CHROM. 4088

High-resolution trimer acid-coated glass capillary columns

Trimer acid (Emery Industries Cincinnati, Ohio), a C_{54}-tribasic acid with about 10 % C_{36}-dibasic acid, has so far received little attention in gas–liquid chromatography. AVERILL[1] pointed out that on a Golay column coated with a solution containing 10% trimer acid and 0.4% dinonylnaphthalenedisulfonic acid in toluene, free fatty acids yield symmetrical peaks. However, these columns have a low efficiency and should be used at temperatures below 160°.

The interesting chemical and physical properties of trimer acid suggested its use as a liquid phase in glass capillary columns. It was found that trimer acid-coated glass capillary columns have a number of interesting features and unusual characteristics for the gas chromatographic determination of essential oils, as they are able to give a degree of resolution not yet obtained with other columns.

Experimental

Glass capillaries made on a conventional glass-drawing apparatus[2] are coated with a layer of carbon, which has been obtained by pyrolysis of methylene chloride according to the method of GROB[3]. To obtain a trimer acid coating, a 10% (w/w) solution of trimer acid in methylene chloride is made to flow through the capillary. The carbonized glass is wetted by the trimer acid solution, and a uniform layer is easily obtained.

Determination of polarity of trimer acid

To obtain information on the selectivity of trimer acid in gas chromatography and to evaluate the uses of this stationary phase, its polarity was determined and compared with the polarity of other phases. Glass capillary columns of trimer acid, squalane, Apiezon L, emulphor, Triton X 305 and diethylene glycolsuccinate (DEGS)

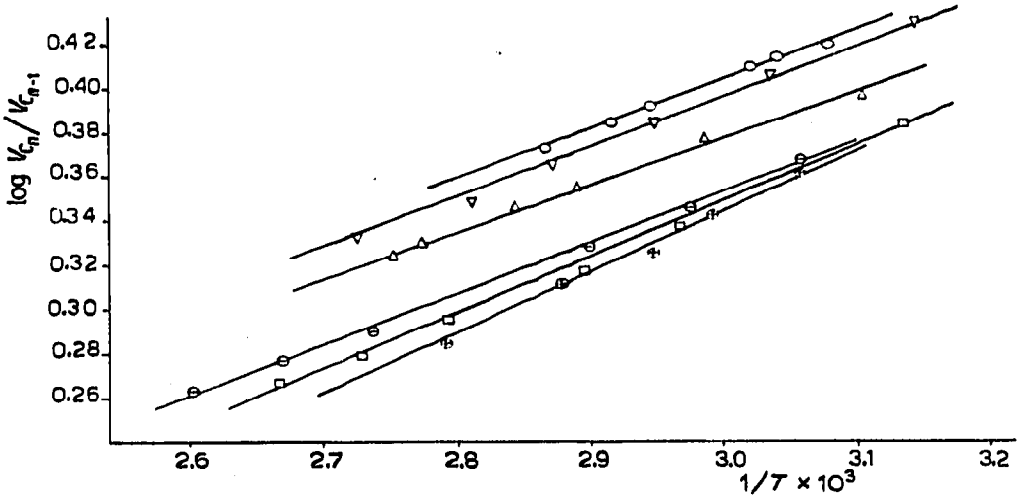


Fig. 1. Logarithm of the ratio of the corrected retention volumes, log V_{Cn}/V_{Cn-1}, *vs.* $1/T \times 10^3$ on glass capillary columns coated with DEGS (○), squalane (▽), Apiezon L (△), trimer acid (⊖), emulphor (□), and Triton X305 (⊕).

TABLE I

αT VALUES

Stationary phase	αT
Squalane	763
Apiezon L	742
Trimer acid	728
Emulphor	662
Triton X 305	616
DEGS	576

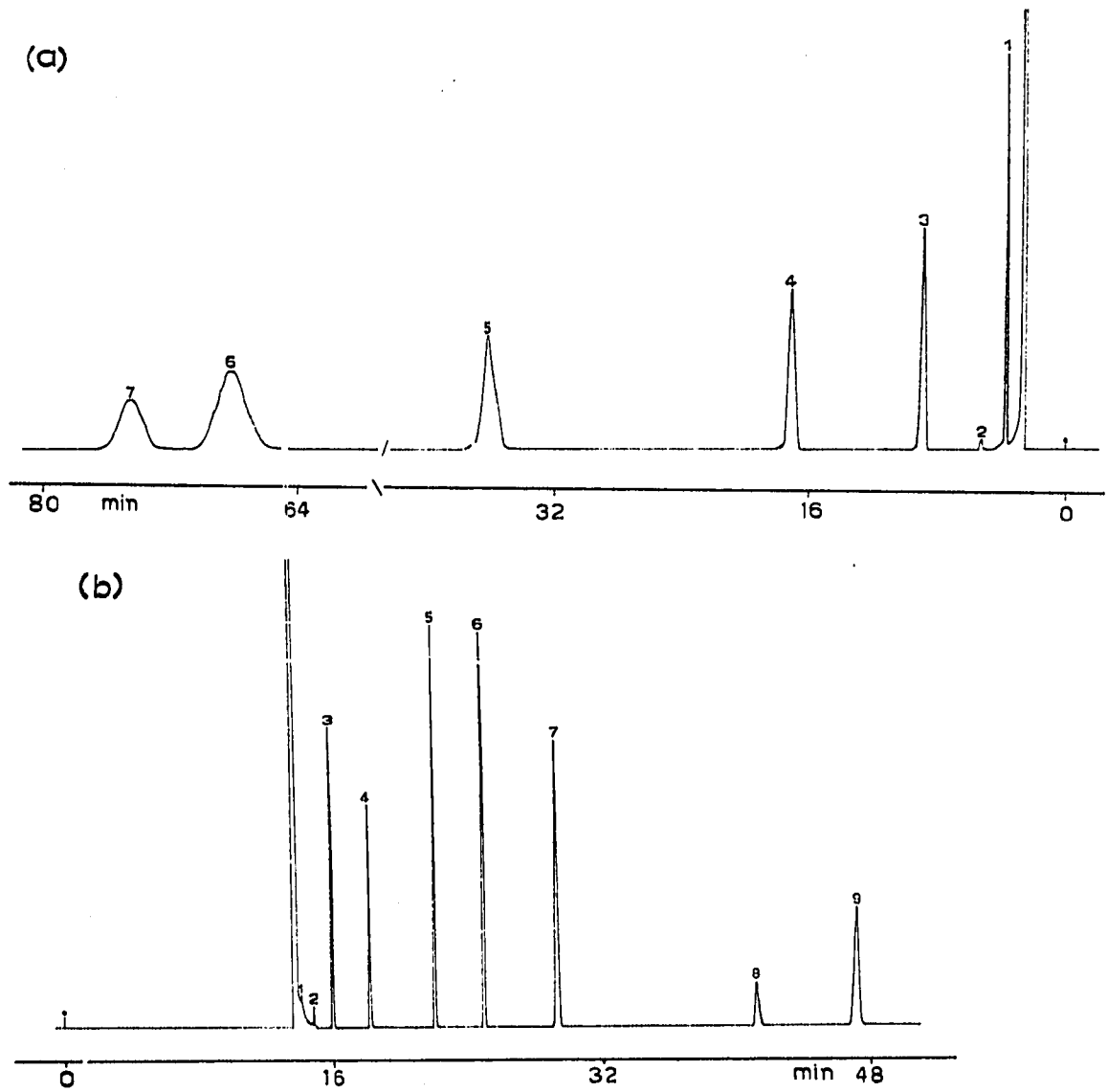


Fig. 2. Gas chromatogram of free fatty acids and aldehydes on 38 m trimer acid-coated glass capillary column. (a) 1 = caprylic acid, 2 = capric acid, 3 = lauric acid, 4 = myristic acid, 5 = palmitic acid, 6 = oleic acid, 7 = stearic acid. Temperature = 194°, N_2-pressure = 2 atm. (b) 1 = valeraldehyde, 2 = caproaldehyde, 3 = enanthaldehyde, 4 = caprylaldehyde, 5 = pelargonic aldehyde, 6 = citronellal, 7 = capraldehyde, 8 = neral, 9 = geranial. Temperature = 120°, N_2-pressure = 0.8 atm.

were prepared and tested by running heptane–octane and undecane–dodecane mixtures on them. The former mixture was used for the non-polar and the latter for other phases.

In Fig. 1 the logarithm of the ratio of the corrected retention volumes, log $V_{C_n}/V_{C_{n-1}} = \alpha$, is plotted *versus* $1/T$. By extrapolation of these lines and following the procedure described by LAZARRE AND ROUMAZEILLES[4], the αT values at the absolute temperature T were calculated, where this product is a constant (see Table I).

Trimer acid is thus a moderately polar stationary phase and might be suitable for use in the analysis of a great variety of chemical compounds. It should be used between 60 and 200°, since no appreciable bleeding is observed in this temperature range.

Preparation of high-resolution glass capillary columns

With the procedure described above high-resolution glass capillary trimer acid columns are easily prepared. As an example of the efficiency of this phase, the separation of free fatty acids which yield symmetrical peaks is shown in Fig. 2. The high degree of efficiency of these columns permits the separation of positional isomers such as *o*-,*p*- and *m*-xylenes and cresols and 2 = 3— and 1 = 2— acetyl thiophenes (Fig. 3a–c).

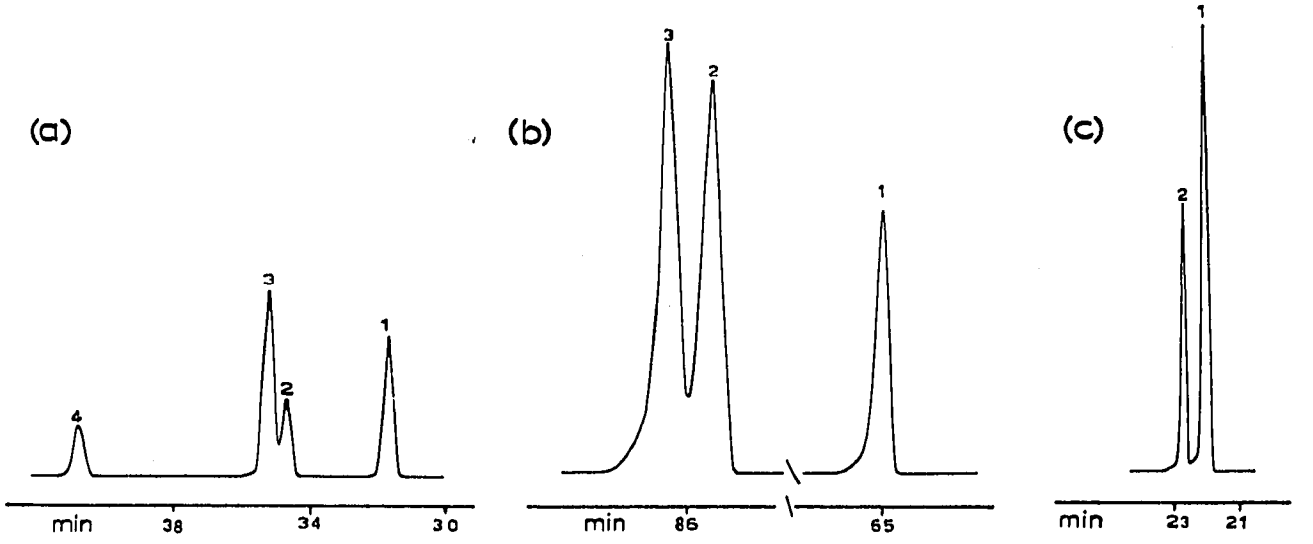
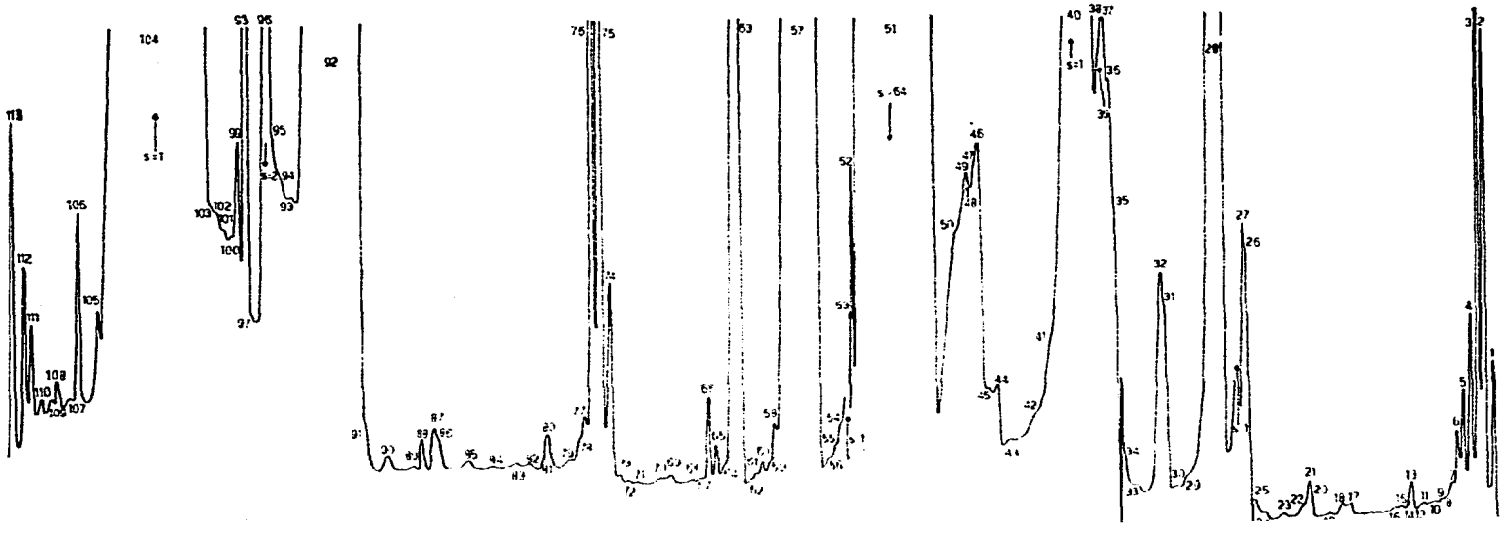


Fig. 3. Gas chromatogram of positional isomers on a 77 m trimer acid-coated glass capillary column. (a) 1 = ethylbenzene, 2 = *p*-xylene, 3 = *m*-xylene, 4 = *o*-xylene. Temperature = 54°, N_2-pressure = 0.8 atm. (b) 1 = *o*-cresol, 2 = *m*-cresol, 3 = *p*-cresol. Temperature = 100°, N_2-pressure = 0.8 atm. (c) 1 = 2-acetyl thiophene, 2 = 3-acetyl thiophene. Temperature = 124°, N_2-pressure = 0.8 atm.

Since most compounds yield symmetrical peaks on trimer acid columns and since this phase is only moderately polar and stable over a wide range of temperatures, these columns have been used to analyse essential oils, in which a large variety of components are present, with excellent results. By using these columns alternatively under isothermal conditions and with programmed temperatures it is possible to demonstrate a much larger number of components in essential oils than previously reported.



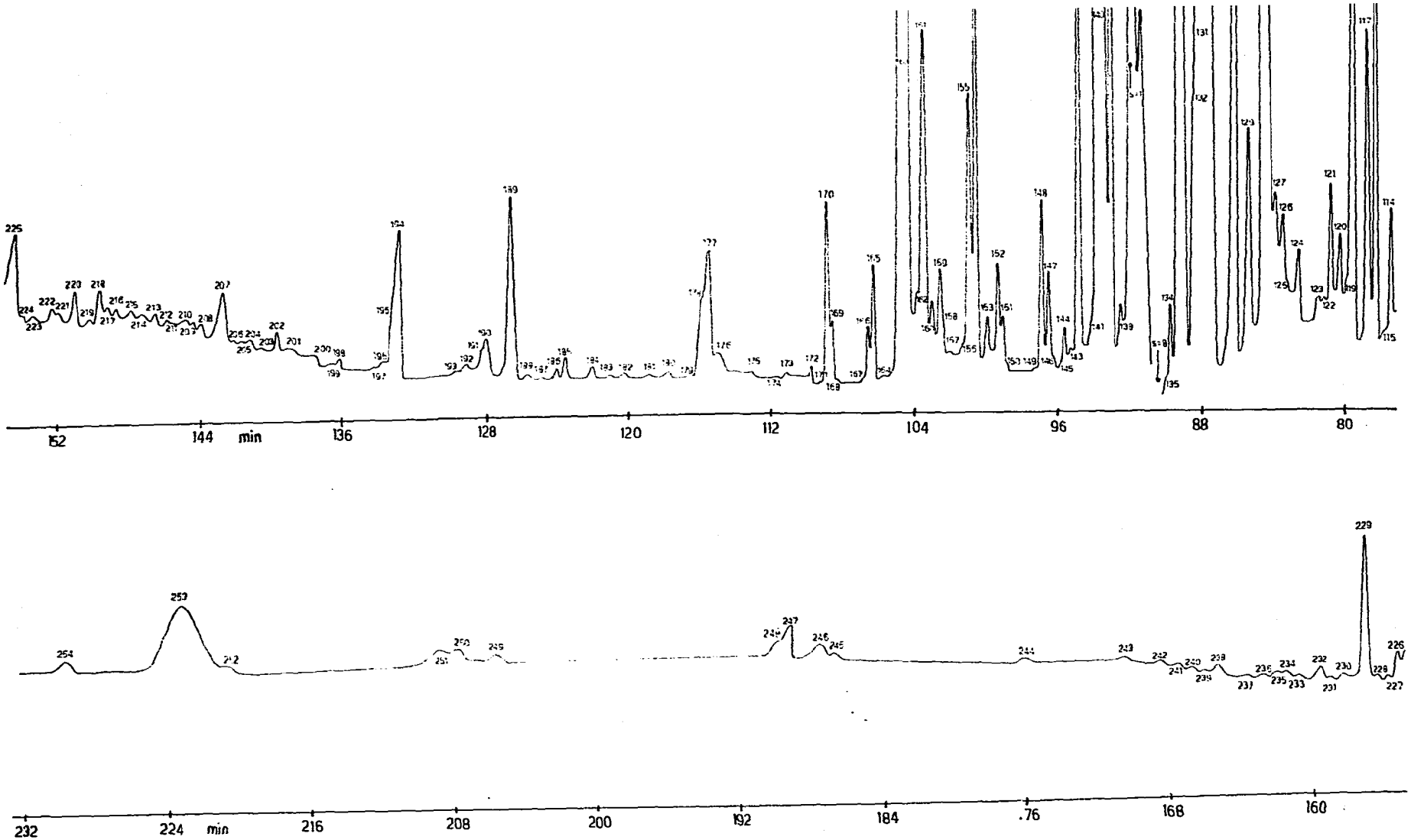


Fig. 4. Gas chromatogram of a bergamot oil on a 77 m trimer acid-coated column. Vaporization temperature = 320°; N_2-pressure = 0.72 kg/cm²; gas flow = 0.5 ml/min.

Fig. 4 shows a gas chromatogram of bergamot oil which was analysed on a 77 m × 0.3 mm (I.D.) trimer acid column, with a capacity ratio for tetradecane at 124° of 2.3; the number of theoretical plates (for this compound) was 132,000.

The chromatography was performed with the following temperature variations: (a) isothermal at 74° for 20 min; (b) programmed temperature, 1.25°/min up to 140°; (c) isothermal at 140° for 10 min; (d) programmed temperature, 1.25°/min up to 186°; (e) isothermal at 186°.

The chromatogram shows that bergamot oil consists of about 250 components. This large number of components is not a specific characteristic of this oil, as almost the same number has been found in other citrus oils. We believe that the use of columns of this kind will greatly aid the study of complex mixtures and the evaluation of essential oils and perfumes.

Istituto di Chimica Analitica,
Università di Roma,
Rome (Italy)

L. ZOCCOLILLO
A. LIBERTI
G. C. GORETTI

1 W. AVERILL, *J. Gas Chromatog.*, 1 (1963) 22.
2 D. H. DESTY, T. M. HARESNAPE AND B. H. F. WHYMAN, *Anal. Chem.*, 32 (1960) 302.
3 K. GROB, *Helv. Chim. Acta*, 48 (1965) 1362.
4 F. LAZARRE AND S. ROUMAZEILLES, *Bull. Soc. Chim. France*, (1965) 3371.

Received April 1st, 1969