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VARIATION OF PERFORMANCE OF POROUS POLYMER BEAD COLUMNS IN GAS CHROMATOGRAPHY

T. A. GOUGH
Laboratory of Government Chemist, Stamford Street, London S.E. 1 (Great Britain)
AND
C. F. SIMPSON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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SUMMARY

A study has been made of the variation of performance of different batches and types of porous polymer bead columns for the analysis of water–alcohol mixtures. The effect of preconditioning of the columns, column wall material, and sample size on quantitative analysis, retention time, peak asymmetry, efficiency and resolution are reported.

INTRODUCTION

Synthetic porous polymer beads have been in widespread use for several years and form a valuable addition to the wide selection of traditional column packings. Porous polymer bead columns are particularly useful for the analysis of aqueous samples and those containing other highly polar compounds, since satisfactory elution profiles may be obtained in contrast to the gross distortions often encountered using conventional stationary phases and supports. HOLLIS AND HAYES[1], in an account of the use of porous polymer beads for the analysis of a variety of aqueous samples, state that little if any loss of water by adsorption occurs on the column packing, although no detailed quantitative data are presented. Adsorption may however occur on the column walls and HOLLIS AND HAYES stress the need to minimise bare metal surfaces. In the present work the effect of different column wall materials on the quantitative analysis of aqueous samples is reported. The effect of sample size on retention time has recently been discussed[2,3] and some data are presented herein. The thermal stability of a column and its ability to maintain a constant level of performance during use are important criteria in the choice of packing material. The stability of porous polymer columns at 200°, after conditioning at 225°, expressed in terms of relative retention time, has been reported by PALFRAMAN AND WALKER[4]. The effect of preconditioning of columns, on quantitative analysis, retention time, peak asymmetry, efficiency and resolution are now reported. HOLLIS[5] has stated that

by proper control of the synthesis of porous polymer beads one could expect to obtain a polymer which would be reproducible from batch to batch, and which would give good retention reproducibility. The present authors have carried out such an investigation in which water–alcohol mixtures were repeatedly analysed on different types and batches of porous polymer bead.

EXPERIMENTAL

All analyses were carried out on a Pye 104 chromatograph fitted with a Gow-Mac Minigade 625 gas density detector. Previous work[6] has shown that although the response of the gas density detector is predictable under some operating conditions, it is advisable to calibrate the device. This was carried out using a mass detector[7], connected in series with the gas density detector.

All columns were 4 ft. × ¼ in. O.D. and were thoroughly cleaned but not silanised prior to use. Column packing was sieved to 80–100 BS mesh. Columns of stainless steel were prepared from three different batches of Porapak Q, one batch of Porapak Q-S (silanised by manufacturers), and one of Chromosorb 102. In addition one glass and one teflon column were packed with the same batch of Porapak Q as one of the metal columns, to compare the contribution of the column wall materials. Details of the columns are given in Table I. The maximum operating temperatures recommended by the manufacturers are 300° for Porapak Q and 250° for Chromosorb 102.

TABLE I

COLUMN DETAILS

Column No.	*Material*	*I.D. (mm)*	*Packing*	*Batch No. of packing*[a]	*Weight of packing (g)*
1	S/steel	5.0	Porapak Q	1	7.9
2	glass	3.0	Porapak Q	1	4.6
3	teflon	4.5	Porapak Q	1	6.4
4	S/steel	5.0	Porapak Q	2	8.0
5	S/steel	5.0	Porapak QS	3	7.7
6	S/steel	5.0	Chromosorb 102	4	7.7
7	S/steel	5.0	Porapak Q	5	8.8

[a] Authors' assignation.

All packing material was white and fairly free flowing prior to conditioning except Porapak Q batch 5 which was yellow and did not flow freely. Each column was filled by forcing the packing into the coiled tubing under a slowly increasing pressure (0–30 p.s.i.g.), accompanied by gentle vibration. Columns were conditioned overnight at 150° in a stream of nitrogen, the packing adjusted to the same height in each column, and the columns plugged with silanised glass yarn. The following experiments were carried out on each of the seven columns. With a 10 μl syringe, 1 μl samples of water–alcohol mixtures were injected. Each sample was injected in triplicate and the injection septum was renewed after every 6th injection. No sample was kept for more than a few hours, and the same syringe was used throughout the

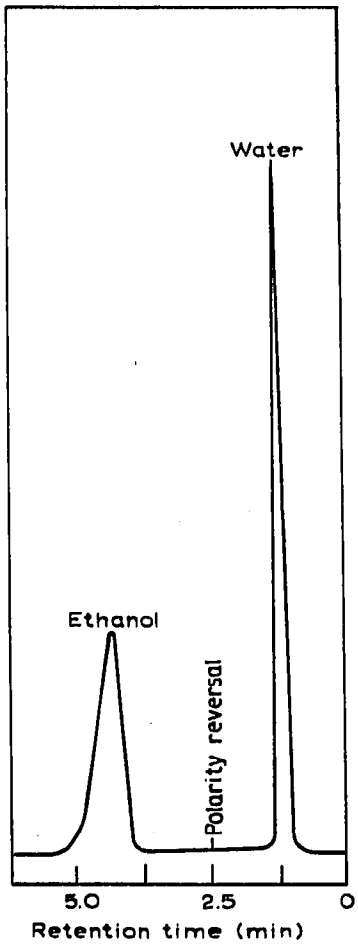


Fig. 1. Chromatogram of water–alcohol mixture.

TABLE II

OPERATING CONDITIONS

Apparatus:	Pye 104
Detector:	Minigade 625 gas density
Carrier gas:	Nitrogen
Carrier gas flow rate:	50 ml min^{-1}
Reference gas flow rate:	100 ml min^{-1}
Column temperature:	125°
Detector temperature:	130°
Detector filament current:	150 mA
Sample size:	1 μl

work. A chromatogram is shown in Fig. 1. Peak area measurements were made using a Kent Chromalog II integrator. The GC operating conditions are given in Table II.

RESULTS

From the chromatograms comparison between the various packings was made on the basis of the quantitative results, retention data, peak asymmetry, efficiency and resolution. The stability of the columns was studied by further conditioning followed

TABLE III

COMPARISON OF QUANTITATIVE RESULTS WITH VARIOUS COLUMNS AND COLUMN CONDITIONINGS

Conditioning		*% Water detected in sample ($\bar{x}$)*							*True % water (x_0)*
Temp. (°C)	*Time (h)*	*1*[a]	*2*	*3*	*4*	*5*	*6*	*7*	
150	16	36.17	35.75	35.33	35.91	36.60	35.33	31.17	35.73
220	12	37.22	36.13	36.62	37.12	36.56	37.00	37.79	36.47
275	12	36.23	36.38	36.64	36.11	36.32	36.52	39.10	36.50
275	336	33.42	32.83	—	33.85	34.30	32.80	26.15	33.33
22	336	33.50	35.88	—	33.79	32.49	30.08	34.49	33.38

[a] For key to column numbers, see Table I.

by a repetition of the experiments described above. A comparison of the quantitative results, expressed in terms of the percentage water detected, is given in Table III.

Due to the small differences in true percentage composition of the various samples, the effects of conditioning on the quantitative results are more readily compared in terms of the percentage bias of the results. Bias values are quoted in Table IV. The analyses were in reasonable agreement with the true values, using all columns except No. 7. There was no evident difference in adsorption losses between any of the packings or between the different column wall materials. Prolonged conditioning of the columns had no effect on the analytical results, although column No. 3 had to be discarded due to deterioration of the teflon. Preconditioning of column No. 4 with 500 μl of water had no effect on the quantitative results. Mean values are

TABLE IV

BIAS OF QUANTITATIVE RESULTS

Conditioning		*Percentage bias*[a]						
Temp. (°C)	*Time (h)*	*1*[b]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	+1.23	+0.06	−1.12	+0.50	+2.43	−1.12	−12.76
220	12	+2.06	−0.93	+0.41	+1.78	+0.25	+1.45	+ 3.62
275	12	−0.74	−0.33	+0.38	−1.07	−0.49	+0.05	+ 7.12
275	336	+0.27	−1.50	—	+1.56	+2.91	−1.59	−21.54
22	336	+0.36	+7.30	—	+1.23	−2.67	−9.92	+ 3.33

[a] Percentage bias, defined as $[(\bar{x} - x_0)/x_0] \times 100$, where $\bar{x}$ = mean experimentally determined % composition, and x_0 = true % composition.

[b] For key to column numbers, see Table I.

TABLE V

EFFECT OF PRECONDITIONING WITH WATER

True % composition	*Experimentally determined % composition*	
	No pretreatment	*Water pretreatment*
36.50	36.11	36.28

given in Table V. Absolute and relative retention distances (ethanol–water) are given in Tables VI and VII respectively.

TABLE VI

ABSOLUTE RETENTION DISTANCES

Conditioning		*Retention distances of water and ethanol (mm)*						
Temp. (°C)	*Time (h)*	*1*[a]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	13.5[b]	9.5	12.3	11.3	10.0	10.5	18.0
		56.7[c]	35.0	50.3	43.0	42.0	35.0	94.0
220	12	12.3	8.7	12.5	11.0	10.0	12.7	20.0
		54.7	32.7	54.7	44.7	41.7	38.5	93.0
275	12	12.2	8.0	12.0	10.8	10.0	11.7	18.0
		55.0	33.0	48.0	46.0	42.7	45.2	95.0
275	336	8.5	5.5	—	12.7	7.5	8.0	11.5
		40.0	26.0	—	59.0	33.5	35.0	63.0
22	336	8.0	6.0	—	11.0	8.0	8.5	11.5
		38.0	25.0	—	53.0	33.5	34.0	62.0

[a] For key to column numbers, see Table I.
[b] Retention distance of water.
[c] Retention distance of ethanol.

TABLE VII

RELATIVE RETENTION RATIOS

Conditioning		*Relative retention ethanol/water*						
Temp. (°C)	*Time (h)*	*1*[a]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	4.20	3.68	4.09	3.81	4.20	3.33	5.22
220	12	4.45	3.76	4.38	4.06	4.17	3.03	4.65
275	12	4.51	4.13	4.00	4.26	4.27	3.86	5.28
275	336	4.71	4.72	—	4.64	4.47	4.37	5.48
22	336	4.75	4.17	—	4.82	4.18	4.00	5.38

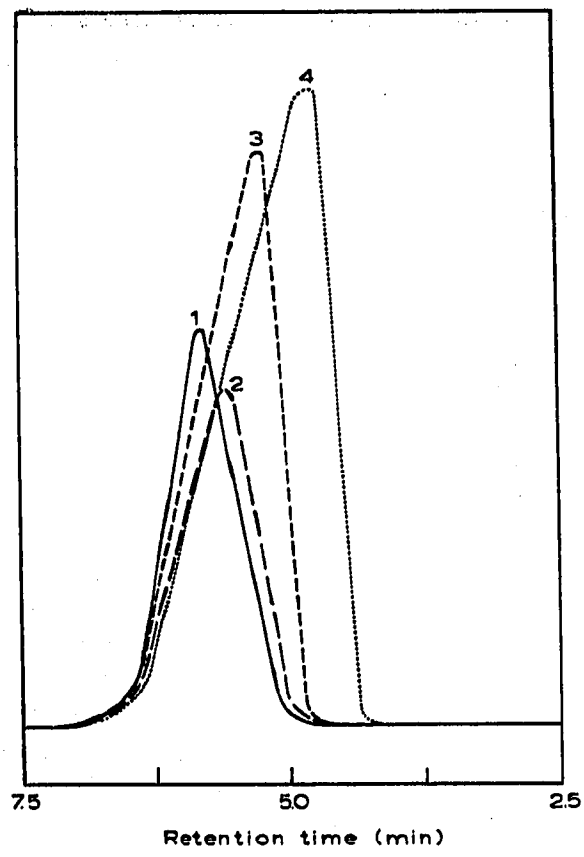
[a] For key to column numbers, see Table I.

Absolute retention distances varied with the extent of conditioning and changed significantly after prolonged treatment at 275°. In general relative retention ratios increased as conditioning progressed. Similar values for retention data were obtained for all columns except No. 7, for which the values were much greater. It has been reported in the literature[3] that retention distance (to the peak maximum) varies with sample size, and this is clearly demonstrated by the results given in Table VIII, which were obtained using column No. 1.

TABLE VIII

VARIATION OF RETENTION DISTANCE WITH SAMPLE SIZE

Compound	*Retention distances (mm)*			
	0.5 µl	*1.0 µl*	*2.0 µl*	*5.0 µl*
Water	14.0	13.5	13.5	12.2
Ethanol	57.8	56.7	54.2	49.2



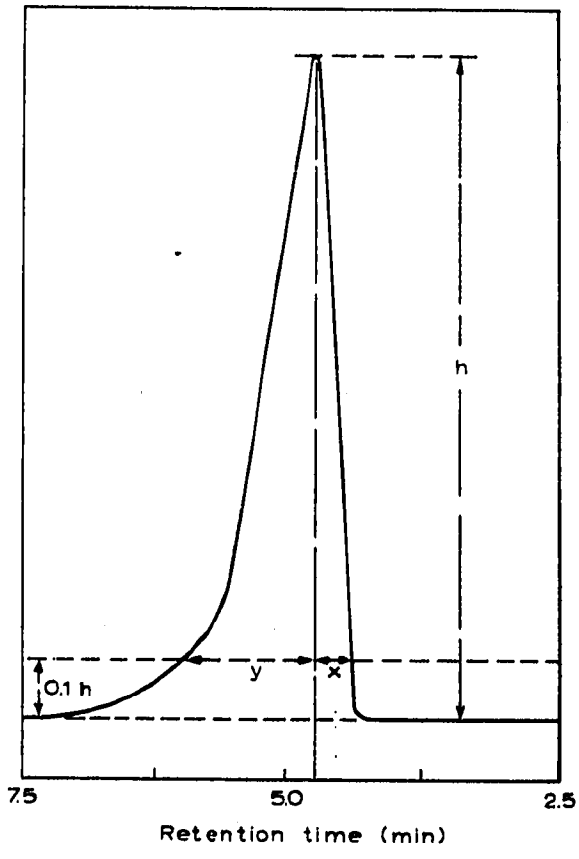


Fig. 2. Chromatogram showing effect of sample load on peak symmetry. 1 = 0.5 μl (attenuation $\times 2$); 2 = 1.0 μl (attenuation $\times 5$); 3 = 2.0 μl (attenuation $\times 5$); 4 = 5.0 μl (attenuation $\times 10$).

Fig. 3. Definition of peak asymmetry.

Fig. 2 shows four superimposed chromatograms obtained under identical conditions using sample sizes of 0.5–5.0 μl.

Mean values of the peak asymmetry (x/y values as defined in Fig. 3) of the alcohol peaks are given in Table IX. Comparison of the data shows that the most symmetrical peaks were obtained using Nos. 4 (unsilanised Porapak Q) and 5 (silanised Porapak Q). The remaining batches of Porapak Q and Chromosorb 102 gave somewhat

TABLE IX

PEAK ASYMMETRY

Conditioning		*Peak asymmetry*[a]						
Temp. (°C)	*Time (h)*	*1*[b]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	0.49	0.44	0.40	0.67	0.75	0.50	0.47
220	12	0.48	0.50	0.33	0.62	0.64	0.42	0.53
275	12	0.50	0.39	0.24	0.71	0.73	0.50	0.60
275	336	0.49	0.54	—	0.56	0.80	0.55	—
22	336	0.55	0.59	—	0.62	0.73	0.56	0.53

[a] A symmetrical peak takes the value 1.00.
[b] For key to column numbers, see Table I.

poorer results. Peak asymmetry was not affected by thermal treatment except in the case of column No. 3, which was attributed to deterioration of the column walls. The results quoted in Table IX refer to a sample size of 1 μl. The changes in peak symmetry with sample size, for column No. 1, are given in Table X, and are illustrated in Fig. 2.

TABLE X

EFFECT OF SAMPLE SIZE ON PEAK ASYMMETRY

Sample size (μl)	0.5	1.0	2.0	5.0
Peak asymmetry	0.56	0.49	0.36	0.22

TABLE XI

COLUMN EFFICIENCY

Conditioning		*HETP (mm)*[a]						
Temp. (°C)	*Time (h)*	*1*[b]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	2.85	3.62	3.65	2.56	1.33	2.73	3.19
220	12	3.27	3.42	3.15	3.01	1.54	1.79	6.33
275	12	4.09	4.34	4.02	3.43	2.56	5.97	14.2
275	336	7.50	5.77	—	3.54	3.54	7.22	26.2
22	336	5.24	4.77	—	6.72	5.35	5.42	16.4

[a] Using the expressions: $n = 5.545 \left(\frac{\text{retention distance}}{\text{peak width at } \frac{1}{2} \text{ height}}\right)^2$ and $\text{HETP} = \frac{\text{column length}}{n}$

[b] For key to column numbers, see Table I.

Column efficiencies were compared by calculating HETP values on the ethanol peaks. These are quoted in Table XI. Efficiencies are somewhat lower than those attainable using conventional coated supports. By far the most efficient column was No. 5 (silanised Porapak Q). Efficiency was not affected very much by conditioning up to 220° (except column No. 7), but deteriorated rapidly on conditioning at 275°. The efficiency of column No. 7 was particularly poor.

Values for the resolution[8] of the water and alcohol peaks are given in Table XII. Column No. 5 (silanised Porapak Q) gave by far the most satisfactory performance. Some deterioration in resolving power after conditioning occurred with all the columns.

TABLE XII

PEAK RESOLUTION

Conditioning		*Peak resolution*						
Temp. (°C)	*Time (h)*	*1*[a]	*2*	*3*	*4*	*5*	*6*	*7*
150	16	4.9	4.6	4.9	4.9	6.6	4.3	4.4
220	12	4.9	5.1	4.7	4.5	5.6	5.2	4.0
275	12	5.0	3.8	4.1	4.4	5.7	3.6	3.1
275	336	4.0	3.7	—	5.6	4.2	3.7	2.3
22	336	4.2	4.2	—	4.2	3.9	3.8	3.0

[a] For key to column numbers, see Table I.

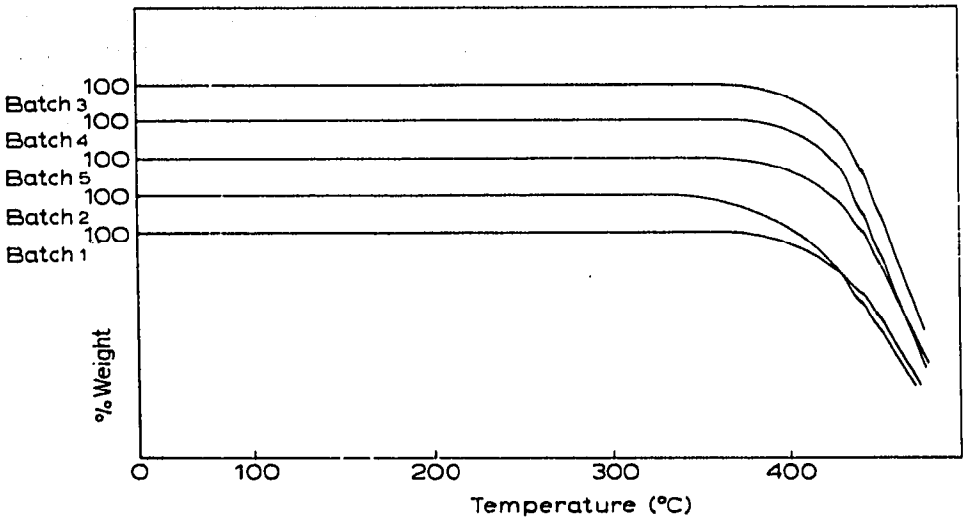


Fig. 4. Thermograms of unused porous polymer beads.

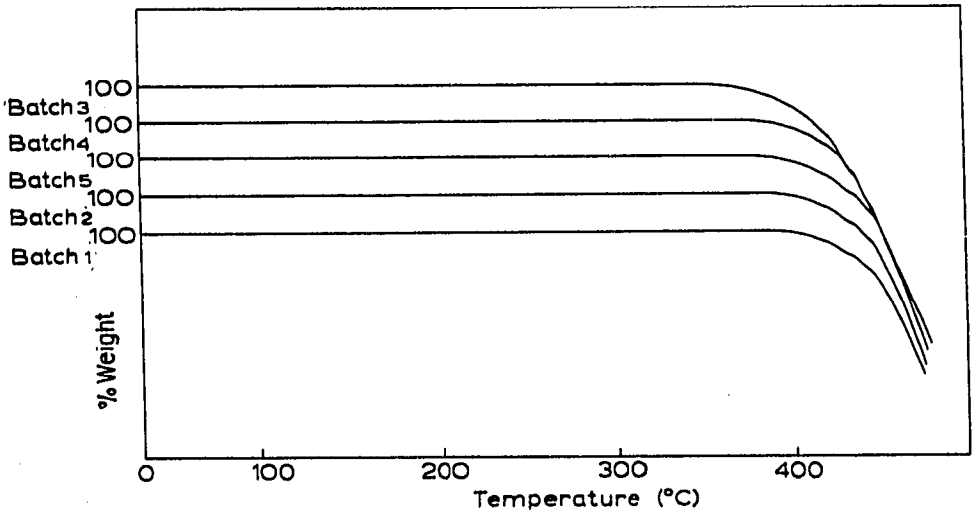


Fig. 5. Thermograms of used porous polymer beads.

TABLE XIII

WEIGHT LOSSES OF POROUS POLYMER BEADS AT 425°

Batch No.	*Percentage weight loss*	
	Before use	*After use*
1	15.6	5.9
2	26.6	6.7
3	10.9	16.4
4	12.2	8.7
5	11.8	6.9

The column packings were examined after completion of the experiments described above. All were found to be off-white except batch 5 which was light brown. Some coagulation of the beads had occurred. 10-mg samples of the beads, taken before and at the end of the experiments, were subjected to thermogravimetric analysis under nitrogen, covering the temperature range 50–475°. Similar thermograms (see Figs. 4 and 5) were obtained in all cases except that of batch 5 beads prior to treatment, which showed weight loss beginning at 250°. Percentage weight losses at 425° for all the samples are given in Table XIII.

CONCLUSIONS

The quantitative analysis of water–alcohol mixtures was found to be satisfactory using all but one of several different batches and types of porous polymer beads. Column wall material had no effect on the analyses. Retention times changed with the extent of column conditioning, and varied with sample size. Peak asymmetry was not affected by column conditioning, but varied with the different column packings and sample size. Column efficiencies and resolution varied with the packing material and deteriorated after prolonged conditioning. One particular batch of Porapak Q gave a very much poorer overall performance than any of the other packings. By far the most satisfactory performance was achieved using Porapak Q-S.

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REFERENCES

1 O. L. HOLLIS AND W. V. HAYES, *J. Gas Chromatog.*, 4 (1966) 235.
2 T. N. GVOSDOVICH, A. V. KISELEV AND YA. I. YASHIN, *Chromatographia*, 2 (1969) 234.
3 L. EEK AND T. GALCERAN, *Chromatographia*, 2 (1969) 541.
4 J. F. PALFRAMAN AND E. A. WALKER, *Analyst*, 92 (1967) 535.
5 O. L. HOLLIS, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Inst. Petrol., London, 1967, p. 71.
6 S. C. BEVAN, T. A. GOUGH AND S. THORBURN, *J. Chromatog.*, 44 (1969) 14.
7 S. C. BEVAN, T. A. GOUGH AND S. THORBURN, *J. Chromatog.*, 44 (1969) 25.
8 R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 429.