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ANALYSIS OF PHENOLS BY GAS–LIQUID–SOLID CHROMATOGRAPHY

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SUMMARY

The use of graphitized Sterling FT has been extended to the analysis of phenolic compounds. This has been made possible by coating the carbon surface with small amounts of a high-boiling, acidic liquid phase, such as FFAP. The effectiveness of this packing material in chromatographing phenols is made evident by the fact that cresols are separated in an analysis time of only 3 min and the fractionation of a mixture of more than twenty phenols is achieved by the use of a single column and with an elution time of not more than 45 min. By varying the liquid:solid ratio, the behaviour of gas–liquid–solid columns was studied.

INTRODUCTION

The analysis of phenols is of interest because of their presence in disinfectant formulations and plant tissues, for example. These compounds have high polarity and low vapour pressure at moderate temperatures, which makes their chromatographic analysis with conventional packed columns difficult and laborious. An additional difficulty arises from the fact that certain pairs of phenolic compounds have almost identical vapour pressures. Recently, the analysis of some of the more polar phenols, such as catechol and pyrogallol, has been performed with a packed column of SE-30[1]. Peak tailing in the elution of such compounds, however, affected the quality of the analysis and did not enable quantitative analysis to be achieved.

The use of conventional capillary columns[2–6] or more sophisticated techniques[7,8] can improve the resolution of phenols and substituted methylphenols. However, some problems, especially in the linear elution of the more polar phenols, still remain.

Graphitized carbon black (GCB) deposited as a thin layer on the walls of glass capillary columns has been shown to be a very effective adsorbing medium for separating phenolic isomers[8]. The planes, essentially non-polar and uniform surface of this adsorbing medium permits the separation of molecules mainly on the basis of differences in their geometric structures. However, the presence of trace amounts of hydrophilic sites on the surface of GCB results in tailed peaks in the elution of small amounts of polar compounds, such that the quality of the analysis is seriously affected[9].

In recent work[10], suitable amounts of non-volatile, acidic liquid phase such as FFAP (Varian Aerograph) were added on the surface of GCB. The results showed that the addition of a small amount of FFAP is very effective in linearizing the adsorption isotherms of free acids. At the same time, although FFAP is added at the rate of one complete monolayer, the ability of the carbon surface to separate structural isomers is still partially preserved.

The addition of even small amounts of liquid phase on an adsorbing surface causes the chromatographic features of a gas–solid column to be considerably altered. The modification to the chromatographic process arises from the combined effects of both the liquid and the solid phase. The elution of a particular compound through a column in which these effects are acting together has been termed gas–liquid–solid chromatography (GLSC) by Purnell[11].

In this work, the use of Sterling FT-G coated with various amounts of FFAP has been extended to the analysis of phenolic compounds, in order to examine the possibility of fractionating mixtures containing about 20 phenolic compounds by making use of a single packed column. The gas chromatographic behaviour of GLSC columns is also briefly discussed.

EXPERIMENTAL

GCB designated as graphitized Sterling FT (Sterling FT-G) was purchased as "Carbopack" from Supelco Inc., Bellefonte, Pa., U.S.A. The preparation of the packing material has been previously described[10].

The apparatus used was a Carlo Erba gas chromatograph, Model GI (Milan, Italy), equipped with a flame ionization detector. The chromatographic apparatus is constructed so as to allow the sample to be injected directly into the column. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

Macromolecules of FFAP added to the Sterling FT-G surface act mainly as a deactivating agent by being preferentially adsorbed on active sites on the carbon surface, so that surface heterogeneities become unavailable for adsorption of eluate molecules. A relative amount of FFAP of about 0.3% suffices to give symmetrical peaks, even for the elution of hydroxyphenols.

On the other hand, the addition of the liquid phase to an adsorbing medium considerably modifies all the chromatographic properties of a GLSC column. By varying the surface concentration of the liquid phase, modifications to the chromatographic process have been evaluated in terms of selectivity and elution time for phenols. Retention volumes per gram of adsorbent of some phenols *versus* the percentage of FFAP on Sterling FT-G are plotted in Fig. 1a.

It can be seen that, depending on the strength of the interactions between the liquid phase and the eluate molecules, the retention volume curves have different shapes. A qualitative interpretation of this behaviour is made by assuming that multilayer deposition of FFAP takes place on the Sterling FT-G surface[12]. In this connection, as previously reported[10], the completion of one monolayer of polymeric macromolecules of FFAP can be approximately fixed at 0.8% FFAP.

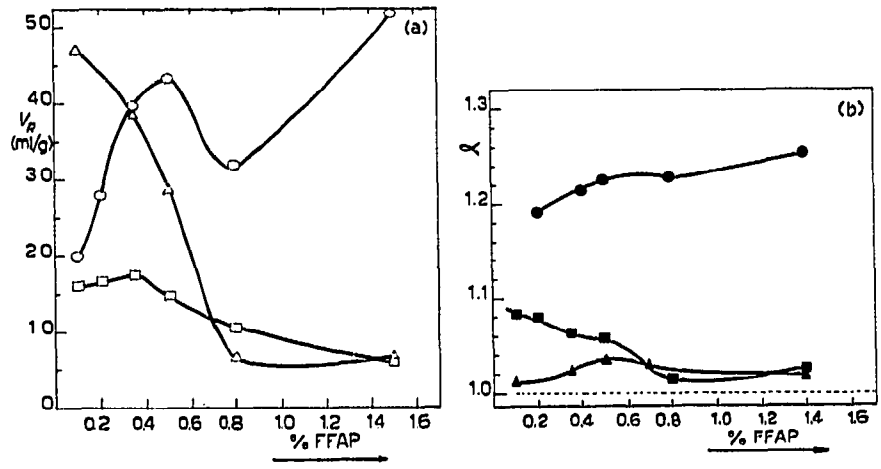

Fig. 1. (a) Plot of retention volume per gram of adsorbent at 208° as a function of the amount of FFAP added on Sterling FT-G. □, Cresol; △, dimethylphenol; ○, hydroquinone. (b) Plot of the separation factors as a function of the amount of FFAP added on Sterling FT-G. ■, *m*-Cresol + *p*-cresol; ▲, 2,4-dimethylphenol + 2,5-dimethylphenol; ●, hydroquinone + resorcinol.

The shape of the retention volume curve for hydroquinone can be used to illustrate modifications due to pre-adsorption of FFAP molecules on the carbon surface. At low percentages of FFAP, an initial increase in the retention volume of hydroquinone is observed. This increase is explained by considering that strong lateral interactions occur between polar groups of adsorbed eluate molecules and of the liquid phase due to specific, long-range forces, thus giving additional effects on the heat of adsorption of hydroquinone.

On the other hand, by increasing the surface concentration of the liquid phase, both the entropy of localization and the solid surface area available for adsorption decrease. Then, starting from a particular surface coverage, these effects outweigh the increase in the heat of adsorption and, consequently, a decrease in the retention volume of the adsorbate is observed. At concentrations of FFAP higher than 0.8%, *i.e.*, in the region of multimolecular adsorption, the retention volume curve of hydroquinone begins to increase, owing to the contribution of the solution in the liquid film that starts to form.

Retention volume curves for other compounds show a similar trend, with differences from the above curve depending on the strength of the interactions between the liquid phase and the eluate molecules.

In GLSC, the addition of molecules of a non-volatile liquid to the adsorbing medium introduces new force centres other than surface carbon atoms. Then, by modifying both the nature and the amount of liquid phase, column selectivity can be continuously adjusted so as to obtain the best resolution for a particular separation problem. By varying the surface coverage of the adsorbent, changes in separation factors, shown in Fig. 1b, can illustrate features of the working mechanism of GLSC columns.

For eluates that have very small differences in polarity or boiling point, such as the *m*-cresol–*p*-cresol pair, separation on a GL column is laborious. On the other

hand, the flat, essentially non-polar surface of GCB is particularly suitable for separating isomers on the basis of differences in geometrical structure, disregarding the presence in the adsorbate of functional groups. Then, GCB coated with the minimum amount needed to obtain symmetrical peaks for the elution of cresols appears to be the best packing material for the separation of the isomeric pair considered (Fig. 2). Obviously, by increasing the liquid:solid ratio, the influence of the carbon surface is attenuated and a consequent decrease in the separation factor of the *m*-cresol–*p*-cresol pair is observed.

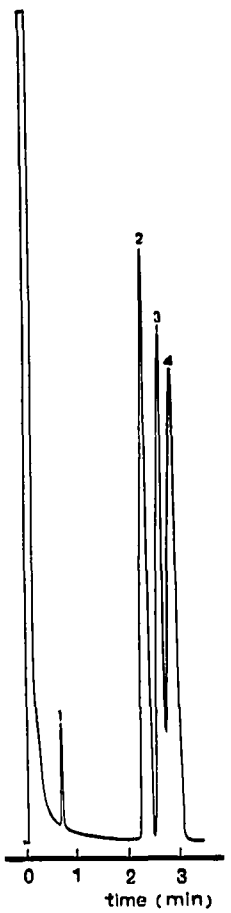

Fig. 2. Chromatogram showing the elution of cresols. Column, 1.7 m × 2 mm; 0.1% FFAP on Sterling FT-G; temperature, 208°; linear carrier gas velocity, 12 cm/sec. 1, Phenol; 2, *o*-cresol; 3, *m*-cresol; 4, *p*-cresol.

For the 2,4-dimethylphenol–2,5-dimethylphenol pair, the components of which differ slightly both in geometrical structure and polarity, the separation factor can be maximized by making use of a carbon surface that is partially shielded by a suitable amount of macromolecules of FFAP, as indicated by the plot considered.

Finally, for the hydroquinone–resorcinol pair, the components of which have

a large difference in polarity, the shape of the separation factor–surface coverage curve does not require discussion.

Each analytical separation involves many factors, which must be carefully considered in order to obtain a "tailor-made" chromatographic column that will yield the best analytical results. For this reason, when using GLSC it is difficult to indicate the "ideal" liquid:solid ratio to be used for a particular separation problem. Nevertheless, from the examination of the separation factor–surface coverage curves, and as deduced in our previous work[12], it appears that the graphitized carbon surface partially coated with the liquid phase so as to obtain an almost complete monolayer is generally the best arrangement for obtaining good separation factors in the chromatographic elution of a mixture of phenols.

To provide experimental evidence of the above conclusion, a chromatogram of a complex mixture of 23 phenols is shown in Fig. 3. The fractionation of the mixture

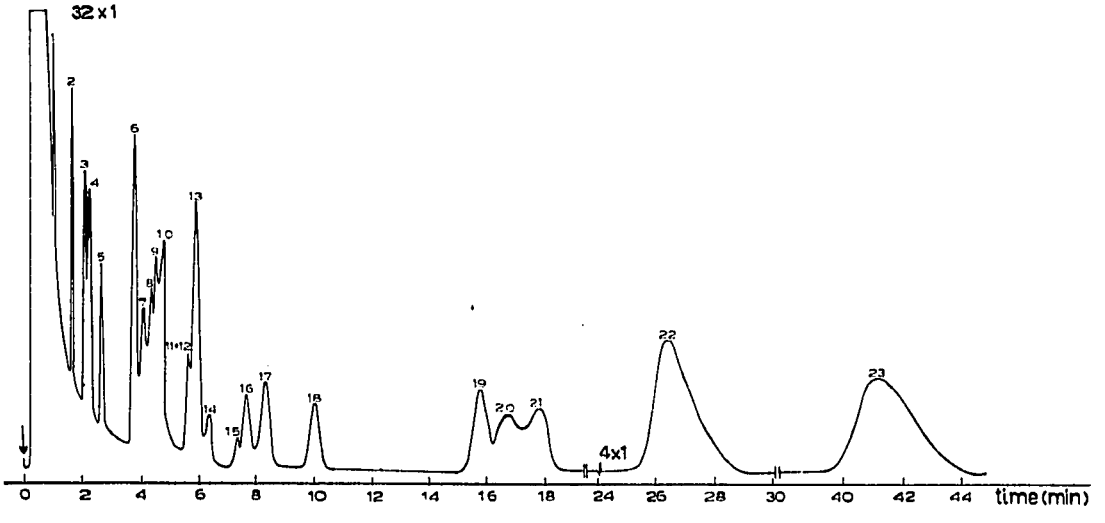

Fig. 3. Chromatogram showing the elution of phenols. Column, 2.4 m × 2 mm; 0.5% FFAP on Sterling FT-G; temperature, 220°; linear carrier gas velocity, 10 cm/sec; sample size of each component, 30–60 ng. 1, Phenol; 2, *o*-cresol; 3, *m*-cresol; 4, *p*-cresol; 5, *o*-nitrophenol; 6, 3,4-dimethylphenol; 7, catechol; 8, 2,3-dimethylphenol; 9, 3,5-dimethylphenol; 10, 2,4-dichlorophenol; 11, 2,4-dimethylphenol; 12, 2,5-dimethylphenol; 13, 2,4,6-trimethylphenol; 14, hydroquinone; 15, 2-methyl-1-nitrophenol; 16, resorcinol; 17, 2,6-dimethylphenol; 18, *o*-vanillin; 19, 3,4,5-trimethylphenol; 20, pyrogallol; 21, vanillin; 22, *m*-nitrophenol; 23, *p*-nitrophenol.

was made possible by the use of a column packed with Sterling FT-G + 0.5% FFAP. Under the experimental conditions used to elute all the components of the mixture, it was not possible to differentiate 2,4-dimethylphenol from 2,5-dimethylphenol. It can be seen that most of the phenols exhibit symmetrical peaks. Some tailing is observed in peaks relating to the elution of very small amounts of catechol, pyrogallol and nitrophenols, probably owing to slight decomposition of the compounds in the chromatographic apparatus.

CONCLUSION

The experimental results show that GCB coated with a suitable amount of FFAP is a very useful packing material for obtaining linear elution of phenols. In particular, we have confirmed the great ability of the carbon surface to separate isomers that have differences in their physicochemical properties that are so slight that their separation by conventional chromatographic techniques is very laborious. This is in addition to other important advantages that are peculiar to the GLSC technique[12].

Finally, it should be pointed out that the Sterling FT-G + FFAP system permits the simultaneous elution of both phenols and acids to be performed with a single chromatographic column.

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