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SEPARATION OF PYRIDINE BASES OF COAL TAR LIGHT OIL BY MEANS OF CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The suitability of glass capillary columns coated with polyethylene glycol 400, polyethylene glycol 400 mixed with 2% potassium hydroxide, Apiezon K mixed with Slovamin 20, Amine 220, and Reoplex 400 stationary phases for the separation of pyridine, aniline, and quinoline derivatives was studied. Optimal conditions for the separation of these compounds were determined and the dependence of the chromatographic behaviour of some derivatives of pyridine and aniline on their structures was verified.

INTRODUCTION

A number of authors[1–17] have studied the separation of pyridine, aniline, and quinoline derivatives. Almost all of the published work was carried out on packed columns which allowed some simple mixtures, such as pyridine and picolines or also lutidines, to be separated. The attempts to separate even more complex mixtures[12] were undertaken later. However, they did not lead to an entire separation of all the components.

The first applications of metal capillary columns were published by Grant[15] and later by Grob[16], who verified by means of this technique the suitability of polyethyleneimine and polypropyleneimine phases which had been synthesized and separated an artificial mixture of methyl and ethyl derivatives of pyridine. Later on, Franken *et al.*[17] separated some pyridine derivatives on a glass capillary column with a thin layer of graphitized carbon black, coated with cobalt phthalocyanine, and demonstrated the separation of some aromatic amines by this system. Metal capillary columns were also used by Zeman and Wirotama[18] for the separation of a mixture of some alkyl amines. However, the total separation of the complex mixture of derivatives of pyridine, aniline, and quinoline contained in coal tar light oil has not yet been carried out.

Therefore, the authors tried to find the optimal combination of high-efficiency capillary columns with selective phases, so that these compounds may be separated.

EXPERIMENTAL

The internal surface of the glass capillaries used was modified by cleaning with chromic acid[19] prior to drawing and by subsequent etching in the gaseous phase[20]. The activated glass capillaries were then coated by the dynamic method with solutions of polyethylene glycol 400 (PEG 400), with PEG 400 mixed with 2% KOH, with Apiezon K mixed with Slovamin 20 (octadecylamine + 20 moles of ethylene oxide; AP + SL), with Amine 220 (1-ethanol-2-heptadecenyl-2-isoimidazole; AM), and with Reoplex 400. The efficiencies of the capillary columns prepared and used are shown in Table I.

TABLE I

PROPERTIES OF THE CAPILLARY COLUMNS USED

Phase	*Length (m)*	*Internal diameter (mm)*	*Number of theoretical plates*	*k'*
5% PEG 400 + 2% KOH	40	0.28	64 000	3.85
10% Amine 220	18	0.23	20 000	2.7
8% Reoplex 400	68	0.26	170 000	2.3
4% Apiezon K + Slovamin 20	25	0.27	33 000	3.6
10% PEG 400	99	0.30	300 000	2.4

The raw basic portion of the light oil and all pure picolines, lutidines, collidines, and isoquinoline were obtained from Urx Chemical Plant, Research Institute of Coal Chemistry, Valašské Meziříčí, Czechoslovakia. Some derivatives of aniline were supplied by Lachema N.E. (Brno, Czechoslovakia), and xylidines were provided by Schweizerische Sprengstoff-Fabrik (Dottikon, Switzerland).

Analyses were carried out on a Carlo Erba Fractovap Model C apparatus (Carlo Erba, Milan, Italy) equipped with a flame ionization detector. Nitrogen served as the carrier gas and a nitrogen–hydrogen mixture (3:1) was used in the burner. Maximum volumes of samples amounting to 0.6–0.8 μl were injected into an injection port which was maintained at a temperature of 180–200°. The sample was divided by a splitter in 1:50 ratio.

Operational conditions were selected in such a way that optimum separation of the compounds under study might be obtained. A temperature of 58° was found optimal for the PEG 400, AP + SL, and Reoplex 400 columns and one of 77° for the AM column for the separation of the members of the pyridine series at a linear flow-rate of the carrier gas of 10 cm/sec. For the separation of aromatic amines and quinoline, a temperature of 95° was found optimal with the AP column, of 110° with the PEG 400 + KOH column, of 114° with the Reoplex 400 column, and of 130° with the AM column.

The retention times were measured on all the columns at constant temperature and carrier gas pressure at the column outlet.

RESULTS AND DISCUSSION

Relative retention times are given in Tables II and III. They were calculated from the retention times measured by substracting the dead time determined by injecting methane. The relative volatility, α, and the separation factor, $S = 36[\alpha/(\alpha - 1)]^2$, are given for the pairs that are difficult to separate. The Kováts retention indices that are given in Tables II and III were calculated only for the stationary phases AM and Reoplex 400.

All the columns used showed an efficiency sufficient for the separation of most of the compounds (see Fig. 1). It is obvious from the figure that the capillary columns coated with AM and AP + SL give symmetrical peaks for individual derivatives of pyridine and aniline, while the shapes of the peaks obtained on the columns coated with PEG 400 and Reoplex 400 are still affected by the glass surface. The descending part of the peaks of the compounds studied is terminated by a slight tailing, which increases as the amount of solute increases. The effect of addition of potassium

TABLE II

RELATIVE RETENTION TIMES, *RRT*, RELATIVE VOLATILITIES, α, RETENTION INDICES, I_R, AND SEPARATION FACTORS, *S*, OF PYRIDINE DERIVATIVES MEASURED ON CAPILLARY COLUMNS COATED WITH FOUR DIFFERENT STATIONARY PHASES

Compound	*PEG 400*		*Reoplex 400*			*AP + SL*		*AM*		
	RRT	α	*RRT*	α	I_R	*RRT*	α	*RRT*	α	I_R
Pyridine	0.331		0.283		1086	0.224		0.222		916
2-Methylpyridine	0.413	1.248	0.374	1.322	1124	0.339	1.514	0.357	1.608	980
2,6-Dimethylpyridine	0.490	1.186	0.483	1.291	1159	0.525	1.548	0.500	1.400	1027
2-Ethylpyridine	0.567	1.156	0.582	1.205	1185	0.595	1.038	0.706	1.173	1066
2-Methyl-6-ethylpyridine	0.591	1.042	0.688	1.044	1207	0.740	1.243	0.774	1.096	1077
3-Methylpyridine	0.674	1.140	0.625	1.074	1195	0.545	1.037	0.565	1.130	1040
4-Methylpyridine	0.737	1.091	0.659	1.132	1202	0.573	1.051	0.602	1.066	1047
2,5-Dimethylpyridine	0.827	1.122	0.809	1.175	1228	0.841	1.136	0.860	1.110	1092
2,4-Dimethylpyridine	0.959	1.158	0.891	1.101	1237	0.910	1.082	0.935	1.087	1101
2,3-Dimethylpyridine	1.000	1.042	1.000	1.122	1255	1.000	1.098	1.000	1.070	1110
2,4,6-Trimethylpyridine	1.081	1.081	1.163		1274	1.369	1.369	1.332	1.332	1142
3-Ethylpyridine	1.115	1.031	1.222							
2,3,6-Trimethylpyridine	1.194	1.105	1.252	1.024*	1283	1.461	1.047	1.463	1.059	1148
4-Ethylpyridine	1.239	1.033	1.326							
2,5-Dimethyl-6-isopropylpyridine		1.308	1.059							
2,4-Dimethyl-6-ethylpyridine		1.344	1.028	1.377						
3,5-Dimethylpyridine	1.361	1.012**	1.404		1299	1.394	1.018§	1.381	1.037	1158
2-Methyl-4-ethylpyridine	1.528	1.123								
3,4-Dimethylpyridine	1.998	1.307	1.993		1346	1.883	1.289	1.953	1.334	1193
2,3,5-Trimethylpyridine	2.004	1.003	2.13		1355	2.470	1.311	2.41	1.234	1225
2,4,5-Trimethylpyridine	2.650	1.323	2.48		1376	2.955	1.196	2.94	1.221	1266
2,3,4-Trimethylpyridine	3.030	1.143	3.10		1406	3.610	1.221	3.38	1.150	1266

* $S = 67\,000$.
** $S = 260\,000$.
§ $S = 115\,000$.

TABLE III

RELATIVE RETENTION TIMES, *RRT*, RELATIVE VOLATILITIES, α, AND RETENTION INDICES, I_R, OF ANILINE DERIVATIVES MEASURED ON CAPILLARY COLUMNS COATED WITH FOUR DIFFERENT STATIONARY PHASES

Compound	*PEG 400*		*Reoplex 400*			*AP + SL*		*AM*		
	RRT	α	*RRT*	α	I_R	*RRT*	α	*RRT*	α	I_R
N,N'-Dimethylaniline	0.195		0.266		1371	0.328		0.446		1268
N,N'-Diethylaniline	0.279	1.431	0.405	1.523	1445	0.662	1.127	0.793	1.098	1368
N-Methylaniline	0.493	1.767	0.567	1.400	1506	0.587	1.022	0.772	1.201	1352
Aniline	0.660	1.338	0.628	1.108	1525	0.574	1.750	0.601	1.347	1320
2-Methylaniline	0.799	1.211	0.829	1.320	1576	0.815	1.232	0.873	1.101	1385
4-Methylaniline	0.898	1.124	0.890	1.073	1589	0.897	1.104	0.927	1.061	1395
3-Methylaniline	1.000	1.113	1.000	1.124	1610	1.000	1.111	1.000	1.079	1408
2,5-Dimethylaniline	1.125	1.125	1.281	1.281	1653	1.443	1.443	1.428	1.428	1470
3,5-Dimethylaniline	1.448	1.288	1.588	1.097	1691	1.773	1.032	1.666	1.077	1497
Quinoline	1.458	1.007	1.406	1.130	1670	1.717	1.190	2.010	1.166	1530
3,4-Dimethylaniline	1.513	1.037	1.774	1.071	1711	2.014	1.136	1.867	1.121	1517
Isoquinoline	1.714	1.133	1.700	1.043	1703	2.100	1.043	2.490	1.238	1567

hydroxide on the improvement of the shapes of the peaks of pyridine derivatives and on the selectivity of the separation process was also studied. The capillary column to which KOH was added was found to have the same behaviour towards the compounds under study as had the column coated with pure PEG 400.

The selectivity of the separation systems used is obvious from Fig. 2. The stationary phases PEG 400 and Reoplex 400 show a similar behaviour. Positions of 3- and 4-methylpyridines, 2-ethylpyridine, 3-ethylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, and all the collidines under study are determined in the spectrum shown in Fig. 2 by the formation of hydrogen bonds. Different selectivity is shown by the other two columns —AM and AP + SL— on which individual compounds are mostly eluted according to their boiling points. Thus a remarkable shift towards higher relative retention values appears with ethyl- and trimethylpyridines. Picolines, on the other hand, are eluted relatively earlier than on the two previous phases.

Similar effects can be noted with both pairs of stationary phases when derivatives of aniline, quinoline and isoquinoline are separated. N,N'-Dimethylaniline is markedly shifted towards toluidines and quinoline and isoquinoline behind xylidines on the two phases that contain nitrogen. Somewhat different behaviour is shown by aniline; its relative retention values are lower on the nitrogen-containing phases than on the other two columns.

When studied in further detail, the behaviour of individual members of the homologous series shows the dependences that are known from work on packed columns. For example, the compounds that contain functional groups in the vicinity of a nitrogen atom are eluted preferentially on such phases that enable a hydrogen bond to be formed with a heterogeneous atom of the molecule. If the possibility of the interaction of a hydroxyl hydrogen does not exist, a shift towards higher relative values (Fig. 2) according to their boiling points appears in the chromatogram with some compounds, *e.g.*, with 2-methyl-6-ethylpyridine or 2,4,6- and 2,3,6-trimethylpyridines

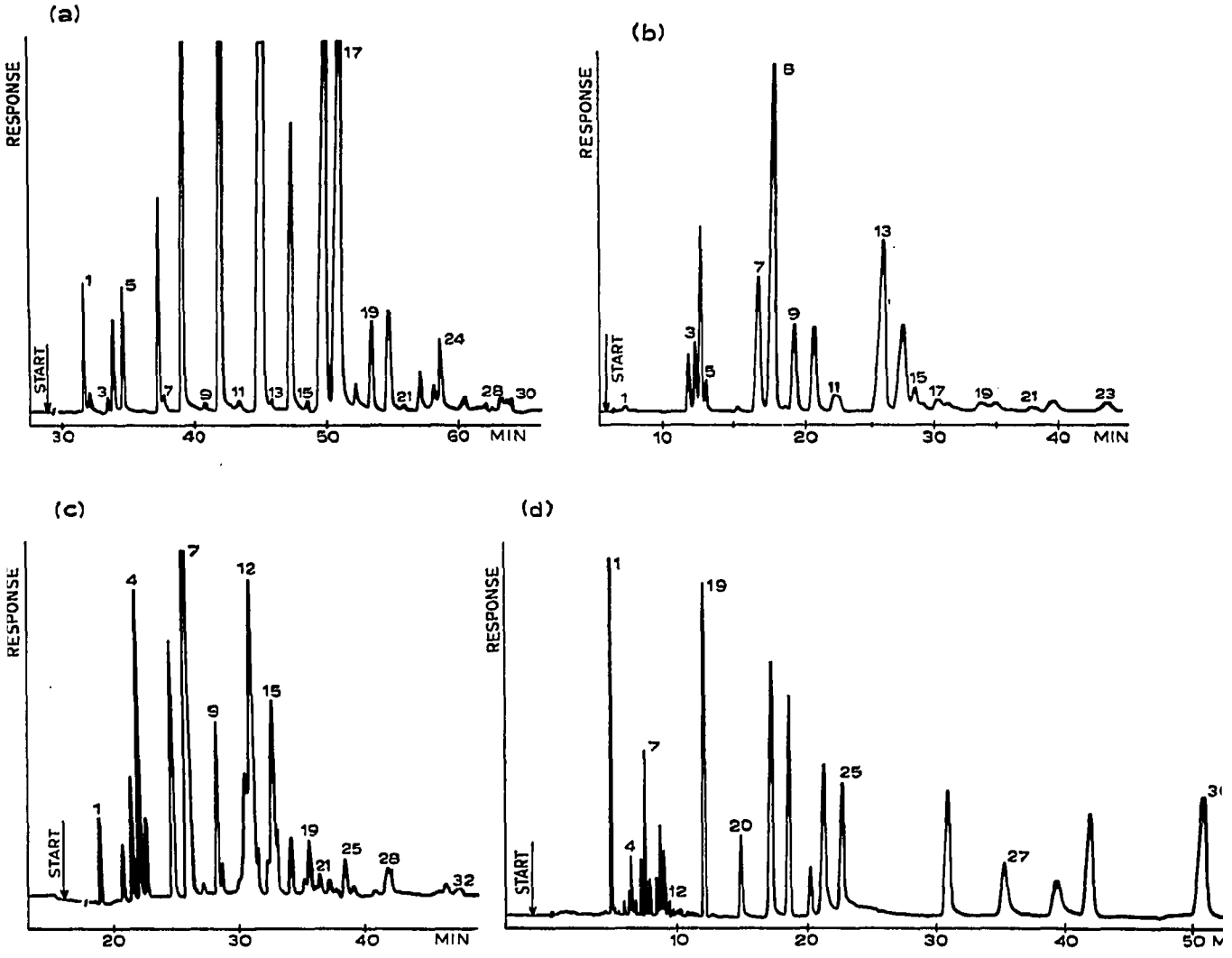

Fig. 1. (a) Chromatogram of a mixture of pyridine derivatives on a capillary column coated with PEG 400 (T_c = 80°). 1 = 2,6-diMePy, 4 = 2-EtPy, 5 = 2-Me-6-EtPy, 6 = 3-MePy, 8 = 4-MePy, 10 = 2,5-diMePy, 12 = 2,4-diMePy, 14 = 2,3-diMePy, 16 = 2,4,6-triMePy, 17 = 2,3,6-triMePy, 18 = 4-EtPy, 19 = 4-Me-2-EtPy, 24 = 3,5-diMePy. (b) Chromatogram of a mixture of pyridine derivatives on a capillary column coated with AP + SL (T_c = 58°). 1 = Py, 2 = 2,6-diMePy, 3 = 3-MePy, 4 = 4-MePy, 5 = 2-EtPy, 6 = 2-Me-6-EtPy, 7 = 2,5-diMePy, 8 = 2,4-diMePy, 9 = 2,3-diMePy, 10 = 3-EtPy, 11 = 4-EtPy, 13 = 2,4,6-triMePy, 14 = 2,3,6-triMePy, 20 = 3,4-diMePy. (c) Chromatogram of a mixture of pyridine derivatives on a capillary column coated with Reoplex 400 (T_c = 58°). 1 = 2,6-diMePy, 2 = 2-EtPy, 3 = 3-MePy, 4 = 4-MePy, 5 = 2-Me-6-EtPy, 6 = 2,5-diMePy, 7 = 2,4-diMePy, 9 = 2,3-diMePy, 12 = 2,4,6-triMePy, 14 = 3-EtPy, 15 = 2,3,6-triMePy, 16 = 4-EtPy, 19 = 3,5-diMePy, 31 = 3,4-diMePy. (d) Chromatogram of a mixture of pyridine and aniline derivatives on a capillary column coated with AM (T_c = 130°). 1 = Py, 2 = 2,6-diMePy, 3 = 3-MePy, 4 = 4-MePy, 6 = 2,5-diMePy, 7 = 2,4-diMePy, 10 = 2,4,6-triMePy, 11 = 2,3,6-triMePy, 19 = N,N'-diMeA, 20 = N-MeA, 21 = N,N'-diEtA, 22 = A, 23 = 2-MeA, 24 = 4-MeA, 25 = 3-MeA, 26 = 2,5-diMeA, 27 = 3,5-diMeA, 28 = 3,4-diMeA, 29 = quinoline, 30 = isoquinoline. (Me = methyl, Et = ethyl, Py = pyridine, and A = aniline.)

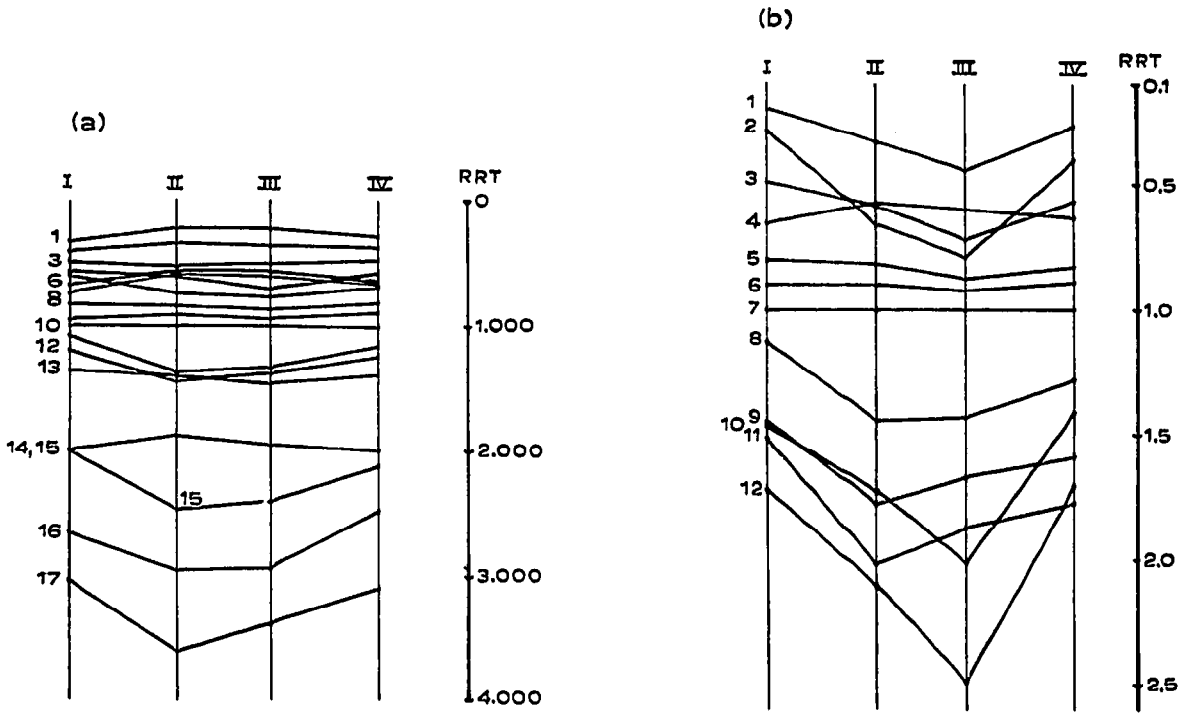

Fig. 2. **(a)** A graph showing the positions of the relative retention times on all the phases used. I = PEG 400, II = AP + SL, III = AM, IV = Reoplex 400. 1 = Py, 2 = 2-MePy, 3 = 2,6-diMePy, 4 = 2-EtPy, 5 = 2-Me-6-EtPy, 6 = 3-MePy, 7 = 4-MePy, 8 = 2,5-diMePy, 9 = 2,4-diMePy, 10 = 2,3-diMePy, 11 = 2,4,6-triMePy, 12 = 2,3,6-triMePy, 13 = 3,5-diMePy, 14 = 3,4-diMePy, 15 = 2,3,5-triMePy, 16 = 2,4,5-triMePy, 17 = 2,3,4-triMePy. **(b)** A graph showing the positions of the relative retention times of aniline and quinoline derivatives on all the phases used. 1 = N,N'-diMeA, 2 = N,N'-diEtA, 3 = N-MeA, 4 = A, 5 = 2-MeA, 6 = 4-MeA, 7 = 3-MeA, 8 = 2,5-diMeA, 9 = 3,5-diMeA, 10 = quinoline, 11 = 3,4-diMeA, 12 = isoquinoline.

and other trimethyl derivatives. The character of the interaction is also demonstrated by the retention indices shown graphically in Fig. 3. The affinity of alkanes is obviously higher towards AM than towards Reoplex 400 and the positions of individual members of the pyridine and aniline series are thus shifted by approximately 150 index units towards greater values on Reoplex 400 than on AM. The greater affinity of hydrocarbons towards the latter stationary phase is caused by the long hydrocarbon chain in this molecule in which —as in 1-ethanol-2-heptadecenyl-2-isoimidazole— according to the character of the solute, either the polar heterocyclic part (as is the case here) or the hydrocarbon chain show decisive effects. The influence of the constitution of this stationary phase also appeared by a higher optimum temperature being necessary for the separation of all the compounds under study.

All the stationary phases used appeared to be nearly equivalent. The use of AM and Reoplex 400 provides certain advantages for the separation of aromatic amines, as the lowest relative volatilities measured for Reoplex 400, 1.043, and AM, 1.062, show that a column having an efficiency of 40,000 theoretical plates for $k' = 2$ is sufficient for the complete separation of all the components studied. A Reoplex 400

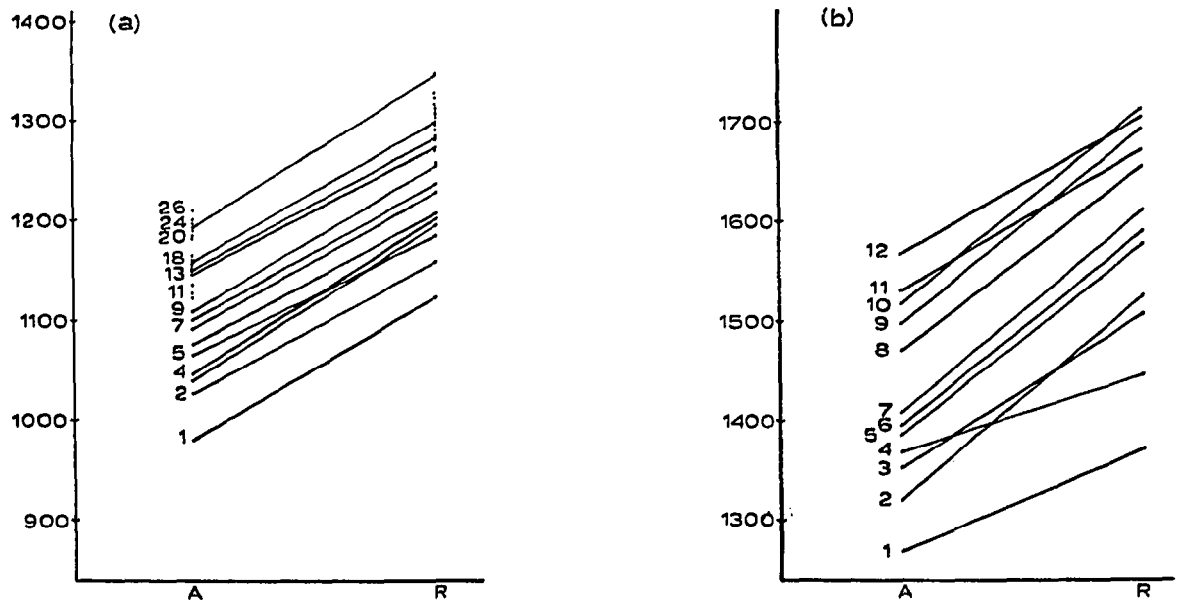

Fig. 3. (a) A graph showing the positions of the retention indices of pyridine derivatives on Reoplex 400 and AM. The sequence of compounds is identical to that in Fig. 2a. (b) A graph showing the positions of the retention indices of aniline derivatives on Reoplex 400 and AM. The sequence of compounds is identical to that in Fig. 2b.

column seems to be most advantageous for the separation of all the pyridine derivatives due to its high selectivity, universal applicability, ease of preparation of the capillary columns and high resolution. Equally wide applicability and ease of preparation

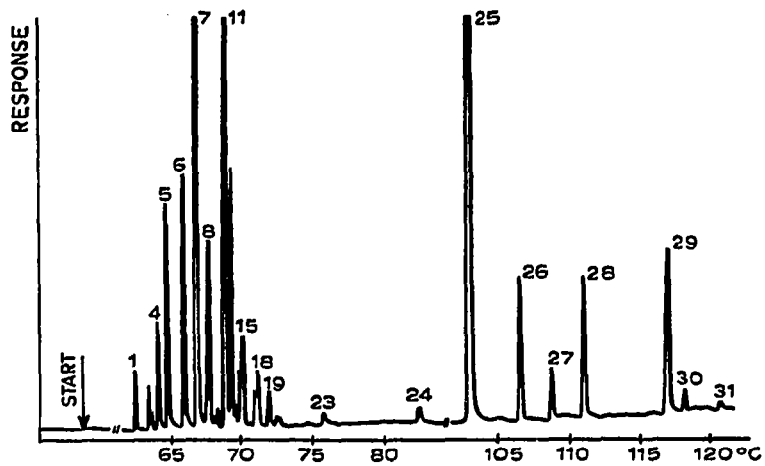

Fig. 4. Chromatogram of pyridine and aniline derivatives on a capillary column coated with PEG 400, temperature programme 1.25°/min. 1 = 2,6-diMePy, 2 = 2-EtPy, 4 = 3-MePy, 5 = 4-MePy, 6 = 2,5-diMePy, 7 = 2,4-diMePy, 8 = 2,3-diMePy, 11 = 2,4,6-triMePy, 12 = 2,3,6-triMePy, 15 = 4-EtPy, 18 = 2,4-diMe-6-EtPy, 19 = 3,5-diMePy, 23 = 3,4-diMePy, 24 = benzonitrile, 25 = A, 26 = 2-MeA, 27 = 4-MeA, 28 = 3-MeA, 29 = quinoline, 31 = isoquinoline.

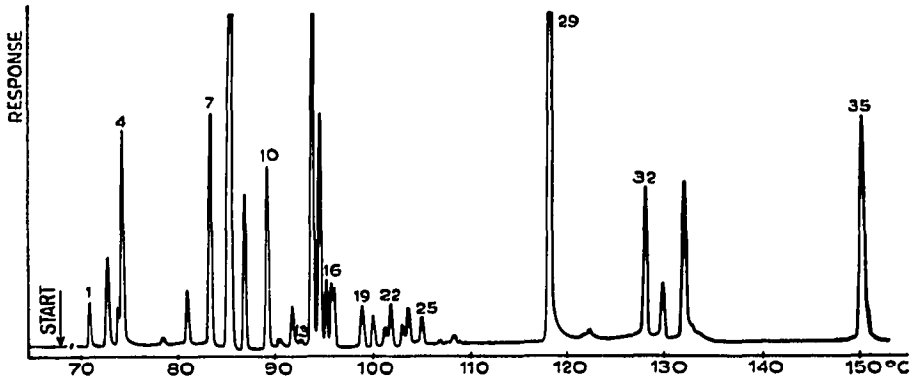

Fig. 5. Chromatogram of pyridine and aniline derivatives on a capillary column coated with AM, temperature programme 1.25°/min. 1 = 2,6-diMePy, 2 = 3-MePy, 4 = 4-MePy, 5 = 2-EtPy, 6 = 2-Me-6-EtPy, 7 = 2,5-diMePy, 8 = 2,4-diMePy, 9 = 2,3-diMePy, 10 = 3-EtPy, 12 = 4-EtPy, 14 = 2,4,6-triMePy, 15 = 2,3,6-triMePy, 19 = 3,4-diMePy, 25 = 2,3,5-triMePy, 29 = A, 32 = 2-MeA, 33 = 4-MeA, 34 = 3-MeA, 35 = quinoline.

apply to capillary columns coated with AP + SL. The stationary phase PEG 400 + KOH can be used to advantage for the separation of basic organic compounds, as a free hydroxyl group is present that can react with other groups in substances (such as phenols etc.) that are part of some natural mixtures.

CONCLUSION

The use of capillary columns gives detailed information about the composition of basic compounds from coal tar oils under mild operational conditions. It allows the use of strongly polar stationary phases, which have lower limiting operational temperatures, and all the present compounds could be separated perfectly. The technique of temperature programming can be used to advantage in order to separate the complex spectrum of pyridine, aniline, and quinoline derivatives entirely, as shown in Figs. 4 and 5.

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