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Note

High-pressure static coating of glass capillary columns

Reproducibility and performance of columns with polyethylene glycol as liquid phase

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It is essential to be able to reproduce retention indices¹ with the upmost accuracy for gas-liquid chromatographic (GLC) analysis of complex mixtures of natural origin. In this paper, examples are given of the preparation of glass capillary columns exhibiting satisfactory index reproducibility.

Previously, we have shown that the high-pressure static method for coating glass capillary columns² in combination with inner surface pre-treatment³ with aqueous hydrofluoric acid-potassium hydroxide produces efficient columns having long life spans. The original procedure was improved by use of a pre-heater (Zelinskii Institute of Organic Chemistry, Moscow, U.S.S.R.) in a more sophisticated compact apparatus. This innovation, also described by Jennings *et al.*⁴, speeds up the coating of glass capillary columns (45-60 min) with no loss of column efficiency.

The estimation of the stability of such columns with PEG-40M as liquid phase is based on the observation that, in a series of PEG columns having different phase ratios the Kováts indices of primary amines are strongly dependent on this ratio, *i.e.*, the greater the proportion of the surface siloxane and silanol groups relative to the liquid phase the greater are the retention indices of the amines. This phenomenon is associated with the strong interaction between the structural elements of the glass surface ($\equiv\text{SiOH}$ and $\equiv\text{SiOSi}\equiv$) and the primary amines. Thus, any loss of liquid phase would result in an increase of the Kováts indices of the amines. Obviously, this process would also be accompanied by a decrease in the corrected retention times of alkanes.

EXPERIMENTAL

Glass columns were drawn from borosilicate glass (SiO_2 , 68.7%; B_2O_3 , 19.0%; K_2O , 4.4%) by a standard procedure⁵. The columns were filled under a pressure of

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nitrogen with a 0.5% aqueous solution of hydrofluoric acid from a polyethylene container and were then left to stand overnight. The acidic plug was flushed out using nitrogen into a flask containing concentrated aqueous ammonia. The ammonia solution and the column eluate usually formed a solid gel of silicic acid. After washing to neutrality with water (5 ml) the column was flushed with 10 ml of a 1% solution of potassium hydroxide in methanol and with 5 ml of methanol and 3 ml of tetrahydrofuran (all operations at a pressure of 5 atm). The column was then filled with a 0.25% solution of PEG-40M in tetrahydrofuran, *ca.* 5 ml of this solution being collected after passage through the column. One end of the column was carefully sealed and the liquid phase solution was evaporated at 200°, the pre-heater being at 350°. When the final coil of the column was reached the pre-heater and feeder were cut off, and after 10–15 min at the thermostat temperature the column was flushed out with dry nitrogen for 15 min.

After cooling, the column was connected to a splitter (all-glass, home-made) in a Chrom Model 4 gas chromatograph and to a flame ionization detector. Chromatographic conditions: carrier gas, nitrogen; column temperature, 110°; splitting ratio, 1:120 to 1:250 (see Table II). Each column was initially conditioned at 200° for 1.5 h. Test mixtures were prepared in pentane (10–15 μ l of each component in 1 ml of pentane). The sample volume injected was 0.5 μ l.

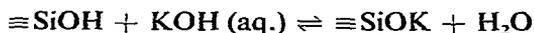
Each of four test columns was in continuous operation for 2–3 days and then interchanged for the next test. This process was repeated continually for 45 days. Retention indices were measured 4, 8, 12, 15 and 45 days after preparation of a column. The results in Table I are the means from 5–7 measurements. The mean deviation does not exceed 1.8 units of Kováts index; the standard deviation is less than 2.2 units.

RESULTS AND DISCUSSION

Retention indices of eight nitrogen-containing organic bases are listed in Table I. It can be seen that all of the columns gave virtually the same values throughout the test period (1.5 months). This stability permits the identification of the components of complex mixtures on the basis of Kováts indices.

All of the PEG columns shown in Table I contain potassium hydroxide in the liquid phase. The presence of a strong base in the liquid phase was demonstrated by special chromatographic indicators: acetylenic carbinols of the type $R_1R_2C(OH)CCH$. Injection of these compounds onto columns containing even trace amounts of "free" bases invariably results in their conversion into acetylene and ketones.

Of special interest is the mode of the introduction of the base. Treatment of hydrofluoric acid-etched columns with aqueous potassium hydroxide and subsequent washing with water to neutrality produces "acid" columns. With nitrogen as the carrier gas, such columns may effect excessive tailing and longer retention times of primary amines. This behaviour is obviously connected with the equilibria:



With excess of water all of the potassium ions are washed out from the weakly acidic silicate surface. The same type of columns ("acid") may be prepared after neutraliza-

TABLE I

THE REPRODUCIBILITY OF KOVÁTS' INDICES OF EIGHT NITROGEN CONTAINING ORGANIC BASES ON COLUMNS WITH PEG-40M AS LIQUID PHASE AT 110°

Column no.	Substance	Interval for the determination of Kováts indices (days)					
		0	4	8	12	15	45
1	Hexylamine	1086	1086	1083	1082	1085	1082
	Heptylamine	1183	1183	1182	1180	1186	1181
	Methyloctylamine	1263	1262	1264	1263	1266	1263
	Octylamine	1284	1284	1283	1283	1286	1283
	2,5-Dimethylpyrazine	1310	1311	1309	1310	1313	1310
	2,4-Dimethylpyridine	1322	1324	1321	1322	1325	1322
	Dimethyldecylamine	1376	1379	1374	1376	1378	1376
	Triamylamine	1463	1466	1461	1463	1465	1463
2	Hexylamine	1082	1080	1082	1082	1080	1080
	Heptylamine	1180	1179	1181	1182	1179	1183
	Methyloctylamine	1263	1264	1263	1263	1262	1265
	Octylamine	1284	1284	1284	1282	1283	1286
	2,5-Dimethylpyrazine	1313	1312	1313	1312	1313	1315
	2,4-Dimethylpyridine	1325	1324	1326	1325	1325	1327
	Dimethyldecylamine	1377	1376	1377	1375	1376	1378
	Triamylamine	1463	1461	1464	1461	1463	1463
3	Hexylamine	1082	1084	1084	1083	1084	1082
	Heptylamine	1185	1186	1186	1186	1185	1185
	Methyloctylamine	1265	1266	1266	1265	1266	1265
	Octylamine	1286	1287	1288	1286	1286	1287
	2,5-Dimethylpyrazine	1310	1309	1309	1310	1310	1309
	2,4-Dimethylpyridine	1323	1322	1324	1324	1323	1322
	Dimethyldecylamine	1378	1376	1377	1377	1376	1377
	Triamylamine	1464	1460	1461	1463	1461	1464
4	Hexylamine	1085	1083	1088	1085	1086	1087
	Heptylamine	1185	1182	1186	1187	1186	1188
	Methyloctylamine	1266	1263	1267	1266	1266	1267
	Octylamine	1287	1286	1289	1287	1286	1289
	2,5-Dimethylpyrazine	1308	1305	1308	1307	1306	1308
	2,4-Dimethylpyridine	1321	1320	1322	1320	1322	1322
	Dimethyldecylamine	1378	1375	1379	1376	1377	1377
	Triamylamine	1463	1462	1463	1463	1462	1461

tion with aqueous ammonia. On the other hand, the use of more basic methanolic potassium hydroxide in combination with the "salting-out" effect of tetrahydrofuran leaves behind a quantity of the base which on subsequent thermal treatment may be transformed into the alcoholate of the chemically bound liquid phase:



Table II summarizes values of the efficiency N and N_{eff} at the optimal carrier gas flow-rate ($u_{\text{opt.}}$). N_{eff} was calculated according to Purnell⁶. The values are reasonably high for the column diameters (see Fig. 1). Somewhat lower values of N_{eff} calculated for primary amines may be associated with the adsorption of the amines on the glass

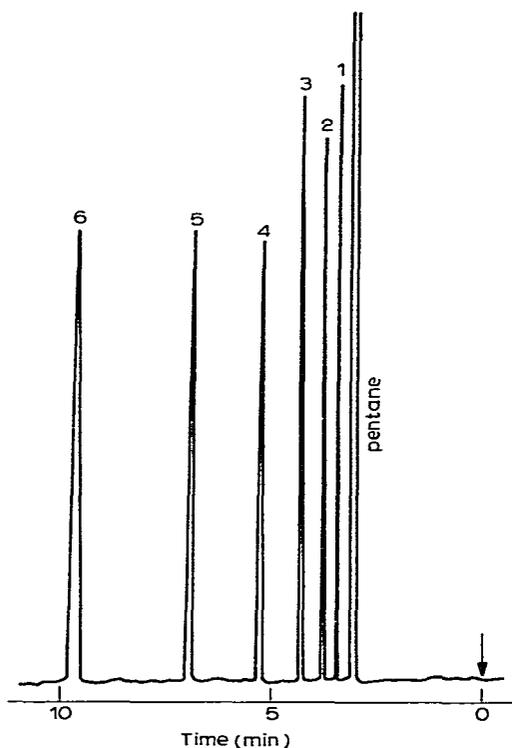


Fig. 1. Chromatogram of a hydrocarbon mixture on PEG-40M. Column no. 2; temperature, 110° ; inlet pressure, 1.20 atm. Peaks: 1 = decane; 2 = undecane; 3 = dodecane; 4 = tridecane; 5 = tetradecane; 6 = pentadecane.

surface but, as can be seen from the chromatogram in Fig. 2, the extent of adsorption is not great.

The storing of open columns for a long time (more than 3 months) results in some deterioration of the peak shapes of primary amines, although the retention in-

TABLE II

THE EFFICIENCY OF GLASS CAPILLARY COLUMNS WITH PEG-40M AS LIQUID PHASE

Column: 0.30 mm I.D.; temperature, 110°

Column no.	1	2	3	4
Length (m)	61	72	61	66
Splitting ratio	1:250	1:120	1:200	1:250
$u_{opt.}$ (ml/min)	0.41	0.55	0.51	0.42
N (m^{-1})	4216	4245	4435	3736
$N_{eff.}$ (m^{-1})	for tetradecane			
N (m^{-1})	1322	1327	1264	1050
$N_{eff.}$ (m^{-1})	for octylamine			
N (m^{-1})	4069	4808	5304	4086
$N_{eff.}$ (m^{-1})	715	867	837	705

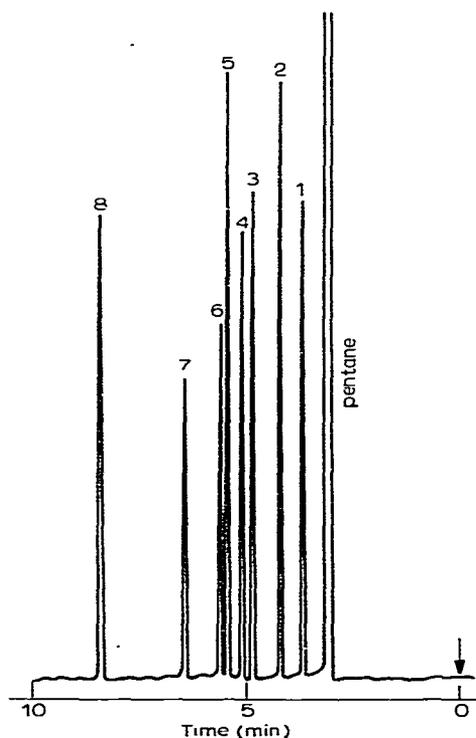


Fig. 2. Chromatogram of mixture of nitrogen-containing organic bases on PEG-40M. Column no. 2: temperature, 110° ; inlet pressure, 1.20 atm. Peaks: 1 = hexylamine; 2 = heptylamine; 3 = methyl-octylamine; 4 = octylamine; 5 = 2,5-dimethylpyrazine; 6 = 2,4-dimethylpyridine; 7 = dimethyl-decylamine; 8 = triamylamine.

dices unaffected. This effect of storing may be associated with moisture or some other factors in the laboratory atmosphere. Thermostating of the sealed columns at 250° for 3 h completely restores the peak shapes, and the retention indices of the amines remain unchanged.

Thus, high-pressure static coating of glass capillary columns is one of the most promising methods for the preparation of columns having a high reproducibility and durability for chromatography of a wide range of compounds including strongly polar ones such as primary amines.

REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 E. L. Ilkova and E. A. Mistryukov, *J. Chromatogr. Sci.*, 9 (1972) 569.
- 3 E. L. Ilkova and E. A. Mistryukov, *Chromatographia*, 4 (1971) 77.
- 4 W. G. Jennings, K. Yabumoto and R. H. Wohleb, *J. Chromatogr. Sci.*, 12 (1974) 344.
- 5 D. H. Desty, J. N. Haresnape and B. H. Whyman, *Anal. Chem.*, 32 (1960) 302.
- 6 J. H. Purnell, *J. Chem. Soc., London*, (1960) 1268.