THE USE OF GEL-COATED GLASS MICROSPHERICAL SUPPORTS FOR IMPROVED COLUMN PERFORMANCE AND THE RAPID SEPARATION OF ISOMERIC COMPOUNDS

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SUMMARY

Columns packed with glass beads coated with a thin layer of Bentone 34, either by itself or in the form of a gel with a suitable liquid modifier, have been found to give high theoretical plate numbers and rapid elution characteristics. Symmetrical elution peaks are obtained for a wide range of chemical types, including hydrocarbons, aldehydes, ketones, esters, amines, alcohols, and phenols, and several types of strong selectivity have been noted. It is suggested that such columns could be applied to a wide variety of gas chromatographic separation problems, to give an improvement in resolution with a considerable decrease in the analysis time.

INTRODUCTION

A review of the development of gas chromatographic (GC) column technology in relation to packed columns reveals that little fundamental progress has been made in the improvement of performance from the viewpoint of separation speed. Most packed columns for routine use are essentially similar to those originally prepared by James and Martin[1], even to the extent of using diatomaceous earth supports. Porous polymers[2] are used fairly widely, particularly for the separation of highly polar substances and permanent gases, but the columns are not very selective towards isomeric compounds, and retention times are often high. Various chemically bonded stationary phases[3-5] have also been developed which give improved thermal stability and are convenient to use but they give no real increase in analysis speed and are not significantly more selective than their more conventional counterparts.

The advent of wall-coated open tubular columns[6] in 1958 probably explains the apparent loss of interest in the improvement of analysis speed in packed columns. The new columns seemed to dispose of many of the earlier disadvantages of packed columns and they were capable of generating very high theoretical plate numbers in a short time. However, these columns have not become as popular as was at first

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predicted in many quarters; they have the theoretical limitations of high phase ratio, which gives rise to a much lower effective plate number[7] than the true plate number, and they are difficult to reproduce and operate successfully. Another disadvantage is that it is not practicable to coat such columns with adsorbents for gas–solid separations, at least not for routine purposes. The main objective in using open tubular columns is to achieve a high theoretical plate number for the resolution of close-boiling compounds or isomers. However, such separations can often be more readily performed by the use of appropriate gas–solid adsorption systems which improve the selectivity. Even small increases in the selectivity of the system will result in a dramatic lowering of the theoretical platage which is necessary to resolve an isomeric pair. This is apparent from the following equation:

$$N = \left[\frac{4\,R}{S-1}\left(\frac{k_a+1}{k_a}\right)\right]^2 \tag{1}$$

Thus the use of selective stationary phases in packed columns gives faster separations, with greater precision and reproducibility, than can be achieved in wall-coated open tubular columns containing non-selective phases. The higher theoretical platage of the latter, however, will be advantageous in the separation of very complex mixtures where the use of more selective but less efficient columns would tend to redistribute the components adversely.

White and Cowan[8] first described the adsorption properties of dimethyl-dioctadecylammonium bentonite when used as a stationary phase for GC. This material is prepared by a cationic exchange reaction between montmorillonite clay and the appropriate quaternary ammonium salt. It is available commercially as Bentone 34[*], or B34, and has a lamellar structure which swells to form a gel when organic solvents are added. B34, modified by the addition of a conventional liquid phase has been used widely for the GC separation of *meta* and *para* isomers, particularly those of the xylenes[9,10].

Columns which contain B34 stationary phases normally give high retention times and consequently many compounds are too strongly retained for them to be separated in reasonable periods of time, even at the maximum temperature at which the gel remains stable. Also, work reported on the effects of gel packings towards polar substances such as alcohols, amines, phenols etc. indicates that tailing of the peaks is normally experienced[9].

The present investigation was initiated to increase the range of application of B34-based stationary phases to higher boiling and more polar substances than have hitherto been studied. Problems arising from the use of diatomaceous supports are obviated by using glass microspheres of low adsorption properties and by coating the B34, or B34 gel evenly over the glass surface. The resulting columns are found to give high theoretical plate numbers, principally because of the resulting low resistance to mass transfer effect. This is attributed to the fact that the B34 gel has the physical properties of a solid and so forms a thin stable layer.

Glass microspheres have been used previously as a support in GC but they have not become popular because they give low theoretical plate numbers. Little-

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[*] Bentone is a trade mark of F. W. Berk and Co. Ltd.

wood[11] claimed that up to 4% by weight of stationary phase could be loaded onto glass bead supports but plate numbers were variable and very high mass transfer coefficients were obtained in most cases. This is explained by the flow of liquid over the spherical surfaces and its accumulation at the points of contact. Also, wet glass beads are difficult to pack efficiently and this too has an adverse effect on the column plate number. Ways of improving the plate performance of such columns have been suggested on theoretical grounds, both by Golay[12] and by Giddings[13]. Golay suggested that the disposition of liquid phase on bead supports could be stabilized if it were adsorbed in a thin porous layer coated uniformly on the surfaces. Successful columns were in fact produced in this way by Halász and Horváth[14] using colloidal metal oxides and diatomaceous earths. Tailing peaks were obtained for polar compounds, however, and the columns were not particularly selective. Etching techniques[15] and mechanical abrasion[16] have been employed to roughen the glass surface to improve the stability of liquid phase coatings, but without a great deal of success in terms of any increased theoretical plate speed and applicability to polar substances. The gel-coated beads described in the present work give a considerable improvement in plate speed, are applicable to polar substances and are easy to prepare.

EXPERIMENTAL

Batches of glass beads were purchased from a number of suppliers but only those from BDH Ltd. and Ballotini Ltd. were found to be suitable. The grades employed were 60 and 100 nominal mesh size, from BDH, and 120–150 mesh from Ballotini. The beads were washed in successive stages using water with added detergent, water alone, acetone, and finally diethyl ether. They were dried on a water-bath and then subjected to heat treatment in a muffle furnace at 400° for several hours.

The gel-coated beads were prepared by weighing out the requisite amounts of Bentone 34 and liquid modifier into a small beaker and adding 5 ml of benzene (Analar reagent grade). The solution was stood on a water-bath at 100° and stirred until homogeneous. It was then added to 50 g of the treated glass beads and thoroughly mixed until the beads were evenly moistened. The benzene was finally removed with constant stirring. This procedure was found to be very critical and uneven coating resulted if the amount of benzene solvent used was either too little or too much.

Standard 1.5-m glass columns were employed throughout. These had an external diameter of 6.4 mm and were packed by the application of a vacuum at one end and drawing the packing into the open end in small batches. Each batch was drawn to the vacuum end of the column onto a plug of silanized glass wool by rotating the column and gentle tapping. When the column had been apparently filled another plug of glass wool was pushed onto the packing at the open end and the column was vibrated using an electrical device. This caused some shrinkage which was made up by introducing more packing into the column. This procedure was continued until no further shrinkage occurred.

Apparatus

A Pye 104 Model 24 flame ionization gas chromatograph operated in conjunction with a Smiths Servoscribe Model RE511-20 potentiometric recorder. The columns were standard Pye 104 glass columns with viton compression seal couplings.
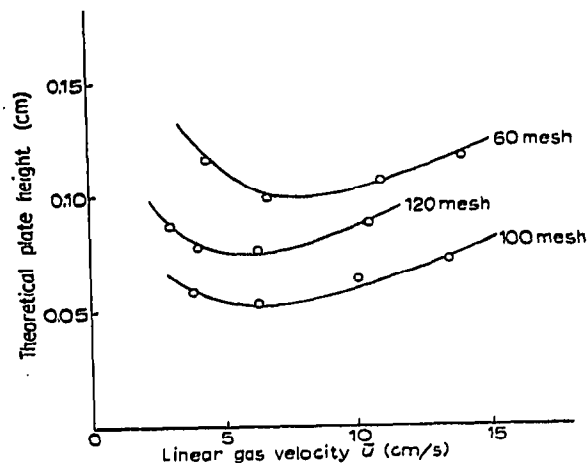
Fig. 1. Effect of bead size on theoretical plate height. Solute, fluorene at 130°; carrier gas, nitrogen.

A preheater was employed adjusted to a temperature of 200°. Hydrogen and air rates were adjusted to the recommended values for the equipment.

Effect of bead size

      The three grades of support were tested for their performance with regard to theoretical plate characteristics. All the mesh sizes were used as supplied without
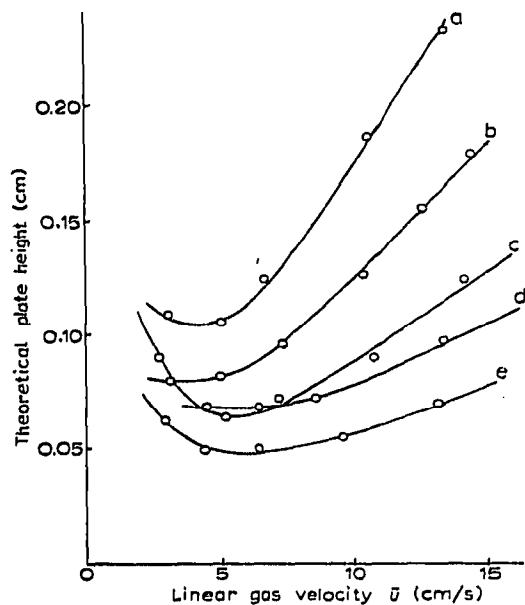

Fig. 2. Effect of stationary phase composition on plate characteristics. 0.08% w/w B34–OV-17 on 100-mesh glass beads. Solute, naphthalene; carrier gas, nitrogen. a = OV-17 only; b = B34–OV-17 (1:3); c = B34 only; d = B34–OV-17 (2:2); e = B34–OV-17 (3:1).

further grading. The mesh size refers to the mean value, the actual gradings being within 52–72 mesh, 72–120 mesh, and 120–150 mesh. The beads were loaded with 0.08% by weight of 50:50 mixtures of B34 and Silicone OV-17 and packed into 1.5-m columns as described earlier. Each column was tested at 130° using fluorene as a test substance and nitrogen as carrier gas. Van Deemter plots are shown in Fig. 1 which show that the 100-mesh beads give the lowest theoretical plate heights. This grade was easier to pack than the 120-mesh beads and a more uniformly packed column was achieved. This would have the effect of lowering the multiple path constant[17]. The higher theoretical platages experienced with the 60-mesh beads would be explained theoretically by the effect of larger particle diameter in the multiple path term $2\lambda d_p$. 100-mesh beads were consequently chosen for the work to be described.

Effects of stationary phase composition

Five columns were packed with 100-mesh glass beads all containing the same loading of 0.08% by weight of the total stationary phase. The stationary phase composition, however, was varied as follows: 100% B34, 75% B34–25% OV-17, 50% B34–50% OV-17, 25% B34–75% OV-17, and 100% OV-17. The theoretical plate and retention characteristics of the columns were tested using nitrogen as carrier gas. Sample sizes were generally 0.1 μl of a 1% solution of the test substances in tetrahydrofuran (THF). Thus the mass of solute in each injection was about 1 μg. The amplifier attenuation was set at between SX100 and SX500 and columns were conditioned at 150° for several hours before use.

Fig. 2 shows Van Deemter plots for naphthalene at 130°. As expected the column coated with OV-17 alone gave a high plate height which increased rapidly with increasing gas velocity. This is indicative of a high liquid phase mass transfer term if we assume the validity of the Van Deemter equation[17], *i.e.*:

$$h = 2\lambda d_p + \frac{2\gamma D_g}{\bar{u}} + C_1\bar{u} \qquad (2)$$

where $2\lambda d_p$ is the multiple path or eddy diffusion term, $2\gamma D_g/\bar{u}$ is the molecular diffusion term, and C_1 is the liquid phase mass transfer coefficient.

The latter term is given by the expression:

$$C_1 = \frac{8\,k d_f^2}{\pi^2(1 + k)^2\,D_1} \qquad (3)$$

TABLE I

EFFECT OF STATIONARY PHASE COMPOSITION ON MINIMUM THEORETICAL PLATE HEIGHTS $h_{min.}$ AND LIQUID PHASE MASS TRANSFER COEFFICIENTS C_1

Column temperature: 130°; test substance: naphthalene.

Percent w/w OV-17 in B34	$h_{min.}$ (cm)	$C_1 \times 10^{-3}$ (sec)
0 (B34 only)	0.065	5.1
25	0.050	4.0
50	0.068	5.8
75	0.079	12.3
100 (OV-17 only)	0.104	17.4

and it is clear that any measure which reduces the mean film thickness d_f would be expected to reduce C_1 critically, and hence the theoretical plate characteristics of the column, particularly at high gas velocities. Table I lists computed values of C_1 derived from the Van Deemter plots in Fig. 2, and also the minimum plate heights.

The presence of the B34 clearly gives a dramatic improvement in both plate heights and in the mass transfer coefficients, the optimum result being obtained for the column which contained 25% OV-17. Surprisingly, the column which contained B34 alone also gave excellent results with no trace of peak asymmetry. Previous published work has indicated that the adsorption isotherms for most substances, with the exception of paraffinic hydrocarbons, are non-linear, and that the presence of a liquid modifier is essential to obtain symmetrical peaks. The work reported here indicates that the isotherms are in fact linear for a number of chemical types if a sufficiently non-active support is used[18]. Thus the apparent non-linearity previously experienced is almost certainly due to adsorption at the surface of the diatomaceous earth or firebrick supports which are usually employed. Even the glass beads, however, have a significant activity which causes tailing with very polar compounds, unless steps are taken to reduce the residual activity by the use of polar liquid modifiers (see Fig. 4). Symmetrical peaks, however, were obtained on all the five columns for hydrocarbons, primary amines, aldehydes, ketones, esters, and heterocyclic compounds.

Fig. 3 shows plots of V_g *versus* percentage liquid modifier in the stationary phase for three isomeric pairs *viz. m-/p*-xylenes, *m-/p*-toluidines, and quinoline/isoquinoline. Each pair is seen to exhibit a different type of behaviour. With the xylenes, there is a rapid decrease in retention volume, and consequently in selectivity, as the liquid phase loading is increased. *m-* and *p*-toluidines, however, give a much more gradual decline in selectivity so that even with 75% of modifier present there is an excellent resolution between the isomers. More surprising is the effect obtained with quinoline and isoquinoline. The B34 alone exhibits no selectivity towards these isomers but adding the liquid modifier induces a strong selectivity which causes isoquinoline to be eluted before the quinoline. On increasing the liquid modifier concentration, the selectivity again decreases, so that at the 50% level the peaks are once again eluted together. Above 50% by weight of liquid modifier quinoline elutes before isoquinoline, presumably due to the difference in their vapour pressures. This result is significant because it implies that the degree of selectivity obtained with liquid modified bentones is not necessarily merely a dilution of that obtained on unmodified bentones, but can, in fact, be higher. High selectivity was also obtained towards β- and γ-picolines, which behaved similarly to the *m-* and *p*-xylenes, and towards anthracene and phenanthrene which were similar in behaviour to the *m-* and *p*-toluidines.

Effects of stationary phase loading

Columns were packed with loadings of 0.008, 0.016, 0.04 and 0.08% by weight of 50:50 mixtures of B34 and OV-17. Van Deemter plots for fluorene, determined at 130° are shown in Fig. 4 and computed values of C_1 and minimum theoretical plate heights are given in Table II.

The 0.008% loaded column gave slight peak tailing which accounts for its poor plate characteristics. The other columns all gave a good performance with low
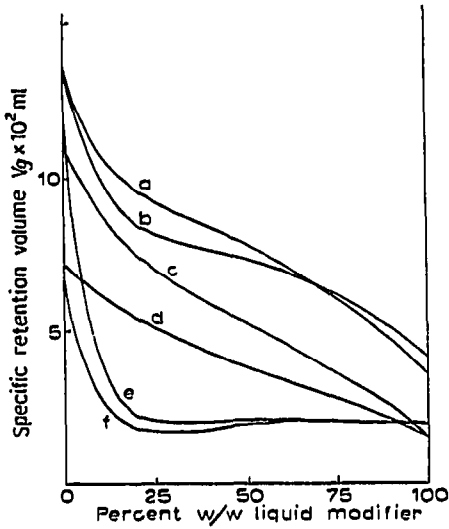
Fig. 3. Effect of liquid modifier concentration on V_g values. a = Isoquinoline; b = quinoline; c = m-toluidine; d = p-toluidine; e = m-xylene; f = p-xylene.
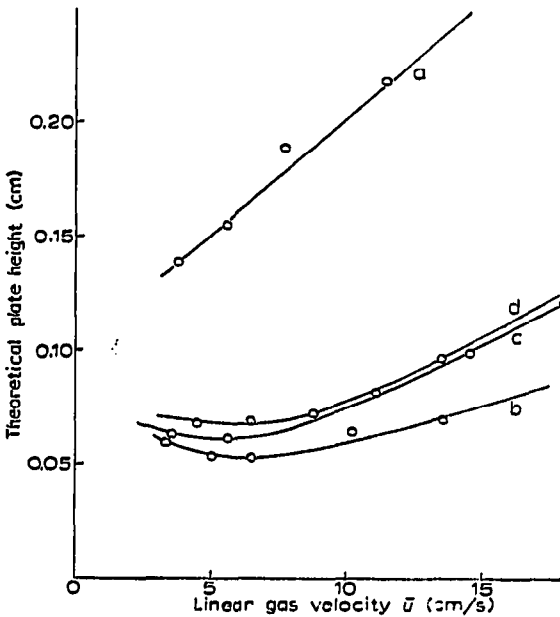

Fig. 4. Effect of stationary phase loading on plate characteristics. Solute, fluorene at 130°; carrier, gas, nitrogen. Stationary phase loading (%): a = 0.008; b = 0.016; c = 0.04; d = 0.08%.

minimum plate heights. Significantly there is no difference in the C_1 values for the 0.04 and 0.08% loadings. This suggests that there is a contribution to the plate height at high gas velocities which is independent of the liquid phase loading. This will be discussed later.

TABLE II

EFFECT OF STATIONARY PHASE LOADING ON MINIMUM PLATE HEIGHTS AND COMPUTED MASS TRANSFER COEFFICIENTS IN GEL-COATED BEAD COLUMNS

Percent loading by weight (50:50 B34–OV-17)	$h_{min.}$ (cm)	$C_1 \times 10^{-3}$ (sec)
0.008	~ 0.1	10.4
0.016	0.053	3.2
0.04	0.062	6.8
0.08	0.067	6.8

Analysis speed

The 0.016% column contained in fact only 6 mg of total stationary phase, which is about one hundred times less than a conventional diatomaceous earth packed column loaded with 5% stationary phase. If we compare the two columns on this basis alone, *viz.* assuming that the theoretical plate and relative retention characteristics are identical, then we should realize an improvement in analysis speed of two orders of magnitude. This follows from the expression:

$$t_r = \frac{L}{\bar{u}}(1 + k)$$

$$\approx \frac{Lk}{\bar{u}} \text{ when } k \text{ large}$$

$$= \frac{Lk\, v_1}{v_g}$$

In fact the improved plate performance of gel-coated beads at high gas velocities and their improved selectivity should increase the speed even more so that analysis times can be measured in terms of minutes or even seconds. Desty *et al.*[19] proposed a useful method for the measurement of this aspect of column performance which was called effective plate speed (EPS). This is defined as the number of effective theoretical plates generated per second measured under conditions in which the com-

TABLE III

ANALYSIS SPEED FOR AROMATIC COMPOUNDS ON COLUMN CONTAINING 0.016% BY WEIGHT OF B34–OV-17 GEL ON GLASS BEADS

Column temperature: 130°; inlet pressure: 20 p.s.i.g.; carrier gas: N_2.

Compound	Adjusted retention time t_r (sec)	Effective plate speed (effective theoretical plates per sec)
Naphthalene	6	250
Biphenyl	24	83
Acenaphthene	39	51
Dibenzofuran	63	32
Fluorene	84	28
Phenanthrene	300	11
Anthracene	370	10

ponent is resolved from its neighbours. The following expression is applicable[20]:

$$EPS = \frac{\bar{u}}{h}\left[\frac{k^2}{(1+k)^3}\right]$$

$$\approx \frac{\bar{u}}{hk} \text{ when } k \gg 1, \text{ as in most packed columns.}$$

For fast analysis the carrier gas velocity can be adjusted to the value which gives a maximum value of $\bar{u}/h$. This is known as the optimum practical gas velocity (OPGV), defined originally by Scott and Hazeldean[21]. Table III gives values of retention times and EPS calculated for the elution of various aromatic compounds in a single run on the 0.016% column loading.

Minimum limit of retention

Fig. 5 shows the effect of stationary phase loading on the retention volume for fluorene at 130°. The retention volume is seen to decrease to a minimum limiting value as the loading decreases owing to a residual adsorptivity on the glass surface. With no loading present the peaks are highly asymmetrical, indicating non-linear adsorption on the glass. Above 0.01 % loading the retention volume increases linearly in accordance with simple theory and the peaks become very symmetrical with no trace of tailing.
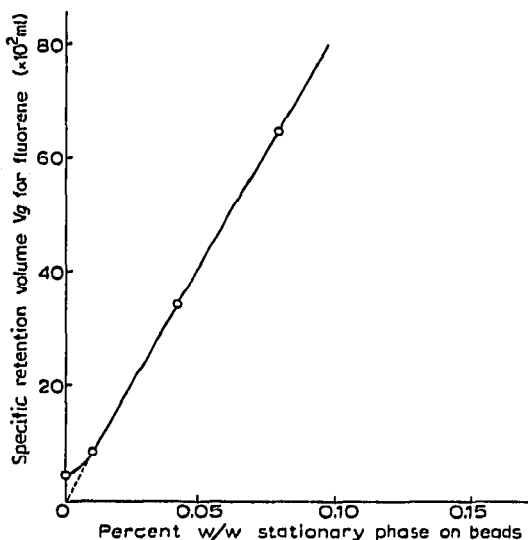

Fig. 5. Effect of stationary phase loading on V_g value of fluorene. Temperature, 130°.

Determination of separate C_g and C_1 values

It was noted earlier that there was evidence for the existence of an additional mass transfer effect independent of the amount of stationary phase present. This is almost certain to arise from gas phase diffusion and Golay[12] in fact first postulated the existence of this in the development of the theory of capillary columns, but it was generally assumed to be insignificant in packed columns. Thus, if we allow for the

presence of a contribution to mass transfer in the gas phase the plate height equation becomes:

$$h = 2\lambda\, d_p + \frac{2\gamma\, D_g}{\bar{u}} + (C_g + C_1)\bar{u}$$

Separate values of C_g and C_1 can be computed by running a column with two different carrier gases and producing simultaneous equations[22]. Values were obtained in this way for a column containing a 0.08% loading of a 50:50 mixture of B34 and trimer acid. This column gave highly symmetrical peaks for hydrocarbons, alcohols, aldehydes, ketones, esters, and amines. The column was run at 130° and theoretical plate characteristics were measured using the compounds biphenyl, acenaphthene, dibenzofuran, and fluorene as test substances. Nitrogen and helium were the two carrier gases employed. Table IV lists the computed mass transfer coefficients.

TABLE IV

COMPUTED C_g AND C_1 AND $(C_g + C_1)$ VALUES FROM EXPERIMENTAL DATA

Column: 0.08% B34–trimer acid (50:50) on 100-mesh beads; temperature: 130°.

Substance	Partition ratio k	Mass transfer coefficients × 10⁻³				
		$(C_g + C_1)$ using N_2 (sec)	$(C_g + C_1)$ using He (sec)	C_g He (sec)	C_g N_2 (sec)	C_1 (sec)
Biphenyl	8.9	8.2	6.2	1.2	3.2	5.0
Acenaphthene	17	6.8	3.3	2.2	5.7	1.1
Dibenzofuran	27	6.8	3.7	1.9	5.0	1.8
Fluorene	38	3.4	1.7	1.0	2.7	0.7

Examination of these values shows that there is in fact a significant contribution from gas phase mass transfer, as was earlier indicated. Both C_g values seem to go through a maximum for acenaphthene and then decrease with increasing k value. However, there is a relatively high error associated with the determination of these values because of the difficulty in measuring theoretical plate heights with any accuracy, particularly at high gas velocities and on rapidly eluted components. The values given for biphenyl may well be low for this reason. The C_1 values clearly decrease appreciably from biphenyl to fluorene and this is explained by the effect of k on C_1 in expression 3. Apparently then the liquid phase mass transfer coefficient is less important than the gas phase mass transfer coefficient in these columns. Theoretically this is of some advantage because it can be shown that where $C_1 \ll C_g$ the minimum plate height becomes almost independent of the nature of the carrier gas[23], viz.

$$h_{\min.} = 2\lambda\, d_p + 2\sqrt{\frac{\gamma\, d_p{}^2(1 + 6\,k + 11\,k^2)}{12(1 + k)^2}}$$

Thus, by using helium as carrier gas we should be able to achieve almost the same theoretical plate number as with nitrogen but at a higher gas velocity in view of the smaller C_g value in helium. This is supported by the results shown in Fig. 6 where
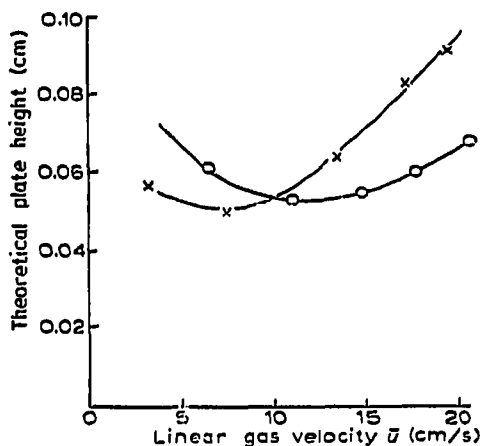
Fig. 6. Effect of carrier gas on plate characteristics. Solute, fluorene at 130°. O—O, helium; ×—×, nitrogen.

the minimum plate heights for fluorene are seen to be very similar for both gases. At higher gas velocities than the optimum, plate heights using helium are appreciably lower than with nitrogen and so one can derive a considerable advantage from the use of helium for fast analysis.

Nature of liquid modifier

We have shown that liquid modified B34 packings coated onto a glass bead support improves the plate characteristics of columns beyond what can be achieved with either liquid phases or B34 used alone. Obviously retention properties are dependent on the amount and nature of the liquid modifier and an infinite number of possibilities exist. Table V gives the properties of five different combinations of liquid modifiers with B34. Particularly interesting are the very low theoretical plate heights obtained using polyphenyl ether and the mixed trimer acid and OV-17 as modifiers.

TABLE V

USE OF VARIOUS LIQUID MODIFIERS WITH BENTONE 34 IN GEL-COATED GLASS BEAD COLUMNS

PPE: polyphenyl ether; TA: trimer acid; Cwx 20M: Carbowax 20M; TA + OV-17: 50:50 mixture of trimer acid and silicone OV-17; (+ +): excellent symmetry; (+): acceptable symmetry; (— —): bad tailing, peaks not measurable; (—) tailing but peaks measurable; n.m.: not measured; MCH: methyl cyclohexanol.

Liquid modifier	Percent w/w loading	$h_{min.}$ (cm)	Separation factors			
			Anthracene Phenanthrene (150°)	m-Cresol p-Cresol (105°)	cis-MCH trans-MCH (120°)	Isoquinoline Quinoline (130°)
OV-17	0.08	0.07	1.25(+ +)	(— —)	(— —)	1.16(+)
PPE	0.08	0.04	1.13(+ +)	(— —)	(— —)	1.00(—)
TA	0.08	0.06	n.m.	1.20(—)	1.22(+)	n.m.
Cwx 20M	0.10	0.05	1.04(+ +)	1.04(—)	(—)	1.21(—)
TA + OV-17	0.12	0.04	1.10(+ +)	1.19(+ +)	n.m.	1.26(+)

These columns gave a plate efficiency of over 800 plates per foot which suggests that the disposition of the gel over the surface of the beads has been further improved in these cases. Also of interest is the peak symmetry obtained for highly polar substances where polar liquid modifiers are used. This enables phenols, alcohols, and probably also highly polar compounds to be separated. High selectivity was achieved between the *m-/p*-cresols and also significantly between the *cis-* and *trans*-methylcyclohexanols. Obviously a further investigation of the *cis–trans* selectivity of these packings should be profitable. Plate speeds also are very high in general.

ACKNOWLEDGEMENTS

LIST OF SYMBOLS

N Number of theoretical plates in column
R Resolution, defined as distance between two adjacent peak maxima divided by their mean peak width
S Separation factor
k Partition ratio
k_a Partition ratio for first eluted component of pair to be resolved
h Height equivalent to a theoretical plate or "plate height"
h_{min}. Minimum plate height
λ Multiple path diffusion constant
d_p Mean particle diameter of solid support
γ Tortuosity constant
D_g Diffusion coefficient of solute in gas phase
D_1 Diffusion coefficient of solute in stationary phase
C_1 Stationary phase mass transfer coefficient
C_g Gas phase mass transfer coefficient
$\bar{u}$ Mean linear carrier gas velocity
d_f Average stationary phase film thickness on support
t_r Measured retention time of any component from injection
L Column length
v_1 Volume of stationary phase in column
v_g Volume of gas phase in column
V_g Specific retention volume

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