CHARACTERIZATION AND INVESTIGATION OF KREMER WHITE AS AN INPAINTING PIGMENT

CNS 614-615

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December 12, 2022

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ABSTRACT

"Kremer White" is a relatively new and unfamiliar white pigment that has been introduced to conservators as an inpainting pigment. Since little to no technical characterization exists for this pigment, an array of analytical techniques was used to create reference data for the material. The pigment's listed composition is zirconium silicate, and research into the compound allowed a more thorough understanding of the pigment's properties. Kremer White was discussed and evaluated in comparison to other common white pigments applied in conservation–primarily titanium white. Tactile experience with the pigment was gained to understand its performance as an inpainting pigment. These initiatives contributed to an investigation of Kremer White as an inpainting pigment in terms of efficacy and suitability.

1. INTRODUCTION

1.1 Background: Kremer White

A white pigment named "Kremer White" manufactured by the company Kremer Pigments Inc. has recently been introduced to the art conservation community as a new white option for inpainting. There is documentation of its use for around 10 years–most significantly through the teaching practice of private paintings conservator James Bernstein, who has led a workshop titled "Mastering Inpainting" across various museum institutions in the United States and at the American Institute for Conservation annual meeting for the past decade. Although Kremer White is documented in Bernstein's workshop manual, the pigment remains less common among paintings conservators in a North American context (Bernstein, pers. comm.).

Kremer White is available on the Kremer Pigments website under product code number 46360. The pigment's composition is listed as pure zirconium silicate with a particle size of 5 microns (Kremer Pigments Inc.). The pigment is marketed as a suitable painting material that is compatible with a range of common artist's binding mediums: acrylic, oil, watercolor, gouache, tempera, and all aqueous media. The pigment is described as having good wettability and that it would be particularly suitable for aqueous binders. Additionally, the product overview states that the pigment is lightfast, less pure than titanium white, and may serve as a non-toxic substitute for lead-based whites. Recommended recipes and images of paint-outs demonstrate the pigment's performance in two examples of acrylic and watercolor media, and its properties are described. Kremer White is also commercially available as a readymade watercolor paint under product code number 463608. The watercolor paint is accompanied by a description sheet that details its properties and performance on various paper supports, and includes images of paint-outs (Kremer Pigments Inc.).

1.2 Zirconium Silicate and its Application as a Pigment

Zirconium silicate is the commercial term for zircon, a naturally occurring mineral derived from deposits of beach sands in Queensland, Australia and Florida, USA (Eastaugh et al.

2004, 409-410). The Zircon Industry Association (ZIA), an independent non-profit trade association, writes in their technical handbook that zircon is sourced from coastlines and major deposits in mainly Australia and South Africa (Dunant et al. 2019). Zircon is mined as a mineral sand from these deposits and then dried and cleaned to remove impurities. This zircon sand may then be further processed and converted into zircon opacifier, which is heavily used in the ceramics industry. The particle size of Kremer White matches the grade of zircon opacifier used in ceramics as listed on the ZIA website as of December 12, 2022, indicating that the pigment is the same opacifying material. In the realm of art and cultural heritage, zircon has been commonly used as an opacifier in decorative ceramics since the early 20th century and included as a pigmentary component in ceramic glazes (Eastaugh et al. 2004, 410). Currently, the ceramics industry remains the most significant market for zircon. Other applications of zircon are primarily industrial and chemical due to its high refractory nature, resistance to high temperatures, and great chemical stability. In example, zircon is used as an abrasive, a catalyst, and a refractory in fire brick, coatings, casting, and other foundry materials (CAMEO).

At present, the application of zirconium silicate as a painting pigment is uncommon and the compound is not widely discussed as an artist's pigment in literature relevant to art conservation. The Pigment Compendium notes that although zirconium silicate was not suitable for other pigmentary applications aside from ceramics due to problems with obtaining appropriate particle sizes, the compound exhibited optical properties that "may suit other applications" (Eastaugh et al. 2004, 410). This description implies zircon's theoretical suitability as a painting pigment. Thus, zirconium silicate may have only been recently formulated and commercially marketed for use as a painting pigment in the last decade or so, and was possibly done to create another non-toxic alternative to lead-based whites. In Analysis of Modern Paints, conservation scientist Thomas Learner writes about the incorporation of small amounts of zirconium compounds as driers in alkyd resin paints and modern oil paints, yet does not specify whether they specifically zirconium silicate (Learner 2004, 20-22). Kremer may be the first to begin explicitly marketing the compound as an artist's painting pigment, as the company was able to apply its proprietary name to pure zirconium silicate.

1.3 Conservation Implications

Historically, the three main white pigments used in art and cultural heritage are lead white, titanium white, and zinc white. Both titanium and zinc whites were developed as modern, non-toxic substitutes for lead white. Conservators similarly began with using titanium and zinc whites in their palettes for inpainting and retouching treatments. In recent years there has been controversy around the use of zinc white as an inpainting medium and its use is now discouraged due to problems in its material stability (AIC Wiki). Various studies have shown that zinc white, which contains zinc oxide, may induce degradation effects in certain paint layers and mediums (Pratali, 2013; Osmond, 2012; Rogala et al. 2010). Thus, titanium white has become the primary and often the sole white pigment used for inpainting. Titanium white is used across all specialties in conservation, yet this study focuses primarily on inpainting in the context of paintings conservation.

The arrival of Kremer White on the market introduces questions with regard to its suitability as an inpainting medium, as the potential to add a second option for white to conservator's palettes will have a profound effect on conservation treatments and approaches. According to James Bernstein, the pigment is a significant addition to the conservator's inpainting palette yet remains unknown to many conservation professionals. Bernstein describes zirconium silicate white as a controllable pigment with adjustable translucency, lower metamerism, and a warmer tone. These qualities are sometimes advantageous over titanium white, a cooler tone with a high tinting strength. Should the need for a white inpainting color arise, Kremer White may become a more suitable option than titanium white.

As more conservators learn of and explore the use of Kremer White, the availability of technical analysis and a formal understanding of the material will be beneficial. Additionally, prior research may become helpful as the pigment becomes more widespread and potentially incorporated as an artist's material in the form of paintings and painted surfaces. The pigment might be encountered in future contemporary works of art that are subjected to study and treatment, since zirconium silicate is now directly marketed as an artist's painting pigment. Other suppliers of artists' materials are also distributing the pigment, such as Case For Making, an independent supplier of watercolor materials that sells a watercolor paint handmade with Kremer White and has it available on their website as of December 12, 2022. Performing a formal study of Kremer White pigment will contribute to and expand upon the existing body of literature on artist' materials in relation to conservation and cultural heritage.

1.4 Current Study

The current study sought to create reference data for Kremer White using an array of analytical techniques and scientific instrumentation. The techniques used were multimodal imaging, polarized light microscopy, x-ray fluorescence spectroscopy, fiber optics spectroscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, and fourier transform infrared spectroscopy. This series of technical analyses characterized the optical behavior of the pigment in different regions of the electromagnetic spectrum and recorded its spectral responses in various ways under different illumination and excitation sources. Experiential data was also obtained by the author to gain an understanding of the pigment's working properties and practical application to conservation.

2. METHODS

2.1 Multimodal Imaging (MMI)

Multimodal imaging (MMI) employs combinations of imaging modes and lighting techniques to photographically capture how different materials reflect, absorb, transmit, and/or emit visible light and invisible wavelengths across the electromagnetic spectrum (Chen and

Smith 2020). Completing MMI is a useful technique for characterizing pigments and paints and may assist in understanding what materials are present in artworks. A Nikon D700 UV-Vis-IR modified digital single-lens reflex camera outfitted with a Coastal Optics UV-Vis-IR 60 mm Apochromatic lens was used to perform MMI on a large sample of dry Kremer White pigment with no binder. Photography was done on a copy stand with the camera positioned directly above the subject. The pigment was photographed using the following imaging techniques: visible light in normal illumination (NORM), longwave ultraviolet-induced visible fluorescence (UVA-Vis), long-wave ultraviolet reflectography (RUVA), near-infrared reflectography (RIR), and visible-induced near-infrared luminescence (IRLUM). The techniques and their associated combinations of illumination or excitation source and filtration on lens are detailed below (see Table 1). Image processing utilized the AIC PhD target and a custom UV-IR target standard to adjust exposure values, and was completed via Adobe Bridge software according to AIC standards (Warda et al. 2011).

Table 1. Summary of multimodal imaging techniques and instrumentation settings.

Technique	**Illumination/Excitation Source**	**Filters**
NORM	Profoto D1 500 W Air Monolight, electronic flash at 5600K, x 2, 30° angle to copy stand	X-Nite CC1
UVA-VIS	UVA Systems SuperBright II UVA lamps, peak at 368 nm, x 2, 45° angle to copy stand	Kodak 2E + PECA 918 + X-nite CC1
RUVA	UVA Systems SuperBright II UVA lamps, peak at 368 nm, x 2, 45° angle to copy stand	B+W 403 + X-Nite CC1
RIR	Profoto D1 500 W Air Monolight, electronic flash at 5600K, x 2, 30° angle to copy stand	X-Nite 1000
IRLUM	Powersmith 50 W LED + Schott BG38 filter (6 mm thick), x 1, axial position to subject	X-Nite 715

2.2 Polarized Light Microscopy (PLM)

Optical microscopy is a widespread and relatively accessible tool for material identification. Polarized light microscopy (PLM) is widely used to observe and compare the morphologies and optical properties of pigment particles to characterize a pigment. PLM was performed to visually examine the Kremer White pigment and confirm its particulate characteristics and optical properties. A small sample of pigment was taken using a needle probe and permanently mounted on a glass microscope slide with Meltmount mounting media with a refractive index of 1.662. Using a Leica DM750 P polarization microscope, the sample's morphologies (particle size, crystal structure, cleavage, and type of agglomeration) and optical properties (shade of color, refractive index via Becke line test, birefringence, extinction angle, anisotropic/isotropic property, interference color, and the presence of pleochroism) were recorded while viewing the sample with a 40x objective. The samples were viewed under plane-polarized light and crossed polars with a full λ compensator plate. Images were also captured using the microscope's Leica ICC50 W camera module and Leica LAS EZ software.

2.3 X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy is a powerful, non-invasive method for elemental analysis, and reveals important information about the chemical composition of a material (Bezur et al. 2020, 17). The technique involves illuminating samples with an X-ray beam to excite them with X-radiation photons. These X-ray photons interact with electrons in the atoms within samples in different ways, the absorption and emission of which are then characterized onto a spectrum of wavelengths (*ibid*, 17). This generated spectral response denotes intensity peaks indicating what elements are present in a sample. An advantage of XRF is its ability to be portable, handheld, mobile, as well as lab-based. XRF can also reveal what trace elements or impurities might be present in a compound.

A sample of Kremer White pigment was analyzed using XRF to determine the elemental composition of the pigment, confirm that it is pure zirconium silicate, and detect whether any impurities were present. Performing XRF also generated a characteristic spectrum for the pigment, which may become useful in the future as XRF is commonly used as an analytical and identification technique for pigments and paintings conservation. An X-ray fluorescence spectrum was collected using a Bruker Artax 400 energy dispersive X-ray spectrometer system. The excitation source was a Rhodium (Rh) target X-ray tube with a 0.2 mm thick beryllium (Be) window, operated at 15 kV and 1450 uA current. The X-ray beam was directed at the artifact through a masked aperture of 0.65 mm in diameter. X-ray signals were detected using Peltier cooled XFlash silicon drift detector (SDD) with a resolution of 146.4eV. Helium purging was used to enhance sensitivity to light elements. Spectral interpretation was performed using the Artax Control software 7.8. Spectra was collected over 120 seconds (live time). No filters were used.

2.4 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS)

Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) was performed to produce a high resolution image demonstrating the morphology and chemical composition of the pigment on a microscopic scale. Performing elemental analysis on the compound at a particulate level contributes further to an understanding of what trace elements might be present in the compound, and may provide insight into the production of the material. Secondary electron and backscatter electrons were obtained using a Tescan Vega3 XMU tungsten variable pressure scanning electron microscope located in the science department at SUNY - Buffalo State. Samples were analyzed under high vacuum at an accelerating voltage of 15 kV. X-ray spectra were collected using an accelerating voltage of 15 kV. The data was processed with an Oxford Instruments 50 mm^2 X-Max^n Silicon Drift Detector (SDD) and AZtecEnergy analysis software. The sample was carbon coated to reduce surface charging.

2.5 Fiber Optics Spectroscopy

Fiber optics spectroscopy is a common, non-invasive technique for the analysis and identification of pigments and a variety of other colorants and materials (Beckett and Shugar 2022). Fiber optics reflectance spectroscopy (FORS) involves using a full-spectrum light source to illuminate a sample via a fiber optics cable and capturing its diffuse spectral response with a spectrometer. Ultraviolet fiber optics spectroscopy (UV-FOS) utilizes the same system modified with an ultraviolet excitation source to measure UV-induced fluorescence emission from samples that fluoresce under UVA irradiation.

FORS and UV-FOS were conducted to measure Kremer White's spectral responses and obtain characteristic spectra. These techniques are non-destructive, meaning no physical sampling is required. FORS provides spectral information in the visible region (color) through the near-infrared (chemical information / functional groups). FORS was completed on samples of Kremer White prepared in dry powdered pigment form and bound in Golden acrylic matte medium painted out on a black ceramic tile. FORS data was also collected for reference pigment paint-outs of lead white, zinc white, and titanium white. An ADS FieldSpec4 Hi-Res FORS was used for analysis. This is a portable spectroradiometer with the ability to report on a spectral range of 350 –2500 nm and has a spectral resolution of 3nm @700 nm and 8nm @1400/2100 nm. The FORS Illumination source was an Ocean Insights HL-2000 providing output from 360-2400 nm through a VIS-NIR fiber optic cable. UV-FOS was conducted on a sample of dry powdered Kremer White pigment. The UV-FOS illumination source was a tightly-banded 365 nm LED excitation source (12 nm FWHM) coupled to an Ocean Insight LSM power source providing output through a UV-Vis fiber optical cable. The fiber optic cables were held in hand at a consistent angle to one another and distance from the sample. The system was calibrated on a white 98% reflectance standard prior to data accumulation. Data was collected over 350-1000 at 136 ms/channel. Resulting color measurements were calculated based on the spectral responses using ColorCalculator version 7.77, and these values were converted and plotted on a CIE 1931 (x, y) color space chromaticity diagram.

2.6 Fourier Transform Infrared Spectroscopy - Transmission (FTIR)

Fourier transform infrared spectroscopy (FTIR) measures the absorption or transmission of infrared (IR) radiation as it passes through a sample. Different materials will absorb or transmit IR radiation at various intensities based on their chemical compositions, generating spectra that represent the molecular "fingerprints" of materials (Derrick, Stulik, and Landry 1999, 13). FTIR-transmission is a type of IR spectroscopy analysis where the radiation passes through the sample. An advantage of the FTIR-transmission system available in the department is that it is coupled with a microscope, allowing the required sample size to be very small. Although the availability of sample size was not an issue with the material in question, it remained useful for the author to perform FTIR-transmission since this technique for sample preparation is widely applicable in the field of art conservation (Derrick, Stulik, and Landry 1999, 45).

An infrared spectrum was collected using a Continuum microscope coupled to a Nicolet 6700 FTIR spectrometer (Thermo Scientific). A sample was prepared by flattening it in a diamond compression cell (Thermo Spectra Tech), removing the top diamond window, and analyzing the thin film in transmission mode on the bottom diamond window (2 mm x 2 mm surface area). An approximately 100 mm x 100 mm square microscope aperture was used to isolate the sample area for analysis. The spectrum is the average of 64 scans at 4 cm^{-1} spectral resolution. Correction routines were applied as needed to eliminate interference fringes and sloping baselines. Sample identification was aided by searching a spectral library of common conservation and artists' materials (Infrared and Raman Users Group, http://www.irug.org) using Omnic software (Thermo Scientific).

2.7 Experiential Paint-outs

A panel of small paint-out tests was created to gain tactile experience and working familiarity with the pigment in application to inpainting. Half of a white artist's board was painted with Golden acrylic black matte paint to include a dark background, which would better visualize the white pigments and transparency of various pigments. Gamblin Galdehyde Resin Solution was selected as a binder due to its common use as an inpainting medium in paintings conservation. The binder was combined with dry pigments and diluted with 1-methoxy-2-propanol. Small swatches of Kremer White, titanium white, and a variety of other colors mixed with the white pigments were painted out using a fine point brush. A diverse range of inpainting pigment colors was selected, and each color was combined with approximately the same amounts of Kremer White and titanium white to observe and compare the effects of mixing in the different whites.

3. RESULTS AND DISCUSSION

3.1 Multimodal Imaging (MMI) Results

The pigment appeared bright white in the RIR image, indicating that it reflects wavelengths in the IR region (Figure 1b). The pigment exhibited little to no amount of luminescence in the IR luminescence image, meaning it does not emit much IR energy (Figure 1c). UVA-induced visible fluorescence imaging revealed that the pigment does fluoresce dimly in a burnt orange color under UVA irradiation (Figure 1d). This UVA fluorescence result confirmed the presence of zircon, since orange-colored fluorescence under ultraviolet irradiation is characteristic of and known to be a widespread phenomenon in the mineral zircon (Gleason, 1960, 148). The reflected UVA technique showed that the pigment reflects wavelengths in the UVA region, as it appears white in the image (Figure 1e).

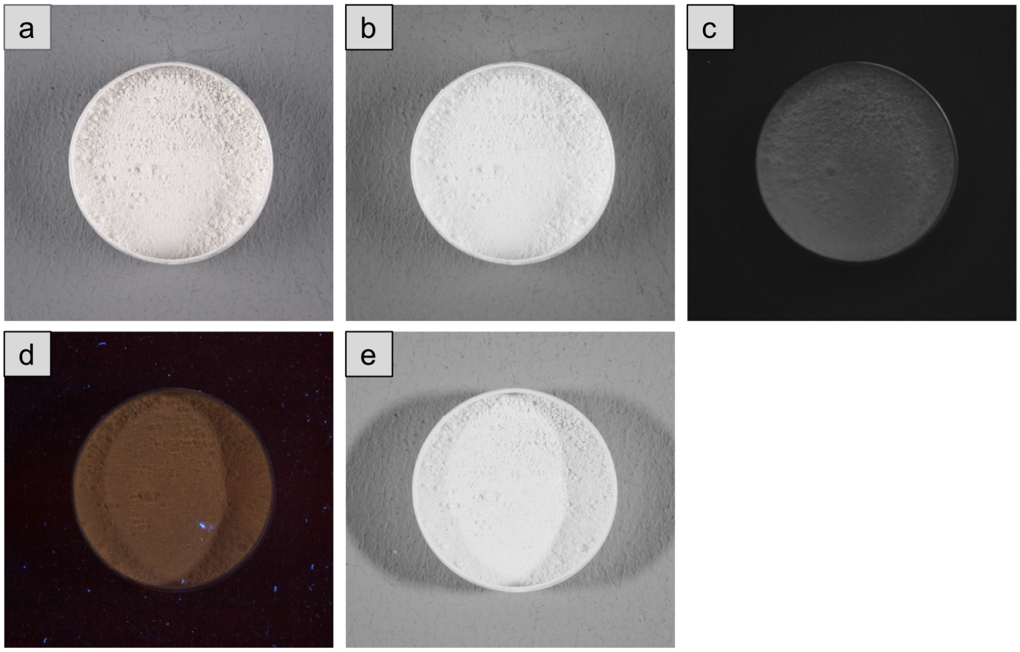

Figure 1. Multimodal images of Kremer White pigment. (a) Visible light, normal illumination, (b) reflected IR, (c) visible-induced IR luminescence, (d) UVA-induced visible fluorescence, (e) reflected UVA.

Documenting the ways in which zirconium silicate white pigment responds in visible light and the non-visible wavelengths of the IR and UVA regions may serve as a useful way for identifying whether the pigment is present in a painting or painted surface, especially as Kremer White gains popularity as an addition to both artists' and conservators' palettes. Multimodal imaging of a wide range of common white pigments had been previously completed, yet did not include Kremer White. The imaging done in this study contributed toward prior studies and created a more complete reference set. The reflectance, absorption, emission, and luminescence properties of titanium white, zinc white, and lead white are known and can be distinguished from one another through MMI. When comparing the modern whites, Kremer White can be differentiated from titanium and zinc whites under reflected UVA since Kremer White reflects UV while the other two absorb it and appear dark (see Appendix 1). UVA-induced visible fluorescence can also distinguish between the three modern whites, since titanium white does not fluoresce, zinc white fluoresces a bright yellow-green, and Kremer White fluoresces a dim orange (see Appendix 1). Since Kremer White is already used by some paintings conservators for inpainting and may potentially become even more common in the future, these imaging techniques may help identify whether titanium white or Kremer White have been used.

3.2 Polarized Light Microscopy (PLM) Results

The following observations were collected after examining a sample of Kremer White under plane-polarized light and crossed polars (Figure 2). Particles of Kremer White appeared individually transparent and colorless, and had a slight gray tint when amassed. The morphology consisted of an irregular crystal habit, a mixed variety of amorphous shapes with sharp and round edges, and tabular or basal cleavage. The state of agglomeration contained singular individual particles. Measuring the particles revealed an average particle size 4.25 microns, with a size range of 1-10 microns. Performing the Becke line test indicated a refractive index greater than 1.662 n_D 25. Viewing the sample under crossed polars demonstrated that the compound was anisotropic with low birefringence and first-order interference colors (Figure 3). The particles had an inclined extinction angle and exhibited complete extinction in an undulose pattern. No pleochroism was observed. Viewing the sample under crossed polars with the compensator in helped determine a positive sign of elongation (Figure 4).

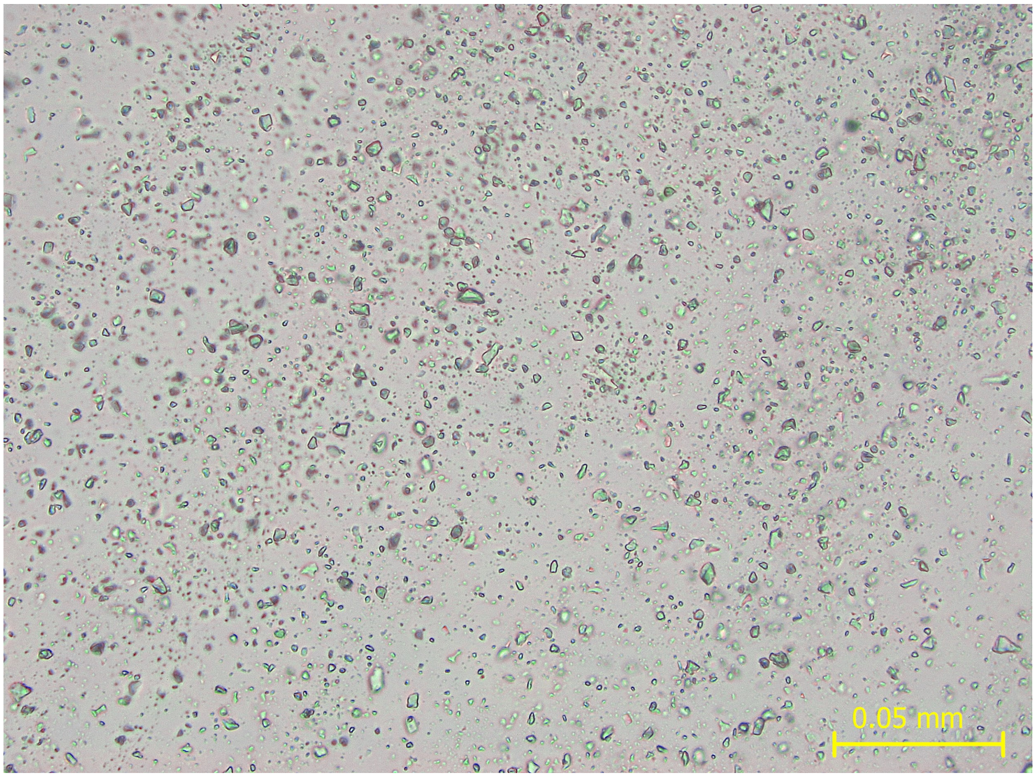

Figure 2. Photomicrograph of Kremer White under plane-polarized light.

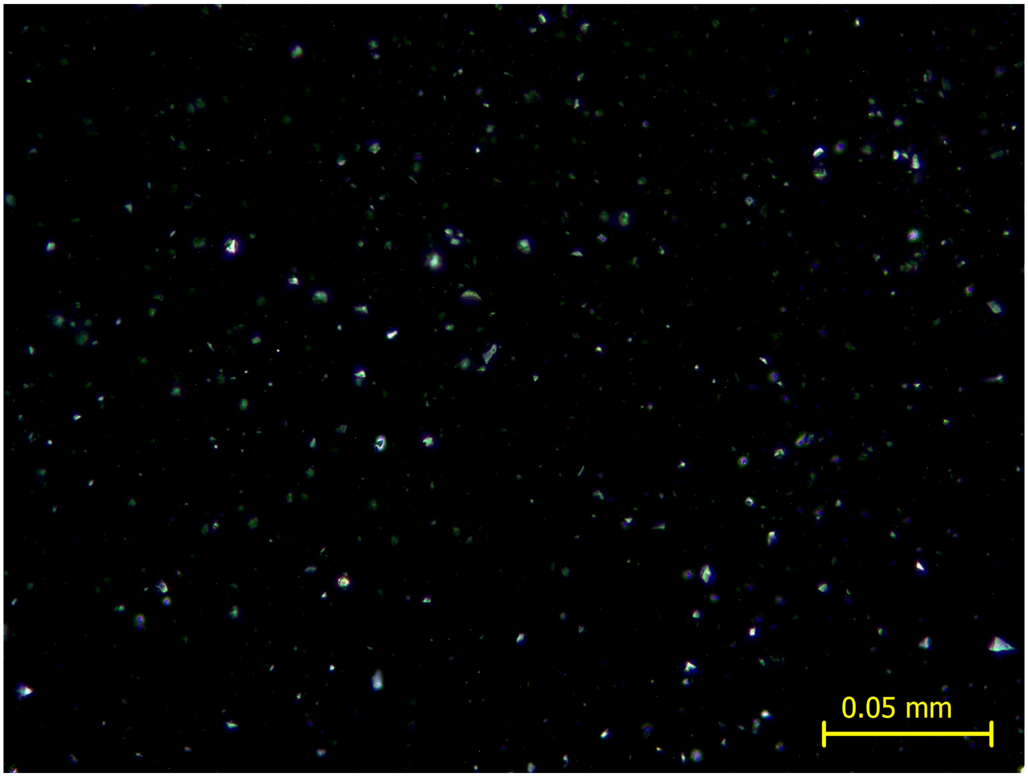

Figure 3. Photomicrograph of Kremer White under crossed polars.

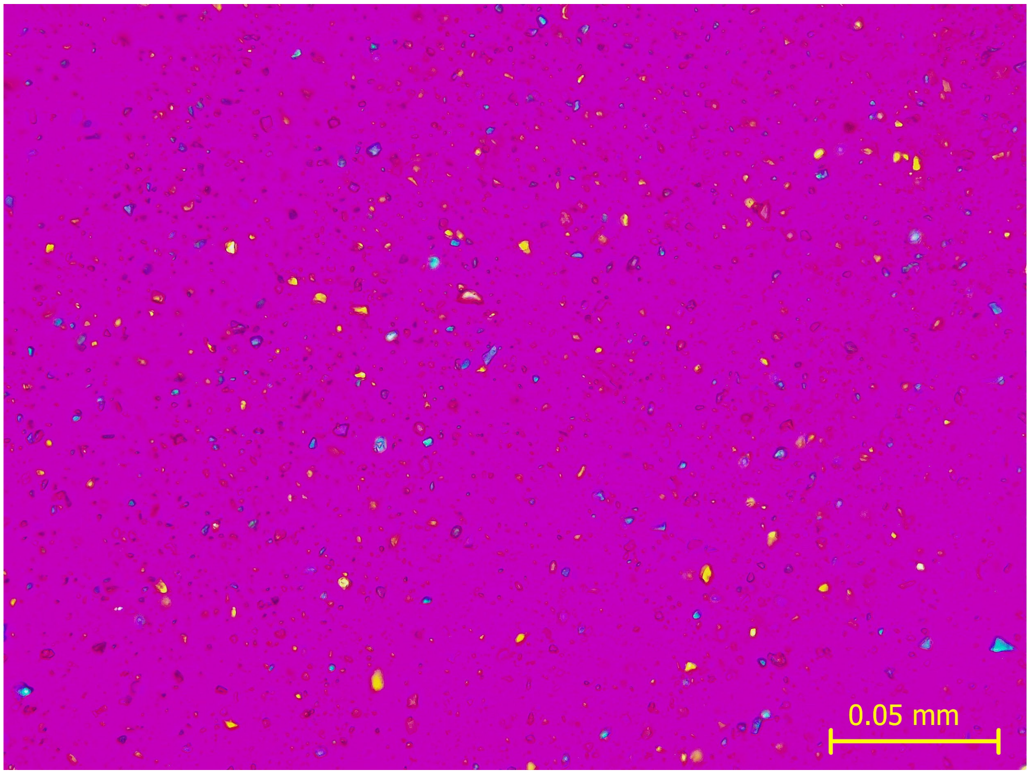

Figure 4. Photomicrograph of Kremer White under crossed polars, analyzer in.

Recording what Kremer White or zirconium silicate particles look like under microscopy may help with identification of the material in the future, since PLM is one of the most prevalent methods for advanced visual examination in conservation. Observing the compound on a microscopic level also contributes to an understanding of why the pigment might work well as an alternative white pigment to titanium white. One of the main characteristics upon which pigments are evaluated is their opacity or covering power. A pigment's refractive index, the measurement of a material's ability to reflect light, affects its level of opacity when combined with different mediums (Johnston-Feller 2001, 190-1). Pigments with higher refractive indices demonstrate higher opacity. Titanium white has the highest refractive index of all whites at a value of 2.71-72, indicating the highest covering power (see Appendix 2). The observed refractive index of the Kremer White sample was higher than that of Meltmount medium at 1.662. This resulting value matches that of zirconium silicate, which is listed on chemical supplier Stanford Advanced Materials' website at 1.93-2.01 as of December 12, 2022. Although Kremer White's refractive index is lower than that of titanium white, 1.93-2.01 is relatively very high and above those of most white pigments (see Appendix 2). Kremer White's refractive index is also comparable to those of lead white and zinc white pigments, attesting to the pigment's covering power and performance as a painting medium (see Table 2).

Table 2. Comparison of refractive indices for white pigments.

Pigment	Refractive Index
Zirconium Silicate White	1.93-2.01
Lead White	1.94-2.09
Zinc White	2.00-2.02
Titanium White	2.71-2.72

3.3 X-ray Fluorescence Spectroscopy (XRF)

The resulting XRF spectrum for Kremer White confirmed that the material was purely zirconium silicate. Only two strong peaks were present and noted as characterizing peaks; these were identified as peaks for silicon and zirconium (Figure 5). A small peak also indicated the presence of hafnium, which is characteristic for zirconium silicate or zircon since hafnium is nearly always present in some amount (McCall 2005). A very small peak indicates the presence of titanium, which may be due to the possible development of minute titanium concentrations as a chemical substitution of elements in zircon (Fu et al. 2008). The ZIA also writes online as of December 12, 2022 that titanium dioxide is also commonly present in zircon as an impurity. However, the titanium peak is extremely small and may not actually be significant. Two other very small peaks indicate the presence of manganese, yet the cause of these is unclear and may be related more to the XRF response instead of what elements are present. Another analysis technique performed in this study similarly revealed trace amounts of manganese that were ultimately inconclusive and will be discussed in the following section.

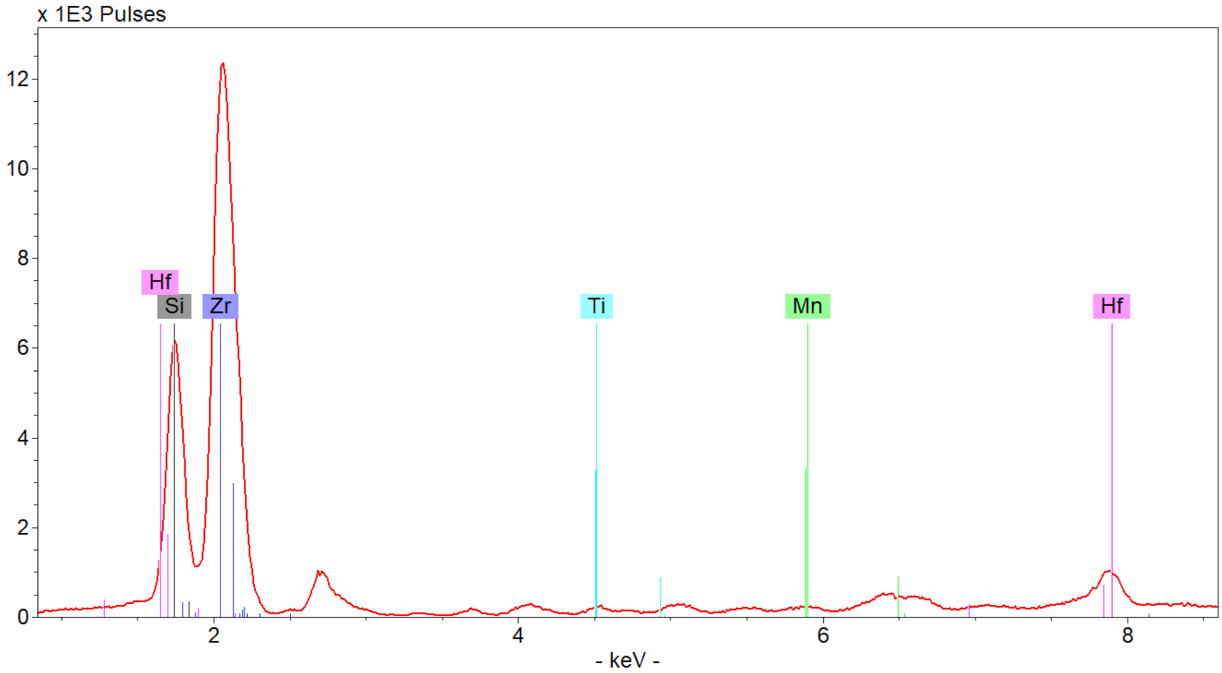

Figure 5. Annotated XRF spectrum for Kremer White.

3.4 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS)

Performing SEM/EDS analysis on a sample of Kremer White provided a high-resolution photographic capture of the particles' physical morphology and identified their compositional makeup on a minute scale. The morphology consisted of irregular shapes with sharp, angular edges, conchoidal fracture, and variable particle sizes. The SEM image scale denoted an average particle size range of 0.5-1 microns, which was smaller than the listed particle size of 5 microns on its technical data sheet. Even under extremely high magnification and resolution via SEM imaging, the particles still appeared very fine and well-dispersed; this morphological property may contribute to the pigment's high refractive index and good wetting ability. The variations in darkness and brightness between the particles represented the overall average atomic numbers of the detected elements, where the brighter areas indicated higher atomic numbers (Figure 6).

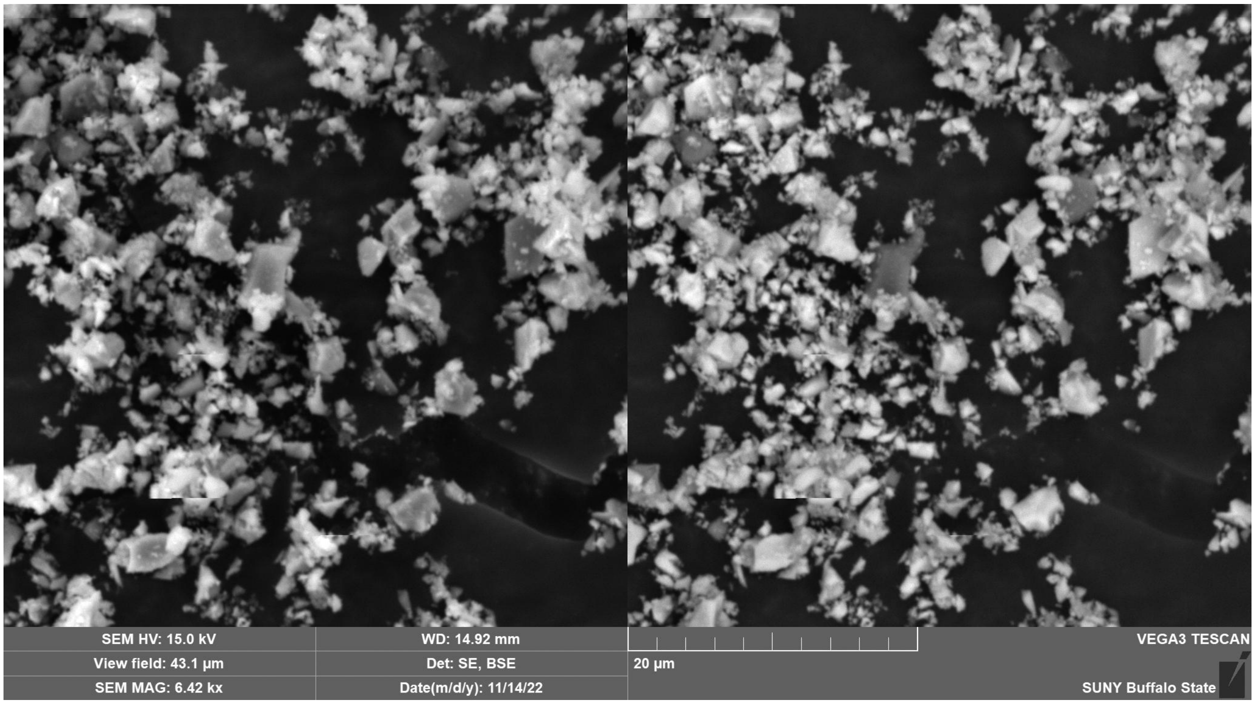

Figure 6. SEM/EDS images for sample of Kremer White.

Three spectra were collected from three different particles in the scanning electron image area and their compositional ratios were recorded (see Appendix 3). One darker particle was selected along with two brighter particles, which resulted in different percentages of zirconium to silicon (Figure 7, Table 3). The first spectrum, or Spectrum 1, was taken for a darker particle and revealed a much lower percentage of zirconium than that of the compositional ratio for zirconium silicate. The chemical composition for zircon is $ZrSiO_4$, so based on molecular weight the compositional percentage of the element zirconium is around 50%. Spectrum 1 indicated that the darker particle contained only around 12% of zirconium. Spectra 2 and 3 were taken for two other brighter particles, which contained around 52% zirconium and around 49% zirconium, respectively. These latter two particles contained percentages of zirconium that matched the compositional ratio for zirconium silicate. This variation in zirconium content may be attributed to the mining, production, and/or processing of the mineral into a distributed chemical compound and specifically as zircon opacifier (see Section 1.2). The zircon content of the source deposits vary in concentration, which may explain why some particles contain more silica or silicon dioxide (Dunant et al. 2019). Zircon sand or opacifier may also inherently vary in elemental composition from particle to particle. Similar to the XRF analysis, a possible trace amount of manganese was also detected yet not enough to qualify it as significant data.

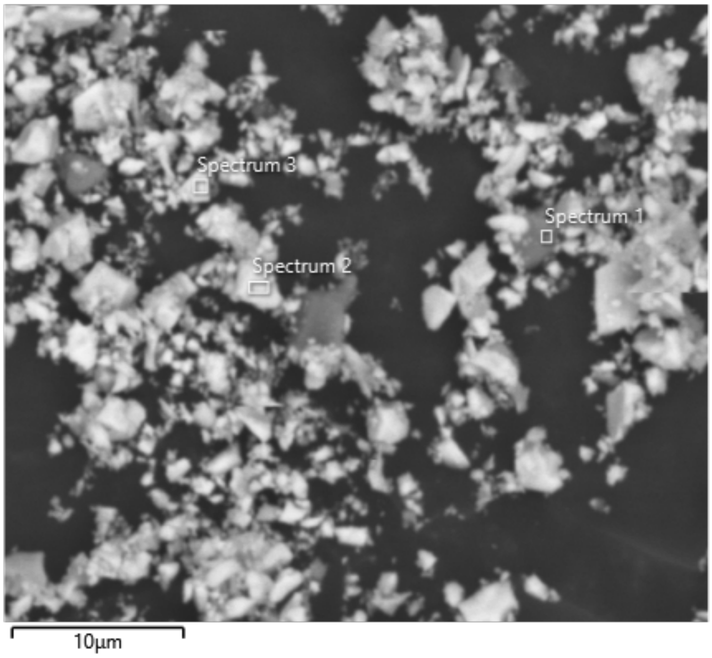

Figure 7. Annotation of SEM/EDS image for collected particle spectra.

Table 3. Summary of SEM/EDS spectral data for Kremer White.

Spectrum #	Weight % of Zr	Weight % of Si	Weight % of O
1	12.10	43.50	44.40
2	51.94	16.48	31.58
3	48.72	14.36	36.92

3.5 Fiber Optics Spectroscopy

Fiber optics reflectance spectroscopy (FORS) produced characteristic spectra for Kremer White in powdered pigment form and in an acrylic binder painted out on a black ceramic tile. Spectra were also generated for reference paint-outs of lead white, titanium white, and zinc white and compared to the spectra for Kremer White (see Figure 8). The FORS spectra generated for both prepared samples of Kremer White matched expected results for a white pigment, which do not contain any key emission peaks or absorption bands. All of the collected spectra reveal absorbance in the UV region, which is characteristic of white pigments and is particularly strong in titanium white and zinc white (Cosentino 2014). The black color of the support used for the paint-out of Kremer White in acrylic binder may have affected the resulting spectrum, and provided a less consistent point of reference when compared with the other white pigment paint-outs. In future testing, preparing a Kremer White paint-out on a white support and collecting FORS measurements for this sample would potentially provide a more accurate datapoint for reference.

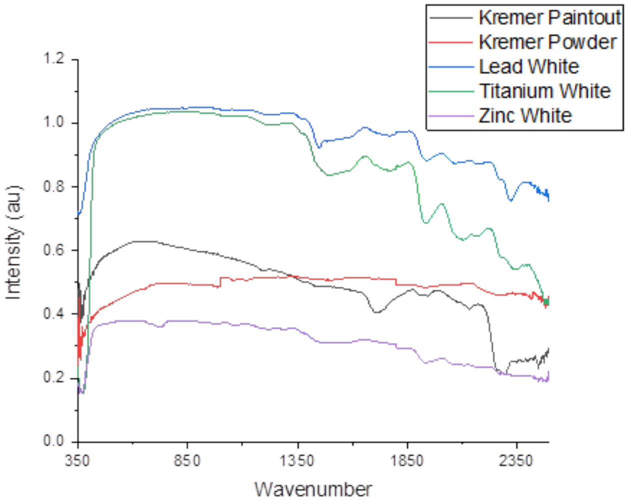

Figure 8. Fiber optics reflectance spectra for prepared Kremer White samples and reference white pigment paint-outs.

The fiber optics spectroscopy system was used to measure ultraviolet (UV)-induced fluorescence emission from a binderless sample of Kremer White pigment. The retrieved spectrum did not contain any significant intensity peaks, yet revealed some strong emission occurring at around the 400 nm wavelength region (Figure 9). The corresponding CIE 1931 (x, y) color space chromaticity diagram plotted the color measurement for Kremer White based upon its UV spectral response (Figure 9). The CIE result revealed a measurement in the blue region and appeared different to MMI findings, where UVA-induced visible fluorescence produced an orange-colored fluorescence (see Section 3.1). This unexpected difference in color measurement may have been due to equipment performance, since the Spectralon white reflectance standard used was possibly totally UV-absorbing and reflected more blue light. Total UV absorbance of the white standard would have caused a greater UV reflectance in the sample response and skewed it toward the bluer region.

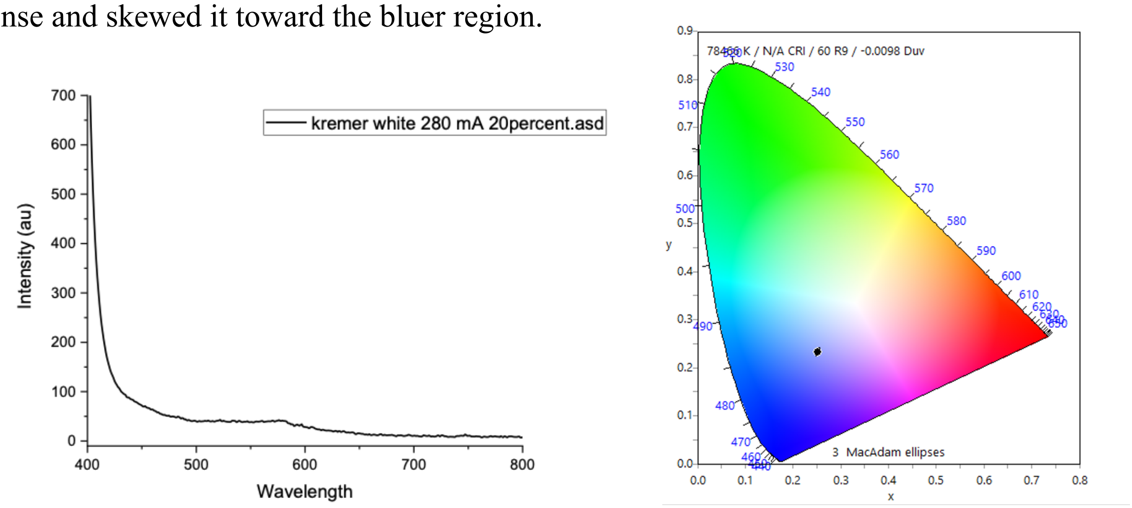

Figure 9. Fiber optics UV-induced spectrum **(left)** and CIE 1931 (x, y) color space chromaticity diagram **(right)** for Kremer White.

3.6 Fourier Transform Infrared Spectroscopy - Transmission (FTIR)

Performing FTIR analysis would generally not reveal as much useful or novel information about this pigment since it is an inorganic material. Nevertheless, FTIR spectroscopy is still used to characterize inorganic compounds and it was previously unknown whether any spectral data already existed in reference libraries for zirconium silicate. A spectrum was retrieved for a sample of Kremer White and compared against reference library data, which generated matches with reference spectra for glass and silica-containing materials. These reference spectra closely matched the sample spectrum, where both sets similarly contained one strong and broad peak at around 1000 nm (Figures 10-11). Thus, this strong peak is likely characteristic for silica or silicon dioxide. The Kremer White spectrum appeared to have some gradual absorption beginning in around the 2000 nm region and beyond, which the reference spectra lacked. This difference might be due to the zirconium content, yet it is unclear whether this represents anything characteristic. A manual text-based search for zircon, zirconium, and zirconium silicate in the reference library was also performed, generating one relevant match for zircon (Figure 12). The reference spectrum did not exactly match that for Kremer White, yet both contained strong absorption bands in roughly the same region. Infrared spectral data for zircon samples were also available in the online RUFF Project spectral database for minerals as of December 12, 2022, and appeared similar to the FTIR response collected for Kremer White (see Appendix 4). Ultimately, this reference FTIR spectrum for Kremer White or zirconium silicate might not be as useful or conclusive when attempting to identify the pigment as it appeared very similar to spectra for silica glass.

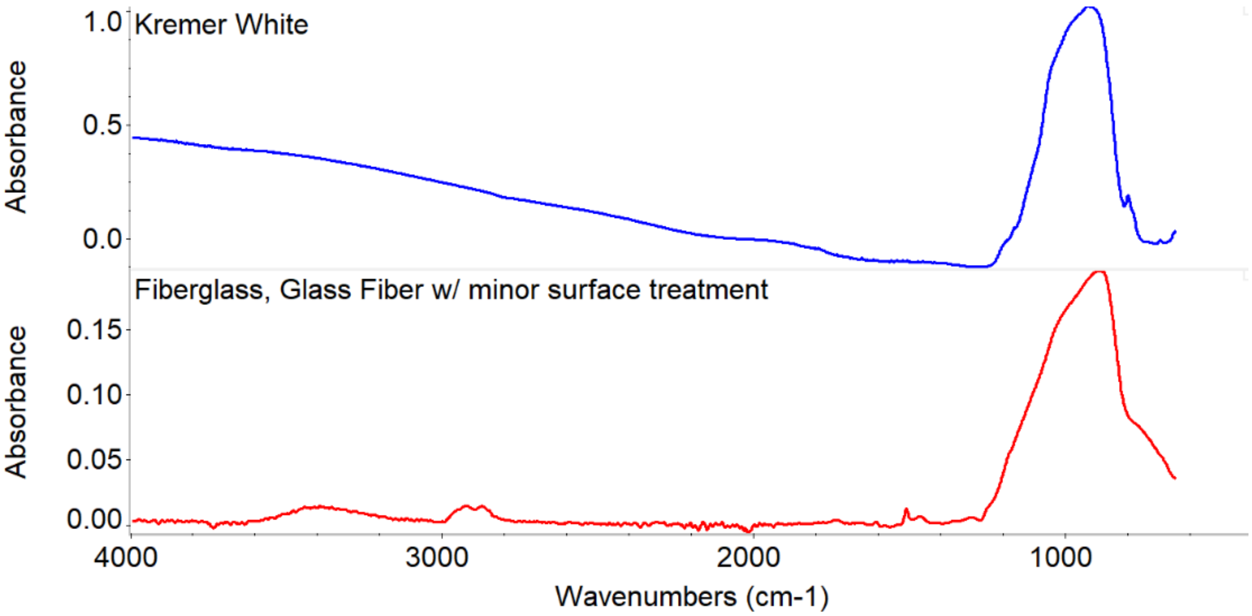

Figure 10. Kremer White spectrum compared against reference spectrum for fiberglass.

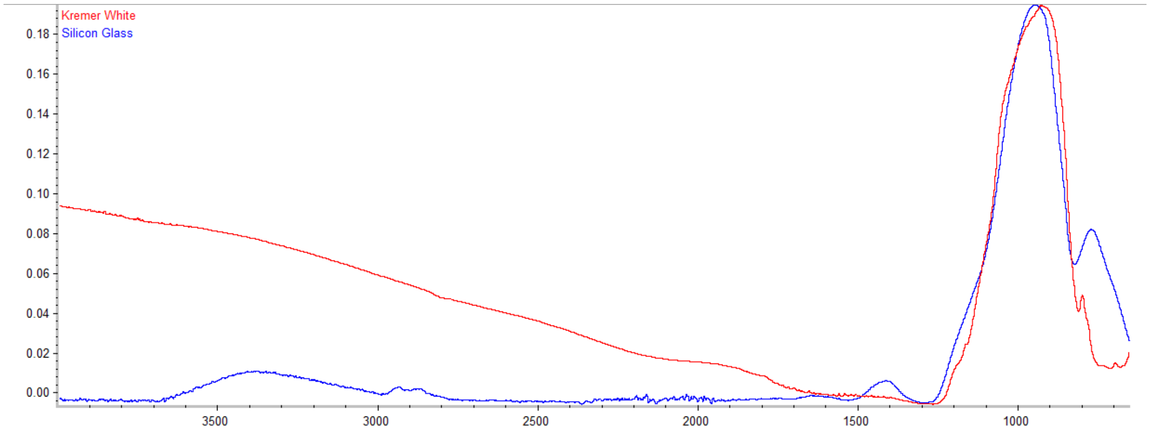

Figure 11. Kremer White spectrum overlaid with reference spectrum for silicon glass.

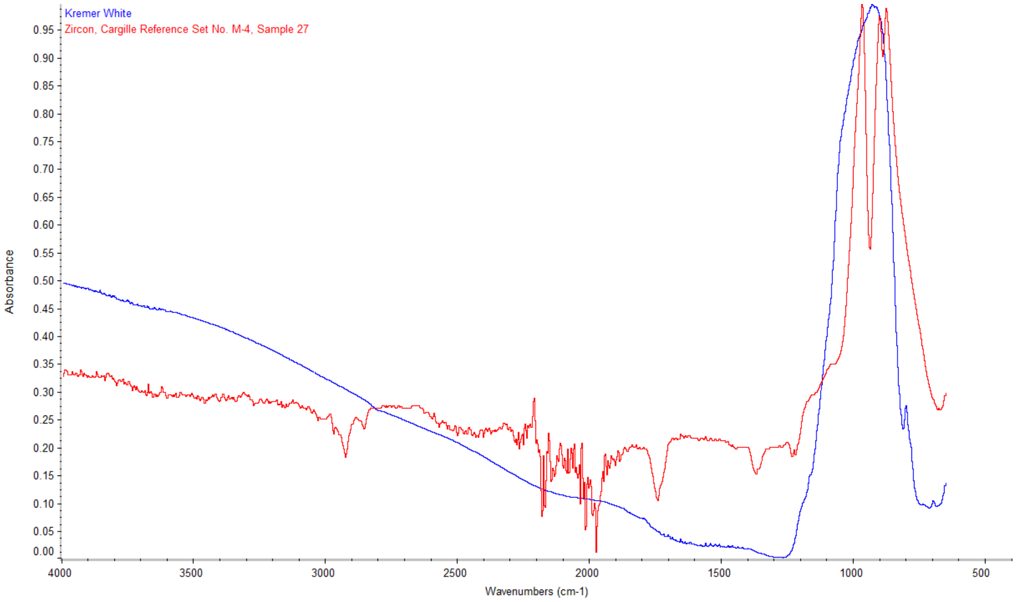

Figure 12. Kremer White spectrum overlaid with reference spectrum for zircon.

2.7 Experiential Paint-Outs: Observations

Painting out small swatches of Kremer White and titanium white alone revealed that Kremer White possessed a warmer, more muted shade than titanium white. Both white pigments demonstrated good wetting ability. Titanium white appeared brighter white, whereas Kremer White had a slight beige tinge similar in color to titanium buff. Kremer White had a significantly lower tinting strength or covering power than titanium white, and required the addition of much more pigment to reduce its translucency and further alter another color. Mixing both whites with a range of pigments produced expected results, where Kremer White imparted a much warmer tone in every color (see Figure 13). Titanium white altered each color more readily due to its high tinting strength and less pigment was required for mixing. In some instances, titanium white produced a slightly dulling or graying effect.

Kremer White's working properties and qualities matched those as described by James Bernstein and on Kremer Pigments' website. The pigment possessed good wetting ability, more translucency, and was easier to control when mixed with other colors due to its lower tinting strength. No issues were encountered when binding the pigment in Gamblin Galdehyde resin. There is great potential for Kremer White to be a useful addition to conservator's inpainting palette–especially since titanium white widely exists as the only option for an inpainting white. Due to the noticeable differences between the effects of Kremer White versus titanium white on various pigments, Kremer White may provide certain advantages and solutions to the limitations of titanium white.

Figure 13. Panel of painted swatches of Kremer White, titanium white, and both whites combined with common inpainting colors.

4. FUTURE WORK

Continuation of this study may entail performing Raman spectroscopy of Kremer White since there are many reference spectra available for comparison. X-ray diffraction (XRD) analysis may also be useful, as it would help understand and document the pigment's crystalline nature. Research may be done to find previously existing XRD analyses of zircon and compare their results with that of Kremer White, which may reveal some insight into the pigment's production and this specific processing or synthesis of zirconium silicate. Creating paint-outs with the pigment in a systematic manner to perform an accelerating aging test on the pigment would demonstrate how the material might react or change over time, which is useful in determining its suitability for conservation. Conducting visible and UV FORS analysis may be attempted on results from an aging test to quantify any color shifts within the pigment. UV FORS might be more useful in identifying any color shifts, since visible FORS is typically less effective on white colorants. MMI may also be performed on an aging test to identify any changes in the material. Another interesting point of departure would be to compare Kremer White with other sources of pure zirconium silicate in the same grade and particle size, as the compound is available from a range of suppliers in the ceramics and chemical industries. Differences and similarities between Kremer's proprietary material and other sources might be beneficial to explore, along with the comparison of price points for economical purposes.

5. CONCLUSION

This investigation into Kremer White, or zirconium silicate white, provided a deeper understanding of the pigment's chemical composition and properties and demonstrated its suitability as an inpainting pigment. Conducting various technical analyses revealed that MMI, XRF, and SEM/EDS are the most useful methods for identifying the pigment. Kremer White was confirmed to be 100% pure zirconium silicate, indicating its reliability as a material with tremendous chemical stability. The pigment contained a high refractive index comparable to that of titanium white, the most widely used white for inpainting, as well as those for common white pigments such as lead white and zinc white. This refractive index value attested to the pigment's ideal opacity and covering power. Kremer White possessed different working properties in comparison to titanium white, which may prove useful for inpainting and greatly impact future conservation treatments. Since Kremer White and the use of zirconium silicate as a painting pigment have not been researched in the past, these characterization findings might serve as useful reference points for future studies–especially as conservators continue to discover and apply Kremer White, and potentially encounter the pigment in contemporary works of art and cultural heritage.

6. ACKNOWLEDGEMENTS

The author would like to thank the following: James Bernstein for generously giving me his time and sharing his knowledge about Kremer White with me, Professor Jiuan Jiuan Chen for her advice with multimodal imaging and providing resources on UV-fluorescent rocks and minerals, and classmate plus dear friend Susan P. Enterline for her guidance in arriving at this research topic.

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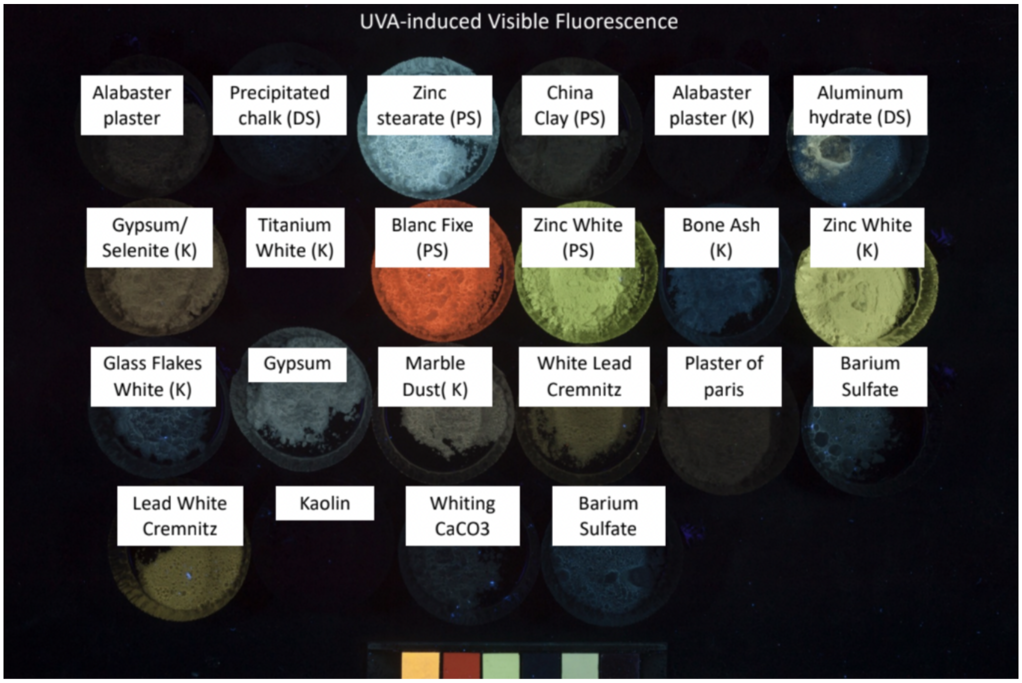
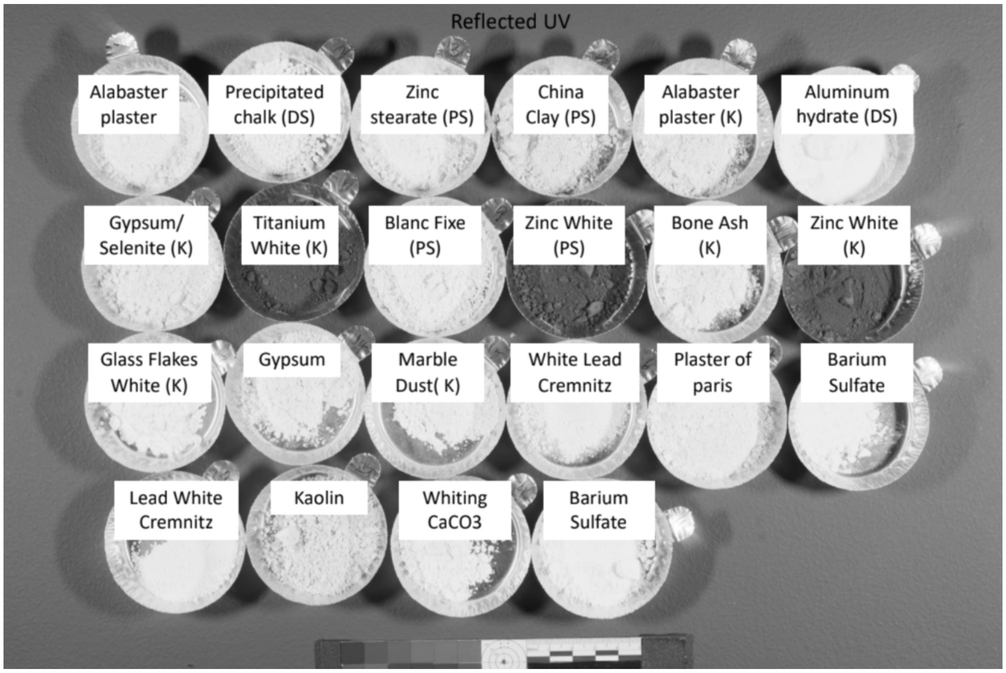
APPENDIX 1: Multimodal Images of Common White Pigments

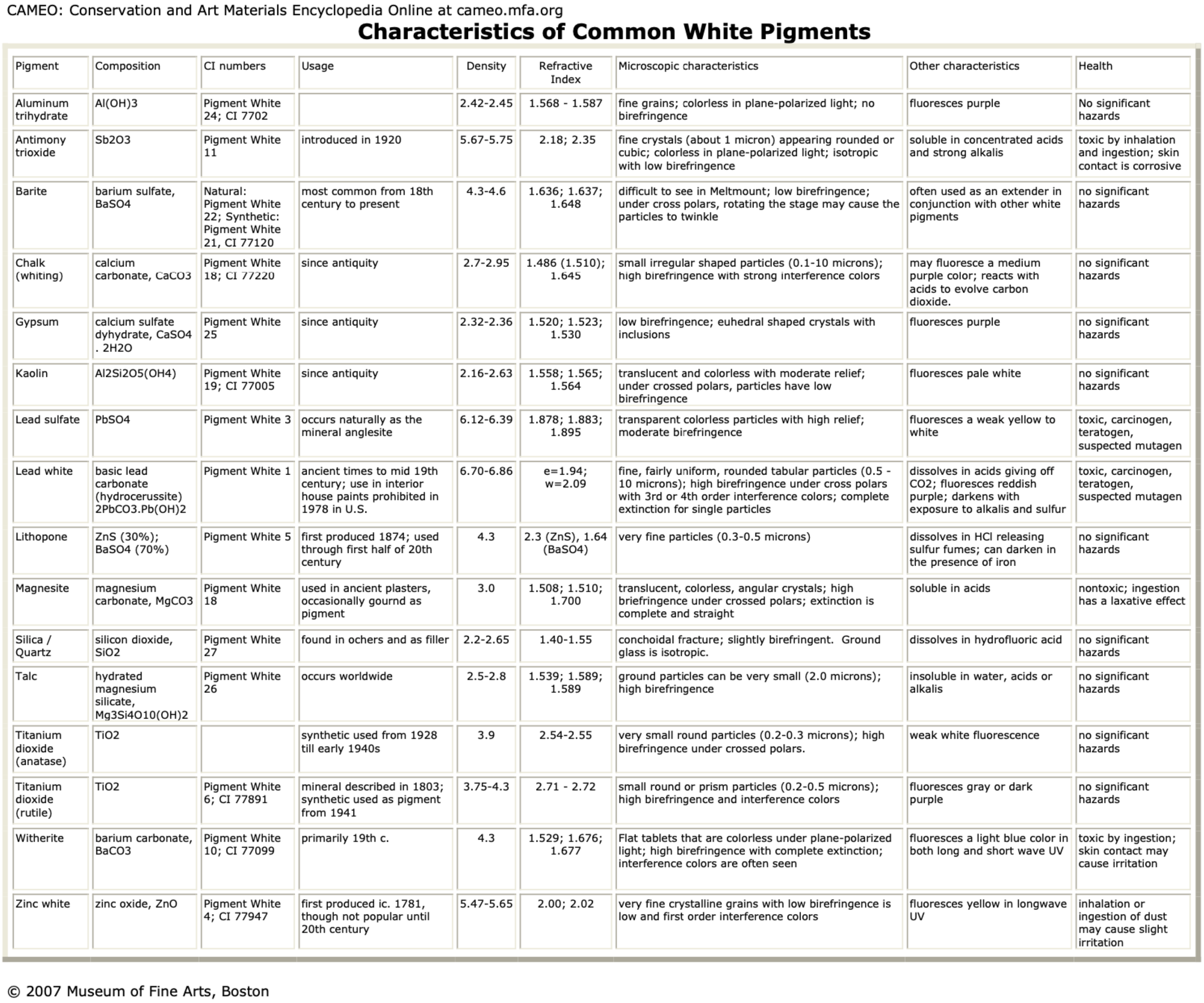


UVA-induced visible fluorescence. Image courtesy of Jiuan Jiuan Chen.



Reflected UVA. Image courtesy of Jiuan Jiuan Chen.

APPENDIX 2: MFA CAMEO Characteristics of Common White Pigments Chart



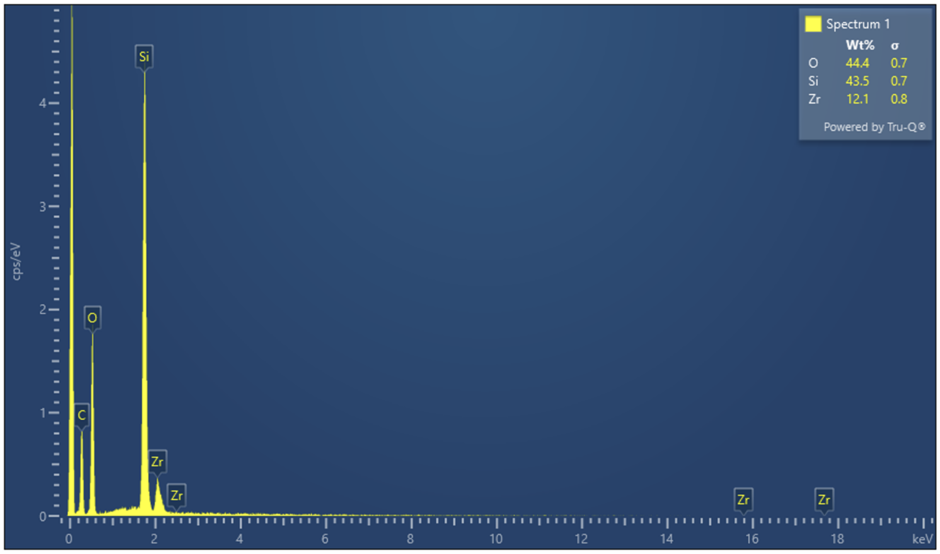
CAMEO: Conservation and Art Materials Encyclopedia Online at cameo.mfa.org

Characteristics of Common White Pigments

Pigment	Composition	CI numbers	Usage	Density	Refractive Index	Microscopic characteristics	Other characteristics	Health
Aluminum trihydrate	Al(OH)3	Pigment White 24; CI 7702		2.42-2.45	1.568 - 1.587	fine grains; colorless in plane-polarized light; no birefringence	fluoresces purple	No significant hazards
Antimony trioxide	Sb2O3	Pigment White 11	introduced in 1920	5.67-5.75	2.18; 2.35	fine crystals (about 1 micron) appearing rounded or cubic; colorless in plane-polarized light; isotropic with low birefringence	soluble in concentrated acids and strong alkalis	toxic by inhalation and ingestion; skin contact is corrosive
Barite	barium sulfate, BaSO4	Natural: Pigment White 22; Synthetic: Pigment White 21, CI 77120	most common from 18th century to present	4.3-4.6	1.636; 1.637; 1.648	difficult to see in Meltmount; low birefringence; under cross polars, rotating the stage may cause the particles to twinkle	often used as an extender in conjunction with other white pigments	no significant hazards
Chalk (whiting)	calcium carbonate, CaCO3	Pigment White 18; CI 77220	since antiquity	2.7-2.95	1.486 (1.510); 1.645	small irregular shaped particles (0.1-10 microns); high birefringence with strong interference colors	may fluoresce a medium purple color; reacts with acids to evolve carbon dioxide.	no significant hazards
Gypsum	calcium sulfate dyhydrate, CaSO4 . 2H2O	Pigment White 25	since antiquity	2.32-2.36	1.520; 1.523; 1.530	low birefringence; euhedral shaped crystals with inclusions	fluoresces purple	no significant hazards
Kaolin	Al2Si2O5(OH4)	Pigment White 19; CI 77005	since antiquity	2.16-2.63	1.558; 1.565; 1.564	translucent and colorless with moderate relief; under crossed polars, particles have low birefringence	fluoresces pale white	no significant hazards
Lead sulfate	PbSO4	Pigment White 3	occurs naturally as the mineral anglesite	6.12-6.39	1.878; 1.883; 1.895	transparent colorless particles with high relief; moderate birefringence	fluoresces a weak yellow to white	toxic, carcinogen, teratogen, suspected mutagen
Lead white	basic lead carbonate (hydrocerussite) 2PbCO3.Pb(OH)2	Pigment White 1	ancient times to mid 19th century; use in interior house paints prohibited in 1978 in U.S.	6.70-6.86	e=1.94; w=2.09	fine, fairly uniform, rounded tabular particles (0.5 - 10 microns); high birefringence under cross polars with 3rd or 4th order interference colors; complete extinction for single particles	dissolves in acids giving off CO2; fluoresces reddish purple; darkens with exposure to alkalis and sulfur	toxic, carcinogen, teratogen, suspected mutagen
Lithopone	ZnS (30%); BaSO4 (70%)	Pigment White 5	first produced 1874; used through first half of 20th century	4.3	2.3 (ZnS), 1.64 (BaSO4)	very fine particles (0.3-0.5 microns)	dissolves in HCl releasing sulfur fumes; can darken in the presence of iron	no significant hazards
Magnesite	magnesium carbonate, MgCO3	Pigment White 18	used in ancient plasters, occasionally gournd as pigment	3.0	1.508; 1.510; 1.700	translucent, colorless, angular crystals; high briefringence under crossed polars; extinction is complete and straight	soluble in acids	nontoxic; ingestion has a laxative effect
Silica / Quartz	silicon dioxide, SiO2	Pigment White 27	found in ochers and as filler	2.2-2.65	1.40-1.55	conchoidal fracture; slightly birefringent. Ground glass is isotropic.	dissolves in hydrofluoric acid	no significant hazards
Talc	hydrated magnesium silicate, Mg3Si4O10(OH)2	Pigment White 26	occurs worldwide	2.5-2.8	1.539; 1.589; 1.589	ground particles can be very small (2.0 microns); high birefringence	insoluble in water, acids or alkalis	no significant hazards
Titanium dioxide (anatase)	TiO2		synthetic used from 1928 till early 1940s	3.9	2.54-2.55	very small round particles (0.2-0.3 microns); high birefringence under crossed polars.	weak white fluorescence	no significant hazards
Titanium dioxide (rutile)	TiO2	Pigment White 6; CI 77891	mineral described in 1803; synthetic used as pigment from 1941	3.75-4.3	2.71 - 2.72	small round or prism particles (0.2-0.5 microns); high birefringence and interference colors	fluoresces gray or dark purple	no significant hazards
Witherite	barium carbonate, BaCO3	Pigment White 10; CI 77099	primarily 19th c.	4.3	1.529; 1.676; 1.677	Flat tablets that are colorless under plane-polarized light; high birefringence with complete extinction; interference colors are often seen	fluoresces a light blue color in both long and short wave UV	toxic by ingestion; skin contact may cause irritation
Zinc white	zinc oxide, ZnO	Pigment White 4; CI 77947	first produced ic. 1781, though not popular until 20th century	5.47-5.65	2.00; 2.02	very fine crystalline grains with low birefringence is low and first order interference colors	fluoresces yellow in longwave UV	inhalation or ingestion of dust may cause slight irritation

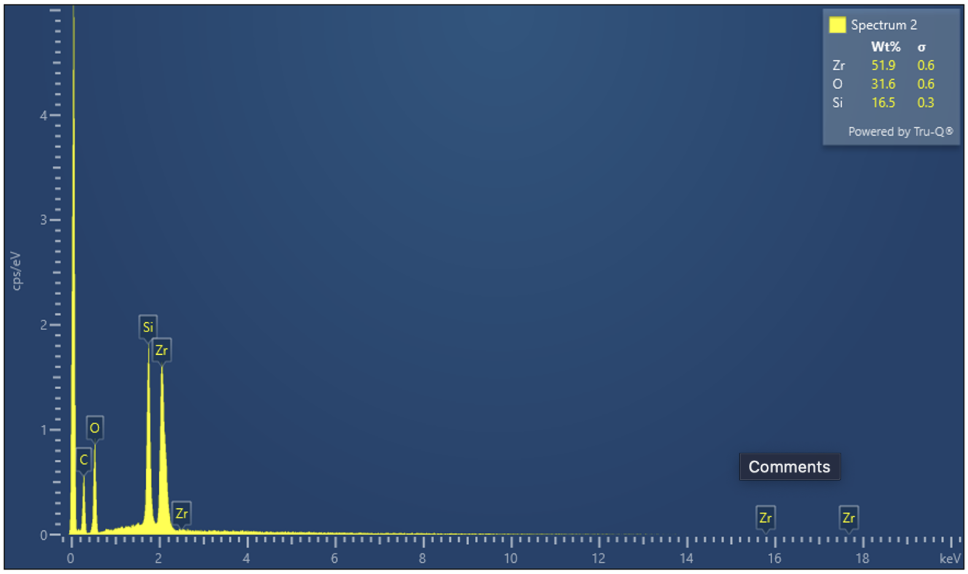
APPENDIX 3: SEM/EDS Spectral Information

Project 1 11/14/2022



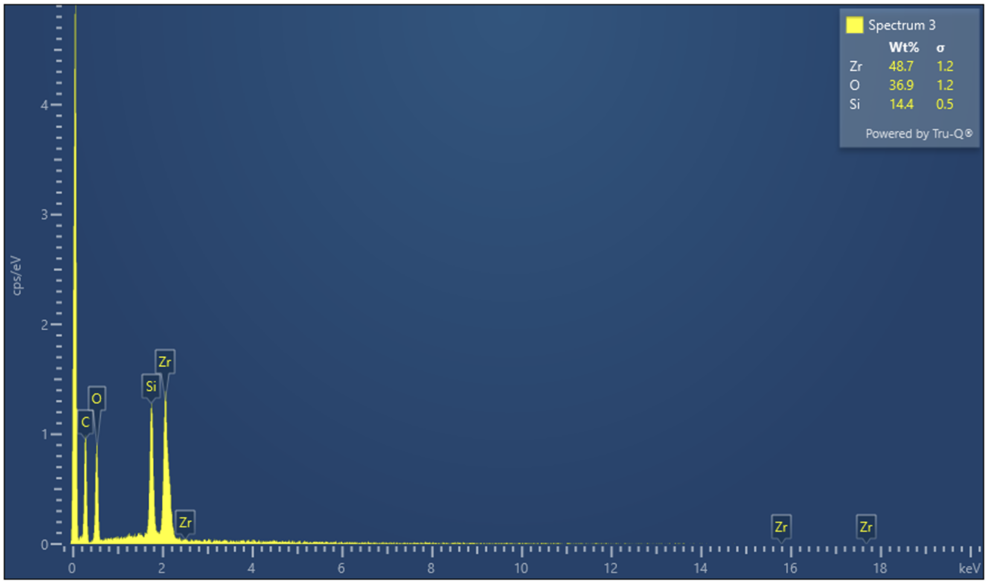
Project 1 11/14/2022

Spectrum 1								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
O	K series	53.67	0.18059	44.40	0.71	SiO2	Yes	
Si	K series	55.97	0.44354	43.50	0.65	SiO2	Yes	
Zr	L series	8.75	0.08745	12.10	0.80	Zr	Yes	
Total:				100.00				



Spectrum 2

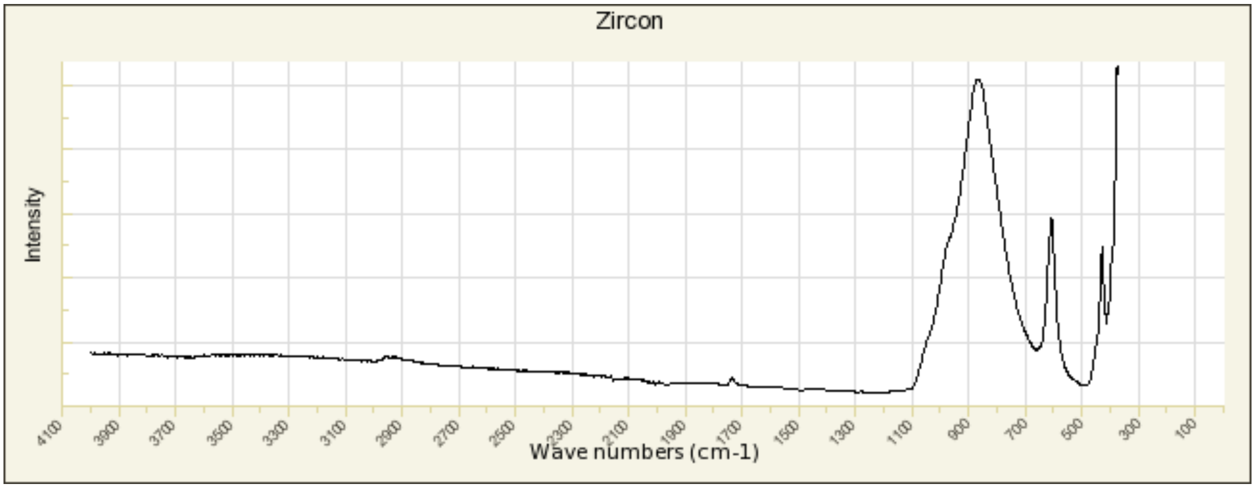
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
O	K series	26.87	0.09042	31.58	0.59	SiO2	Yes	
Si	K series	22.20	0.17593	16.48	0.30	SiO2	Yes	
Zr	L series	47.64	0.47639	51.94	0.63	Zr	Yes	
Total:				100.00				



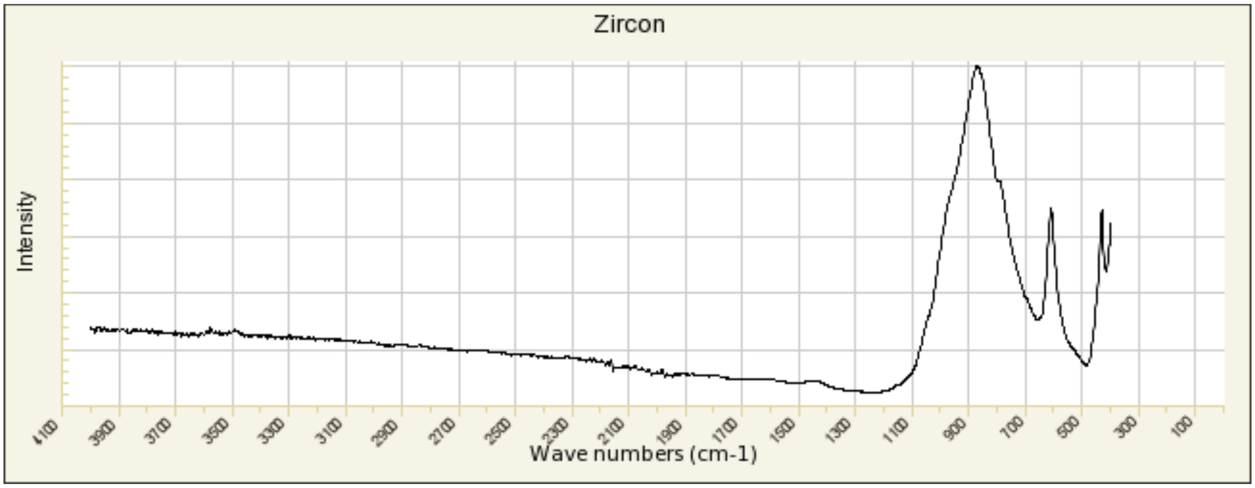
Spectrum 3

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
O	K series	30.99	0.10429	36.92	1.20	SiO2	Yes	
Si	K series	17.74	0.14059	14.36	0.55	SiO2	Yes	
Zr	L series	41.66	0.41659	48.72	1.25	Zr	Yes	
Total:				100.00				

APPENDIX 4: The RRUFF Project FTIR Spectra for Zircon Samples



FTIR-ATR spectrum for ID R050203. Source: https://rruff.info/chem=Si,Zr,O/display=default/R050203



FTIR-ATR spectrum for ID R050034. Source: https://rruff.info/chem=Si,Zr,O/display=default/R050034