

extreme accuracy is not required or where accuracy cannot be obtained in any event because of errors introduced by other steps in the analytical procedure. However, it is always desirable to improve the accuracy of a convenient method, and this can sometimes be done when sources of inaccuracy are known. For this reason I welcome Dijkstra's critical comment on the method for estimation of peak areas.

K. K. CARROLL

Collip Medical Research Laboratory,
University of Western Ontario,
London, Ontario.

Behaviour of 5A Molecular Sieve in Subtractive Gas Chromatography

5A molecular sieve can be used to remove selectively normal paraffins from hydrocarbon samples in the gas phase at the inlet of a gas liquid chromatographic column^{1,2}. This subtraction technique has formed the basis of analytical procedures for the determination of the normal paraffins in complex petroleum fractions and has been applied in conjunction with both packed and capillary columns³.

It has also been shown that at high temperatures (c. 300° C.) normal paraffins could be removed in a similar manner from waxes but in this molecular weight-range only 2-methyl eicosane and the highly branched paraffin squalane were available to test the selectivity of the molecular sieve. Neither of these compounds was sorbed by the sieve at a temperature of 320° C.

Recently, Murray *et al.*⁴ have reported that unspecified single methyl branched paraffins in the wax range are completely removed from the gas phase by 5A sieve. This affinity for the singly branched paraffins was destroyed by repeated passage of these compounds through the sieve until no further sorption occurred. However, the sieve was still capable of retaining the normal paraffins.

We have now studied the behaviour of the single methyl branched hydrocarbons in greater detail using in particular a sample of 2-methyl dotriacontane synthesized in our laboratories⁵. In these experiments a pre-column 6 cm. long and 6 mm. internal diameter was packed with activated 30–60 B.S. mesh 5A molecular sieve. This pre-column was attached to the inlet of an 86-cm. gas-liquid chromatography column, also of 6 mm. diameter, containing 26 per cent wt. of silicone grease E.301 on 52–60 B.S. mesh 'Sil-O-Cel' firebrick. The pre-column was maintained at 320° C. and the gas-liquid chromatography column at 296° C. These conditions had been used previously for wax separations and were known to be satisfactory for such mixtures³. 10- μ l samples of pure paraffin hydrocarbons were introduced into the pre-column and their behaviour is shown in Table 1.

At C₃₃ the 2-methyl paraffin is completely sorbed whereas at C₂₄ and below this type of compound is not

sorbed by the sieve. Also, when the branching occurs in the middle of the molecule the C₄₃-branched paraffin is retained, but the similar C₂₆ compound is not sorbed. At some critical chain-length between the limits indicated, single methyl branched paraffins start to be sorbed by the 5A sieve.

Further work on the selectivity of the sieve will be carried out as more reference hydrocarbons in this range become available.

We wish to thank Mrs. M. Colwell for the synthesis of some of the paraffins used in the work.

E. R. ADLARD
B. T. WHITHAM

'Shell' Research Ltd.,
Thornton Research Centre,
P.O. Box 1,
Chester.

¹ Brenner, N., and Coates, V. J., *Nature*, **181**, 1401 (1958).

² Whitham, B. T., *Nature*, **182**, 391 (1958).

³ Adlard, E. R., and Whitham, B. T., Reprints, Intern. Gas Chromatography Symp. (Instrum. Soc. Amer., 1961).

⁴ Downing, D. T., Kranz, Z. H., and Murray, K. E., *Austral. J. Chem.*, **13** (1), 80 (1960).

⁵ Colwell, M. (to be published).

Improved Gas Chromatography of Unesterified Fatty Acids

It has been demonstrated by Böttcher *et al.*¹ and by Hunter *et al.*² that unesterified fatty acids can be separated, by gas chromatography, by the use of 'liquid' phases of the polyester type. Metcalfe³ has pointed out the necessity to have a highly acidic 'liquid' phase in order to suppress the association of the carboxyl group of the fatty acids, and has shown that the separation of C₄–C₂₂ fatty acids is very much improved by the incorporation of phosphoric acid in the polyester 'liquid' phase. Using a column packing of 'Celite 545' previously coated with 25 per cent of diethylene glycol adipate polyester and 2 per cent of phosphoric acid, mixtures of fatty acids were separated at temperatures of 220–235° C., yielding well-defined symmetrical peaks and separating saturated and unsaturated acids from each other.

The development of the argon ionization detector has resulted in higher sensitivities of detection, allowing a reduction of sample size. This reduction of sample size itself improves column efficiency and, in addition, allows the use of columns with lower content of 'liquid' phase, which in turn leads to improved resolution and a faster analysis. A faster analysis is particularly important with the separation of fatty acids which are more thermo-labile than their corresponding methyl esters. However, the choice of solid support is important when low ratios of 'liquid' phase to solid support are considered. The use of a solid support having a large surface area per unit weight, such as 'Celite', is not particularly suitable in some respects, since treatment with the 'liquid' phase could leave much of the surface area uncoated, allowing the solid support to act as an absorbent and thus to interfere with the distribution of the analysis sample between the 'carrier' gas and the liquid phase.

Bohemen and Purnell⁴ have discussed the requirements of an efficient solid support. These authors have shown that, as predicted by the van Deemter, Zuiderweg and Klinkenberg rate equation⁵, high column efficiencies are attained when the columns have the following characteristics: (a) narrow range of particle sizes; (b) spherical shape of particle; (c) small quantity of 'liquid' phase.

Table 1. BEHAVIOUR OF PARAFFIN HYDROCARBONS IN A GAS-LIQUID CHROMATOGRAPHY PRE-COLUMN CONTAINING 5A MOLECULAR SIEVE

Completely sorbed from the gas phase		Not sorbed from the gas phase	
Docosane	C ₂₂	2-Methyl eicosane	C ₂₁
Tetraacosane	C ₂₄	2-Methyl tricosane	C ₂₃
Hexacosane	C ₂₆	13-Methyl pentacosane	C ₂₅
Octacosane	C ₂₈		
Dotriacontane	C ₃₂		
2-Methyl dotriacontane	C ₃₃		
22-Methyl tritetracosane*	C ₄₄		

* Gas-liquid chromatography column temperature, 350° C.