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Note

Kaolin pre-coated glass capillary columns for the analysis of acidic compounds

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It is well known that the gas chromatographic analysis of acidic organic compounds is difficult owing to their low volatility and their interaction with the active sites of the chromatographic support. These limitations are overcome either by preparing derivatives or by using stationary phases, with added surface modifiers such as phosphoric[1] or trimesic acid[2] in order to elute organic acid compounds as such. Capillary columns for this purpose have been prepared by coating the glass surface with trimer acid[3], free fatty acid phase (FFAP)[4,5] Ucon[6], 1,15-pentadecanedicarboxylic acid[7] and polyethylene glycol (PEG 20M)[8]. Recently effective separations of free acids up to caprylic acid have been obtained by Hrivnac *et al.*[9] on columns pre-coated with acidic silica deactivated with benzyltriphenylphosphonium chloride (BTPPC) and Carbowax 1000.

The interesting features of the recently developed kaolin pre-coated glass capillary columns[10], the simplicity of their preparation and their thermal stability suggest their application for the analysis of these substances. This paper describes a number of applications in which these columns, additional coated with FFAP, can be used.

EXPERIMENTAL

Glass capillary columns pre-coated with kaolin were prepared according to the procedure described by Goretti and co-workers[10].

A suspension of British kaolin (200 mg) was obtained by adding it to a mixture of carbon tetrachloride (35 ml), methylene chloride (15 ml) and FFAP (40 mg) and exposing it for 60 min to ultrasonic vibrations (20–24 kHz frequency, 2 μm amplitude) supplied by a drilling machine.

The suspension (2 ml) was made to flow forwards and backwards twice through a glass capillary column (0.2–0.3 mm I.D.) that had been thoroughly prewashed with dichloromethane. The column was then washed with two 10-ml volumes of dichloromethane, the solvent was removed under a flow of nitrogen and the column was then conditioned in an oven overnight at 400°C (carrier gas nitrogen) in order to dehydrate the kaolin. The columns were subsequently coated dynamically using a 12% solution of FFAP in dichloromethane.

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All experiments were carried out with a Dani 3900 gas chromatograph (Dani, Monza, Italy) with an inlet splitter and a flame-ionization detector equipped with a Leeds and Northrup Model XL 681 recorder and with a Hewlett-Packard Model 3385A integrator.

The fatty acids used were supplied by Supelco (Bellefonte, PA, U.S.A.); all other products were obtained from Carlo Erba (Milan, Italy).

RESULTS AND DISCUSSION

The column capillary efficiency was evaluated by carrying out the gas chromatography of standard mixtures of phenols and fatty acids at different temperatures using hydrogen as the carrier gas. Some experimental results are summarized in Table I. They show that these columns have a high efficiency for acids and for phenols as the number of theoretical plates per meter is in the range 2700–3800 for compounds with capacity ratios (k') of 9–49.

TABLE I

CHARACTERISTICS AND CHROMATOGRAPHIC DATA FOR DIFFERENT COLUMNS

Column number	*Compound*	*Length (m)*	*I.D. (mm)*	*T (°C)*	*k*	*Plates per metre*	u_{opt} *(cm sec)*	TZ_{acids}
1	Capronic acid	13	0.35	150	13.1	2700	40.1	30.0 C_9/C_{10}
2	Myristic acid	16	0.30	200	9.2	2950	38.5	27.1 C_{13} C_{14}
3	3,4-dimethylphenol	16	0.30	150	13.6	2770	43.7	–
4	Myristic acid	13	0.30	170	43.0	3000	39.3	28.6 C_{11} C_{12}
	Stearic acid			200	42.1	3420	39.4	27.8 C_1- C_{18}
	3,4-Dimethylphenol			150	16.6	2760	43.3	–
5	Myristic acid	14	0.20	170	48.7	3640	38.7	29.7 C_{11}, C_{12}
	Stearic acid			200	47.3	3800	39.1	29.9 C_1-/C_{18}

The separation numbers (Trennzahl; *TZ*), which are in the range 27–30 for columns of length 13–16 m, are comparable to values obtained by Hrivnac *et al.*[9]. It is worth noting that interesting results were obtained in the analysis of a free acids mixture in the range nC--nC$_{18}$ shown in Fig. 1. The gas chromatogram was obtained with column 4 (Table I) under isothermal conditions at 200 C with a linear gas velocity, $\bar{u}$, of 62 cm sec. Such a column can thus be used for the evaluation of fatty acids from vegetable oils and of any complex mixture. Typical examples are shown in Figs. 2 and 3: the former is a gas chromatogram of the free acids obtained from hydrolysis of olive oil, carried out at 200°C and $\bar{u}$ = 127 cm/sec on column 3 (Table I), which shows the fractionation of various components from caprylic acid up to behenic acid in about 30 min; the latter is a gas chromatogram of the free acids from lemon wax, a by-product obtained from cold storage of lemon essential oil, carried out at 210°C and $\bar{u}$ = 110 cm/sec on column 1 (Table I).

An interesting application of these columns is their use in the analysis of oxyacids and bicarboxylic acids. Lactic, glycolic, succinic, glutaric, asparic and fumaric acids yield symmetrical peaks and are easily fractionated (Fig. 4), so that the use of these columns for biological applications can be envisaged. This separation has been obtained with column 3 (Table I).

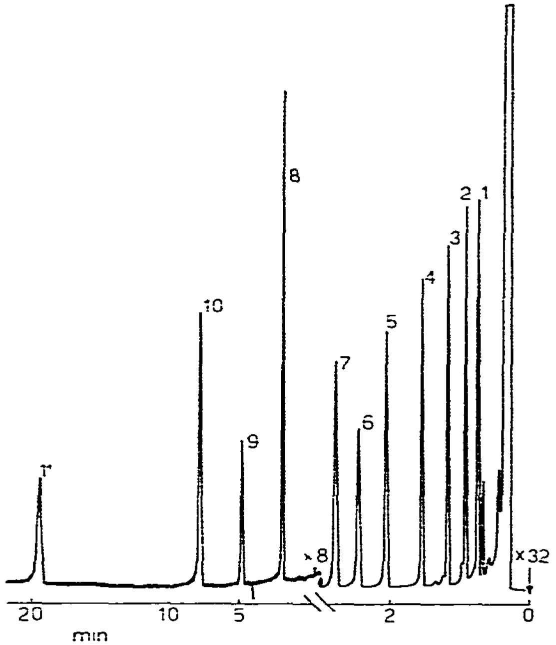


Fig. 1. Gas chromatogram of a fatty acid mixture. Sample injected, 3 µl; concentration of each compound, 0.1 µg ml; splitting ratio, 1:50. Peaks: 1 = heptanoic; 2 = caprylic; 3 = pelargonic; 4 = capric; 5 = undecenoic; 6 = undecylenic (0.07 µg µl); 7 = lauric; 8 = myristic; 9 = hydrocarbon C_{26} (0.05 µg/µl); 10 = palmitic; 11 = stearic acid.

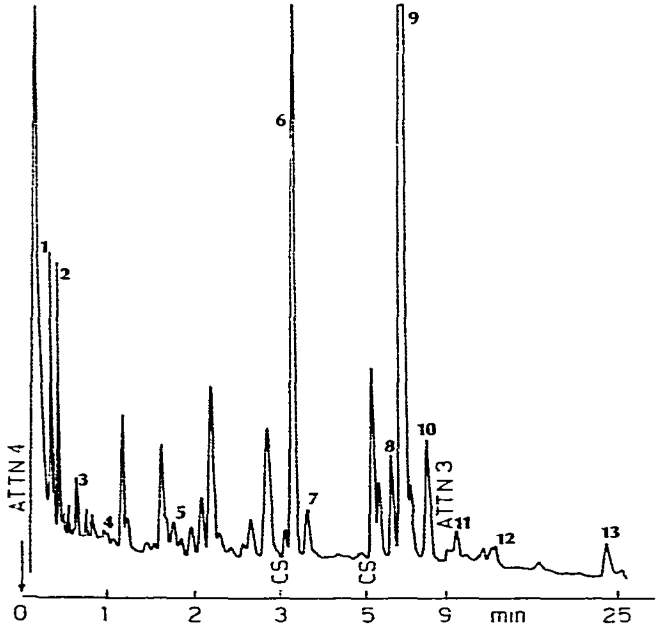


Fig. 2. Olive oil analysis. Peaks: 1 = caprylic; 2 = pelargonic; 3 = capric; 4 = lauric; 5 = myristic; 6 = palmitic; 7 = palmitoleic; 8 = stearic; 9 = oleic; 10 = linoleic; 11 = linolenic; 12 = eicosanoic; 13 = behenic acid.

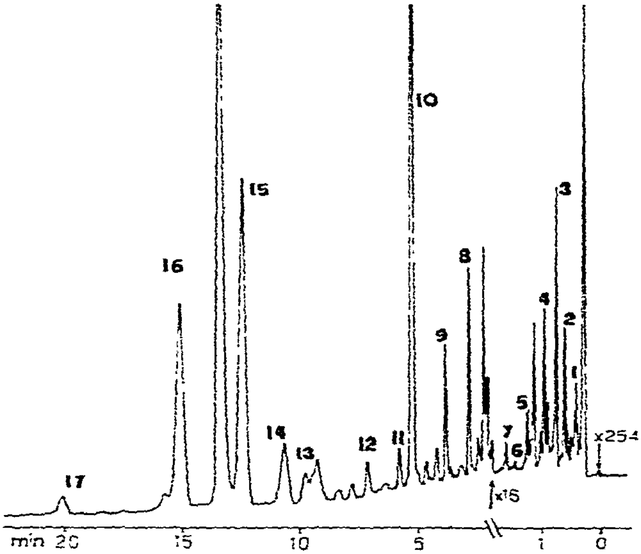
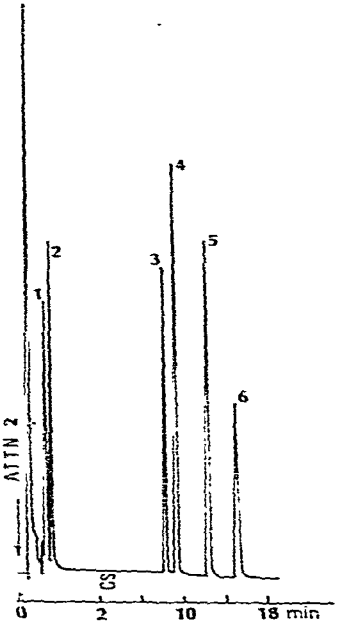


Fig. 3. Analysis of free acids from lemon wax. Peaks: 1 = caproic; 2 = heptanoic; 3 = caprylic; 4 = pelargonic; 5 = capric, 6 = undecenoic; 7 = undecylenic; 8 = lauric; 9 = myristic; 10 = palmitic; 11 = palmitoleic; 12 = heptadecenoic; 13 = stearic; 14 = oleic; 15 = linoleic; 16 = linolenic; 17 = eicosanoic acid.



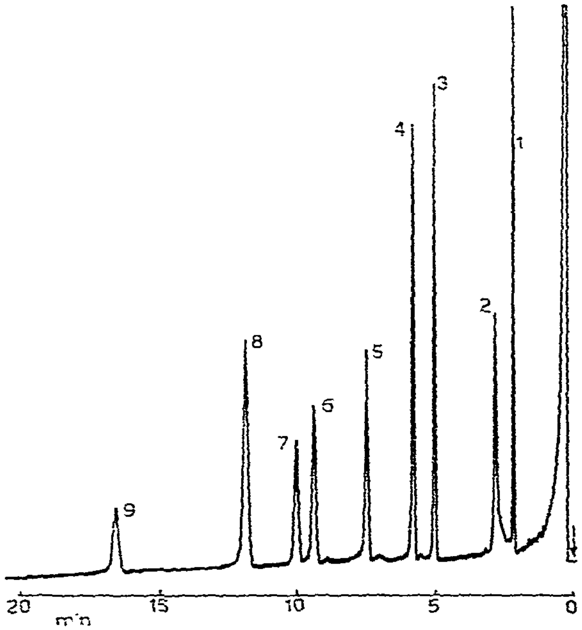


Fig. 4. Gas chromatogram of oxyacid and bicarboxylic acids at 200°C and $\bar{u}$ = 110 cm/sec. Sample injected, 4 μl; concentration of each compound, 1 μg/ml; splitting ratio, 1:50. Peaks: 1 = lactic; 2 = glycolic; 3 = succinic; 4 = glutaric; 5 = aspartic; 6 = fumaric acid.

Fig. 5. Gas chromatogram of phenols. Sample injected, 4 μl; concentration of each compound, 1 μg/ml; splitting ratio, 1:40. Peaks: 1 = 2-bromophenol; 2 = catechol; 3 = α-naphthol; 4 = β-naphthol; 5 = hydroquinone; 6 = resorcinol; 7 = 3-nitrophenol; 8 = 4-phenylphenol; 9 = 4-nitrophenol.

Phenols and chlorophenols also yield symmetrical peaks, as shown in Fig. 5, which is a gas chromatogram of a mixture of mono- and polyphenols and various derivatives. It was obtained on column 5 (Table I) under isothermal conditions at 200°C and $\bar{u} = 93$ cm/sec.

CONCLUSION

Kaolin pre-coated glass capillary columns, additionally coated with FFAP, are effective for the separation of acidic compounds; free fatty acids, some oxyacids and phenols yield symmetrical peaks so that their use is suggested for the analysis of oils as well as of complex acid mixtures.

REFERENCES

1 W. K. Lee and R. M. Bethea, *J. Gas Chromatogr.*, 6 (1968) 582.
2 Di Corcia, R. Sanperi, E. Sebastiani and C. Severini, *Chromatographia*, 14 (1981) 86.
3 L. Zoccolillo, A. Liberti and G. C. Goretti, *J. Chromatogr.*, 43 (1969) 497.
4 G. Goretti, A. Liberti and G. Pili, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 143.
5 M. Verzele and P. Sandra, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 303.
6 P. Sandra, M. Verstappe and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 28.
7 J. L. Marshall and D. A. Parker, *J. Chromatogr.*, 122 (1976) 425.
8 R. D. Dandenau and E. H. Zeremer, *3rd International Symposium on Glass Capillary Column Gas Chromatography, Hindelang, 1979.*
9 M. Hrivnac, L. Sykora-Cechova and M. Muller-Aerne, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 323.
10 G. Goretti, F. Geraci and M. V. Russo, *Chromatographia*, 14 (1981) 285.