Short Communications

Response of the β-ray ionization detector to unesterified lower fatty acids in gas–liquid chromatography

According to the theory of the β-ray detector given by LOVELOCK[1], response per unit mass for any molecular species will decrease strongly with rising molecular weight up to a molecular weight of about 100, and tend to a constant level at values over 200. This theory was moderately well borne out by the compounds tested by LOVELOCK.

Before using the β-ray detection method for a quantitative analysis of mixtures of monobasic saturated straight-chain fatty acids (4–10 carbon atoms) in the unesterified state it was necessary to check LOVELOCK's theory for these acids, since his experiments included fatty acid methyl esters but not free fatty acids.

Our stationary phase was a polyester of maleic acid, adipic acid and ethylene glycol (see BÖTTCHER et al.[2] for details), which gave well-defined peaks, with much less tailing than was obtained on a mixture of Apiezon L (80 %) and behenic acid (20 %). The apparatus and β-ray detector were supplied by Messrs. W. G. Pye and Co., Ltd., Cambridge, England. The potential across the detector was 1000 V and the carrier gas argon, at a flow rate of 35 ml/min, the outlet of the column being at atmospheric pressure. Column temperature was 175°, and sample sizes were of the order of 0.02 μl.

The values for the peak areas relative to that for pelargonic acid per unit mass and per mole, obtained from our measurements on known mixtures of pure acids, are shown in Table I.

TABLE I

PEAK AREAS OF FATTY ACIDS PER MOLE AND PER UNIT MASS
(Relative to those of pelargonic acid)

Compound	Relative peak area per mole	Relative peak area per unit mass
Butyric acid (C_4)	0.09	0.16
Valeric acid (C_5)	0.35	0.54
Caproic acid (C_6)	0.53	0.72
Enanthic acid (C_7)	0.74	0.90
Caprylic acid (C_8)	0.86	0.94
Pelargonic acid (C_9)	1.00	1.00
Capric acid (C_{10})	1.09	1.00

The relative peak areas per unit mass are plotted against molecular weight in Fig. 1. In the same figure the dotted line indicates the values according to LOVELOCK's

formula[1]. Instead of a decrease of the areas per unit mass with increasing molecular weight, as predicted by the latter formula, we find with the fatty acids a marked increase for molecular weights up to 150. The curve shows a tendency to reach a constant value for the higher molecular weights.

Similar anomalous behaviour with this type of detector has been observed by LOVELOCK et al.[3] for highly halogenated and nitro-compounds, and this was attributed to the capture of free electrons by the relevant groups. The same effect may be operative in the case of the carboxyl group of the free fatty acids. We have evidence that this phenomenon may be observed for other compounds with a large proportion of carbonyl oxygen in the molecule: for example, the peak area per mole of dimethyl succinate (C_4) is only about 0.4 times that of dimethyl sebacate (C_{10}).

The effect is not attributable in any way to trans-esterification of the acids on the polyester stationary phase, since similar results were obtained on the Apiezon-
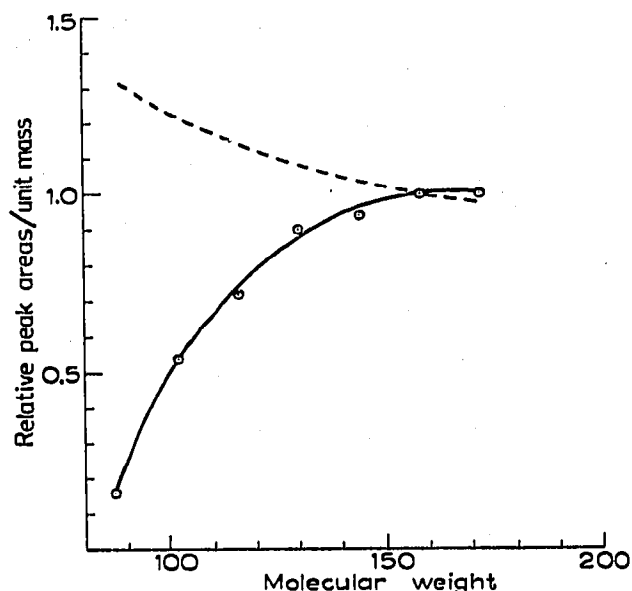

Fig. 1. Observed peak areas per unit mass of monobasic straight-chain saturated fatty acids (relative to that of pelargonic acid) as a function of molecular weight. The dotted curve indicates the relationship predicted by LOVELOCK's formula[1].
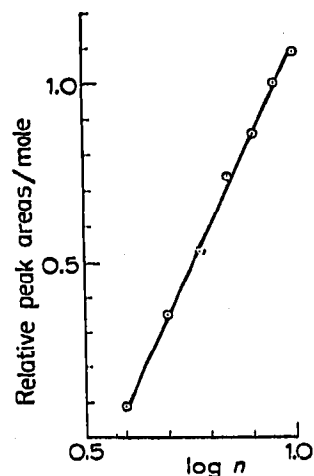

Fig. 2. Observed peak areas per mole of monobasic straight-chain saturated fatty acids (relative to that of pelargonic acid) as a function of $\log_{10} n$, where n is the number of carbon atoms in the molecule.

behenic acid phase mentioned above, although they could not be made quantitative because of excessive tailing.

The relative peak areas A_r per mole of the investigated fatty acids follow quite closely the empirical equation:

$$A_r = 2.5 \log_{10} n - 1.41$$

where n is the number of carbon atoms in the molecule, and the peak area per mole of pelargonic acid is again chosen as unity. This relationship is shown in Fig. 2.

These results indicate that careful calibration of the apparatus is necessary for

compounds of molecular weight less than 100; on the other hand such effects may be useful in indicating the nature of unknown compounds in mixtures.

Department of Physical Chemistry, University of Leiden
(The Netherlands)

C. J. F. BÖTTCHER
G. F. G. CLEMENS
C. M. VAN GENT

[1] J. E. LOVELOCK, *J. Chromatog.*, 1 (1958) 35.
[2] C. J. F. BÖTTCHER, F. P. WOODFORD, E. BOELSMA-VAN HOUTE AND C. M. VAN GENT, *Rec. trav. chim.*, 78 (1958) 794.
[3] J. E. LOVELOCK, A. T. JAMES AND E. A. PIPER, *Ann. N.Y. Acad. Sci.*, 72 (1959) 720.

Paper chromatography of inorganic ions in nitrate media
II. Separation of Se–Te–Po and RaD–RaE–Po

The tendency of polonium to form nitrate complexes in solution is higher than that of its usual radioactive parents (RaD–RaE) and of its homologues (Se–Te). Nitrate media should therefore be useful for chromatographic separations of these elements.

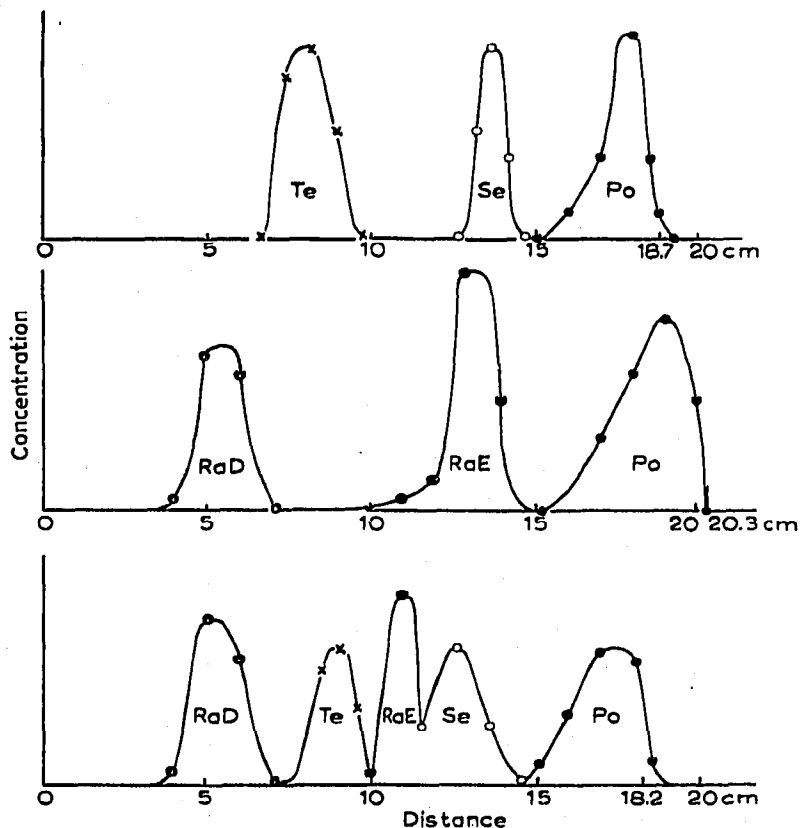A separation by paper chromatography of Se and Te, in the selenite–tellurite

Fig. 1.