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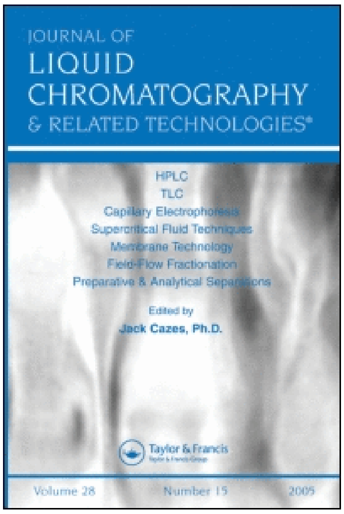

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Analysis of Organic Nitrogen Compounds Using Paired Ion Chromatography. Applications to the Analysis of Coal-Derived Liquids

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To cite this Article Holy, Norman L. and Lin, Tay-Yean(1979) 'Analysis of Organic Nitrogen Compounds Using Paired Ion Chromatography. Applications to the Analysis of Coal-Derived Liquids', Journal of Liquid Chromatography & Related Technologies, 2: 5, 687 — 695

To link to this Article: DOI: 10.1080/01483917908060096

URL: http://dx.doi.org/10.1080/01483917908060096

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JOURNAL OF LIQUID CHROMATOGRAPHY, 2(5), 687-695 (1979)

Analysis of Organic Nitrogen Compounds Using Paired Ion Chromatography. Applications to the Analysis of Coal-Derived Liquids

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ABSTRACT

Evaluation of HPLC as a possible method by which the nitrogen compounds in coal-derived liquids could be analyzed has met with mixed results. Some chromatography fractions display very different HPLC traces in methanol compared with those obtained in a MeOH-HOAc-PIC mixture, but others are insensitive to the change in eluent. HPLC of several model compounds has revealed basic nitrogen compounds generally have longer retention times in paired ion chromatography (PIC) solutions, but that some actually have shorter times. Heterocyclic nitrogen compounds all give longer retention times in PIC solution than in methanol.

INTRODUCTION

With the resurgence of research interest in coal and coal-derived products has come the need to find new techniques for separating and identifying components. Since the nitrogen compounds in coal-derived liquids are detrimental to its fuel qualities, methods are being sought by which the nitrogen may be removed.[1] With respect to the nitrogen compounds in coal-derived liquids there is, however, an even more fundamental need: since the identities of the nitrogen compounds are uncertain, there is need of an analytical technique by which the nitrogen-containing compounds can be distinguished from the myriad of other compounds. We considered that High Performance Liquid Chromatography (HPLC) might be a candidate since the mild operating conditions presumably would avoid sample degradation, and the large number of theoretical plates would facilitate separation of the many compounds.

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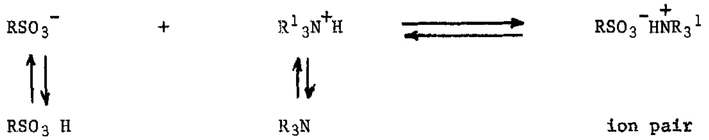
An HPLC approach that is very effective in separating nitrogen-containing compounds involves the paired-ion concept.[2] This is a reversed-phase technique using a C_{18} column; the eluent generally is aqueous methanol that is 1.0M in acetic acid and there is a low concentration of one of the "PIC" reagents (alkyl sulfonic acid). The nitrogen compounds are protonated (pH~2) in this environment and combine with the alkyl sulfonate to form tight ion pairs that interact with the C_{18} units



$$\begin{tikzcd} RSO_3^- \arrow[d, shift left] & + & R^1{}_3N^+H \arrow[d, shift left] \arrow[r, shift left] & RSO_3^-H\overset{+}{N}R_3{}^1 \arrow[l, shift left] \\ RSO_3\,H \arrow[u, shift left] & & R_3N \arrow[u, shift left] & \text{ion pair} \end{tikzcd}$$

of the column. Separation is considered to reflect the degree of protonation, i.e., the basicity of the nitrogen compounds and the Van der Waals interaction of the ion pair with the C_{18} side-chain.

To distinguish the nitrogen compounds in coal-derived liquids from the many other components, it was considered that by comparing HPLC results of a coal liquid using just methanol as eluent with those obtained using the PIC reagents, it might be possible to see a shifting in the retention times of the nitrogen compounds. It was considered that as other components were not likely to form tight ion pairs under the acidic conditions their retention times would be less sensitive to the change of eluent. The changes in retention times of non-nitrogen compounds, if any, were anticipated to be mainly a consequence of differences in solvent dielectric constants.

This paper then examines two concepts. We have evaluated the usefulness of HPLC, within the context of a paired ion approach, to detect nitrogen containing compounds in a coal liquid. Secondly, using model compounds, ion pair formation and retention have been studied.

EXPERIMENTAL

Compounds utilized for the HPLC studies were obtained from either Dr. Art Fort, Institute for Mining and Minerals Research, Lexington, Kentucky, or from Aldrich Chemical Company. They were used without purification. Methanol was freshly distilled through a 1.0m Widmer column. Reagent grade glacial acetic acid was used directly. The PIC-B5 and PIC-B7 were used as obtained from Waters Associates.

The HPLC used in these studies was a Waters ALC/202 equipped with a M6000 pump, UV detector at 254 nm and a 30 cm/8mm Bondapac C_{18} column. Retention times were obtained at a flow rate of 0.4 ml/min. Normally aqueous methanol solutions are used in studies with PIC reagents, but the insolubility of coal-liquids in aqueous media precluded such solvents here. A 240 g sample of H-Coal liquid (Run 130-79, Syncrude Mode, Ashland Oil Company, bp 400-650°F) was placed on a 70 x 5 cm alumina column (1800 g alumina, Baker Analyzed Reagent,pH = 7) and eluted successively with hexane (hydrocarbons, 200 g, 83.3%) methanol (polars, 29.8 g, 12.4%) and glacial acetic acid (polars, 1.1 g, 0.5%).

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For ion-exchange chromatography of the polar fractions, Macroreticular Amberlyst Ion Exchange Resin, Grade 26, from Rohm and Haas, was chosen. This resin has trimethylammonium groups. The beads were soaked in 0.1M methanolic sodium acetate for 24 hr before use. They were then placed on the column (300 g, 70 x 5 cm).

Early fractions from this column contained sodium acetate; this was removed by evaporating the methanolic solutions to dryness, adding chloroform, filtering, and evaporating the chloroform. The dioxane fraction was obtained by removing the beads from the column and heating (65°C) with dioxane for 1 hr, then filtering and evaporating.

RESULTS AND DISCUSSION

Coal-derived liquids could be described very broadly as being composed of nonpolar hydrocarbons and polar compounds. Since the polar components contain most of the nitrogen, this is the fraction which we were most interested in characterizing. To accomplish a separation of the components in coal-derived liquids, several groups have performed a separation on the bulk material.[3] We view this practive as inefficient and wasteful. We would propose that a preliminary separation into polar and nonpolar fractions is both faster and requires far less solvent and adsorbant than is required if attempts are made to characterize the nitrogen-containing materials all in one column chromatography. The results for the preliminary separation of one coal-derived liquid are shown in Table 1.

The polar materials were then placed on an anion exchange resin and eluted in such a manner (Table 2) that the basic compounds could be considered to be in the uncharged form, the acids significantly in their anionic form. Consequently, we anticipated that the basic nitrogen compounds would be among the early fractions, along with polar neutrals, while the acids (probably phenolics for the most part) were considered to be among the later fractions. The preparative fractions were analyzed by HPLC using either methanol or methanol plus PIC as solvent.

Figure 1 shows results of the HPLC of Fraction 3 of the coal liquid. Appreciable differences using methanol and the PIC solution are seen. This figure reflects typical changes seen in fractions 1 - 6. Later fractions (except fraction 16) did not reflect substantial changes; the traces of the PIC curves were virtually superimposable on the curves obtained when only methanol was used.

Thus it would appear, on the basis of the HPLC results, that nitrogen compounds could be distinguished by employing the two eluent systems. To determine if the HPLC results were reliable, elemental analyses were performed on several fractions. These results (Table 2) demonstrate that while the nitrogen is concentrated in early fractions, nitrogen compounds were present also in most later fractions. Thus, HPLC, using the paired-ion approach, is not able to detect all types of nitrogen compounds present in H-Coal.

To determine which types of compounds do not respond to eluent changes, a series of aromatic amines was evaluated. Two criteria were utilized in compound

Table 1. Bulk Separation of H-Coal Into Nonpolar and Polar Components 240.0 g of H-Coal, BP 400-650 F

Fraction	Eluent	Weight (g)	Volumn (ml)	Percentage
1	Hexane	200.0	1,500	83.3
2	Methanol	29.8	800	12.4
3	Glacial acetic acid	1.1	600	0.5
		TOTAL		96.2

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selection. One, the preponderance of nitrogen-containing compounds in coal-derived liquids were assumed to be aromatic. Two, since the coal-derived liquid used in this study (H-Coal) was produced via hydrogenation it was assumed that oxidized forms of nitrogen (e.g., nitro, nitroso) were either absent or present only in very low concentrations.

The results in Table 3 reveal that nitrogen compounds indeed display quite varying behavior in methanol and PIC eluents. The ratio of retention times (PIC/MeOH) varies from 5.2 to 0.82 for the nitrogen compounds tested.

Table 2. Treatment H-Coal (Methanol Fraction) with Base Ion-exchange (S-26) H-Coal 2.20 g, S-26 Ion Resin 300 g.

Sample Number	Eluting Solvent	Volume	Weight (gram)	C	H	N
1	0.1M Sodium Acetate in Methanol	100	0.1172	60.74	8.09	0.46
2	"	"	0.0669			
3	"	"	0.0904	66.47	8.33	1.82
4	"	"	0.1134			
5	"	"	0.1214	71.60	8.55	2.13
6	Methanol	"	0.0937			
7	"	"	0.1938			
8	"	"	0.1974	78.64	8.27	1.53
9	0.1M HCl in Methanol	"	0.1385			
10	"	"	0.1211			
11	"	"	0.0691	85.45	7.01	1.25
12	"	"	0.0455			
13	Acetic Acid 20% Methanol 80%	50	0.0281	66.54	5.90	0.82
14	"	"	0.0450			
15	"	"	0.0386	73.78	6.06	1.37
16	Chloroform	1000	0.1241	43.24	6.74	0.08
17	Dioxane	1000	0.5896			
		TOTAL	2.19 g			

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Table 3. HPLC Retention Characteristics[a] of Model Compounds

Compound	Retention Time(min)		RATIO	pK_b[c]
	MeOH	PIC[b]		
2,7-Dimethylquinoline	3.1	16.0	5.2	8.9
Acridine	3.0	15.0	5.0	9.9
3-Ethylpyridine	3.1	10.0	3.2	
4-Azafluorene	3.5	9.1	2.6	
Nicotinic Acid	1.3	3.0	2.3	
Phenathridine	3.0	6.0	2.0	
4-Phenylimidazole	2.6	5.3	2.0	8.9[d]
7,8-Benzoquinoline	2.6	5.3	2.0	
2,4-Lutidine	6.0	11.9	2.0	
3,5-Lutidine	3.5	6.3	1.8	
N-Methylaniline	3.2	5.6	1.8	
3,4-Lutidine	5.9	10.0	1.7	
5,6-Benzoquinoline	4.9	9.0	1.8	
p-Toluidine	2.8	4.4	1.6	
Lepidine	4.3	6.9	1.6	
Isoquinoline	3.0	4.9	1.6	8.7
Pyridine	4.2	6.6	1.6	8.8
3,4-Dimethylaniline	3.1	4.7	1.5	
Tribenzylamine	2.9	4.3	1.5	
p-Anisidine	3.0	4.1	1.4	
2,6-Dimethylquinoline	3.1	4.2	1.4	
2,6-Lutidine	5.5	8.6	1.5	
N,N-Dimethylaniline	4.0	5.5	1.4	
p-Toluic acid	2.2	2.8	1.3	
5-Hydroxyisoquinoline	5.0	6.2	1.2	
2,5-Diethoxyaniline	2.9	3.6	1.2	
13H-Dibenzo[ai]carbazole	2.6	2.8	1.1	
N-Ethylaniline	3.4	3.9	1.1	
Diphenylamine	2.9	3.3	1.1	13.1

(continued)

Table 3 (continued)

Compound	Retention Time(min) MeOH	Retention Time(min) PIC[b]	RATIO	pK_b[c]
Benzanilide	2.9	3.2	1.1	
2,4,6-Collidine	6.2	7.0	1.1	
Benzylamine	2.7	2.9	1.1	4.6
m-Toluidine	3.0	3.3	1.1	9.1
Dimethylterephthalate	2.8	3.0	1.1	
Benzophenone	2.7	3.0	1.1	
Phenylacetic acid	2.7	3.0	1.1	
3-Methylindole	2.6	2.8	1.1	>16[e]
Salicyclic Acid	2.7	3.0	1.1	
Phthalimide	2.8	3.0	1.1	
Acetanilide	2.9	3.0	1.0	15.7
Benzamide	2.7	2.8	1.0	
Quinaldine	4.1	4.3	1.0	8.4
Carbazole	2.7	2.8	1.0	
Thianaphthalene	3.0	3.0	1.0	
2-Phenylindole	2.7	2.6	1.0	
5-Hydroxyindole	2.8	2.8	1.0	
2-Phenylacetamide	2.8	2.8	1.0	
o-Toluidine	3.9	3.3	0.85	9.6
Dibenzylamine	4.9	4.1	0.84	
Aniline	4.0	3.3	0.82	9.4

[a] Bondapac C_{18}, 1/4" x 30 cm, flow 0.4 ml/min.
[b] MeOH/1.0M HOAC/0.005M PIC-B7.
[c] From "Titrations in Nonaqueous Solvents", Walter Huber, Academic Press, New York 1967, pp 222-223.
[d] For imidazole.
[e] For indole.

Previously it had been considered that the ability of the PIC reagents to separate nitrogen compounds was based on subtle differences in basicity and Van der Waals forces.[2] From the pK_b values listed in Table 3, it can be seen that these explanations are insufficient. They seem to hold for the indole derivatives whose

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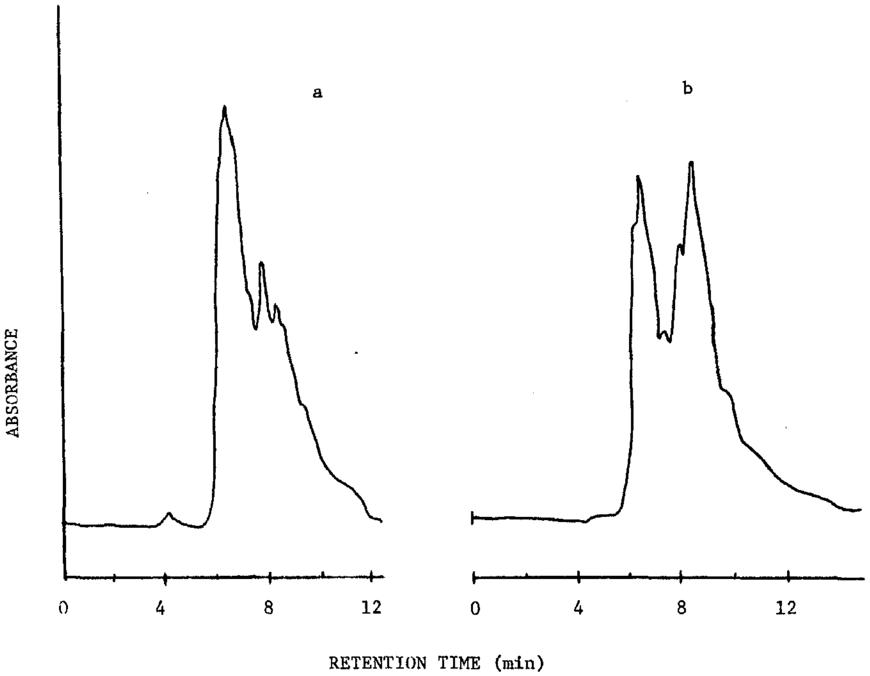

Figure 1. HPLC of Fraction 3, Table 2. a) MeOH eluent
b) MeOH/ 1.0 M HOAc/0.005 M PIC-B7 eluent

insensitivity to the change in eluent would be consistent with the low basicity (pK_b = 16) of these compounds; indole derivatives apparently are not extensively protonated in PIC solutions. But basicity differences would not explain the behavior of aniline, for example, compared with that of acridine.

Acridine and aniline have similar pKs, yet while acridine is very responsive to the PIC eluent, giving much longer retention times, aniline actually demonstrates a shorter retention time in the PIC eluent than in methanol. If one examines the nitrogen compounds in Table 3, it becomes apparent that heterocyclic nitrogen compounds (with the exception of the weakly basic indole derivatives) yield much longer retention times in PIC than do anilines or benzyl amines. Apparently the heterocyclic nitrogen compounds form tight ion pairs with the PIC reagents and interact strongly with the C_{18} side-chain. Since aniline has a shorter retention time in PIC than in methanol alone, it looks as though the anilinium ion is so extensively solvated that it does not form an ion pair. The solvated anilinium

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ion, then, being more polar, has less attraction for the C_{18} unit then the neutral form. Differences in solvation between heterocyclic amines and aniline derivatives would seem to reflect steric effects.

Acknowledgement: The authors wish to thank the Institute of Mining and Minerals Research for financial support.

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