Physical Characterization of Silica Nanoparticles in Extreme Environments

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Abstract

Silica-based consolidation is an important treatment used in the conservation of objects and architectural works. There is limited scientific literature that explores the behavior of silica nanoparticles under fluctuating environmental conditions. This research aims to identify the changes silica undergoes when used in treatments on materials used in artworks such as Beech wood and Portland cement. The stability and durability of silica will be monitored through exposure to hot and cold environments similar to those experienced in the mid-Atlantic region. The stability of silica can be evaluated through monitoring morphological changes on the surface and within the layered structures, as well as shifts in particle arrangement, using AFM and ESEM. Durability will be assessed through changes in oxidation state, elemental composition, and bond vibrations, using *in situ* XAFS, EDX, and ER-FTIR, respectively. This research can contribute to creating sustainable conditions for works housed indoors, and predict the behavior of silica-treated works that are kept outdoors.

Introduction

In the research field of conservation science within cultural heritage, there are two predominant scientific applications. The first involves the use of physical characterization techniques to assess artwork, such as identifying elements present and monitoring changes in surfaces, to inform conservators in choosing the best method of treatment. The second involves conducting experiments to develop and improve conservation treatments that best maintain the integrity of the artwork. One of the most pressing concerns in developing conservation treatments is the longevity and interactions of the treated material with the work.

One type of conservation treatment used to treat outdoor works is consolidation. Consolidation involves the use of chemicals to reinforce deteriorating materials. It's most commonly used on objects and architectural works. The use of nanomaterials in consolidation is a growing area of research interest. Specifically, silica, (SiO_2) is a material of interest due to its many protective properties including fire resistance, hydrophobicity providing resistance to water damage, and scratch resistance.[1]

Previous research reveals that the impregnation method for the use of silica-based consolidation is the most common. Impregnation is a form of treatment method that involves the solution entering into the treated object and layered structures, as opposed to a topical treatment that would remain on the surface. The positive effects that silica has on treating works includes reducing swelling and providing reinforcement. One study revealed Beech wood treated with silica resulted in a decrease in swelling.[2] This is beneficial for wood-based works in potentially prolonging their life. Another study used silica nanoparticles to repair degraded Portland cement, a type of concrete.[3] Silica nanoparticles were revealed to react with Portland cement to form a side product, calcium silicate hydrate, that strengthened the concrete material. This is an example of how concrete-based works may be reinforced by silica.

There is currently a gap in knowledge regarding the longevity of silica, specifically under fluctuating environmental conditions. This proposal aims to close that gap through research that works to understand the behavior of silica nanoparticles in different environmental conditions. The hypothesis for the results of this research are that in fluctuating environmental conditions, silica will alter the tested materials more so than in a stable environment; this alteration will worsen the treated samples through shortening the lifespan of the materials.

Specific Aims

There are two specific aims of this study that will be answered in addition to addressing the hypothesis.

1. Examine the effect of relative humidity and temperature on the stability of silica nanoparticles applied to different media (wood and concrete)
2. Determine the durability of silica nanoparticles applied to different media through elemental composition

Project Description

Experimental overview

The goal of this research is to conduct a materials characterization study to assess silica nanoparticles within different sample materials when exposed to extreme environments. The preparation of silica nanoparticles for treatment will begin with creating a silica and water-based solution. Water was chosen as the solvent as it's an inert substance to silica, limiting interactions to silica and the test material. The applied mediums to be tested are Beech wood and Portland cement. Both of these materials have previously been studied and shown to successfully interact with silica. The impregnation method will be used for treatment. The ideal treatment length for both impregnation and exposure to each environment will be determined using the following test periods: 2 hours, 1 day, 2 days, and 1 week.

The impregnated silica-media samples will then be exposed to the test environments using an artificial aging oven. Samples will first be exposed to the "hot" environment, followed by the "cold" environment. This order was specifically chosen as outdoor conservation treatments are applied in warmer weather, so treated works will experience warmer weather first before transitioning into a cooler climate. The "hot" environment will hold samples at 38°C and 90% RH (relative humidity). The "cold" environment keeps samples at 0°C and 40% RH. These temperatures and relative humidity values represent the high and low points of a season in the mid-Atlantic region. A triplicate of control samples for each material will also be treated using impregnation, but kept at ambient conditions (22°C, 65% RH) for the same time as the experimental samples.

Five physical characterization techniques will be used to gather data before exposure to the environmental conditions, as well as after exposure to both the hot and cold environments. AFM and ESEM will be used to address specific aim 1 regarding the stability of silica nanoparticles on different media. Durability, in specific aim 2, will be assessed using *in situ* XAFS, EDX, and ER-FTIR techniques.

Stability Assessment

Stability will be assessed through analyzing both the surface and layered structures of wood and concrete treated with silica. The physical techniques AFM and ESEM will be used to learn more about discrepancies in surface morphology and particle arrangement, respectively.

AFM monitors surface morphology and particle distribution to an extent

The AFM technique was selected to provide information regarding changes in morphology on the surfaces of the silica-treated test materials. AFM is the optimal technique to choose as it's a surface-specific technique and can capture the silica particles on the micron scale. The AFM technique will be used in the contact and tapping mode. Contact mode provides information about the physical properties of the test materials. Tapping mode is useful for phase imaging in detecting changes in material properties. Non-contact mode should not be used in case silica-water liquid droplets are present on the surface. The use of a flexible tip is ideal when using contact mode to limit tip damage. Expected observations in the use of AFM relate to discrepancies in surface roughness as the experiment is carried out. Specifically, in alignment with the hypothesis, it is predicted that surface roughness will increase as the treated samples are exposed to the fluctuating environments in comparison to the control samples. Additionally, the formation of surface defects on the micron scale may be observed more severely in the experimental samples. The distribution of silica nanoparticles on the surface of both Beech wood and Portland cement will be noted as uneven and the particle shapes will also deform with exposure.

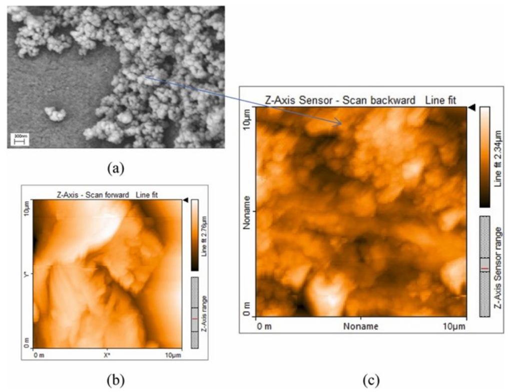

Figure 1. Use of Ag-doped TiO_2 nanoparticles in their application of wood surface treatments. (a) SEM image of Ag-doped TiO_2 nanoparticles. AFM images depicting (b) untreated wood and (c) TiO_2-coated wood. Adapted from reference 4.

The expected observations for AFM have previously been studied in scientific literature. The work performed by *Jafarpisheh* et al. reveals differences in surface morphology through their use of the AFM technique.[4] The goal of this research was to determine whether Ag-doped TiO_2 nanoparticles could be used to enhance the antibacterial activity of wood. The authors monitored the application of titania nanoparticles onto the wood surface using AFM. Figure 1b depicts the surface of the wood without coating while Figure 1c illustrates the wood surface that has been coated with the nanoparticles. The surface roughness increased as a result of the coating application. Additionally, AFM detected an uneven distribution of particles on the surface.

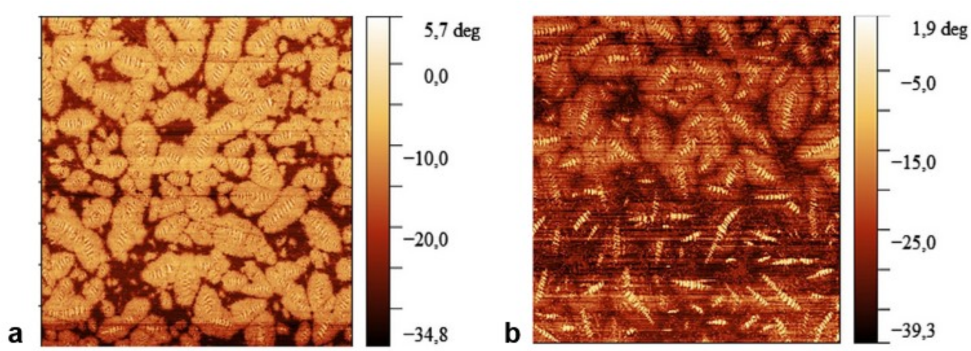

Figure 2. Analysis of aging process in asphalt binders. AFM morphological diagrams of asphalt binders (a) before aging and (b) after aging. Adapted from reference 5.

Another study that supports the expected observations is by *Chen* et al. who researched the aging process of different asphalt binders.[5] The artificial aging process revealed losses in surface coatings and an uneven aging of material. Figure 2a depicts a sample of the asphalt binder prior to the aging process. The authors noted that the surface layer of the sample was not smooth, and contained a thick coating. Figure 2b illustrates that the asphalt particles aged unevenly on the surface, which may be an expected observation in the proposed research. Additionally, the initial coating appeared to have disappeared entirely as a result of artificial aging. This could confirm that the environmental conditions will worsen the silica's effects on the test materials.

ESEM monitors the physical arrangement and shapes of silica

ESEM was chosen as the analytical technique best suited to monitor the physical arrangements and shapes of silica nanoparticles within the test materials that would maintain their experimental conditions. ESEM can analyze non-conductive samples, which is ideal for the studied samples in this proposed research. Additionally, ESEM can maintain the environmental conditions these samples were stored at, including temperature and relative humidity. TEM was considered as a possible technique to monitor particle arrangement and physical shape. However, it would be difficult to create samples thin enough from wood and concrete.

ESEM would be used with a heating/cooling stage while using an ultra variable-pressure detector, as opposed to Everhart-Thornley. Images of samples will be collected without the use of a coating, but the non-conductive surfaces may introduce issues with charging, so the use of a carbon coating may need to be employed. In this experiment, ESEM can be used for two purposes: the first is to verify the successful impregnation treatment of samples and the second, to monitor the shape, size, and arrangements of silica both on the surface and within the structure of the treated materials over time. This technique, coupled with AFM, can give insight into the arrangement of the particles on the surface of each material. While AFM can monitor the distribution, ESEM can provide images of the physical shapes and arrangement of the nanoparticles as well. Expected observations in accordance with the hypothesis predict ESEM will reveal the silica nanoparticles will migrate and deform more in shape when exposed to fluctuating environmental conditions in comparison to samples in a stable environment.

Scientific literature reveals that SEM has previously been used to monitor oxide nanoparticle size and shape. *Jafarpisheh* et al. used SEM to detect the shape and size of the titania nanoparticles on the surface of the wood, as seen in Figure 1a.[4] The titania nanoparticles were shown to be spherically shaped and roughly the same size. The proposed research would use ESEM to monitor the size and shape of silica nanoparticles throughout the experiment.

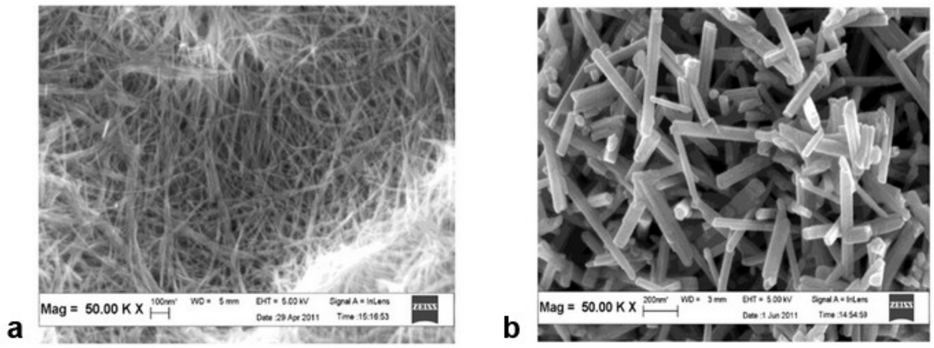

Figure 3. Characterization of TiO_2 nanoparticles during exposure to hydrothermal treatments. FESEM images of TiO_2 nanoparticles (a) after synthesis and (b) two hours of hydrothermal treatment at 700°C. Adapted from reference 6.

An additional article supports the expected observations in showing the distortion of titania nanoparticle shape when exposed to high temperatures. *Razali* et al. aimed to explore the thermostability of titania nanotubes through exposure to different heat treatments.[6] Figure 3 depicts the change in nanoparticle structure after exposure to a temperature of 700°C; the structure of the nanotubes morphed from nanotubes into nanorods after exposure. FESEM was able to reveal that extreme temperature changed the shape of the nanoparticles. The proposed research will reveal similar results in changes in silica nanoparticle shape on the surface, and with cross-sections of the test materials, within the layered structures as well. The fluctuating environments will reveal a greater degree of distortion in silica nanoparticles compared to those stored in a stable environment.

<u>Durability Assessment</u>

The durability of silica-treated materials will be assessed through collecting elemental information. The *in situ* XAFS technique can monitor the formation of side products while EDX and ER-FTIR will detect elements present and changes in silica, respectively.

In situ XAFS monitors changes in oxidation state of silicon

In situ XAFS was chosen due to its ability to provide information about potential side reactions that may occur between silica and the test materials, wood and concrete. XAFS, specifically the XANES portion of a spectrum, provides information regarding oxidation states of the given materials. The *in situ* conditions would allow for the samples to remain in their simulated environment. This is important during data collection to eliminate any additional reactions and changes in oxidation state of silicon and oxygen that may occur through shifts in temperature and humidity.

In situ XAFS would be used to monitor changes in the oxidation state of silicon through collecting spectra throughout the experiment. This is a bulk technique and will not be surface specific due to the preparation of the samples; the impregnation treatment will embed silica throughout the sample. Changes in oxidation state can be monitored by observing changes in the

K-edges of the XAFS spectra. In accordance with the hypothesis, silica is more likely to react in a fluctuating environment compared to stable, resulting in a greater amount of change in oxidation state. This will be visible in XAFS spectra of the fluctuating environment samples through a greater change in K-edges.

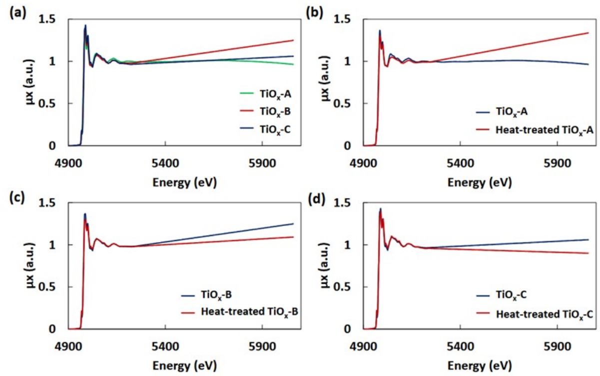

Figure 4. Analysis of the formation of TiO_x phases. XAFS spectra representing (a) three sets of TiO_x particles, and each set of particles before and after heat treatment (b-d). Adapted from reference 7.

Scientific literature supports the expected observations in which extreme environments can alter the oxidation state of a sample. *Arif* et al. monitored the formation of a specific phase of titania nanoparticles at elevated temperatures through exposure to a heat treatment.[7] Their use of XAFS confirmed the formation of the desired phase by comparing fractions of different oxidation states of titanium present. The authors were interested in oxidation states Ti^{3+} and Ti^{4+}. Figure 4 reveals that two sets of titania particles decreased in Ti^{4+} while increasing in one set. This revealed that elevated temperatures could affect the ratio of oxidation states. In the proposed research, results will similarly reveal the exposure of test materials to extreme environments, including elevated temperature, can impact the amount of Si^{4+}, the oxidation state of silicon in silica, present.

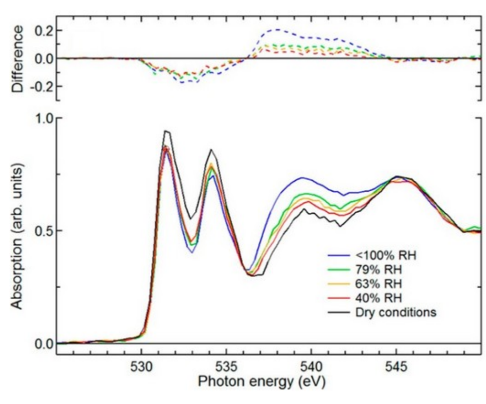

Figure 5. NEXAFS spectra of different humidity conditions of TiO_2 nanoparticles at various relative humidity (RH) conditions. Adapted from reference 8.

XAFS has also been used to illustrate the effect of humidity on changes in oxide nanoparticles. *Orlando* et al. examined titania nanoparticles when exposed to different percentages of relative humidity.[8] Figure 5 depicts the XAFS spectra collected for titania particles when exposed to humidity conditions ranging from dry to 100% RH. The authors examined the O K-edge and determined the presence of water, at higher RH percentages, enhances the absorption features of TiO_2. These differences in TiO_2 features were identified through shifts in the edge positions. This research will similarly reveal that humidity can affect silica by examining shifts in K-edge. In alignment with the hypothesis, samples exposed to fluctuating humidity will experience a greater difference in edge shifts than those stored in a stable environment.

EDX provides elemental maps to qualitatively determine discrepancies over time

EDX was selected as the technique to best monitor the qualitative changes in elements present over reaction time through 2D elemental maps. EDX is a technique that can provide qualitative information regarding elements present in an image. This was key in the ability to monitor the presence of silica throughout the sample over the course of the environmental treatments. This technique was also chosen for efficiency purposes as EDX can commonly be coupled with SEM.

EDX will be used in combination with ESEM. The resolution may be less than that which can be achieved using TEM, but it was previously mentioned that TEM is not an optimal technique for this proposal. In accordance with the hypothesis, EDX mapping will reveal that silica migration is more prominent in test materials exposed to fluctuating environmental conditions compared to samples stored at stable conditions. This can be evident through examining images of the surface and cross-sections of each sample, with an emphasis on the silicon and oxygen element maps.

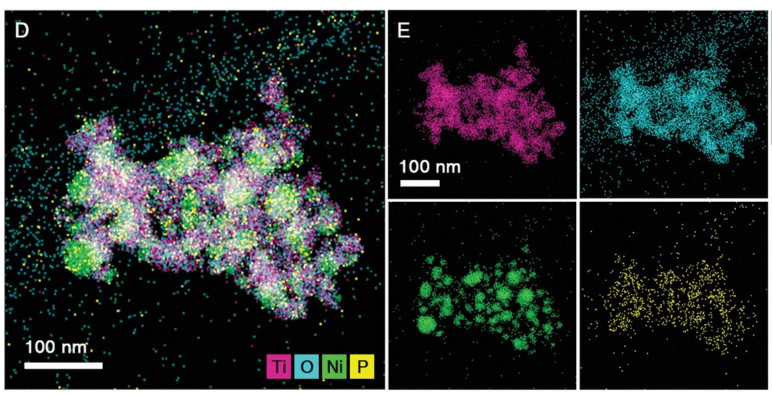

Figure 6. P-doped nickel nanoparticles on TiO_2 support. EDX maps of (d) total elements and (e) individual elements. Pink is titanium, cyan is oxygen, nickel is green, and phosphorus is yellow. Adapted from reference 9.

The distribution of oxide nanoparticles has previously been monitored with EDX mapping. *Li* et al. explored the use of phosphorus-doped nickel nanoparticles on a titania support.[9] Figure 6e depicts the EDX maps collected for the elements of titania, titanium and oxygen, and their spatial distribution within the image. The signals created by titanium and oxygen were observed to be closely overlapped. This led the authors to conclude that the titania support was unaffected by the reactions between nickel and phosphorus. The expected results for the proposed research will reveal similar information. The presence of silica will be evident through the proximity of silicon and oxygen signals on their respective elemental maps. Predictions, in accordance with the hypothesis, indicate that silicon and oxygen are more likely to migrate under fluctuating environmental conditions, which will be evident in their elemental signals being farther from each other.

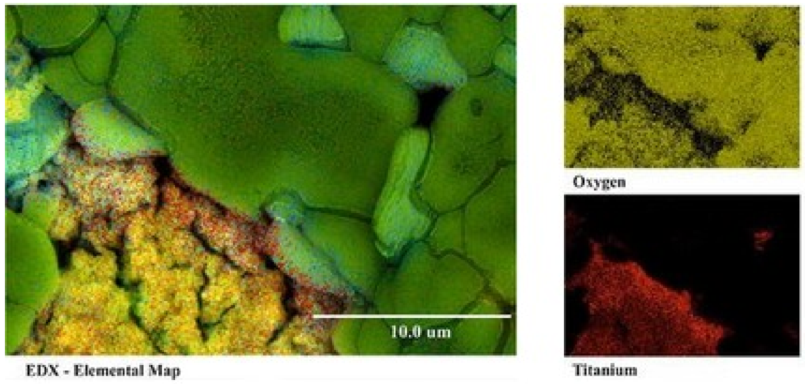

Figure 7. EDX maps of $TiOSO_4$ precursors showing total elements, oxygen in yellow, and titanium in red. Adapted from reference 10.

Additional studies use EDX mapping for the purpose of monitoring the formation of oxide nanoparticles. *Lasfargues* et al. used EDX to confirm the successful formation of titania.[10] Figure 7 depicts the EDX maps generated for the elements associated with titania, titanium and oxygen. The authors determined titania had been successfully formed as the elemental maps of titanium and oxygen superimposed each other. The proposed research will similarly monitor the presence of silica through the proximity of silicon and oxygen; conversely, this research will confirm the potential disruption of silica if the silicon and oxygen maps do not superimpose each other.

ER-FTIR allows for cross-comparison to data collected from real works of art

The ER-FTIR technique was primarily selected to use in this research to cross-compare data that can be collected on real works of art. Unlike experimental sample materials, the physical techniques that can be used on works of art are limited, as the priority is to preserve and maintain them. FTIR in the external reflectance (ER) mode is a non-contact technique and can therefore be used on artworks. An ER-FTIR spectrum is obtained by measuring IR radiation that reflects off a sample. ER-FTIR spectra collected in this proposed research can be directly compared to data from objects and architectural works.

ER-FTIR would be used to monitor the molecular vibrations of silica in both the experimental and control sample test materials. Silica is associated with distinct characteristic peaks in an FTIR spectrum. Disruptions to the silica nanoparticles may be interpreted through a measured change in the shapes of these peaks. In alignment with the hypothesis, it is predicted that the silica exposed to fluctuating environmental conditions is more likely to be disrupted than silica in a stable environment. Expected results indicate the characteristic Si-O peaks will deform with respect to broadness and intensity in the fluctuating environment samples.

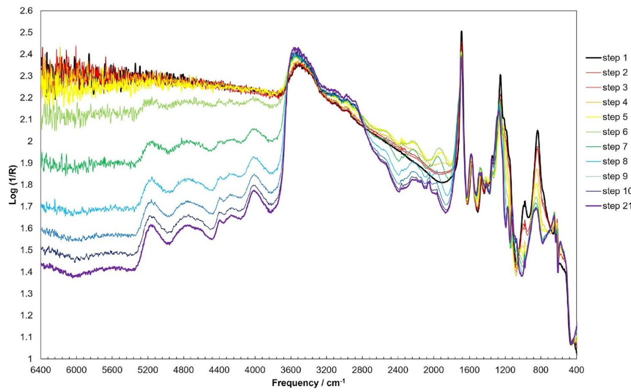

Figure 8. ER-FTIR spectra for different density points on a matte silver gelatin print. Adapted from reference 11.

ER-FTIR has previously been used to monitor the presence of silica on works of art. *Walker and Berrie* used ER-FTIR to examine the differences in various coatings on paper.[11] Figure 8 depicts multiple ER-FTIR readings that were performed on a paper sample containing gelatin. Silica was identified as present through a characteristic absorption at 1070 cm^{-1} with differences in intensity across various locations within the same sample. Comparisons of these spectra revealed additional elements were not detected at every location. The research in this proposal will similarly use ER-FTIR to monitor silica molecular vibrations across the various test materials. Multiple readings will be taken at various points to ensure all molecular vibrations may be measured in case the distribution of silica nanoparticles is not uniform. Expected results indicate that the characteristic silica peaks will be distorted in the samples exposed to a fluctuating environment.

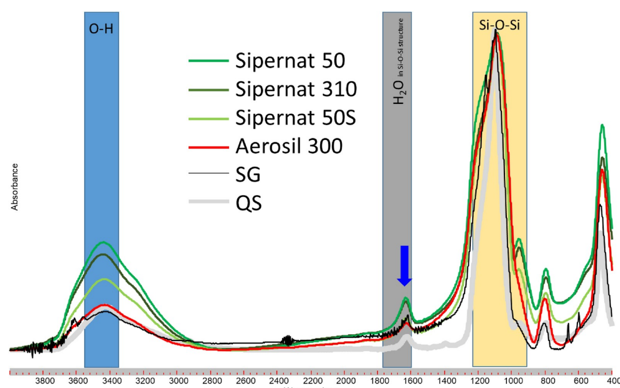

Figure 9. Transmission FTIR spectra of various Si species including amorphous silica, calcium silicate, and sodium silicate. Adapted from reference 12.

Additional studies have used FTIR to monitor characteristic vibrations associated with silica. *Ellerbrock* et al. employed transmission FTIR to characterize different forms of silica and silicate species.[12] Figure 9 reveals that the measured bands for silica vary between each sample. For example, the Si-O-Si band highlighted in the figure is less broad for the silica gel (SG) sample compared to the Sipernat and Aerosil samples. This aligns with the expected results for this research. The peaks associated with silica may differ in broadness, with more drastic changes in peak characteristics in the fluctuating environment samples. While this article used transmission FTIR, the proposed research will use ER-FTIR. Although both modes generate vibrational spectra, each has a different form of sample preparation and thus may have discrepancies in measured bands.

Conclusion

The longevity of silica-based consolidation can be evaluated through research that assesses the physical behavior of silica nanoparticles when exposed to fluctuating environments. The physical characteristics of silica can be monitored through the use of five analytical techniques. The stability of silica can be determined through changes in surface morphology as well as the shape and distribution of silica nanoparticles. AFM reveals information regarding surface morphology changes and provides some insight into the distribution of silica on the surface level. ESEM is a technique that allows for samples to be studied in their environmental housing conditions, and can provide information about nanoparticles both on the surface and within the layered structures. The durability of silica can be assessed through monitoring elemental changes. *In situ* XAFS can monitor changes in the oxidation state of silicon, providing helpful insight into the potential formation of side products. EDX is a technique that provides elemental maps which can be used to identify elements that are present and monitor the presence of silica within the layered structures, when coupled with ESEM. ER-FTIR analysis is helpful to monitor changes in silica through its association with characteristic vibrations; this technique was primarily selected as it's one of the few analytical techniques that are able to be used directly on works of art due to its non-destructive nature, which allows for cross-comparison of results to real works.

The significance of this research is vital to the realm of conservation science. Consolidation is a treatment that can be used on works stored both in protected housing and those unable to be kept in a controlled environment. For objects that can be stored indoors, this research can serve as a guide to creating more sustainable housing conditions. For outdoor objects and architectural works, this research can serve as a predictor for how these pieces may behave at extreme temperatures and humidities. The broader impact of this research includes its contribution to the knowledge of the longevity of materials used in conservation treatments.

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