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SELECTIVITY OF COLUMN PACKING TO PORPHYRIN ELUTION

Authors & Affiliation:

[1]Ibe, K.A. and [2]Ogwuche, C.E.

[1] Department of Chemistry, Federal University of Petroleum Resources, P.M.B. 1221 Effurun, Nigeria.

[2].Department of Chemistry, Federal University of Petroleum Resources, P.M.B. 1221 Effurun, Nigeria.

Corresponding Author:

Kenneth A. Ibe

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Abstract:

The selectivity of column packings to porphyrin elution was investigated. A total of eighteen different column packings by column length and column weight ratios (comprised of three existent and fifteen novel column packings) were investigated for their relative elution of nickel and vanadium porphyrins from ten outcrop sediment samples by column chromatography using silica gel and alumina as the stationary phase. Column packings by column length ratio, AS (1:1) and SA (1:1) eluted the maximum concentration of nickel porphyrin, 790mmole with a mean of 521±55.42 and vanadium porphyrin, 152mmole with a mean concentration of 92.56 ±12.56 while the column packings by weight ratio, SA (1:2) and AS (1:2) eluted the minimum concentration of nickel porphyrin, 9mmole with a mean concentration of 27±6.02 and vanadium porphyrin, 10mmole with a mean concentration of 25.78± 5.16. Some of the novel column ratios investigated eluted significantly higher concentrations of the porphyrins than the three existing column ratios used by different workers at 95% confidence limit.

Keyword: Porphyrin; elution; column packing; chromatography; bottom water sediment; Ethiope river.

Introduction:

Organic matter rich sediments which act as source rocks in oil forming basins are the result of the process of sedimentation during geological time. Conditions during sedimentation may vary, and hence the quality and quantity of organic matter both vertically and laterally may change depending on the environmental conditions during and after deposition of sediments(Moldowan et al; 1985). The Lower Toarcian shales in Europe (Kuspert, 1983) and the Calabar shales in Nigeria(Essien et al; 2005) are typical examples.

Source input variations and diagenetic reactions in the sediment during and shortly after deposition may result in changes in geochemical properties of organic matter in the sediments. For example, it has long been known that phytol diagenetic reaction pathways differ in reducing as opposed to non- reducing conditions in the sediment (Didyk et al; 1978). Porphyrins in crude oils and bitumen occur complexed to either nickel or vanadium. The proportionality of nickel to vanadium may be attributed to Eh, P^H and sulphide concentrations in the environment in which the source rocks were deposited. The inter- relationships and limitations for Eh and P^H of various water bodies have been discussed in detail by(Friedman and Sanders, 1978).The most important in highly reducing marine sediments(low Eh) is the bacterially mediated reduction of sulfate to sulphide which preferentially reacts with Ni^{2+} to form Ni^{2+} sulfide. Thus Ni^{2+} is removed from solution and only VO^{2+} remains to complex with free-base porphyrins. In a less reducing environment sulphate reducing bacteria are absent and sulphate is the dominating form of sulphur. This leaves both Ni^{2+} and VO^{2+} in solution competing for complexation with free base porphyrins. Since the equilibrium constant for the formation of nickel porphyrins is much higher than that of vanadyl porphyrins, a relatively less reducing (higher Eh) leads to predominance of nickel porphyrin. Nickel and vanadyl porphyrins constitute a class of biomarkers that are sensitive to geochemical variations in the environment. Hence, their use in correlation studies and as source parameters(Boduszynski, 1987).

Nickel and vanadium are significantly present in oil – rich geo- ecological environments and have high levels in petroleum coke (Barwise and Whiteland, 1980). Both have equally been shown to be essential trace elements and in excessive physiological concentration are toxic (Vincent, 2004).

From the foregoing, their optimum quantitation becomes imperative. However, since the quantity of recoveries from geochemical samples are method dependent (Ogunsuyi et al; 2008) and (Akpan, 2005), analytical scheme of different column packings were explored with the aim of determining the column packing that would give optimum recoveries. Though the current methods of separation and recovery are instrumental using high pressure liquid chromatography (HPLC), gas chromatography and mass spectrometry (GC/MS) but the cost of purchasing the equipment or cost of the analysis is high and not easily affordable by an average researcher in Nigeria. Hence, the investigation.

Bottom water sediments from Ethiope River in Delta State, South South Nigeria were used.

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^o and 6.05^o North and longitude 5.30^o and 6.05^o 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, Aghalokpe, Aragba-Okpe, Adarweran, Egbeku, Ibada, Eko, Amukpe, Okirigwhre, Sapele, Jesse, Oghara are communities traversed by the Ethiope river(Okumagba and Ozabor,2014)

Sampling:

Ten bottom water sediments were sampled at fixed intervals of 50m in Ethiope River. Traces of surficial dirts and plant materials were carefully and thoroughly removed. The samples were dried at 25^0C for 48 hours before been pulverized and subsequently sieve through 200 mesh size

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

Determination of soluble organic matter (SOM):

To preserve the integrity of the samples, all glass wares were cleaned with soap and water, rinsed with distilled water, heated in an oven at 550^0C for 8hrs; and pre- extracted with methanol and toluene mixture to get rid of any traces of surficial organic matter. The thimble and glass wools were pre- extracted before being used for sample extraction. The samples were extracted for 48hours in a soxhlet apparatus with methanol- toluene (2:1)v/v [1]. The extracts obtained are the soluble organic matter (SOM), which contain the porphyrins among other constituents

Column Chromatography:

Deashphaltation of the extracts were carried out following the procedures described by (Schoell et al; 1983) and (Wehner and Teschner, 1981) by precipitation in a mixture of dichloromethane and petroleum ether (bp 40- 60^0C) at 1: 30 ratio in a centrifuge at 3,000rpm for about 20minutes.

The separation of the deasphaltened extracts was accomplished by liquid chromatography using silica gel 70/230 mesh, and alumina (neutral). The silica gel was activated for 6hrs at 400^0C and the alumina for 2hrs at 700^0C. The silica gel and alumina (stationary phase) were packed in the column in different ratios of column length and weight of the stationary phase as follows:

SA (1:1) = Column packing, where equal height or weight of silica gel and alumina were packed in the column with silica gel at the base and alumina overlying it

SA (1:2)= Column packing, where half the height or weight of silica gel to alumina or twice the height or weight of alumina to silica gel were packed in the column with silica gel at the base and alumina overlying it.

SA (2:1) = Column packing, where twice the height or weight of silica gel to alumina were packed in the column with silica gel at the base and alumina overlying it.

AS (1:1) = Column packing, where equal height or weight of alumina and silica were packed in the column with alumina at the base and silica gel overlying it.

AS (1:2) = Column packing, where twice the height of silica gel to alumina were packed in the column with alumina at the base and silica gel overlying it

AS (2:1) = Column packing, where twice the height of alumina to silica were packed in the column with alumina at the base and silica gel overlying it.

S= Column packing with only silica gel

A= Column packing with only alumina

MSA (2:1) = Modified **SA (2:1)** is actually **(SAS 1:1:1),** that is1/3 of the height or weight being silica gel was packed at the base, 1/3 of the height or weight being alumina in the middle and another 1/3 of the height or weight being silica gel was on top.

MAS (2:1) = Modified **AS (2:1)** is actually **(ASA1:1:1),** that is 1/3 of the height or weight being alumina was packed at the base, 1/3 of the height/ weight being silica gel in the middle and another 1/3 of the height or weight being alumina was on top.

After the removal of the saturated and aromatic hydrocarbons from the deasphaltened extract, nickel porphyrin was eluted with 2:3v/v dichloromethane- hexane mixture and vanadyl porphyrin eluted with 100% dichloromethane (Smyth, 1989). The analytical method was enabled to monitor small changes as significant based on the estimated reproducibilities monitored through standards The solvents were reduced in a rotary evaporator and then in a nitrogen rich atmosphere. The dried nickel and vanadyl porphyrin were re-dissolved in dichloromethane($3.5cm^3$) and their absorbance determined using HACH DR 3000 spectrophotometer ultraviolet visible at 550nm(molar extinction coefficients, ϵ= $33.1Lmmol^{-1}cm^{-1}$) and 570nm(ϵ =$31.6Lmmol^{-1}cm^{-1}$) for Ni(II) and Vo(II) porphyrins respectively(Ibe et al; 2006). Employing Beer- Lambert's law, A = ϵCL, the concentrations(C) of the porphyrins were calculated in millimole, where A= absorbance, ϵ= molar extinction coefficient, c= concentration and L= pathlength of the cell.

The column chromatographic procedure was protected from sunlight to prevent photodecomposition, a particularly important precaution when working with porphyrin bearing functional groups.

Results/Discussion:

The ten different column length ratios used in this investigation comprised of three existent column length ratios, already used by different workers and seven novel column ratios created by the authors. Eight column weight ratios were used which comprised of two weight ratios already used by different workers and six novel column ratios created by the authors.

Nickel porphyrin - Column length ratio:

The maximum concentration of nickel porphyrin by column length ratio was 790mmole from AS (2:1) with a mean of 521.20 ±175.25. The minimum concentration was 10mmole from SA (1:2) (Yang, 2000).

The statistical test of homogeneity of variances and ANOVA showed that a significant difference exists between the means at 0.05 confidence limit. Then, Post Hoc tests were performed on the means to find out which of the method(s) had significant mean difference from the others at the same confidence limit of 0.05.

The results showed that there was no significant difference in the mean yield of SA (1:1) (Ekpo, et al; 2005) and the mean of the rest of the methods. However, AS (2:1), MSA (2:1) and A had significantly higher mean difference from the other methods. Thus, the three methods could be preferred in that order for quantitative estimation of nickel porphyrins.

Table 1: Concentrations of nickel porphyrin by column length ratio (mmole)

S/N	Column length ratio	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1.	SA(1:1)[Ekpo et al; 2005]	700	450	530	643	210	315	111	90	217	20
2.	SA(2:1)[Oderinde & Olajire, 1996]	300	125	157	317	80	90	121	79	80	131
3.	SA(1:2)[Yang, 2000]	10	14	30	17	39	19	11	13	45	35
4.	AS(1:1) "	125	110	200	65	70	139	100	103	59	71
5.	AS(2:1) "	600	550	790	621	705	500	420	509	306	211
6.	AS(1:2)	287	15	487	300	100	112	153	101	37	49
7.	S	91	57	69	125	213	123	178	201	90	57
8.	A	300	421	537	419	215	303	297	300	421	320
9.	MSA2:1	360	570	613	490	287	494	578	421	296	410
10.	MAS2:1	200	191	317	121	375	218	100	87	98	312

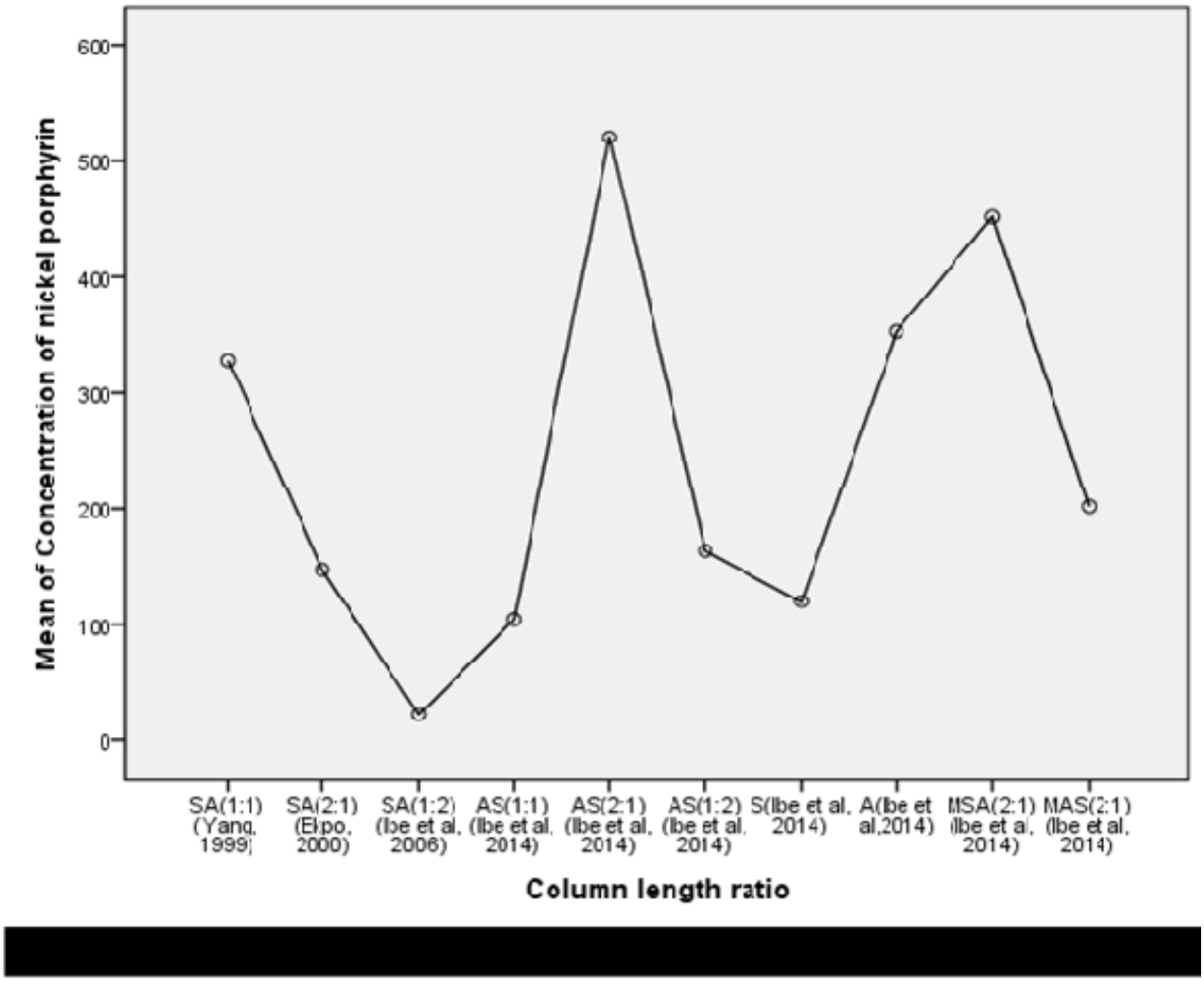

Figure2: Mean plot of nickel porphyrin concentration by column length ratio

Nickel porphyrin- Weight ratio:

The maximum concentration of nickel porphyrin by weight ratio is 97mmole from AS (1:1) with a mean concentration of 61±30.07mmole. The minimum concentration was 9mmole from SA (1:1) with a mean concentration of 27±18.06mmole.

One way analysis of variance at 0.05 confidence showed that showed that a significant difference exists in the concentration of nickel porphyrin by column weight ratios AS(1:1), AS(2:1) and the other six weight ratios.

Table 2: Concentration of nickel porphyrin by column weight ratio (mmole)

S/N	Column weight ratio	1	2	3	4	5	6	7	8	9	10
1.	SA(1:1)[Ekpo et al; 2005]	Nil	40	29	60	78	57	43	92	33	13
2.	SA(2:1) [Yang,2000]	Nil	50	47	80	73	23	37	41	57	41
3.	SA(1:2)	Nil	13	32	9	18	24	21	56	57	13
4.	AS(1:1)	Nil	10	45	97	71	84	67	83	74	19
5.	AS(2:1)	Nil	15	70	63	57	91	48	97	50	56
6.	AS(1:2)	Nil	48	53	64	34	48	19	26	38	51
7.	MSA(2:1)	Nil	53	10	11	29	53	70	29	40	39
8.	MAS(2:1)	Nil	17	14	23	11	14	27	32	37	42

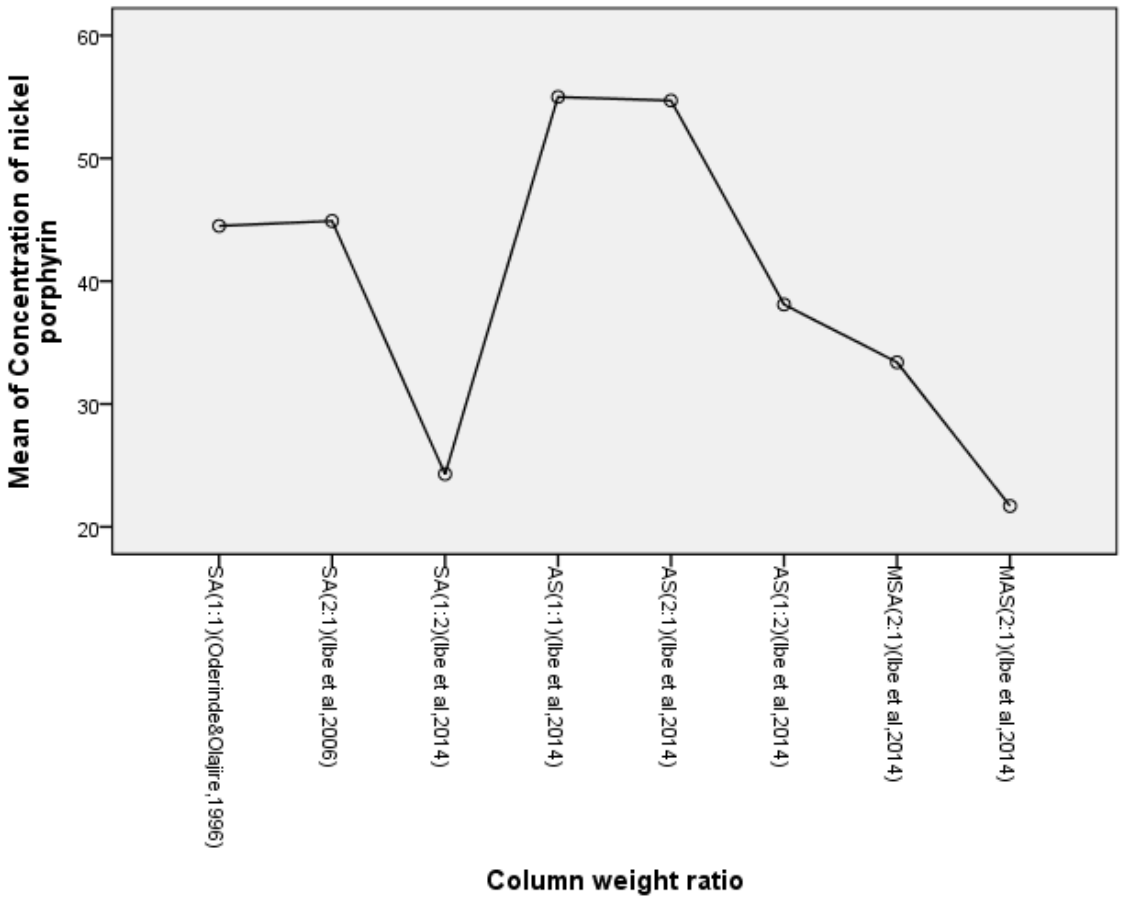

Figure3: Mean plot of nickel porphyrin concentration by weight ratio

Vanadium porphyrin- column length ratio:

The maximum concentration of vanadium porphyrin by column length ratio is 152mmole from SA (1:1)(Ekpo et al; 2005) with a mean concentration of 92.56 ±37.56mmole while the minimum concentration is 17mmole from AS (1:1), S, A, MAS (2:1) with a mean concentration of 20.22±4.21mmole.

Statistical test of homogeneity and one way analysis of variance at 0.05 confidence level showed that a significant difference exists within the mean concentrations eluted by different column length ratios.

The Post Hoc Test showed that the mean concentration obtained from SA (1:1)(Ekpo et al; 2005), AS (1:2), SA (2:1)(Oderinde and Olajire,1996) and AS (1:1) are significantly different from the mean concentrations obtained from the other four column ratios. So, AS (1:2) and AS (1:1) compare very well with the column length ratios previously used by (Ekpo et al; 2005) and (Oderinde and Olajire, 1996).

Table 3: Concentrations of vanadium porphyrin by column length ratio (mmole)

S/N	Column length ratio	1	2	3	4	5	6	7	8	9	10
1.	SA(1:1)[Ekpo et al; 2005]	80	79	123	141	152	Nil	87	71	53	47
2.	SA(2:1)[Oderinde & Olajire, 1996]	53	82	34	91	42	Nil	72	41	50	52
3.	SA(1:2)[Yang,2000]	33	27	82	45	73	Nil	34	29	31	18
4.	AS(1:1)	17	32	35	39	72	Nil	47	83	91	80
5.	AS(2:1)	27	83	70	63	93	Nil	118	125	138	120
6.	AS(1:2)	50	73	90	48	37	Nil	61	52	61	43
7.	S	20	32	41	52	33	Nil	43	27	31	17
8.	A	17	24	47	19	20	Nil	61	20	27	31
9.	MSA2:1	23	32	42	31	28	Nil	30	33	42	31
10.	MAS2:1	19	17	28	19	18	Nil	27	19	18	17

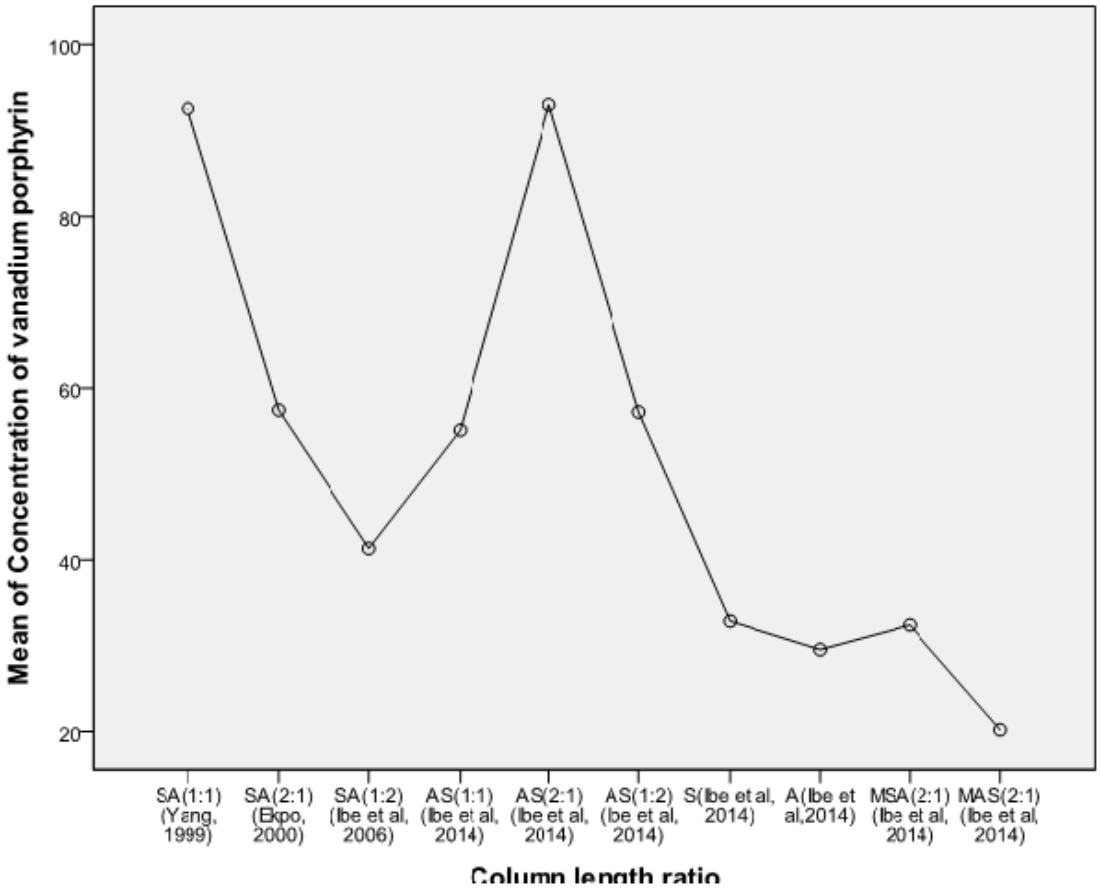

Figure4: Mean plot of vanadium porphyrin concentration by column length ratio

Vanadium porphyrin – Weight ratio

The maximum concentration of vanadium porphyrin by column weight ratio is 87mmole by SA (2:1) with a mean concentration of 56.78±17.10 while the minimum concentration is 10mmole by AS (1:2) with a mean concentration of 25.78±15.48mmole.

The statistical test of homogeneity and one way analysis of variance at 0.05 confidence level showed a significant difference within the mean concentrations eluted by different column weight ratios.

The Post Hoc test showed that the mean concentration obtained by SA (2:1) (Ibe et al; 2006), SA (1:2) and SA (1:1) (Shaw, 1991) are significantly different from the mean concentrations obtained from the other methods. So, SA (1:2), one of the novel column ratios investigated by the authors, compared well with SA (2:1 and SA (1:1) previously used by (Yang, 2000) and (Shaw, 1991).

According to (Ekop and Eddy, 2005), adsorption from solution always involves competition between solute and solvent or between the components of a liquid mixture for the adsorption sites. Adsorption from solution behavior can often be predicted qualitatively in terms of polar/ non polar nature of the solid and of the solution components. The implication is that the relative differences in competition; the polarity of the stationary phase and the mobile phase or the eluate and the ratio of the stationary phase in the column might have contributed to the relative differences in the concentration of the eluted porphyrin.

Table 4: Concentration of vanadium porphyrin by column weight ratio (mmole)

S/N	Column weight ratio	1	2	3	4	5	6	7	8	9	10
1.	SA(1:1)[Oderinde & Olajire, 1996]	37	42	53	65	Nil	42	27	48	50	32
2.	SA(2:1)[Yang, 2000]	42	57	58	72	17	87	30	53	67	45
3.	SA(1:2)	59	70	43	51	19	62	43	20	37	36
4.	AS(1:1)	60	52	71	20	Nil	15	17	21	31	29
5.	AS(2:1)	40	21	35	18	Nil	32	18	32	33	38
6.	AS(1:2)	33	47	54	17	21	10	13	18	21	19
7.	MSA(2:1)	29	30	17	21	Nil	19	21	27	15	21
8.	MAS(2:1)	11	28	19	31	7	13	15	19	23	31

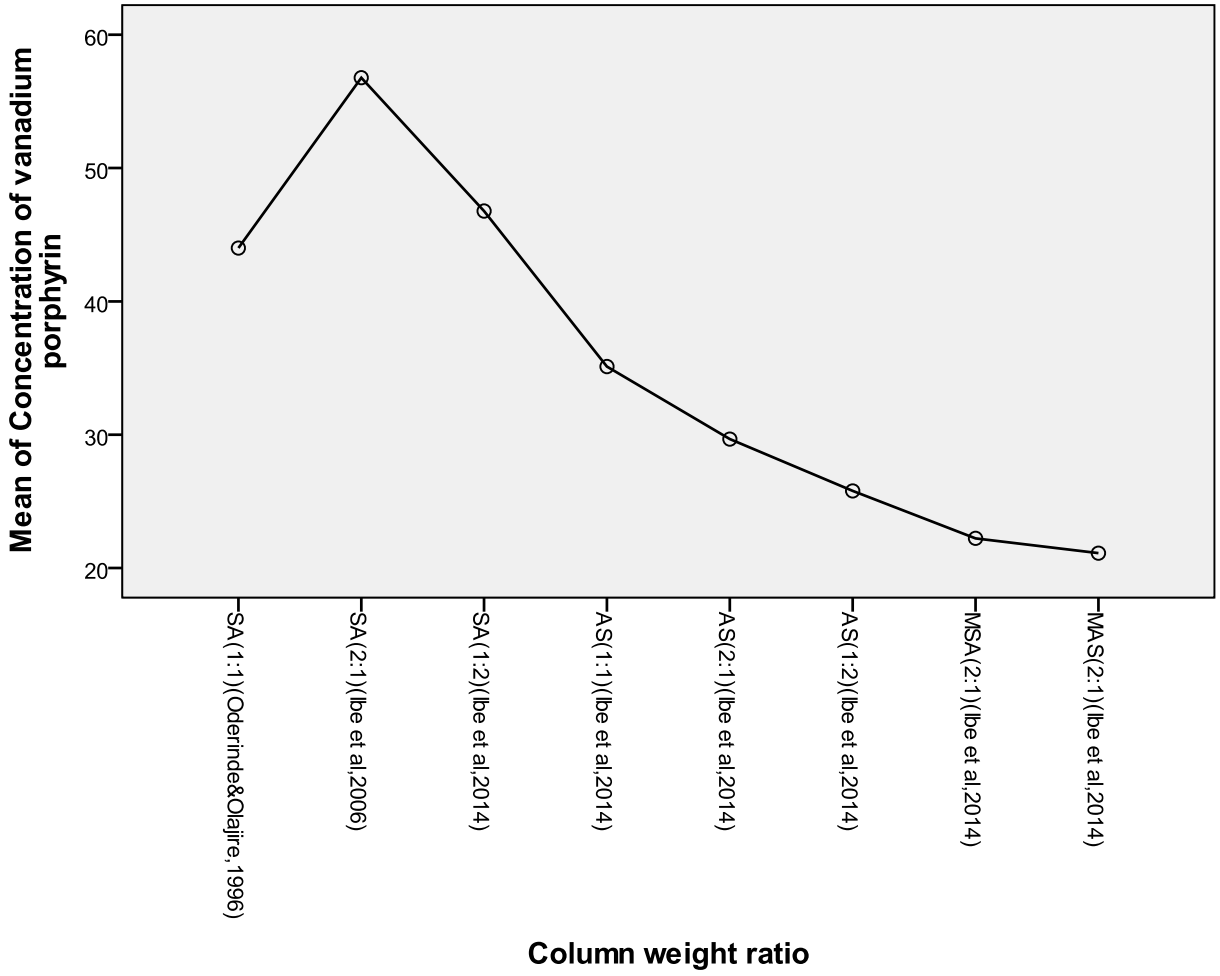

Figure5: Mean plot of vanadium porphyrin concentration by weight ratio

Conclusion:

The results of this investigation showed that some of the novel column packings eluted higher porphyrin concentrations than the existing column packings. Generally, the column packing by column length ratio eluted significantly higher concentrations of nickel and vanadium porphyrins than the column packing by column weight ratio. The relative differences in competition; the polarity of the stationary phase and the mobile phase and the ratio of the stationary phase in the column might have contributed to the relative differences in the concentration of the eluted porphyrin.

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