

AND POTTERAT<sup>6</sup>; the developing solvent was ethanol-*n*-amyl alcohol-water (1:1:1), and the developing time 25 min. The results are given in Table II.

TABLE II  
THIN-LAYER CHROMATOGRAPHY OF SOME SUBSTANCES  
OF THE VITAMIN B<sub>6</sub> GROUP

| <i>As dye of</i>           | <i>R<sub>F</sub></i> |
|----------------------------|----------------------|
| Pyridoxol                  | 0.85                 |
| Bis-4-pyridoxyl disulphide | 0.80                 |
| 4-Pyridoxthiol             | 0.52                 |

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<sup>1</sup> F. W. BERNHART, E. D'AMATO AND R. M. TOMARELLI, *Arch. Biochem. Biophys.*, 88 (1960) 267.

<sup>2</sup> O. MANOUŠEK AND P. ZUMAN, *Collection Czechoslov. Chem. Commun.*, in the press.

<sup>3</sup> M. PAVLIČEK, J. ROSMUS AND Z. DEYL, *J. Chromatog.*, 7 (1962) 19.

<sup>4</sup> G. WENDT AND F. W. BERNHART, *Arch. Biochem. Biophys.*, 88 (1960) 270.

<sup>5</sup> I. M. HAIS AND K. MACEK, *Papírová chromatografie*, ČSAV, Prague, 1959.

<sup>6</sup> M. MOTTIER AND M. POTTERAT, *Anal. Chim. Acta*, 13 (1955) 46.

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## A note on the use of partially-overloaded $\beta$ -ray ionization detectors in gas chromatography\*

One of the characteristics of the LOVELOCK  $\beta$ -ionization detector is that its response to a fraction becomes less than linear when, at a given instant, the concentration of that fraction in the detector exceeds a critical value<sup>1</sup>. The instantaneous concentration of component in the detector can be reduced by diluting the sample or by lowering column temperature or gas flow rate but changes of this nature tend to prolong the analysis or cause fractions with early emergence times to be hidden in the solvent peak. Moreover, it is not always possible to anticipate the situation and, occasionally, repetition of the analysis with a diluted sample is not possible.

Studies of the fatty acid composition of single seeds often involve a minute quan-

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tity of an oil that contains one component present at the 80 % level as well as material representing less than 1 % of the fatty acids. A typical chart and the corresponding percentage composition is shown in Fig. 1. To cope with unsymmetrical curves produced in situations of this type, the following steps were taken.

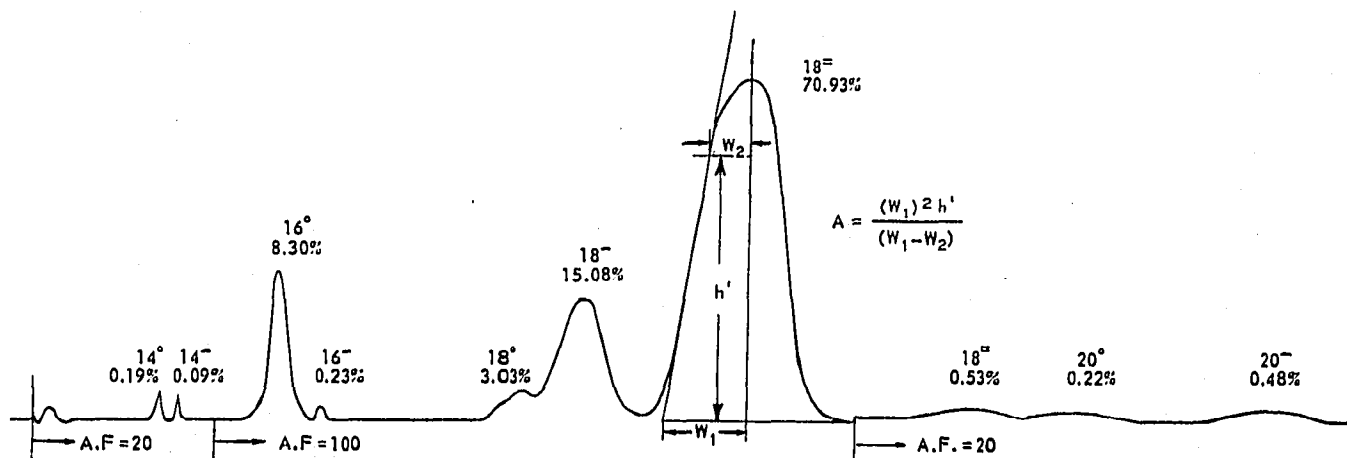


Fig. 1. 6 ft.  $\times$  1/4 in. column containing 5.5 g celite 545 (60-80 mesh) bearing 11 % (w/w) ethylene glycol succinate at 160°. Argon flow = 37 ml/min at 20 p.s.i.; chart rate = 40 in./h; emergence time for 16° = 6.31 min.

(1) The leading edges of 15 large, unsymmetrical peaks were tested by the method of BARTLETT AND SMITH<sup>2</sup> to determine whether they formed part of normal distribution curves. All curves tested showed constancy of  $\sigma$  up to and including 0.607  $h$ .

TABLE I

EFFECT OF MODE OF CALCULATION ON PERCENTAGE COMPOSITION AND IODINE VALUE OF OIL FROM FLAX NO. 7779

| Fatty acid      | Sample diluted 10:1 | Undiluted sample |          |          |
|-----------------|---------------------|------------------|----------|----------|
|                 |                     | mode (a)         | mode (b) | mode (c) |
| 14°             | 1.14                | 1.33             | 1.33     | 1.41     |
| 14 <sup>-</sup> | 0.10                | 0.13             | 0.13     | 0.14     |
| 14 <sup>=</sup> | 0.37                | 0.31             | 0.31     | 0.32     |
| 16°             | 5.91                | 5.57             | 5.58     | 5.91     |
| 16 <sup>-</sup> | 0.43                | 0.37             | 0.37     | 0.40     |
| 16 <sup>=</sup> | 0.50                | 0.35             | 0.35     | 0.37     |
| 18°             | 5.45                | 4.55             | 4.56     | 4.83     |
| 18 <sup>-</sup> | 17.00               | 16.43            | 16.47    | 17.43    |
| 18 <sup>=</sup> | 9.86                | 9.54             | 9.57     | 10.12    |
| 18 <sup>≡</sup> | 61.01               | 60.78            | 60.69    | 58.40    |
| 20 <sup>-</sup> | —                   | 0.63             | 0.63     | 0.67     |
| Chemical I.V.   | 190.1               | 190.1            | 190.1    | 190.1    |
| Calculated I.V. | 190.42              | 189.59           | 188.64   | 184.44   |

(a) = as described in this note.

(b) = leading edge used but triangulation completed on added sheet.

(c) = no allowance made for detector overloading.

(2) Tangents to the leading edges were then drawn between  $0.044 h$  and  $0.607 h$  and produced upward.

(3) Where the peak of the curve could be readily estimated, the triangle was completed and the area determined by mensuration. In the event that the peak was off-scale or insufficiently defined, the system was treated as a truncated triangle<sup>3</sup>:

$$\text{Area} = (W_1)^2 h^1 / (W_1 - W_2)$$

where  $h^1$  is an arbitrary height no greater than  $0.6 h$ . A crude estimate of the height of an off-scale peak has proved sufficient for locating  $h^1$ .

Table I contains data obtained with a Research Specialties Series 600 gas chromatograph equipped with a <sup>90</sup>Sr ionization detector which was supplied with a potential of 750 V. They demonstrate the effect of several modes of calculation on the resultant percentage composition and iodine value of a linseed oil.

These data suggest that provided allowance is made for detector overloading the mode of calculation of area does not affect the results.

The reproducibility of the method described here is shown by the data in Table II.

A statistical assessment of precision has not been attempted. The data in Table II,

TABLE II  
PRECISION OF ANALYSIS OF A SYNTHETIC SAFFLOWER OIL  
MIXTURE USING 0.2  $\mu$ l OF UNDILUTED SAMPLE

| Sample         | 16°  | 18°  | 18"   | 18"   | Iodine value |
|----------------|------|------|-------|-------|--------------|
| Given          | 3.03 | 2.01 | 25.59 | 69.37 | 141.51       |
| Chart 96*      | 3.46 | 1.53 | 26.52 | 68.49 | 140.79       |
| Chart 157*     | 3.15 | 1.80 | 26.47 | 68.58 | 140.90       |
| Outside Lab.** | 2.8  | 1.4  | 26.7  | 69.1  | 141.99       |

\* Methyl ester mixture kept in solution under nitrogen in a deep freeze between analyses.

\*\* Analysis made with a Pye Argon Chromatograph using a 0.01  $\mu$ l sample.

however, are typical of a large number of paired experiments made with flax and safflower seed oils.

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<sup>1</sup> J. E. LOVELOCK, *Ann. N.Y. Acad. Sci.*, 72 (1958-1959) 720.

<sup>2</sup> J. C. BARTLETT AND D. M. SMITH, *Can. J. Chem.*, 38 (1960) 2057.

<sup>3</sup> M. KATES, personal communication.

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