

CHROM 22 075

Confirmation and application of transmission near infrared absorption technique for absolute quantitation of functional groups on silica gel

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(First received March 16th, 1989; revised manuscript received October 6th, 1989)

SUMMARY

A transmission near infrared (NIR) technique has been demonstrated to be useful for the qualitative and quantitative measurement of silica surface functionalities. Confirmation of this method's quantitative capabilities has been performed using a newly developed deuterium-exchange method and the more established methods of tritium radioisotopic exchange and carbon analysis.

This NIR technique has been utilized for the evaluation of surface modification reactions for reducing the silanol content of modified silicas. This effort led to the development of "direct butylation" as a promising method for deactivation of porous silica surfaces. Complementary surface characterization information was obtained using solid state NMR, BET adsorption, mercury intrusion porosimetry and gas chromatography.

INTRODUCTION

Silanol groups on silica gels and other siliceous materials are known to be major centers for solute-surface interaction in chromatography¹. Adsorption of solutes at these sites can be the desired mechanism of retention as in normal-phase liquid chromatography. However, the strong interaction between solutes and silanols is often an undesired secondary retention mechanism causing tailed peaks² and resulting in subsequent difficulties for qualitative and quantitative analysis. Because of their importance in chromatographic processes, much research has focused on (1) techniques for quantitating silanols and other surface functionalities on the silica surface^{3–5}, and (2) physical and chemical methods for modifying or removing silanol contributions to retention^{6–8}.

As described in a previous paper⁹, a transmission near infrared (NIR) absorption technique has been developed in our laboratory for the non-destructive

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evaluation of surface groups on silica gel. In the present paper, this system's utility in the quantitation of silanols and hydrocarbon functionalities on the silica surface will be shown. The NIR technique is compared to more established quantitative techniques such as carbon analysis and tritium radioisotopic exchange and a newly developed technique using deuterium isotopic exchange combined with NIR spectroscopy.

In addition, we will present surface modification reactions we have developed with the aid of the NIR technique. The direct silylation of silicon dioxide using alkyl lithiums has thus been optimized for use with porous silicas. The chromatographic possibilities of these surfaces is shown using gas-solid chromatography.

EXPERIMENTAL

Materials

An irregular silica gel, Davison 62 (Davison, U.S.A.) with a BET surface area of 267 m²/g was used. Reagent-grade carbon tetrachloride and pyridine from Fisher Scientific (Fair Lawn, NJ, U.S.A.) were dried over molecular sieve 4A. The diethyl ether was vacuum evaporated from the methyl lithium (1.5 M in diethyl ether) (Aldrich, Milwaukee, WI, U.S.A.) and dry tetrahydrofuran (THF) added back to form a 0.75 M solution. Butyl lithium (2.7 M in hexanes) (Aldrich) was diluted with THF to 1.4 M. Trimethylchlorosilane (TMCS) and phosphorus pentachloride (Aldrich); Scintiverse scintillation cocktail (Fisher); hydrogen chloride gas (Carolina Specialty Gases, Raleigh, NC, U.S.A.); deuterated water (99.5 atom% ²H by NMR) (Sigma, St. Louis, MO, U.S.A.); and tritiated water (5 μCi/ml) (Amersham, Arlington Heights, IL, U.S.A.) were all used as received.

Equipment

Transmission spectra in the NIR were obtained on a Varian (Palo Alto, CA, U.S.A.) Cary 17 UV-VIS-NIR scanning spectrometer in the absorbance mode. The NIR cell (for description see ref. 9), deuterium-exchange apparatus, tritium-exchange apparatus and flow-through reaction apparatus were all fabricated in-house and treated with TMCS to minimize surface silanols. Scintillation counting was done on an Isocap/300 6872 liquid scintillation system (Searle Analytic, Des Plaines, IL, U.S.A.). Gas chromatographic analyses were performed using a Varian Series 1400 gas chromatograph equipped with a flame ionization detector. Data were acquired using a UNC microcomputer (Chapel Hill, NC, U.S.A.) using an interface and statistical moment² software developed in-house. A Blue M (Blue Island, IL, U.S.A.) laboratory oven was used for heating silica samples. Integration of NIR spectral peaks was performed using a planimeter.

Procedures

(1) *NIR analysis.* The silica sample was placed in the NIR cell and dried by simultaneous heating (180°C) and helium purging of the sample. CCl₄ was added as a refractive index matching medium, the helium bubbles removed and the silica packed using flow, gravity and a glass wool plug. The spectrum was then scanned from 2400–1200 nm (4167–8333 cm⁻¹) (for details, see ref. 9.)

(2) *Deuterium-exchange method.* The NIR cell was modified by adding vacuum stopcocks in place of standard PTFE stopcocks for better system sealing. About three

grams of silica gel were added to the cell and dried. A preliminary "blank" spectrum was taken of the silica gel and the CCl_4 was driven off. A 500- μl volume of deuterated water was then added and allowed to equilibrate for more than 5 h at 80°C . The equilibrated water was driven off at 180°C with helium flow for 5 h, CCl_4 added, and a spectrum taken. This process was repeated until the NIR spectrum showed no further change indicating the complete exchange of surface silanols to the deuterated form. After CCl_4 removal, the cell was weighed and the weight of dried silica obtained by difference.

Under dry nitrogen, 1200 μl of distilled water were added to the cell which was then sealed and allowed to equilibrate for 12 h at 80°C . The water was subsequently driven off using helium flow and heat and condensed in a liquid nitrogen cold trap. The trapped water was then pipetted into a 1-cm pathlength cuvette and placed in the sample beam of the Cary 17. The spectrum was scanned against distilled water ($^1\text{H}_2\text{O}$) in the reference beam from 1800–1500 nm at 0.1 nm/s and the absorbance measured at 1670 nm. A standard series of $^2\text{HO}^1\text{H}$ solutions were prepared, the absorbance measured and then plotted. The concentration of deuterium in the condensed water was obtained by interpolation of the least squares fit (correlation = 0.995).

(3) *Tritium-exchange method.* This experimental procedure for the radioisotopic exchange of silica was derived from work done by Unger¹⁰ with some changes for experimental convenience. The apparatus used is shown in Fig. 1. About 2 g of the silica sample were added to disconnected component 1 at joint 3. Samples rested on the

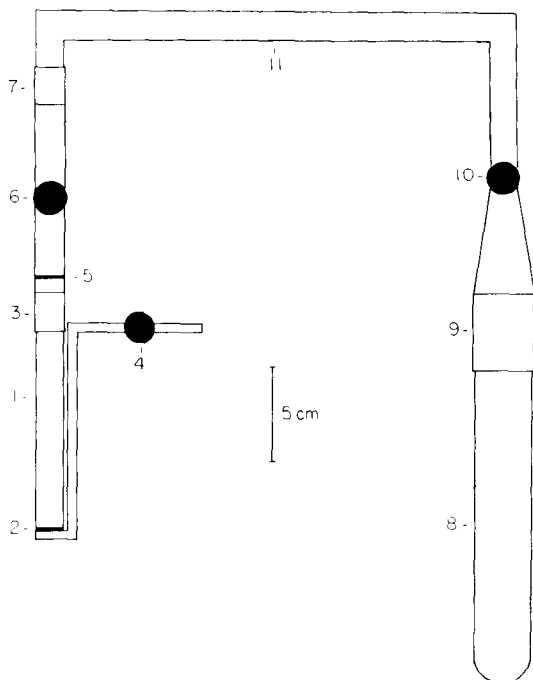


Fig. 1. Tritium (HTO) exchange apparatus. 1 = "Silica component": glass tubing; 2,5 = coarse glass frit; 3,7,9 = ground glass joint; 4,6,10 = PTFE vacuum stopcock; 8 = "ampule component": round-bottom glass tubing; 11 = connecting glass tubing.

sintered glass frit 2. The silica was dried as before with heat and helium flow, component 1 sealed and weighed and the weight of dry silica obtained by difference.

Under a dry nitrogen atmosphere component 1 was reconnected to the apparatus. Meanwhile, a sealed ampule containing a weighed amount (± 0.1 mg) of tritiated water (*ca.* 50 μ l; 10 μ Ci/ml) and a stir bar were placed in component 8 which was then connected to the rest of the apparatus at 14/40 joint 9. The entire system was made vacuum tight by sealing the ground glass joints 3, 7 and 9 with high vacuum grease and by using vacuum stopcocks 4, 6 and 10 for evacuation control. A vacuum was pulled on the entire system through stopcock 4. The stopcock was then closed while the other two stopcocks 6 and 10 remained open to permit free flow of water vapor in the system. After breaking the ampule with the stir bar, the entire apparatus was allowed to equilibrate at 80°C for 12 h. Condensation of the equilibrated vapor was then accomplished by heating component 1 at 180°C while cooling component 8 with liquid nitrogen for 5 h. Heating tape was wrapped around the exposed apparatus to minimize vapor condensation and prevent "freeze-up" of the vacuum grease in joint 9. Stopcock 10 was then closed and the entire system brought to room temperature.

The vacuum was released for component 1 and component 11 by opening stopcocks 4 and 6 successively and component 1 was removed from the apparatus. Sintered disc 5 prevented silica from being pulled into the rest of the system. Stopcock 10 was then opened releasing the vacuum to component 8. Scintiverse and dioxane (15 ml each) were added to the condensed water and stirred for 30 min. A 15-ml portion of the resulting solution was aliquoted into a scintillation vial and counted. System blanks were performed by carrying out this procedure without the silica gel sample. "Simple" blanks were carried out by counting a 15-ml aliquot of a solution of 15 ml dioxane, 15 ml Scintiverse and a weighed amount (*ca.* 50 μ l) of tritiated water. Comparison of the system blank to the simple blank (both in units of counts per minute per gram of tritiated water) revealed a tritium recovery of 99.4% (2% relative standard deviation) for the system blank.

(4) *Carbon analysis.* Carbon analysis of modified and unmodified silica gels was performed by Galbraith Labs. (Knoxville, TN, U.S.A.).

(5) *Surface modification.* All surface modification reactions were carried out in the double necked flow through reaction flask (Fig. 2). The silica rested on the coarse sintered glass frit 1. This arrangement allowed for the easy removal of reagents through the PTFE stopcock 2 and limited exposure of air or water sensitive surfaces to the atmosphere. Because of the air/water sensitivity of many of the reagents and silica surfaces, all reactions and transfers were carried out under nitrogen and all glassware was dried before use. *Safety note:* alkyl lithium reagents are extremely pyrophoric! Great care must be observed in their use.

(a) *Silylations.* A variety of silane coverages were provided by varying reagent amounts in the following general procedure for silylation of silica gel: About 10 g of dried silica gel were added to the flow-through vessel. A solution of 70 ml CCl_4 , up to 30 ml TMCS and up to 5 ml pyridine, was added to the silica gel. After refluxing overnight, the silica was finally washed with CCl_4 , CHCl_3 , CH_2Cl_2 , acetone, THF, water and THF.

(b) *Chlorination-methylation.* A 4-g amount of PCl_5 was dissolved in 100 ml of dry CS_2 . The PCl_5 - CS_2 solution was added to 3 g dried silica in the reaction vessel.

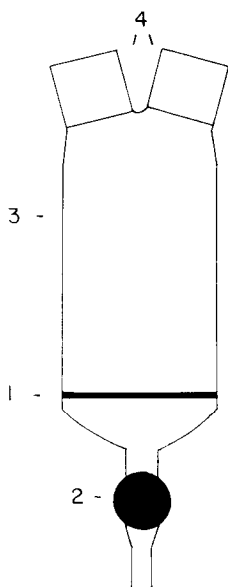


Fig. 2. Flow through reaction flask. 1 = Coarse glass frit; 2 = PTFE stopcock; 3 = large-bore glass tubing; 4 = 19/22 female ground glass joints.

After refluxing the mixture for 5 h, the silica was then washed with dry CS_2 and dried with helium flow and heat. Next 50 ml of methyl lithium (0.75 M in THF) were added and the mixture swirled occasionally for 15 min. The solution was slowly forced into (under the surface of) isopropanol with nitrogen pressure in order to destroy excess methyl lithium. After washing with fresh THF, the silica was dried with helium flow and heat. The silica was neutralized by alternatively pulsing hydrogen chloride gas and helium gas (to cool silica) through the flask. Finally the silica was washed with 4 M hydrochloric acid, water, and THF, the silica dried and the NIR spectrum taken.

(c) Methyl lithium only. Procedure is the same as above except no prior chlorination step was used.

(d) Butyl lithium. A 100-ml volume of butyl lithium (1.4 M in THF/hexanes) was added to 6 g of dried silica. After swirling occasionally over a 15-min period, the butyl lithium was slowly forced into isopropanol with nitrogen pressure (as with methyl lithium). The silica was washed with fresh THF and dried with helium flow and heat. Hydrogen chloride and helium were alternately pulsed through the cell followed by washing with 4 M hydrochloric acid, water, THF, water and THF. After drying, the NIR spectrum was obtained.

(6) *Solid state NMR*. All NMR spectra were obtained at the Colorado State University Regional NMR Center on a modified Nicolet NT-200 (^{29}Si) or NT-150 (^{13}C) spectrometer. (For further details, see refs. 11–13.)

(7) *Gas chromatography*. Weighed amounts of silica adsorbents were packed via tapping into 1 m \times 1/8 in. O.D. stainless-steel tubing. The columns were coiled and preconditioned at 225°C for 12 h. Sample introduction was performed by syringe injections of saturated acetone vapor at room temperature. Methane was used as a dead time marker.

RESULTS AND DISCUSSION

Since developing the NIR technique previously described⁹, we have focused our attention in two directions: (1) evaluation of the quantitative applicability of the technique and (2) application of the technique to the development of useful surface reactions for silica.

First a methodology for quantitation using the NIR method was adopted. Quantitative comparisons were then performed by a deuterium isotopic exchange method recently developed in our laboratory and by two literature methods, tritium radioisotopic exchange and carbon analysis. From the first procedure we obtained a measure of the surface concentration of silanols on the unmodified silica. The more established techniques were used to evaluate the unmodified silica and several TMCS-modified silicas of various surface coverages. Results were then compared to NIR data on the same samples.

Concurrent with these studies novel surface modification routes were explored with the NIR technique. Of particular interest is the direct alkylation of the surface with alkyl lithium which was further evaluated with solid state NMR and gas solid chromatography.

Confirmation of NIR technique

Calculation of percent silanol removal. As shown in Fig. 3, the removal of silanols on silica gel can be monitored in the NIR by comparing traces from unmodified (dotted line) and TMCS-modified (solid line) samples⁹. If the sample has been properly dried (as monitored by removal of the water combination band at 5277 cm^{-1}) the peak at 7220 cm^{-1} can be attributed solely to the overtone of the silanol stretch ($2\nu_s$)⁹ while the bands grouped near 5800 cm^{-1} can be attributed to various overtones of the methyl C-H stretches.

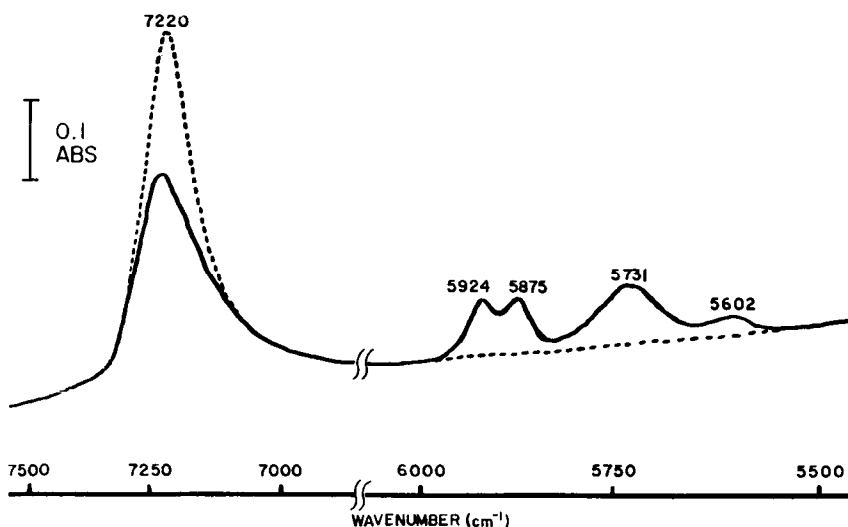


Fig. 3. NIR absorption as a function of trimethylchlorosilane reaction with the silica surface. Broken curve: unmodified silica gel (dry); solid curve: trimethylchlorosilane modified silica.

Silanol removal can be quantitated by drawing a baseline tangent under the OH overtones for both the modified and unmodified silicas. The areas are then measured and percent removal obtained from the ratio. In practice two corrections must be applied as shown in the following equation:

$$P = \frac{M_{7220} - (CM_{5800} + D_{7220}) \cdot 100}{U_{7220} - D_{7220}} \quad (1)$$

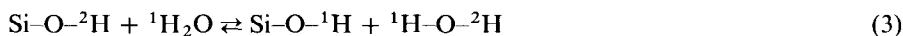
where P is the percent unreacted silanol, and M_{7220} and U_{7220} are the integrated absorbances for the peak at 7220 cm^{-1} for the modified and unmodified silica, respectively. D_{7220} is the area of the silanol overtone for a silica gel that has been exhaustively exchanged with deuterated water (approximately 5% of total silanol). This correction accounts for the contribution to the silanol peak of "buried" silanols¹⁴ which are inaccessible to $^2\text{H}_2\text{O}$ and therefore also inaccessible to reagents and chromatographic solutes.

The second correction factor, C , is needed to account for the overlap of the silanol overtone with weak C–H combination bands due to any alkyl functionalities bound to the silica surface. C was obtained for methyl groups by taking the NIR spectrum of an analogue, tetramethylsilane in CCl_4 , at several tetramethylsilane concentrations. A plot of integrated absorbance for the C–H peaks at 7220 cm^{-1} (y axis) versus the C–H peaks at 5800 cm^{-1} (x axis) yielded a straight line of equation:

$$y = Cx \quad (2)$$

where the slope, C , was found to be 0.304. For modified silicas the area of the C–H peaks overlapping with the silanol overtone at 7220 cm^{-1} (y value) can be obtained by multiplying C by M_{5800} which is the area under the C–H overtone peaks grouped at 5800 cm^{-1} (x value). The value of 0.304 for C has been found to be valid for other alkyl groups including butyl and octadecyl¹⁵ functionalities.

Deuterium-exchange technique. Silanol concentration in the unmodified silica was studied by the method described in procedure 2. This method exploits the equilibrium between ^2H and ^1H in the system:



After exhaustive deuteration and drying of the silica surface, the only sources of exchangeable hydrogen are the deuterated (^2H) silanols (we have found that any contribution from the apparatus is insignificant). Therefore, when a known volume of excess $^1\text{H}_2\text{O}$ (approximately 19-fold excess of exchangeable ^1H) is added to the system, allowed to equilibrate and then separated from the surface and condensed, the number of deuterium atoms displaced and consequently the concentration of deuterium atoms in that known volume of water can be related to the number of silanols on the surface. Even with the large excess used, this number must be corrected for the minority of deuterium atoms left behind on the surface by the partition equilibrium effect.

The number of mmoles of ^2H in the condensed water, $n_w(^2\text{H})$ is:

$$n_w(^2\text{H}) = \frac{2C_v V \rho(^2\text{H}_2\text{O})}{M(^2\text{H}_2\text{O})} \quad (4)$$

where C_v is the concentration of deuterium in the condensed water (volume fraction of ^2H in total hydrogen), V the volume of water after equilibration (ml), $\rho(^2\text{H}_2\text{O})$ the density of deuterated water (g/ml) and $M(^2\text{H}_2\text{O})$ the molecular weight of deuterated water (g/mole). The factor 2 converts moles of water to moles of hydrogen. Similarly, the number of mmoles of ^1H in the condensed water, $n_w(^1\text{H})$ can be calculated from the equation:

$$n_w(^1\text{H}) = \frac{2(1 - C_v)V\rho(^1\text{H}_2\text{O})}{M(^1\text{H}_2\text{O})} \quad (5)$$

where $\rho(^1\text{H}_2\text{O})$ and $M(^1\text{H}_2\text{O})$ are the density and molecular weight, respectively of water ($^1\text{H}_2\text{O}$).

The equilibrium constant for eqn. 3 can be expressed as

$$K = \frac{n_s(^1\text{H}) \cdot n_w(^2\text{H})}{n_s(^2\text{H}) \cdot n_w(^1\text{H})} \quad (6)$$

where K is the equilibrium constant and $n_s(^1\text{H})$ and $n_s(^2\text{H})$ are the mmoles of silanol in the ^1H and ^2H form, respectively. For our purposes we will assume K to be 1. (Even changing the K value to 1.5 would result in only a 4% difference in the surface concentration of silanols). The assumption that $K = 1$ will be justified later in the paper. Since $n_w(^2\text{H})$ and $n_w(^1\text{H})$ are already calculated and since the mmoles of ^1H silanol equals the mmoles of displaced ^2H in the water [*i.e.* $n_s(^1\text{H}) = n_w(^2\text{H})$], eqn. 6 can be used to calculate $n_s(^2\text{H})$. The total mmoles of silanol hydrogen, n_s :

$$n_s = n_s(^1\text{H}) + n_s(^2\text{H}) \quad (7)$$

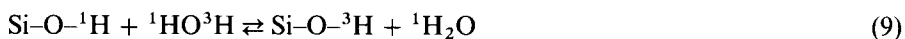
can then be used to calculate the surface concentration of silanols, α_{OH} ($\mu\text{mole}/\text{m}^2$), by the equation:

$$\alpha_{\text{OH}} = \frac{n_s \cdot 10^3}{Sm} \quad (8)$$

where S is the surface area (m^2/g) and m is the mass (g) of the silica gel. The factor 10^3 converts mmoles to μmoles . Table I gives values for duplicate runs of this experiment. The average α_{OH} value of $9.5 \mu\text{moles}/\text{m}^2$ corresponds well with literature values¹⁶.

Tritium-exchange method. TMCS-modified silicas of various coverages were obtained by procedure 5a, the NIR spectrum taken and the results listed in Table II. We then characterized these batches of silica by the tritium exchange (procedure 3) and carbon analysis (next section).

The tritium-exchange method employs the exchange of tritiated water with surface silanols:



Before the surface concentration of silanols can be calculated, two assumptions are made. First, we assume that hydrogen exchange at the surface of the apparatus is

TABLE I

DEUTERIUM-EXCHANGE METHOD

$\rho(^2\text{H}_2\text{O}) = 1.105 \text{ g/ml}$; $M(^2\text{H}_2\text{O}) = 20.03 \cdot 10^{-3} \text{ g/mmol}$; $\rho(^1\text{H}_2\text{O}) = 0.998 \text{ g/ml}$; $M(^1\text{H}_2\text{O}) = 18.02 \cdot 10^{-3} \text{ g/mmol}$; $K = 1$; $S = 267 \text{ m}^2/\text{g}$.

Run No.	C_v	V	$n_w(^2\text{H})$	$n_w(^1\text{H})$	$n_s(^2\text{H})$	n_s	m	α
1	0.055	1.20	7.28	125.6	0.42	7.70	3.01	9.58
2	0.057	1.20	7.55	125.3	0.45	8.00	3.19	9.39
Average								9.5

insignificant and that the only important sources of exchangeable hydrogen are silanols and water. Therefore, the total mmoles of hydrogen, n_t , can be expressed as:

$$n_t = n_s + n_w \quad (10)$$

where n_s and n_w are the mmoles of hydrogen due to silanol and water, respectively. This assumption is reasonable since the percent recovery for the system blank (see procedure 3) was found to be virtually 100% indicating essentially no loss of tritium to the apparatus.

Secondly, it is supposed that the isotopic equilibrium effect between ^1H and ^3H is negligible or non-existent. In other words, the probability that any given ^3H atom will end up on the surface is the same as the probability that any given ^1H atom will end up on the surface. The reasonableness of this condition will be examined below.

Given these two assumptions, if a weighed amount of tritiated water of a known specific activity, a_0 (counts per minute per gram of tritiated water), is allowed to equilibrate with the surface silanols in a dried silica sample and if the resulting equilibrated water is removed from the surface and condensed (procedure 3), the amount of tritium (and therefore the specific activity of the tritium) on the silica gel, a_s , is directly proportional to the number of silanols and the activity of tritium remaining in the water, a_w , is directly proportional to the number of hydrogen atoms in the water.

The initial specific activity, a_0 , is equal to the total activity of the system, a_t (counts $\text{min}^{-1} \text{ g}^{-1}$) and can be related to a_s and a_w :

$$a_0 = a_t = a_s + a_w \quad (11)$$

TABLE II

NIR ANALYSIS OF TMCS COVERAGES

$D_{7220} = 3.1$; $C = 0.304$; $P = \% \text{ unreacted silanol}$.

Batch No.	U_{7220}	M_{7220}	M_{5800}	P
0	79.4	—	—	100%
1	—	74.6	2.3	93%
2	—	70.0	7.1	85%
3	—	60.7	11.3	71%
4	—	53.1	19.0	58%

Finally we can calculate the number of moles of silanol using the equation:

$$\frac{a_w}{a_t} = \frac{n_w}{n_t} = \frac{n_w}{n_w + n_s} \quad (12)$$

The concentration of silanols assuming no isotope effect ($\alpha_{OH(T)}$, $\mu\text{mole}/\text{m}^2$), can then be calculated using eqn. 8.

Triplicate samples of the unmodified silica were analyzed by this method and $\alpha_{OH(T)}$ values of 9.32, 9.51 and 9.42 $\mu\text{moles}/\text{m}^2$ were obtained. The average of 9.42 ± 0.10 is essentially the same within the precision of the experiments as the value of 9.5 ± 0.1 $\mu\text{moles}/\text{m}^2$ obtained from the deuterium method. Since the isotope equilibrium effect was assumed to be absent in both cases and because the same answer is derived using that assumption, we conclude that contrary to previously published results¹⁰ the isotopic effect on equilibrium is very small or non-existent. This can be restated as:

$$K = \frac{n_s(^2\text{H}) \cdot n_w(^1\text{H})}{n_s(^1\text{H}) \cdot n_w(^2\text{H})} = \frac{n_s(^3\text{H}) \cdot n_w(^1\text{H})}{n_s(^1\text{H}) \cdot n_w(^3\text{H})} = 1 \quad (13)$$

and:

$$\alpha_{OH} = \alpha_{OH(T)} \quad (14)$$

Data from the radioisotopic (tritium) analysis of the modified and unmodified silica gels are given in Table III. A plot of surface coverage by tritium exchange (α in Table III) versus percent unreacted silanol by NIR (Table II) is presented in Fig. 4. Note the good linear relationship. The NIR technique is quantitative for silanols over a wide range of coverages. The y intercept for 0% silanol by NIR (totally reacted surface) is very close to the zero silanol surface coverage by ^3H exchange. This makes good physical sense since there would be no silanol coverage NIR signal if all the silanols were reacted.

TABLE III
SURFACE SILANOL COVERAGE BY TRITIUM EXCHANGE

$S = 267 \text{ m}^2/\text{g}$.

Sample	a_w/a_t	n_w	n_s	m^a	$\alpha_{OH(T)}$
Batch 0	0.535	5.44	4.73	1.90	9.32
	0.532	5.54	4.87	1.92	9.51
	0.522	5.44	4.98	1.98	9.42
Batch 1	0.538	5.33	4.58	1.91	8.98
	0.537	5.40	4.66	1.93	9.05
Batch 2	0.572	5.36	4.01	1.88	7.99
	0.573	5.28	3.93	1.83	8.04
Batch 3	0.612	5.37	3.40	1.83	6.97
	0.625	5.37	3.22	1.87	6.45
Batch 4	0.661	5.26	2.70	1.83	5.52

^a Mass corrected for weight of TMS groups added to the surface using carbon analysis data.

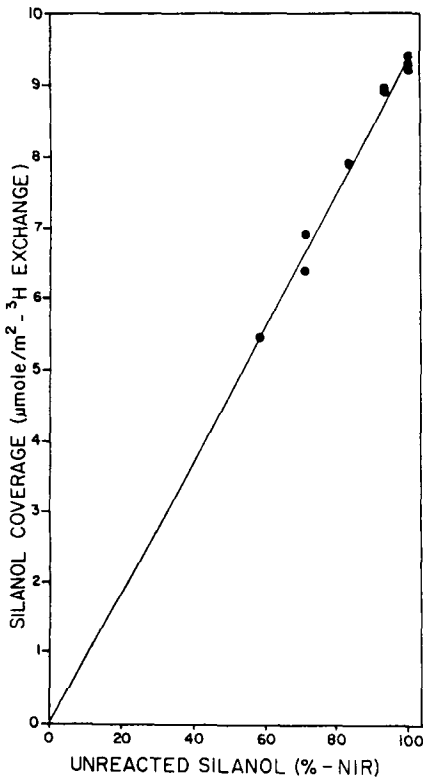


Fig. 4. Silanol coverage by tritium exchange *versus* percent unreacted silanol by NIR spectroscopy (See Tables II and III for data. Line represents least-squares fit of data (intercept = $1.7 \cdot 10^{-3}$; $r = 0.993$).

Carbon analysis

Samples from batches 0–4 were sent out for carbon analysis (procedure 4). The received %C data were converted to total carbon coverage $\alpha_{\text{TMS}(u)}$ ($\mu\text{mole}/\text{m}^2$), by the equation¹⁷

$$\text{TMS}(u) = \frac{\%C \cdot 10^6}{12 \cdot N \cdot 100 \left(1 - \frac{\%C \cdot M_s}{12 \cdot N \cdot 100} \right)} \cdot S \quad (15)$$

where N is the number of carbon atoms in the silane (three for TMCS), M_s the molecular weight of the silane reagent less the reactive group (73 for TMCS) and S is the surface area. The total carbon coverage, $\alpha_{\text{TMS}(u)}$ was then corrected to the “true” TMCS coverage, α_{TMS} ($\mu\text{mole}/\text{m}^2$), by subtraction of the carbon coverage value for the unmodified silica (batch 0), α_{uc} .

The contribution from the unmodified silica is apparently due to ubiquitous carbon physically adsorbed to the surface and to inaccuracies in the carbon analysis method for small amounts of carbon. The values resulting from eqn. 15 are given in

TABLE IV
CARBON ANALYSIS OF TMCS SURFACE COVERAGE

Batch No.	%C	α_{uc}	$\alpha_{TMS(u)}$	α_{TMS}
0	0.49	0.51	—	—
1	0.81	—	0.86	0.35
2	1.57	—	1.69	1.18
	1.87	—	2.02	1.51
3	2.54	—	2.79	2.28
4	3.67	—	4.13	3.62

Table IV and plotted *versus* NIR coverage as shown in Fig. 5. Once again a linear plot is obtained further confirming the quantitative abilities of the NIR technique. A y intercept of $8.69 \mu\text{moles}/\text{m}^2$ is lower than expected from the silanol coverage values observed with previous methods ($9.5 \mu\text{moles}/\text{m}^2$ —see above). The relative difference of 9% is probably due to the lower precision of the total carbon measurements (17% difference for the duplicate determinations for batch 2), the uncertainty introduced by a relatively large blank value (batch 0), and the inability to produce data for higher coverages ($>42\%$ —see *Surface modification* section below).

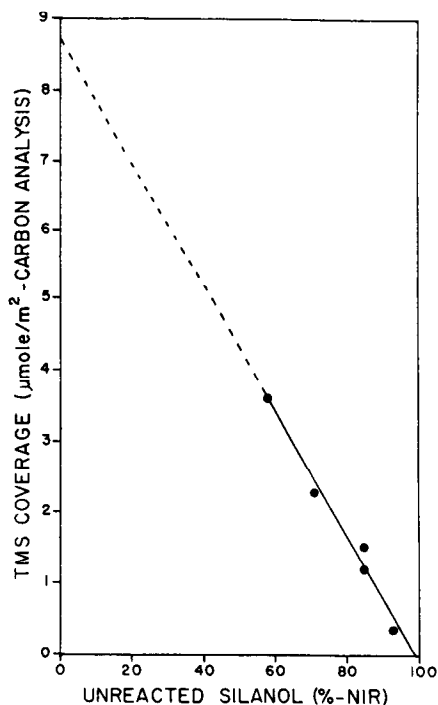


Fig. 5. Trimethylsilyl (TMS) coverage by carbon analysis *versus* percent unreacted silanol by NIR spectroscopy. See Tables II and IV for data. Line represents least-squares fit of data (intercept = $8.6 \mu\text{moles}/\text{m}^2$; $r = 0.991$).

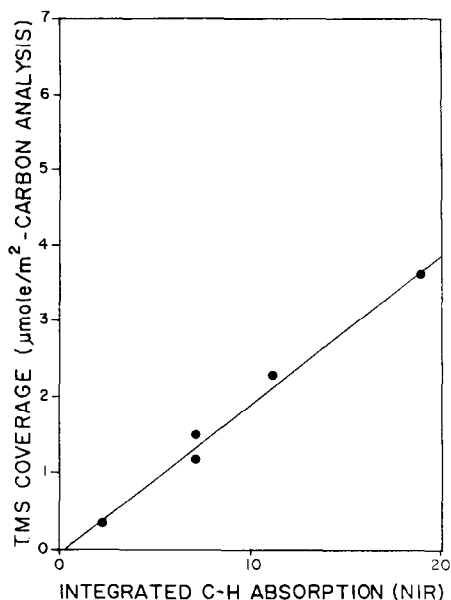
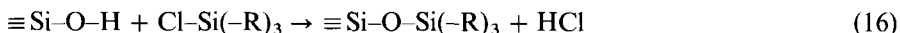


Fig. 6. Trimethylsilyl (TMS) coverage by carbon analysis *versus* integrated NIR C-H overtone absorption (near 5800). See Tables II and IV for data. Line represents least-squares fit of data (intercept = $9.4 \cdot 10^{-2}$ $\mu\text{moles}/\text{m}^2$; $r = 0.993$).

If the TMS coverage values (Table IV) are plotted against M_{5800} values for C-H absorption (Table II) the plot in Fig. 6 results. The linearity of this graph shows that the NIR technique can also be used to quantitate C-H groups on the surface.

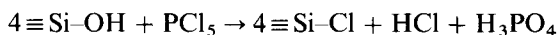
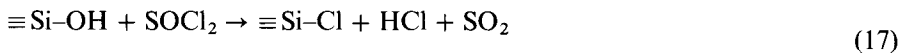
Surface modification

Silylation. The most popular means for the modification of siliceous chromatographic materials is to react surface silanols with various silanes, in particular chlorosilanes:

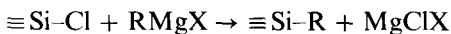


where R can correspond to a variety of functionalities. Even when using the smallest silanes ($\text{R} = \text{CH}_3$; TMCS), both literature studies and our own studies (see batch 4 above) have shown that a maximum of about 40–50% of the surface silanols are removed.

Chlorination/alkylation. We feel that one important reason for this incomplete silylation is simply steric, *i.e.*, the trimethylsilyl groups are too large to pack closely enough on the surface for greater than 50% removal of silanols. Therefore, we looked to a two-step reaction route found in the literature¹⁸ where the silanols are first chlorinated to $\equiv\text{Si}-\text{Cl}$ groups by chlorinating reagents such as SOCl_2 or PCl_5 :



The chlorinated surface is then reacted with an organolithium or Grignard reagent to form a Si-C bond:



If R was chosen to be a small enough functionality such as a methyl group, we felt that the reduced steric hindrance might allow for a more complete removal of silanol groups.

Effects of both chlorination and methylation steps in the modification procedure 5b are shown in Fig. 7. The top broken line corresponds to the unmodified silanol overtone (U_{7220}). The bottom broken line corresponds to the silanol overtone for the silica after the chlorination step and represents a 54% removal of silanols from the silica surface (and therefore 54% surface coverage of $\equiv\text{Si-Cl}$). Unfortunately, after the methylation step the silanol signal rebounded to 90% of the unmodified band's intensity indicating only a 10% reaction of silanols. However, we found that by repeatedly cycling the silica through the two steps we could reduce the apparent silanol content of the silica gel to the point that only 35% of the silanols were remaining by the NIR technique.

Several observations made about the adsorbents resulting from this repeated reaction of the silica surface did not fit with the previously stated reaction scheme (eqns. 21 and 22). First, polysilicic acid was observed in the methyl lithium-THF solution during its removal through the sintered glass disc and into the isopropanol. In addition the silica became more "flocculent" (*i.e.*, its packing density decreased) with

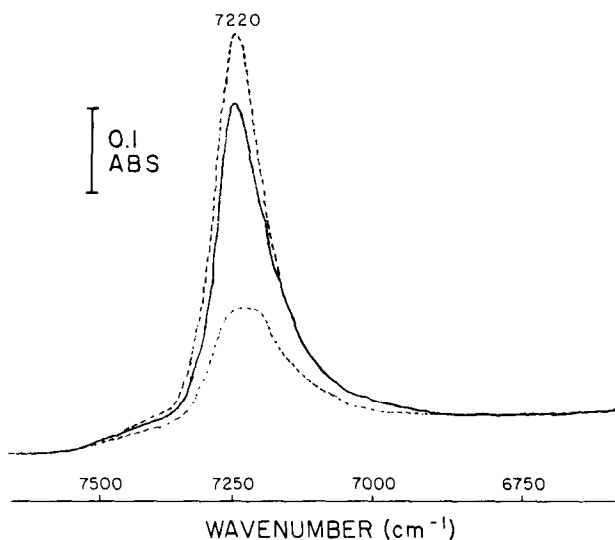


Fig. 7. NIR absorption as a function of surface reaction with phosphorous pentachloride and methyl lithium. Top broken curve: unmodified silica (dry); bottom broken curve: intermediate spectrum of PCl_5 chlorinated surface; solid curve: spectrum after addition of methyl lithium.

repeated reaction. These two observations indicated some sort of break-up of the silica network. Finally, it was noted from the NIR spectrum of the silica that the increase in C-H adsorption (5800 cm^{-1}) as compared to the reduction in silanol absorption (7220 cm^{-1}) was significantly more than would be expected from a one for one replacement of hydroxyl groups (or $\equiv\text{Si}-\text{Cl}$ groups) with methyl groups.

Direct alkylation. In an attempt to explain these unexpected observations we proceeded to monitor what happened if the silica surface was reacted with methyl lithium alone (procedure 5c). We found as above that polysilicic acid formed during methyl lithium addition, that flocculence increased, and that relatively large amounts of methyl were being added to the surface. Fig. 8 shows the NIR spectra of a silica that has been cycled seven times through procedure 5c.

Unmodified silica samples were also reacted with butyl lithium (procedure 5d) so that a broader view of alkyl lithium-silica reactions could be built. During the initial reaction cycle polysilicic acid was observed in the butyl lithium-hexanes-THF mixture indicating, as with the methyl lithium, some sort of silica network break-up. However, this effect lessened with later cycles, and unlike the methyl lithium reaction, packing density and mechanical stability seemed to stay constant. (Possible reasons for these observed differences will be given below.) A relatively large increase in butyl coverage was also observed (see Fig. 9).

Apparently two different reactions occur at the silica surface upon addition of alkyl lithium. Silanols can react directly with the alkyl lithium reagents:



(This reaction has been used to evaluate the silanol coverage of silica gels¹⁹.) On the other hand the break-up of the silica lattice can be attributed to a second reaction with siloxanes¹⁸:

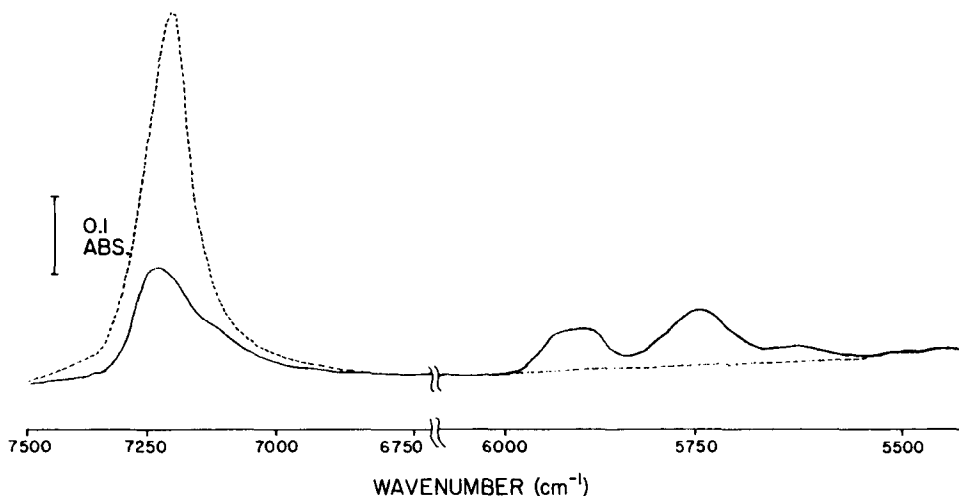
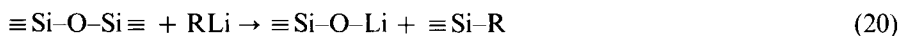


Fig. 8. NIR absorption for a repeatedly methylated (methyl lithium) silica. Broken curve: unmodified silica (dry); solid curve: silica subjected to seven cycles of direct methylation.

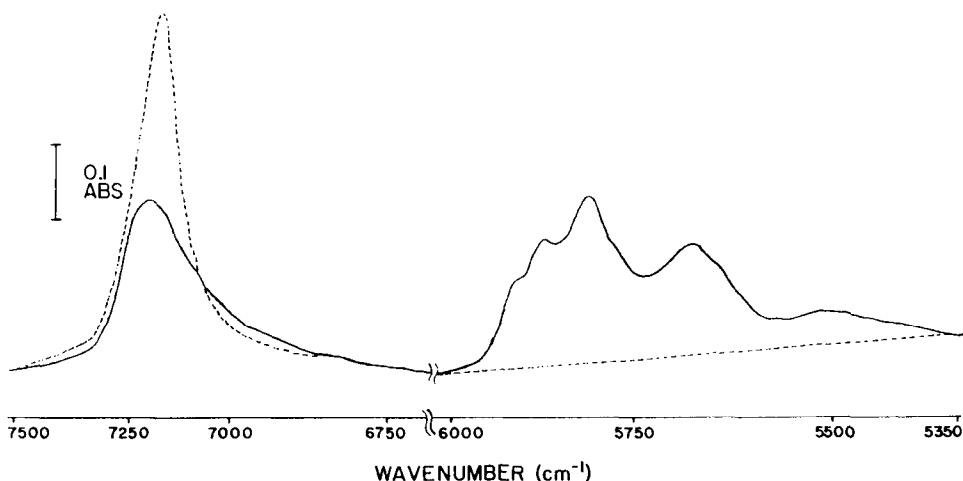


Fig. 9. NIR absorption for a repeatedly butylated (butyl lithium) silica. Broken curve: unmodified silica (dry); solid curve: silica subjected to eight cycles of direct butylation.

resulting in carbon directly bonded to the surface. In our alkylation procedures any remaining alkyl lithium is then removed, and the Si-O-Li groups formed in eqns. 19 and 20 are (exothermically) neutralized to the silanol:

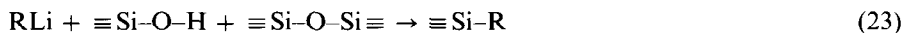


If these silanol groups are close enough together they are known to condense with heat:



to reform stable siloxane bonds.

We propose that the net effect of these reactions (19–22) is an overall loss of silanol and a significant gain in alkyl coverage:



The overall reaction scheme 23 is meant only as a statement of net gains and losses of silica surface functionalities. No overall balanced equation is written due to the disruptive nature of the alkyl lithium reaction with the silica (*i.e.*, “chunks” of polysilicic acid are removed from the silica network). Depending on the conditions of the reaction cycle(s), the increase in alkyl coverage is usually 2–3 times greater than the loss of silanol.

The evidence for direct methylation and direct butylation of the silica surface is given separately below.

Direct methylation. As already noted the case for methyl lithium’s disruption of the silica surface is supported both by the formation of polysilicic acid and the increased flocculence of the silica. In addition the BET surface area of the silica was found to increase by up to 25% upon repeated reaction and the pore size distribution

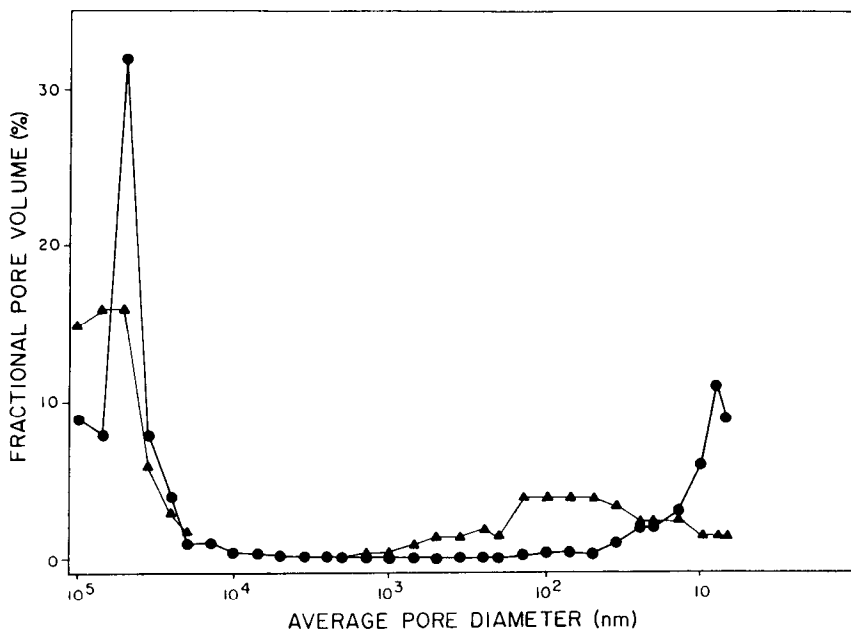


Fig. 10. Fractional pore volume versus average pore diameter for methylated silica. ● = Unmodified silica gel; ▲ = methylated silica.

dispersed greatly in the 10–100-nm region from the sharp maximum at 10 nm for the unmodified silica (see Fig. 10).

The NIR spectrum of the methylated silica (Fig. 8) has a four peak pattern (5924, 5875, 5731, 5602 cm^{-1}) in the C–H overtone region which is peculiar to methyl groups (see Fig. 3). This methyl coverage has been shown to be non-extractable by monitoring the C–H overtone bands before and after washing the adsorbent with THF, methylene chloride, acetone, 4 M hydrochloric acid (aq.), and water, and heating the silica up to 200°C. The identical spectra obtained confirm that the absorptions are due to chemically bonded methyl groups (as opposed to being only physically adsorbed). There is no evidence in the C–H overtone region for any other type of hydrocarbon groups.

Solid state NMR has also been used in order to obtain complementary surface information (see procedure 6). In the carbon-13 spectrum (see Fig. 11a) we have only one absorption at 0 ppm which corresponds to a methyl group bonded directly to Si^{13} [as with the solid reference tetra (trimethylsilyl) methane]. The ^{29}Si spectrum (Fig. 11b) gives a peak corresponding to silicon bound to methyl¹² (near –21 ppm) as well as a broad peak for silanol and siloxane silicons (–98 and –110 ppm, respectively). These spectra further confirm formation of Si–CH₃ bonds via direct methylation.

Direct butylation. Like the methyl lithium, butyl lithium causes disruption of the silica network as evidenced by the formation of polysilicic acid in the initial reaction cycles (procedure 5d). However, after a few cycles this effect diminishes. We believe that this diminution is due to the larger steric volume of the butyl lithium than methyl lithium in solution coupled with the bulky butyl groups bonded to the surface. That is,

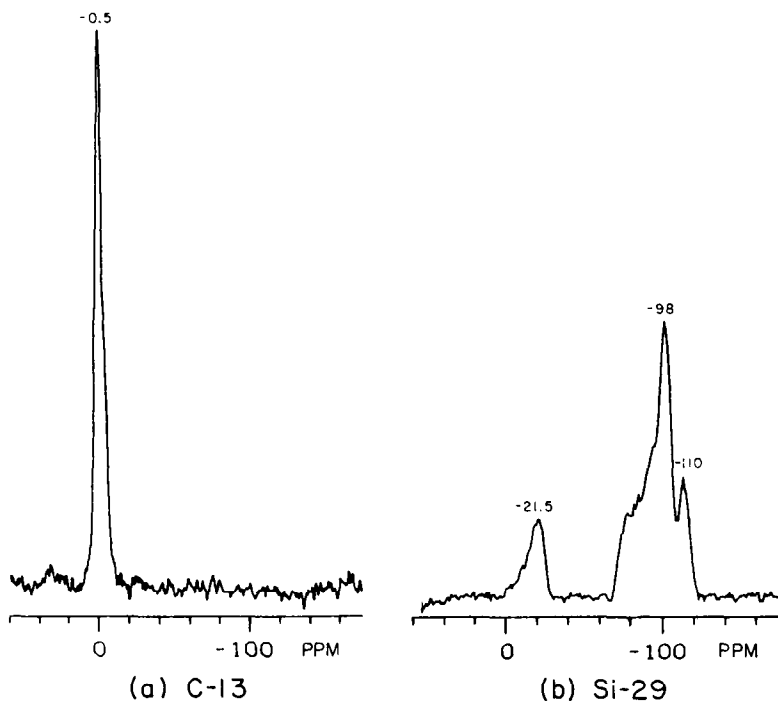


Fig. 11. Solid state cross-polarization magic angle spinning NMR spectra for methylated silica. All numbers in units of ppm. (a) Carbon-13 NMR of methylated silica. Peak at -0.5 ppm corresponds to methyl bound to silicon: $\equiv\text{Si}-\text{CH}_3$. (b) Silicon-29 NMR of methylated silica. Peak assignments: -21.5 ppm, silicon bound to methyl; -98 ppm, silicon bound to silanol; -110 ppm, silicon bound to siloxane only.

the butyl lithium causes less disruption than methyl lithium after initial cycles, because bound butyl sterically hinders butyl lithium from reaching more siloxanes. Due to this effect there is no great loss of mechanical stability and packing density. In fact we have found that the surface area actually decreases (from 267 to 213 m^2/g). This is apparently due to the analogous effect seen when silica is treated with silanes (for example batch 4 above has a surface of 211 m^2/g .) The pore size data (Fig. 12) show a slight dispersion from the unmodified silica. However, the effect is much smaller than for the methylated silica which is also indicative of the smaller amount of surface disruption caused by butyl lithium.

As with methyl groups on the methylated silica, the NIR technique reveals that a relatively large number of non-extractable butyl groups have been chemically bonded to the butylated silica gel. The carbon-13 NMR displays a three peak pattern (Fig. 13) corresponding to (1) methyl bound to carbon, (2) methylene bound to silica and (3) two methylenes bound to carbon. This is the expected pattern for a butyl group bonded directly to silicon. The silicon-29 spectrum was not obtained.

As with the methyl lithium, the evidence supports the breakage of siloxane bonds to form silicon-carbon bonds.

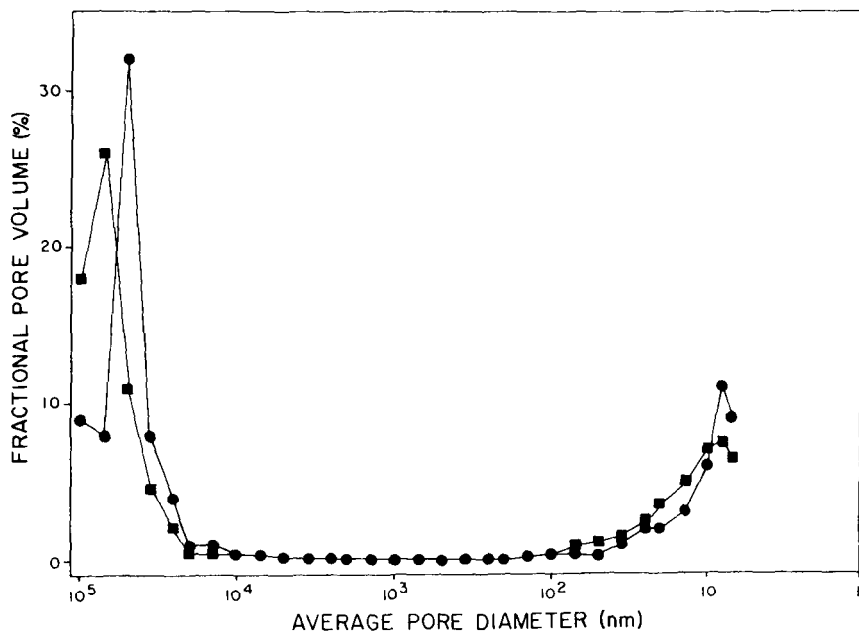


Fig. 12. Fractional pore volume versus average pore diameter for butylated silica. ● = Unmodified silica gel; ■ = butylated silica.

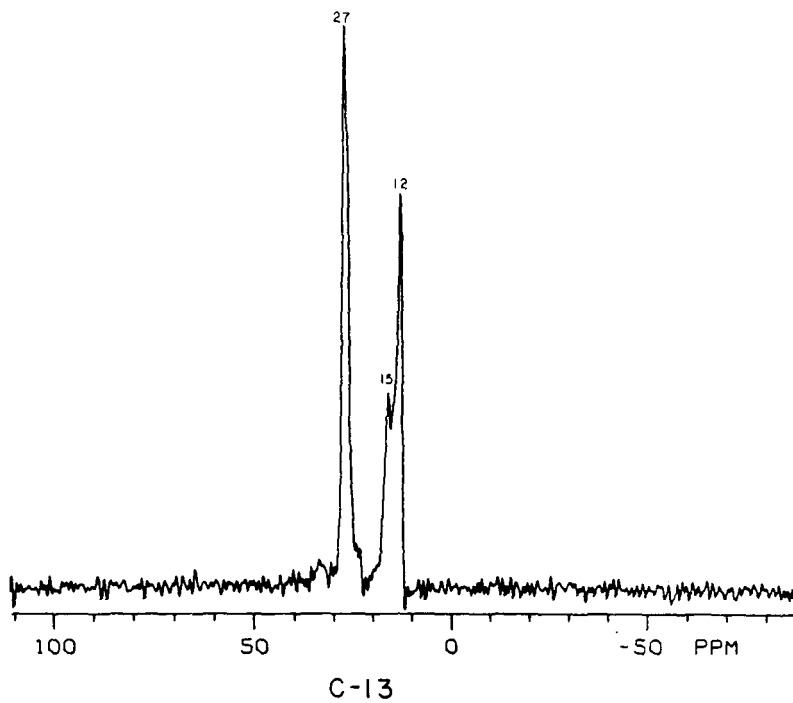


Fig. 13. Solid state cross-polarization magic angle spinning NMR spectra of butylated silica. All numbers in units of ppm. Peak assignment: $\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, where peak 1 = 12 ppm; 2 = 15 ppm; 3 = 27 ppm.

Gas chromatography

Since our final goal was to produce interesting and hopefully useful chromatographic surfaces, the ultimate test of the adsorbents produced was chromatography. Gas-solid chromatography (GSC) was chosen because of the relative simplicity of interactions between solute and adsorbent (*i.e.*, there are no additional interactions with a liquid mobile or supported phase as in liquid chromatography or gas-liquid chromatography). Acetone was chosen as polar probe of the silica surface, because of its strong physical interactions²⁰ with silanols on the silica surface. The butylated adsorbent was chosen as a representative alkylated silica because of its mechanical stability.

Initially comparisons were attempted between the unmodified silica and the butylated silica, but it was found that the acetone was too highly retained on the native silica even under extreme conditions of column temperature and flow-rate. We therefore used a fully reacted TMCS silica (batch 4 above) for a direct comparison with the butylated silica. The results of this comparison are summarized in Fig. 14 and Table V. The conditions are given in the figure legend. Note that for equivalent

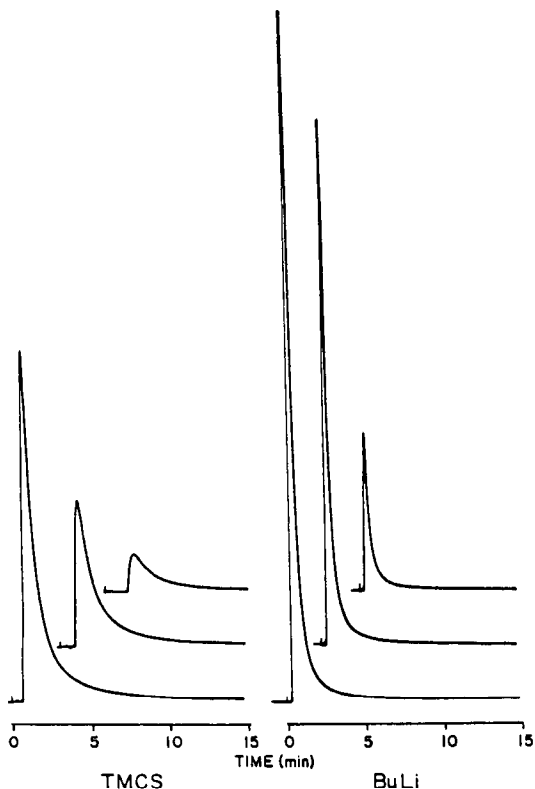


Fig. 14. Direct gas chromatographic comparison of acetone retention profiles for a TMCS (batch 4) and a butylated silica. All conditions are the same for each column. Column temperature: 200°C; flow-rate: 17 ml/min; weight of adsorbent: 1.6 g. The traces for each column correspond to 5 (bottom trace), 2 (middle trace), and 0.5 μ l (top trace) of saturated acetone vapor. "Tics" shown on traces correspond to injection times. BuLi = Butyl lithium.

TABLE V

GSC RETENTION DATA FOR ACETONE ON SILYLATED AND BUTYLATED COLUMNS

Retention time and capacity factor calculated using statistical moments.

Column (adsorbent)	Injection volume (μl)	Retention time (s)	Capacity factor (k')
TMCS	0.5	219	17
	2	170	13
	5	146	11
Butyl lithium	0.5	59	3.8
	2	61	4.0
	5	63	4.1

injection volumes (5, 2 and 0.5 μl of acetone vapor) the chromatographic peaks are sharper and less tailed for the butylated silica column as compared to the silylated silica column. In addition, both the average and range of the retention times and the capacity factors (both calculated using statistical moments) for these chromatograms (Table V) are significantly smaller for the butylated column.

Evidently the interaction with the polar acetone molecule is less intense for the butylated column. This is probably due to two reasons. First, the calculated surface concentration of silanols (eqn. 22) for the butylated and silylated silica were 5.0 and 5.5 $\mu\text{moles}/\text{m}^2$, respectively. Secondly, the calculated surface coverage of alkyl groups for the butylated and silylated silica were 9.5 and 3.7 $\mu\text{moles}/\text{m}^2$, respectively. Apparently the 10% lower silanol content for the butylated adsorbent means fewer high energy silanol sites are available while the dramatically higher alkyl coverage (2.6 times higher) does a better job of sterically restricting solute access to the remaining silanols. The combination gives a less active chromatographic surface.

CONCLUSION

The NIR technique has been shown to be a useful technique for studying silica gel modification. It is non-destructive, gives good qualitative and quantitative information for important surface functionalities, is relatively convenient and is inexpensive. One possible limitation of this technique in its application is the method for correcting silanol absorption for C-H combinations (eqn. 1). For silicas with very high carbon coverages, the correction becomes relatively large and the approximation of a baseline for integration (M_{7220}) is more difficult. This problem can be solved by using computer aided peak subtraction and integration.

The present work with alkyl lithium confirms and expands on the direct alkylation of silica done by Boehm *et al.*¹⁹, and sheds a new light on the chlorination/alkylation methods found in the chromatographic literature (*e.g.* ref. 7). The preliminary GSC data given in this paper indicate that direct alkylation (particularly butylation) may have a useful role to play in the deactivation and modification of siliceous materials for chromatography.

SYMBOLS

a_0	Initial specific activity of tritiated water
a_s	Specific activity of tritiated silanols (after equilibration)
a_t	Total specific activity
a_w	Specific activity of tritiated water (after equilibration)
C	Correction factor for C-H combination bands at 7220 cm^{-1}
C_v	Volume fraction of deuterium in total hydrogen
%C	Percent weight of carbon in modified silica gel
D_{7220}	Integrated absorbance at 7220 cm^{-1} for deuterated silica
K	Equilibrium constant
m	Mass of silica gel (g)
M_{5800}	Integrated absorbance at 5800 cm^{-1} for modified silica
M_{7220}	Integrated absorbance at 7220 cm^{-1} for modified silica
$M(^1\text{H}_2\text{O})$	Molecular weight of water
$M(^2\text{H}_2\text{O})$	Molecular weight of deuterated water
M_s	Molecular weight of silane minus reactive group
N	Number of carbon atoms in the silane
n_s	mmoles of hydrogen in silanol
$n_s(^1\text{H})$	mmoles of ^1H in silanol
$n_s(^2\text{H})$	mmoles of ^2H in silanol
$n_s(^3\text{H})$	mmoles of ^3H in silanol
n_t	Total mmoles of hydrogen
n_w	mmoles of hydrogen in condensed water
$n_w(^1\text{H})$	mmoles of ^1H in condensed water
$n_w(^2\text{H})$	mmoles of ^2H in condensed water
$n_w(^3\text{H})$	mmoles of ^3H in condensed water
P	Percent unreacted silanol
S	Specific surface area of silica (m^2/g)
U_{7220}	Integrated absorbance at 7220 cm^{-1} for unmodified silica
V	Volume of water after equilibration (ml)
α_{OH}	Surface concentration of silanols
$\alpha_{\text{OH(T)}}$	Surface concentration of silanols by tritiation method
α_{TMS}	Surface coverage of TMS groups
$\alpha_{\text{TMS(u)}}$	Uncorrected surface coverage of TMS groups
α_{uc}	Carbon coverage for unmodified silica
$\rho(^1\text{H}_2\text{O})$	Density of water
$\rho(^2\text{H}_2\text{O})$	Density of deuterated water

ACKNOWLEDGEMENTS

NMR spectra were obtained at the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE-8208821. We acknowledge the help of Drs. Mark Miller and Richard Linton in obtaining the NMR spectra. We also acknowledge the help of Kevin Bruce in obtaining surface area and porosimetry data.

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