

Notes

A rapid method for evaluating gas-liquid chromatography stationary phases

Introduction

The liquid used as stationary phase in the G.L.C. column should be chemically stable and involatile at the operating temperature and should preferably be thoroughly evaluated before use. Since the analyst requires reproducible retention data, evaluation of the stationary phase with respect to the constancy of retention data is more significant than investigations of chemical changes¹ or redistribution of the liquid phase in the column^{2,3} or measurement of the loss of material from the column^{4,5}.

Previous attempts to detect changes in retention^{3,6} have employed specific retention volumes which are difficult and time consuming to measure reliably and are irrelevant in the context of relative retention data. As the evaluation of stationary phases is of prime importance to gas chromatography the author proposes to describe a simple and rapid method which can be run in conjunction with the routine analytical work of a laboratory.

Procedure

The method involves the following steps:

1. Preparation and conditioning of the column.
2. Determination of the maximum operating temperature.
3. Preparation of suitable calibration solutions.
4. Chromatography of the calibration solutions whilst the column temperature is alternated between a convenient temperature in the range 60° to 100° and the maximum operating temperature.
5. Calculation of relative retentions in retention index units and processing of the data.

1. The column packing should be coated by the usual technique and the column conditioned at moderate temperatures (not exceeding 100°) thus ensuring minimum thermal degradation of the stationary phase.

2. The most probable maximum operating temperature should be obtained by measurement of the detector signal due to stationary phase bleed preferably using one of the ionisation detectors. The retention data subsequently obtained will serve to confirm whether or not this was the highest temperature at which constant retentions can be obtained.

3. The calibration solution should be a mixture containing at least four *n*-alkanes, preferably successive homologues, and at least five solutes which have retentions between those of the *n*-alkanes. The solutes should be selected so as to

have as wide a range of solvent interactions as possible. Therefore molecules with either strong dipoles, or hydrogen bond acceptor or donator properties or readily polarisable groups should be included. Only compounds which give symmetrical peaks on the chromatogram should be used. The mixtures should be made up as ~ 5 % w/v solutions in a volatile solvent, 30-40 petrol or *n*-heptane.

4. The column temperature should be alternated daily between a convenient temperature in the range 60-100° and the maximum operating temperature. The column temperature should remain constant within the period the chromatograms are obtained (drift not to exceed 0.2°) and be reproducible from day to day (within ± 0.2°). The carrier gas flow rate should also remain constant within a run and be reproducible.

5. Retention distances should be measured from the point of injection to peak maxima on the recorder chart and the retention indices calculated according to KOVATS⁷ using the expression:

$$I = 100 N + 100 n \left(\frac{\log R_S - \log R_N}{\log R_{N+n} - \log R_N} \right)$$

where N = the carbon number of the first *n*-alkane used and $N + n$ that of the second,

R_S = the retention of the solute,

R_N = the retention of *n*-alkane carbon number N ,

R_{N+n} = the retention of *n*-alkane carbon number $N + n$.

The constancy of the retention data can be tested by plotting against the column life. Since no column dead volume correction (which will vary from column to column) is applied, the retention data is not suitable for documentation.

Experimental and results

In order to illustrate the method of evaluation one of the new nitrile silicone stationary phases was examined.

Chromatograms were obtained using an apparatus consisting of glass columns (5 ft. long and 4 mm I.D.) with a modified flame ionisation detector⁸. The carrier gas was a 3:1 (by volume) mixture of hydrogen and nitrogen. The flow rate was controlled solely by a standard BHR 12 regulator (British Oxygen Gases). The column was packed with a 20 % w/w mixture of nitrile silicone fluid XF-1150 (General Electric Company of U.S.A.) and acid washed 60-70 mesh celite. The column was heated by means of a vapour jacket, methanol 65° and *n*-pentanol 138°. The carrier gas which was dried over linde molecular sieve was allowed to flow continuously, the column being maintained at elevated temperature during the day (~ 8 h) and left at room temperature overnight. The calibration solutions were introduced by means of stainless steel capillary pipettes.

The results which are summarised in Table I reveal that nitrile silicone XF-1150 stationary phase is capable of giving constant retention data at temperatures up to 138° over a period of at least 120 h (approximately 15 working days).

Conclusions

The method described is capable of giving constant retention data with stationary phases which do not undergo chemical changes with column usage. The particular

TABLE I

THE CONSTANCY OF RETENTION DATA WITH COLUMN USAGE

Column: 20% nitrile silicone XF 1150, celite; carrier gas flow rate: 60 ml/min at 65° and 138°.

Substance	Temp. (°C)	$I_{initial}$	I_{final}	δI	I_{mean}	σ
<i>n</i> -Hexane thiol	65	1141	1142	+ 1	1143	1.2
Pentan-1-ol	65	1181	1181	Nil	1182	1.2
<i>n</i> -Butyl cyanide	65	1252	1255	+ 3	1255	1.8
Di- <i>tert.</i> -butyl disulphide	65	1329	1330	+ 1	1330	0.7
1-Iodoheptane	65	1358	1360	+ 2	1360	1.0
Methyl fumarate	138	1718	1719	+ 1	1719	0.9
Octadec-1-ene	138	1850	1850	Nil	1850	0.4
Dodecan-1-ol	138	1955	1955	Nil	1955	0.8
Di- <i>n</i> -heptyl ketone	138	2076	2076	Nil	2076	1.1
1-Chlorohexadecane	138	2137	2137	Nil	2137	0.6

Where $I_{initial}$ and I_{final} are the initial and final retention indices and I_{mean} the mean of 7 determinations carried out over a period of 3 weeks.

δI is the change of retention index between initial and final observations.

σ is the standard deviation in retention index units.

attractions of the method are its simplicity and rapidity. Chromatograms need not take longer than 3 h for duplicate determinations, and the calculations less than 30 min as no dead volume correction need be computed⁹. Thus it should be possible to evaluate a number of stationary phases at one time, the columns being available for routine analysis purposes after a day's calibrations have been completed. Once stationary phases have been evaluated by this technique methods of column characterisation may then be investigated. Such an investigation is now in progress at N.R.P.R.A.

The Natural Rubber Producers' Research Association,
Welwyn Garden City, Herts. (Great Britain)

M. B. EVANS

¹ D. H. DESTY AND J. C. HAWKES, in D. H. DESTY (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 266.

² H. S. KNIGHT AND R. L. PECSOK, *Principles and Practice of Gas Chromatography*, John Wiley and Sons, New York, 1959.

³ R. BATE, B. COSTA, P. FORMAN AND R. A. KELLER, *J. Chromatog.*, 8 (1962) 157.

⁴ *Materials for Gas Chromatography*, May and Baker Ltd., Dagenham, England, 1958.

⁵ W. GERRARD, S. J. HAWKES AND E. F. MOONEY, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 266.

⁶ G. W. TAYLOR AND A. S. DUNLOP, *Gas Chromatography*, Academic Press, New York, 1958, p. 73.

⁷ E. KOVATS, *Helv. Chim. Acta*, 41 (1958) 1915.

⁸ J. F. SMITH, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 114.

⁹ M. B. EVANS AND J. F. SMITH, *J. Chromatog.*, 9 (1962) 147.

Received October 31st, 1962