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Note

Analysis of pyridine bases isolated from a high-temperature coal tar by capillary gas chromatography *

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The composition of the pyridine base fraction of high-temperature bituminous coal tar can be determined reliably and precisely by gas chromatography[1–7]. For the separation of multi-component mixtures of isomeric alkylpyridines, polar stationary phases[1,7] and the method of capillary gas chromatography have been used[8,9].

It has already been shown that the analysis of a complex mixture of basic plant biosubstrates can be carried out on an Amine 220 (1-ethanol-2-heptadecenyl-2-isoimidazole) phase[9,10]. The relative retention (pyridine = 1) of alkylpyridines de-

TABLE I

RELATIVE RETENTION INDICES (R) OF PURE ALKYLPYRIDINES ON A COLUMN PACKED WITH CELITE 545 WITH 20% OF AMINE 220 (PYRIDINE = 1.00)

Compound	*R*	*Compound*	*R*
2-Methylpyridine	1.42	2,4,6-Trimethylpyridine	4.25
3-Methylpyridine	2.22	2,3,6-Trimethylpyridine	4.59
4-Methylpyridine	2.31	2,3,5-Trimethylpyridine	7.45
2,6-Dimethylpyridine	1.93	2,4,5-Trimethylpyridine	8.57
2,5-Dimethylpyridine	3.12	4-Methyl-2-ethylpyridine	4.83
2,4-Dimethylpyridine	3.26	6-Methyl-3-ethylpyridine	5.54
2,3-Dimethylpyridine	3.48	2,4-Dimethyl-6-ethylpyridine	5.73
3,5-Dimethylpyridine	4.89	2,6-Dimethyl-3-ethylpyridine	7.31
3,4-Dimethylpyridine	6.27	2,6-Dimethyl-4-ethylpyridine	7.39
2-Ethylpyridine	2.23	2-Butylpyridine	7.00
3-Ethylpyridine	3.96		
4-Ethylpyridine	4.24		

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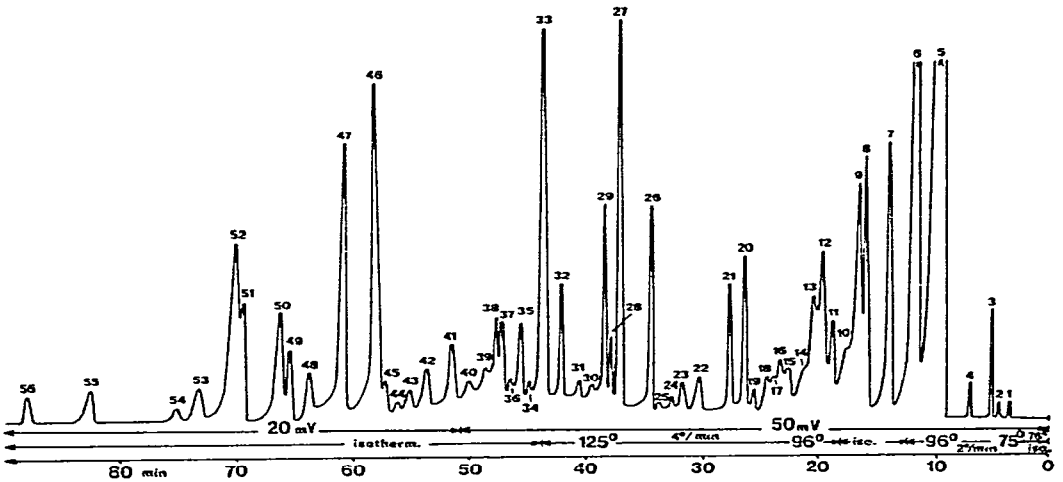

Fig. 1. Chromatogram of basic fraction of high-temperature bituminous coal tar (stainless-steel capillary column coated with Amine 220).

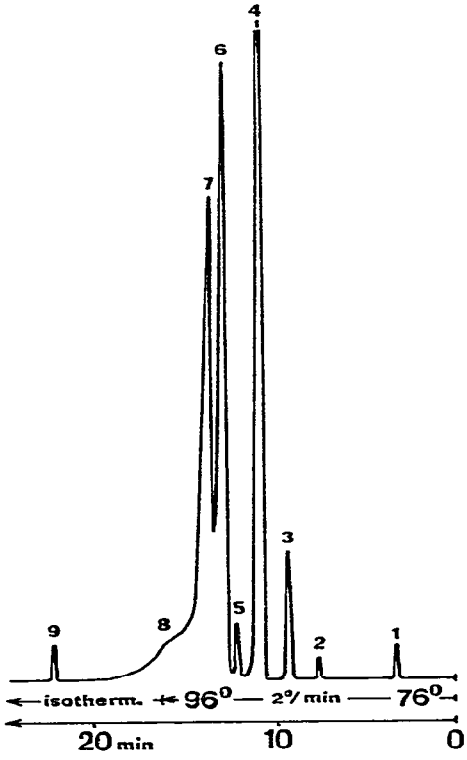

Fig. 2. Chromatogram of β-picoline fraction of tar bases (stainless-steel capillary column coated with Amine 220).

termined on a column packed with Celite 545 prepared by treatment with 1% potassium hydroxide solution using Amine 220 stationary phase indicate the good selectivity of Amine 220 for the separation of their isomers, as demonstrated in Table I.

These results correlate with those obtained using a capillary column on a Chrom 41 (Laboratory Instruments, Prague, Czechoslovakia) gas chromatograph equipped with a flame-ionization detector. The pressure of the carrier gas (nitrogen) at the inlet of the column was 29.3 kPa. A stainless-steel capillary column (25 m × 0.26 mm I.D.) was coated with Amine 220 stationary phase, the splitting ratio being 1:100 and the evaporator temperature 250°C (523°K). As the sample substances had a wide range of boiling points, temperature programming was applied.

A low-boiling mixture of pyridine derivatives isolated from a high-temperature bituminous coal tar (Fig. 1) and of a β-picoline fraction prepared by rectification were analysed (Fig. 2).

The main fraction of the crude pyridine bases consists of pyridine, methylpyridines, 2,6-dimethylpyridine, 2,4-dimethylpyridine, aniline, methylaniline, quinoline,

TABLE II

ELUTION SEQUENCE OF PYRIDINE BASES OF COAL TAR ON A STAINLESS-STEEL CAPILLARY COLUMN COATED WITH AMINE 220

Sample size: 0.15 μl.

Sequence in chromatogram (Fig. 1)	*Substance identified*	*Sequence in chromatogram (Fig. 1)*	*Substance identified*
1–4	Unidentified	25	Unidentified
5	Pyridine	26	Aniline
6	2-Methylpyridine	27–29	Unidentified
7	2,6-Dimethylpyridine	30	N-Methylaniline
8	3-Methylpyridine	31	N,N-Diethylaniline
9	4-Methylpyridine	32	Unidentified
10	Unidentified	33	2-Methylaniline
11	2,5-Dimethylpyridine	34	Unidentified
12	2,4-Dimethylpyridine	35	4-Methylaniline
13	2,3-Dimethylpyridine	36	Unidentified
14	3-Ethylpyridine	37	3-Methylaniline
15	4-Ethylpyridine + 2,4,6-trimethyl pyridine	38	2,6-Dimethylaniline
		39	Unidentified
16	2,3,6-Trimethylpyridine	40	Unidentified
17	2-Ethyl-5-methylpyridine	41	2,5-Dimethylaniline + 2,4-dimethylaniline
18	2-Ethyl-4-methylpyridine + 3,5-dimethylpyridine	42	3,5-Dimethylaniline
19	3-Ethyl-6-methylpyridine	43	3,4-Dimethylaniline
20	3,4-Dimethylpyridine + aromatic hydrocarbon	44	Unidentified
		45	2,3-Dimethylaniline
21	Aromatic hydrocarbon	46	Quinoline
22	2,3,5-Trimethylpyridine + 2,6-dimethyl-3-ethylpyridine + 2,6-dimethyl-4-ethylpyridine	47	2-Methylquinoline + 8-methylquinoline
		48	Isoquinoline
23	2,4,5-Trimethylpyridine + 2,3,4-trimethylpyridine	49–51	Unidentified
		52	2,8-Dimethylquinoline
24	N,N-Dimethylaniline	53–56	Unidentified

methylquinoline and some aromatic hydrocarbons. The use of a capillary column with temperature programming column made it possible to identify 2,3,6- and 2,4,6-trimethylpyridines in the β-picoline fraction. These substances have not previously been identified in the crude pyridine base fraction of high-temperature coal tar[11,12].

TABLE III

ELUTION SEQUENCE OF ALKYLPYRIDINES IN PICOLINE FRACTION OF TAR ON A STAINLESS-STEEL CAPILLARY COLUMN COATED WITH AMINE 220

Sample size: 0.6 μl.

Sequence in chromatogram (Fig. 2)	*Substance identified*	*Sequence in chromatogram (Fig. 2)*	*Substance identified*
1	Unidentified	6	3-Methylpyridine
2	Unidentified	7	4-Methylpyridine
3	Pyridine	8	2,4-Dimethylpyridine + 2,5-dimethylpyridine
4	2-Methylpyridine		
5	2,6-Dimethylpyridine	9	2,4,6-Trimethylpyridine + 2,3,6-trimethylpyridine

The results obtained are also summarized in Tables II and III, and demonstrate the applicability of this method for the process control of the manufacture of pyridine bases based on coal tar.

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