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KINETIC PROPERTIES OF BONDED SILICAS AS STATIONARY PHASE SUPPORTS IN GAS CHROMATOGRAPHY: IMPROVEMENT OF PACKED COLUMN EFFICIENCY*

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SUMMARY

New supports for gas-liquid chromatography were prepared by bonding macroporous silicas and diatomites and were tested with various common stationary phases, both polar and apolar. The results were interpreted by drawing height equivalents to a theoretical plate *versus* gas flow-rate curves and by calculating gas- and liquid-phase mass transfer coefficients. Significant improvements in efficiency over the usual supports were obtained, the classical methylsilanized supports being the worst. We succeeded in reconciling deactivation and efficiency even by coating with phases as polar as cyanosilicone OV-275. The unusual wetting properties of thick-bonded monolayers which govern the correct fitting of the graft and the stationary phase are emphasized.

INTRODUCTION

Modifying a siliceous support in gas-liquid chromatography with packed columns may have two different objectives. The first purpose is the “deactivation” of the support to prevent the half-reversible adsorption of polar solutes. This objective is well fulfilled by the usual methylsilanized diatomites, in spite of the survival of about half of the surface silanol groups for steric reasons². The second purpose is the improvement of the wettability of the surface in order to stabilize a thin and regular layer of stationary phase, a necessary condition for obtaining high-efficiency columns. However, as far as this objective is concerned, the usual supports are poor.

Many chromatographers are conscious of the mediocrity of commercial silanized diatomites and, as a consequence, the corresponding untreated materials are still commercially available for various analyses of slightly polar compounds. However, non-wetting of the usual silanized supports has long been ignored³ and few papers have been devoted to this significant problem, except recently for capillary column pre-treatment studies.

* This paper is part of the Thesis of C. Gaget¹.

The preparation in our laboratory of very densely bonded silicas for high-performance liquid chromatography (HPLC) by means of dimethylaminosilanes according to Kováts encouraged us to test these materials as supports for liquid stationary phases in packed column gas chromatography.

To a large extent, the wetting problems of porous silica particles and glass capillary substrates are similar, but preparing a good capillary column according to modern sophisticated techniques is a very long task with sometimes variable results. This is the reason why a systematic study of many grafts and many stationary phases with many repetitions of the experiments is hardly possible with this type of column. We have undertaken such a study¹ on classical silica-packed columns. Besides, most analyses by gas chromatography are still carried out with this technique.

In an attempt to study the chromatographic performance of a new branched-chain C₈₇ hydrocarbon stationary phase, Boksanyi and Kováts⁴ coated a densely alkyl-bonded Chromosorb W diatomite and interpreted their results in terms of global Van Deemter mass coefficients and wetting angles.

In a recent paper⁵, we reported the improvement in efficiency obtained by using a C₁₈-bonded silica instead of a trimethylsilylated support with the classical apolar stationary phase squalane.

This paper describes the preparation of various macroporous bonded silicas, their comparison with other materials as supports of polar and apolar stationary phases and the interpretation of the results in terms of the coefficients of the kinetic equations of Giddings, "coupled" or "non-coupled".

EXPERIMENTAL

Preparation of bonded supports

The bonding reagents, trimethyl(dimethylamino)silane, octyldimethyl(dimethylamino)silane, octadecyldimethyl(dimethylamino)silane, phenyldimethyl(dimethylamino)silane, diphenylmethyl(dimethylamino)silane, triphenyl(dimethylamino)silane, γ -cyanopropyldimethyl(dimethylamino)silane and heptadecafluorodecyldimethyl(dimethylamino)silane, were prepared in the laboratory, starting from the corresponding chlorosilanes⁶. The bonding process has been described by Kováts and Boksanyi⁷.

The properties of the siliceous substrates and bonded supports are summarized in Table I. Surface areas are given after our own BET nitrogen adsorption measurements⁸ on unbonded materials. Particles were sieved and washed with dichloromethane in a Soxhlet extractor prior to the bonding. We are aware that the broad particle-size range of our materials is not particularly favourable for the preparation of high-efficiency columns, but our only purpose was to compare different supports prepared under reproducible conditions.

The preparation of Carbowax 20M non-extractable layers on silicas was carried out according to Vogt and Aue⁹.

The percentage of bonded carbon was determined by the Service d'Analyse du CNRS (Solaize, France).

Gas chromatography

The stationary phases were commercial products of gas chromatographic qual-

TABLE I
 PROPERTIES OF SUBSTRATES AND BONDED SUPPORTS

Mean pore diameters of the substrates are 300 and 130 nm for the Spherosils and about 1 μm for the Chromosorb.

Parameter	Spherosil XOC 005*									
	Specific surface area (m ² /g)	9.8	13.6	9.8	9.8	9.8	9.8	9.8	9.8	9.8
Bonded radical Γ ($\mu\text{mol}/\text{m}^2$)	C ₁ >4	C ₈ 3.5	C ₁₈ 0.8	C ₁₈ 2.7	C ₁₈ 3.5	C ₁₈ 4.6	C ₁₈ ** 3.3	Phenyl 4.3	Diphenyl 3.0	
	Spherosil XOC 005					Spherosil XOB 015		Chromosorb P***		
Specific surface area (m ² /g)	9.8		9.8			27.7	27.7	4		
Bonded radical Γ ($\mu\text{mol}/\text{m}^2$)	Triphenyl 1.7		C ₂ H ₄ C ₁₀ F ₂₁ 4.2			C ₁ >4	C ₁₈ 4.3	C ₁₈ 4.3		

* Rhône Poulenc, Paris, France.

** From chlorosilane.

*** Johns Manville, Denver, CO, U.S.A.

ity: squalane and cyanopropylphenylsilicone OV-225 (Merck, Darmstadt, F.R.G.), methylsilicone OV-101 and phenylsilicone OV-17 (Interchim, Montluçon, France) and cyanosilicone OV-275 (Applied Science Labs., State College, PA, U.S.A.).

Standard 1/8 in. stainless-steel tubing of length 1.50 m was used for the columns.

A home-made chromatograph with a very small dead volume was employed. The thermal conductivity detector (Gow-Mac, Madison, WI, U.S.A.) had a volume of 75 μl . The injector made in the laboratory had a dead volume of 20 μl . The temperature of the column was regulated with a classical $\pm 0.1^\circ\text{C}$ oil-bath thermostat.

The height equivalent to a theoretical plate (HETP) is given by

$$h = \frac{L}{5.54} \left(\frac{W_{0.5}}{t_r} \right)^2 \quad (1)$$

where t_r is the retention time, $W_{0.5}$ the peak width at half-height and L the column length.

The flow-rate (Q) at the outlet of the column was measured by means of a thermostated soap-bubble flow meter. A quantity proportional to the carrier gas rate is given by

$$U_s = \frac{Q}{60S} \cdot \frac{T_C}{T_B} \cdot \frac{p_o - p_v}{p_o} \quad (2)$$

where S is the tube cross-section, T_C and T_B the temperatures of the column and the flow meter, respectively, p_o the pressure at the outlet of the column (atmospheric pressure) and p_v the vapour pressure of water at $T_B^\circ\text{K}$.

Eight solutes, *n*-pentane, *n*-hexane, *n*-heptane, chloroform, carbon tetrachloride, benzene, toluene and perfluorooctane, were studied in samples of 0.05 μ l. However, only results for *n*-alkanes and benzene are reported here; the results for the other solutes are similar.

In all the experiments the column temperature was 80°C and the injector temperature was 110°C. All the columns were preconditioned at 80°C overnight. The carrier gas was hydrogen ("U" standard, l'Air Liquide, Paris, France).

The reproducibility of the experiments was systematically tested. All of the bonding reactions were at least duplicated. All of the column-filling operations were reproduced.

THEORETICAL

Kinetic equations

The kinetic equations taken into account*, in order of increasing complexity, were as follows:

Van Deemter *et al.*¹⁰:

$$h = A + B/U + CU \quad (3)$$

Golay¹¹:

$$h = A + B/U + C_g U + C_l U \quad (4)$$

Giddings *et al.*¹²:

$$h = (A + B/p_o U_o + C_g p_o U_o) f + C_l U_d j \quad (5)$$

Giddings and Robison¹³:

$$h = \left(\frac{1}{1/A + 1/C_g p_o U_o} + C'_g p_o U_o + B/p_o U_o \right) f + C_l U_d j \quad (6)$$

A, *B* and *C* are constants related to the dispersion of the paths (eddy diffusion), molecular diffusion and mass transfer, respectively; *C_g*, *C'_g* and *C_l* are the mass transfer coefficients in mobile gas phase, stagnant gas phase and liquid phase, respectively; and *j* and *f* are the compressibility correction factors of James and Martin and the coefficient of Giddings, respectively, expressed as

$$j = 3/2 \left(\frac{P^2 - 1}{P^3 - 1} \right) \quad (7)$$

* There are many other types of kinetic equations, a few of which are quoted in ref. 1.

and

$$f = 9/8 \left[\frac{(P^2 - 1)(P^4 - 1)}{(P^3 - 1)^2} \right] \quad (8)$$

where $P = p_i/p_o$ is the ratio of inlet to the outlet pressure of the column.

Many theoretical expressions have been proposed for C_1 . None of them can be used, owing to the complexity of the particle texture, but all of these expressions involve a rapid increase of C_1 with the mean thickness of the film.

The kinetic aspects of gas-liquid chromatography were broadly discussed in the 1960s (e.g., refs. 10-17). However, only a few authors really calculated the kinetic constants for the interpretation of experimental results.

Calculation of constants

Different graphical or numerical methods^{15,18-23} have been reviewed and tested^{1,24}.

First, we discarded eqns. 3 and 4 because they are not able to discriminate the mass transfer resistance in the gas and liquid phases. This discrimination is of paramount importance for the interpretation of the wetting properties of silica. Subsequently, we calculated the coefficients of eqn. 5 by a least-squares method and the coefficients of eqn. 6 by an heuristic method, the so-called flexible polyhedron method.

In most instances, the best fitting of the experimental curves was obtained with eqn. 5, the coefficients being determined by a multiple linear regression^{25,26}. We limited the value of A to 0 and 0.15 because it corresponds to the actual particle diameter, d_p , by taking

$$A = 2\lambda d_p \quad (9)$$

where λ is the "eddy diffusion coefficient" characteristic of the packing¹⁰, and

$$2\lambda = 1 \quad (10)$$

as is generally agreed^{13,17}.

In practice, we first calculated A , B , C_g and C_l . Using the limitations that if $A < 0$ we take $A = 0$ and if $A > 0.15$ we take $A = 0.15$, we recalculated B , C_l and C_g by the least-squares method. Subsequently we were able to calculate the different contributions to the HETP: $h_A = Af$, $h_B = Bf/p_o U_o$, $h_{C_g} = C_g p_o U_o f$ and $h_{C_l} = C_l U_o j$.

In the tables, we report the components of the HETP at the fixed and relatively high flow-rate of 75 cm sec⁻¹. The interpretation of these last results is more straightforward than at the optimal flow-rate of the carrier gas. In addition, they suggest the possibility of high-speed analysis.

RESULTS AND DISCUSSION

Squalane as stationary phase

Influence of bonded alkyl chain length. Figs. 1 and 2 for hexane and benzene as solutes show H as a function of U for Spherosil XOC 005 bonded with normal alkyl radicals of various chain lengths. Table II reports the contributions of the different kinetic factors in the same experiments (coating percentage 10%).

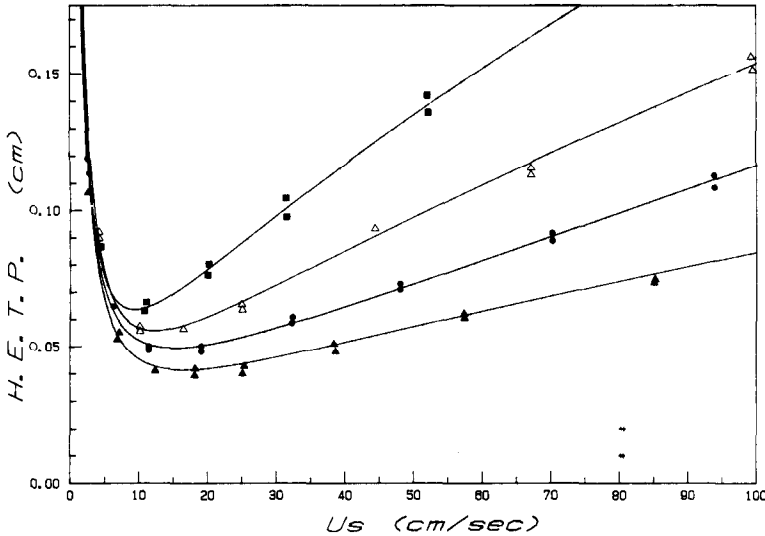


Fig. 1. h versus U curve for *n*-hexane as solute and squalane as stationary phase on C_1 -bonded (■), untreated (●), C_8 -bonded (△) and C_{18} -bonded (▲) Spherosil XOC 005. Squalane loading, 10% (w/w).

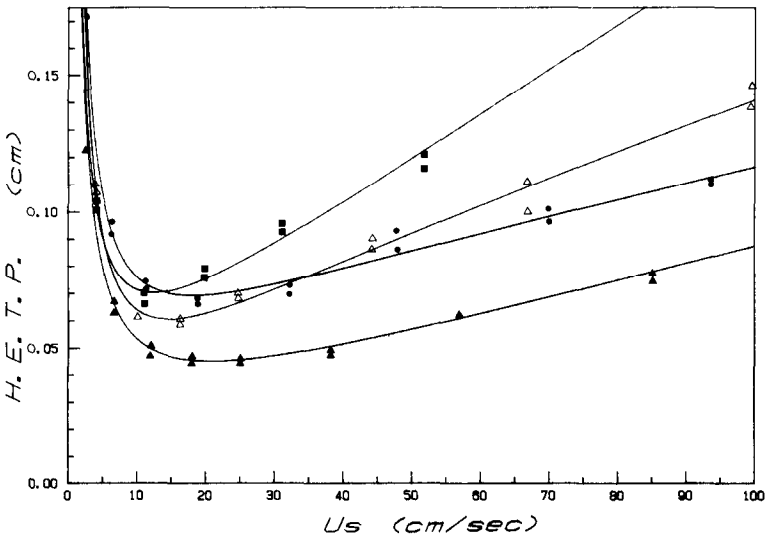


Fig. 2. h versus U curve for benzene as solute and squalane as stationary phase on C_1 -bonded (■), untreated (●), C_8 -bonded (△) and C_{18} -bonded (▲) Spherosil XOC 005. Squalane loading, 10% (w/w).

TABLE II

CONTRIBUTIONS OF THE DIFFERENT TERMS OF THE KINETIC EQUATION TO THE HETP AT 75 cm sec⁻¹ GAS FLOW-RATE FOR VARIOUS ALKYL-BONDED SPHEROSILS XOC 005 AND THE RAW SILICA AS SUBSTRATES, *n*-HEXANE OR BENZENE AS SOLUTE AND SQUALANE AS STATIONARY PHASE

Optimal conditions are reported in the last two rows.

Solute	Support	h_A	h_B	h_{C_9}	$h_{C_{11}}$	h_{75}	h_{min}	U_{min}
<i>n</i> -Hexane	Non-bonded support	0.000	0.004	0.034	0.058	0.096	0.049	13.9
	C ₁ bonded	0.000	0.004	0.058	0.114	0.176	0.065	9.3
	C ₈ bonded	0.000	0.005	0.049	0.073	0.126	0.057	12.3
	C ₁₈ bonded	0.000	0.004	0.022	0.046	0.072	0.041	16.8
Benzene	Non-bonded support	0.0152	0.006	0.017	0.065	0.102	0.069	18.5
	C ₁ bonded	0.016	0.005	0.099	0.041	0.161	0.069	12.1
	C ₈ bonded	0.016	0.005	0.066	0.029	0.116	0.062	15.8
	C ₁₈ bonded	0.015	0.004	0.047	0.006	0.073	0.045	21.1

These results show that the improvement observed in the efficiency with increasing bonded chain lengths may be broadly ascribed to the decrease in the contribution of the liquid phase mass transfer resistance to the HETP.

The results also indicate the very good wetting of the C₁₈ bonded silica by squalane (see Discussion and Conclusion). At the same time, they are in agreement with the observations of Serpinet²⁷ on the non-wetting of methylsilanized supports, with results of Riedo *et al.*²⁸ obtained by contact angle measurements on bonded glass and with the imbibition of long-chain alkyl bonded silicas by squalane brought out by inverse gas chromatography²⁹.

As far as the untreated, non-deactivated silica is concerned, the interpretation must take into account the parasitic adsorption of "polar" solutes such as benzene, which results in a broadening of the peaks and an apparent increase in the mass transfer coefficients. Accordingly, the HETPs obtained by injection of hexane are good, although the values are significantly higher than with octadecyl bonded silica. However, the measured efficiency is appreciably worse for benzene because of the lack of deactivation of the substrate.

High values of h_C for the methylsilanized support may be interpreted by partial occlusion of the pores by capillary condensate and droplets in the non-wetted support. In addition, as we shall see, this situation results in faulty column filling, which has to be taken into account in explaining high h_C values.

Density of packing and nature of the bonding reagent. Surprisingly, the influence of the surface density of the graft is limited between 0.8 and 3.5 $\mu\text{mole/m}^2$ and non-existent for dense layers (Fig. 3).

Nevertheless, replacing our octadecyldimethyl(dimethylamino)silane by the usual chlorosilane, even with the same surface density of alkyl groups, leads to a clear decrease in efficiency, which is perfectly reproducible (Fig. 4). A study of the structure of these layers by spectral methods is in progress. However, it seems that the alkyl layer from dimethylaminosilane is more regular as a result of the order of

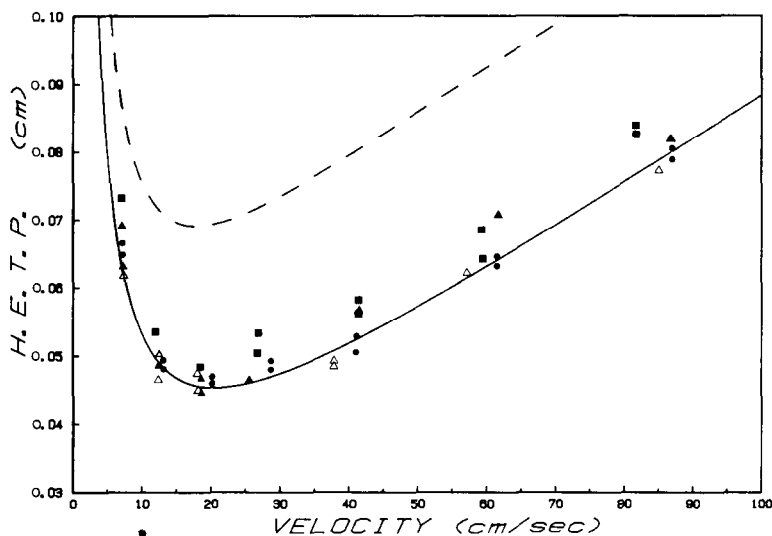


Fig. 3. h versus U curve for benzene as solute and squalane as stationary phase on C_{18} -bonded Spherosil XOC 005 of various densities: \blacktriangle , 4.0; \blacksquare , 3.5; \bullet , 2.7; \triangle , $0.8 \mu\text{mol}/\text{m}^2$. —, Unbonded support. Squalane loading, 10% (w/w).

the previously physisorbed layer of the reagent. In addition, $(\text{CH}_3)_2\text{NH}$ is much more readily eliminated than HCl.

Percentage of squalane. Changing the percentage of squalane considerably does not modify the HETP very much, as shown in Figs. 5 and 6. C_{18} silica from aminosilane is always the most efficient support. Trimethylsilylated silica is the worst,

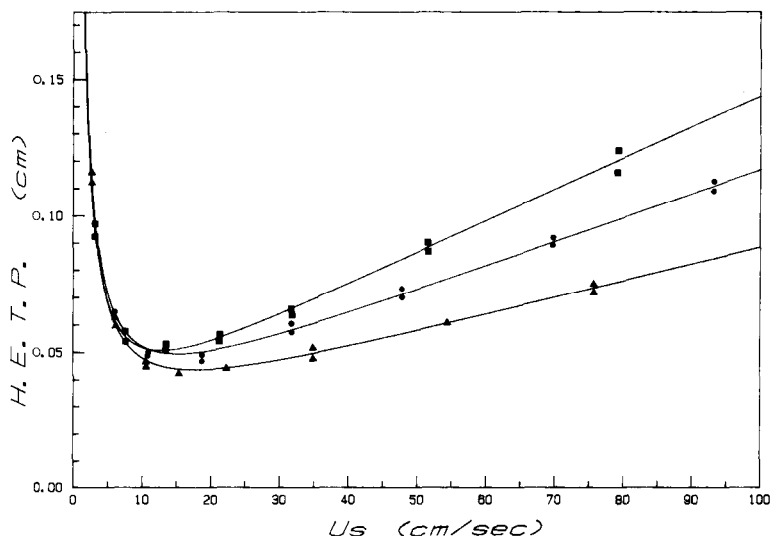


Fig. 4. h versus U curve for n -hexane as solute and squalane as stationary phase on Spherosil XOC 005: \bullet , untreated; \blacksquare , C_{18} -bonded from chlorosilane, \blacktriangle , C_{18} -bonded from dimethylaminosilane. Squalane loading, 10% (w/w).

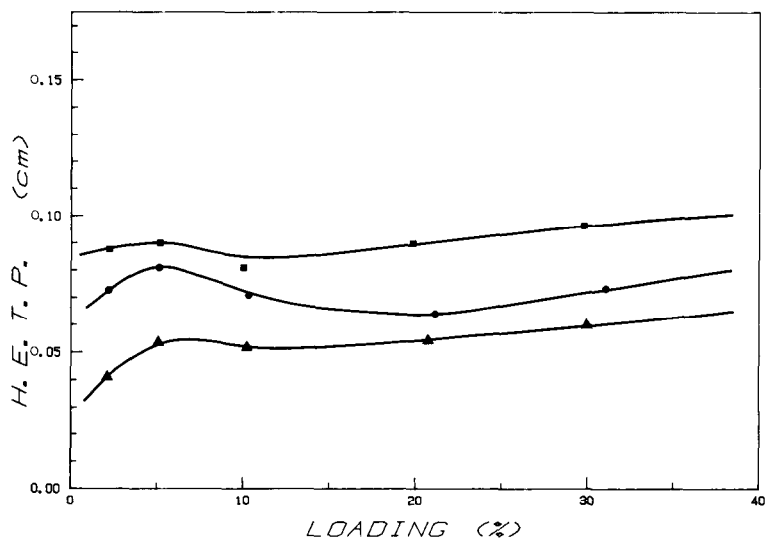


Fig. 5. h_{min} versus squalane loading for *n*-hexane as solute and Spherosil XOC 005 as support: ●, untreated; ■, C_1 -bonded; ▲, C_{18} -bonded.

except for very low percentages with the "polar" solute, where the untreated silica is still worse. As shown in Fig. 7, the increase in C_1 with increasing percentage of squalane in the case of the C_{18} graft brings about progressive thickening of the layer, whereas the constancy of h_{C_1} indicates the lack of occlusion of the pores. In contrast, a rapid increase in h_{C_1} for C_1 silica brings about increased inhomogeneity of the so-called "liquid layer".

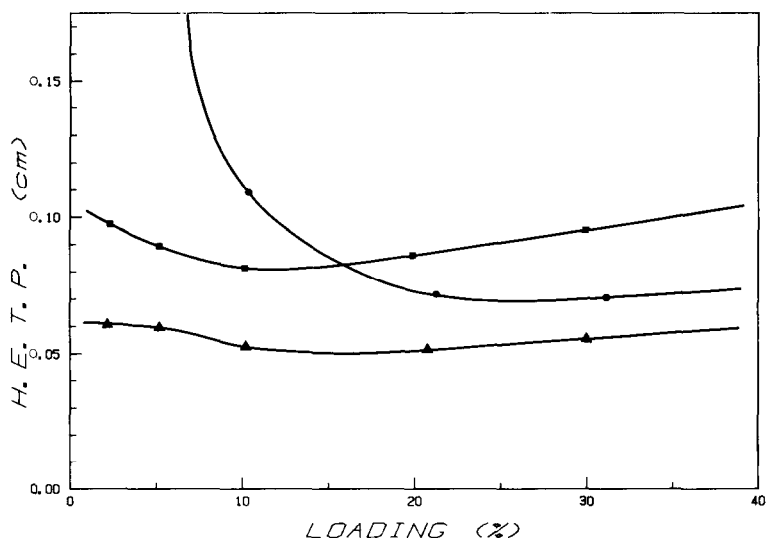


Fig. 6. h_{min} versus squalane loading for benzene as solute and Spherosil XOC 005 as support: ●, untreated; ■, C_1 -bonded; ▲, C_{18} -bonded.

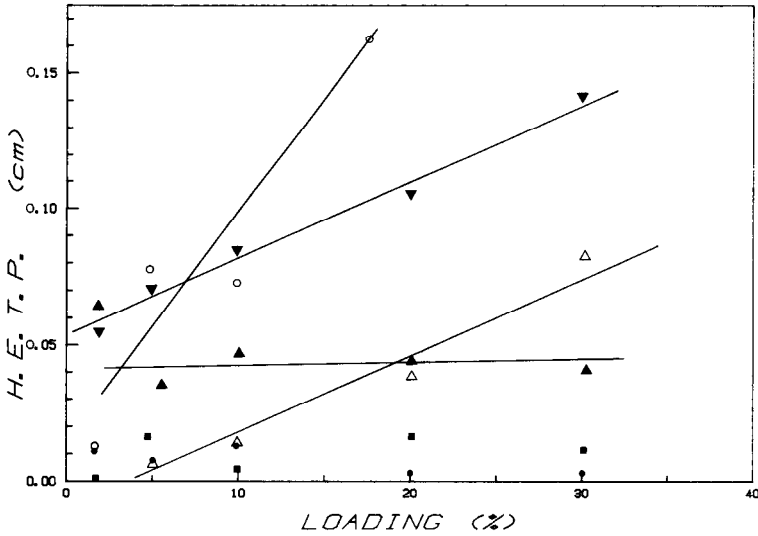


Fig. 7. Different contributions to the HETP at 75 cm sec^{-1} gas flow-rate for *n*-hexane as solute on squalane-covered C_{18} -bonded Spherosil, as a function of the squalane loading: \blacksquare , h_A ; \bullet , h_B ; \triangle , h_{C1} ; \blacktriangledown , h_{C2} ; ∇ , h (total). On the same scale the h_{C1} values for a C_1 -bonded silica are also represented (\circ).

Changing the graft. Fluorine atoms in the bonded chain result in a significant decrease in efficiency (Fig. 8). This observation and the values of the coefficients of the Giddings equation (not reported) are in perfect agreement with the very low surface energy of perfluorinated surfaces and their defective wetting properties as studied by Jarvis and Zisman³⁰.

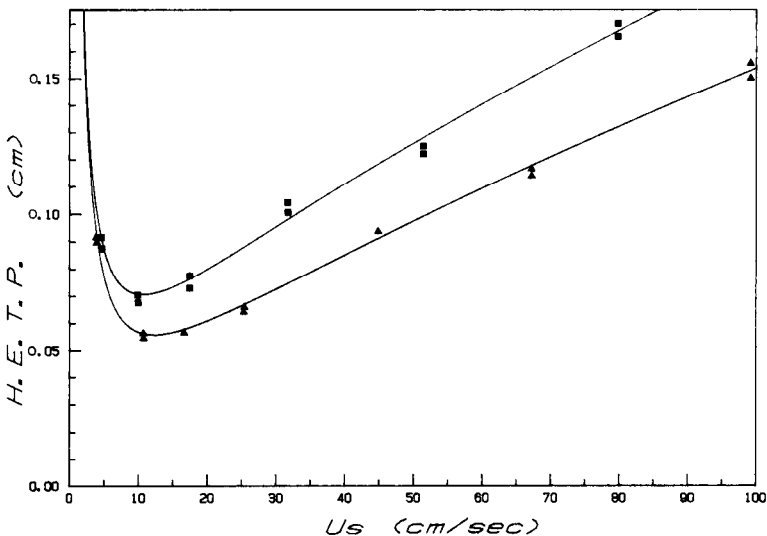


Fig. 8. h versus U curve for *n*-hexane as solute and squalane as stationary phase on C_8H_{17} -bonded (\blacktriangle) and $\text{C}_2\text{H}_4\text{-C}_8\text{F}_{17}$ bonded (\blacksquare) Spherosil XOC 005. Squalane loading, 10% (w/w).

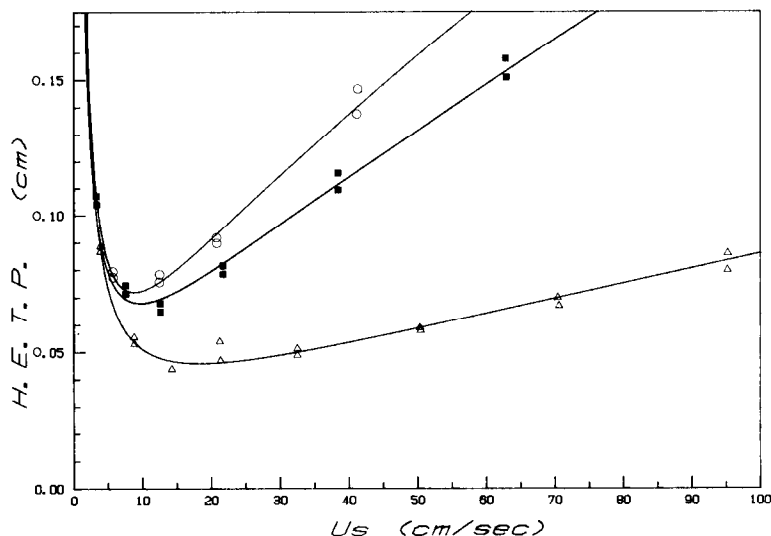


Fig. 9. h versus U curve for n -hexane as solute and squalane as stationary phase on various phenyl-bonded Spherosil XOC 005: ■, phenyldimethyl; ○, diphenylmethyl; △, triphenyl. Squalane loading, 10% (w/w).

As far as phenylbonded silicas are concerned, the superiority of the triphenylated support is obvious (Fig. 9). It is as if the wetting properties were chiefly governed by the number of methyl groups. In these cumbersome radicals, the carbon-attractive centres are kept distant from the external molecules. Therefore, the critical surface tension of wetting is much lower for the methylated than for the phenylated surfaces²⁹.

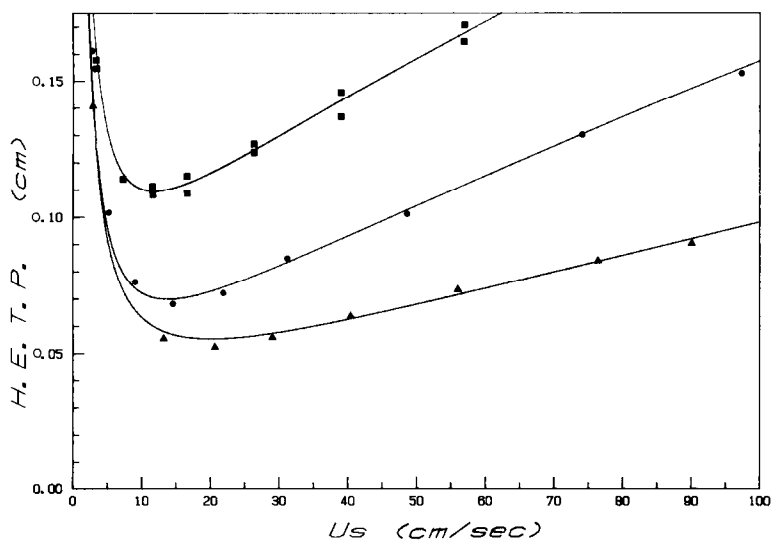


Fig. 10. h versus U curve for benzene as solute and squalane as stationary phase on variously deactivated Spherosil XOC 005: ■, untreated; ●, PEG deactivated; ▲, C_{18} -bonded.

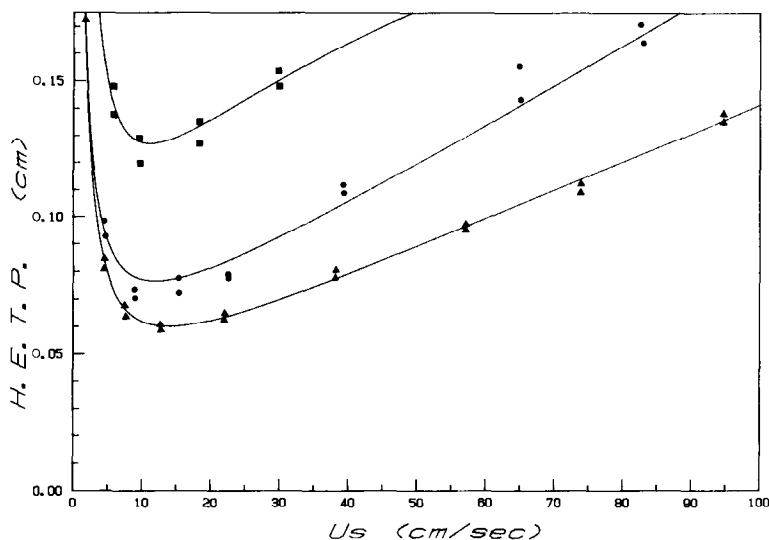


Fig. 11. h versus U curve for benzene as solute and squalane as stationary phase on Spherosil XOB 015 as support: ■, untreated; ●, C_1 -bonded; ▲, C_{18} -bonded. Squalane loading, 10% (w/w).

Modification of the silica surface with an unextractible layer of PEG 20M according to Aue⁵ results in a low efficiency (Fig. 10 for benzene solute). In a similar manner, the unfavourable results obtained with hexane and the high values of h_{C_1} observed for all the solutes indicate the good deactivation and the marked apolar character of this paradoxical material.

Changing the siliceous substrate. The improvement in efficiency with our C_{18} bonding process was confirmed for a less macroporous silica, Spherosil XOB 015 (Fig. 11).

Bonding of a Chromosorb P diatomite with extremely large pores (1 μm) by octadecyldimethyl(dimethylamino)silane leads to a much more efficient support than the commercial Chromosorb P DMCS for all of the test solutes. In fact, the advantage over the unbonded acid-washed Chromosorb is limited for an n -alkane (Table III), but it is very significant for benzene (Fig. 12) and polar solutes. In the analysis

TABLE III

CONTRIBUTIONS OF THE DIFFERENT TERMS OF THE KINETIC EQUATION TO THE HETP AT 75 cm sec^{-1} GAS FLOW-RATE FOR VARIOUS CHROMOSORBS AS SUPPORTS, n -HEXANE AS SOLUTE AND SQUALANE AS STATIONARY PHASE

Optimal conditions are reported in the last two rows.

Support	h_A	h_B	h_{C_0}	h_{C_1}	h_{75}	h_{min}	U_{min}
Chromosorb P AW (commercial)	0.016	0.006	-0.025	0.095	0.093	0.076	20.9
Chromosorb P DMCS (commercial)	0.000	0.007	0.008	0.061	0.076	0.054	21.6
C_{18} silanized	0.010	0.006	0.024	0.020	0.059	0.044	26.2

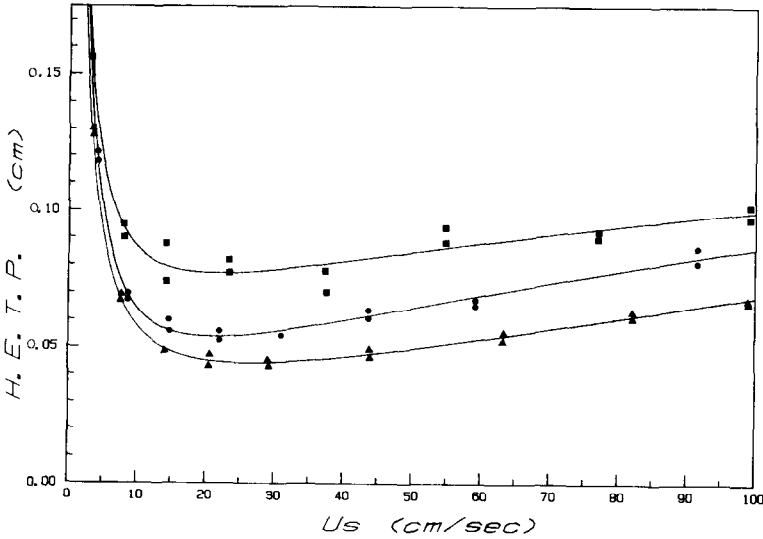


Fig. 12. h versus U curve for benzene as solute and squalane as stationary phase on Chromosorbs as support: ●, P DMCS (commercial); ■, P AW (commercial non-silanized); ▲, C_{18} -bonded P AW. Squalane loading, 7.5% (w/w).

of these compounds, the octadecyl treatment makes it possible to reconcile good efficiency and perfect deactivation.

Apolar polysiloxane phase

Coating the alkyl-bonded supports by the (apolar) polymethylsiloxane OV-101 leads to the same order of increasing efficiencies as for squalane: $C_1 < C_8 < C_{18}$

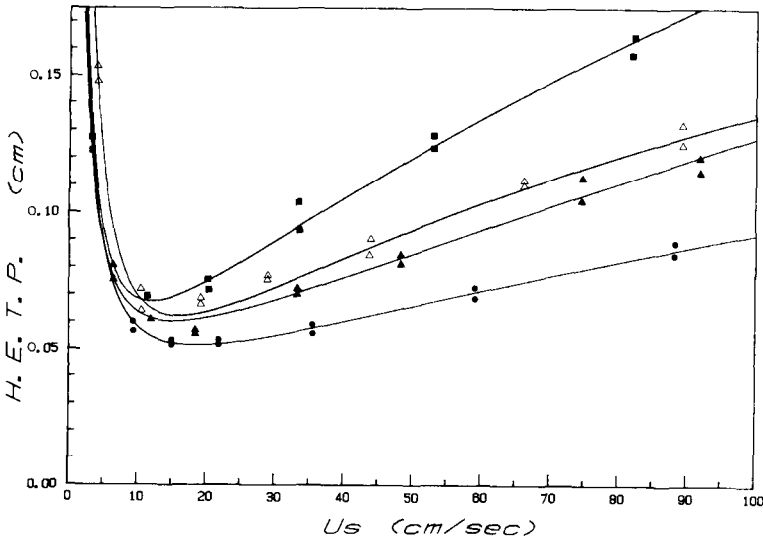


Fig. 13. h versus U curve for benzene as solute and OV-101 as stationary phase on Spherosil XOC 005 as support: ●, untreated; ■, C_1 -bonded; △, C_8 -bonded; ▲, C_{18} -bonded. OV-101 loading, 5% (w/w).

TABLE IV

CONTRIBUTIONS OF THE DIFFERENT TERMS OF THE KINETIC EQUATION TO THE HETP AT 75 cm sec^{-1} GAS FLOW-RATE FOR VARIOUS SUBSTRATES, *n*-HEXANE AS SOLUTE AND OV-101 AS STATIONARY PHASE

Optimal conditions are reported in the last two rows.

Support	h_A	h_B	h_{C_g}	h_{C_l}	h_{75}	h_{min}	U_{min}
Untreated silica	0.014	0.004	0.060	0.011	0.089	0.047	16.3
C ₁ bonded	0.011	0.004	0.067	0.070	0.152	0.065	11.6
C ₈ bonded	0.013	0.004	0.054	0.052	0.123	0.062	13.3
C ₁₈ bonded	0.006	0.004	0.047	0.046	0.103	0.051	14.2
Phenyl bonded	0.000	0.006	0.084	0.067	0.157	0.065	13.3
Diphenyl bonded	0.013	0.004	0.053	0.037	0.106	0.053	13.7
Triphenyl bonded	0.007	0.004	0.052	0.012	0.074	0.039	17.8
Cyanopropyl bonded	0.012	0.004	0.038	0.018	0.085	0.043	18.5

(Fig. 13). However, the best support of the polymethylsiloxane is the untreated silica itself. This fact suggests that imbibition of the bonded alkyl layers by OV-101 is not as easy as by squalane, for steric reasons. On the other hand, adsorption in a regular layer of the methylsiloxane by the silica surface may be favoured by the steric concordance of the siloxane chains in the polymer and in the adsorbing material. The difficult decontamination of silicone-treated glass is notorious in laboratories. In any case, the very low value of h_{C_l} (Table IV) confirms the particularly good wetting of the untreated substrate.

As in experiments with squalane, we point out the excellent properties of tri-

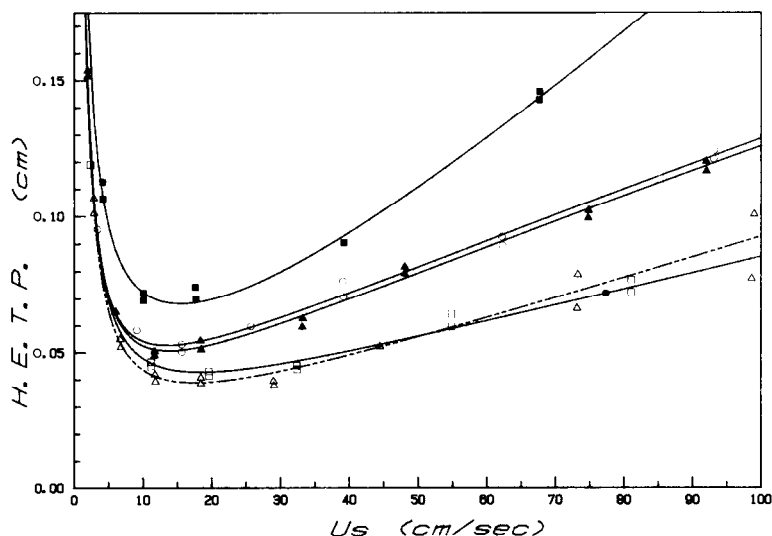


Fig. 14. h versus U curve for *n*-hexane as solute and OV-101 as stationary phase on Spherosil XOC 005 as support: ■, phenyl-bonded; ○, diphenyl-bonded; △, triphenyl-bonded; □, cyanopropyl-bonded; ▲, C₁₈-bonded. OV-101 loading, 5% (w/w).

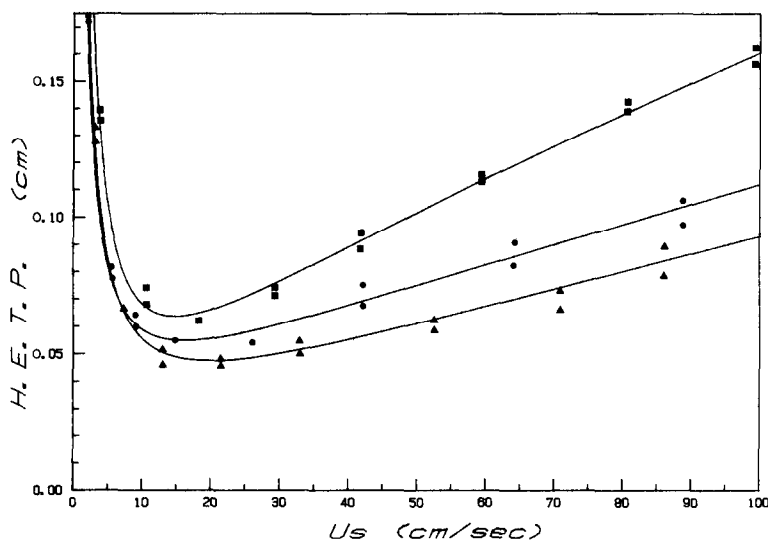


Fig. 15. h versus U curve for benzene as solute and OV-17 as stationary phase on Spherosil XOC 005 as support: ●, untreated; ■, C_1 -bonded; ▲, C_{18} -bonded. OV-17 loading, 5% (w/w).

phenylsilica as a support for OV-101 (Fig. 14), but here the phenyldimethyl support is the least satisfactory, almost as unsatisfactory as the trimethylsilanized silica. In addition, the efficiency of the columns prepared with cyanopropyl-, triphenyl- and octadecylsilica are approximately the same.

Nevertheless, for the analysis of apolar solutes, no column of OV-101 has ever reached the efficiency of the squalane-covered octadecyl-bonded silica.

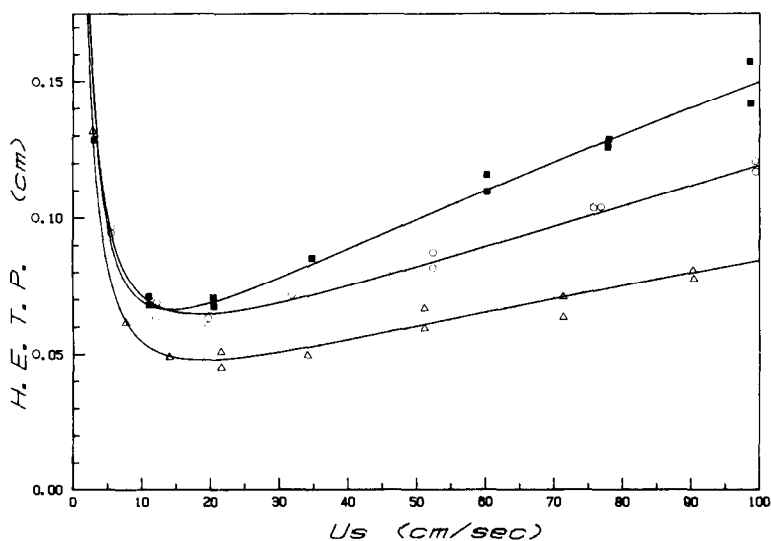


Fig. 16. h versus U curve for benzene as solute and OV-225 as stationary phase on Spherosil XOC 005 as support: ■, phenyl-bonded; ○, diphenyl-bonded; △, triphenyl-bonded. OV-225 loading, 5% (w/w).

Polyphenylmethylsiloxane OV-17

Once again the C_{18} support leads to efficient columns, even more efficient in fact than those filled with raw silica (Fig. 15). Again the C_1 support is the worst as a consequence of its bad wetting and the high C_1 contribution to the HETP (not reported).

However, this time the triphenylsilica (Fig. 16) proves to be an excellent support, better than the cyanopropyl, which may hardly be compared to the raw substrate itself, except for its deactivation properties.

Polyphenylcyanopropylsiloxane OV-225

The behaviour of OV-225 is similar (Fig. 16), although the wetting of the trimethylsilylated support is still worse, as a consequence of the increased polarity of the stationary phase (curve not reported). Again, as far as the efficiency of the columns is concerned, the cyanopropyl, triphenyl and C_{18} supports may be compared (curves not reported).

In addition, a few experiments with the PEG-modified silica confirmed not only the favourable deactivation of this support but also its poor wettability and the poor efficiency of the columns prepared with this material (contribution to HETP and curves not reported).

Cyanosilicone OV-275

Experiments with this stationary phase are of particular significance, because it is one of the most polar. In addition, the difficulty of spreading it as a thin film on the surface of silica substrates, for example on capillary columns, is notorious.

Our results indicate the possibility of surpassing in efficiency the methylsilanized silicas and even the untreated high-energy supports.

C_{18} silica leads to good columns but, in comparison with the raw substrate,

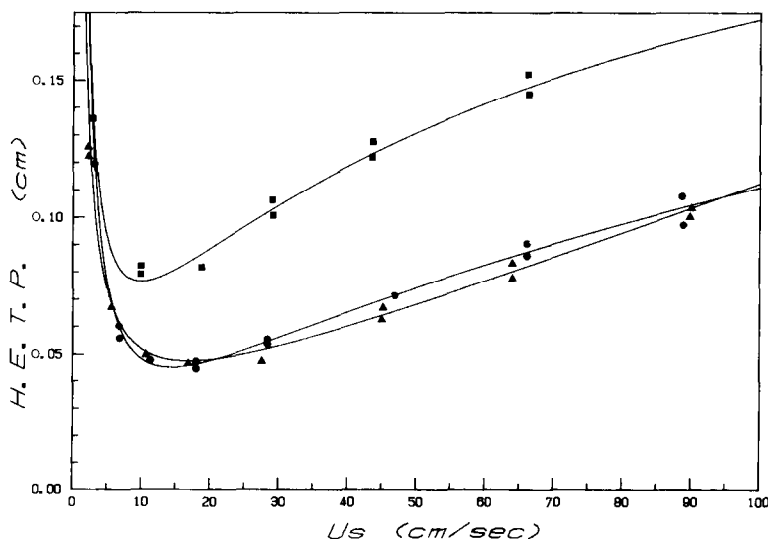


Fig. 17. h versus U curve for n -hexane as solute and OV-275 as stationary phase on Spherosil XOC 005 as support: ●, untreated; ■, C_1 -bonded; ▲, C_{18} -bonded. OV-275 loading, 5% (w/w).

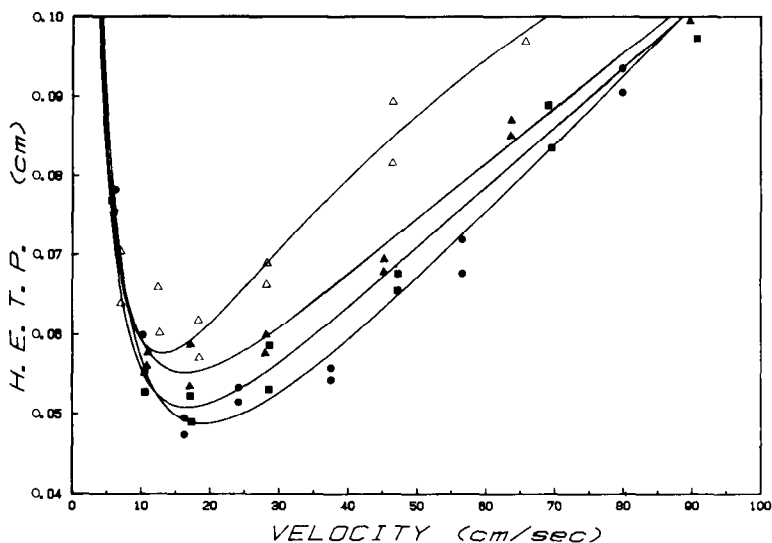


Fig. 18. h versus U curve for benzene as solute and OV-275 as stationary phase on Spherosil XOC 005 as support: Δ , untreated; \blacktriangle , C_{18} -bonded; \blacksquare , triphenyl-bonded; \bullet , cyanopropyl-bonded. OV-275 loading, 5% (w/w).

the improvement in efficiency is not striking (Fig. 17), except of course for benzene (curves not reported).

As supports of OV-275, phenylated silicas behave well, similarly to the case with OV-225, but it is worth noting that the best efficiency is obtained with the γ -cyanopropylsilylated support (Fig. 18). It is as if the similarity of the graft and the stationary phase were resulting in a particularly regular thin film, more efficient than the films formed at the surface of C_{18} alkylated and untreated supports.

The contributions of the liquid phase mass transfer resistance (Table V) to the HETP confirm these observations, which leads to our conclusion that the cyanopropyl-bonded silica is really wetted by the cyanosilicone OV-275.

TABLE V

CONTRIBUTIONS OF THE DIFFERENT TERMS OF THE KINETIC EQUATION TO THE HETP AT 75 cm sec^{-1} GAS FLOW-RATE FOR VARIOUS BONDED SILICAS AND THE RAW SUBSTRATE, BENZENE AS SOLUTE AND OV-275 AS STATIONARY PHASE

Optimal conditions are reported in the last two rows.

Support	h_A	h_B	h_{C_g}	h_{C_l}	h_{75}	h_{min}	U_{min}
Non-bonded	0.000	0.005	0.011	0.087	0.103	0.061	15.2
C_1 bonded	0.000	0.007	0.031	0.127	0.164	0.077	11.7
C_{18} bonded	0.008	0.005	0.026	0.052	0.091	0.055	16.8
Phenyl bonded	0.000	0.006	-0.006	0.160	0.160	0.085	12.4
Diphenyl bonded	0.000	0.006	0.028	0.075	0.109	0.062	16.6
Triphenyl bonded	0.003	0.005	0.033	0.048	0.090	0.051	17.0
CN bonded	0.005	0.006	0.058	0.019	0.088	0.049	19.3

TABLE VI

PERMEABILITY ($\times 10^7$ cm²) OF COLUMNS PREPARED IN THE SAME WAY WITH VARIOUS BONDED SUPPORTS AND VARIOUS STATIONARY PHASES

The corresponding minimal HETPs (cm) are reported in parentheses.

Graft	Stationary phase				
	Squalane	OV-101	OV-17	OV-225	OV-275
Raw spherosil XOC 005	0.90 (0.049)	0.95 (0.046)	0.89 (0.045)	0.93 (0.047)	1.01 (0.045)
C ₁ bonded	1.45 (0.064)	1.78 (0.065)	1.42 (0.070)	1.39 (0.070)	1.66 (0.079)
C ₈ bonded	1.34 (0.056)	1.38 (0.062)	—	—	—
C ₁₈ bonded	0.97 (0.040)	1.06 (0.050)	0.91 (0.041)	0.97 (0.047)	0.69 (0.043)
Phenyl bonded	1.26 (0.066)	1.85 (0.068)	1.43 (0.065)	1.49	1.41 (0.058)
Diphenyl bonded	1.92 (0.075)	1.26 (0.051)	2.02 (0.068)	1.07 (0.048)	0.80 (0.054)
Triphenyl bonded	0.89 (0.045)	0.93 (0.040)	0.93 (0.040)	0.97 (0.040)	0.86 (0.042)
CN bonded	—	0.92 (0.041)	1.01 (0.046)	0.91 (0.042)	0.66 (0.037)

Permeability of column and wettability

As Table VI shows for hexane as a solute, the more permeable the column, the less efficient it is. It seems that the presence of a non-wetting liquid on the external surface of the particles impedes the correct compact packing of the column. Consequently, there is a decrease in efficiency owing to the increase in the gas phase mass transfer resistance. This situation may explain the unexpected correlation between the high values of h_{C_8} and h_{C_1} observed for methylsilanized supports and most of the stationary phases studied.

DISCUSSION AND CONCLUSION

Our results and calculations confirm the paramount importance of the wetting properties of the support for the efficiency of packed columns, and indicate the possibility of a very significant improvement in the present commercial supports for gas-liquid chromatography. Methylsilanized siliceous substrates are the least satisfactory for effecting good separations.

Concerning the wetting properties of various densely bonded silicas, certain results agree well with simple classical concepts, such as the critical surface tension according to Zisman. This is also the case for the bad wetting properties of trimethylated and perfluorinated surfaces.

In general, however, these theories, taking into account the surface energy of the external atom groups of the layer, are considerably oversimplified. As already quoted by Kováts², a C₁₈ layer of 23.5 dyn/cm surface energy is wetted by squalane (surface tension 28.5 dyn/cm) and even by OV-17 (32.3 dyn/cm).

In all of these instances, the concept of imbibition of the layer must be substituted for the concept of surface energy. A thick-bonded monolayer must be considered as a real solvent. Its affinity for the coating stationary phase depends on the possibility of specific interactions in the inner part of the layer.

In contrast, the poor wetting of the C₁₈ silica by silicone OV-101 (20.5 dyn/cm) may be explained by steric hindrance. Bonded surfaces are "deep" surfaces. Their physico-chemical properties are still not very well known.

Our experiments, for example with OV-17 and OV-275, confirm the advantage of using grafts which are chemically related to the coating stationary phase.

In conclusion, the dimethylaminosilanes are of interest for the preparation of gas chromatographic supports which are well deactivated and also efficient. As an example, a support leading to an improvement in very polar OV-275 columns has been prepared.

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