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USE OF SPECIFIC RETENTION VOLUMES IN THE EVALUATION OF VARIOUS TYPES OF COLUMNS FOR USE IN THE TRACE DETERMINATION OF ETHYLENE GLYCOL BY GAS CHROMATOGRAPHY

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SUMMARY

Various types of column packings were evaluated for use in the gas chromatographic determination of ppm concentrations of ethylene glycol in aqueous systems. The columns were evaluated by determining specific retention volumes and observing peak shapes for progressively smaller concentrations of ethylene glycol in water injected on to the column. An increase in the specific retention volume, accompanied by significant peak tailing, was taken to indicate that quantitative analysis would not be feasible below a certain concentration range, because of chemisorptive effects. The most desirable column for quantitative analysis at trace levels (10 ppm or more injected on to the column) was selected on the basis of comparative evaluation. Acid-washed and silane-treated diatomaceous supports coated with Carbowax 20M, uncoated porous polymers (Chromosorb 101 and 102), and Chromosorb 102 coated with Carbowax 20M were considered unsatisfactory. Super-Pak 20M coated with Carbowax 20M was marginally successful, while Chromosorb 101 coated with Carbowax 20M was clearly the column packing of choice. These results are discussed in terms of column support adsorption effects.

INTRODUCTION

The determination of trace levels of polar organic compounds by conventional gas–liquid chromatography (GLC) on diatomaceous supports is often difficult because of adsorption effects resulting in increasing retention volumes accompanied by peak tailing and irreproducible responses. These effects are usually caused by hydroxyl groups on the surface of the support. This problem is not confined to low loads of stationary phase where incomplete surface coverage might be implicated, but can exist with completely coated supports[1–3]. The use of silane-treated supports may improve performance in this respect. However, adsorption problems have been reported that could be attributed to poor silanization of commercially available supports of this type[4] or possible adsorption at the silyl group[5].

An alternative choice for the gas chromatographic stationary phase is to use porous polymers produced from divinylbenzene and either styrene or ethylvinyl-

benzene. Presumably no hydroxyl groups are present in these materials to strongly adsorb polar compounds. However, unreacted vinyl groups[6], residual transition metals[7,8] and unspecified causes[9,10] have been implicated in adsorption of compounds such as amines[6,8], volatile free fatty acids[6,9] and alcohols[6,10] at low solute concentrations. Some workers[6,8,11–13] have improved performance in trace analysis by coating porous polymers with common liquid phases.

In our work to determine ethylene glycol (EG) migrating at trace levels from poly(ethylene terephthalate) bottles into aqueous food-simulating solvents, we observed problems similar to those often encountered in the chromatography of polar compounds. To select an appropriate GLC column, we evaluated various types of columns by determining specific retention volumes and observing peak shapes for progressively smaller concentrations of EG in water injected on to the columns. This comparative evaluation resulted in the selection of a column which is being used for EG analysis with a minimum of adsorption-related problems.

EXPERIMENTAL

Apparatus and general procedure

The gas chromatograph used for this study was a Hewlett-Packard 5840A equipped with a flame ionization detector. Nitrogen carrier gas was passed through an oxygen trap installed in the carrier gas line to the instrument. The injection port was maintained at 195° and the detector at 225°.

The various column packings were packed with gentle tapping and vacuum into 6 ft. × 2 mm I.D. glass coils to allow "on-column" injection of the sample. All columns were evaluated at 170° by determining specific retention volumes (as defined in Results and discussion) and observing peak shapes for EG as a function of the quantity of EG injected. Triplicate 5 μl injections were made of each solution of EG in distilled water, in the concentration range of 8 ppm to 2 parts per thousand (v/v). The EG retention times for each concentration were averaged to calculate retention volumes.

Coated diatomaceous supports

An approximate 10% Carbowax 20M on 80–100 mesh Chromosorb W AW packing was prepared by standard solution coating from chloroform. The exact loading was determined by Soxhlet extraction with chloroform. Residual oxygen was purged from the column at room temperature using nitrogen flow for 30 min. After conditioning with flow for 2 h at 270°, the column was cooled to 170° and evaluated. The same column was then further conditioned at 270° for an additional 16 h and re-evaluated. The column was finally conditioned at 270° for 68 h more and re-evaluated. Immediately after the final evaluation, the amount of Carbowax 20M remaining on the support was determined by Soxhlet extraction of the packing removed from the column.

A similar procedure was followed for a column packed with 10% Carbowax 20M on Super-Pak 20M (mesh size not specified by manufacturer) and a column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb WHP.

Carrier gas flow-rates for all evaluations of the coated diatomaceous supports were 28–30 ml/min. Column head pressures were *ca.* 30, 19 and 49 p.s.i.g. for the

Chromosorb W AW, Chromosorb W HP and Super-Pak 20M support groups, respectively.

Porous polymers and coated porous polymers

Chromosorb 101 and 102 (80–100 mesh) columns were purged with nitrogen at ambient temperature for 30 min. The columns were conditioned with flow at 200° for 4 h, after which they were evaluated. After the initial evaluation each column was brought to ambient temperature under continued nitrogen flow. To assess the effect of residual oxygen during conditioning the following routine was performed. The carrier gas line of the gas chromatograph was disconnected from the nitrogen source and connected to a source of air of breathing quality. The flow-rate was set at 50 ml/min and continued for 30 min at ambient temperature. The carrier gas line was reconnected to the nitrogen source, the flow was initiated, and the column oven temperature was immediately raised to 200° and held for 4 h. After this procedure, the columns were again evaluated . Chromosorbs 101 and 102 from the same lots as the above were each coated with 3 and 6% Carbowax 20M by solution coating from chloroform. Each column was purged with nitrogen at ambient temperature for 30 min, conditioned with flow for 4 h at 200° and evaluated.

Evaluations of the porous polymers were performed at carrier gas flow-rates of 22.0 and 24.0 ml/min for the Chromosorb 101 and 102 groups, respectively. This was done to avoid the variation within each group of retention volumes with the carrier gas flow-rate, which has been reported to occur for porous polymers[14,15]. Column head pressures were *ca.* 27 and 44 p.s.i.g. for uncoated Chromosorbs 101 and 102, 39 p.s.i.g. for both 3 and 6% Carbowax 20M on Chromosorb 101, and 41 p.s.i.g. for both 3 and 6% Carbowax 20M on Chromosorb 102. Two columns were packed from each lot of prepared packing material. Since the results were in general agreement for all sets of duplicate columns, results for only one column from each set are presented.

RESULTS AND DISCUSSION

Coated diatomaceous supports

Fig. 1 shows the "apparent" specific retention volumes for EG after the various conditioning periods for the Carbowax 20M on Chromosorb W AW column. We define "apparent" specific retention volume as follows:

$$V_g^{T\prime} = V_n / W_s'$$

where $V_g^{T\prime}$ is the "apparent" specific retention volume (at 170°), V_n is the net retention volume corrected for dead volume and pressure drop[16], and W_s' is weight of stationary phase in the unconditioned packing. Since *ca.* 50% of the initial load on the support was lost during the total conditioning and evaluation procedure, the apparent values are not true specific retention volumes as required for the determination of thermodynamic parameters. They deviate increasingly from the true values for the more highly conditioned columns. The slopes of the curves for the highly conditioned columns are also less than what would be observed if actual specific retention volumes were used. However, any dependence of retention volume on the concentration of EG injected is still evident. Retention volumes are expressed relative to the unconditioned

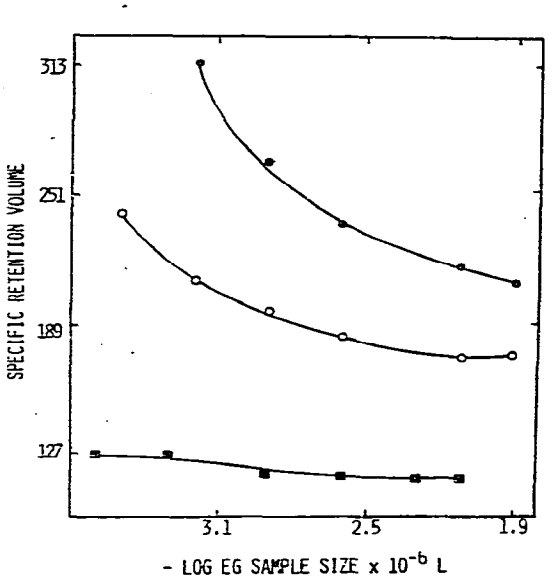

Fig. 1. "Apparent" specific retention volume at 170° (per gram of Carbowax 20M present in the unconditioned packing) *vs.* EG sample size, for a column of 10% Carbowax 20M on Chromosorb W AW conditioned at 270° for ● 2 h, ○ 18 h and ■ 96 h.

packing to allow for the evaluation of stationary phase bleed, for a single column through the progressive conditioning process. This would be indicated by decreasing apparent specific retention volume values during the cumulative conditioning process.

A concentration dependence of the apparent specific retention volume, such that it increases as smaller amounts of solute are injected, usually indicates solute adsorption at active sites on the support surface. A progressive bleed of stationary phase accompanied by a progressive lessening of support adsorption of EG is indicated by Fig. 1. The latter observation agrees with findings of Aue *et al.*[17], who observed a similar deactivation of the surface of Chromosorb W by Carbowax 20M when such high-temperature conditioning was employed.

However, EG exhibited severe tailing (Fig. 2) with poor response for the initial two evaluations. The dependence of retention volume on quantity injected lessened considerably for the evaluation of the column conditioned for 96 h. However, double peaking due to ghosting was observed, as previously reported in adsorption-plagued analyses[18,19]. Thus, after 96 h of cumulative conditioning at 270° and with 4.6% stationary phase still remaining. Chromosorb W AW was not a satisfactory support for the trace analysis of EG.

Apparent specific retention volumes for EG after the various conditioning periods for the Carbowax 20M on Chromosorb W HP column are shown in Fig. 3. This support also lost *ca.* 50% of its original stationary phase load during the cumulative conditioning process, accounting for the progressive decrease in apparent specific retention volume. Support adsorption effects are clearly evident for each evaluation. However, the effects present during the initial evaluation are considerably less than those observed for the Chromosorb W AW support and are only slightly lessened during the cumulative conditioning process.

These observations indicate that the silanized diatomaceous support offers a

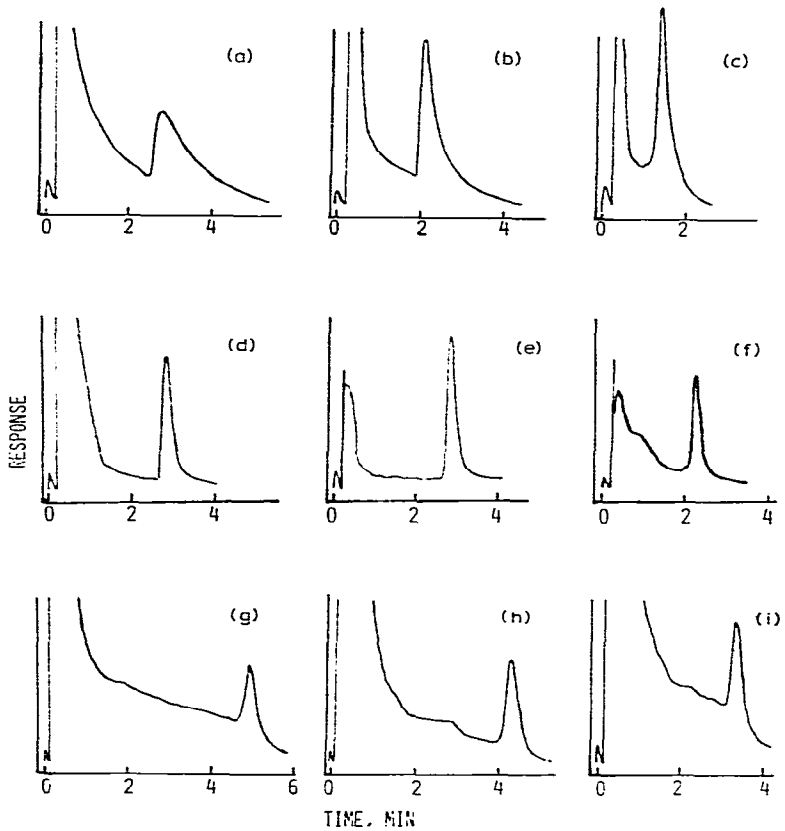

Fig. 2. EG peak shapes obtained at 170° for: (a)–(c), 10% Carbowax 20M on Chromosorb W AW; (d)–(f), 20% Carbowax 20M on Chromosorb W HP; (g)–(i), 10% Carbowax 20M on Super-Pak 20M. Conditioning: (a), (d) and (g), 2 h; (b), (e) and (h), 18 h; (c), (f) and (i), 96 h.

less adsorptive surface than its acid-washed counterpart, as would be expected. However, the potential for achieving further support deactivation through conditioning, when a relatively polar stationary phase is employed, may be discouraged by the hydrophobic nature of the surface of the silanized support. This is evidenced by the observation that after 96 h of cumulative conditioning, the acid-washed support exhibited less support activity than the silanized support. Tailing of EG peaks observed for this column is shown in Fig. 2. Because of persistent adsorption effects, we considered this support unsatisfactory for the chromatography of small amounts of EG. Recognizing, however, that commercially available supports of this type may exhibit widely varying degrees of support activity, it is not unlikely that more carefully silanized supports of this type would exhibit improved performance[4].

The evaluation of the column of Carbowax 20M on Super-Pak 20M is shown in Fig. 4. Once again a *ca.* 50% stationary phase bleed occurred during the cumulative conditioning process, accounting for the progressive decrease in the apparent specific retention volumes. However, this support exhibited virtually no dependence of apparent specific retention volume on sample size during the initial evaluation. Support effects evidenced by changing apparent specific retention volumes were observed

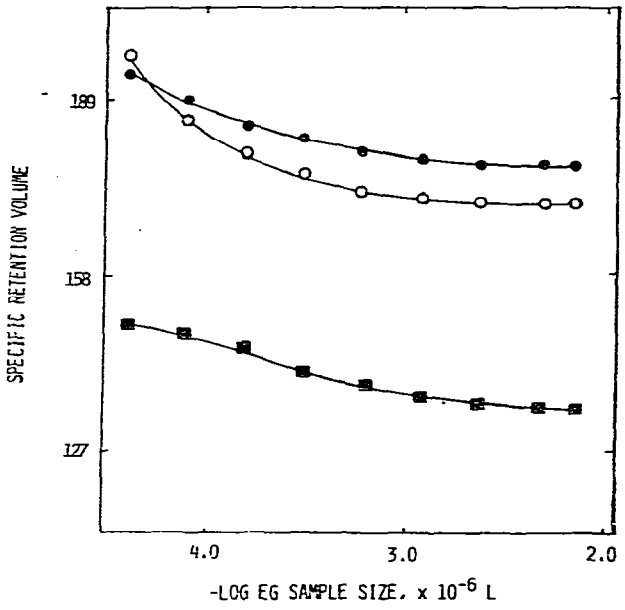

Fig. 3. "Apparent" specific retention volume at 170° (per gram of Carbowax 20M present in the unconditioned packing) *vs.* EG sample size, for a column of 20% Carbowax 20M on Chromosorb W HP conditioned at 270° for ● 2 h, ○ 18 h and ■ 96 h.

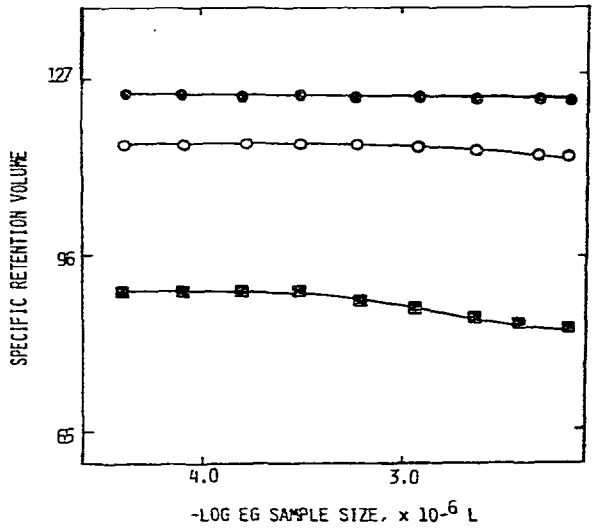

Fig. 4. "Apparent" specific retention volume at 170° (per gram of Carbowax 20M present in the unconditioned packing) *vs.* EG sample size, for a column of 10% Carbowax 20M on Super-Pak 20M conditioned at 270° for ● 2 h, ○ 18 h and ■ 96 h.

for the later evaluations. Excessive high-temperature conditioning is evidently ruinous to the support, as indicated by the manufacturer.

Super-Pak 20M is a specially prepared, deactivated diatomaceous support based on the work of Aue *et al.*[17]. The progressive deactivation of Chromosorb W AW

which we observed (Fig. 1) is commercially employed to produce Super-Pak 20M, with the result that this support as supplied is clearly the most suitable diatomaceous type of support for this analysis.

EG peak shapes obtained for this column are nearly symmetrical for the initial evaluation, as shown in Fig. 2. However, curves for response *vs.* amount of EG injected for the 2 h conditioned column showed considerable irreproducibility of integration values for EG peaks, indicating that some support adsorption may still be occurring. For this reason it was decided to evaluate non-diatomaceous supports in an attempt to ascertain what would be an optimal column for this analysis.

Porous polymers and coated porous polymers

Figs. 5 and 6 show specific retention volumes (at 170°) expressed per gram of Chromosorb 101 and 102, respectively, for these two uncoated porous polymers conditioned with and without residual oxygen present in the column. For both of the uncoated porous polymers which have been purged of residual oxygen prior to conditioning, trace analysis of EG is complicated by active-site adsorption effects. Such effects are attributed to the presence of unreacted vinyl groups and residual transition metals in the porous polymers, as previously mentioned.

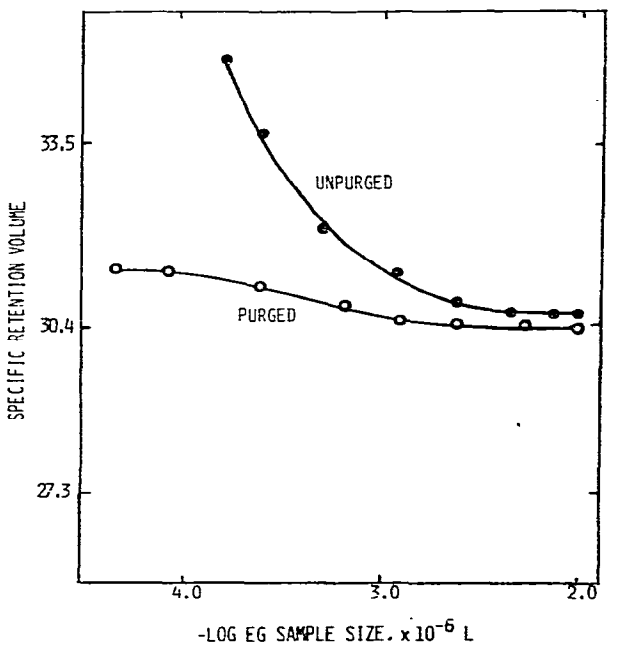

Fig. 5. Specific retention volume at 170° (per gram of Chromosorb 101) *vs.* EG sample size, for uncoated Chromosorb 101 conditioned with (●) and without (○) residual air present in the packed column.

It is especially detrimental to the performance of these porous polymers if they are not purged of residual oxygen prior to high-temperature conditioning. Neumann and Morales T have associated the formation of conjugated carbonyl compounds with a reduction of residual vinyl content in Chromosorb 102 heated at 200°

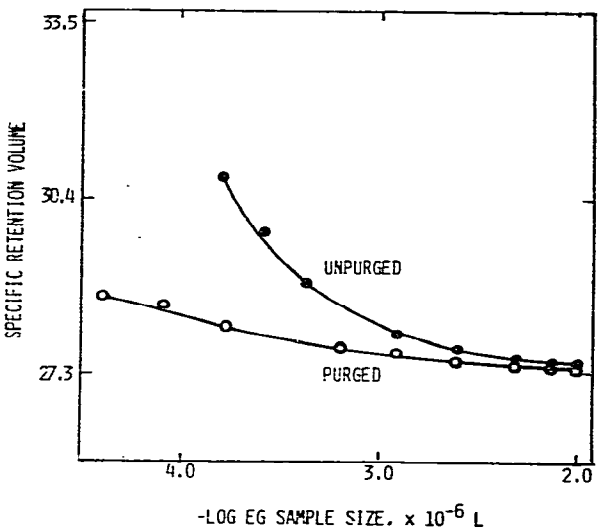

Fig. 6. Specific retention volume at 170° (per gram of Chromosorb 102) *vs.* EG sample size, for uncoated Chromosorb 102 conditioned with (●) and without (○) residual air present in the packed column.

in an oxygen-containing nitrogen flow[20]. The formation of carbonyls on the surface of these porous polymers presents the potential for an enhanced interaction with compounds possessing hydroxyl groups such as EG. Peak shapes for EG obtained for these columns are shown in Fig. 7A–D. As expected, increased tailing is observed for the columns which were not purged of residual oxygen prior to conditioning at the elevated temperature.

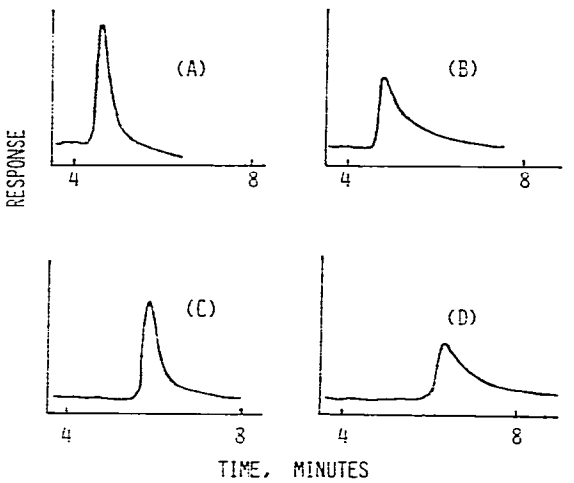

Fig. 7. EG peak shapes obtained for uncoated Chromosorb 101 and 102 columns. Chromatograms A and B represent Chromosorb 101 columns conditioned without and with residual air present in the packed column. Chromatograms C and D are the equivalent pair for Chromosorb 102. The EG sample size in each case is *ca.* 5 times larger than the minimum amount detectable.

The effect of coating Chromosorb 101 with a liquid phase is illustrated in Fig. 8. With 3 and 6% loads of Carbowax 20M, there is no dependence of the specific retention volume (per gram of Chromosorb) on the amount of EG injected. Furthermore, peak shapes are nearly symmetrical for small amounts of EG injected, as shown in Fig. 9A–B, and EG peak integration values are reproducible. However, for 3 and 6% loads of Carbowax 20M on Chromosorb 102, a dependence of the specific retention volume on the amount of EG injected still exists, although this dependence is less for the 6% column as shown in Fig. 10. Peak shapes shown in Fig. 9C–D indicate tailing for small amounts of EG injected.

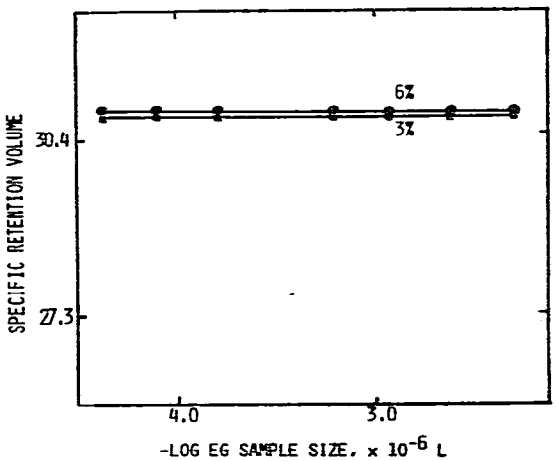

Fig. 8. Specific retention volume at 170° (per gram of Chromosorb 101) *vs.* EG sample size for coated Chromosorb 101, where the liquid phase is (●) 6% Carbowax 20M and (■) 3% Carbowax 20M.

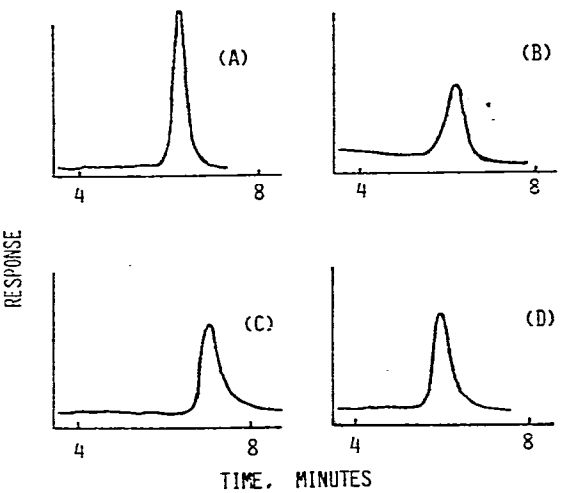

Fig. 9. EG peak shapes obtained at 170° for coated Chromosorb 101 and 102 columns. Chromatograms A and B represent coated Chromosorb 101 where the liquid phase is 3% and 6% Carbowax 20M. Chromatograms C and D are the equivalent pair for coated Chromosorb 102. The EG sample size in each case is *ca.* 5 times larger than the minimum amount detectable.

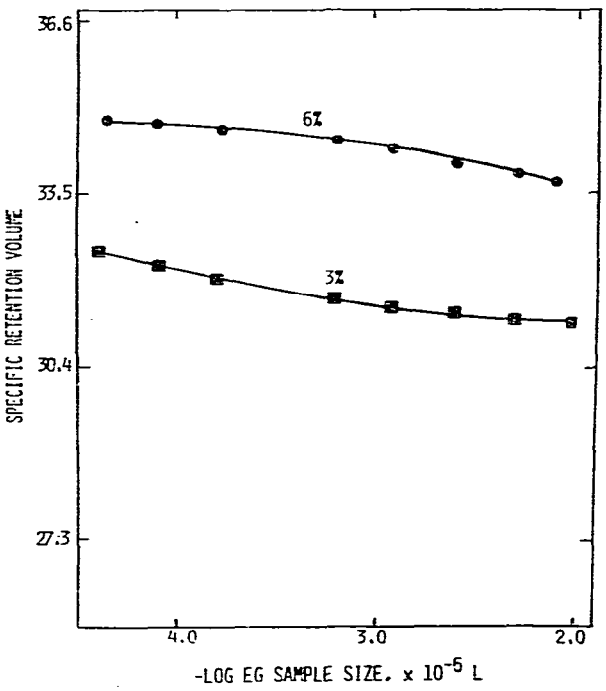

Fig. 10. Specific retention volume at 170° (per gram of Chromosorb 102) *vs.* EG sample size for coated Chromosorb 102, where the liquid phase is (●) 6% Carbowax 20M and (■) 3% Carbowax 20M.

When examining the effect of 3 and 6% Carbowax 20M on the specific retention volumes per gram of Chromosorb 101 and 102, it is apparent that the presence of a liquid phase has a much greater effect relative to the uncoated porous polymer for Chromosorb 102. Although these two materials are chemically similar, they are markedly dissimilar with respect to surface area and average pore diameter, with corresponding values of 40 m^2/g and 3000–4000 Å and 300–400 m^2/g and 85 Å for Chromosorbs 101 and 102, respectively[21].

The microporous structure of Chromosorb 102 probably leads to a pore-filling effect upon coating with Carbowax 20M such that bulk liquid phase deposited in the micropores contributes to a substantial increase in the specific retention volume of EG relative to uncoated Chromosorb 102. While bulk liquid phase is pooled in micropores upon coating, portions of the support surface remain relatively uncoated, contributing to the observed adsorption effects when coated Chromosorb 102 is evaluated. This represents a combination gas–solid and gas–liquid chromatography, as reported for coated Porapak Q[8], with significant support adsorption effects present even at a 6% liquid phase load.

For coated Chromosorb 101, the microporous structure of this support probably favors the deposition of a thin layer of Carbowax 20M which possesses non-bulk properties, since the specific retention volumes relative to the uncoated support increased only slightly. The more complete surface coverage attained in the absence of pooling of the liquid on this support accounts for the superior suppression of adsorp-

tion effects on coated Chromosorb 101. Specific retention volumes relative to uncoated Chromosorb 101 indicate that a somewhat modified gas–solid chromatography occurs for the coated Chromosorb 101 columns.

The suppression of support adsorption effects obtained for the coated Chromosorb columns is attributed to a physical blocking of active sites on the surface of the porous polymer, as discussed by Hertl and Neumann[6]. They suggested that treating porous polymers containing residual vinyl groups with HF would be a more desirable method for deactivating these active sites. Merely coating the surface of the polymer with a liquid phase presents the possibility for loss of the liquid phase through bleeding and an eventual availability of active sites on the support surface.

We found the columns of 3 and 6% Carbowax 20M on Chromosorb 101 to be suitable for determination of low concentrations of EG as long as the above limitation is recognized. There does seem to be a sudden onset of irreproducible integration values for EG peaks if a column has been in continuous use at 170° for a month or so. This may be due to a gradual bleed of liquid phase resulting in a subsequent availability of support active sites as mentioned earlier. We are now reducing the temperature of the column oven to 50° when analyses are not being performed, in the hope of extending column life as recommended by Ives and Giuffrida[22].

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