Journal of Chromatography, 115 (1975) 250–255
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CHROM. 8577

Note

Rubidium benzenesulphonate as a stationary phase in the gas chromatography and separation of isomers of phenols and pyridine bases

ASIT BHATTACHARJEE and A. BHAUMIK
Central Fuel Research Institute, P.O. FRI, Dhanbad, Bihar (India)
(First received November 13th, 1974; revised manuscript received July 4th, 1975)

The selectivity of rubidium benzenesulphonate as a stationary phase in gas–solid chromatography (GSC) had been reported in a previous paper[1], and it was found that tailing of peaks was the main disadvantage for quantitative work. In the present study, peak tailing has been eliminated and isomers such as cresols, lutidines and picolines have been separated. The mechanism of the retention of phenols has been found to apply also to pyridine bases.

EXPERIMENTAL

Equipment

A Perkin-Elmer 810 gas chromatograph fitted with a flame ionization detector and a Honeywell I-MV recorder was used. Experiments were carried out in stainless-steel columns (6 ft. × 1/8 in. O.D.) with nitrogen as the carrier gas (flow-rate 30 ml/min). The packing materials for the following two columns were prepared by slurrying the stationary phases with the support in a water–methanol mixture followed by removal of the solvent by heating:

Column A: 40% rubidium benzenesulphonate + 2% Carbowax 20M + 2% ascorbic acid on Chromosorb P (60–80 mesh).

Column B: 40% rubidium benzenesulphonate + 2% Carbowax 20M on Chromosorb P (60–80 mesh).

The columns were pre-conditioned at 120° for 1 h under a flow of nitrogen. As there was no separation of β- and γ-picolines or 2,4- and 2,5-lutidines on column B, or *m*- and *p*-cresols on column A, at 120°, the columns were further conditioned at 160° for 1 h. This activation of the columns enabled the separation of the above pairs to be achieved at 120°. The results reported in this paper were obtained on an activated column.

Chemicals

The following pure-grade chemicals were used for quantitative work: 2,4-xylenol and 2,5-xylenol (BDH, Poole, Great Britain); 2,4-lutidine (Riedel, Hannover, G.F.R.: dried over sodium hydroxide pellets); 2,5-lutidine (L. Light, Colnbrook, Great Britain; dried over sodium hydroxide pellets); *o*-cresol (E. Merck, Darmstadt, G.F.R.); *m*-cresol (BDH); *p*-cresol (Naarden, Naarden, The Netherlands); and ascorbic acid (BDH).

RESULTS AND DISCUSSION

In a previous study[1], it was suggested that some sort of clathration holes or channels[2,3] were present in rubidium benzenesulphonate crystals and that these holes or channels collapsed as the temperature of the column was increased to 160°. For the first time, differential thermal analysis (DTA) on rubidium benzenesulphonate clearly showed a third endothermic change at 160° (Fig. 1). As there was no weight loss at that temperature, the change can be attributed to some structural rearrangement caused, in this instance, by the collapse of clathration holes. The first and second endothermic changes were due to the expulsion of moisture whereas the fourth was due to its melting.

Phenols

The analysis of phenols on a packed column by GC is difficult, firstly owing to the tailing of peaks caused by non-linear adsorption on the solid support and secondly to the non-availability of a suitable stationary phase for the complete separation of isomers such as cresols and xylenols, particularly 2,4- and 2,5-xylenols. Several workers[4–7] have reported the use of different stationary phases, none of which, however, resulted in the complete separation of all the cresols or 2,4- and 2,5-xylenols. Peak symmetry has been achieved in some instances[5,8,9] by converting the phenols into their alkyl or silyl ethers. In the present work, peak tailing has been successfully eliminated by using 2% Carbowax 20M and 2% ascorbic acid together with 40% rubidium benzenesulphonate (column A). Surprisingly, Carbowax 20M and ascorbic

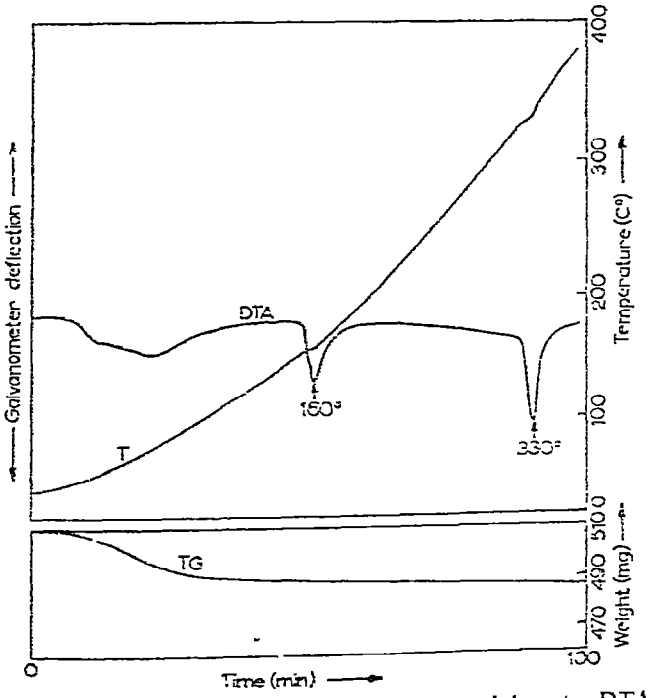
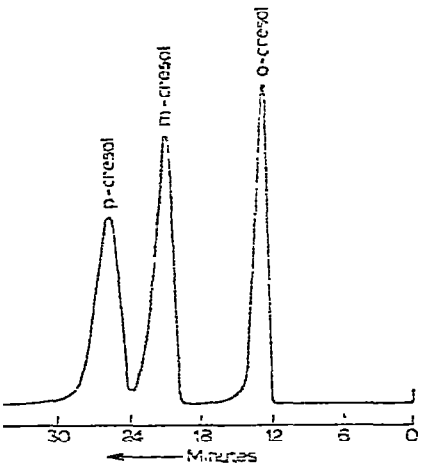


Fig. 1. Derivatogram of rubidium benzenesulphonate. DTA = Differential thermal analysis; T = temperature; TG = thermogravimetry.



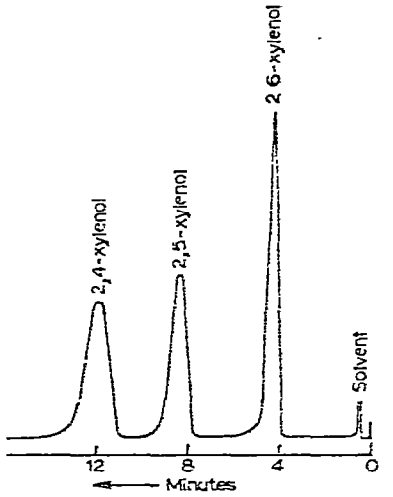


Fig. 2. Separation of *o*-, *m*- and *p*-cresols at 135° on column A.
Fig. 3. Separation of 2,6-, 2,5- and 2,4-xylenols at 145° on column A.

acid, when used individually with rubidium benzenesulphonate, failed to eliminate tailing. Figs. 2 and 3 show the chromatograms of *o*-, *m*- and *p*-cresols and 2,6-, 2,5- and 2,4-xylenols, respectively. The complete separation of these two groups of isomers on a single stationary phase has not been reported elsewhere. Table I gives the relative

TABLE I

RELATIVE RETENTION TIMES OF PHENOLS ON COLUMN A AT 145°

Compound	*Boiling point (°C)*	*Relative retention time*
Phenol	181.7	1.00
o-Cresol	190.8	0.80
2,6-Xylenol	200.6	0.52
p-Cresol	201.5	1.50
m-Cresol	202.1	1.26
2,4-Xylenol	211.3	1.44
2,5-Xylenol	211.5	1.00
2,3-Xylenol	217.1	1.37
3,5-Xylenol	221.0	1.69
3,4-Xylenol	227.0	2.14
2,6-Di-*tert.*-butylphenol	—	0.21
Anisole	154.0	0.10

TABLE II

ANALYSIS OF SYNTHETIC MIXTURES OF CRESOLS ON COLUMN A AT 135°

Compound	*Mixture I (% w/w)*		*Mixture II (% w/w)*		*Mixture III (% w/w)*	
	Found	*Present*	*Found*	*Present*	*Found*	*Present*
o-Cresol	28.8	29.0	35.4	35.3	31.6	31.2
m-Cresol	37.7	37.7	11.4	11.9	51.0	51.5
p-Cresol	33.5	33.3	53.2	52.8	17.4	17.3

TABLE III

ANALYSIS OF SYNTHETIC MIXTURES OF XYLENOLS ON COLUMN A AT 145°

Compound	*Mixture I (% w/w)*		*Mixture II (% w/w)*		*Mixture III (% w/w)*	
	Found	*Present*	*Found*	*Present*	*Found*	*Present*
2,6-Xylenol	35.9	36.0	25.7	25.6	33.7	33.4
2,5-Xylenol	29.2	28.9	12.6	12.0	54.3	53.3
2,4-Xylenol	34.9	35.1	61.7	62.4	12.0	13.3

retentions of some phenols, the elution of which follow the mechanism already reported[1]. As several mixtures of cresols and xylenols have been successfully determined on this column (Tables II and III), the prospect seems good for its use for analytical purposes.

Pyridines

As with phenols, peak tailing of pyridine bases on a rubidium benzenesulphonate column was a major disadvantage for quantitative work. Carbowax 20M has been found to be effective in eliminating tailing[10] of hydrocarbons in GSC. We used this procedure in order to achieve symmetrical peaks for pyridine bases on column B. Fig. 4 shows the chromatogram of 2,6-, 2,5- and 2,4-lutidines, indicating a complete separation. Several stationary phases[11–14] have been used for the separation of pyridine bases, but none achieved the complete separation of 2,4- and 2,5-lutidines. The present stationary phase has been found to be most suitable for the separation of this pair of isomers, the separation factor for which $\alpha = 1.26$ is so far the highest reported. β- and γ-picolines are not resolved completely on this phase. The relative retention times of some pyridine bases are presented in Table IV. The elution of pyridine bases

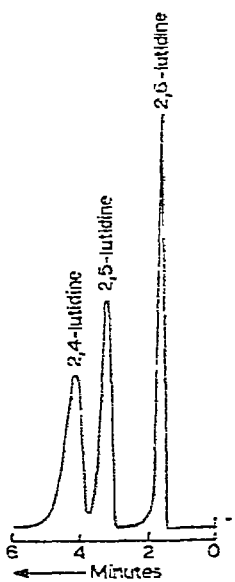


Fig. 4. Separation of 2,6-, 2,5- and 2,4-lutidines at 115° on column B.

TABLE IV

RELATIVE RETENTION TIMES OF PYRIDINE BASES ON COLUMN B AT 115°

Compound	Boiling point (°C)	Relative retention time
Pyridine	115.3	1.00
2-Picoline	129.4	0.95
2,6-Lutidine	144.0	0.87
3-Picoline	144.1	1.83
4-Picoline	145.4	2.10
2,5-Lutidine	157.0	1.70
2,4-Lutidine	157.9	2.13
4-Ethylpyridine	167.7	3.14
2-Methyl-5-ethylpyridine	178.3	1.75

TABLE V

ANALYSIS OF SYNTHETIC MIXTURES OF LUTIDINES ON COLUMN B AT 115°

Compound	Mixture I (% w/w)		Mixture II (% w/w)		Mixture III (% w/w)	
	Found	Present	Found	Present	Found	Present
2,6-Lutidine	32.4	33.4	45.6	45.8	34.9	35.0
2,5-Lutidine	33.3	34.2	3.2	2.9	49.5	50.4
2,4-Lutidine	34.3	32.4	51.2	51.3	15.6	14.6

was found to be governed by the interaction of the metal ion and the lone pair of electrons on the nitrogen atom. Three synthetic mixtures of lutidines were analyzed on this column and the results were found to be satisfactory (Table V).

In general, both columns A and B deteriorate after a few days, as shown by the loss of resolution of the isomers examined. The original performance of the column can be restored merely by activation of the column at 160° for about 1 h under a flow of nitrogen. The fact that the efficiency of the columns increases with activation may be due to "frozen equilibrium"[15], which occurs with some alkali metal salts. The increase in the number of accessible Rb^+ ions interacting with the lone pair of electrons on the nitrogen or oxygen atom at the activation temperature remains unchanged for a considerable time even at lower column temperatures, thereby effecting the separation of the isomers.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. S. N. Mukherjee for the DTA experiment and to Dr. C. S. B. Nair for his constant encouragement and helpful suggestions.

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