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Note

Alkali metal salt additives and chromatographic performance of glass capillary columns with polyethylene glycol as the stationary phase

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In a previous paper we reported the preparation of efficient and reproducible glass capillary columns of PEG 40M with a wide range of applications, including primary amine analysis¹. These columns were prepared by high-pressure static (HPS) coating on a glass surface containing trace amounts of "bound" potassium hydroxide. Such columns were optimized in relation to a specific salt (potassium hydroxide) and were prepared by eluting excess of the base with methanol. Naturally, the procedure is applicable only to this particular compound, which is capable to form chemical bonds with acidic components of the glass surface, e.g., $\geq\text{SiOH}$. The properties of "free" and "bound" potassium hydroxide differ considerably with respect to their effects on the chromatographic system glass surface-PEG 40M. If elution with methanol was omitted and excess of the base was remained on the surface, such columns, after application of a liquid phase, showed strong catalytic effects with decomposition of test compound 14 and equilibration of *cis*- and *trans*-isomers of compound 15 (Table I).

It was therefore interesting to attempt to find some other salt additives, the effects of which would not be so dependent on concentration. However, these salts, which are chemically non-reactive with the glass surface and act by means of the salting-out effect, present special problems in their application. In this respect, our earlier unsuccessful attempts to modify glass surface by converting $\geq\text{SiOH}$ (after etching with hydrofluoric acid) completely into $\geq\text{SiOK}$ by treatment with the blue solution of potassium in naphthalene-tetrahydrofuran (THF) or incorporation of KOCH_3 (ca. 10% from PEG 40M) in PEG 40M-THF solution for HPS coating are of interest. The first columns were of poor efficiency owing to the extremely poor wetting of the $\geq\text{SiOK}$ surface by PEG 40M. Visual inspection of such columns revealed distinct pools of the liquid phase and areas of uncovered glass. The application of the HPS procedure to the second columns resulted in "empty" capillaries

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because of the total destruction (depolymerization) of PEG under the catalytic action of KOCH_3 in the pre-heater and thermostat¹. This last example illustrates the importance of the use of a base in combination with the HPS coating procedure.

This paper reports the development of the *n*-hexane plug method for the application of basic salts (potassium carbonate and trisodium orthophosphate) on to hydrofluoric acid pre-treated inner surfaces and the evaluation of the chromatographic properties of such glass capillary columns.

EXPERIMENTAL

Columns were prepared from borosilicate glass¹ and treated with 10 ml of 1% hydrofluoric acid under a nitrogen pressure of 5 atm; the acidic solution was flushed out and was followed by 5 ml of water and 5 ml of methanol. Then the columns were filled with a 0.1% solution of sodium orthophosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) or potassium carbonate in methanol, a certain volume (*ca.* 2–3 ml) being collected after passage through the column. A plug of *n*-hexane (*ca.* 5 ml) was applied immediately after the salt solution.

The columns were dried in a stream of nitrogen for 2 h and filled with a 0.25% solution of PEG 40M in dry THF; the first 5–6 ml were collected and the HPS coating procedure was carried out². Conditioning of the columns was carried out in the same apparatus at 200° for 3 h in a stream of nitrogen.

For analysis 10–15 μl of each of the test compounds (Table I) were dissolved in 1 ml of *n*-pentane and 0.5 μl of the mixture were injected. A Chrom Model 4 gas chromatograph with a flame-ionization detector was modified to accommodate glass capillary columns; the nitrogen pressure was 1.5 atm, and the splitting ratio and column parameters are given in Table II.

TABLE I
TEST COMPOUNDS FOR EVALUATION OF BASIC ADDITIVES TO PEG 40M

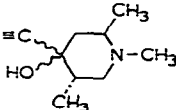
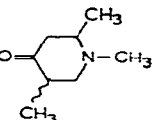

Compound No.	Substance	Compound No.	Substance
1	C_{10} – C_{15} <i>n</i> -Alkanes	10	Triethylamine
1a	<i>n</i> - $\text{C}_{13}\text{H}_{28}$	11	<i>N,N</i> -Dimethylcyclohexylamine
2	Amylamine	12	<i>N</i> -Methylcyclohexylamine
3	Hexylamine	13	Cyclohexylamine
4	Heptylamine	14	 (isomer mixture) at C_4
5	Methyloctylamine	15	 (<i>cis</i> - and <i>trans</i> - isomer mixture)
6	Octylamine		
7	2,5-Dimethylpyrazine	16	1,2-Diaminopropane
8	2,4-Dimethylpyridine	17	2-Hydroxypropylamine
9	Dimethyldecylamine	18	 Triethylenediamine

TABLE II
CHROMATOGRAPHIC PARAMETERS OF GLASS CAPILLARY COLUMNS OF PEG 40M

Column	Inner surface treatment (salt additives)			
	Na_3PO_4 (I)*	K_2CO_3 (II)*	KOH (III)*	KOH ("bound") (IV)**
Length (m)	65	65	69	70
Internal diameter (mm)	0.32	0.30	0.37	0.30
Splitting ratio	1:100	1:150	1:100	1:120
Carrier gas flow-rate (ml·min ⁻¹)	0.53	0.38	0.47	0.49
Plates per metre:				
For $n-C_{13}H_{28}$ (110°)	3040	4379	1933	5420
For octylamine (110°)	3405	4686	1935	3379

* Treatment by *n*-hexane plug method.

** Columns treated with methanolic KOH and subsequent washing with pure methanol.

RESULTS AND DISCUSSION

From Table II, it can be seen that the efficiency of type IV columns (chemically bound potassium hydroxide) is higher for $n-C_{13}H_{28}$ than for octylamine. This difference, which is more pronounced if treatment with methanol-potassium hydroxide after treatment with hydrofluoric acid is omitted, is indicative of an interaction between the acidic centres of the glass surface (*i.e.*, $\equiv SiOH$) and the amine. On the other hand, the efficiency of type III columns (prepared by the *n*-hexane plug method) is almost the same for both test compounds 1a and 6. Therefore, it can be assumed that these columns contain more basic component than do the type IV columns. As a result, in addition to blocking the acidic centres on the glass surface, a small excess of the base exercises a salting-out effect and makes the amine peaks more symmetrical and narrow. At the same time, this excess of base is sufficiently small not to cause decomposition of test compound 14 or isomerization of compound 15 (for the chromatograms see Fig. 1).

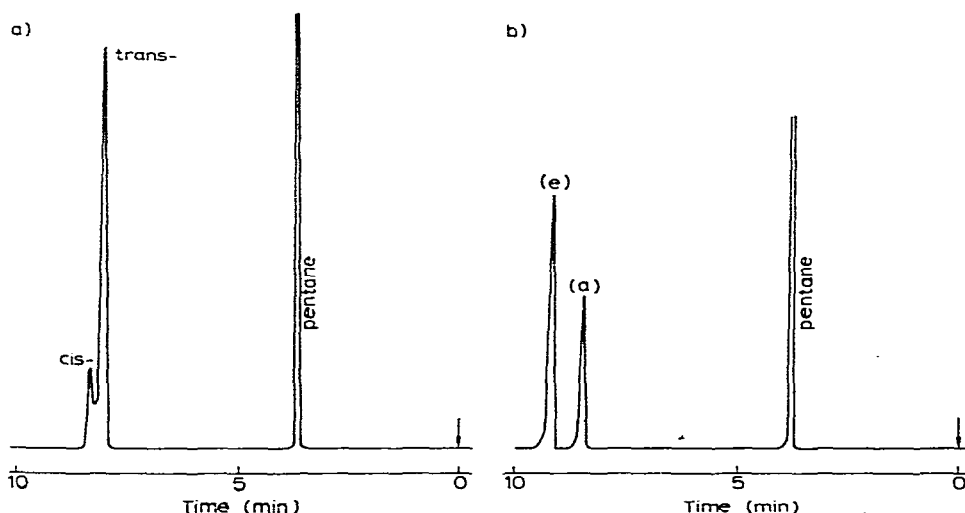


Fig. 1. Chromatograms of (a) *cis*- and *trans*-isomer mixture 15 and (b) mixture 14 on the column type III.

TABLE III

KOVÁTS RETENTION INDICES OF NINE NITROGEN-CONTAINING ORGANIC BASES ON COLUMNS OF PEG 40M AT 110°

The results are the means from 5-7 measurements. The mean deviation does not exceed 2.1 units; the standard deviation is less than 2.5 units.

Substance	Inner surface treatment (salt additives)			
	Na_3PO_4 (I)	K_2CO_3 (II)	KOH (III)	KOH ("bound") (IV)
Amylamine	981	986	981	981
Hexylamine	1078	1082	1085	1080
Heptylamine	1179	1182	1185	1181
Methyloctylamine	1262	1264	1267	1264
Octylamine	1280	1283	1287	1283
2,5-Dimethylpyrazine	1310	1314	1318	1310
2,4-Dimethylpyridine	1322	1326	1330	1322
Dimethyldecylamine	1376	1377	1379	1377
Triamylamine	1463	1464	1464	1464

From Table III, it can be seen that for most of the test compounds the potassium hydroxide columns III and IV (Table III and Fig. 2) are similar to the sodium orthophosphate (I) and potassium carbonate (II) columns. An interesting feature of the phosphate and carbonate columns is their high efficiency for amines, which even surpasses that for hydrocarbons (Table II). Nevertheless, a difference between the salts tested does exist and becomes noticeable when easily isomerizable (15) or strongly polar (17) compounds are compared. As can be seen from Fig. 3, mixture 15

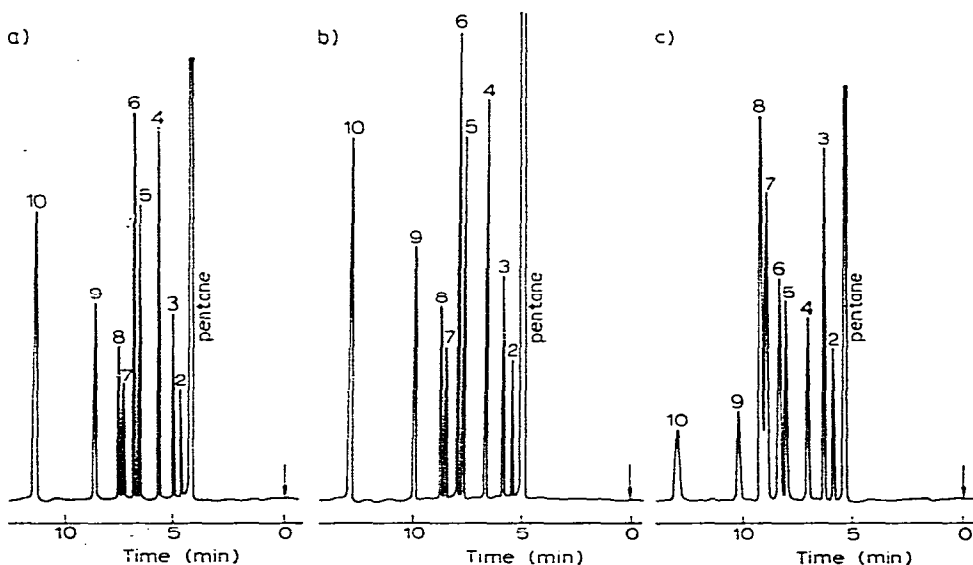


Fig. 2. Chromatograms of nitrogen-containing organic bases on PEG 40M columns. Treatment of inner glass surface: (a) Na_3PO_4 ; (b) K_2CO_3 ; (c) KOH. Peak numbers according to Table I.

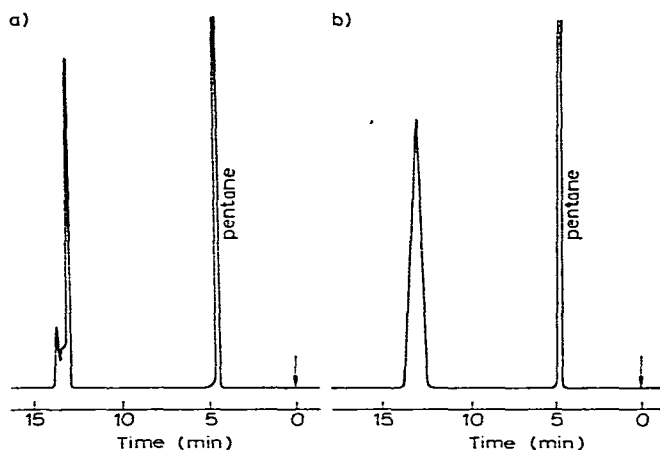


Fig. 3. Chromatogram of *cis*- and *trans*-isomer mixture 15. (a) Column type I; (b) column type II.

emerges as a single broad peak on the potassium carbonate column and as a pair of partially separated peaks on the sodium orthophosphate column.

All three salts also differ when compounds 16, 17 and 18 are used for column evaluation (see Fig. 4). An interesting test mixture for PEG columns is the mixture of cyclohexylamine and its mono- and dimethyl derivatives (11, 12 and 13). None of the salt-PEG 40M compositions tested separates monomethyl- and cyclohexylamines (12 and 13). The separation of this mixture can be achieved only on "acidic" PEG 40M columns (*e.g.*, ammonia-neutralized hydrofluoric acid-treated glass), the efficiency of which is not high for amines.

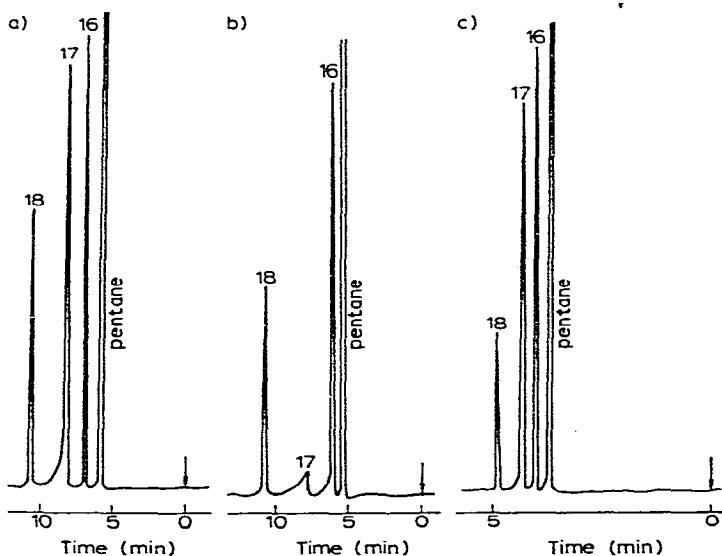


Fig. 4. Chromatograms of compounds 16, 17 and 18 on PEG 40M columns. Treatment of inner glass surface: (a) Na_3PO_4 ; (b) K_2CO_3 ; (c) KOH.

In conclusion, carbonates or neutral phosphates of alkali metals can be used successfully for "basification" of the PEG liquid phase for chromatography of amines of medium polarity. For the application of these salts, the *n*-hexane plug method appears to be the most convenient and reproducible. Superficially, this method is similar to the mercury plug procedure for the application of a liquid phase to glass capillary columns³, but differs from it in the mode of action of the plug. In fact, whereas the mercury plug exercises only a mechanical action in levelling up the liquid film on the inner glass surface, the *n*-hexane plug in the contact zone precipitates salts from methanolic solution on to the glass by virtue of its admixture with methanol. The same procedure can be applied to coating glass capillary columns with liquid phase (*i.e.*, dichloromethane solution followed by an *n*-hexane plug).

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