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Free fatty acid phase high resolution capillary columns

Free fatty acid phase (FFAP), a product of the reaction between Carbowax 20M and 2-nitroterephthalic acid developed by Varian Aerograph, has been found to be a very effective liquid phase for the gas chromatography (GC) of free fatty acids[1]. Interesting results have also been obtained in the analysis of aliphatic oxygenated compounds[2], though LEE AND BETHEA[3] found it more convenient to modify FFAP with phosphoric acid to eliminate the undesirable tailing which occurred in the GC of some aldehydes.

As most compounds yield symmetrical peaks on FFAP columns, this substance seems to be one of the most convenient general-purpose liquid phases and might be used in the analysis of complex mixtures containing a variety of compounds such as essential oils. It has been shown that these oils[4] may be conveniently fractionated on trimer acid-coated glass capillary columns, but this stationary phase has been criticised because some compounds such as alcohols might be retained on it.

The aim of this investigation was the preparation and the evaluation of high resolution FFAP capillary columns. It was shown that a high efficiency is obtained also with capillary columns of moderate length.

Experimental

Glass capillaries made on a conventional glass-drawing apparatus were coated with FFAP. No special treatment of the glass surface was required: a 10–15% FFAP solution in methylene chloride solvent was made to flow very slowly (20 min/m)

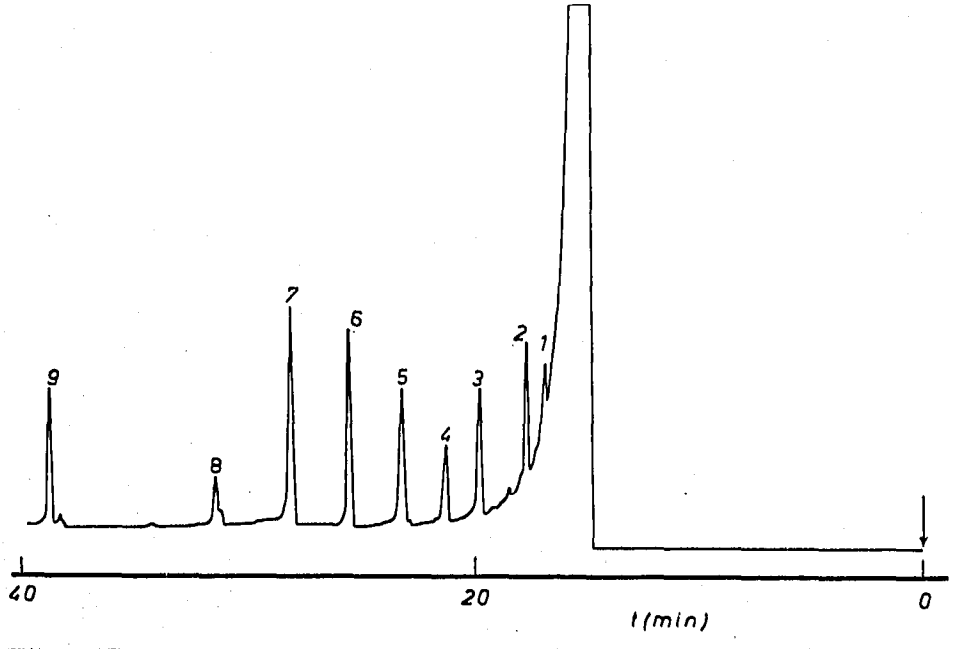


Fig. 1. Programmed-temperature gas chromatogram of a mixture of aldehydes and hydrocarbons. Conditions: 70-m glass capillary column coated with FFAP; 80–130° at 1.25°/min; N_2, 0.5 ml/min. 1 = undecane, 2 = heptanal, 3 = octanal, 4 = tridecane, 5 = nonanal, 6 = tetradecane, 7 = decanal, 8 = pentadecane, 9 = hexadecane.

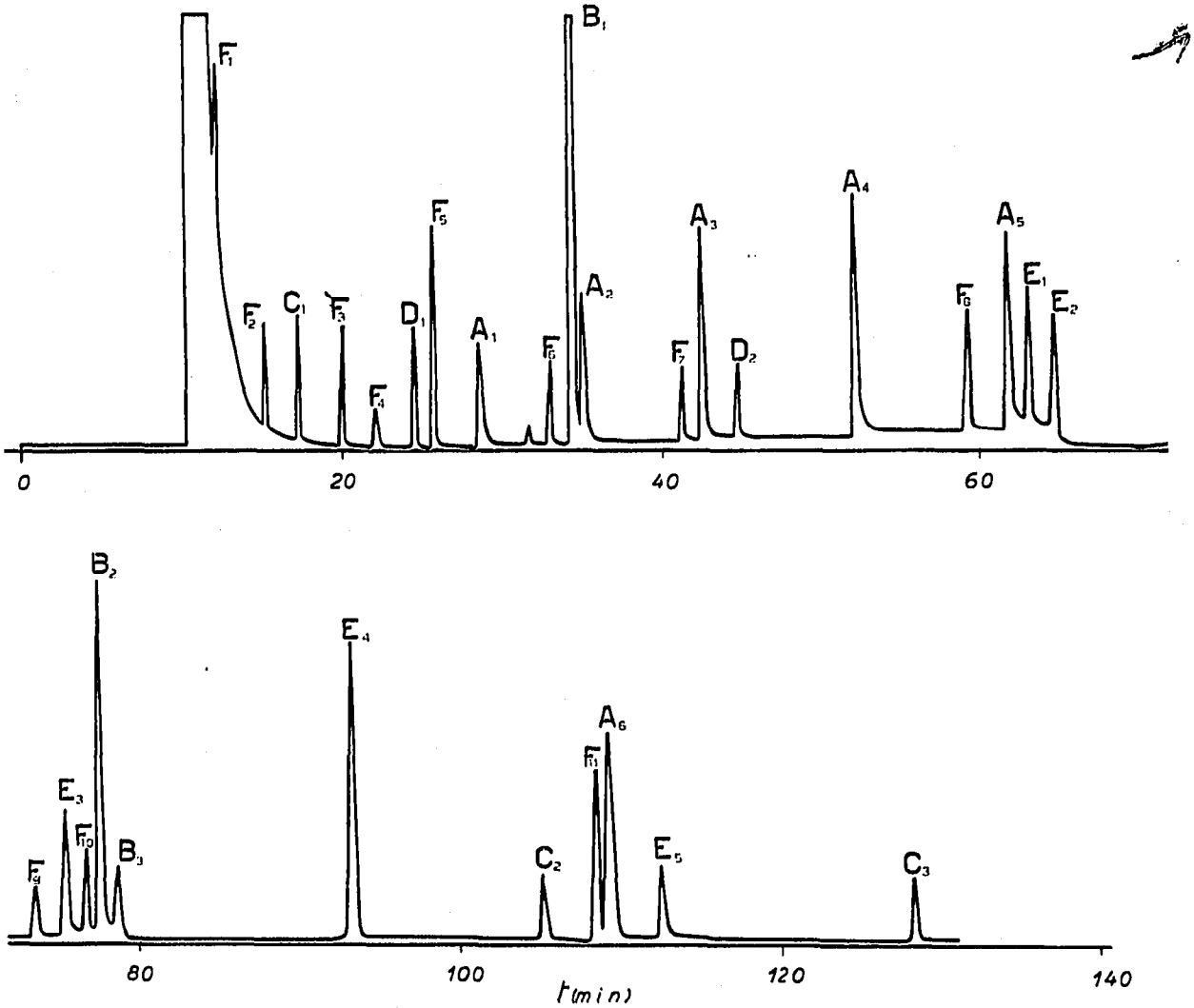


Fig. 2. Programmed-temperature gas chromatogram (80–230° at 1.25°/min; N_2, 0.5 ml/min) on a 45-m glass capillary column coated with FFAP of a mixture of (A) acids: 1 = acetic, 2 = propionic, 3 = *n*-butyric, 4 = valeric, 5 = capronic, 6 = benzoic; (B) aldehydes: 1 = benzaldehyde, 2 = anisaldehyde, 3 = cinnamaldehyde; (C) esters: 1 = acetic, isobutyl ester, 2 = benzoic, ethyl ester, 3 = phthalic, isobutyl ester; (D) ethers and ketones: 1 = ethyl phenyl ether, 2 = acetophenone; (E) alcohols and phenols: 1 = guaiacol, 2 = benzyl alcohol, 3 = phenol, 4 = *m*-xylenol, 5 = hydroxydiphenyl; (F) hydrocarbons: 1 = undecane, 2 = decahydronapthalene, 3 = tridecane, 4 = trimethylbenzene, 5 = tetradecane, 6 = pentadecane, 7 = hexadecane, 8 = octadecane, 9 = diphenyl, 10 = eicosane, 11 = tetracosane.

through the capillary (I.D. 0.25–0.30 mm) and the solvent was then volatilised in a stream of nitrogen.

Several columns were prepared, assembled on Carlo Erba gas chromatographs and used over a wide temperature range (55–240°). To illustrate the efficiency of the columns, a 45-m column (I.D. 0.28 mm) yields 73 000 theoretical plates for *n*-hexadecane at 108° and a 73-m column yields 145 000 theoretical plates for the same compound at 99°.

Polarity of FFAP

The polarity of FFAP was determined following the procedure of LAZARRE AND

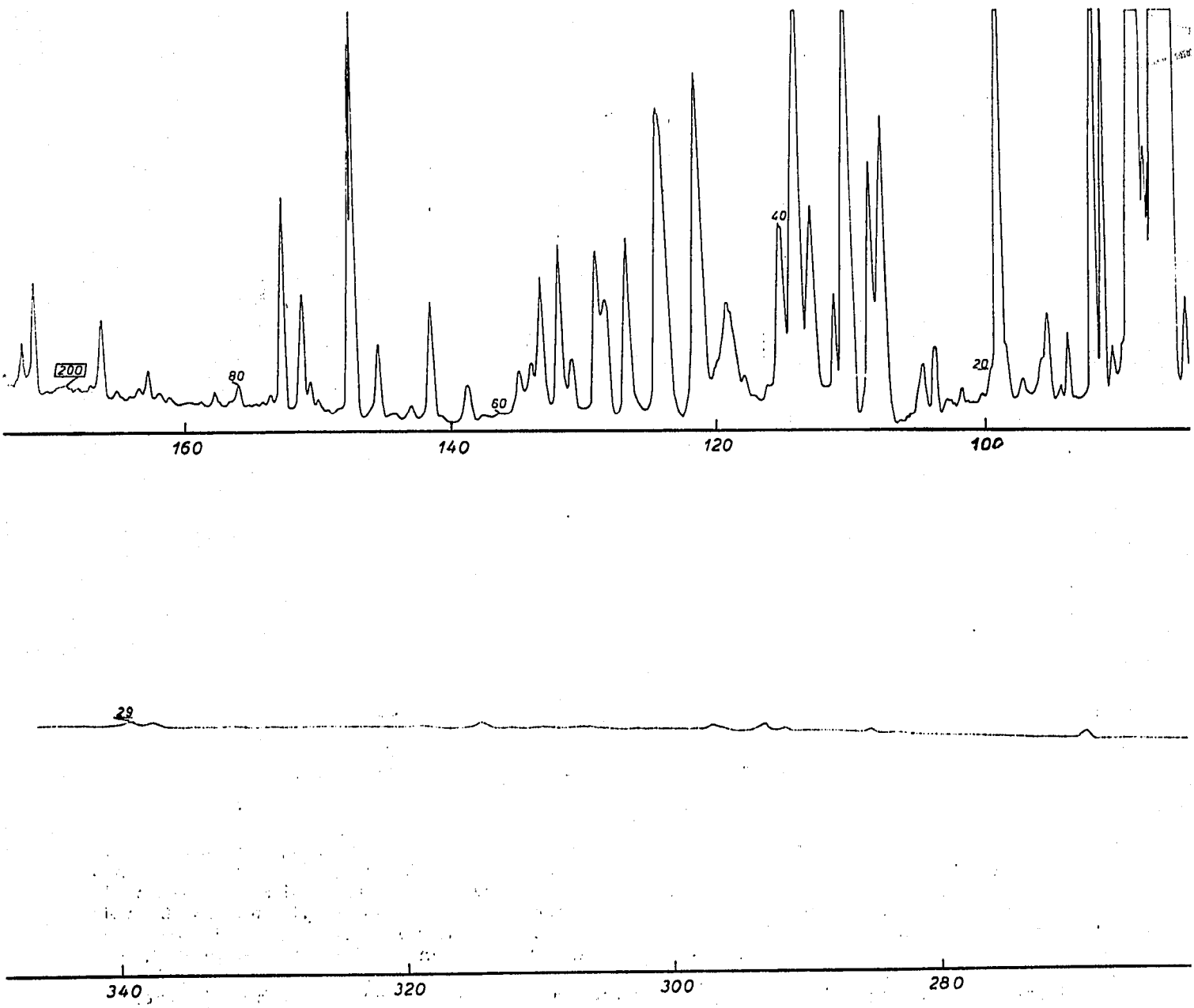
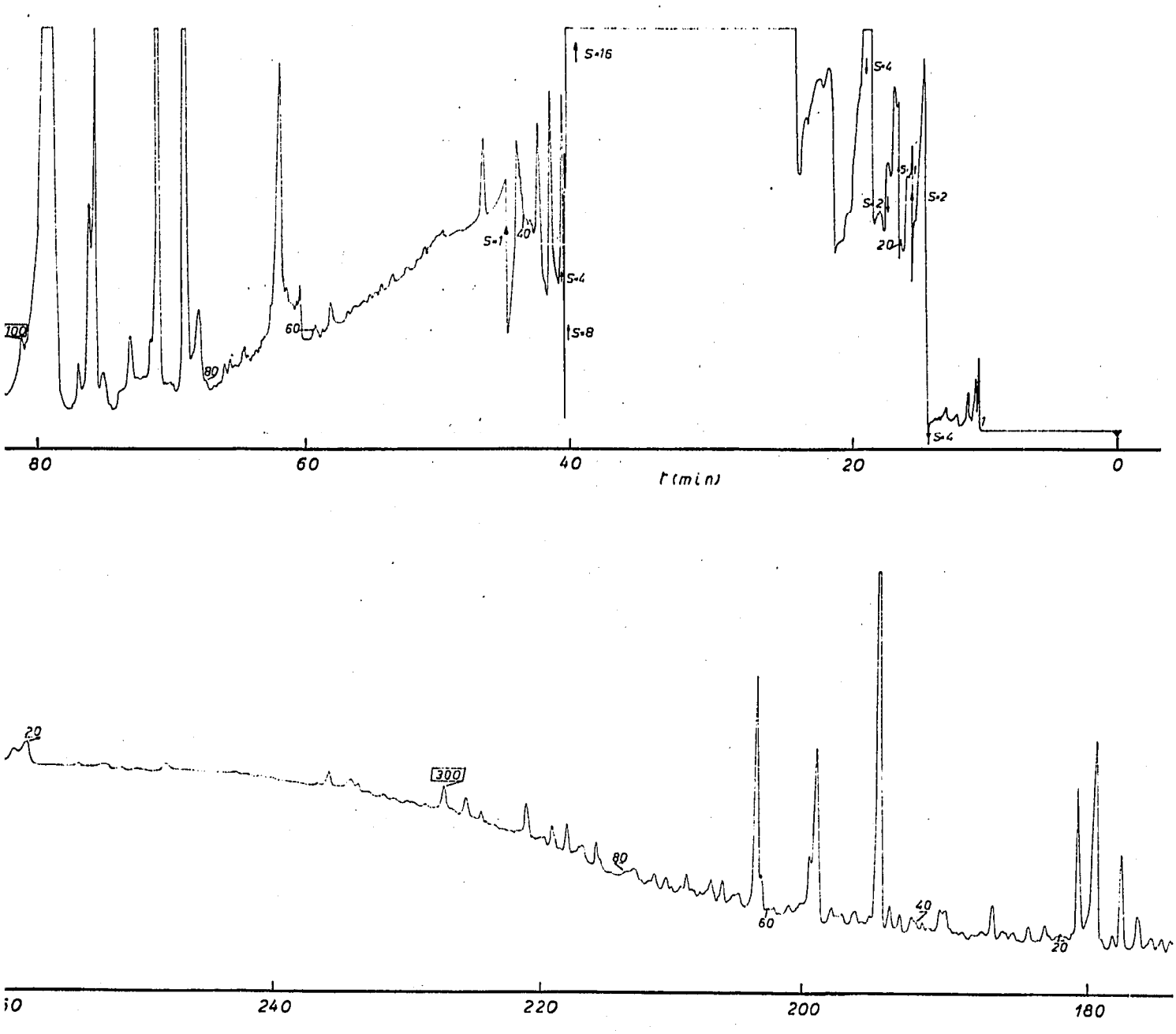


Fig. 3. Gas chromatogram of an orange oil from Reggio Calabria Italy, on a 45-m glass capillary column coated with FFAP (programmed and isothermal temperature; N_2, 0.5 ml/min).

ROUMAZEILLES[5]; polarity can be expressed by means of a numerical value obtained from a study of the function αT *versus* T, where α is the ratio between the corrected retention volumes of two *n*-paraffins, $V_{N(n)}/V_{N(n-1)}$, eluted at the same temperature For FFAP, a value of 671 is obtained which is higher than the values obtained for emulphor (662), triton X305 (616) and DEGS (576), but lower than those for trimer acid (728) Apiezon L (742) and squalane (762) columns. FFAP can thus be considered as a moderately polar stationary phase.



Chromatographic separations

Fig. 1 shows the separation of mixtures of aldehydes and hydrocarbons on a 70-m column, and Fig. 2 shows the separation of (A) acids, (B) aldehydes, (C) esters, (D) ethers and ketones, (E) alcohols and phenols, and (F) hydrocarbons, at programmed temperatures from 80° to 230° on a 45-m column. The peaks are quite symmetrical, well defined and tailing is almost negligible. This excellent response indicates that FFAP-coated capillary columns may be used successfully for the analysis of complex mixtures.

The behaviour of these columns in the analysis of essential oils and of complex mixtures related to aroma evaluation is outstanding. Experiments performed on citrus oils and by operating alternately under isothermal and programmed temperature conditions showed these oils to consist of a much larger number of components than previously reported, because of the high efficiency of FFAP columns. It was previously shown[4] that about 250 compounds were present in citrus oils. Chromatograms produced on an FFAP column of moderate length showed about 330 peaks in an orange oil (Fig. 3) and almost the same number in other citrus oils.

The chromatogram was obtained under the following operating conditions: isothermal at 62° for 43 min; programmed at 1.25°/min up to 110°; isothermal at 110° for 55 min; programmed at 1.25°/min up to 220°; isothermal at 220°.

An FFAP column has been used to obtain information on the nature of odour emission from diesel engines. Exhaust gases from a diesel engine operating under controlled conditions were condensed in a cold trap and extracted with ether. The gas chromatogram of the ether extract was obtained with temperature programming (1.25°/min) from 80° to 232° and then under isothermal conditions on a 70-m column. The presence of 200 components was demonstrated.

Conclusion

FFAP-coated glass capillary columns exhibit an efficiency much greater than that of any other phase for the analysis of complex mixtures; this stationary phase seems to be the most convenient and versatile fractionating tool for the evaluation of essential oils and for the definition of aroma.

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