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SPECIFIC SURFACE AREA: THE NEGLECTED PARAMETER IN CHROMATOGRAPHY

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SUMMARY

The specific surface area of chromatographic supports, the importance of which has long been recognized, is still a neglected parameter. Nevertheless, this parameter can open up new possibilities in chromatography in general.

The specific surface area appears in the theoretical retention time expression and the rules that govern separation in gas and liquid chromatography are similar. When applied in partition gas chromatography, large values of this parameter permit high-speed analyses and high resolution on very short columns, which could lead to new possibilities in process gas chromatography and air pollution analysis. When applied in adsorption liquid chromatography, a large specific surface area permits the use of a low pressure and inexpensive high-performance liquid chromatography by using short, efficient columns.

The use of Spherosil with a large specific surface area in both gas and liquid chromatography is illustrated by some typical examples.

INTRODUCTION

In general, the use of supports with large specific surface areas is unpopular in chromatography as some workers consider these materials as possible catalysts that could modify the sample composition, or they consider that the specific surface area might be a source of undesirable effects such as strong and/or irreversible adsorption phenomena, giving rise to tailing peaks and poor results in quantitative analysis.

On the contrary, however, this neglected parameter should be considered as very important, provided that it is used in the right way. In adsorption liquid chromatography [or liquid-solid chromatography (LSC)], the specific surface area can transform high-performance liquid chromatography (HPLC) into a low pressure technique (below 50 bar or 700 p.s.i.). In modified adsorption gas chromatography [or modified gas-solid chromatography (GSC)], this parameter permits high-speed GC analysis to be performed without difficulty.

In 1962, Dal Nogare and Juvet¹ wrote that solid supports should have the following characteristics: "chemical inertness, large surface area per unit volume, thermal stability, mechanical strength and low pressure drop". Spherosil for either

GC or LC meets nearly all of the above requirements, especially that for specific surface area. Table I gives the main physical characteristics and applications of the different grades of Spherosil that are now commercially available.

TABLE I

PHYSICAL CHARACTERISTICS OF VARIOUS GRADES OF SPHEROSIL SUITABLE FOR DIFFERENT CHROMATOGRAPHIC PROCESSES

Grade	Range of specific surface area, S (m^2/g) [*]	Pore diameter (Å)	Porous volume, V_p (ml/g)	Particle size, \bar{d}_p (μm)	Applications
XOA 400	300-500	80	1	100-200 μm , 40-100 μm , <40 μm	GPC, GC and preparative LC
XOA 200	140-230	150	1		
XOB 075	75-125	300	1		
XOB 030	37- 62	600	1		
XOB 015	18- 31	1250	1		
XOC 005	5- 15	3000	1		
XOA 600, Normatom	540-660	60	0.9	$\bar{d}_p = 5-7 \mu m$, 90% of the fraction between	HPLC HPLC
XOA 800, Normatom	720-880	40	0.6	$\bar{d}_p \pm 2 \mu m$	

* BET measurement

THE ROLE OF THE SPECIFIC SURFACE AREA OF SUPPORTS IN CHROMATOGRAPHY

The influence of specific surface area is manifested in the retention time (t_R), which is given by the well known relationship²

$$t_R = \frac{L}{U} (1 + k') \quad (1)$$

where L is the column length, U the linear velocity of the mobile phase and k' the capacity factor. k' can be converted into the distribution coefficient:

$$k' = KV_S/V_M \quad (2)$$

where K is the distribution coefficient and V_S and V_M are the volumes of stationary phase and mobile phase, respectively.

In gas or liquid partition chromatography, K becomes K_p (the partition coefficient) and V_S can be expressed by the equation

$$V_S = S_T d_f = S p d_f \quad (3)$$

where S_T is the total surface area of the support, S the specific surface area of the support, p the weight of the support in the column and d_f the film thickness of the liquid stationary phase. The retention time then becomes

$$t_R = \frac{L}{U} \left(1 + K_p \cdot \frac{S p d_f}{V_M} \right) \quad (4)$$

In gas or liquid adsorption chromatography V_S can be replaced with the specific surface area only³ and the retention time is now expressed by

$$t_R = \frac{L}{U} \left(1 + K_{ad} \cdot \frac{Sp}{V_M} \right) \quad (5)$$

where K_{ad} is the adsorption coefficient. However, in chromatography one is mainly interested in the adjusted retention time of solutes rather than their absolute retention times:

$$t'_R = t_R - t_0$$

where t_0 refers to the unretained solute or the column dead time. Then eqns. 4 and 5 become, respectively:

in partition GC or LC:

$$t'_R = \frac{L}{U} \cdot K_p \cdot \frac{Sp d_f}{V_M} \quad (6)$$

in adsorption GC or LC:

$$t'_R = \frac{L}{U} \cdot K_{ad} \cdot \frac{Sp}{V_M} \quad (7)$$

From eqns. 6 and 7, it can be deduced that in a chromatographic process the adjusted retention time is, to a first approximation, a function of the product of the specific surface area and the column length.

If this statement is valid, then it must be possible to obtain identical adjusted retention times or separations of superimposable peaks by just balancing S and L in order to keep constant the product SL .

Verification of the statement $SL = \text{constant}$ in partition GC

Fig. 1 shows as an example the separation of a synthetic mixture of methane, benzene, toluene, ethylbenzene and styrene on three different columns of Carbowax 20M coated Spherosil, the so-called "toasted Spherosil"⁴, for which the product SL is constant. The column characteristics to be compared are given in Table II.

From Table II and Fig. 1, it is obvious that the product SL for each chromatogram is constant and the t'_R values of the different components are identical. On the other hand, the amount of the liquid stationary phase Carbowax 20M is proportional to the specific surface area of the three grades of Spherosil, in order to keep theoretically constant the average film thickness, d_f :

$$d_f = \frac{W}{Sp\rho} \quad (8)$$

where W and ρ are the weight and density, respectively, of the stationary phase.

It can also be seen that alterations to the carrier gas flow-rate are concomitant with column length variations and carrier gas compressibility. In partition GC, the partition coefficient, K_p , is independent of S , and depends only on the nature of the liquid phase; hence k' (eqn. 2) and consequently t_R (eqn. 4) vary linearly either with

TABLE II
 CHARACTERISTICS OF THREE DIFFERENT COLUMNS (1 mm I.D.) PACKED WITH SPHEROSIL/CARBOWAX 20M USED FOR THE SEPARATION OF AN AROMATIC HYDROCARBON MIXTURE BY PARTITION GAS CHROMATOGRAPHY

Column	Specific surface area, S (m^2/g)	Column length, L (cm)	SL	Amount of liquid stationary phase, W (g per 100 g)	Theoretical film thickness, d_f (\AA)	N_2 flow-rate (ml/min)	k' (peak No. 3)	$t_{R3} - t_0$	$t_{R3/2} = \frac{t_{R3} - t_0}{2}$
A	28	500	14,000	2	7.08	32	2.45	1.71	1.71
B	96	148	14,208	6.70	7	9.70	7.50	1.72	1.72
C	200	70	14,000	14	7	4.35	15.10	1.71	1.71

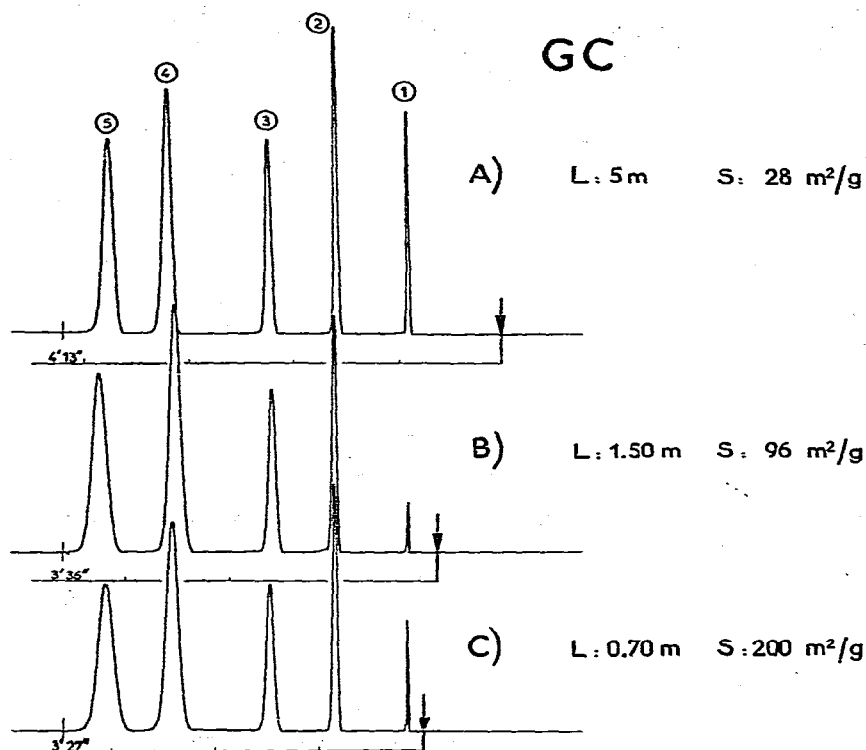


Fig. 1. Gas chromatograms of (1) methane, (2) benzene, (3) toluene, (4) ethylbenzene and (5) styrene. (A) Column, 1 mm I.D., $L = 5$ m. Spherosil, $28 \text{ m}^2/\text{g}$ ($d_p = 160 - 180 \mu\text{m}$) + Carbowax 20 M (2 g per 100 g). Flow-rate (N_2) = 0.85 l/h. Temperature = 130° . $\Delta P = 5$ bar. (B) Column, 1 mm I.D., $L = 1.50$ m. Spherosil, $96 \text{ m}^2/\text{g}$ ($d_p = 80 - 100 \mu\text{m}$) + Carbowax 20M (6.70 g per 100 g). Flow-rate (N_2) = 0.58 l/h. Temperature = 130° . $\Delta P = 5$ bar. (C) Column, 1 mm I.D., $L = 0.70$ m. Spherosil, $200 \text{ m}^2/\text{g}$ ($d_p = 80 - 90 \mu\text{m}$) + Carbowax 20M (14 g per 100 g). Flow-rate (N_2) = 0.26 l/h. Temperature = 130° . $\Delta P = 2$ bar.

respect to the column length or with the specific surface area of the constant d_f coated support, as shown in Fig. 2. Further, t'_R will remain constant when an increase in S of the coated support is followed by a corresponding decrease in L .

In practice, both the specific surface area and column length can be considered as the final parameters to be adjusted in order to achieve very fast analyses without difficulty. A previous paper⁵ was devoted to this problem; high-speed analysis will be of great interest mainly for the future process GC analyser, included in a closed-loop control, either to monitor chemical processes with rapid kinetics, or to increase the analytical credibility by averaging the results of several analytical measurements carried out within the response time of the process.

Fig. 3 illustrates the high-speed GC analysis of some chlorinated hydrocarbons, performed within 60 sec on a 15-cm, 1-mm I.D. micropacked column with Spherosil- β, β' -oxydipropionitrile (ODPN).

Such a performance has to be considered as the cumulative result of several properties of a modified gas-solid chromatography process: the small resistance to mass transfer offered by monolayers of liquid stationary phases, the flatness of the

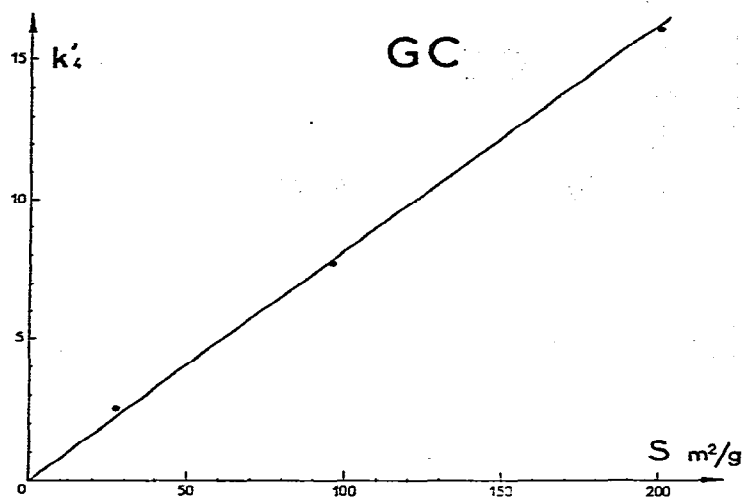


Fig. 2. GC plot of capacity factor, k' (ethylbenzene, peak 4 in Fig. 1) versus the specific surface area of Carbowax 20M coated Spherosil.

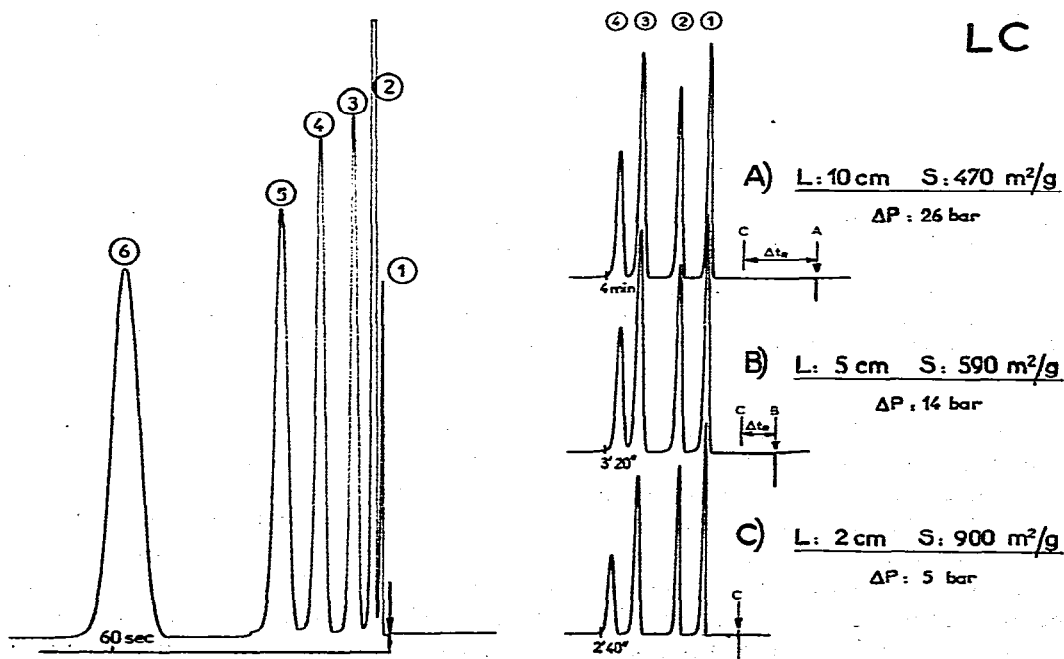


Fig. 3. High-speed GC separation of (1) vinyl chloride, (2) vinylidene chloride, (3) methylene chloride, (4) benzene, (5) 1,2-dichloroethane and (6) 1,1,2-trichloroethane. Column, 1 mm I.D., $L = 15$ cm. Spherosil, $200 \text{ m}^2/\text{g}$ ($d_p = 25\text{--}40 \mu\text{m}$) + ODPN (14 g per 100 g). Flow-rate (N_2) = 1.25 l/h. Temperature = 85° . $\Delta P = 2$ bar.

Fig. 4. Liquid chromatograms of (1) toluene, (2) naphthalene, (3) biphenyl and (4) anthracene. (A) Column, 4 mm I.D., $L = 10$ cm. Spherosil, $470 \text{ m}^2/\text{g}$ ($d_p = 5.6 \mu\text{m}$). Mobile phase = dry n -hexane. Flow-rate = 0.9 ml/min. Temperature = ambient. $\Delta P = 26$ bar. (B) Column, 4 mm I.D., $L = 5$ cm. Spherosil, $590 \text{ m}^2/\text{g}$ ($d_p = 5.3 \mu\text{m}$). Mobile phase = dry n -hexane. Flow-rate = 0.9 ml/min. Temperature = ambient. $\Delta P = 14$ bar. (C) Column, 4 mm I.D., $L = 2$ cm. Spherosil, $900 \text{ m}^2/\text{g}$ ($d_p = 5.3 \mu\text{m}$). Mobile phase = dry n -hexane. Flow-rate = 0.9 ml/min. Temperature = ambient. $\Delta P = 5$ bar.

Van Deemter curve, which allows faster linear flow velocities with a negligible decrease in column efficiency, and the very short but still efficient micropacked columns obtained by increasing S and decreasing L and by using a small particle size (20–40 μm).

An original application of very short micropacked columns containing toasted Spherosil is their use in portable GC chromatographs for atmospheric pollutant measurements at ambient temperature.

Verification of the statement $SL = \text{constant}$ in adsorption LC

Fig. 4 shows separations of a synthetic mixture of aromatic hydrocarbons (toluene, naphthalene, biphenyl and anthracene) performed under three different sets of operating conditions, by varying both the specific surface area of the Spherosil and the column length in opposite directions. It can be seen that the adjusted retention time does not depend on the product SL only, which can be explained by assuming that the adsorption coefficient, K_{ad} , is not independent of the specific surface area but depends on the surface activity, K^0 , of the adsorbent⁶. K_{ad} should be independent of the specific surface area if the surface activity, K^0 , is constant for each grade of the adsorbent⁷.

Differences in surface activities may be created during thermal activation of the support and/or by variations in the process, giving different specific surface areas^{6,7}. To illustrate this statement, the mixture of aromatic hydrocarbons shown in Fig. 4 but containing an additional component (phenanthrene) was separated, the conditions being identical (hexane flow-rate, column temperature, particle size, etc.), on columns of identical I.D. (4 mm) and length (10 cm), but packed with Spherosil of increasing specific surface area: 470, 590 and 900 m^2/g . The chromatograms, shown in Fig. 5, clearly reveal an exponential separation of peaks, which is supported by the plot of k' versus S in Fig. 6. It must be borne in mind that in adsorption chromatography t'_R refers to both the specific surface area (S) and surface activity (K^0).

Under these conditions, eqn. 7 can be written as

$$t'_R = \frac{L}{U} \cdot k' = \frac{L}{U} \cdot K_{\text{ad}} \cdot \frac{SpK^0}{V_M} \quad (9)$$

where K^0 is the surface activity as defined by Snyder⁶.

For instance, the anthracene–phenanthrene pair, which is hardly separated on Spherosil with the lowest specific surface area (470 m^2/g), is almost separated on that of 590 m^2/g and finally shows a complete resolution on Spherosil of 900 m^2/g (Fig. 5).

In Fig. 7, the separation of a mixture of benzocaine and procaine and tetra-caine chlorohydrates shows different peak elution orders on Spherosil XOA 600 and XOA 800, which indicates that the surface activities are not only quantitatively but also qualitatively different, as has already been pointed out previously⁸.

It is obvious from Figs. 4 and 5 that the specific surface area can serve a double purpose, either for achieving very difficult peak resolutions or for transforming HPLC into a low-pressure technique. The former process is feasible by increasing S alone or both S and L , while the latter is effected by an increase in S and a reduction in L much more than linearly, because of the concomitant variation of the surface activity, K^0 , of the support.

Finally, the higher the specific surface area, the shorter is the column and

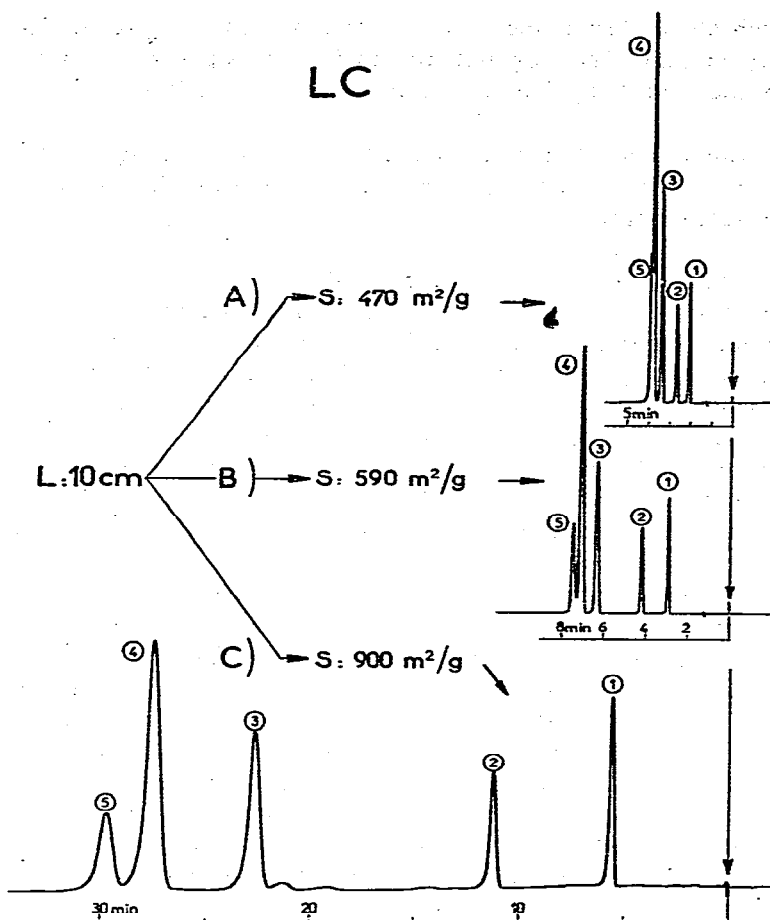


Fig. 5. Influence of specific surface area of support on LC separation of (1) toluene, (2) naphthalene, (3) biphenyl, (4) anthracene and (5) phenanthrene. Conditions as in Fig. 4 except column length = 10 cm.

the lower the pressure drop and analysis time. In practice, this means that HPLC can be now performed on very short columns (5–15 cm), requiring inexpensive pumping systems because the column pressure drops are usually below 50 bar.

As in this new concept of HPLC pressure is the price to be paid, all parameters must be optimized in order to keep the column pressure drop as low as possible.

Optimization of the parameters in the Darcy relationship

The pressure drop of a packed column is given by the well known Darcy relationship:

$$\Delta P = \frac{U\eta L}{\phi d_p^2} \quad (10)$$

where U is the linear flow velocity, η the liquid carrier viscosity, L the column length, d_p the average particle size and ϕ the permeability coefficient. Each term of this

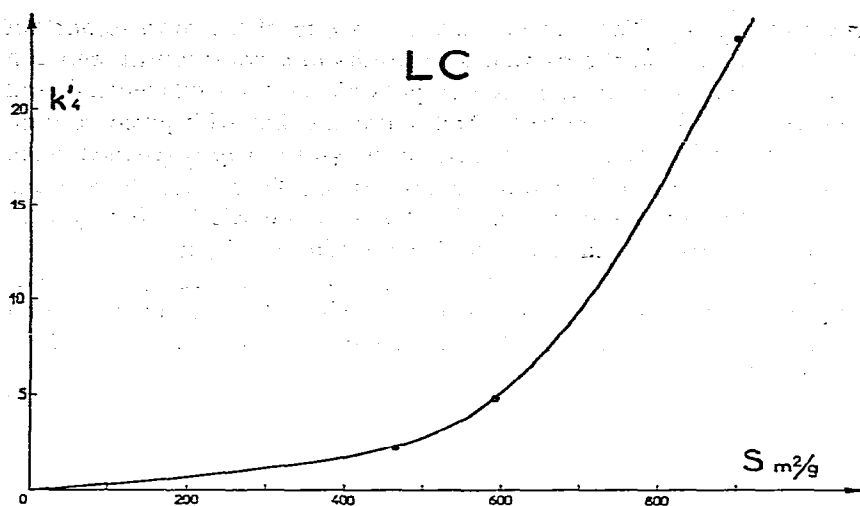


Fig. 6. LC plot of capacity factor, k' (anthracene, peak 4 in Fig. 5), versus the specific surface area of different grades of Spherosil.

equation has to be optimized in order to satisfy the requirements of low-pressure HPLC: high column efficiency, short analysis time and low column pressure drop.

Column length, L. It just has been seen that shortening the column length is now possible as a consequence of an increase in the specific surface area of the support. In addition to the corresponding decrease in pressure drop, shortening the column also meets the other two requirements. Being shorter, the columns are more homogeneously packed and achieve very high efficiencies. On the other hand, the analysis time will be reduced because of the smaller column dead volume.

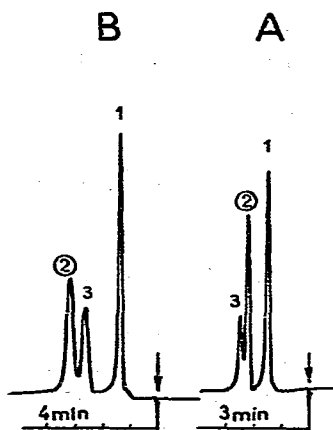


Fig. 7. LC separation of (1) benzocaine, (2) procaine chlorohydrate and (3) tetracaine chlorohydrate. (A) Column, 4 mm I.D., $L = 10$ cm. Spherosil XOA 600 ($d_p = 6.5 \mu\text{m}$). Mobile phase = 2,2,4-trimethylpentane-diisopropyl oxide-methanol-triethylamine-water (39.92:49.55:9.63:0.20:0.70). Flow-rate = 1 ml/min. $\Delta P = 25$ bar. Temperature = ambient. (B) Column, 4 mm I.D., $L = 10$ cm. Spherosil XOA 800 ($d_p = 5.3 \mu\text{m}$). Mobile phase, as in A. Flow-rate = 0.8 ml/min. $\Delta P = 34$ bar. Temperature = ambient.

Average particle size, d_p . The particle size, d_p , is one of the most important parameters in LC. With Spherosil the particle size results in a compromise between decreasing the particle size to attain the highest possible column efficiencies⁹ and an optimization model by Martin *et al.*^{10,11} which indicates that with given column efficiency, analysis time and k' , the minimum column pressure drop is reached when the average particle size is $7 \mu\text{m}$ and column length 10 cm. Therefore, the average particle diameter of the two grades of Spherosil XOA 600 and XOA 800 may vary between 5 and $7 \mu\text{m}$ with a narrow particle size distribution of $\pm 2 \mu\text{m}$.

An average of 800 theoretical plates per centimetre can be easily obtained; the upper limit of column efficiency is shown in Fig. 8, with 12,750 plates measured on the anthracene peak ($k' = 23$) separated on a 10-cm column, *i.e.*, an HETP of $8 \mu\text{m}$ or a reduced HETP of $h = 1.50$.

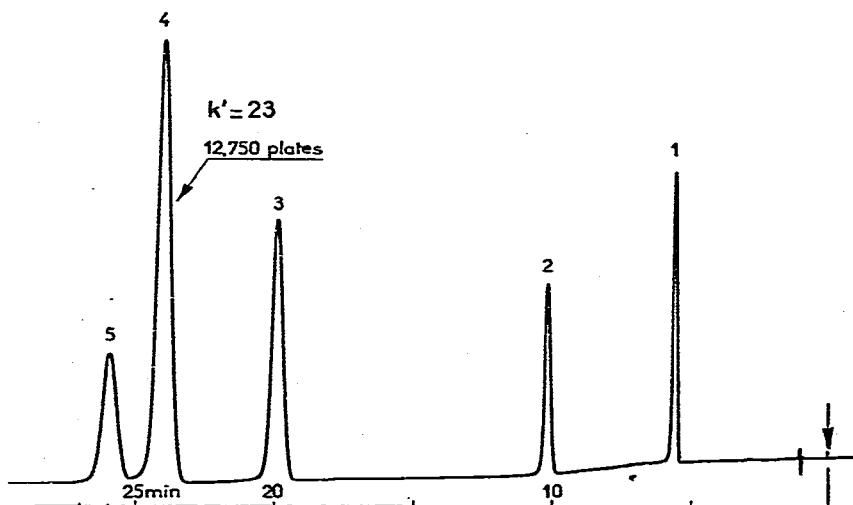


Fig. 8. Maximum LC column efficiency obtained on anthracene (peak 4): $k' = 23$ under the following conditions: column, 4 mm I.D., $L = 10$ cm; Spherosil XOA, 800 ($d_p = 5.3 \mu\text{m}$); mobile phase, dry *n*-hexane; flow-rate = 0.9 ml/min; $\Delta P = 21$ bar; temperature = ambient.

Thus, this size of particles allows one to operate HPLC at a reduced pressure drop.

Permeability coefficient, φ . As Spherosil consists of spherical microbeads, the permeability coefficient, φ , is at a maximum and consequently ΔP will be at a minimum.

The use of short columns of Spherosil with a large specific surface area forces the user to keep the column efficiency at the maximum and to operate at the minimum of the $\text{HETP} = f(U)$ curve⁸. Working under these conditions allows one to obtain the best resolution, the lowest mobile phase consumption, a short analysis time and, of course, a minimum column pressure drop.

Mobile phase viscosity, η . A judicious choice of a solvent with a low viscosity will avoid too large a pressure drop, but the most important parameter to consider is the column temperature; several bars pressure may be gained by working at 10° or 20° above ambient temperature. On the other hand, separations are faster and

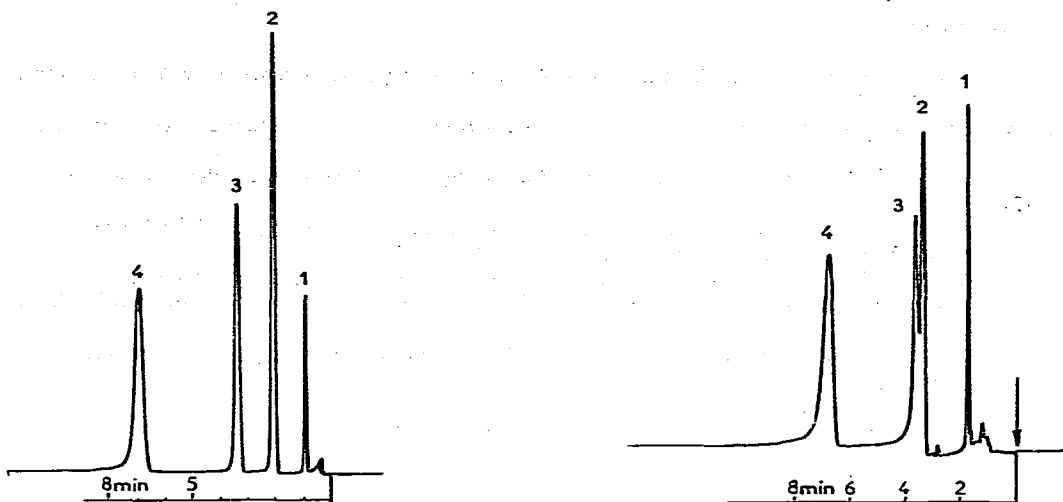


Fig. 9. LC separation of (1) phenobarbital, (2) amidopyrine, (3) caffeine and (4) nicotinamide. Column, 4 mm I.D., $L = 5$ cm. Spherosil XOA 800 ($d_p = 5.3 \mu\text{m}$). Mobile phase = 2,2,4-trimethylpentane-diisopropyl oxide-methanol-triethylamine-water (34.93:49.51:14.58:0.20:0.78). Flow-rate = 0.9 ml/min. Temperature = ambient. $\Delta P = 14$ bar.

Fig. 10. LC separation of free phthalic acids: (1) Benzoic acid; (2) terephthalic acid; (3) isophthalic acid; (4) orthophthalic acid. Column, 4 mm I.D., $L = 10$ cm. Spherosil XOA 600 ($d_p = 6.3 \mu\text{m}$). Mobile phase = *n*-hexane-isopropanol-acetic acid (88:10:2). Flow-rate = 0.85 ml/min. $\Delta P = 28$ bar. Temperature = ambient.

sometimes better because of the influence of temperature on the adsorption coefficient.

To illustrate the potential of this type of HPLC, Fig. 9 shows the separation of phenobarbital, amidopyrine, caffeine and nicotinamide on a 5-cm column packed with Spherosil XOA 800, with a special mobile phase composition and a flow-rate of 0.8 ml/min at room temperature.

Fig. 10 gives another illustration of low-pressure HPLC applied to free phthalic acids separated in adsorption chromatography.

CONCLUSION

Although the importance of the specific area surface area of the support in gas and liquid chromatography had been predicted theoretically, it remained neglected because no support with a wide range of specific surface areas was commercially available. As a result of the introduction of new supports, powerful but inexpensive gas and liquid chromatographic techniques may now be developed, leading to new trends in chromatography.

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EDITOR'S NOTE

A very similar treatment was recently presented by J. F. K. Huber and F. Eisenbeiss at the Salzburg Symposium (*J. Chromatogr.*, 149 (1978) 127). This paper had not yet appeared when the present paper was submitted to the editor.

The general problem was recognised some time ago, for example, in ion-exchange paper chromatography where R_F values can be varied by changing the capacity of the paper (see, for example, G. Alberti, V. Caglioti and M. Lederer, *J. Chromatogr.*, 7 (1962) 242).