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CHROMATOGRAPHIC CHARACTERIZATION OF SURFACE-MODIFIED SILICA GELS*

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SUMMARY

Wide-pore silica gels with different surface areas have been prepared and deactivated with non-extractable monomolecular layers of Carbowax 20M. The resulting materials were characterized by their visual and chromatographic properties. They hold promise as easily prepared and easily modified stationary phases in chromatography.

INTRODUCTION

Among absorbents, the man-made silica gels have been some of the most thoroughly researched and characterized materials[1]. Their importance in gas–solid chromatography (GSC) is well established; however, they have found little use so far in the gas chromatography (GC) of higher, especially polar, organics. In this area, the much less well characterized, "natural" diatomaceous earths are the supports of preference in an overwhelming number of applications. This is easy to understand since GSC or gas–liquid chromatography (GLC) on silica gel phases is plagued by irreversible adsorption, decomposition, or, at least, excessive retention of polar organic molecules.

In an earlier study, we have demonstrated the deactivation of silica gel surfaces by what may be described as a monomolecular, non-extractable film of Carbowax 20M. This technique was assisted by a prior treatment with liquid water at elevated temperatures and by the well-known method of humidifying the GC carrier gas[2].

In the present study, we attempted to define further the effects of a monomolecular layer on the chromatographic properties of various silica gels. The silica gels in question were to be prepared from an inexpensive, wide-pore commercial product by reaction with liquid water at various temperatures in an autoclave; *i.e.* by "hydrothermal treatment" (HT).

Aside from the primary question of chromatographic performance, the materials

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to be developed were interesting in a number of contexts. First, "hydrothermal treatment" is a method which has been researched extensively by Kiselev and coworkers[3-6,9-11], but has found little chromatographic application so far in the Western hemisphere. In our earlier paper[2], we had expressed our uncertainty whether or not we had truly reproduced the Russian technique. On closer study of all available information, some of this uncertainty remained. The Russian papers refer to steam or water vapor when the physical state of water is specified[3-6]. Steam was apparently supplied, at least in some cases, by a high-pressure line entering the bottom of the autoclave[7]. The influence of the temperature and partial pressure of steam on the structure of cracking catalysts (*e.g.* ref. 8) has, of course, been a much-studied item; and hydrothermal treatment could be considered a high-pressure corollary to these early studies (ref. 9, first footnote). These gas-phase treatments contrast with our approach of keeping the silica gel well-covered by liquid water. In an early Russian publication, however, a suspension of aerosil in water is mentioned[9] and some papers refer to "silica solutions"[10,11]. The latter term, incidentally, would not be entirely incompatible with the assumption of silica gel being treated in the gas phase — say above a liquid water reservoir in an autoclave — since dissolution and precipitation of silica on the surface is likely under the high water-vapor pressures and relatively low temperatures.

Yet the published temperature–pressure data do not all coincide with the *p–T* curve for water, suggesting that (in a pure water–silica gel system) the autoclave was filled with only liquid water in some cases, with only gaseous water in others. This is shown in Fig. 1, where the *p–T* curve for water is superimposed on data from Russian publications, and on our own data from a treatment of silica gel covered by water in an autoclave. The importance, which we attach to the specification whether silica gel was suspended in liquid water or gaseous water, stems from the differences

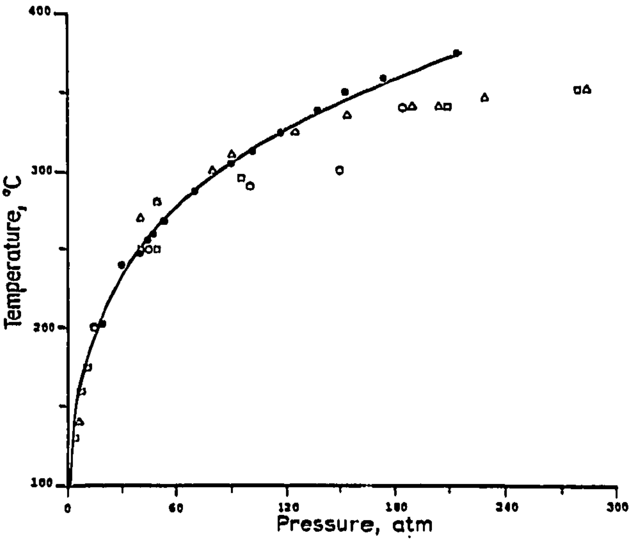


Fig. 1. Vapor pressure curve of water (from ref. 19); superimposed are: ● own data from silica gel and water in autoclave, and data from □ ref. 5, △ ref. 4, ○ ref. 11.

one would expect in the dissolution and precipitation of silica during the hydrothermal treatment and during cool-down of the autoclave. The mechanics of structural changes and especially transport phenomena in the gas phase (*e.g.* ref. 12) should show significant differences from that in the liquid phase. All information considered then, we assume that the treatment as described by Kiselev *et al.*[3–6] relates to the gas phase while ours relates to the liquid phase (below the critical point). However, since the results reported in this paper, *i.e.* the reduction in surface area if not the chromatographic performance, is similar to the results obtained by the pioneering Russian group, the same term "hydrothermal treatment" will be used from here on.

As a second point of interest, silica gels have a much larger surface area than the diatomaceous earths; and this study thus afforded us a welcome opportunity to obtain preciser data on the thickness of the Carbowax 20M layer. This we had considered information of prime importance in our early development[13] of techniques for preparing non-extractable polymer coatings, but the problem was never completely resolved due to the experimental difficulties posed by the extremely small amounts of polymer bonded to Chromosorb particles.

Third, we were interested in the supposedly detrimental effects of silanol groups on the chromatography of polar substances. On one hand, silanol groups of various chemical types are commonly held responsible for peak broadening and peak tailing, if not for irreversible adsorption and decomposition of solute molecules. On the other hand, we had some prior evidence which suggested that support silanol groups could be present in substantial numbers even during delicate GC analyses. The fully hydroxylated silica gels resulting from the hydrothermal treatment were therefore interesting materials to test with polar solutes, especially alcohols.

Fourth, we were interested in observing the difference between the chromatographic behavior of polar and non-polar compounds as the surface area changed from the high values characteristic of silica gel adsorbents to the low values more often associated with diatomaceous earths.

EXPERIMENTAL

Acid-washing

A large batch of wide-pore silica gel Davison grade 62, 40–60 mesh (Fisher Scientific Co., St. Louis, Mo., U.S.A.) was acid-washed in a Soxhlet (Kontes Model K-585100) with concentrated HCl as described earlier[2]. The acid was occasionally replaced, and the extraction was considered complete if a new batch of acid, after several hours of extraction, appeared free of yellow hue at ambient or boiling temperatures. (This extraction should be performed in a well-functioning hood, since the concentration of the refluxing acid will slowly change toward the constant-boiling mixture and HCl will distill off. In some of our arrangements, a long tube connected the reflux condensor to the sink, where the constant flow of cooling water disposed of the excess acid.) After acid-treatment, the silica gel was washed with deionized water to neutrality.

Hydrothermal treatment

Portions of the acid-washed silica gels were well covered with deionized water in a borosilicate glass insert tube and hydrothermally treated at temperatures ranging from 180 to 380° in a high-temperature bomb (Parr Model 4740), much as described earlier[2], *i.e.* the bomb was lowered in the evening into a large muffle furnace preset at the temperature chosen, left there overnight, removed from the hot muffle furnace with due caution, and left to cool down in a safe place. The heat-treatment period thus lasted approximately 18 h, and the cool-down period approximately 5 h. The treated silica gels were acid-washed as before in order to remove any traces of metals originating from the bomb.

Deposition of polymer layer

Approximately one-half of both non-treated and hydrothermally treated silica gels was coated by the conventional rotary evaporation technique. Coated silica gels were heat-treated under a slow flow of pure nitrogen at 270° for 18 h, and then extracted with methanol in a Goldfisch apparatus for 48 h; similar to the procedure developed for diatomaceous supports[13].

Extracted materials were dried in vacuum at 100° overnight, before being packed into 1.8 × 2 mm I.D., U-tube borosilicate glass columns. The GC characteristics of all packings were evaluated in terms of retention temperature, separation, and peak shape for various *n*-alkanes and *n*-alkanols. Some of these compounds were selected for obtaining apparent heats of sorption (log k' *vs.* $1/T$) plots; as well as k' *vs.* C(solute) plots, the latter essentially representing adsorption isotherms.

Small amounts of selected phases were examined by scanning electron microscopy (SEM) (Naval Ordnance Labs.), elemental analysis (PCR, Gainesville, Fla., U.S.A.) and surface area determination (Micromeritics Instruments, Norcross, Ga., U.S.A.).

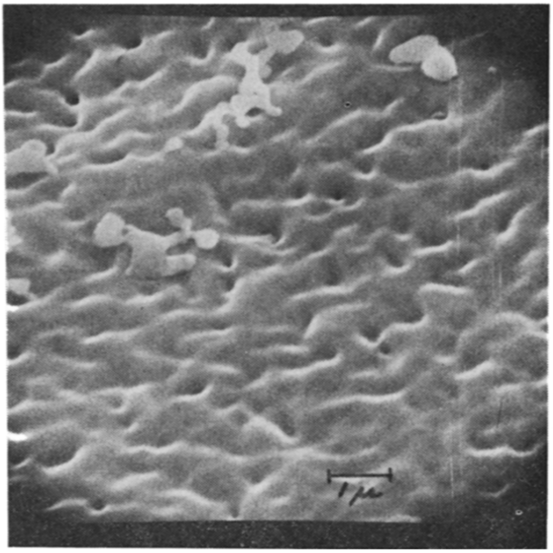
RESULTS

As anticipated from the literature, hydrothermal treatment provided us with a number of materials of different surface areas and pore diameters. Figs. 2–8 show a few selected scanning electron micrographs of silica gel particles, some of which have been cleaved to expose the interior and allow a comparison of the internal pore structures with those found at the periphery.

The information value of the SEM pictures (all at 10,000 × magnification) was limited by inadequate resolution; however, some conclusions could be drawn for the materials hydrothermally treated at 340 and 380°. The visual pore-size distribution did not vary within one particular particle from the surface to the core. However, different particles of the same batch (especially of the HT-380 material) varied somewhat: The most pronounced difference found is shown in Figs. 2 and 3. The materials HT-380 and HT-340, with respective surface areas of 2 and 50 m^2/g, can be clearly distinguished from each other and from the "Non-HT" material, with 350 m^2/g.

As a sideline, it is instructive to look at one of the materials, HT-340, under the viewpoint of peak broadening in liquid chromatography. The area seen in Fig. 5 corresponds to the cross-section of a minute 10-μ particle with unusually wide pores. Even under these extremely favorable circumstances, it is obvious that great differences must exist between the relative velocities of solutes migrating around, and those of solutes migrating through the particle.

Fig. 9 shows a quasi-Arrhenius representation of the effects of hydrothermal treatment on surface area. Based on these areas and the elemental analyses of materials that were coated with Carbowax 20M and exhaustively extracted, an estimate of liquid phase load could be obtained. In Table I, these loads are expressed as the average thickness of the liquid layer. Although the silica gels, due to their larger



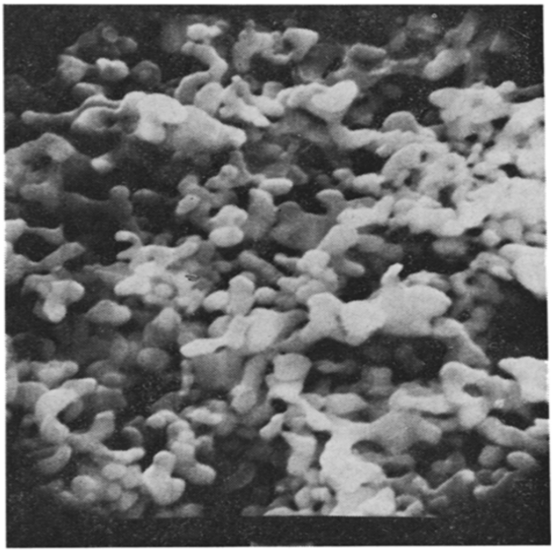
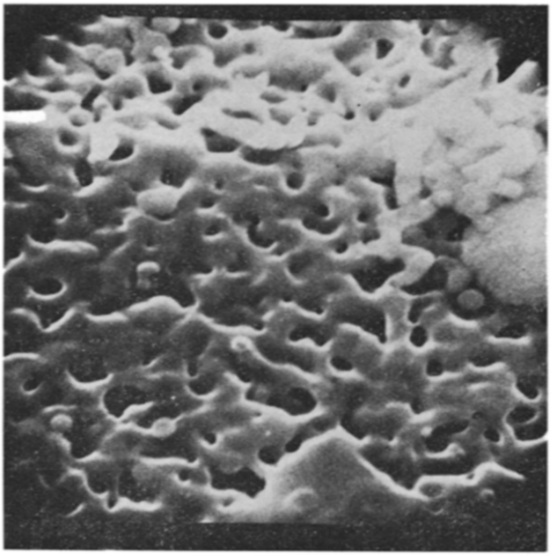


Fig. 2. Scanning electron micrograph of silica gel 62, hydrothermally treated at 380°, particle exterior.

Fig. 3. Silica gel 62, hydrothermally treated at 380°, particle exterior.



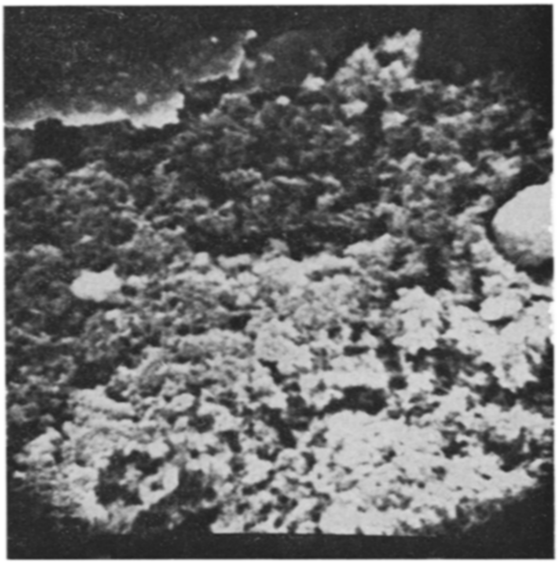


Fig. 4. Silica gel 62, hydrothermally treated at 380°, particle interior.

Fig. 5. Silica gel 62, hydrothermally treated at 340°, particle exterior.

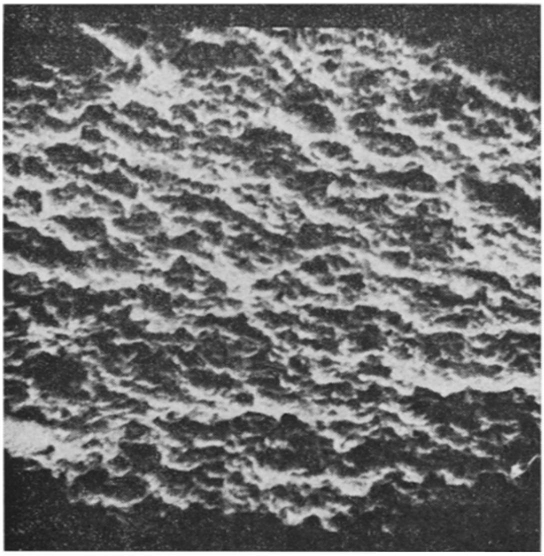


Fig. 6. Silica gel 62, hydrothermally treated at 340°, particle interior.

Fig. 7. Untreated silica gel 62, particle exterior.

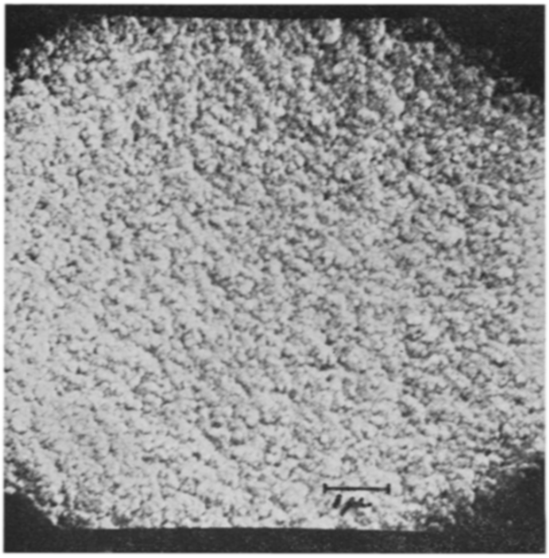


Fig. 8. Untreated silica gel 62, particle interior.

surface areas, can be expected to yield preciser values, we still regard the presented data as estimates. Not only do the uncertainties of analysis enter the picture, but a variety of other aspects can make such assessments doubtful[13].

It seems clear, however, that most layers are but a few Å thick; and whatever chromatography there is must occur under the influence of surface forces and in contact with (probably oriented) polymer chains of Carbowax 20M. The increase

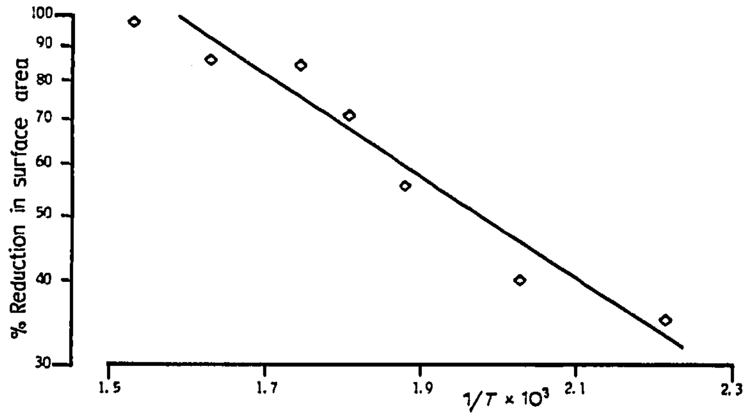


Fig. 9. Reduction in silica gel surface area as a function of hydrothermal treatment temperature.

TABLE 1

EFFECT OF HYDROTHERMAL TREATMENT TEMPERATURE ON SILICA GEL SURFACE AREA AND POLYMER LAYER THICKNESS

Hydrothermal treatment (°C)	*Surface (m^2/g)*	*Carbowax 20M layer thickness estimated (Å)*
None	350	1.1
180	228	1.7
220	209	0.8
260	152	2.0
300	55	1.1
340	49	6.3
380	2.2	34.3

in layer thickness observed on materials that were hydrothermally treated at relatively high temperatures is interesting but as yet unexplained. It would seem to mimic Carbowax layers on Chromosorbs, whose thickness may reach 15 Å. Only a more thorough study of the 300–380° temperature range of hydrothermal treatment, however, would permit more definite conclusions.

Most of the following figures demonstrate, in one form or another, the difference between bare and coated silica gels of various surface areas. All tested silica gels gave good chromatography for hydrocarbons; with the exception of the HT-380 sample as shown in Fig. 10. This material represents an exception in other regards as well: Its visual appearance is notably different from that of the other samples, and its surface area is considerably lower. Whether the fact that it was treated with water just above the critical point had anything to do with it, is an open question.

Figs. 11 and 12 show selected chromatograms of alcohols on bare and coated silica gels, respectively. A comparison of the two figures demonstrates the definite improvement in chromatographic properties which the monomolecular layers of Carbowax 20M confers upon the silica gel structure. The efficiency of the material

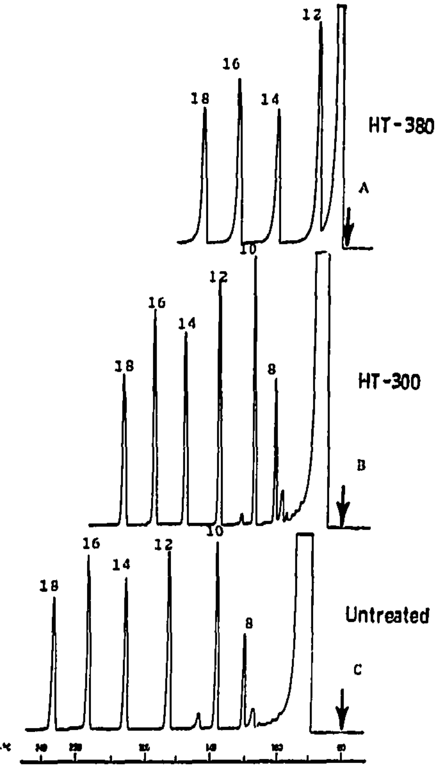


Fig. 10. Separation of even numbered *n*-alkanes (octane through octadecane) on bare silica gels. Temperature program, 60–240°, 6°/min.

obtained by hydrothermal treatment at 340°, in coated form, comes close to rivaling the common GLC packings on Chromosorb.

This is definitely surprising since regular silica gels could hardly be considered suitable supports for GC of alcohols. Even bare silica gels, whose hydrothermally treated surface can be safely assumed to bear a dense cover[14] of the often-maligned silanol groups, yield a passable separation of the alcohols (Fig. 11, upper traces).

To some degree, this situation is reflected by a comparison of the apparent heats of sorption given in Table II. Hydrothermal treatment and coating with a polymer layer cause only small changes in the interaction of hydrocarbons with the surface, while their effect on the chromatography of alcohols is definitely more noteworthy.

Actual chromatography demonstrates this situation: The effects of Carbowax 20M on the characteristic chromatographic parameters of retention, efficiency, and peak asymmetry are much more pronounced with alcohols than with hydrocarbons as solutes; as could be expected from a wealth of similar data in the literature[15,16]. Yet while there is a definite decrease of alcohol retention time or temperature caused by the polymer layer on a particular silica gel, even greater changes in retention can be brought about by the choice of temperature in the hydrothermal treatment. These effects are also demonstrated in Figs. 13 and 14, where the conveniently mea-

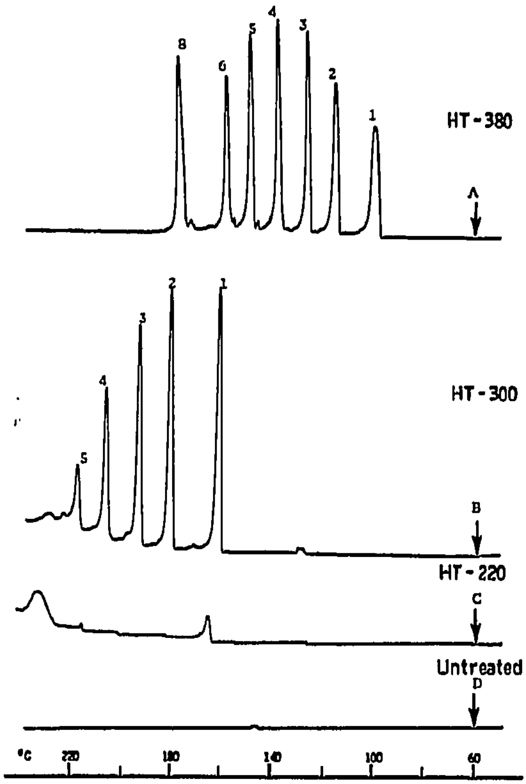


Fig. 11

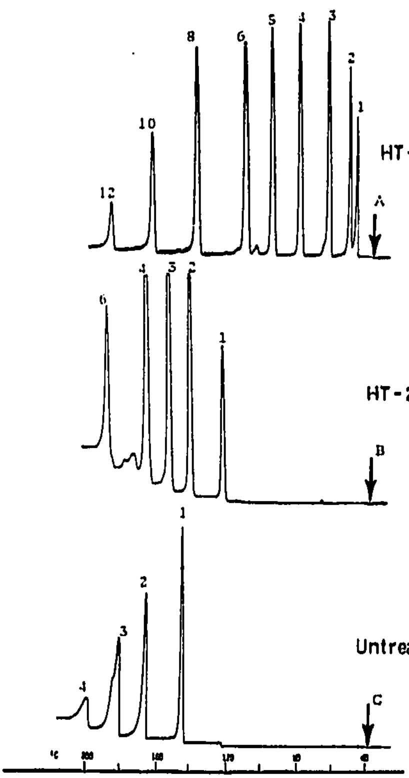


Fig. 12

Fig. 11. Separation of *n*-alkanols on bare silica gel 62, hydrothermally treated at different temperatures.

Fig. 12. Separation of *n*-alkanol standards (methanol through dodecanol) on Carbowax 20M-coated silica gels.

TABLE II

TEMPERATURE DEPENDENCE OF HYDROCARBON AND ALCOHOL CHROMATOGRAPHIES (APPARENT HEATS OF SORPTION FROM LOG k' *vs.* $1/T$ PLOTS, KCAL/MOL, UNCORRECTED)

Hydrothermal treatment (°C)	*Bare silica gel*		*Coated silica gel*	
	n-dodecane	*n-butanol*	*n-dodecane*	*n-hexanol*
None	14.8	—	14.4	—
340	13.4	18.3	12.5	13.1
380	14.5	16.0	13.4	12.8

sured retention temperatures of a standard GC temperature program serve to characterize both bare and coated silica gels.

The influence of the surface is apparent not only in regard to retention time and temperature, but also in terms of peak asymmetry; or in terms of a closely

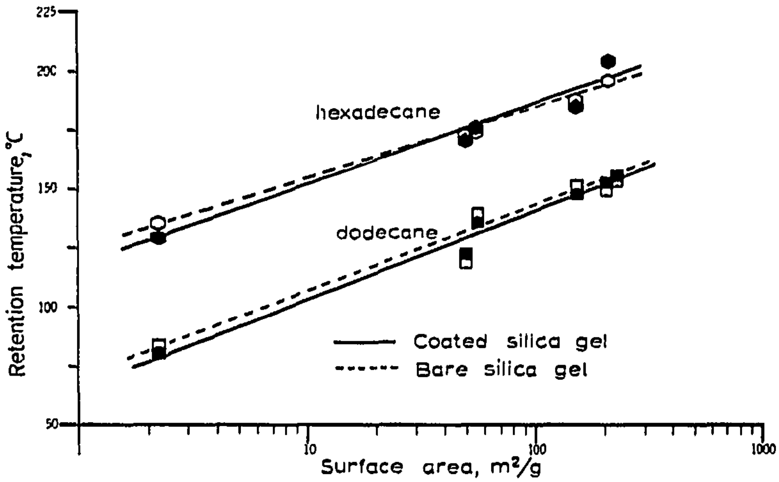


Fig. 13. Retention temperatures of *n*-alkanes on bare and coated silica gels of different surface areas.

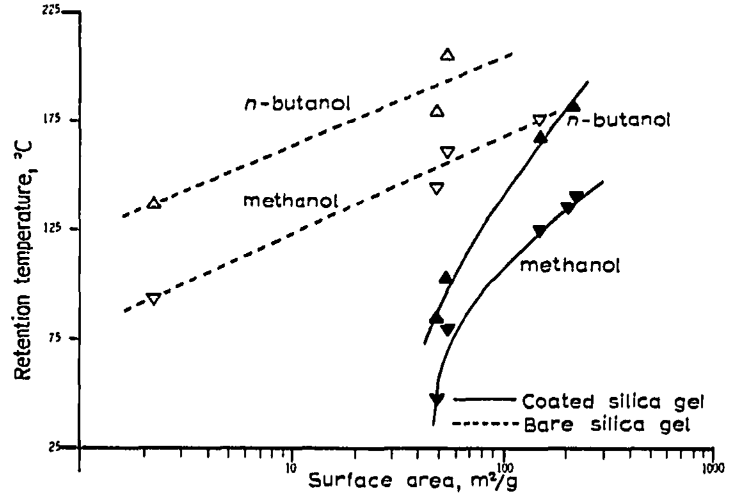


Fig. 14. Retention temperatures of *n*-alkanols on bare and coated silica gels of different surface areas.

related function, the dependence of retention on the amount of solute injected. In GLC, retention (as expressed in this study by k', the ratio of solute molecules in the stationary to those in the mobile phase) is not affected by solute concentration over a wide range, *i.e.* the partition isotherm is linear. The adsorption isotherms of GSC, in contrast, show, if any, much more restricted linear ranges. In place of these more conventional sorption isotherms, we have used an essentially equivalent representation, which is better suited for this study, namely a plot of the distribution ratio k' *versus* solute concentration (flame ionization detector peak height × attenuation).

Figs. 15 and 16 show a comparison of such plots obtained with hydrocarbons on bare and coated silica gels, respectively. Due to the large differences introduced by the hydrothermal treatment, it would not have been possible to determine all these isotherms with the same compound at the same temperature. Our choice of parameters therefore does represent a compromise. Nevertheless, some beneficial effect of the monomolecular Carbowax 20M layer is clearly demonstrated, most notably by a comparison of the materials obtained via hydrothermal treatment at 260 and 340°. These, in a coated state, have linear isotherms in the surveyed range. The other two curves, representing temperature extremes, indicate curvatures one

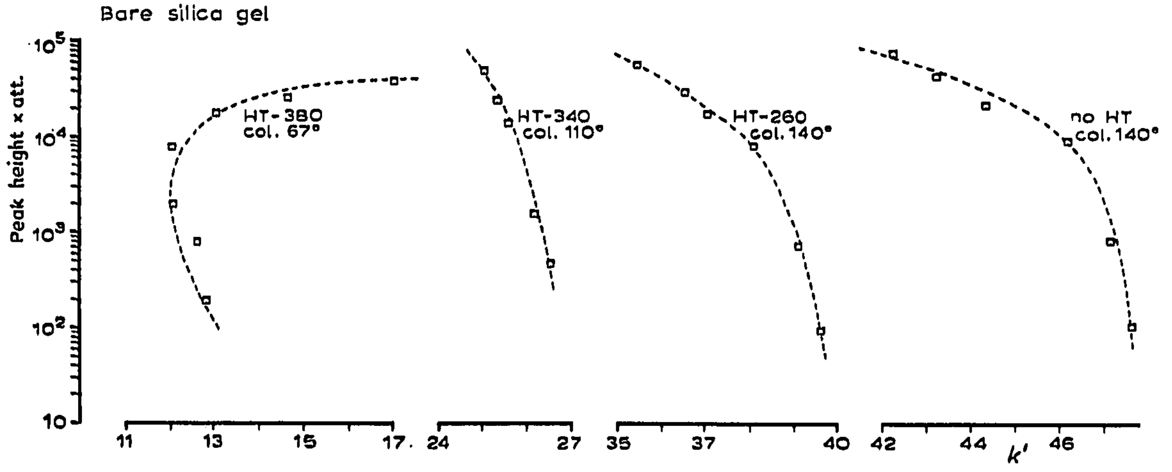


Fig. 15. Non-linearity of the adsorption isotherm, expressed by the dependence of GC retention on solute concentration. Bare silica gels, hydrothermally treated at different temperatures, are tested with *n*-dodecane as solute.

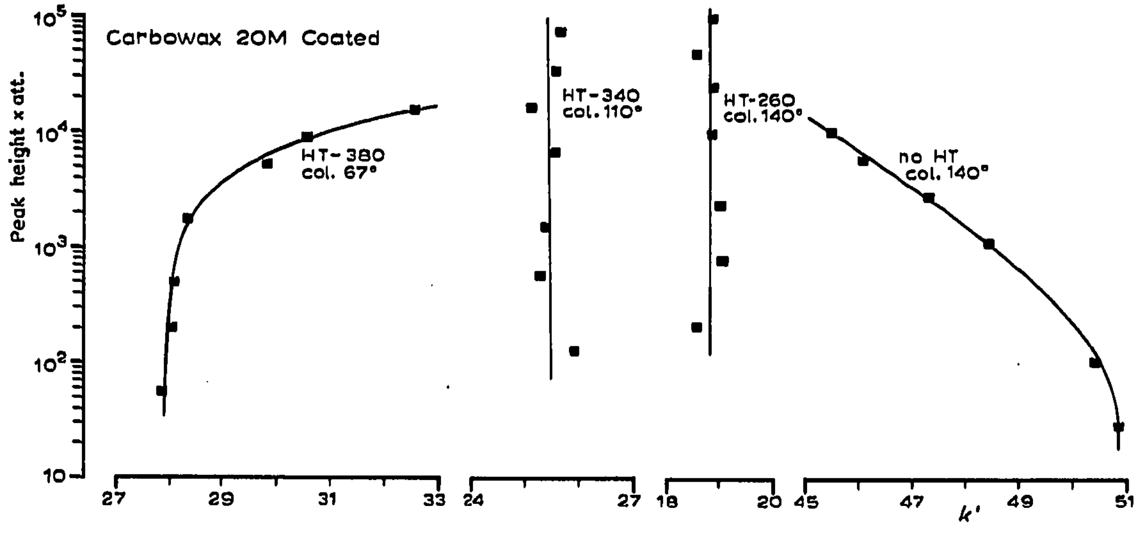


Fig. 16. *n*-Dodecane chromatographed on various silica gels coated with Carbowax 20M.

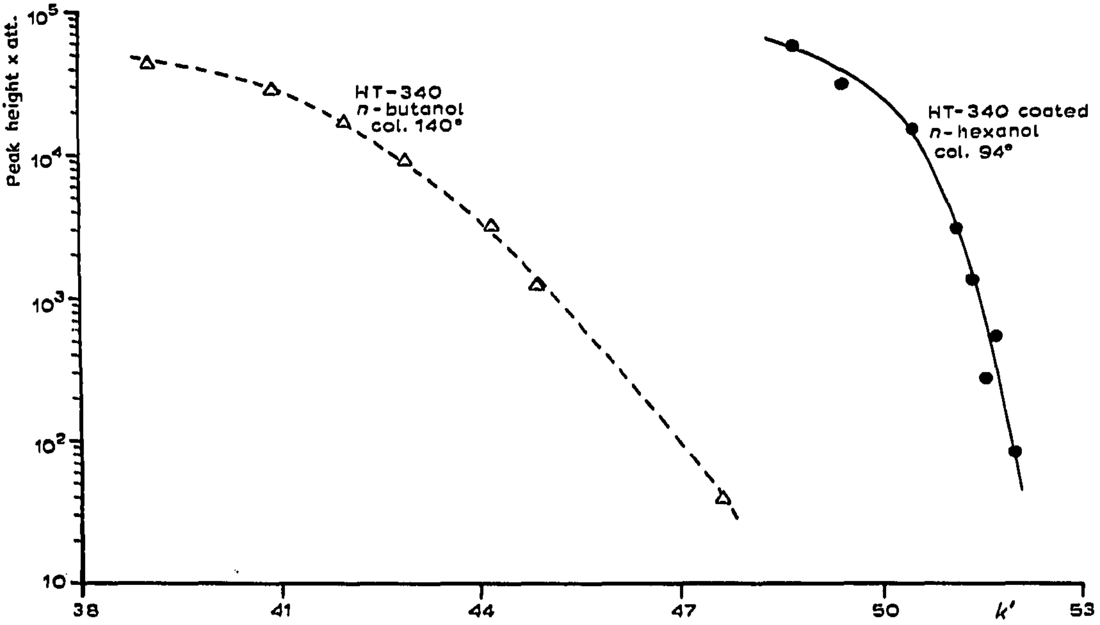


Fig. 17. Chromatography of alcohols on bare and coated silica gel HT-340 (hydrothermally treated at 340°).

might have predicted: a (conventionally) convex adsorption isotherm in the case of the untreated phase, and a concave one in the case of the material treated at 380°.

Hydrocarbons, however, are much less influenced by the polar polymer layer than alcohols. Fig. 17 shows its effect on silica gel HT-340; a material that, even in a non-coated state, is capable of good alcohol chromatography. In order to achieve a similar retention, the bare support was tested with a lower alcohol and at a higher temperature (*n*-butanol at 140°) than the coated one (*n*-hexanol at 94°). Both curves represent conventionally convex isotherms, but the deviation from linearity is much more pronounced in the case of the uncoated material.

DISCUSSION

While the microstructure of diatomaceous earths is determined by their natural origin, most silica gels are man-made and span an extremely wide range of surface area, pore volume and pore diameter. Despite the apparent simplicity of their synthesis, the chemistry involved in the production and chromatographic application of defined products is highly complex and still not completely understood. Yet, the variety of obtainable materials, even though it haunts the chromatographer with problems of selection and reproducibility, should ultimately prove its biggest asset in chromatography[1].

This study, although primarily concerned with the effects of non-extractable polymer layers, made extensive use of one particular form of geometric modification, *i.e.* a version of the so-called hydrothermal treatment. The reduction in surface area seems similar to the results obtained by Kiselev *et al.* (*e.g.* refs. 10 and 11). Yet the chromatographic effects appear to be more pronounced — as demonstrated, for instance, by the separation of alcohols in Fig. 11. We did not investigate, at this time, whether the increased possibilities of silica movement through the liquid water phase in the hydrothermal treatment, or the rather elaborate acid-washing of the material, contributed significantly to the striking improvement in chromatographic properties of the materials produced. This apparent change toward a more homogeneous surface, however, was greatly aided by the deposition of Carbowax 20M films.

These non-extractable polymer layers, presumably physically bonded to the surface, are in the monomolecular range. The term "monomolecular" unfortunately assumes ambiguity when applied to the so-called "bonded" chromatographic phases. Condensation reactions between the surface silanol groups and a variety of suitable materials, *i.e. chemical* reactions, lead to monomolecular layers of the "brush" type; as opposed to the reaction of silanol groups with multi-functional monomers, which can be further condensed to build up thick layers. In *physical* bonding, *i.e.* multipoint adsorption of larger molecules on the surface, the thickness of a truly monomolecular layer should be calculable from the Van der Waals dimension of the "stretched-out" polymer chains, closely packed side by side[16]. Our definition in this study, involving a polyethylene glycol with a molecular weight between 15,000 and 20,000, is obviously closer to the latter case. Since the experimental errors and ambiguities, however, do not allow a precise thickness to be assigned, we like to think of the monomolecular layer in chromatographic terms; *i.e.* one which permits fast, efficient elution of polar compounds, yet allows the influence of surface forces to be felt strongly, for instance in the separation of closely related compounds.

In spite of these forces, there is no doubt that the surface is well-deactivated. It is surprising, in fact, how strong the effect of layers with average thickness of only a couple of Å really is. The monomolecular layer results in a significant reduction in retention time or temperature and an increase in chromatographic efficiency for polar compounds such as alcohols, for which silica gel had little to offer in the past. It should, perhaps, be mentioned at this point that gas chromatographies on silica gel and associated problems of deactivation date back to the early nineteen-forties, *i.e.* much farther than is commonly assumed[17].

To state that the polyethylene oxide structure modifies the silica gel surface sites responsible for alcohol retention, represents merely a restatement of the experimental findings; although it appears likely that strong hydrogen bonds exist between the surface silanol groups and the ether oxygens of the polymer[18]. A more accurate portrayal of the complex phenomena involved would have to play in atomic dimensions and, at least for now, in experimental darkness.

Practical applicability may be easier to come by. It appears that silica gels could be modified to a point —which, incidentally, is not quite attained yet— where surface deactivation and GC efficiency would be equivalent to those obtained on diatomaceous earths. The silica gels described in this study come close; and it should be an interesting proposition to investigate whether particular traditional advantages of silica gels, such as their efficiency in isomer separations, can still be put to use in spite of the extensive modification these materials have undergone.

ACKNOWLEDGEMENTS

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