

ENHANCEMENT OF AROMATIC AND SATURATED HYDROCARBON BY MODIFIED COLUMN CHROMATOGRAPHIC TECHNIQUE

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ABSTRACT

Three sediment samples collected from the Qua Iboe River System 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 (silica 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 hydrocarbon; sediment I, 287ppm; sediment II, 347ppm; sediment III, 337ppm. The modified SA(2:1) column length ratio eluted the highest amount of aromatic hydrocarbons, 119ppm for sediment I; 90ppm for sediment II and 123ppm for sediment III. The modified AS2:1 weight ratio eluted the least amount of saturated hydrocarbon, sediment I, 19ppm; sediment II, 30ppm and sediment III, 20ppm while the SA1:1 weight ratio eluted the least amount of aromatic hydrocarbon, sediment I, 8ppm; sediment II, 3ppm and sediment III, 12ppm. Generally, the packing by column length ratios eluted higher concentrations of saturated and aromatic hydrocarbons than the packing by weight ratio and the difference is statistically significant. These differences in the yields of the aromatic and saturated hydrocarbons are due to 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.

KEYWORDS: Hydrocarbon, enhancement, column length ratio, weight ratio, adsorption.

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.

In the Niger Delta region of Nigeria the major industrial activity is petroleum exploration and hydrocarbons are known to be the major components of crude oil and petroleum products (Britton, 1984) and their presence in the sediment above regulatory consent limits indicates pollution. Incessant cases of oil pipeline rupture and leakages in the region expose the aquatic environment to excess load of these hydrocarbons (Akpan et al, 1998). 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 concentration 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 the recoverable aromatic and saturated hydrocarbons in a sediment is necessary for a more valid assessment of the levels of these hydrocarbons in the medium. Although interest is growing in frontal analysis, a sorption technique either by liquid-liquid chromatography or liquid-solid chromatography (Cannavacciuolo et al., 1980) but owing to the dearth of instruments for such analysis presently in Nigeria, a classical scheme on column chromatography is re-appraised and better explored using the sediments from the Qua Iboe River system as case study. The Qua Iboe River (Fig. 1) lies within latitude $4^{\circ}31'$ to $4^{\circ}45'N$ and longitude $7^{\circ}30'$ to $8^{\circ}00'E$ on the South Eastern coast line of Nigeria. The river originating from Umuahia hills, traverses mainly sedimentary terrains of Cretaceous to Recent ages and develops into extensive meanders before emptying into the Atlantic Ocean within the Gulf of Guinea (Ekwere et al., 1992).

The Qua Iboe River is fronted by several offshore oil well pipelines and flanked to the east by other oil producing facilities of Mobil Oil Producing Company Nigeria (Unlimited). Gas flaring is also carried out in this area. Because of the intensive oil activities in the area, the Qua Iboe River System is selected for this study.

MATERIALS AND METHODS

Sampling

Sediment samples were collected with a Van Veen grab sampler from three stations in the Qua Iboe River and Douglas Creek (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.

- (i) All the organic solvents were re-distilled at least twice and solvent purity checked by boiling point determination.
- (ii) Only glass wares were used and effort was made not to get the extracts in contact with any rubber or plastic material.
- (iii) Adsorbents were activated before another column is prepared in order to make the activity of the adsorbent constant.
- (iv) 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 200 mesh (40 nanometer) sieve. 100g of the sieved samples were Soxhlet extracted with chloroform-methanol (3:1 v/v) for 48 hours (Lichtfouse et al., 1997). Elemental sulphur was removed with activated copper turnings (Hostettler and Kvenvolden, 1993). The extracts were collected in preweighed flasks. After evaporation of the solvent the extracts were quantified by weight difference.

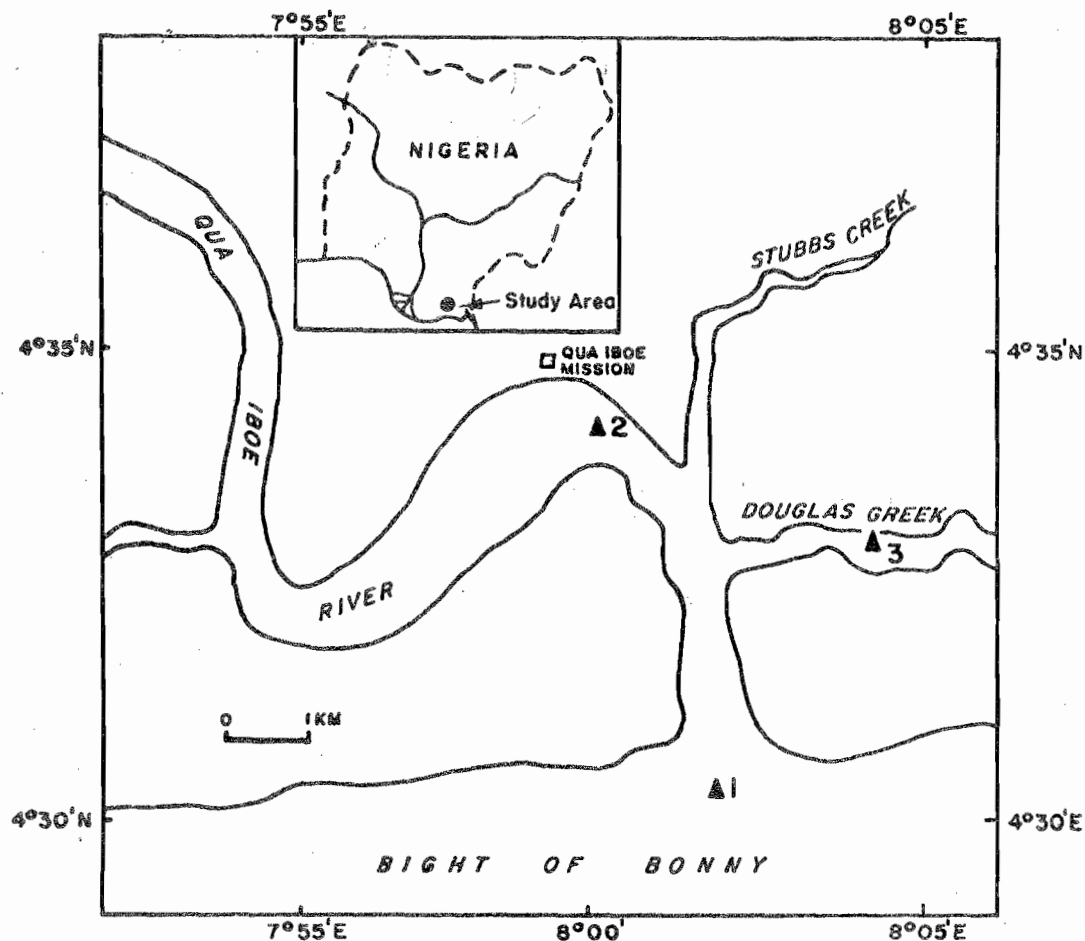


Fig 1: Map showing sample location

KEY

▲ Sample Station

Column Chromatography

The extracts were de-asphalted by the method of Schoell et al. (1983) and Wehner and Teschner (1981). This is by precipitation in a mixture of dichloromethane-petroleum ether (B.P. 40 – 60°C) at 1:30 v/v ratio in a centrifuge at 3,000 rpm for about 20 minutes. The neutral alumina (80 – 200 mesh) was fully activated for 16 hours at 400°C and the silica gel (70 – 230 mesh) was equally activated for 16 hours but at 265°C (Olajire and Odeinde, 1996).

Ten columns (0.65cm id x 35 cm 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 was at the bottom while alumina 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 MSA2:1 is 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, MAS2:1 is ASA1:1:1. The column length was measured from the top of the glass wool base. 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 SA 2:1 implies 10g of silica gel to 5g of alumina and vice versa. SA 1:1 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 deasphalted 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 for 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 solvent (50mls). The column was also flushed with another batch of toluene (25mls) and the eluent examined spectrophotometrically (uv - vis, camag universal-uv lampe 29200) to ensure the complete removal of the recoverable aromatic hydrocarbon 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 ($\mu\text{g/g}$) of the sediment weight.

RESULTS AND INTERPRETATION

Tables 1 and 2 show the concentrations of saturated and aromatic hydrocarbons in the three sediments I, II and III obtained by column length and weight ratios.

Table 1: Concentrations of saturated and aromatic hydrocarbons obtained by column length ratio

S/N	Column Length Ratio	SHC (PPM)				ARO (PPM)			
		I	II	III	MEAN	I	II	III	MEAN
1	SA (1:1) (Yang, 1999)	99	106	104	103 ± 3.6	88	87	85	86.7 ± 1.5
2	SA (2:1) (Ekpo, 2000)	150	153	151	151.3 ± 2.3	39	16	42	32.3 ± 14.2
3	SA (1:2)	287	347	337	323.7 ± 32.1	55	12	74	47.0 ± 22.6
4	AS (1:1)	113	134.3	127	124.8 ± 10.8	62	7	65	44.7 ± 32.7
5	AS (2:1)	67	81	71	73.0 ± 7.2	39	11	112	54.0 ± 52.1
6	AS (1:2)	75	180	89	114.7 ± 57.0	63	62	63	62.7 ± 0.58
7	S	74	114	76	88.0 ± 22.5	40	36	86	54.0 ± 27.8
8	A	66	68	68	67.3 ± 1.2	21	10	54	28.3 ± 22.8
9	MSA (2:1)	30	201	87	106.0 ± 87.1	119	90	123	10.7 ± 18.0
10	MAS (2:1)	29	43	36	36.0 ± 7.0	13	8	27	16.0 ± 9.8

Table 2: Concentrations of saturated and aromatic hydrocarbons obtained by column weight ratio

S/N	Column Weight Ratio	SHC (PPM)				ARO (PPM)			
		I	II	III	MEAN	I	II	III	MEAN
1	SA (1:1) (Oderinde & Olajire, 1996)	79	120	96	98.3 ± 20.6	8	3	12	7.7 ± 4.5
		7	54	67	49.3 ± 20.4	40	13	79	44 ± 33.2
2	SA (2:1)	39	70	40	49.7 ± 18.0	12	5	23	13.3 ± 9.07
3	SA (1:2)	29	42	36	35.7 ± 6.5	43	36	50	43.0 ± 7.0
4	AS (1:1)	78	99	95	90.7 ± 11.2	51	35	62	49.3 ± 13.6
5	AS (2:1)	65	82	79	75.3 ± 9.07	18	12	21	17.0 ± 4.6
6	AS (1:2)	73	93	80	82.0 ± 10.1	36	34	46	38.7 ± 6.4
7	MSA (2:1)	19	30	20	23.0 ± 6.1	17	15	25	19.0 ± 5.3
8	MAS (2:1)								

Column Length Ratio

In table 1, No. 3 the composition SA (1:2) column length ratio gave the highest concentration of saturated hydrocarbons for sediments I, II and III. However, its aromatic hydrocarbon yield ranked 5th of the ten compositions by column length under investigation. No. 9, MSA (2:1) eluted the highest concentration of aromatic hydrocarbons in sediments I, II and III. This suggests that the relative elution of the saturated and aromatic hydrocarbons is differently influenced by the composition of the column packing.

The saturated hydrocarbons do not adsorb well on the alumina relative to silica gel due to polarity difference.

Therefore, descending the comparatively longer length of the alumina (SA 1:2) 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 hydrocarbon may be as a result of the first contact of the aromatic hydrocarbons 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. 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 consequent 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 reasons adduced above enhanced their elution. However, the same does 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. Therefore, this suggests that having alumina at the bottom and the top with silica gel in between ASA (1:1:1) immensely disrupts the dispersion interaction of the saturated and aromatic hydrocarbons. Consequently, their respective concentration is considerably 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 4 degrees of freedom shows that a significant difference exists between the aromatic hydrocarbon concentrations obtained from the column length ratios SA2:1, no. 2 and MSA2:1, no. 9 (t-calculated = 3.43 and t-critical = 2.78). For no. 1, SA1:1 and no. 4, AS 1:1; no. 5, AS2:1 and no. 9, MAS 2:1; no. 2, SA2:1 and no. 3, SA1:2 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, AS2:1 and no. 10, MAS2:1; no. 2, SA2:1 and no. 3, SA1:2 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 :1 weight ratios exhibited significant differences in the concentrations of the aromatic hydrocarbon obtained from them, t-calculated, 4.11 and 2.94 respectively against the critical value of 2.78. For no. 2, SA(2:1) and no. 7, MSA(2:1) there was no significant difference (t-calculated = 0.22 against the 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 amount of aromatic and saturated hydrocarbons than the packings by weight ratio. This is supported by the calculated t-values of 2.81 for MSA (2:1) column length ratio and AS (2:1) weight ratio in the aromatic

hydrocarbon concentration. Similarly, SA 1:2 column length ratio and SA 1:1 weight ratio showed a significant difference in the concentrations of the saturated hydrocarbon as the calculated t-value is 3.63.

However, there were few cases where the column packing by weight ratio eluted higher amounts of aromatic hydrocarbons (SA2:1; MAS2:1) and saturated hydrocarbon (SA1:1; AS2:1; MSA2:1), but no significant differences in the aromatic and saturated hydrocarbon concentrations existed 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.

CONCLUSION

In column chromatographic separation, the modification of the column packing by column length ratio and weight ratio influence the concentration 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).

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