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USE OF GRAPHITIZED CARBON BLACK IN ENVIRONMENTAL ANALYSIS

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SUMMARY

The versatility of graphitized carbon black as a column material for various environmental analytical problems is shown by studies on the gas chromatography of sulphur compounds and olefins in air. Its feasibility for use in the analysis of unknown complex mixtures with widely different volatilities is reported.

It is also shown that good results are obtained using graphitized carbon black as an adsorbent to trap and release air pollutants, ensuring the absence of impurities that arise from the sampling technique.

INTRODUCTION

In the past, a large amount of research has been devoted to the study of adsorption properties of graphitized carbon blacks (GCBs) and it was shown that these materials behave essentially as Gaussian adsorbents and that some of them also exhibit a narrow energy distribution of active sites^{1,2}.

The excellent and peculiar behaviour of GCBs as stationary phases in gas chromatography have been emphasized by Kiselev and co-workers^{3,4}, who made interesting correlations between static adsorption measurements and the chromatographic properties of the adsorbents.

Several other groups of researchers have investigated interesting applications of GCBs in gas chromatography, mainly Halász and Horvath⁵, Guiochon and co-workers^{6,7} and Liberti and co-workers^{8,9}. Starting from these studies, GCBs have been extensively exploited as solid supports in gas-liquid-solid chromatography (GLSC) by our group, and we have shown their versatility for use in the elution of trace amounts of polar compounds both in GLSC¹⁰ and in GSC¹¹. More recently, it was shown that by changing the type and the amount of the liquid phase, one can achieve the most suitable column for a particular separation problem¹²⁻¹⁵.

On the other hand, the problems connected with environmental analysis by gas chromatography are related mainly to column characteristics as highly sensitive and specific detectors are available nowadays. Such problems can be summarized as follows:

(a) the column should be versatile in order to permit the elution of different classes of compounds which may be present in the organic material contained in air or water;

- (b) the large amount of water usually present in air or water concentrates should be eluted without destroying the column or yielding large and diffuse peaks;
- (c) rapid analysis is required for repetitive measurements;
- (d) reactive compounds such as sulphur dioxide and other sulphur compounds must be linearly eluted at the parts per billion* concentration level;
- (e) the column should be selective so as to permit the separation of compounds of similar structure such as saturated hydrocarbons and olefins.

Moreover, the adsorbents used for the concentration of large air or water pollutant samples should have the following characteristics:

- (1) capability of retaining all of the compounds at low temperature and to release them at high temperature without any appreciable chromatographic process;
- (2) to keep their properties after repetitive cooling and heating operations in the presence of large amounts of water and oxygen;
- (3) high purity so as to ensure that very low or no blank compounds are injected into the gas chromatograph or extracted by the solvents.

In this paper, we describe the possibilities of using GCBs in order to solve the problems mentioned above, using them both as column material and sampling adsorbents.

EXPERIMENTAL

Apparatus and materials

All measurements were made with Carlo Erba (Milan, Italy) Model GI 450 gas chromatographs equipped with flame ionization detectors (FID). Sulphur-containing gases were analyzed by equipping such a chromatograph with a flame photometric detector (FPD) supplied by Tracor (Austin, Texas, U.S.A.).

The column for the analysis of sulphur-containing gases was made with graphitized carbon black Carbopack B HT (Supelco, Bellefonte, Pa., U.S.A.) treated as described previously¹⁶, while Carbopack B coated with 2.6% of Carbowax 1500 was used as the column packing for the analysis of light hydrocarbons in air.

C₇-C₂₂ organic compounds in air were analyzed with a column of Carbopack A HT coated with 1.5% of PPE 20 (Supelco). A new type of graphitized carbon black was used for the separation of high-boiling compounds; this material has the same chromatographic properties as Carbopack A, but its surface area is slightly lower, so that retention times are shorter.

Glass system for sulphur analysis

Previous work by our group on the analysis of sulphur-containing gases in air showed that PTFE should be always used as the material for the column and exponential dilution flask^{16,17}. In the present work, we used Pyrex glass for the connecting lines, column and exponential dilution flask. The same results were obtained as when PTFE was used provided that the system was thoroughly dried by passing a stream of dry helium or hydrogen through the entire system while heating it at 130° for 6 h. The flow-rate was about 200 ml/min. Under these conditions, no appreciable

* Throughout this article the American billion (10⁹) is meant.

adsorption takes place on the glass lines and on the column wall; of course, the carrier and diluting gases must be dried before entering the glass system. The calibration curve for sulphur dioxide made with the apparatus modified with glass showed a slope of 1.7, and the detection limit was slightly better than in earlier work¹⁷.

Sampling device for organic compounds in air

The sampling device is shown in Fig. 1A. It consists of a 3-l Dewar flask containing liquid nitrogen; a double-walled cylindrical brass container (a) with a 4-mm interspace between the walls is placed in the Dewar and suspended by three supports (b) spaced at 120° apart. The trap (c) consists of a 15 cm × 4 mm I.D. stainless-steel tube connected via Swagelok-type connectors to two stainless-steel tubes. The trap is filled with 40–60 mesh Carbopack A. The inlet tube (d) is 2 mm I.D., while the outlet tube (e) is 1 mm I.D., in order to prevent the use of a narrower inlet tube causing the occlusion of the trap because of condensation of water. The outlet tube is narrow in order to prevent high dead volumes in the injection phase. The thermocouple (f) measures continuously the trap temperature. A system of five electrically controlled valves (Skinner, Roosendaal, The Netherlands), shown schematically in Fig. 1B, allows sampling and injections.

For field sampling, the part of the apparatus enclosed within the broken lines in Fig. 1B is removed. With such a system, the organic substances comparable in volatility with C₁–C₈ hydrocarbons are sampled.

Sampling and solvent extraction of higher-boiling compounds in air is made with a system similar to that described by Grob and Grob¹⁸.

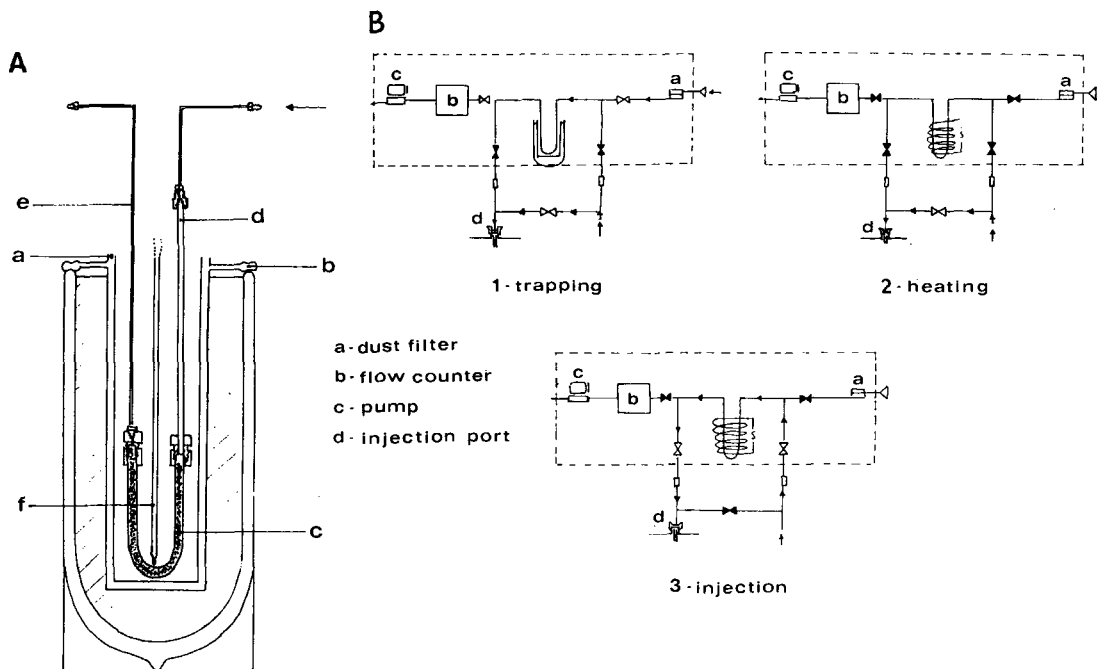


Fig. 1. Sampling and injection system: (A) trap; (B) overall system. For details of components, see text.

RESULTS AND DISCUSSION

Monitoring of sulphur compounds in air

The major advantage of using glass as the column material is that the number of theoretical plates is about 1500 per metre, compared with 500 per metre obtained with the PTFE column. This makes the resolution greater by a factor of 1.7 and permits the linear gas velocity to be doubled, with a corresponding decrease in the analysis time. The chromatogram in Fig. 2 shows that hydrogen sulphide and methanethiol, which might interfere in the measurement of sulphur dioxide, are well separated from this compound and from air in only 1 min, which makes the gas chromatographic method continuous in practice. The results obtained with the glass column, together with the automatic sampling and injecting device described previously¹⁶, make the gas chromatographic method competitive with the manual method and other automatic methods in terms of sensitivity, reliability and the possibility of continuous use. It also appears superior because of the absence of interferences in the measurement of sulphur dioxide and of wet-chemical operations.

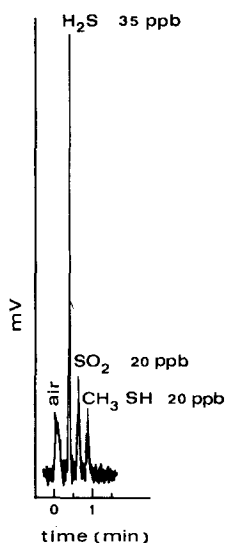


Fig. 2. Analysis of trace amounts of sulphur compounds in air with an FPD detector. Column: 1.6 m \times 0.4 mm I.D. glass, Carbo-pack B, 40–60 mesh, + 0.7% H_3PO_4 + 0.7% XE-60. Φ = 120 ml/min; T = 40°.

Fig. 2 shows one of the merits of using carbon black, which guarantees the selectivity of GLSC and the possibility of eluting trace amounts of polar compounds.

By using Carbo-pack A and temperature programming, sulphur compounds from hydrogen sulphide, carbonyl sulphide and sulphur dioxide up to pentanethiol and thiophenes can be separated on a 4-m column. Such analyses are useful in the analytical problems that are frequently encountered in the determination of odours in the vicinity of chemical or petrochemical plants.

Determination of olefins in air

The determination of olefins in air is an interesting problem in environmental analysis because these compounds, together with aldehydes, are the precursors of photochemical smog.

The most widely used technique for analyzing light hydrocarbons in air consists in trapping them by means of an adsorbent at an appropriate temperature, heating the adsorbent and injecting the desorbed compounds into a chromatographic column.

A careful choice of the adsorbent is imperative in order to ensure complete recovery. Altshuller¹⁹ pointed out some advantages and disadvantages of different adsorbents. One problem is the choice of the trapping and heating temperatures; generally, if one uses a "strong" adsorbent, the trapping temperature may be higher, say about room temperature, which, for obvious reasons, would be more convenient. On the other hand, with such an adsorbent, there is a serious risk that in the desorbing stage higher-boiling compounds could be only partially released and that a chromatographic effect would take place in the trap itself; this affects the reproducibility of the retention times and very often gives tailing peaks. Moreover, decomposition of the thermally unstable compounds easily takes place.

In order to obviate such undesirable effects, some workers^{20,21} coated various supports with high-boiling liquid phases. The disadvantages of such a technique are first that in many instances the liquid phase may react with some of the compounds, for example, Dexsil 300 will not release alkaline compounds, and secondly, the impurities of the liquid phase may bleed into the column and contaminate the sample. Nicotra *et al.*²² used SE-30 or OV-17 on Chromosorb W to trap air pollutants. They found a very strong effect due to desorption of water and, in order to eliminate this effect, they were obliged to use a dehydrating agent. This leads to another problem, that is, the selective adsorption of the compounds by the dehydrating agent. Only saturated hydrocarbons are, in fact, virtually unadsorbed, while for other compounds, the more polar the molecule, the lower is the recovery.

The difficulties pointed out above can be solved by using graphitized carbon black. In Fig. 3, two chromatograms reporting "bad" results show that the efficiency of the trap is very important for the performance of the analysis. The same column as in Fig. 4 was used, but in the case of Fig. 3a the trap was made with the activated charcoal employed in filter cigarettes, while in the case of Fig. 3b it was silver nitrate and Carbowax 20 M on Carbopack A.

These two chromatograms indicate two of the common problems involved with the trapping methods. The activated charcoal used in filter cigarettes acts like a "bad" chromatographic column, yielding strongly tailing peaks with very high retention times. However, the elution of water seems not to be a serious problem in this instance. This result is in agreement with the findings of Kaiser²⁰ using Carbosieve B. With the silver nitrate–Carbowax 20M trap there is an improvement in peak shape and retention times, but water, which is always present, considerably affects the baseline, making quantitative analysis unlikely.

The use of pure Carbopack A solved this problem as this material is able to elute large amounts of water rapidly, even at room temperature²³, without making changes in the baseline or affecting the elution of the peaks. The necessity of using liquid nitrogen in the trapping phase may be a problem, but this appears to be minor

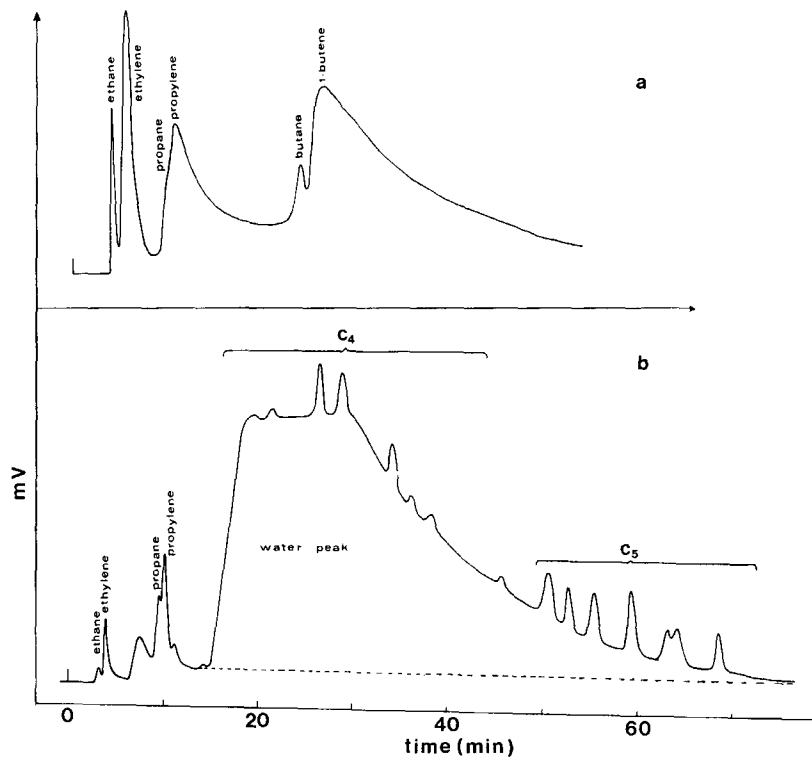


Fig. 3. Chromatograms of light hydrocarbons collected with unsatisfactory traps. (a) Activated charcoal used in filter cigarettes; (b) 10% AgNO_3 + 10% Carbowax on Carbowax A. Column as in Fig. 4.

compared with the advantage of the complete release of even the high-boiling trapped compounds.

In Table I, the efficiency of the trapping system described in Fig. 1 is reported. It appears that trapping efficiency is near to 100% for all of the compounds of interest

TABLE I
TRAPPING EFFICIENCY

Compound	Sample recovery* (%) (2 l N_2)	Sample recovery* (%) (3 l N_2)
Ethylene	95	62
Ethane	98	70
Propene	100	98
Propane	100	100
Isobutane	100	100
1-Butene	100	100
Isobutene	100	100
<i>n</i> -Butane	100	100
<i>cis</i> -2-Butene	100	100
<i>trans</i> -2-Butene	100	100

* Average of 10 measurements.

if 2 l of nitrogen are passed through the trap after injecting the standard mixture into it, while a significant loss of the C₂ compounds is observed when larger amounts of N₂ are passed. The trap temperature during sampling was -160°, which is about the minimum for avoiding any air condensation. On the other hand, a higher temperature results in too severe losses of the lighter compounds. The amount of air sampled is usually sufficient to collect a sufficient amount of pollutants for a chromatographic analysis in polluted areas.

Fig. 4 shows the analysis of the low-boiling organic fraction of an air sample collected in a Rome park, about 100 m away from traffic-bearing roads. All of the significant olefin peaks are separated sufficiently to permit their quantitative determination. The unlabelled peaks correspond to polar compounds or aromatic compounds which are still unidentified.

The column used was made of Carbowax B (90 m²/g) coated with 2.6% of Carbowax 1500 and was prepared according to Di Corcia and Samperi²⁴. This corresponds to about the maximum value of the lateral interactions which ensures maximum selectivity. The advantages of using a polar liquid phase for the elution of non-polar compounds on graphitized carbon black was discussed earlier¹². Briefly, the "squeezing" effect of the polar liquid phase makes retention times shorter, the selectivity with respect to the geometrical structure being still preserved. A different column prepared with 0.3% of squalene on Carbowax A gave analogous results, but resolution was lower and the peaks of *cis*-2-butene, *n*-butane and butadiene completely overlapped. The column was prepared with the aim of separating the olefins and saturated hydrocarbons up to C₆, because this is the lower limit of the solvent extraction method used in this work.

A complete analysis of the organic compounds found in air is obtained only if the trapping technique already described is coupled with solvent extraction; this is shown in Fig. 5. In this case, the trap is made of activated charcoal as used in filter cigarettes and the solvent is carbon disulphide. A 6 m × 0.7 mm I.D. micropacked column is used. This technique starts from the C₇ hydrocarbons, which is the upper limit of the heating stripping technique. The amount of air sampled was 250 l and the results obtained (number of peaks) were similar to those shown by Grob and Grob¹⁸, who used a 120-m high-efficiency glass capillary column.

The organic compounds contained in water may include many types, even very-high-boiling compounds. It is usually considered that graphitized carbon black has the disadvantage that high-boiling compounds cannot be eluted unless prohibitively high temperatures are used. The new type of material we are now using overcomes this difficulty and, at the same time, it enables low-boiling compounds to be separated on the same column. Fig. 6 shows a chromatogram of a synthetic mixture containing some reference compounds. The mixture was made with the aim of showing the wide range of compounds that can be eluted by a single column starting from room temperature and increasing the temperature to 320°. Fig. 6 also shows a characteristic and unique feature of GLSC, that is, the possibility for the same column to be operated with the same resolving power and efficiency over a much wider range of temperature than in GLC. In the latter technique, the efficiency of the column is adversely affected if the liquid phase becomes solid, so that different columns should be used for low-boiling and high-boiling compounds. The reverse is true in GLSC because in this type of gas chromatography the chromatographic technique is con-

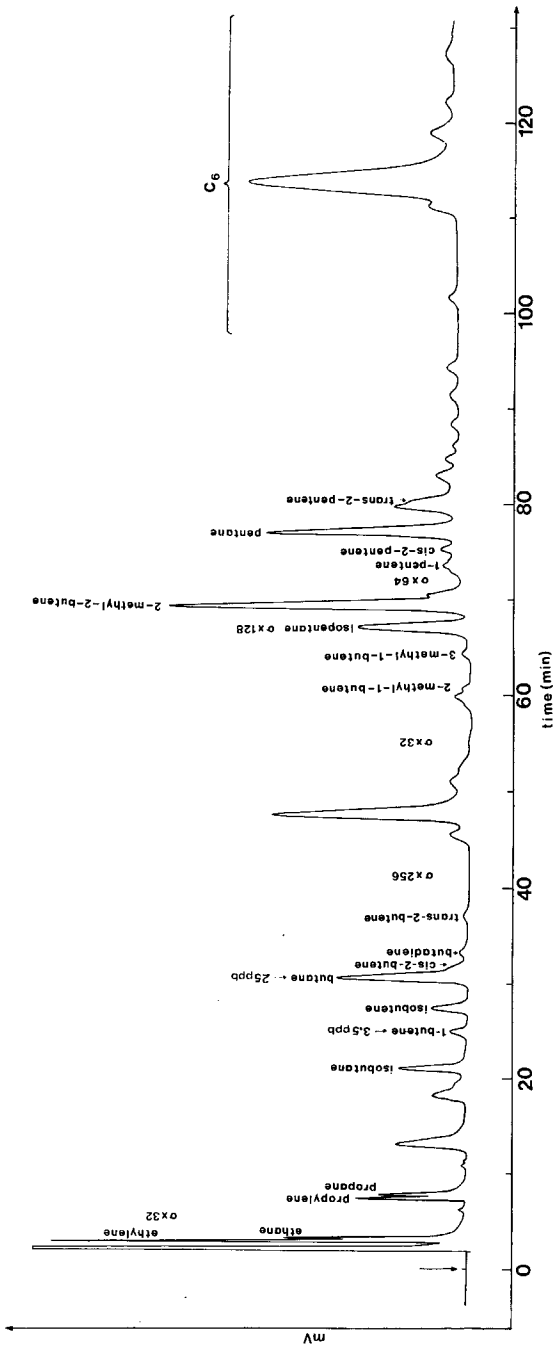


Fig. 4. Chromatogram of light hydrocarbons from air collected with a pure Carboxpack A trap. Injection temperature: 200°. Column: 4 m × 4 mm I.D., Carboxpack B + 2.6% Carbowax 1500, 80-100 mesh. Chromatographic conditions: inlet pressure, 2.5 kg/cm² (N₂); temperature, isothermal at 50° for 40 min, then programmed at 2°/min to 110°.

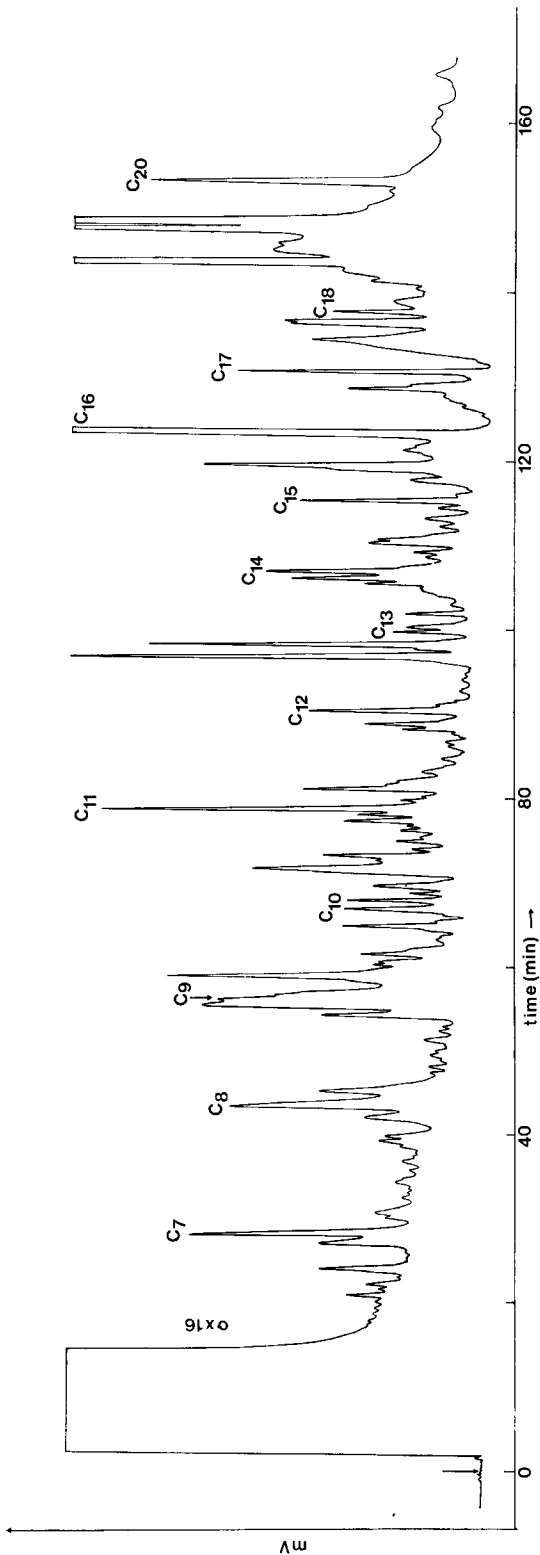


Fig. 5. Analysis of high-boiling organic compounds in air. Column: 6 m × 0.7 mm I.D., micropacked Carbo-pack A + 1.5% PPE 20, 100-120 mesh. Pressure: 5 kg/cm² (H₂). Temperature: 50° for 10 min, then programmed at 2°/min to 300°.

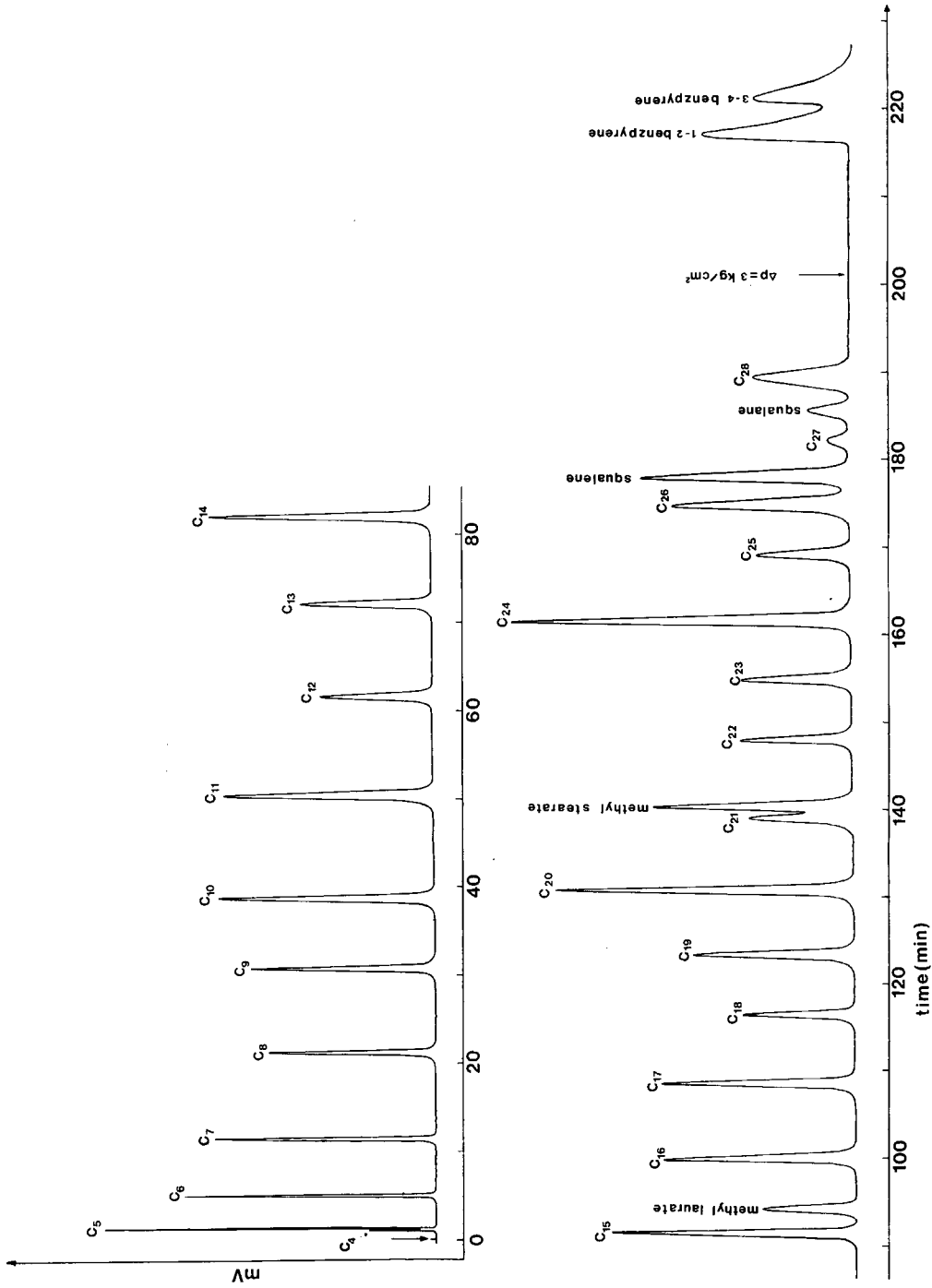


Fig. 6. Analysis of an artificial organic mixture. Column: 1.5 m \times 0.7 mm I.D., micropacked graphitized carbon black (12 m²/g), coated with 5% PPE 20, 100–120 mesh. $\Delta p = 1.5 \text{ kg/cm}^2$ (H_2) for 200 min, then 3.0 kg/cm². Temperature: 20° for 5 min, then programmed at 1.5°/min to 320°.

trolled by the solid support and the liquid phase does not serve to make a solution of the compounds eluted, as already demonstrated¹². The separation of the two benzo-pyrenes obtained on a column only 2 m long again shows the great separating power of carbon black for geometrical isomers. Finally, Fig. 6 shows that the column is of general use for water pollution analysis, where both polar and non-polar, relatively low-boiling and high-boiling compounds may be present. The use of PPE 20, a neutral and low-bleeding phase, is of great help in this type of analyses²⁵.

In Fig. 7, the analysis of a mixture of polynuclear hydrocarbons (run on the same column) is shown. According to recent work²⁶, the use of Apiezon L grease as the liquid phase in the analysis of polynuclear hydrocarbons seemed to give good results for the separation of isomeric compounds. We tried a column of the new type of carbon black coated with 2.5% of Apiezon L. The separation of 1,2- and 3,4-benzopyrene was achieved in about 1 h, with a 2-m micropacked column. However, when the use of the column was prolonged, retention times became increasingly longer because of the bleeding, so that it appeared unsuitable for use at 300°. This problem was solved by the use of PPE 20. Two features should be noted: the separation achieved between the pairs anthracene-phenanthrene and 1,2-benzopyrene-3,4-benzopyrene, and the short analysis time. This shows that the gas chromatography of polynuclear hydrocarbons can now be carried out by a very simple technique and routine analysis is now possible, the separation and identification of the most important compounds being ensured without the use of sophisticated techniques²⁷.

The results show that graphitized carbon black has many interesting applications in environmental analysis. Its use as general stationary phase makes this material

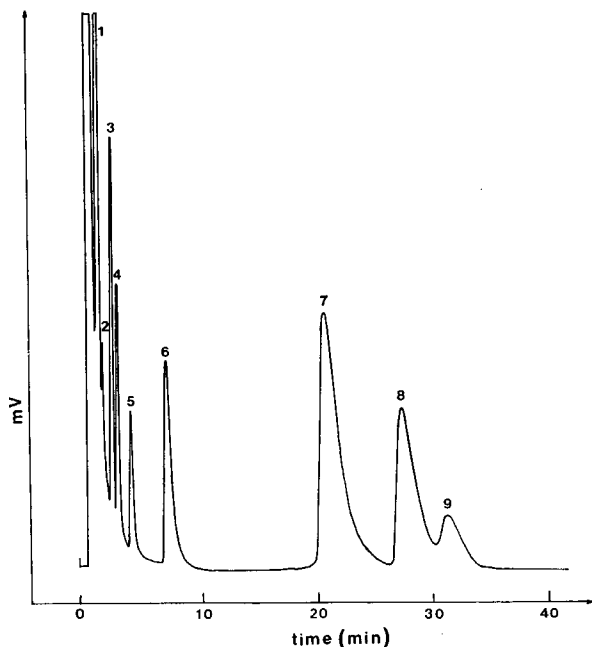


Fig. 7. Analysis of polynuclear hydrocarbons. Column as in Fig. 6. Temperature: 320° (isothermal). $\Delta p = 3 \text{ kg/cm}^2$ (H_2). 1 = Phenanthrene, 2 = anthracene, 3 = pyrene, 4 = fluoranthene, 5 = 3-methylpyrene, 6 = crysene, 7 = 3,4-benzofluoranthene, 8 = 1,2-benzopyrene, 9 = 3,4-benzopyrene.

most useful in the analysis of completely unknown and heterogeneous mixtures. Its major characteristics as a sampling adsorbent are that blanks are practically absent, and owing to its thermal stability the same trap* can be used for an unlimited number of sampling operations.

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* After completion of this manuscript, a paper by Raymond and Guiochon²⁸ came to our notice, in which the use of a similar trap was described.