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WATER ADSORPTION BY POROUS POLYMER BEAD GAS CHROMATOGRAPHY COLUMNS

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SUMMARY

Porous polymer gas chromatographic columns are used in the quantitative estimation of water in organic samples. The reliability of using porous polymer beads for water–alcohol analyses has been studied and the quantitative results are presented. Variations in the results were attributed to preferential losses by adsorption of water within the columns. This was demonstrated qualitatively by introducing pure deuterated water into the gas chromatograph, allowing the water to elute, and then detecting any residual water by raising the temperature of the column and passing the effluent into a mass spectrometer. A measure of the amounts of water lost was made by injecting known amounts of pure water onto the column, allowing the water to elute, and then driving off any residual water for subsequent detection with a calibrated gas density detector.

INTRODUCTION

The analysis by gas chromatography (GC) of samples containing water is facilitated by using porous polymer bead columns, and several papers have been published describing the quantitative analysis of water with these materials. NEUMAN[1] has stated that water can be estimated at a level of 0.01 μg in a 10-μl sample of propanol using Porapak R at 140°, with an error of 20%; for greater amounts (about 1 μg) the error decreases to about 8%. Unfortunately no details of technique are given and no substantiating quantitative results are presented. The water content of 50-μl chlorophyll solutions has been estimated using a Porapak Q packing at 110°, in which 5–10-μg amounts of water were determined with an accuracy of $\pm$ 10%, using a calibrated katharometer[2]. The determination of water in 1-μl aliquots of dextran solutions at the 0.15-μg level, using Porapak QS has also been reported[3]. The water content of organic solvents has been estimated using Porapak Q; the accuracy was 20% at the 1-μg level and 3–6% in the milligram range, using 100-μl samples[4]. It has recently been shown[5] that essentially quantitative elution of water and ethanol can be achieved from porous polymer bead columns when the proportion

of water in the mixture is high (35 %). It was also shown that column wall material had no effect on quantitative elution. However, should the water content of the sample be low, then a small absolute loss of water can become significant in cases where small sample sizes ($< 1\ \mu l$) are analysed. The present work investigates such a situation. Water–ethanol samples with water contents in the range 1–30 % have been quantitatively analysed. A qualitative demonstration of water adsorption using combined GC and mass spectrometry (MS) is described, and a technique for the direct quantitative estimation of adsorbed water, in which varying amounts of pure water are introduced into the gas chromatograph, is presented. The method offers several advantages over the conventional GC method of determining adsorption losses. The estimation of adsorbed water has been taken to the level of the background water in the carrier gas, and to the detection limit of the gas density detector (3×10^{-6} mmoles ml^{-1}).

The analysis of smaller absolute quantities of water ($< 5\ \mu g$) would necessitate the use of a more sensitive detector (the micro-katharometer). It is difficult to prepare standards containing known amounts of water and to inject these into a gas chromatograph without contamination from atmospheric moisture[2], so that for such a study a completely closed system is envisaged.

TABLE I

COLUMN DETAILS

Column No.	*Packing*	*Batch No.*[a]	*Weight of packing (g)*
8	Porapak Q	7	7.40
10	Porapak QS	8	7.49
13	Porapak Q–HMDS	7	7.52

[a] = Authors' assignation.

RELATIVE COMPOSITION ANALYSES

Experimental

The quantitative analyses of water–ethanol mixtures were carried out on a Pye 104 chromatograph fitted with a gas density detector. Nitrogen was used as carrier gas, and was dried by passing through freshly activated charcoal, prior to entering the gas chromatograph. All columns were 1.25 m × 4 mm I.D. stainless-steel packed with 80–100 BS mesh Porapak, as detailed in Table I.

The packing for column 10 was silanized by the manufacturers using dichlorodimethyl silane[6]. The packing for column 13 was silanized by the authors with hexamethyldisilazane (HMDS)[7], using the same batch of packing from which column 8 was prepared. The columns, which had not been used for any analyses prior to this work, were conditioned for 15 h at 230° before use. The water–alcohol samples were contained in phials fitted with septa. The alcohol was dried by distillation from magnesium ethoxide and the residual water content estimated by the GC analysis of 5-μl aliquots using column 8 (which is subsequently shown to adsorb relatively little water). Using column 8, each mixture was analysed three times at each of four different sample sizes. The compositions of the mixtures are given in Table II. The

peak areas of the resulting chromatograms were measured using a Kent Chromalog II integrator.

OPERATING CONDITIONS

Apparatus	Pye 104 chromatograph
Detector	Minigade 625 gas density, 2 filament
Carrier and reference gas	nitrogen
Carrier gas flow-rate	47 ml min^{-1}
Reference gas flow-rate	100 ml min^{-1}
Column temperature	120°
Detector temperature	125°
Detector filament current	150 mA
Sample sizes	0.5, 1.0, 2.0, 5.0 μl

After completion of the quantitative analyses on column 8, the column was conditioned for 15 h at 230° in a stream of dry nitrogen, and silanized *in situ* at 180° with 5 × 10-μl injections of bis(trimethylsilyl)acetamide (BSA). The column was conditioned for a further 2 h at 200° after which 10 × 10-μl injections of water were made to ensure the removal of any residual BSA. The water–alcohol analyses were repeated.

TABLE II

RELATIVE COMPOSITION ANALYSES — COLUMN 8

Sample size (μl)	x_0[a]	*Prior to BSA treatment*		*After BSA treatment*	
		$\bar{x}$	*% Bias*	$\bar{x}$	*% Bias*
0.5	1.47	1.83	+24.5	0.86	−41.5
1.0		1.41	− 4.08	0.82	−44.2
2.0		1.43	− 2.72	1.12	−23.8
5.0		1.44	− 2.04	1.41	− 4.08
0.5	6.46	6.26	− 3.25	4.94	−23.5
1.0		6.13	− 5.11	6.28	− 2.79
2.0		6.30	− 2.48	6.11	− 5.42
5.0		6.25	− 3.25	5.99	− 7.28
0.5	10.82	10.30	− 4.81	9.19	−15.1
1.0		10.42	− 3.70	10.44	− 3.51
2.0		10.35	− 4.34	9.95	− 8.04
5.0		10.45	− 3.42	8.94	−17.4
0.5	29.44	28.49	− 3.23	24.79	−15.8
1.0		28.31	− 3.84	29.70	+ 0.88
2.0		28.40	− 3.53	27.49	− 6.62
5.0		28.54	− 3.06	27.19	− 7.64

[a] x_0 = true percentage composition, corrected for the moisture content of ethanol (0.19%).

For the purposes of comparison, water–alcohol mixtures were also analysed under the same conditions on columns 10 and 13. The attempt to perform quantitative analyses on column 10 was abandoned, due to its very poor performance. The column was then silanized with BSA, and further analyses were carried out.

Results

The results are presented in Tables II–IV and give the mean percentage water detected ($\bar{x}$ values) and the percentage bias of these values for each column at each sample size.

On the basis of the results presented in Table II, the performance of column 8 prior to BSA treatment was regarded as satisfactory. Accuracy of the results did not vary significantly either with sample size or with the proportion of water in the sample.

The percentage bias of all the results was between 2 % and 5 %. Note, however, that all bias values, except one, are negative. However, after BSA treatment, results were substantially lower and were particularly poor for the mixture containing the smallest proportion of water. The variations of the results at different sample sizes were far greater than corresponding values obtained prior to BSA treatment.

Column 8 after BSA treatment, was conditioned for a further 72 h at 230° and the analyses repeated at a single sample size of 1 μl. The results are presented in Table III.

TABLE III

RELATIVE COMPOSITION ANALYSES — COLUMN 8

x_0	$\bar{x}$	% *Bias*
2.72	2.36	−13.2
5.07	4.45	−12.2
9.23	8.23	−10.8
22.64	21.49	− 5.06

There was no improvement in performance, and it was concluded that BSA treatment, far from improving quantitative analysis, had a detrimental effect. The Porapak QS column (No. 10) gave completely unsatisfactory quantitative results, although this is in contrast to the performance of a similar column used in some previous work[5], thus demonstrating again the variation of performance of porous polymer beads from batch to batch.

TABLE IV

RELATIVE COMPOSITION ANALYSES — COLUMN 13

Total conditioning time (h)	x_0	$\bar{x}$	% *Bias*
15	1.03	0.99	− 3.88
	4.86	3.66	−24.6
	9.36	8.14	−13.1
	22.79	21.88	− 3.99
87	1.60	1.49	− 6.87
	3.33	3.40	+ 2.10
	9.59	9.46	− 1.36
	24.02	24.17	+ 0.63

The results of the analyses carried out on column 13, after 15 h and a further 72 h conditioning are presented in Table IV, and refer to a sample size of 1 μl. Bias values are rather high for most analyses although there is some improvement with conditioning.

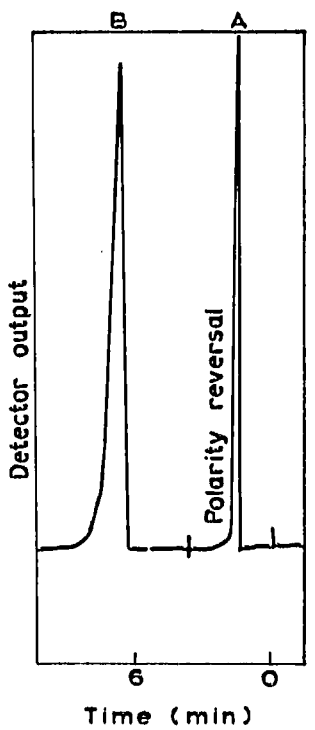
Asymmetry factors[5] and retention times for the water and ethanol peaks for both untreated and treated columns are given in Table V. The values refer to 1-μl aliquots of the sample containing 30% water.

TABLE V

RETENTION AND ASYMMETRY DATA — COLUMNS 8, 10, AND 13

	Column 8	*+ BSA*	*Column 10*	*+ BSA*	*Column 13*
Retention time (sec)					
Water	85	80	135	133	102
Ethanol	384	390	700	623	357
Relative retention	4.52	4.87	5.18	4.70	3.51
Asymmetry					
Water	0.19	0.17	0.21	0.28	0.08
Ethanol	0.25	0.27	0.20	0.28	0.08

BSA treatment has a negligible effect on the retention times on column 8, and on column 10 only the ethanol retention was decreased. Retention times are almost double on column 10 compared with column 8, although the relative retentions are



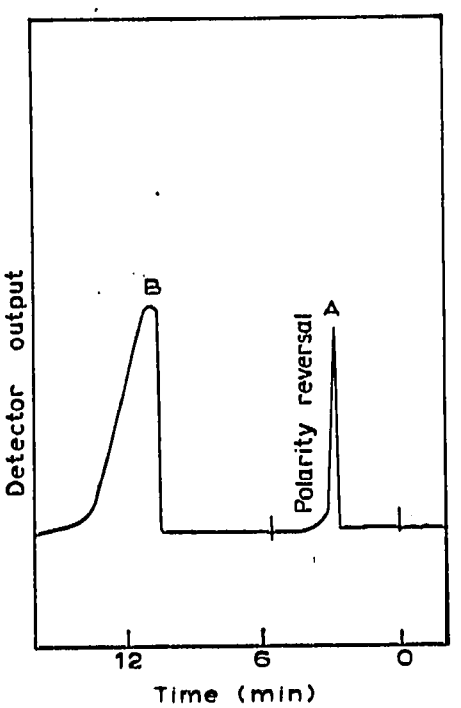


Fig. 1. Chromatogram of water–ethanol mixture (column 8), sample size, 1 μl. A = H_2O (attenuation × 2); B = ethanol (attenuation × 5).

Fig. 2. Chromatogram of water–ethanol mixture (column 10), sample size, 1 μl. A = H_2O (attenuation × 2); B = ethanol (attenuation × 5).

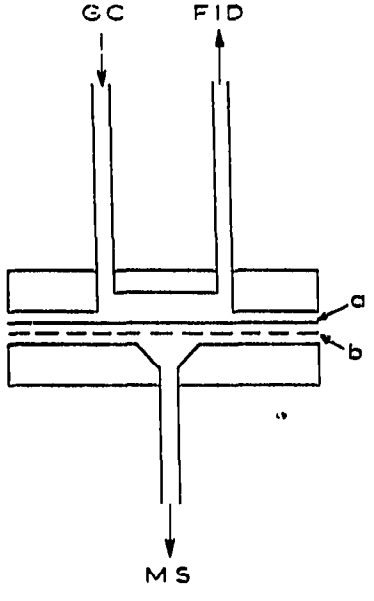
of the same order. There was no change in asymmetry factors on column 8 but some improvement took place on column 10 after silanization. Chromatograms from columns 8 and 10 prior to BSA treatment are shown in Figs. 1 and 2, respectively. The symmetry of the peaks on column 13 was extremely poor.

GC–MS ANALYSIS

Experimental

The differences in behaviour between silanized and unsilanized columns may be the result of sample adsorption which, using untreated column 8, was either negligible or of the same order for both water and ethanol. The detection of traces of adsorbed water and alcohol was attempted by directly coupling a Pye 104 chromatograph to an Edwards 60° mass spectrometer using a membrane separator[8]. The separator was designed at the University of Sussex and is shown diagrammatically in Fig. 3. The interface is a disc of 0.05-mm silicone rubber supported on a glass sinter, and clamped between stainless-steel flanges. The flanges are sealed with silicone rubber moulding paste capable of withstanding temperatures up to 250°. The column effluent was fed into a pneumatically operated 6-port switching valve, such that the effluent was either vented to atmosphere or passed into the mass spectrometer via the separator. During venting pure helium was passed over the separator interface. The switching valve and separator were both housed in the GC oven, and the transfer line from the separator to the mass spectrometer was maintained at 120°.

The objective of the GC–MS experiments was to study the fate of water introduced into the GC column, and hence all injections were of pure water, rather than



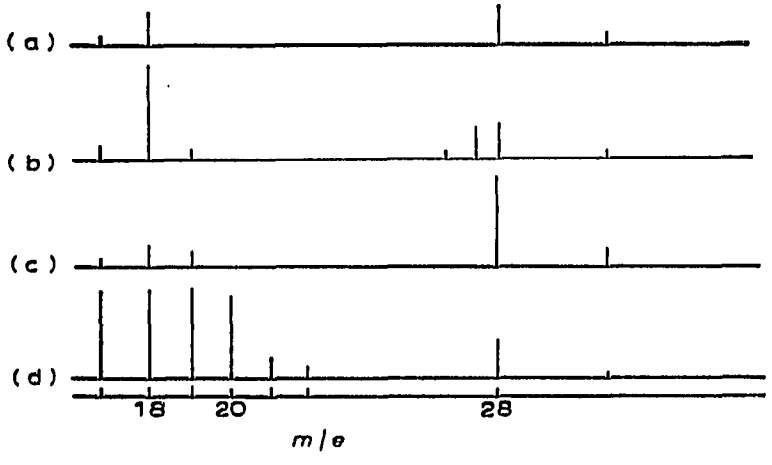


Fig. 3. Diagram of separator. a = silicone membrane; b = glass sinter.

Fig. 4. Background mass spectra. (a) Column 9 effluent to vent; (b) column 9 effluent at 200° to MS; (c) column 9 effluent at 120° to MS, after elution of D_2O; (d) mass spectrum of desorbed D_2O from column 9 at 200°.

water–alcohol mixtures. In view of the ubiquitous nature of water, deuterated water was used to ensure that the water detected by the mass spectrometer arose only from injected samples. It was therefore not necessary to attempt the task of eliminating all extraneous water from the system, although reasonable precautions were taken. The column under study (see Table VI) was heated in the GC oven at 200° for 15 h, with dried helium carrier gas flowing at 50 ml min^{-1} vented to atmosphere. A background spectrum was recorded (Fig. 4a), the column effluent switched to the mass spectrometer and a second spectrum run (Fig. 4b). The column and separator were cooled to 120° and 50 μl of deuterated water were injected on to the GC column and vented until all the water was eluted. Column effluent was then switched to the spectrometer and a spectrum run to check that the peak at *m/e* 20 was at background level (Fig. 4c). The carrier gas flow through the column was turned off, and the column heated for 10 min at 200°, after which the flow was resumed and the effluent swept into the mass spectrometer. Spectra were recorded (Fig. 4d). A similar series of runs were carried out using 50-μl samples of ethanol. Fig. 5a shows the spectrum resulting from ethanol desorption, and Fig. 5b the corresponding background spectrum. Details of the columns used for these analyses are given in Table VI.

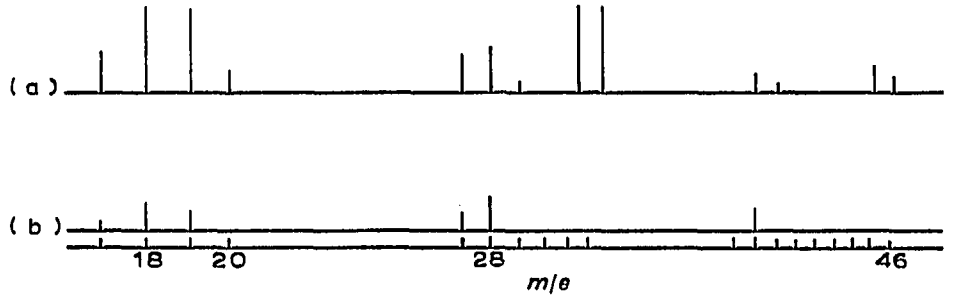


Fig. 5. (a) Mass spectrum of desorbed ethanol from column 9 at 200°; (b) background mass spectrum of column 9 effluent 5 min after ethanol desorption.

TABLE VI

COLUMN DETAILS

Column No.	*Packing*	*Batch No.*	*Weight of packing (g)*
9	Porapak Q	7	7.14
11	Porapak QS	8	8.28
12	—	—	—

Column 9 is directly comparable with column 8, and column 11 with No. 10 (Table I). An empty column (No. 12) was included to assess the contribution of the column wall material to adsorption.

Results

Some spectra obtained for the desorption experiments from column 9 are shown in Figs. 4 and 5. Adsorption of both water and ethanol has taken place, and heating the column to 200° was sufficient to desorb at least some of the adsorbate. Similar

spectra were obtained using column 11. The contribution of the column walls to adsorption was small; a spectrum, obtained using column 12, is shown in Fig. 6 and is comparable with Fig. 4d. Spectra run at higher sensitivities showed that the porous polymer beads continued to bleed substantial amounts of material at 200°, even after conditioning for 72 h at 230° (see Fig. 7).

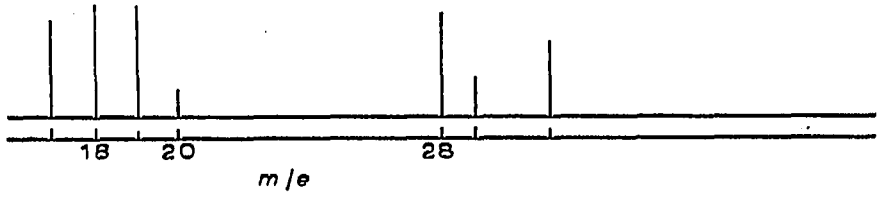


Fig. 6. Mass spectrum of desorbed D_2O from column 12 at 200°.

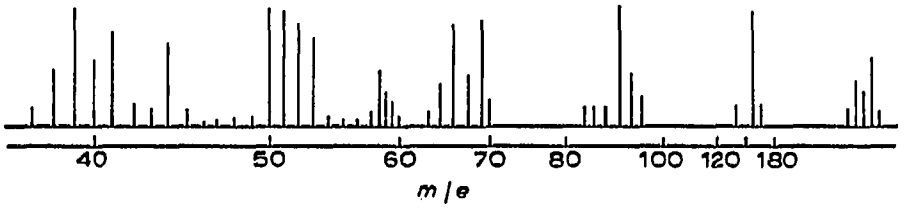


Fig. 7. Mass spectrum of effluent from column 9 at 200°.

QUANTITATIVE ADSORPTION ANALYSIS

The qualitative results obtained using a combined GC–MS system show that both water and ethanol are adsorbed by Porapak columns. It is clearly necessary to estimate the proportion of injected water which is lost by adsorption on the porous polymer beads in order to place some reliance on water analyses at low concentrations. The standard GC procedure for such a determination is to inject progressively smaller amounts of the material on to the column and to extrapolate to the limit at which no detector response is predicted for a finite volume of sample[9]. This procedure is only satisfactory where detector response is linear within the region under study, and the amount of sample lost by adsorption is relatively high (*i.e.*, of the same order as the smallest amount of sample which can be reliably injected and detected). Serious errors may result in cases where detector response is non-linear and where excessive extrapolation is necessary.

Experimental

For the present work a method was devised by which the adsorbed material itself is detected after desorption from the column at an elevated temperature. A diagram of the system is shown in Fig. 8. The column under study, the switching valve and the delay column were contained in a GC oven. The detector was housed in a separate oven. The trap to collect desorbed material consisted of a copper U-tube in which was held 300 mg of activated charcoal. All transfer lines were of 0.5 mm I.D. stainless-steel tubing, and those outside the GC oven were contained within 12-mm O.D. flexible metal conduit wrapped in heating tape, thus ensuring uniform heating of the lines.

Procedure. With the switching valve in position b (Fig. 8), the sample of water

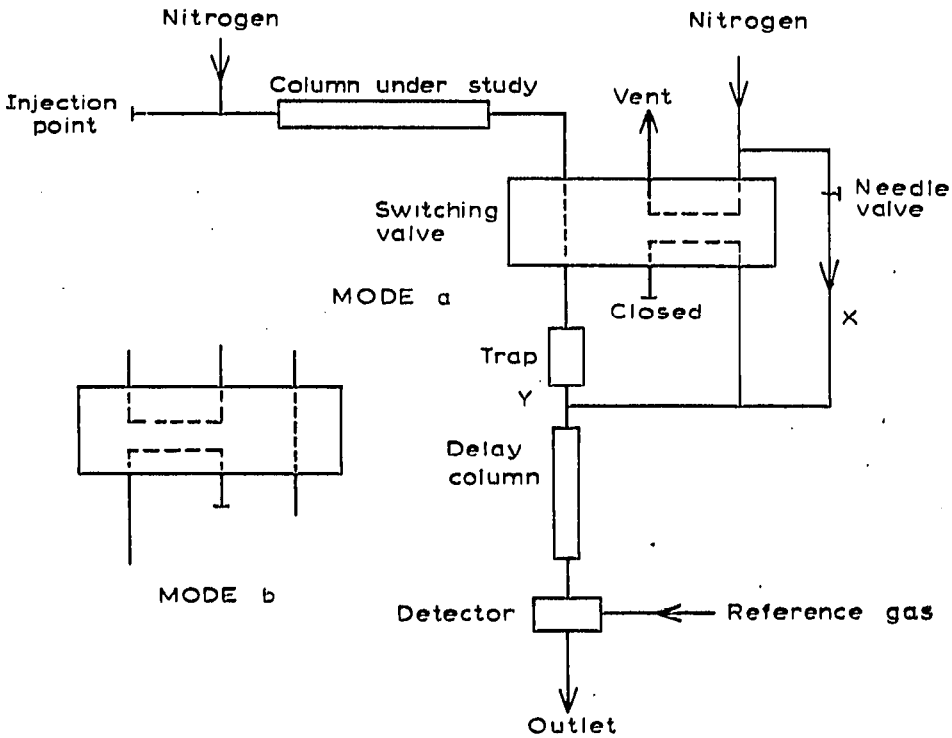


Fig. 8. Diagram of adsorption apparatus.

TABLE VII

OPERATING CONDITIONS

Gas chromatograph	Pye 104
Detector	Minigade 625 gas density, 4 filament
Switching valve	Servomex type SV 220
Carrier and reference gas	nitrogen dried over molecular sieve
Gas flow rates	
Carrier	30 ml min^{-1} (2 streams)
Bleed	1 ml min^{-1}
Reference	90 ml min^{-1}
Column oven temperature	
Elution	110°
Desorption	200°
Trap temperatures	
Collection	−196°
Sweep	+200°
Detector temperature	110°
Transfer line temperature	205°
Detector filament current	125 mA

is injected and allowed to elute in the conventional manner, and vented to atmosphere. The valve is switched to position a, the trap cooled with liquid nitrogen, and the column oven temperature rapidly raised to induce desorption. Adsorbed water is collected for a known time (15 min) after which the valve is returned to position b whilst the trap is heated to 200°. This ensures that no water can escape from the trap

during the heating period (1.5 min). Finally the valve is returned to position a and the water swept from the trap into the detector. The delay column is incorporated to allow the detector to stabilize before the water reaches the detector. The disturbance is kept to a minimum by ensuring that the gas flow rate to the detector is the same whether the valve is in position a or b. A continuous small bleed of nitrogen is maintained along line x to prevent back diffusion of water at the tee-junction y when the trap is swept.

Operating conditions and apparatus details are given in Table VII.

The delay column consisted of a 1.5 m × 2 mm I.D. stainless-steel column containing Porapak T. The weight of packing was 1.3 g, *i.e.*, small compared with the weight of Porapak in the column under study (see Table VIII). Hence adsorption by the delay column can be discounted particularly as water only comes into contact with this column at 200°.

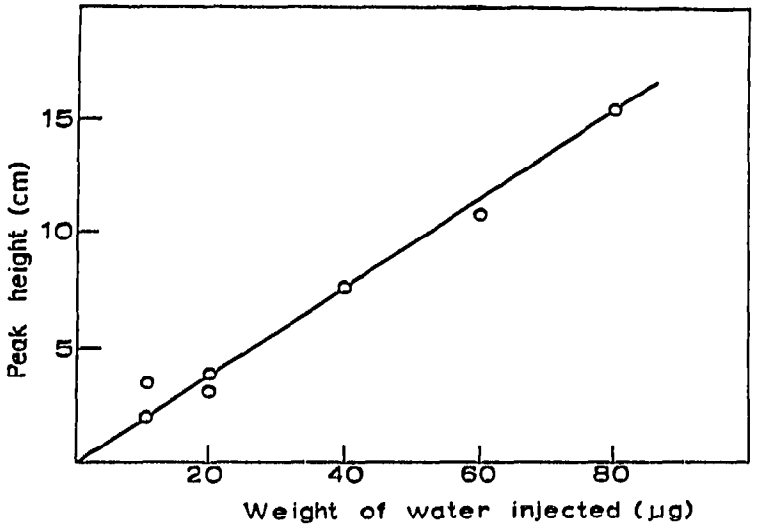


Fig. 9. Detector calibration.

TABLE VIII

COLUMN DETAILS

Column No.	*Packing*	*Batch No.*	*Weight of packing (g)*
4	Porapak Q	5	8.00
8	Porapak Q–BSA	7	7.40
9	Porapak Q	7	7.14
11	Porapak QS	8	8.28
13	Porapak Q–HMDS	7	7.52
14	Porapak Q	7	7.04
15	Porapak N	9	10.11
16	Porapak T	10	9.96

Preliminary experiments were carried out to establish that (a) the majority of adsorbed water could be desorbed at 200° in a reasonable time, (b) the trap was equally efficient for all sample sizes, (c) all eluted material was water and not organic matter for column bleed, and (d) a sufficient venting time was allowed to clear the tail

of the water elution peak for the largest amount of water injected. The moisture content of the carrier gas was monitored daily, by the same technique. The detector was calibrated by injecting into the system at 200° water–propanol mixtures containing known amounts of water and collecting the water in the trap for subsequent detection. The adsorption runs were carried out by injecting known volumes of water covering the range 0.1–20 μl and the amounts lost by adsorption estimated using the calibration graph (Fig. 9). To confirm that negligible adsorption of water occurred on the column walls and within the switching valve, water was injected into an empty column. The amount of water collected was identical to that contained in a carrier gas blank.

The syringes used in this work were calibrated by injecting known nominal volumes of water into a small sealed vessel containing an absorbent, via a septum.

The increase in weight of the vessel was measured using an electro-microbalance which itself was calibrated using NPL* standard weights. It is recognized that the conditions used to calibrate the syringes are less onerous than those for an injection into a gas chromatograph. It nevertheless serves as a useful indication of the absolute amounts of water introduced into the system. The columns used for the quantitative adsorption study are listed in Table VIII.

All packings were 80–100 BS mesh, and columns were conditioned at 210° for a minimum of 15 h (see also below). It will be noted that columns 8, 9, 13 and 14 were all prepared from the same batch of Porapak and this enables comparisons to be made between the unsilanized material (column 9), an *in situ* silanized column (No. 8), Porapak silanized prior to packing (No. 13), and the effects of conditioning (*cf.* Nos. 9 and 14). Prior to the adsorption determinations, column 8 had been conditioned for several hundred hours at 230°, and column 14 for only 50 h at 200°. Column 4, used in an earlier study[5], had been conditioned for about 400 h at 275°. Columns 15 and 16 were included in order to make comparisons between porous polymer beads of varying polarities.

TABLE IX

SYRINGE CALIBRATION

Syringe capacity (μl)	*Nominal volume injected* (μl)	*Weight detected* (mg)
1	0.25	0.29
	0.50	0.54
	0.75	0.78
10	1.0	0.95
	2.5	2.56
	5.0	5.10
	7.5	7.60
50	10.0	10.13
	12.5	12.66
	15.0	15.37
	17.5	17.78
	20.0	20.35

* NPL = National Physical Laboratory.

Results

Calibration of the syringes for each of the various volumes used, is expressed in terms of milligrams for each nominal volume, and is given in Table IX. Each value is the mean of three injections.

The detector calibration graph is shown in Fig. 9, from which the quantity of adsorbed water for each amount injected on each column, was read. Note that there is no necessity to calibrate the detector for any amount of material greater than the amounts lost by adsorption. The maximum amounts of water adsorbed by each column are listed in Table X. The variations of amounts adsorbed with sample size for several of the columns are shown in Figs. 10–12.

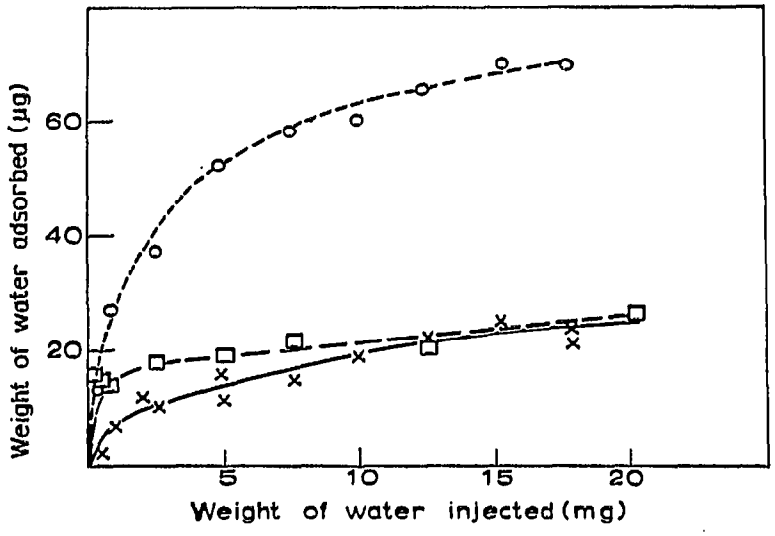


Fig. 10. Water adsorption on Porapak Q batch 7. ×, column 9; ○, Column 13; □, column 14.

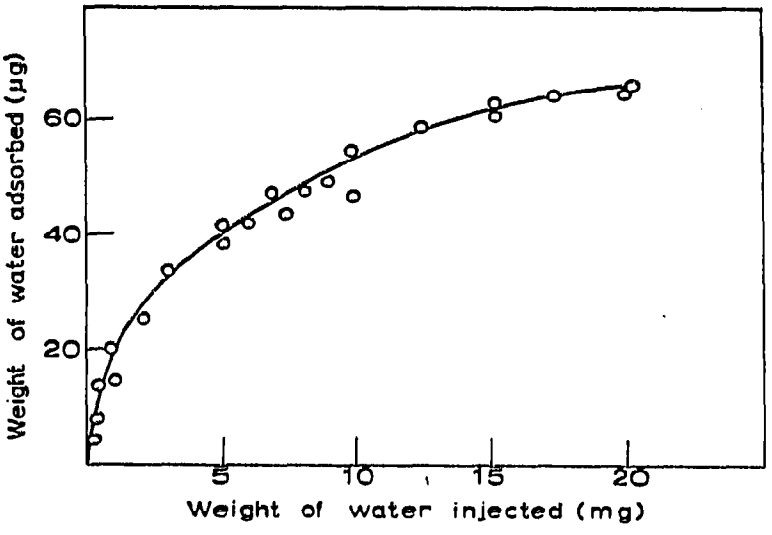


Fig. 11. Water adsorption on Porapak QS column 11.

All columns adsorbed water, but the extent of adsorption varied with the packing. There was no change in the adsorption characteristics of batch 7 Porapak with the extent of conditioning at 230° (*cf.* columns 9 and 14), but HMDS treatment significantly increased the capacity of the material to adsorb water (*cf.* columns 9 and 13).

Column 11, treated with dichlorodimethyl silane, also showed substantial adsorption. Column 8 (BSA treated) gave a higher adsorption than the same batch of untreated Porapak (column 9). Column 4, which had been conditioned for 400 h at 275°, showed negligible adsorption, as did a sample of Porapak N and Porapak T.

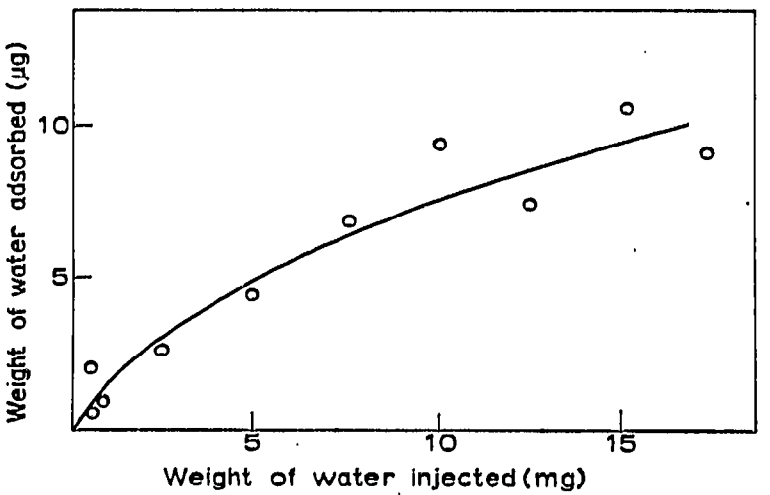


Fig. 12. Water adsorption on Porapak N column 15.

TABLE X

ADSORPTION CAPACITY OF COLUMNS

Column No.	*Maximum amount of water adsorbed*		*Fig. No.*
	µg	*µg per g of packing*	
4	7	0.9	—
8	34	4.6	—
9	24	3.4	10
11	66	8.0	11
13	70	9.3	10
14	24	3.4	10
15	10	1.0	12
16	4	0.4	—

The two columns exhibiting substantial water adsorption were further studied by the same technique, covering the range 0.1 to 1.0 mg of injected water. An essentially linear variation of adsorption with the amount injected was observed (see Fig. 13).

The proportion of water lost by adsorption on any of the columns studied for a given weight of water injected is obtained directly from the slope of the appropriate graph (Figs. 10–12). As an example the variation of the percentage water lost with the amount injected on to column 13 is shown in Fig. 14.

On the assumption that water is adsorbed to a greater extent than any organic compound, the effect on the percentage composition analysis of an aqueous sample is to induce a negative bias, which will depend both on the proportion of water in the sample and on the total sample size injected. Values of percentage water adsorbed and percentage bias values (Tables II–IV and ref. 1) can be compared directly, and

this has been done in an attempt to explain the variation of the relative composition analyses of the water–ethanol mixture with different columns.

The column giving the most satisfactory quantitative analyses adsorbed a maximum of only 0.9 $\mu g\ g^{-1}$ of packing (see Table X). The bias of the results was negligibly small (+ 0.8 %) and within the precision of peak area measurement[10] and detector response[11]. Bias values were negative for all columns showing significant adsorption, and the spread of bias values is relatively large for columns showing high adsorption of water. Asymmetry factors alone did not give a reliable guide to the extent of adsorption, a fact recently noted with reference to adsorption by polytetrafluoroethylene (PTFE)[12].

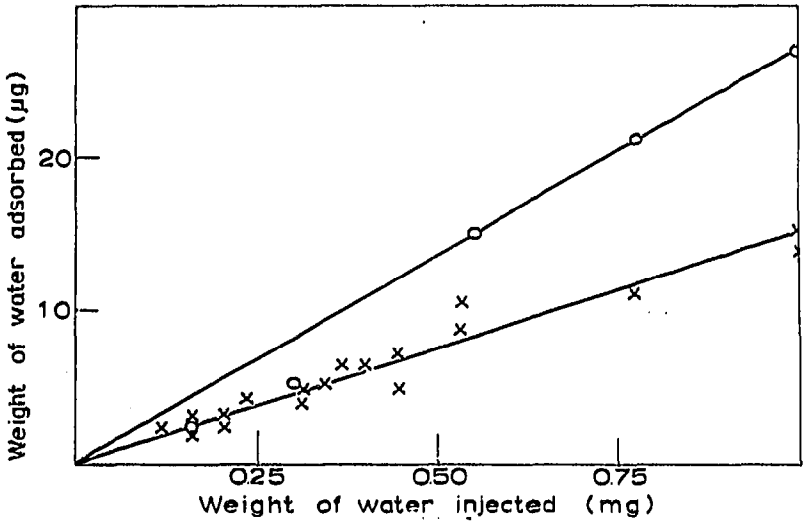


Fig. 13. Water adsorption on column 11 and 13. ×, column 11; ○, column 13.

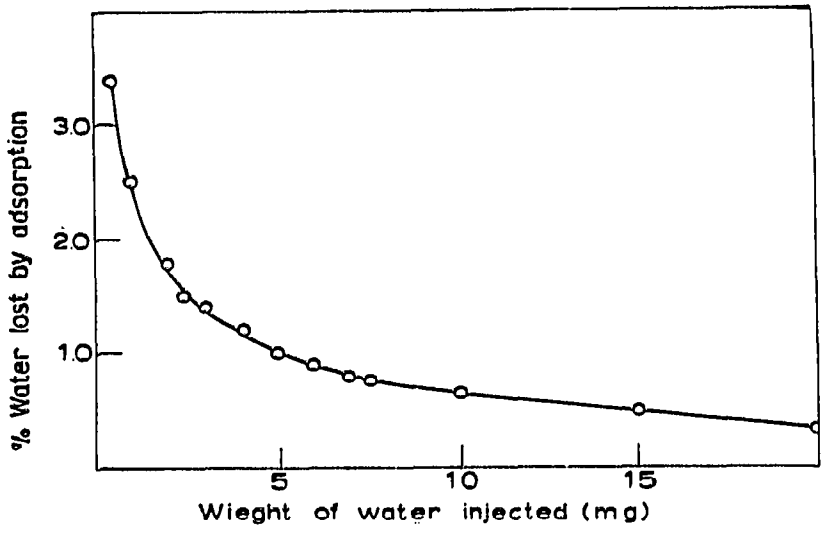


Fig. 14. Proportion of water lost by adsorption on column 13.

CONCLUSIONS

Confirming earlier work it is found that the characteristics of Porapak vary between batches, but that given a satisfactory batch, the material is suitable for the

analysis of samples in which the proportion of water is at least as low as 1 %. However, the mass spectral analysis of GC effluent demonstrates that both water and alcohol are adsorbed by Porapak columns. A quantitative assessment of the extent of water adsorption using a new technique, showed that poor percentage composition analyses with large bias values are associated with columns having high adsorption capacities for water. Quantitative elution of water is not enhanced by prolonged thermal treatment or by silanization. Indeed silanization can produce the opposite effect.

A porous polymer bead column for quantitative use must be chosen with care, and can be selected on the basis of the technique described in this work. Further, to minimize adsorption, analyses should be carried out at the highest practicable temperature.

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