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COMPARISON OF PHYSICAL AND GAS CHROMATOGRAPHIC PROPERTIES OF STERLING FT AND CARBOPACK C GRAPHITIZED CARBON BLACKS*

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SUMMARY

A comparison of Sterling FT, a graphitized carbon black used widely in adsorption and gas chromatography, and Carbopack C, a commercially available graphitized carbon black, was made in terms of retention parameters, heats of adsorption and their behaviour at various coating percentages.

The effects induced by hydrogen treatment at high temperature are compared, and it is shown that graphs of the heat of adsorption *versus* percentage of liquid phase added are very useful in understanding the difference in the surface properties of the two materials. The advantages of the two carbon blacks in practical gas chromatography are discussed.

INTRODUCTION

Graphitized carbon blacks are among the most homogeneous adsorbents available (*e.g.*, ref. 1) and many studies have been carried out² to show the large influence of graphitization on the linearity of the adsorption process. The peculiar characteristics of graphitized carbon blacks as adsorbents for gas-solid chromatography³ and for liquid-modified gas-solid chromatography^{4,5} have also been shown.

A decisive improvement in the chromatographic performance of graphitized carbon blacks, especially in the elution of polar compounds, is observed when the product undergoes thermal treatment with hydrogen^{6,7} at 1000°.

In general, the differences observed in the chromatographic behaviour of carbon blacks are attributed to differences in the surface area, these being mainly responsible for the variation in retention volumes. Such a generalization is usually valid for saturated aliphatic hydrocarbons, which undergo non-specific interactions with the carbon surface, but fails when polar compounds are eluted. In this instance, specific interactions take place with the chemical impurities, which act as specific

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active sites, and the chromatographic behaviour depends on the manufacturer of the carbon black and the production process.

About 3 years ago, graphitized carbon blacks made specially for use in gas chromatography became commercially available (Supelco, Bellefonte, Pa., U.S.A.) and these are also widely used for routine analysis. A careful investigation of the constancy of the chromatographic properties and of the differences between carbon blacks from different sources was thus desirable, as it is generally felt that columns involving gas-solid processes give poorly reproducible results.

In this paper, a comparison between Sterling FT (Cabot Corp., Boston, Mass., U.S.A.) and Carbo-pack C (Supelco) is made in terms of retention parameters, adsorption of polar compounds and modifications induced by thermal treatment with hydrogen. One of the aims is to predict, on the basis of the thermodynamic properties, the coating conditions for the best chromatographic separations.

EXPERIMENTAL

Graphitization and hydrogen treatment

Graphitization of Sterling FT was carried out by the Research and Development Division of Elettrocarbonium S.p.A., Narni, Italy, at 2700°. Carbo-pack C was kindly supplied already graphitized by Supelco.

Hydrogen treatment was carried out in a cylindrical oven with a 70-cm long heated zone. The carbon black was placed in an iron tube (40 cm × 3.5 cm I.D.) that had previously been treated with hydrogen under the same conditions at 1100° for 30 h.

Extra-pure hydrogen ($O_2 < 2$ ppm; $H_2O < 3$ ppm) was used and the flow-rate was 300 ml/min. Before heating, hydrogen was allowed to flow through the oven for 1.5 h. After the treatment, the hydrogen flow was maintained until room temperature was attained. Cooling the oven and substituting hydrogen with helium did not affect the results to a significant extent.

The oven temperature was maintained at 1100° in order to give a temperature of at least 1000° in the centre of the bulk of the carbon black; stricter temperature control was found to be unnecessary so far as reproducibility of the results was concerned.

A Carlo Erba Model GI gas chromatograph was used for all experiments; the temperature control was better than $\pm 0.5^\circ$. Heats of adsorption were calculated from retention data as previously described⁵. A series of glass columns of the same length, internal diameter and shape (1.5 m × 2 mm I.D.) was used and packed with 80–100-mesh packings. The mesh range and packing conditions were carefully checked; under these conditions, the pressure required to obtain the same flow-rate on different columns was the same with a maximum scattering at $\pm 5\%$.

Coating of carbon black with small amounts of modifiers requires special care. Not less than 100 g of the material were used to prepare packings with low percentages of modifiers. It is imperative to allow the solvent to evaporate without heating, with very gentle stirring at intervals. Once the solvent has evaporated, fresh solvent should be added in order to collect any modifier present on the walls of the container in order to redistribute it homogeneously on the carbon black.

Surface area measurements were carried out in our laboratory using a modification of the continuous flow method⁸ described previously.

RESULTS AND DISCUSSION

Fig. 1 shows electron micrographs of the two graphitized carbon blacks taken under the same conditions. The characteristic polygonal shape of the particles is present in both instances in Fig. 1a and 1b; this shows that the graphitization process brings both carbon blacks to a very similar fine structure, as could be inferred by the fact that they have the same origin (Fine Thermal Blacks). In Fig. 1c and 1d, which show the surface of a broken particle under a scanning microscope, a fine structure is observed for Sterling FT, which is probably due to the higher surface area of this material. However, it should be borne in mind that it is very hazardous to compare the optical appearance with the chemical behaviour and this can lead to errors.

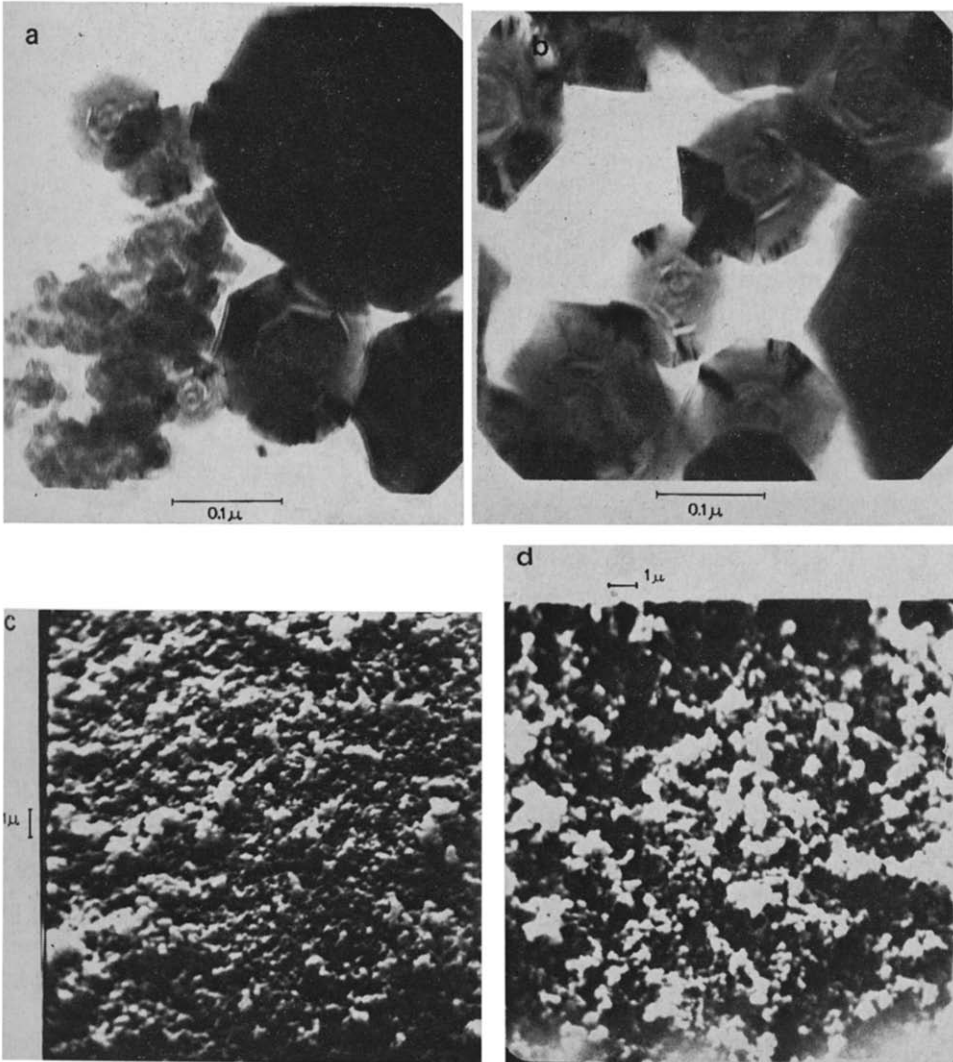


Fig. 1. Electron micrographs of carbon blacks. a and c, Sterling FT; b and d, Carbopack C; a and b, transparency micrographs ($\times 120,000$); b and c, scanning micrographs ($\times 5000$).

Table I compares some of the most significant physical properties of Sterling FT and Carbopack C. According to Rappeneau *et al.*⁹, the greater the particle size, the better is the response to graphitization. In this view, Carbopack C should be graphitized to a greater extent, but there is no evidence to support this from the electron microscope photographs, which indicate that the particles of the carbon blacks.

TABLE I
PHYSICAL PROPERTIES OF GRAPHITIZED CARBON BLACKS

Property	Carbopack C	Sterling FT
Grade	Fine Thermal	Fine Thermal
Graphitization temperature (°C)	2,700	2,700
Average particle size (Å)	2,000	1,500
Pycnometric density	2.160	2.159
Loose weight (g/cm ³)	0.76	0.66
Surface area (B.E.T.) (m ² /g)	9	15
Surface area (continuous flow) (m ² /g)	8	15
Surface area (m ² /cm ³)	6	10

The same is true for the pycnometric density, although this parameter is not a guide to the effectiveness of graphitization. The difference in loose weight is significant, being strictly related to the packing density in chromatographic columns. However, as the particles size in carbon black packings is the result of the random adherence of smaller particles, the higher density of Carbopack C leads only to a greater tendency of the particles to aggregate, leaving a smaller number of empty spaces within the particles. This is in agreement with the higher mechanical resistance of Carbopack C packings.

The most important difference as far as gas chromatography is concerned is the surface area, which is much lower for Carbopack C. Assuming that the nature of the surface is the same in each instance, which can be inferred by the fact the two carbon blacks are both of the Fine Thermal class and that they undergo identical graphitization processes, one should predict lower retention volumes for Carbopack C, in agreement with what is found for Graphon and FT¹⁰.

However, very different behaviour is observed on comparing the retention data for the two materials. Fig. 2 shows graphs of K' (capacity ratio) versus the percentage of liquid phase, the data for Sterling FT in Fig. 2 being taken from ref. 5.

Squalane and glycerol were chosen as liquid phases because they represent the extreme cases of non-polar and polar modifiers, so that any differences induced can be clearly seen.

n-Pentane is eluted much later on pure Carbopack C than on pure Sterling FT, and the difference is opposite to that which could be inferred from the difference in surface areas. However, even very small amounts (0.1 %) of liquid phase are sufficient to induce a sharp decrease in K' so that whenever the surface is covered with the liquid phase, the retention on Carbopack C is lower than that on Sterling FT. Further, the maximum value of K' , due to the combined effects of adsorption and lateral interactions, always present on Sterling FT⁵, is not found on Carbopack C. According

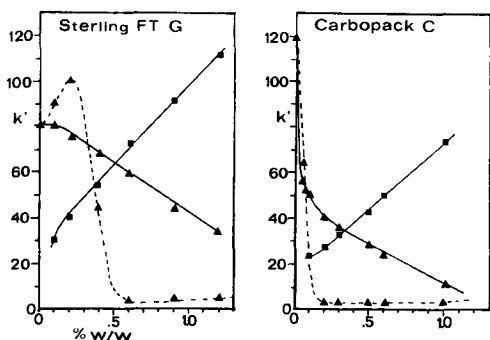


Fig. 2. K' versus percentage (w/w) of liquid phase. Broken line, squalane; solid line, glycerol; ■, *n*-Propanol, ▲, *n*-pentane. Temperature, 46°.

to Young⁸, this is related to the inhomogeneity of the surface, as confirmed by gas chromatographic measurements⁵. A further source of information on the difference in the surfaces of Carbopack C and Sterling FT is given by the graphs showing the change of K' for *n*-propanol with the percentage of glycerol. With Sterling FT, the lower part of the curve shows a deviation from linearity (lower values of K'), which is attributed to a decrease in hydrogen-bond type interactions between glycerol and *n*-propanol when the liquid phase is present in small amounts.

The K' value in this instance approaches that of *n*-butane at zero coverage, the polarizability of the adsorbed molecule being mainly responsible for the retention on pure carbon black.

It is important to notice that on both carbon blacks a linear increase in K' is observed for *n*-propanol, which shows the very important role of the polar liquid phase when a polar compound is eluted. In this instance, the overall value of K' is given by the sum of the adsorption and the retention due to the liquid phase. The effect of the polar liquid phase on the elution of non-polar compounds is to decrease the retention linearly, this being due to the "squeezing effect"⁵.

The following conclusions can be drawn as a first approach on the basis of these results:

(1) Very active non-specific adsorption sites are present on the surface of Carbopack C, so that *n*-pentane is more retained on the pure solid than on Sterling FT, in spite of the lower surface area.

(2) Such active sites also yield specific interactions, which are responsible for the higher retention of alcohols at low coverages.

(3) The interaction of the active sites, either specific or not, is masked by coating the surface even at a very small extent, as shown by the linearity of the curve of K' for *n*-propanol versus percentage of liquid phase at higher coverages.

As was shown previously^{6,7}, hydrogen treatment changes the surface of graphitized carbon black by eliminating most of the active sites and we used this method to study whether or not the two carbon blacks undergo different surface modifications. For this purpose, they were kept in a flow of hydrogen at 1000° for various times and then the capacity ratios (K') were measured for *n*-pentane. From the results shown in Fig. 3, it can be seen that also in this respect a considerable difference exists between Sterling FT and Carbopack C. The change in K' is rather

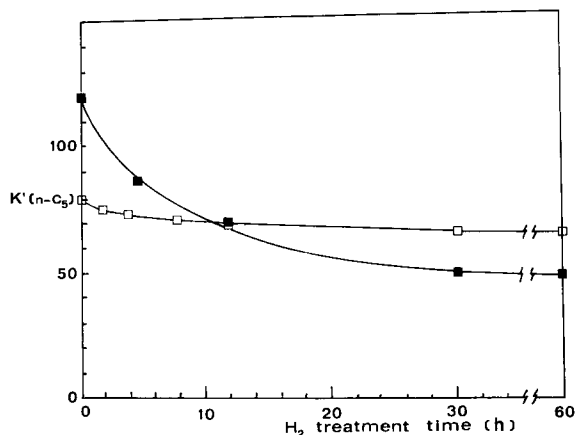


Fig. 3. K' versus time of hydrogen treatment at 1000° . \square , Sterling FT; \blacksquare , Carbopack C.

low for Sterling FT, and constancy is attained after about 8 h, the total decrease being 18%.

For Carbopack C, on the other hand, K' decreases from 120 to 50 and constancy is attained after not less than 30 h of treatment with hydrogen. Measurements of isosteric heats of adsorption (Q_s) on the materials simply graphitized and on those treated with hydrogen for 30 h as a function of the percentage of liquid phase are shown in Fig. 4, and the changes in K' are also reported for the sake of comparison.

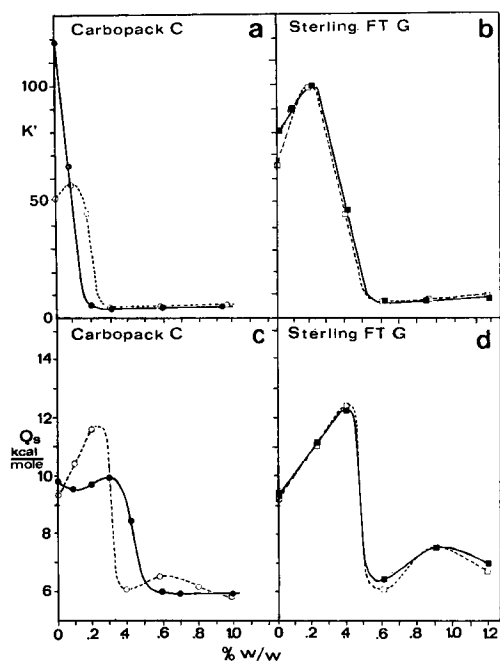


Fig. 4. Comparison of isosteric heats of adsorption and K' versus percentage (w/w) of squalane for n -pentane. Solid line, normal; broken line, hydrogen treated (30 h). \square , Sterling FT, hydrogen treated; \blacksquare , Sterling FT, normal; \circ , Carbopack C, hydrogen treated; \bullet , Carbopack C, normal.

The most important modifications are found for Carbo-pack C, its behaviour being strikingly different before and after hydrogen treatment. The characteristic maximum on the curve of K' versus coverage is present for the HT form, approaching the behaviour of Sterling FT, which shows this feature in both the HT and normal forms. So far as heats of adsorption are concerned, three features before and after the hydrogen treatment should be noted:

(1) The heat of adsorption at zero coverage is lower for the HT form.

(2) The curve of Q_s versus coverage of the HT form is very similar to that for Sterling FT, with a very pronounced maximum and a steep decrease when the first monolayer of liquid phase is formed. A secondary maximum, during the formation of the second monolayer, is also observed.

(3) For Sterling FT, the modifications made by hydrogen treatment are less important, and minor changes are observed in the heats of adsorption. The only marked difference is found for the values of K' at zero coverage, as pointed out before.

From the graphs in Fig. 4, the following conclusions can be drawn:

(1) The values found for Q_s at zero coverage for both Sterling FT and Carbo-pack C are in good agreement with those in the literature. In fact, for the heats of adsorption of *n*-pentane, Vidal-Madjar *et al.*¹¹ reported 8.88 and 8.83 kcal/mole for the normal and HT forms, respectively, while Kiselev *et al.*¹² reported 9.15 kcal/mole for both the normal and HT forms. Di Corcia and Samperi⁷ found values of 8.82 and 8.55 kcal/mole for the normal and HT forms, respectively. It should be noted that the value of 8.55 kcal/mole was found at a lower temperature, so that a further decrease can be expected in Di Corcia and Samperi's experiments. In the present work, values of 9.35 and 9.25 kcal/mole, respectively, were found. These values are almost identical, the error involved in our measurements being about ± 0.05 kcal/mole. It should be noted that the value of Q_s calculated by Kiselev¹³ is 9.0 kcal/mole and those measured on graphite are 8.6 kcal/mole¹⁴. With Carbo-pack C, the value found in this work is 9.80 kcal/mole for the normal form and 9.25 kcal/mole for the HT form. The latter value is in agreement with most of the figures cited and we can conclude that Carbo-pack C is equivalent to Sterling FT when the HT forms are compared.

(2) From the value of Q_s found in this work for the untreated form of Carbo-pack C (9.8 kcal/mole), one might easily conclude that this material is very similar to other graphitized carbons. In fact, one of the values obtained from the literature¹⁵ is 10 kcal/mole, showing that the values of Q_s at zero coverage are insufficient to be correlated with even marked differences in the chromatographic properties of graphitized carbon blacks.

(3) In order to obtain more detailed information about the surfaces of adsorbents, the complete curve of Q_s versus coverage should be explored, at least to the second monolayer. In fact, the curves in Fig. 4c and 4d are much more significant than the crude values of the heats of adsorption at zero coverage. In Fig. 4c, the initial decrease in the heat of adsorption with increasing coverage is the most significant demonstration of the presence of very strong active sites on the untreated Carbo-pack C surface. Further, the lack of a pronounced maximum and the smooth decrease of the curve for the untreated form indicates a non-uniform energy distribution of active sites, which covers the effect of lateral interactions⁵, as is also shown by the complete lack of the secondary maximum¹⁶.

(4) Apparently, hydrogen treatment "smoothes" the Carbo-pack C surface and makes it very similar to that of Sterling FT, provided that the differences in surface areas are considered. In fact, the inflection point is found at a lower percentage coverage for Carbo-pack C than for Sterling FT, but the ratio between the percentage of liquid phase corresponding to one monolayer and the ratio of the surface areas is 2.1 for Carbo-pack C and 1.66 for Sterling FT for the untreated forms. These ratios become 1.56 and 1.66, respectively, when the HT forms of the materials are compared. This is a further indication of the fact that a regular monolayer is formed only when the adsorbent shows a smooth surface, *i.e.*, a uniform distribution of the energy of the active sites. In fact, a higher percentage of liquid phase is necessary in order to obtain the inflection point of the curve for the untreated form. This result is probably due to the fact that on strong active sites, clusters of liquid-phase molecules are formed, while void zones are still on the surface, as suggested by Kiselev¹⁷. The irregular formation of the monolayer is also the reason for the smoother decrease of the curve at the inflection point¹⁶.

In order to obtain better information about the effect of the hydrogen treatment on specific active sites, measurements of irreversible adsorption of aliphatic amines were made on the two carbon blacks. Fig. 5 shows the effect of hydrogen treatment on the elution of *n*-butylamine. The ratio of peak area to amount injected is constant when a column properly prepared for the linear elution of aliphatic amines down to the 0.5-ng level¹⁸ is used, as shown by the broken line. For both carbon blacks, which for this experiment were packed without any coating, this ratio is lower even after treatment for 30 h, although the linearity of the curves for longer treatment times shows a constant tendency towards the broken line.

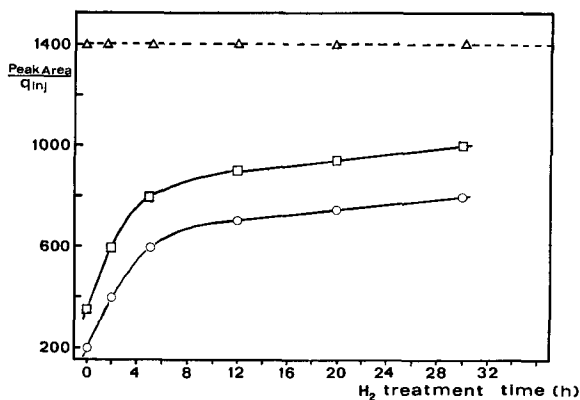


Fig. 5. Irreversible adsorption on two carbon blacks. Compound eluted: *n*-butylamine. Δ , Carbo-pack C + 0.3% KOH + 1.2% PEI or Sterling FT + 0.5% KOH + 2% PEI; \square , Sterling FT, uncoated, hydrogen treated (30 h); \circ , Carbo-pack C, uncoated, hydrogen treated (30 h).

Fig. 6 shows calibration graphs prepared with three columns; the broken line refers to the specific packing for amines used for the graphs in Fig. 5; the linearity of the graph shows that there is no evidence of irreversible adsorption even when a few nanograms are injected. The other two lines, which refer to Sterling FT and Carbo-pack C, both treated for 30 h and uncoated, curve towards the abscissa when

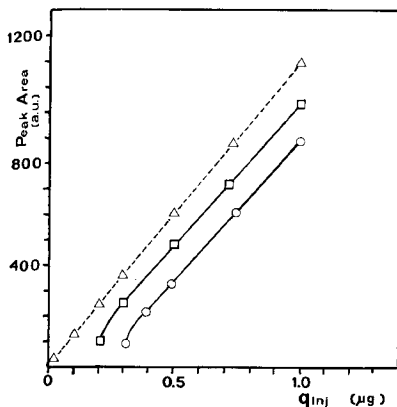


Fig. 6. Calibration graphs for *n*-butylamine. Δ , Carbo-pack C + 0.3% KOH + 1.2% PEI or Sterling FT + 0.5% KOH + 2% PEI; \square , Sterling FT, uncoated, hydrogen treated (30 h); \circ , Carbo-pack C, uncoated, hydrogen treated (30 h).

amounts lower than 0.3 and 0.4 μg of *n*-butylamine are injected on Sterling FT and Carbo-pack C, respectively.

This result shows that hydrogen treatment does not eliminate the specific active sites completely. Di Corcia and Samperi¹⁹ reported that linear isotherms are obtained for *n*-propylamine on Sterling FT after hydrogen treatment. However, the errors involved in their measurements of adsorption isotherms, as reported by the authors themselves, are much too high to permit the evaluation of non-linearity at low coverage. Further, in the present work, we were able to compare the results on uncoated materials with those obtained with the column capable of the linear elution of very small amounts of aliphatic amines.

Calculations made on the basis of the results in Fig. 6 show that about 100 ng of *n*-butylamine are irreversibly adsorbed by 1 g of Sterling FT at the experimental temperature; the corresponding value for Carbo-pack C is 150 ng.

From simple calculations, taking into account the surface areas of the two materials, it is found that the number of specific (in particular acidic) active sites per unit area is about 3.4 times higher on Carbo-pack C HT than on Sterling FT HT.

It should be noted that by heating the two carbon blacks under a flow of carrier gas at 200° for 20 min, the amine is completely desorbed. Each measurement in Figs. 5 and 6 was made after this operation.

An investigation are some analytical applications of graphitized carbon blacks is useful in order to use the data reported in the literature for Sterling FT, which is commercially unavailable, for the evaluation of the possibilities of Carbo-pack C. Fig. 7 reports the classical separation of C_1 - C_5 alcohols on Sterling FT coated with Carbowax 1500, reported by Di Corcia *et al.*²⁰. The four chromatograms compare the separations obtained on the two materials coated with the appropriate amount of liquid phase. Ottenstein²¹ found that the separation of C_1 - C_5 alcohols obtained on Sterling FT can be repeated on Carbo-pack C provided that the concentration of Carbowax 1500 used is 0.2% instead of 0.4%. The chromatograms in Fig. 7 show that this is approximately true and that the optimal concentration of Carbo-

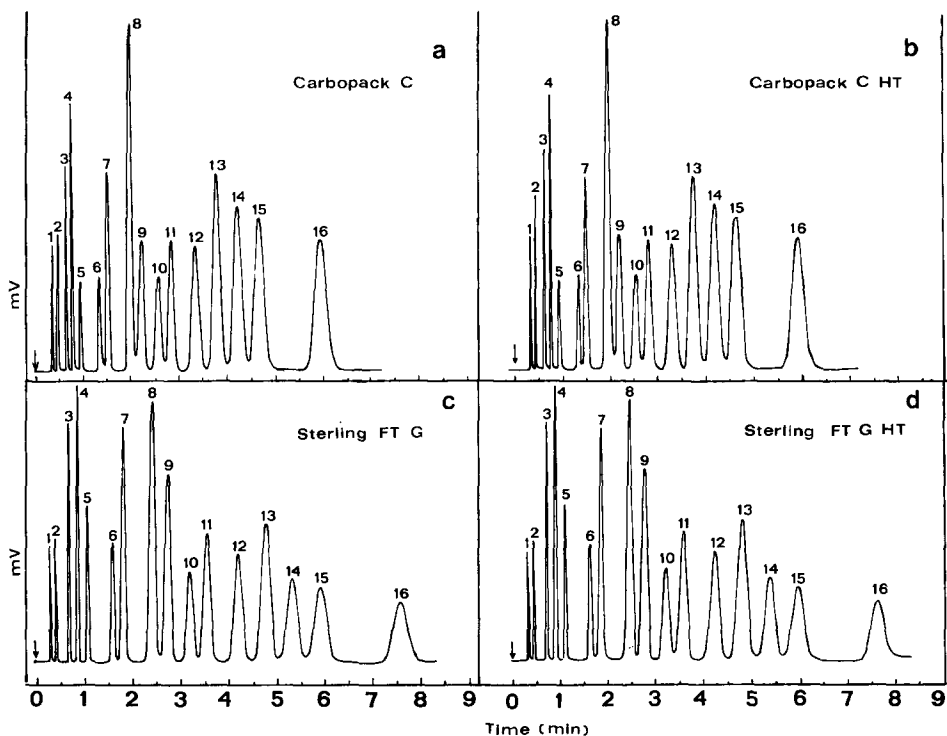


Fig. 7. Comparative chromatograms of the performance of HT and normal forms of Sterling FT and Carbopack C. Columns: Carbopack C (normal) and HT + 0.23% Carbowax 1500; Sterling FT (normal) and HT + 0.4% Carbowax 1500. Column length 1.5 m; I.D. 2 mm; temperature 135°. Elution of C_1 - C_5 alcohols: (1) 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-metanol-2-butanol; (12) 3-pentanol; (13) 2-pentanol; (14) 2-methyl-1-butanol; (15) 3-methyl-1-butanol; (16) 1-pentanol.

pack C is 0.23%. In this instance, the separation factors for particular compounds are identical, within experimental error. The most interesting result is that there is no difference in practice if one uses the normal or the HT form. This is due to the fact that the effect of hydrogen treatment is remarkable on the uncoated packing or when a non-polar liquid phase is used. The polar liquid phase masks the specific active sites and the difference is no longer observed, even for Carbopack C, where the hydrogen treatment plays an important role, as shown by Fig. 4.

For the separation considered, there is no effect on retention times, which is in disagreement with Fig. 4. However, it should be borne in mind that the graphs in Fig. 4 were obtained with squalane as the liquid phase. The results are in agreement with those in Fig. 2, where it is shown that with a polar liquid phase (glycerol) the K' values increase. Carbowax 1500 is intermediate, in terms of polarity, between squalane and glycerol, so that for the same material, whether in the normal or the HT form, no changes in K' values are observed in practice.

The advantage of using Carbopack C is in the shorter separation time (about 25%).

The effect of hydrogen treatment is evident in the chromatograms in Fig. 8, showing the elution of aniline, phenol and *n*-undecane on Carbopack C in the normal and HT forms. The 1.5% PPE 20 was chosen because of the need to use a liquid phase of very low polarity, without hydroxyl groups, and to coat the adsorbent with more than a monolayer, in order to check the influence of the adsorbent even when it is fully coated. Both aniline and phenol show greater tailing of the peaks when they are eluted on the normal form, while *n*-undecane is much less retained on the HT form, in agreement with Fig. 2. From these results, it is clear that hydrogen treatment eliminates either specific and non-specific active sites, even though the former are still present in significant amounts after treatment. Further, it can be said that the excess of non-specific active sites is eliminated in Carbopack C, which, after hydrogen treatment, behaves in a similar manner to Sterling FT, considering the lower surface area. It should be noted that the same compounds as shown in Fig. 8 yield the same chromatogram on Sterling FT, no difference being observed for the two forms.

The retention times on the two carbon blacks in the normal form, which is the

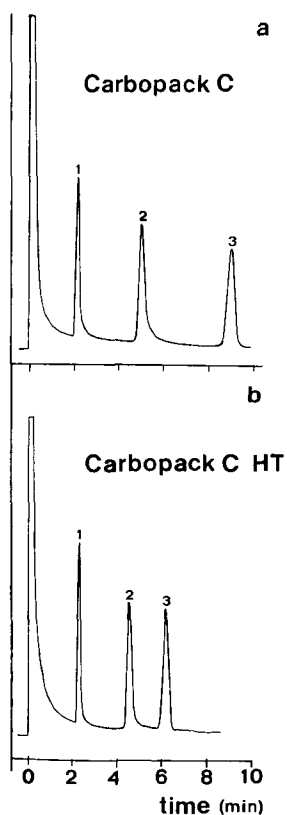


Figure 8

Fig. 8. Effect of hydrogen treatment on the elution of aniline (1), phenol (2) and *n*-undecane (3) on Carbopack C. Column: 1.5 m packed with Carbopack C + 1.5% PPE 20 in both instances. Temperature, 120°. Amount injected: 0.3 μg of each component.

most widely used form, are given in Table II. The most important feature of Carbo-pack C is that on this adsorbent the retention times are lower, so that compounds of higher molecular weight can be eluted. This allowed us to separate the two benzopyrene isomers²², which could not be achieved with Sterling FT.

TABLE II

CORRECTED RETENTION TIMES FOR *n*-ALKANES

Starting temperature: 100°, programmed at 2°/min to 270°. Columns: Sterling FT + 1.5% PPE 20; Carbopack C + 1.5% PPE 20. Retention times obtained with a Hewlett-Packard 3380A integrator.

<i>n</i> -Alkane	Sterling FT		Carbopack C	
	<i>t_r</i> (min)	<i>T</i> (°C)	<i>t_r</i> (min)	<i>T</i> (°C)
C ₁₁	8.40	118	5.29	112
C ₁₂	14.08	130	9.41	120
C ₁₃	20.72	142	14.74	131
C ₁₄	27.86	157	20.98	144
C ₁₅	34.75	170	27.10	156
C ₁₆	41.63	184	33.17	168
C ₁₇	48.52	198	39.49	180
C ₁₈	55.06	212	45.07	193
C ₂₀	67.58	236	55.81	218
C ₂₂	79.54	262	65.92	236
C ₂₄	94.76	Final isothermal	76.48	250

CONCLUSION

The results have shown that Carbopack C and Sterling FT behave in a different manner, in spite of the similarity of their structures. The differences are not related only to differences in surface area, but also depend on the energy distribution of active sites. The greater number of non-specific active sites on Carbopack C is eliminated by hydrogen treatment, so that the treated forms of the two packings are more similar than in the original materials. Specific active sites are present in both carbon blacks, but to a greater extent on Carbopack C. The effects of such active sites are eliminated when a strongly polar liquid phase is added, so that the only differences are related to the surface areas.

Finally, hydrogen treatment improves the quality of Carbopack C as an adsorbent for general use, with the possibility of eluting polar compounds even though it is coated with a non-polar liquid phase. Carbopack C, once it has been treated with hydrogen and coated with a liquid phase, yields lower retention times.

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