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Note

Gas chromatography of low-boiling pyridine bases

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The characterization of the low-boiling tar base fraction, the only potential natural source of pyridines, is a difficult problem in gas chromatography with respect to the satisfactory separations of pyridine and 2-methylpyridine and of 3- and 4-methylpyridine, etc., as well as the time of elution of the bases. Several stationary phases, e.g., glycerol¹⁻⁴, diglycerol⁵, Bentone 34 + DC 710⁶, polyphenyl ether⁷, PEG 400⁸, Tide⁹ and Tween 20¹⁰, have been used for the analysis of pyridines. The major disadvantages of the above phases are long analysis times, unsatisfactory separations of pyridine and 2-methylpyridine and of 3- and 4-methylpyridine, peak tailing and column deterioration. The time of elution of pyridines on the above phases varies from 10 to 50 min. The most widely used stationary phase, glycerol, also suffers from evaporation loss, leading to column deterioration.

In this study attempts have been made to develop a stationary phase that overcomes these difficulties. In this respect, diglycerol, which has a low vapour pressure⁵ at the column temperature, has been found in this laboratory to be an ideal stationary phase after modification with Bentone 34. Studies have been made of the separation and analysis of pyridine, 2-, 3- and 4-methylpyridine and 2,6-dimethylpyridine, which are present in the tar base fraction boiling up to 146°C. The characterization of this fraction is very important because the more valuable constituents such as pyridine and methylpyridines, which are used as starting materials for the production of dyestuffs, drugs, agrochemicals, etc., occur in this boiling range.

EXPERIMENTAL

Experiments were carried out in a Perkin-Elmer 810 gas chromatograph fitted with a flame-ionization detector and a 1-mV Honeywell recorder. Nitrogen was used as the carrier gas (flow-rate 20 ml/min). The following three columns (6 ft. × $\frac{1}{8}$ in. O.D., stainless steel) were prepared using a conventional method: I, 30% glycerol on Chromosorb P (80-100 mesh); II, 30% diglycerol on Chromosorb P (80-100 mesh); and III, 30% diglycerol + 2% Bentone 34 on Chromosorb P (80-100 mesh).

Pyridine, 2-, 3- and 4-methylpyridine and 2,6-dimethylpyridine were of pure grade and the chemicals were dried over potassium hydroxide pellets.

The resolution ($R_{i,j}$) of a pair of compounds was calculated from the following equation¹¹:

$$R_{i,j} = 100 \left[\frac{f}{g} + \frac{\Delta d}{2(W_{h/2,i} + W_{h/2,j})} \right]$$

where g = length of the perpendicular drawn from the baseline through the minimum of the valley between two partially resolved peaks to the line the two peak maxima, f = portion of the perpendicular between the line joining the peak maxima and the minimum of the valley, $W_{h/2,i}$ and $W_{h/2,j}$ = width at half-height of peaks i and j , respectively, and Δd = portion of the baseline intercepted between two peaks.

RESULTS AND DISCUSSION

Table I compares the elution characteristics of the five pyridine bases on the three columns. The time of elution of all the bases was minimal on column III. Such

TABLE I
RELATIVE RETENTION TIMES OF PYRIDINES ON DIFFERENT STATIONARY PHASES

Compound	Boiling point (°C)	Relative retention time		
		Column I at 115°C	Column II at 135°C	Column III at 135°C
Pyridine	115.3	1.00	1.00	1.00
2-Methylpyridine	129.4	0.84	0.89	0.86
2,6-Dimethylpyridine	144.0	0.61	0.67	0.67
3-Methylpyridine	144.1	1.39	1.41	1.37
4-Methylpyridine	145.4	1.65	1.63	1.58

TABLE II
RESOLUTION OF PYRIDINE BASES ON DIFFERENT COLUMNS

Calculated from the chromatogram of the tar base fraction (initial boiling point 146°C).

Compound	Resolution ($R_{i,j}$)		
	Column I	Column II	Column III
2,6-Dimethylpyridine	97.5	98.8	100.0
2-Methylpyridine	90.0	79.0	92.0
Pyridine	98.2	100.0	166.0
3-Methylpyridine	87.0	85.5	91.5
4-Methylpyridine			
Time of elution (min)	9	8	7

a short time of elution (7 min) of these bases on packed columns has not been reported elsewhere. Tailing of peaks, especially that of 2,6-dimethylpyridine, was minimal on column III (Fig. 1). The resolutions of pairs of compounds (Table II), clearly indicate the suitability of column III for the analysis of low-boiling pyridine bases.

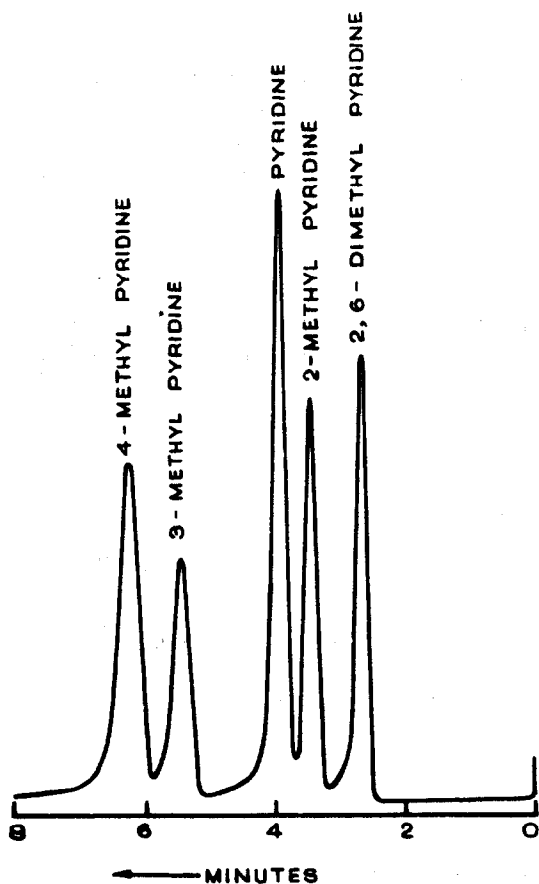


Fig. 1. Chromatogram of a synthetic mixture of pyridines.

TABLE III

ANALYSIS OF SYNTHETIC MIXTURES OF PYRIDINE BASES ON COLUMN III

The figures quoted are percentages by weight.

Compound	Mixture 1		Mixture 2		Mixture 3	
	Found	Present	Found	Present	Found	Present
2,6-Dimethylpyridine	11.2	11.8	15.8	16.1	10.8	9.8
2-Methylpyridine	11.5	12.1	16.2	16.9	25.1	23.2
Pyridine	42.1	40.8	29.3	30.1	15.9	16.7
3-Methylpyridine	12.9	12.0	14.4	13.8	19.3	18.1
4-Methylpyridine	22.3	23.3	24.3	23.1	28.9	32.2

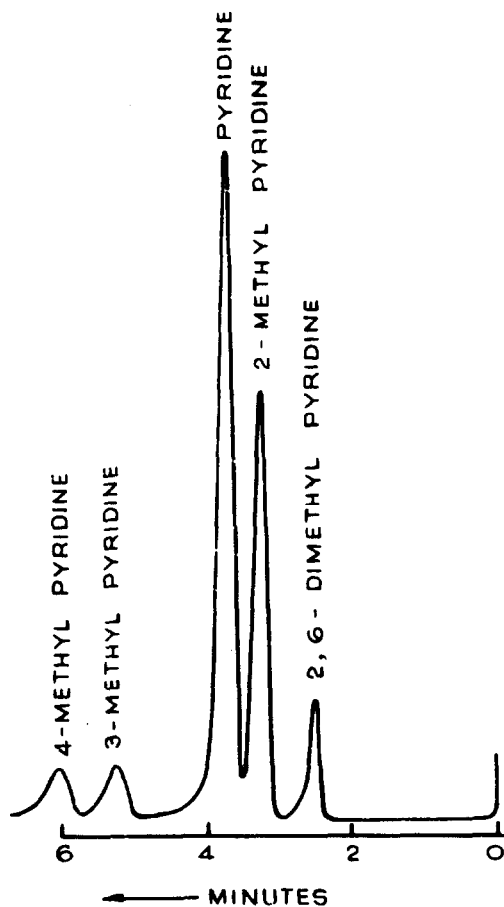


Fig. 2. Chromatogram of tar base fraction (initial boiling point 146°C).

Regarding the life of the columns, the deterioration was slowest for column III, the resolution of pyridine and 2-methylpyridine decreasing from 92% to only 80% after 60 days of use. Thus column III is capable of analysing low-boiling pyridine bases in a short time with satisfactory resolution of peaks. The method was verified with several synthetic mixtures of the above pyridines (Table III) and was found to be highly suitable for the analysis of the tar base fraction (boiling up to 146°C) derived from saturator liquor (Fig. 2).

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