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TRANSMISSION NEAR-INFRARED TECHNIQUE FOR EVALUATION AND RELATIVE QUANTITATION OF SURFACE GROUPS ON SILICA

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SUMMARY

A qualitative and quantitative infrared method for surface group determination on silica gel is presented. Carbon tetrachloride is used to reduce scattering so that the sample transmits light throughout the region of interest (near-infrared: 8000–4000 cm^{-1}). The technique is shown to be useful in studying water adsorption, $^2\text{H}_2\text{O}$ exchange and trimethylchlorosilane reaction with silanol groups on the silica surface.

INTRODUCTION

Silanol (hydroxyl) groups on the surface of silica gel have been shown to be major centers for solute adsorption¹. Because of their importance in chromatographic and catalytic processes, characterization and quantitation of silanols have been done by a variety of techniques both chemical²⁻⁵ and physical⁶⁻²². Spectroscopic methods including solid-state nuclear magnetic resonance (NMR)⁸⁻¹⁰ and reflectance¹¹, photoacoustic¹² and transmission¹³⁻²² infrared spectroscopy have been particularly important.

Transmission infrared (IR) in the fundamental region (4000–700 cm^{-1}) has received intense interest^{13,15,17,20,21} because of strong fundamental bands for various silica surface functionalities including "free" and "bound" (or hydrogen-bonded) silanols^{13,15} (see Fig. 5), physically adsorbed water¹³, deuterated silanols^{15,17} and various organic modifiers including organosilanes²⁰. Unfortunately, the overlap of bands for O–H stretching vibrations of bound silanols and physically adsorbed water in this region have caused problems in qualitative and quantitative assessment of these groups. This problem can be alleviated by studying the less intense combination and overtone bands in the near-IR^{14,16,18,19} (8000–4000 cm^{-1}). It has been shown that the combination (stretch and bend) bands for silanols and physically adsorbed water are easily resolved resulting in more reliable quantitation¹⁹.

In transmission IR, scattering must be reduced in the silica gel sample so it will be reasonably transparent to the incident radiation. Traditionally this has been accomplished by pressing the silica into pellets at high pressures^{13,15}. However, the pressures needed to form stable pellets cause loss of particle integrity²⁰ which may

result in an altered surface with concurrent changes in the IR spectrum. Also, it is difficult to get reproducibly uniform samples for good quantitation. Alternatively, the sample may be slurried with a liquid of similar refractive index. Carbon tetrachloride^{14,16,19,21} and polychlorotrifluoroethylene²⁰ have been used successfully as refractive index matching media in the near-IR and fundamental IR. Although interactions between any adsorbed species and surface functionalities cause shifts in absorption frequencies²², carbon tetrachloride exerts a relatively minor influence¹⁴.

In our laboratory we have developed quantitative/qualitative transmission techniques in both the fundamental and near-IR using carbon tetrachloride as a refractive index matching medium. Carbon tetrachloride is effective as it gives no significant absorption from 8000 to 2300 cm^{-1} . This paper focuses on the near-IR technique, because of the additional information available from the combination bands of this region and because of comparative ease in sample handling technique. A cell has been designed that allows for *in situ* drying and reaction of the silica gel, subsequent addition of carbon tetrachloride and recording of spectra. This cell avoids exposure of sample to air and especially water vapor. The application of this system to studying the effectiveness of the surface modification of silica gel is of primary interest.

EXPERIMENTAL

Materials

A spherical silica gel, Porasil B (Supelco, Bellefonte, PA, U.S.A.), 80–100 mesh, with a BET surface area of 197 m^2/g was used. Reagent-grade carbon tetrachloride from Fischer Scientific Co. (Fair Lawn, NJ, U.S.A.) was distilled and dried over molecular sieve 4A. Deuterated water (99.8 atom%²H) (Sigma, St. Louis, MO, U.S.A.), and trimethylchlorosilane (Petrarch Systems, Levittown, PA, U.S.A.) were used as received.

Equipment

Transmission spectra in the near-IR were obtained on a Varian (Palo Alto, CA, U.S.A.) Cary 17 UV-vis-IR scanning spectrometer in the absorbance mode. The near-IR cell (Fig. 1) was fabricated in-house. A piece of square glass tubing (1), roughly $1 \times 1 \times 22$ cm, acts as both reaction chamber and spectroscopic cell. The path length was found to be 1.02 cm by calibration against a 1.000 cm cuvette using copper(II) sulfate solution at a wavelength of 790 nm. The sample rests on a sintered glass disc (2) which permits free flow of gases and liquids but keeps the silica gel in place. This is connected to a 22-cm length of 1 mm bore glass capillary (3) which in tandem with the $1 \text{ m} \times \frac{1}{4}$ in. I.D. glass coil (4) allows for easy removal of gas bubbles from the sample upon addition of carbon tetrachloride. The two temperature-resistant, greaseless, PTFE stopcocks (5) allow control of gas liquid flow and prevent contamination of the sample with atmospheric water. A 14/20 ground-glass joint (6) allows for both convenient cell cleaning and retrieval of the silica-carbon tetrachloride slurry for subsequent experiments. A PTFE sleeve and springs allow for effective sealing of the joint. The length of the square tubing and capillary section of the cell permits insertion of the silica gel into the constant-temperature region of a tube furnace or oven for drying, and assists addition of carbon tetrachloride. Because of

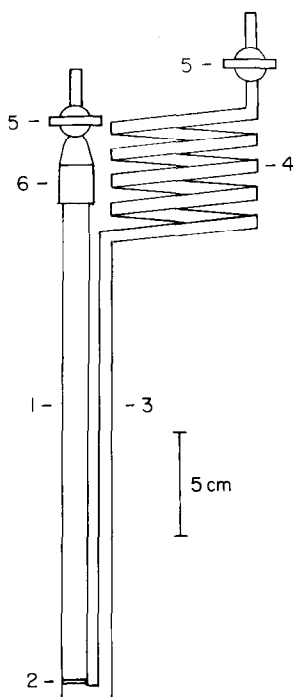


Fig. 1. Near-IR cell. 1 = Square tubing with path length of 1.02 cm; 2 = coarse glass frit; 3 = 1 mm bore glass capillary; 4 = 1 m coil of 1/4 in. glass tubing; 5 = PTFE stopcocks; 6 = 14/20 ground-glass joint.

the cell's height, a special sample compartment cover for the Cary 17 had to be constructed to prevent room light from interfering with the spectra. A Lindberg (Watertown, WI, U.S.A.) temperature controller/tube furnace and a Blue M (Blue Island, IL, U.S.A.) laboratory oven were used for heating samples. Integration of absorbance peaks was performed using a planimeter. Photoacoustic near-IR spectra were taken on a Model 6001 Princeton Applied Research (Princeton, NJ, U.S.A.) UV-vis-near-IR spectrometer with a xenon source.

Procedures

(1) *Samples.* Approximately 2.1 g of Porasil B were weighed to a precision of 0.1 mg and added to the cell. This amount of silica adequately fills the incident radiation beam. The large cell dimensions lead to reproducible packing of silica in the beam.

For spectra about 20 ml of dry carbon tetrachloride were added by syringe through the stopcock and trapped gas bubbles removed by gentle agitation. The cell was inserted into the Cary 17 and the near-IR region scanned from 2400 to 1200 nm (4167 to 8333 cm^{-1}) at a scan rate of 1 nm/sec for a total scan time of 20 min. The slit width varied from 0.4 to 1.0 mm, giving an instrument spectral bandwidth of 1–2 nm.

(2) *Drying.* Originally drying was performed by passing helium (10 ml/min) over the silica at $>200^\circ\text{C}$ for at least 5 h. The silica was allowed to cool for 1/2 h in

gas flow before dry carbon tetrachloride was added. The resulting spectra had no band corresponding to physically adsorbed water (5277 cm^{-1} ; see Table I). Unfortunately, drying at more than 200°C caused discoloration of the silica (presumably due to decomposition of adsorbed organics) and resulted in a less transparent sample after several cyclings of the silica (as in procedures 3 and 4 below). This caused diminution of the integrated absorbance of the peaks of interest and necessitated changing the silica after several cycles. To avoid this effect we now dry the silica at 180°C which causes no noticeable discoloring and still removes all detectable water (5277 cm^{-1}).

(3) *Standard water addition.* Silica gel was dried and then 1–40 μl of distilled water were added via a syringe through the stopcock. The silica gel and water were then allowed to equilibrate for 3 h at 90°C . Carbon tetrachloride was added and the spectra were taken.

(4) *Deuteration.* Excess of deuterated water (2 ml) was added to dried silica gel and permitted to equilibrate at 90°C for 3 h. The silica was then dried at 200°C in He flow for 2 h to remove excess of $^2\text{H}_2\text{O}$. Carbon tetrachloride was added and the spectrum recorded.

(5) *Silylation.* To a round-bottomed flask were added 5 ml (40 mmol; 10-fold excess) of trimethylchlorosilane, 2 ml of dry pyridine and 25 ml of carbon tetrachloride. The dried silica (2.1 g) was added, a reflux column and nitrogen bubbler were attached and the solution was heated for 12 h at just under reflux. The resulting modified product was washed with carbon tetrachloride, methylene chloride, THF and water, dried in the cell and the spectrum taken.

(6) *Photoacoustic spectroscopy (PAS).* The trimethylchlorosilane-modified Porasil B (procedure 5) was loaded into a stainless-steel disc with a cavity volume of 0.10 ml. Static charges on the particles were neutralized with a Zerostat antistatic pistol (Discwasher, Columbia, MO, U.S.A.) and then the sample cell was screwed together and inserted in the spectrometer. The spectra were collected with a chopping frequency of 40 Hz and divided by a carbon black reference for source compensation. The slit width of 4.0 mm gives an instrument spectral bandwidth of 64 nm. Five scans were signal averaged at a scan rate of 200 nm/min for a total data collection time of 40 min.

RESULTS AND DISCUSSION

In our experience, any exposure of dry silica gel to the atmosphere will cause water to be rapidly, physically adsorbed on the surface. The resulting absorption in the fundamental IR overlaps with silanol absorption making quantitation of silanols difficult if not impossible. For this reason we have focused our efforts in the near-IR where contributions from silanols and physically adsorbed water can be distinguished. The cell described above was used to study interactions of the silica surface with water, deuterated water and trimethylchlorosilane.

Assignment and quantitation of OH bands

In Table I fundamental, combination and overtone bands for various surface OH functionalities observed in both the fundamental IR and near IR are listed. Our experimental values given in column 5 are shifted to lower values from the literature

TABLE I
ASSIGNMENT OF SPECTRAL BANDS OF SILICA TO OH FUNCTIONAL GROUPS

Functional group	Band assignment	Band frequencies (cm^{-1})			
		Literature		Experimental	
		Vacuum	CCl_4		
Silanol	Bend (δ_s)	870 ¹⁵	—	—	
	Stretch (ν_s)	3750 ¹³	3700 ²¹	3670	
	H-bonded stretch (ν_s)	3500 ¹³	—	3480	
	Combination ($\delta_s + \nu_s$)	4550 ¹⁸	—	4515	
	Overtone ($2\nu_s$)	7326 ¹⁴	7220 ¹⁴	7220	
	H-bonded Overtone ($2\nu_s$)	7140 ¹⁴	—	7140	
	Deuterated silanol	Deuterated stretch (ν_D)	2760 ¹⁵	—	2710
	Deuterated overtone ($2\nu_D$)	—	—	5362	
Water	Bend (δ_w)	1635 ¹⁵	—	1600	
	Stretch (ν_w)	3400 ¹³	—	3200	
	Combination ($\delta_w + \nu_w$)	5260 ¹⁴	5265 ¹⁹	5277	
	Overtone stretch ($2\nu_w$)	6850 ¹⁴	—	6850	

values obtained in vacuum (column 3) due to carbon tetrachloride adsorption on the OH functionalities¹⁴. The literature values for carbon tetrachloride in column 4 correspond closely to our values. Because the overtone band for the silanol ($2\nu_s$: 7220 cm^{-1}) and combination band for water ($\delta_w + \nu_w$: 5277 cm^{-1}) are totally resolved, they seem to be ideal for studying the silica surface. Therefore we have used the integrated silanol stretch overtone for quantitation of silanol. This is valid as long as the water combination band at 5277 cm^{-1} is absent indicating absence of adsorbed water, so that the peak at 7220 cm^{-1} is due only to silanols and not to a water overtone ($2\nu_w$). This is the case after drying (procedure 2). Results for the integration of the overtone band for four dried Porasil B samples are given in Table II. As can be seen, the results are very consistent with a relative standard deviation of 1.7%.

TABLE II
SILANOL QUANTITATION BY INTEGRATION OF PEAK AT 7220 cm^{-1} FOR PORASIL B

Sample	Integrated peak area (cm^2)
1	33.5
2	33.5
3	34.4
4	33.0
Average	33.6
Standard deviation	0.58
Relative standard deviation	1.7%

Standard addition of water

In order to gain an understanding of the effect of water on the near-IR spectrum and to see if quantitation of surface groups was possible using our technique, we carried out a series of standard additions of water to the silica gel (procedure 3). The amounts of water added were 1, 2, 5, 10, 20 and 40 μl . As was expected, a gradual increase in the intensity of the water combination band (5277 cm^{-1}) was observed, as shown in Fig. 2. The bands were then integrated and the results plotted *versus* amount of added water [monolayers were calculated using 12.5 \AA^2 area for H_2O (ref. 23) on the silica surface] as shown in Fig. 3. The resulting linear plot agrees with the results obtained by Klier *et al.*¹¹ using reflectance near-IR spectroscopy. Our technique can be used for quantitation of surface water. Fig. 4 shows the effect of addition of water on the silanol overtone band (7220 cm^{-1}). The broken line corresponds to the band resulting from dried silica whereas the solid line represents the same band with 40 μl of adsorbed water per 2.1 of silica (*ca.* 0.4 monolayers). Note that the dried silica has a band at 7220 cm^{-1} corresponding to non-hydrogen-bonded "free" silanols¹⁴ and to "bound" hydrogen bonded silanols¹⁴. After water adsorption, the band at 7140 cm^{-1} has increased significantly with the peak at 7220 cm^{-1} becoming much less intense. An additional peak at 6850 cm^{-1} also appears. The peaks at 7140 and 6850 cm^{-1} are thought to be due to overtones of several functionalities

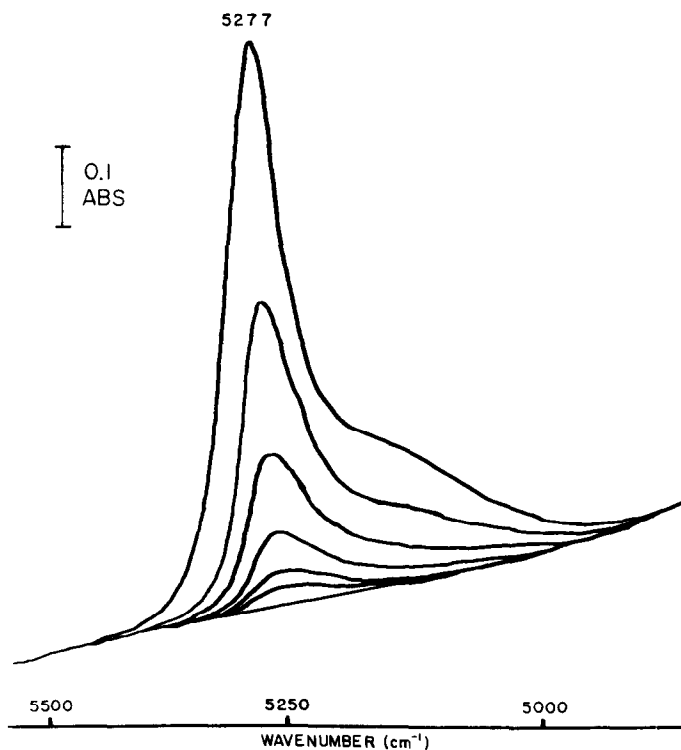


Fig. 2. Near-IR absorption as a function of water added to the silica sample. Curves correspond to dry silica (bottom curve) and 1, 2, 5, 10, 20 and 40 μl (top curve) of added water per 2.1 g of silica. $5277\text{ cm}^{-1} =$ water combination band ($\delta_w + \nu_w$).

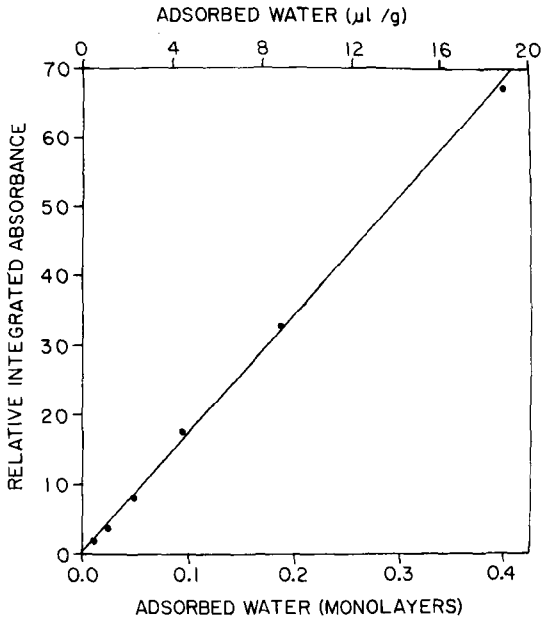


Fig. 3. Relative integrated absorbance of the peak at 5277 cm^{-1} (water combination; $\delta_w + \nu_w$) as a function of added adsorbed water in monolayers (bottom abscissa) and in μl of water per gram of silica (top abscissa). The line corresponds to a least-squares fit of the data. Correlation coefficient = 0.9995.

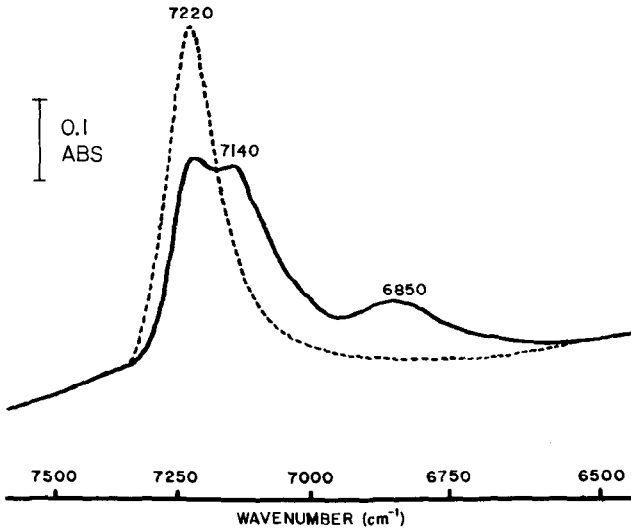


Fig. 4. Near-IR absorption as a function of adsorbed water added to the silica sample. Broken curve: dry silica. Solid curve: $40\ \mu\text{l}$ of water per $2.1\ \text{g}$ of silica. $7220, 7140, 6850\ \text{cm}^{-1}$ = silanol and water overtones (see text).

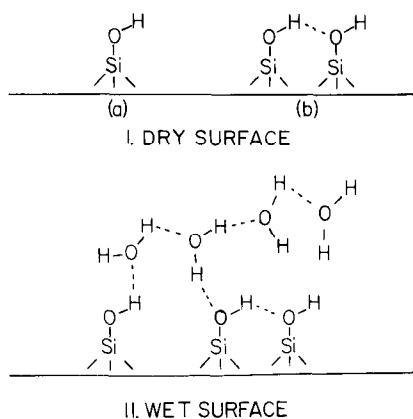


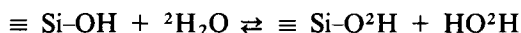
Fig. 5. Models for silica surface functionalities as a function of dryness. I, Dry silica surface: (a) "lone" silanol; (b) "bound" or hydrogen-bonded silanol. II, Wet silica surface (see text). Solid lines = covalent bonds; broken lines = hydrogen bonds.

(see Fig. 5) including (1) silanols interacting with adsorbed water and (2) physically adsorbed water. A dried silica surface leads to easier interpretation and quantitation of results.

At this point it is important to explain the reason for the slanting baselines seen in our near-IR spectra. Because the refractive indices of liquids (carbon tetrachloride) and solids (silica) vary at different rates with wavelength, carbon tetrachloride and silica only "match" refractive indices at one wavelength. Consequently, as the wavelength is varied in either direction from the matching point, the refractive indices of the two mediums diverge causing the slurry to scatter more light. Since the matching point for silica and carbon tetrachloride is in the visible region, scanning from the visible to longer wavelengths in the near-IR causes a simultaneous increase in scattering. This increase in scattering is seen as a steady rise in the baseline of all spectra shown. Fortunately this effect is minor and has little effect on quantitative and qualitative interpretation.

Deuteration of silanols

Deuteration of surface silanols by exchange with deuterated water:



has been shown¹⁷ to be indicative of whether silanols being observed in the fundamental or near IR are due to surface groups or "buried" silanols. Buried silanols are trapped inside the silica gel during its manufacture. These groups should be inaccessible to chromatographic solutes and therefore can be discounted when attempting modification of the surface. We deuterated the surface of Porasil B according to procedure 4 repeatedly (driving off the carbon tetrachloride with helium and readmitting ${}^2\text{H}_2\text{O}$, etc.) until subsequent addition of ${}^2\text{H}_2\text{O}$ did not decrease the silanol overtone band (7220 cm^{-1}) any further. In Fig. 6 we see the silanol overtone (7220 cm^{-1}) before (broken trace) and after (solid trace) repeated deuteration. From integration of these peaks we concluded that 95% of the silanols were on the surface and

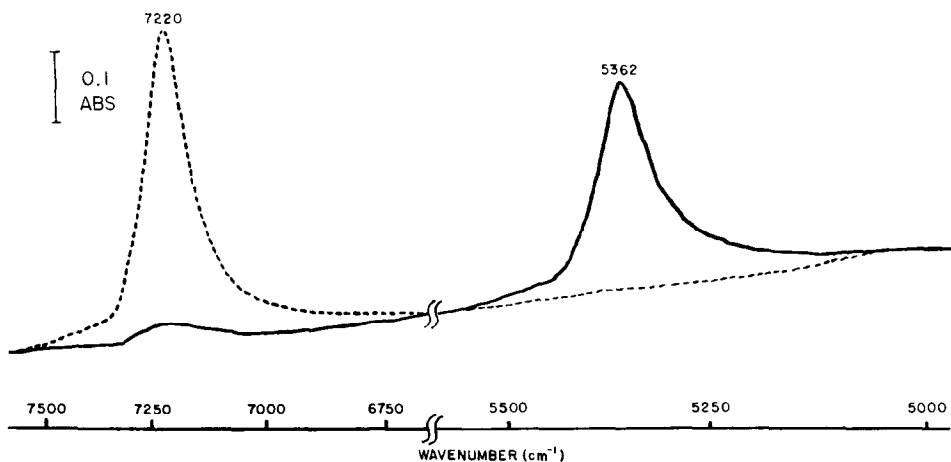


Fig. 6. Near-IR absorption as a function of deuteration of the silica surface. Broken curve: dried silica before deuteration. Solid curve: deuterated silica. 7220 cm^{-1} = silanol overtone ($2\nu_s$); 5362 cm^{-1} = deuterated silanol overtone ($2\nu_D$).

that the contribution of buried silanols to the spectrum could be compensated for. Fig. 6 also shows the appearance of a band (solid trace) at 5362 cm^{-1} corresponding to deuterated silanol (see Table I). The broken curve corresponds to dried silica before deuteration.

Surface modification

Silanol interaction with solutes²³ in both gas and liquid chromatography can

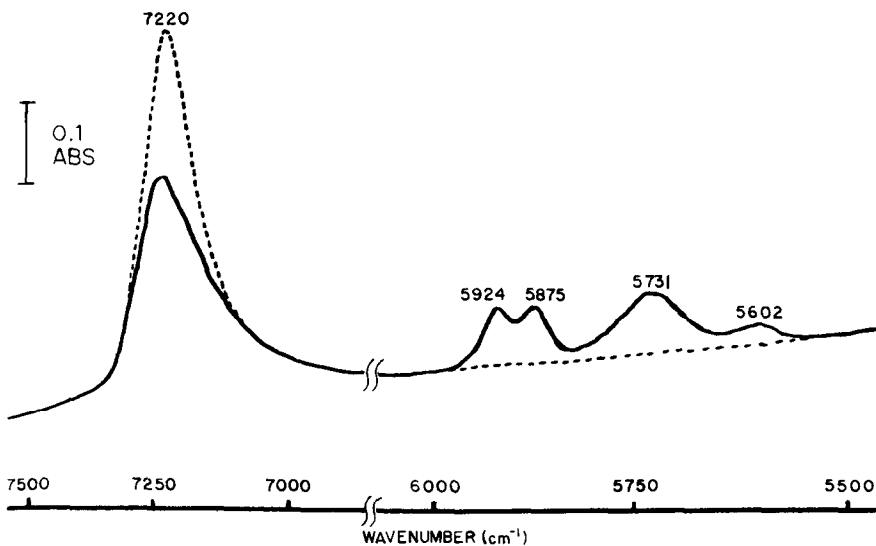


Fig. 7. Near-IR absorption as a function of trimethylchlorosilane reaction with the silica surface. Broken curve: dried silica. Solid curve: trimethylchlorosilane-modified silica. 7220 cm^{-1} = silanol overtone ($2\nu_s$); 5924 , 5875 , 5731 , 5602 cm^{-1} = C-H overtone and combinations (see Table III).

cause tailing peaks resulting in poor resolution and concurrent difficulties in qualitative and quantitative measurements. The main goal in developing the above technique was to study surface modification methods for reducing silanol contributions to a minimum. To show how our technique could be applied to this end, we silylated Porasil B as described in procedure 5. Fig. 7 shows the spectra of the silica gel before (broken line) and after (solid line) silylation. As was expected a decrease in the amount of silanol (7220 cm^{-1}) with a simultaneous increase in the amount of surface hydrocarbon ($5924, 5875, 5731$ and 5602 cm^{-1} ; column 2) occurs. From Table II we can see that those latter peaks are due to various combinations of C-H stretch frequencies. These frequencies were confirmed by taking the analogous spectra for trimethylchlorosilane (column 3) and tetramethylsilane (column 4) in carbon tetrachloride and comparing them with literature data on the gas phase spectra for chloromethane in column 5. Because of differences between samples used and inherent differences between gas phase and solution spectra the match is not exact.

By comparing the integrated areas of unmodified Porasil B and trimethylchlorosilane-modified Porasil B and correcting for buried silanols we were able to determine that approximately 40% of surface silanols reacted, which compares well with other studies of limiting coverages for trimethylsilyl groups reported in the literature²⁴.

The modified silica gel was also analyzed using photoacoustic spectroscopy for comparative purposes. A photoacoustic near-IR spectrum (procedure 6) of the silylated Porasil B is presented in Fig. 8. Because of inadequate drying procedures there is a large water peak ($\delta_w + \nu_w$: 5320 cm^{-1}) and a broad silanol peak ($2\nu_w$: 7250 cm^{-1}) with a shape similar to the wet silica absorption band in Fig. 4. A group of poorly

TABLE III
ASSIGNMENT OF SPECTRAL C-H BANDS OF TRIMETHYLSILYL-MODIFIED SILICA

<i>Band assignment</i> ²⁵	<i>Band frequencies (cm⁻¹)</i>			<i>Literature</i> ²⁵ : <i>CH₃Cl</i> <i>in vacuum</i>
	<i>Experimental</i>			
	<i>Trimethylsilyl-silica in CCl₄</i>	<i>Trimethylchlorosilane in CCl₄ (1 M)</i>	<i>Tetramethylsilane in CCl₄ (1 M)</i>	
Symmetric bend (δ_2)	—	—	—	1355
Asymmetric bend (δ_5)	—	—	—	1455
Symmetric stretch (ν_1)	2890	2890	2880	2966
Asymmetric stretch (ν_4)	2950	2945	2945	3042
$\delta_2 + 2\delta_5$	4158	4158	4148	4175
$\nu_1 + \delta_2$	4216	4219	4202	4229
$\nu_4 + \delta_2$	4348	4359	4357	4383
Unassigned	5602	5602	5602	—
$\nu_4 + \nu_1$	5731	5731	5731	5900
$2\nu_4$	5875	5875	5865	6013
$2\nu_4$	5924	5928	5910	6076

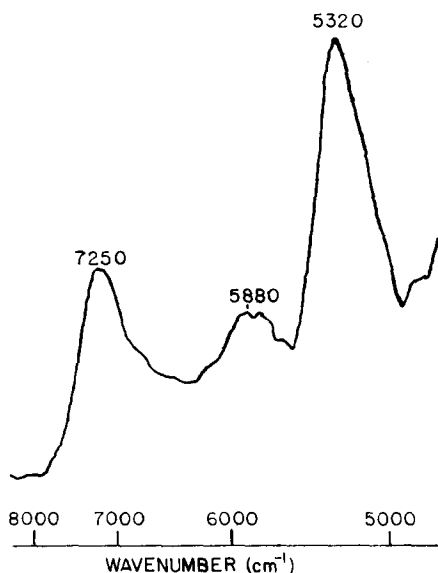


Fig. 8. Near-IR photoacoustic spectrum of trimethylchlorosilane-modified silica. 7250 cm^{-1} = silanol overtone ($2\nu_s$); 5880 cm^{-1} = C-H overtones and combinations; 5320 cm^{-1} = adsorbed water combination ($\delta_w + \nu_w$).

resolved bands corresponding to C-H overtones and combinations can be seen in the 5880 cm^{-1} region. The transmission near-IR technique described is superior in sensitivity, speed and resolution to the photoacoustic technique presented. In addition the near-IR cell allows for the *in situ* drying of the silica essential for quantitative interpretation of results. The necessity of some exposure to air in the loading of the PAS cell results in significantly increased water adsorption and hinders surface silanol characterization using our near-IR PAS. One advantage of the photoacoustic technique is that no refractive index matching material is needed since light scattering does not affect acoustic emission signals which reflect gas pressure fluctuations in the PAS cell enclosure caused by sample heating and cooling at the light source modulation frequency. Thus, spectral shifts resulting from the adsorption of refractive index matching materials in transmission IR are not encountered in PAS. However, as noted earlier the shifts caused by the carbon tetrachloride are predictable and insignificant in terms of quantitative and qualitative analysis. Small sample size (0.1 ml) and ease of sample preparation are other advantages of the PAS technique.

CONCLUSION

The above technique has several advantages over previously reported transmission IR methods. The near-IR cell is convenient for use in routinely available absorption instruments. The cell also allows for versatility in silica treatment with various reagents and prevents exposure of silica to atmospheric water allowing for the study of reactive intermediates. The non-destructive nature of sample preparation allows for the modified silica to be used subsequently in preparation of chromatographic columns for correlation of chromatographic properties with spectral data.

Our laboratory is currently using this technique to study several possible methods for further reducing silanol activity over present methods. Applications to studies of chromatographic support deactivation and chemically bonded stationary phases are manifold.

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REFERENCES

- 1 K. K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979, pp. 76-83.
- 2 Ref. 1, pp. 64-68.
- 3 J. J. Fripiat and J. Uytterhoeven, *J. Phys. Chem.*, 66 (1962) 800.
- 4 C. Armistead, A. Tyler, F. Hambleton, S. Mitchell and J. Hockey, *J. Phys. Chem.*, 73 (1969) 3947.
- 5 L. Nondek and V. Vyskočil, *J. Chromatogr.*, 206 (1981) 581.
- 6 I. Y. Băbkin and A. V. Kiselev, *Russ. J. Phys. Chem.*, 37 (1963) 118.
- 7 J. Taylor and J. Hockey, *J. Phys. Chem.*, 70 (1968) 2169.
- 8 G. E. Maciel and D. W. Sindorf, *J. Amer. Chem. Soc.*, 102 (1980) 7606.
- 9 G. E. Maciel, D. W. Sindorf and V. J. Bartuska, *J. Chromatogr.*, 205 (1981) 438.
- 10 M. Holík and B. Matějková, *J. Chromatogr.*, 213 (1981) 33.
- 11 K. Klier, J. H. Sen and A. C. Zettlemoyer, *J. Phys. Chem.*, 77 (1973) 1458.
- 12 C. H. Lochmuller and D. R. Wilder, *Anal. Chim. Acta*, 118 (1980) 101.
- 13 R. S. McDonald, *J. Phys. Chem.*, 62 (1958) 1168.
- 14 A. V. Kiselev and V. I. Lygin, in L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, 1966, 9.
- 15 H. A. Benesi and A. C. Jones, *J. Phys. Chem.*, 63 (1959) 179.
- 16 G. Wirzing, *Naturwissenschaften*, 51 (1964) 211.
- 17 V. Y. Davydov and A. V. Kiselev, *Russ. J. Phys. Chem.*, 27 (1963) 1404.
- 18 J. H. Anderson and K. A. Wickersheim, *Surface Sci.*, 2 (1964) 252.
- 19 J. Erkelens and B. G. Linsen, *J. Colloid Interface Sci.*, 29 (1969) 464.
- 20 J. Van De Venne, J. Rindt and G. Coenen, *J. Colloid Interface Sci.*, 74 (1980) 287.
- 21 S. Läufer, *J. Mol. Struct.*, 60 (1980) 409.
- 22 R. S. McDonald, *J. Amer. Chem. Soc.*, 79 (1957) 850.
- 23 A. L. McClellan and H. F. Harnsberger, *J. Colloid Interface Sci.*, 23 (1967) 577.
- 24 K. K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979, p. 118.
- 25 G. Herzberg, *Infrared and Raman Spectra*, Vol. 2, Van Nostrand, New York, 1945, p. 313.