

Notes

CHROM. 4819

Separation of mono- and dibasic fatty acids by gas chromatography

The separation and quantitative determination of complex mixtures of mono- and dicarboxylic acids by gas chromatography (GC) is not simple when the carbon number of the components varies over a large range and when branched acids and straight-chain acids are present together.

Many GC procedures have been reported in the literature for a single class of acids or for mixtures having a limited number of components. GC separation of the free fatty acids or of their heavier esters (butylesters) is preferred when low carbon number components are present, while a separation as their methyl esters is chosen with acids heavier than C_8 - C_{10} (refs. 1-3).

APPLEBY AND MAYNE⁴ have recently suggested the separation of C_4 - C_{20} fatty acids and C_8 - C_{12} dicarboxylic acids as their *n*-propyl esters, using 3% polyethylene glycol or 3% Embaphase silicone oil on 100-120 mesh Celite as the stationary phase.

In our present work, it was necessary to analyze complex mixtures of oxidized

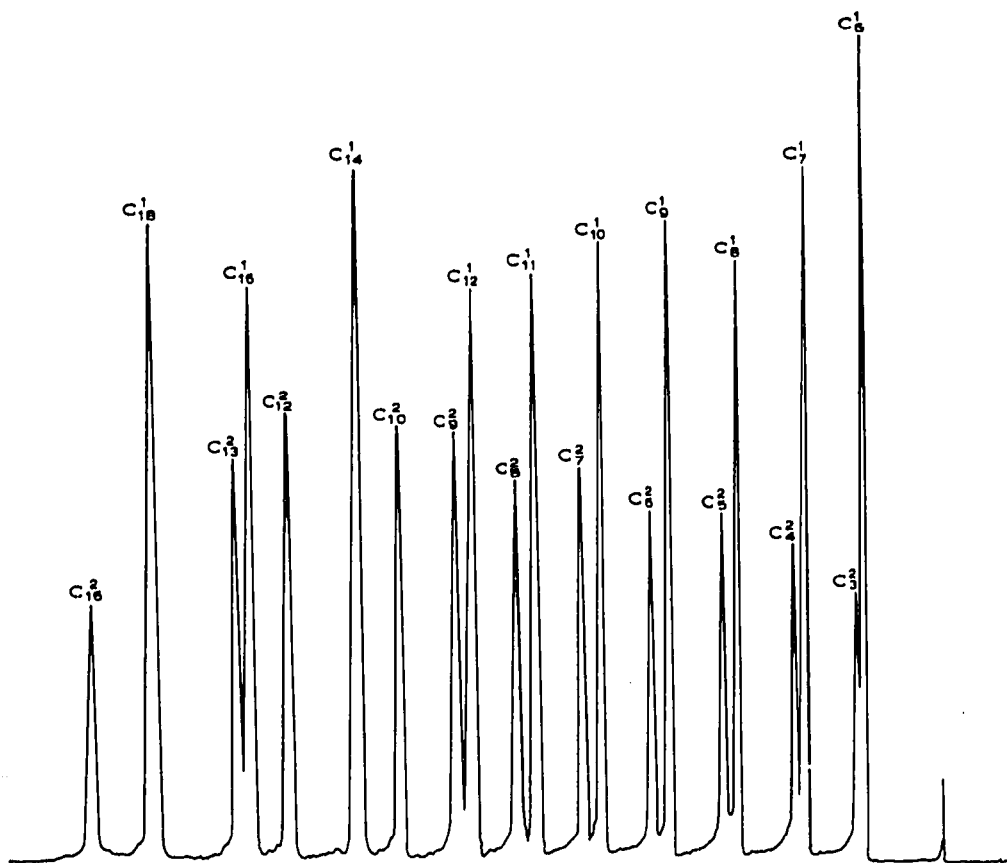


Fig. 1. Chromatogram of the calibration mixture of the methyl esters of the C_6 - C_{18} monoacids and C_4 - C_{10} diacids. See Table I for GC conditions.

TABLE I

CHROMATOGRAPHIC ANALYSIS CONDITIONS

Apparatus:	Perkin Elmer Model 900 gas chromatograph
Detector:	Flame ionization
Column:	4 ft. \times 1/8 in., 5% SE-52 on Chromosorb G AW, 60-80 mesh
Temperature:	programmed 4°/min from 50° to 330°
Carrier gas:	helium 50 ml/min
Recorder:	5 mV span
Chart speed:	4 mm/min
Sample:	1 μ l

products containing C₆-C₂₇ monocarboxylic acids and C₄-C₁₆ dicarboxylic acids. It was found that a GC procedure using 5% of silicone gum rubber, SE-52, on 60-80 mesh Chromosorb G AW as the stationary phase was a possible approach. This

TABLE II

RETENTION TIMES AND RESPONSE FACTORS, RELATIVE TO C₁₀¹, OF THE METHYL ESTERS OF MONO- AND DICARBOXYLIC ACIDS

Component	Purity ^a	Retention time (min)	Response factor	
			FID	TCD
C ₆ ¹	p	2.8		0.90
C ₃ ²	pp	3.6	4.55	1.06
C ₇ ¹	99.9 p	4.9	1.17 \pm 0.05	0.91
C ₄ ²	p	5.3	2.69 \pm 0.10	1.05
C ₈ ¹	99.8 p	7.5	1.08 \pm 0.02	1.00
C ₅ ²	p	8.1	2.34 \pm 0.10	1.07
C ₉ ¹	p	10.6	1.06 \pm 0.04	0.97
C ₆ ²	99 p	11.4	1.86 \pm 0.06	1.05
C ₁₀ ¹	99.9 p	13.7	1.00	1.00
C ₇ ²	p	14.6	1.74 \pm 0.06	1.07
C ₁₁ ¹	99.8 p	16.9	0.96 \pm 0.01	1.01
C ₈ ²	p	17.7	1.70 \pm 0.05	1.09
C ₁₂ ¹	99.7 p	19.8	0.96 \pm 0.01	1.03
C ₉ ²	pract.	20.7	(1.41 \pm 0.10)	1.07
C ₁₃ ¹	—	22.8	—	—
C ₁₀ ²	—	23.5	1.40 \pm 0.10	1.13
C ₁₄ ¹	99.9 p	25.4	0.95 \pm 0.02	1.05
C ₁₁ ²	—	26.2	1.30	—
C ₁₅ ¹	—	28.0	—	—
C ₁₂ ²	p	28.8	1.20 \pm 0.07	1.13
C ₁₆ ¹	p	30.5	0.86 \pm 0.02	1.03
C ₁₃ ²	techn.	31.2	(1.48 \pm 0.07)	1.28
C ₁₇ ¹	—	32.7	—	—
C ₁₄ ²	—	33.4	—	—
C ₁₈ ¹	p	35.1	0.86 \pm 0.02	1.08
C ₁₆ ²	—	35.8	—	—
C ₁₉ ¹	—	37.3	—	—
C ₁₆ ²	—	38.3	1.17	—
C ₂₀ ¹	—	39.3	—	—

^a p = pure; pp = very pure.

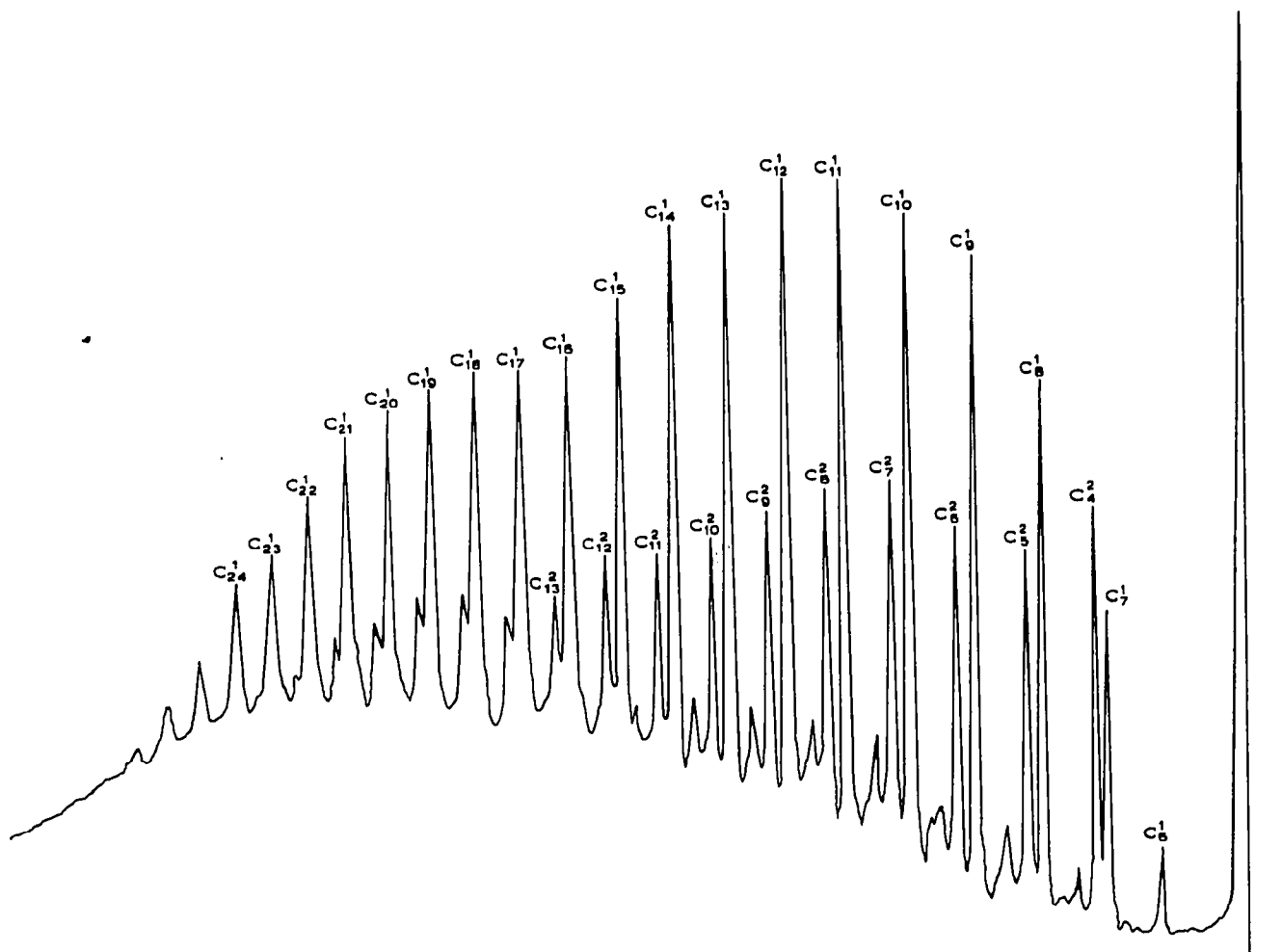


Fig. 2. Chromatogram of methylated acids separated from an oxidation product. See Table I for GC conditions.

stationary phase is stable at high temperatures and allows a final programmed temperature as high as 350°. Therefore a determination of the components with a carbon number higher than C₂₀ is possible.

The gas chromatographic conditions used are given in Table I. Table II shows the retention times of the straight-chain mono- and dicarboxylic acids and the response factors for the flame ionization and for the thermal conductivity (filament) detectors (TCD).

A mixture of the methyl esters of C₆–C₁₈ monoacids and C₄–C₁₀ diacids was prepared from pure components supplied by Merck or Fluka and used for calibration purposes; a typical chromatogram of this mixture is given in Fig. 1.

Fig. 2 is a chromatogram of a mixture of acids separated from an oxidized product methylated according to the methanol–BF₃ method of METCALFE AND SCHMITZ⁵. This chromatogram shows a high background which is mainly due to the methyl esters of branched acids, above which the normal components emerge as well-defined peaks. Normal alkanes mixed with branched and cyclic hydrocarbons give a similar chromatogram when analyzed on the same column.

Some individual branched acids—if present in a comparatively large quantity—could contribute to the area of the *n*-acid peaks; furthermore, when the dicarboxylic ester content is 4–5 times less than that of the monocarboxylic esters, their determination is impossible as is the case of the C₁₃ diacid in chromatogram 2, where its peak is overlapped by the C₁₆ monoacid.

Flame ionization allows higher sensitivities than thermal conductivity but the relative FID response factors for low molecular weight components are rather high. This is because of the considerable influence of the carboxylic acid group in the lighter components as stated by ACKMAN AND SIPOS⁶. For this reason TCD is to be preferred for the analysis of low carbon number components when no sensitivity problems are foreseen.

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