Assessment of a Portable Near-Infrared Spectroscopy NIRS Instrument in Cultural Heritage Materials

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Abstract

This study presents the first approach to the use of the pocket-size molecular sensor *SCiO* in the field of cultural heritage. The portable, non-invasive, and compact instrument was developed in 2014 as a Startup project of Consumer Physics (Tel Aviv, Israel), bringing Near-Infrared Spectroscopy NIRS to consumers mostly interested in the agricultural field.

The main purpose of the project was to explore possible areas of application in cultural heritage in which SCiO could be useful, evaluating the performance and suitability of the instrument, same as future lines of work and improvements. The methodology and results obtained, including the analysis of the spectra, can be a point of reference for future studies using SCiO or similar devices that use NIR.

The materials tested in this study were paintings materials; pigment, binder, and varnish reference samples, a canvas painting reproduction, and five paintings of the Italian artist Lino Piccoli (1926-2010), selected as case studies to make possible the exploration of the painter's palette.

Keywords: SCiO (Consumer Physics), Near Infrared spectroscopy NIRS, portable, non-invasive, paintings, Lino Piccoli.

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List of abbreviations

Abbreviation	**Term**
IRS	Infra-red spectroscopy
NIR	Near infrared spectroscopy
PCA	Principal component analysis

Introduction

The chemical and physical characterization of works of art through analytical techniques grants a deeper level of understanding of the materiality, and therefore contributes to further research in many areas such as archaeology, history, art history, and conservation. Therefore, the development and application of scientific approaches to give light to the cultural heritage questions are considered essential for the study of objects, their conservation, and valorization.

Bearing in mind the importance and challenges implied in the analysis of artistic and historic works of art, the introduction of novel devices with desired characteristics into the field, must be contemplated as a major contribution to the study of cultural heritage. Employing non-invasive portable devices, such as SCiO NIRS molecular sensor, provides an opportunity for a broader sample and data collection given that no samples or preparation are needed, and the materials are not destroyed or affected when carrying out analyses. Also, being a quick method that permits the obtention of data almost immediately, allows doing a fast check of the suitability of the data for interpretation and a better decision making on areas to be sampled, or the relevance of performing further analysis.

Despite its good performance in the agricultural and pharmaceutical analysis (Beć, Grabska, Plewka, & Huck, 2021; Kaur, Künnemeyer, & McGlone, 2017; McVey, Gordon, Haughey, & Elliott, 2021; Wiedemair, Langore, Garsleitner, Dillinger, & Huck, 2019; Wilson, Kaur, Allan, Lozama, & Bell, 2017; Zgouz et al., 2021), *SCiO* was never tested in heritage objects. The same applies to most instruments using the Near-Infrared range (800-1200 nm), in which only overtones and combination bands can be observed, making the interpretation of spectrum more complex (Boselli et al., 2009); however, in the recent years there has been an increasing interest in the development of chemometrics approaches to NIRS given the many advantages of this technique (Cséfalvayová, Strlič, & Karjalainen, 2011; Lugli et al., 2021; Strlič et al., 2010).

This study presents the results of the analysis performed with the SCiO molecular sensor on painting materials. A small group of binders and varnishes applied on the surface of a canvas, and the Pigments Checker v.5 chart produced by CHSOS, were employed as reference samples. The Gorgias reflectance library of spectra was used to establish comparison and verification of the results, given that the Gorgias Reflectance System is a more robust instrument.

Subsequently, a reproduction of an oil on canvas painting elaborated by Matteo Positano from Emmebi Diagnostica Artistica was tested to assess possible variation on more complex paint mixtures. Finally, five canvas paintings of the artist Lino Piccoli were selected to test the performance of SCiO on real case studies evaluating the possibility of characterizing the painter´s color palette.

Lino Piccoli (1926-2010) was cubo-futurist contemporary artist, from the Veneto region in Italy. Piccoli was very active around the world, and worked especially in the region of Puglia, where he transferred in the 80´s and lived for around three decades until he died. Representations of Puglia´s landscapes and traditions, mainly Alberobello and surrounding towns, were a recurrent topic found in his paintings; this can be observed in three landscape paintings selected as case studies.

His oil painting technique is more or less consistent throughout his career, but his color palette changes dramatically depending on the themes and places represented in his works of art.

This thesis work is divided in 4 parts:

The part *1. Theoretical Background*, consist of a summary of the technical details and physical processes involved in Infrared spectroscopy, especially in the Near-Infrared range, and the characteristics of SCiO molecular sensor; aspects necessary to put in context and understand the line of the work and contribution of this research project. A brief state of the art of previous studies where SCiO was employed, was also included for reference.

The part *2. Experimental*, gives an overview of the materials and methods employed in the research project, parameters, data acquisition, pre-processing, and data analysis, same as the Gorgias reflectance library used for comparison of the spectra.

The part *3. Results and discussion*, explains the developments of this thesis work. It includes the spectrum and principal component analysis, a description of the results obtained, together with the interpretation of the data.

The final part of this work, *4. Conclusions*, presents the final remarks and considerations of the materials, methods, advantages, disadvantages, and challenges faced during the project, assessing the suitability of SCiO for the study of cultural heritage, paintings in this case, suggesting future lines of work.

The appendix section contains three parts the A. *Pigments checker* spectrum database for future studies reference; *B. Points of analysis* of the case studies; C. *Lino Piccoli*, shows a further record of the activities developed in the framework of the Lino Piccoli valorization project, which comprehends a field trip to Puglia and a thorough literature review of his biographical information and career activities.

1. Theoretical background

1.1 Infrared Spectroscopy

Infrared spectroscopy is a type of vibrational spectroscopy technique widely used in cultural heritage for elucidating the chemical composition of materials. It consists of the study of the interactions of Infrared light with matter, giving place to vibrations of the molecules (Derrick R., Michele ; Stulik, Dusan; Landry M., 1999).

Considering that Infrared uses a lower energy than the visible, ultraviolet, and X-ray, it can only induce fundamental vibrational transitions, in a range lower than the necessary for electronic transitions (Pasquini, 2003). Therefore, its field applications are directed to the study of compounds that present small differences in the rotation and vibration of the molecules when excited. The vibration of the molecules is divided into stretching, a change in the interatomic distance (symmetric or asymmetric); and bending: a change in the angle between two bonds (rocking, scissoring, wagging, twisting).

When IR light interacts with the sample, it can be reflected, absorbed, or transmitted, depending on the physical and chemical properties of the material, giving place to the different modes in which spectral information is displayed in the Y axis.

The infrared IR region covers the range between 780 to 1 mm, it is divided into three ranges: Near 780-2500 nm, Mid 2500-5000 nm, and Far 5000-10.000nm. Although the Mid-infrared range, presenting the fingerprint region, is the most used for the analysis of materials, nevertheless, the Near-Infrared range has had a large application field in the agriculture, food, and medicine industries.

1.2 Near-Infrared NIR

As mentioned before, the NIR region comprehends the range between 780-2500 nm (12.820-4000 cm^{-1}), right after the visible red region. Given that it is accessible through optical components, low cost, fast measurements, easy handling, miniaturization reducing the size and weight. Nevertheless, this poses a challenge to preserve the wavelength range and resolution.

NIR is divided into 3 regions: region I: from 780-1200 nm, also called the “Herschel” region, where electronic transitions can be observed, presents overtones and combination bands; the region II: 1200-1800 nm, presents the first overtones, and the region III: 1800-2500 nm, presents combination bands.

The spectra produced in the NIR region comprise overtone and combination bands that come from the fundamental vibrations of the mid-IR region, producing overlapping bands; for this reason, “single band spectroscopy and qualitative band assignments are nearly impossible”(Derrick R., Michele ; Stulik, Dusan; Landry M., 1999, p. 27). Like the visible range, the values in this region are measured in wavelength (nm) instead of wavenumber (cm^{-1}).

The main applications for the NIR region in cultural heritage are related to multispectral and hyperspectral imaging studies (Cséfalvayová et al., 2011; Lugli et al., 2021; Mahgoub, Gilchrist, Fearn, & Strlič, 2017), as well as quantitative chemical analysis through chemometric multivariate analysis (Carlesi et al., 2016; Romero, 2011; Strlič et al., 2010)

The term chemometrics refers to the implementation of mathematical and statistical techniques for the manipulation of analytical chemistry data (Pasquini, 2003, p. 211). It has been widely applied in spectroscopy, especially in the field of NIR analyses for the improvement of spectral data and development of quantitative analysis in large datasets, given their complexity. One of the most largely used in the cultural heritage field is Principal Component Analysis PCA, within the multivariate analysis field (Romero, 2011), as it helps to display graphically groups of data from a matrix within a spectral range, generating principal components, in this case, used to distinguish between painting samples based on their differing compositions, facilitating the interpretation of large datasets (Carlesi et al., 2016).

1.3 SCIO

1.3.1 Specifications

SCiO mini version 1.0

Size: 54 x 36.4 x 15.5 mm

Weight: 35 g

Range: 750-1070 nm (13514 – 9346 cm^{-1})

Wavelength selector: Bypass filter

Source: LED

Wavelength resolution: < 10 cm−1

Spectral resolution: 28 nm average (McVey et al., 2021, p. 3)

Scan time: 2-5 s

Non-invasive: 2 cm distance

Silicon photodiode (CMOS) array detector (12 elements)

Figure 1-1: SCiO Molecular Sensor by Consumer Physis logo.

The molecular sensor SCiO is a low-cost, portable, and non-invasive NIR spectrometry device developed by Consumer Physics (Tel Aviv – Israel), and commercially launched in 2014. It uses micro-optical components for the miniaturization, according to Consumer Physics, still providing sensitivity and accuracy comparable to a benchtop device. “The low power consumption and zero warm up time make it highly responsive and extremely efficient, allowing it to perform hundreds of scans from a small rechargeable battery” (Wiedemair et al., 2019).

1.3.2 The Lab Application

Consumer physics has developed a certain purposed Cloud-based data analysis software called The Lab, which can be connected to SCiO and operated via Bluetooth; it serves for the pre-established calibration, data acquisition, spectrum visualization in real-time, data storage, chemometric prediction models creation, amongst other features constantly improved and implemented into the app.

All these features can be applied automatically using the software; hence, technical knowledge in physics or chemistry is not necessary for using SCiO or The Lab app, making it extremely consumer friendly. Nevertheless, the patented software is closed, and the processing methods are in most cases unknown. Besides it requires a Researcher profile with a cost of 3000USD for data download, and access to features such as model creation.

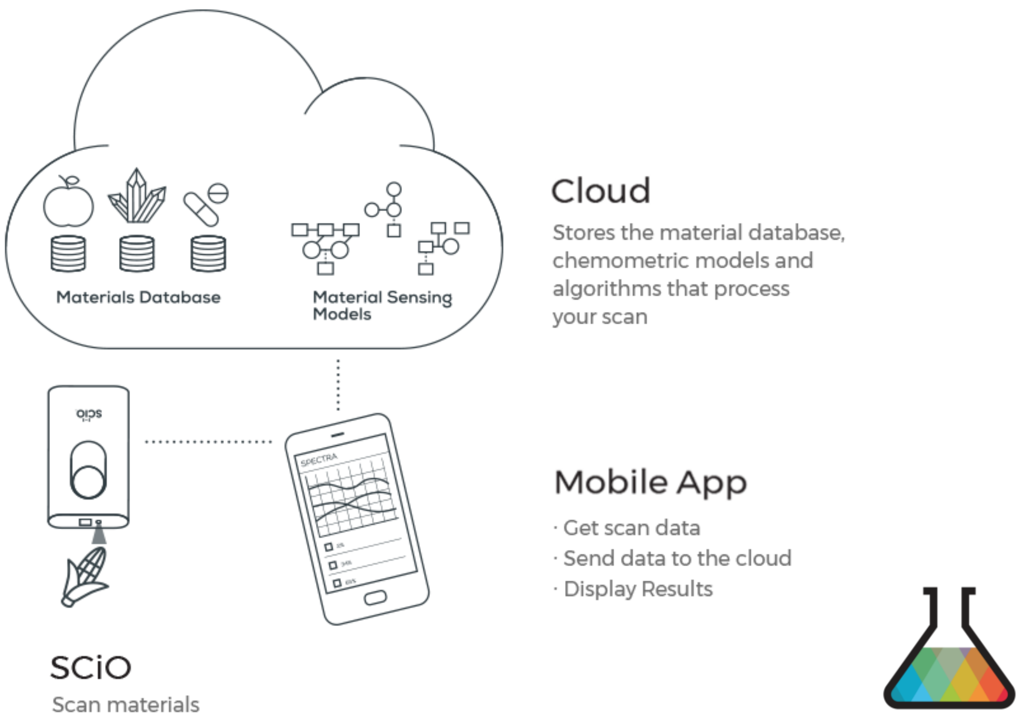


Figure 1-2: The Lab mobile application[1]

[1] https://www.consumerphysics.com/technology/

2. Experimental

2.1 Materials

Reference materials and reliable reproduction samples of painting materials were selected due to the wide use of pigments, binders, and additives in the elaboration of historical and artistic objects, potentially providing important information about the context of production.

2.1.1 Reference Samples

The reference materials constitute samples of known composition which serve as a base to establish comparison based on the color and spectra obtained. In this study pigment and binder samples were used, as they constitute, they main components to be characterized in order to obtain technical information about pictorial layers.

A small number of artistic binders and varnishes commonly used for paint purposes served as a reference for the analysis of paintings' reproductions and case studies. The materials selected were linseed oil, egg tempera, dammar resin, acrylic varnish, rabbit glue, gouache varnish, Arabic gum, and an industrial water-based varnish. They were applied in liquid on an industrial canvas using a brush and air-dried. In the case of the solid materials (rabbit glue and Arabic gum) these were dissolved in warm water.

The Pigments Checker v.5 developed by Cultural Heritage Science Open Source CHSOS (Cosentino, 2019) consists of a chart with 69 historic and modern pigment samples on acrylic binder, and the corresponding acrylic binder reference.

Figure 2-1: Pigments Checker v.5 reference samples. (CHSOS)

2.1.2 Reproduction Canvas Painting

A reliable reproduction of an oil on canvas painting, elaborated by Matteo Positano from the Emmebi laboratory that contains 40 samples of historic pigments including pure pigments and mixtures on different preparation layers.

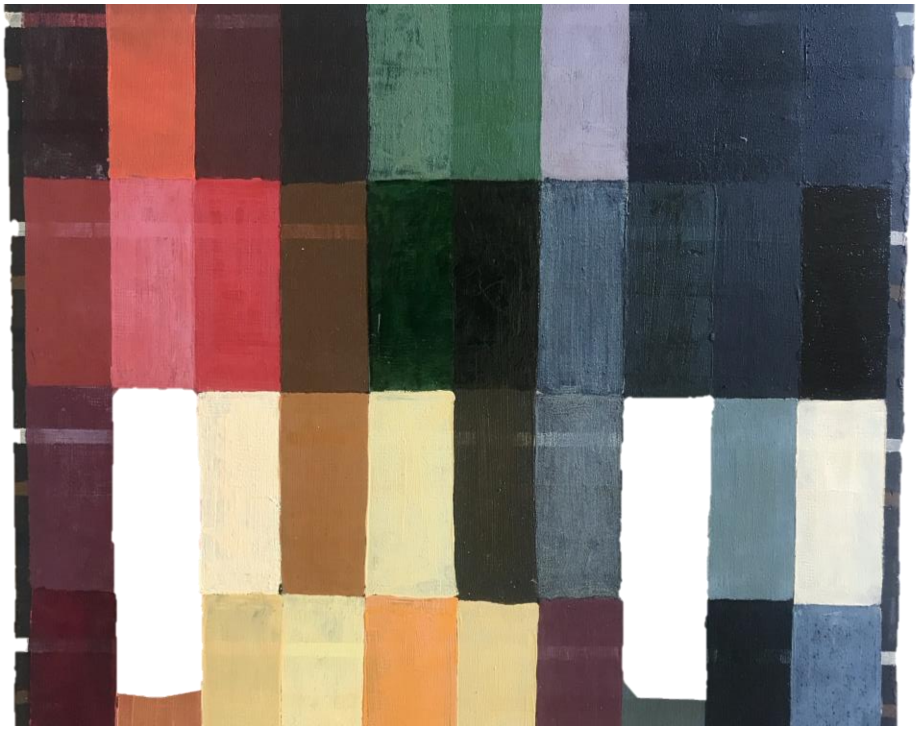


Figure 2-2: Oil on canvas paintings reproduction. (Emmebi Diagnostica Artistica)

2.1.3 Case studies: Lino Piccoli Canvas Paintings

After obtaining enough information from the reference and reproduction samples, five canvas paintings of Lino Piccoli, from different periods and displaying a similar color palette, were selected to be analyzed with SCiO in search of the painter's palette.

The paintings depicting landscapes of Puglia land still lifes belong to a private collection. The main criteria for the selection of the paintings of Lino Piccoli as case studies were the rich palette and wide areas of color employed by the artist, as well as the absence of a protective topcoat such as a varnish, allowing the direct analysis of the oil-based paint layers applied over a canvas.

Title Alberobello
Author Lino Piccoli
Technique Oil on canvas
Size 70 x 90 cm
Year 2003

Figure 2-3 Case study I.

Title *Natura Morta Cubista 1*
Cubist Still Life
Author Lino Piccoli
Technique Oil on canvas
Size 25 x 35 cm
Year 2004

Figure 2-4 Case study II.

Title *Natura Morta Cubista 2*
Cubist Still Life
Author Lino Piccoli
Technique Oil on canvas
Size 25 x 35 cm
Year 2004

Figure 2-5 Case study III.

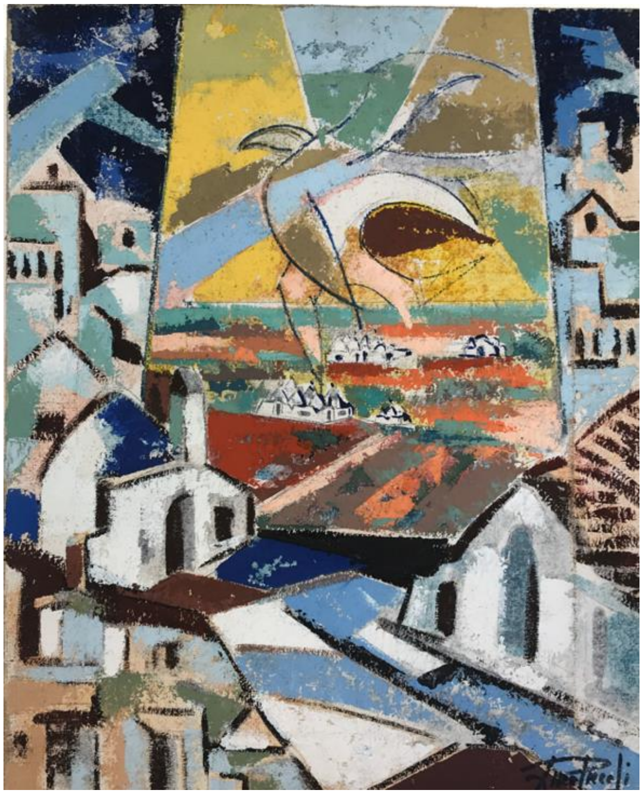


Figure 2-6: Case study IV.

Title Valle D´Itria

Author Lino Piccoli

Technique Oil on canvas

Size 40 x 60 cm

Year 1988

Figure 2-7: Case study .

Title *Finestra sul Mare*

Window over the Sea

Author Lino Piccoli

Technique Oil on canvas

Size 40 x 60 cm

Year 1996

2.2 Methods

The molecular sensor SCiO (Consumer Physics -Tel Aviv, Israel) was used to acquire spectrum from the reference materials, reproduction samples, and case studies, connected via Bluetooth through The SCiO Lab mobile application, and fast-checked in real time through the SCiO Lab web application.

The data was also processed and plotted using Excel and MATLAB to avoid the introduction of unknown algorithms and pre-processing methods applied automatically by the SCiO Lab application.

2.2.1 Parameters

The parameters for calibration and sampling interval of 1 nm, were automatically fixed by the Lab application after creating a Collection of samples.

The calibration was performed by introducing SCiO inside of its case facing down the white tile designed for this purpose; this happened automatically before any measurement, and after approximately 10 scans; it can also be done manually, always through the SCiO Lab application. A background spectrum was also acquired before the analysis of the sample; its purpose is to be extracted during the data processing to avoid possible external signals.

Figure 2-8: SCiO case, outside and inside.

2.2.2 Data Acquisition

When the calibration was finished the instrument was flipped out and positioned with the light window facing directly over the sample mounted on a shade that acted as a barrier to maintain a 2 cm distance, and a consistent vertical position necessary to allow the interactions of the light emitted by the LED source and avoiding external light noise. SCiO was actioned to start scanning either through the Lab App “Scan” feature or through the button in the center of the device.

Figure 2-9: SCiO components.

2.2.3 Data Pre-processing

The data was automatically pre-processed, immediately available for visualization after the acquisition, and simultaneously through the mobile and desktop SCiO Lab application, displaying spectra in which further processing algorithms can be applied.

The processing method consists of the extraction of the background from the sample raw date generating values displayed as spectrum data that can be downloaded in CSV format and identified as *spectrum raw.* Other algorithms and processes applied by the SCiO Lab app are unknown.

According to information provided by Consumer Physics, the custom processing mode “It is equivalent to applying a preprocess of: log, 1st derivative with a window of 35 and polynomial degree of 2, subtract average”.

The data was plotted again using MATLAB, and Excel to re-organize the information, this with the aim of observing a non-processed spectra in contrast with The SCiO Lab spectra

2.2.4 Analysis of results

The results were analyzed considering the information consigned in the literature review: on one hand about the general framework of materials in cultural heritage, on the other about the materials identified in similar case studies.

In this case, the Gorgias Reflectance Spectral Library, obtained from a Pigments Checker chart with the Gorgias Reflectance Spectrometry System, a more robust device that works in the spectral range 200-1000 nm (VIS-NIR), coincides for the most part with the range of SCiO (740-1070 nm); proving very useful for comparison of results. However, given that the charts versions used are different, some pigments references tested with SCiO do not exist in the Gorgias spectral database

Figure 2-10: Gorgias Reflectance Spectrometer for Art Examination[2]

[2] https://chsopensource.org/reflectance-spectroscopy-system/

Furthermore, the results obtained from the reference and reproduction samples were the basis for the interpretation of the Piccoli case studies spectrum. This allowed us to verify and determine the possible contributions of SCiO for testing the pigments reference samples.

2.2.5 Principal Component Analysis PCA

PCA multivariate analysis of the five case studies was carried out with the purpose of predicting possible variations, employing the Lab App to generate the graphs in which the distribution of point of analysis could be observed along a 3D space.

3. Results and discussion

3.1 Reference Materials

3.1.1 Pigments Checker V. 5

Pigments are the main component of pictorial layers, providing the color to the paint mixture. Relevant spectra of the pigments reference samples from the Pigments Checker chart (CHSOS) are displayed in comparison to the Gorgias Spectral Library; both plotted using MATLAB. A full account of the Pigments Checker spectrum collection can be found in the Appendix A.

The results with the best correlation were the ones obtained from the blue and green pigments. For instance, two spectrum examples of ultramarine (figures 3-1 & 3-2) and chrome oxide (figures 3-3 &3-4) for both SCiO and Gorgias can be observed below.

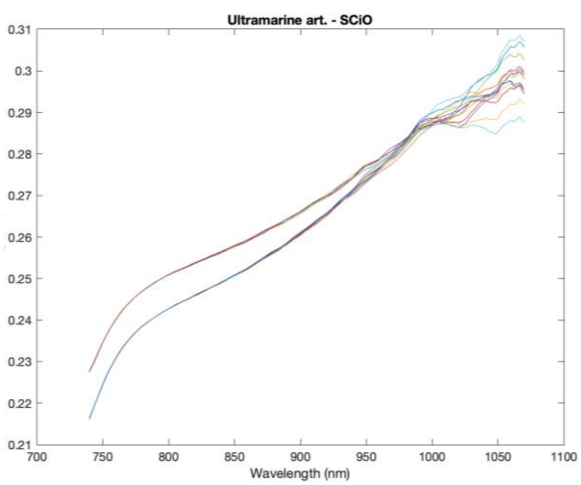


Figure 3-1: Ultramarine art - SCiO.

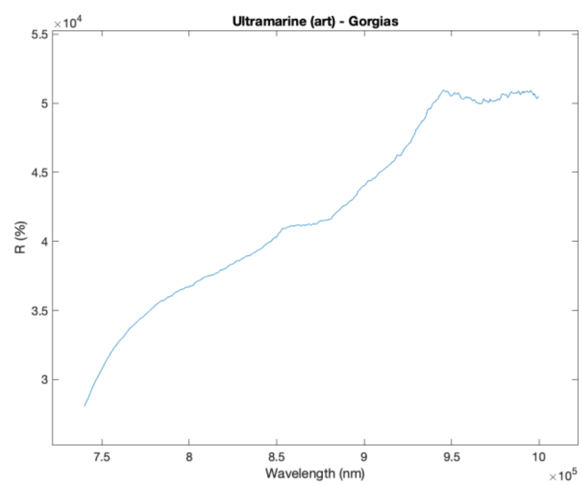


Figure 3-2: Ultramarine art - SCiO.

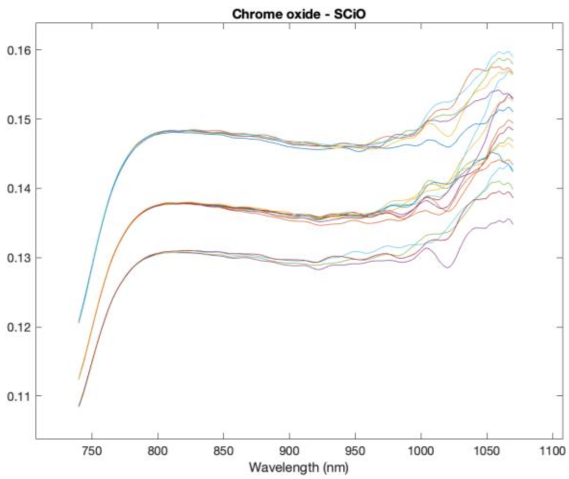


Figure 3-3: Chrome oxide - SCiO.

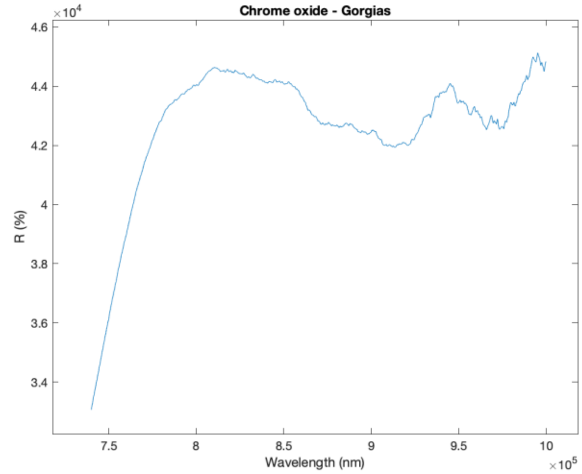


Figure 3-4: Chrome oxide - Gorgias.

As for the red and yellow pigments, the correlation depends largely on the composition of the samples, earth pigments such as ochres (figures 3-5, 3-6, 3-7 & 3-8) present good correlation, but pigments such as artificial vermillion (figures 3-9 & 3-10) present large differences in the spectrum.

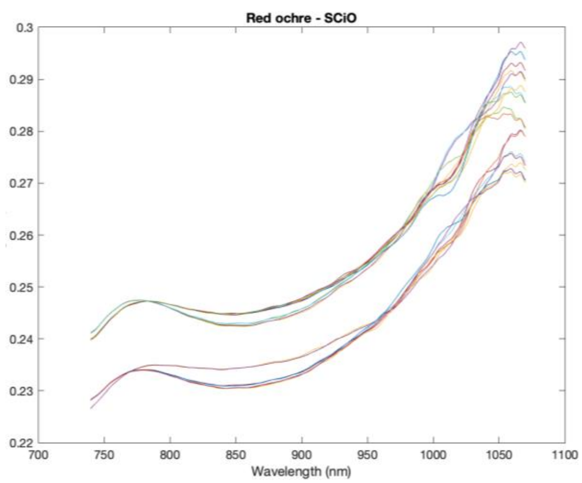


Figure 3-5: Red ochre - SCiO.

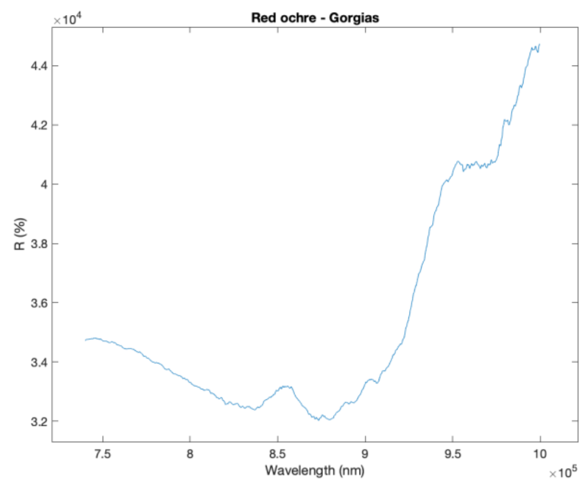


Figure 3-6: Red ochre - Gorgias.

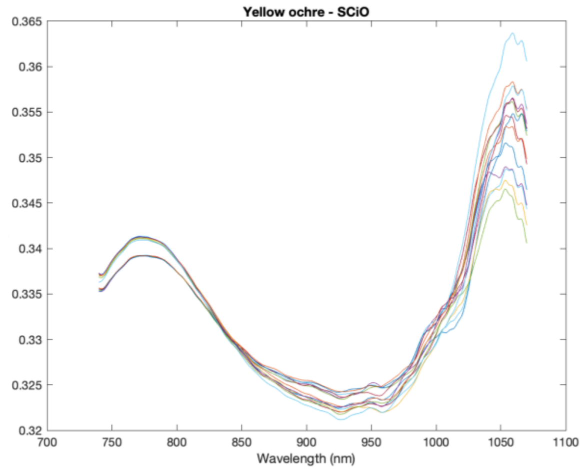


Figure 3-7: Yellow ochre - SCiO.

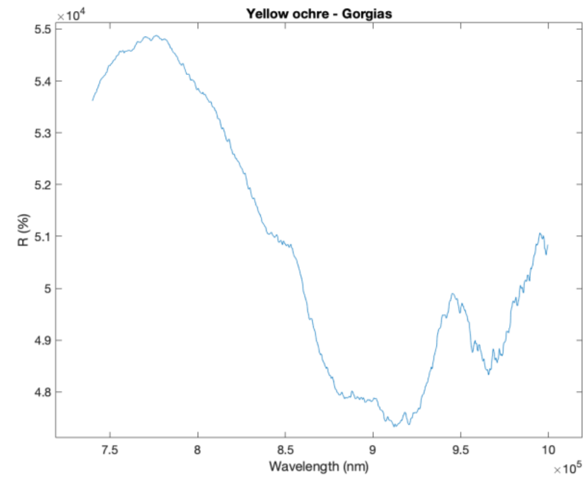


Figure 3-8: Yellow ochre - Gorgias.

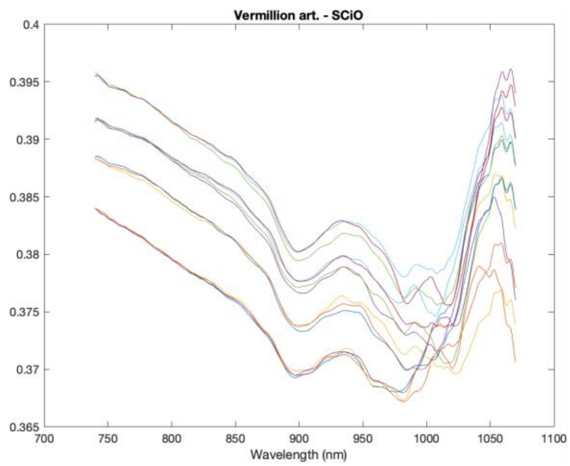


Figure 3-9: Vermillion (art) - SCiO.

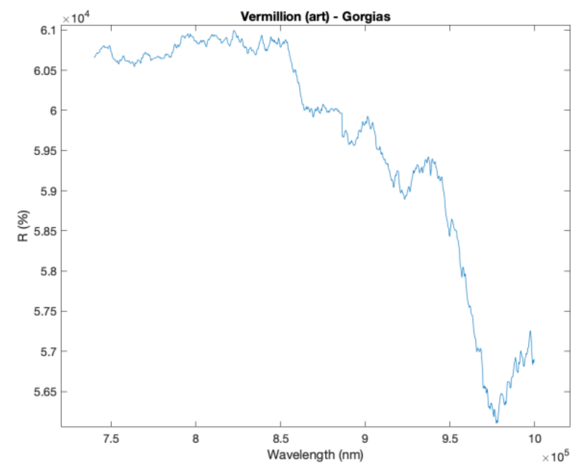


Figure 3-10: Vermillion (art) - Gorgias

In white and black pigments, the correlation is poor in most cases. For the white pigments there is a lot of noise in the Gorgias spectra (figure 3-12), making it impossible to stablish a good comparison with the SCiO spectra (figure 3-11); for the black pigments, the opposite happens, the spectra look all very similar, impeding the differentiation between samples. Nonetheless, in specific cases such as lithopone (figures 3-13 & 3-14), and Iron gall (figure 3-15 &3-16) a good correlation of spectra can be observed.

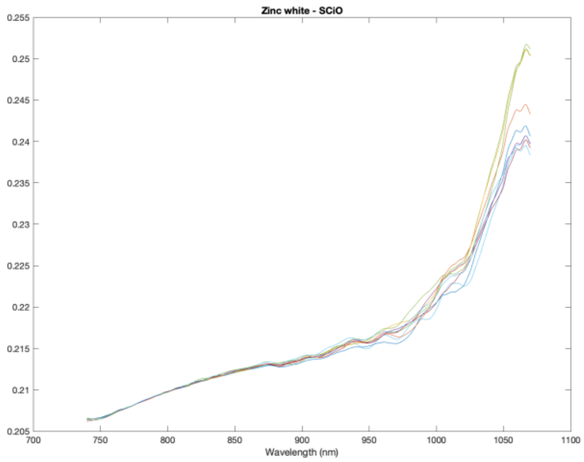


Figure 3-11:Zinc white - SCiO.

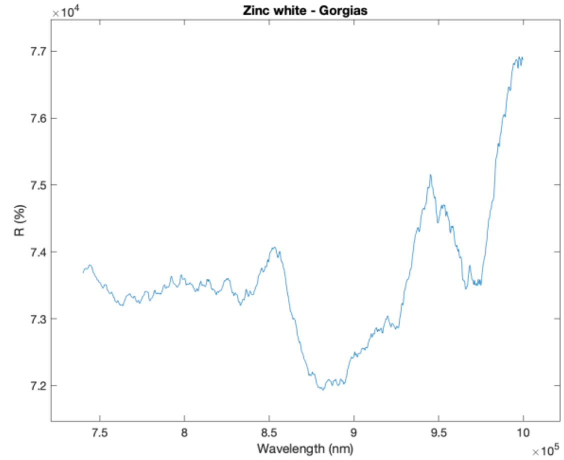


Figure 3-12: Zinc white - Gorgias.

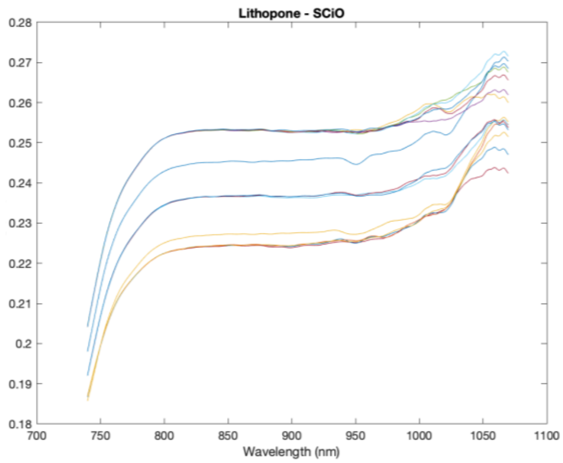


Figure 3-13: Lithopone - SCiO.

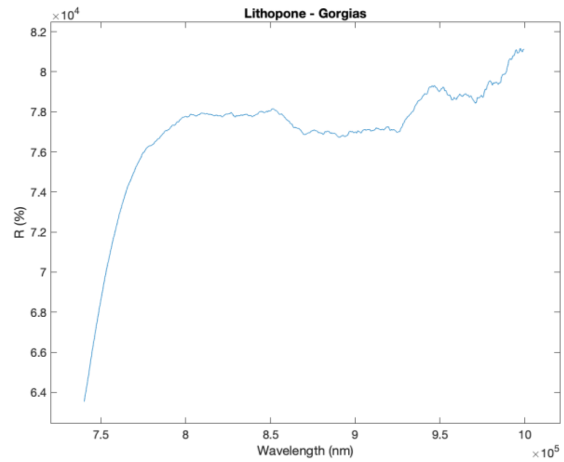


Figure 3-14: Lithophone - Gorgias.

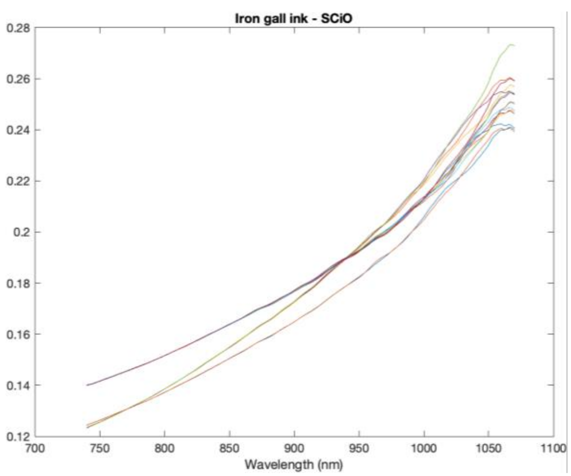


Figure 3-15: Iron gall - SCiO.

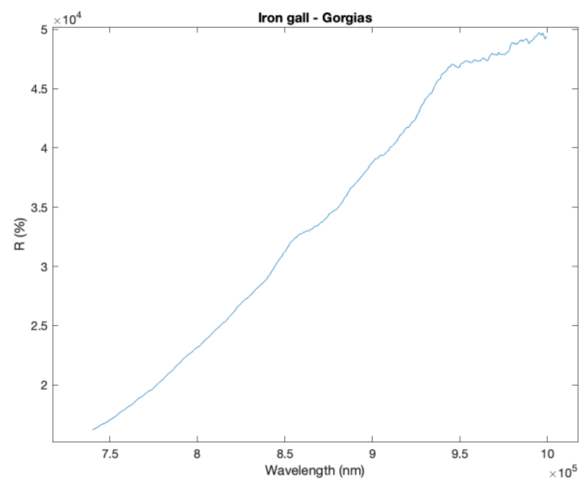


Figure 3-16: Iron gall - Gorgias.

3.1.2 Binder reference samples

Binders determine the pictorial technique, and depend mostly on the support used:; for instance, tempera employs a protein binder and is mostly used in panel paintings, oil paintings are used in canvas paintings, and the use of acrylic binders (synthetic polymers) is widely spread.

The spectrum obtained from this collection (figure 3-17) appear similar in most cases,

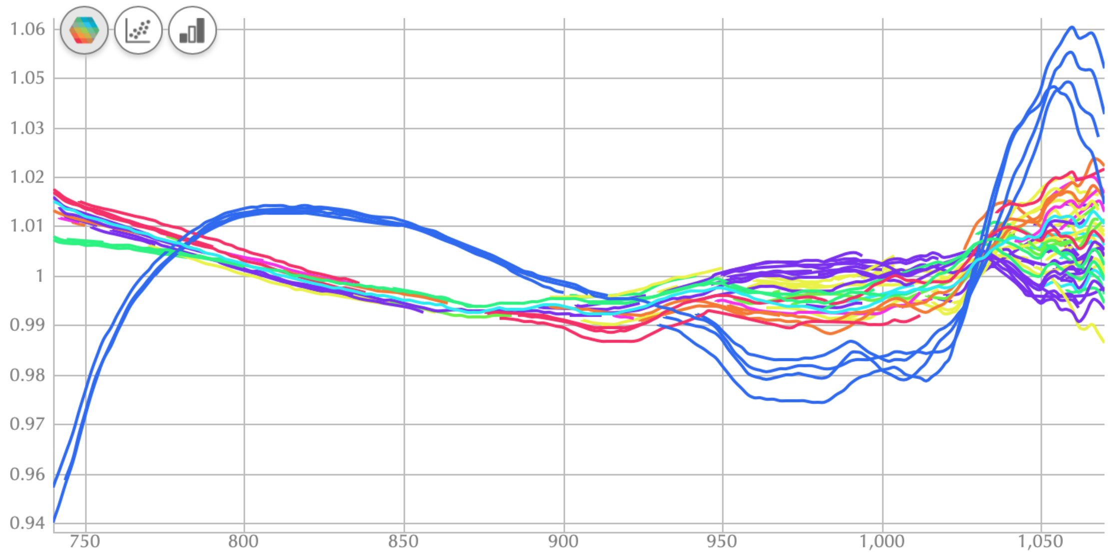


Figure 3-17: Binder reference collection spectrum. (SCiO Lab app)

As it can be observed in the figures below, the linseed oil and rabbit glue spectra, processed using MATLAB, present the same characteristics.

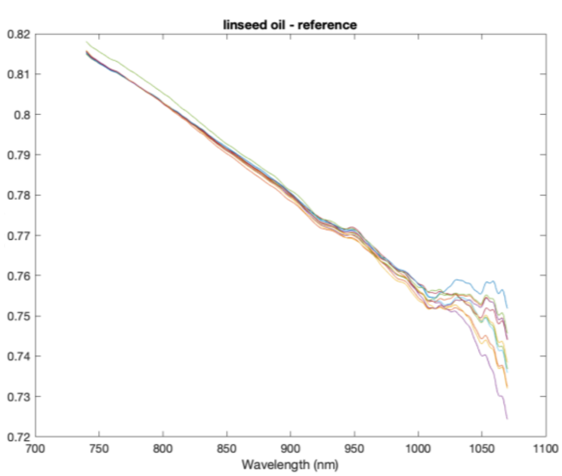


Figure 3-18: Linseed oil reference spectrum.

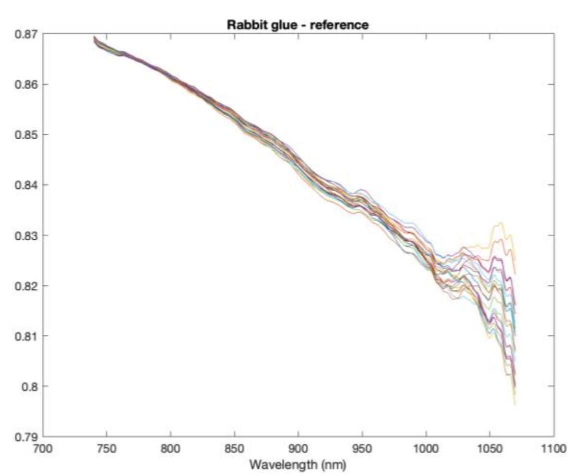


Figure 3-19:Rabbit glue reference spectrum.

The only exception is the acrylic binder (in blue) displayed in the processed spectra obtained through the SCiO Lab application (figure 3-17), comparable to the *figure 3-20: Acrylic binder* reference spectrum plotted with MATLAB without any further processing.

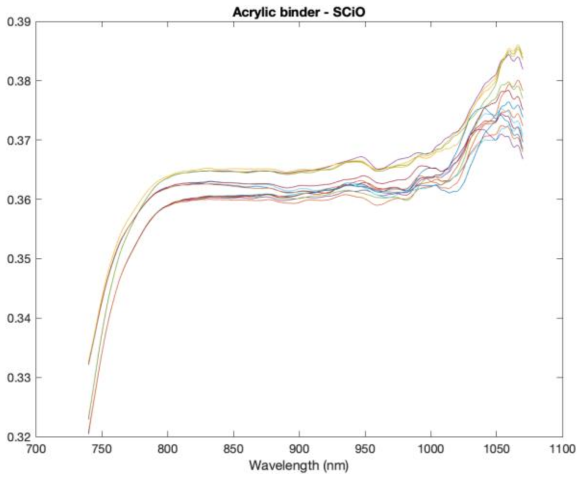


Figure 3-20: Acrylic binder – SciO

3.2 Reproduction canvas painting

The spectrum obtained from the reproduction canvas painting present a direct correlation with the reference materials spectrum, presenting in most cases a good spectrum.

Below a few examples of single pigments can be observed.

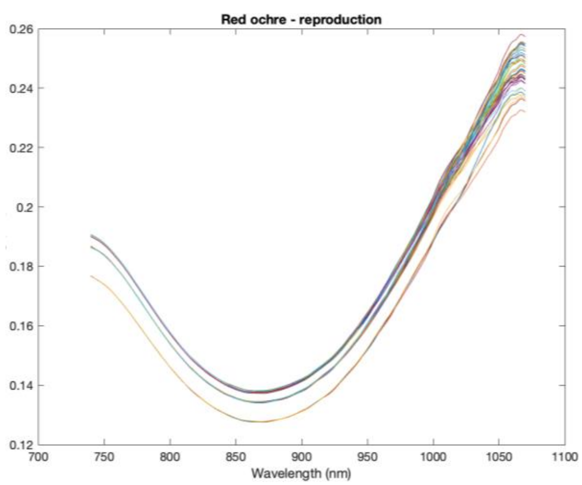


Figure 3-21: Red ochre reproduction spectrum.

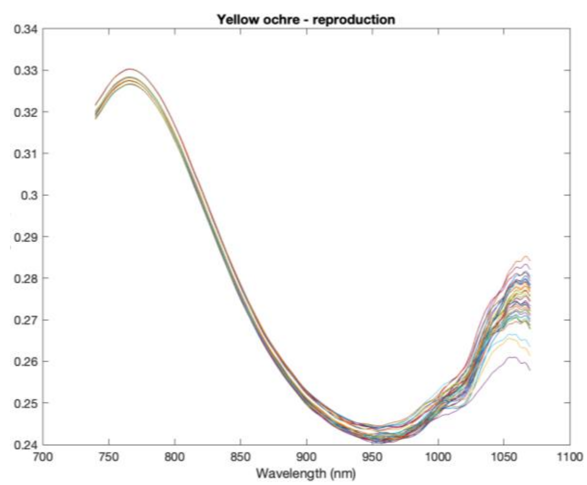


Figure 3-22: Yellow ochre reproduction spectrum.

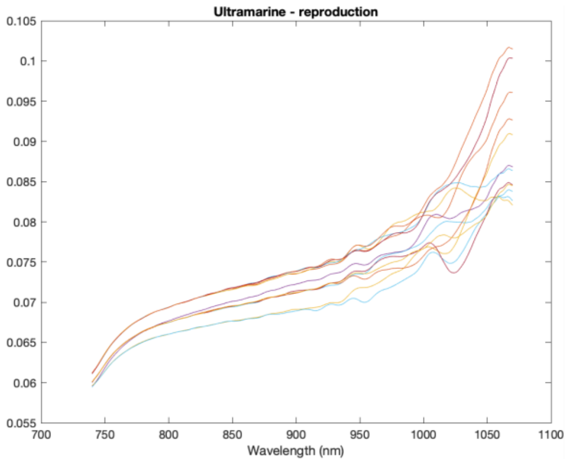


Figure 3-23: Ultramarine reproduction spectrum.

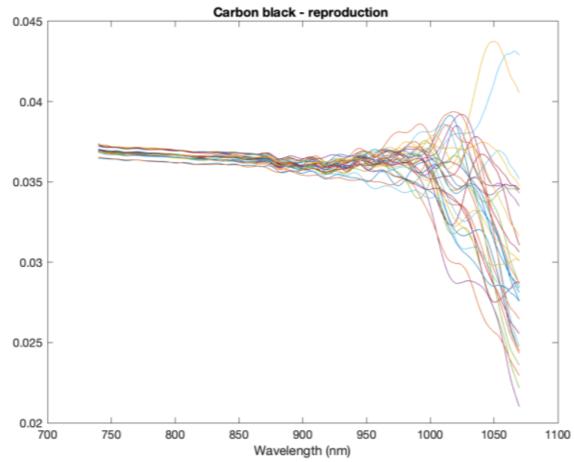


Figure 3-24: Carbon black reproduction spectrum.

3.3 Case studies

For the five case studies, the areas to be measured where selected according to the colors present: white, black, blue, red, yellow, orange, and green, further analysis were performed including different hues from light to dark, and other possible mixtures.

3.3.1 Spectrum

Blue

The spectrum obtained from the blue points of analysis display similar characteristics matching the reference spectra of ultramarine blue.

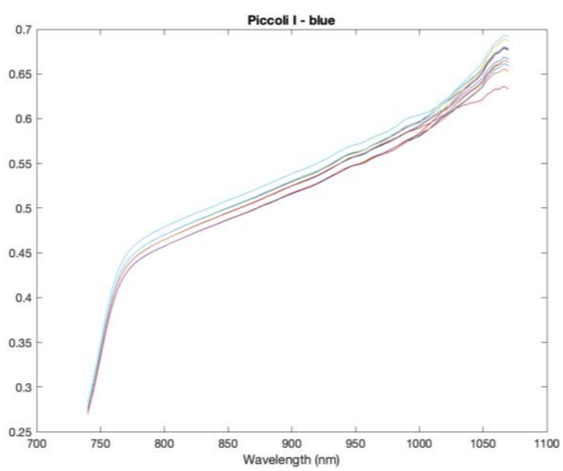


Figure 3-25: Case study I, blue.

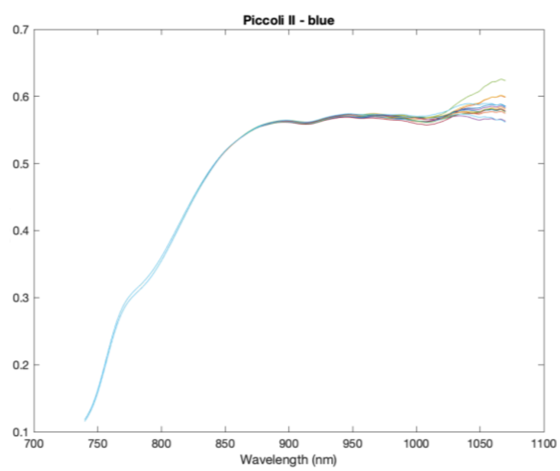


Figure 3-26: Case study II, blue.

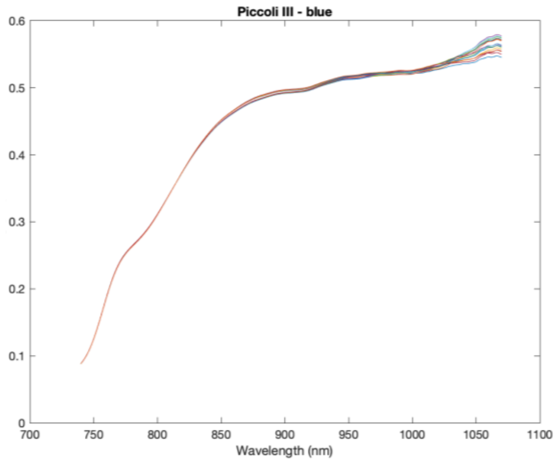


Figure 3-27: Case study III, blue.

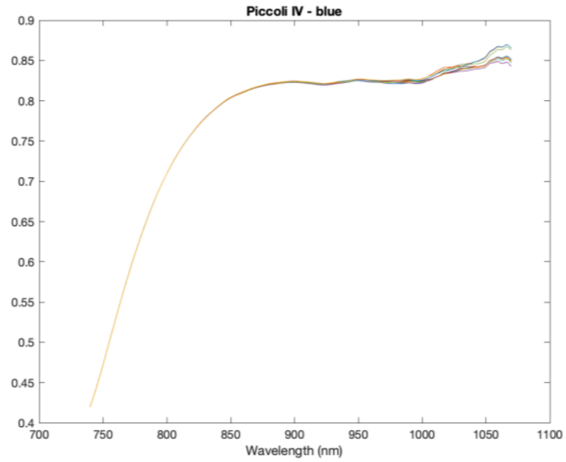


Figure 3-28: Case study IV, blue.

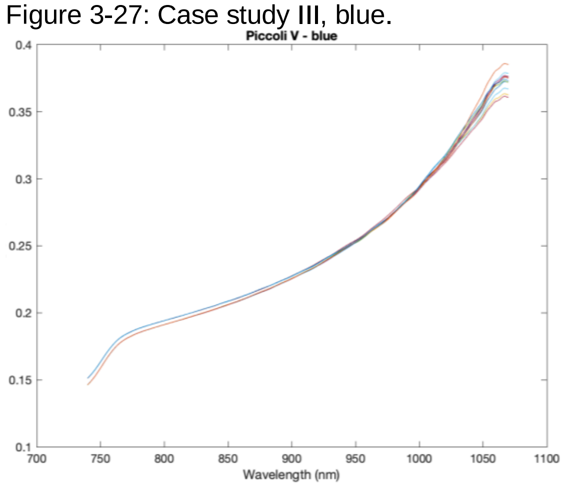


Figure 3-29: Case study V, blue.

Green

All of the green spectra present the same characteristics and match the reference spectra of Green earth.

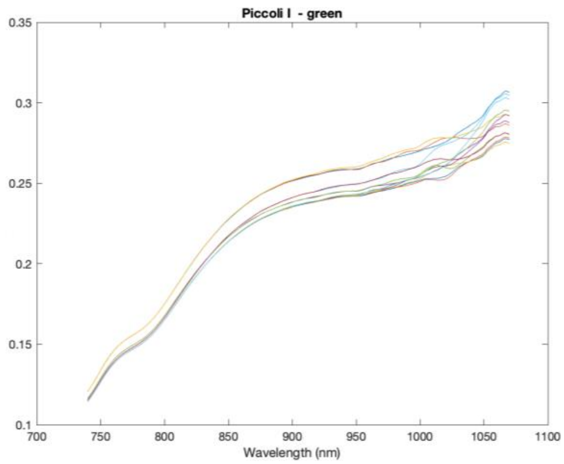


Figure 3-30: Case study I, green.

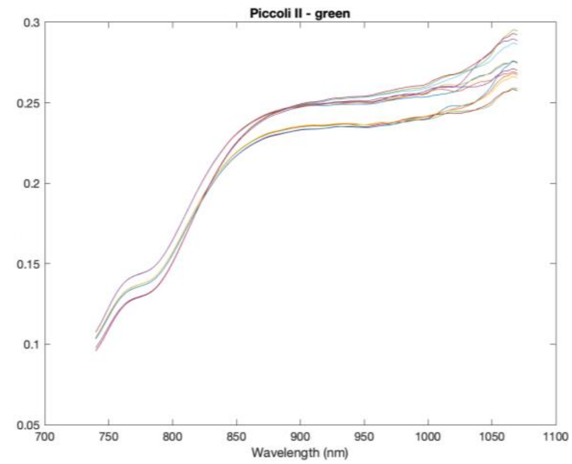


Figure 3-31: Case study II, green.

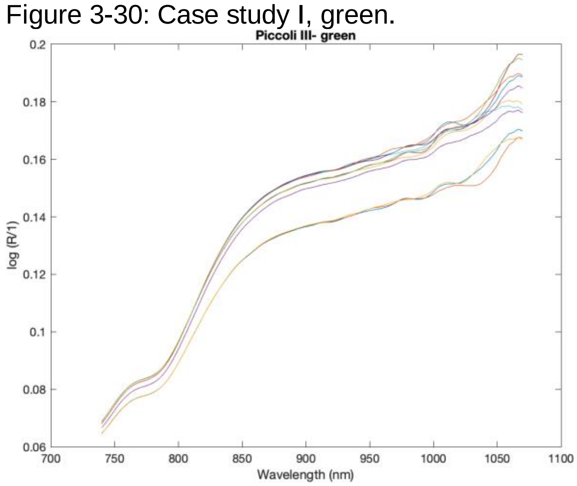


Figure 3-32: Case study III, green.

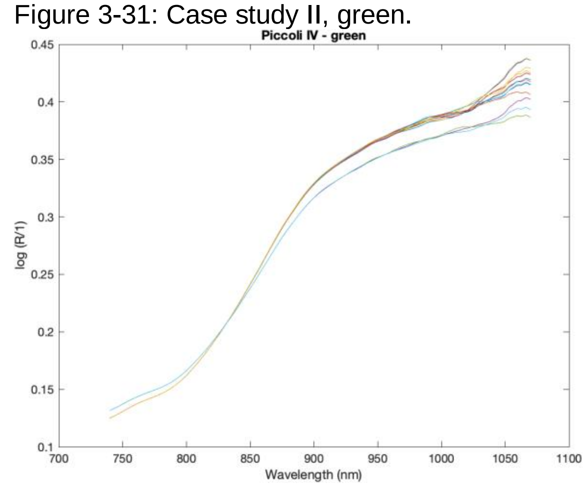


Figure 3-33: Case study IV, green.

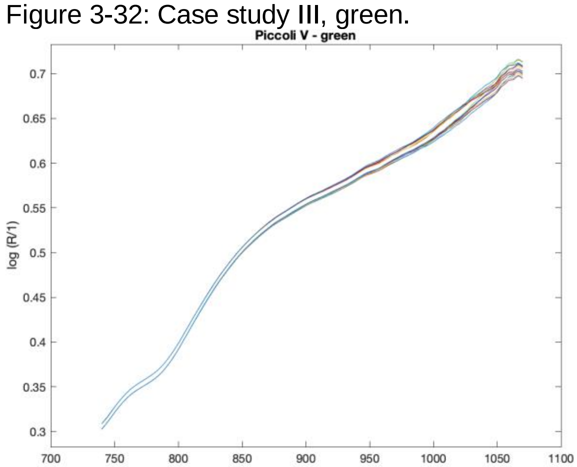


Figure 3-34: Case study V, green.

Red

The spectra obtained from the case studies I, II and III, present similarities that match the reference spectra of natural vermillion, however, the case study IV presents a spectra that matches the reference spectra of red ochre, indicating the use of two different pigments used as red in the palette of Lino Piccoli.

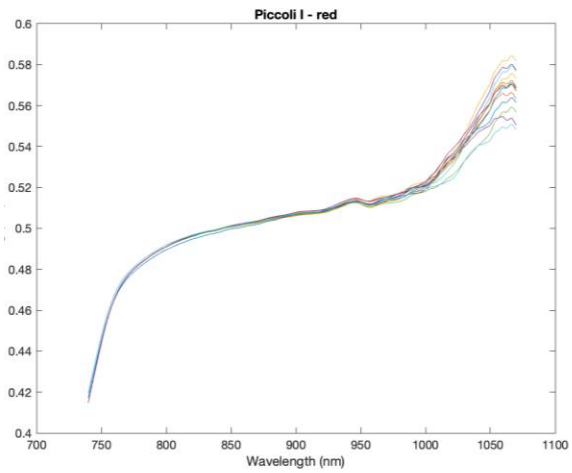


Figure 3-35: Case study I, red.

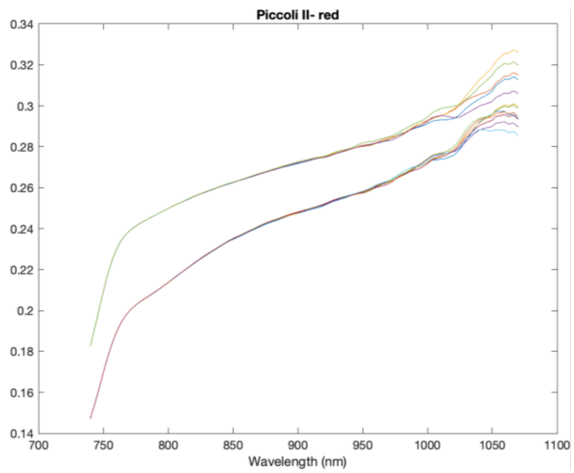


Figure 3-36: Case study II, red.

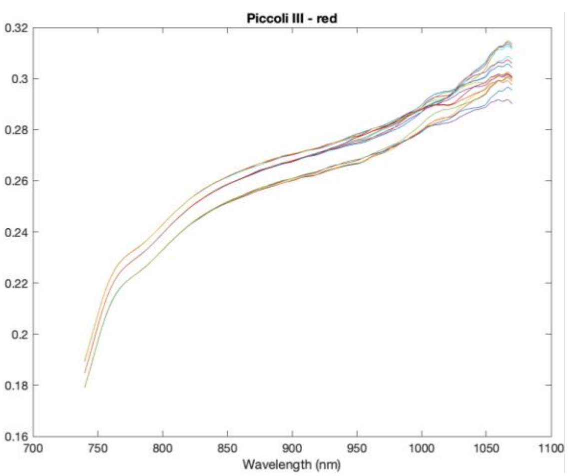


Figure 3-37: Case study III, red.

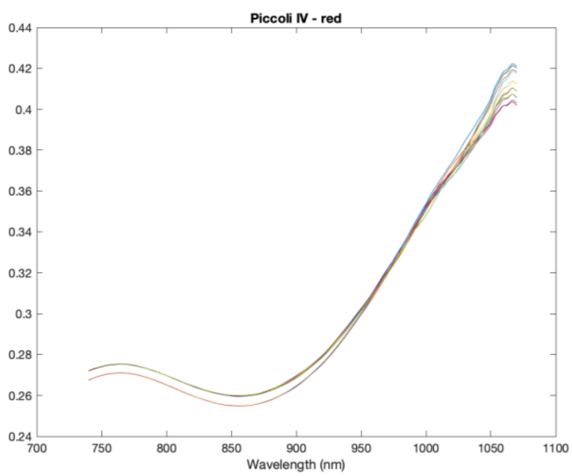


Figure 3-38: Case study IV, red.

Note: the case study V does not have red paint.

Yellow

The spectra from the case studies I, II and IV are consistent with the presence of yellow ochre, nevertheless, the case study V shows a different spectrum, possibly correponding to led tin yellow II; this coould be confirmed through elemental analysis.

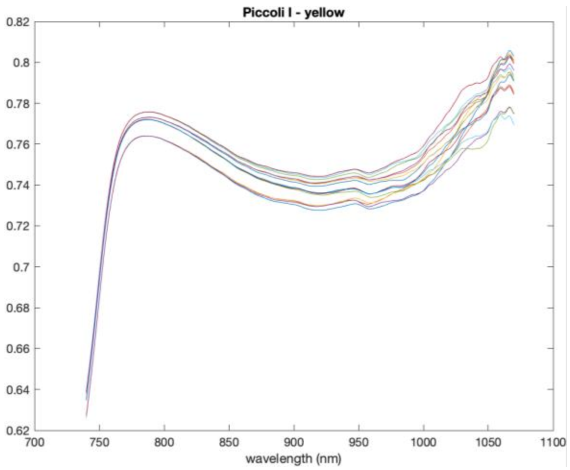


Figure 3-39: Case study I, yellow.

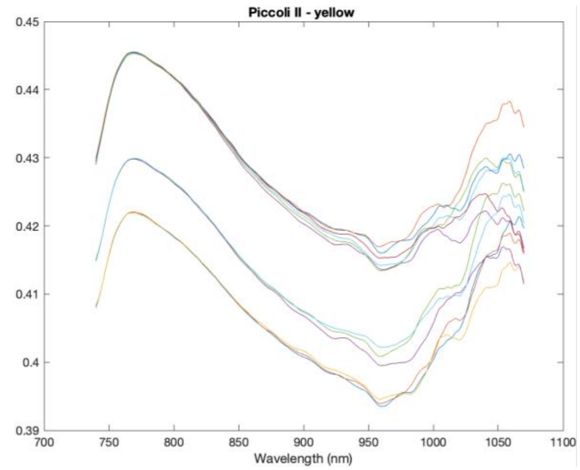


Figure 3-40: Case study II, yellow.

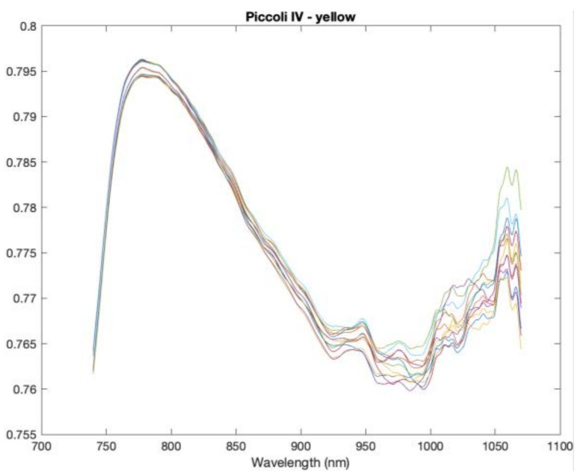


Figure 3-41: Case study IV, yellow.

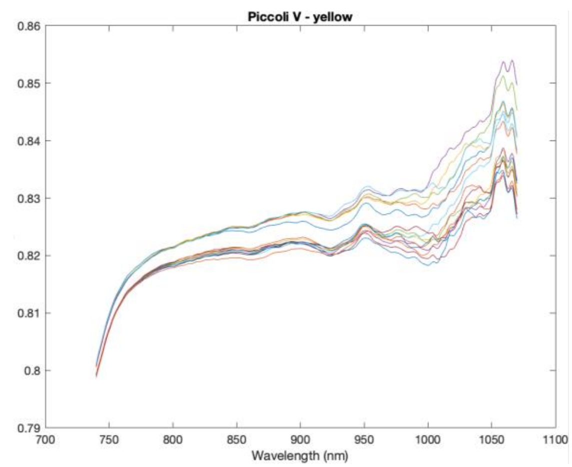


Figure 3-42: Case study V, yellow.

Note: the case study III does not have yellow paint.

Orange

For the case studies I, II, III and IV, it was possible to correlate the spectra with those of the ochres, nevertheless for the case study V it ws not possible to find a coincidence.

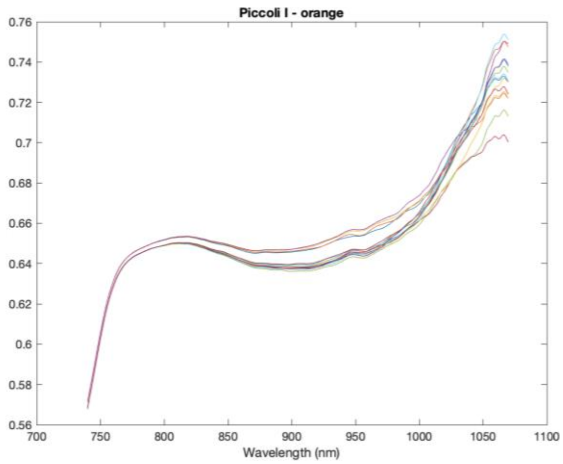


Figure 3-43: Case study I, orange.

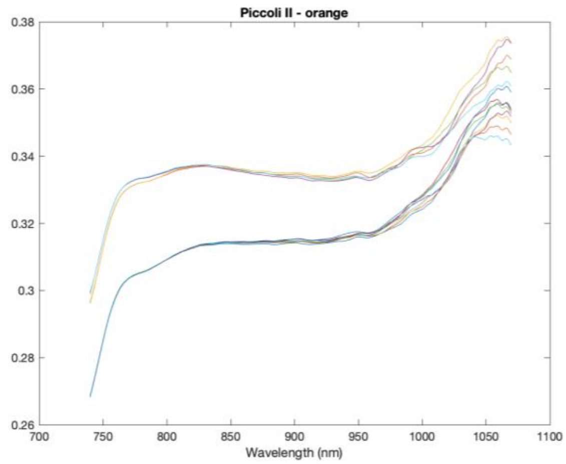


Figure 3-44: Case study II, orange.

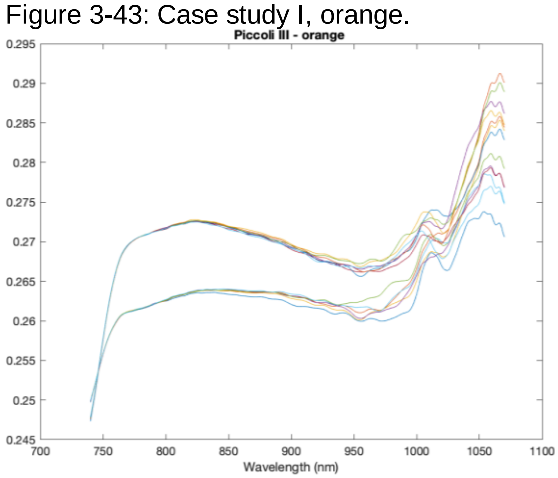


Figure 3-45: Case study III, orange.

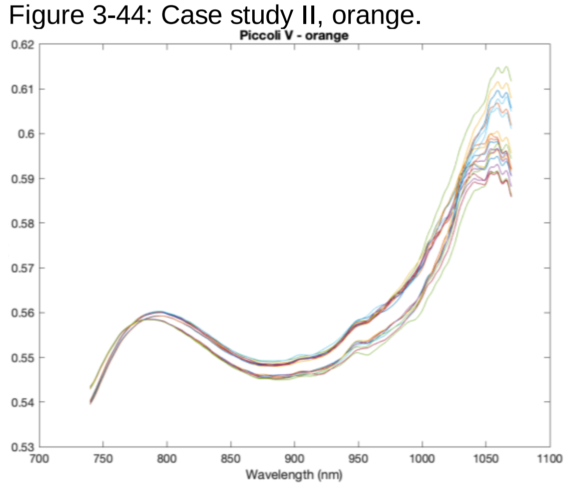


Figure 3-46: Case study V, orange.

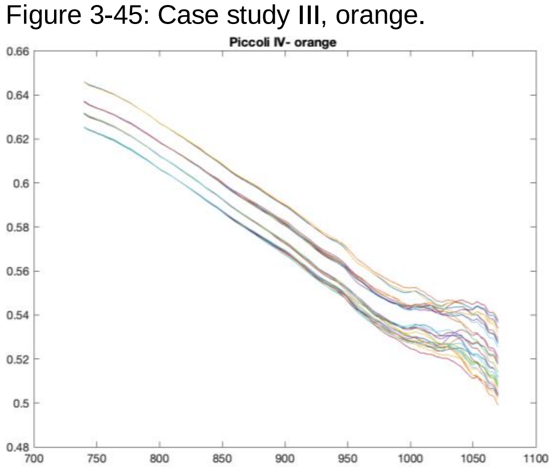


Figure 3-47: Case study IV, orange.

White

In this case it is possible to establish there is a coincidence in the spectra obtained fro m all the white spots of analysis.

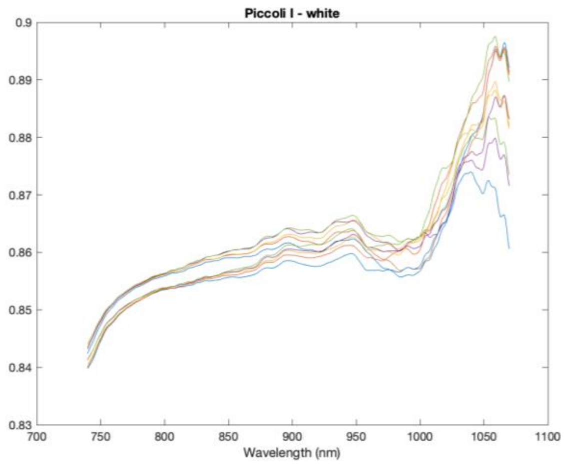


Figure 3-48: Case study I, white.

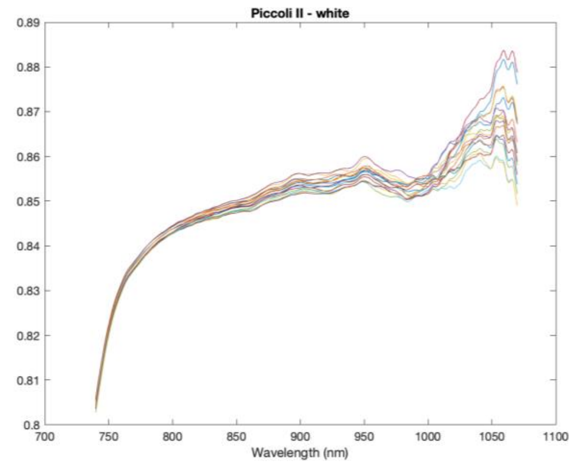


Figure 3-49: Case study II, white.

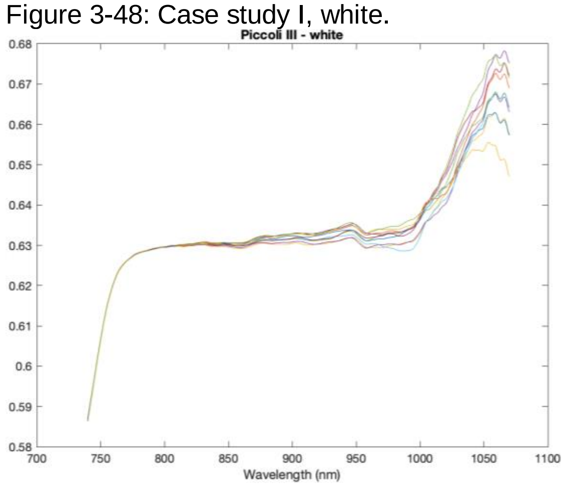


Figure 3-50: Case study III, white.

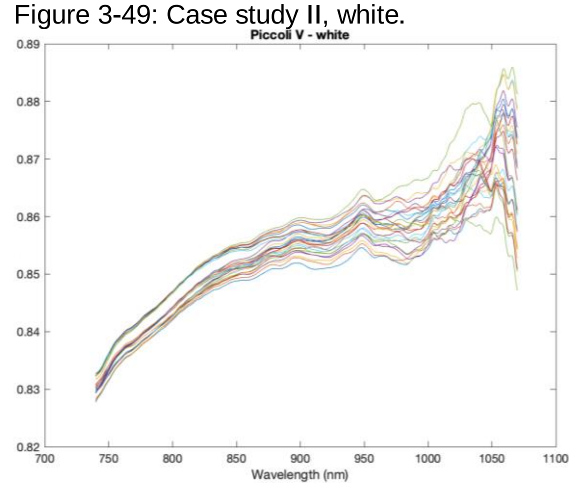


Figure 3-51: Case study IV, white.

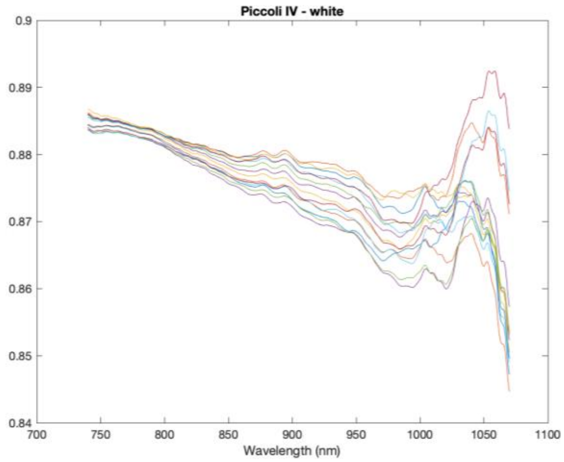


Figure 3-52: Case study V, white.

Black

For the first three case studies it was not possible to establish a coincidence, however, the case studies IV and V present a large coincidence with the spectra of carbon black obtained from the reproduction canvas.

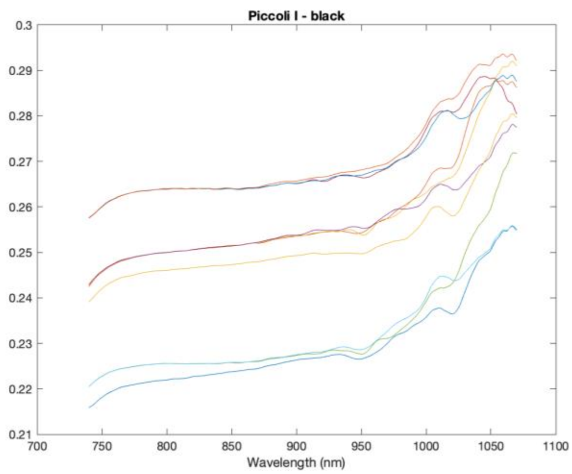


Figure 3-53: Case study I, black.

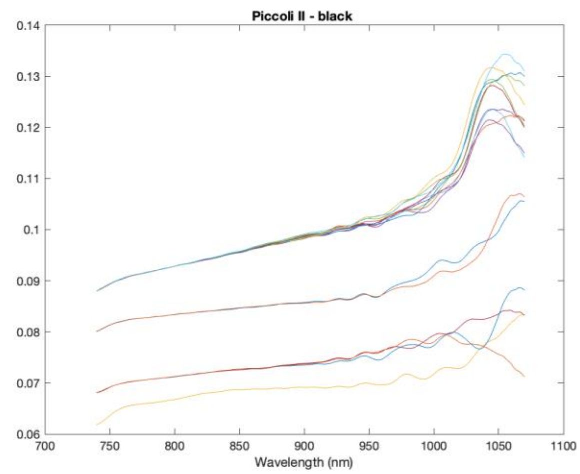


Figure 3-54: Case study II, black.

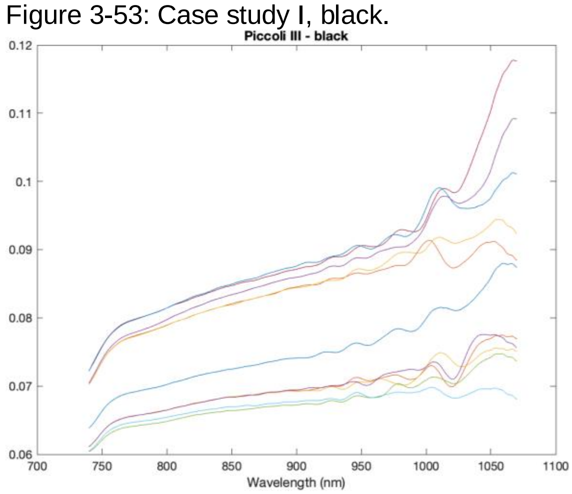


Figure 3-55: Case study III, black.

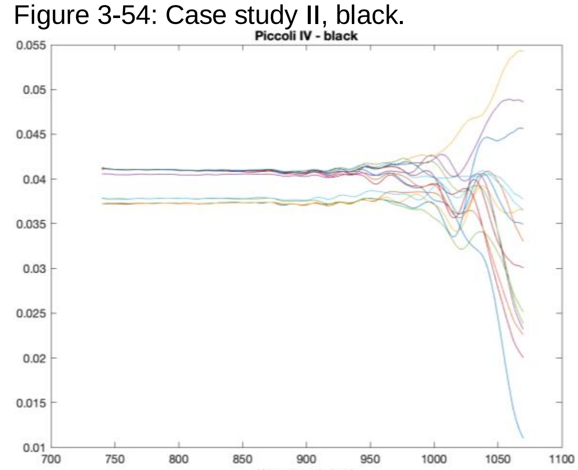


Figure 3-56: Case study IV, black.

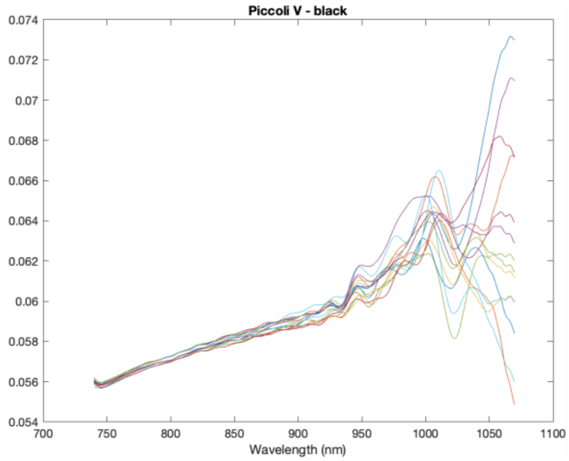


Figure 3-57: Case study V, black.

3.3.2 Principal Component Analysis PCA

It was necessary to apply PCA multivariate analysis in order to differentiate the large datasets of points of analysis, establishing relations mainly between areas of the same color.

Case Study I

In this case, yellow, orange, and red points of analysis are all located in the far-left part of the graph, same as black and white areas which displayed lower reflectance values in the proximity to 0 (black dash and dotted line).

The blue areas points of analysis measured (blue dotted line), are all dispersed to the right part of the PC1, same as the green points of analysis, distancing the most from 0, except for the light green point (light green dotted line).

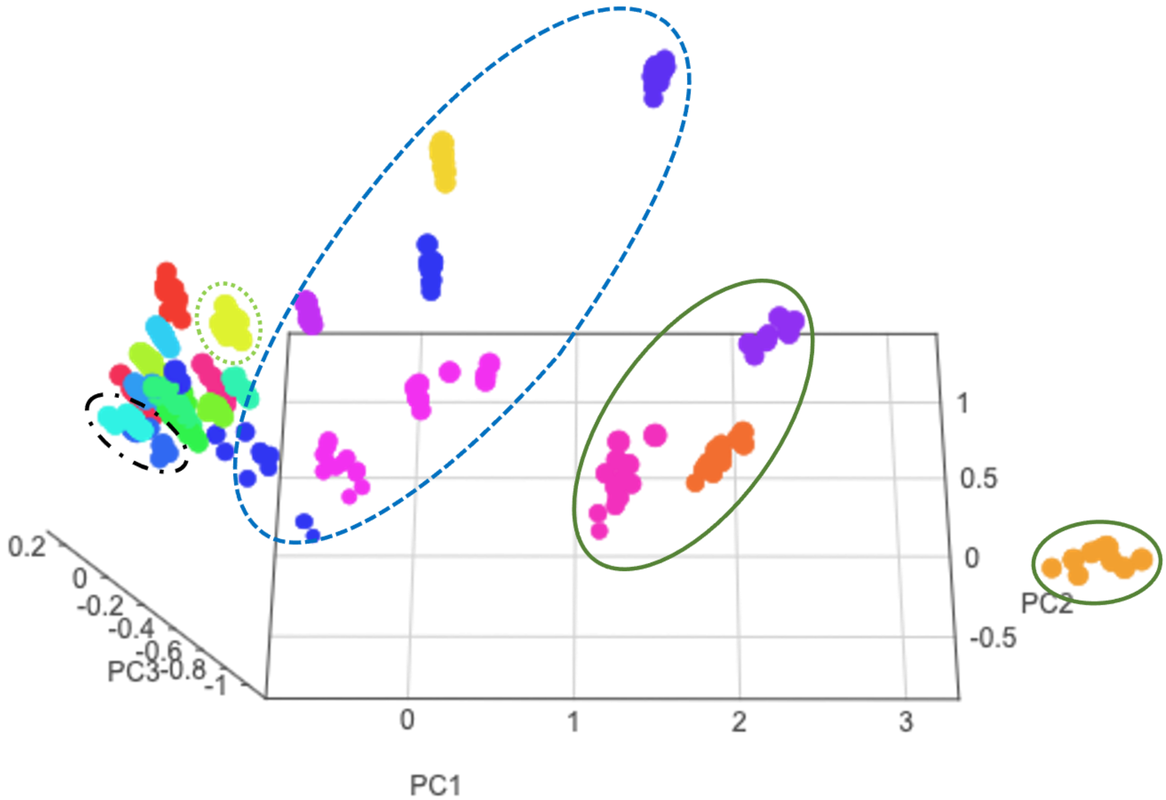


Figure 3-58: PCA, Case study I.

Case Study II

Different from all the other case studies, the blue points of analysis seem the ones to distance most from 0 in both the PC2 and PC2. It is interesting to observe a couple points of blue which locate in the proximity to the red, orange, black and white points, which could indicate the presence of a mixture or different composition.

The green points of analysis are clearly differentiated from the rest in the far-right of the graph distancing from 0 in the PC1, but not that of the PC2.

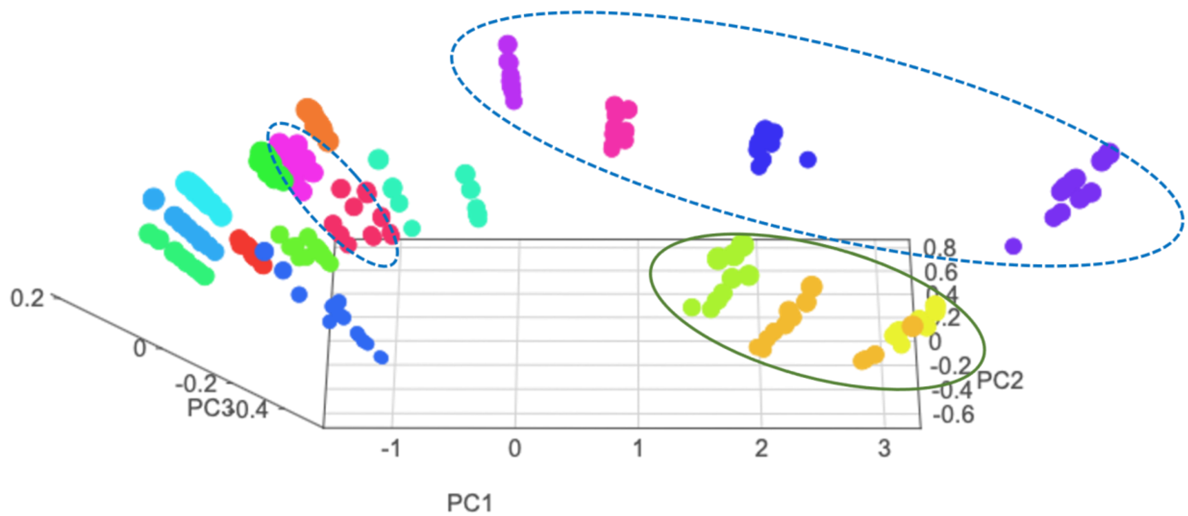


Figure 3-59: PCA, Case study I.

Case Study III

The green points of analysis remain the most distant from 0 in the PC1 and PC2, followed by the blue points of analysis largely distributed along the PC2 and distancing from 0 in the PC1, except for one point in the proximity to the red, orange, white and black points of analysis. Differing from the rest of red samples, there is one point that seems to slightly distance in the PC1.

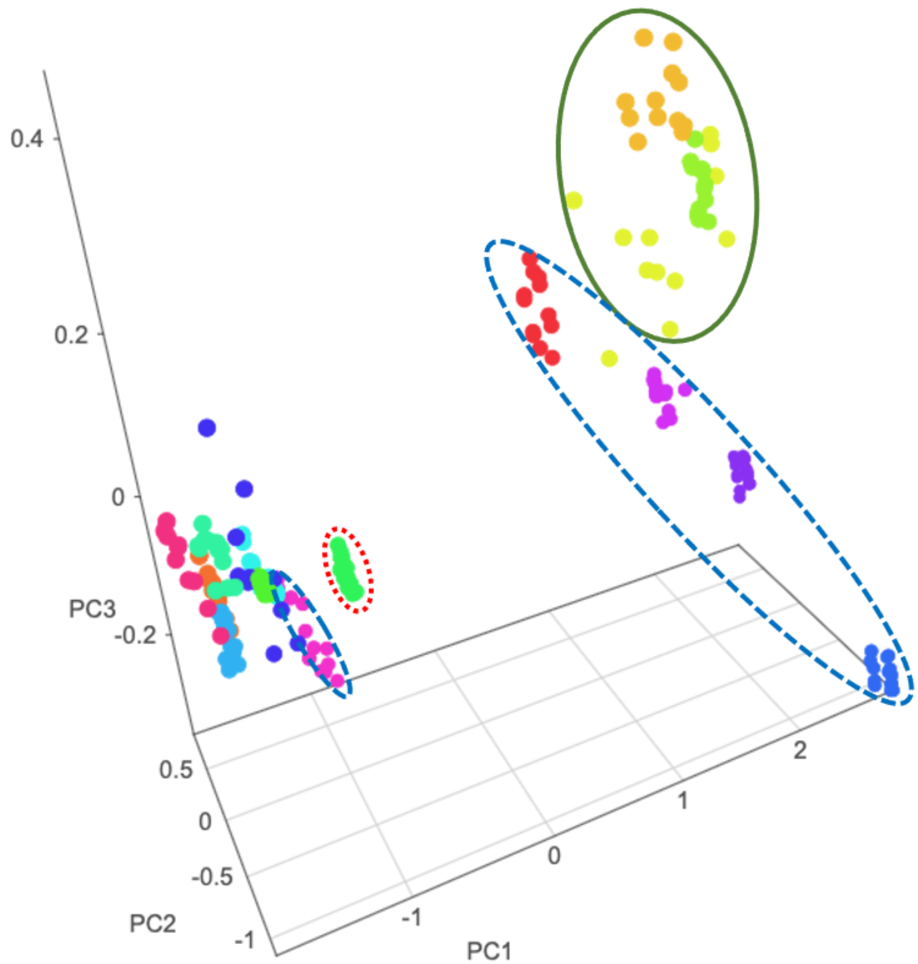


Figure 3-60: PCA, Case study I.

Case Study IV

While red, orange, brown and white points of analysis remain in the proximity to 0 in the PC1 and PC2, the black point of analysis seems disperse along the Z axis; also, light hues of blue (light blue dotted oval) seems fall in the proximity this area, while darker hues of blue remain differentiated distancing from 0 both in the PC1 and 2, same applies for the green points of analysis which remain the farthest from 0.

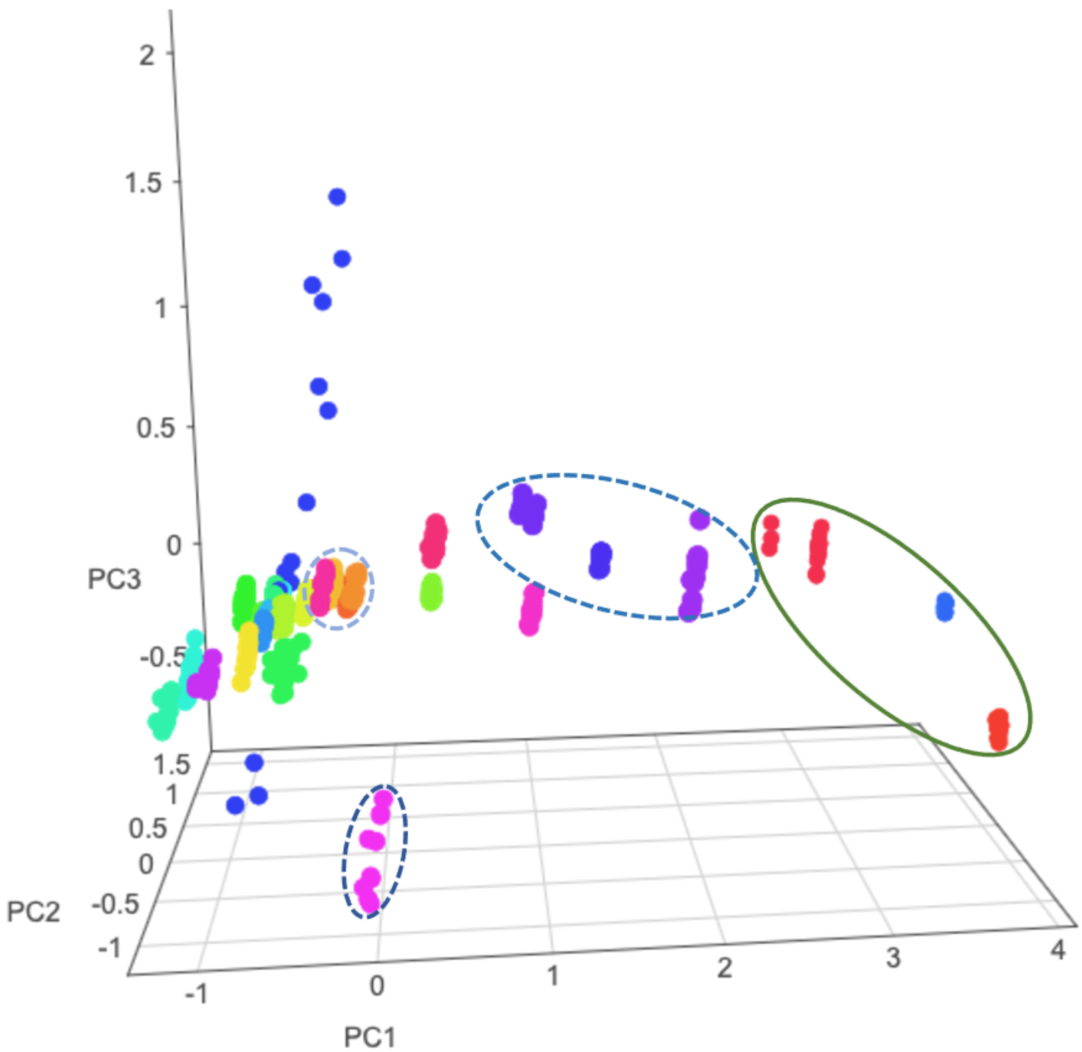


Figure 3-61: PCA, Case study I.

Case Study V

From all the paintings, this case study presents the largest variability in the distribution of points of analysis of the same color. Even though red, orange, white and black points are still located in the proximity to 0 in the PC1 and PC2, light blue points (light blue dotted ovals) seem to coincide for the most part with the distribution of some of the green points of analysis; darker hues of blue remain differentiated, same as some hues of green which distance from 0.

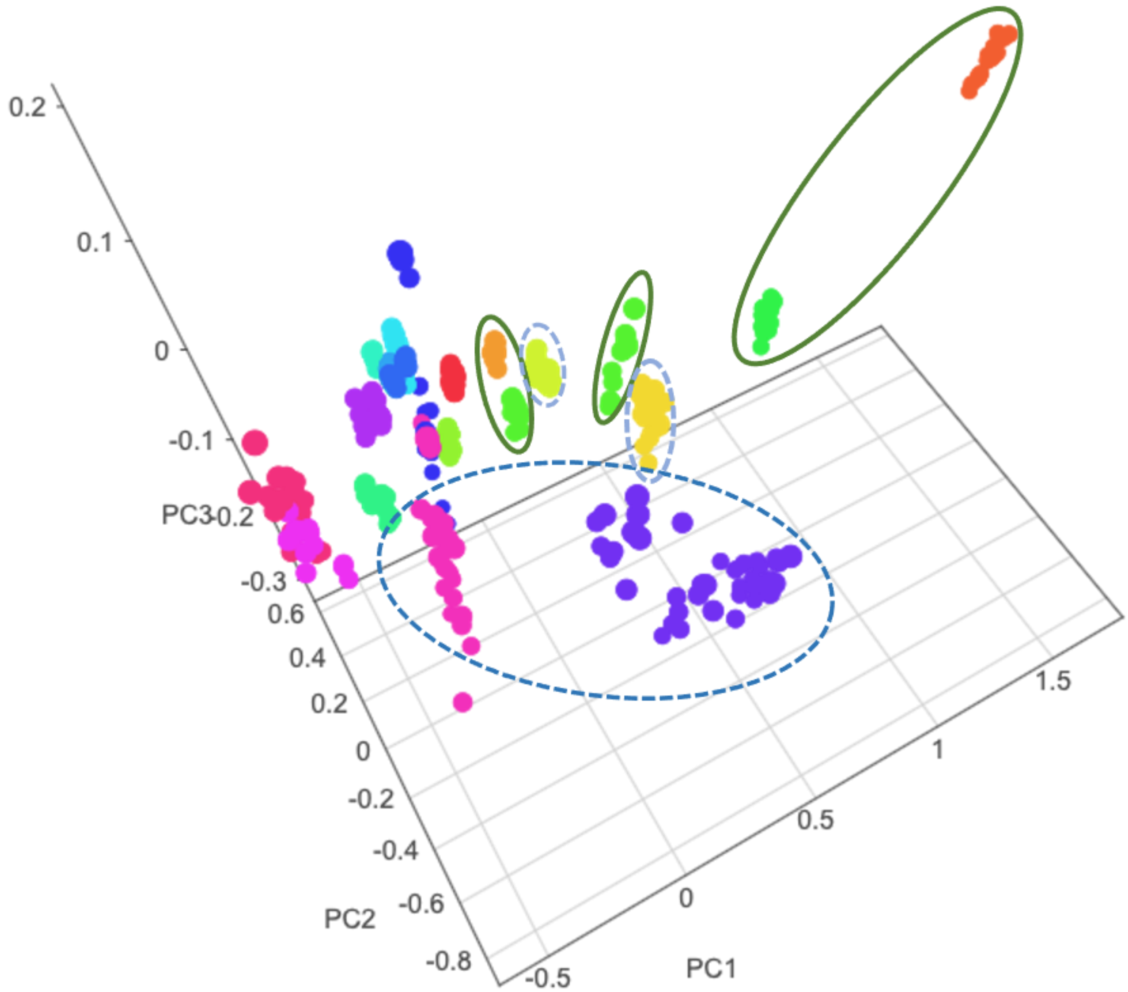


Figure 3-62: PCA, Case Study V.

3.3.3 Interpretation

Lino Piccoli used a large variety of typical commercially available modern pigments matched qualitatively through spectral comparison; it is recommended to perform complementary analysis for confirmation.

According to the results obtained, the palette consists of a rich and not homogeneous distribution of materials, containing mixture of different pigments, and displaying a wide gamma of colors which differ according to the themes represented for the paintings selected.

Even though in some cases there are variations, in general the paintings correspond to a similar palette; also showing a similar technique, consisting of the application of monochrome impaste of defined lines, characteristic of the cubo-futurist style.

As for the binder, it was known that oil was used, this information was verified in the spectra of paintings where pigments with low reflectance values were used, this is the case of the black surfaces.

Multivariate analysis using PCA allowed to plot and determine and correlate the position of areas of similar colors measured, which can correspond to the use of mixtures, but most importantly to the use of pigments of various compositions.

The five case studies analyzed display similar distributions in PC1 (X axis) and PC2 (Y axis) corresponding to reflectance values and wavelength respectively; being the black and white pigments in the proximity of 0 on the X axis, followed by yellow, orange, and red areas of colors. Blue and green areas presented the higher reflectance response distancing from 0 in most cases, except for lighter or darker hues, which can also affect the reflectance values for materials of the same composition. The Z axis for PC3 was not held into account.

4. Conclusions

4.1 SCiO

As it was mentioned before, the many advantages of SCiO are its portability, size, rechargeability, non-invasive character, high speed, low cost of analysis, and the possibility to use The Lab cloud-based software, making automatic the transfer of data, enabling the immediate obtention of processed spectra and fast-check of results in real-time.

These aspects make the device ideal for consumer-focused use. Nevertheless, this can prove counterproductive for researchers given that: The Lab software is closed, and therefore the processing methods are not known, the parameters for calibration and other settings cannot be controlled, and the instruments cannot be modified or synced to other analysis software. Also, not being scientist or researchers the main target, very little is known about the technical specifications, or data processing or algorithms employed, also, if a model for specific materials does not exist a new model has to be created.

In this study, it was necessary to download the raw data to be able to visualize the values and plot the spectra without any pre-processing. The data download feature requires a Researcher License that costs €3000 per year, which was granted by Consumer Physics for a limited time of one week.

The researcher license also includes the model creation feature, which can be useful to improve the quality of the data through the creation of certain-purposed databases and processing methods.

The contribution of this study in the context of heritage science consists mainly in the exploration of SCiO considering the characteristics of the instrument, the quality of the data obtained, and the possible developments to make further improvements using SCiO or other NIR spectroscopy instruments in the field.

4.2 Near-Infrared spectroscopy

The limited existence of NIR spectral libraries of cultural heritage material constitutes at the moment the main barrier to the use of this technique in the field. It is important to remark that, as these libraries broaden, so does the field of application for analysis on a wider range of materials that can throw considerably useful data under the NIR range, employed by the SCiO instrument. Likewise, the development of a spectrum analysis software for automatic matching, as it exists for Infrared spectroscopy in the Middle IR region, would be a further step in the field.

Also, the development of certain-purposed data processing models, especially for calibration, could be an important advance to achieve better data quality and implement quantitative analysis using chemometrics. Also, improvements in the instrumentation, such as the expansion of the range into the VIS region, could prove useful in the field.

4.3 Paintings

A considerable amount of painting samples and analysis employing SCiO was necessary to establish the first database. However, it does not provide enough information to perform a visual match for some of the spectra obtained from real case studies given the complexity of the samples, and as already mentioned, the lack of comprehensive reference materials and spectral libraries for association.

About the complexity of the case studies, and modern canvas paintings in general, it is relevant to remark the large number of possible materials used as pigments, which in most cases requires more sophisticated data processing tools for a more accurate matching and differentiating pigments of similar composition. In addition, mixtures of pigments, binder and/or additives, possible degradations products, and deterioration materials on the surface of the paintings pose a challenge for the identification of spectra.

The changes in the light, temperature and vibration conditions for the measurements can cause variations in the spectra obtained from the same sample at different times and places. Given that the tests were done in different locations in approximately five months, this is an important consideration in possible differences and the presence of outline spectra.

4.4 Case Studies

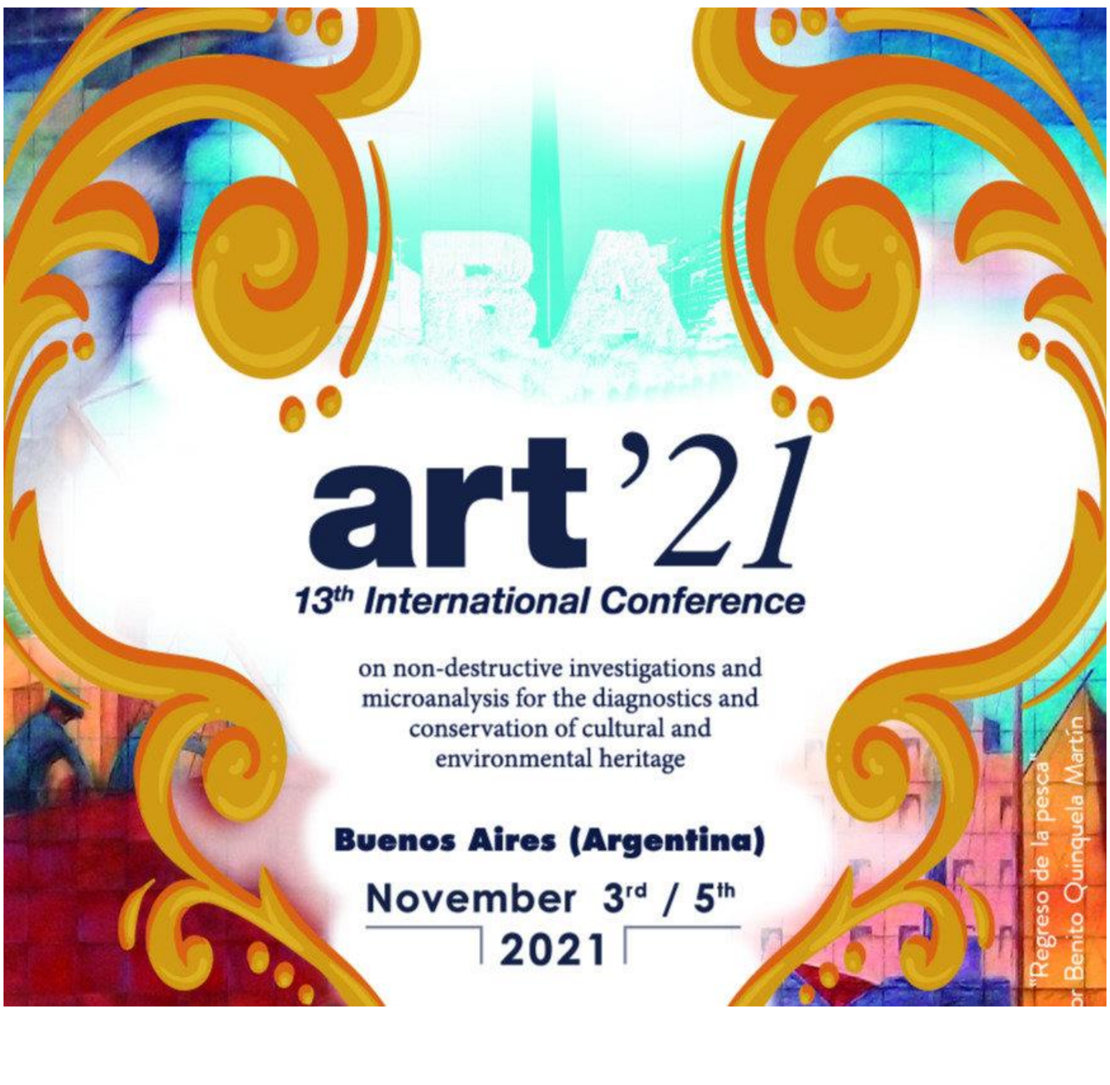
The knowledge about the composition of a painting materials, a painter palette, and the techniques used is crucial not only for artistic studies, but also determine conservation aspects. In this project, the choice of five oil on canvas painting by Lino Piccoli as case studies yielded results relevant for a first approach to the painter's palette, showing the potential and benefits of using the SCiO molecular sensor, or other NIR portable devices for the study and screening of paintings materials as a preliminary analysis technique.

Even though the use of spectra for qualitative matching proved challenging, multivariate analysis using PCA can provide clues to differentiate variability in samples of the same color, which can be attributed to different compositions or the use of mixtures.

Outcomes of the thesis work

Oral Presentation: *Assessment of Portable Near-Infrared Spectrometer SCiO for the Study of Canvas Paintings.*

Art21 - 13th International Conference on non-destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage.



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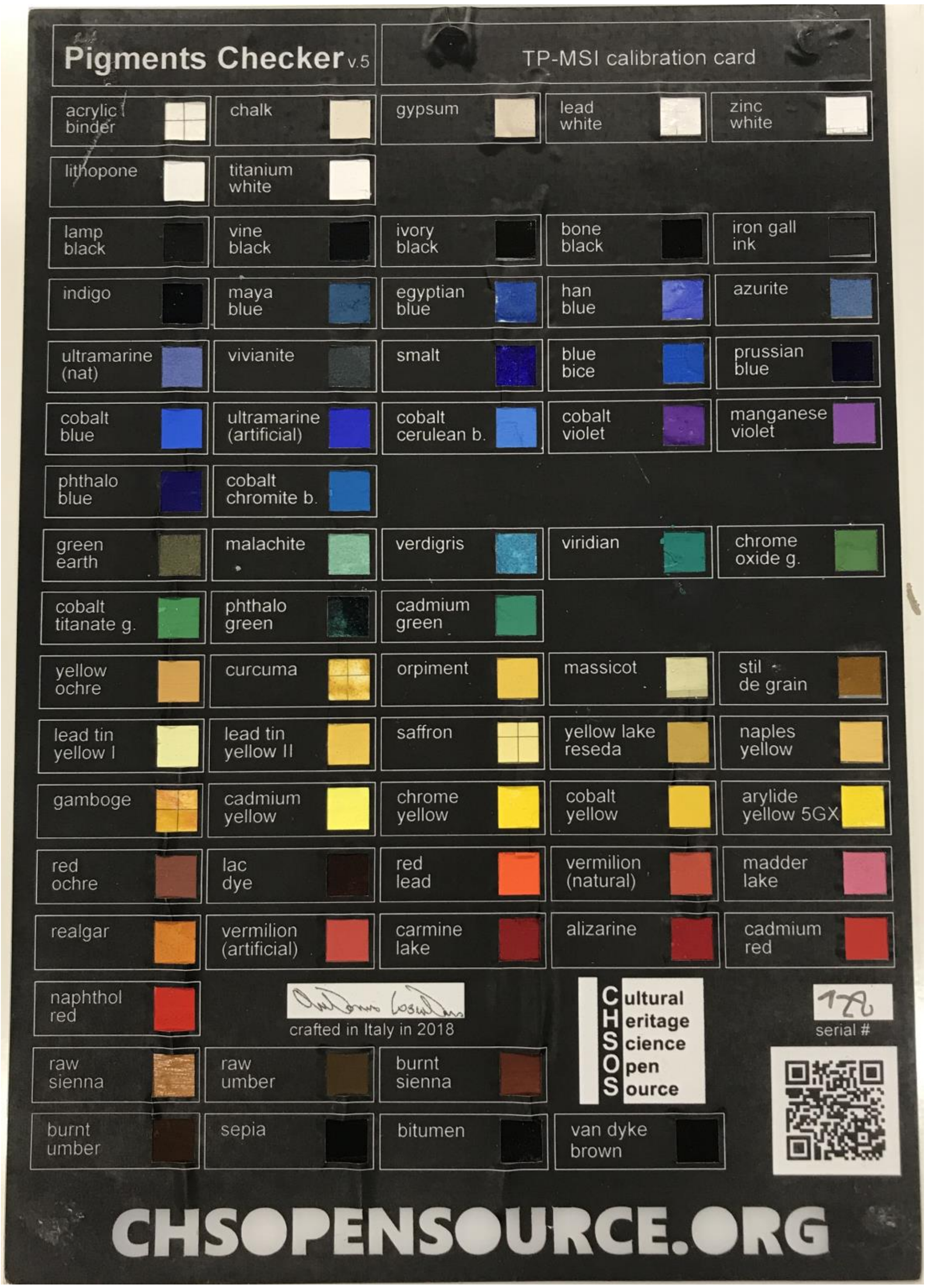
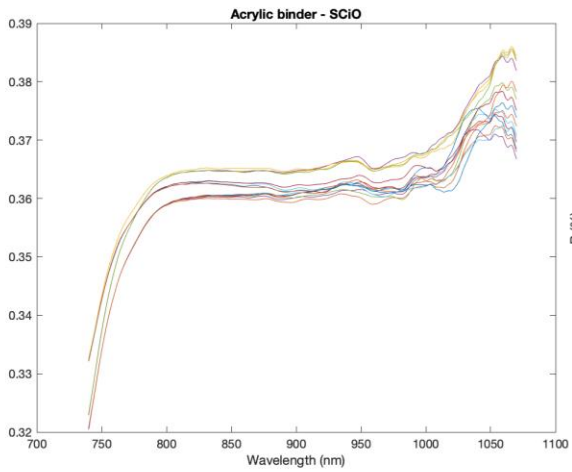
A. Appendix: Spectrum

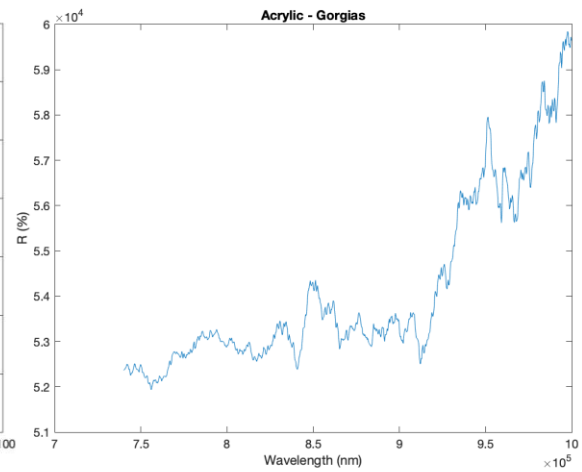
Pigments Checker v.5



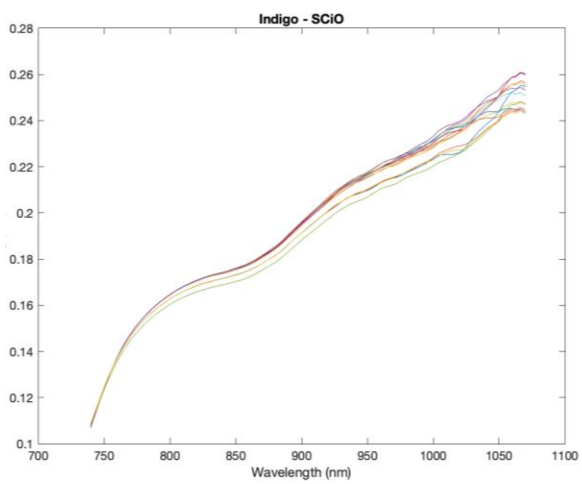
Spectrum

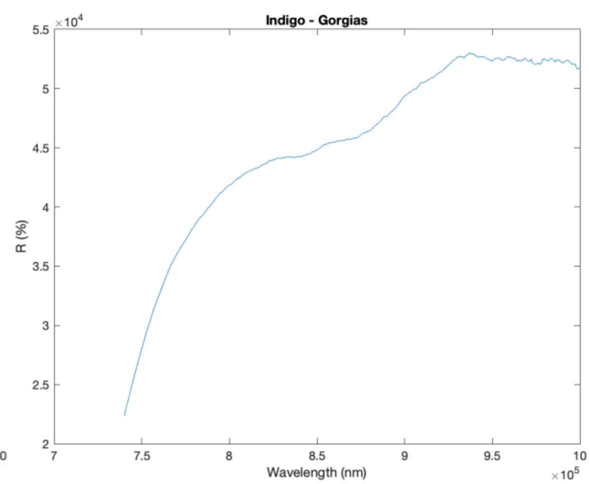
Acrylic

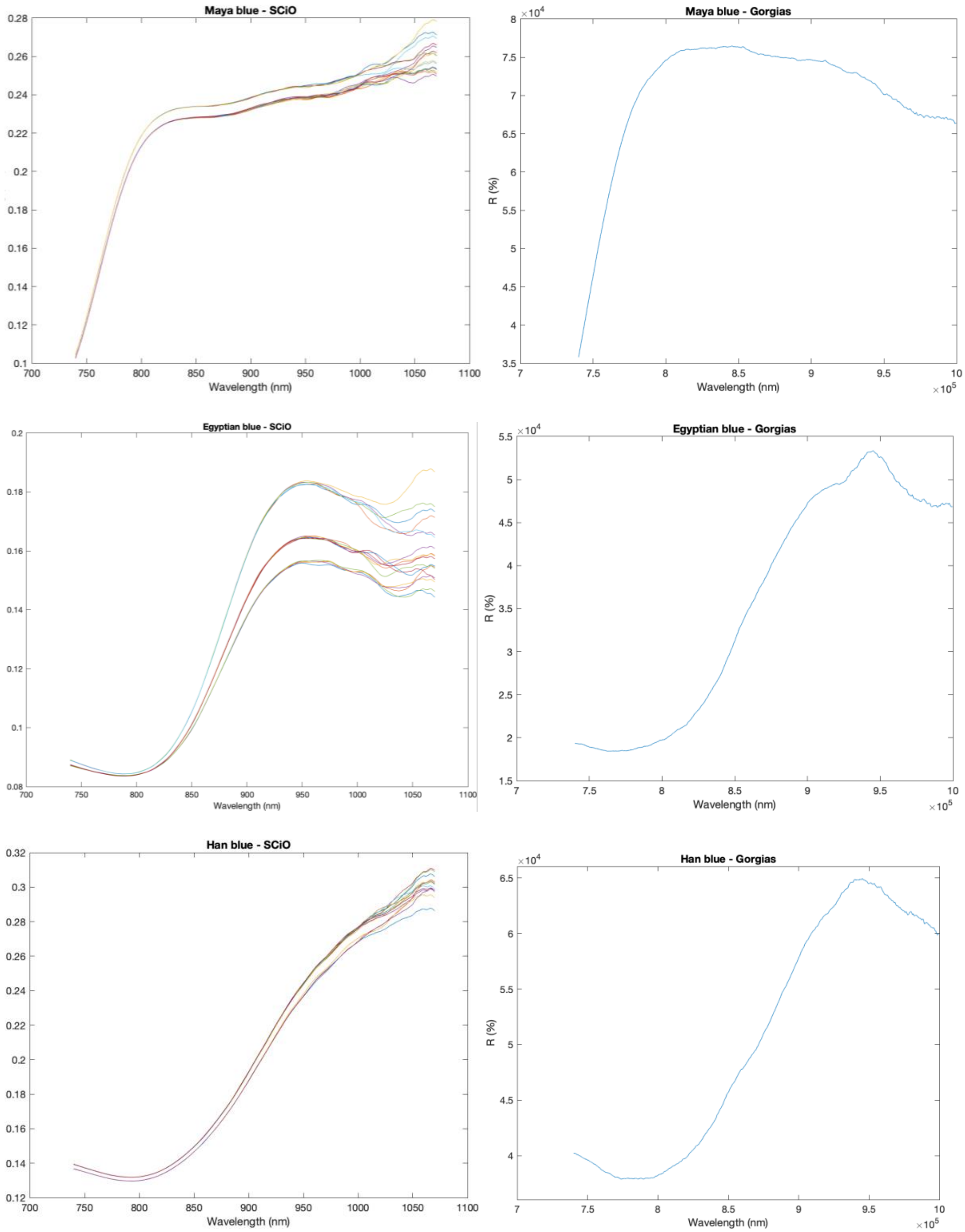




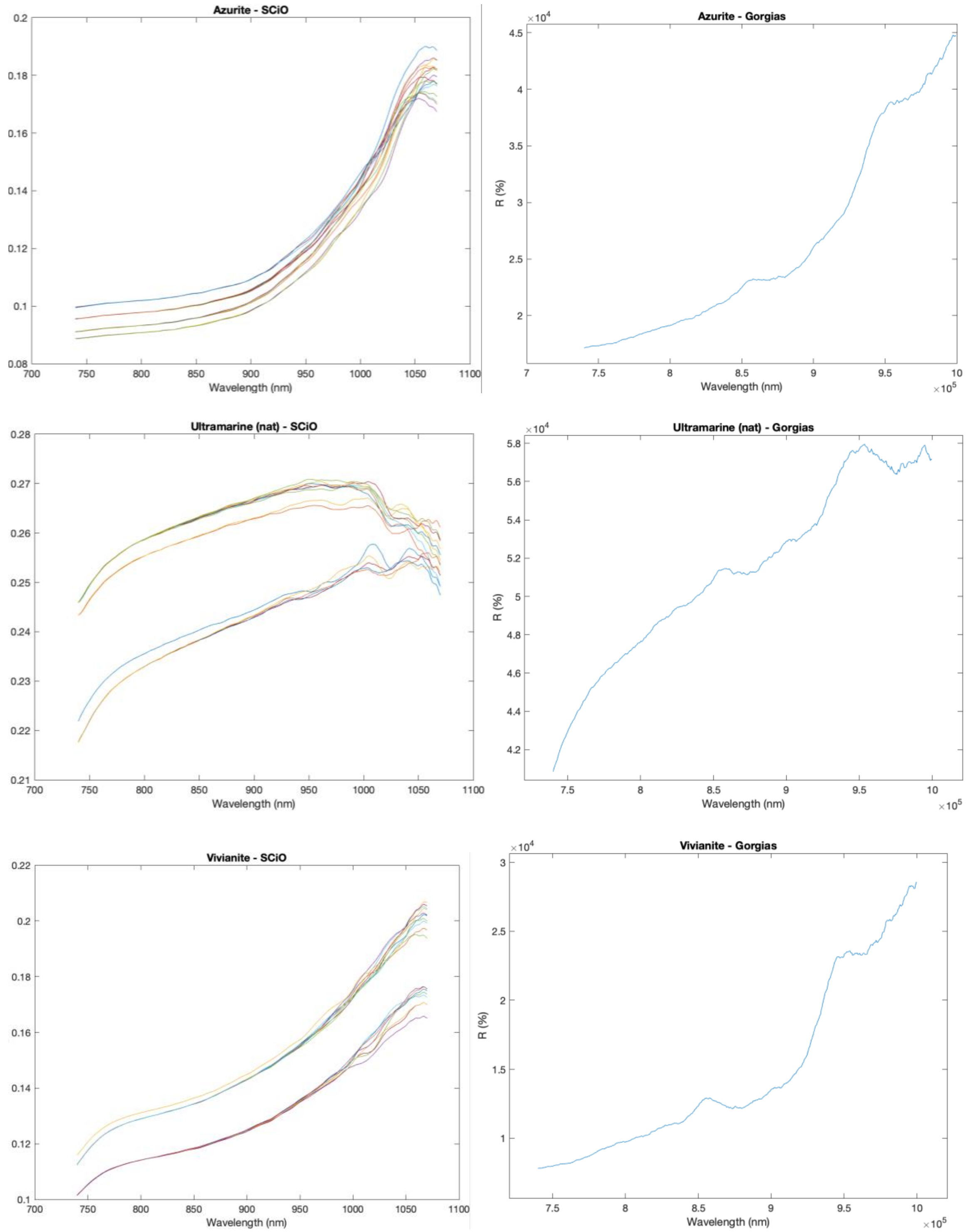
Blue pigments

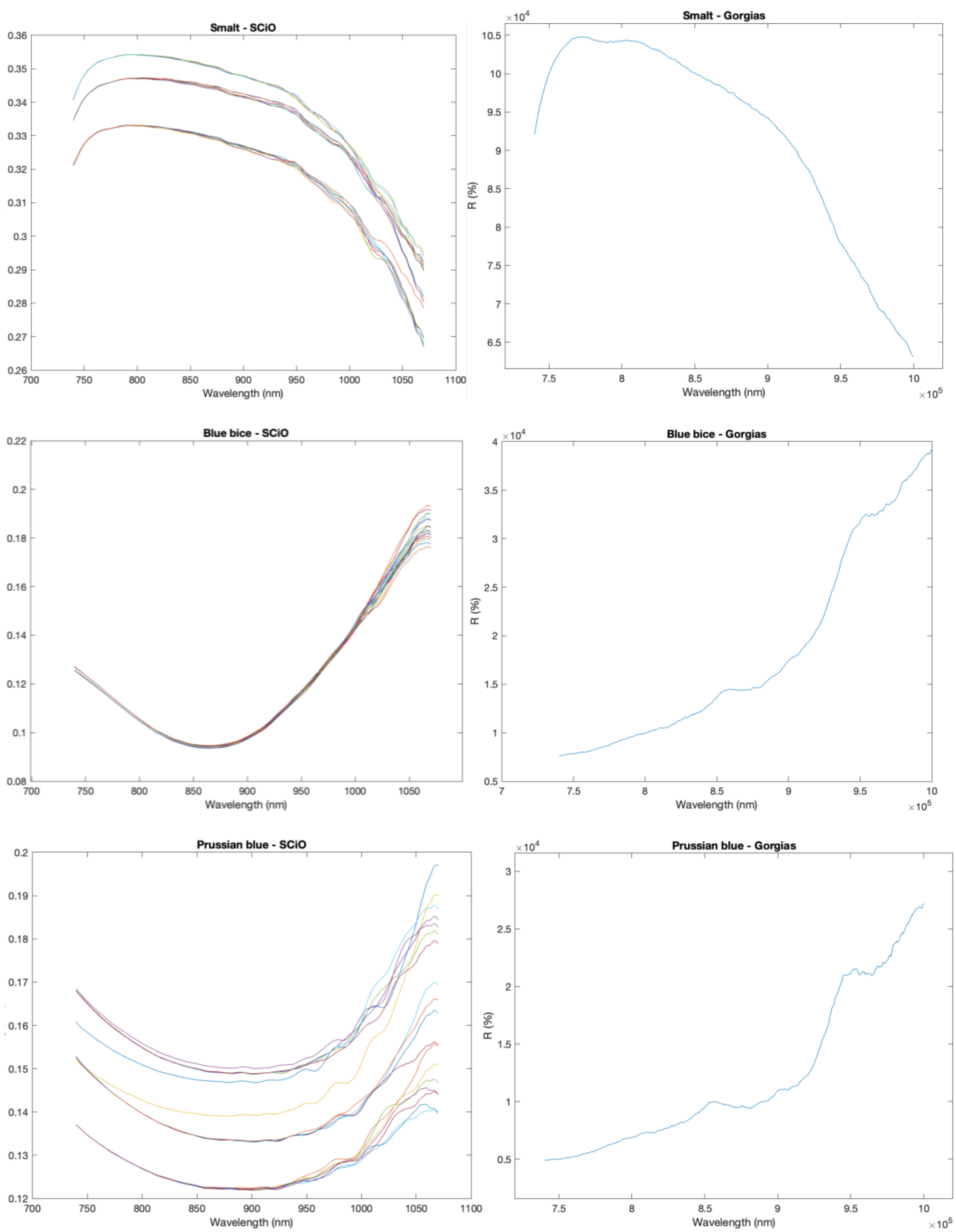


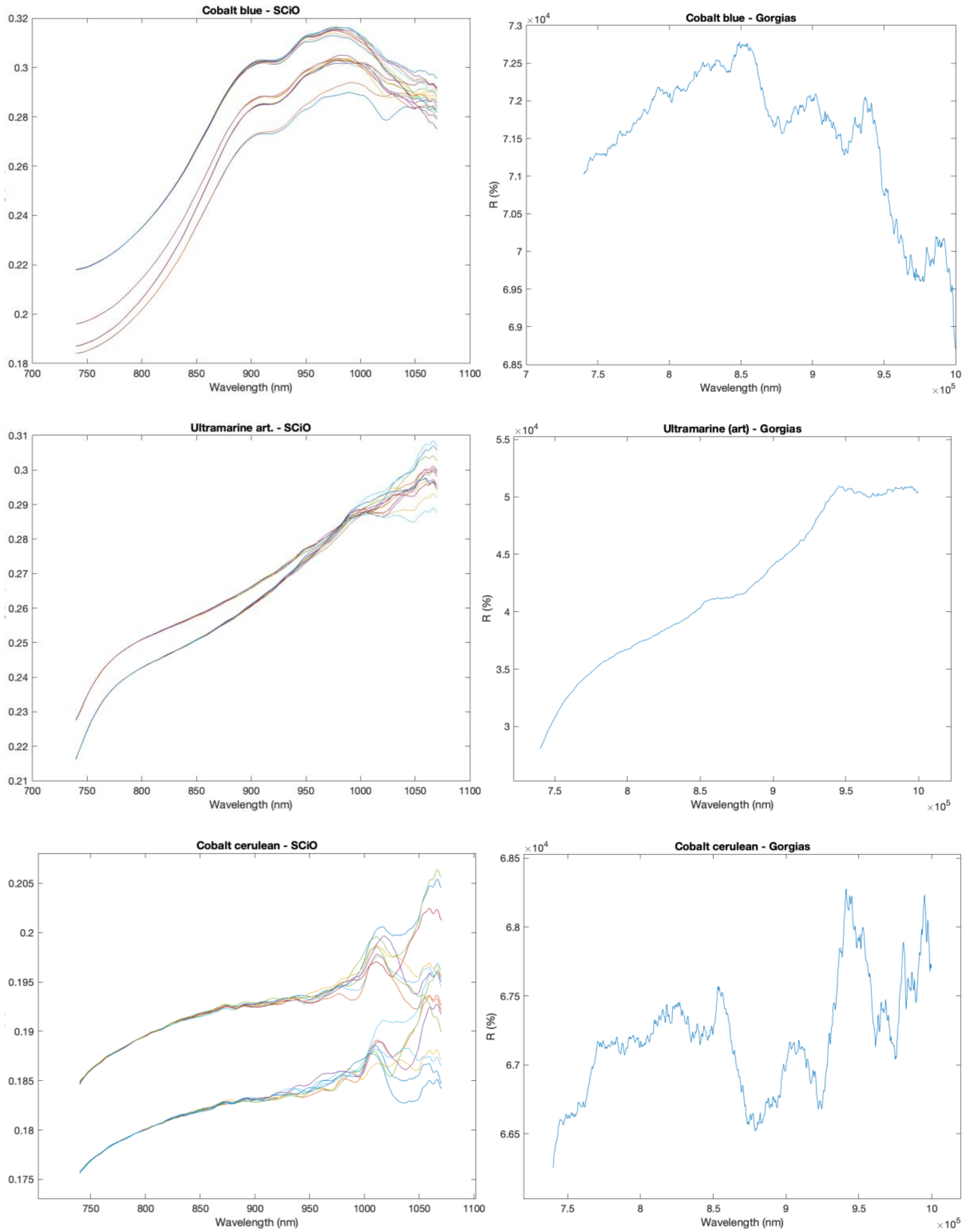


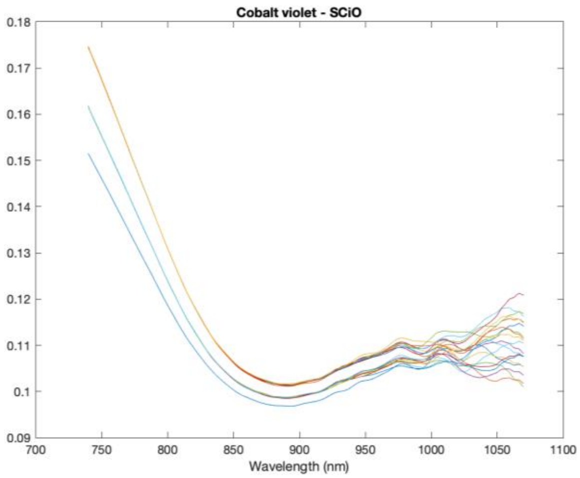


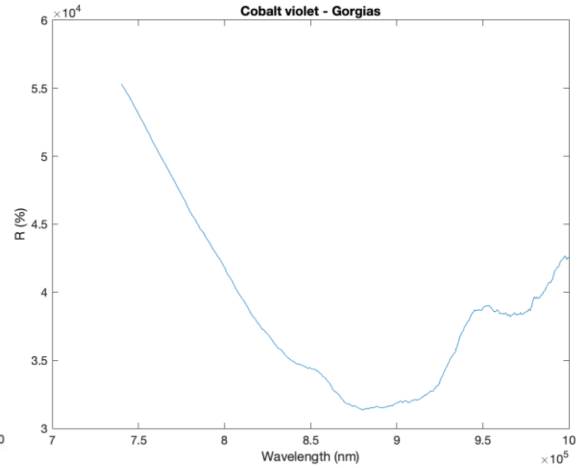
Maya blue - SCiO
Wavelength (nm)
Maya blue - Gorgias
R (%)
Wavelength (nm)
Egyptian blue - SCiO
Wavelength (nm)
Egyptian blue - Gorgias
R (%)
Wavelength (nm)
Han blue - SCiO
Wavelength (nm)
Han blue - Gorgias
R (%)
Wavelength (nm)

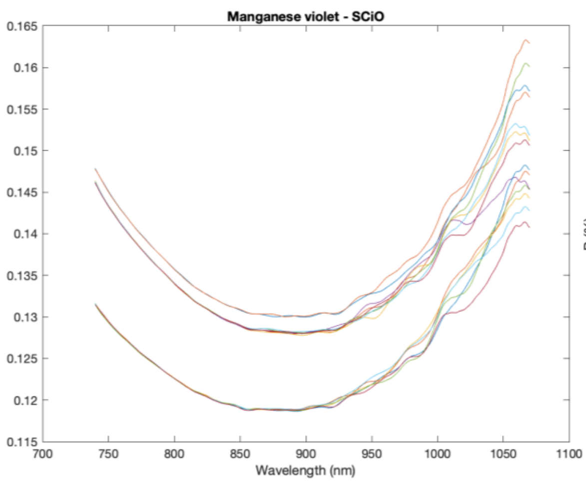

Azurite - SCiO
Wavelength (nm)
Azurite - Gorgias
R (%)
Wavelength (nm)
Ultramarine (nat) - SCiO
Wavelength (nm)
Ultramarine (nat) - Gorgias
R (%)
Wavelength (nm)
Vivianite - SCiO
Wavelength (nm)
Vivianite - Gorgias
R (%)
Wavelength (nm)

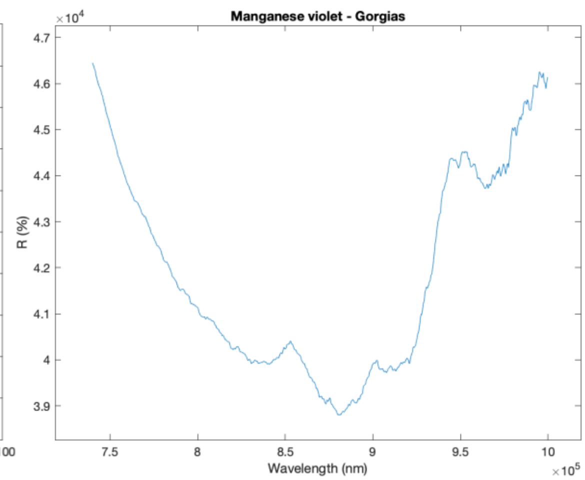

Smalt - SCiO
Wavelength (nm)
Smalt - Gorgias
R (%)
Wavelength (nm)
Blue bice - SCiO
Wavelength (nm)
Blue bice - Gorgias
R (%)
Wavelength (nm)
Prussian blue - SCiO
Wavelength (nm)
Prussian blue - Gorgias
R (%)
Wavelength (nm)

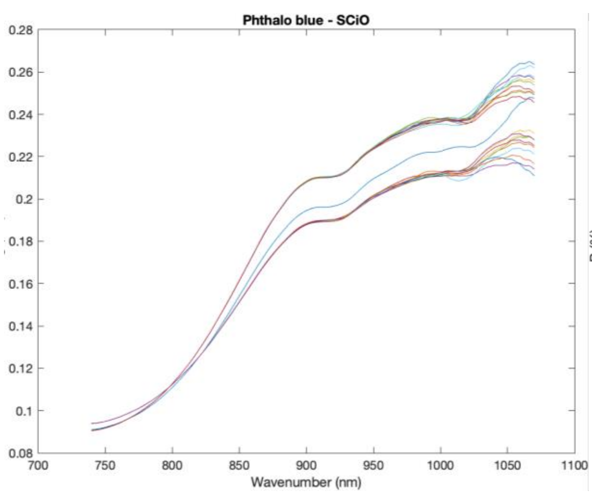

Cobalt blue - SCiO
Wavelength (nm)
Cobalt blue - Gorgias
R (%)
Wavelength (nm)
Ultramarine art. - SCiO
Wavelength (nm)
Ultramarine (art) - Gorgias
R (%)
Wavelength (nm)
Cobalt cerulean - SCiO
Wavelength (nm)
Cobalt cerulean - Gorgias
R (%)
Wavelength (nm)

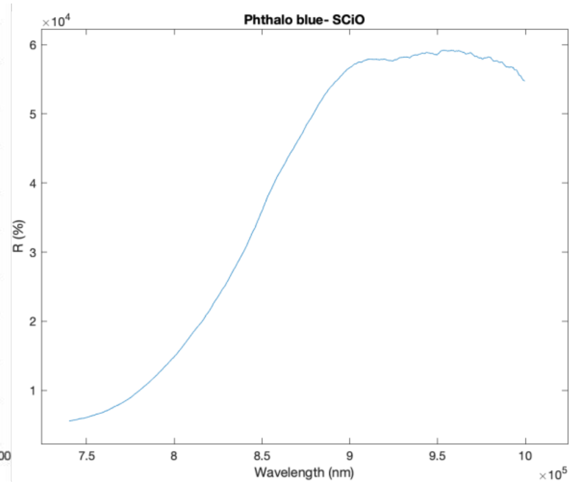

Cobalt violet - SCiO
Wavelength (nm)

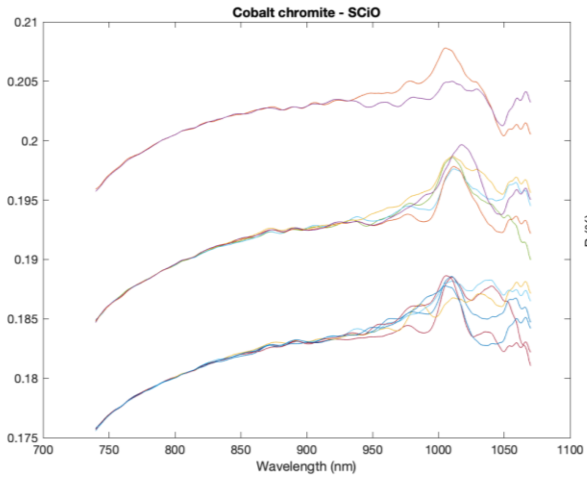

Cobalt violet - Gorgias
R (%)
Wavelength (nm)
×10^4
×10^5

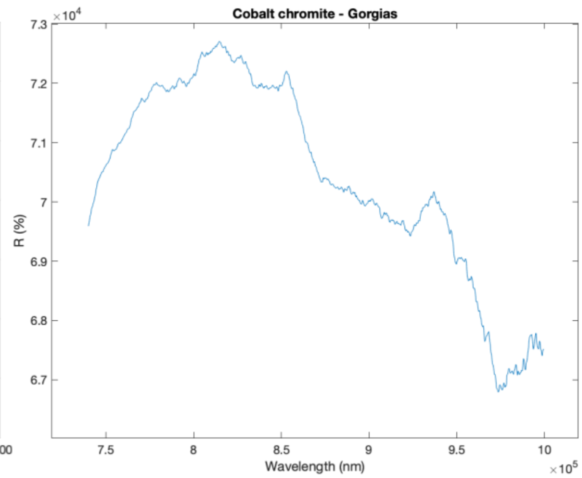

Manganese violet - SCiO
Wavelength (nm)


Manganese violet - Gorgias
R (%)
Wavelength (nm)
×10^4
×10^5

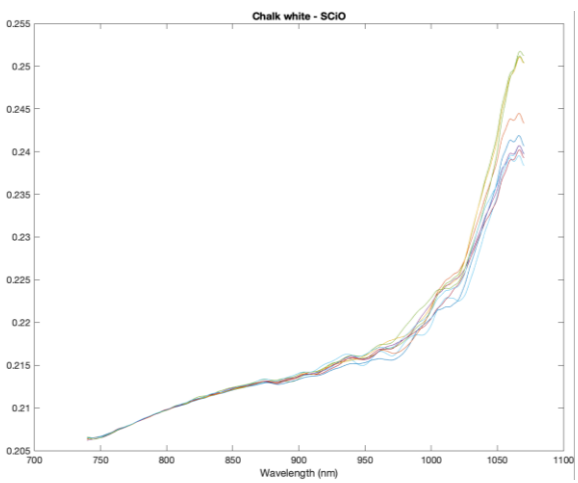

Phthalo blue - SCiO
Wavenumber (nm)

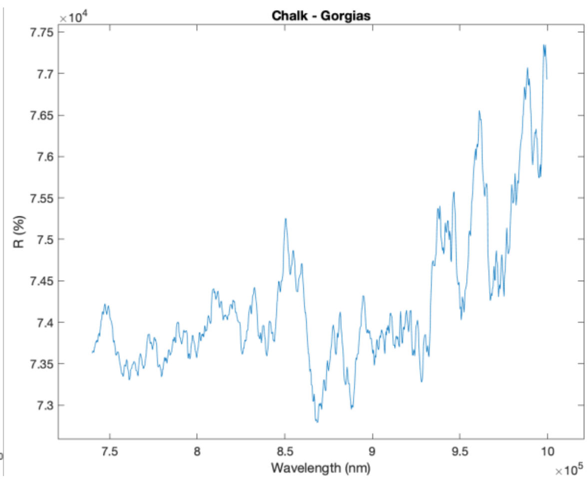

Phthalo blue- SCiO
R (%)
Wavelength (nm)
×10^4
×10^5

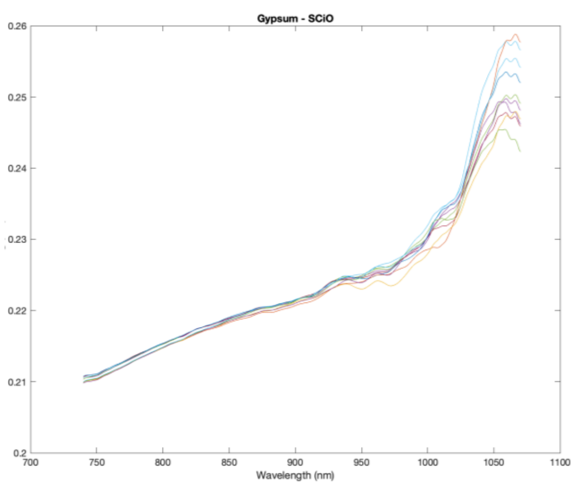


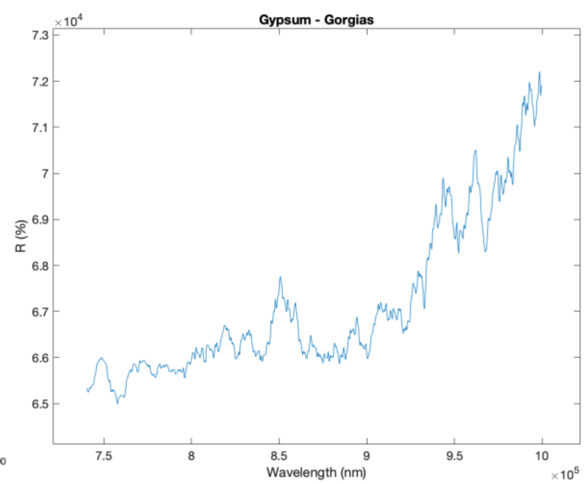


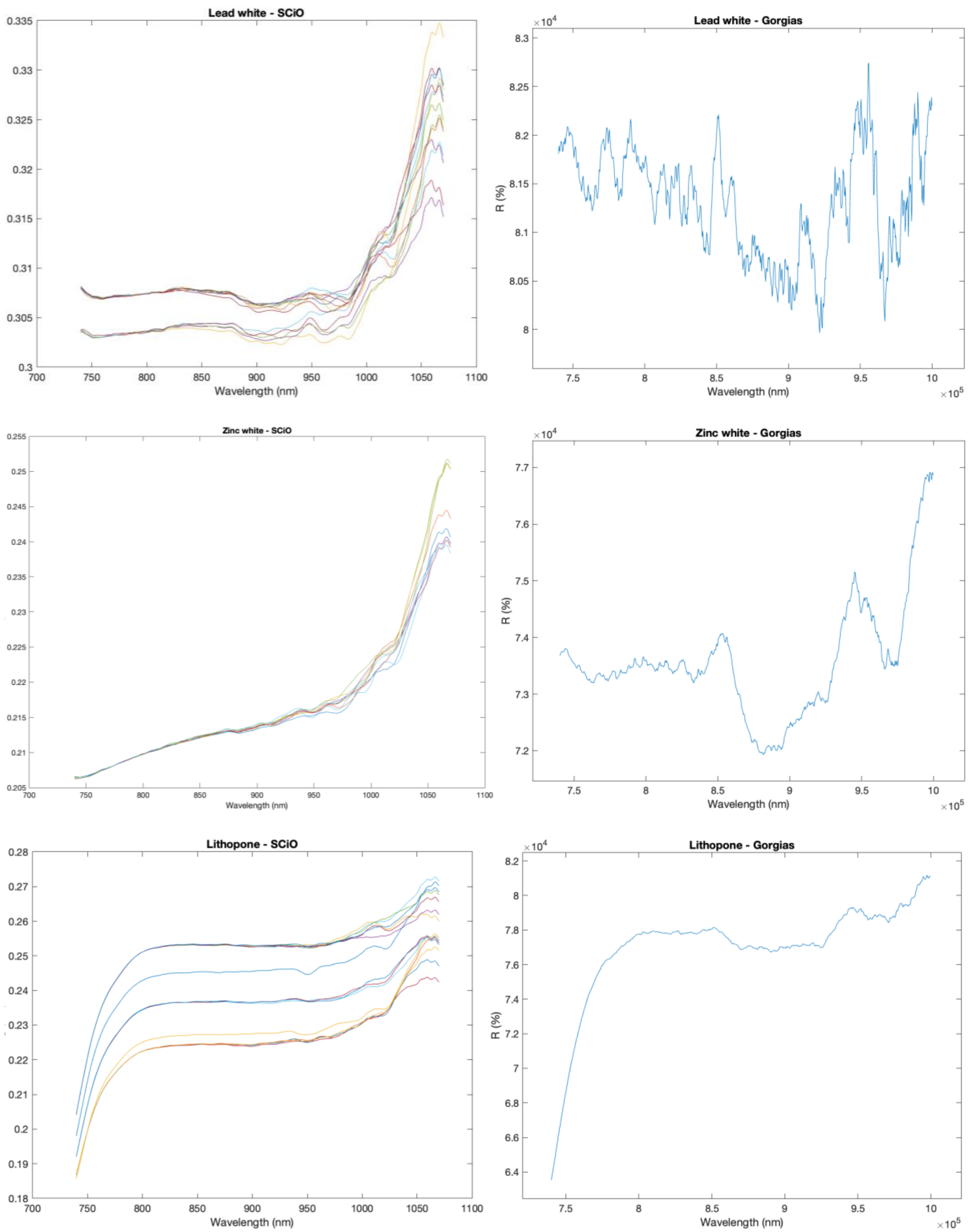
White pigments

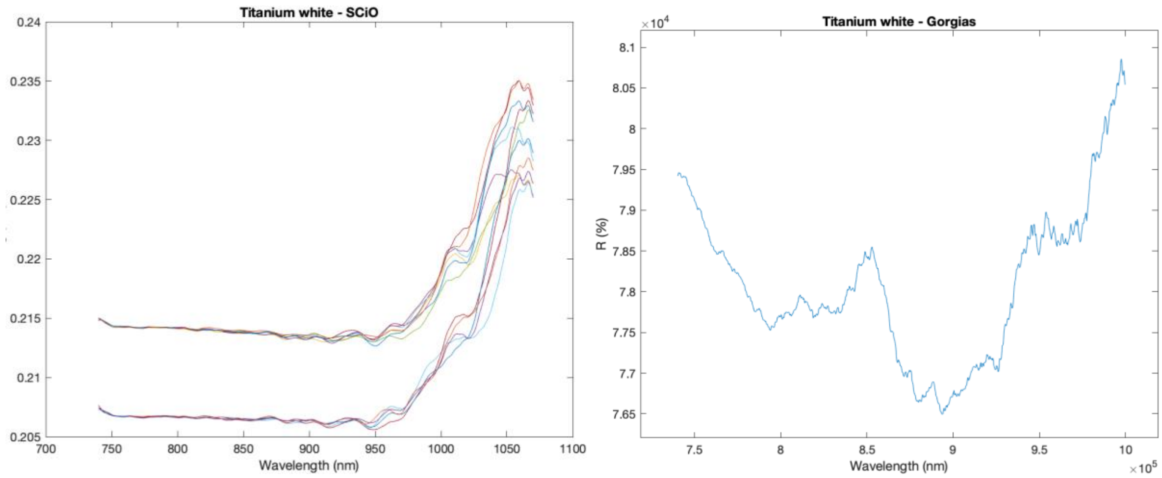




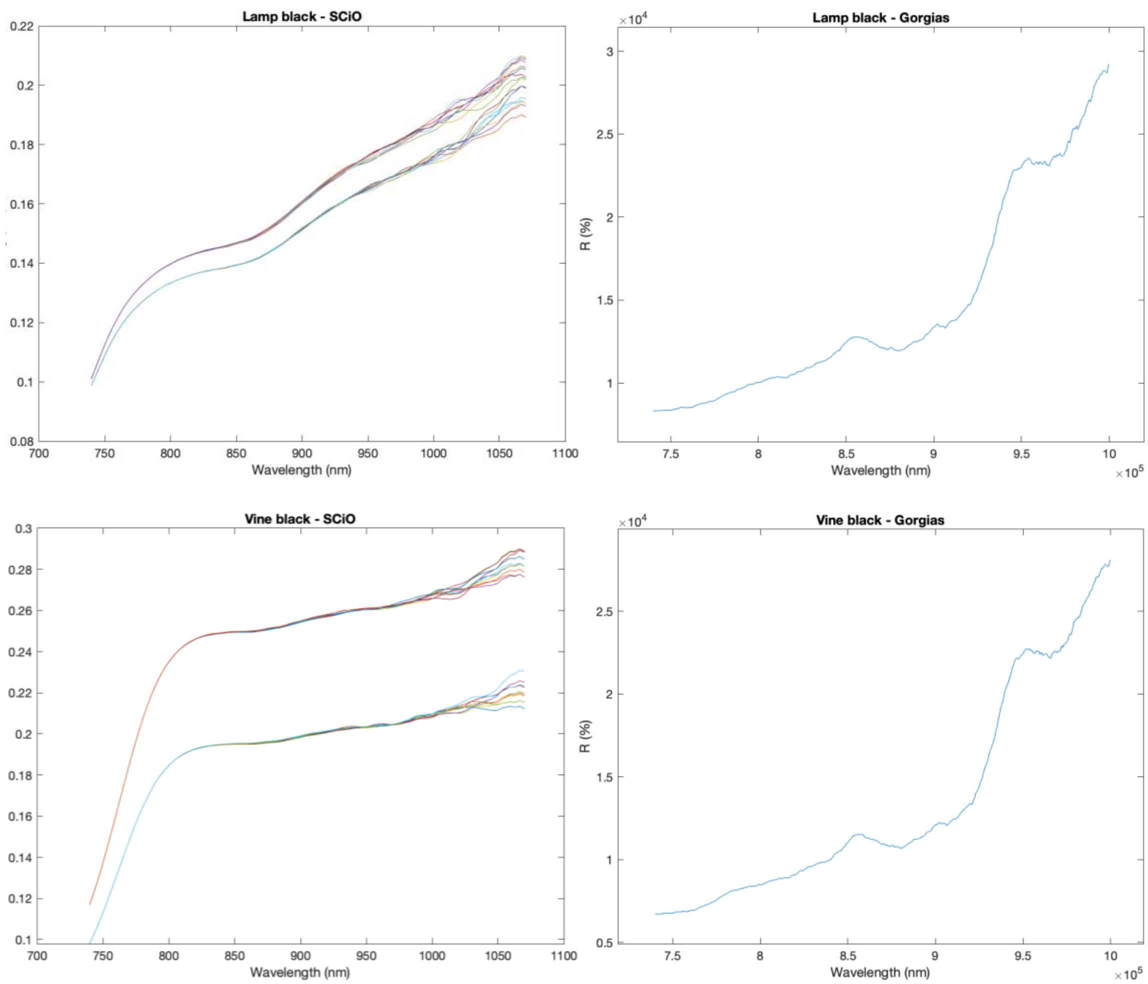


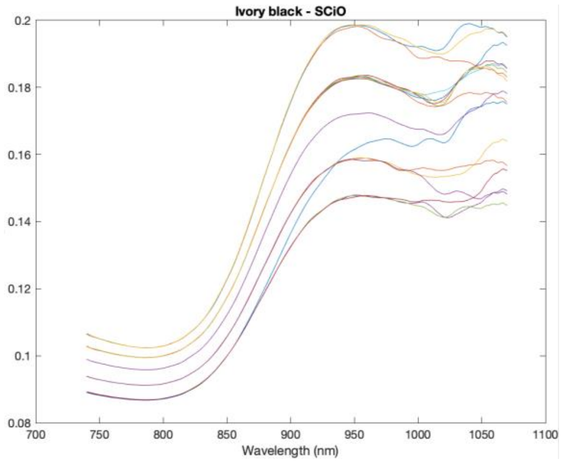


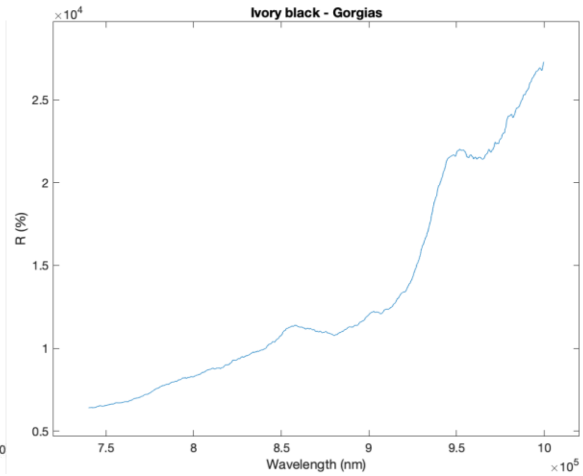

Lead white - SCiO
Wavelength (nm)
Lead white - Gorgias
R (%)
Wavelength (nm)
Zinc white - SCiO
Wavelength (nm)
Zinc white - Gorgias
R (%)
Wavelength (nm)
Lithopone - SCiO
Wavelength (nm)
Lithopone - Gorgias
R (%)
Wavelength (nm)

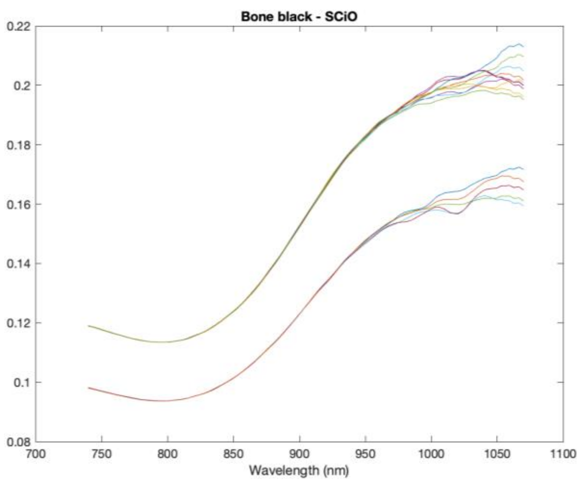


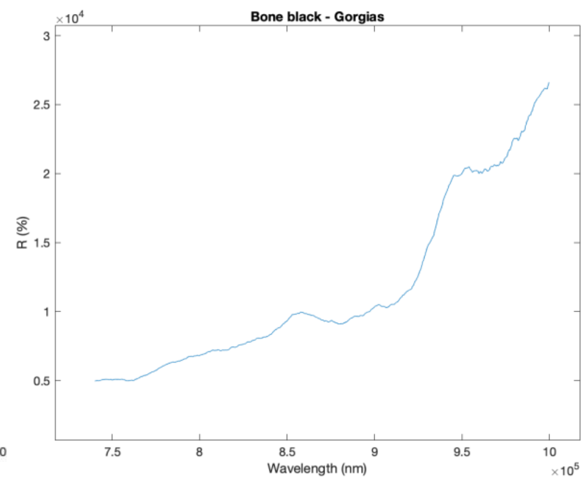
Black pigments

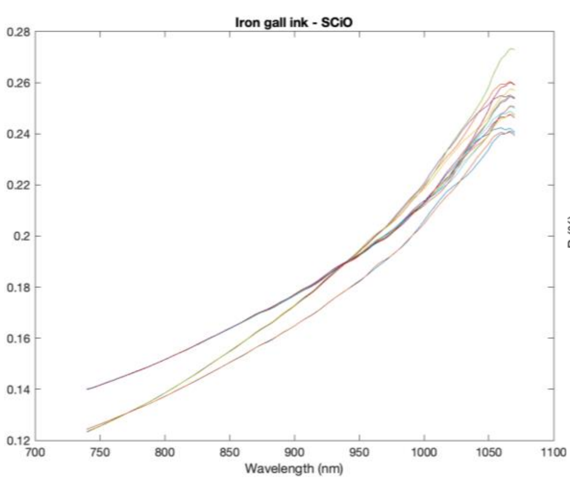


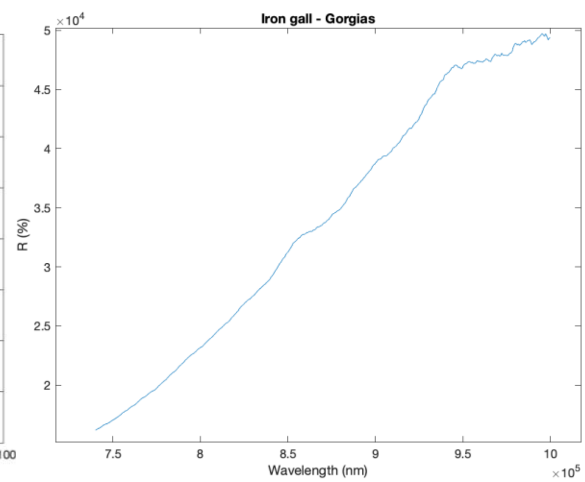

Ivory black - SCiO
Wavelength (nm)


Ivory black - Gorgias
R (%)
Wavelength (nm)

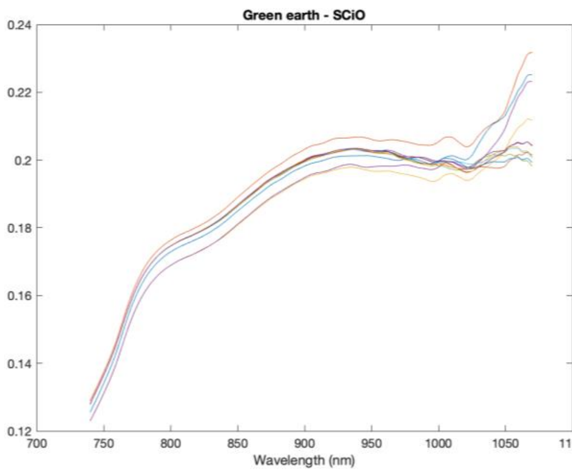

Bone black - SCiO
Wavelength (nm)

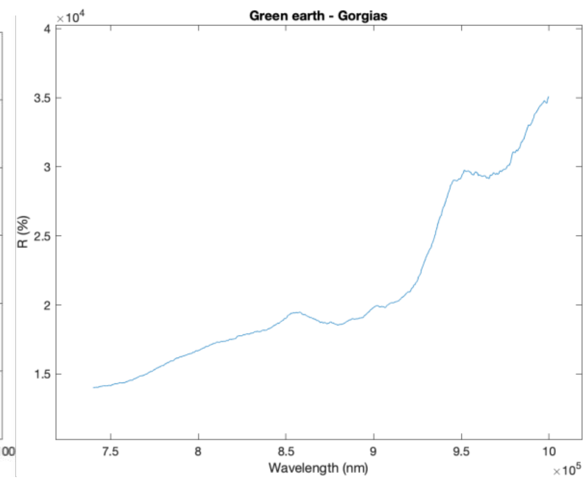

Bone black - Gorgias
R (%)
Wavelength (nm)

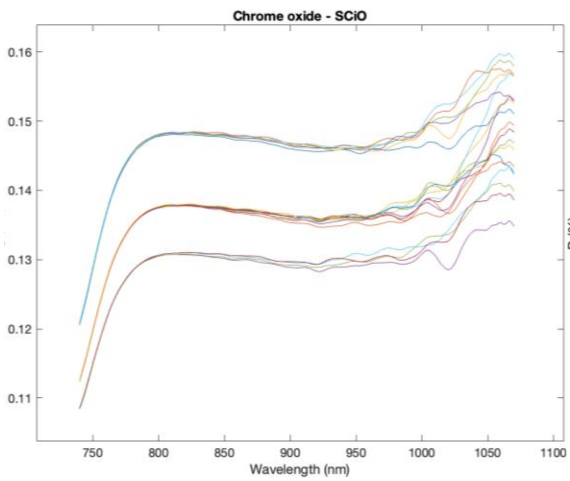

Iron gall ink - SCiO
Wavelength (nm)

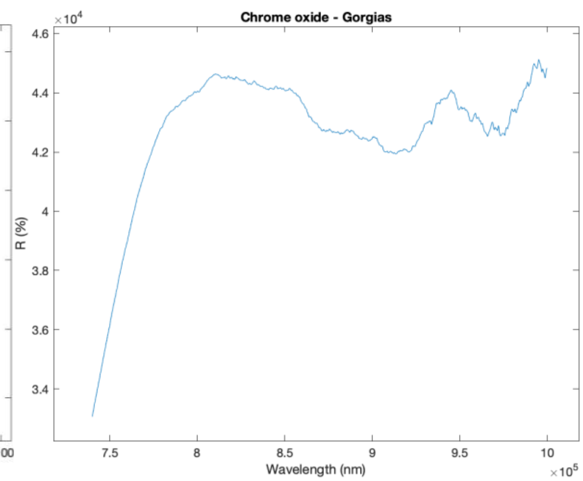

Iron gall - Gorgias
R (%)
Wavelength (nm)

Green pigments

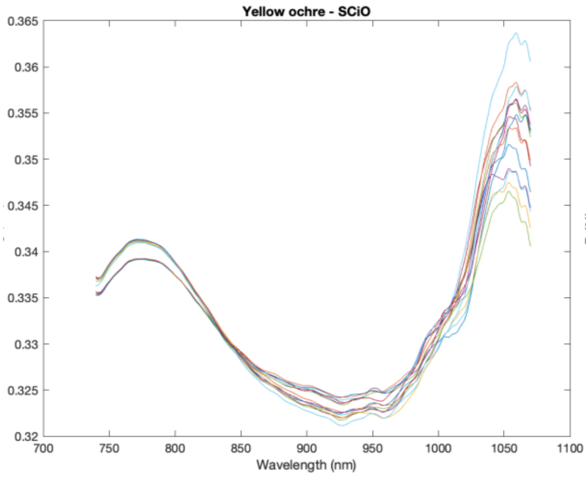


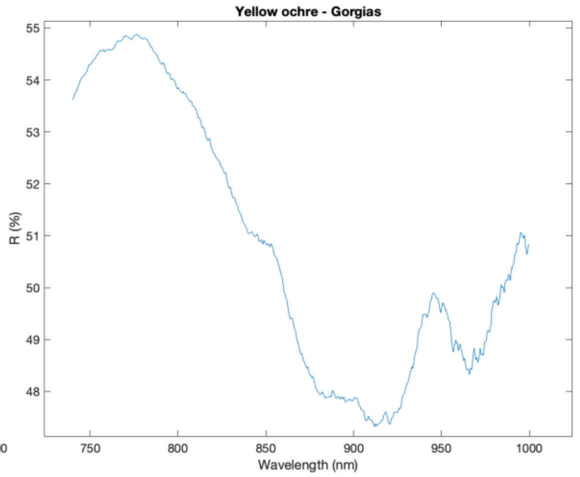


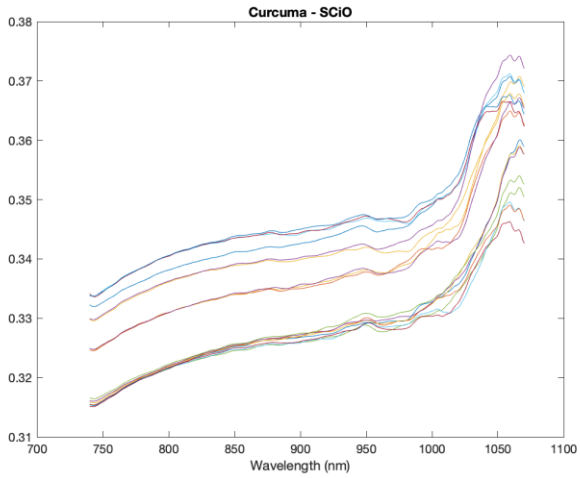


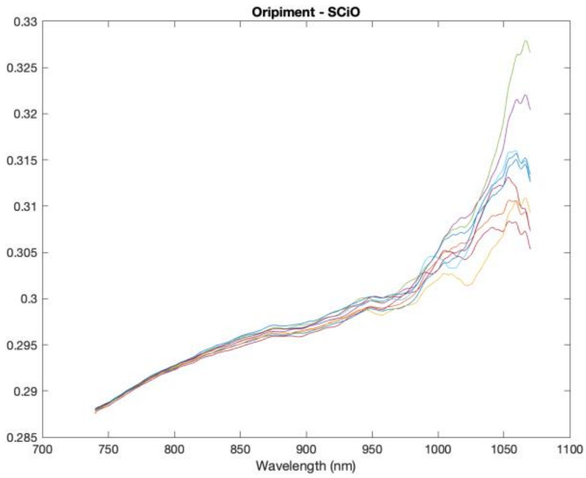


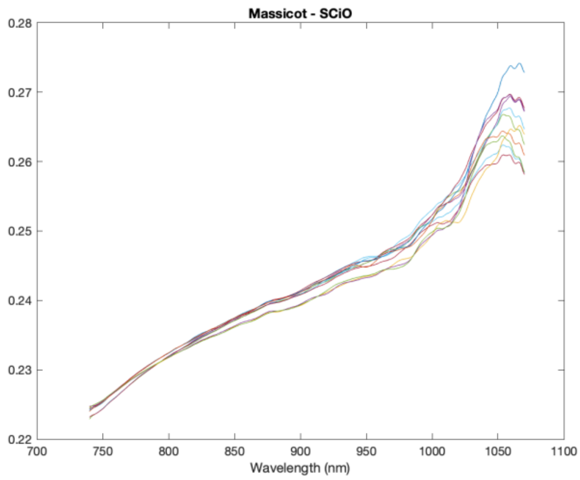
Yellow pigments

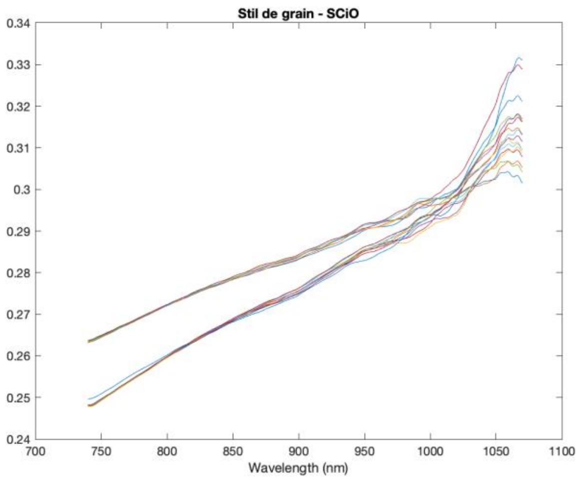


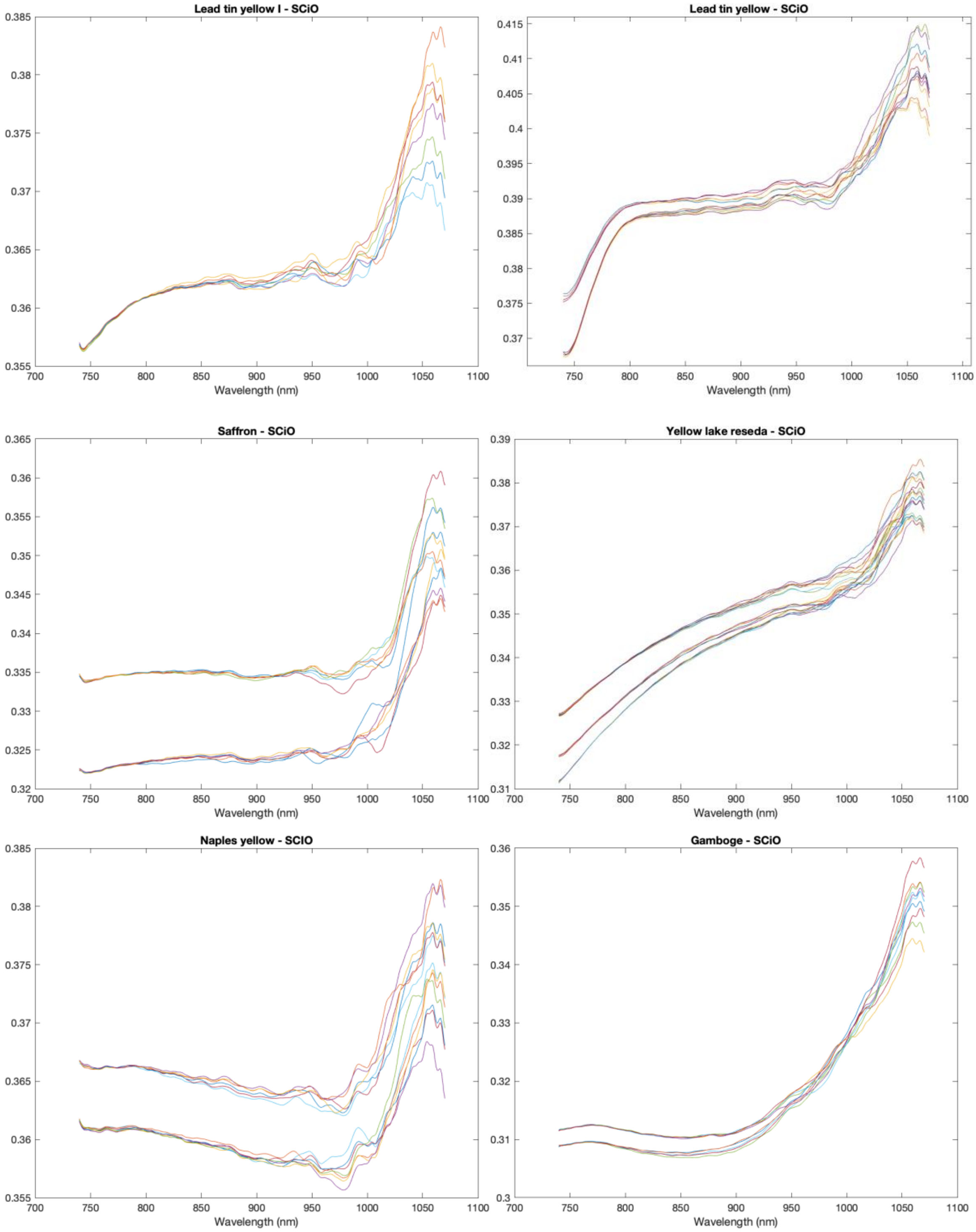


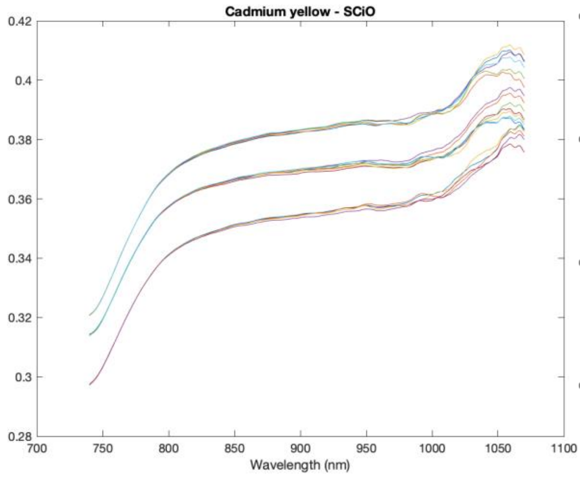


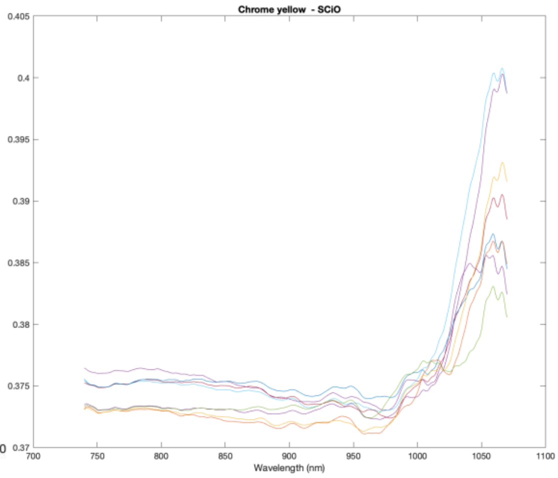




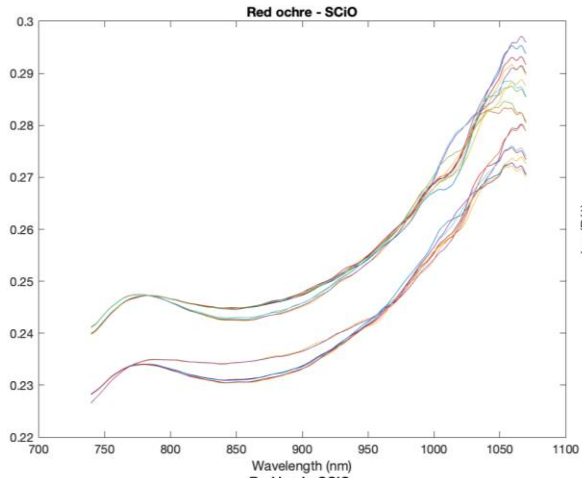


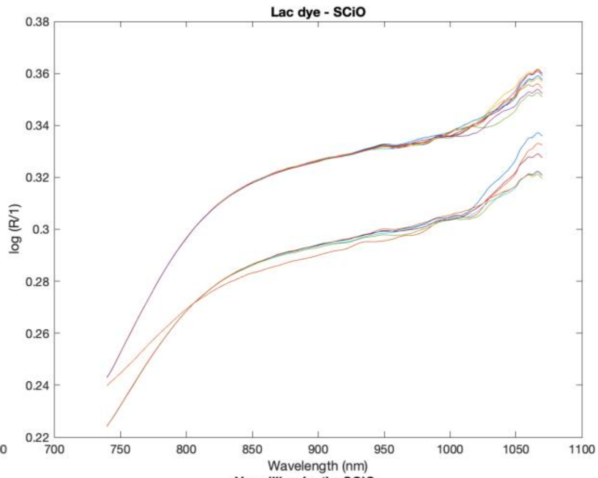

Lead tin yellow I - SCiO
Wavelength (nm)
Lead tin yellow - SCiO
Wavelength (nm)
Saffron - SCiO
Wavelength (nm)
Yellow lake reseda - SCiO
Wavelength (nm)
Naples yellow - SCIO
Wavelength (nm)
Gamboge - SCiO
Wavelength (nm)

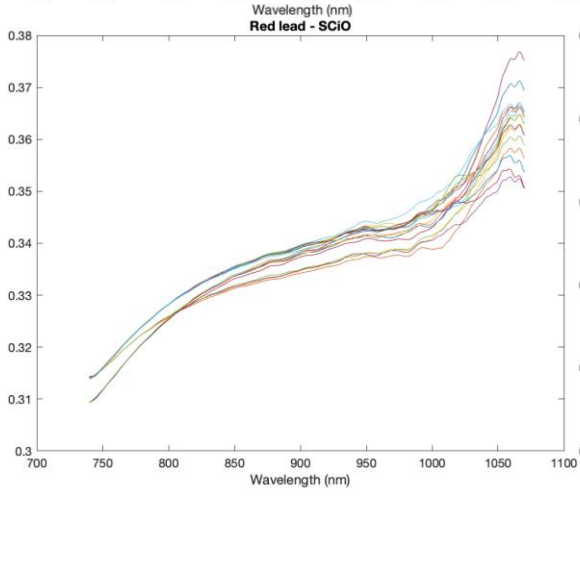


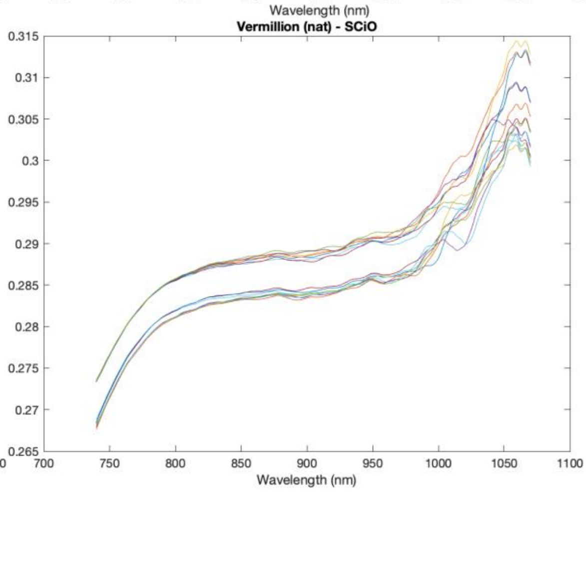


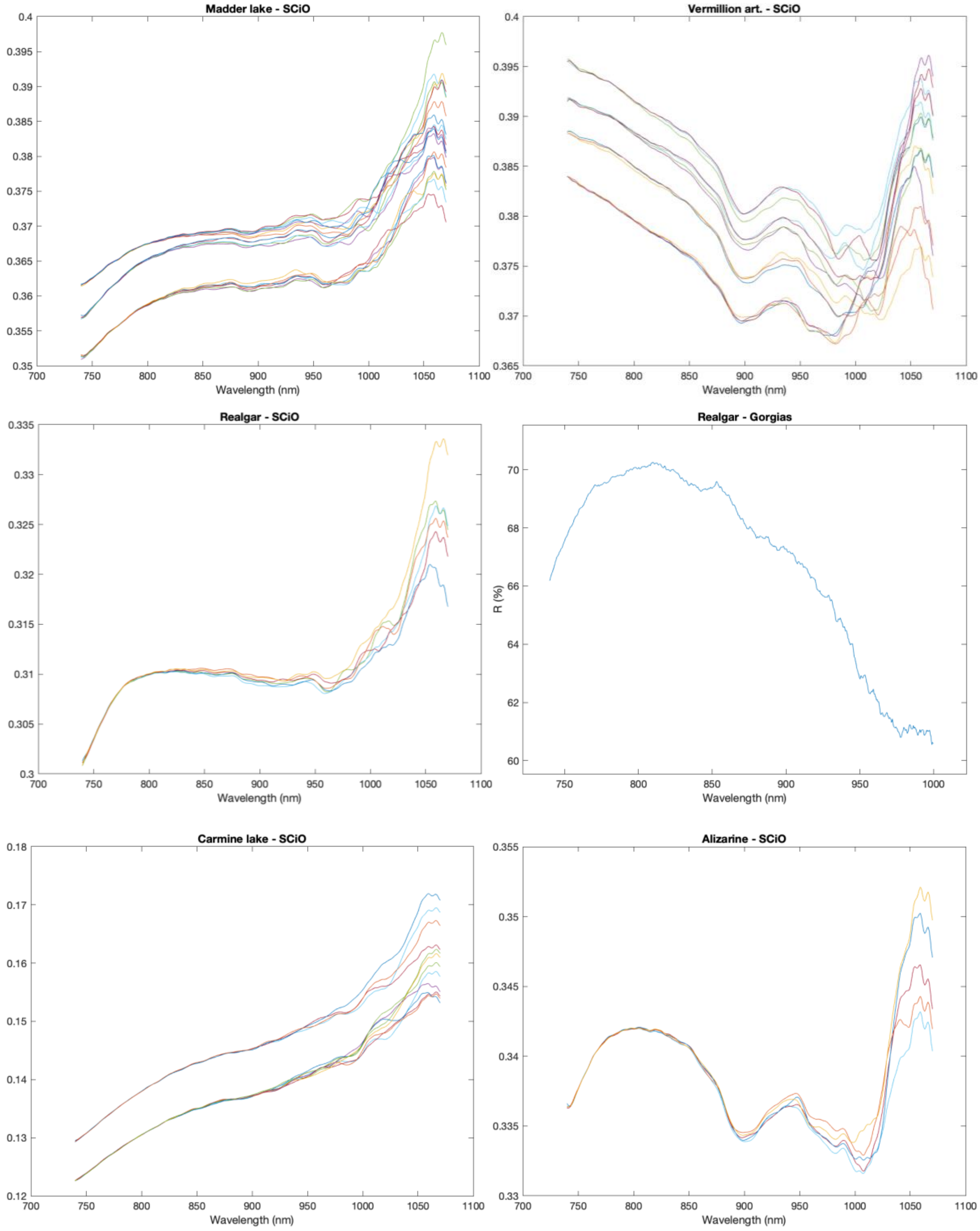
Red pigments

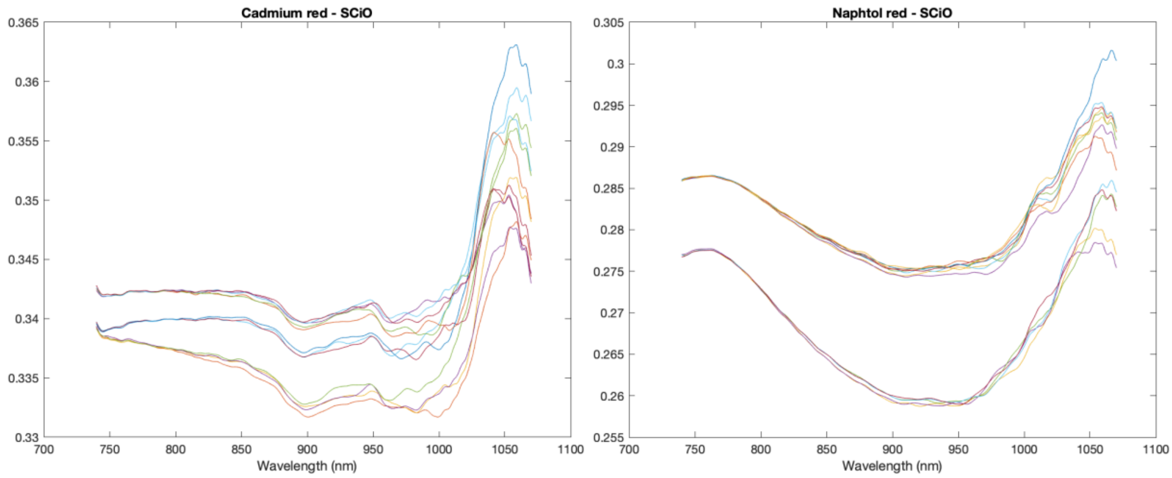






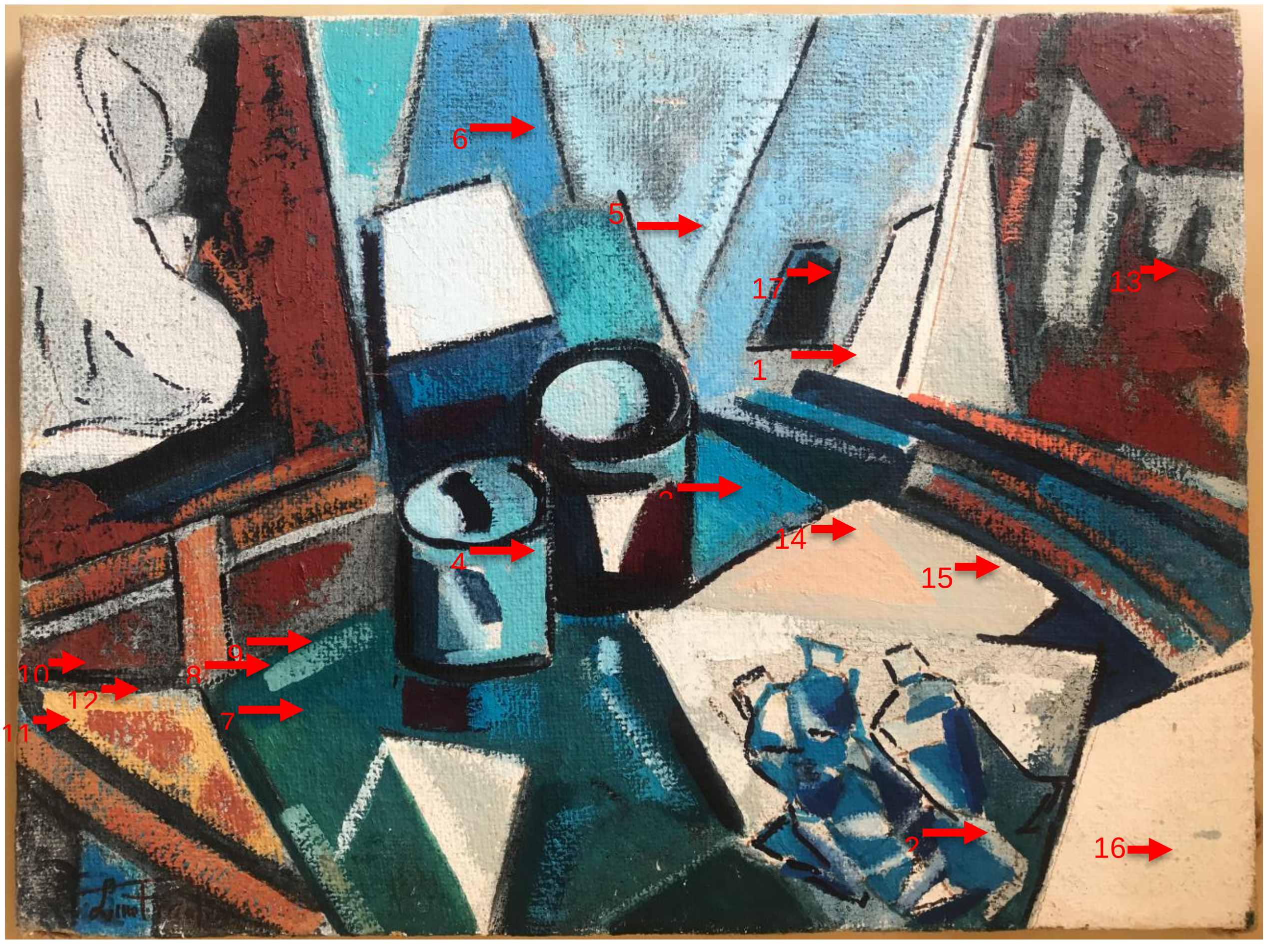



Madder lake - SCiO
Wavelength (nm)
Vermillion art. - SCiO
Wavelength (nm)
Realgar - SCiO
Wavelength (nm)
Realgar - Gorgias
R (%)
Wavelength (nm)
Carmine lake - SCiO
Wavelength (nm)
Alizarine - SCiO
Wavelength (nm)

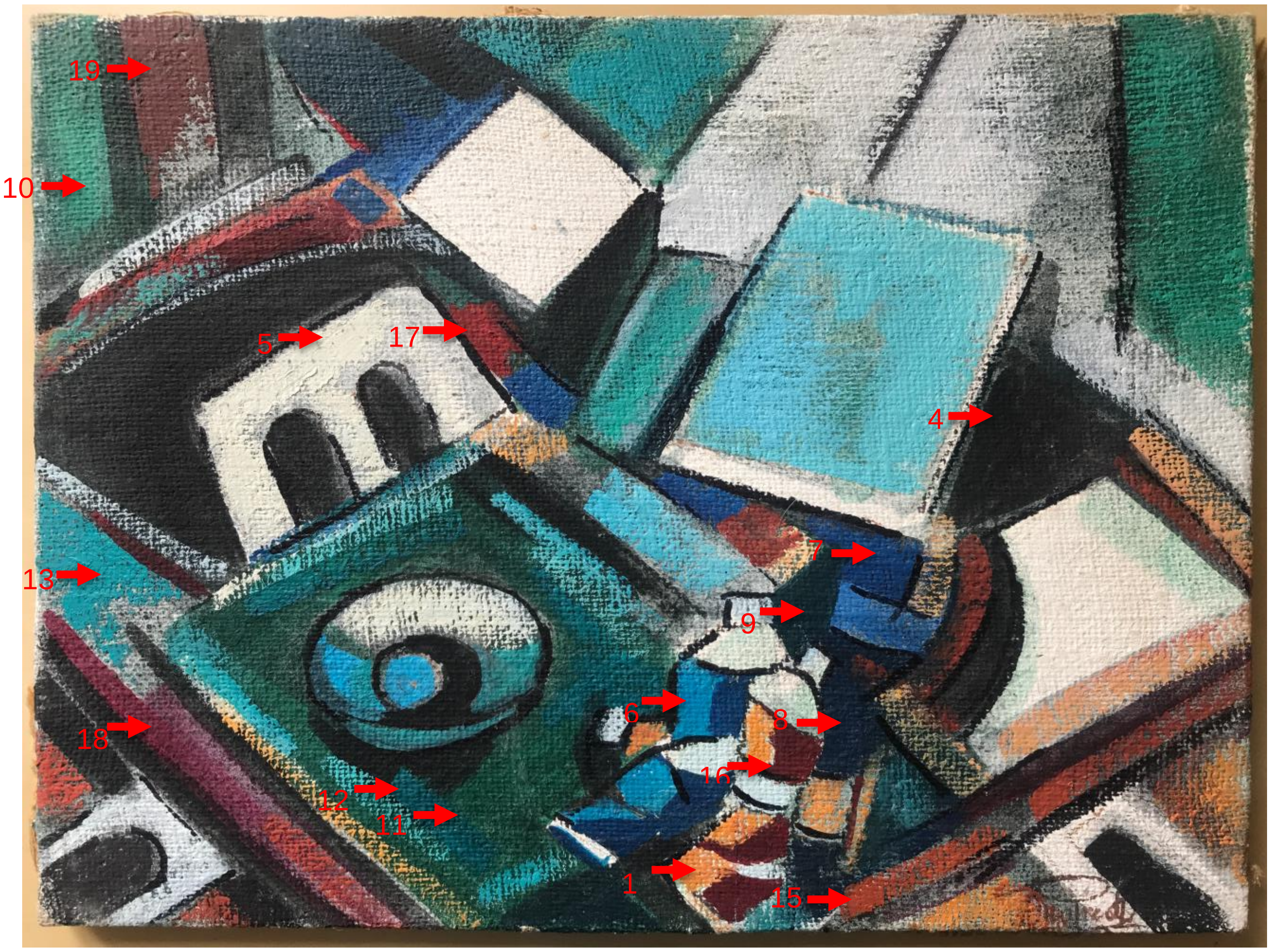

Cadmium red - SCiO
Wavelength (nm)
Naphtol red - SCiO
Wavelength (nm)

B. Appendix: points of analysis

CASE STUDY II



CASE STUDY III



CASE STUDY IV

CASE STUDY V