

Notes

Displacement effect of water in gas chromatography

It has been found that when a mixture of water and organic components passes through a gas chromatographic column, the retention volumes of substances more strongly retained than water are reduced by comparison with their values in the absence of water. This effect is shown in the three superimposed chromatograms illustrated in Fig. 1 obtained with a hydrogen flame ionisation detector. The chromatogram of water alone was recorded at a much higher instrument sensitivity than the other two. Operating conditions, together with retention data and peak dimensions,

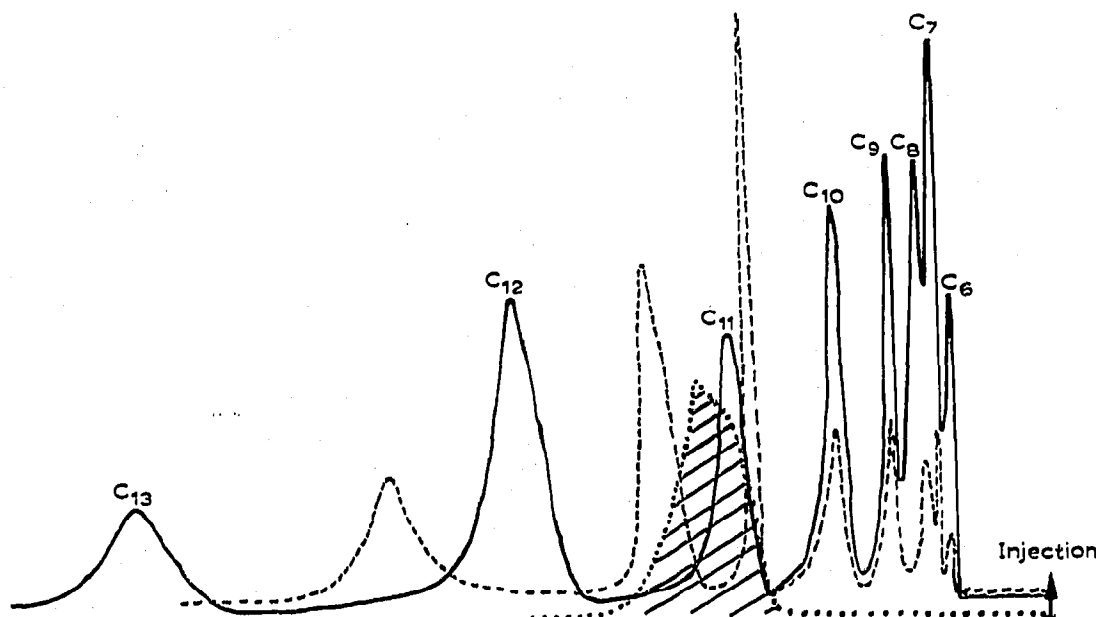


Fig. 1. Chromatograms of *n*-alkanes on polyethylene glycol in the presence, and the absence, of water. (—) *n*-alkanes alone; (---) *n*-alkanes plus water; (····) water alone (water peak hatched).

are given in Table I. A similar effect was observed when an apolar silicone oil column was used instead of one containing the polar glycol. Results for the silicone column are given in Table II.

The principal features shown by these chromatograms are:

(i) Substances which normally elute before the water "front" have identical retention times in the presence and absence of water.

(ii) A substance having an almost identical retention to water emerges, in its presence, just ahead of the water "front" and, under these conditions, the peak is very much sharper.

(iii) Substances normally eluting after the water "front" are eluted more rapidly in the presence of water, although they do not overtake the water "front".

TABLE I

RETENTION DISTANCES OF *n*-ALKANES-POLAR COLUMN

Column: 6', 10% polyethylene glycol 4000 on 60-100 mesh celite; temperature: 101°; carrier gas flow rate: 75 c.c.s. min⁻¹ nitrogen at column exit; chart speed: 64" h⁻¹; samples and size: (a) 0.2 μl *n*-C₆-*n*-C₁₃ alkane blend, (b) as (a) with 7 μl water added.

<i>n</i> -Alkane	Retention distances (mm)		Peak width at half height (mm)	
	(a)	(b)	(a)	(b)
Hexane	21	21	—	—
Heptane	24	24	—	—
Octane	27	27	—	—
Nonane	33	33	2.0	2.0
Decane	43	43	3.8	3.0
Undecane	65	58	5.6	1.9
Dodecane	107	77	10.0	6.3
Tridecane	184	110	17.0	11.0

Water front appears at 57 mm.

(iv) The presence of a water peak is revealed by a hydrogen flame ionisation detector despite the generally accepted belief that this detector does not respond to water¹.

Discussion

As the retention times of substances which travel through a column more rapidly than water are unaffected, it follows that the influence of water is effected in the column, not at the point of injection. The unexpected sharpness of the *n*-undecane peak (Fig. 1 and Table I) which emerges with the water "front" can be attributed to a displacement effect of the water. This displacement may arise from a change in stationary phase character. In the vicinity of a water peak, as it passes through a column, the stationary phase is considered to be a mixture of the particular phase used and water. Consequently, partition coefficients, particularly of hydrophobic

TABLE II

RETENTION DISTANCES OF *n*-ALKANES-APOLAR COLUMN

Column: 6' 10% silicone oil on 60-100 mesh celite; temperature: 124°; carrier gas flow rate: 70 c.c.s. min⁻¹ nitrogen at column exit; chart speed: 64" h⁻¹; samples and sizes: (a) 0.2 μl *n*-C₆-*n*-C₉ alkane blend, (b) as (a) with 7 μl water added.

<i>n</i> -Alkane	Retention distances (mm)	
	a	b
Hexane	74	65
Heptane	108	100
Octane	169	163
Nonane	286	283

Water front appears at 42 mm.

materials, will be decreased in this region of the column. In the example cited, *n*-undecane is probably virtually insoluble in the polyethylene glycol-water mixture postulated and therefore passes through the column as a very sharp "slug" just ahead of the water "front".

The unexpectedly rapid elution of substances retained more strongly than *n*-undecane is interpreted as reflecting that the water and the substance proceed together through the column for a period of time. The time during which water and the solute are proceeding together through the column is roughly inversely proportional to the difference in their retention times. During this period the partition coefficient of the solute is lower than normal and the component therefore moves more rapidly than normal, though not as fast as the water. The solute eventually falls behind the water peak region and for the remainder of its passage through the column partitions normally into the stationary phase. These observations show that identifications based on retention data obtained in the absence of water are suspect when applied to the analysis of aqueous solutions.

Conclusions

It is concluded that the gas chromatographic analysis of dilute aqueous solutions of hydrocarbons requires either the selection of a column which retains water after all of the component of interest have passed (a very polar column) or the calibration of the column with aqueous solutions of pure components prior to the running of unknown samples.

If the explanation of the origin of the displacement effect of water is correct, it is expected that the retentions of small amounts of substances eluting close to a major component will also be changed; the magnitude of the change would depend on both the quantity and the chemical nature of the major component. Thus, in trace analysis, difficulties in identification based on retention parameters obtained with pure substances can be anticipated. Very recently an effect of this type has been reported in the separation of esters of long chain fatty acids².

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¹ A. B. LITTLEWOOD, *Gas Chromatography*, Academic Press, London, 1962, p. 294.

² R. G. ACKMAN, *J. Gas Chromatog.*, 3 (1965) 15.

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