

Visualizing Chemical Compositions and Kinetics of Sol–Gel by Near-Infrared Multispectral Imaging Technique

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Kinetics of sol–gel formation were studied using the recently developed near-infrared (NIR) multispectral imaging instrument. This imaging spectrometer possesses all the advantages of conventional spectrometers. It also has additional features that NIR spectrometers cannot offer, namely, its ability to provide kinetic information at different positions within a sample. The high spatial resolution and sensitivity of the InSb camera make it possible for the imaging spectrometer to determine the kinetic from data recorded by a single pixel. Kinetics of sol–gel reactions, determined by this multispectral imaging instrument, show that the initial hydrolysis of the TEOS, MTES, or a mixture of these two alkoxysilanes is relatively inhomogeneous. The inhomogeneity is dependent on the number of pixels used to calculate the spectrum for each spot. Data calculated from a single pixel provide the largest inhomogeneity. No inhomogeneity was observed when an average of a large number of pixels (e.g., 10×10) is used for calculation. The inhomogeneities observed for TEOS sol–gels are different from those for the MTES sol–gels, and those for sol–gels prepared from a mixture of TEOS and MTES are relatively larger and more similar to those of the MTES sol–gels. A variety of reasons might account for the observed inhomogeneities including differences in the structure of the TEOS sol–gels and MTES sol–gels and the inability of the TEOS to mix well with MTES with the latter being more hydrophobic.

The sol–gel method has been widely used to prepare silica glasses as well as mixed-metal oxides.^{1–3} The popularity stems from the fact that, compared to traditional technologies, this method has several advantages including high reactivity and better purity and possibility control of the structure of the material at all stages of the process. Specifically, it is known that the chemical and physical properties of the ceramic formed are dependent on kinetics of hydrolysis and condensation reactions, and these reactions can be easily modified by changing types of reactants, their relative concentrations, and reaction pH.¹ It is, therefore,

hardly surprising that the kinetics of sol–gel formation have been studied extensively by many different spectroscopic techniques.^{4–15} Among them, the near-infrared (NIR) technique is relatively more popular as the technique has the sensitivity and selectivity, is nondestructive and noninvasive, and requires no sample preparation.^{13–15} In fact, NIR technique has been used to study the kinetics of sol–gel formation.^{13–15} It is, however, important to realize that care must be taken for such studies to avoid possible errors. The concerns are due to the nature of the sol–gel and the NIR instrument used for measurements. Specifically, the chemical homogeneity of the sol–gel is known to be strongly dependent on the kinetic factors and that rates of hydrolysis and condensation may be different at different positions in a sample.^{1–15} As a consequence, the sol–gel end product may not be chemically homogeneous. Since chemical and physical properties of glasses formed depend on their chemical compositions, the presence of chemical inhomogeneity will have pronounced effects on their properties. It is, therefore, important that rates of each step of the sol–gel formation be measured at different positions in a sample in order to determine the presence of any chemical and kinetic inhomogeneity. Unfortunately, to date, NIR-based kinetic methods rely on the use of NIR spectrometers equipped with single-channel NIR detectors.^{13–15} As such, it has not been possible to simultaneously determine the kinetics of reaction at different positions in a sol–gel sample. A NIR multispectral imaging spectrometer is needed for such purpose.

A multispectral imaging spectrometer is an instrument that can simultaneously record spectral and spatial information of a sample.^{16–22} Chemical homogeneity of the sample can be eluci-

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dated from recorded images. In these instruments, the spatial distribution of the sample is obtained by a camera, and the spectral information is gained by scanning a dispersive element.^{16–22} To be used for kinetic determination, the instrument must be able to sensitively and rapidly record spectral images of a sample. These requirements can be satisfactorily met with the instrument recently developed in our laboratory.^{20–25} In this instrument, an acoustooptic tunable filter (AOTF) is used for spectral scanning and an InGaAs area camera is for recording NIR images.^{20–25} AOTF is a electronic tunable filter based on the diffraction of light by an acoustic wave in an anisotropic medium. It has rapid scanning ability (μs), high diffraction efficiency ($>90\%$), wide spectral tuning range (from UV to NIR), and high resolution.^{26–28} Because of these advantages, the multispectral imaging instrument based on an AOTF has high sensitivity and can rapidly record spectral images of a sample. This imaging spectrometer makes it possible for us to perform studies that to date were not possible using existing techniques. These include the authentication of documents, the determination of chemical inhomogeneity of ethylene/vinyl acetate copolymers and kinetic inhomogeneity of curing of epoxy by amine, and the determination of identity and sequences of peptides synthesized by combinatorial solid-phase method.^{20–25}

The information presented is indeed provocative and clearly indicates that it is possible to use the AOTF-based multispectral imaging instrument to determine the chemical and kinetic inhomogeneity of sol–gel. Preliminary results on the kinetics of sol–gel prepared from one component or a mixture of alkoxysilanes are reported in this paper.

EXPERIMENTAL SECTION

Chemicals. Tetraethyl orthosilicate (TEOS 98%, Aldrich), methyltriethoxysilane (MTES, Aldrich), absolute ethanol (Pharmco), *N,N*-dimethylformamide (99%, Aldrich), and hydrofluoric acid (48%, Mallinckrodt) were used as received.

Acid-catalyzed sol–gels from TEOS, MTES, or a mixture of the two alkoxysilanes were synthesized in ETOH and DMF. Mole ratios of alkoxysilane: $\text{H}_2\text{O}/\text{ETOH}/\text{DMF}$ were adjusted to be 1:7.5:3.6:1.7. By adding an appropriate amount of HF to the reaction mixture, the rates of the sol–gel formation reaction can be adjusted to be fast or slow. In this study, HF mole ratios were adjusted to be 0.01 to provide relatively slow hydrolysis. Typically, the reaction mixture was prepared by vigorously mixing the organic components with an appropriate amount of the HF aqueous solution. After complete mixing (~ 1 – 2 min), the solution was transferred with a Pasteur pipet to a variable-path length microcell equipped with sapphire windows. After removal of air

bubbles in the reaction mixture, the cell path length was reduced to 0.5 mm.

Instrumentation. The NIR multispectral imaging instrument used in this study is similar to the imaging spectrometer used in our previous studies.^{20–22,25} Essentially, in this instrument, a 250-W, 12-V halogen–tungsten lamp was used as the light source. A 2.5-cm-focal length ZnSe lens was used to collimate the incident white light from the lamp into a noncollinear AOTF (Crystal Technologies). The AOTF was driven by a home-built rf generator. The rf signal from the generator was amplified by a rf power amplifier before being connected to the AOTF. Light diffracted by the AOTF was transmitted through the sample and recorded by an NIR camera. Different from previous studies, which used an InGaAs camera,^{12–14} in this work, a liquid N_2 -cooled, indium antimonide (InSb) camera equipped with 320×256 pixels (Santa Barbara Focal Plane, Goleta, CA) was used to record NIR images. This camera was selected because it is sensitive in a relatively wider region, namely, from 1 to 5 μm . A cold filter was installed in the camera to reduce background noise. This filter also limits the response of the camera to the region from 1 to 3 μm . Recorded images were grabbed and transferred to a personal computer by a frame grabber (Dipix Technologies model XPG-1000). A software written in C++ language was used to control the frequency and the power and to scan the applied rf signal. The same software also facilitated the frame grabbing and saving data in appropriate formats for subsequent analysis.

RESULTS AND DISCUSSION

Sol–Gel from Tetraethoxysilane. Hydrofluoric acid was used to catalyze sol–gel formation from TEOS. The reaction mixture containing TEOS, H_2O , ETOH, DMF, and HF was mixed thoroughly and its images were recorded, in a 0.5-mm-path length cell, by the InSb camera for each wavelength from 1950 to 2650 nm at 2-nm intervals (by scanning the AOTF). As described in the introduction, the scanning speed of the AOTF is the speed of the acoustic wave in the crystal, which is on the order of microseconds. However, the rate at which an image is recorded by this NIR imaging instrument is much slower than the scanning speed of the AOTF. This is because of the additional time required by other components of the instrument including the camera (time for exposure and for recording an image) and the frame grabber (to grab the image and to transfer it to the computer). In this study, the exposure time of the InSb camera was set at 32 ms. When the time to grab the picture, to transfer, and to store the picture in the computer is added to this exposure time, the total time it takes to record one picture is ~ 411 ms. The total time it takes to record the whole set of 350 pictures is, therefore, 144 s. It is important to point out that this recording time can be reduced substantially by narrowing the wavelength range, increasing the wavelength interval (at the expense of spectral resolution) and reducing the camera exposure time. For instance, it is possible to record 118 frames/s by reducing the exposure time of the camera to 0.6 μs . It seems that 118 frames/s is the limited speed for the camera and frame grabber used in this work. At this speed, it takes only 8.5 ms to record one frame and 3 s to record a whole set of 350 pictures. As stated previously, the total time required to record whole set of pictures can be further reduced by narrowing the wavelength range and increasing the wavelength interval. As a consequence, the imaging instrument is suitable

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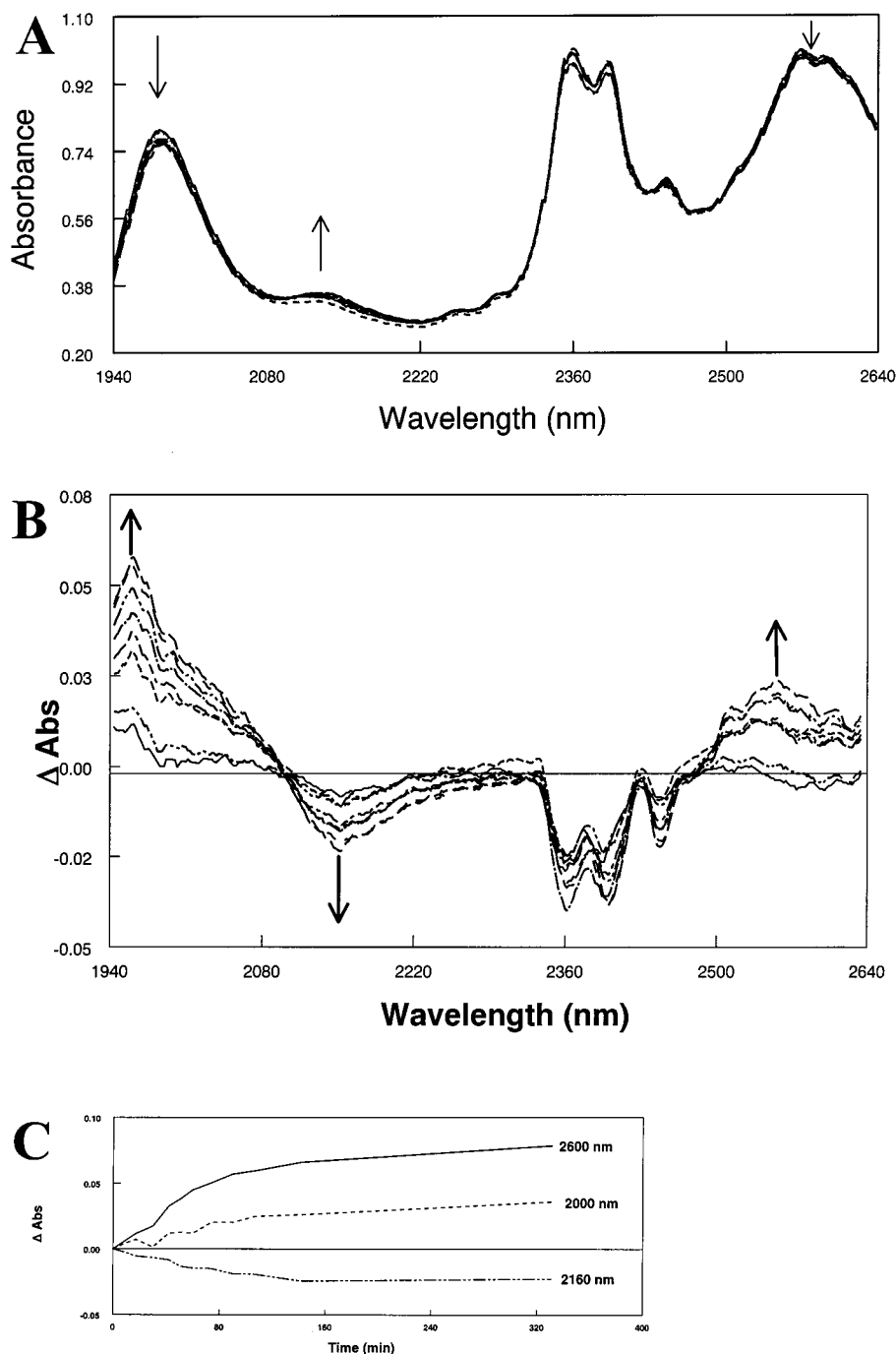


Figure 1. (A) NIR spectra of TEOS reaction mixture (in 0.5-mm-path length cell) at different times. The spectra were calculated by taking average of a square of 60×60 pixels; (B) Differential spectra calculated from Figure 2A by subtracting spectrum at $t = 0$ from spectra at various times, and (C) changes in the absorbance for O–H band of water and silanol at 2000, 2600, and 2160 nm, respectively, plotted as a function of time.

for determination of kinetics of reactions as fast as a few hundreds milliseconds.

NIR spectra at various locations within the sample can be obtained by comparing the intensity of the corresponding pixel in each image. Shown in Figure 1A are the NIR spectra of the TEOS reaction mixture, taken at various times. These spectra were obtained by taking averaged intensity of a 60×60 pixel square from the same position of each recorded image. As illustrated, there are several bands. The cluster of bands center at ~ 2392 nm can be attributed to the overtone and combination transitions of the C–H group.^{3,6,22} The broad band at 2000 nm may be due

to the overtone and combination transitions of the O–H group of water whereas the band at 2156 nm and at 2600 nm are probably due to the O–H of ethanol and silanol.^{7,10,29} It is known that hydrolysis of the TEOS involves the consumption of water and the generation of ethanol, and the subsequent condensation reaction will lead to the production of water. It is, therefore, possible to determine the kinetics of these reactions by monitoring the C–H and O–H of water, ethanol, and silanol as a function to time. In fact, Figure 1A contains several spectra taken at various

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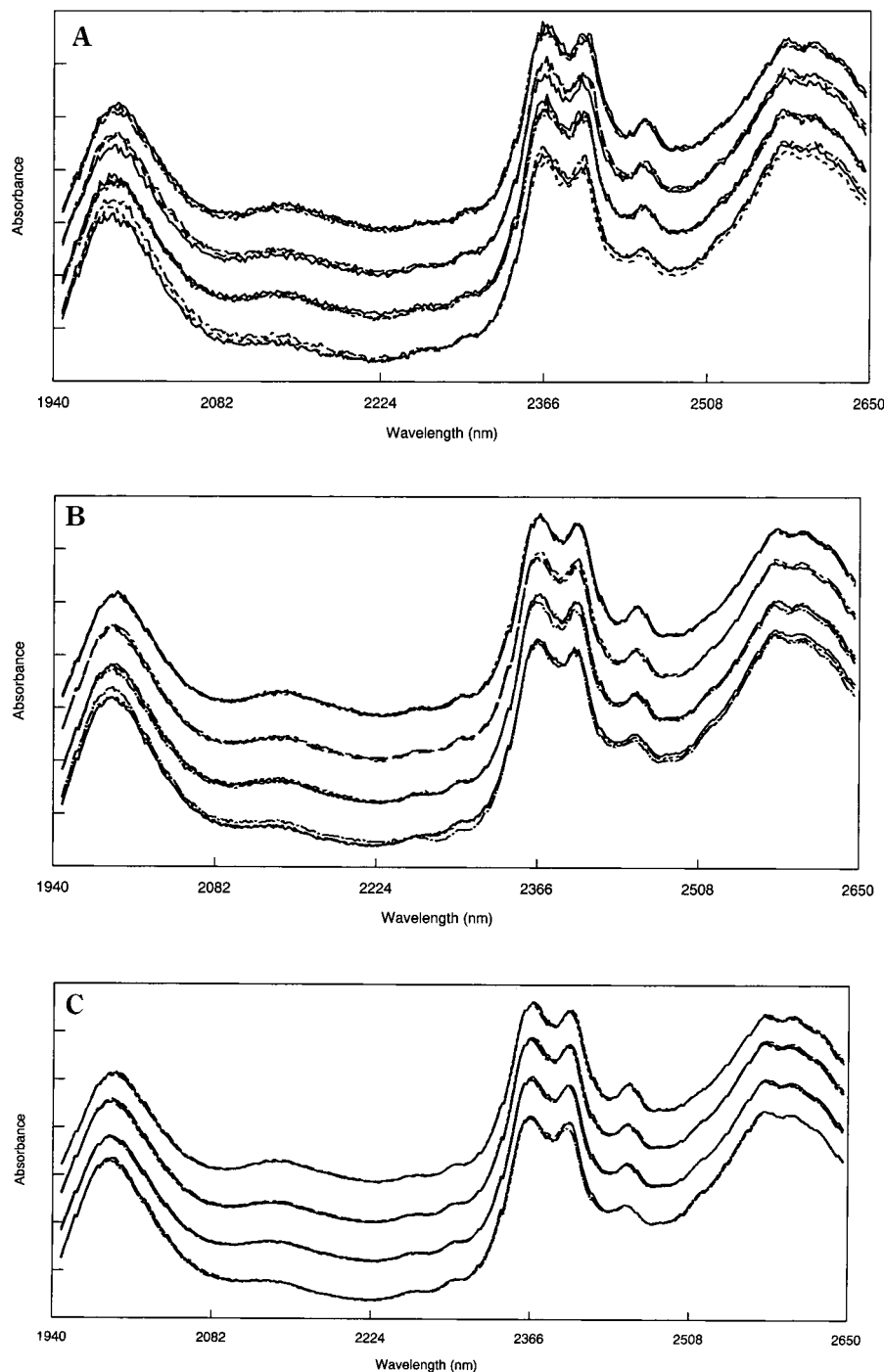


Figure 2. (A) Spectra of TEOS reaction mixture, taken at different times (from bottom to top: 8, 64, and 82 min and 16 h) at three different positions in the sample. Spectra were calculated using data taken from a single pixel for each spot; (B) and (C) are the same as in (A) except the spectra were calculated using data taken from a square of 3×3 pixels (B) and 10×10 pixels (C) for each of the same spot as in (A).

time intervals. As illustrated, the O–H bands of water at 2000 nm and at 2600 nm decreased concomitantly with time. The O–H band of ethanol and silanol at 2156 nm increased with time whereas the changes of the C–H band at 2392 nm were very small. Better visualization can be seen in Figure 1B and C, which plots the differential spectra, i.e., spectra obtained by subtracting spectra at various times from that at time $t = 0$, as a function of wavelength (B) and time (C). The differential spectra clearly illustrate the changes (i.e., decrease in the absorbance compared to that at $t = 0$; i.e., an increase in ΔA as a function of time) in

the intensity of the O–H bands of water at 2000 nm and at 2600 nm and the changes (increase in the absorbance compared to that at $t = 0$; i.e., a decrease in ΔA as a function of time) in the intensity of the O–H band of ethanol and silanol at 2156 nm as a function of time. The C–H bands at 1760 and 2398 nm also changed with time but the changes are, as expected, much smaller than that of the O–H bands. These results are in agreement with hydrolysis reactions in which the concentration of water is decreased and the concentration of alcohol and silanol is increased.

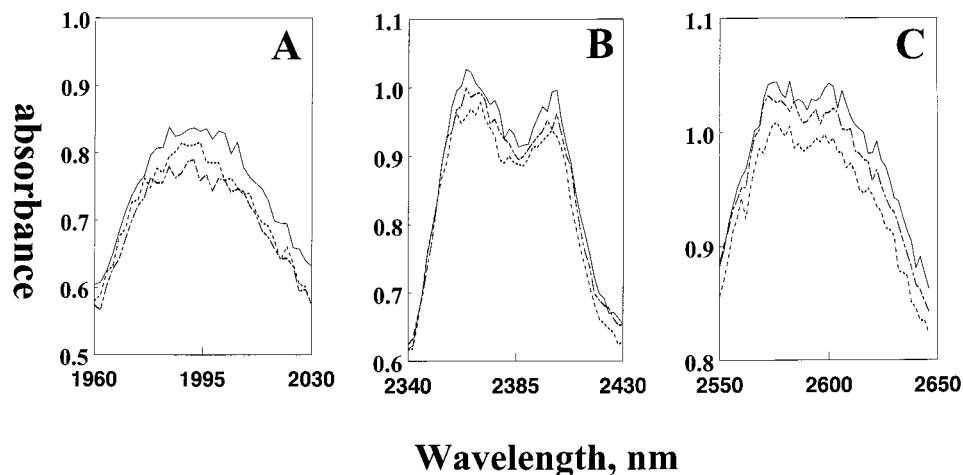


Figure 3. Expansion of three major bands of the set of three spectra calculated using data from a single pixel at time $t = 8$ min in Figure 2A.

As described in the introduction, in contrast to spectrometers, a multispectral imaging instrument is based on the use of an area camera to record spectral images of a sample. The NIR camera used in this work was equipped with 320×256 pixels. Due to its high sensitivity, data from a single pixel can be used to calculate a spectrum at a single location in a sample. As a consequence, the imaging spectrometer can simultaneously measure NIR spectra at 81 920 different positions within a sample. This feature make it particularly suited for the determination of any inhomogeneity in the chemical compositions and kinetics of sol–gel reactions. Data from a single pixel at three different positions within a sol–gel sample were used to calculate its NIR spectra, and the results are shown in Figure 2A. This figure also shows spectra of the same three locations taken at different times; i.e., it contains four sets of spectra at different times (8, 64, and 82 min and 16 h), and each set contains three spectra at three different locations in the sample. Spatial inhomogeneity was clearly observed in the sample at all stages of sol–gel formation from the very beginning up to 16 h. Interestingly, the inhomogeneity seems to be more pronounced at the beginning of the reaction processes. It is important to point out that the differences among spectra at different positions are not due to any optical aberration of the multispectral imaging instrument but rather due to the inhomogeneity within the sample. This is because exactly the same NIR spectrum was obtained at these three positions for a sample of ethanol.

For clarity, three major bands of the set of three spectra at time $t = 8$ min of Figure 2A were expanded and shown in Figure 3. It is evident that there are pronounced differences in absorption at different positions within the same sample. A difference as high as 7% was observed for bands at 2364 nm (Figure 3B).

The inhomogeneity can only be observed when spectra are simultaneously determined at different positions in the sample with a camera having high spatial resolution. In other words, the observed inhomogeneity is dependent on the spatial resolution of the imaging spectrometer. No inhomogeneity were observed when signals from all or a large number of pixels were averaged. This conclusion is based on the results in Figure 2B and C, which show spectra at the same timing intervals (as in Figure 2A) but obtained by calculation using not a single pixel but rather a square of 3×3 (B) and 10×10 pixels (C) for each spot. Inhomogeneity

was still observed when 3×3 pixels were used (Figure 2B) but at much smaller magnitude than that with a single pixel (A). However, when the size of the square pixels was increased to 10×10 , inhomogeneity was not observed at the beginning as well as the end sol–gel reactions.

The spatial resolution of the imaging instrument was determined to be $\sim 10 \mu\text{m}/\text{pixel}$. Since the InSb camera is equipped with 320×256 pixels, this corresponds to a recording an area of $3.2 \text{ mm} \times 2.56 \text{ mm}$ of a sample. The exact size of the inhomogeneous pocket within a sample was not accurately measured. However, based on the observation that inhomogeneity was still observed for a square of 3×3 pixels and disappeared when 10×10 pixels were used, it seems to suggest that each inhomogeneous pocket can be as large as $30 \mu\text{m} \times 30 \mu\text{m}$.

In this study, the TEOS reaction mixture was selected to react relatively slowly; namely, rates of hydrolysis are slow, and the changes observed in the NIR are due mainly to the hydrolysis. It is expected that a condensation reaction may also occur but only at the very end of the measurements. Consequently, the inhomogeneity observed at the beginning probably is due to the differences in the hydrolysis. A variety of reasons might account for the inhomogeneity, including differences in the relative concentrations of starting compounds. As stated in the Experimental Section, the TEOS reaction mixture was mixed thoroughly for ~ 2 min. However, it is known that TEOS has rather low solubility, even in the mixture of water and ethanol. As a consequence, there may be some possible aggregation of the TEOS to form a few small aggregates. This would lead to inhomogeneity of the kinetics of the hydrolysis. Chemical inhomogeneity of the starting materials will decrease as the reaction proceeds, which leads to the disappearance of the inhomogeneity in the kinetics. The observed inhomogeneity may also be due to changes in the structure of the silica as well as the sol–gel. In fact, it has been demonstrated in previous studies, using IR, near-field fluorescence spectroscopy, and neutron scattering, that compared to conventional polymers (e.g., poly(butylmethacrylate) sol–gel is relatively chemically inhomogeneous.^{12,30–33}

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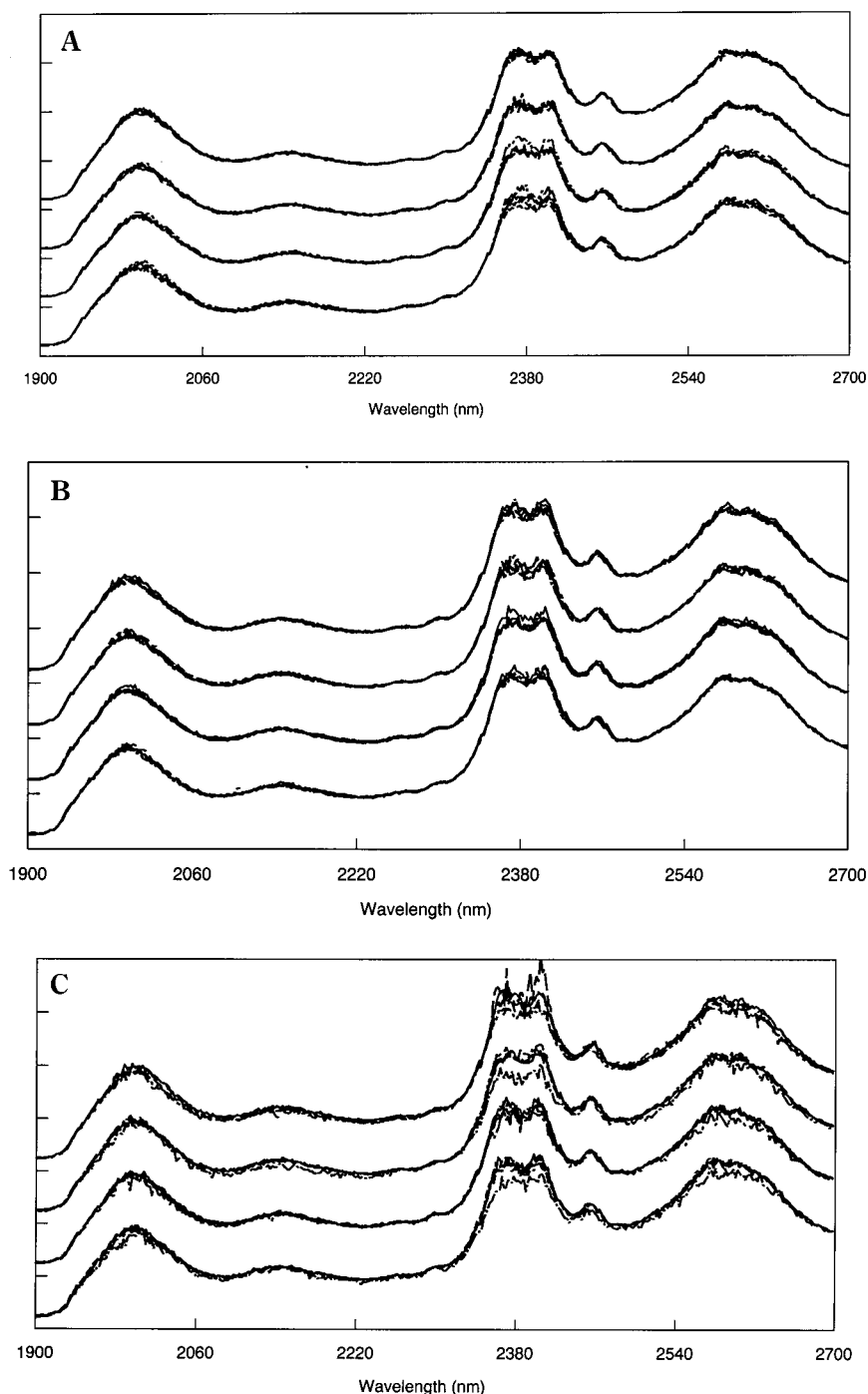


Figure 4. Spectra calculated using data taken from a single pixel for each spot at three different positions in a sample of (A) MTES at different times (from bottom to top: 0, 10, and 25 min and 13 h); (B) a mixture of 60:40 MTES/TEOS, at different times (from bottom to top: 0, 5, 9, and 193 min); and (C) a mixture of 40:60 MTES/TEOS, at different times (from bottom to top: 0, 4, 8, and 169 min).

Sol-Gel from Methyltriethoxysilane. Similar to the sol-gel synthesized from TEOS, NIR images of sol-gel prepared from MTES were recorded using the NIR imaging spectrometer from 1900 to 2700 nm at 2-nm intervals. From a set of 400 images, NIR spectra at various locations within the sample were calculated from either a single pixel or square of pixels. Shown in Figure 4A are

spectra calculated by using data from a single pixel at five different positions within the sample. This figure also shows other sets of spectra of the same five locations taken at four different reaction times (0, 10, and 25 min and 13 h).

As expected, these spectra are relatively similar to those of TEOS sol-gel samples. For instance, bands due to the overtone and combination transitions of the C-H group were observed at ~ 2392 nm, the O-H band of water is at 2000 nm, whereas the bands at 2156 nm and at 2600 nm are probably due to the O-H of ethanol and silanol.^{3,6,9}

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Information on the inhomogeneity of the MTES sample can be readily obtained from the set of spectra in Figure 4A. As illustrated, within each set (i.e., spectra of the sample at the same reaction time but at different locations) there are pronounced differences among five spectra. It seems that spatial inhomogeneity was present at all stages of sol-gel formation from the very beginning up to 13 h. Interestingly, the inhomogeneity seems to be more pronounced at the beginning of the reaction processes. Again similar to TEOS, inhomogeneity was not observed when signals from all or from a large number of pixels were averaged. This conclusion is based on spectra obtained at different reaction times, calculated using not a single pixel but rather a square of 3×3 and 10×10 pixels for each spot, respectively (spectra not shown). Inhomogeneity was still observed when 3×3 pixels were used but with much smaller magnitude than that of the single pixel. However, when the size of the square pixels were increased to 10×10 , inhomogeneity was not observed at the beginning as well as the end.

It is of particular interest to note that the observed inhomogeneity in MTES is different from that in TEOS. Specifically, for the MTES, any set of five spectra at five different locations within a sample, calculated using either a single pixel or a square of 3×3 or 10×10 pixels, seems to have the largest differences for bands at ~ 2392 nm, which corresponds to C-H bands, i.e., backbone of the sol-gel (Figure 4A). There are also differences at other regions of the spectra including those corresponding to the O-H bands at about 2000, 2156, and 2600 nm (Figure 4A). However, these differences are relatively smaller than those for the C-H bands. Conversely, for the TEOS, it seems that differences are relatively the same for the C-H and O-H bands (Figures 2 and 3). A variety of reasons might account for this observation including difference in reaction rates between MTES and TEOS, but the most likely one might be that the structure of the MTES sol-gel is different from that of the TEOS sol-gel. That is, the packing of the MTES sol-gel is different from that for TEOS. Because of the structural differences, any inhomogeneity produced by different kinetics will be magnified.

Sol-Gel from Mixtures of MTES and TEOS. Sol-gels were also prepared from mixtures of MTES and TEOS. Shown in Figure 4B and C are spectra of sol-gels prepared from 60:40 and 40:60 mixtures of MTES/TEOS, respectively, calculated using data from a single pixel at five different positions in the samples. As illustrated, inhomogeneity was observed for both mixtures. The inhomogeneity is similar to those observed for sol-gels prepared from a single MTES or TEOS; namely, the inhomogeneity is largest when a single pixel was used to calculate the spectrum, and the inhomogeneity is more pronounced at the beginning of the reaction. The inhomogeneity for both mixtures is not the same for all regions of the spectra but seems to be largest at bands correspond to C-H transitions. This is of particular interest as these sol-gels were prepared from mixtures containing both MTES and TEOS (40:60 and 60:40), but their inhomogeneities seem to be similar to those prepared from MTES and different

from those from TEOS. Furthermore, the inhomogeneity observed for the 40:60 mixture (Figure 4C) is largest, i.e., it is larger than that for the 60:40 mixture (Figure 4B) as well as the TEOS sol-gel (Figure 2A) and MTES sol-gel (Figure 4A). It is known that MTES is relatively more hydrophobic than TEOS, and as a consequence, it may not mix well with TEOS. Furthermore, based on the observed inhomogeneity for sol-gels from either TEOS and MTES (Figures 2A and 4A, respectively), it seems to indicate that the structure of the TEOS sol-gel is relatively more ordered than that of the MTES. The combined effect of poor mixing and less ordering (of the MTES) may be responsible for the observed similar inhomogeneity among the MTES sol-gel and the 60:40 and 40:60 mixture sol-gels.

CONCLUSIONS

In summary, it has been demonstrated that the high sensitivity and fast scanning ability of the multispectral imaging make it suitable for kinetic determination of sol-gel reactions. The imaging spectrometer possesses all the advantages of conventional spectrometers. It has, however, additional features that NIR spectrometers cannot offer, namely, its ability to provide kinetic information at different positions within a sample. The high spatial resolution and sensitivity of the InSb camera make it possible to determine the kinetics from data collected by a single pixel in the camera. Kinetics of sol-gel reactions, determined by this multispectral imaging instrument, shows that the initial hydrolysis of the TEOS, MTES, or mixtures of these two alkoxysilanes is relatively inhomogeneous. The inhomogeneity is dependent on the number of pixels used to calculate the spectrum for each spot. No inhomogeneity was observed when an average of a large number of pixels (e.g., 10×10) is used for calculation or if a single detector (such as those used in conventional spectrometers) is used for detection. Of particular interest is the fact that the observed inhomogeneity for TEOS sol-gel was found to be different from that of the MTES sol-gel. Structural differences between the two sol-gels may be account for this observation; namely, the structure of the TEOS sol-gel seems to be more ordered than that of the MTES sol-gel. Sol-gels prepared from mixtures of TEOS and MTES (40:60 and 60:40) also exhibit inhomogeneity, and the inhomogeneity of mixture sol-gels is not only larger than that of sol-gels prepared from a single alkoxysilane but also is similar to that of the MTES sol-gel (and different from that of the TEOS sol-gel). These seem to suggest that TEOS is not mixed well with MTES with the former being less hydrophobic than the latter. As a consequence, sol-gels prepared from a mixture of these two alkoxysilanes will have more inhomogeneity, and their structure is more similar to that of the MTES sol-gel, i.e., less ordered.

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