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INCREASE IN PACKED COLUMN EFFICIENCY IN GAS-LIQUID CHROMATOGRAPHY BY USE OF C₁₈-BONDED SILICA INSTEAD OF A METHYLSILANIZED SUPPORT

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SUMMARY

A significant increase in packed column efficiency in gas-liquid chromatography has been obtained by use of very densely C₁₈-bonded silica instead of methylsilanized silica as the support and squalane as the stationary phase. Graphs of the height equivalent to a theoretical plate versus carrier gas flow-rate were plotted for four supports: a macroporous untreated silica and the same substrate C₁ and C₁₈ silanized and PEG 20M modified. In all instances and for any liquid loading the best efficiency was obtained with the C₁₈-bonded silica for both *n*-hexane and benzene as solutes. This observation confirms the poor wettability of the methylsilanized support and shows the much better spreading of the liquid on the surface of the C₁₈-bonded silica.

INTRODUCTION

Methylsilanized siliceous supports are widely used in gas-liquid chromatography^{1,2}. They are generally prepared by reaction of dimethyldichlorosilane, trimethylchlorosilane or hexamethyldisilazane with surface hydroxyl groups of the substrate³⁻⁵. The main purpose of the reaction is the deactivation of the support. For the same purpose, Aue *et al.*⁶ proposed a technique for the preparation of non-extractable polymer layers (polyethylene glycols or polysiloxanes) at the surface of diatomites or silicas.

Numerous investigations in gas chromatography have been carried out on the nature of the retention mechanisms on supports bonded with various organic radicals without any liquid phase⁷⁻⁹. Some techniques for the characterization of the modified surfaces have been suggested¹⁰. Likewise, the thermodynamics of exchanges on these surfaces were studied¹¹, whereas very little is known about the kinetics of the chromatography.

So far, little research has been carried out on the use of chemically bonded siliceous materials as supports in gas-liquid chromatography^{12,13}.

By means of retention volume measurements Serpinet¹⁴ and Kourini¹⁵ showed

that methylsilanized supports are not wetted by most polar or non-polar stationary phases. By contact angle measurements Riedo *et al.*¹⁶ studied silica surfaces chemically modified by alkyl dimethylsiloxanes. They showed that the surface energy and the critical tension of wetting of bonded silica surfaces increase with increasing length of the alkyl radical. Measurements were made with different wetting agents including squalane.

On the one hand, we can suppose that the spreading of the thin liquid film which is placed on the support must have a significant effect on column efficiency. On the other hand, using aminosilanes as monofunctional bonding reagents, according to the Kováts technique, we are able to prepare well defined, very densely covered C₁₈-bonded silicas.

This paper reports the column efficiencies obtained by using these C₁₈-bonded silicas as the supports for a squalane stationary phase. They are compared with an untreated silica gel, a classical methylsilanized silica and a Carbowax-modified silica used as the supports for the same liquid stationary phase. In all instances the reproducibility was studied by the preparation of several batches for each kind of bonded Spherosil.

EXPERIMENTAL

Two batches of Spherosil XOC005 (Rhône Poulenc, Paris, France) (particle diameter 100–200 μm and mean pore diameter 280 nm) were used.

Preparation of bonded supports

The bonding reagents, trimethyl(dimethylamino)silane and octadecyldimethyl(dimethylamino)silane, were prepared in our laboratory as described by Morel and Serpinet¹⁷. The bonding process has been described by Kováts and Boksanyi¹⁸. The characteristics of the different bonded supports are given in Table I. The specific surface areas of the two substrates are 13.0 and 13.6 m²/g according to the BET nitrogen adsorption method¹⁹. The percentages of bonded carbon were determined by the Service Central d'Analyse du CNRS (Solaize, France).

The preparation of the Carbowax 20000 non-extractable layers on the same Spherosil was carried out according to Vogt and Aue²⁰.

TABLE I
CHARACTERISTICS OF BONDED SUPPORTS

Property	Support No.				
	1	2	3	4	5
Alkyl group	C ₁	C ₁	C ₁₈	C ₁₈	C ₁₈
Bonded C (%)	0.4*	0.5*	1.3	1.5	1.2
Surface coverage ($\mu\text{mol}/\text{m}^2$)	>6*	>6*	4.1	4.6	4.0

* Values of less significance because of the low percentage of bonded carbon.

Gas chromatography

The support was dried at 150°C for 3 h prior to coating with squalane (Merck, Darmstadt, G.F.R.). Freshly distilled dichloromethane was used as the coating solvent. Standard 1/8-in. stainless-steel tubing was used as a 1.5 or 1.2 m × 2.2 mm I.D. column.

A home-made chromatograph as described by De Ford *et al.*²¹ and Amouroux *et al.*²² was used with a thermal conductivity detector (TCD) (GowMac, Madison, NJ, U.S.A.). In this device, the injector is located before an empty stainless-steel reference column (1.5 m × 2.2 mm I.D.), the reference cell of the detector and the packed tested column. All of these components were contained in a thermoregulated air-bath. The use of two columns in series makes it possible to distinguish between the initial peak broadening and the broadening originating from the column under test.

The height equivalent to a theoretical plate, H , is given by²¹

$$H = \frac{L}{5.545} \cdot \frac{(\Delta t_0^2 - \Delta t_i^2)}{(t_0 - t_i)^2}$$

where t_i and t_0 are the times of the peak maxima registered by the reference and sample cells of the TCD, and Δt_i and Δt_0 are the widths of these peaks at half-height.

n-Hexane and benzene (Fluka, Buchs, Switzerland) were used as solutes. The liquid sample size was 0.05 μ l. In all experiments the column temperature was maintained at 80°C. Each column was preconditioned overnight at 80°C. The carrier gas was hydrogen (U-grad; L'Air Liquide, Paris, France).

RESULTS AND DISCUSSION

Figs. 1 and 2 show H as a function of the linear velocity of the carrier gas (u) for *n*-hexane and benzene as solutes and 10 and 30% (w/w) of squalane as stationary phase on four different supports: unmodified Spherosil XOC005 and the same substrate methylsilanized (C_1 -bonded), C_{18} -bonded and Carbowax 20M modified. The curves obtained for 2, 5 and 20% of squalane were similar and are not exhibited here.

Figs. 3 and 4 show the minimum theoretical plate height as a function of the liquid loading of squalane on unbonded, C_1 -bonded, C_{18} -bonded and Carbowax 20M-modified Spherosil XOC005 as supports with *n*-hexane and benzene as solutes.

Fig. 5 shows the H versus u curves obtained for three different batches of C_{18} -bonded Spherosil XOC005 coated with 10% of squalane.

In all instances, the H versus u curve for C_{18} -bonded Spherosil lies well below the curves for unbonded, C_1 -bonded and Carbowax 20M-modified Spherosils. In most instances the upper curve corresponds to the C_1 -bonded Spherosil, except with benzene as solute and stationary phase loadings lower than 15%. In that event, the poor efficiency of the unbonded and low-loaded silica can be ascribed to the "polarity" of benzene and to adsorption phenomena at the surface of the badly deactivated support.

Good deactivation of the Carbowax 20M-modified silica is obvious after the fairly high efficiency obtained for benzene as a solute. However, the H values are relatively high with this support with *n*-hexane and, in any case, they are much higher than those of the C_{18} -bonded support.

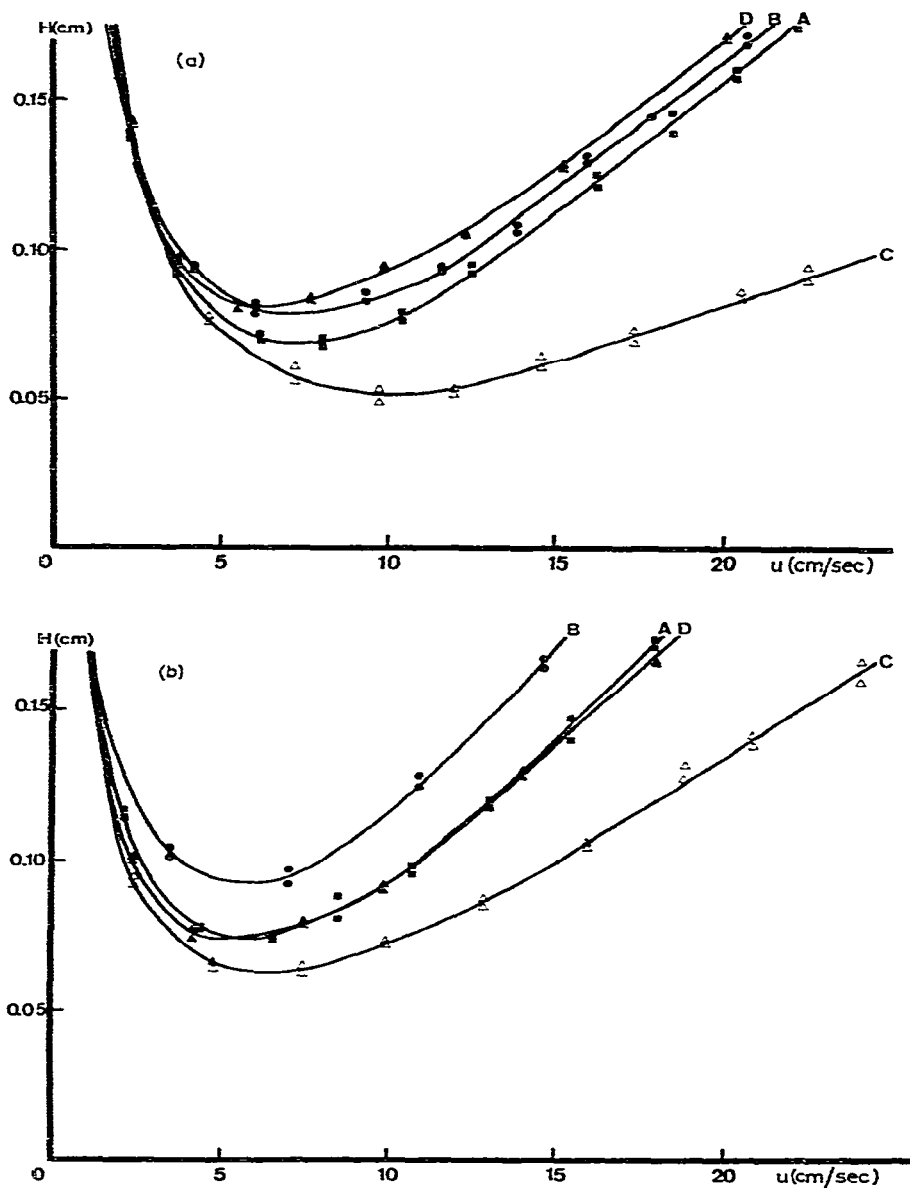


Fig. 1. H versus u curves for n -hexane as solute and squalane as stationary phase on C_1 -bonded (\bullet), untreated (\blacksquare), C_{18} -bonded (\triangle) and Carbowax 20M-modified (\blacktriangle) Spherosil XOC005. Squalane loading: (a) 10% (w/w); (b) 30% (w/w).

As far as column efficiency is concerned, the excellence of the C_{18} -Spherosil at any stationary phase loading is confirmed by Figs. 3 and 4. The significance of this result is emphasized by the relative reproducibility of the H versus u curves from one batch to another: all of the curves in Fig. 5 lie well below the curve for other supports in Fig. 1.

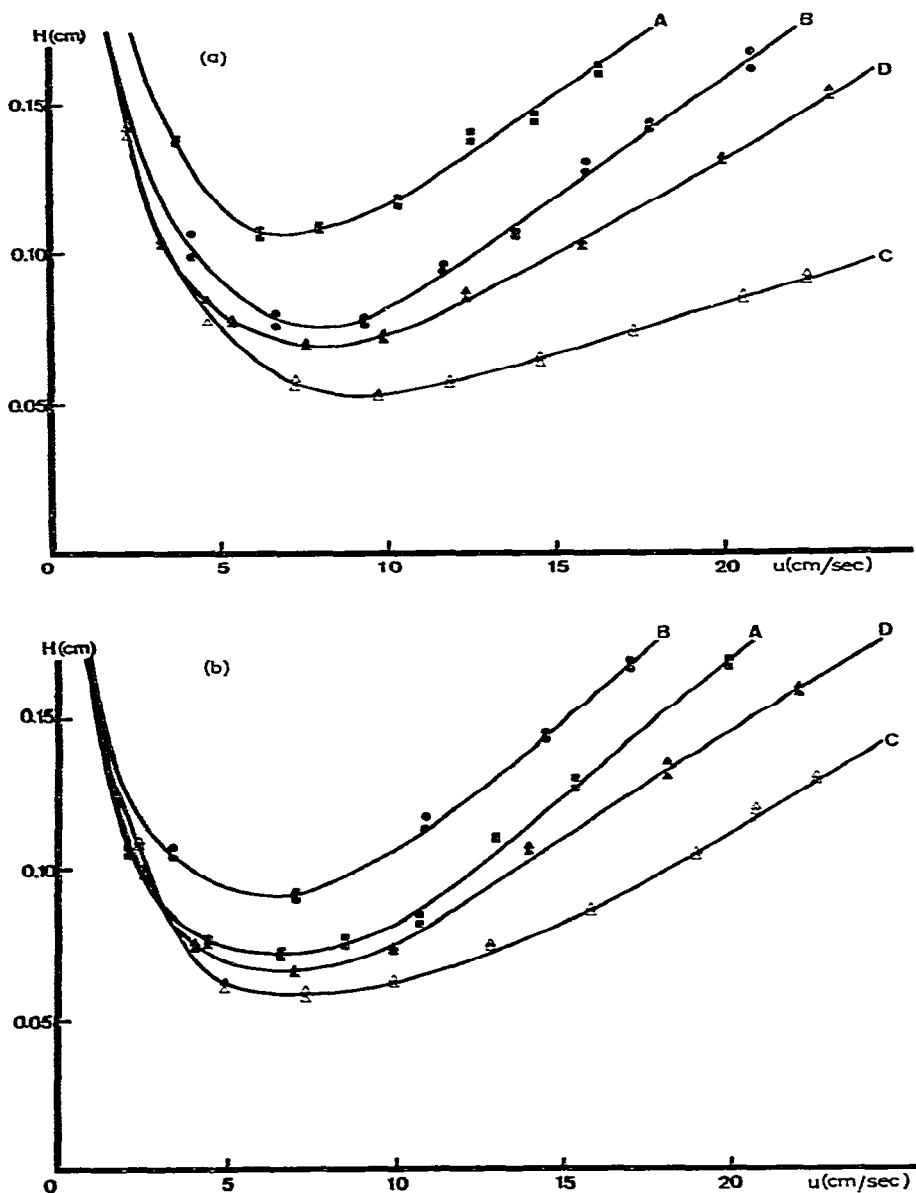


Fig. 2. H versus u curves for benzene as solute and squalane as stationary phase on C_1 -bonded (\bullet), untreated (\blacksquare), C_{18} -bonded (\triangle) and Carbowax 20M-modified (\blacktriangle) Spherosil XOC005. Squalane loading: (a) 10% (w/w); (b) 30% (w/w).

More than 2300 theoretical plates per metre were achieved with 1.2-m C_{18} -columns packed with beads of large particle size (100–200 μm). If smaller and more homogeneous particles were used, higher efficiencies could be expected. The slope of the right-hand side of the H versus u curve is smaller for C_{18} -bonded silica than for other packings. As this slope is proportional to the mass transfer coefficient (C) of the

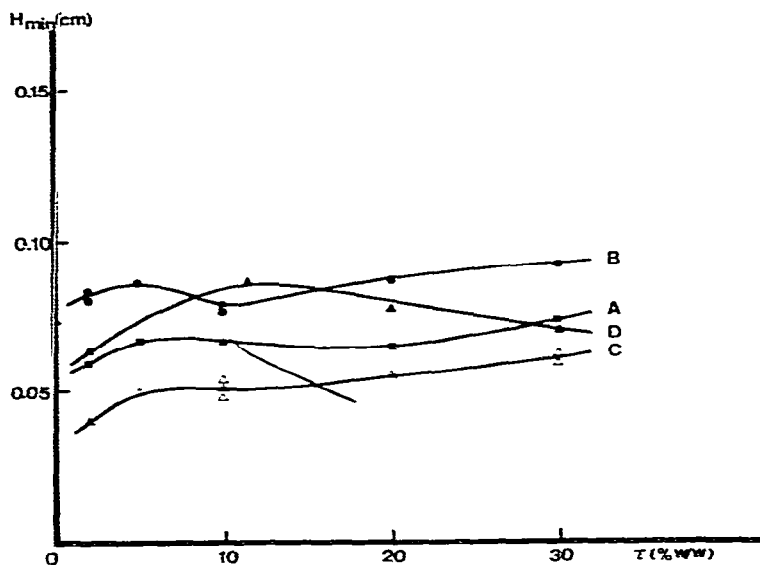


Fig. 3. Variation of minimum theoretical plate height with squalane stationary phase loading (τ) for *n*-hexane as solute and C_1 -bonded (●), untreated (■), C_{18} -bonded (△) and Carbowax 20M-modified (▲) Spherosil XOC005 as supports.

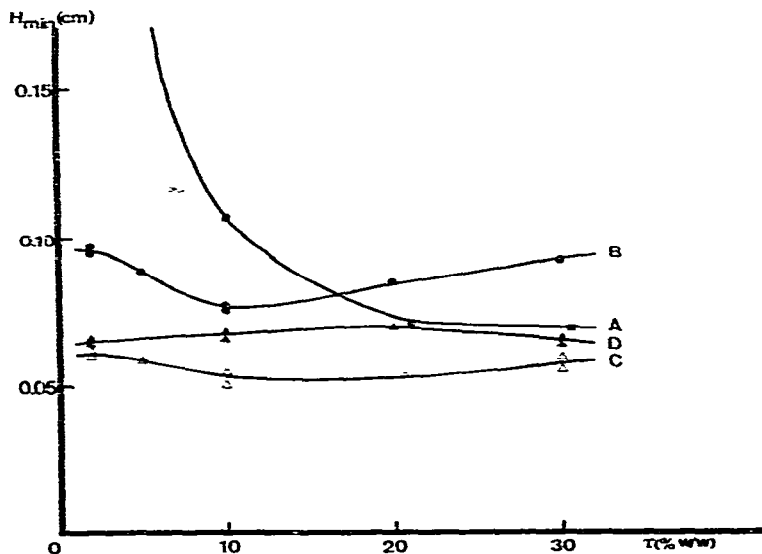


Fig. 4. Variation of minimum theoretical plate height with squalane stationary phase loading (τ) for benzene as a solute and C_1 -bonded (●), untreated (■), C_{18} -bonded (△) and Carbowax 20M-modified (▲) Spherosil XOC005 as supports.

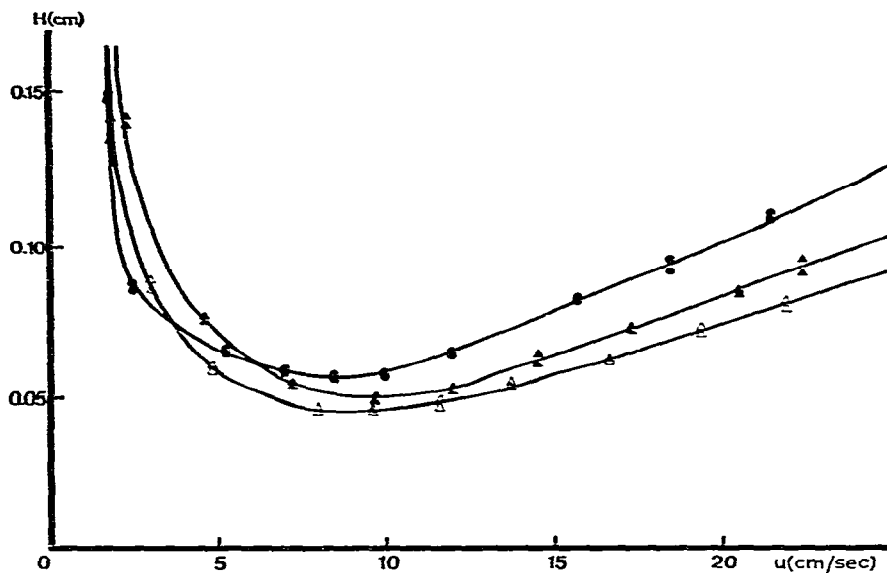


Fig. 5. H versus u curves for n -hexane as solute and squalane as stationary phase on three C_{18} -bonded batches of the same Spherosil XOC005. Squalane loading: 10% (w/w).

Van Deemter equation and as the pore sizes of the very macroporous supports are identical, this seems to indicate a more favourable disposition of the liquid phase for the C_{18} -bonded packing as a consequence of better wetting of the support by squalane. This observation is in agreement with the wetting experiments of Riedo *et al.*¹⁶ on alkyl-bonded glasses. Its consequence is the ability of long-chain alkyl bonded silicas to allow rapid analysis without a significant decrease in efficiency.

In contrast, the poor efficiency and large slope of the ascending branch of the Van Deemter curve for C_1 -bonded and Carbowax 20M-modified Spherosils imply poor wetting of these supports. These results agree well with the conclusions of Serpinet¹⁴ on the non-wettability of the usual (methyl) silanized supports by most stationary phases. They are also in good agreement with the observations of Jönsson²³ on the particularly poor wettability of Carbowax-modified silicas, as shown by the location of curve D in Fig. 1a.

Results presented in this paper emphasize the interest of C_{18} -bonded silicas as supports in gas-liquid chromatography with a non-polar stationary phase. Extension of this work to other bonded radicals, to other stationary phases (such as OV-17) and to other materials (*e.g.*, Chromosorb) is now in progress and will be reported later.

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