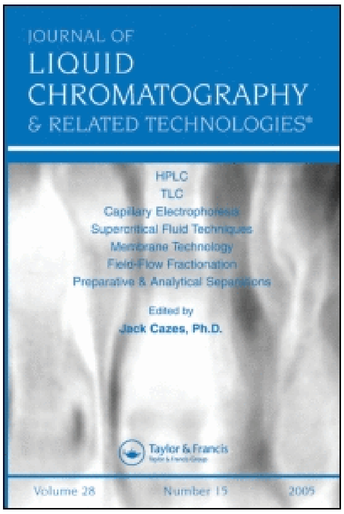

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SURFACE MODIFICATION OF SILICAGELS. EVALUATION OF THERMALLY - TREATED COMMERCIAL SILICAGELS.

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ABSTRACT

The chromatographic properties and the structure and texture of thermally treated silicagels have been studied. Commercial silicagels (Partisil and Lichrosorb) were thermally modified at 300, 400, 500, 600, 700, 800 and 900°C. The evolution of specific surface, pore volume and distribution of mean pore diameter as a function of temperature was investigated. It is shown that the modification at 600°C is the most interesting one : reducing the hydroxyl concentration of a silicagel by a controlled thermal treatment, all the surface hydroxyl groups could be involved in a chemical modification.

INTRODUCTION

In a previous article (1), two methods of deactivation of silica gels have been studied : deactivation by addition of water in the chromatographic system and deactivation by thermal treatment. The latter method was studied mainly from the chromatographic point of view. In this work, we were particularly interested in the structure and texture of thermally treated silicagel, a study which could

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provide a better understanding of their chromatographic behaviour.

Scott and Kucera have shown (2), by studying thermally treated silicagels, that the retention of a solute on such an adsorbent depends only on its water or hydroxyl group content, and little, if at all, on siloxane groups. The surface characteristics of silica gels greatly influence the chromatographic parameters in liquid-solid chromatography (3-6). These characteristics are closely linked with the method of preparation, as well as the subsequent treatments of the silica gel.

The nature of silica gel surfaces has been the object of a number of articles. The interactions of surface hydroxyl groups with several adsorbents and reagents have been widely examined (7-13). Several authors have examined the influence of thermal treatment on the water and silanol groups on silica gel surfaces. De Boer and Vleeskens (4) consider that physisorbed water is removed by heating to 120°C ; on the other hand, Lange (15) has shown that strongly physisorbed water is not removed below 180°C, at which temperature Young and Bursh (16) think that the silanol groups begin to condense with water elimination. According to Snyder and Ward (17), silica gel loses a significant number of hydroxyl groups from 200°C upwards. Other workers go much further : they consider that a temperature of 300°C is necessary to remove all the physisorbed water (18) and even suggest that water strongly bound to silica gel surface can stay right up to 600°C (19).

As for the complete dehydration of silica gels, a temperature over 1000°C is required. Up until 400°C, the reactions which take place on the silica gel surface are not reversible at room temperature and beyond 400°C the reaction is completely irreversible (20). A porous silica gel undergoes modifications during a thermal treatment. Young (21) has shown that sintering begins at 900°C and that the decrease in specific surface varies linearly with thermal treatment time. Sintering is a very complex phenomenon in which several factors seem to play a role :

- mineral impurity content,
- constitutional hydroxyl content,
- adsorbent texture and, in particular, its porosity type.

EXPERIMENTAL

Thermal treatment. They were carried out on 3 g fractions of support. The silica gels modified were LICHROSORB SI 60 5 µm (batch EF 54) (MERCK - Darmstadt GFR), Partisil 5 (Batch A 311) and Partisil 20 (Batch A 266) (Whatman - Ferrières - France). The silica gel was placed in a quartz crucible ; all of which was put in a furnace whose temperature was fixed and regulated to ± 1°C. The temperature range studied was 300 - 900°C. For all modifications the treatment time was 5 hours. After treatment, the silica gel fractions were left at room temperature, without taking any special precautions.

Reagents-Products. The solvents used as eluents were analytical grade dichloromethane and isooctane (MERCK). Dry solvents were obtained by percolation on activated silica gel (MERCK silica gel 60, 0.063 - 0.200 mm) through a glass column (60 cm x 3 cm). They were then stored on a molecular sieve. The water content of eluents was controlled by Karl Fischer titration with an automatic Karl Fischer titrator E 547 (Metrohm, Herisau, Switzerland).

Chromatographic apparatus. The chromatographic study was carried out either with a Spectraphysics 3520 chromatograph or with an apparatus assembled in the laboratory and consisting of : Model AE-10-4 Orlita pump (Sedere - Paris), a damping system, a RHEODYNE valve (70-10) and a model 2-1428-3 Varian UV 254 nm photometer. All measurements were made at room temperature.
The columns were packed with silicagels modified according to a technique developed in the laboratory (22). The column dimensions were 10 cm x 4.6 mm I.D. for Lichrosorb SI60 and Partisil 5 and 25 cm x 4.6 mm I.D. for Partisil 20. All measurements were made at room temperature and in isocratic conditions. The column characteristics for the various modified silica gels are shown in Tables 1 and 2.

It can be noted that the external porosity varies only slightly with the temperature while the internal porosity decreases

Table 1

Column Properties for Thermally Modified Lichrosorb SI 60

LICHROSORB SI 60

T°C	Weight of Silica gel in column(g)	Column Dead volume (ml)	External porosity ε_e	Internal porosity ε_i	Total porosity ε_t
un-treated	0.757	1.30	0.47	0.31	0.78
350	0.774	1.22	/	/	/
400	0.773	1.23	/	/	/
450	0.770	1.23	/	/	/
500	0.786	1.25	0.45	0.30	0.75
600	0.742	1.25	/	/	/
650	0.808	1.24	/	/	/
700	0.823	1.24	0.47	0.27	0.74
800	1.016	1.16	0.51	0.19	0.70
900	1.415	0.96	0.56	0.02	0.58

significantly from 800° onwards, reaching almost zero at 900°C. In order to estimate the pore volume of a silica gel, it can be treated to 1000°C so that it undergoes a sintering ; then pack two identical columns : one with the modified silica gel, the other with the untreated silicagel. The pore volume can be determined as the difference between the two column dead volumes.

DENSITY MEASUREMENTS

With the apparatus used (22), the pycnometer can be filled under a 10^{-2} torr vacuum after the sample has been degassed for 2 hours at 150°C. Benzene was used as pycnometric liquid. Table 3 shows that for the two silica gels studied, the increase in density as a function of thermal treatment only reaches 10 % at 1200°C, with respect to untreated silica gel.

Table 2

Column Properties for Thermally Modified PARTISIL 20

T°C	Weight of Silica gel in Column (g)	Column Dead volume (ml)	External porosity ε_e	Internal porosity ε_i	Total porosity ε_t
un-treated	2.09	2.96	0.43	0.28	0.71
400	2.05	3.04	/	/	/
500	2.05	3.07	0.43	0.31	0.74
600	1.97	2.97	0.47	0.24	0.71
700	2.28	3.19	0.45	0.32	0.77
800	2.92	2.79	0.46	0.21	0.67
900	4.21	2.14	/	/	/

ε_e is the external porosity = fraction of column volume between silica particles.

ε_i is the internal porosity = total pore volume available to the mobile phase, expressed in fraction of column volume.

ε_t is the total porosity $\varepsilon_t = \varepsilon_e + \varepsilon_i$

SPECIFIC SURFACE, PORE VOLUME AND DISTRIBUTION OF MEAN PORE DIAMETER

The specific surfaces of thermally treated silicagels were obtained by the BET method using nitrogen as adsorbent at - 195°C. The calculation of pore diameter distribution was done according to PIERCE's method (23) as modified by ORR and DALLA VALLE (24) using the nitrogen desorption branch. The pore volumes were measured from the same isotherms for a relative pressure of 0.95 according to the Gurvitsch rule (25). The pore diameter distribution curves show a double distribution in the case of untreated LICHROSORB SI 60

Table 3

Density values of Thermally Modified Silica Gels

Lichrosorb SI 60

T°C	untreated	400°C	500	600	700	800	900	1200
Density	2.05	2.09	2.14	2.17	2.18	2.19	2.21	2.24
V_s specific volume $cm^{-3}g^{-1}$	0.487	0.478	0.467	0.461	0.459	0.457	0.452	0.447
Partisil 20								
Density	2.09	2.14	2.16	2.17	2.18	2.20	2.21	2.26
$V_s\, cm^3 g^{-1}$	0.478	0.467	0.464	0.460	0.459	0.454	0.452	0.442

(Fig. 1) for $\bar{r}_p$ = 2 nm and $\bar{r}_p$ = 2,9 nm. The second distribution ($\bar{r}_p$ = 2.9 nm) is less important than the distribution with a maximum at 2.0 nm. This double distribution is seen again, but shifted towards the wider pores, for the different thermal modifications. For thermally treated and untreated PARTISIL 20, there is a single distribution with a maximum at 3 nm (Fig. 1).

The decrease in specific surface becomes significant from 700°C upwards (Tables 4 and 5). At 900°C, the sintering is considerable and for PARTISIL, there is no more adsorption whatsoever, even for P/p_o = 1. The evolution of pore volume follows that of specific surface : the decrease in pore volume begins at 600-700°C ; at 700°C, it is 9 % for LICHROSORB SI 60 and 15 % for PARTISIL 20.

The evolution of the BET constant, C_{BET} as a function of thermal treatment is interesting : C_{BET} is directly related to the net adsorption heat, its value therefore giving an indication of surface activity. C_{BET} decreases slowly from unmodified support up to 600°C, then remains constant at a relatively high value for subsequent tem-

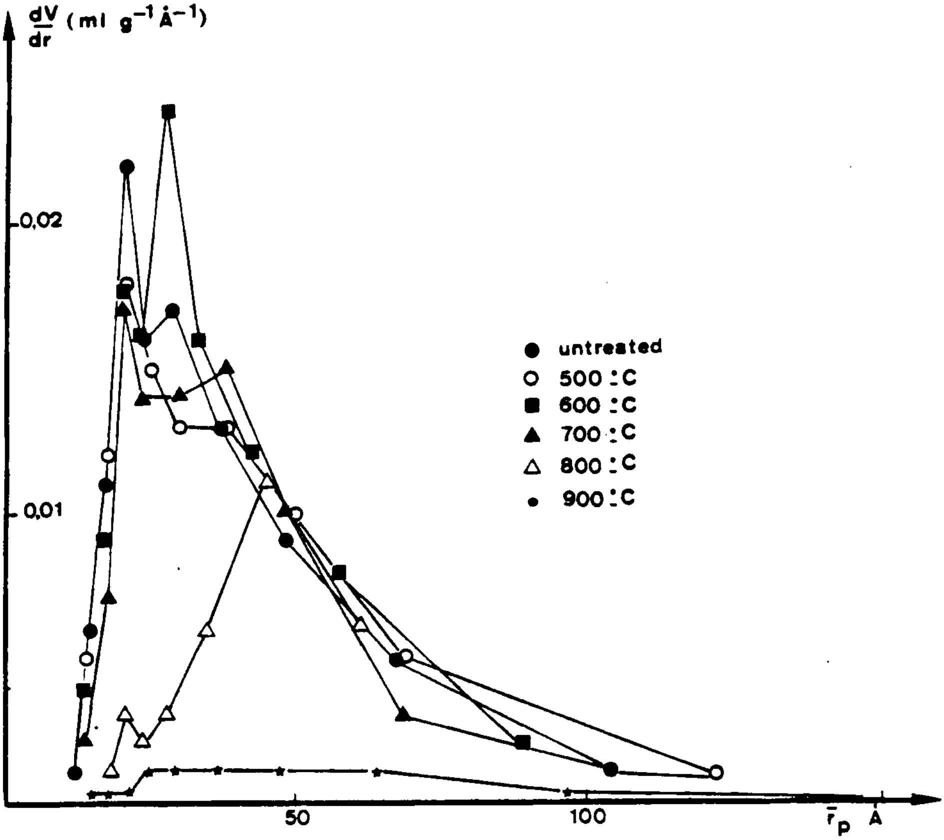

FIGURE 1 - Lichrosorb SI 60. Relative pore volume distributions for the various thermal treatments.

Table 4

Variation of Pore Structure and Surface Parameters by Means of Thermal Modification - LICHROSORB SI 60

T°C	untreated	400	500	600	700	800	900
S_{BET} $m^2.g^{-1}$	463	441	455	472	367	186	39
$V_p(N_2)cm^3.g^{-1}$	0.661		.686	.661	.602	.349	.066
$\bar{r}_p$ (nm)	2.0,2.9		2.0 3.0-3.8	2.0 2.8	2.0 3.8	2.0 4.5	2.5 6.4

Table 5

Variation of Pore Structure and Surface Parameters by Means of Thermal Modification - PARTISIL 20

T°C	untreated	500	600	700	800
$S_{BET} m^2.g^{-1}$	403	380	398	312	169
C_{BET}	99	94	87	87	88
$V_p (N_2) cm^3.g^{-1}$	0.65	0.69	0.65	0.55	0.30
$\bar{r}_p$ nm	2.9	3.0	2.9	3.0	2.9-3.2

S_{BET} = specific surface area using the B.E.T. method

V_p = pore volume $\bar{r}_p$ = most frequent pore radius of the relative pore volume distribution

peratures. This decrease in C_{BET} up to 600°C expresses the surface deactivation by thermal modification ; however the surface remains just as active after a 800°C treatment as after a 600°C one. This is confirmed by the chromatographic behaviour of these modified silicagels which shows very little evolution between 600 and 800°C.

EVOLUTION IN WATER CONTENT OF THERMALLY MODIFIED SILICAGELS

Chemisorbed Water Content : The chemisorbed water content (surface hydroxyl groups) was determined by loss on ignition at 1200°C. All measurements were made on 1 g samples of silicagel. The silicagel was given a preliminary 5 hour treatment in a stove at 120°C, weighted after cooling and then treated at 1200°C for 5 hours. After cooling again, it was dried at 120°C for the same length of time. The difference between the two weights represents the quantity of chemisorbed water in the silicagel. One then determines W in g %, the percentage of chemisorbed water. The same operation was carried out on the modified silicagels. The results can be used to calculate the average surface occupied by one OH :

$$\text{average surface}/_{OH} = \frac{3S.10^{-3}}{2\ W} \quad (nm^2)$$

S = specific surface according to the BET method.
W = % chemisorbed water content

The OH number per unit surface (nm^2) was calculated using the following relation :

$$N\ OH/_{nm^2} = \frac{2 \times 10^3}{3} \quad \frac{W}{S}$$

The concentration of surface hydroxyls, α_{OH}, obtained for a modified silicagel (Table 6) is significantly higher than the generally accepted value of 8 μmole.m^{-2} (26,27).

According to KOVATS, too high surface hydroxyl values are inherent in the method used for their determination (27) and could correspond to water inclusions in the silicagels. Table 6 shows that the OH concentration decreases considerably from the untreated to

Table 6

Chemisorbed Water Content of Thermally Modified Silicagels

Lichrosorb SI 60

T°C	untreated	400	500	600	700	800	900
W g %	4.42	2.44	1.97	1.65	1.14	.34	.61
Surface area /OH (nm^2)	.15	.27	.35	.43	.48	.30	.09
N OH/nm^2	6.4	3.7	2.9	2.3	2.1	3.4	10.4
average distance between OH groups (nm)	.39	.52	.59	.65	.69	.54	.31

Partisil 20

T°C	untreated	400	500	600	700	800	900
W g %	3.6	2.5	2.2	1.8	1.7	1.2	1.0
Surface area /OH (nm^2)	.17	.24	.26	.33	.27	.21	
N_{OH}/nm^2	5.9	4.1	3.8	3.0	3.6	4.7	
average distance between OH groups (nm)	.41	.49	.51	.57	.52	.46	

the treated silicagel at 400°C. From this temperature right up to 600-700°C, the decrease is much less marked and there is even an increase from 700°C upwards which, in fact, does not correspond to a real increase in the number of OH, but to an increase in surface hydroxyl concentration due to a decrease in specific surface.

This is confirmed by Figure 2 which shows the chemisorbed water content W as a function of the specific surface S. From 600°C upwards, W varies linearly as a function of S for both silicagels. The temperature range from 600 to 700°C seems interesting in so far as such a treatment provides a material which presents a fairly homogeneous surface activity and a good hydroxyl distribution while keeping a high specific surface. Such material will be used for chemical surface modification in a subsequent work.

Physisorbed water.

Water fixation from the vapour phase. Water adsorption isotherms from the vapour phase were established as has already been described (28).They are given in Fig. 3 and 4. Up to 500°C, the water content fixed by the silicagel decreases with increasing thermal treatment temperature ; from 90 % relative humidity onwards,the quantity of adsorbed water is more or less constant. This can be explained as

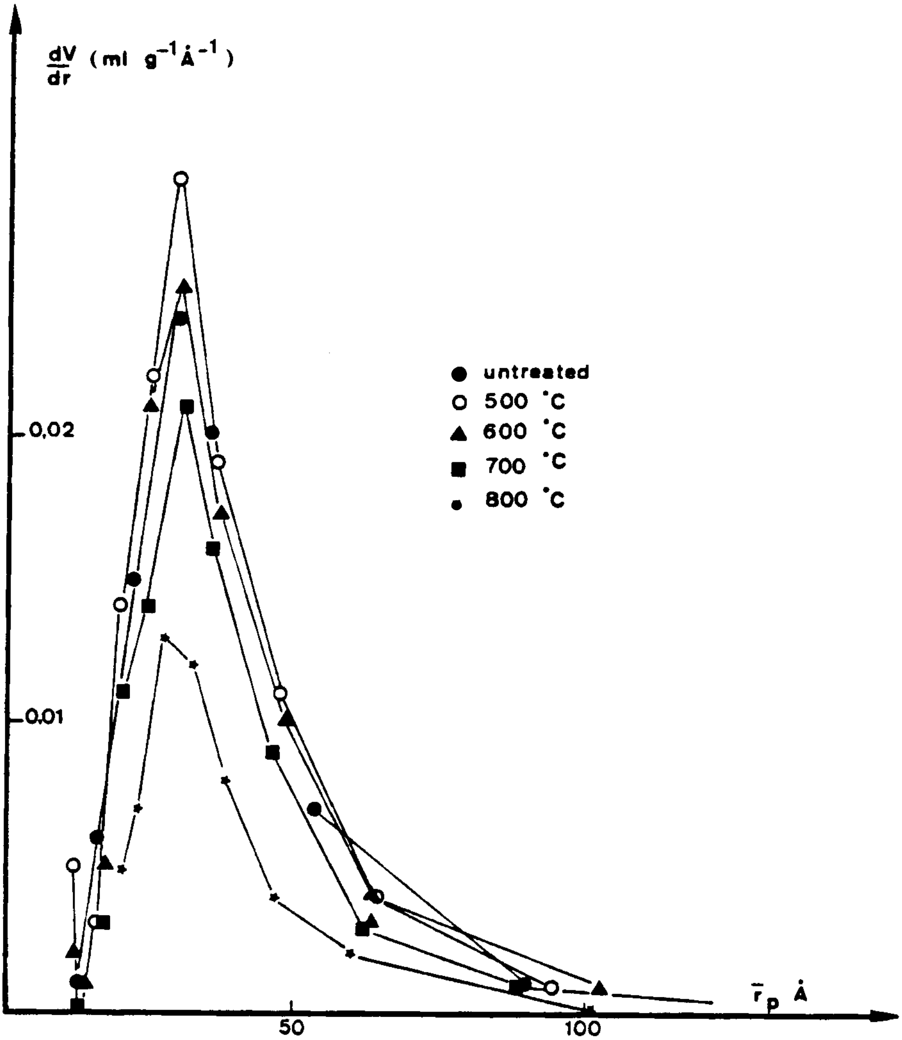

FIGURE 2 - Partisil 20 - Relative pore volume distributions for the various thermal treatments.

follows : up to 500°C, thermal treatment results in the removal of the most reactive hydroxyls, responsible for water fixation in the low and average relative humidity range ; at the same time, the pore volume does not change, which explains the identical isotherms for 90 % relative humidity onwards.

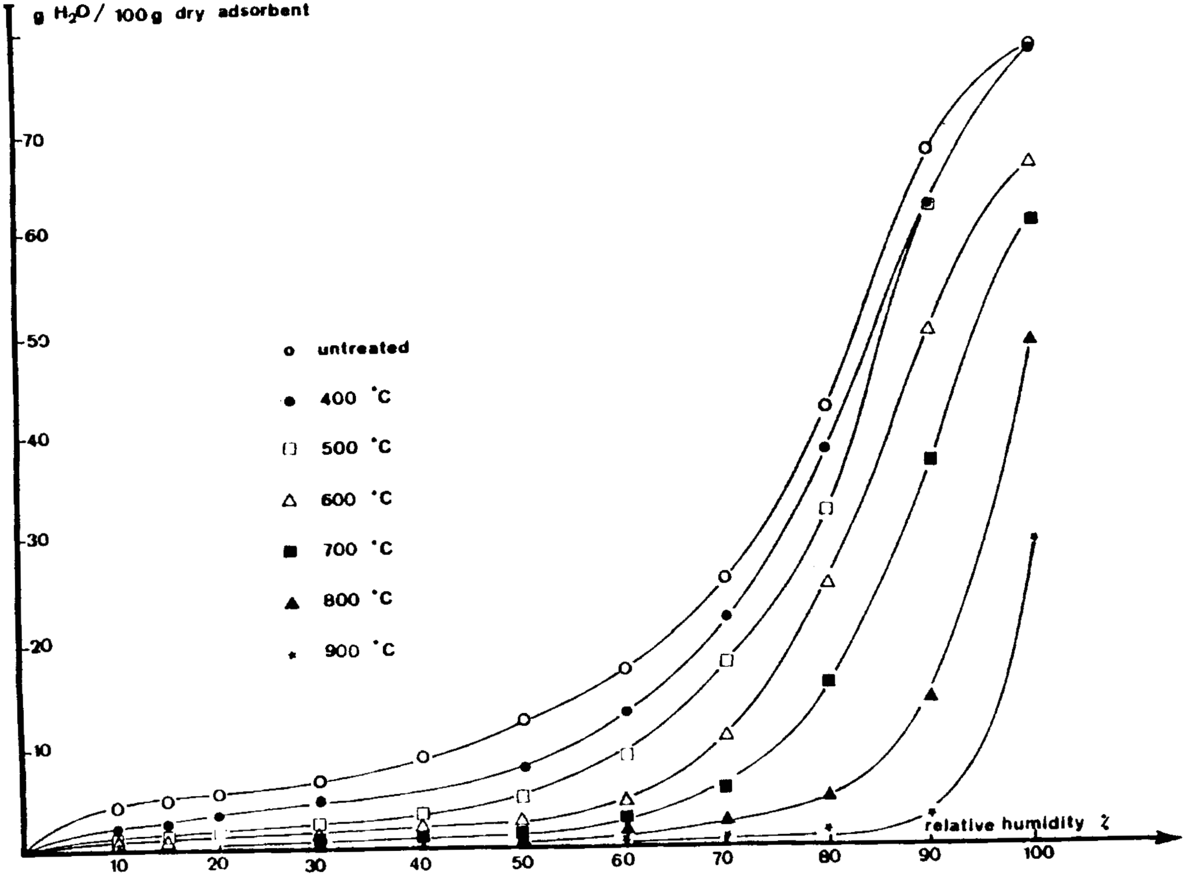

FIGURE 3. Lichrosorb SI 60 - Water adsorption isotherms from vapour phase.

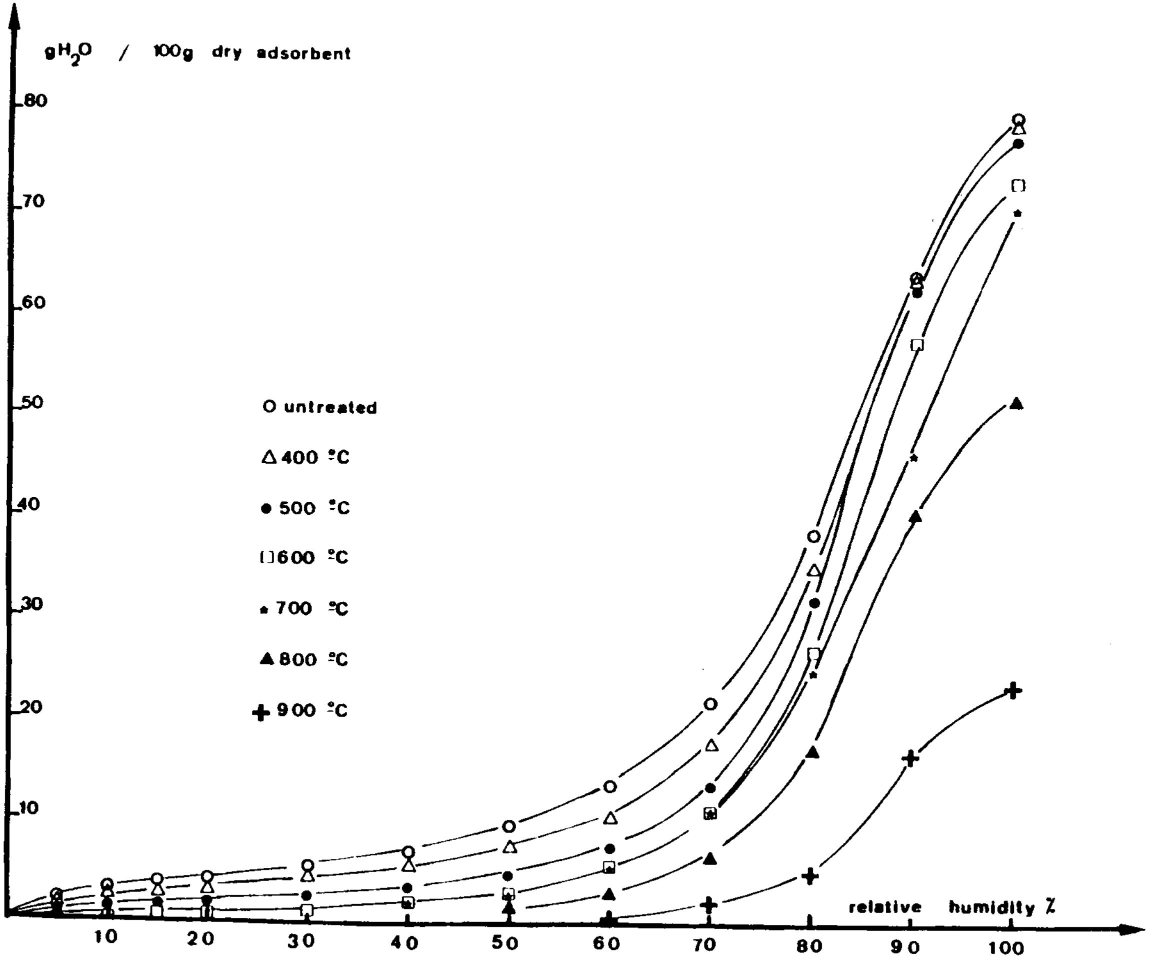

FIGURE 4. Partisil 5 - Water adsorption isotherms from vapour phase.

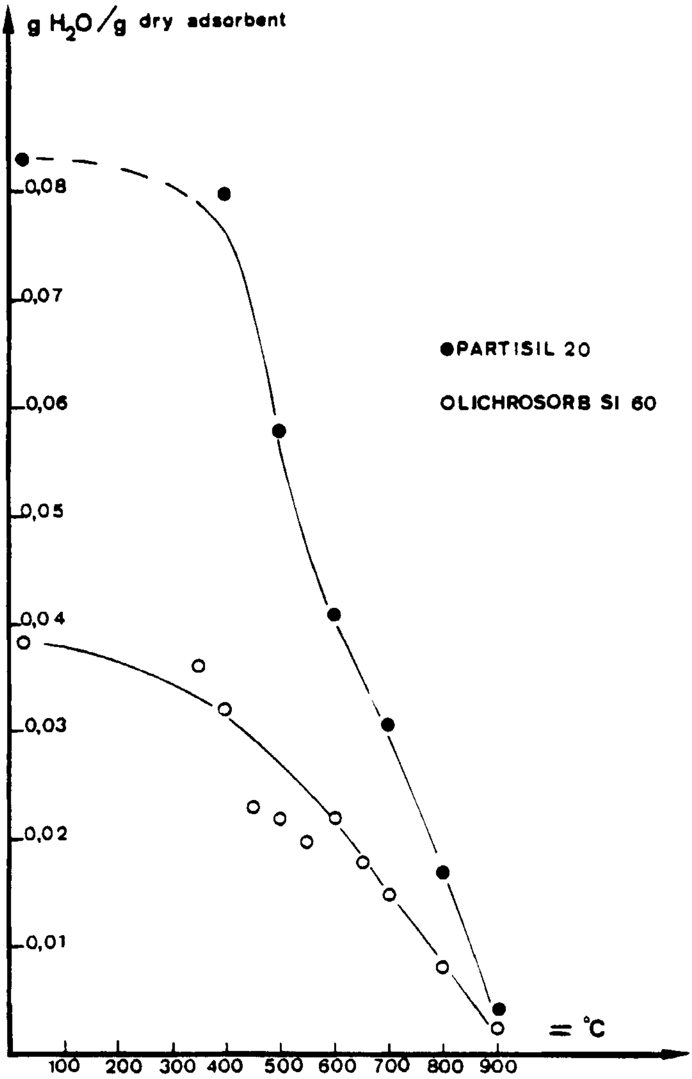

FIGURE 5 - Water fixation from liquid phase as a function of the temperature of thermal treatment.

● Partisil 20 - CH_2Cl_2 + 1440 ppm H_2O

○ Lichrosorb SI 60 - CH_2Cl_2 + 1100 ppm H_2O

From 600°C onwards, the quantity of water fixed by the silicagel decreases progressively with increasing temperature, this being so for all relative humidities. This could have two origins : firstly, the removal of chemisorbed water and secondly the decrease in pore volume due to sintering for temperatures above 650-700°C.

Water fixation from the liquid phase. Each column packed with thermally treated silicagel was activated with dry eluent (dichloromethane). The different columns thus activated were then deactivated with the same water content eluent. Equilibrium having been reached (this is controlled by successive injections of a test solute), the measurement of water fixed on each column was carried out according to the method described previously (29). The curves representing the quantity of water fixed (in grams) per gram of modified silicagel are shown in the Fig.5. Although the eluents are not the same in both cases, the behaviour of the two silicagels is identical ; the quantity of water fixed decreases progressively with increasing thermal treatment temperature ; this obviously comes from the decrease, by condensation, of the number of surface hydroxyl groups which are responsible for molecular water fixation. From 600°C onwards, for both silicagels, the quantity of water fixed is half that fixed by the untreated silicagel.

INFLUENCE OF THERMAL TREATMENT ON RETENTIONS

Two chromatographic systems have been tested with dry and water modified mobile phases : isooctane and dichloromethane. With dry mobile phases, the silicagel surface is in its highest activation state. In this case (Fig. 6 and 7), retentions depend on hydroxyl surface concentration and texture characteristics. Considering the previous results (Tables 4, 5 and 6), it can be argued that, in a first step, for low temperatures (> 650 - 700°C), the fall in k' values is caused by the decrease in the number of surface hydroxyl ; in a second step, for high temperatures, the decrease in retentions is above all caused by the texture modification of the silicagel.

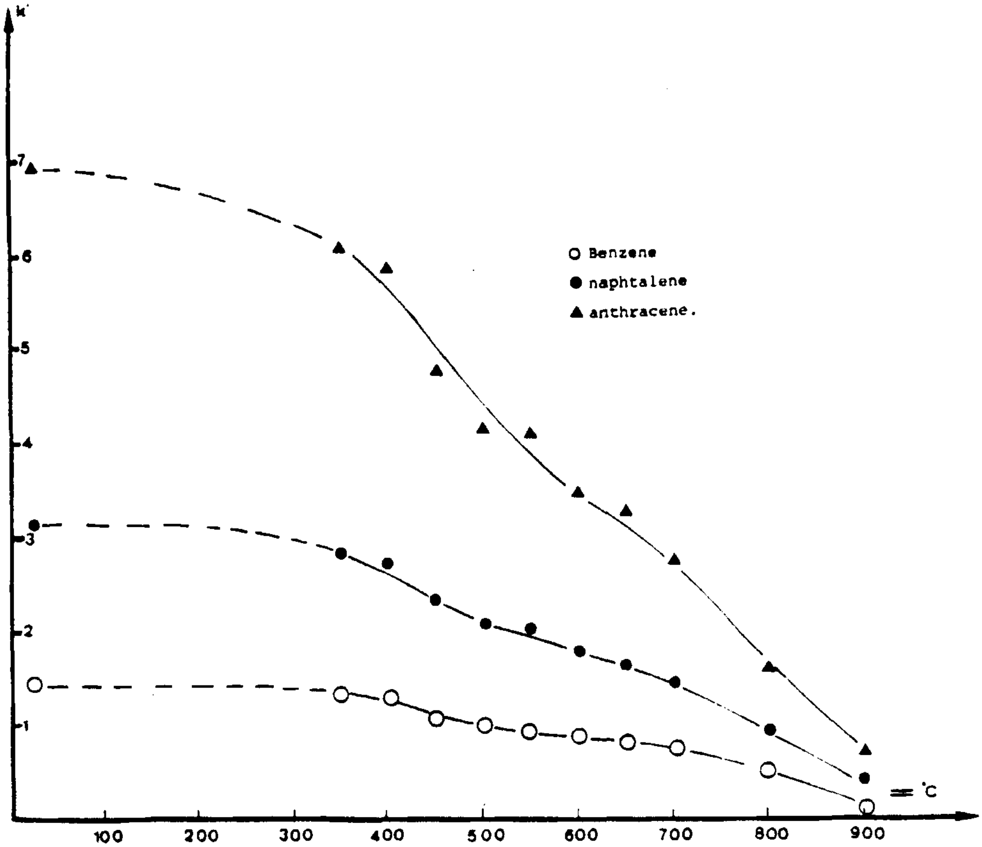

FIGURE 6 - Plot of k' values versus the temperature of thermal treatment. Lichrosorb SI 60 - Dry isooctane.

Retentions depend also on nature of interactions between solutes and available sites on the silicagel surface. With dry dichloromethane (Fig. 8 and 9), linuron is eluted with the same k' value up to 600°C ; for higher temperatures, k' linuron decreases rapidly.

With water containing mobile phases (Fig. 8 - 10) we already noticed (28) the presence of a maximum in the curves k' = f (T°C). From data obtained in the evolution of chemisorbed water and texture characteristics as a function of thermal treatment temperature, 3 steps can be considered :

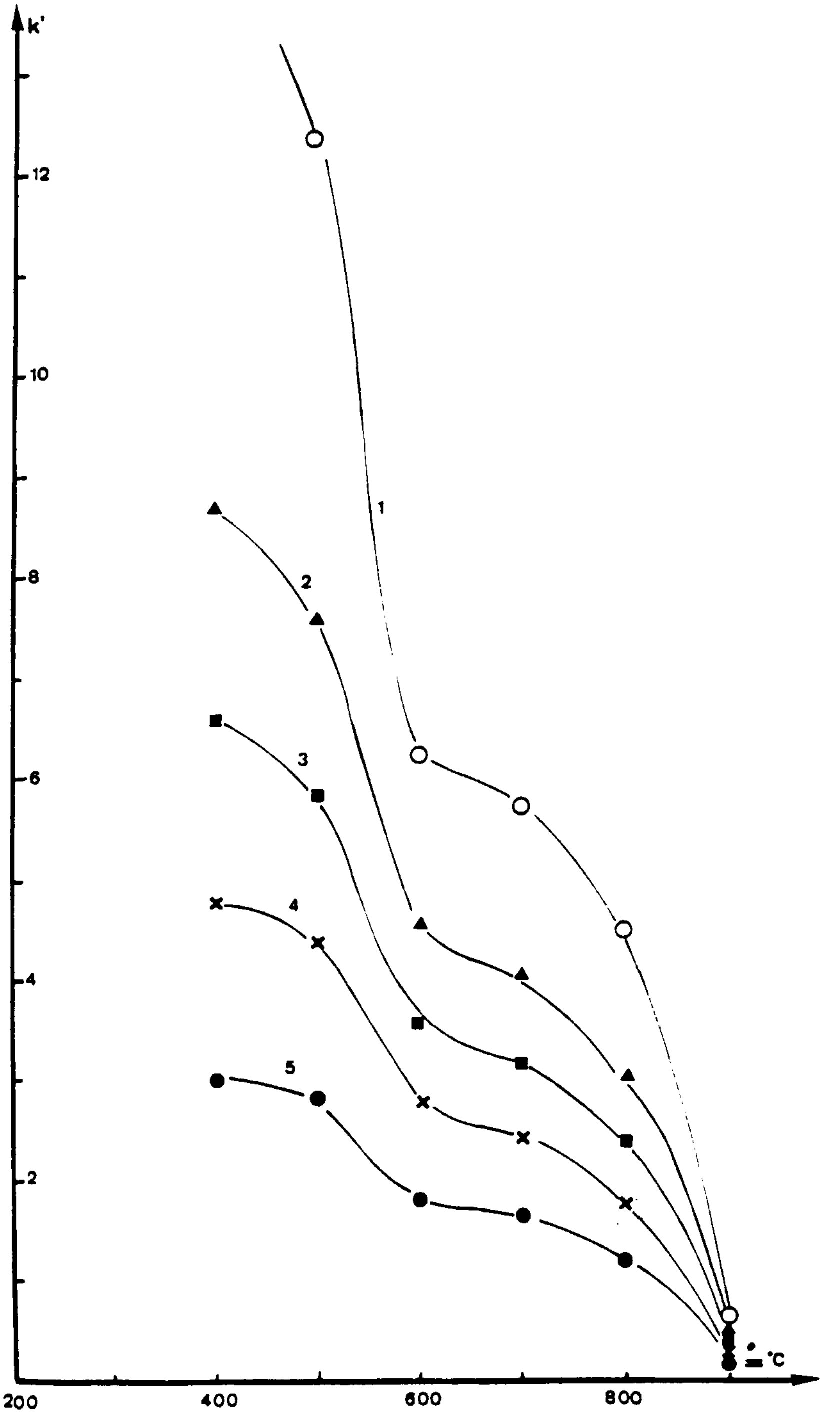

FIGURE 7. Plot of k' values versus the temperature of thermal treatment. Partisil 20 - Dry isooctane. Solutes: 1-triphenylene, 2-fluoranthene, 3-anthracene, 4- acenaphtylene, 5- naphthalene.

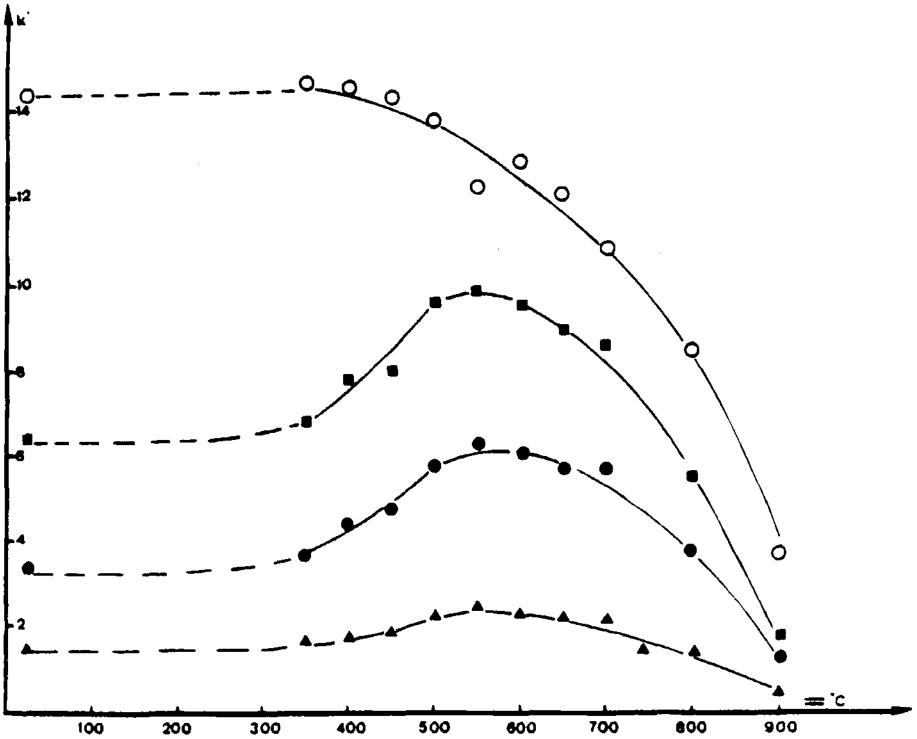

FIGURE 8 - The k' values of herbicides ((linuron, neburon, phenobenzuron) as a function of the temperature of thermal treatment. Lichrosorb SI 60

● Linuron - Dry dichloromethane

▲●■ Linuron, neburon, phenobenzuron - CH_2Cl_2 + 1100 ppm H_2O

- Below 350°, the retentions are identical with those obtained with untreated silica. In this temperature range, the number of hydroxyl per unit surface is the same and columns are in a similar "activation state".

- Between 350 and 650°C, the retentions increase and reach a maximum which corresponds to a decrease in the amount of water on silica ; mean while, texture and surface characteristics don't change. IR measurements (30) have shown that the number of surface hydroxyls increases and reach a maximum too.

- From 600-650°C, the decrease in retentions corresponds to the decrease in the specific surface area.

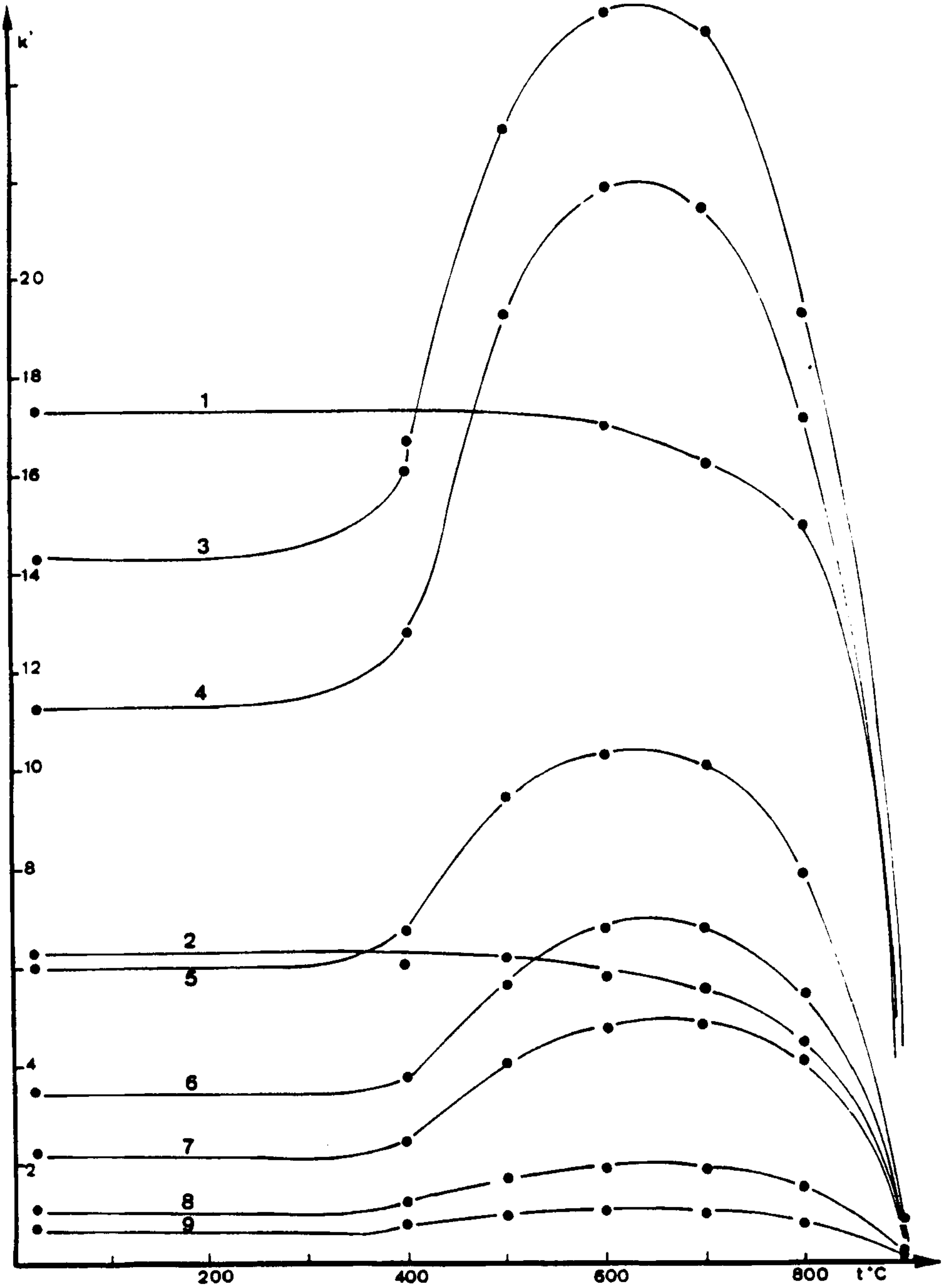

FIGURE 9. k' values of herbicides as a function of the temperature of thermal treatment. Partisil 20. 1,2-Dry dicloromethane, 3,9-Dicloromethane + 1440 ppm H_2O. Solutes: 1,8- linuron, 2,9- acetophenone, 3-fenuron, 4-isoproturon, 5-diuron, 6-phenobenzuron, 7-neburon.

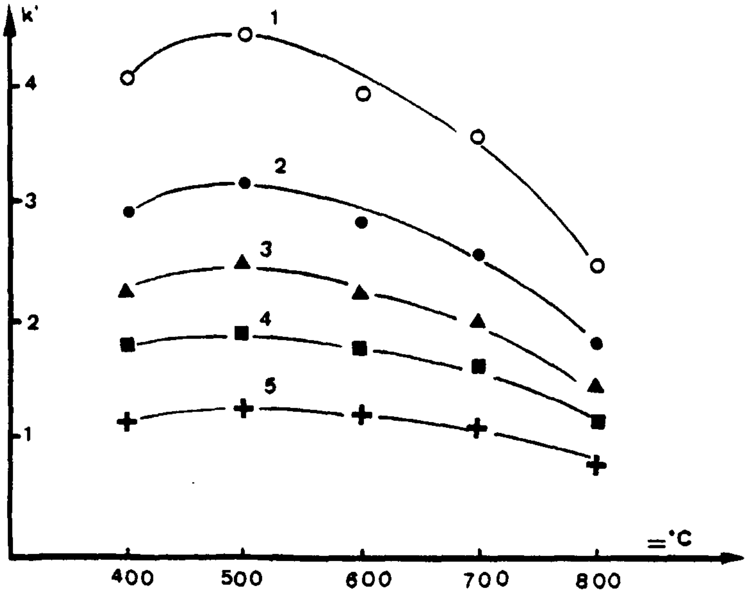

FIGURE 10 - Plot of k' values versus the temperature of thermal treatment. Partisil 20 - Water saturated isooctane. Solutes as in Fig. 7.

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