

PHOTOACOUSTIC STUDY OF SILICA-SILANE COUPLING REAGENT INTERACTIONS

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Summary

Photoacoustic spectroscopy is an effective technique for studying filler-coupling reagent interactions. The use of coupling agents with inorganic fillers necessitates a thorough understanding of the binding activity that takes place. The binding of vinyltriethoxysilane to the hydroxyl groups on a silica surface was identified. Whereas the visible part of the photoacoustic spectra revealed that strong binding took place, the near IR characterized the surface binding groups.

1. Introduction

The use of mineral fillers in a resin matrix has been the subject of increased research activity. In addition to reducing materials cost [1, 2], these fillers also reduce shrinkage, thus improving water resistance and weathering properties [3 - 5]. To allow better dispersion of the inorganic filler in the organic polymer, coupling agents such as silanes and titanates [6] are being used. These reagents are bifunctional and thus have the ability to react through their silane group with the surface of the filler and with a second group, such as a vinyl group, which reacts with the polymer.

For binding with the filler surface, only one hydrolyzable group is required per silane molecule [7]. However, most of the commercially available silanes have three hydrolyzable groups. Though this should make their application to fillers easier, there is a possibility of polyhydroxysilanes condensing with each other. In this work it is intended to establish whether chemical binding of vinyltriethoxysilane (VTES) to the silica surface or self-condensation polymerization is prevalent. This problem has been dealt with extensively before, using IR transmission and reflection spectroscopy [8 - 10], Raman spectroscopy [11] and inelastic tunnelling spectroscopy [12]. In

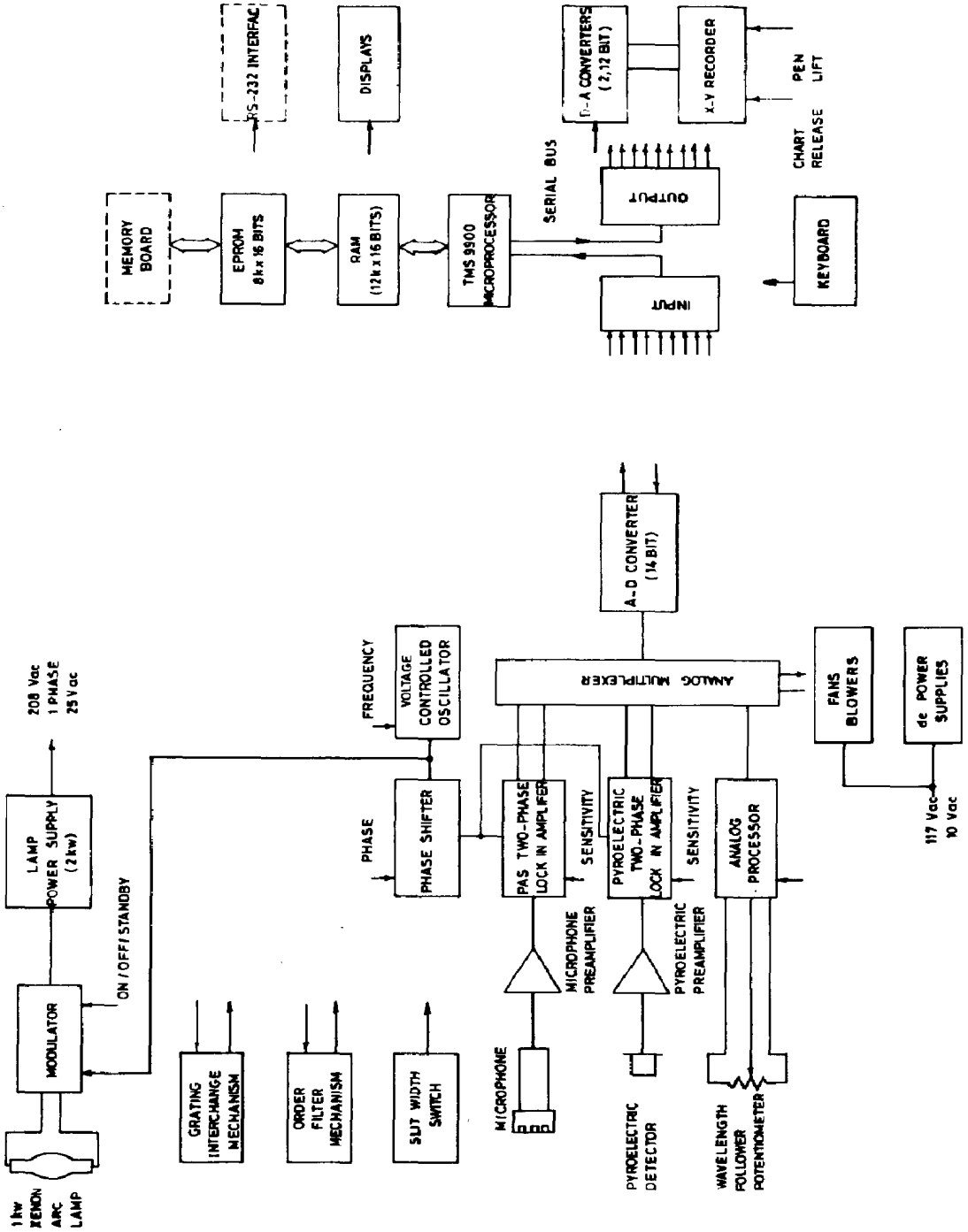


Fig. 1. A block diagram of the photoacoustic spectrometer.

this paper we report the binding of VTES to sand (99.6% purity; 7 μm in diameter), using the photoacoustic technique. This technique is a powerful one for this kind of study as it does not involve sample preparation [13] and thus does not result in a perturbed spectrum. It is immune to light scattering and reflection. It is also a non-destructive technique and spectra of completely opaque or transparent samples can be easily obtained.

2. Experimental procedure

2.1. Samples and sample preparation

Sand was washed with distilled water, dried in a vacuum oven at 60 °C overnight, rinsed with acetone and redried under the same conditions overnight. The silane used in this study, VTES, was obtained from Fluka. The reagent was applied drop by drop from a freshly prepared solution (1% VTES by weight) of VTES in aqueous ethanol (90% ethanol by volume). The treated sand was then kept at 105 °C for 2 h after it had been dried in vacuum at 40 °C. In a concurrent experiment, a few milliliters of the VTES solution were treated similarly as described but sand was omitted. On drying, a white material was obtained which did not melt below 320 °C.

2.2. Photoacoustic spectrometer

A block diagram of the photoacoustic spectrometer used in this work is shown in Fig. 1. A schematic diagram of the optical components and the

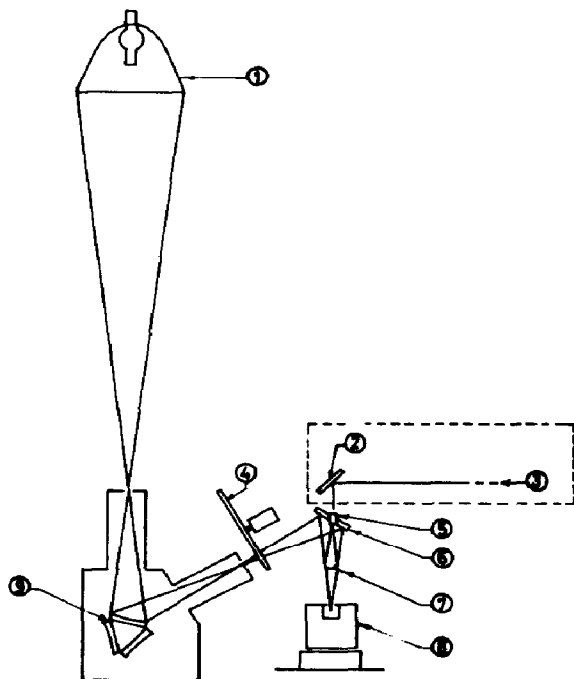
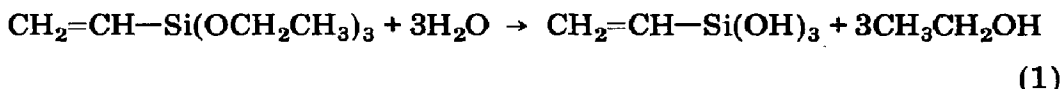


Fig. 2. A schematic diagram of the optical components and the sample cell: 1, 1 kW xenon arc lamp, F/4.2 ellipsoidal reflector; 2, plane mirror; 3, external laser beam; 4, order-sorting filters; 5, pyroelectric reference detector; 6, off-axis ellipsoidal reflector; 7, fused silica beam splitter; 8, sample cell; 9, turret three gratings.

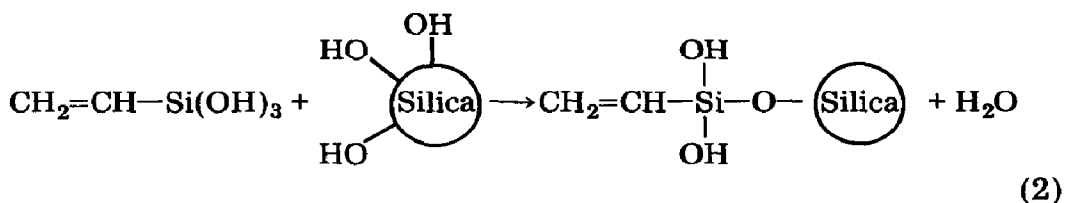
sample cell is shown in Fig. 2. A 1 kW xenon lamp was used as the excitation source in this experiment. Any variation in the lamp intensity is automatically compensated for by the pyroelectric detector. The spectral range of this equipment is from 200 to 2600 nm at any modulated frequency between 10 and 2 kHz and at any scanning rate from 1 to 200 nm min⁻¹. The sample cell is made of high quality quartz and accepts samples of size 5 mm × 8 mm × 2 mm in liquid or solid phases. The exit slit of the monochromator can be varied for optimization of the signal-to-noise ratio. Two slit widths were used in this experiment. One value was 2 mm at which the resolution of the spectrometer is 8 nm. The other slit width was 4 mm which results in a resolution of 16 nm. It was found necessary to use both these slit widths, as will be indicated later. Carbon black was used as the reference against which all the spectra were normalized. Air was used as the coupling media between the sample and the microphone. The equipment is completely controlled and operated by a microprocessor.

3. Results and discussion

The hydrolysis of VTES is expected to proceed according to the reaction



The self-condensation polymerization [5] product is expected to give either linear or branched polysiloxanes (PSs). The reaction of VTES with the filler is expected to proceed according to



The photoacoustic spectra (PASs) were classified into two distinct regions. The first region is the UV-visible part of the spectrum between 200 and 750 nm. The second region is the near IR: it extends between 810 and 2600 nm.

The UV-visible range of the PAS for VTES, PS, silica and VTES added to silica is shown in Figs. 3 - 6. The PAS for VTES (Fig. 3) is characterized by its two sharp peaks at 205 and 257 nm. At wavelengths greater than 350 nm, VTES exhibits little or no absorption. The PAS for PS is shown in Fig. 4. A sharp peak at 212 nm and a shoulder at about 373 nm are evident. The features of the spectrum are in general much broader than those of VTES. This is a result of the polymerization of VTES molecules forming PS polymers. The silica PAS is shown in Fig. 5. It is broad and almost structure-

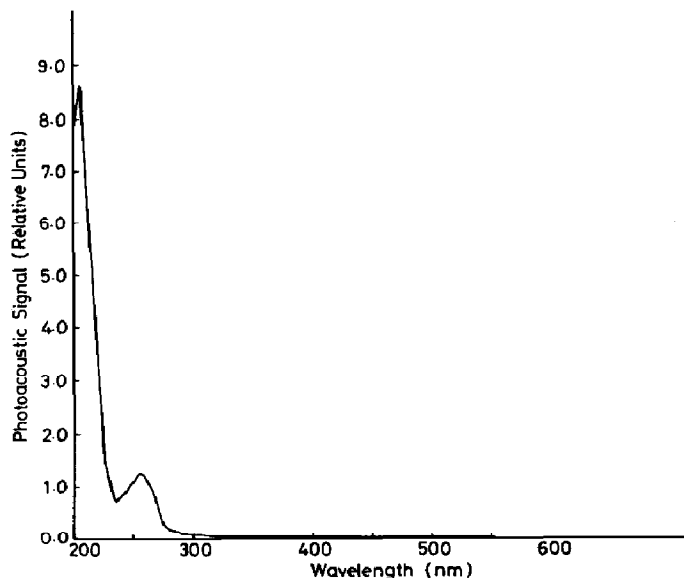


Fig. 3. A UV-visible PAS for VTES (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

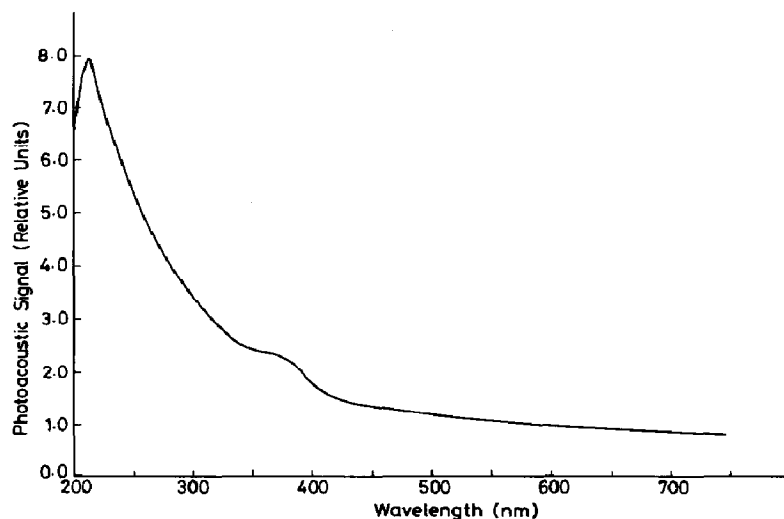


Fig. 4. A UV-visible PAS for PS (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

less. The PAS for VTES added to silica is shown in Fig. 6. It is completely different from any of the previous spectra. It is not a superposition of the spectra of silica and VTES and/or PS, which would be an indication of strong chemical binding between silica and VTES. Since our experiment can detect parts per million amounts, if silica did not bind with VTES or if it partially binds with a fraction of the VTES, we would expect the spectrum to contain

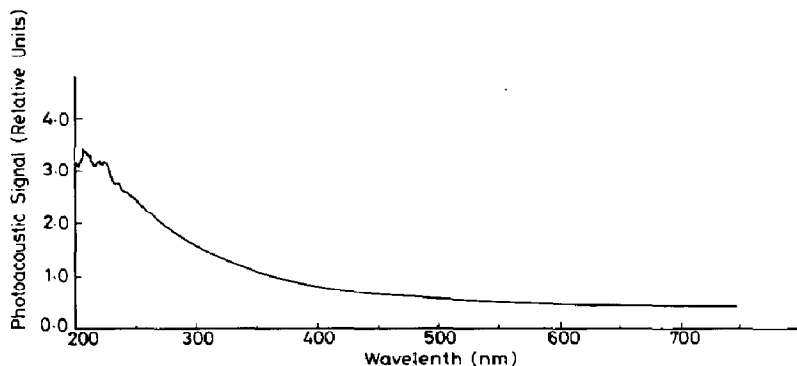


Fig. 5. A UV-visible PAS for silica (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

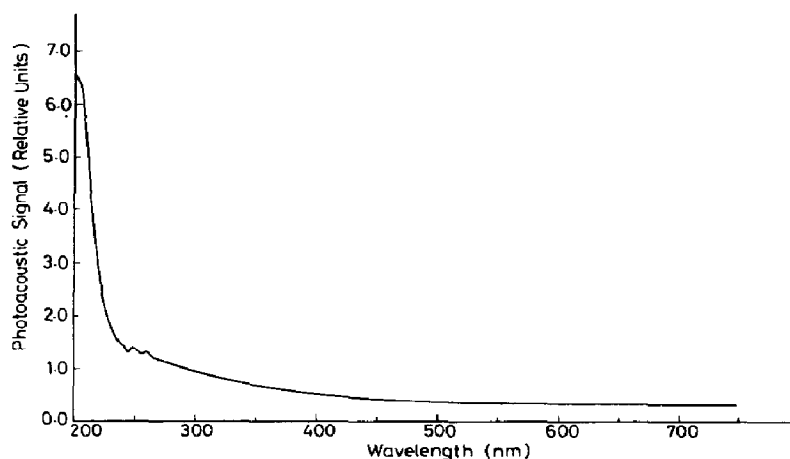


Fig. 6. A UV-visible PAS for VTES added to silica (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

that of VTES (or PS spectra if polymerization of VTES took place). This was not observed.

The near-IR PAS of VTES is shown in Fig. 7. The terminal vinyl group exhibits characteristic absorption peaks at 1.64 and 2.15 μm [14, 15]. The peaks at 1.69 and 2.46 μm were assigned to saturated $-\text{CH}_2-$ groups. The peak at 2.29 μm is due to aliphatic [16] $-\text{CH}_3-$ groups. Owing to the abundance of C_2H_5 groups, these peaks result in more intense signals than those of the terminal vinyl group.

As a result of polymerization of VTES to form PS, we expect a relative reduction in the intensity of the peaks at 1.69 and 2.46 μm compared with the peaks at 1.64 and 2.15 μm . This is clearly shown in Fig. 8. In this figure, the spectrum of PS was also recorded after the sample had been wetted with triply distilled water. The peaks at 1.38 and 1.89 μm were found to arise from adsorbed water. However, there are two more peaks at 1.98 and 2.235

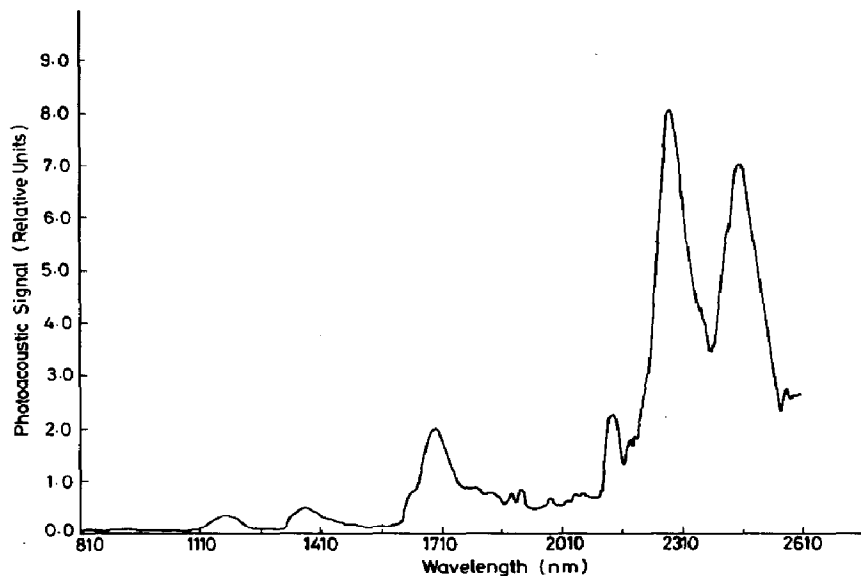


Fig. 7. A near-IR PAS for VTES (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

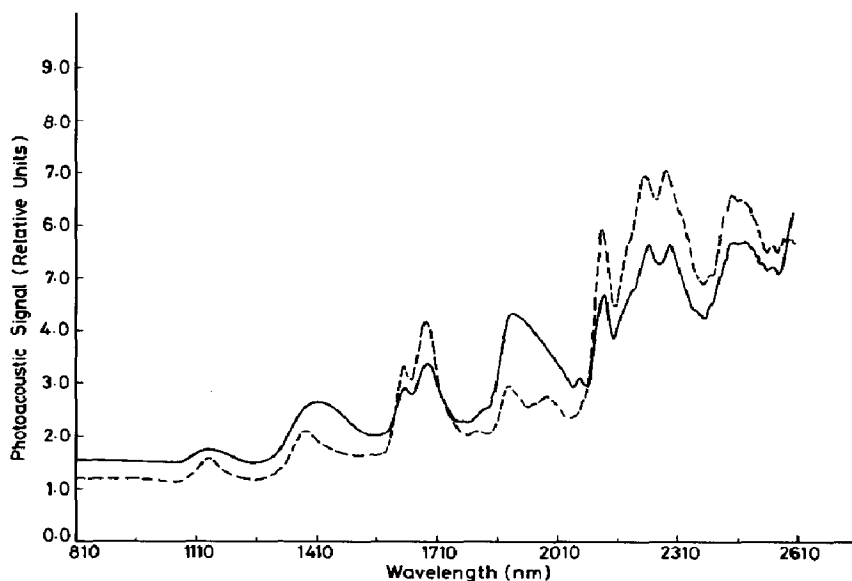


Fig. 8. A near-IR PAS for PS (—) and for PS after it had been wetted with triply distilled water (---) (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

μm in the spectrum of PS with no corresponding peaks in the spectrum of VTES. These two peaks are possibly due to ether bond $-\text{Si}-\text{O}-\text{Si}-$ vibrations. Supporting evidence for the assignment of these two peaks will be indicated later.

The near-IR PAS for silica is shown in Fig. 9. It has a sharp peak at $1.38 \mu\text{m}$ which is due to the surface silanol group. The first overtone of this peak is at $2.67 \mu\text{m}$. The bending and stretching vibrations of the silanol groups are at $2.28 \mu\text{m}$. This peak should appear at $2.22 \mu\text{m}$ but owing to adsorbed water it appears at a slightly longer wavelength. The peak at $1.4 \mu\text{m}$ (which appears as a shoulder to the peak at $1.38 \mu\text{m}$) and the peak at $1.9 \mu\text{m}$ are due to adsorbed water introduced during the exposure of silica to air while obtaining the spectra. These peaks become much more pronounced and broader on wetting silica with triply distilled water. They overshadow the rest of the silica spectrum peaks and are shifted to slightly longer wavelengths.

The PAS for VTES added to silica is also shown in Fig. 9 together with the spectrum of PS for comparison of all spectra under the same experimental resolution (16 nm). It was found to be necessary to change the slit width of the spectrometer from 2.0 to 4.00 mm and to sacrifice better resolution in order to obtain a better signal-to-noise ratio in the PASs of silica and of VTES added to silica. The PASs for these last two samples at a monochromator slit width of 2 mm (which corresponds to 8 nm resolution) are shown in Fig. 10 and Fig. 11, respectively. No meaningful information can be obtained from these spectra.

The PAS of VTES added to silica resembles that of silica except that it is reduced in intensity. However, it has peaks around 2.0 and $2.35 \mu\text{m}$ which do not appear in the spectrum of silica. This spectrum is neither a superposition of the spectrum of silica nor the spectrum of VTES and/or PS, as has been observed by Gent and Hsu [7]. If binding between VTES and silica is complete and occurs according to eqn. (2), we would expect its PAS to arise

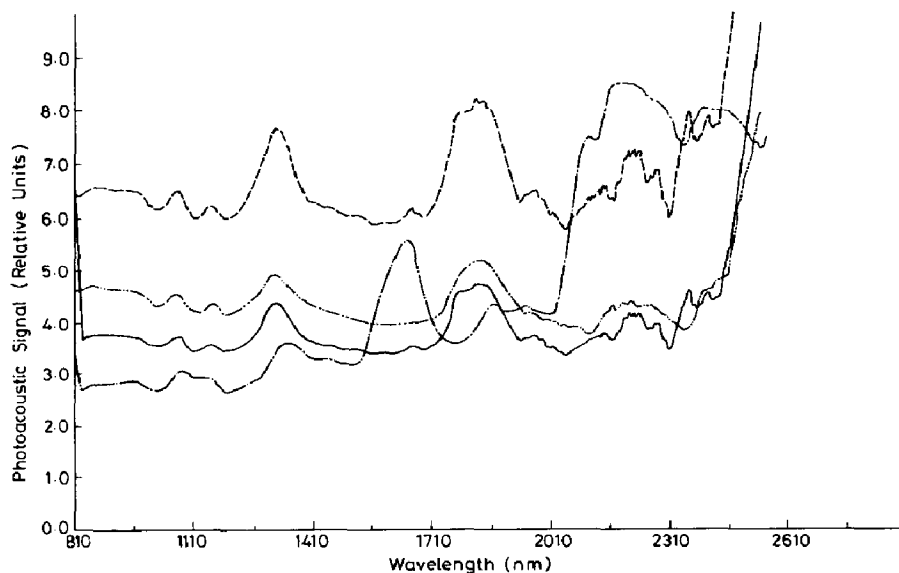


Fig. 9. Near-IR PASs (lamp modulation frequency, 40 Hz ; spectral resolution, 16 nm): ---, PS, $\times 0.25$; —, VTES added to silica; - · - ·, silica; - - - -, VTES added to silica, $\times 1.75$.

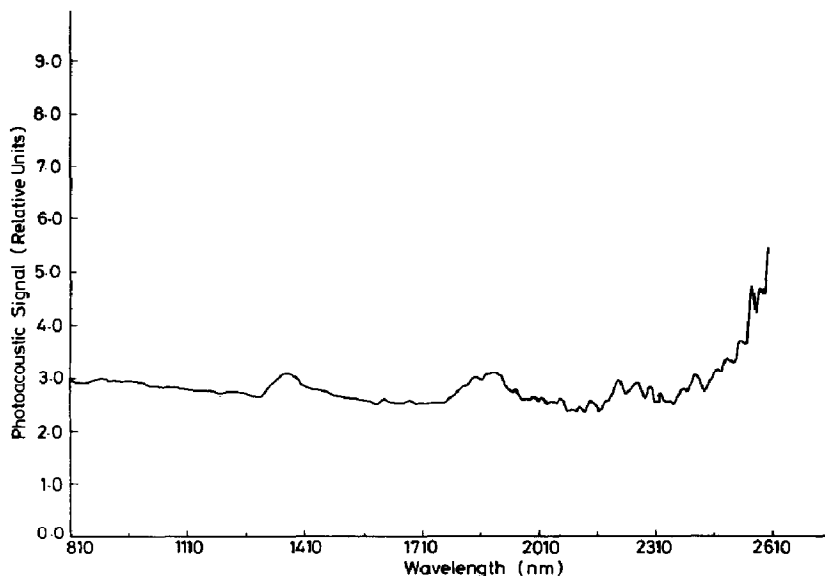


Fig. 10. A near-IR PAS for silica (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

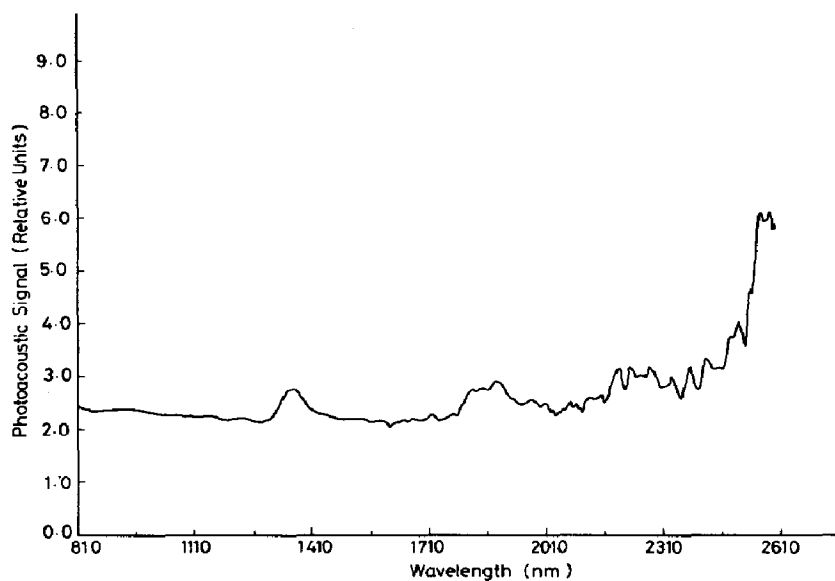


Fig. 11. A near-IR PAS for VTES added to silica (lamp modulation frequency, 40 Hz; spectral resolution, 8 nm).

mainly from a silica spectrum superposed on the spectrum resulting from ether bond $-\text{Si}-\text{O}-\text{Si}-$ vibrations. The peaks that appear at 2.0 and 2.260 μm in the PAS of VTES added to silica are identified to be from $-\text{Si}-\text{O}-\text{Si}-$ groups. These two peaks appeared at 1.98 and 2.235 μm in the spectrum of PS. The second peak is shifted by 0.025 μm to a longer wavelength for VTES added to silica. This is due to the fact that silica has its bending and stretch-

ing spectrum located around 2.28 μm , which results in an apparent shift in the position of the peak at 2.235 μm . If binding between VTES and silica is not complete or if it does not take place at all, as was previously discussed, the spectrum of silica added to VTES would be a mere superposition of the PASs of silica and VTES and/or PS (if polymerization of VTES took place). As mentioned before, we did not observe this. Instead our spectra indicate a complete chemical binding between silica and VTES.

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