Gas–liquid–solid chromatography with coated graphitized carbon black

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Abstract - The exceptional properties of graphitized carbon blacks
in gas chromatography are described and the explanation of their
behaviour is explained in terms of the thermodynamic functions related
to the chromatographic process and of the kinetics of adsorption.
Analytical applications using both packed and capillary columns using
the working mechanism of gas liquid solid chromatography are reported.

INTRODUCTION

The term "Gas Liquid Solid Chromatography" (GLSC) was introduced by Purnell (ref.1)
to indicate the particular technique where a liquid modifier is added to an adsorbent
in order to reduce the peak tailing usually obtained in gas solid chromatography (ref.2).
The great advantages of using Graphitized Carbon Blacks (GCB) in adsorption gas chromato-
graphy have been shown at a large extent by Kiselev and his coworkers in many papers
and a detailed discussion of the entire topic is reported extensively in his book (ref.3).

WORKING MECHANISM

Graphitized carbon blacks are substantially non porous or macroporous adsorbents. This
leads to outstanding properties when they are coated with different amounts of a liquid
modifier. In Figure 1 the behaviour of the isosteric heat of adsorption Q_s at zero
surface coverage of n-pentane, when the adsorbent surface is coated with increasing
amounts of a non polar liquid phase like squalane, is reported. In the case of GCB, one
can clearly see that a maximum of Q_s is reached just before a monolayer is formed,
while a continous decrease is observed using a porous material such as silica gel.

This feature is a very important one, since on GCB the "lateral interactions" with the
liquid modifier are very effective and play an important role in the selectivity of
the adsorbent toward the structural characteristics of the molecules eluted. The working
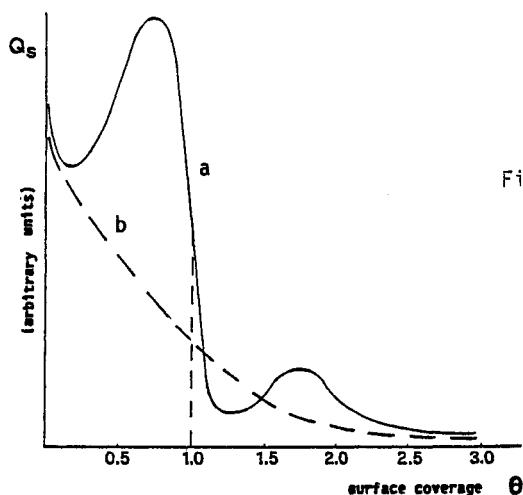mechanism is explained very simply by the model shown in Fig. 2.

Fig. 1.
Typical behaviour of the heat of adsorption of
n-pentane on porous and non porous adsorbents.
Liquid phase: squalane.
Solid line: Graphitized Carbon Black Sterling FT.
Dotted line: silica gel.

When the surface is perfectly clean, the molecule coming from the gas phase is preferentially adsorbed on the active sites of the graphitic surface, namely cracks, crevices and, in general, high electron density adsorptive sites. When a few molecules of a non volatile liquid modifier are added to the adsorbent, these will be preferentially adsorbed on the most active sites, so that in this situation, the molecules eluted will be adsorbed on lower energy sites. This explains the initial decrease of the heat of adsorption (Fig. 2B) and the molecules of the organic modifier acts as a deactivating agent, making the adsorbent a more "gaussian" one. This effect is common to all adsorbents when coated with a modifier and this can be simply taken as a tail reducer, giving rise to more symmetrical peaks in chromatographic experiments because the adsorption isotherm is linearized.

A striking difference between a porous and a non porous material is observed when the organic modifier covers the surface at a higher extent. If the adsorbent is a non porous one, a very homogeneous distribution of the modifier may occur and "lateral" interactions of the molecules take place. This means that the molecule eluted interacts not only with the surface, but also with the molecules of the modifiers.

This results in an increase of the heat of adsorption (Fig. 2C). Once the monolayer is formed a sharp decrease of the heat of adsorption occurs because of the "shielding effect" of the adsorption forces operated by the modifier (Fig. 2D). If the adsorbent is very homogeneous a second maximum is observed by further increasing the amount of modifier, due to the formation of a second layer (Fig. 2E).

This behaviour is not observed with a porous material, mainly due to the impossibility of forming a regular monolayer, becuase of pore filling and other disturbing phenomena.

It should be also noted that, for different molecules eluted on the same adsorbent and the same modifier, the monolayer may occur at different percentages of the modifier (ref.4).

RESULTS

Chromatographic efficiency and selectivity are strongly enhanced in the region of maximum lateral interactions (maximum Q_s values) and deeply affected by the presence of different functional groups (OH, COOH, NH_2, etc.) in the modifier. An example of the counteracting effect of the same modifier on molecules of different structure is given in Fig. 3, where the values of the capacity ratio k' are reported against the percentage of two different modifiers, glycerol and squalane. For n-pentane, when squalane is the modifier, the effect of lateral interactions and the shielding effect of the monolayer formation are clearly seen (dashed line). The same compound, when glycerol, a highly polar liquid phase, is used, shows a linear decrease of k'. This is due to the fact that the only effect of glycerol is to decrease the surface area of the adsorbent, since no lateral interaction with the eluate occur.

On the contrary, if n-propanol is eluted on glycerol, the retention increases linearly with the percentage of the liquid phase, due to the increasing number of alcoholic -OH groups that interact with the alcoholic function of n-propanol.

Further, it should be observed that, by coating the surface of the adsorbent with a polar modifier, the separation of aliphatic hydrocarbon isomers is not affected.

In this case the driving force of the process is gas adsorption on liquid (ref. 5).

On the basis of these facts one comes to the conclusion that using modified non porous adsorbent as stationary phases in gas chromatography, tailor made columns can be made and a high selectivity may be reached.

An example of the effectiveness of GLSC as compared to GLC is given in Fig. 4, where the separation of some harbicides is reported and obtained on a GLC capillary column with about 60.000 theoretical plates (a) and on a packed column having about 5.000 plates (b). The packed column works in GLSC and the three compounds, atrazine, simazine and propazine are better separated in a much shorter time.

In Fig. 4c and d the same columns are used to separate nine compounds and similar results are obtained on the capillary and packed column. As a matter of fact, from the chromatogram it may be seen that the higher number of theoretical plates of the capillary column is not fully used; a cluster of five peaks is eluted within less than two minutes, while wide regions of the chromatogram do not show any peaks (ref.6).

From these facts it may be inferred that using a capillary column with the working mechanism of gas-liquid-solid chromatography, outstanding results could be obtained.
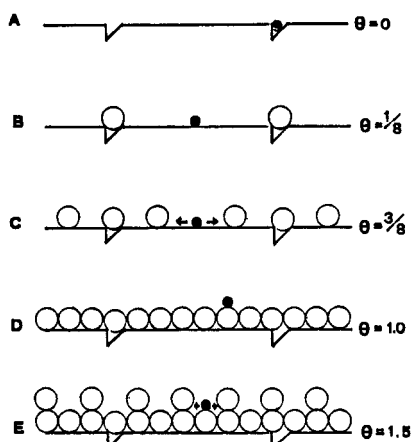
Fig. 2. Model explaining the behaviour
of Q_S with surface coverage θ of
Fig. 1. ○ Molecule of the modifier.
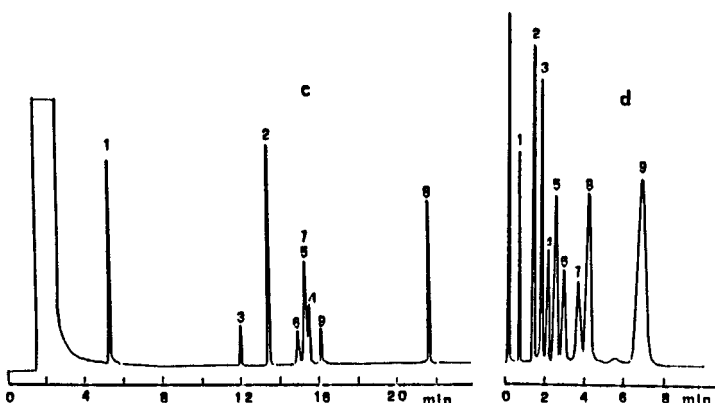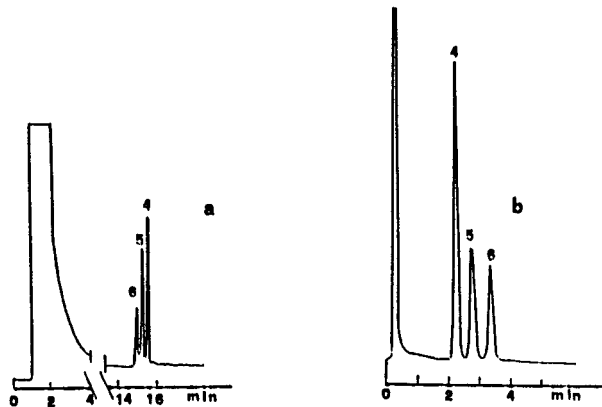● Molecule of the compound eluted.

Fig. 4. Separation of herbicides on a capillary column (a and c) containing
SE-54 (30m x 0.24mm 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 of Carbopack F
(6.0 sq.m/g)   coated with 0.3 % SP1000 (1m x 2mm i.d., 240 °C
isothermal). Flame ionization detection. Peaks: 1=diclobenil;
2=trifluralin; 3=2,4-D ME; 4=propazine; 5=atrazine; 6=simazine;
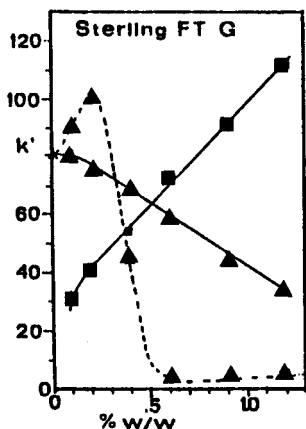7=Silvex ME; 8=2,4,5-T ME; 9=DCPA.

Fig. 3. k' versus percentage (w/w) of liquid phase.
Broken line: squalane; solid line: glycerol, ■ n-propanol,
▲ n-pentane. Temperature: 46 °C.

Further, the kinetics in gas adsorption chromatography are much faster than in the
GLC mode. For this reason, according to Giddings (ref. 7) the C term of the Van Deemter
equation should have a much lower value with respect to GLC.
In Fig. 5, a comparison of the Van Deemter curves obtained for two capillary columns
of the same geometrical characteristics, one working in GLC and the other one in GLSC
with graphitized carbon black, is reported. One order of magnitude is gained in the
decrease of the mass transfer term. This allows faster analysis still having a high
efficiency in terms of theoretical plates (ref. 8).

The practical effects of what stated above are well represented in Fig. 6, where the
same preparation of Fig. 4 is reported and the results are better than those obtained
with both the GLSC packed columns and the GLC capillary column.
The outstanding properties of GCB coated with polar liquid phases are furtherly shown
by the chromatogram of Fig. 7, where the separation of polar compounds, such as phenols
and alcohols are shown on a capillary column working in GLSC with Carbowax 20M.
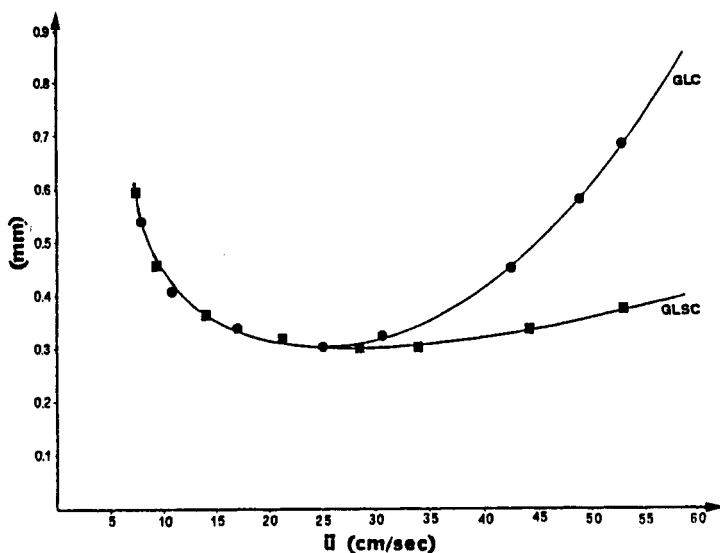It should be noted that the column is only 9m in length (ref. 8).

Fig. 5. Van Deemter plots obtained on two fused silica capillary columns with the same geometrical character- istics (20m x 0.25mm i.d.). Coatings: ■ = graphitized carbon black, Carbopack F + 0.3 % SP1000; ● = SP1000; film thickness 0.25 μm. Sample = n-hexadecane.
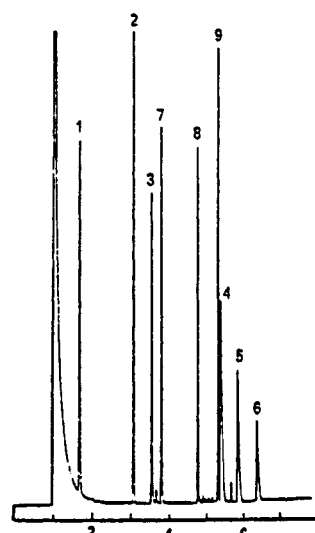

Fig. 6. Separation of some herbicides on a GLSC capillary columns. 1=diclobenil; 2=trifluralin; 3=2,4-DME; 4=propazine; 5=atrazine; 6=simazine; 7=Silvex ME; 8=2,4-STME; 9=DCPA.
Fused silica capillary column (20m x 0.25mm i.d.) coated with Carbopack F + 0.3% SP1000. Temp. progr. 140 °C for 2 min, then increased at 18 °C/min to 230 °C.
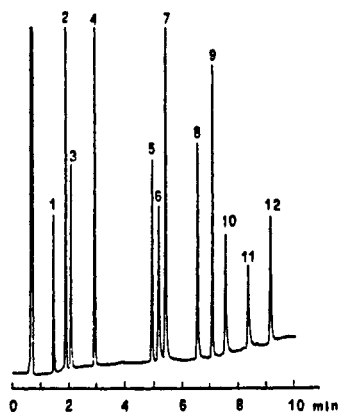

Fig. 7. Separation of alcohols and phenols. 1=hexanol; 2=2-octanol; 3=1-heptanol; 4=1-octanol; 5=1-de- canol; 6=2-nitrophenol; 7=2-chloro- phenol; 8=phenol; 9=2,4-dimethylphe- nol; 10=2,4-dichlorophenol; 11=2,4, 6-trichlorophenol; 12=4-chloro-3- methylphenyl. Fused silica capillary column (9m x 0.25mm i.d.) coated with Carbopack F + 0.3% Carbowax 20M. Temp. progr.: 90 °C for 1 min, then increased at 12 °C/min to 140 °C, followed by 25 °C/min to 220 °C.

REFERENCES

1) H. Purnell, Gas Chromatography, p. 375, Wiley, New York (1962).

2) F. T. Eggertsen and H. S. Knight, Anal. Chem. 30, 15-21 (1958).

3) A. V. Kiselev anf Y. I. Yashin, "Gas Adsorption Chromatography", Plenum Press, New York 1969.

4) F. Bruner, P. Ciccioli, G. Crescentini and M. T. Pistolesi, Anal. Chem. 45, 1851-1859 (1973).

5) R. L. Martin, Anal. Chem. 33, 347-351 (1961).

6) F. Mangani and F. Bruner, J. Chromatog. 289, 85-94 (1984).

7) J. C. Giddings, Anal. Chem. 36, 1170-1179 (1964).

8) F. Bruner, G. Crescentini, F. Mangani, P. Palma and M. Xiang, J. Chromatog. 399, 87-97 (1987).