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Gas-liquid/solid chromatography of hydrogen-bonding compounds

In the last few years we have investigated some interesting features concerning the use of graphitised carbon blacks as stationary phases in gas chromatography. These materials, introduced by KISELEV and his school^{1,2}, offer various advantages as compared with other adsorbents available, the most important being their high selectivity with respect to the geometrical structure of adsorbates, regardless of the possible presence in these molecules of very active functional groups. Graphitised carbon blacks are, in fact, classified as non-specific adsorbents³ and their mutual interaction with the molecules eluted is attributed to dispersion forces alone. On the other hand, graphitised carbon blacks have some disadvantages, common to other adsorbents, which can be summarised as follows: very high retention volumes and, due to the presence of some active sites on the adsorptive surface, peak tailing even for scarcely polar compounds and, in the case of hydrogen-bonding compounds, almost irreversible adsorption and "ghosting" phenomena.

In a recent paper⁴, we showed that these obstacles can be overcome by coating the adsorbent surface with very polar liquids bearing functional groups capable of neutralising the active centres of the adsorbent. The limiting factor of this technique is that, owing to the relatively high volatility of these deactivating liquids, the elution of compounds with high boiling points is hindered because one can only just operate at temperatures up to about 100°. More recently, we partially overcame this limit, by heating graphitised carbon blacks in a hydrogen stream at 1000° (ref. 5). This procedure, suggested by MILLARD and coworkers in a paper on water adsorption on carbon black⁶, serves to eliminate every residual oxygenated group from the carbon surface. The results of this procedure were quite satisfactory, allowing the elution of small amounts of very polar compounds, such as aliphatic amines and free carboxylic acids by gas-solid chromatography. However, the problem of high retention still remained. It is well known that by coating the support surfaces with small amounts of liquid phases, so that a thin film is formed, the support can be made to play an important role in the chromatographic process. We have already shown⁴ that this contribution of the solid can be employed to achieve a new type of selectivity, if both the liquid phase and the solid support are properly chosen. Obviously, this technique, called gas-liquid/solid chromatography (GLSC), can be used only if a highly homogeneous support is available. On the other hand we found that, by coating the graphitised carbon black surface, previously treated with hydrogen at high temperatures with variable amounts of a non-polar liquid with a high boiling point, the retention times were greatly reduced. Moreover, if the surface coverage is properly chosen, the adsorptive characteristics of the carbon black are partially preserved, depending on the thickness of the liquid phase layer. In this way, the elution of high-boiling compounds at fairly low temperatures is possible, in some cases avoiding possible pyrolysis of the compounds being analysed.

Finally, the use of hydrogen-treated carbon black avoids peak tailing even with polar and multifunctional compounds, and permits the exploitation of the selectivity of GLSC for these compounds. This paper reports the first results obtained with this technique.

Experimental and results

Sterling FT, obtained from Cabot Corp., having a surface area of about $15 \text{ m}^2/\text{g}$, was treated with hydrogen at 1000° according to the procedure previously described⁵. The adsorbent was then coated with the liquid phase in the usual way and packed into glass columns. For our purpose, a new poly-carboranesiloxane non-polar stationary phase (Analabs, North Haven, Conn.), called Dessim 300 GC, stable up to 400° , was used. Experiments were carried out on a Carlo Erba (Milan, Italy) GI gas chromatograph, equipped with a FID detector.

In Fig. 1, the behaviour of the corrected retention volumes per gram of adsorbent as a function of the percentage of liquid phase is reported. As can be seen, in the first region, say about up to 1.5% liquid phase, there is a linear decrease of the retention volumes as the surface coverage increases. This is the range in which further addition of liquid phase if, as in our case, the liquid has no particular affinity with the adsorbates only, has the effect of reducing the surface area of the adsorbent. So, this region can be denominated of "reduced adsorption". As soon as a monolayer is obtained, no further decrease of retention volume is observed and a more or less pronounced slight increase takes place. This region, starting from about 1.5% liquid phase, is the range where the interactions of both liquid phase

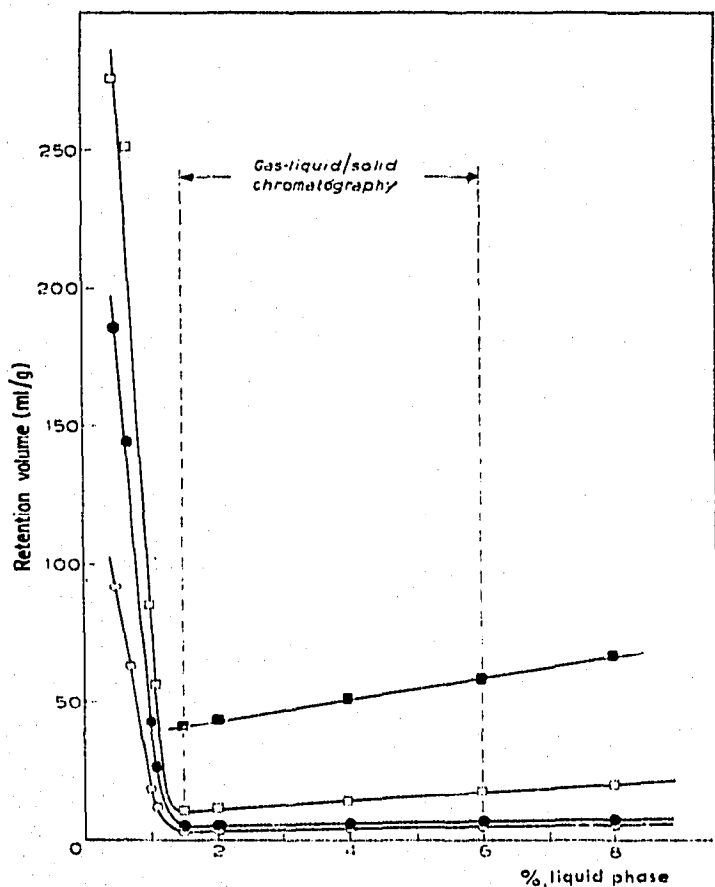


Fig. 1. Plot of the specific retention volumes for various compounds vs. the percentage of the liquid phase. ○, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$; ●, $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$; □, $(\text{C}_6\text{H}_5)_2\text{O}$; ■, $(\text{C}_6\text{H}_5)_2\text{NH}$.

and adsorptive surface are acting synergistically with the molecules being eluted, yielding a characteristic chromatographic process. The upper coverage limit of the region of GLSC is of course indefinite and one can hardly say at which stage gas-liquid partition becomes the only process. Moreover, it has not been possible to investigate the behaviour of Sterling FT at coverages higher than 8% of liquid phase because a uniform coating could no longer be obtained. We have arbitrarily limited the region of GLSC to about 6% of liquid phase for Sterling FT, but the range of interest lies considerably lower, *i.e.* between 1.5% and 3%.

As an example of the applicability of this technique to the solution of particular problems, we report the analysis of a reaction mixture, supplied by M. L. FORCELLI, in Fig. 2. The second compound is unresolved from the third, when analysed with a gas-liquid column with Dexsil as liquid phase⁷, while the separation on our GLSC column is quite large. Furthermore, the peaks due to unknown impurities show up well.

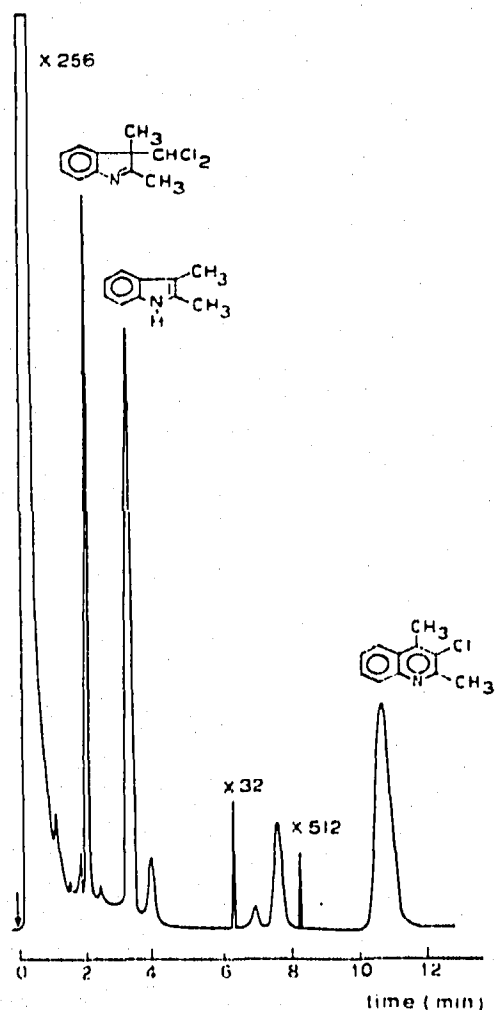


Fig. 2. Chromatogram showing the elution of some heterocyclic compounds. Column: 1.7 m \times 2 mm hydrogen-treated Sterling FT + 2% Dexsil; temperature, 250°; carrier gas, hydrogen.

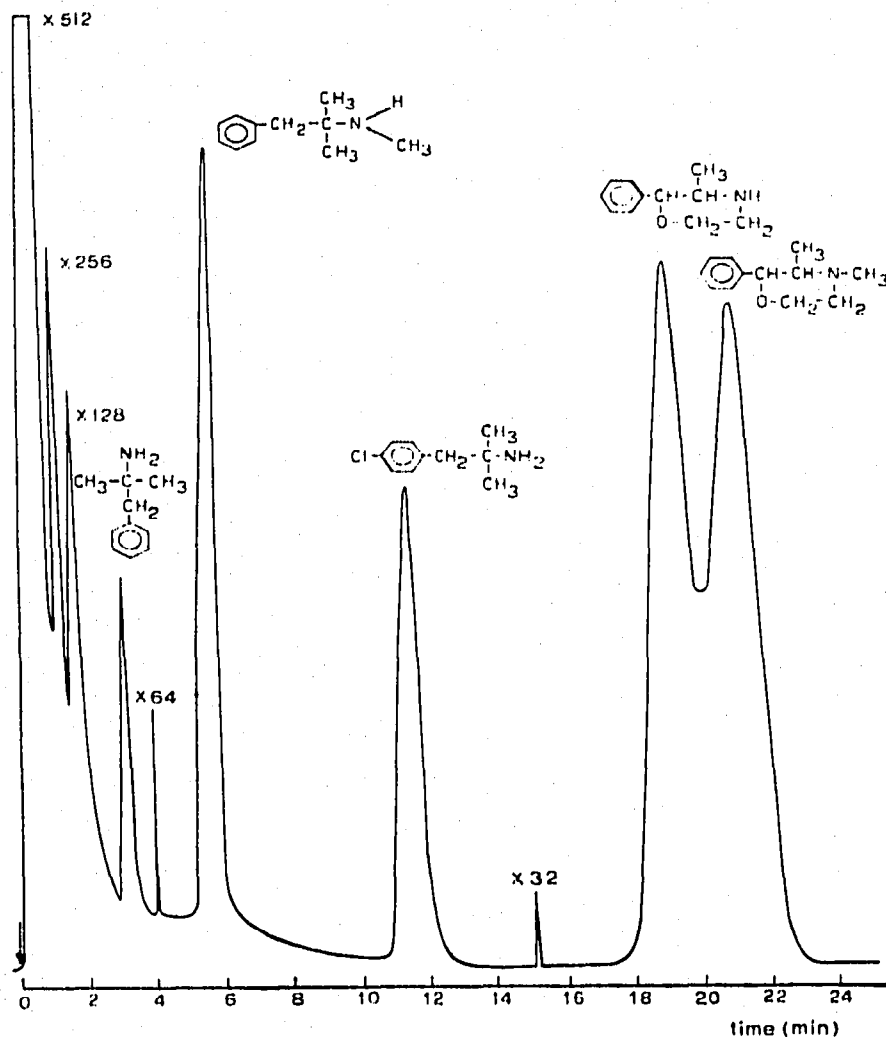


Fig. 3. Chromatogram showing the elution of some amphetamine-type compounds. Column: 0.8 m \times 3 mm, hydrogen-treated Sterling FT + 2% Dexsil; temperature, 110°; carrier gas, hydrogen.

The separation of some amphetamine-type compounds is shown in Fig. 3. A very good separation also occurs, in this case the elution temperature being about the same as with GLC. This result shows that GLSC can also be competitive with GLC as far as the working temperature is concerned.

Discussion

The high efficiency of the GLSC column is noteworthy. In both cases shown, the column efficiency measured on the compounds eluted was about 1600 theoretical plates per meter.

Several authors in the last few years have coated carbon blacks with monolayers of various liquid phases^{7,8}. The main novelty of this paper is that, due to the hydrogen treatment, small amounts of hydrogen-bonding compounds can be eluted

on this material, and this enlarges the field of use of GLSC to practically all classes of organic compounds.

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