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Short communication

Separation of low-boiling pyridine bases by gas chromatography

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Abstract

The analysis of the low-boiling pyridine and its alkyl derivatives is a difficult task for gas chromatography due to their close vapor pressures and polarities. The methods described in the paper employ columns packed with N,N,N',N'-tetrakis(hydroxyethyl)ethylenediamine and metal transition compounds on diatomaceous supports which permit a rapid and reliable separation.

1. Introduction

Owing to the importance of applications in chemical industries of pyridine and its alkyl derivatives considerable attention has been given to their chromatographic separation and determination. The analysis of the low-boiling tar base fraction, the β -picoline fraction, is a complex problem in gas chromatography. On account of their close vapor pressures and polarities it is difficult to separate some compound pairs, i.e. 4-methyl- and 3-methylpyridine.

The use of capillary columns and adequate stationary phases diminish these difficulties. Polar liquids such as N,N-bis(hydroxyethyl)trimethylenediamine [1] have produced an acceptable separation but with tailing peaks. Pretreatment or addition of strong bases, i.e. potassium hydroxide, to Carbowax 1540 [2] or to

β -cyanoethylpolysiloxane [3] have allowed better symmetries but without the necessary selectivities. Other applications include the use of non-polar phases [4–7] and a wide variety of polar phases such as Amine-220 [8,9], amine-treated Carbowax 20M [6,10] and Reoplex 400 [4,5,8]. According to Novrocíková et al. [5] a soft sodium–calcium glass column with Reoplex 400 can resolve, with identification purposes, 72 pyridine alkyl homologues, except three pairs and one triad compounds.

Numerous chromatographic papers have been published using packed columns [11–25]. Since the first steps of chromatography it has been well known that glycerol, triethanolamine and polyethyleneglycol [11,12] were used as liquid phases to separate a few pyridine bases mixtures. In most of these studies the solid support was deactivated by means of surface silylation, additions of non-volatile organic compounds or potassium hydroxide in order to improve the symmetry of the peaks, but they suffer from long

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analysis times, partially resolved pairs or, in some cases, tailing. It is important to point out the high selectivities of 4-methyl-/3-methylpyridine on glycerol and on benzoic acid derivative [19].

Finally, metal transition stearates or oleates [20,26], or their mixtures with Apiezon M [27,28] have been exploited as stationary phases for pyridine bases separation. Studies of systems such as Co-phthalocyanine supported on carbon black, in packed and porous-layer open tubular columns [29]; squalane plus Ni- β -ketoamine complexes [30] and 1,2,3-tris(2-cyanoethoxy)propane plus cupric chloride [31] were tried with limited success.

The industrial-scale fractionation of pyridine bases is carried out by distillation, consequently the β -picoline fraction could contain compounds whose boiling points are lower than 150°C as principal components and small quantities of other alkylpyridines, i.e. lutidines or collidines. The aim of the present work is to develop a suitable packed column for a rapid and reliable separation of components of the β -picoline fraction and of binary samples of 4-methyl- and 3-methylpyridine when one of them is in a higher ratio concentration.

2. Experimental

Konik 3000 and Hewlett-Packard 5880A gas chromatographs equipped with a flame ionization detectors were used in this study. The columns were 1/4 in. O.D. \times 2 mm I.D. (1 in. = 2.54 cm) silanized glass tubing, with lengths ranging between 1 and 2 m. Analytical-grade nitrogen, previously passed through humidity (Analabs HGC-145) and oxygen (Analabs HGC-224) traps, was used as carrier gas at 15–20 ml min⁻¹. The flame ionization detector was operated at 150°C and the injector port at 140°C. Samples of 0.5 μ l of 0.5% (w/w) solutions were injected by means of 5- or 10- μ l syringes (Hamilton 75N or 701N).

The pyridine (Py), 2,4,6-collidine (2,4,6-C) and six lutidines or dimethylpyridines (2,3-; 2,4-;

2,5-; 2,6-; 3,4-; and 3,5-L) were from Aldrich and picolines or methylpyridines (2-MP; 3-MP and 4-MP) and 2-ethylpyridine (2-EtP) were from Fluka; analytical-grade *n*-hexane (Merck) was used to prepare sample solutions. The solid support, Chromosorb P AW, 100–120 mesh, was from J. Manville. The stationary phases were from various suppliers.

Metallic stearates were prepared as described by Whitmore and Lauro [32] from stearic acid and inorganic metal salts, all analytical reagents. Column packings were prepared by mixing a solid support with a solution which contains the required quantity of stationary phase in an adequate solvent, chloroform for a single liquid phase; chloroform plus benzene for a binary phase; and methanol for N,N,N',N'-tetrakis(hydroxyethyl)ethylenediamine (THEED) plus cupric chloride. The solvent was slowly removed in a rotary evaporator (Büchi) under a nitrogen stream and gentle heating.

The column performance has been compared by means of the following parameters: (1) the symmetry of the pyridine peak, defined as the ratio of the back width and the front width of the peak, measured from a vertical line traced through the peak maximum, at one tenth of the peak maximum; and (2) the number of theoretical plates/m for pyridine and its alkyl derivatives.

3. Results and discussion

Peak shape and column efficiency improved when siliceous solid supports were deactivated by means of a liquid stationary phase or treated with a silanizing reagent or with an adequate additive. For those purposes, in the first stage of the present work, we have employed a series of high-polarity phases such as glycerol, diglycerol, AT-220, Quadrol and THEED, all of them between 2 and 6% (w/w).

Asymmetries lower than 1.2, measured at 90°C, were observed with AT-220 (the best), THEED and Quadrol, and the numbers of theoretical plates were approximately the same, 2500–2200 theoretical plates/m. A good balance

between peak symmetry, relative retention, analysis time and temperature was obtained with 4% liquid phase. The results with the use of THEED are expressed as selectivities and they are summarized in Table 1. At 70°C all pairs between pyridine and 2,5-L gave satisfactory results, except 2,6-L/2-EtP, but the analysis time was very long, approximately 20 min. At higher temperature an improved resolution of the above-mentioned pair was obtained. However, large drops in selectivities were observed with 2-MP/2,6-L and 4-MP/2,5-L; obviously, analysis time decreased considerably.

We intended to improve selectivities by adding transition metal organic salts. Several columns containing 3% THEED plus increased cadmium stearate [Cd(St)₂] concentrations ($X = 0.023, 0.045, 0.086$ and 0.16 ; where X denotes mol fraction) were studied. The best separations were obtained at higher metal salt concentrations. So a better balance was reached between selectivity and temperature for the pairs mentioned above compared to the results we obtained with THEED. The selectivities are summarized in Table 1. The efficiency of binary liquid phases

presented a small drop with increased metal salt concentration.

Nickel stearate and THEED mixtures behaved similarly as cadmium salt (Table 1). Therefore, both mixtures of stearates (Ni or Cd) plus THEED can be used for separation of the β -picoline fraction components with a packed column 1.5 m long, at temperatures between 80 and 90°C. Fig. 1 shows a typical chromatogram, obtained for a sample of seven pyridine bases on an 1.5 m column packed with 3.1% THEED plus Ni(St)₂ ($X = 0.16$) at 90°C. The behavior described above was compared to that obtained for a Carbowax Amine fused-silica capillary column [33,34]. The results indicate that our packed column has had a good performance.

The zinc stearate as liquid phase has been specially indicated for its high selectivity [26,35]. However, its mixture with THEED did not lead to important improvements with respect to cadmium and nickel salts. The results in Table 1 show higher selectivities for Py/2-MP and 4-MP/2,5-L and lower for 2-EtP/3-MP. Furthermore, it was observed that efficiency drops to 1500 theoretical plates/m at $X = 0.16$.

Table 1
Selectivities of pyridine bases on liquid stationary phases

	Selectivity															
	100°C				90°C				80°C				70°C			
	Cd	Ni	Zn	THEED	Cd	Ni	Zn	THEED	Cd	Ni	Zn	THEED	Cd	Ni	Zn	THEED
Pyridine	1.26	1.26	1.32	1.22	1.30	1.29	1.36	1.26	1.33	1.33	1.40	1.30	1.36	1.37	1.45	1.35
2-MP	1.22	1.22	1.22	1.09	1.25	1.26	1.25	1.12	1.29	1.23	1.29	1.16	1.33	1.34	1.34	1.20
2,6-L	1.13	1.13	1.13	1.12	1.14	1.13	1.13	1.11	1.14	1.13	1.12	1.10	1.13	1.12	1.12	1.10
2-EtP	1.24	1.27	1.19	1.34	1.24	1.26	1.18	1.32	1.23	1.24	1.16	1.30	1.23	1.23	1.14	1.28
3-MP	1.12	1.13	1.11	1.12	1.12	1.13	1.11	1.13	1.13	1.14	1.12	1.13	1.13	1.15	1.12	1.14
4-MP	1.10	1.08	1.17	1.08	1.12	1.11	1.20	1.11	1.14	1.14	1.24	1.14	1.16	1.17	1.28	1.18
2,5-L	1.12	1.13	1.12	1.15	1.13	1.13	1.13	1.16	1.13	1.14	1.13	1.16	1.13	1.14	1.13	1.16
2,4-L	1.04 ^a	1.04 ^a	1.04 ^a	1.03 ^a	1.04 ^a	1.04 ^a	1.04 ^a	1.03 ^a	1.04 ^a	1.04 ^a	1.04 ^a	1.03 ^a	1.04 ^a	1.04 ^a	1.04 ^a	1.03 ^a
2,3-L	1.16	1.17	1.18	1.05	1.19	1.23	1.21	1.09	1.23	1.23	1.25	1.12	1.23	1.23	1.25	1.12
2,4,6-C	1.35	1.36	1.26	1.34	1.34	1.33	1.23	1.30	1.33	1.31	1.20	1.27	1.33	1.31	1.20	1.27
3,5-L	1.42	1.45	1.42	1.46	1.44	1.47	1.43	1.48	1.46	1.49	1.45	1.50	1.46	1.49	1.45	1.50
t'_R 3,4-L (min)	15.1	10.4	12.4	12.3	22.4	15.4	18.0	18.3	34.5	22.6	26.7	29.1	34.5	22.6	26.7	29.1

Columns: Cd: 2 m × 2 mm I.D., 3.2% THEED plus cadmium stearate (0.16 mol fraction); Ni: 1.5 m × 2 mm I.D., 3.1% THEED plus nickel stearate (0.16 mol fraction); Zn: 6 ft. × 2 mm I.D., 3.1% THEED plus zinc stearate (0.16 mol fraction); THEED: 2 m × 2 mm I.D., 4.1% THEED.

^a Selectivities were determined injecting binary mixtures of 2,5-L plus 2,4-L and 2,5-L plus 2,3-L.

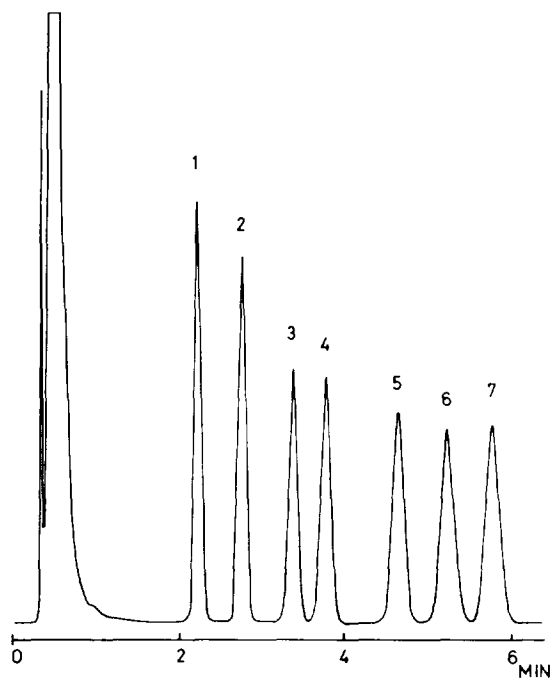


Fig. 1. Chromatogram on 1.5 m \times 2 mm I.D. glass column of 3.1% THEED plus nickel stearate (0.16 mol fraction) on Chromosorb P AW, 100–120 mesh, at 90°C. Peaks: 1 = Py; 2 = 2-MP; 3 = 2,6-L; 4 = 2-EtP; 5 = 3-MP; 6 = 4-MP; 7 = 2,5-L.

It is relevant to point out that with the studied metal stearates it was possible to get a better separation of the β -picoline fraction, but the improvement in selectivity, respect of pure THEED, was not obtained for 4-MP/3-MP pair.

In aqueous solution pyridine interaction with cupric ion is higher than with Ni(II) and Cd(II); thus, the logarithms of the equilibrium constants are 2.41, 1.78 and 1.27 respectively [36] and its *o*-alkyl derivatives are strongly affected by steric impediments. A mixture of Cu(St)₂ ($X = 0.22$) in 3% THEED as liquid phase reverse the gas chromatographic retentions of Py, 2-MP and 2,6-L, but selectivities were not high enough for separation, and the 4-MP/3-MP pair selectivity reached 1.4. However, this behavior was blurred by an unstable retention, which remained although the column was maintained 100 h at 100–120°C. A mixture of cupric chloride ($X =$

0.16) plus 4.1% THEED has produced: (1) a better retention stability ($\pm 4\%$ fluctuation in a period of 8 h); (2) a low efficiency, only 1200–1300 theoretical plates/m, and (3) selectivities for the 4-MP/3-MP pair of 1.29 and 1.27 at 80°C and 90°C, respectively. Fig. 2 shows a chromatogram obtained for a solution of 3-MP (Fluka, purity higher than 98%) in *n*-hexane on a column packed with the above-mentioned binary stationary phase at 85°C. This column failed when applied to a 2,3- and 2,4-L mixture, it provided a higher retention for 2,4-L (an inverted behavior of Cd, Ni and Zn salts plus THEED) and a 1.08 selectivity at 70–90°C. Higher cupric chloride concentrations packings have produced columns of lower efficiency; at

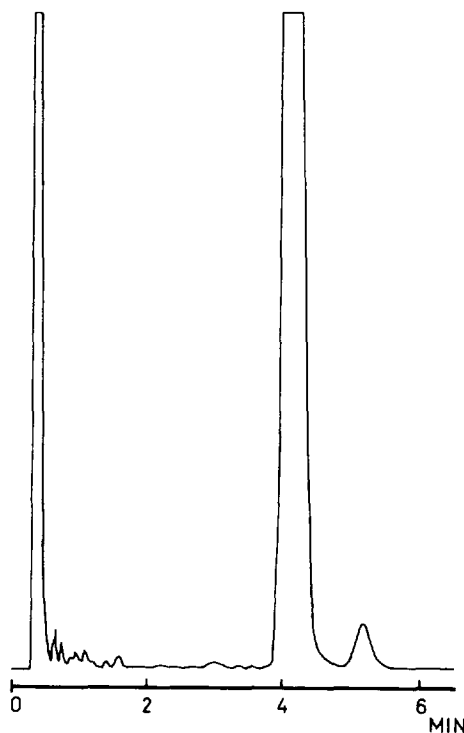


Fig. 2. Chromatogram on 4 ft. \times 2 mm I.D. glass column (1 ft. = 30.48 cm) of 4.1% THEED plus cupric chloride (0.16 mol fraction) on Chromosorb P AW, 100–120 mesh, at 85°C. Sample 0.5 μ l of 4% solution of 3-MP (Fluka, purity higher than 98%) in *n*-hexane.

present we continue working with another cupric organic salts to improve selectivity and retention stability.

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