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# RAPID GAS CHROMATOGRAPHIC ANALYSIS ON SPHEROSIL

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## SUMMARY

Rapid gas chromatographic analyses are necessary in industrial routine control operations that are carried out by means of laboratory or process gas chromatography.

A reduction in the analysis time by a factor of 2–5 can be easily achieved without the need for additional chromatographic equipment by using micropacked columns of Spherosil. In order to carry out rapid analyses on Spherosil in either gas–solid or modified gas–solid chromatography, several parameters can be varied: carrier gas linear velocity, column diameter, particle size range, etc.

Some examples are given to show the potentialities of Spherosil in separating various molecules.

## INTRODUCTION

The problem of rapid analysis is considered here only in connection with routine control, either in the laboratory or in the plant, with process gas chromatographs.

In general, in routine process control, rapid analysis has virtually not been considered, although it was developed as early as 1957 with the Golay open tubular columns[1]. The present problem is to decide whether rapid analysis is useful for control purposes, and if so, why such a development has been limited. Although time saving is always the aim, at present other factors have to be considered. First of all, in plants, the amount of analysis to be undertaken is increasing, whereas the number of personnel is decreasing. But the increasing use of computers for closed-loop control is perhaps one of the main reasons; such a development implies greater credibility and reliability of analyses, which may be achieved by statistical, rather than, unitary measurements at a particular time. It is probably true that rapid analysis would have been developed earlier in process control if the use of capillary columns did not raise more problems than it solved in this type of application.

Capillary columns are difficult to prepare and require special equipment and skilled personnel. In order to avoid overloading during sample injection, the use of a stream splitter is essential, the linearity of which must always be proved in quantitative analysis. At present, process gas chromatographic (GC) injectors cannot repeatedly deliver volumes of liquid less than 1 $\mu$l. As the injection volumes required by capillary columns are so small, the choice of detector is limited to the flame ionization detector (FID) because of its sensitivity and dead volume.

However, some of these disadvantages were overcome with the development of the packed capillary columns of Halász and Heine[2] and of Landault and Guiochon[3], prepared by drawing out a packed glass tube, but because of their fragility, such columns have never been used in process GC.

More recently, Cramers *et al.*[4] and Landault and Guiochon[5] have shown the usefulness of micropacked columns of I.D. 0.5–1 mm, which have many advantages over capillary and normally packed columns.

By using micropacked columns of Spherosil[6–8], rapid analyses are not only feasible, but are also compatible with the requirements of routine control in the laboratory or plant.

In this paper, a rapid analysis is defined as one giving a time saving of a factor of 2–5 with respect to present analysis times of 15–30 min.

## PREPARATION OF MICROPACKED COLUMNS OF SPHEROSIL

### *Coating procedure*

Spherosil can be used in either gas–solid[7] or modified gas–solid chromatography (GSC) with various stationary phases[8] that can be used successfully for the four groups of molecules according to Kiselev's classification[9].

The coating procedure is similar to that used for classical supports, apart from some specific differences. For this procedure, the use of a rotating evaporator is recommended, in which the following steps are carried out. (*a*) Dehydration of Spherosil at 150° for 2 h in a vacuum. This essential step prevents the bleeding of the liquid phase by the steam absorbed into the pores when Spherosil is used above 100°. (*b*) Cooling the Spherosil to room temperature in a vacuum. Air and gases have to be avoided in order to give a better distribution of the coating solution in the pores. (*c*) Addition of the pure, dried solvent so that the Spherosil is completely immersed. The solvent must be polar in order to be compatible with the hydroxyl groups of Spherosil and the liquid phase itself. The preferred solvents are alcohols, ketones, etc. (*d*) Addition of the liquid phase diluted with the solvent. The amount of liquid phase to be coated on the Spherosil depends on the specific surface area of the particles; with Spherosil the term "film thickness" of the liquid phase instead of "percentage", as with classical supports, is used. For the common stationary phases, with a film thickness of 10–20 Å, the nomograph shown in Fig. 1 gives the correspondence between the film thickness ($e_A$=20 Å) and the amount in grams of the liquid phase of density $\rho$, for 100 g of Spherosil of specific surface area $S$. (*e*) The mixture of solvent, liquid phase and Spherosil is stirred for 1 h before evaporating. (*f*) Removing the solvent. The solvent is conveniently evaporated by applying heat from an infrared source, while the coated support is gently stirred in the rotating evaporator. (*g*) Baking the Spherosil. In order to create mechanical or physical forces or even chemical bonding, the baking procedure can take place either before filling the column or *in situ* after it has been filled with the coated support. The temperature of baking depends on the nature of the stationary phase:

| | |
|---|---|
| $\beta,\beta'$-Oxydipropionitrile . . . . . | 110° for 2 h |
| Carbowax 20M . . . . . | 250° for 2 h |
| Squalane . . . . . | 150° for 10 h |

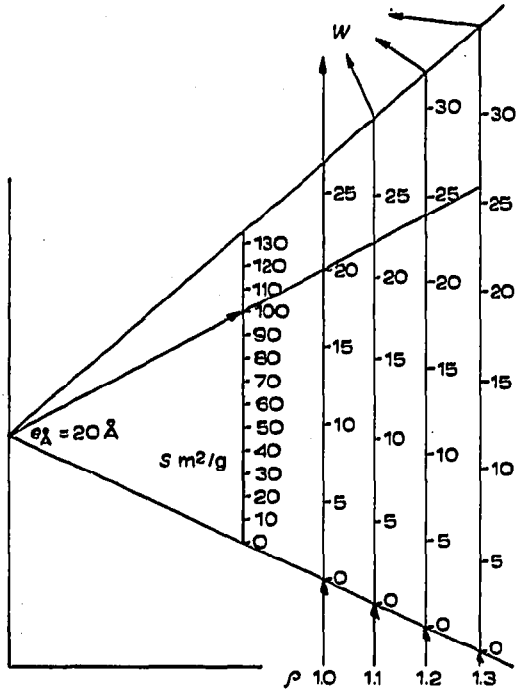



Fig. 1. Nomograph giving the weight of stationary phase of density $\varrho$ to be coated on 100 g of Spherosil of given specific surface area $S$, and for a film thickness $e_A$ of 20 Å. $W = e_A \cdot \varrho \cdot S \cdot 100$.

In general, as a result of this baking, the temperature limit at which the liquid phases can be used is higher than that recommended by the manufacturers. For instance, $\beta,\beta'$-oxydipropionitrile can be heated up to 110° without baseline drift (see Fig. 18). In order to reflect the difference between the classical coating procedure and this special coating and baking procedure with Spherosil, we suggest the name "toasted Spherosil", because it is as difficult to remove the liquid phase from this support as it is to scrape butter from warm toast.

When the bonding is of an ester type, Si–O–R, moisture is to be avoided in order to prevent any hydrolysis of such bonds.

For GC applications, Spherosils of specific surface areas 5–100 $m^2/g$ are recommended, but as a rule the specific surface area chosen will be smaller, the higher is the polarizability of the molecules to be separated[8].

*Packing procedure*

In order to pack columns of 1 mm I.D., the empty clean tube of good quality (to avoid wall adsorption effects, good quality tubing should be used) is connected upstream to a reservoir filled with coated Spherosil and downstream to a vacuum pump. The reservoir is connected to an inert gas cylinder. During the packing operation, the coiled column is submitted to vibrations by using a vibrator or by tapping it while first a vacuum and then progressively the pressure of the inert gas (up to 15 bars) are applied.

All of the narrow particle size distributions used were obtained by sieving the commercial particle size range of 100–200 $\mu$m.

## OPTIMIZATION OF ANALYSIS TIME

Several parameters contribute to the optimization of the analysis time when using micropacked columns of Spherosil, and they are examined below in order of importance.

*Linear velocity of the carrier gas*

It is well known that the velocity of mass transfer in adsorption chromatography is high[9–12]; the main reasons being the high diffusivity of gaseous molecules inside and outside the pores of the adsorbant particles, and the low coefficient of resistance to mass transfer of the molecules relative to the surface energy of the adsorbent. Because of such instantaneous equilibria, the band spreading, or in other words the loss of column efficiency, which appears when the linear velocity of the carrier gas is increased, is not so high in adsorption as in partition chromatography.

The contribution of the $C\bar{u}$ term of the Van Deemter equation[13]

$$H = A + \frac{B}{\bar{u}} + C\bar{u}$$

being a minimum, the graphs of $H=f(\bar{u})$ are flat, which is characteristic of this type of chromatography. Fig. 2, curve A, shows such a curve for adsorption chromato-

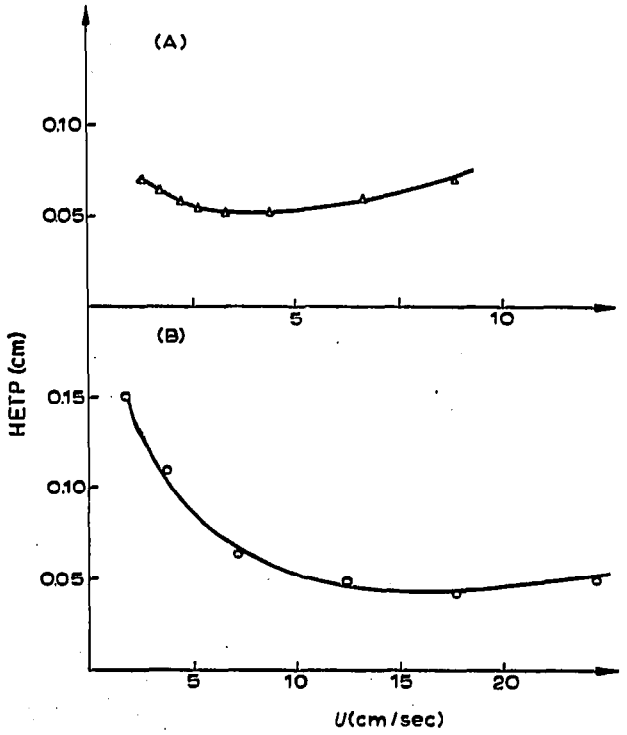



Fig. 2. Plots of HETP *versus* linear velocity of the carrier gas at the column outlet. (A) Spherosil in gas–solid chromatography ($S=77$ m²/g). (B) Spherosil in modified gas–solid chromatography ($S=28$ m²/g coated with Carbowax 20M, 2 g per 100 g; $e_A \approx 10$ Å).

graphy using a Spherosil of specific surface area 77 $m^2/g$. In this particular case, increasing the velocity by a factor of 2 involves a 25% loss in the number of theoretical plates.

Fig. 3 illustrates this phenomenon by showing a mixture of chlorofluorohydrocarbons eluted at different carrier gas flow-rates. With a flow-rate seven times higher, the time required for such an analysis has been reduced by a factor of 3, with almost identical resolutions between the peaks (resolution between peaks 5 and 6: 2.50 with 2 l/h of He and 2.34 with 15 l/h of He).

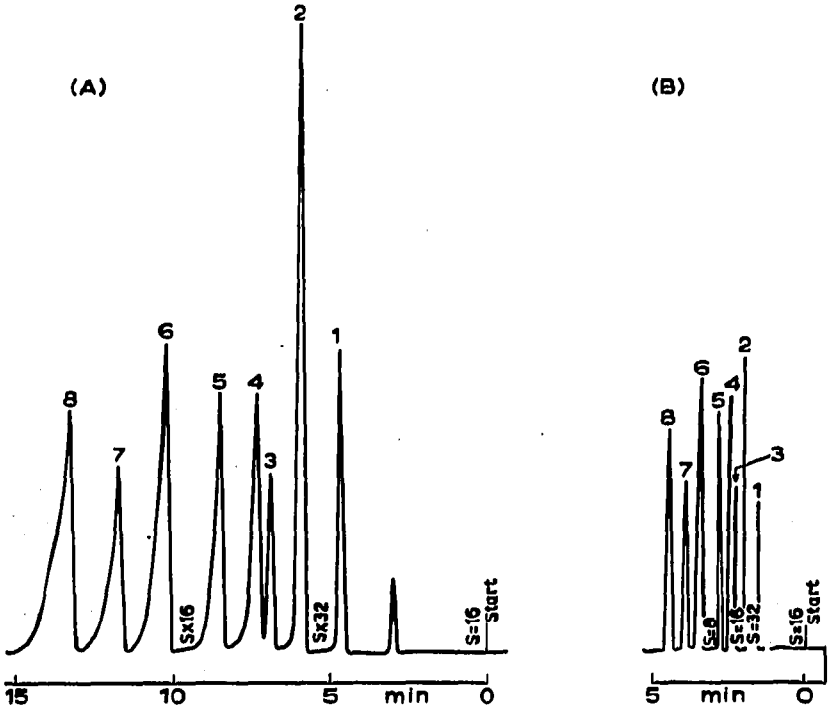



Fig. 3. Influence of carrier gas flow-rate on the separation of some hydrocarbons and halogenated hydrocarbons by GSC on Spherosil. Spherosil XOB 075 (50 $m^2/g$); column length 6 m; isothermal temperature 70°. (A) He flow-rate 2 l/h; (B) He flow-rate 15 l/h. 1, Propane; 2, $F_{12}$ ($CF_2Cl_2$); 3, isobutane; 4, *n*-butane; 5, $F_{22}$ ($CHF_2Cl$); 6, $F_{114}$ ($C_2F_4Cl_2$); 7, vinyl chloride; 8, $F_{11}$ ($CFCl_3$).

In spite of this important property of adsorbents, their use is limited to the first two groups of molecules according to Kiselev's classification[9], *i.e.*, saturated and unsaturated hydrocarbons. For polar molecules with oxygen atoms, such as alcohols, aldehydes, etc., separation on an adsorbent is impossible. However, Guillemin *et al.*[8] have shown recently that Spherosil, used in modified GC, when coated with thin layers of stationary phases, may be useful for the separation of polar compounds and in rapid analysis.

Owing to the small resistance to mass transfer offered by monolayers, higher flow-rates are possible with a minimum loss in column efficiency, as shown in Fig. 2, curve B, for a Spherosil of specific surface area 28 $m^2/g$ coated with Carbowax 20M (2 g per 100 g). As an illustration of this phenomenon, Fig. 4 shows the separation

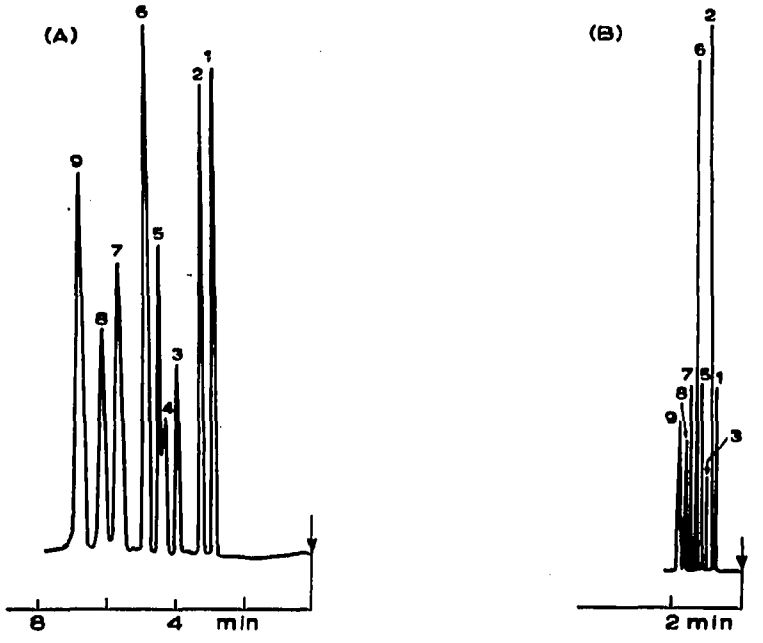



Fig. 4. Influence of carrier gas flow-rate on the separation of some chlorinated $C_1$ and $C_2$ hydrocarbons in modified GSC on Spherosil. Spherosil XOB 030 (27 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Particle size range, 100–200 $\mu$m. Column length, 4 m. Isothermal temperature, 100°. (A) $N_2$ flow-rate, 3 l/h for column of I.D. 4 mm, $\Delta P = 3$ bars. (B) $N_2$ flow-rate, 1.5 l/h for column of I.D. 1 mm, $\Delta P = 6$ bars. 1, Vinylidene chloride; 2, *trans*-dichloroethylene; 3, methylene chloride; 4, 1,1-dichloroethane; 5, carbon tetrachloride; 6, 1,1,1-trichloroethane; 7, *cis*-dichloroethylene + trichloroethylene; 8, chloroform; 9, 1,2-dichloroethane.

of chlorinated hydrocarbons carried out on the same material but with two different linear velocities of the carrier gas. By increasing the velocity by a factor of 8, the analysis time was shortened from 8 to 2 min, with about the same resolution.

*Column diameter*

Increase the carrier gas flow-rate with classical columns of 3 or 4 mm I.D. may be incompatible with usual industrial detectors, such as thermal conductivity and flame ionization detectors. On the one hand, high flow-rates can disturb the absolute or even the relative response of these detectors, and on the other hand, the carrier gas is consumed in this technique. As the volumetric flow-rate increases with the square of the diameter, this problem can be solved by decreasing the column diameter. From Fig. 3, a simple calculation shows that a flow-rate of 15 l/h with a column of I.D. 4 mm becomes 0.95 l/h with a column of I.D. 1 mm. However, Fig. 4 shows that a flow-rate of 24 l/h is necessary in order to obtain an analysis time of 2 min with a column of I.D. 4 mm, which is both technically and economically unreasonable.

*Particle size range*

An increase in the flow-rate inevitably leads to an increase in the pressure drop, and this increase will be higher, the lower is the column permeability. In fact,

Darcy's equation shows that under normal GC conditions, the gas velocity is proportional to the pressure gradient and to the permeability[12]:

$$U = -\frac{K}{\eta} \cdot \frac{dP}{dx} \qquad (1)$$

where $K$ is the column permeability, $\eta$ the viscosity of the carrier gas and $dP/dx$ the pressure gradient. $K$ depends on the particle size range and on the density of the packing in the column[15,16]:

$$K = \frac{\psi^2 {d_p}^2}{180} \cdot \frac{{\varepsilon_0}^3}{(1-\varepsilon_0)^2} \qquad (2)$$

where $d_p$ is the average diameter of particles, the shape factor of which is $\psi$, and $\varepsilon_0$ is the porosity of the column, which does not include the internal volume of the particles. It should also be noted that to a first approximation, $K$ is independent of the column I.D.

In practice, spherical porous particles such as Spherosil give a column permeability a little lower than that expected according to theory, and a higher pressure drop than columns filled with a classical support, because of the inner porosity. Fig. 4 shows that a pressure drop of 3 bars with a linear velocity of 6.6 cm/sec (column I.D. 4 mm, flow-rate 3 l/h) becomes 6 bars with a linear velocity of 53 cm/sec (column I.D. 1 mm, flow-rate 1.5 l/h). However, too great a pressure drop in the column is to be avoided for two reasons: (*a*) the influence of Martin's pressure factor on column performance[13], and (*b*) the use of commercial chromatographs. It is possible to avoid this difficulty by varying the column permeability and the particle size range ($K$ is proportional to the square of the average diameter of the particles, eqn. 2).

Fig. 5 shows the separation of some alkyl bromides on a column I.D. 1 mm filled with Spherosil of specific surface area 28 $m^2/g$ coated with Carbowax 20M at 2 g per 100 g ($e_\lambda \approx 10$ Å) of different particle size ranges, 90–100 $\mu$m (A) and 180–200 $\mu$m (B). In the first case (A), the pressure drop is 4 bars with a flow-rate of 0.33 l/h, whereas in the second case (B), the pressure drop reaches only 3 bars for a flow-rate 3.5 times higher (1.16 l/h).

Another conclusion that can be drawn from Fig. 5 is that the analysis time of 7 min (A) has been reduced to $2^1/_2$ min (B) with still sufficient resolution between, for instance, peaks 1 and 2: $R=2$ (B) compared with 4.5 (A). However, by drastically increasing the linear velocity of the carrier gas and the particle size range, the high column efficiency of 3250 plates/m ($\approx$16.5 plates/sec) has decreased to 600 plates/m ($\approx$10 plates/sec). This decrease in column efficiency can be explained, as a first approximation, by the longer path length to be covered by the molecules through the deep pores of the larger particles, and the increased difference between the velocities of the carrier gas inside and outside the pores. Finally, the narrower the particle size distribution, the better are the permeability and efficiency; 3250 theoretical plates/m have been obtained with a particle size range of 90–100 $\mu$m, *i.e.*, a ratio of average diameter of particles to column diameter of close to 0.1 (ref. 8). For Spherosil, just as for any other packing, a compromise has to be found between analysis time and peak resolution.

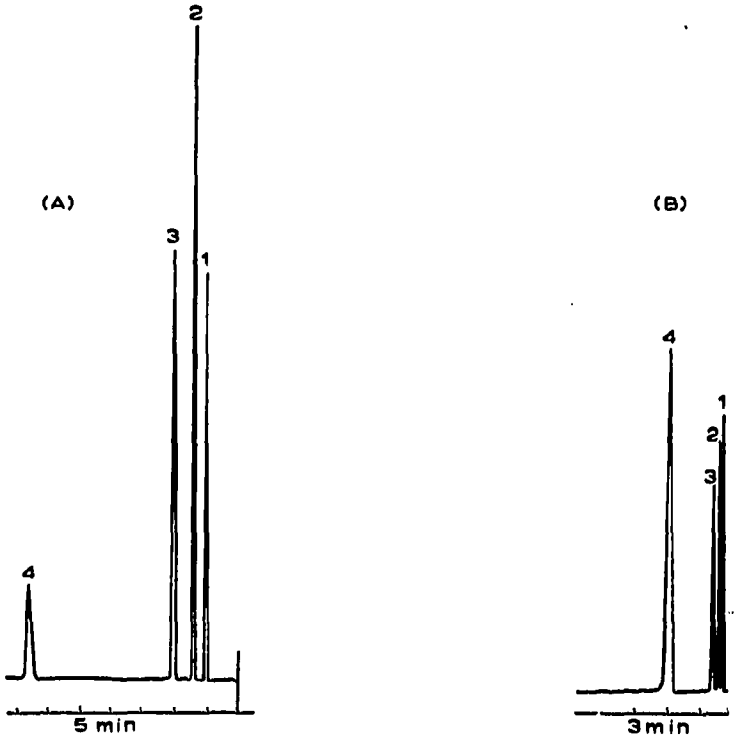



Fig. 5. Influence of particle size distribution of Spherosil and carrier gas flow-rate on the separation of some brominated hydrocarbons. Spherosil XOB 030 (28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Column I.D. 1 mm, length 2 m. (A) Particle size range, 90–100 $\mu$m; $N_2$ flow-rate, 0.33 l/h; $\Delta P = 4$ bars; isothermal temperature, 110°. (B) Particle size range, 180–200 $\mu$m; $N_2$ flow-rate, 1.16 l/h; $\Delta P = 3$ bars; isothermal temperature, 90°. 1, Ethyl bromide; 2, *n*-propyl bromide; 3, *n*-butyl bromide; 4, bromobenzene.

*Amount of stationary phase to be coated on Spherosil*

It has already been shown[8] that the retention volume of a solute is a function of the thickness of the stationary phase coated on Spherosil. The retention volume first decreases (Fig. 6), then passes through a minimum and finally increases upon further addition of liquid phase. In the present case, the mixture to be separated was diethyl ether–acetone–methyl ethyl ketone–methyl isobutyl ketone on Spherosil of specific surface area 64 $m^2/g$ coated with different layer thicknesses of stationary phase at an isothermal temperature of 110°.

It is an original property of this material that the same chromatographic separation can be obtained with Spherosils of different specific surface areas, provided that the liquid film has a constant thickness; *i.e.*, the amount of stationary phase has to be proportional to the specific surface area of Spherosil[8]:

$$e_A = \frac{W_L}{\rho \cdot S \cdot p} \qquad (3)$$

where $W_L$ is the weight of stationary phase in grams per 100 g of Spherosil, $\rho$ the density of the stationary phase, $S$ the specific surface area of Spherosil and $p$ the weight of Spherosil.

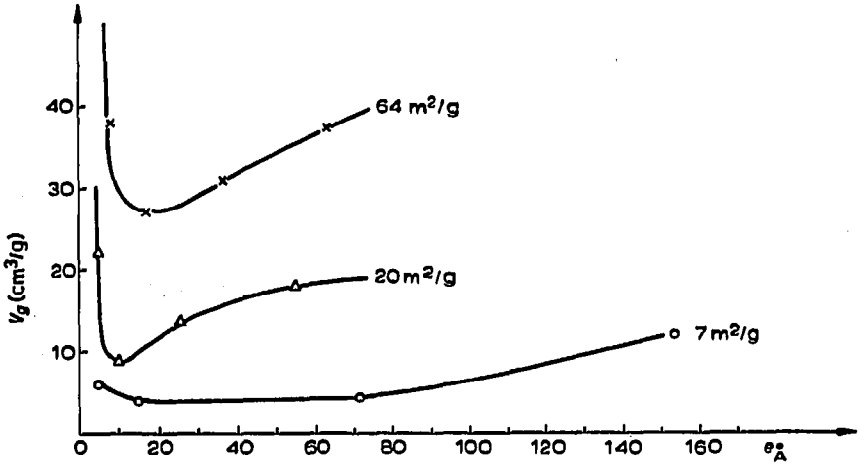



Fig. 6. Plots of the specific retention volume ($V_g$) of methyl isobutyl ketone *versus* the film thickness ($e_A$) of $\beta,\beta'$-oxydipropionitrile coated on Spherosils of different specific surface areas.

With $\beta,\beta'$-oxydipropionitrile, as with other stationary phases, the minimum in the curve in Fig. 6 is situated between 10 and 20 Å, but in practice, to ensure that the coating is homogeneous, a film thickness of 20 Å is recommended (see nomograph, Fig. 1).

The specific surface area still has a part to play in rapid analysis. Fig. 7 shows the plots of the minimum retention volume, $V_{g\,(min.)}$, of the different curves (Fig. 6) *versus* the specific surface area of Spherosil. This relationship is linear, so that the smaller the specific surface area, the more rapid is the analysis; it should not be forgotten, however, that the choice of Spherosil also depends on the nature of the molecules to be separated[8].

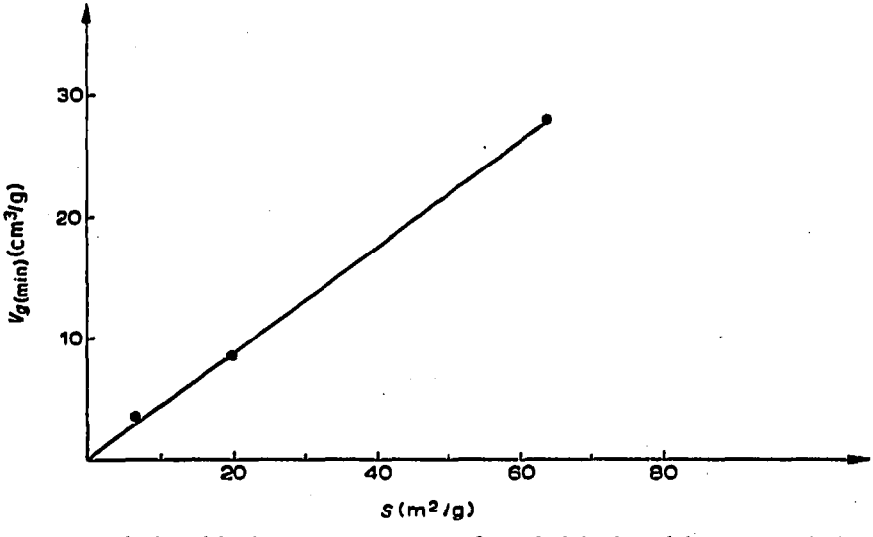



Fig. 7. Relationship between $V_{g\,(min.)}$ of methyl isobutyl ketone and the specific surface area of Spherosil.

## INJECTION CAPACITY

Before using such micropacked columns of Spherosil in routine industrial control carried out with either laboratory or process gas chromatographs, two points remained to be checked, *viz.*, the injection capacity and quantitative analysis.

Up to now, the liquid sampling systems in process GC have not been suitable for injecting amounts below 1 $\mu$l. Such a restriction has prevented the use of capillary columns and restricted the development of rapid analysis in process GC. This particular problem can be solved by using micropacked columns of Spherosil.

Fig. 8 shows the analysis of some impurities in 1,2-dichloroethane, *viz.*, trichloroethylene, benzene, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, separated on Spherosil of specific surface area 55 $m^2/g$ coated with hexakiscyanoethoxy-

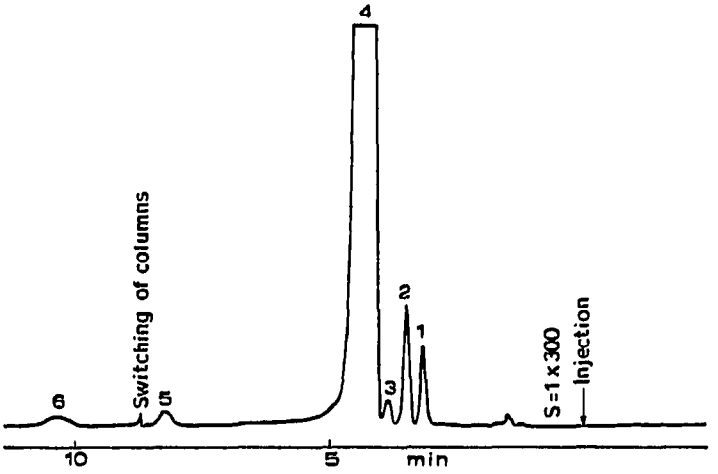



Fig. 8. Analysis of some impurities in 1,2-dichloroethane. Spherosil XOB 075 (55 $m^2/g$) coated with hexakiscyanoethoxyhexane at 9 g per 100 g ($e_A \approx 17$ Å); particle size range, 90–100 $\mu$m; column I.D. 1 mm, length 2.50 m; $N_2$ flow-rate, 0.36 l/h; isothermal temperature, 108°; injection volume, 1.29 $\mu$l. 1, Trichloroethylene; 2, benzene; 3, perchloroethylene; 4, 1,2-dichloroethane; 5, 1,1,2-trichloroethane; 6, 1,1,2,2-tetrachloroethane.

TABLE I

ACCURACY OF QUANTITATIVE ANALYSIS USING COATED SPHEROSIL AS A COLUMN PACKING

The relative response factors used for this analysis were determined by the gas density balance calibration technique[19,20]. Corrections have been made for trace impurities contained in the major component, 1,2-dichloroethane.

| *Components* | *Synthetic mixture (p.p.m.)* | *Results* | |
|---|---|---|---|
| | | *Average of 3 runs (p.p.m.)* | *Deviation (%)* |
| Methylene chloride | 66 | 71 | +7 |
| 1,1-Dichloroethane | 102 | 101 | −1 |
| Internal standard (benzene) | 41 | | |
| Trichloroethylene | 94 | 89 | −5 |
| 1,2-Dichloroethane | Major component | | |

hexane at 9 g per 100 g ($e_A \approx 17$ Å). This process analysis was carried out with a switching column procedure and the injection was made with a Siemens liquid valve of volume 1.29 $\mu$l (the volume was measured by the acidimetric technique[18]). In spite of the 1 mm I.D. of the column used, no overloading was observed; the major peak shows no tailing and the chromatogram is satisfactory. The analysis time was 11 min instead of about 30 min with a classical column.

## VALIDITY OF THE USE OF SPHEROSIL IN QUANTITATIVE ANALYSIS

In general, adsorbents are often suspected of giving asymmetrical chromatographic peaks, thus restricting their use in quantitative analysis. Table I gives the quantitative results of the trace analysis of a synthetic mixture containing methylene chloride, 1,1-dichloroethane and trichloroethylene in 1,2-dichloroethane, separated on Spherosil of specific surface area 83 $m^2/g$ coated with polyethylene glycol 400 at 5 g per 100 g. The results are perfectly valid at this level of concentration.

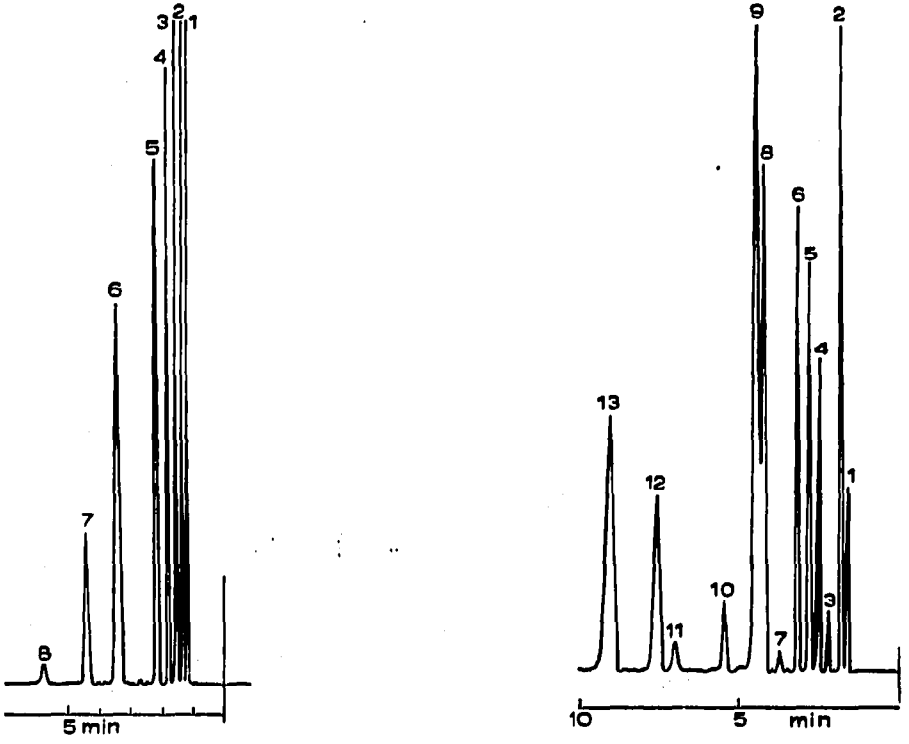



Fig. 9. Separation of high-boiling $C_{10}$–$C_{18}$ aliphatic hydrocarbons. Spherosil XOB 015 (28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Particle size range, 90–100 $\mu$m; column I.D. 1 mm, length 2 m; $N_2$ flow-rate, 0.25 l/h; isothermal temperature, 250°. 1, $C_{10}$; 2, $C_{11}$; 3, $C_{12}$; 4, $C_{13}$; 5, $C_{14}$; 6, $C_{16}$; 7, $C_{17}$; 8, $C_{18}$.

Fig. 10. Separation of alcohols up to $C_6$. Spherosil XOB 015 (28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Particle size range, 90–100 $\mu$m; column I.D. 1 mm, length 2 m; $N_2$ flow-rate, 0.35 l/h; isothermal temperature, 105°. 1, Ethanol; 2, isopropanol; 3, unknown; 4, 1-propanol; 5, 2-butanol; 6, 2-methyl-2-butanol; 7, unknown; 8, 3-methyl-2-butanol; 9, 1-butanol; 10, 2-methyl-2-pentanol; 11, 2-methyl-1-butanol; 12, 4-methyl-2-pentanol; 13, 2-hexanol.

## APPLICATIONS

In order to show the potentialities of Spherosil in rapid analysis, especially in routine control, all of the following applications were carried out under isothermal conditions.

*Spherosil XOB 015 (specific surface area 28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å)*

Fig. 9 shows the separation of high-boiling aliphatic hydrocarbons from $C_{10}$ to $C_{18}$. The analysis time of this separation was only 6 min and the column, of I.D.

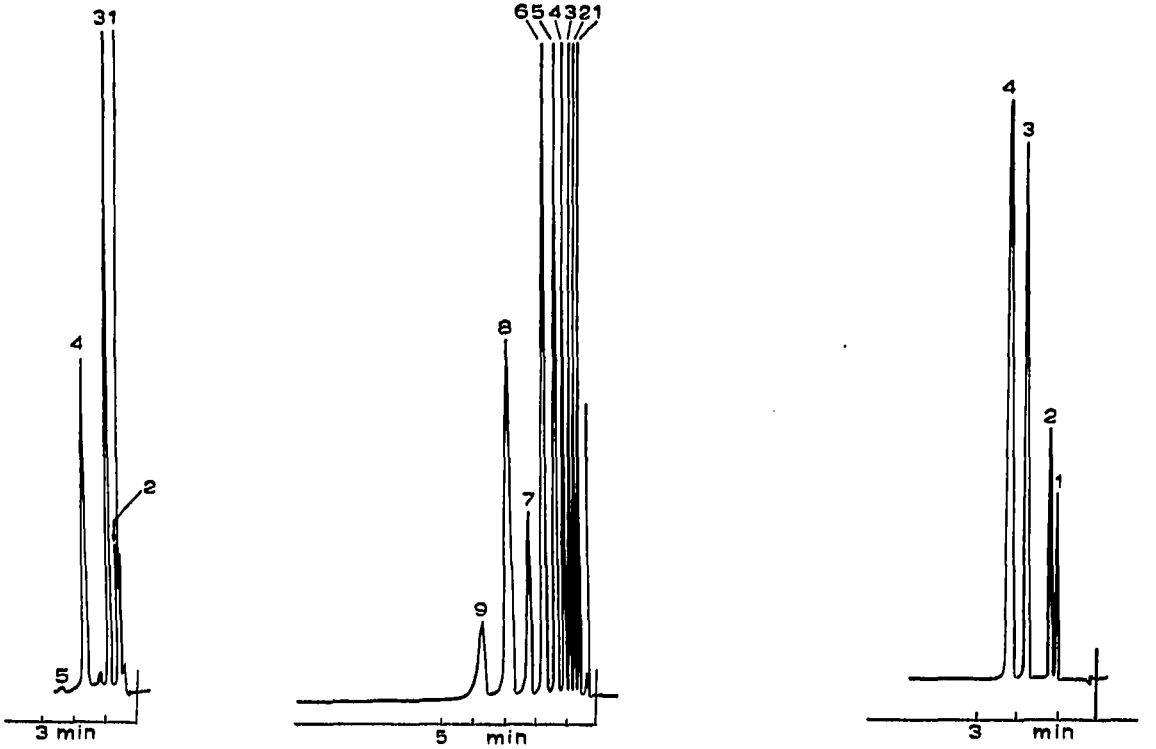



Fig. 11. Separation of phthalic esters. Spherosil XOB 015 (28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Particle size range, 180–200 $\mu$m; column I.D. 1 mm, length 2 m; $N_2$ flow-rate, 1.5 l/h; isothermal temperature, 300°. 1, Methyl phthalate; 2, unknown; 3, ethyl phthalate; 4, butyl phthalate; 5, hexyl phthalate.

Fig. 12. Separation of saturated $C_{11}$–$C_{19}$ fatty acid methyl esters. Spherosil XOB 015 (28 $m^2/g$) coated with Carbowax 20M at 2 g per 100 g ($e_A \approx 10$ Å). Particle size range, 180–200 $\mu$m; column I.D. 1 mm, length 1.85 m; $N_2$ flow-rate, 0.40 l/h; isothermal temperature, 250°. 1, $C_{11}$ (methyl undecanoate); 2, $C_{12}$ (methyl laurate); 3, $C_{13}$ (methyl tridecanoate); 4, $C_{14}$ (methyl myristate); 5, $C_{15}$ (methyl pentadecanoate); 6, $C_{16}$ (methyl palmitate); 7 $C_{17}$ (methyl heptadecanoate); 8, $C_{18}$ (methyl stearate); 9, $C_{19}$ (methyl nonadecanoate).

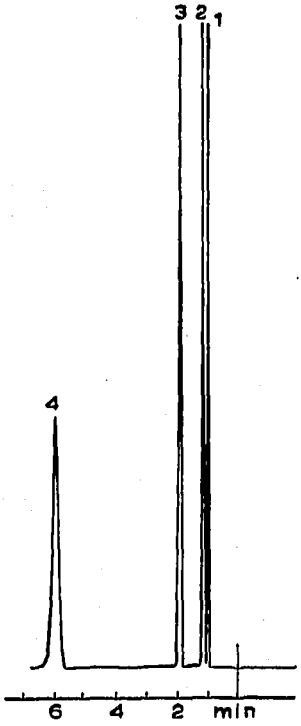
Fig. 13. Separation of acetic esters. Spherosil XOB 075 (75 $m^2/g$) coated with Carbowax 20M at 5 g per 10 g ($e_A \approx 10$ Å). Particle size range 90–100 $\mu$m; column I.D. 1 mm, length 2.50 m; $N_2$ flow-rate 0.26 l/h; isothermal temperature 202°. 1, Methyl acetate; 2, ethyl acetate; 3, butyl acetate; 4, isoamyl acetate.

1 mm and operating at 250°, showed no bleeding of the liquid phase and no baseline drift.

Fig. 10 shows the separation of alcohols up to $C_6$. The separation of these 13 alcohols by modified GSC on Spherosil was possible within 10 min, with good resolution and symmetrical peaks.

Fig. 11 shows the separation of phthalic esters. This separation is remarkable not only in the analysis time, but also for the temperature limit at which this packing was operating, *i.e.*, 300°. Such a column, after several days of operation at 300°, still gave the same separations of previously used mixtures (*n*-paraffins and $C_6$ alcohols).

Fig. 12 shows the separation of saturated fatty acid methyl esters ($C_{11}$–$C_{19}$). The complete separation of the nine esters was achieved within 5 min at 250°.



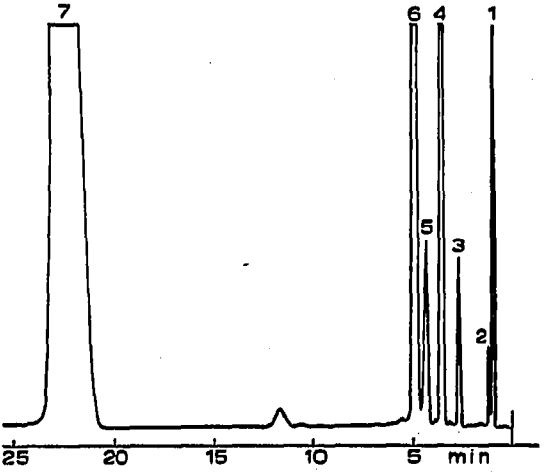




Fig. 14. Separation of acrylic esters. Spherosil XOB 075 (75 $m^2/g$) coated with Carbowax 20M at 5 g per 100 g ($e_\lambda \approx 10$ Å). Particle size range, 90–100 $\mu$m; column I.D. 1 mm, length 2.50 m; $N_2$ flow-rate, 0.56 l/h; isothermal temperature, 202°. 1, Methyl acrylate; 2, ethyl acrylate; 3, butyl acrylate; 4, ethylhexyl acrylate.

Fig. 15. Separation of benzene and some oxygen-containing compounds. Spherosil XOB 075 (75 $m^2/g$) coated with Carbowax 20M at 5 g per 100 g ($e_\lambda \approx 10$ Å). Particle size range, 90–100 $\mu$m; column I.D. 1 mm, length 2.50 m; $N_2$ flow-rate, 0.70 l/h; isothermal temperature, 203°. 1, Benzene; 2, unknown; 3, benzaldehyde; 4, *o*-toluidic anhydride; 5, citraconic anhydride; 6,$\alpha$,$\alpha'$-dimethylmaleic anhydride; 7, phthalide.

*Spherosil XOB 075 (specific surface area 75 $m^2/g$) coated with Carbowax 20M at 5 g per 100 g ($e_A \approx 10$ Å)*

Fig. 13 shows the separation of four acetic esters, which were separated in less than 3 min without any difficulty.

Fig. 14 shows the separation of acrylic esters. This separation was carried out without the addition of a tail reducer on Spherosil. The efficiency of the column calculated on ethylhexyl acrylate was 2500 plates/m.

Fig. 15 shows the separation of benzene and some oxygen-containing compounds such as anhydrides. The separation of such molecules is not easy, but by using Spherosil in modified GSC, the separation of a mixture containing some anhydrides was possible, with good resolution and peak shape.

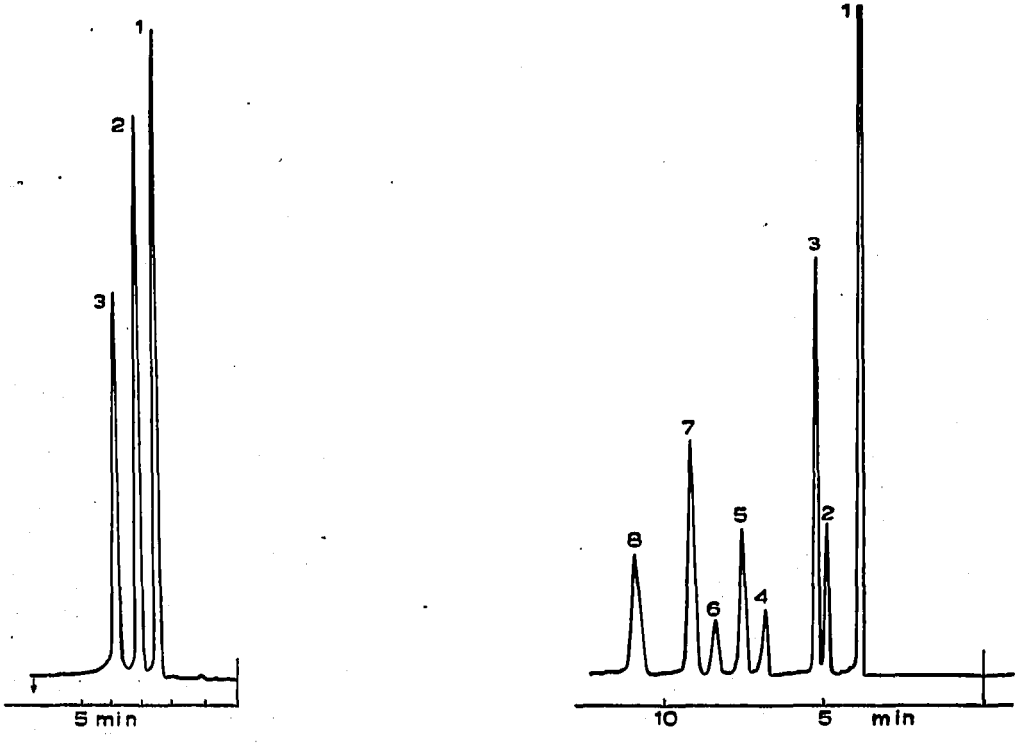



Fig. 16. Separation of some $C_8$ alcohols. Spherosil XOC 005 (7 $m^2/g$) coated with Carbowax 1500 at 14 g per 100 g (partition chromatography). Particle size range, 100–125 $\mu$m; column I.D. 1 mm, length 3 m; $N_2$ flow-rate, 0.56 l/h; isothermal temperature, 200°. 1, 2-Octanol; 2, 2-ethylhexanol; 3, 1-octanol.

Fig. 17. Separation of some aromatic hydrocarbons and butyl acetate. Spherosil XOB 030 (28 $m^2/g$) coated with ethylhexyl sebacate at 5 g per 100 g ($e_A \approx 20$ Å). Particle size range, 80–100 $\mu$m; column I.D. 1 mm, length 3.80 m; $N_2$ flow-rate, 0.175 l/h; isothermal temperature, 165°. 1, Benzene; 2, 2-ethyl-1-hexene; 3, toluene; 4, butyl acetate; 5, *m*- and *p*-xylenes; 6, *o*-xylene; 7, cumene; 8, *p*-ethyltoluene.

*Spherosil XOC 005 (specific surface area 7 $m^2/g$) coated with Carbowax 1500 at 14 g per 100 g (partition chromatography)*

Fig. 16 shows the separation of some $C_8$ alcohols. This separation has only been achieved on Spherosil coated with Carbowax 1500, but in partition chromatography $e_A > 200$ Å. In this case, the column efficiency reached only 1000 plates/m.

*Spherosil XOB 015 (specific surface area 28 $m^2/g$) coated with ethylhexyl sebacate at 5 g per 100 g ($e_A \approx 20$ Å)*

Fig. 17 shows the separation of some aromatic hydrocarbons and butyl acetate.

*Spherosil XOB 030 (specific surface area 64 $m^2/g$) coated with β,β'-oxydipropionitrile at 10 g per 100 g ($e_A \approx 17$ Å)*

Fig. 18 shows the separation of ketones. In this particular case, the optimization of analysis time was not achieved by increasing the carrier gas flow-rate, as in the previous examples, but by decreasing the column length. Chromatogram A shows an excellent separation of four oxygenated compounds with a resolution of 4 between peaks 2 and 3. As the analysis time increases as the cube of the resolution[12], a simple calculation indicates that the complete separation of these compounds (resolution of 2 between peaks 2 and 3) can still be obtained with a column length of only 25 cm. This calculation has been verified, and chromatogram B shows the separation of the same mixture carried out in 4 min instead of 20 min with a 30-cm column and a predicted resolution of 2 between peaks 2 and 3.

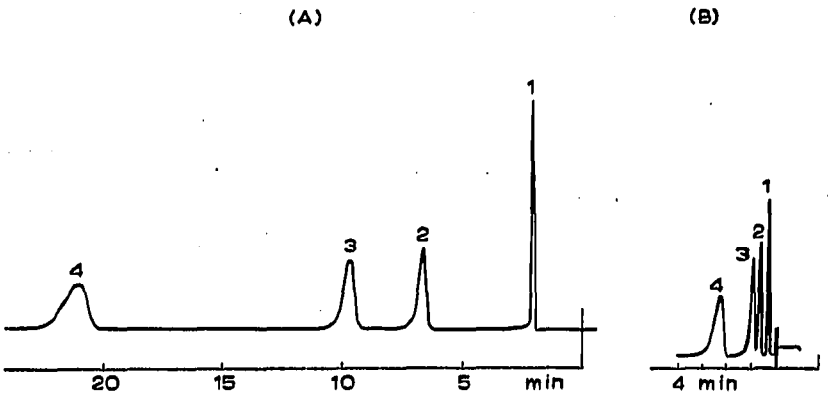



Fig. 18. Separation of ketones. Spherosil XOB 030 (64 $m^2/g$) coated with β,β'-oxydipropionitrile at 10 g per 100 g ($e_A \approx 17$ Å). Particle size range, 125–160 μm; column I.D. 1 mm, length (A) 2 m and (B) 0.30 m; $N_2$ flow-rate, 0.2 l/h; isothermal temperature, 110°. 1, Diethyl ether; 2, acetone; 3, methyl ethyl ketone; 4, methyl isobutyl ketone.

## CONCLUSIONS

Spherosil seems to provide a means of developing rapid analysis in routine control without the need for additional investment. The use of Spherosil in either GSC or modified GSC is simple and does not require any special skill from the operator; furthermore, the 1-mm I.D. columns are already in use as classical columns.

From the point of view of chromatographic hardware, the micropacked columns with Spherosil do not need any special equipement for either laboratory or process GC.

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