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Note

Rubidium benzenesulphonate —an efficient stationary phase for the separation of close-boiling organic isomers by gas chromatography

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The similarity of the physical and chemical properties of close-boiling aromatic and heterocyclic isomers poses serious problems in their separation. Techniques such as distillation, liquid chromatography, thin-layer chromatography and counter-current distribution frequently suffer from long analysis times, poor resolution and complexity of operation. Gas chromatography (GC) promises to be a fast, simple and efficient technique for this purpose and has been studied by various workers.

Various stationary phases have been used for the separation of close-boiling isomeric pairs such as *m*- and *p*-xylenes[1–3], *m*- and *p*-dichlorobenzenes[4,5], *m*- and *p*-tolualdehydes[6], *m*- and *p*-tolunitriles[7], 1- and 2-methylnaphthalenes[8], 3- and 4-methylpyridines[9–11], 2,4- and 2,5-dimethylpyridines[10,12], quinoline and isoquinoline[11,13], *m*- and *p*-toluidines[14], *m*- and *p*-cresols[15–17] and 2,4- and 2,5-xylenols[15,18]. However, no work appears to have been published on the GC separation of 3- and 4-cyanopyridines, 3- and 4-acetylpyridines, *m*- and *p*-dibromobenzenes or *m*- and *p*-bromobenzaldehydes. Even Bentone 34 (occasionally modified with a suitable liquid phase), which had been tried for the resolution of the largest number of isomeric pairs, was not universally satisfactory in terms of resolution, efficiency, peak symmetry, elution time, etc.

Rubidium benzenesulphonate (RBS) has been found to be an efficient stationary phase for the complete separation of 2,4- and 2,5-xylenols[19–21], an isomeric pair that had hitherto defied all attempts at a satisfactory separation by other workers. RBS was also found equally suitable for the separation of 2,4- and 2,5-dimethyl pyridines[19] and *m*- and *p*-cresols[19,21]. This paper considers the potential of RBS for the separation of other close-boiling isomers.

EXPERIMENTAL

The close-boiling isomeric pairs used in this study were chosen according to their availability. Whenever possible, pure chemicals were used; impure materials were purified by distillation or recrystallization. Two acidic, six basic and seven neutral isomeric pairs were studied (Table I).

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Experiments were carried out with a Perkin-Elmer 810 gas chromatograph fitted with a flame-ionization detector and a 1-mV Honeywell recorder. Stainless-steel columns (6 ft. × 1/8 in. O.D.) were used with nitrogen as the carrier gas (30 ml/min). The packing materials were prepared by slurrying the stationary phase, dissolved in a water–methanol mixture, with support, followed by removal of the solvent by heating.

Two columns were prepared as follows: A, 40% RBS + 2% Carbowax 20M + 2% ascorbic acid on Chromosorb P NAW (80–100 mesh); B, 40% RBS + 2% Carbowax 20M on Chromosorb P NAW (80–100 mesh). Column A was used for phenolic isomers and column B was used for the other isomers. Column A was activated at 175°C for 2 h under a flow of nitrogen. The temperature of activation was maintained below 181°C, as ascorbic acid decomposes above this temperature. Column B was similarly activated at 200°C for 3 h. The sample size was about 0.2 μl.

The separation factor (SF) was calculated using the following equation

$$\mathrm{SF} = \frac{d_{R_a}}{d_{R_b}} \tag{1}$$

where, d_{R_a} and d_{R_b} are retention distances of components a and b, respectively (see Table I).

The general eqn. 2 for determining the resolution (R) was not found suitable for partially resolved peaks, particularly for studying the decrease in resolution.

$$R_{i,j} = 1.18 \cdot \frac{d_{R_j} - d_{R_i}}{W_{h/2,i} + W_{h/2,j}} \tag{2}$$

where $W_{h/2,i}$ and $W_{h/2,j}$ denote peak width at half-height for compounds i and j, respectively. The following equation[22] was ultimately used throughout for determining the resolution:

$$R = \frac{f}{g} \cdot 100 \tag{3}$$

where g is the length of the perpendicular drawn on the baseline through the lowest point of the trough between two resolved peaks up to the line joining the uppermost points of the two peaks, and f is the portion of the perpendicular from the lowest point of the trough to the point of intersection with the line joining the uppermost points of the two peaks. For two completely separated peaks the resolution is 100.

RESULTS AND DISCUSSION

Table I presents the resolutions and other characteristics for the isomeric pairs studied on the activated column. No universal and unique parameter could be identified that governs the retention behaviour of all of the isomeric pairs studied. Probably it is the concerted effect of ligand (lone electron pairs of the isomers)–Lewis acid (Rb^+ ion) interactions, hydrogen bonding, dipole–dipole interactions, etc., with varying contributions that determine the elution characteristics. It is worth mentioning that the separation factor (2.02) and the extent of separation (Fig. 1) for quinoline and isoquinoline achieved in this work are probably the highest among those reported so

far. The elution times of the completely separated pairs such as *m*- and *p*-dichlorobenzenes (Fig. 2) and *m*- and *p*-dibromobenzenes are also the shortest reported so far.

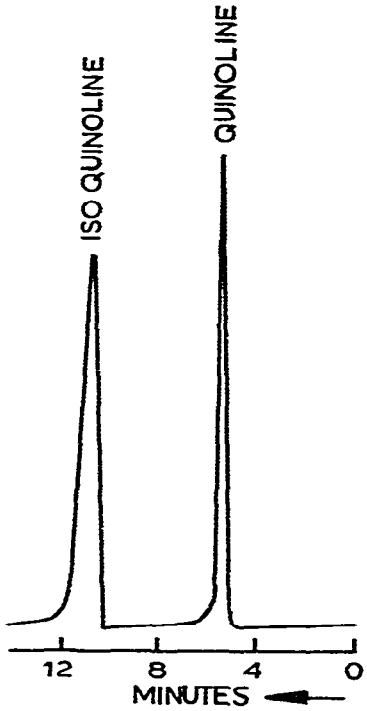
Activation plays a crucial role in enhancing the effectiveness of the stationary phase. It has been observed that significant resolution is possible only when the column is activated[19]. In this work, the decrease in resolution as a function of time, when an activated column was subjected to prolonged use, was studied. Necessarily,

TABLE I

RESOLUTIONS AND OTHER CHARACTERISTICS OF DIFFERENT ISOMERIC PAIRS

Isomers	*Boiling point (°C)*	*Column temperature (°C)*	*Column*	*SF*	*R (%)*	*Time of elution (min)*
(a) *p*-Xylene (b) *m*-Xylene	138.0 139.0	80	B	0.79	88.5	11
(a) 4-Methylpyridine (b) 3-Methylpyridine	145.4 144.0	110	B	1.20	91.5	10
(a) 2,4-Dimethylpyridine (b) 2,5-Dimethylpyridine	158.0 157.0	130	B	1.30	97.5	6
(a) *p*-Toluidine (b) *m*-Toluidine	200.5 203.3	130	B	1.21	94.0	27
(a) *p*-Tolualdehyde (b) *m*-Tolualdehyde	204.0 199.0	145	B	1.17	87.2	18
(a) 1-Methylnaphthalene (b) 2-Methylnaphthalene	245.0 241.0	150	B	1.25	97.0	9
(a) *p*-Dichlorobenzene (b) *m*-Dichlorobenzene	174.0 172.0	150	B	1.47	100.0	4
(a) *p*-Tolunitrile (b) *m*-Tolunitrile	217.0 210.0	150	B	0.83	97.0	17
(a) *p*-Dibromobenzene (b) *m*-Dibromobenzene	219.0 219.5	170	B	1.27	100.0	5
(a) *p*-Bromobenzaldehyde (b) *m*-Bromobenzaldehyde	Subl. 233.0	174	B	0.86	96.5	15
(a) 4-Acetylpyridine (b) 3-Acetylpyridine	214.0 220.0	175	B	0.80	96.5	11
(a) Isoquinoline (b) Quinoline	242.0 238.0	175	B	2.02	100.0*	12
(a) 4-Cyanopyridine (b) 3-Cyanopyridine	Subl. 240.0	180	B	0.80	97.0	8
(a) *p*-Cresol (b) *m*-Cresol	201.0 202.0	150	A	1.21	95.0	29
(a) 2,4-Xylenol (b) 2,5-Xylenol	211.3 211.5	160	A	1.44	100*	14

* Peaks are widely separated.



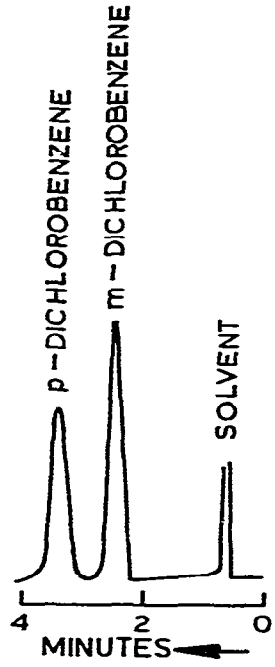


Fig. 1. Separation of quinoline and isoquinoline on column B at 175°C.

Fig. 2. Separation of *m*- and *p*-dichlorobenzenes on column B at 150°C.

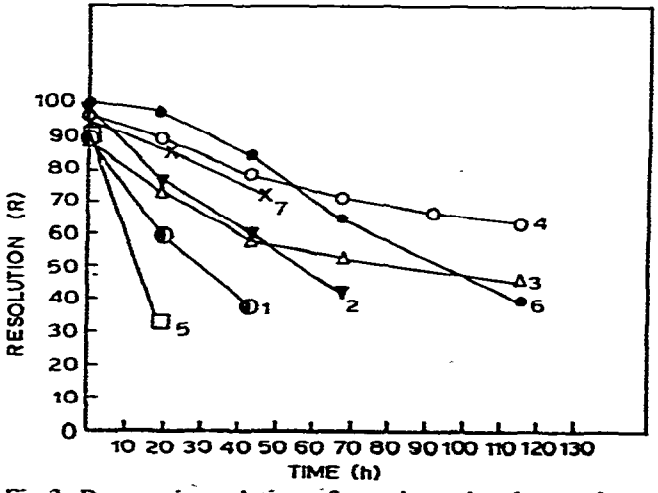


Fig. 3. Decrease in resolutions of seven isomeric pairs on columns A and B. 1 = *m*- and *p*-xylenes; 2 = 2,4- and 2,5-lutidines; 3 = *m*- and *p*-tolualdehydes; 4 = 1- and 2-methylnaphthalenes; 5 = *m*- and *p*-toluidines and 6 = *m*- and *p*-dichlorobenzenes on column B; 7 = *m*- and *p*-cresols on column A.

studies were conducted only on those isomeric pairs for which the column temperatures were low enough to preclude any *in situ* reactivation of the columns. Seven isomeric pairs were chosen for this purpose. Studies on the corresponding resolutions were determined at an interval of 20–24 h. Fig. 3 shows the gradual deactivation behaviour of columns A and B, activated (once only) at 175°C for 2 h and at 200°C for 3 h, respectively. Column deactivation and the decrease in resolution can be seen to be the fastest for *m*- and *p*-toluidines and the slowest for 1- and 2-methylnaphthalenes.

CONCLUSION

Fifteen close-boiling isomeric pairs were efficiently separated on a single stationary phase (RBS modified with Carbowax 20M, with or without ascorbic acid) probably for the first time. Some of the separations were highly satisfactory. Column deactivation studies were carried out in order to obtain an idea about the column life for specific isomeric pairs.

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