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# CHROMATOGRAPHIC PROPERTIES AND ANALYTICAL APPLICATIONS OF A LOW-SURFACE-AREA GRAPHITIZED CARBON BLACK

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## SUMMARY

Retention data and heats of adsorption on a new low-surface-area graphitized carbon black have been determined and are compared with values for other adsorbents. The new adsorbent has been applied to gas chromatography of polar compounds such as alcohols, free fatty acids and phenols, and to environmental analyses.

## INTRODUCTION

The advantages of liquid-modified adsorption gas chromatography using several kinds of graphitized carbon black (GCB) have been demonstrated in a large number of papers published in the last 15 years. A review of the theory and analytical applications appeared in 1976[1]. Pioneering work on the gas chromatographic (GC) theory and applications of GCBs has been carried out by Kiselev, Halàsz, Liberti, Guiochon and their co-workers[2–6]. While the advantages of high selectivity and those connected with the possibility of linear elution of highly polar compounds, such as alcohols, aliphatic amines, free fatty acids and phenols, are well known, the use of these materials in GC are limited by the high retention of heavier organic compounds due to the high surface area, ranging between 10 and 100 $m^2/g$. A particular type of GCB, Sterling MT, has a lower surface area[7], but its softness has discouraged its use as a chromatographic support for routine analytical problems.

Recently, a new type of graphitized carbon became available to us, which has a surface area of about 6.0 $m^2/g$. This low-surface-area graphitized carbon black (LSGCB) is available in pellets and is hard enough to be used as a column material without particular problems. No details about its preparation have been furnished by the supplier (Supelco).

In this paper we present the first results on the characterization of this chromatographic material in respect of its adsorptive properties and analytical applications.

## EXPERIMENTAL

The graphitized carbon was sieved to yield a mesh range of 80–100, coated with the liquid phase as previously described[8], and then sieved again. The error

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involved in the amount of liquid phase does not exceed 1%. Heats of adsorption were calculated from the isosteres obtained by plotting the logarithm of the capacity ratio against the reciprocal of the absolute temperature. The same care was taken for the reproducibility of GC columns and temperature controls as in previous work[7,8]. Gas chromatographs from DANI (Monza, Italy) and Carlo Erba (Milan, Italy) were used. For mass spectrometric measurements a VG 70-70H double focusing magnetic instrument was used coupled via a jet separator interface to a DANI Model 3800 gas chromatograph, equipped with both capillary and packed columns. A PTV injector was used for capillary columns. A 30-m fused-silica capillary column, 0.25 I.D., coated with SE-54 (0.25 $\mu$m) (Supelchem, Milan, Italy) was used. Packed columns were made of Pyrex glass (1.5 mm I.D.) of various lengths.

## RESULTS AND DISCUSSION

### *Retention data*

Retention measurements, reported as $k'$ values show that the new carbon black is less retentive compared to the most widely used adsorbents of this type. A comparison is made with Sterling FT and Carbopack C, which are the most similar insofar as the chromatographic behaviour is concerned. The $k'$ values for *n*-pentane found for these three carbons when uncoated at 46°C are 80, 50 and 29 respectively, in good agreement with the surface areas, 15.0, 10.0 and 6.0 $m^2/g$ respectively. The ratios $k'$/surface area for the same compound at the same temperature are 5.3, 5.0 and 4.8 respectively. This is the best indication that the three carbons differ in practice only in their surface areas.

In order to explore the effects of the surface coating on retention, the values of $k'$ were measured for different surface coverages by the liquid phase. Actually, comparisons of the retentions of different chromatographic materials are correctly made through the retention volumes. In our preliminary experiments it was found that, if packing mesh size, column dimensions and pressure drop are kept constant, the $k'$ values are only dependent upon the surface area for non-porous adsorbents, such as graphitized carbon blacks. In fact, under such conditions, the retention volume of an unretained compound, $V_0$, can be taken as constant within the experimental errors. On the other hand, the errors involved in the measurement of the net retention volume, $V_g$, and $V_0$ are higher than those involved in assuming $k'$ is proportional to $V_g$. Furthermore, such measurements are rather troublesome.

The choice of the liquid phases was made with the aim of obtaining results for the extreme cases of a polar and a non-polar liquid and because these liquid phases have a well defined molecular weight and chemical structure. Squalane and glycerol were tested and the values found are reported in Fig. 1. The curves are similar to those previously obtained with Sterling FT and Carbopack C[8,9]. The retention of *n*-pentane with squalane as liquid phase increases relative to that on the uncoated surface until a monolayer of the liquid phase is formed. At this point, a sharp fall in retention occurs, and after that, when a second monolayer is being formed, a new increase is observed. The same hydrocarbon eluted with different percentages of glycerol behaves in a different way, the retention decreasing linearly. This is due to the fact that the polar layer of glycerol hinders the interactions of the non-polar molecules with the carbon surface and the effect is similar to that of a decrease in the surface area. Adsorption on the liquid is the driving force at high surface coverages[10].

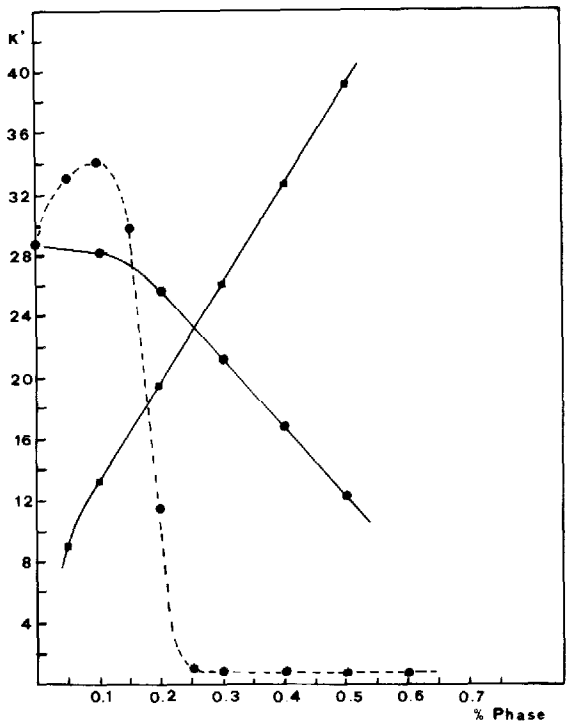


Fig. 1. Plots of $k'$ *vs.* percentage (w/w) of liquid phase ( —, squalane; - - -, glycerol). Solutes: ■, *n*-propanol; ●, *n*-pentane. Temperature: 46°C.

When *n*-propanol is eluted with increasing amounts of glycerol the retention increases linearly with the percentage of liquid phase, because the interactions of the –OH groups of the solute and the liquid phase are the driving forces of the chromatographic process in this instance.

It should be noted that the very different behaviour of polar and non-polar solutes on polar liquid phases can be exploited in order to increase the selectivity of the stationary phases in practical analytical applications, as will be discussed later.

In Fig. 2 the heats of adsorption, $Q_s$, of *n*-pentane measured at different surface coverages by squalane are reported and compared to those obtained with Sterling FT[8] and Carbopack C[9]. The behaviour of the new graphitized carbon is very similar to that of Carbopack C when the latter is treated with hydrogen at high temperature[11]. The only substantial difference is due to the lower surface area, as shown by the inflection point of the $Q_s$ curve; for the carbon presently investigated this occurs at 0.25% of squalane, while for Carbopack C it occurs at 0.31%. The ratio of the surface area and the per cent of squalane at which formation of a monolayer is observed is different for the three carbons, but this is probably due to entropy effects.

*Analytical applications*

The separation of all sixteen $C_1$–$C_5$ alcohols can be used to demonstrate the characteristic selectivity of graphitized carbon blacks. With the present carbon the chromatogram shown in Fig. 3 was obtained. The graphitized carbon was coated

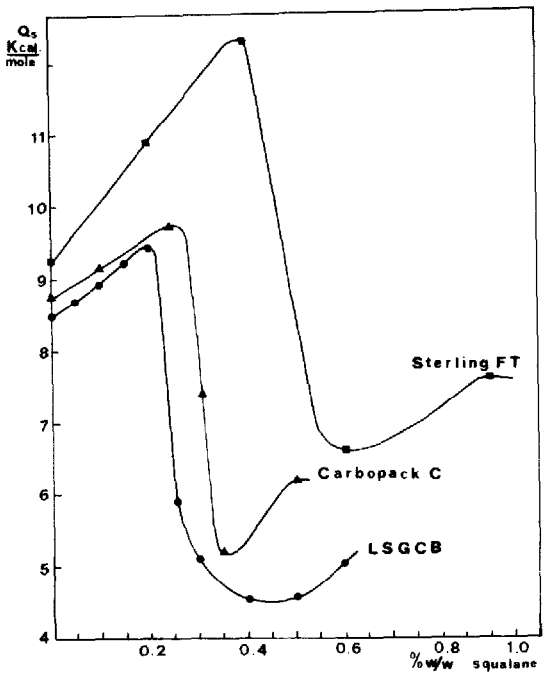


Fig. 2. Isosteric heats of adsorption as a function of the percentage of squalane on the surface of three different GCBs.

with 0.15% Carbowax 1500. By comparing this chromatogram with that obtained with Carbopack C coated with 0.2% Carbowax 1500 it is seen that the total analysis time is reduced to one half that of the best separation obtained on a commercially available GC column[12]. This is due to the lower surface area, while maintaining the separating power. The amount of liquid phase is a very critical parameter for the selectivity of gas–liquid–solid chromatography, and as an example we show in Fig. 3a the same separation carried out on a column with the new carbon black coated with a higher amount of Carbowax 1500, *i.e.*, 0.19%. The analysis time is reduced further to 3.8 min, but selectivity is lost since some of the peaks are not fully separated. This shows again the very important rôle played by the liquid phase–adsorbent–solute interactions and usefulness of the chromatographic method for careful investigations of such interactions. A liquid phase coverage of 0.15% corresponds to the maximum in the interactions of the solute molecules with the liquid phase. The aliphatic part of alcohol molecule interacts preferentially with the adsorbent, thus enhancing structural differences.

The alcohol functional group interacts with the polar functions of the liquid phase, resulting not only in linear adsorption isotherms and symmetrical peaks even at very low concentrations, but also enhancing the differences among the various alcoholic molecules, *e.g.*, the nature of the –OH group (primary, secondary or tertiary). Such a double differentiation, structural and functional, forms the basis of the unique selectivity of the column and it is understandable that very slight modifications in the nature of the surface will cause large changes in the relative retention volumes.

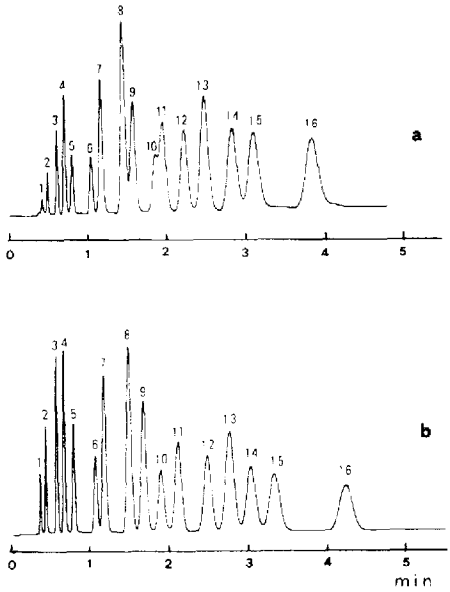


Fig. 3. Separation of $C_1$–$C_5$ alcohols on 80–100 mesh LSGCB coated with 0.19% (a) and 0.15% (b) Carbowax 1500. Column: glass, 2 m × 2 mm I.D. Temperature: 128°C. Flame ionization detection. Peaks: 1 = methanol; 2 = ethanol; 3 = 2-propanol; 4 = 1-propanol; 5 = 2-methyl-2-propanol; 6 = 2-butanol; 7 = 2-methyl-1-propanol; 8 = 1-butanol; 9 = 2-methyl-2-butanol; 10 = 2,2-dimethyl-1-propanol; 11 = 3-methyl-2-butanol; 12 = 3-pentanol; 13 = 2-pentanol; 14 = 2-methyl-1-butanol; 15 = 3-methyl-1-butanol; 16 = 1-pentanol.

Another interesting chromatogram is presented in Fig. 4, which shows the separation of $C_2$–$C_5$ carboxylic acids at the ppm level in water, using the new graphitized carbon coated with 0.24% Carbowax 1500. The adsorbent was previously acid washed[13].

A rapid separation of phenols is shown in Fig. 5 where the adsorbent was coated with 0.25% SP1000. This coating corresponds to more than a monolayer of liquid phase, as in the example of fatty acids, and this is due to the need for a very acidic surface to elute both classes of compounds. It is interesting to note that the characteristic feature of graphitized carbons, their ability to separate isomers, is retained in spite of the relatively high surface coating, as shown by the good separation obtained for the three valeric acid isomers.

In Fig. 6 the separation of all the chlorinated solvents included in the list of priority pollutants is reported and again the main feature is the rapid analysis and good separation of compounds of similar structures. From the relative retention times it can be inferred that both molecular polarizability, that is the main driving force in the adsorption process, and structure are important. For example, carbon tetrachloride is eluted before many compounds of lower molecular weight due to its spherical structure which hinders strong interactions of the chlorine atoms with the adsorbent surface.

In the course of our research on the separation and quantitative analysis of herbicides in environmental samples, we have recently set up an extraction and pre-

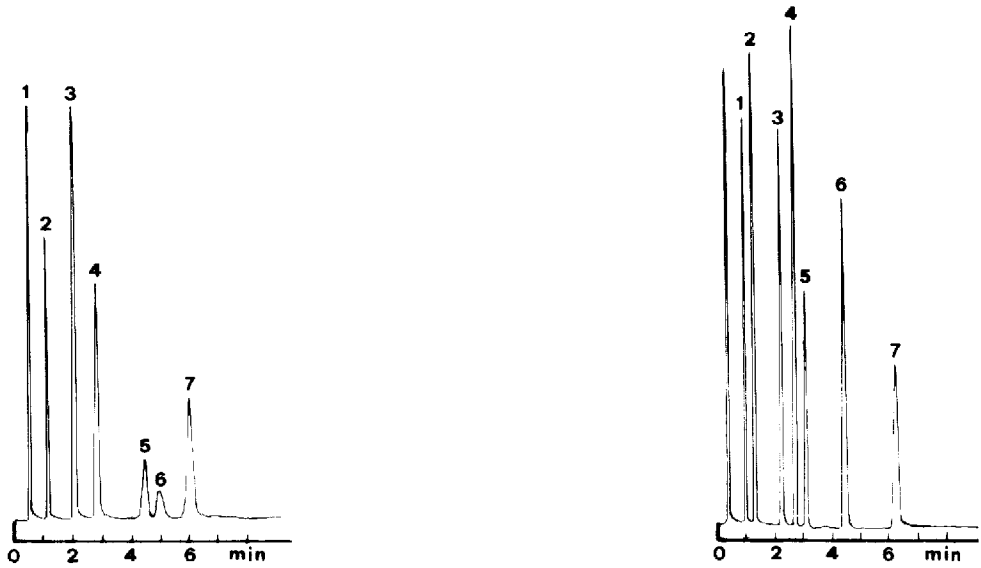


Fig. 4. Separation of $C_2$ $C_5$ fatty acids on 80–100 mesh LSGCB AW coated with 0.24% Carbowax 1500. Column: glass, 2 m × 1.5 mm I.D. Temperature: 140°C. Flame ionization detection. Peaks: 1 = acetic; 2 = propionic; 3 = isobutyric; 4 = *n*-butyric; 5 = 2-methylbutyric; 6 = 3-methylbutyric; 7 = *n*-valeric acid.

Fig. 5. Separation of phenols on 80–100 mesh LSGCB coated with 0.25% SP1000. Temperature: 215°C to 250°C, at 20°C/min. Other details as in Fig. 4. Peaks: 1 = phenol; 2 = 2-chlorophenol; 3 = 2-nitrophenol; 4 = 2,4-dimethylphenol; 5 = 2,4-dichlorophenol; 6 = *p*-chloro-*o*-cresol; 7 = 2,4,6-trichlorophenol.

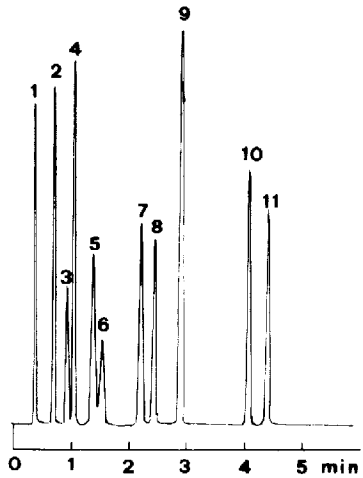


Fig. 6. Separation of chlorinated solvents on 80–100 mesh LSGCB coated with 0.26% SP1000. Temperature: 60°C to 200°C, at 20°C/min. Other details as in Fig. 4. Peaks: 1 = methylene chloride; 2 = 1,1-dichloroethane; 3 = 1,2-dichloroethane; 4 = chloroform; 5 = 1,1,1-trichloroethane; 6 = carbon tetrachloride; 7 = 1,2-dichloropropane; 8 = trichloroethylene; 9 = 1,1,2-trichloroethane; 10 = perchloroethylene; 11 = 1,1,2,2,-tetrachloroethane.

concentration method for pesticides and herbicides using adsorption on graphitized carbon black from water, followed by elution with an appropriate solvent mixture[14–16]. The GC separation of most commonly used herbicides presents some difficulties because the very similar structures of *s*-triazines, propazine, atrazine and simazine hinders a complete separation of these compounds when they are mixed with other herbicides. We have solved this problem by using a packed column (2 m

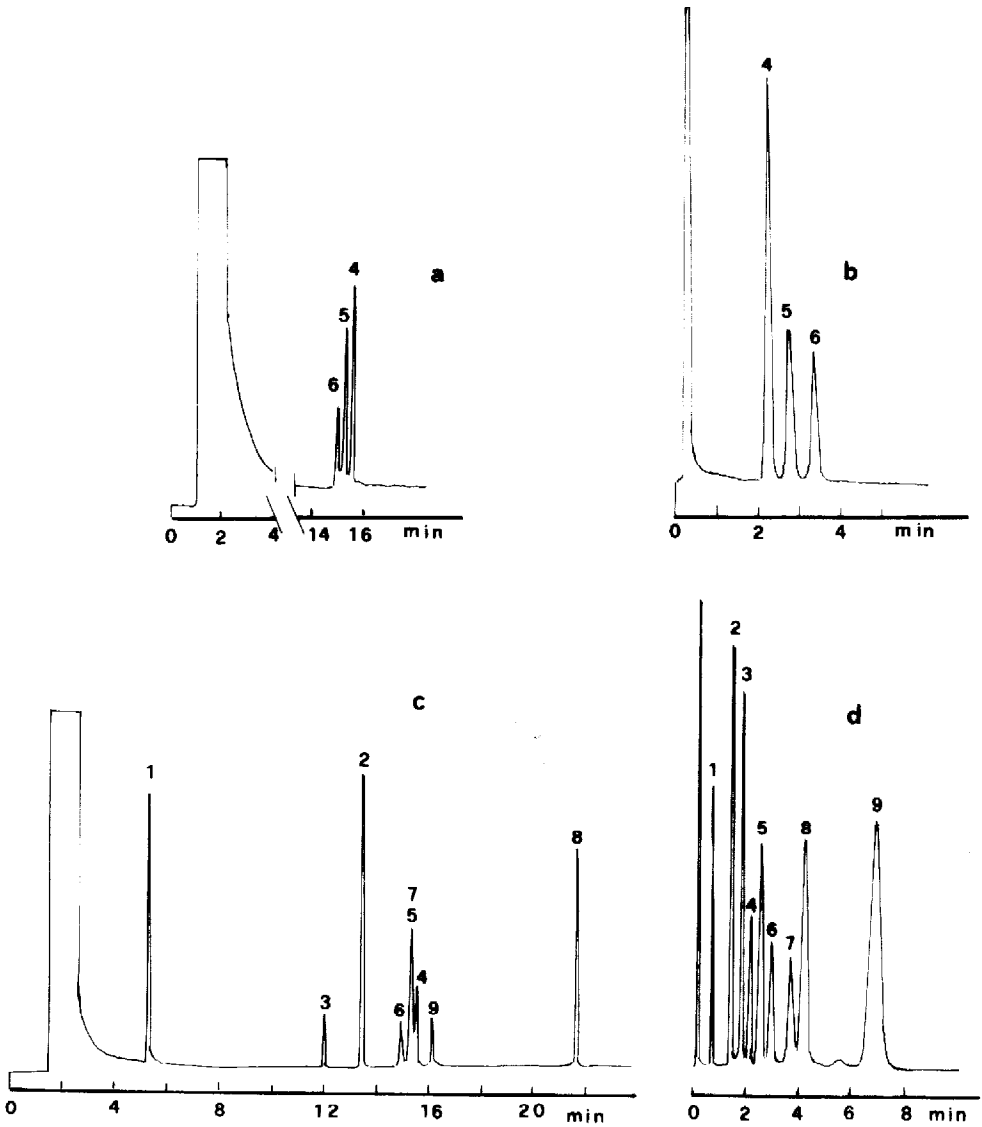


Fig. 7. Separation of herbicides on a capillary column (a and c) containing SE-54 (30 m × 0.25 mm I.D.; 130°C, 2 min then to 230°C at 4°C/min) and a packed column (b and d) containing 80–100 mesh LSGCB coated with 0.26% SP1000 (1 m × 2 mm I.D., 240°C isothermal). Flame ionization detection. Peaks: 1 = diclobenil; 2 = trifluralin; 3 = 2,4D ME; 4 = propazine; 5 = atrazine; 6 = simazine; 7 = Silvex ME; 8 = 2,4,5T ME; 9 = DCPA.

× 2 mm I.D.) containing Chromosorb W coated with 1.5% SP2250 + 1.95% SP2401. On this column only one peak is obtained for the three triazines, while the other herbicides are fully separated from each other and from the first three compounds.

By using gas chromatography–mass spectrometry (GC MS) in the selected ion monitoring (SIM) mode, triazines can be identified and quantitated from their fragment peaks[15]. In our efforts to simplify such analysis for routine use in any laboratory, we attempted the separation on a fused-silica capillary column (30 m × 0.25 mm I.D.) coated with SE-54 having about 70,000 theoretical plates under the operating conditions. The result was an almost complete separation of the three triazines, although with a rather high analysis time (Fig. 7a). However, when the mixture of the nine most commonly used herbicides has been eluted, the separation is incomplete because Silvex ME shows the same retention time as atrazine (Fig. 7C). Thus, the silicon rubber phase is not selective enough to obtain the separation of certain compounds, while the retention time of other herbicides is very high.

An attempt to use the graphitized carbons commercially available failed because of the high retention times obtained at reasonable temperatures. We therefore tested the new LSGCB and the results are reported in Fig. 7a and 7d. The adsorbent was coated with 0.26% SP1000, a polar acidic phase. A complete separation of the triazines is achieved in 3 min, and when a mixture of the nine herbicides is eluted a very good separation is obtained for all of them. The elution order is reversed with respect to the molecular weight due branching of the aliphatic chain when the isopropyl group is present. Simazine, which has two ethyl groups, shows the highest retention time, while propazine is eluted first. The branched chain hinders a close interaction of the methyl group with the graphite surface.

This shows that the selectivity of the graphitized carbon together with the possibility of eluting rather high boiling compounds makes this material competitive in some instances with capillary columns. It is interesting to note that the maximum selectivity of the carbon black–liquid phase system is obtained when a polar liquid phase is used, even when non-polar compounds are eluted. Because adsorption takes place on the liquid, isomers are well separated, and the rôle of the liquid phase is to decrease the retention times, as discussed before, while retaining the selectivity of adsorption chromatography for isomeric compounds.

These results show that, in spite of the obvious advantages of capillary columns in the analysis of complex and thermolabile mixtures, classical GC on packed columns can be competitive in particular instances, because it is possible to use the higher separation factors that are obtainable by exploiting the large number of stationary phases available. A small increase of the separation factor is much more effective for the resolution than a large increase in the number of theoretical plates.

A final example to show the usefulness of the new adsorbent is reported in Fig. 8. The chromatogram refers to the GC–MS analysis of a rather complex mixture of oxygenated polar compounds, such as free carboxylic acids and phenols, present as the products of wood distillation. The substances are present as low percentages in a large amount of water. The composition of the mixture is reported in Table I, which shows again the high selectivity of the column used and the possibility of elution of highly polar compounds.

A peculiarity of carbon black is that one can inject water solutions without

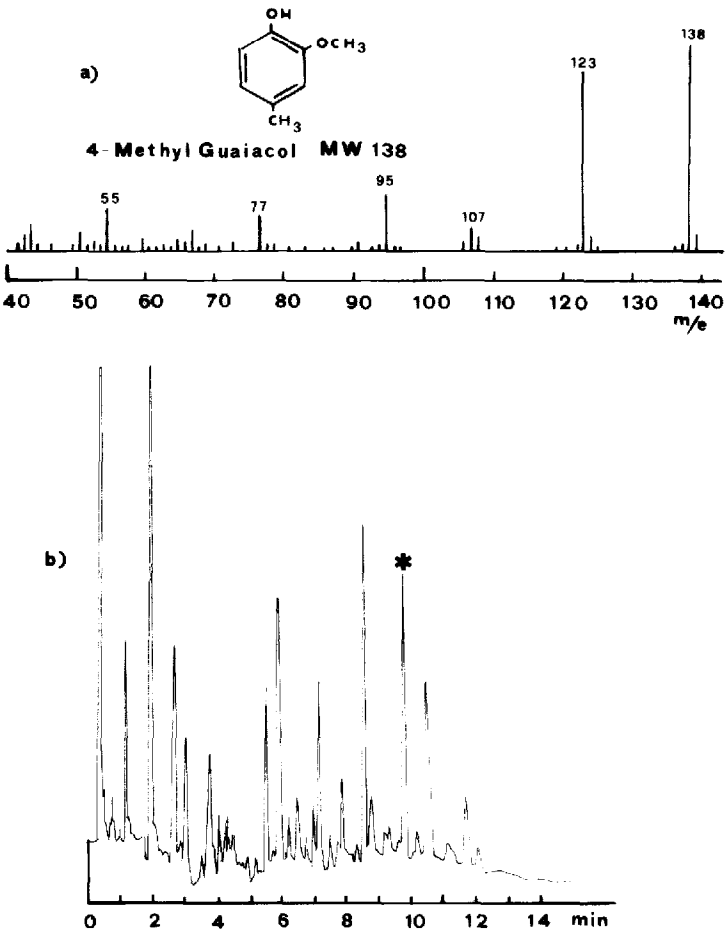


Fig. 8. (a) Mass spectrum of component (*) (most normalized) in chromatogram b, identified as methylguaiacol. (b), Separation of wood distillation products, contained in water, on 80–100 mesh LSGCB AW coated with 0.26% SP1000. Column: glass, 2 m × 2 mm I.D. Temperature: 70°C to 220°C, at 10°C/min. Mass spectrometric detection. Amount injected: 1 μl solution in water.

significantly affecting the efficiency. In Fig. 8a the mass spectrum of 2-methoxy-4-methylphenol is reported. The spectrum is not normalized and the peaks are reported as they appeared on the chart from the UV recorder. It can be interpreted without any difficulty, due to the absence of column bleeding. The possibility of injecting large amounts of organic samples dissolved in water, together with the high efficiency, makes this new adsorbent very useful in routine GC MS work. The columns also exhibit long lives under conditions that are prohibitive for other columns, especially highly sophisticated capillary columns.

In conclusion, the main advantages of the new graphitized carbon with respect to those commercially available are as follows:

(i) capability of elution of compounds of higher molecular weight

(ii) high purity, which allows coating with very low amounts of liquid phases.

TABLE I

INTERMEDIATE FRACTION OF WOOD DISTILLATE IN WATER

| *Compound* | *% in water* |
|---|---|
| Methanol | 0.35 |
| Methyl acetate | 0.03 |
| Ethyl acetate | 0.02 |
| Acetic acid | 5.09 |
| Propionic acid | 0.32 |
| Furfural | 0.35 |
| 5-Methylfurfural | 0.07 |
| 2,3,5-Trimethylfurfural | 0.08 |
| Phenol | 0.03 |
| Guaiacol | 0.15 |
| *o*-Cresol | 0.01 |
| *m* + *p*-Cresol | 0.01 |
| 4-Methylguaiacol | 0.10 |
| 4-Ethylguaiacol | 0.08 |

As a consequence,

(iii) very high selectivity

(iv) short analysis time.

More studies are necessary in order fully to exploit the unique properties of this material.

ACKNOWLEDGEMENTS

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