

CHROM. 6403

## CARBON-COATED GLASS BEADS AS A GAS CHROMATOGRAPHIC SUPPORT MATERIAL

LELIO ZOCOLILLO AND ARNALDO LIBERTI

*Istituto di Chimica Analitica, Città Universitaria, 00185 Rome (Italy)*

---

### SUMMARY

A new gas chromatographic support material obtained by coating glass beads with a thin layer of carbon is described. The layer is obtained by the pyrolysis of methylene chloride in a closed vessel at 550°.

The operating conditions for this material are described; the working characteristics are superior to those of untreated glass beads.

Separations of polar and non-polar compounds with various stationary phases are reported.

---

### INTRODUCTION

Micro glass beads are used extensively as a solid support for gas-liquid chromatography in the preparation of columns whose geometrical characteristics are known. Glass beads were originally considered to be a non-active material, but as this is not so<sup>1</sup>, a variety of procedures has been developed to improve their properties. Some workers replaced soda-lime glass with silica<sup>2</sup> or sodium silicate<sup>1</sup>, and others carried out specific surface treatments such as grooving or roughening by acid or alkali leaching<sup>3,4</sup>, by silylation<sup>5</sup> or by coating with metal oxides<sup>6</sup>.

Glass beads have a very uniform size but exhibit undesirable adsorption properties, which might be due to active groups such as the hydroxyl groups present on the surface; to these sites might be attributed the tailing and poor resolution for polar compounds. An additional cause of limited efficiency is the "pudding effect", due to the formation of pockets of liquid substrates which might be drawn by capillary action to points of contact among beads. As the nature of the surface and its wettability are responsible for these effects, the coating of glass beads with a uniform layer of inert material should improve the efficiency of this support material, as suggested by GOLAN<sup>7</sup>. This paper describes the preparation of carbon-coated glass beads obtained by the pyrolysis of methylene chloride, and the evaluation of this new material.

### EXPERIMENTAL

Commercially available soda-lime beads were sieved and the fraction of 75-84 mesh was used to determine the layer thickness that yields the most satisfactory results.

### Preparation of carbon-coated glass beads

The procedure described by GROB<sup>8</sup> for coating a carbon layer in glass capillaries was adapted for the preparation of carbon-coated glass beads. A weighed amount of glass beads is transferred into a vial and the calculated amount of methylene chloride is added. The vial is flame-sealed and placed in an oven at 550°.

It has been found that, with the selected mesh size, the amount of methylene chloride required is about  $3 \times 10^{-2} \mu\text{l}$  per gram of beads, which corresponds to a carbon layer of about 0.4 nm. In order to measure the small volume of methylene chloride required, the use of a tared glass capillary which is set into the vial containing the beads, which are kept in ice, is recommended. After flame-sealing the vial, it is transferred into a hot water-bath and then heated in an oven at 550°.

When using glass beads of different mesh sizes with an average diameter of  $d$  mm, the volume of  $\text{CH}_2\text{Cl}_2$  in microlitres to be added per gram is calculated by means of the expression  $V = K/d$ , where  $K$  is  $7 \times 10^{-3} \text{ mm}^4$ , this value being obtained by geometrical considerations and by taking into account the density of the carbon layer, which was found to be  $1.5 \text{ g/cm}^3$ .

### RESULTS AND DISCUSSION

The gas chromatographic behaviour of carbon-coated glass beads was determined by coating them with small amounts of stationary phase (0.05% (w/w) of SE-52); a column about 2 m long and 0.4 cm I.D. was filled and the plate heights at 120° for the elution of *n*-hexadecane at various linear velocities were determined.

The values obtained are shown in Fig. 1 (curve A) together with the data for

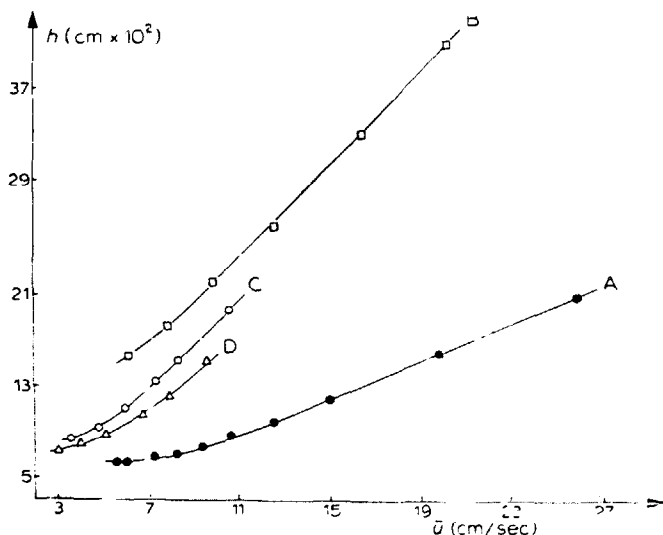


Fig. 1. Graphs of HETP against  $\bar{u}$  for normal saturated hydrocarbons: (A) on carbon-coated glass beads, (B) on untreated glass beads, (C) on silanized Chromosorb G, (D) on silanized Chromosorb W. A and B: glass column, 190 cm long, I.D. 0.3 cm; glass beads sieve fraction, 75-84 mesh; coating, 0.05% SE-52 silicone oil; carrier gas, nitrogen with  $p_{\text{min.}} = 0.10 \text{ kg/cm}^2$ ; sample, *n*-hexadecane;  $T_c = 120^\circ$ ; detector, FID. C and D: Conditions as for A and B except coating, 1.0% and 2.0%, respectively, SE-52 silicone oil; carrier gas,  $p_{\text{min.}} = 0.50 \text{ kg/cm}^2$ ; sample, *n*-tridecane.

a column prepared in the same way with untreated glass beads (curve B). A noticeable improvement is obtained, with a faster mass transport between the stationary liquid substrate and the mobile gas phase. In the same figure are also reported the same measurements made with similar columns prepared with Chromosorb G coated with 1% (w/w) of SE-52 (curve C) and Chromosorb W coated with 2% (w/w) of SE-52 (curve D) in the elution of *n*-tridecane.

The thin layer of carbon on glass beads has a good mechanical strength and reproducible results are obtained by packing columns several times.

It may be interesting to compare this new support in the elution of some compounds that are usually used as reference compounds. It is well known that benzophenone interacts strongly with Lewis acid sites through coordination of its lone pair of electrons. Fig. 2 shows a gas chromatogram obtained on Corning GLC 100

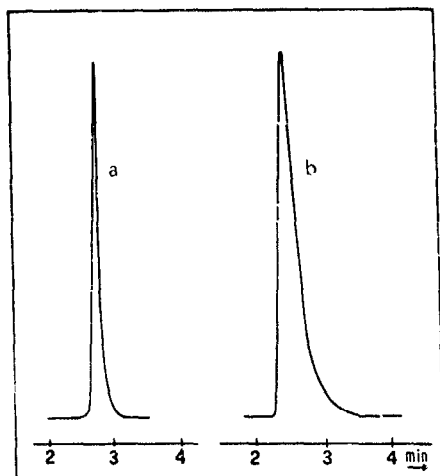


Fig. 2. Shape of benzophenone peak obtained (a) on carbon-coated soda-lime glass beads and (b) on textured Corning GLC 100 glass beads<sup>1</sup>. Glass beads sieve fraction, 75-84 mesh; coating, 0.05% SE-52 silicone oil; temperature, 150°; sample, (a) 0.4  $\mu$ g, (b) 1.5  $\mu$ g; attenuation, 1  $\times$  8.

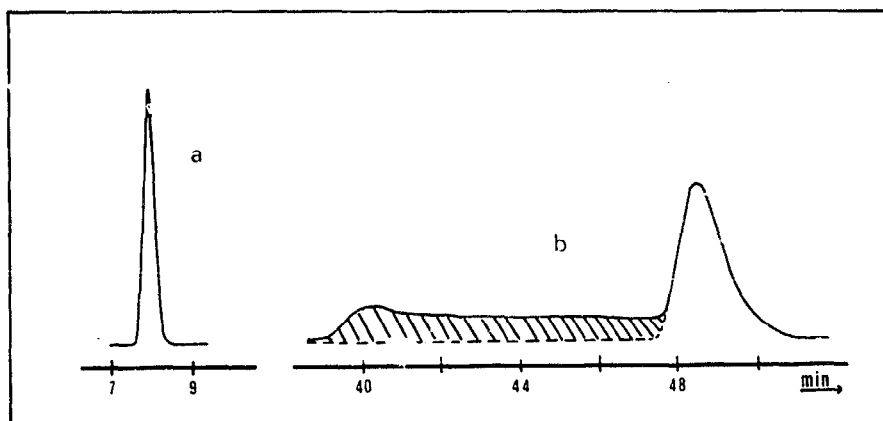


Fig. 3. Pentamethylbenzylacetate on (a) carbon-coated soda-lime glass beads and (b) silanized Chromosorb G (decomposition). Same columns as (A) and (C) in Fig. 1. Temperature, 170°.

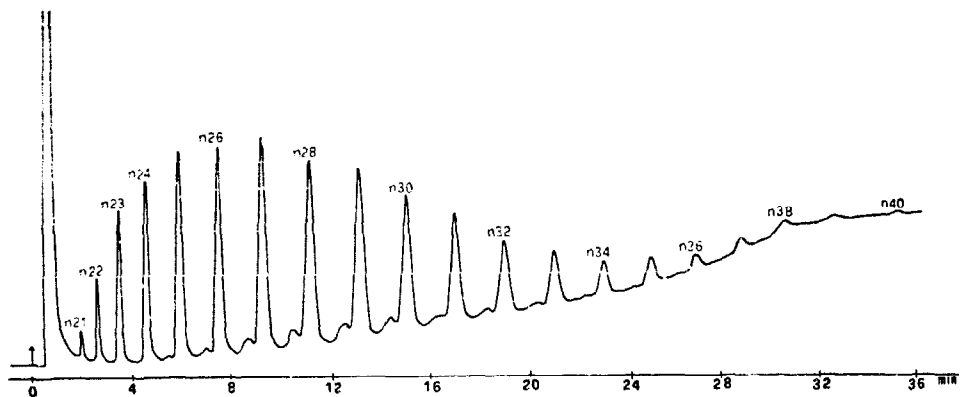


Fig. 4. Normal and *iso*-saturated hydrocarbons of a paraffin wax. Glass column, 190 cm long, I.D. 0.3 cm; glass beads sieve fraction, 60-80 mesh; coating 0.05% SE-52 silicone oil; temperature: programmed from 200° to 290° at 3°/min.



Fig. 5. Separation of phenols: (1) 2,4,6-tri-*tert*-butylphenol; (2) 2,4,6-trimethylphenol; (3) phenol; (4) 2,4-xyleneol; (5) 2,3-xyleneol; (6) 3,5-xyleneol; (7) 3,4-xyleneol; (8) 2,6-xyleneol; (9) 3,4,5-trimethylphenol; (10) *p*-methoxyphenol; (11) *p*-chlorophenol. Stainless-steel column, 500 cm long, I.D. 0.5 cm; glass beads sieve fraction, 50-60 mesh; coating: 0.10% FFAP; carrier gas, nitrogen with  $p = 0.95 \text{ kg cm}^{-2}$  and flow-rate 60 ml/min; temperature, 182°.

glass beads coated with SE-52 and on carbon-coated soda-lime glass beads with the same stationary phase at the same operating temperature; with the latter, an almost symmetrical peak is obtained.

The elution of substances such as pentamethylbenzyl acetate, which on Chromosorb G coated with 1% of SE-52 undergoes decomposition, yields a symmetrical peak on carbon-coated glass beads (Fig. 3).

The low loading of the stationary phase on this support enables the chromatography of complex mixtures to be carried out in a fairly short time. Fig. 4 shows the chromatographic analysis of a paraffin wax that was carried out in order to evaluate the distribution of normal and isoalkanes.

High-efficiency carbon-coated glass beads columns are also obtained with polar stationary phases. As an example of the interesting feature exhibited by this support, Fig. 5 shows a gas chromatogram of a mixture of phenols. They are eluted on an FFAP column at 182° in a fairly short time, yielding symmetrical peaks.

The gas chromatographic behaviour of this new support shows that the thin layer of carbon built up on the glass beads eliminates surface irregularities, prevents the action of active groups and renders the beads more wettable by any liquid phase. The increased effectiveness of this new support material should be attributed to the elimination of the effects that are responsible for poor efficiency. The carbon layer does not change the surface area appreciably; it has to be considered as an "inactive layer" as far as the elimination of active sites is concerned so that the composition of the solid support becomes of minor importance. One of the most interesting features is the increase in the wettability due to the variation of contact angle<sup>9</sup>. Liquid phases of any polarity are spread on the beads more easily and uniformly, as a better distribution of the liquid substrate is achieved and a lower concentration is required with a column of higher efficiency.

It seems that carbon-coated glass beads, which require a low loading of stationary phase and permit a fast time of analysis, might yield columns that are useful for the coupling of gas chromatography with mass spectrometry.

#### REFERENCES

- 1 J. G. NIKELLY, *Anal. Chem.*, **36** (1964) 2244.
- 2 C. L. GUILLEMIN, M. LE PAGE AND A. J. DE VRIES, *J. Chromatogr. Sci.*, **9** (1971) 470.
- 3 R. W. OHLINE AND R. A. JOJOLA, *Anal. Chem.*, **36** (1964) 1681.
- 4 A. M. FILBERT AND M. L. HAIR, *J. Gas Chromatogr.*, **6** (1968) 218.
- 5 H. L. MACDONALL, *Anal. Chem.*, **40** (1968) 221.
- 6 I. HALASZ AND C. NORVATH, *Anal. Chem.*, **36** (1964) 1178.
- 7 M. J. E. GOLAY, in K.P.W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 139.
- 8 K. GROB, *Helv. Chim. Acta*, **48** (1965) 136.
- 9 A. LIBERTI, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 95.