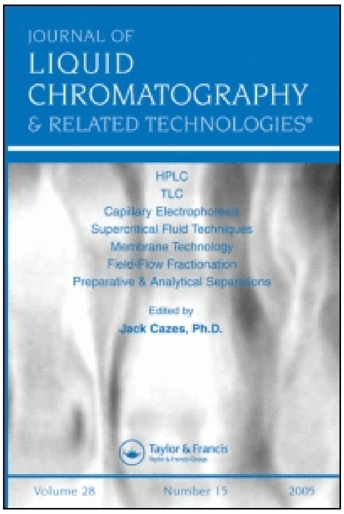

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CHEMICAL MODIFICATION OF SILICA GELS AFTER PRELIMINARY THERMAL TREATMENT.

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ABSTRACT

Chemically bonded phases have been prepared using thermally treated silicagels as basic material. Four bonding reactions with trimethylchlorosilane (TMCS) were successively performed on each silicagel in order to obtain the maximum coverage.

The effect of the chemical modification on the surface structure of packings and on their retention behaviour in reversed-phase chromatography was investigated. The maximum coverage with trimethylsiloxy groups was observed with silicagels previously treated at 300-400°C while the minimum concentration of hydroxyl groups was calculated for silicagels previously treated at 600°C.

Significant differences in retention were observed for these phases in reversed-phase chromatography. Silicagels with maximum coverage were found to be the most convenient for the analysis of apolar solutes while silicagels with minimum hydroxyl group concentration were the most convenient for the analysis of polar solutes.

INTRODUCTION

The reversed-phase chromatographic technique (RPLC) is now the method of separation most widely used by chromatographers. G. Guiochon (1) thinks that a few years from now 70 % of all

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analyses will be carried out using RPLC. Already this percentage seems to have been exceeded. Initially, RPLC was used essentially for the separation of apolar or slightly polar substances, based on the size or alkyl group structure of the molecules. Some authors such as Karger (2) think that this technique can be a powerful and selective tool for a separation based on polarity differences. A large number of studies concerning the separation and the characterization of chemically bonded phases have been published, the most complete with respect to their synthesis being certainly that of E.Sz. Kovats (3).

The main object in the manufacture of such phases is to obtain as high a modification as possible, that is, to bond the maximum surface hydroxyl groups. Indeed, it is well known at present that accessible residual silanol groups contribute to the chromatographic mechanism (4-12), particularly in the case of basic substances (7).

The aim of the chemical modification of the surface is therefore a two fold one :

- to maximize the bonded phase coverage
- to minimize the number of residual silanol groups.

The limit surface concentration reported in the literature for trimethylsiloxy groups is 4.0umole/m^2 (3,12) and 3.5umole/m^2 for the other alkyl dimethylsiloxy groups (3). These limit values were obtained by Kovats (3) after three repeated treatments of the silicagel. The use of alkyl dimethylchlorosilane molecules eliminates the possibility of polymerization as well as the formation of silanol groups by hydrolysis of unreacted Si-Cl bonds (12).

In a number of cases, the bonding reaction is followed by a silanization in order to reduce the number of accessible residual silanols. In a previous article (13), we have shown that by thermally treating the silicagel, the number and the average distance of the surface hydroxyl groups can be controlled as has also been reported by Scott (14). The aim of this article is to describe the preparation and the chromatographic properties of silicagels which have undergone first a thermal treatment and subsequently a chemical surface modification by bonding trimethyl siloxy groups.

EXPERIMENTAL

Chromatographic Apparatus.

The liquid chromatograph consisted of the following components : Model 380 Altex pump (Touzart & Matignon - Vitry s/Seine - France), a damping system, a Chromatem septum injection valve (Touzart & Matignon), Model 2-1428-3 Varian UV photometer. All measurements were made at room temperature.

Reagents.

The compositions of the eluents are indicated in volume/$_{\text{volume}}$ the methanol used for their preparation, RP Normapur quality (Prolabo - Paris) and the acetonitrile, Spectrosol grade (SDS - Peypin - France) were used without further purification. The deionized water was distilled ; once the mobile phase have been prepared, it was degassed in an ultrasonic bath. The trimethyl chloro silane TMCS used for the bonding reaction was supplied by Interchim (Montluçon - France).

Column materials and packings.

The silicagel used as basic material for the bonding reaction was Partisil 5 (Whatman - Reeve Angel - Ferrières - France) thermally treated at 300, 400, 500, 600, 700 and 800°C. No special precautions were taken in the conservation of the silicagel after thermal treatment. The texture and structure characteristics of these thermally modified phases have been pointed out in the preceding article (13). The stationary phases were packed into columns of 10 cm x 4.6 mm I.D. tubing (Touzart & Matignon - Vitry s/Seine France) according to a technique described in the literature (15).

PREPARATION OF CHEMICALLY MODIFIED SILICA GELS

The bonding reaction :

$$\equiv Si - OH + (CH_3)_3Si - Cl \rightarrow \equiv Si - O - Si(CH_3)_3 + HCl$$

is carried out in an apparatus identical to that described by Unger (11,16). 5 g of silicagel were placed in the apparatus and physisorbed water was removed by heating at 200°C and 10^{-1}, 10^{-2} torr during 10 hours. After cooling, the glass ampoule containing an excess of TMCS was broken and the silane distilled on the silicagel. The reaction was continued by heating to 70°C for 10-12 hours. Once the reaction had ended, the sample of silica was heated again to 200°C under vacuum during 10 hours in order to remove excess TMCS and the hydrochloric acid produced by the reaction. The silicagel was finally washed in ether and THF then dried at 120°C for 3 hours. A sample is then microanalysed for carbon content.

For each phase, four successive treatments were carried out, following the same process. Part of the bonded phase was used to pack the column (10 cm x 4.6 mm I.D.), the rest being used for other determinations (% C, specific surface, pore volume distribution).

RESULTS - DISCUSSION

Stationary phase characteristics.

All experiments were carried out with Partisil 5. The specific surface areas, S_{BET}, of the packings were obtained from nitrogen sorption measurements at - 195°C according to the BET method using an apparatus set up in the laboratory as described by S.J.Teichner and al (17). From the values indicated in Table 1, one can see that the decrease in specific surface area, expressed in % with respect to the basic material is of the order of 20 to 24 %, with the exception of the bonded silicagel after thermal treatment at 800°C, in which case the decrease is only 7 %.

The pore volume was calculated from the nitrogen adsorption isotherm at a relative pressure of 0.95 ($P/p_0 = 0.95$). The pore volume is significantly reduced with respect to that of the basic material except in the case of silicagel G^4_{800}, where the pore volume is of the same order of magnitude as that of the basic material (Table 1). Obviously, an increase in the bonding phase coverage considerably increases the fraction of the pore volume occupied by the alkyl bonded groups.

TABLE 1

Variation of Pore Structure Parameters

Original silica	Untreated silica	300°C	400°C	500°C	600°C	700°C	800°C
S_{BET} $m^2.g^{-1}$	400	414	432	402	399	368	200
C_{BET}	102	73	86	98	80	71	77
V_p $cm^3.g^{-1}$	0.65*	-	-	0.69*	0.65*	0.55*	0.30*
Bonded silica	G^4	G^4_{300}	G^4_{400}	G^4_{500}	G^4_{600}	G^4_{700}	G^4_{800}
S_{BET} $m^2.g^{-1}$	310	321	328	322	307	293	186
C_{BET}	19	18	24	30	27	49	37
ΔS %	22.5	22.5	24.1	20	23.1	20.4	7
V_p $cm^3.g^{-1}$	0.56	0.51	0.52	0.52	0.63	0.51	0.31
$\bar{r}_p$ nm	2.0** 2.8***	2.9** 2.0 , 2.4***	2.0** 2.8***	2.0** 2.8***	2.0** 2.8***	2.9**	3.4**

* values measured for Partisil 20

** first maximum (more important)

*** second maximum

It is difficult to make a clear distinction between the free space and the volume occupied by the bonded layer, because as noted by Unger (12), the latter shows an open network which can be penetrated by molecules and which perhaps shows swelling properties.

From the calculation of the distribution of mean pore diameter, using the nitrogen desorption isotherm, according to the method of Pierce (18), as modified by Orr and Dalla Valle (19), one can evaluate the texture modification due to bonding. As we have indicated previously (13), thermally treated silica gels give a single distribution of mean pore diameter with a maximum at $\bar{r}_p \simeq 2.9$ nm. After

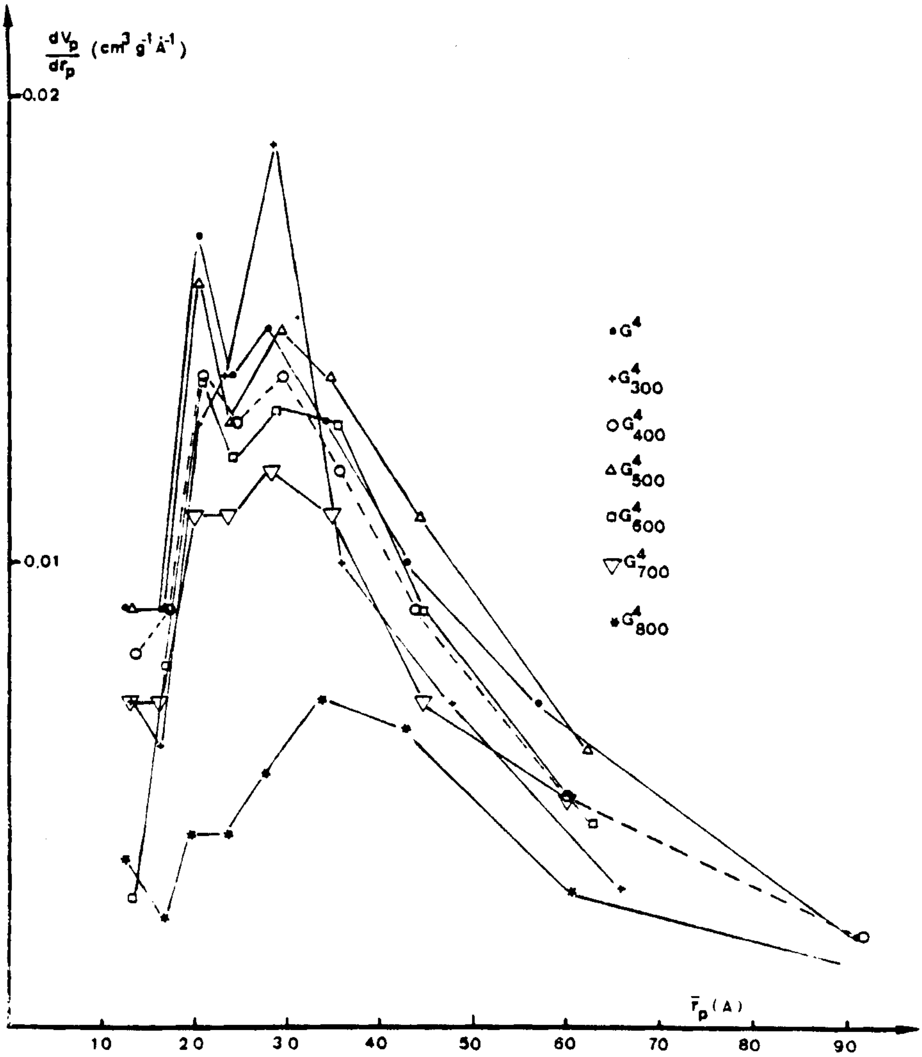

FIGURE 1 - Relative pore volume distributions of bonded silicagels.

bonding, one sees (Figure 1) a double distribution for all of the silicagels. For silicagels G^4, G^4_{400}, G^4_{500} and G^4_{600}, the two maxima are seen to be at $\bar{r}_p$ = 2.0 nm and $\bar{r}_p \simeq$ 2.8-2.9 nm. In the case of G^4_{700} and G^4_{800}, the first distribution becomes less important and the second moves toward the large pores ($\bar{r}_p$ = 3.4 nm for G^4_{800}).

Two stages can be distinguished in the evolution of texture size :

- up to 600°C, thermal treatment does not produce noticeable changes in texture (pore volume, specific surface area). The original silicagel gives a single distribution of pore volume. After bonding, a double distribution is observed, one of which corresponds to a pore diameter smaller than that of the initial silicagel and a decrease in the pore volume and in the specific surface.
- for temperatures above 600°C, the pore volume and the specific surface of the original silicagel decrease with the temperature of thermal treatment.

Assuming that this decrease arises from the removal of the narrowest pores, the addition of a bonded layer in the widest pores no longer appreciably modifies the pore volume and the specific surface (case of G^{4}_{800}).

Concentration of remaining surface hydroxyl groups.

At present, none of the bonded phase characterization tests is entirely satisfactory. The first characterization method is based on the results of the elemental analysis which gives the carbon Content C % (Table 2). From these values, the surface coverage can be calculated using the formula :

$$\alpha_{exp}(\mu\text{mole.m}^{-2}) = \frac{C\,\%}{1.2\ N_c\left(1000 - C\,\%\ .\ {}^{M}/(N_c \times 12)\right)\ S_{BET}.10^{-6}}$$

C % = Carbon content obtained by elemental analysis.

M = molar weight of the bonded functional group

N_c = number of carbon atoms in the bonded silane molecule

S_{BET} = specific surface area of the starting support ($m^2.g^{-1}$)

In Table 2, G^{x}_{y} represents a silicagel which has undergone a preliminary thermal treatment at y°C, than x reactions with TMCS.

TABLE 2

Properties of Silanized Supports

Designation of product	Original Silica	% C	Surface Concentration α_{exp}. µmole.m^{-2}
G^1	Partisil 5	3.09	2.29
G^2		4.05	3.07
G^3		4.06	3.07
G^4		4.24	3.23
G^1_{300}	Partisil 5	3.24	2.33
G^2_{300}	thermally treated	3.90	2.84
G^3_{300}	at 300°C during	4.04	2.96
G^3_{400}	5 hours	4.33	3.19
G^1_{400}	Partisil 5	3.56	2.47
G^2_{400}	thermally treated	3.70	2.57
G^3_{400}	at 400°C during	3.74	2.60
G^3_{400}	5 hours	3.78	2.63
G^1_{500}	Partisil 5	1.77	1.27
G^2_{500}	thermally treated	2.45	1.78
G^3_{500}	at 500°C during	2.43	1.77
G^4_{500}	5 hours	2.68	1.96
G^1_{600}	Partisil 5	2.47	1.81
G^2_{600}	thermally treated	2.15	1.56
G^3_{600}	at 600°C during	2.25	1.64
G^4_{600}	5 hours	2.37	1.73
G^1_{700}	Partisil 5	1.08	0.83
G^2_{700}	thermally treated	1.34	1.04
G^3_{700}	at 700°C during	1.43	1.11
G^4_{700}	5 hours	2.03	1.60
G^1_{800}	Partisil 5	0.55	0.77
G^2_{800}	thermally treated	0.88	1.25
G^3_{800}	at 800°C during	1.22	1.74
G^4_{800}	5 hours	1.62	2.33

The α_{exp} values show that the surface coverage remains more or less constant up to 300°C (3.2 mole.m^{-2}) then decreases from a 400°C preliminary thermal treatment onwards.

A second characterization test for the bonded phases is the determination of the residual surface hydroxyls. By considering on the one hand the values of surface concentration in silanol sites (13), expressed in μmole.m^{-2}, and on the other hand the surface concentration in bonded groups deduced from elemental analysis, one can then estimate for each silicagel the percentage OH which has reacted. The results are shown in Table 3. W represents the quantity of chemisorbed water (%), determined as described previously (13).The values of the total concentration of surface hydroxyls, deduced from the chemisorbed water content W_{H_2O}, are appreciably higher than the generally accepted mean value of 8 μmole OH.m^{-2} (3,11).

According to Kovats (3) and identical results of Taylor and Hockey (20) commercial silicagels contain water inclusions in variable quantity. The high values (9.9 μmole.m^{-2}) found for the surface hydroxyl concentration probably result from the method used in their determination (13).

The maximal modification was obtained with a silicagel pretreated at 400°C for which 42 % of the surface hydroxyls had reacted.

TABLE 3

Surface Coverage of Silanized Supports

Original Silica	Partisil 5	400°C	500°C	600°C	700°C	800°C
W g %	3.6	2.5	2.2	1.8	1.7	1.2
$S_{BET} m^2.g^{-1}$	400	432	403	399	368	200
μmole OH.m^{-2}	9.9	6.3	5.9	4.9	4.9	6.6

Bonded Silica	G^4	G^4_{400}	G^4_{500}	G^4_{600}	G^4_{700}	G^4_{800}
α_{exp}	3.23	2.63	1.96	1.73	1.60	2.33
% of reacted OH	33 %	42 %	33 %	35 %	33 %	35 %

For temperatures over 400°C, the conversion rate remains more or less constant ($\simeq$33 - 35 %) and equal to that obtained with untreated silicagel. It should be noted that, in all cases, the α values are lower than those of 4 μmole.m^{-2} generally indicated in the literature (3,11,21). This difference probably comes from the original silicagel which has a relatively high specific surface area (400 m^2.g^{-1}) and a relatively small mean pore diameter (6 nm). By bonding trimethyl siloxy groups to silicagels with specific surface areas of 211 m^2.g^{-1} and 301 m^2.g^{-1}, Unger (11) has obtained a decrease in α from 4.5 (211 m^2.g^{-1}) to 4.1 μmole.m^{-2} (301 m^2.g^{-1}), which seems to indicate that the specific surface area and there fore the pore volume exert a significant influence on the bonding coverage.

CHROMATOGRAPHIC BEHAVIOUR OF CHEMICALLY BONDED PHASES

Straight Phase System.

A judicious method for testing the residual OH in a silicagel after bonding consists in measuring the retention of small polar solutes molecules with a dry eluent (heptane, isooctane) (11,12). The silicagel is then used as a polar adsorbent. Benzene, nitrobenzene, acetophenone and phenol have been used to test the surface coverage of bonded silicagels. k' values for these aromatic species are shown in Table 4.

TABLE 4

Capacity Factors (k') of Solutes on Silanized Supports in Dry Isooctane Eluent

Silica	G^4	G^4_{300}	G^4_{400}	G^4_{500}	G^4_{600}	G^4_{700}	G^4_{800}
k' benzene	0.24	0.20	0.31	0.35	0.24	0.31	0.23 0.45
k' nitrobenzene	2.24	1.92	3.23	3.68	2.48	3.65	1.76 2.31
k' acetophenone	13.10	7.58	12.91	22.18	11.90	25.92	8.88
k' phenol	21.7	11.00	11.82	10.69	3.98	6.76	3.93

For the least polar molecules (benzene, nitrobenzene), k' values are small and hardly differ from one silica gel to another. On the other hand, for acetophenone and phenol, liable to give strong H-bonding with the unreacted hydroxyls, the retentions remain considerable. An important decrease in the k' values is observed for G^4_{600}; referring to Table 3, G^4_{600} is the silicagel for which the number of residual hydroxyls per unit surface α_{OH}/m^2 is the lowest.

Although authors are not all in agreement as to the chromatographic role of these remaining OH even after silanization (2,12,21) it is obvious that the hydroxyl groups play some role, in particular with respect to polar species. B.L. Karger (2) has observed differences in retention of 20 % with two bonded silicagels from the same batch and having both been further silanized. We agree with this author in saying that the residual silanol test with a dry eluent is a more conclusive test than the determination of the bonded coverage α_{exp} using C and H % microanalysis.

Reversed-Phase Chromatography.

Numerous publications point out the linearity of the relations : log k' = f (% modifier in eluent) and log k' = f (N_c) for an homolo-

TABLE 5

k' Values of Barbiturates - MeOH/H_2O 60/40

Bonded silica / Barbiturate	G^4	G^4_{300}	G^4_{400}	G^4_{500}	G^4_{600}	G^4_{700}	G^4_{800}
Bartibal	1.03	1.08	1.05	0.78	0.87	0.77	0.60
Allobarbital	1.13	1.96	1.73	1.25	1.50	1.18	0.95
Phenobarbital	1.96	2.27	2.23	1.71	2.18	1.55	1.32
Tetrallobarbital	3.35	3.82	3.36	2.39	2.95	2.27	1.91
Hexobarbital	3.52	4.31	4.76	4.0	5.45	4.14	3.55
Prominal	3.78	4.53	4.86	3.62	4.85	3.59	2.80
Amobarbital	4.91	5.77	5.32	4.32	5.45	4.35	3.20
Secobarbital	6.22	7.41	6.73	4.85	6.03	4.73	3.72
Thiogenal	10.17	12.49	11.55	8.70	12.18	9.18	5.86

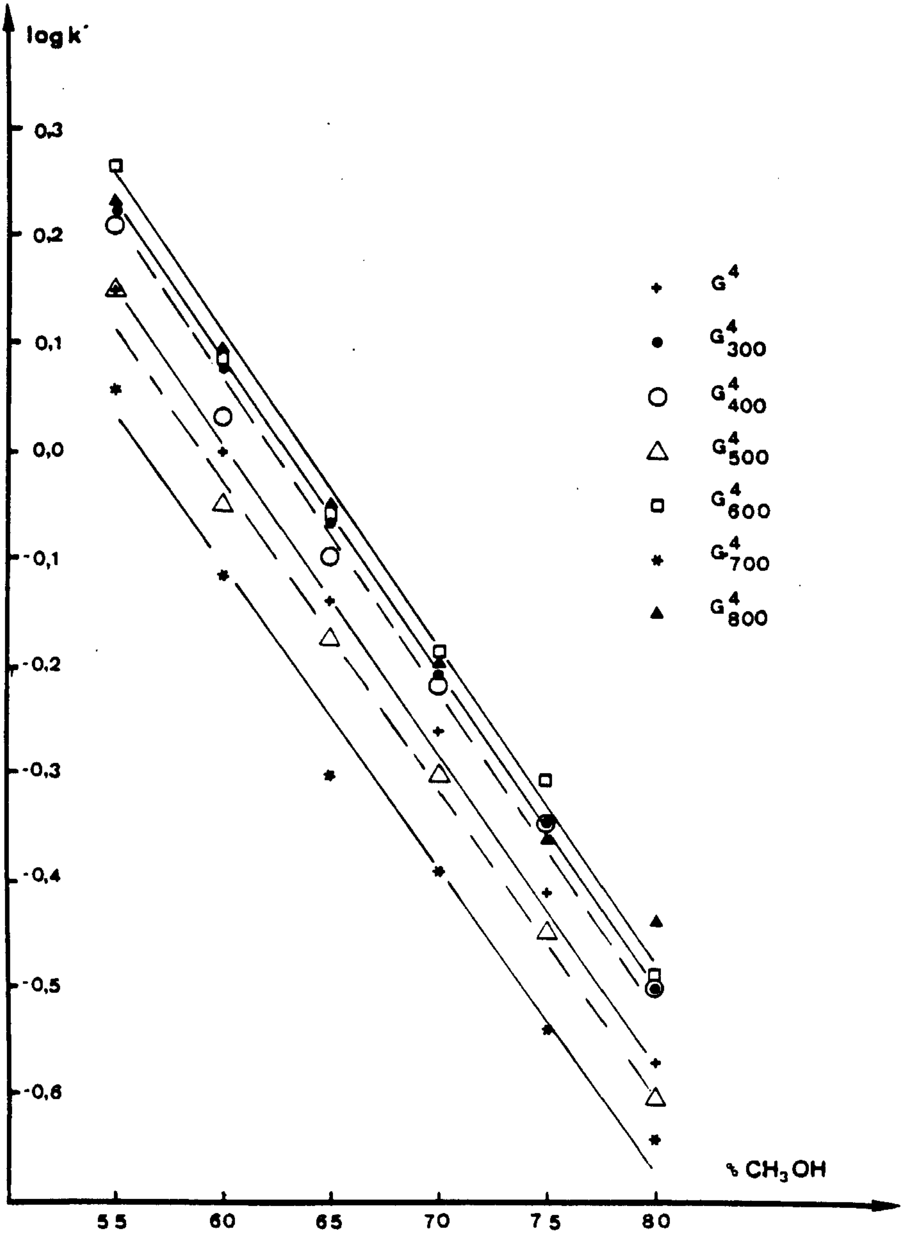

FIGURE 2 - Plot of log k' versus % MeOH in the mobile phase. Solute : toluene.

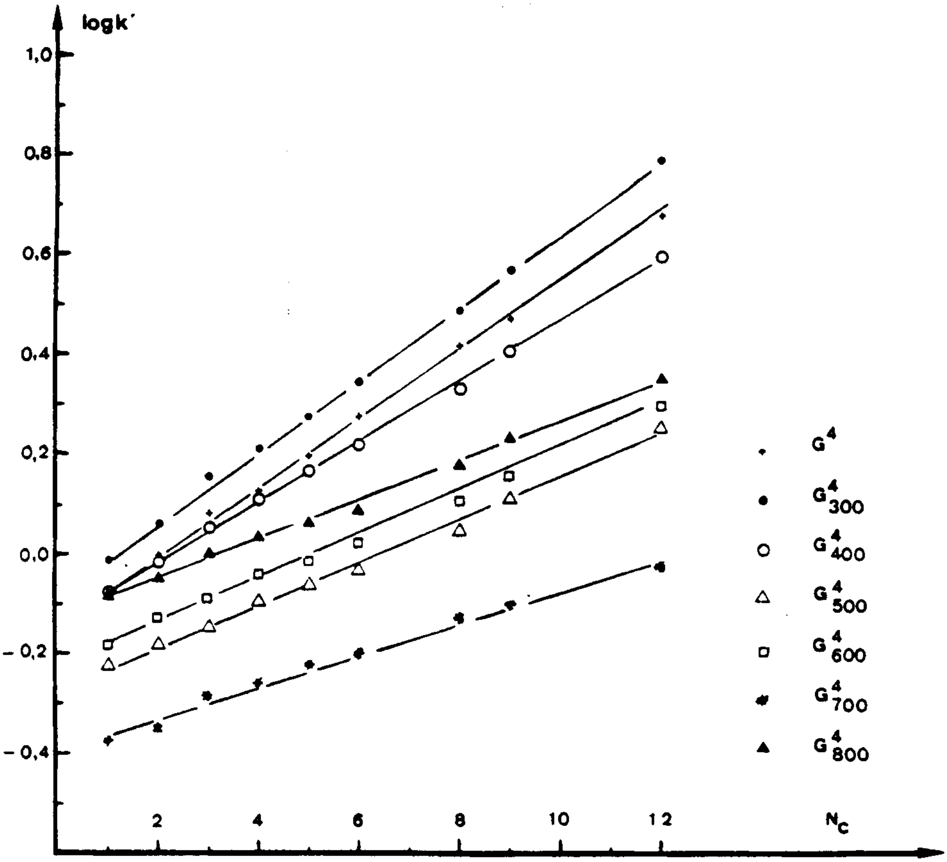

FIGURE 3 - log k' against carbon number of n-alkyl benzenes. Mobile phase : Acetonitrile - H_2O, 70-30 v/v.

gous series. Such relations have also been obtained for our bonded phases, as shown in Figures 2 and 3. The changes in slope of the lines log k' = $f(N_c)$ express the changes in selectivity for the same family of solutes and the same eluent when one goes from one stationary phase to another.

The best selectivities and the highest retentions are observed for silica gels G^4_{300}, G^4 and G^4_{400}, that is, for the maximal values of α_{exp}. For slighty polar solutes (n-alkylbenzenes), retention and selectivity, in reversed phase chromatography, seem to depend above

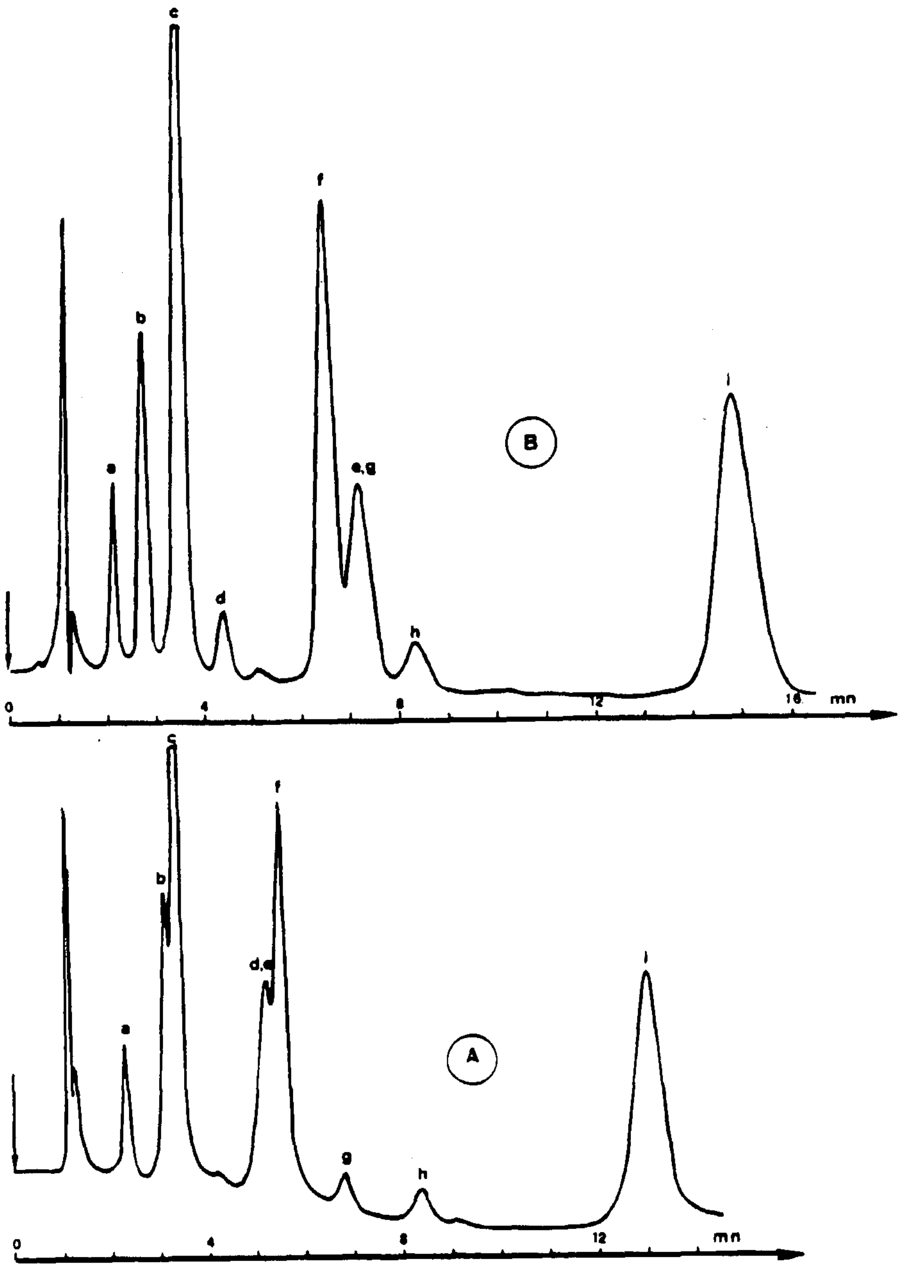

FIGURE 4. Chromatograms of barbiturates. (a) G^4 silicagel. (b) G^4_{600} silicagel. Mobile phase: MeOH - H_2O 40-60 v/v, Flow rate: 1 ml/mn, UV Detection 254 nm, s = 0.16, Injection volume: 3 μl, solutes: a- barbital, b- allobarbital, c- phenobarbital, d- tetrallobarbital, e- hexobarbital, f- prominal, g- amobarbital, h- secobarbital, i- thiogenal.

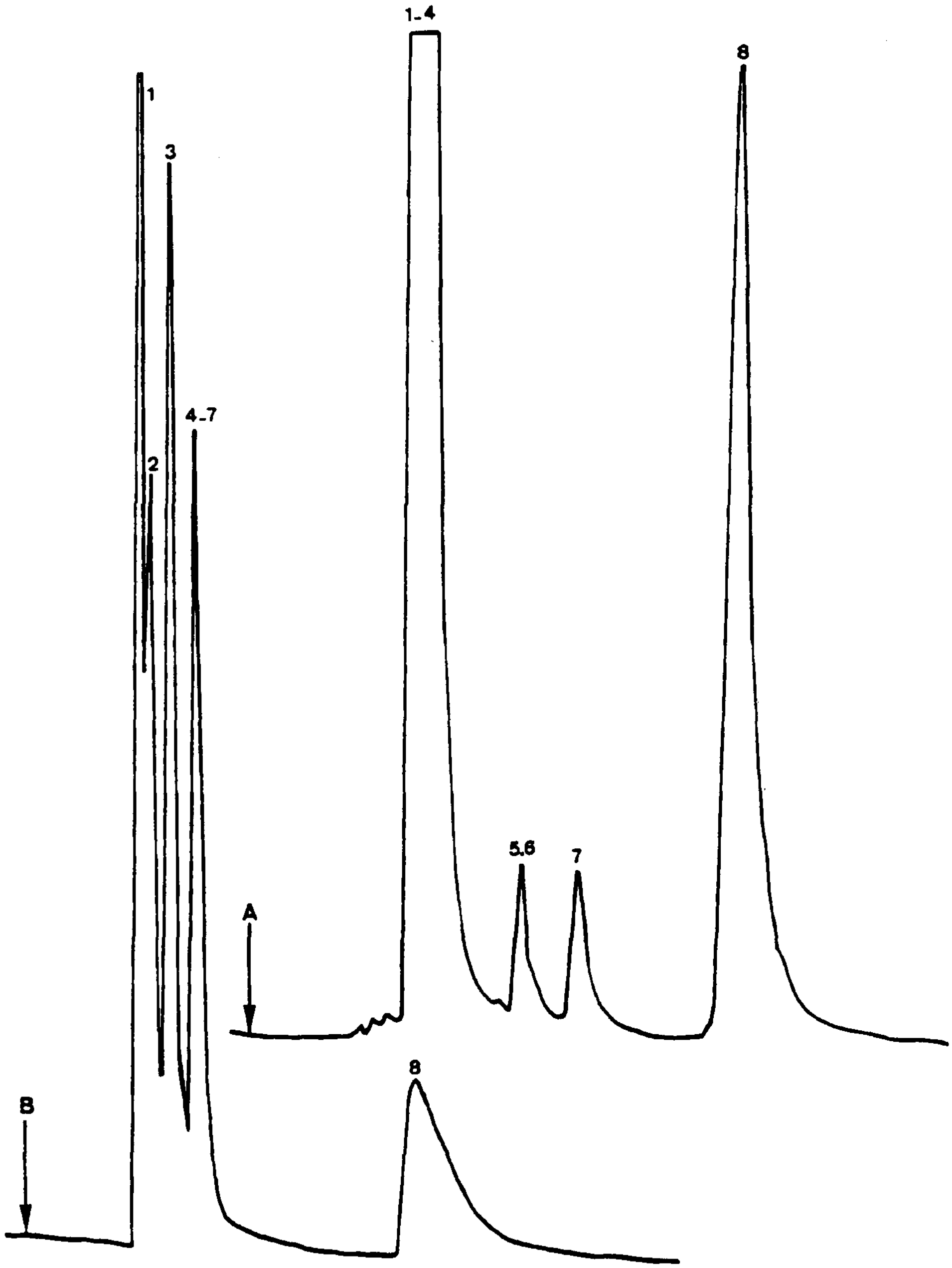

FIGURE 5. Chromatograms of phenols. (A) G^4_{300} silicagel (B) G^4_{600} silacagel. Mobile phase MeOH - H_2o 50-50 v/v pH 3. Flow rate: 0.6 ml/min ΔP = 40 bars. UV detection 254 nm. Solutes: 1- 2,4,6-trinitrophenol, 2- 4-nitrophenol, 3- 2,4-dinitrophenol, 4- 2-nitrophenol, 5- m-tertiobutylphenol, 6- p-tertiobutylphenol, 7- o-tertiobutylphenol, 8-2,4-dinitro 6-tertiobutylphenol.

all on the bonded phase coverage of the silicagel in organic group. Examining the chromatographic behaviour of these stationary phases with respect to the more polar solutes, the barbiturates, it can be seen (Table 5 and Figure 4) that the best selectivity is obtained (for the most polar solutes 1, 2, 3, 4) for the stationary phase G^4_{600}, that is for a minimal α_{OH} value.

One can therefore put forward the following hypothesis about the behaviour of these bonded phases in RPC.

- in the case of apolar or slightly polar solutes, retention and selectivity are above all determined by α_{exp}, the bonded surface coverage in organic species.

- in the case of polar solutes, retention and selectivity are strongly influenced by α_{OH}, the number of remaining hydroxyls on the surface of the support. Then, the most convenient stationary phases are those with minimal α_{OH} values.

This hypothesis is confirmed in the present case by the analysis of phenol derivatives : o, m, p-tertiobutyl phenols and nitrophenols. Figure 5 shows that the most polar components (nitrophenols) are well resolved for silicagel G^4_{600} while the selectivity is less good for the tertiobutyl phenols. Exactly the opposite occurs in the case of silicagel G^4_{300}, that with the maximal bonded coverage.

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