CHROM. 10,077

HIGH-SPEED GAS CHROMATOGRAPHIC ANALYSIS IN PROCESS CONTROL*

C. L. GUILLEMIN and F. MARTINEZ

Centre de Recherches Rhone-Poulenc Industries, 93308 Aubervilliers (France)

(First received November 12th, 1976; revised manuscript received March 10th, 1977)

SUMMARY

Among the different criteria for a process gas chromatograph to be included in a closed loop control, the analytical credibility is one of the most important and can be improved by averaging the results of several analyses carried out during the response time of the process. This criterion resulted in high-speed gas chromatographic analysis being developed.

Modified adsorption chromatography with Spherosil is one means of reducing the time of analysis to 1 min without difficulty. Several examples are presented to show the potential of such a technique in process gas chromatography.

INTRODUCTION

In order to be included in a closed loop system for the control of chemical processes, some types of on-line analysers must have their analytical credibility increased. With a process gas chromatograph the analytical credibility can be improved by averaging the results of several analytical measurements carried out within the response time of the process.

These requirements led to the development of high-speed chromatography.

The problem of reliability has already been solved with a technique called the "deferred standard"[1-4], which consists on on-line checking of the process chromatograph. High-speed chromatographic analysis has been known for many years; there are examples in the literature as early as 1957[5] of separations performed within 1 min on capillary columns. However, for use in process gas chromatography (PGC) a simpler solution with similar performances is required.

SIMPLE AND ECONOMIC HIGH-SPEED GC ANALYSIS

In a previous paper on PGC[6], the properties of modified adsorption chroma-

---

tography were summarized, leading from classical analysis times (15–30 min), to accelerated analysis (5–15 min) and then to rapid analysis (1–5 min). The final step, the achievement of ultra-rapid analysis, with analysis times less than 1 min, is the result of studies undertaken during several years on Spherosil in modified gas–solid chromatography (GSC)[7-9].

When modified with thin layers of stationary phases, the main properties of Spherosil are as follows: decreased coefficient of mass transfer owing to a layer thickness of stationary phase between 10 and 20 Å (ref. 10); flatness of the Van Deemter curve, allowing faster carrier gas flow-rates, with a minimum loss in column efficiency; and efficient micro-packed columns, usable with common detectors; the final parameter to be considered in order to achieve very rapid analyses is the specific surface area. By considering these properties consecutively, the time of an analysis can be reduced by a factor of up to 30 without any difficulty.

As an illustration of this improvement, Fig. 1 shows the same mixture of five chlorinated hydrocarbons separated in different ways. In Fig. 1A, classical partition chromatography effects the separation in 25 min. In Fig. 1B, the separation is now achieved in 5 min, simply as a result of using modified adsorption instead of partition chromatography. This step is called "accelerated analysis". In Fig. 1C, the separation time is halved again by increasing the linear velocity of the carrier gas. However, in order to keep the volumetric flow-rate compatible with common industrial detectors (thermal conductivity or flame ionization), the column diameter has to be decreased. This is the "rapid analysis" step. In general, micro-packed columns of I.D. 1 mm are more efficient than 1/4-in. columns packed with the same material. Fig. 1D corresponds to "ultra-rapid analysis", which can be considered the cumulative result of the different properties considered above.

It has been shown[7-9] that the straightforward rules which govern any separation in modified gas–solid chromatography with Spherosil are as follows: at a constant specific surface area, S, and with a variable film thickness, d_f, the selectivity is variable; and with a variable S but constant d_f, the selectivity is constant. The latter rule means that superimposable chromatograms can be obtained on Spherosil of different specific surface areas, provided that the total surface energy is the same for the different columns. In other words, if d_f is constant, the product of the specific surface area of Spherosil and the column length has to be a constant, to first approximation:

$$S \cdot L = \text{constant} \tag{1}$$

By assuming that a homogeneous and reproducible packing is obtainable, the weight, W, of the packing can be replaced with the column length, L. Shortening an analytical sequence will involve increasing the specific surface area and reducing the column length, and consequently the dead volume of the column will be smaller.

Fig. 2 is an illustration of superimposable chromatograms of chlorinated hydrocarbons separated on two different types of Spherosil, with $S = 28$ and 200 m²/g, but coated with a constant layer thickness of stationary phase. It can easily be seen that the amount of stationary phase is proportional to the specific surface area:

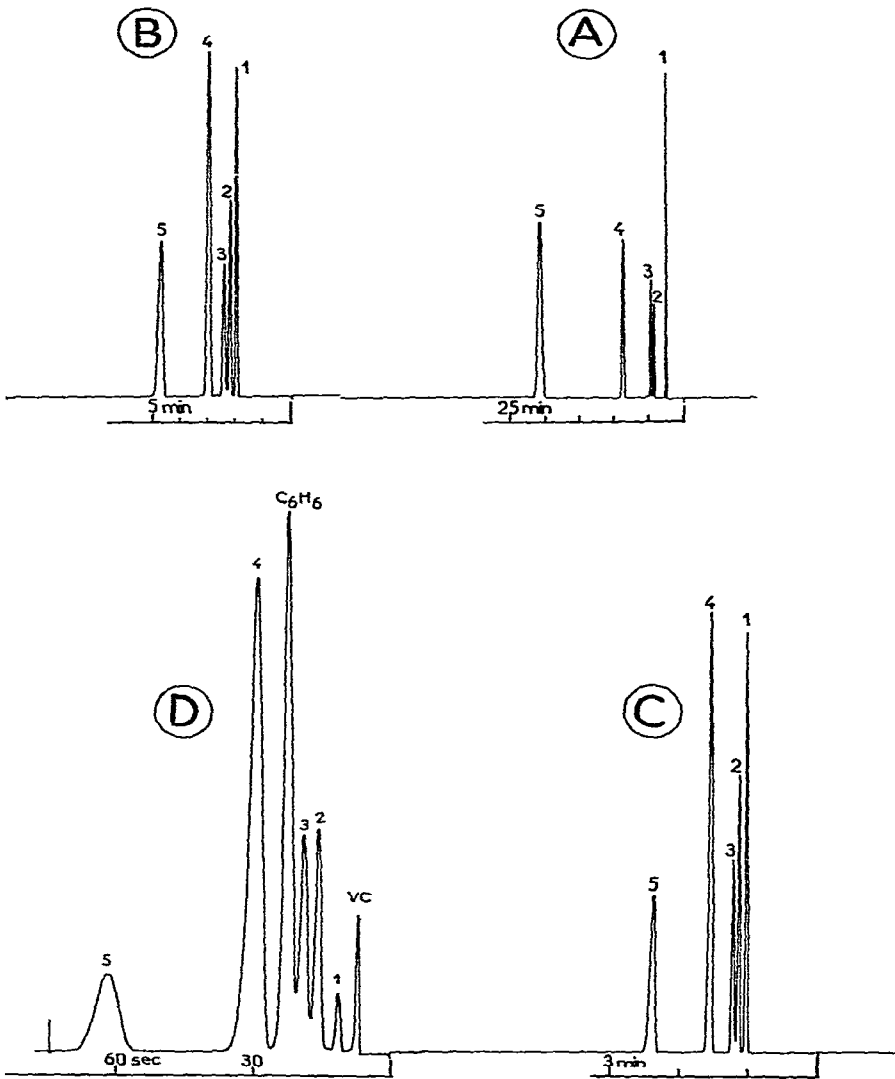$$\frac{W_1}{S_1} = \frac{W_2}{S_2} \qquad \frac{2}{28} \approx \frac{14}{200} = 0.07$$

Fig. 1. Separation of a mixture of chlorinated hydrocarbons. Peaks: (1) vinylidene chloride; (2) methylene chloride; (3) carbon tetrachloride; (4) 1,2-dichloroethane; (5) 1,1,2-trichloroethane; VC, vinyl chloride; C_6H_6, benzene. (A) Partition chromatography (classical analysis). Column, 4 m × 4 mm I.D., Chromosorb P (d_p = 145–175 μm) + Carbowax 20M (20 g per 100 g); temperature, 130°; flow-rate (N_2), 3 l/h; Δp, 1.8 bar; injection, 1 μl of liquid. (B) Modified gas–solid chromatography (accelerated analysis). Column, 4 m × 4 mm I.D. Spherosil (28 m²/g, d_p = 125–200 μm) + Carbowax 20M (2 g per 100 g); temperature, 130°; flow-rate (N_2), 3 l/h; Δp, 2.5 bar; injection, 1 μl of liquid. (C) Modified gas–solid chromatography (rapid analysis). Column, 5 m × 1 mm I.D. Spherosil (28 m²/g, d_p = 125–200 μm) + Carbowax 20M (2 g per 100 g); temperature, 130°; flow-rate (N_2) 0.9 l/h; Δp, 5 bar, injection, 1 μl of liquid. (D) Modified gas–solid chromatography (ultra-rapid analysis). Column, 0.7 m × 1 mm I.D. Spherosil (200 m²/g, d_p = 80–90 μm) + Carbowax 20M (14 g per 100 g); temperature, 130°; flow-rate (N_2), 1.25 l/h; Δp, 5 bar; injection, 0.05 μl of liquid.
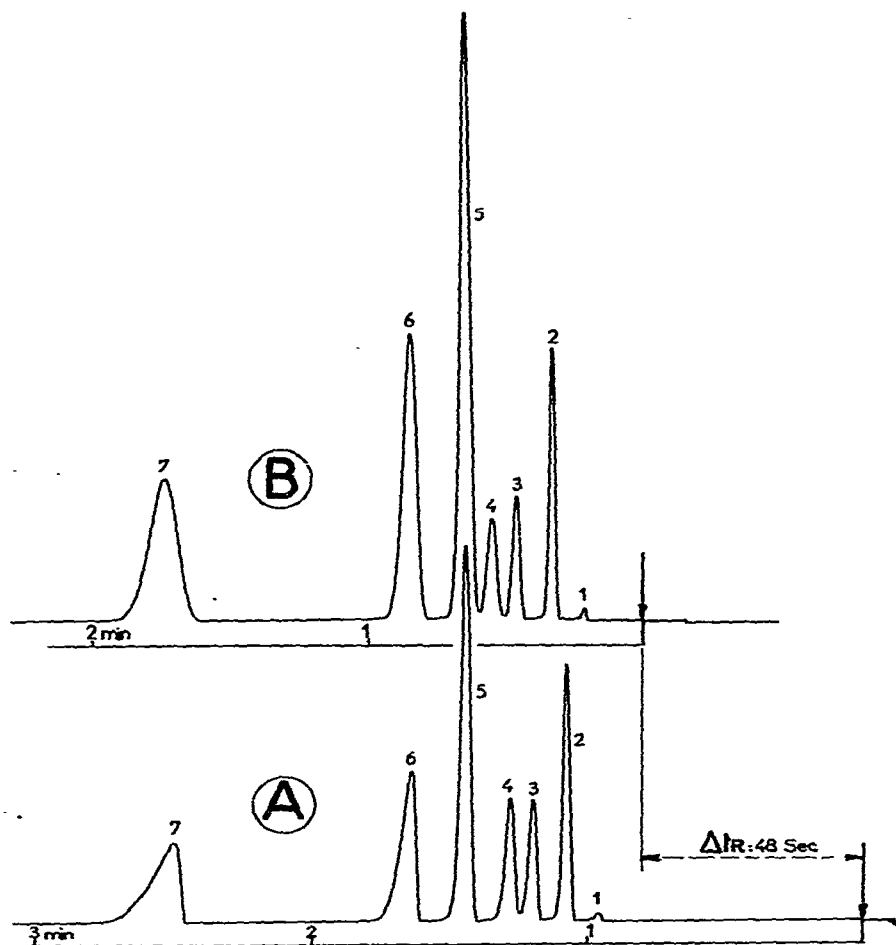
Fig. 2. Superimposable chromatograms of chlorinated hydrocarbons obtained on two different types of Spherosil. (A) Column, 5 m × 1 mm I.D. Spherosil (28 m²/g, d_p = 125–200 μm) + Carbowax 20M (2 g per 100 g) temperature, 130°; flow-rate (N₂), 3 l/h. (B) Column, 0.7 m × 1 mm I.D. Spherosil (200 m²/g, d_p = 80–90 μm) + Carbowax 20M (14 g per 100 g); temperature, 130°; flow-rate (N₂), 0.40 l/h. Peaks: (1) vinyl chloride; (2) vinylidene chloride; (3) methylene chloride; (4) carbon tetrachloride; (5) benzene; (6) 1,2-dichloroethane; (7) 1,1,2-trichloroethane.

and that the product $S \cdot L$ is constant:

$$S_1 \cdot L_1 = S_2 \cdot L_2$$

$$28 \cdot 5 = 200 \cdot 0.70 = 140$$

By applying the above properties (using a micro-packed column of coated Spherosil, increasing S, reducing L and increasing the carrier flow-rate), the mixture of chlorinated hydrocarbons containing two additional compounds (vinyl chloride and

benzene) is now separated in 72 sec on a column of I.D. 1 mm and length 70 cm packed with Spherosil (200 m²/g) coated with Carbowax 20M (14 g per 100 g).

In addition, it must be pointed out that under the conditions used 950 theoretical plates (1350 plates/m) generated by the 70-cm column were sufficient to perform this separation, in spite of the 6-fold higher flow-rate than the optimum. Increasing the flow-rate still further would lead to an analysis time within the 60 sec required, but the resolution between the peaks would be poorer, despite the fact that the Van Deemter curve is rather flat in modified GSC (Fig. 3), and that the flow-rate can be increased.
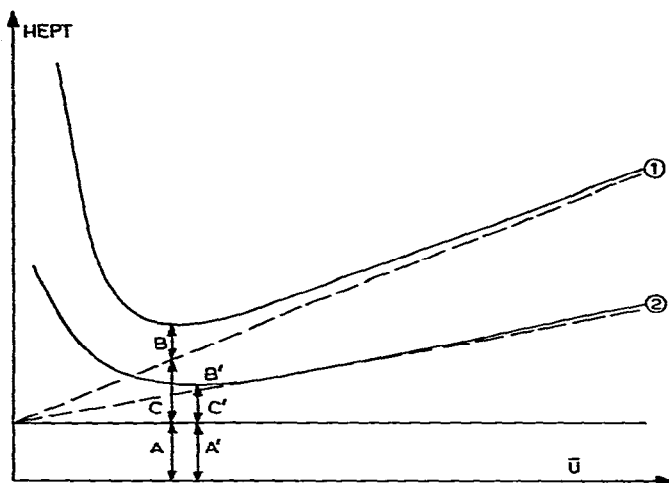

Fig. 3. Schematic curves of Van Deemter equation: HETP = f(u). (1) In partition chromatography; (2) in modified adsorption chromatography.

The resolution (R), which depends on the column efficiency and selectivity, is given by the well known equation

$$R = \frac{1}{4} \left(\frac{\alpha-1}{\alpha}\right) \cdot \left(\frac{k'_2}{1 + k'_2}\right) \sqrt{N_2}$$

where

α = relative retention, i.e. the ratio K_2/K_1 of the partition coefficients of components 2 and 1;

k'_2 = capacity factor of component 2;

N = number of theoretical plates, calculated on peak 2.

In modified GSC on Spherosil, a decrease in resolution can be partly balanced on the one hand by using higher specific surface areas, which gives a higher selectivity[8] (see Figs. 5A and 5B), and on the other hand by trying to increase the total number of theoretical plates or, better, the number of effective plates per second as speed of analysis is the main concern.

The solution of the last problem was given by Huber et al.[11], who recommended that the particle size should be reduced to 30–50 μm in GC, by analogy with the effect of particle size in high-performance liquid chromatography. According to Huber et al., column efficiencies of 10,000 plates/m are feasible, but there is a pressure drop, which in this instance can reach 30–50 bar. However, when applied to shorter columns

of coated Spherosil, this concept may be convenient and compatible with the present PGC technology, which tolerates no more than 8–10 bar of back-pressure in the pneumatic circuits.

Figs. 4A and 4B illustrate the Huber *et al.* theory combined with the effect of a high specific surface area of Spherosil and the selectivity of the liquid stationary phase. The same mixture of chlorinated hydrocarbons is still separated within 60 sec, but in this instance a column only a 8 cm long and 1 mm I.D. of Spherosil (200 m²/g) coated with β,β'-oxydipropionitrile (ODPN, 14.5 g per 100 g), with a particle size distribution between 25 and 40 μm, was sufficient to achieve this separation (Fig. 4A). Despite a 4-fold greater flow-rate than the optimum, the column back-pressure was only 1.9 bar and the column generated 250 theoretical plates (3,125 plates/m) or 5 N_{eff}/sec. Fig. 4B shows the limits of the technique: a 4-cm column filled with the same packing still allows a useful separation of the mixture.
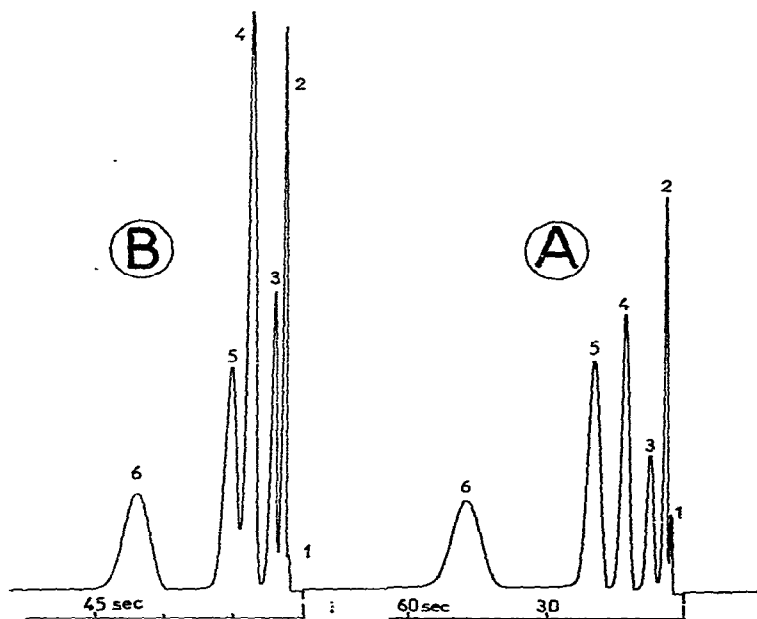

Fig. 4. Separation of chlorinated hydrocarbons on a short GC column. (A) Column, 8 cm × 1 mm I.D. Spherosil (200 m²/g, d_p = 25–40 μm) + β,β'-oxydipropionitrile (14.5 g per 100 g); temperature, 85°; flow-rate (N₂), 0.66 l/h; Δp, 1.9 bar; injection, 0.05 μl of liquid. (B) Column, 4 cm × 1 mm I.D. Spherosil (200 m²/g, d_p: 25–40 μm) + β,β'-oxydipropionitrile (14.5 g per 100 g); flow-rate (N₂), 0.22 l/h; Δp, 0.75 bar, injection, 0.02 μl of liquid. Peaks: (1) vinyl chloride; (2) vinylidene chloride; (3) carbon tetrachloride; (4) benzene; (5) 1,2-dichloroethane; (6) 1,1,2-trichloroethane.

This technique of shortening the column in GC when using a support with a higher specific surface area is similar to that already used in high-performance liquid chromatography[12].

Although these column performances can be increased by using suitable chromatographs avoiding dead volumes up- and down-stream of such short columns, or by improving the packing technique for small particles, etc., it must be borne in mind

that the aim is not to attain spectacular performances but only to perform high-speed PGC analyses with a reduced operating cost. A compromise among the different parameters such as column length, specific surface area of Spherosil, particle diameter and amount of sample injected has to be found when the existing equipment is to be used. However, a process gas chromatograph specially designed for short columns would be able to overcome the problem of the installation of the analyser with regard to the location of the sample injection. The compact analytical unit of such a chromatograph could be located very close to the sample probe, so that the influence of the nature and the response time of the sampling system would be minimized.

EXAMPLES OF HIGH-SPEED GC ANALYSIS

All of the experiments were carried out on a Carlo Erba 2400 laboratory chromatograph equipped with flame-ionization detectors. The shortest columns were connected to the injection port and to the detector, with intermediate empty tubes, respectively, of length 15 cm, I.D. 1 mm, and length 15 cm, I.D. 0.25 mm.

Figs. 5A and 5B show a synthetic blend of normal aliphatic C_6–C_{16} hydrocarbons separated at 180° on 1-mm I.D. column, under the following conditions: In Fig. 5A, the separation was achieved in $3\frac{1}{2}$ min by using a 35-cm column of Spherosil (93 m²/g) coated with Carbowax 20M (20 g per 100 g) and a nitrogen flow-rate of 0.24
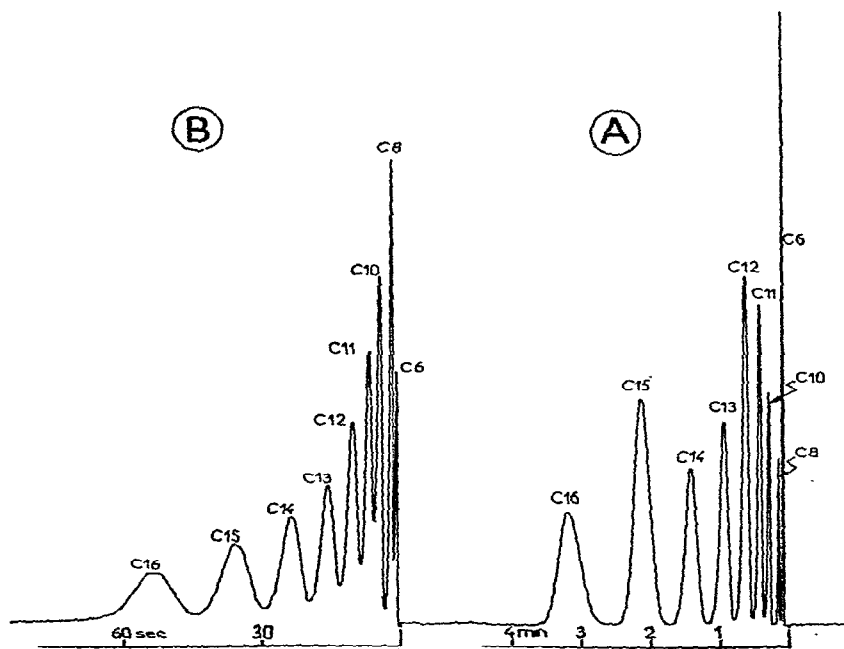

Fig. 5. Separation of saturated C_6–C_{16} aliphatic hydrocarbons. (A) Rapid analysis. Column, 35 cm × 1 mm I.D. Spherosil (93 m²/g, d_p = 150–160 μm) + Carbowax 20M (20 g per 100 g); temperature, 180°; flow-rate (N_2), 0.25 l/h; Δp, 0.8 bar; injection, 0.1 μl of liquid. (B) Ultra-rapid analysis. Column, 35 cm × 1 mm I.D. Spherosil (200 m²/g, d_p = 100–125 μm) + Carbowax 20M (40 g per 100 g); temperature, 180°; flow-rate (N_2), 2 l/h; Δp, 4.8 bar; injection, 0.1 μl of liquid.

l/h; in Fig. 5B, the separation was achieved in 65 sec with a 17-cm column of Spherosil (200 m²/g) coated with Carbowax 20M (40 g per 100 g) in order to obtain the same film thickness. In this instance the carrier gas flow-rate was increased to 2 l/h in order to decrease the analysis time. It must be pointed out that in Fig. 5B the first peaks emerge very rapidly (*ca.* 1 sec) and good quantitative results can be obtained only with a computerized data reduction system.

A complex mixture of nine alcohols, the composition of which is given in Fig. 6, was separated in 4 min on a 70-cm, 1-mm I.D. column of Spherosil (200 m²/g) coated with Carbowax 20M (14 g per 100 g) at 160°. In spite of the high specific surface area of the support, the peaks are well shaped; this result is probably due to a homogeneous coating of stationary phase.
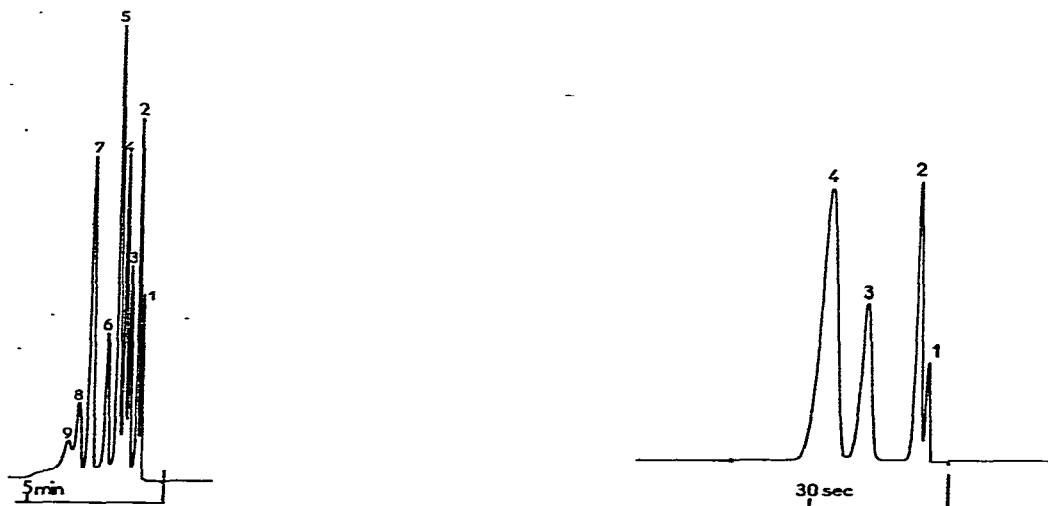

Fig. 6. Separation of a mixture of alcohols. Column, 70 cm × 1 mm I.D. Spherosil (200 m²/g, d_p = 80–90 μm) + Carbowax 20M (14 g per 100 g); temperature, 160°; flow-rate (N₂), 0.2 l/h; Δp, 1.6 bar; injection, 0.05 μl of liquid. Peaks: (1) ethanol; (2) isopropanol; (3) 1-propanol; (4) 2-butanol; (5) 2-methyl-2-butanol; (6) 3-methyl-2-butanol; (7) 2-methyl-1-pentanol; (8) 2-methyl-1-butanol; (9) 3-methyl-1-butanol.

Fig. 7. Separation of acetates. Column, 17 cm × 1 mm I.D. Spherosil (93 m²/g, d_p = 80–90 μm) + Carbowax 20M (20 g per 100 g); temperature, 130°; flow-rate (N₂) 0.2 l/h; Δp, 1 bar; injection, 0.05 μl of liquid. Peaks: (1) methyl acetate; (2) ethyl acetate; (3) butyl acetate; (4) isoamyl acetate.

Fig. 7 illustrates the separation of four acetate esters in 35 sec with a 17-cm, 1-mm I.D. column packed with Spherosil (93 m²/g) coated with Carbowax 20M (20 g per 100 g) at 130°. The resolution of the peaks is satisfactory, and a faster analysis could easily be achieved by increasing the carrier gas flow-rate.

An air-pollution analysis of four components (vinyl acetate, ethyl acrylate styrene and butyl acrylate) is carried-out in 40 sec by using an 8-cm, 1-mm I.D. column of Spherosil (200 m²/g) coated with triscyanoethoxypropane (25 g per 100 g)

(Fig. 8). In this instance, an efficiency of 400 theoretical plates in 8 cm was obtained (5,000 plates/m or 10 N_{eff}/sec) owing to the use of a small particle size (20–25 μm).

Trace analysis is possible in high-speed GC with short columns: impurities at concentrations below 200 ppm in 1,2 dichloroethane have been separated easily on an 8-cm, 1-mm I.D. column of Spherosil (200 m²/g) coated with β,β'-oxydipropionitrile (14 g per 100 g) at 85° (Fig. 9). In spite of the small column dimensions, no overloading was observed; the major peak showed no tailing and the chromatogram was satisfactory.
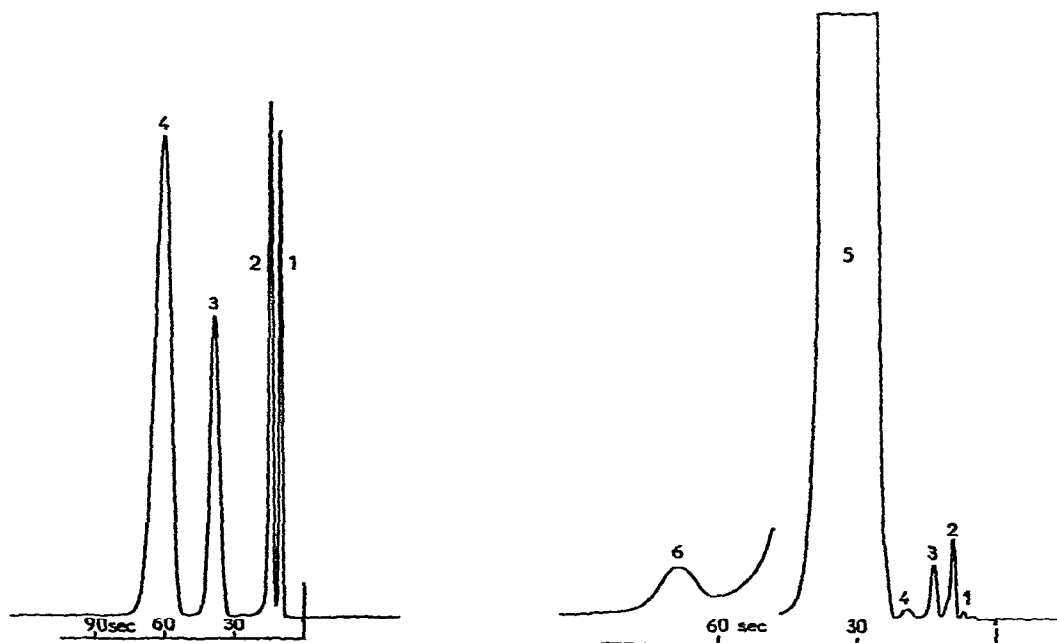

Fig. 8. Separation of airborne pollutants. Column, 8 cm × 1 mm I.D. Spherosil (200 m²/g, d_p = 25–40 μm) + triscyanoethoxypropane (25 g per 100 g); temperature, 100°; flow-rate (N₂), 1 l/h; Δp, 4.75 bar; injection, 0.05 μl of liquid. Peaks: (1) vinyl acetate; (2) ethyl acrylate; (3) styrene; (4) butyl acetate.

Fig. 9. Analysis of trace impurities in 1,2-dichloroethane. Column, 8 cm × 1 mm I.D. Spherosil (200 m²/g, d_p = 25–40 μm) + β,β'-oxydipropionitrile (14 g per 100 g); temperature, 85°; flow-rate (N₂), 0.2 l/h; Δp, 1 bar; injection, 0.04 μl of liquid. Peaks: (1) vinyl chloride; (2) vinylidene chloride; (3) methylene chloride; (4) carbon tetrachloride; (5) 1,2-dichloroethane; (6) 1,1,2-trichloroethane.

CONCLUSION

The characteristics of Spherosil (specific surface area and particle size) have been shown to allow tailor-made chromatographic performances from classical to ultra-rapid. Owing to the straightforward rules developed for this support in modified gas–solid chromatography, high-speed PGC analysis becomes economically feasible in comparison with other techniques such as the use of capillary columns. However, interest in high-speed analyses with Spherosil lies not only in a simple comparison with other techniques; a new trend in PGC can be foreseen. The process GC analyser

could be miniaturized as a result of the use of short columns, would be more reliable owing to the deferred standard technique, and its response more credible by increasing the number of analyses averaged by the incorporated miniprocessor. By setting it close to the sample injection point in the process, the sample line would be shortened and simplified and the total response time of the analysis would be considerably reduced. With such a process gas chromatograph, a further step towards process automation could be made.

REFERENCES

1 C. L. Guillemin, J. Vermont, P. Juston, P. Ferradini and P. Peyron, *J. Chromatogr. Sci.*, 9 (1971) 155.
2 C. L. Guillemin, *Mesures*, No. 4 (1972) 87.
3 C. L. Guillemin, *Mesures*, No. 5 (1972) 99.
4 C. L. Guillemin *Instrum. Technol.*, April (1975) 43.
5 L. S. Ettre, *Open Tubular Columns in GC*, Plenum Press, New York, 1965, p. 48.
6 C. L. Guillemin, *Mesures*, No. 7/8 (1976) 41.
7 C. L. Guillemin, M. Le Page and A. J. de Vries, *J. Chromatogr. Sci.*, 9 (1971) 470.
8 C. L. Guillemin, M. Deleuil, S. Cirendini and J. Vermont, *Anal. Chem.*, 43 (1971) 2015.
9 S. Cirendini, J. Vermont, J. C. Gressin and C. L. Guillemin, *J. Chromatogr.*, 84 (1973) 21.
10 J. C. Giddings, *Dynamics of Chromatography, Part I, Principles and Theory*, Marcel Dekker, New York, 1965.
11 J. F. K. Huber, H. H. Lauer and H. Poppe, *J. Chromatogr.*, 112 (1975) 377.
12 J. Vermont, M. Deleuil, A. J. de Vries and C. L. Guillemin, *Anal. Chem.*, 47 (1975) 1329.