

Applications of Advanced ATR-FTIR Spectroscopic Imaging to Objects of Cultural Heritage

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I would like to dedicate this thesis to Wolfgang, 與在臺灣的家人

Declaration of Originality

This doctoral thesis documents the results of research conducted within the Department of Chemical Engineering at Imperial College London from November 2019 to August 2023, under the supervision of Professor Sergei Kazarian. Except where acknowledged, all the material presented is the original work of the author, and all information has been referenced appropriately. No part of this thesis has been submitted for a degree at any other university.

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Abstract

The aim of this thesis was to create innovative methods for scientific examination of cultural heritage objects. These methods were intended to enhance Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopic imaging approaches using new designs and implementations, optimising experimental procedures. It is hoped that the results of the case studies, including oil paintings, antique photographs, and painted sculptures, along with the advancement of knowledge in this thesis, can aid in the development of scientifically supported and improved conservation strategies.

The analysis of the pigments used by Martiros Saryan was firstly performed in this thesis. The results shed light on the chemical characterisation of the pigments, as well as the formation of degradation products in the pigments such as metal carboxylates and oxalates.

The second case study of oil paintings involved two cartoons by Edward Poynter from the Heritage Collections at the UK Parliament, which have suffered from white crusts. The results of the cross-sectional samples have provided conservators with guidance for cleaning treatments of the white crusts. Metal carboxylates with different crystallinity were successfully characterised. This has explained the possible degradation process associated with the relocation of metal ions from ground layers to form the white crusts on the surface of the paintings.

Subsequent to the study of the oil paintings, the focus of this thesis moved on to three types of 19th–20th black and white antique photographs: salt prints, albumen photographs, and silver gelatine photographs. Successful classification of the three antique photographs and chemical characterisation of different layers within each photograph were achieved. Furthermore, three-dimensional depth profiling experiments were conducted to investigate the surface of the photographs.

The final case study in this thesis examines Donatello's Virgin and Child sculptures. F. Polarisation measurements were implemented to study polarisation behaviours and structural inhomogeneity of the detected chemical components.

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List of Symbols

Symbol	Description	Unit
E	Energy of radiation	J
h	Planck's constant	J × s
ν	Frequency of light	s ⁻¹
$\tilde{\nu}$	Wavenumber of light	m ⁻¹
V_c	Speed of light	ms ⁻¹
k	Force constant	N/m
μ	Reduced mass	kg
m	Mass of an atom	kg
N	Number of atoms in a molecule	–
T	Transmittance of the Light beam	–
I	Intensity of light beam	–
A	Absorbance of light	–
ε	Molar absorptivity of sample	L × mol ⁻¹ × m ⁻¹
c	Concentration of sample	mol × L ⁻¹
l	Effective path length	m
n	Refractive index	–
λ	Wavelength of light	m
θ	Angle of incidence	°
dp	Penetration depth	m
de	Effective thickness	m
r	Lateral spatial resolution	m
ν_{sy}	Symmetric stretching vibration	–
ν_{as}	Anti-symmetric stretching vibration	–
δ	Bending vibration	–

List of Acronyms

2D	Two-dimensional
ATR	Attenuated Total Reflection
CA	Cluster analysis
EDS	Energy Dispersion Spectroscopy
EM	Electromagnetic
FIR	Far-Infrared
FOV	Field Of View
FPA	Focal Plane Array
FTIR	Fourier Transform Infrared
GC-MS	Gas Chromatography-Mass Spectrometry
HeNe	Helium-Neon
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IR	Infrared
IRE	Internal Reflection Element
LA	Linear Array
LDA	Linear Discriminant Analysis
LED	Light-Emitting Diode
LM	Light Microscopy
MCT	Mercury Cadmium Telluride

MIR	Mid-Infrared
MU-ATR	Metal Underlayer-Attenuated Total Reflection
NA	Numerical Aperture
NIR	Near-Infrared
NMR	Nuclear Magnetic Resonance
O-PTIR	Optical Photothermal Infrared
OPLS	Orthogonal Partial Least Squares
PCA	Principal Component Analysis
PLS	Partial Least Squares
PTIR	Photothermal-Induced Resonance
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
SG	Savitzky-Golay
S/N	Signal-To-Noise
SORS	Spatially Offset Raman Spectroscopy
SR	Synchrotron Radiation
UK	United Kingdom
UV	Ultraviolet
V&A	Victoria and Albert
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Publications and Conferences

The results presented in this thesis are described in the following publications:

1. Liu, G. L., & Kazarian, S. G. (2022). Recent advances and applications to cultural heritage using ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging. *Analyst*, 147(9), 1777-1797.
2. Liu, G. L., Guerreiro, E., Babington, C., & Kazarian, S. G. (2023). ATR-FTIR spectroscopic imaging of white crusts in cross sections from oil cartoons by Edward Poynter in the Heritage Collections at UK Parliament. *Journal of Cultural Heritage*, 62, 251-267.
3. Liu, G. L. & Kazarian, S. G. (2023). Characterisation and Degradation Analysis of Pigments in Paintings by Martiros Sarian: Attenuated Total Reflection Fourier Transform Infrared Spectroscopic Imaging and X-ray Fluorescence Approach. *Heritage*, 6, 6777-6799.
4. Liu, G.L., Chen, T. C., & Kazarian, S. G. (2024). Identification of black and white antique photographs via non-destructive microscopic and spectroscopic techniques coupled with chemometric approaches. *Microchemical Journal*, 200, 110297.

Other Publications (not included in this thesis):

- Liu, G. L., Chang, H. K., Chuang, Y. C., Lin, Y. M., & Chen, P. Y. (2020). Reversible Underwater Adhesion: The Unique C-shaped Suckers of Net-winged Midge Larvae (*Blepharicera* sp.). *Scientific Report*, 10, 9395.

Conferences:

- Science and Engineering Research for Cultural Heritage (SERCH) Conference 2023 Imperial College London, UK. Oral presentation and Poster.

1 Introduction

The utilisation of infrared (IR) spectroscopic technique, specifically Fourier transform infrared (FTIR), in the imaging of cultural heritage objects has witnessed significant growth in research over the last two decades (Liu & Kazarian, 2022; Rosi, Cartechini, et al., 2019b), starting with its first application in 1999 in reflection mode to an oil painting, *The Anatomy Lesson of Dr Nicolaes Tulp* (Heeren et al., 1999). In contrast to conventional spectroscopy, which only allows for recording a single spectrum for each measurement, FTIR spectroscopic imaging can obtain spatial and spectral information simultaneously, revealing the two-dimensional (2D) chemical distribution over an area of the detected samples. Furthermore, FTIR spectroscopic imaging measurements conducted in ATR mode have minimal or no requirements for sample preparation and can provide high lateral spatial resolution. It is especially beneficial for ATR-FTIR spectroscopic imaging to be employed in the chemical visualisation and identification of original materials and/or degradation products within cross-sections of cultural objects that have a multi-layer structure.

A wide variety of scientific techniques have been utilised to examine cultural heritage objects. These techniques can be non-invasive, meaning the analysis requires no sampling; non-destructive, meaning the analysis may or may not need sampling, but the sample remains intact during analysis and is thus available for future analyses; or even destructive, meaning the sample is destroyed after the analysis. The ATR-FTIR spectroscopic imaging technique is classified as a non-destructive technique, which is significantly useful for the scientific investigation of cultural objects. It should be noted that ATR-FTIR spectroscopic imaging cannot replace other non-destructive techniques but rather complements the acquired findings to build a broader, deeper and more accurate interpretation for the results of scientific research on the cultural objects.

ATR-FTIR spectroscopic imaging has recently gained popularity in the scientific investigation of cross sections of oil paintings or other painted objects of cultural heritage over the last fifteen years. Its first two applications to analyse cross-sectional

samples containing heterogenous layers occurred in 2008 (Goodall et al., 2008; Spring et al., 2008). With the advantage of ATR-FTIR spectroscopic imaging, distributions of degradation products and original materials in the cross-sections of cultural objects can be resolved, assisting in exploring the artist's techniques and delving into mechanisms of the degradation. In this thesis, two case studies of oil paintings were explored through the application of ATR-FTIR spectroscopic imaging.

In addition to oil paintings or other painted objects of cultural heritage, ATR-FTIR spectroscopic imaging was employed to examine cross-sections of albumen photographs (Ricci et al., 2007), which have an organic binder layer thinner than 10 μm . However, limited imaging research has been conducted to analyse other types of black and white antique photographs in addition to albumen ones. The appearances of these black and white antique photographs may be too similar for archivists to distinguish. Therefore, there is a growing need to establish a database for FTIR imaging analysis of black and white antique photographs. To rigorously assess the FTIR spectra for better identification of various types of antique photographs, chemometric analyses are often applied. In this thesis, chemometric analyses such as Principal Component Analysis (PCA) and k-means clustering were demonstrated to classify the antique photographs.

Another advantage of ATR-FTIR spectroscopic imaging is that this technique can be versatile when equipped with various devices to conduct different measurements. For instance, a variable angle approach utilising apertures that can control different angles of IR incidence can be coupled with ATR-FTIR spectroscopic imaging to probe the sample at different depths (Chan & Kazarian, 2007; Chan et al., 2008; Wrobel et al., 2015). As a result, depth profiling of the sample is attainable. It has also been demonstrated that this variable angle approach can reduce or even prevent band shifts and spectral distortions caused by anomalous dispersion in the ATR mode (Wrobel et al., 2015). Another example is the polarisation method, which utilises p-polarised and s-polarised light that have different directions of the electric field. Different chemical information from the detected sample can be gathered using the polarisation method, which has been demonstrated to acquire the molecular orientation of the detected

materials and/or their degradation conditions (Chrabaszcz et al., 2021; Grégoire et al., 2020; Hikima et al., 2019). However, neither the variable angle approach nor the polarisation method has ever been adopted to investigate cultural objects. Consequently, in this thesis, apertures and a polariser were equipped onto the ATR-FTIR spectroscopic imaging system to explore the versatile usefulness of this technique.

The final goal of this thesis is to develop an effective and innovative experimental protocol that utilises ATR-FTIR spectroscopic imaging to study objects of cultural heritage, coupled with other non-destructive analytical techniques, within the context of scientific investigation. It is anticipated that the findings derived from the case studies and the advancements of this imaging technique presented in this thesis can contribute to the scientifically supported understanding of artwork, establishing reliable strategies for cultural heritage conservation.

1.1 Objectives

The research in this thesis primarily aims to identify and characterise original materials and degradation products of cultural heritage objects using the micro and macro ATR-FTIR spectroscopic imaging technique. Additionally, it seeks to develop novel approaches for this purpose. The subjects of this research encompass oil paintings by Martiros Sarian from the Martiros Sarian House-Museum in Armenia, oil cartoon paintings by Edward Poynter from the Heritage Collections at UK Parliament, three types of black and white antique photographs from college archives and private collections, and Donatello's Virgin and Child sculptures provided by the Victoria and Albert (V&A) Museum. This research has specific objectives, which are listed as follows:

- Demonstrate how the combination of ATR-FTIR spectroscopic imaging and XRF offers significant guidance in the preliminary characterisation of oil paintings that are from a museum where access to scientific investigation is limited.

- Investigate the white crusts found on the surface of oil cartoon paintings to reveal heterogeneity of white crusts and better understand migration processes of materials from the ground layers.
- Apply ATR-FTIR imaging coupled with the chemometric analysis and the variable angle approach to the identification of antique photographs with heterogenous compositions.
- Illuminate how ATR-FTIR spectroscopic analysis can supplement the interpretation of results obtained from other techniques, while also demonstrating the pioneering application of polarised ATR-FTIR measurements to cultural collections from a museum.

2 Literature Review

This section is adapted from: Liu, G. L., & Kazarian, S. G. (2022). Recent advances and applications to cultural heritage using ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging. *Analyst*, 147(9), 1777-1797. (Liu & Kazarian, 2022)

2.1 Scientific investigation of cultural heritage objects

Archaeometry, archaeological science (Tite, 1991) and conservation science (Winter, 2005) are research fields that utilise analytical methods to examine objects of cultural heritage or items in museum collections such as oil paintings, manuscripts, textiles, potteries and metallic artefacts for the purpose of understanding the original manufacturing techniques and materials, as well as tackling and solving problems concerning heritage conservation or preservation (Artioli & Angelini, 2010). There are two main issues related to the preservation of cultural heritage, firstly, degradation which results from interaction between the materials used to produce the artworks, and secondly environmental influences such as light, heat and pollution. Conducting pre-emptive diagnosis measures will lead to effective, early identification of these problems and therefore prompt conservation of important objects of cultural heritage, leading to a time and cost reduction. Another problem is art fraud/forgery which must be recognised because forged copies may jeopardise authentic artworks. As a result, authentication is an important contribution to art history and curatorship (Craddock, 2009).

A wide variety of analytical techniques can be performed to investigate objects of cultural heritage. Each of these methods operate at specific energy levels, spatial scales, spatial resolutions, and has distinct limits of detection and sensitivity. Consequently, the analytical techniques may yield highly varied results and information. These intricacies should not be considered problematic; rather, they should be regarded as a valuable set of tools for obtaining complementary data to address issues

related to cultural heritage objects. These analytical techniques typically use electromagnetic (EM) radiation to probe the material of interest. It should be realised that as well as EM radiation beam incident particle beams such as electrons, neutrons, and protons can also be utilised. According to Maxwell's classical theory, light is a form of EM radiation, characterised by oscillating electric and magnetic field vectors perpendicular to each other (Maxwell, 1865). These fields are synchronised and propagate as sine waves, as depicted in Figure 2.1a. The absorption of light corresponds to the interaction between the electric field of light and matter. In addition to the classical theory, light can be understood from a quantum perspective, as elucidated by Albert Einstein in 1905 regarding the photoelectric effect of light (Einstein, 1905). In Einstein's quantum theory, light consists of particles known as photons, which exhibit wave-like properties. A compilation of light at various frequencies constitutes the electromagnetic spectrum, as illustrated in Figure 2.1b.

The velocity of electromagnetic wave propagation in a vacuum is a constant value of 3×10^8 m/s, known as the speed of light (V_c). The relationship between energy and wavelength for photons can be expressed as

$$E = \frac{hV_c}{\lambda} = h\nu = hc\tilde{\nu} \quad (2.1)$$

where E represents the energy of the radiation or the amount of energy absorbed when a molecule is excited from the ground state to a higher energy state; h denotes Planck's constant, with a value of 6.626×10^{-34} Js; ν signifies the frequency of light, and $\tilde{\nu}$ corresponds to the wavenumber. When a material is exposed to radiation or particles, it interacts with the incident beam, emitting scattered radiation and/or particles. The emitted radiation and/or particles are then analysed to obtain information about the chemical or physical state of the constituent atoms or molecules. Table 2.1 summarises common analytical techniques used in heritage science with information of the types of incident probe and detected signal. These analytical techniques are categorised as spectroscopy, diffraction and imaging, according to Gilberto Artioli's definition on page 20 of *Scientific Methods and Cultural Heritage* (Artioli & Angelini,

2010).

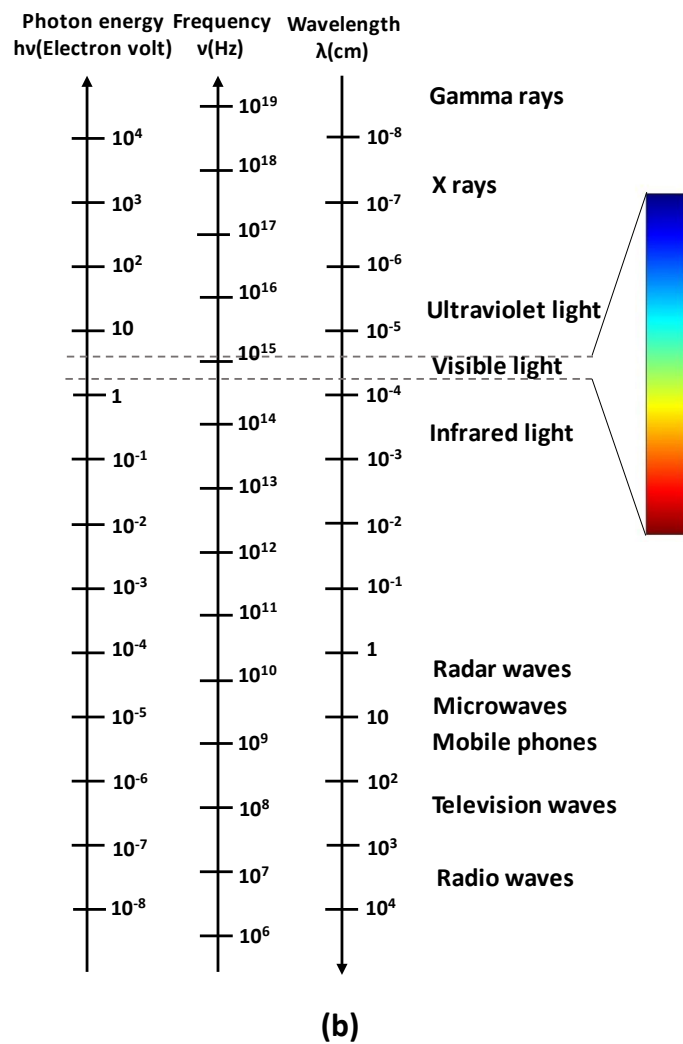
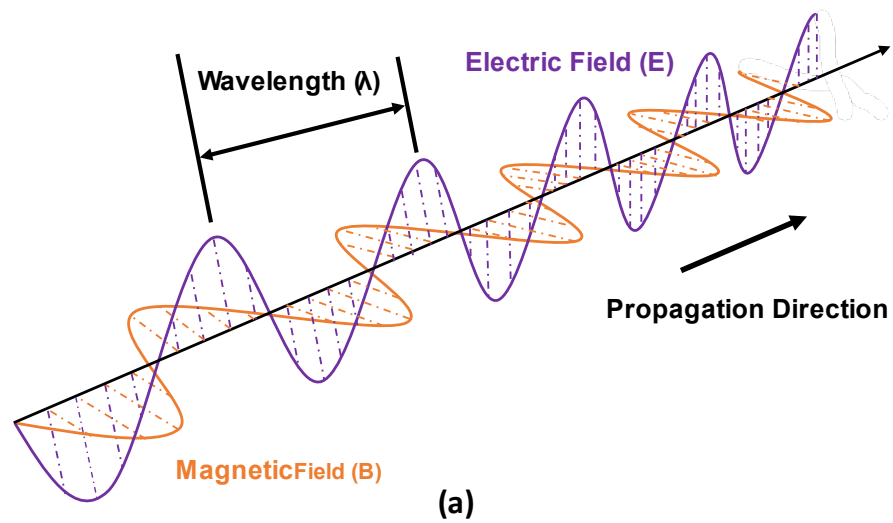


Figure 2.1 (a) Electromagnetic wave and (b) spectrum

Table 2.1 Photon-based analytical techniques used in heritage science

Categorisation	Techniques	Incident probe	Detected signal
Spectroscopy	X-ray fluorescence, XRF	X-rays	X-rays
	Infrared spectroscopy, IR	Infrared	Infrared
	Raman spectroscopy, RS	Visible	Visible
	X-ray photoelectron spectroscopy, XPS	X-rays	Electrons
	Proton induced X-ray fluorescence, PIXE	Protons	X-rays
	Atomic absorption spectroscopy, AAS	Visible	Visible
	Optical emission spectroscopy, OES	Temperature	Visible
	Auger electron spectroscopy, AES	Electrons	Electrons
	Ultraviolet spectroscopy, UV	Ultraviolet	Ultraviolet
	Visible spectroscopy, Vis	Visible	Visible
Diffraction	X-ray diffraction, XRD	X-rays	X-rays
	Neutron diffraction, ND	Neutrons	Neutrons
	Electron diffraction, ED	Electrons	Electrons
Imaging	Scanning electron microscopy-energy dispersive spectroscopy, SEM-EDS	Electrons	Electrons and X-rays
	Optical microscopy, OM	Visible	Visible
	X-rays or neutron radiography	X-rays or neutrons	X-rays or neutrons
	X-rays or neutron computed tomography, CT	X-rays or neutrons	X-rays or neutrons
	Reflectography	X-rays, neutrons, protons, UV, visible or IR	X-rays, neutrons, protons, UV, visible or IR

Because of the uniqueness, value and significance of cultural heritage, the removal of cultural heritage for sampling and the damages caused by sample preparation should be as minimal as possible to minimise the loss of cultural heritage. Even in the case sampling is needed, it is beneficial that the sample can be left intact after the analysis because more information on this specific sample can be acquired by applying other complementary techniques. Non-invasive analysis requires no sampling, while

non-destructive analysis may or may not need sampling but the sample is intact during analysis and thus available for future analyses. Non-invasive techniques, such as portable X-ray Fluorescence (XRF), X-ray radiography and portable UV/IR and Raman spectroscopy, are beneficial for scientific investigation of cultural heritage. These non-invasive techniques can also be employed in situ, offering identification of chemical heterogeneity of cultural heritage objects. Despite the usefulness of the non-invasive techniques, there are some limitations such as they are not able to provide detailed and/or stratigraphic characterisation of the samples.

Although it is ideal for the conservation field to adopt non-invasive approaches, there may be a fundamental need to obtain more unambiguous and detailed identification of the cultural heritage objects, the information which non-invasive approaches may not be sufficient to yield. As a result, micro-invasive analysis (Artioli & Angelini, 2010; Trentelman, 2017), where a small amount of samples is extracted from cultural heritage objects using a micro-scale system, is necessary. Micro-invasive techniques can be non-destructive, allowing the samples to be intact for further study. The most common non-destructive analytical techniques that conservators and scientists employ in laboratories are Light Microscopy (LM), Scanning Electron Microscopy (SEM) in combination with Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.

FTIR spectroscopy is an established analytical tool which has been applied to material identification of cultural heritage due to its sensitivity and specificity (Peets et al., 2017). In recent decades, FTIR spectroscopic imaging systems have been developed which can obtain spatial and spectral information simultaneously, showing the chemical distribution over an area of the samples.

Common FTIR spectroscopy and spectroscopic imaging techniques implemented to investigate cultural heritage and ancient artefacts include transmission, external reflection and attenuated total reflection (ATR) mode (Derrick et al., 2000; Rosi, Cartechini, et al., 2019a; Salzer & Siesler, 2014). In the next section, we delve into the fundamentals of FTIR spectroscopy and spectroscopic imaging, with a specific emphasis on the ATR-FTIR mode. This mode holds particular significance within the

context of this thesis.

2.2 Fundamental of ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging

2.2.1 Fundamental background of IR spectroscopy

Infrared (IR) spectroscopy is a pivotal tool in analytical chemistry and utilises the principle that IR radiation absorbed by molecules. As shown in Figure 2.1, IR light is characterised as a spectral range that encompasses a broad spectrum of wavelengths, ranging from 700 nm (7×10^{-5} cm) to ~ 1000 μ m (10^{-1} cm), or equivalently, spanning wavenumbers from 14000 cm^{-1} to $\sim 10^{-1}$ cm^{-1} (Ball, 2003). The IR region can be divided more specifically into three distinct segments: the Near-Infrared (NIR) extending from $\sim 14\,000$ cm^{-1} to ~ 4000 cm^{-1} , the Mid-Infrared (MIR) extending from $4,000$ cm^{-1} to 400 cm^{-1} , and the Far-Infrared (FIR), extending from 400 cm^{-1} to 200 cm^{-1} .

Vibrations, along with certain contributions from rotations, can induce vibrational motion in molecules, which occurs within the infrared (IR) region owing to the resonance with the molecules' specific frequencies. At this resonant frequency, the atoms within the molecules exhibit a more pronounced vibrational magnitude, resulting in alterations in intramolecular distances and bond angles. The model of molecular oscillators is often employed to elucidate the vibrational degrees of freedom. Moreover, molecular vibrations are approximately described using a classical harmonic oscillator. The vibrational frequency, ν , in this classic harmonic oscillator is determined by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (2.2)$$

where k is the bond force constant, measuring the strength of the molecular bond

between the two masses. The reduced mass, μ , equals:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2.3)$$

where m_1 and m_2 are the two masses. A photon can be absorbed by a molecule only if its frequency corresponds to the molecular vibration's frequency. This means that only equidistant vibrational levels are allowed, with energy transitions primarily occurring between adjacent levels. However, in real-world experiments, we also observe transitions between non-adjacent levels. The transitions between two vibrational energy levels are reflected as absorption bands in an IR spectrum. The vibrational energy levels are given by:

$$E_n = h\nu \left(n + \frac{1}{2} \right) \quad (2.4)$$

where n is the vibrational quantum number, which have integer values. When a vibrational transition takes place between the ground vibrational state ($n = 0$) and the first vibrational level ($n = 1$), it is referred to as the fundamental transition, which is the most common type of vibrational transition at room temperature (Chalmers & Griffiths, 2002). Vibrational transitions between the ground state vibrational level and the second ($n = 2$) or the third ($n = 3$) vibrational level known as overtone bands, while transitions among multiple excited vibrational levels ($n > 0$) produce combination bands. All of these transitions can be observed in the NIR and MIR regions.

When IR light is absorbed by a molecule, various types of vibrations, including vibrational or normal modes, can occur. The number of these modes depends on whether the molecule is linear or nonlinear, determined by $3N - 5$ or $3N - 6$, respectively, where N represents the number of atoms. These modes encompass stretching vibrations of molecular bonds, which can be symmetric or anti-symmetric, as well as angle deformation (bending) vibrations, categorised as in-plane or out-of-plane bending. The MIR range, which is where most fundamental transitions in organic

and inorganic molecules are detected, is commonly employed for the examination of cultural heritage materials (Casadio & Toniolo, 2001; Low & Baer, 1977). This thesis exclusively focuses on research conducted within this MIR spectral range. Materials that lack vibrations in the MIR region, such as certain sulfides and oxides, can be analysed using an FIR detector, as these materials are more likely to absorb in the FIR region, as discussed in the other literature sources (Derrick et al., 2000; Kendix et al., 2008).

An IR spectrum represents absorbance or transmittance bands in a sample as a function of frequency, which is usually displayed in wavenumbers, due to the proportionality of frequency to photon energy. Absorption bands consist of lines arising from rotational transitions induced by discrete IR light absorption, which are observable only in gaseous samples. Absorbance (A) is the base -10 logarithmic reciprocal of transmittance (T), defined as the ratio of light intensity with the sample (I) to that without (I_0) in Equation 2.5 and 2.6:

$$T(\%) = \frac{I}{I_0} \quad (2.5)$$

$$A = \log \frac{I_0}{I} \text{ or } A = \log \frac{1}{T} \quad (2.6)$$

While both absorbance and transmittance find widespread acceptance, the absorbance spectrum appears to be more meaningful and aptly suited for quantitative analysis due to its linear correlation with the concentration of the measured sample. This correlation is explained by Beer-Lambert's Law, which states that:

$$A = \varepsilon cl \quad (2.7)$$

where ε stands for the molar absorptivity of the sample, c for its concentration, and l for the effective path length of measurement. Based on Equation 2.7, it is important to note that absorbance depends on the length of the path the light travels through the

sample. Therefore, the thickness of the sample must be carefully controlled to prevent total absorption of peaks in the spectrum. This is especially vital when using transmission mode for measurement. However, in the case of ATR, sample thickness doesn't pose an issue, as explained further in Section 2.2.2.

2.2.2 ATR-FTIR spectroscopy

One of the first papers using IR spectroscopy to investigate ancient artefacts was published in 1966 (Casadio & Toniolo, 2001). Here, an improvement of spectral resolution and detection limit was noted due to the development of FTIR spectroscopy in place of dispersive IR; the former technique has contributed enormously to archaeometry and conservation of cultural heritage since 1980s (Low & Baer, 1977; Messerschmidt & Harthcock, 1988). A standard FTIR spectroscopy design consists of an IR source, an interferometer, an accessory for sample placement, a detector, and a personal computer for spectral data analysis. The core component of an FTIR spectrometer is the Michelson interferometer, a two-beam interferometer, as illustrated in Figure 2.2. The IR source emits the light beam which is then split using the beam splitter. The beam splitter directs the IR light beam towards two mirrors: one that moves and one that is fixed. The optical pathlength of the IR light beam directed to the moving mirror changes as the mirror moves, while the optical pathlength of the IR light beam directed to the fixed mirror remains unchanged. The difference between the two optical pathlengths is described as optical retardation. When the two beams, having travelled varying distances, return to the beam splitter, they recombine either constructively or destructively, producing an interference pattern, which is recorded as an interferogram. In physics, when the waves are in phase, meaning the peaks of one wave align with the peaks of another wave of the same frequency at the same point (or the troughs align with the troughs), constructive interference occurs, resulting in an increased amplitude. Conversely, when waves are out of phase, where the peak of one wave meets the trough of another wave, destructive interference occurs, resulting in a decreased amplitude (Stark, 2023). The recombined IR light beam is subsequently

directed towards the sample, and the interferogram is recorded and collected using a detector. To establish a reliable reference of the optical path for the moving mirror, a Helium-Neon (HeNe) laser is used, which serves as an indicator of the path of the IR light beam within the instrument, especially when aligning the optics in an accessory is required. Since the interferogram is a time domain signal, it is converted into an IR spectrum in the frequency domain using the Fourier transform algorithm, as detailed in Equation 2.8:

$$f(t) = \int_{-\infty}^{\infty} F(\tilde{\nu}) e^{i2\pi\tilde{\nu}t} d\tilde{\nu} \leftrightarrow f(\tilde{\nu}) = \int_{-\infty}^{\infty} F(t) e^{-i2\pi\tilde{\nu}t} dt \quad (2.8)$$

where t is time and $\tilde{\nu}$ is the wavenumber.

FTIR spectroscopy typically utilises transmission, external reflection, and ATR modes, as illustrated in Figure 2.3. In a transmission measurement, infrared light

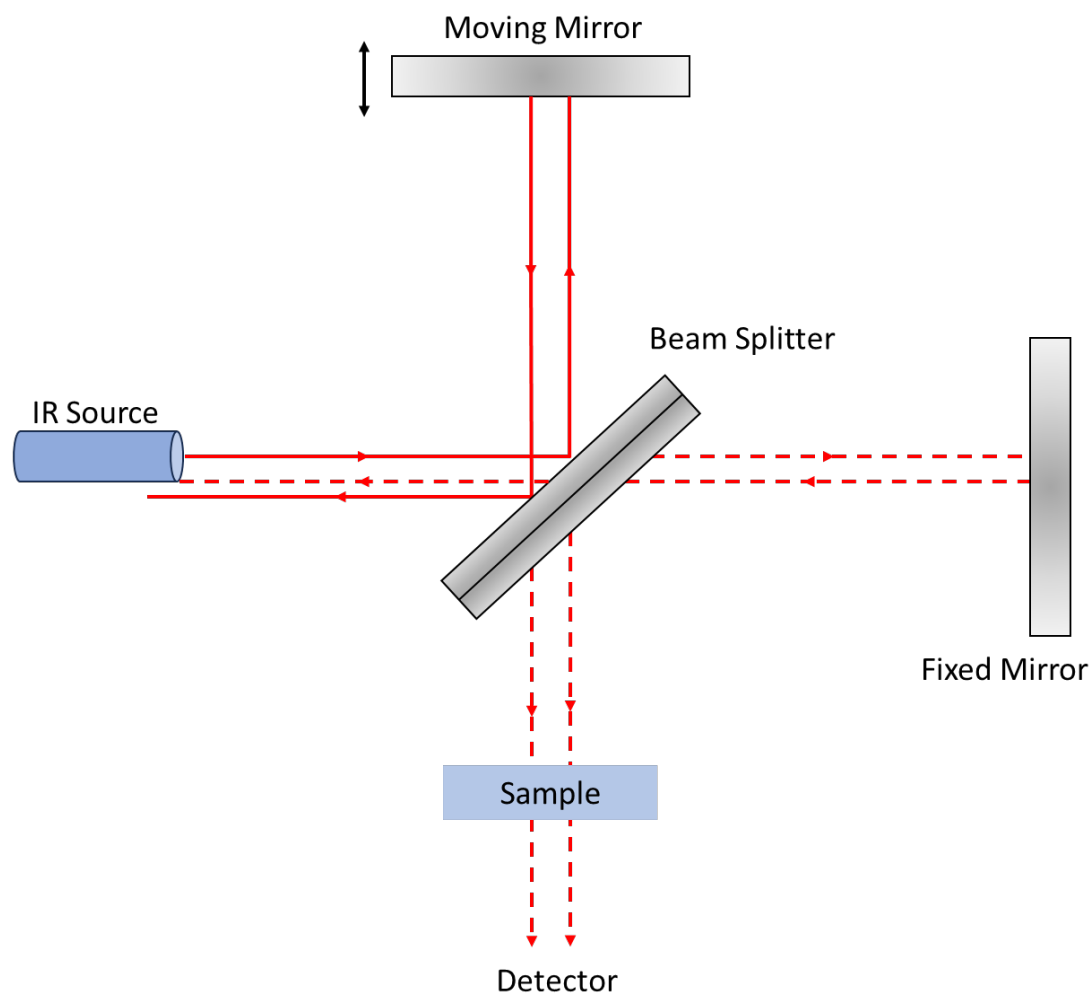


Figure 2.2 Schematic of the Michelson interferometer inside an FTIR spectrometer

passes through a sample, whilst in external reflection and ATR modes, the infrared light is reflected off the external or internal surfaces of the sample. External reflection and ATR are reflection modes which have simpler sample preparation compared to that for transmission mode requiring thin sections of samples which are generally between 3 and 10 μm to ensure that absorbance of all spectral bands is not out of scale. In an ATR measurement, the beam of infrared light is directed through an infrared transparent medium which has higher refractive index to the sample which has lower refractive index, but in an external reflection measurement, the infrared beam is not directed through the infrared transparent medium. This means that in ATR measurements, adequate contact between the IRE (see below) and the studied sample is necessary to achieve high-quality spectra (Chan & Kazarian, 2003; Joseph et al., 2010). In ATR measurements, absorption spectra are recorded, leading to no spectral distortion attributed from the variable contributions of both volume and surface reflection which can be seen in external reflection measurements (Miliani et al., 2012; Ploeger et al., 2011). As a result, spectral results produced by ATR-FTIR spectroscopy are comparable to that produced by transmission FTIR spectroscopy. However, a type of spectral distortions such as anomalous dispersion may happen in an ATR

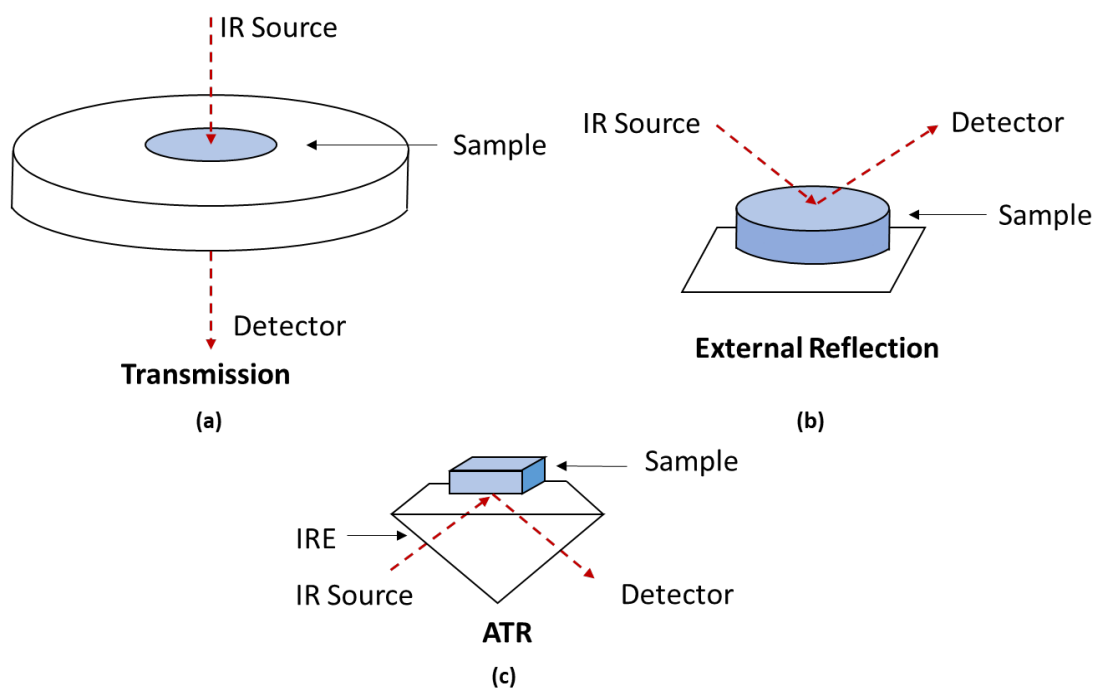


Figure 2.3 Three typical modes of FTIR: (a) transmission, (b) external reflection and (c) attenuated total reflection (ATR) modes

measurement when the angle of incidence is close to the critical angle. This type of spectral distortion is commonly observed particularly for samples with high refractive indices or when dispersion of the refractive index for samples is close to the wavelength of an absorbance band. As a result, this may cause significant shift in position of spectral band compared to the position of spectra band measured in transmission spectra. This minor problem may cause spectral misinterpretation if reference transmission mode spectra are directly used to explain acquired ATR spectra. In the author's laboratory it has been demonstrated that it is possible to reduce the distortion of spectral bands by increasing angle of incidence, which significantly reduces the effect of anomalous dispersion. This approach was demonstrated in macro ATR-FTIR spectroscopic imaging (Chan et al., 2008) as well as in micro ATR-FTIR spectroscopic imaging (Wrobel et al., 2015) which has been discussed in these review articles (Chan & Kazarian, 2016; Kazarian & Chan, 2013) where the phenomenon of anomalous dispersion and the ways of its mitigating were presented in details.

In ATR-FTIR spectroscopy, an Internal Reflection Element (IRE) with a high refractive index (n_1) is brought into contact with an optically non-transparent sample which has a lower refractive index (n_2). IRE is often a hemi-sphere or a prism and most often made of diamond, silicon (Si), zinc selenide (ZnSe) or germanium (Ge). When the beam of IR is directed at above a certain angle, called the critical angle, total internal reflection occurs, where a standing wave of radiation called an evanescent wave is generated by IR light totally reflecting inside the IRE. This evanescent wave then interacts with the sample, attenuating the IR beam. The attenuated IR beam exits the IRE and reaches the detector, where the resulting signal is converted to an IR spectrum. The electric field of the evanescent wave exponentially decays to a distance from the surface of the IRE to e^{-1} of the maximum, which is known as the depth of penetration (dp) for non-absorbing materials. dp varies with the wavelength (λ), as shown in Equation 2.9, and dp is also dependent on the angle of incidence of IR light and the refractive indices of both the sample and the IRE. the depth of penetration (dp) can be calculated by:

$$dp = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - n_{21}^2}} \quad (2.9)$$

where n_{21} stands for n_2/n_1 . The depth of penetration (dp) is a frequently employed metric for estimating the measurement depth within the sample, and its validity has been established for materials with low absorption characteristics (Mirabella, 1983). The depth of penetration (dp) should not be confused with the concept of effective thickness (de), which is defined as the sample thickness that results in an equivalent absorbance in transmission when compared to the ATR measurement (Kazarian & Chan, 2010b). The determination of effective thickness (de) is feasible through the employment of Harrick's polarised light equations, denoted as s-polarised (Equation 2.10) and p-polarised (Equation 2.11) light:

$$de(S) = \frac{\lambda n_{21} \cos \theta}{\pi(1-n_{21}^2) \sqrt{\sin^2 \theta - n_{21}^2}} \quad (2.10)$$

$$de(P) = \frac{\lambda n_{21} \cos \theta (2 \sin^2 \theta - n_{21}^2)}{n_1 \pi (1-n_{21}^2) [(1+n_{21}^2) \sin^2 \theta - n_{21}^2] \sqrt{\sin^2 \theta - n_{21}^2}} \quad (2.11)$$

Here, λ represents the wavelength, θ is the angle of incidence, and n_{21} represents the ratio of refractive index of the sample to that of the ATR, n_2/n_1 . The parameters in Equation 2.10 and 2.11 are the same as those in Equation 2.9. The mean values of $de(S)$ and $de(P)$ can be regarded as the effective pathlength of non-polarised light de , as acquired from Equation 2.12:

$$de = de(S) + de(P) \quad (2.12)$$

As the wavelength increases, both de and dp increase. Additionally, dp and de also exhibit an increase when ATR crystals with a lower refractive index (n_1) are used or when measuring a sample with a higher refractive index (n_2). Determined from

Equation 2.9–2.12, when $\frac{n_{21} \cos \theta}{(1-n_{21}^2)} \left(1 + \frac{2 \sin^2 \theta - n_{21}^2}{(1+n_{21}^2) \sin^2 \theta - n_{21}^2} \right)$ approaches 1, regardless of the wavelength of the illuminating beam, the value of dp converges toward that of de . The application of altering dp and de using a variable-angle approach is explored in Section 4.4, which focuses on the research related to depth profiling antique photographs.

2.2.3 ATR-FTIR spectroscopic imaging

An FTIR spectrometer coupled with an infrared array detector can be employed to simultaneously collect IR spectra and spatial locations within the sample, generating two-dimensional (2D) chemical images. These 2D chemical images indicate areas of high absorbance at a wavenumber for different materials over a region of the sample. Previously, these images where spectral and spatial information are acquired simultaneously were produced by point-by-point mapping using a single element detector, generally Mercury Cadmium Telluride (MCT). With the development of infrared array detectors, 2D chemical images can be obtained in more timesaving methods, such as line mapping and imaging (Rosi, Cartechini, et al., 2019a) which both utilise multiple element detectors (usually MCT). The difference between the detectors of line mapping and imaging is that the line mapping detector is arranged in a linear array format, as known as Linear Array (LA), and the imaging detector is arranged in a square or rectangular array format, as known as Focal Plane Array (FPA), of which size is varied from 64×64 , 128×128 to 256×256 elements (pixels). As a result, line mapping using LA enables spectra to be acquired through scanning rows of the static sample and then mapping into an image, whereas true imaging using FPA detector allows thousands of FTIR spectra from the whole sample area to be collected simultaneously into an image, thus allowing the studies of dynamic systems. Both methods have advantages and disadvantages which are not discussed in this thesis but can be referred to elsewhere (Kazarian & Chan, 2013; Steiner & Koch, 2009). Illustration of these three different methods for producing 2D chemical images is shown in Figure 2.4.

ATR-FTIR spectroscopic imaging using an FPA detector can be operated in two modes: micro and macro. The micro setup utilises a microscope to spatially locate the detected area of the sample. In addition, the IRE used in the micro mode is often a Ge crystal which provides a high lateral spatial resolution. In this thesis, axial resolution is disregarded, and only lateral resolution is considered as the spatial resolution. The lateral spatial resolution (r), defined as the minimum distance between two distinguishable points, is restricted by the diffraction limit as shown in Equation 2.13:

$$r = \frac{0.61\lambda}{NA} \quad (2.13)$$

where λ is the wavelength of light and NA is the Numerical Aperture of the objective. NA is defined as $n = \sin \alpha$ where n is the refraction index of the imaging medium between the objective and the sample and α is half the angular aperture.

Micro ATR-FTIR spectroscopic imaging provides high lateral spatial resolution

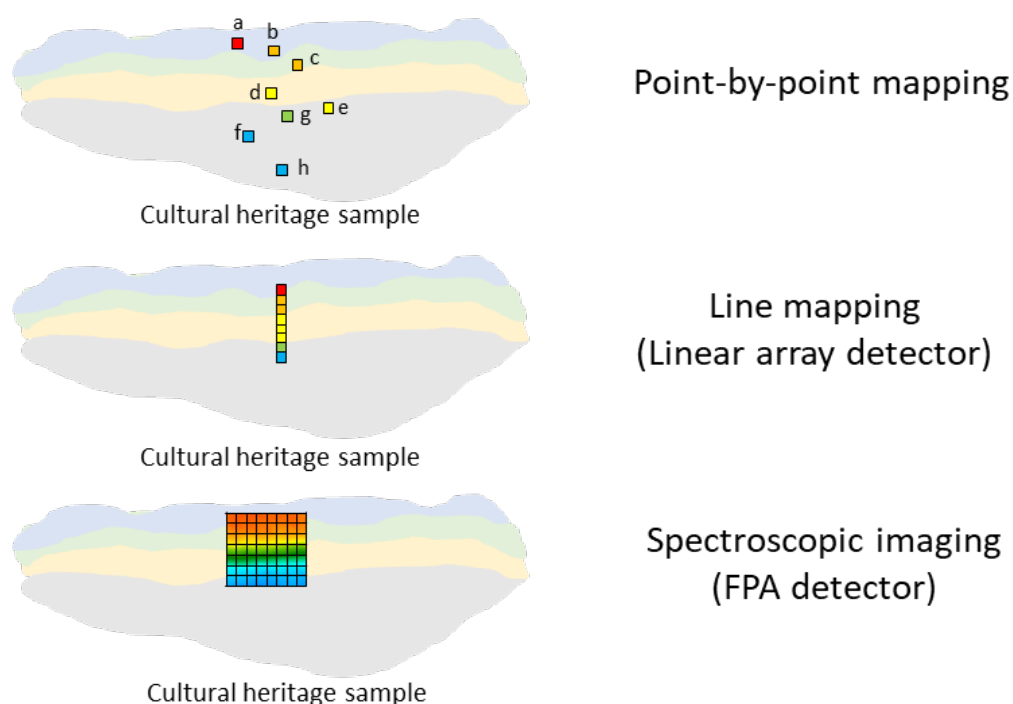


Figure 2.4 Schematic of point-by-point mapping, line mapping and spectroscopic imaging. The colours of pixels represent concentration of an investigated component. Red/orange colours represent a high concentration of the component while blue/green region shows a low concentration.

because of much higher NA (n for Ge = 4). Compared to the micro setup, the macro setup is performed without using a microscope and the IRE used in the macro mode is an inverted prism that can be made of ZnSe, Ge, Si, and diamond. The IRE is installed on an ATR accessory in a large sample compartment that connects to an FTIR spectrometer. Macro ATR-FTIR imaging offers possibilities for scanning large sample areas consisting of a complex heterogeneous matrix. Table 2.2 summarises the different measurement fields of view and the lateral spatial resolutions using different ATR imaging accessories from the author's laboratory (Ewing & Kazarian, 2017; Ricci et al., 2006). ATR-FTIR spectroscopic imaging in its macro and micro modes has been applied to a wide variety of research field ranging from biological systems (Song & Kazarian, 2019), polymers (Hikima et al., 2019), pharmaceuticals (Ewing & Kazarian, 2018) and forensic science (Bailey et al., 2012). There is a perception among some researchers that pressure required to achieve a good contact may cause damage on the cultural heritage sample. Therefore, ATR-FTIR spectroscopic imaging cannot be considered a non-destructive technique. However, from the experience of the author's laboratory, a good contact can be achieved without the need to apply much pressure and thus would not damage the sample or leaving a mark. In ATR-FTIR spectroscopic imaging it is possible to observe the quality of contact of Ge crystal with the sample in live touching using FPA detector and to measure the smallest pressure for taking measurements.

Table 2.2 Measurement parameters of ATR-FTIR spectroscopic imaging accessories. Reprinted with permission, (Ewing & Kazarian, 2017) copyright (2017) The Royal Society of Chemistry

ATR accessory	Image size	Lateral spatial resolution ^a
Germanium micro ATR crystal in a microscope objective	64 μm $\times$ 64 μm	4 μm
Zinc selenide crystal (Oil analyser, Specac Ltd.) in macro ATR imaging	2.5 mm $\times$ 3.6 mm	40 μm
Diamond crystal (Golden Gate, Specac Ltd.) in macro ATR imaging	500 μm $\times$ 700 μm	15 μm

^a Lateral spatial resolution is estimated based on using a wavenumber of 1700 cm^{-1} .

Various types of cultural heritage can be characterised for molecular analysis using ATR-FTIR spectroscopic mapping and imaging. Cultural objects which have multi-layered structures or are polychrome, such as oil paintings, historical paper and polychrome sculptures, are typical examples. These multi-layered structures of cultural heritage may be composed of heterogeneous mixtures of organic/inorganic materials and possible deterioration products. ATR-FTIR spectroscopic mapping and imaging can offer identification and spatial location of these various components of cultural heritage, contributing to addressing specific analytical issues and conservation problems. The recent applications of using ATR-FTIR spectroscopic mapping and imaging are highlighted in Section 2.3.

2.2.4 Sample preparation

As discussed in Section 2.2.2, commonly used acquisition modes for investigation of cultural heritage include external reflection, ATR and transmission. The choice of acquisition modes depends on the type, nature and amount of available samples and the research questions. Sampling, which is the process of extracting a small portion of material for further analysis, is often necessary for ATR-FTIR spectroscopic analyses. Because of the fragile state, the preciousness and the aesthetic properties of cultural heritage objects, lower amount of sampling is preferred. Micro-sampling (Artioli & Angelini, 2010) which requires small amount of the material ($\sim 100 \mu\text{m}^2$ or $\sim 0.05\text{--}0.1$ g, dry weight) to be taken can be used for ATR-FTIR spectroscopic measurements because of its high sensitivity and specificity. Micro sampling may reduce or even avoid noticeable damages to cultural heritage objects. Furthermore, samples taken from cultural heritage objects can be measured repeatedly using this non-destructive ATR-FTIR spectroscopic technique and other non-destructive analytical equipment.

Powder and fragments are common types of samples for the analysis in ATR-FTIR spectroscopic measurements. Fragments contain cross-section and thin-section approaches which work in reflection and transmission mode, respectively. As mentioned in Section 2.2.2, thin sections which generally require thicknesses of

samples to be between 3–10 μm is a more difficult sample preparation, especially for investigating complex artwork stratigraphy samples. Therefore, cross sections are more commonly prepared. Sample preparation of both cross and thin sections is conducted by immersing a fragment sample in an embedding material as support which hardens in a short period of time. These embedding materials are often organic polymers such as polyester resins or acrylate (van Der Weerd et al., 2002). However, these organic polymers might permeate into the sample fragments, causing acquisition of spectral signal of the polymers that impede the IR bands of the sample fragments. This problem can be solved using alternative IR-transparent salts such as silver chloride (AgCl) or potassium bromide (KBr) (Pouyet et al., 2014; Prati et al., 2012; Prati et al., 2013; van der Weerd et al., 2004). The spectral interferences caused by polyester resins or acrylate can be eliminated with these alternative IR-transparent salts. Nonetheless, AgCl encounters darkening and accelerated corrosion problems. In addition, KBr is a hygroscopic salt that causes unfeasible preservation for the fragment sample and reduces spectral quality shortly after sample preparation. Because KBr is more fragile than organic polymers, when a polishing procedure is needed it may lead to damage to the sample. Other feasible approaches may be coating the sample with cyclododecane ($\text{C}_{12}\text{H}_{24}$) before the sample is embedded in the organic polymer. This approach avoids penetration of the organic polymers into the sample (Martin de Fonjaudran et al., 2008; Papiaka et al., 2015), but $\text{C}_{12}\text{H}_{24}$ sublimates at room temperature, leaving a gap between the sample and the embedding material. This gap may cause nonoptimal sample-ATR crystal contact when conducting ATR measurements, leading to poor spectral quality. Furthermore, depending on the roughness of the sample it is not always possible to obtain adequate contact between the ATR and the sample. To overcome such challenge, an immersion medium can be used on the cross-sections of different samples of cultural heritage objects embedded in polyester resin. For example, adding droplet of water to fill air gaps allows us to obtain high quality spectra from the paint cross-sections and successfully localise either inorganic compounds or organic substances present as painting materials studied by macro ATR-FTIR spectroscopic imaging (Joseph et al.,

2010).

2.3 Selected applications for cultural heritage analysis

using ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging

This section introduces selected applications of using ATR-FTIR spectroscopic techniques to investigate objects of cultural heritage, such as multi-layered painted artworks, paper, and inorganic substances. It is worth noting that this section does not aim to cover the entire field but rather to discuss applications related to the samples of interest in this thesis.

2.3.1 Multi-layered painted artworks

2.3.1.1 FTIR spectra of materials used for multi-layered painted artworks

FTIR spectroscopy is an ideal tool to examine oil paintings because the paintings consist of multiple layers, which have a variety of organic and inorganic components that can be identified with FTIR spectroscopy or spectroscopic imaging. Typically, an oil painting may be layered with varnish, glazing, paint layer, underpainting, underdrawing, ground, canvas and wooden stretcher, from the top to the bottom. Among these layers, especially the upper layers, pigments, fillers and binders are often investigated and identified using FTIR spectroscopy and Raman spectroscopy. Both organic and inorganic pigments in paintings have been studied extensively (Bacci, 2000; Castro et al., 2003; Genestar & Pons, 2005; Kuckova et al., 2005; Pięta et al., 2019; Prati et al., 2010). The inorganic pigments have metal elements which can be detected with XRF. However, details such as complex structures of these pigments can only be further investigated with FTIR spectroscopy and Raman spectroscopy.

Databases of these inorganic materials used in paintings have been studied and built (Castro et al., 2003). Compared to inorganic pigments, organic pigments may have more complex IR spectra and are more likely to suffer from degradation, especially photochemical degradation due to light exposure (Ion et al., 2018). Metal Underlayer-Attenuated Total Reflection (MU-ATR) spectroscopy which is an enhanced sensitivity spectroscopic technique has been employed to investigate organic pigments by analysing a few ng of sample (Prati et al., 2016). This new enhanced FTIR method can reduce the amount of sample, which can be promising for the analysis of trace amount of organic pigments in paintings or textiles. The detailed analytical procedure and applications of MU-ATR-FTIR spectroscopy are described elsewhere (Prati et al., 2016; Quintero Balbas et al., 2019; Sciutto et al., 2017). Identification of pigments is of importance because it can provide early detection of degradation and prompt conservation, and also interpretation of the techniques and palette of artists.

Binders used in paintings have been greatly characterised using FTIR spectroscopy (Nodari & Ricciardi, 2019; Ortega-Avilés et al., 2005; Pilc & White, 1995). Widely used binders are egg tempera, linseed oil, gum arabic and animal glue. The purpose of using these binders in the painting is to mix with organic/inorganic pigments powders, maintaining uniform pigments. It is worth noticing that there may be overlap in spectra between these different binders in complex paint samples. For example, both egg tempera and linseed oil contain triglycerides which have C–H stretching bands at around 2923 and 2872 cm^{-1} , so it may be difficult to distinguish these two binders when interpreting spectra. However, egg tempera also contain protein, so two strong characteristic bands at around 1650 cm^{-1} (amide I, C=O stretching) and 1550 cm^{-1} (amide II, N–H bending) can be used to identify the egg. The FTIR spectroscopic results can be supported and strengthened in combination with a more complete characterisation using Gas Chromatography-Mass Spectrometry (GC-MS), which provides qualitative and quantitative analysis of different analytes (Andreotti et al., 2006; Platania et al., 2020).

Vahur et al. has contributed to building ATR-FTIR spectral databases of materials used on painting including paint materials (inorganic pigments, fillers, binders), oil

paints and protective coatings (Vahur et al., 2009; Vahur et al., 2010; Vahur et al., 2016). These databases can be freely searched online (Vahur et al., 2016). In these databases, the IR region is extended to include MIR and FIR region. Painting materials are often complex mixed organic and inorganic components which may have similar or overlapped characteristic bands in the MIR region, leading to difficult identification. This problem can be solved by examining spectral bands in the FIR region. Most organic constituents such as ester and proteins have spectral bands in the MIR region but have no absorption in the FIR region, while some inorganic substances have absorption in both MIR and FIR regions. Therefore, by examining spectral bands in the FIR region these inorganic substances can be identified (Vahur et al., 2016).

2.3.1.2 Case studies: Paintings

For investigation of oil paintings, non-invasive techniques such as analytical single point devices (e.g. Fibre Optic Reflectance Spectroscopy (FORS)) as well as hyperspectral imaging systems in visible and Near-Infrared (NIR) regions have been exploited to analyse original materials, retouching and degradation (Corradini et al., 2020; Cucci et al., 2016; Delaney et al., 2016). Although these techniques are non-invasive and can be used to discriminate chemical components in the paintings, their spectra are often hard to interpret and needs further confirmation using other analytical techniques such as Raman and FTIR spectroscopies (Corradini et al., 2021). More detailed information can be acquired by examining the stratigraphy of paintings. Non-invasive approaches such as Optical Coherence Tomography (OCT) (Ford et al., 2021), Nuclear Magnetic Resonance (NMR) (Di Tullio & Proietti, 2020), Terahertz imaging (Doria et al., 2020), confocal XRF (Conti et al., 2018; Woll et al., 2004) and micro-Spatially Offset Raman Spectroscopy (micro-SORS) (Conti et al., 2018) can be performed to investigate and characterise the layer successions, but they are not able to provide the 2D distribution of compositional information of the materials. ATR-FTIR spectroscopy can be combined with multivariate techniques to analyse spatial and compositional information of the stratigraphy of a painting (Izzo et al., 2021; Martin de

Fonjaudran et al., 2008). It is of great importance to obtain stratigraphic component information to clarify the original manufacturing technique, deterioration phenomena and subsequent conservation history of the painting. For example, a wall painting may be fresco or secco that can be hard to determine with the naked eye. The main difference between these two types of wall paintings is that the binders of fresco and secco are inorganic and organic compounds respectively. Furthermore, in fresco, calcium hydroxide solution (lime water paste) was added to mix with pigments of the wall paintings (Ergenç et al., 2018; Germinario et al., 2018). ATR-FTIR spectroscopy can be used to confirm whether the fresco or secco technique was used in the manufacturing of wall paintings by detecting the binder areas (Duran & Perez-Rodriguez, 2020; Ergenç et al., 2018).

Metal carboxylates, as known as metal soaps, are a typical deterioration problem in paintings. This problem is caused by the interaction between metal ions from pigments and fatty acids from binders (Casadio et al., 2019). Metal carboxylates might be protrusions on the surface of paintings or aggregated crystals between paint layers. These two forms of deterioration product, protrusions and aggregated crystals, would either affect aesthetical and structural properties of the paintings (Casadio et al., 2019; Gabrieli et al., 2017; Higgitt et al., 2003). Issues of metal carboxylates have been fully explored and discussed in a comprehensive book (Keune et al., 2019). Micro ATR-FTIR spectroscopic imaging has been used for the first time to identify metal soaps owing to COO^- bands in studies by Spring et al (Spring et al., 2008). High lateral spatial resolution of micro ATR-FTIR spectroscopic imaging allows to resolve layers of a few micrometres in the samples from the corresponding paintings and thus reveal the chemical distribution and identify degradation process of metal soaps (Gabrieli et al., 2017). The use of Synchrotron Radiation (SR) sources for FTIR spectroscopic techniques can increase Signal-To-Noise (S/N) in obtained spectra and improve spatial resolution in mapping approaches (Salvadó et al., 2013; Salvadó et al., 2009). However, it is often preferred conducted in transmission mode which requires thin-section preparation, making sampling more challenging. ATR-FTIR spectroscopy has been used to distinguish different metal soaps by examining the positions of COO^-

bands with different metal ions which are shifted to different frequencies (Robinet & Corbeil-a, 2003). Metal ions that interact with fatty acid forming metal soaps such as zinc (Christiansen, Baadsgaard, et al., 2017; Hermans & Helwig, 2020; Hermans et al., 2015), copper (Mazzeo et al., 2008; Spring et al., 2008), lead (Henderson et al., 2019; Spring et al., 2008), cadmium and chromium (Christiansen, Sørensen, et al., 2017) have been examined using ATR-FTIR spectroscopic mapping and imaging. To confirm metal ions more precisely in the metal carboxylates, SEM-EDX is often employed. Figure 2.5 shows an example of chemical characterisation of a white paint cross-section from Jackson Pollock's *Alchemy* (1947) (Gabrieli et al., 2017). ATR-FTIR 2D chemical images and SEM-EDX elemental images are reported to indicate the distribution of metals (Al, Zn and Ti) and location of Zn carboxylates, ZnSt₂ and AlSt(OH)₂, featuring the band at 1590 cm⁻¹, 1540 cm⁻¹ and 1588 cm⁻¹, respectively. Another research using SEM-EDX and ATR-FTIR imaging, where pigments, extenders and binding media were identified in the stratigraphy of a painting claimed to be painted

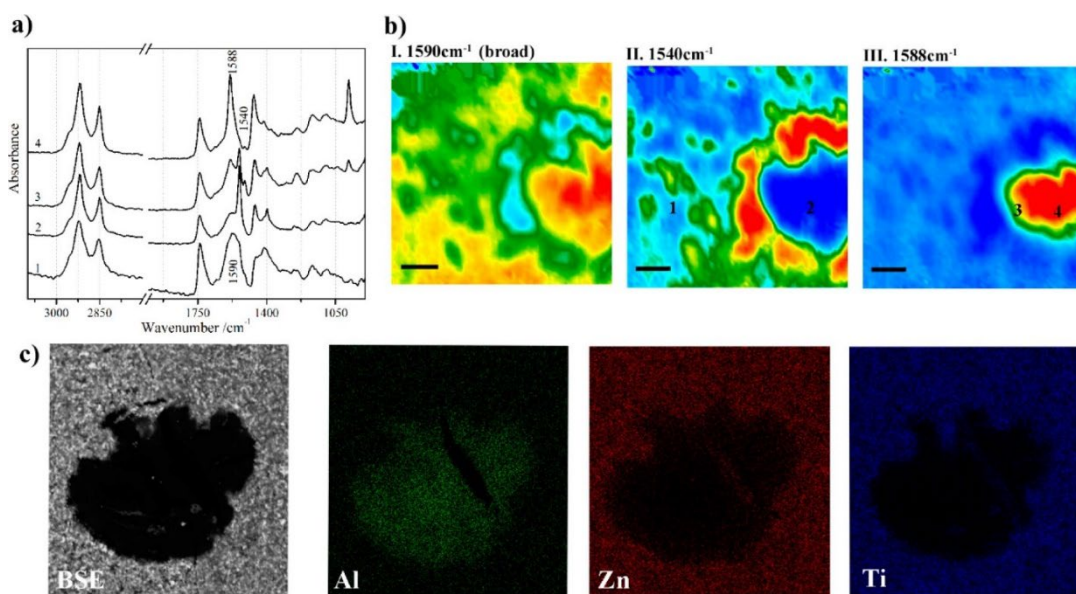


Figure 2.5 Chemical characterisation of a white paint cross-section from Jackson Pollock's *Alchemy* (1947). (a) Extracted ATR-FTIR imaging spectra corresponding to four locations in (b) chemical images of the cross section. The chemical images are acquired by integrating absorbance at 1590, 1540 and 1588 cm⁻¹, which are characteristic bands of Zn carboxylates, ZnSt₂ and AlSt(OH)₂, respectively. (c) SEM and EDX images of the metal soaps in the cross section. Reprinted with permission, (Gabrieli et al., 2017) copyright (2016) American Chemical Society.

by Vincent van Gogh, detected deterioration products such as cadmium oxalate and zinc palmitate/stearate for the first time (Kaszowska et al., 2013). In addition to the identification of painting materials and deterioration products, ATR-FTIR spectroscopic imaging is also a powerful technique to study the formation of metal soaps by discussing dynamic processes of fatty acid and metal diffusion (Baij et al., 2018a; Baij et al., 2018b). In conservation of paintings, it is important to discuss cleaning solvent diffusion and paint swelling. Time-resolved ATR-FTIR spectroscopy can accurately monitor diffusion and swelling processes (Baij et al., 2018b). The chemical composition of polymer materials that are used in conservation works have been researched using ATR-FTIR spectroscopy (Chércoles Asensio et al., 2009). Recently, chemometric methods such as Partial Least Squares (PLS) or Orthogonal Partial Least Squares (OPLS) have been utilised in conjunction with ATR-FTIR spectroscopy to quantify pigments and coatings (Hayes et al., 2014) and estimate ages of paints (Ortiz-Herrero et al., 2019).

2.3.1.3 Case studies: Other cultural heritage subject to metal soaps

Apart from oil paintings, micro ATR-FTIR imaging can also be utilised for investigation of other artefacts consisting of oil-based paint materials that are subjected to saponification. Figure 2.6 shows the identification of organic and inorganic substance distributions in the cross-sectional layer of a cold painted terracotta statue (Possenti et al., 2021a) using micro ATR-FTIR spectroscopic imaging. Demonstrated by the ATR-FTIR spectroscopic images, a complex sequence of seven layers can be observed in the painted materials on the terracotta statue. The distributions of these substances in the chemical images contribute to the chemical identification of pigments, binders and deterioration products and shed light on a possible cause of the formation of metals soaps. In a separate study, samples of cross-sections from terracotta altar-piece were studied with the greater Field Of View (FOV) using macro ATR-FTIR spectroscopic imaging, where the composition of complete stratigraphy was obtained (Joseph et al.,

2010).

As discussed above, metal soaps formed in paintings or oil-based painted materials are due to the reaction between metal ions from pigments and fatty acids from organic binders. Nevertheless, metal soaps can occur in other cultural heritage samples as a result of a mixture of metal ions and fatty acids. Leather is one of the striking examples where metal soaps are formed because a combination of metal oxide and fat residue remained on the skin during the manufacturing process. The mechanism of these metal soaps can be investigated using macro ATR-FTIR imaging. In a case study of 17th and 18th century leather book covers from Armenia (Vichi et al., 2018). ATR-FTIR spectroscopic images indicate the formation mechanism of calcium stearates which is a kind of calcium soaps, as shown in Figure 2.7. The formation mechanism of Ca soaps

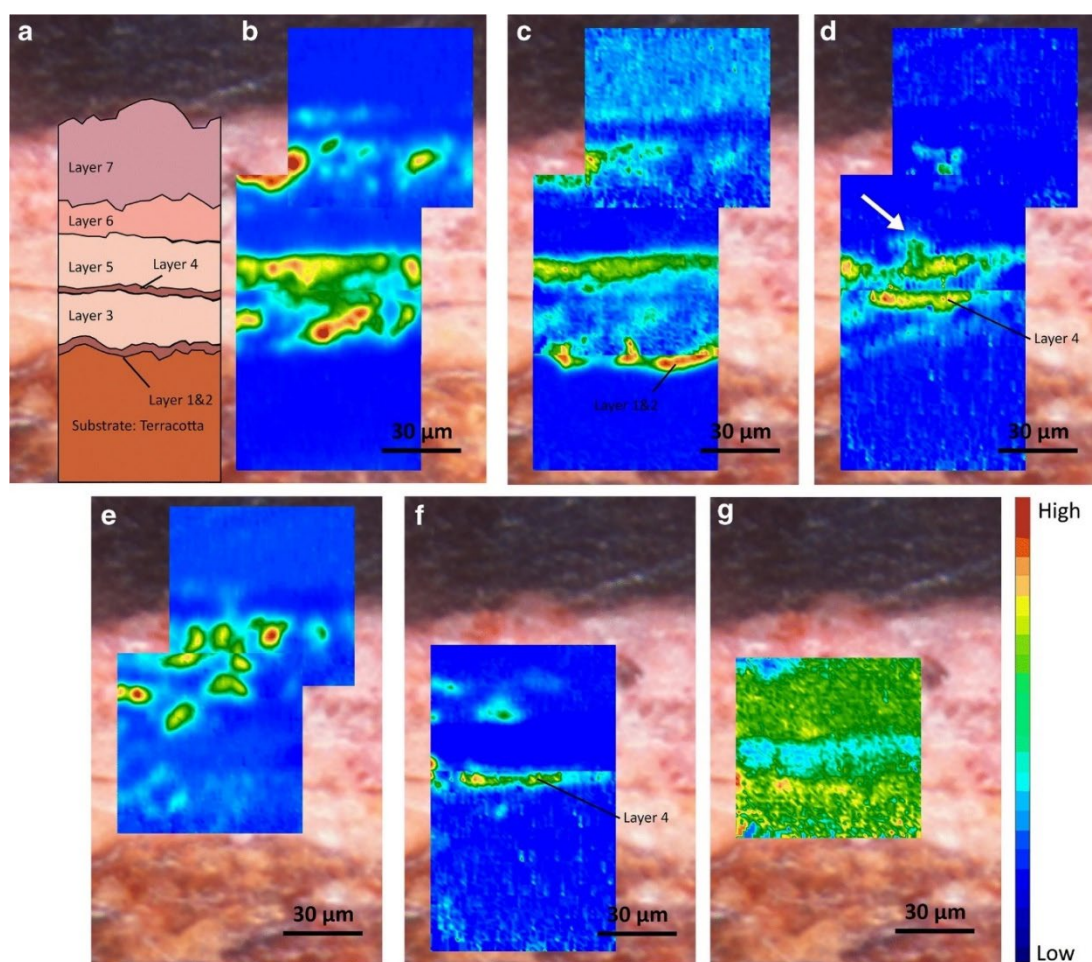


Figure 2.6 (a) Optical microscopic image of the cross section from the 7-layer painted materials on the terracotta statue. Chemical images displaying the distribution of (b) lead white (c) lipid—siccative oil (d) lead carboxylates and (e) gypsum. Reprinted with permission, (Possenti et al., 2021a) copyright (2021) Springer Nature.

(saponification) can be explained by quantitative analysis of Ca soaps with regard to calcium carbonate (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by looking at the spatial distribution of stearate, carbonate and gypsum in the ATR-FTIR images. In the spectra of the selected consecutive five pixels from the ATR-FTIR images, the absorbance of stearate increases as the absorbance of the carbonate and sulfate decreases. The spatial distribution and spectral variation analyses using ATR-FTIR imaging offer the evidence of saponification of original CaCO_3 and gypsum in the leather book covers.

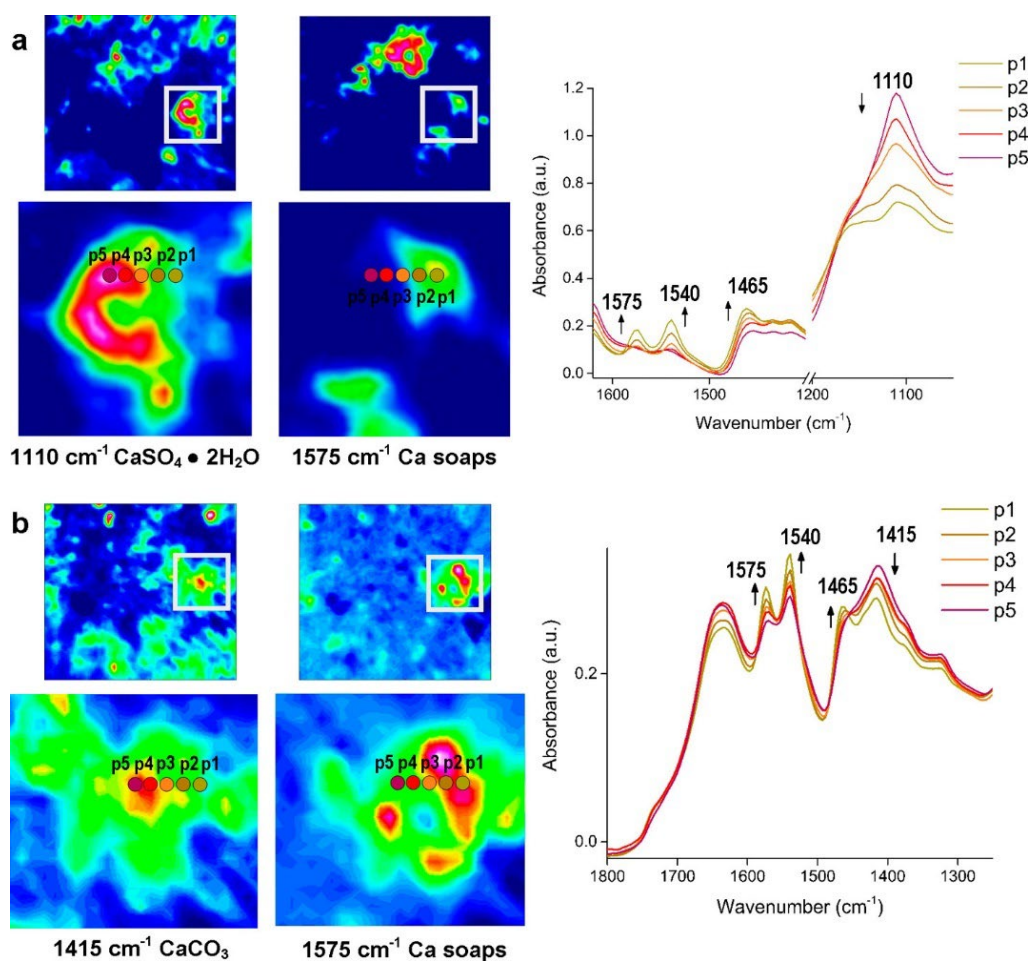


Figure 2.7 ATR-FTIR spectroscopic imaging of the samples from surface of two leather books: (a) 17th century manuscript, showing the distribution of gypsum (1110 cm^{-1}) and Ca stearate (1575 cm^{-1}) and (b) the manuscript dated 1750, showing the distribution of CaCO_3 (1415 cm^{-1}) and Ca stearate. P1 to p5 represent pixel 1 to 5 where FTIR spectra are extracted. The chemical images of the integrated absorbance and the locations (p1 to p5) show the increasing absorbance of the Ca stearate as decreasing absorbance of the carbonate and sulfate. Reprinted with permission, (Vichi et al., 2018) copyright (2018) American Chemical Society.

2.3.2 Paper

2.3.2.1 FTIR spectra of paper materials

The main constituent of paper is cellulose, which is a polysaccharide composed of a linear chain of D-glucose units. These D-glucose units are linked by β -(1,4)-glycosidic bonds and the number of the D-glucose in cellulose can be hundreds to thousands. (Crawford, 1981; Updegraff, 1969) In FTIR spectra of paper, a strong and broad band at around 3330 cm^{-1} attributed to O–H stretching vibration of H-bonded hydroxyl groups can be observed (Hinterstoisser et al., 2001; Maréchal & Chanzy, 2000). Other typical bands in the spectra of paper cellulose includes bands at 2900 cm^{-1} (C–H stretching), 1630 cm^{-1} (H_2O molecule absorption), 1428 cm^{-1} (CH_2 bending), 1367 cm^{-1} (C–H bending), 1028 cm^{-1} (C–O stretching) and 897 cm^{-1} (C–O–C stretching) (Fackler et al., 2011; Hospodarova et al., 2018; Xu et al., 2013; Yan et al., 2019). Among these typical bands, the band at 1428 cm^{-1} is correlated to the crystallinity of cellulose, whereas the band at 897 cm^{-1} is associated with the amorphous zones in cellulose (Åkerholm et al., 2004). Nelson and O'Connor (Nelson & O'Connor, 1964) proposed an IR crystallinity index determined by the ratio between the bands at 1428 cm^{-1} and 897 cm^{-1} . This calculated index using FTIR spectra has been employed to analyse changes in cellulose crystallinity by a great amount of research (Kljun et al., 2011; Široký et al., 2010; Yan et al., 2019).

In addition to cellulose, other components to manufacture paper might include organic and/or inorganic matters such as hemicellulose, lignin, clay, kaolin, titanium dioxide (TiO_2), calcium carbonate (CaCO_3), etc (Kumar et al., 2017; Udriștioiu et al., 2012). The chemical compositions of paper vary depending on manufacture approach. Knowledge of chemical compositions can contribute to authentication and discovering provenance of ancient paper heritage. However, paper materials typically constitute a wide variety of components, which might be difficult to be distinguished based solely on IR spectra. For example, absorbance at 1732 cm^{-1} could indicate the presence of hemicelluloses (Adami et al., 2016; Bjarnestad & Dahlman, 2002), but this absorbance

might result from oxidation of lignin, which is also a deterioration phenomenon (Pandey, 2005). Therefore, it is necessary to combine other scientific analytical equipment to obtain comprehensive characterisation of paper heritage.

2.3.2.2 Case studies

Originating in China, paper has been developed and utilised as the main material for recording words or information for many centuries (Hunter, 1943). Properties of paper have altered and varied region by region as the technology of paper production transferred from China through central Asia to the West. In Europe, the manufacture of paper has evolved, and compositions of paper include cellulose, wood pulp, sizing agents, fillers and coatings. A research study (Gorassini et al., 2008) investigating paper heritage from 12th century to date using ATR-FTIR spectroscopy discovered that between 1100–1300 A.D., paper was made up of rag sized with starch, while between 1400–1700 A.D., paper was composed of rag sized with gelatine. In the 1800–1960 (ca.) A.D. samples, wood pulp was characterised by the lignin absorption bands. This finding is crucial because the use of wood pulp as raw materials would lead to rapid deterioration of paper (Librando et al., 2011). Modern paper (1960–today A.D.) utilised CaCO₃ as fillers to stabilise acid reaction. The presence of CaCO₃ can be detected with ATR-FTIR spectroscopy (Gorassini et al., 2008; Librando et al., 2011). If large quantities of CaCO₃ are used in manufacture of paper, it can affect the mechanical properties of paper.

Islamic paper, manufactured in Islamic cultural areas including the Arab, Persian or Turkic realm, is distinct from other regions due to its unique papermaking process (Loveday, 2001). In ATR-FTIR spectra for the Islamic paper, proteinaceous coatings such as casein or egg white can be detected by detecting the peaks of amide group bonds at 1533 and 1639 cm⁻¹ (Mahgoub et al., 2016). Papermaking approaches travelled from the Arabic countries to Italy (Bloom, 2017), and it is in Italy that a technological evolution occurred leading to creation of a new kind of paper. This new kind of paper replaced the previous kind which originated from China and earned a

name of “the manufactured western paper” (Proietti et al., 2020). A research study analysed a series of Italian paper samples from Fabriano and Camerino which were produced between 13th–15th century (Proietti et al., 2020). In both areas, starch (which has the peak at 998 cm⁻¹) was not detected and possible use of animal gelatine (which has the peptide bond at 1540 and 1645 cm⁻¹) was proposed based on ATR-FTIR spectra results. Restoration using Tylose, a cellulose ether, might have caused the gelatine peaks less obviously. Furthermore, ATR-FTIR spectroscopy successfully identified the presence of CaCO₃, the alkali carbonate added in the manufacture of modern paper by looking at the characteristic bands at around 1410–1430 cm⁻¹.

Back to China, the birthplace of papermaking, technology of paper manufacture has been refined and a wide variety of paper artefacts could be seen in the history of traditional handmade paper.(Needham & Tsuen-Hsuin, 1985) *La Jian*, invented in Sui-Tang period (6th–10th centuries) and massively produced in Qing dynasty (17th–20th centuries), is famous for its aesthetic decoration with gold or silver flecks (Luo et al., 2019). In a study *La Jian* was investigated with ATR-FTIR spectroscopy and it was discovered that the dyed surface was coated with Chinese insect wax (Luo et al., 2019) which has carboxyl group band at 1722 cm⁻¹. *Fen Jian*, another example of Chinese paper artefact that was commonly used in calligraphy, was examined in a project (Wei et al., 2018). Chemical distribution and spectra of pigments (lead white: 1415, 1046, 681 cm⁻¹), paper fibre (cellulose: 1036, 1060, 1111, 1162 cm⁻¹) and ground ash (talc: 3674 cm⁻¹, lime: 1405, 876 cm⁻¹, and clay minerals: 1021 cm⁻¹, Si–O anti-symmetric stretching vibration) were confirmed using the ATR-FTIR mapping approach.

2.3.3 Inorganic substances: stone, ceramics and glasses

Although FTIR spectroscopy is especially useful for studying organic and complex samples, there has been an increasing amount of research that utilises FTIR spectroscopy to investigate inorganic objects, such as stone (La Russa et al., 2018; La Russa et al., 2017; Lamhasni et al., 2019), ceramics (Centeno et al., 2012; De Benedetto et al., 2002; Ion et al., 2011; Lavat et al., 2007; Lettieri, 2015; Medeghini et

al., 2016), and glasses (MacDonald et al., 2000; Thickett & Pretzel, 2020; Vilarigues & da Silva, 2004) due to the well-established and comprehensive IR databases of minerals (Farmer, 1974; Ferraro & Laboratories, 1982; Gadsden, 1975; Lafuente et al., 2016; Price et al., 1998; Price et al., 2007). Minerals are the main ingredient to produce ceramics and glasses. The dissimilarity between ceramics and glasses is that ceramics are crystalline, while glasses are amorphous. The mineral compounds for manufacturing ceramics are generally oxides, nitrides, carbides and borides. These mineral compounds have their characteristic IR bands and therefore can be identified with FTIR spectroscopy (Barilaro et al., 2005; Maritan et al., 2006). Glasses have wide composition ranges; however, the main contents are generally silicate-based materials. Glasses may experience structural changes resulting from the leaching of alkaline and earth alkaline glass compounds. The structural changes cause shifts of wavenumber and changes of intensities to the non-bridging and bridging Si–O stretching bands at 950 cm^{-1} and 1050 cm^{-1} , which can be detected with FTIR spectroscopy (Vilarigues & da Silva, 2004).

Stone heritage may be likely to suffer from changes in environmental conditions including the presence of water, air pollutants and biodegradation. Deposits on the surface of stone heritage attributed from environmental impacts can be effectively diagnosed using the FTIR techniques (Maravelaki-Kalaitzaki, 2005; Rampazzi et al., 2004). Limestone and marble (CaCO_3), worldwide used for stone heritage as well as historical architecture, have been suffered from degradation due to air pollutants in urban areas (La Russa et al., 2018; La Russa et al., 2017; Lamhasni et al., 2019). In ATR-FTIR spectra, bands at around 1405 , 872 and 712 cm^{-1} are typical vibrations of CaCO_3 (Vahur et al., 2016), corresponding respectively to anti-symmetric C–O stretch, C–O out-of-plane bend and C–O In-plane bend in CO_3^{2-} . The degradation products can be detected using ATR-FTIR spectroscopy (La Russa et al., 2018; Lamhasni et al., 2019) including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) due to SO_2 attack and oxalate ($\text{CaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$) due to biological weathering. Typical bands assigned to identify these degradation products are at 1110 cm^{-1} (anti-symmetric stretch vibration mode of SO_2) for gypsum and at 1618 and 1321 cm^{-1} (anti-symmetric and symmetric CO_2 stretching

modes, respectively) for calcium based oxalate (Lamhasni et al., 2019). In a very recent study of the Carrara marble and its treatment was studied in situ via ATR-FTIR spectroscopy and with macro ATR-FTIR spectroscopic imaging (Possenti et al., 2021b).

In the case of ceramics, FTIR spectroscopy is able to identify mineralogical compositions (Medeghini et al., 2016), firing temperature and atmosphere (Lavati et al., 2007). ATR-FTIR spectroscopy combined with Principal Component Analysis (PCA) has been utilised to classify Hellenistic and Roman ceramic shards and determine their firing temperature (Tarhan et al., 2021). XRD is the most commonly used technique to conduct qualitative and quantitative analysis of mineralogical sample (Zhou et al., 2018). ATR-FTIR spectroscopy combined with Partial Least Squares (PLS) regression method has been utilised as an alternative technique to XRD to quantify seven groups of minerals in archaeological and cultural heritage samples containing clay material (Vahur et al., 2021). Compared to a rather large amount of sample required for XRD measurements (~0.5–1 g), smaller amount (~a few mg) is needed for ATR-FTIR spectroscopic measurements, one of the advantages for investigating cultural heritage when considering minimising the loss of the cultural heritage objects. In the case of glasses, ATR-FTIR spectroscopy can be employed to detect the degree of degradation (MacDonald et al., 2000). 19th century daguerreotypes have been investigated their glass degradation using ATR-FTIR spectroscopy (Thickett & Pretzel, 2020). These studies and applications demonstrate that ATR-FTIR spectroscopic technique is a potential and useful tool for the analysis of cultural heritage objects composed of inorganic materials.

2.4 Summary

FTIR spectroscopy is a well-established analytical technique that has been applied in the cultural heritage field for identification and characterisation of original materials, degradation and conservation products, and monitoring of cleaning treatments. ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging are very suitable methods for investigation of cultural heritage materials due to its minimal requirements for sample preparation and its provision for high resolution. Furthermore, ATR-FTIR spectroscopic measurement can be not only traditional single spectrum collection, but also 2D mapping and imaging, which is especially beneficial for multi-layered structure cultural objects such as painting, historical paper and polychrome sculptures. Applications of ATR-FTIR spectroscopy and spectroscopic imaging on cultural heritage have been explored and the findings are of significance to archaeology and conservation management of cultural heritage. This chapter has reviewed the fundamentals of ATR-FTIR spectroscopy and spectroscopic imaging and highlighted their applications to investigation of cultural heritage materials related to samples of interest in this thesis, such as multi-layered painted artworks, paper, and inorganic substances. Although ATR-FTIR spectroscopy and spectroscopic imaging techniques are widely used as powerful analysis tools for cultural heritage, there is still some potential for more advanced development and applications, a prospect explored in the subsequent sections of this thesis.

3 Experimental Methods

3.1 Instrumentation

3.1.1 ATR-FTIR spectroscopy

The ATR-FTIR spectroscopy used for collecting a single spectrum for each measurement in this thesis was using the Alpha spectrometer (Bruker Optics, Baden-Württemberg, Germany). The Alpha spectrometer can be either portable or lab-based spectroscopy, and it contains an IR source, an interferometer, and a single-element DTGS detector. The sampling mode of the Alpha spectrometer can be transmission, external reflection, or ATR. In this thesis, only the ATR mode was used, as displayed in Figure 3.1. The ATR mode is composed of a prism-shaped diamond crystal that is



Figure 3.1 Photograph of the Alpha spectrometer

fitted into a measuring surface of $2 \times 2 \text{ mm}^2$ where the sample is placed, along with an anvil that can be pressed down to ensure proper contact between the sample and the crystal for measurements. This Alpha spectrometer allows for rapid measurements, typically taking less than one minute, depending on the selected parameters.

3.1.2 Macro ATR-FTIR spectroscopic imaging

The macro ATR-FTIR spectroscopic data in this thesis were collected using a macro ATR-FTIR spectroscopic imaging system. This system consists of a Tensor 27 FTIR spectrometer attached to an IMAC macro chamber (Bruker Optics, Baden-Württemberg, Germany) coupled with a 64×64 Focal Plane Array (FPA) detector (Santa Barbara Focalplane, USA) and a diamond imaging Golden Gate ATR accessory (Specac, UK), as depicted in Figure 3.2. The ATR diamond crystal has a refractive index of approximately $n \approx 2.43$ and offers a Field Of View (FOV) measuring $0.6 \text{ mm} \times 0.55 \text{ mm}$ with a spatial resolution of $10\text{--}15 \text{ }\mu\text{m}$. The diamond crystal is inserted into a top plate of the Golden Gate accessory, with an anvil that is positioned above the top plate and can be pressed down to ensure proper contact, serving the same function as the anvil in ATR-FTIR spectroscopy introduced in Section 3.1.1. Dried air is continually purged into the system, and KBr windows are present in the macro chamber to maintain low and stable levels of water vapor and CO_2 .

A schematic illustration of the path of the IR light traveling across mirrors and lenses in the Golden Gate accessory is provided in Figure 3.3. By employing apertures on the illuminating lens, various angles of incident IR light (θ_i) can be acquired, providing the capability for depth profiling analysis (Chan et al., 2008; Vichi, 2018), which is introduced in Section 4.4. The alignment of the Golden Gate accessory to achieve optimal sample illumination and precise focusing of FTIR images is performed by adjusting the positions of the illumination and focus lenses, as well as by rotating the angles of mirrors for the IR light successfully passing through the Golden Gate accessory, as shown in Figure 3.3. Shifting the location of the Golden Gate accessory along the path of the IR light in the IMAC macro chamber also affects the alignment.

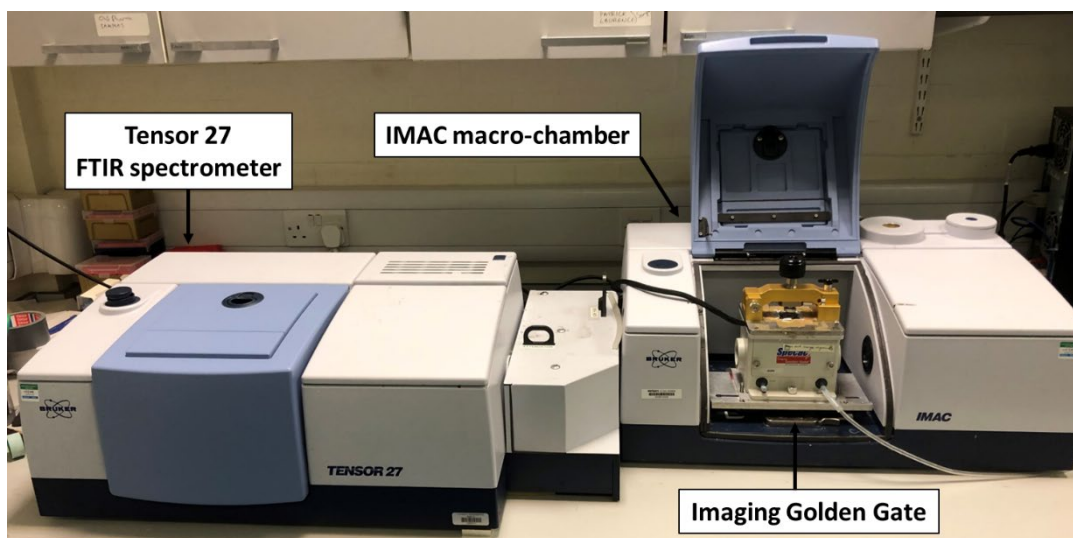


Figure 3.2 Macro ATR-FTIR spectroscopic imaging system, consisting of a Tensor 27 FTIR spectrometer attached to an IMAC macro chamber, coupled with a 64×64 FPA detector and a Diamond Imaging Golden Gate ATR accessory. The FPA detector, not visible in this figure, is installed at the rear of the IMAC chamber.

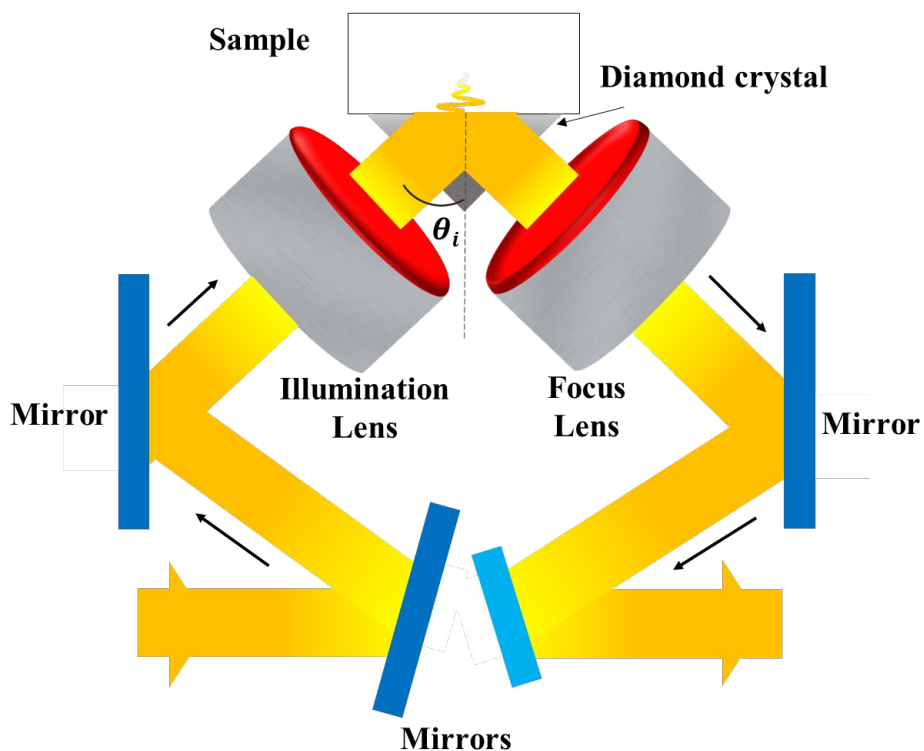


Figure 3.3 Schematic illustration of the path of the IR light traveling across mirrors and lenses in the Golden Gate ATR accessory

3.1.3 Micro ATR-FTIR spectroscopic imaging

The micro ATR-FTIR spectroscopic imaging measurements were conducted using a Cary 620 IR microscope coupled with an Agilent-Varian 670 FTIR spectrometer operating in continuous scan mode with a 64×64 -pixel 2D Focal Plane Array (FPA) detector (Agilent Technologies, Inc., Santa Barbara, CA, USA), as depicted in Figure 3.4. The microscope is equipped with a $15\times$ Cassegrain objective (with a Numerical Aperture (NA) of 0.62) and a slide-on germanium (Ge) crystal as the internal reflective element (IRE). The Ge crystal has a refractive index of approximately $n \approx 4.00$, enabling a high spatial resolution of $2\text{--}4\text{ }\mu\text{m}$, depending on wavelength. The size of a spectroscopic image obtained is approximately $70\text{ }\mu\text{m} \times 70\text{ }\mu\text{m}$. This micro ATR-FTIR system setup is capable of measuring a range of wavenumbers from 850 to 3850 cm^{-1} when using the FPA detector with a good Signal-To-Noise (SN) ratio (Vichi, 2018). Similar to the macro ATR-FTIR spectroscopic imaging system, dried air is constantly purged into the micro ATR-FTIR spectroscopic imaging system to reduce the concentration of water vapour and CO_2 .

A schematic illustration of the path of the IR light passing through the Cassegrain objective fitted with the ATR Ge crystal is provided in Figure 3.5. By varying the angles (θ_i) or polarisation direction of the IR light incident on the Ge crystal, depth profiling and polarisation measurements can be conducted, which are introduced in Sections 4.4 and 4.5, respectively. The alignment of the ATR-FTIR spectroscopic imaging system to achieve proper focusing of the FTIR image on the focal plane of the FPA detector is carried out by adjusting the height of the ATR Ge crystal on the slide-on accessory along the Z-direction. Additionally, the location of the ATR Ge crystal in the X and Y-directions can be adjusted.

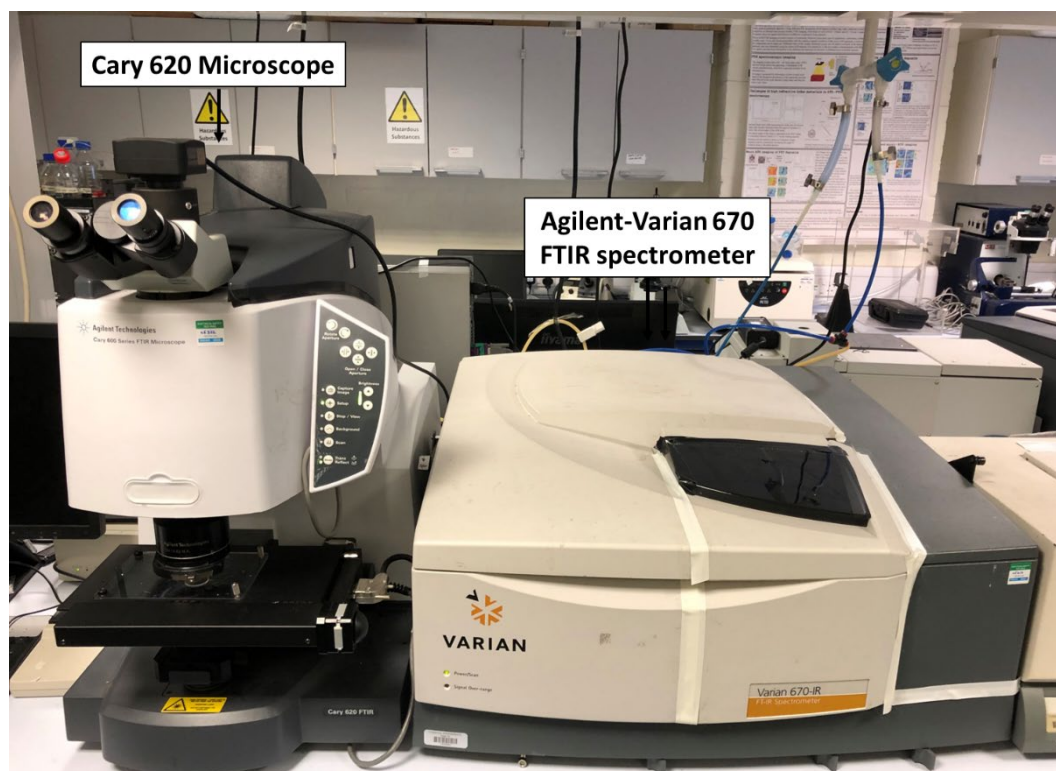


Figure 3.4 Micro ATR-FTIR spectroscopic imaging system, consisting of a Cary 620 IR microscope coupled with an Agilent-Varian 670 FTIR spectrometer, coupled with a 64×64 FPA detector. The FPA detector, not visible in this figure, is installed at the rear of the IR microscope.

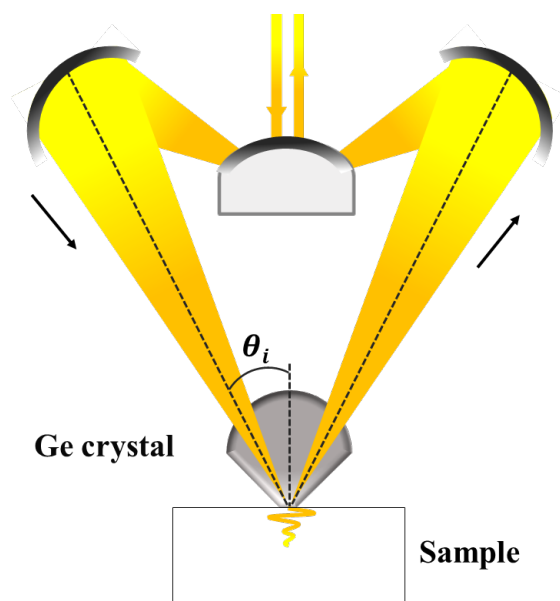


Figure 3.5 Schematic illustration of the path of the IR light passing through the Cassegrain objective fitted with the ATR Ge crystal

3.1.4 Scanning Electron Microscopy (SEM)/ Energy Dispersive X-Ray analysis (EDX)

Scanning Electron Microscopy (SEM), in combination with Energy Dispersive X-Ray analysis (EDX), was performed to complement the ATR-FTIR spectroscopic data. This technique utilises electron beams with energy ranging from 10^2 to 10^4 eV, which falls within a wavelength range of 0.123–0.012 nm (Artioli & Angelini, 2010). Electrons have shorter wavelengths compared to light, including infrared and ultraviolet, as illustrated in Figure 2.1. Due to the use of electrons instead of light, SEM can capture images at magnifications exceeding 100,000 times, in contrast to the highest magnification achievable by light microscopes, which is about 1,000. In addition to image acquisition, chemical elemental information can be obtained using the SEM instrument equipped with an EDX spectrometer. The EDX spectrometer utilises characteristic X-rays to identify elements within the analysed sample. The characteristic X-ray lines of specific elements can be assigned, and 2D elemental distribution maps can then be generated.

Since most cultural heritage samples are not electron-conductive, SEM analysis can be enhanced by applying a coating (in this thesis, platinum was used) to the surface of the sample being analysed. Furthermore, samples must be measured in a vacuum condition (below 10^{-3} Pa) to prevent the air molecules, such as N_2 , O_2 , H_2O or CO_2 from absorbing or scattering the electrons (Goldstein et al., 2018). The SEM instruments performed in this thesis are a Zeiss SigmaTM VP SEM (ZEISS Group, Germany) in Section 4.2 and a JEM-7100F SEM (JEOL Ltd., Japan) in Section 4.3.

3.1.5 X-ray Fluorescence (XRF) spectroscopy

X-ray Fluorescence (XRF) spectroscopy, a commonly used tool for elemental analysis of cultural heritage objects, as described in Section 2.1, was applied for the supplementary investigation of ATR-FTIR spectroscopic imaging systems. The fundamentals of this XRF technique are as follows: High-energy X-rays expel core electrons of an atom, leading to the unstable ionised state of the atom. This atom tends

to relax to its ground state by a series of electrons jumping from the outer orbits to the vacancies at the inner orbits where the core electrons have been expelled by the X-rays. These electron transitions from the outer orbits subsequently emit fluorescence photons in the X-ray region, revealing and representing the quantum structure of the atom. This fluorescence emission is known as secondary X-rays or characteristic X-rays, the spectrum of which can be used for the identification and semi-quantification of the detected chemical elements, as also mentioned in the EDX spectrometer in Section 3.1.4.

XRF measurements in this thesis were performed using an Epsilon 3XLE ED-XRF from PANalytical (Almelo-Netherland) equipped with an Ag anode tube (maximum voltage = 50 keV) at 1200 s acquisition time for each sample. Five set-ups of voltage/current intensity/ filter/ medium were employed for each measurement contributing to final data collection: 50 keV/ 300 μ A/ Ag/ air, 50 keV/ 300 μ A/ Cu/ air, 20 keV/ 750 μ A/ Al/ air, 12 keV/ 1250 μ A/ Al/ air, and 9 keV/ 1666 μ A/ Ti/ He. The system was equipped with a 10-position sample holder allowing sample spinning during measurement, as shown in Figure 3.6. The samples were placed in holders with 4 μ m polypropylene films. The qualitative and semi-quantitative analyses of the XRF



Figure 3.6 Epsilon 3XLE ED-XRF with a 10-position sample holder

spectral data were performed and calibrated using the PANalytical analytical program, Omnic software. The Omnic software was used to search, align, and manually inspect peaks from the scanning atlas, after which the data were processed to obtain the final results.

3.2 Spectral data processing

Acquired ATR-FTIR spectral data can be processed and analysed using the software that Agilent and Bruker provide, Resolutions Pro for micro ATR-FTIR spectroscopic data and Opus for macro ATR-FTIR spectroscopic data. Chemical images were produced by plotting the integrated absorbance of a spectral band of interest in all 4096 spectra as a function of all pixels of the array, representing the spatial distribution of the absorbance of the specific spectral band of interest. Integration methods are introduced in Section 3.2.1. However, to conduct more advanced data processing such as spectral derivatives and chemometrics which are introduced in Section 3.2.2 and 3.2.3, respectively, the acquired ATR-FTIR spectral data were exported to Matlab.

3.2.1 Integration methods for spectroscopic images

Figure 3.7 demonstrates several univariate analysis methods of integration for producing spectroscopic chemical images of lead white in a wavenumber region of 1280–1480 cm^{-1} . Method A integrates the entire area below the peak of the absorbance with the absolute baseline set at an absorbance value of 0, while method B integrates the area with a local tangential baseline, as shown in Figure 3.7a and b, respectively. The integration formulas for method A and method B are defined as Equation 3.1 and 3.2, respectively (Hofko et al., 2018):

$$I_{method\ A} = \int_{w_l}^{w_u} a(w) dw \quad (3.1)$$

$$I_{method\ B} = \int_{w_l}^{w_u} a(w) dw - \frac{a(w_u) - a(w_l)}{2} \times (w_u - w_l) \quad (3.2)$$

Here, $a(w)$ represent the absorbance value at wavenumber, w ; w_u is the upper wavenumber limit and w_l is lower wavenumber limit, in this case of integrating the spectral band of lead white, 1490 and 1280 cm^{-1} , respectively.

Although method A has been widely used for spectral processing, throughout this thesis, only method B was adopted to produce chemical images. This choice is made because method B eliminates the influence of baseline variation among pixels, generating chemical images of higher quality. Another method for dealing with spectral

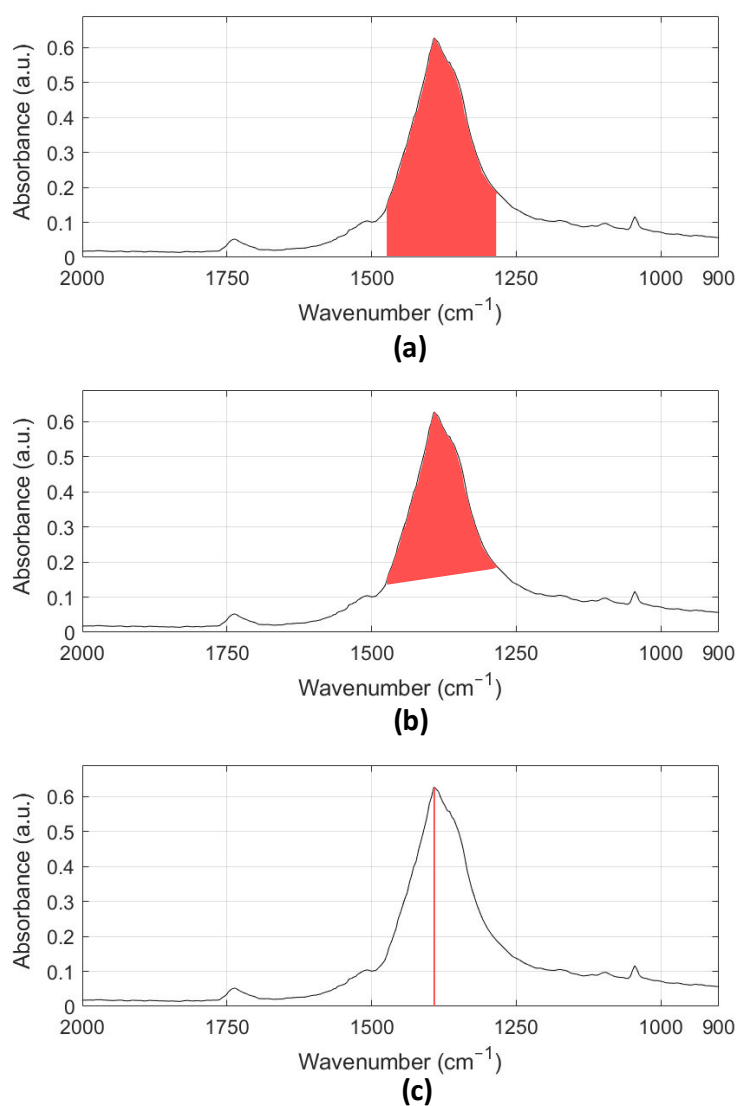


Figure 3.7 Illustration of the three integration methods used in univariate analysis of ATR-FTIR spectroscopic data: (a) method A, (b) method B, and (c) method P

bands of absorbance is called method P, which simply uses the absorbance value of the chosen spectral band with respect to the absolute baseline at an absorbance value of 0, as shown in Figure 3.7c. Method P was applied to the calibration of apertures inserted on micro and macro ATR-FTIR spectroscopic systems, as introduced in Section 4.4, and to the dichroic ratio in the polarisation measurements, as introduced in Section 4.5.

3.2.2 Spectral derivatives and smoothing

Applying simple calculus such as derivatives to process spectral data offers numerous advantages. One of the significant advantages is the elimination of spectral offset, resulting in baselines situated at zero. The first derivative is employed to identify points where the slope of an absorbance band is zero, pinpointing the peak of the absorbance band. The second derivative is utilised to measure the change in slope (Smith, 2002), enhancing the accuracy of peak position determination for the analysed absorbance band. A second derivative spectrum may exhibit a curve with three sections: a positive value, followed by a negative value, and another positive value. The minimum of this curve signifies the peak position of the analysed absorbance band. Moreover, in comparison to the first derivative, the second derivative, or higher derivatives, can effectively deconvolve or separate overlapping spectral bands.

To perform derivative calculations, simple mathematical techniques are applied to the spectrum using a constant wavenumber interval. For FTIR spectral data, this wavenumber interval corresponds to the spectral resolution $\Delta\tilde{\nu}$, which in this thesis was set to 4 or 8 cm^{-1} . The calculation of the first and second derivatives can be achieved by employing Equation 3.3 and 3.4, respectively:

$$D_{first} = \frac{A_{\tilde{\nu}+\Delta\tilde{\nu}} - A_{\tilde{\nu}}}{\tilde{\nu}} \quad (3.3)$$

$$D_{second} = \frac{A_{\tilde{\nu}-\Delta\tilde{\nu}} - 2A_{\tilde{\nu}} + A_{\tilde{\nu}+\Delta\tilde{\nu}}}{\Delta\tilde{\nu}^2} \quad (3.4)$$

where $A_{\tilde{\nu}}$ represents the absorbance value of the analysed band at a certain wavenumber, $\tilde{\nu}$. Despite the mentioned merits, derivative spectra may exhibit increased noise. To enhance the signal of the spectra, a smoothing algorithm is employed in conjunction with the utilisation of derivatives.

Smoothing functions can be found in FTIR software packages, including the Agilent Resolution Pro software on the micro ATR-FTIR spectroscopic imaging system and Bruker OPUS software on the macro ATR-FTIR spectroscopic imaging system. Smoothing algorithm coding using Matlab can also be performed for smoothing spectra, which was utilised in this thesis for smoothing second derivative spectra in Section 4.4. The smoothing algorithm used is the Savitzky–Golay (SG) algorithm (Savitzky, 1989; Savitzky & Golay, 1964), a polynomial smoothing algorithm that relies on the least squares principle. Initially, the number of points in the smoothing window is selected, which can be a 5-, 7-, 9-, or higher odd integer point. The higher the number of points in the window, the larger the amplitude of smoothing, resulting in smoother spectra; however, the distortion of the signal may be increased (Zimmermann & Kohler, 2013). The next step involves fitting a polynomial function to the set of data points in the smoothing window. The degree of this polynomial function can be 0, 1, 2, or 3. The lower the degree of the polynomial function, the smoother the spectra obtained. The concept of this algorithm is that because the degree of the polynomial function is less than the number of points in the window, the polynomial function is not able to fit all the points in the window, resulting in the acquisition of a smooth approximation of the spectral data. This smoothing algorithm is only adopted for second derivative spectra in Section 4.4 in this thesis.

3.2.3 Chemometrics

Chemometrics is the discipline that utilises mathematics, statistics, and computer science to enhance the efficiency of experimental designs and assist in realising the chemical information extracted from extensive and intricate datasets (Varmuza &

Filzmoser, 2009). Common tools for conducting chemometrics analysis of spectral data include Principal Component Analysis (PCA), Cluster Analysis (CA), Partial Least-Squares (PLS), and Linear Discriminant Analysis (LDA), among others (Peris-Díaz & Krężel, 2021). In this thesis, PCA and k-means clustering were employed as chemometrics tools to analyse spectral datasets for the classification of samples.

PCA is the most important and frequently employed exploratory method for chemometric analysis of spectroscopic data (Peris-Díaz & Krężel, 2021; Varmuza & Filzmoser, 2009). Often utilised as an unsupervised machine learning algorithm, PCA requires no labels or outcomes when processing data, meaning no prior knowledge of the sample is needed (Lever et al., 2017). The primary concept of PCA is to reduce the dimensionality of the data by projecting correlated features in the higher-dimensional subspace to a lower-dimensional subspace, resulting in uncorrelated features known as Principal Components (PCs). The mathematical algorithms of PCA can be rather complicated. Here, the simple and understandable equation by Granato et al. (Granato et al., 2018) is employed to explain how the data are projected and transferred when using PCA. The matrix X , composed of $(I \times J)$, can be broken down with the following equation:

$$\mathbf{X} = \mathbf{TP}^t + \mathbf{E} \quad (3.5)$$

where $\mathbf{T}$ is the $(I \times A)$ scores matrix representing data in a new reduced subspace; $\mathbf{P}$ is the $(J \times A)$ loadings matrix indicating the effectiveness of variables explained by model components; $\mathbf{E}$ is the $(I \times J)$ residuals matrix, and A is the number of PCs, an essential parameter for meaningful PCA results. In Section 4.3 and 4.4 of this thesis, PCA results were presented using score plots that explain the differences in spectral data. The first two or three PCs, accounting for the total variance of the data, were chosen to generate these score plots. Loading plots showing significant spectral features of the PCs were provided alongside these score plots.

Cluster analysis (CA) is another frequently used exploratory method for the chemometric analysis of spectroscopic data, and it can be hierarchical or non-hierarchical. While hierarchical CA can be useful, it tends to be more time-consuming

than non-hierarchical CA. One of the most employed non-hierarchical CA tools is k-means clustering, which was utilised in this thesis. To initiate k-means clustering analysis, the number of clusters, denoted as k , needs to be specified and decided first. Subsequently, the data being processed are separated into k different clusters. The distances between the data points should be sufficiently large, ensuring effective separation. A centroid, representing the centre of each cluster, is then calculated and produced. Each data point is assigned to a specific cluster based on the closeness and similarity between its features and the centroid of that cluster. The fundamental concept of k-means clustering analysis is to minimise the total intra-cluster variance or the objective function, as expressed in the following equation:

$$J = \sum_{j=1}^k \sum_{i=1}^n \left\| x_i^{(j)} - c_j \right\|^2 \quad (3.6)$$

where J is the objective function; k is the number of clusters; n is the number of cases; $x_i^{(j)}$ represents the case i , and c_j represent the centroid for cluster j . $\left\| x_i^{(j)} - c_j \right\|$ is the Euclidean distance, serving as a metric and variance measure for cluster scatter. Due to the random assignment of centroids and subsequent variation in Euclidean distances, the results may differ in different implementations of k-means clustering analysis. Similar to PCA, k-means clustering is an unsupervised learning algorithm that does not require labelled data. In comparison to the chemical images produced by plotting integrated absorbance, as introduced in Section 3.2.1, the chemical images resulting from k-means clustering are multivariate and thus can enhance the information content of spectroscopic imaging data. The implementation details of PCA and k-means clustering are summarised in Section 4.3.

4 Results and Discussion

This chapter comprises five primary investigations, each designed to provide insights into the challenges and research gaps discussed in the backgrounds of Sections 4.1–4.5. The motivation behind each of these investigations is outlined here:

Section 4.1 presents a preliminary scientific examination of the pigments used by Martiros Sarian, a prominent Armenian artist renowned for his vibrant and evocative paintings. This study focuses on five paintings by Sarian, spanning the 1900s to the 1940s, with the aim of illustrating the valuable insights provided by the combined use of ATR-FTIR spectroscopic imaging and XRF in the analysis of oil paint layers. This is particularly relevant in instances where access to scientific examination is restricted within museum settings.

Section 4.2 aims to investigate the white crusts found on the cartoons painted by Edward Poynter from the Parliamentary Art Collection, Heritage Collections at the UK Parliament. Micro ATR-FTIR spectroscopic imaging was employed to explore the complex stratigraphy of the Edward Poynter cartoons for the first time, focusing on the characterisation of white crusts, metal carboxylates, and materials such as pigments and fillers used by the artist. The findings in this paper are expected to provide insights into the origin and formation of the surface white crusts. Other analytical approaches, including Light Microscopy (LM) and Scanning Electron Microscopy Energy Dispersive X-ray (SEM-EDX) microanalysis, were used to support the results obtained from micro ATR-FTIR imaging¹.

Section 4.3 discusses characterisation and classification of three types of antique photographs created in different years between 19th and 20th centuries. The novelty of this work is applying micro and macro ATR-FTIR spectroscopic imaging coupled with

¹ This work was conducted in collaboration with Ms. Elsa Guerreiro at International Fine Art Conservation Studios Ltd. and Dr. Adel El-Turki from the University of Bristol in 2022. The LM figures and images of paintings were captured at International Fine Art Conservation Studios Ltd., while SEM images were saved and stored in Dr. Adel El-Turki's laboratory.

the chemometric analysis to the identification of antique photographs which have heterogenous compositions but have similar appearance that even cannot be distinguished by the conservators and archivists. Other non-destructive techniques utilised in this section includes confocal light and laser microscopy, XRF, and SEM-EDX².

Section 4.4 extends the findings from Section 4.3, where depth profiling of antique photographs was conducted using the variable angle approach. The objective of this section is to qualitatively and semi-quantitatively analyse the acquired ATR-FTIR images. It is anticipated that the depth profiling method can significantly contribute to the non-invasive and non-destructive analysis of a broader range of samples and cultural heritage objects.

Section 4.5 delves into the utilisation of ATR-FTIR spectroscopic imaging to examine four cross-sectional samples extracted from Donatello's Virgin and Child, provided by the Victoria and Albert (V&A) Museum. Additionally, this section explores the pioneering application of polarised ATR-FTIR measurements—a technique widely employed in diverse fields but not previously applied in the realm of cultural heritage.

² This work was undertaken in collaboration with Mr. Tai-Cheng Chen at the National Atomic Research Institute in 2021. The operations involving confocal light and laser microscopy, as well as SEM-EDX, were conducted in the laboratories of the National Atomic Research Institute.

4.1 Characterisation and degradation analysis of pigments in paintings by Martiros Sarian: ATR-FTIR spectroscopic imaging and XRF approach

This section is adapted from: Liu, G. L. & Kazarian, S. G. Characterisation and Degradation Analysis of Pigments in Paintings by Martiros Sarian: Attenuated Total Reflection Fourier Transform Infrared Spectroscopic Imaging and X-ray Fluorescence Approach. *Heritage*, 6, 6777-6799. (Liu & Kazarian, 2023)

4.1.1 Background

Martiros Sarian (1880–1972) is a highly influential figure in twentieth-century Armenian art, often regarded as the key proponent of the Armenian national style of painting (Azatyan, 2012). Sarian received his artistic training at the Moscow School of Painting, Sculpture, and Architecture from 1897 to 1903, where he honed his skills under renowned painters Konstantin Korovin and Valentin Serov (Sahakyan, 2021). He promptly joined a circle of Symbolist artists in Moscow and began showcasing his vibrant and vividly coloured paintings. Throughout his journeys to Constantinople (now Istanbul) in 1910, Egypt in 1912, southwestern Armenia in 1913, and Persia (now Iran) in 1914, Sarian drew inspiration for a series of large-scale fresco-like works, aiming to convey the evocative qualities of Middle Eastern landscapes. These experiences also lead to the incorporation of Persian motifs into several of his paintings. Similar to many Russian artists in the early 20th century, Sarian drew significant inspiration from Impressionism. Furthermore, his admiration for French artists Henri Matisse (1869–1954) and Paul Gauguin (1848–1903) is evident in his utilisation of areas of simplified, flat colours (Britannica, 2023).

Despite Sarian being acknowledged as a symbolic Armenian artist, there exists limited information regarding Sarian's painting technique and the materials he utilised. The acquisition of such knowledge through scientific investigation plays a pivotal role

in unravelling the methodologies employed in creating these artworks and ensuring their optimal preservation. Remarkably, prior to this study, no scientific research had been conducted on this subject, underscoring the novelty and significance of this contribution in shedding light on the colour palette employed by Sarian.

This section aims to characterise pigments from paintings created by Martiros Sarian, which are housed at the Martiros Sarian House-Museum in Yerevan, the capital of the Republic of Armenia. To our knowledge, these paintings have never been studied using scientific techniques before. Due to the unavailability of scientific equipment at the museum and the inability to transport the paintings, small fragments were carefully extracted from the edges and corners of the artwork by the curators and the conservators at the museum. The edges and corners of the artwork contained pigments and were chosen to minimise any invasive harm to the paintings. It is worth noting that the samples were exclusively taken from the upper layers of the paintings; however, it remains plausible that these extracted pigment samples might contain tiny portions of components from the underlying ground layers. The extracted pigment samples were then sent to Imperial College London, UK, for scientific analysis. The analysed paintings in this paper include *Morning in Stavrino*, *Arabian Dancer*, *Caravan*, *Yerevan Zangu River* and *Kirovakan*, dated 1909, 1913, 1926, 1931 and 1948, respectively. These specific paintings were selected to investigate the artist's evolving techniques and materials over distinct 10-year periods: the 1910s, 1920s, 1930s, and 1940s. Characterisation of the pigments is conducted using non-destructive methods, including micro Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopic imaging (Liu & Kazarian, 2022) and X-Ray Fluorescence (XRF) (Streli et al., 2017). The application of micro ATR-FTIR imaging (Gabrieli et al., 2017; Kaszowska et al., 2013; Liu et al., 2023; Spring et al., 2008) and XRF (Pięta et al., 2015; Van der Snickt et al., 2012) for pigment characterisation in oil paintings has been well-established, demonstrating the suitability of these techniques for non-destructive analysis. This section demonstrates how the combination of micro ATR-FTIR spectroscopic imaging and XRF offers significant guidance in the preliminary characterisation of oil paint layers that are from museums where access to scientific

investigation is limited.

4.1.2 Experimental setting up

Pigment samples were extracted from 17 locations at the edges and corners of the paintings: *Morning in Stavrinio* (blue, green and yellow pigments), *Arabian Dancer* (blue, green and red pigments), *Caravan* (brown, red, yellow, blue, green and blue-green pigments), *Yerevan Zangu River* (blue, green and dark green pigments) and *Kirovakan* (orange and light blue pigments), as displayed in Figure 6.1 in Appendices. The extracted pigment samples each weigh around 200 mg, except for the dark green pigment from *Yerevan Zangu River*, which consists of merely two powders. The extracted pigment samples were first subjected to XRF analysis, followed by investigation using micro ATR-FTIR spectroscopic imaging.

The pigment samples extracted from the paintings were placed onto a 2-mm thick CaF_2 window (Crystran Ltd., UK) for micro ATR-FTIR spectroscopic imaging measurements. The micro ATR-FTIR imaging measurements were conducted using an Agilent 670 FTIR spectrometer operating in continuous scan mode with a 64×64 -pixel 2D Focal Plane Array (FPA) detector. Spectra were collected with 4 cm^{-1} spectral resolution in the range $3,900\text{--}750 \text{ cm}^{-1}$ using 64 scans. The XRF measurements were performed using an ED-XRF Epsilon 3XLE (Malvern Panalytical Ltd.) equipped with an Ag anode tube (maximum voltage = 50 keV) at 1200 s acquisition time for each pigment sample. It should be noted that XRF is a semi-quantitative technique, requiring a reasonable amount of material—typically 2 to 3 grams—to ensure sufficient counts for quantitative analysis. In this study, the XRF results are utilised for providing qualitative compositional information, while the quantitative results are for reference. Detected elements were categorised based on their concentration as major ($>1\%$), minor ($0.1\%\text{--}1\%$) and trace ($<0.1\%$) for each pigment, as detailed in Table 6.1– 6.4 in Appendices. The primary lines ($K\alpha$ and/or $L\alpha$) in the spectra of the minor and trace elements were utilised for manual inspection to confirm the presence of these elements.

4.1.3 Results

4.1.3.1 Study of the blue pigments

Table 4.1 Summary of XRF results of the blue pigments

Colour	Painting	Detected chemical elements with XRF
Blue	<i>Morning in Stavrino (1909)</i>	Major: Zn, Ca, S, Si, Cr, Al, Pb, Cl, Fe Minor: Ti, Cu, As, P, Cd, Co Trace: Mn, Ga, Ni, Sr
	<i>Arabian dancer (1913)</i>	Major: Zn, Si, S, Al, Ca, Pb, Fe Minor: K, Cl, P, Cd, Cr, As, Ga, Co, Cu Trace: Ti, Mn, V
	<i>Caravan (1926)</i>	Major: Pb, Ca, Co, Al, Fe, Zn, S, Cd Minor: Cl, Cr, V Trace: Sr, Ga
	<i>Yerevan Zangu River (1931)</i>	Major: Zn, Sn, Co, Si, Ca, Fe, Cl, Cr Minor: As
Light blue	<i>Kirovakan (1948)</i>	Major: Zn, Ca, Sn, Co Minor: Si, S, Cl, Fe, Trace: Cu, As, Cr, P

In this section, the blue pigments under investigation include those extracted from *Morning in Stavrino*, *Arabian Dancer*, *Yerevan Zangu River*, *Caravan*, *Yerevan Zangu River* and the light blue pigments extracted from *Kirovakan*. The XRF results of these pigments are detailed in Table 4.1.

The blue pigment sample extracted from *Morning in Stavrino* and *Arabian Dancer* can be identified as ultramarine, which was traditionally acquired from the mineral lapis-lazuli (Plesters, 1993). Lapis-lazuli is a complex mineral that contains sodium, calcium, aluminium, silicon (Na, Ca, Al, Si)-based mineral such as lazurite (major) and other mineral impurities such as calcium carbonate (CaCO_3) and pyrite (FeS). Synthetic ultramarine, which was invented in 1826, is a more likely candidate and is chemically identical to lapis lazuli but boasts even more vibrant colours. Figure 4.1 and 4.2 show the ATR-FTIR chemical images of ultramarine blue and calcium carbonate. The band of $\nu_{\text{as}}(\text{O}-\text{Si}-\text{O})$ at around 1000 cm^{-1} is assigned to lazurite (Silva et al., 2006;

Vahur et al., 2016), while the bands at 1414 cm^{-1} ($\nu_{\text{as}}(\text{CO}_3^{2-})$) and at 874 cm^{-1} ($\delta_{\text{out-of-plane}}(\text{CO}_3^{2-})$) are assigned to calcium carbonate (Salter et al., 2019). XRF results (Table 4.1) show the detection of iron (Fe) and sulfur (S), which may support the existence of

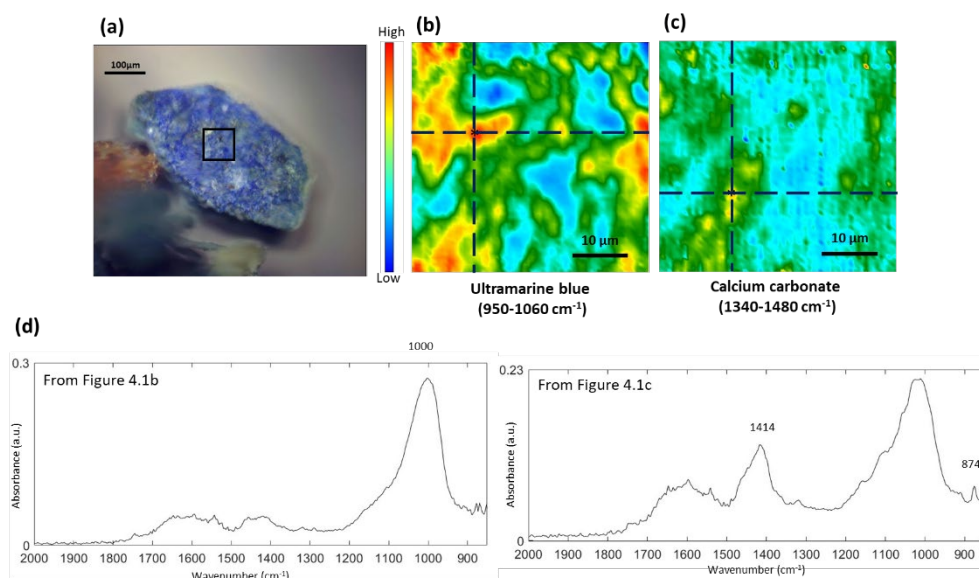


Figure 4.1 (a) Microscopic image of the blue pigment taken from Morning in Stavirino where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the blue pigments showing the distribution of (b) ultramarine blue and (c) calcium carbonate. (d) ATR-FTIR spectra extracted from pixels of the chemical images.

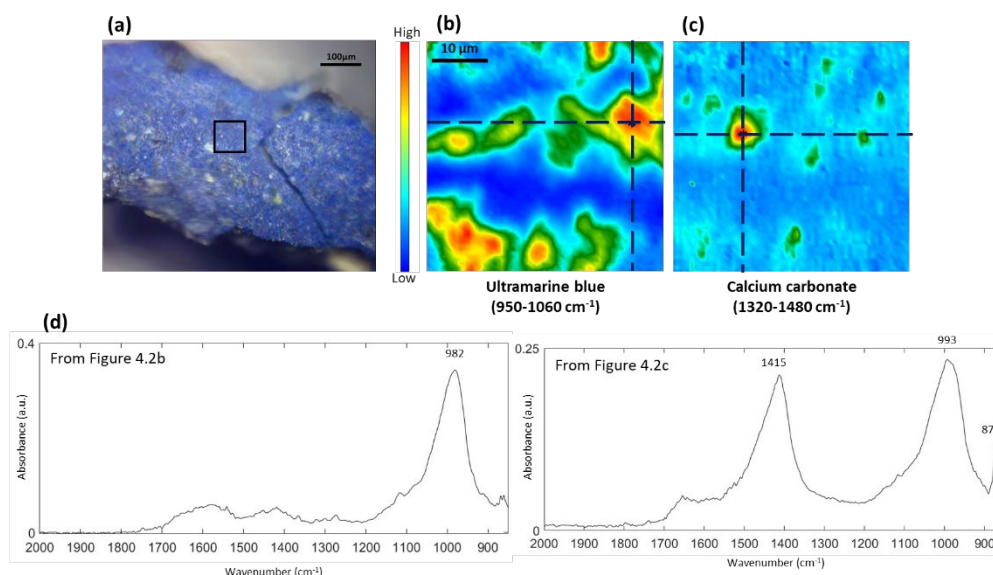


Figure 4.2 (a) Microscopic image of the blue pigment sample taken from *Arabian dancer* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the blue pigment showing the distribution of (b) ultramarine blue and (c) calcium carbonate. (d) ATR-FTIR Spectra extracted from pixels of the chemical images.

pyrite. However, it is important to note that S is also present in ultramarine blue. Future research may employ other molecular techniques to further elucidate the source of S. Chromium (Cr) was detected as a major element from the XRF results, implying the sample may contain Cr-based components. Chlorine (Cl) was also detected as a major element in the XRF results of this blue pigment and is commonly found in other pigment samples as well (Table 4.1–4.4). This presence could be attributed to chlorinated salts or Cl-containing degradation products. However, these compounds were not identified using the ATR-FTIR spectroscopic imaging technique. Further analysis is required to elucidate these Cr-based components and Cl-containing degradation products.

The ATR-FTIR imaging results show the presence of lead white and gypsum in the blue pigment from *Caravan* (Figure 4.3a). This observation finds support in the identification of high concentrations of Pb and Ca, as indicated by the XRF results (Table 4.1). Notably, there is no apparent detection of ultramarine blue, recognisable by its characteristic bands at approximately 1000 cm^{-1} in the ATR-FTIR spectrum. The use of XRF analysis enabled the detection of Co and Sn (Table 4.1), thereby corroborating the prevalence of cobalt cerulean blue ($\text{CoO}\cdot n\text{SnO}_2$, cobalt stannate)

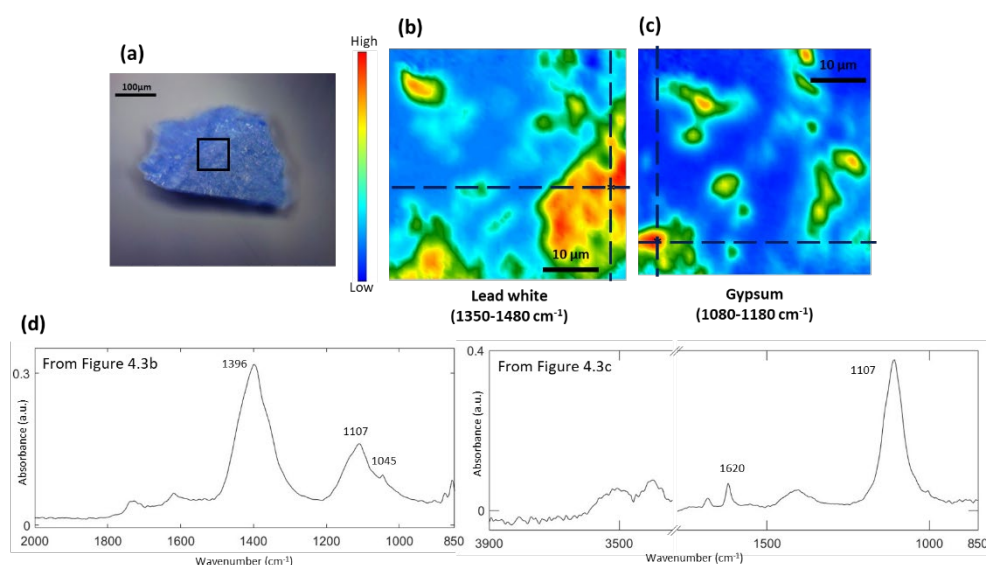


Figure 4.3 (a) Microscopic image of the blue pigment sample taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the blue pigment showing the distribution of (b) lead white and (c) gypsum. (d) ATR-FTIR spectra extracted from pixels of the chemical images.

(Haddad, Rogge, et al., 2022) as one of the components of this blue pigment sample.

The detection of Al from the XRF results indicate the possibility that cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) might also have been used in the painting. The ATR-FTIR imaging results show the presence of lead white and gypsum by assigning the spectral bands at 1396 cm^{-1} (Brooker et al., 1983; Liu et al., 2023; Spring et al., 2008) and 1107 cm^{-1} (Bishop et al., 2014; Vichi et al., 2018), respectively. (Figure 4.3b, c and d). The detection of cadmium (Cd) and sulfur (S) as major elements in the XRF results implies that this blue pigment may contain cadmium yellow (CdS), which is uncommon for blue pigments. This could be attributed to the artist's blending of colours, although microscopic images do not reveal any apparent greenish hues. Cd was also detected as a minor element in other blue and green pigments in this study (Table 4.1 and 4.2), which may be due to contamination from brushes or the palette.

The ATR-FTIR imaging results of the blue pigment sample from *Yerevan Zangu River* (Figure 4.4) show chemical images of silicates, calcium carbonate, metal carboxylates and an unidentified compound. The presence of silicates was identified by assigning the absorbance at 1026 cm^{-1} and 1034 cm^{-1} (Figure 4.4b and f) and the detection of Si from the XRF results. These detected silicates may be fillers mixed with the blue pigment. The presence of Co and Sn detected with XRF may suggest that cobalt cerulean blue ($\text{CoO} \cdot n\text{SnO}_2$) is the main component of this blue pigment from the paint layer. It is noteworthy that metal carboxylates, characterised by distinct bands of $\nu_{\text{as}}(\text{COO}^-)$ within the spectral range of 1520 cm^{-1} to 1630 cm^{-1} , were notably abundant within this blue pigment sample. The broad band of $\nu_{\text{as}}(\text{COO}^-)$ in this blue pigment sample indicate these metal carboxylates have a non-crystalline structure. The unidentified compound identified in this blue pigment shows characteristic bands at 1115 cm^{-1} , which may indicate the presence of gypsum (Figure 4.4e and f). Nonetheless, this absorbance, assumed to be $\nu_{\text{as}}(\text{SO}_4^{2-})$, is at a higher wavenumber compared to the gypsum detected in the other samples, which is around $1107\text{--}1111 \text{ cm}^{-1}$ (Figure 4.3, 4.7, 4.9, 4.15). The other absorbance peaks of gypsum, such as the one at 1620 cm^{-1} , and water absorption at 3398 and 3529 cm^{-1} , overlap with the absorbance of the metal oxalates detected in the blue pigment from *Yerevan Zangu River*. Furthermore, the detection of S is absent from the XRF results. As a result,

gypsum cannot be identified in this blue pigment.

The presence of lipids, metal soaps, and calcium carbonate was identified in the

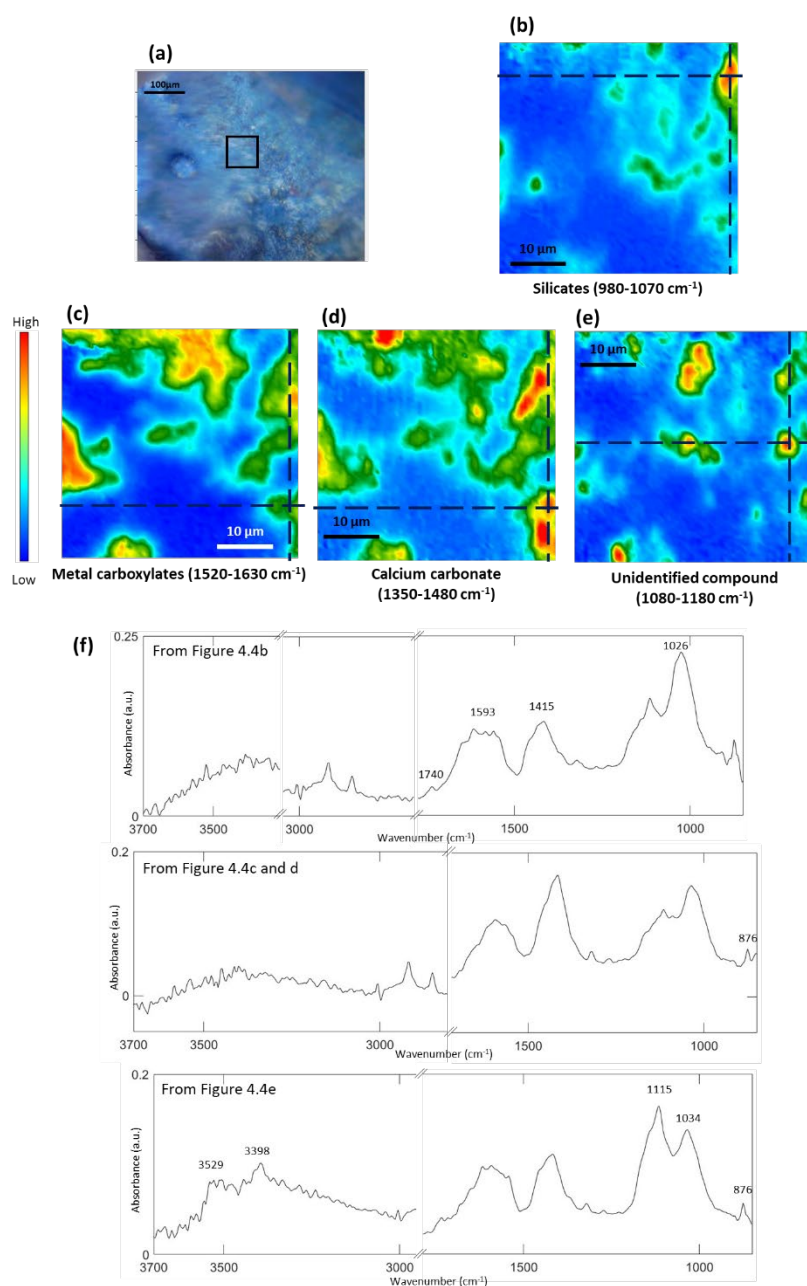


Figure 4.4 (a) Microscopic image of the blue pigment taken from *Yerevan Zangu River* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the blue pigments showing the distribution of (b) silicate, (c) metal carboxylates, (d) calcium carbonate and (e) an unidentified compound of which images were produced by plotting integrated absorbance between 1080 and 1180 cm⁻¹. (f) ATR-FTIR spectra extracted from pixels of the chemical images.

light blue pigment sample from *Kirovakan* using ATR-FTIR spectroscopic imaging (Figure 4.5). The detection of Sn and Co using XRF may suggest that cobalt cerulean blue ($\text{CoO} \cdot n\text{SnO}_2$) is the primary component of the light blue pigment (Table 4.1). The possibility of cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) is not considered due to the absence of Al detection using XRF. The relatively strong vibrational bands located at 1740 cm^{-1} , 2856 cm^{-1} , and 2929 cm^{-1} , assigned to the $\nu_{\text{sy}}(\text{C}=\text{O}\text{ ester})$, $\nu_{\text{sy}}(\text{CH}_2)$, and $\nu_{\text{as}}(\text{CH}_2)$, respectively, suggest the presence of a lipidic binder (Figure 4.5c and f), most likely associated with a siccative oil, such as linseed oil. The extensive distribution of this lipidic binder detected within the light blue pigment as shown from the ATR-FTIR image could be associated with the widespread occurrence of metal carboxylates (Figure 4.5d), which exhibit a broad $\nu_{\text{as}}(\text{COO}^-)$ peak in the ATR-FTIR spectrum (Figure 4.5f), indicating their non-crystalline structure. These metal carboxylates can be amorphous zinc carboxylates as XRF detected a high amount of Zn (Table 6.1 in Appendices). In addition, zinc lactate, another degradation product of oil paints, was detected as demonstrated by the spectral bands at 1047 cm^{-1} , 1092 cm^{-1} , 1122 cm^{-1} and 1270 cm^{-1} (Figure 4.5e and f), which closely resemble the spectrum of zinc lactate (Chua et al., 2022; Helwig et al., 2014). It is known that zinc lactate can form as localised aggregates infused into the matrix of zinc soaps, in accordance with descriptions in the literature (Chua et al., 2022). This observation is consistent with our ATR-FTIR chemical images (Figure 4.5d and e).

XRF analysis reveals Zn as the most abundant element detected in the blue pigments from *Morning in Stavrino*, *Arabian Dancer*, *Yerevan Zangu River* and *Kirovakan*, suggesting the possible presence of zinc white (ZnO). However, it is worth noting that the spectral band of zinc white typically appears around 450 cm^{-1} , which falls beyond the spectral range detectable by our ATR-FTIR spectroscopic technique. To validate the presence of zinc white in these blue pigments, further investigations could involve the use of FTIR spectroscopy with the far-IR region, capable of detecting spectral bands at lower wavenumbers. Additionally, complementary techniques like Raman spectroscopy could also be employed.

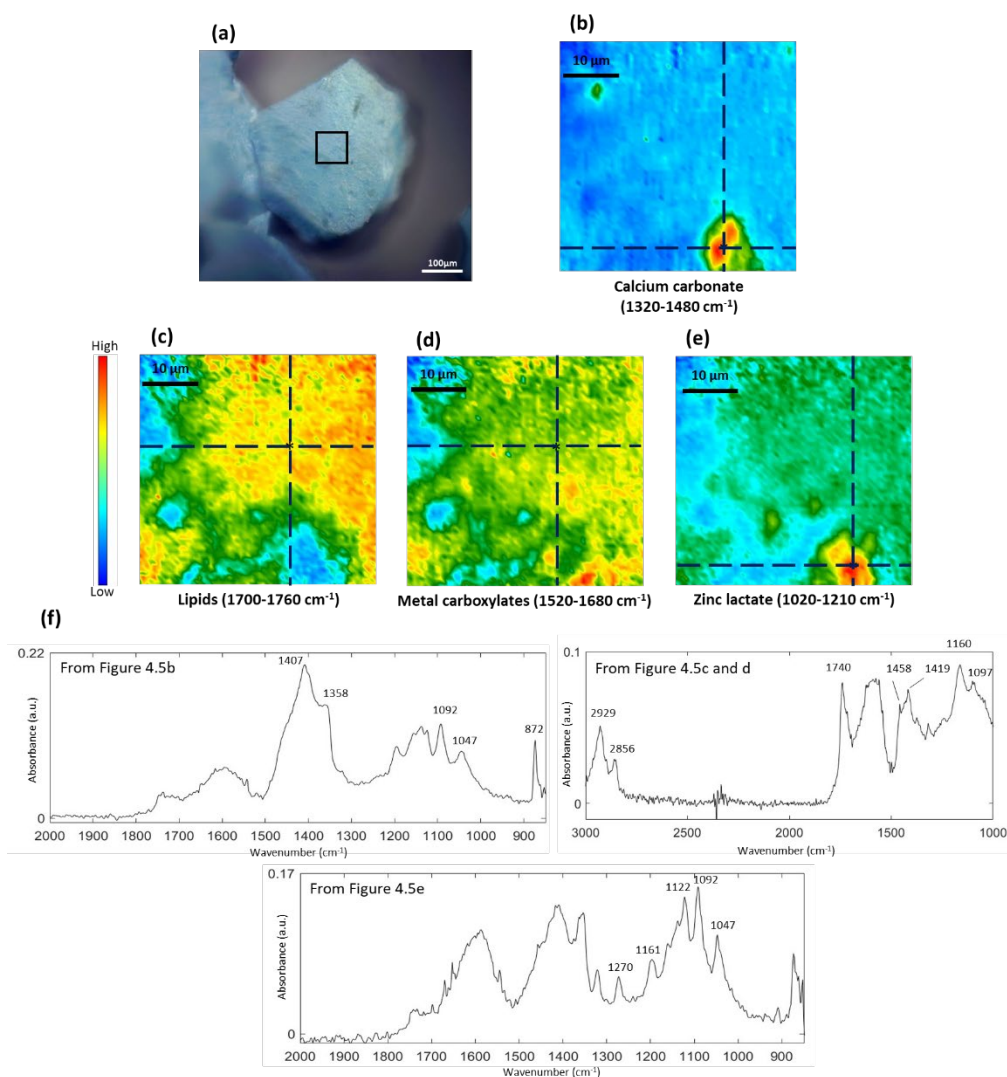


Figure 4.5 (a) Microscopic image of the light blue pigment sample taken from *Kirovakan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the light blue pigment sample showing the distribution of (b) calcium carbonate, (c) lipids, (d) metal carboxylates and (e) zinc lactate. (f) ATR-FTIR spectra extracted from pixels of the chemical images.

4.1.3.2 Study of the green pigment

In this section, the focus turns to the exploration of green pigments, encompassing those derived from *Morning in Stavrino*, *Arabian Dancer*, *Yerevan Zangu River*, *Caravan*, and the blue green pigment from *Caravan*, the dark green pigment from *Yerevan Zangu River*. The XRF results of these pigments are detailed in Table 4.2.

Table 4.2 Summary of XRF results of the blue pigments.

Colour	Painting	Detected chemical elements with XRF
Green	<i>Morning in Stavrino (1909)</i>	Major: Ca, Cr, Si, S, Al, Fe, Zn, Cl, P Minor: Pb, Co, Ti, Cu Trace: As, Mn
	<i>Arabian dancer (1913)</i>	Major: Zn, Na, S, Si, Ca, Al, Cr, Fe, Pb, Ti Minor: P, Cl, Co, Cd Trace: Sn, As, Sr
	<i>Yerevan Zangu River (1931)</i>	Major: Zn, Pb, Si, Ca, Al, Fe, S, Cl, Cr, Co Minor: As, Er, V, Ga Trace: Mn
	<i>Caravan (1926)</i>	Major: Pb, Ca, Cr, Mg, Fe, Zn Minor: Cd, Cl, Ti Trace: Sr, Mn, Zr
Blue green	<i>Caravan (1926)</i>	Major: Pb, As, Cu, Ca, Co Minor: Zn, Fe, Cl, Sn Trace: Sr, Cr, Ti, Zr
Dark green	<i>Yerevan Zangu River (1931)</i>	N/A

The ATR-FTIR images (Figure 4.6b and c) shows chemical distributions of ultramarine blue and calcium carbonate in the green pigment from *Morning in Stavrino*, which is in line with the results of the blue pigment sample from *Morning in Stavrino*. Our XRF results (Table 4.2) reveal high concentration of calcium (Ca), aligning with our identification of calcium carbonate in the blue pigments. In addition, a spectrum extracted from the measured area of this green pigment sample exhibits two absorption bands at 1252 cm^{-1} and 1286 cm^{-1} , indicating a presence of hydrated chromium oxide ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) (Vahur et al., 2016), also known as viridian (Figure 4.6d). The spectra also exhibit an O–H bending band at approximately 1640 cm^{-1} , which confirms the presence of water molecules in the hydrated chromium oxide. The absorption bands at 1252 cm^{-1} and 1286 cm^{-1} are attributed to a by-product, which was assumed to be a chromium bearing borate in the literature (Zumbuehl et al., 2009). Interestingly, these two absorption bands are not commonly identified in modern post-war samples, possibly due to the application of different manufacturing techniques in

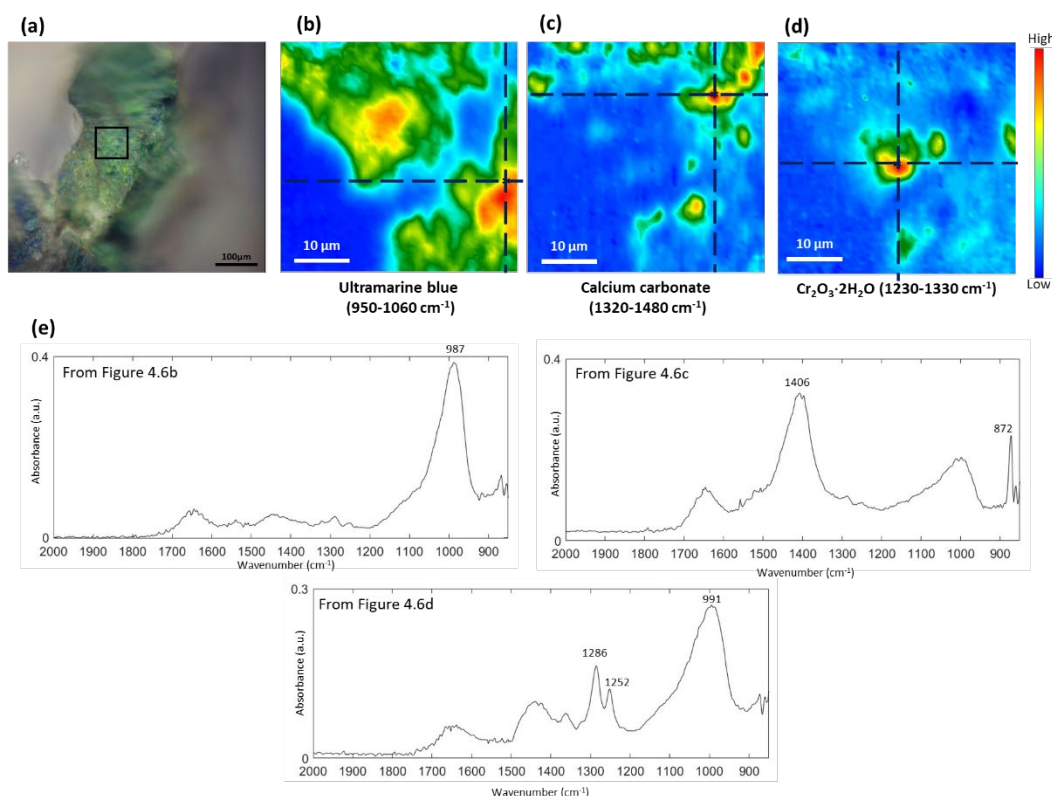


Figure 4.6 (a) Microscopic image of the green pigment taken from *Morning in Stavrino* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the green pigments showing the distribution of (b) ultramarine blue (c) calcium carbonate and (d) $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. (e) ATR-FTIR spectra extracted from pixels of the chemical images.

the production of viridian pigments (Newman, 1997). However, our XRF results do not detect boron (Table 4.2) due to the limitations of XRF in detecting light elements. The XRF results of this green pigment sample do confirm the presence of Cr, supporting the presence of viridian. It should be noted that in certain literature (Vahur et al., 2016), $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ exhibits distinct peaks at approximately 1063 cm^{-1} and 792 cm^{-1} , which are not observed in our results. The absence of absorption bands at 1063 cm^{-1} and 792 cm^{-1} may be explained by the specific synthesis conditions of this viridian pigment, involving a higher temperature range and a prolonged calcination period (Zumbuehl et al., 2009).

The ATR-FTIR analysis reveal the presence of ultramarine blue, calcium carbonate, and hydrated chromium oxide in the green pigment from *Arabian Dancer* (Figure 4.7b-d), which is consistent with the results obtained for the green pigment used in

Morning in Stavrinio (Figure 4.6), except for the detection of sulfates and gypsum (Figure 4.7e and f). The sulfates observed in the green pigment sample may be attributed to the presence of chrome yellow, which can be either lead chromate PbCrO_4 or a mixture of lead chromate and lead sulfate ($\text{PbCrO}_4 \cdot \text{PbSO}_4$) (Monico et al., 2011), as yellow hues are visible on the mineral particles of this green pigment (Figure 4.7a). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) could either be an original material or a product of degradation. The spectral band at 1107 cm^{-1} is assigned to the anti-symmetric stretching mode of sulfate ($\nu_{\text{as}}(\text{SO}_4^{2-})$), while the bands at 3396 cm^{-1} and 1620 cm^{-1} correspond to the stretching and bending vibrational modes of water, respectively. The detection of Cr revealed in the XRF results (Table 4.2) may provide supporting evidence for the potential existence of chrome yellow (Figure 4.7e and g) and hydrated chromium oxide (Figure 4.7d and g) within the green pigment, as indicated by the ATR-FTIR results. The detection of Zn as the element with the highest concentration in the XRF results could be attributed to the potential utilisation of zinc white. This hypothesis needs verification through additional complementary techniques, such as FTIR spectroscopy within the far-IR spectral region or Raman spectroscopy.

The distribution of $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ in the green pigment from *Caravan* was obtained by plotting the integrating absorbance bands at 1250 cm^{-1} and 1284 cm^{-1} (Figure 4.8b). XRF analysis also confirmed the presence of Cr (Table 4.2). Lead white and gypsum were identified from the ATR-FTIR imaging results (Figure 4.8c) and Pb and Ca were detected from the XRF results.

The ATR-FTIR imaging results (Figure 4.9) show chemical images of metal oxalates as a degradation product, and distribution of calcium metal carboxylates, calcium carbonate, gypsum, and silicates in the green pigment from *Yerevan Zangu River*. The presence of silicates in this green pigment sample was identified by assigning Si-O stretching modes (Farmer, 1974) at 1030 cm^{-1} (Figure 4.9f and h) or at 952 cm^{-1} (Figure 4.9g and h). The detection of Zn, Cr, and Co from the XRF results (Table 4.2) implies that the green pigments may contain cobalt green ($\text{CoO} \cdot \text{ZnO}$) and chromium oxide green (Cr_2O_3). We do not observe the spectral bands at 1252 cm^{-1} and 1286 cm^{-1} that are attributed to boron-containing by-products in hydrated chromium oxide which

can be seen in the green pigments from *Arabian Dancer* (Figure 4.7f and g) and *Caravan* (Figure 4.8b and f). In addition to the cobalt green pigment, which was relatively uncommon, a more plausible explanation could involve the mixture of small amounts of cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) into this green pigment to achieve the desired hue. The substantial presence of As (9.707%, Table 6.2 in Appendices) from the XRF results

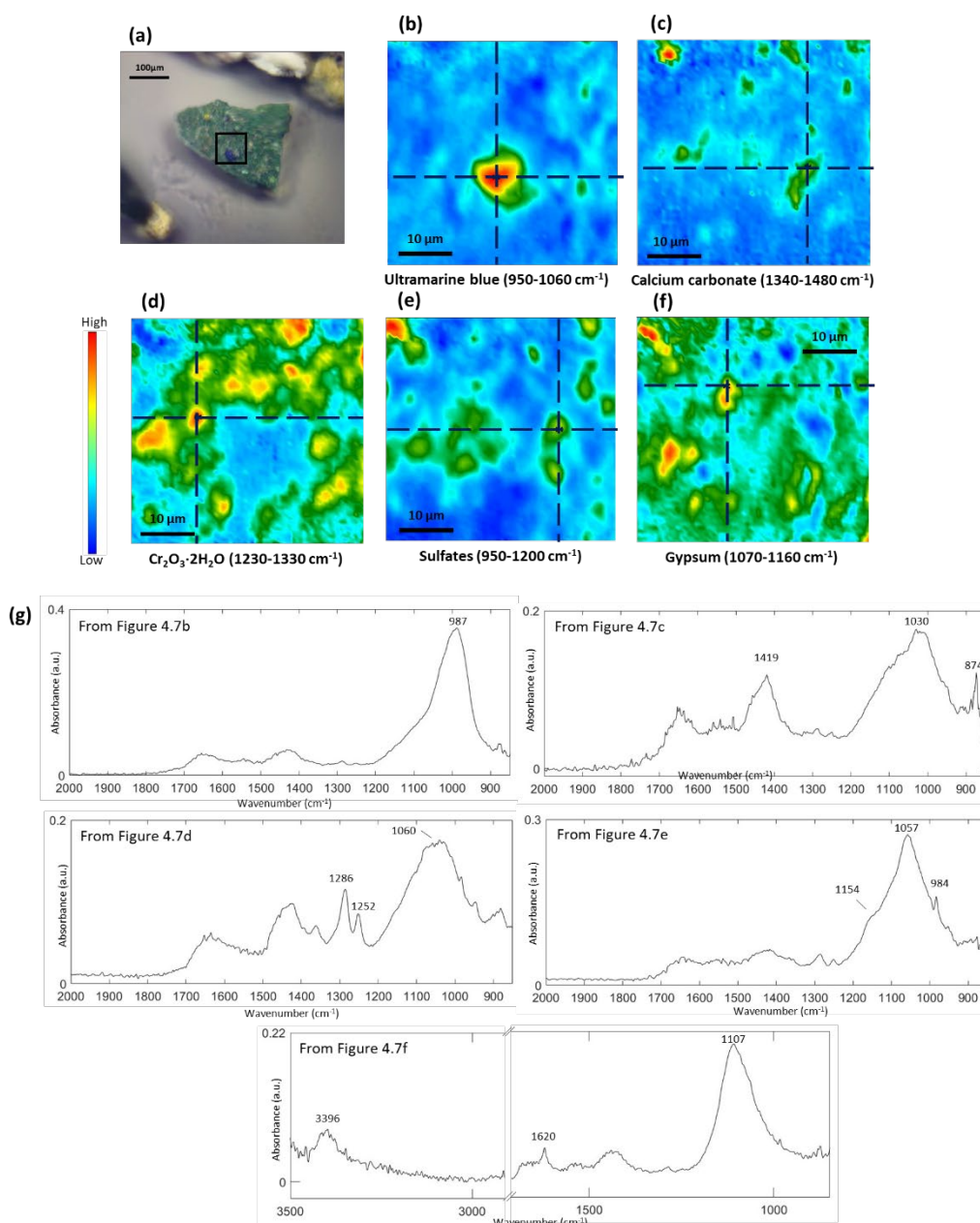


Figure 4.7 (a) Microscopic image of the green pigments taken from *Arabian dancer* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the green pigments showing the distribution of (b) ultramarine blue, (c) calcium carbonate, (d) $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, (e) sulfates and (f) gypsum. (g) ATR-FTIR spectra extracted from pixels of the chemical images

of the blue-green pigment from *Caravan* (Table 4.2) suggests a high likelihood of a Cu-based pigment, emerald green (copper acetoarsenite, $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$) (Fiedler & Bavard, 1997). Emerald green was highly esteemed by artists in the 19th century due to its vividness and long-lasting properties (Fiedler & Bavard, 1997).

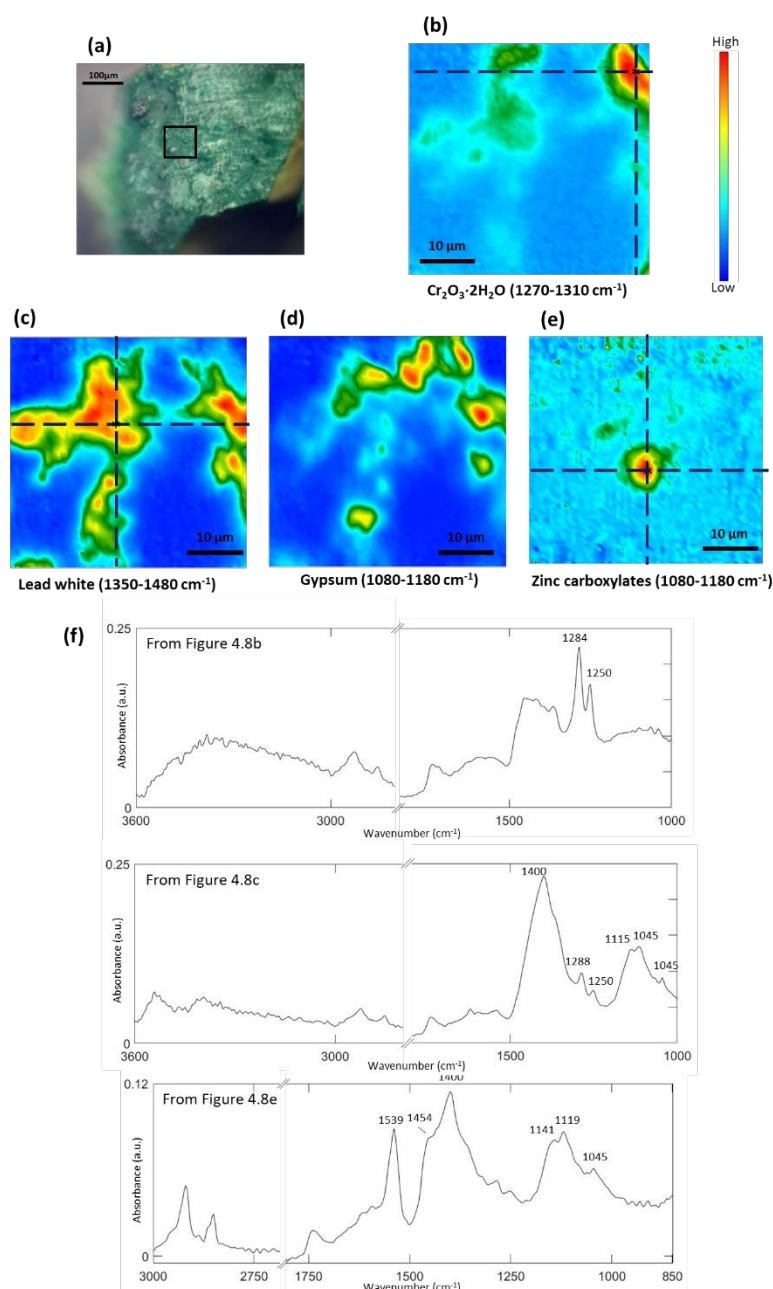


Figure 4.8 (a) Microscopic image of the green pigment taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the green pigments showing the distribution of (b) $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, (c) lead white, (d) gypsum and (e) zinc carboxyalates. (f) ATR-FTIR spectra extracted from pixels of the chemical images.

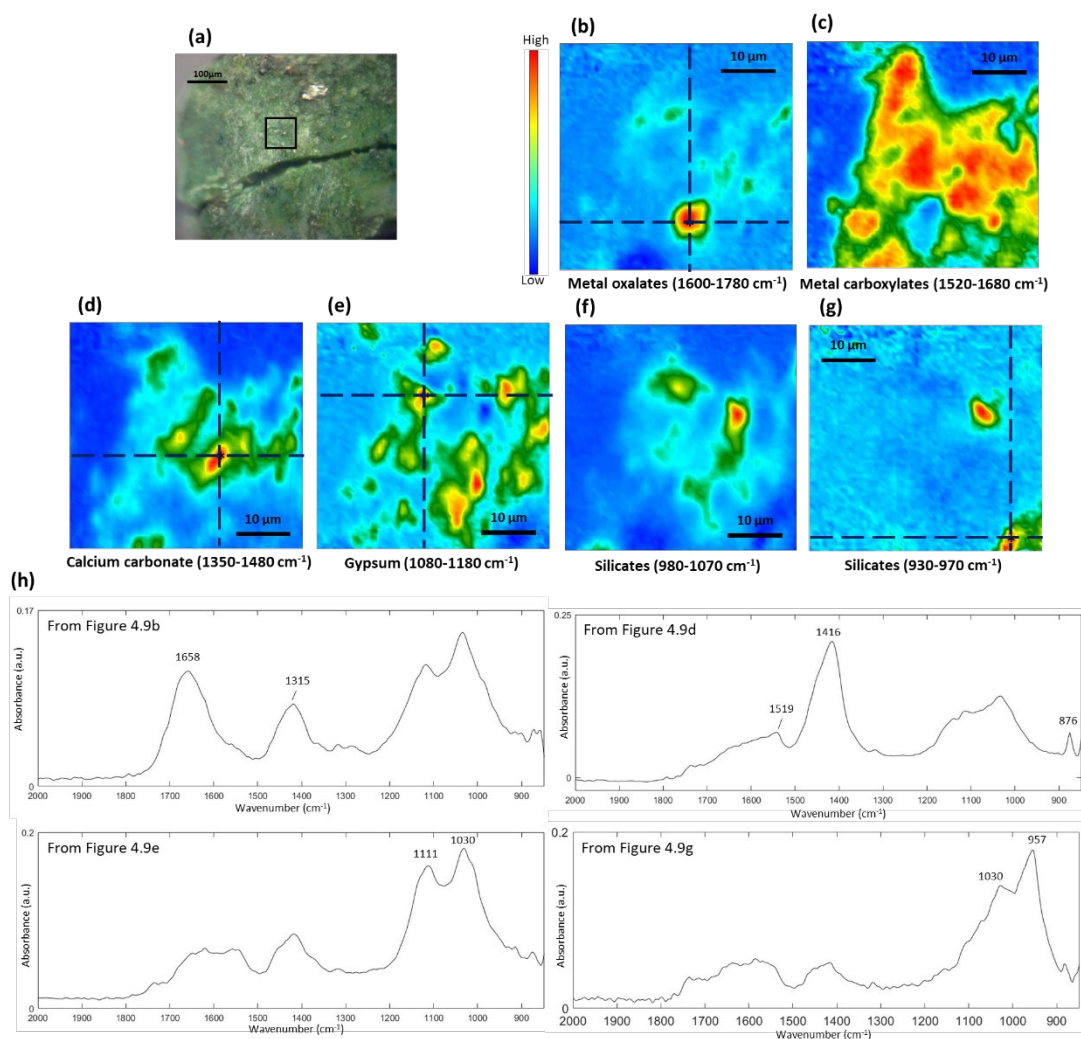


Figure 4.9 (a) Microscopic image of the green pigment taken from *Yerevan Zangu River* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the green pigments showing the distribution of (b) metal oxalates, (c) metal carboxylates, (d) calcium carbonate, (e) gypsum, and silicates with absorbance at (f) 980–1070 cm^{-1} and (g) 930–970 cm^{-1} . (h) ATR-FTIR spectra extracted from pixels of the chemical images.

Nevertheless, its production was ultimately discontinued by the 1960s due to the severe toxicity associated with the pigment (Lipscher). Other possibilities of Cu-based green pigments could include malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and azurite ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), potentially indicated by the identification of carbonates by assigning the spectral bands of the carbonate group at 1400 cm^{-1} and 862 cm^{-1} in our ATR-FTIR results (Figure 4.10b and d). However, it is worth noting that malachite, an ancient pigment, was not commonly employed in the 20th century. Furthermore, both

malachite and azurite exhibit multiple peaks of $\nu_{\text{as}}(\text{CO}_3^{2-})$ in the region of 1380 cm^{-1} and 1490 cm^{-1} (Vahur et al., 2016), these carbonates are more likely to be attributed to lead white. The substantial presence of Pb, as evident in the XRF results, further supports the assumption that the carbonates within this blue-green pigment are primarily derived from lead white. Additionally, the detection of Co and Zn also suggests the possible presence of a small amount of cobalt green ($\text{CoO}\cdot\text{ZnO}$) (Vermeulen et al., 2022). Zinc carboxylates, characterised by spectral bands of $\nu_{\text{as}}(\text{COO}^-)$, were identified as a degradation product in this blue-green pigment, exhibiting a split doublet at 1531 cm^{-1} and 1546 cm^{-1} (Helwig et al., 2014) (Figure 4.10c and d). The spectral bands of $\nu_{\text{as}}(\text{COO}^-)$ at 1454 and 1546 cm^{-1} may also be attributed to the carboxylic group of copper acetoarsenite (Klisińska-Kopacz et al., 2023), thus supporting the presence of emerald green.

Apart from the green pigment, another green pigment that is darker was also taken from *Yerevan Zangu River* (Figure 4.11a). The ATR-FTIR spectrum extracted from a chemical image was created by plotting absorbance between 930 and 1000 cm^{-1} and show two spectral bands at 957 cm^{-1} , 972 cm^{-1} and a shoulder at 1072 cm^{-1} , which can be ascribed to a distortion of the Si-O bond in-plane (Moretto et al., 2011). The

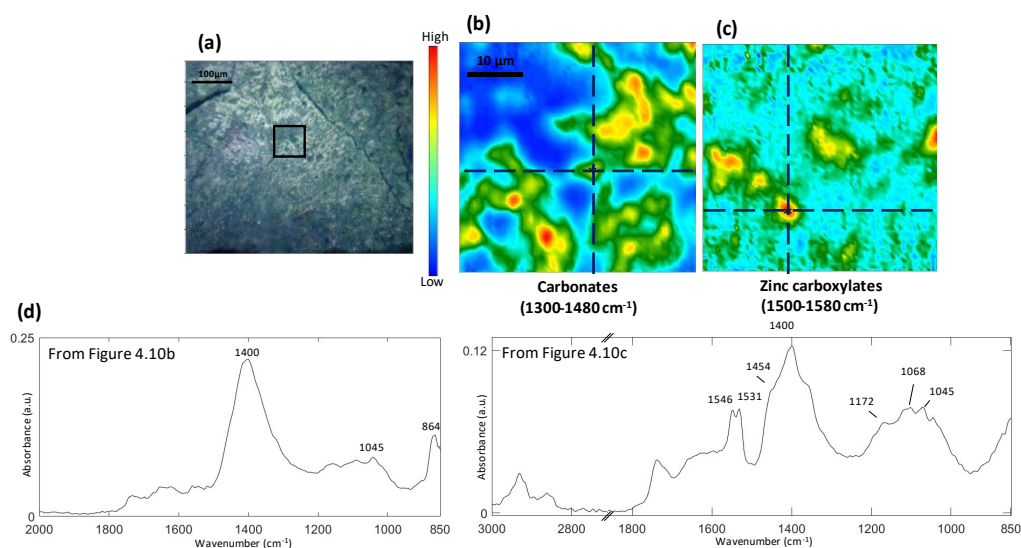


Figure 4.10 (a) Microscopic image of the blue-green pigment taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the blue-green pigment showing distribution of (b) carbonates and (c) zinc carboxylates. (d) ATR-FTIR spectra extracted from pixels of the chemical image are placed next to the chemical images.

ATR-FTIR imaging results show that the dark green pigment used in *Yerevan Zangu River* may be celadonite ($\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})[\text{Si}_4\text{O}_{10}](\text{OH})_2$) (Figure 4.11). However, the amount of dark green sample (two separate powders) is too low to get reliable results to confirm the presence of K, Mg and Al.

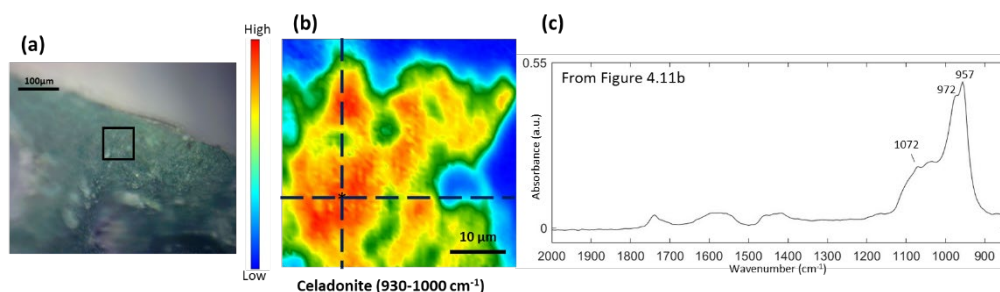


Figure 4.11 (a) Microscopic image of the dark green pigment taken from *Yerevan Zangu River* where the black square displays the area identified using ATR-FTIR imaging. (b) ATR-FTIR chemical image of the dark pigments showing distribution of celadonite. (c) ATR-FTIR spectra extracted from pixels of the chemical images of celadonite.

4.1.3.3 Study of the yellow and brown pigments

In this section of the pigment investigation, we delve into the analysis of yellow pigments from *Morning in Stavrino* and *Caravan*, and a brown pigment from *Caravan*. The XRF results of these pigments are detailed in Table 4.3.

Table 4.3 Summary of XRF results of the yellow and brown pigments.

Colour	Painting	Detected chemical elements with XRF
Yellow	<i>Morning in Stavrino</i> (1909)	Major: Si, Ca, Zn, Cl, Pb, S, Fe, Cr, Sn, Ti Minor: As
	<i>Caravan</i> (1926)	Major: Pb, Ca, Cd, Ti, Cl Minor: Fe, Zn, V, Cr Trace: Sr, Zr
Brown	<i>Caravan</i> (1926)	Major: Pb, Ca, Cd, Zn Minor: Al, Fe, Cr, Co Trace: Sr, Ti, Cu, Zr, Rb

The ATR-FTIR imaging results (Figure 4.12) reveal the detection of sulfates in the yellow pigment sample taken from *Morning in Stavrino*, as indicated by the spectral

bands at 984 cm^{-1} , 1068 cm^{-1} , and 1182 cm^{-1} ($\nu(\text{SO}_4^{2-})$). The bands at 1068 cm^{-1} and 1182 cm^{-1} are attributed to $\nu_{\text{as}}(\text{SO}_4^{2-})$, while the band at 984 cm^{-1} corresponds to $\nu_{\text{sy}}(\text{SO}_4^{2-})$ (Lane, 2007). The XRF results (Table 4.3) do not detect any cadmium (Cd), indicating that the possibility of cadmium yellow can be ruled out. Additionally, chrome yellow is composed of PbCrO_4 and PbSO_4 (Monico et al., 2011). The ATR-FTIR spectra display the presence of $\nu_{\text{sy}}(\text{CrO}_4^{2-})$ at approximately 850 cm^{-1} . The detection of Cr from the XRF results suggests that chrome yellow may be the main component of the yellow pigment. It is important to emphasise that a substantial amount of Si, Ca, Zn, and Fe was detected using XRF (Table 6.3 in Appendices). The presence of Si and Fe could suggest the inclusion of Fe-containing yellow earth in this chrome yellow pigment. Similarly, the identification of Ca and Zn might indicate the incorporation of CaCO_3 and zinc white (ZnO), respectively, into the yellow pigment. However, the absorption bands associated with Fe-containing yellow earth and CaCO_3 are obscured by the strong spectral bands of $\nu(\text{SO}_4^{2-})$ and $\nu_{\text{sy}}(\text{CrO}_4^{2-})$ originating from the chrome yellow pigment. Verification of this hypothesis may necessitate the utilisation of alternative techniques.

The brown-coloured sample extracted from *Caravan* has a pale almond tone mixing with an orange matrix (Figure 4.13a). ATR-FTIR analysis reveals the presence of carbonates, potentially lead white and calcium carbonate (Figure 4.13b), which was supported by the detection of Pb and Ca from the XRF results (Table 4.3). The presence of Cd and Zn in the XRF results may indicate the identification of cadmium yellow (CdS and ZnS) in the brown-coloured sample. However, the absence of S in

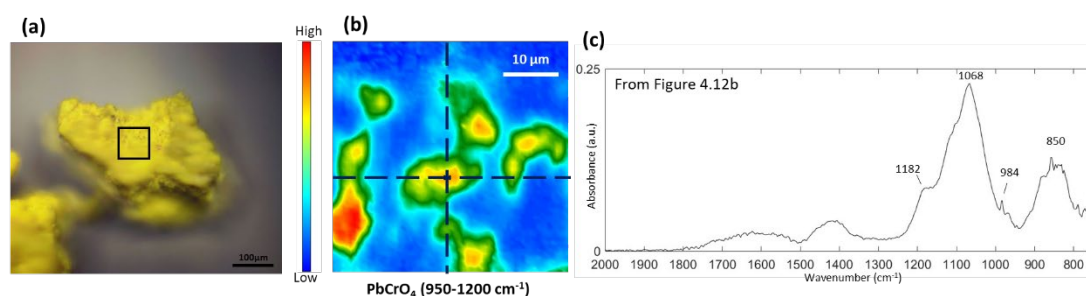


Figure 4.12 (a) Microscopic image of the yellow pigment sample taken from *Morning in Stavrino* where the black square displays the area identified using ATR-FTIR imaging. (b) ATR-FTIR chemical image of the yellow pigment sample showing the distribution of PbSO_4 and (c) ATR-FTIR spectrum extracted from a pixel of the chemical image.

the XRF results may raise concerns regarding the identification of cadmium yellow. Unfortunately, the Cd–S vibrational bands fall within the spectral range of 300–230 cm^{-1} (Vahur et al., 2010), which exceeds the capability of our ATR-FTIR technique. Consequently, the verification of CdS through the ATR-FTIR results is unattainable. Nonetheless, the presence of CdCO_3 and CdSO_4 is commonly observed when identifying CdS in cadmium yellow pigment. This is due to the utilisation of CdSO_4 and CdCO_3 as reagents in the wet and dry process syntheses of CdS, respectively (Fiedler & Bayard, 1986; Topalova-Casadiegos & Plahter, 2011). Furthermore, CdSO_4 and CdSO_3 are degradation products resulting from the photooxidation of CdS (Mass, Opila, et al., 2013). Therefore, the detection of carbonates in this yellow pigment sample can also be assigned to CdCO_3 .

Despite the slightly different colours exhibited by the brown and yellow pigments from *Caravan* (Figure 4.13a and 4.14a), their ATR-FTIR imaging and XRF results are

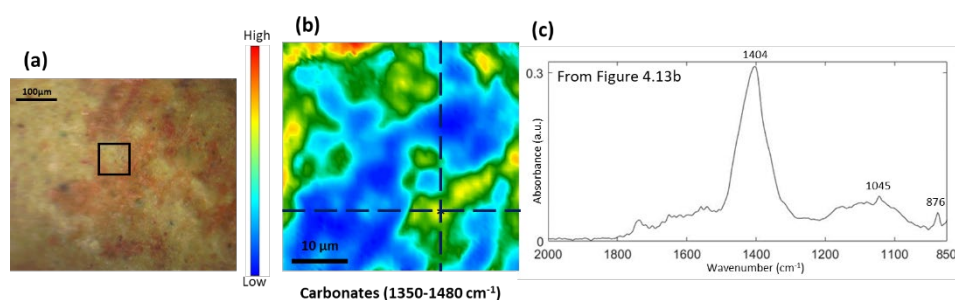


Figure 4.13 (a) Microscopic image of the brown pigment taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. (b) ATR-FTIR chemical image of the brown pigments showing the distribution of lead white and calcium carbonate. (c) ATR-FTIR Spectra extracted from pixels of the chemical images.

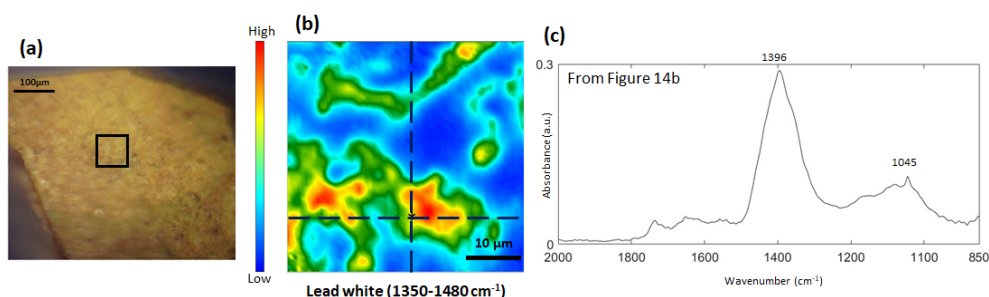


Figure 4.14 (a) Microscopic image of the yellow pigment sample taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. (b) ATR-FTIR chemical image of the yellow pigment sample and (c) ATR-FTIR spectrum extracted from a pixel of the chemical image.

similar. Carbonates, including lead carbonate (lead white), calcium carbonate, and cadmium carbonate, were identified, as shown in Figure 4.13b and Table 4.3. The measured Zn content in the brown pigment sample from XRF results is 1.055% (Table 6.3 in Appendices), categorising it as a major element. However, the yellow pigment sample contains 0.737% of Zn (Table 6.3), designating it as a minor element.

4.1.3.4 Study of the red and orange pigments

Red pigments from *Arabian Dancer* and *Caravan*, and an orange pigment extracted from *Kirovakan* are examined and discussed in this section. The XRF results of these pigments are detailed in Table 4.4.

Table 4.4 Summary of XRF results of the red and orange pigments.

Colour	Painting	Detected chemical elements with XRF
Red	<i>Arabian dancer (1913)</i>	Major: Zn, Na, S, Ca, Al, Si, Cd, Fe, P
		Minor: Cl, K, As, Cr, Ti
		Trace: Co, Mn
	<i>Caravan (1926)</i>	Major: Pb, Cl, Co, Ca, P, Fe, Zn, Er Minor: Cr Trace: Ga
Orange	<i>Kirovakan (1948)</i>	Major: Zn, Si, Ca, Fe, Cl, S Minor: Ti, Cr, V, As, Co

The ATR-FTIR imaging results demonstrate the presence of gypsum in the red pigment from *Arabian dancer* (Figure 4.15b), and gypsum might have been used as an extender or a filler. The detection of silicates (Figure 4.15c) may indicate the presence of red ochre, as ochre is a mixture of ferric oxide, clay, and silicate-containing sand. The detection of aluminium (Al) and silicon (Si) and iron (Fe) in the XRF results (Table 4.4) also corroborates the hypothesis that the red pigment contains red ochre. It is important to note that based on the XRF results, the presence of cadmium (Cd), zinc (Zn), and sulfur (S) was also detected. Therefore, the possibility of cadmium yellow (CdS and ZnS) should not be excluded. Additionally, the identification of oxalates as degradation products was observed (Figure 4.15d).

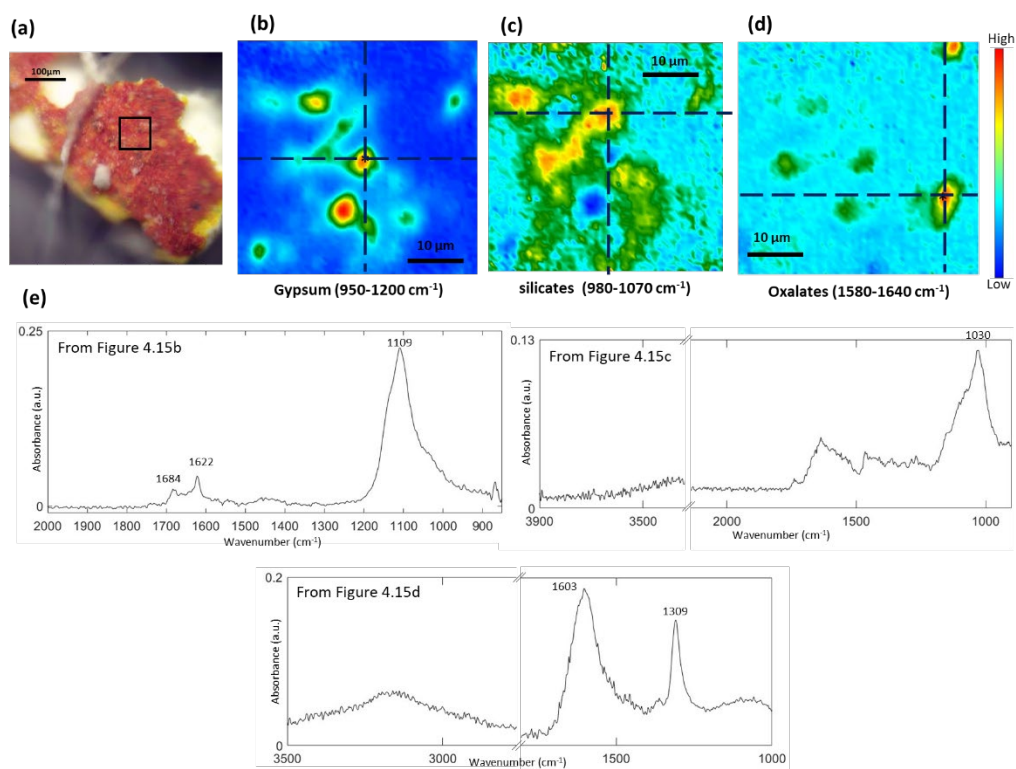


Figure 4.15 (a) Microscopic image of the red pigments taken from *Arabian dancer* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the red pigments showing distribution of (b) gypsum, (c) silicates and (d) metal oxalates. (e) ATR-FTIR spectra extracted from pixels of the chemical images.

ATR-FTIR imaging results reveal the presence of silicates, gypsum, an unidentified compound, and carbonates in the red pigment from *Caravan* (Figure 4.16). By assigning spectral bands at 934 cm^{-1} , 1018 cm^{-1} , and 1033 cm^{-1} attributed to different silicates and clay mixtures, red ochre can be identified (Figure 4.16b and g). The detection of Fe from the XRF results supports the possibility of red ochre, but the lack of Si detection may weaken this hypothesis. The unidentified compound identified in this red pigment displays characteristic bands at 927 cm^{-1} , 976 cm^{-1} , 1431 cm^{-1} , and 1462 cm^{-1} (Figure 4.16d, e and g). These bands may suggest a potential association with the elevated levels of chlorine (Cl), phosphorus (P), and erbium (Er) detected in the XRF results (Table 4.4). However, due to the limited existing literature on the application of Er-based components in oil paintings, confirming whether this unidentified compound is genuinely related to the Er-based components remains challenging. A pixel from this red pigment shows the presence of an intense band at

1400 cm^{-1} that may be characteristic carbonates (Salter et al., 2019) (Figure 4.16f and g). Combined with the XRF results indicating a high concentration of Pb and Ca, we cannot exclude the presence of lead white and CaCO_3 . Notably, Co was detected in the XRF results. Therefore, it is reasonable to hypothesise that Co-based pigments were mixed with this red pigment to give it a somewhat violet appearance.

Red ochre (Fe_2O_3 + kaolin) was identified in the orange pigment from *Kirovakan* by assigning spectral bands at 912 cm^{-1} (inner-surface OH in-plane bending), 1005 cm^{-1} and 1028 cm^{-1} (equatorial Si-O bond anti-symmetric stretching) (Figure 4.17a, b and

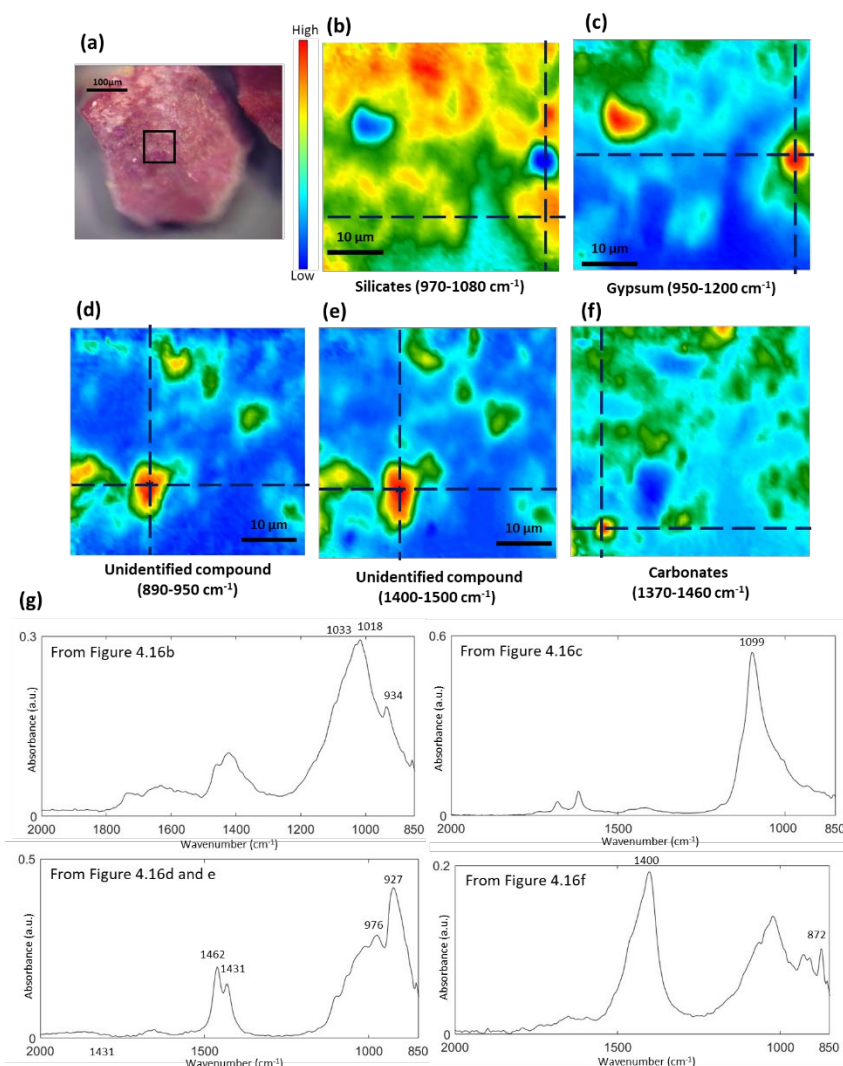


Figure 4.16 (a) Microscopic image of the red pigments taken from *Caravan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the red pigments showing the distribution of (b) silicates, (c) gypsum, an unidentified compound of which images were produced by plotting integrated absorbance between (d) 890 and 950 cm^{-1} and (e) 1400 and 1500 cm^{-1} , and (f) carbonates. (g) ATR-FTIR spectra extracted from pixels of the chemical images.

d). The detection of Fe and Si further supports the presence of red ochre in the orange pigment. Impurities such as calcium carbonate (Elias et al., 2006) were also identified (Figure 4.17c).

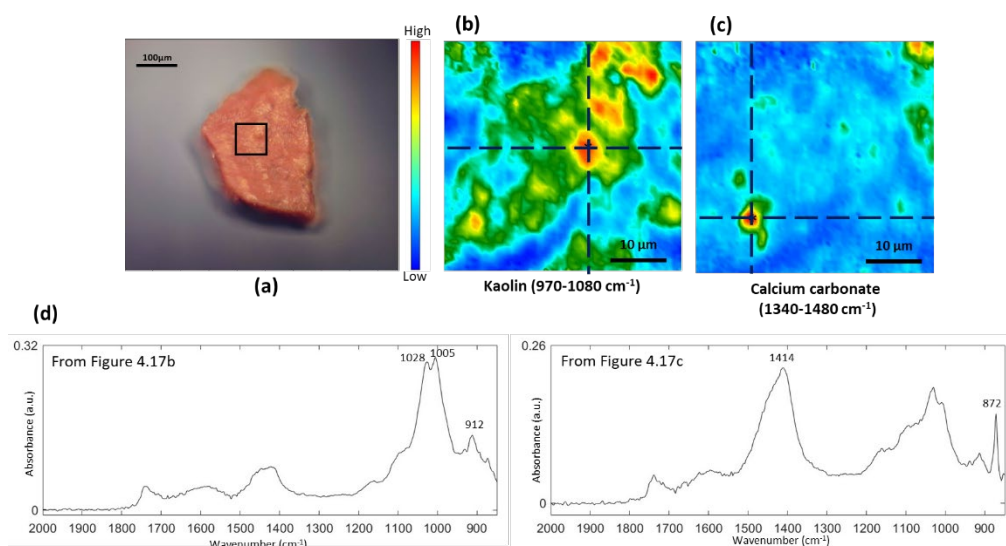


Figure 4.17 (a) Microscopic image of the orange pigment sample taken from *Kirovakan* where the black square displays the area identified using ATR-FTIR imaging. ATR-FTIR chemical image of the orange pigments showing the distribution of (b) kaolin and (c) calcium carbonate. (d) ATR-FTIR spectra extracted from pixels of the chemical images.

4.1.3.5 Formation of metal carboxylates and oxalates in oil paints

Calcium carbonate is commonly found in all ochres (Elias et al., 2006). Our results confirmed the presence of calcium carbonate in the ochre pigments through the identification of specific vibrational modes. The band of $\nu_{\text{as}}(\text{CO}_3)$ was observed within the range of $1404\text{--}1415\text{ cm}^{-1}$, accompanied by a distinct peak at approximately 872 cm^{-1} ($\delta(\text{CO}_3)$). Calcium carbonate in oil paintings has been found to form degradation products such as calcium carboxylate (Higgs & Burnstock, 2019; Izzo et al., 2021) and calcium oxalate (Rampazzi, 2019). Identification of calcium carboxylate and calcium oxalate can be acquired by assigning to a doublet of $\nu_{\text{as}}(\text{COO}^-)$ at around $1540/1575\text{ cm}^{-1}$ (Vichi et al., 2018) and a spectral band of $\nu_{\text{as}}(\text{C=O})$ at 1650 cm^{-1} (Klaassen et al.,

2019), respectively.

The formation of metal soaps in oil paintings occurs spontaneously due to the interaction between the fatty acid constituents of drying oils used as binders and the cations present in inorganic pigments (Noble, 2019; Ordonez & Twilley, 1997). These metal soaps play a significant role in the generation of protrusions and distortions within the paint layers (Gabrieli et al., 2017). Similarly, the calcium ions present in the calcium carbonate within the analysed pigment samples potentially undergo a saponification reaction with the fatty acids present in an oil-based binder, resulting in the formation of calcium soaps or calcium carboxylates. Upon conducting a detailed examination, a notable observation was made: the absorbance of carbonate decreased while the absorbance of metal carboxylates increased (Figure 4.18a). However, the data revealed that these metal carboxylates exhibit the broad spectral band of $\nu_{as}(\text{COO}^-)$ at 1570 cm^{-1} , indicating the presence of a non-crystalline structure (Hermans, Keune, van Loon, et al., 2016). Additionally, a shoulder at 1454 cm^{-1} , attributed to $\delta(\text{CH}_2)$ of the typical soap aliphatic chain, was observed in the spectra, which represents a characteristic spectral pattern of metal carboxylates.

In addition to the saponification of CaCO_3 that gives rise to metal soaps, CaCO_3 is also responsible for the formation of metal oxalates, as illustrated in Figure 4.18b. It was observed that the carbonate absorbance at 1415 cm^{-1} decreased as the oxalate absorbance at 1655 cm^{-1} increased. It is noteworthy that the intensity of the $\nu_{as}(\text{COO}^-)$ of calcium soaps at 1543 cm^{-1} decreased in the region where the metal oxalates were identified, as depicted in P4 and P5 in the ATR-FTIR image of metal oxalates (Figure 4.18b). Therefore, calcium is likely to be the metal ion present in these oxalates. Metal oxalates are predominantly found in association with organic binding media, indicating their probable formation as a result of the degradation of organic matter (Salvadó et al., 2019). However, some studies have also reported that metal oxalates can originate from metal carboxylates (Le Brun, 2021).

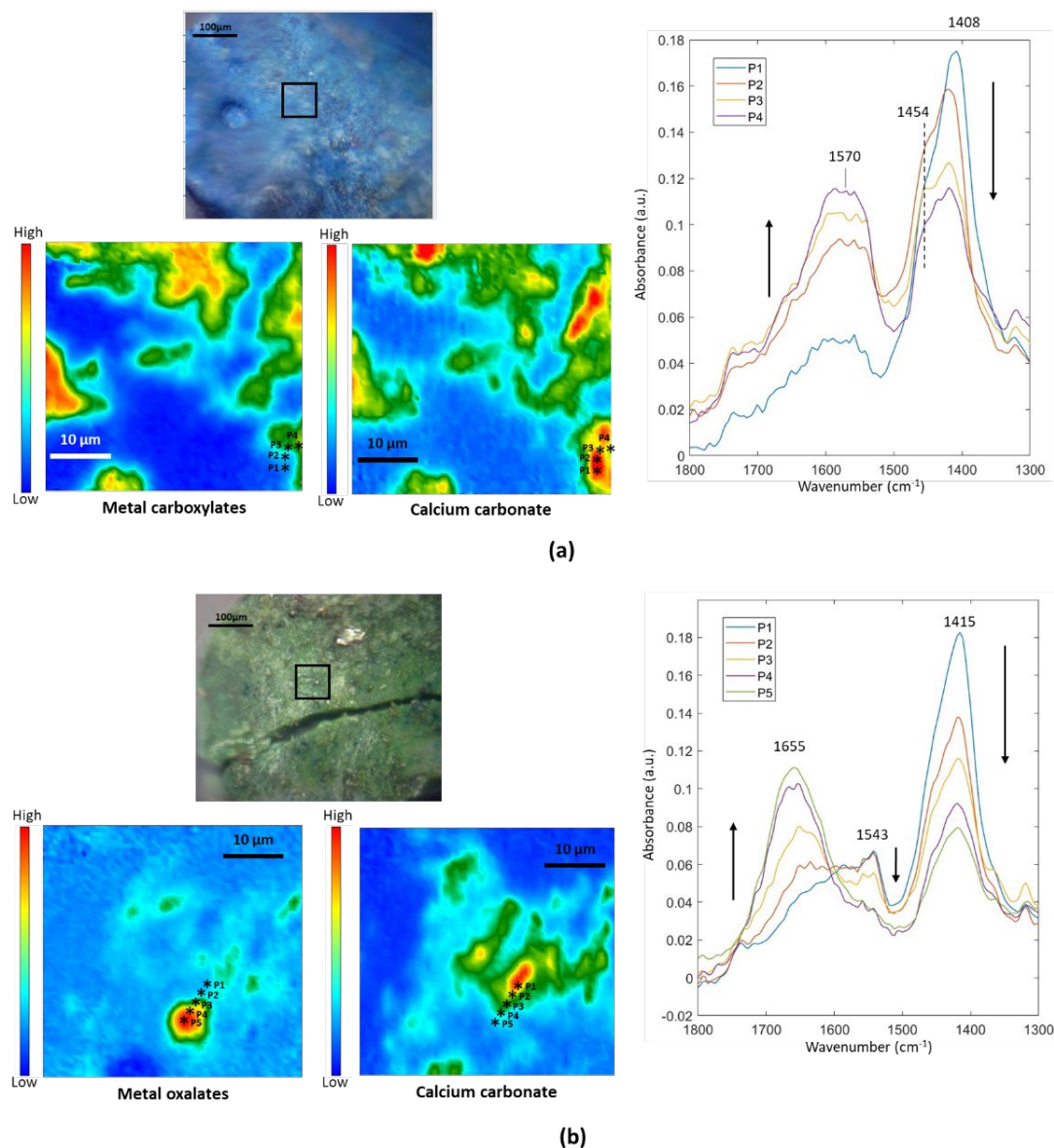


Figure 4.18 Micro ATR-FTIR spectroscopic imaging of the top external surface of two pigments samples from *Yerevan Zangu River*: (a) blue pigment and (b) green pigment. The images of the integrated absorbance of calcium carbonate (1415/1408 cm^{-1}), metal carboxylates (1570 cm^{-1}) and metal oxalates (1655 cm^{-1}) and the ATR-FTIR spectra extracted from pixels (P1 to P4 in Figure 4.18a and P1 to P5 in Figure 4.18b) clearly show that absorbance of the metal oxalates and metal carboxylates increases as absorbance of the calcium carbonate decreases.

4.1.4 Discussion

The results of ATR-FTIR spectroscopic imaging coupled with XRF made it possible to identify the chromatic palette used by Martiros Sarian. The pigments identified in Sarian's works during this research are comparable to the ones employed by his influential artists, Henri Matisse (Haddad, Pastorelli, et al., 2022; Mass, Sedlmair, et al., 2013; Pouyet et al., 2015) and Paul Gauguin (Christensen, 1993; Defeyt et al., 2018; Vermeulen et al., 2021), as well as other notable Impressionist and Post-Impressionist painters of the era (Januszczak, 1980; Pollack, 2020). As described in the results section, these pigments include ultramarine blue, cobalt blue, cobalt cerulean blue, viridian or chromium oxide, emerald green, cobalt green, celadonite green, cadmium yellow, chrome yellow, yellow ochre, red ochre, lead white, zinc white and calcium carbonate. Due to the high spatial resolution of ATR-FTIR spectroscopic imaging ($\sim 3\text{--}4\text{ }\mu\text{m}$), the mixture of pigments within a single colour can be successfully resolved, and each component can be identified. The green pigments like viridian and emerald green have been frequently mentioned in technical studies of Impressionist and Post-Impressionist artists, including Monet, Pissarro and Munch (Gutierrez & Burnstock, 2013; Roy, 2007; Singer et al., 2010; Vermeulen et al., 2022). However, it is worth noticing that in these five investigated paintings created by Sarian, no presence of Prussian blue was identified. Prussian blue ($\text{Fe}_7(\text{CN})_{18}$, or $\text{Fe}_4[\text{Fe}(\text{CN})_6]3\cdot n\text{H}_2\text{O}$), a vivid blue pigment that emerged during the early 18th century, has been recognised as the pioneering pigment among its modern counterparts (Berrie, 1997). The presence of Prussian blue has been identified in numerous Impressionist and Post-Impressionist paintings. Notably, Matisse and Gauguin demonstrated an affinity for Prussian blue (Christensen, 1993; Defeyt et al., 2018; Haddad, Pastorelli, et al., 2022; Matisse & Courthion, 2013). Despite being widely used as a blue pigment from the early 18th century to the late 20th century (Berrie, 1997), Prussian blue has not been found in the palettes of some painters, such as Paul Cézanne (Butler, 1984) and Georges Seurat (Fiedler, 1984). Further research would be of interest to examine additional paintings by Sarian to ascertain whether Prussian blue was absent from his

palette. Additionally, it is important to note that the XRF results (Table 4.1–4.4) demonstrate a significant presence of Pb in the pigments from *Caravan*. It appears that Sarian used both lead white and zinc white simultaneously in some paintings, but only *Caravan* showed a higher abundance of lead compared to zinc in this study. *Caravan* was painted in 1926. From 1926 to 1928, Matiro Sarian lived and worked in Paris, but most works from this period were destroyed in a fire aboard the boat on which he returned to the Soviet Union. Future work may also focus on investigation of paintings produced in this period to understand Sarian's choice of white.

Ultramarine blue was identified in *Morning in Stavrino* (1909) and *Arabian Dancer* (1913), while cobalt-containing blue pigments, such as cerulean blue and/or cobalt blue, were identified in *Caravan* (1926), *Yerevan Zangu River* (1931), and *Kirovakan* (1948). It remains uncertain whether Sarian utilised different blue pigments during different periods of his artistic career. However, our findings indicate that Sarian incorporated ultramarine blue in paintings created during earlier years (1909 and 1913), whereas he employed cobalt-containing blue pigments in paintings from later years (1926, 1931, and 1948). Furthermore, chromium-containing green pigments were used in the paintings from 1909, 1913, 1926, and 1931, albeit with slight variations in their combinations. In the paintings from 1909 and 1913, Viridian (hydrated Cr_2O_3) was mixed with ultramarine blue, while in the painting from 1926, it was mixed with lead white. The painting from 1931 featured a dehydrated form of chromium-containing pigment, likely Cr_2O_3 , which was mixed with cobalt green and celadonite. Regarding red pigments, variations were observed in the paintings dating from 1926, 1931, and 1948. It is worth noting that while ultramarine blue was identified using ATR-FTIR spectroscopic imaging, the XRF results did not quantify Na in the blue pigment and the green pigment from *Morning in Stavrino*, as can be seen in Table 4.1 and 4.2. This could be attributed to the fact that, although Na is among the lightest elements detectable using ED-XRF (Brouwer, 2010), its detection is sometimes hindered due to its very low energy fluorescence (<1 keV). The air between the sample and the detector may be too dense for the fluorescence to pass through. To better confirm the presence of Na, other techniques such as atomic absorption spectroscopy or Inductively

Coupled Plasma Optical Emission Spectroscopy (ICP-OES) can be conducted in future work.

Degradation products, such as metal oxalates and metal carboxylates, were successfully identified in the pigments of this paper. The detected metal carboxylates exhibited either a crystalline nature, characterised by a sharp $\nu_{as}(\text{COO}^-)$ band, or a non-crystalline nature, indicated by a broad $\nu_{as}(\text{COO}^-)$ band in the ATR-FTIR spectra. Zinc carboxylates described in this study displayed a single peak (Figure 4.8) or a doublet (Figure 4.10) in the ATR-FTIR spectra, which may be attributed to the different symmetry of the components (Helwig et al., 2014). As demonstrated in Section 4.1.3.5, the formation of metal carboxylates and metal oxalates may be attributed to the presence of CaCO_3 , as revealed by the ATR-FTIR spectroscopic imaging results displayed in Figure 4.18. Previous research has primarily focused on investigating calcium oxalate due to its high occurrence in cultural heritage objects, including oil paintings and stone artifacts (Bordignon et al., 2008). Although gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) could potentially serve as a source of Ca ions for the formation of calcium oxalate, we did not observe a decrease in gypsum absorbance at around 1110 cm^{-1} with increasing oxalate absorbance at 1655 cm^{-1} , as observed in the case of CaCO_3 (Figure 4.18b). Ca ions derived from CaCO_3 are more likely to form calcium oxalate, which is consistent with previous literature findings (Zoppi et al., 2010) that demonstrated CaCO_3 can react with even very low concentrations of oxalic acid to produce calcium oxalate.

To support these findings regarding the paint surfaces and to achieve a more comprehensive understanding of the utilised colour palette by Sarian, further investigation into the compositional analysis of the oil paintings is needed. This should encompass the identification of additional pigment samples extracted from Sarian's artworks spanning the 1950s, 1960s, and 1970s, as well as stratigraphic imaging through cross-sectional analysis. Non-invasive portable XRF is recommended for the museum to conduct in-situ semi-quantitative investigations of their paintings. Additionally, the application of additional scientific techniques like Raman spectroscopy and SEM-EDX is recommended to complement and strengthen the

outcomes presented in the present study.

4.1.5 Summary

This section has provided valuable insights into the pigments used by Martiros Sarian in five of his paintings. By employing micro ATR-FTIR spectroscopic imaging in conjunction with XRF, successful characterisation of pigments was achieved. Ultramarine blue was identified in earlier paintings, while cobalt-containing blue pigments, including cerulean blue and cobalt blue, were present in later works. Chromium-containing green pigments, including viridian and chromium oxide, were utilised with slight variations in combination. The formation of degradation products in the pigments, such as metal carboxylates and metal oxalates, were also explored in this section. Calcium carbonate was found to play a significant role in the formation of these degradation products. Zinc and lead carboxylates were identified as crystalline structure carboxylates by the presence of the sharp band of $\nu_{\text{as}}(\text{COO}^-)$. Other amorphous metal carboxylates exhibited broad $\nu_{\text{as}}(\text{COO}^-)$ bands in the ATR-FTIR spectra.

4.2 ATR-FTIR spectroscopic imaging of white crusts in cross sections from oil cartoons by Edward Poynter in the Heritage Collections at UK Parliament

This section is adapted from: Liu, G. L., Guerreiro, E., Babington, C., & Kazarian, S. G. ATR-FTIR spectroscopic imaging of white crusts in cross sections from oil cartoons by Edward Poynter in the Heritage Collections at UK Parliament. *Journal of Cultural Heritage*, 62, 251-267. (Liu et al., 2023)

4.2.1 Background

In 1847, the Fine Arts Commission led by Prince Albert planned four monumental mosaics in the central lobby hall at the heart of the Palace of Westminster (Cannadine et al., 2000; Port, 1976). These four monumental mosaics depict the patron saints of the four nations of United Kingdom (UK): St George in England, St David in Wales, St Patrick in Northern Ireland, and St Andrew in Scotland. It was only in the late 1860s that work on the programme began and it would be almost six decades before it was completed. The St George and St David mosaics were installed in 1870 and 1899 respectively, based on designs by Sir Edward Poynter (1836–1919). The other two mosaics of St Andrew and St Patrick were designed by Robert Anning Bell and unveiled in 1923 and 1924.

The focus of this study includes eleven to-scale painted canvas cartoons (a set of five and a set of six) created by Sir Edward Poynter as designs for the mosaics. The six cartoons were made for St David between 1897 and 1899, which now exhibit highly disfiguring efflorescent white crusts (Figure 6.2 in Appendices), while the other five cartoons were made for St George in 1869 and do not have the issue of white crusts. The cartoon designs were sent to Italy to the workshop of Salviati and Company, which

later became the Venice and Murano Glass and Mosaic Company, who made the mosaics. To directly transfer the scale images from the cartoon designs to the mosaics, rectangles of translucent paper were tacked to the cartoons with animal glue, so the images could then be traced. There are remnants of this design transfer process visible on both sets. These cartoons were returned to the UK and acquired into the Ministry of Works: St George in 1873 and St David in 1901. It should be noted that these cartoons were created as designs for the mosaics and were not originally intended for display. Due to the way these cartoons had been directly used to lay out the mosaics and the way they were transported, they were in a very poor condition, with fragile damaged canvas, unstable paint layers, and significant dirt build up. These cartoons were safely stored at the Victoria and Albert (V&A) Museum until their recent treatment mentioned in this study. The two sets of cartoons would likely have experienced a similar environment following their arrival at the V&A Museum, but earlier differences in the conditions during transportation and transfer may have affected the two sets. No technical studies or formal conservation of these cartoons had been previously carried out. Ownership was formally transferred to the Parliamentary Art Collection in 2019. These cartoons have an inherent value for research and have potential for display. As a result, scientific investigation is of importance for identifying and evaluating the current condition of the cartoons. Appropriate and prompt conservation treatments can be developed based on the obtained scientific information.

A common deterioration product in oil paintings are metal carboxylates, also known as metal soaps. These metal carboxylates are caused by interactions between metal ions which are from pigments, fillers and extenders, and fatty acids which are from binding media (Noble, 2019). A variety of metal carboxylates with different metal ions such as zinc (Hermans & Helwig, 2020; Hermans et al., 2015), copper (Mazzeo et al., 2008; Spring et al., 2008), lead (Henderson et al., 2019; Spring et al., 2008), cadmium (Christiansen, Sørensen, et al., 2017) and chromium (Christiansen, Sørensen, et al., 2017) have been identified over a range of multi-layered oil painted artworks. FTIR spectroscopic imaging has been used to characterise different metal carboxylates

based on the band shifts in the spectra of COO^- bands associated with different metal ions (Robinet & Corbeil-a, 2003). Due to the use of lead white in ground and paint layers, lead carboxylates are likely the most commonly encountered metal carboxylates in oil paintings, which result in two main degradation problems:

- 1) Lead carboxylates can form aggregates that may protrude through the paint layer (Sawicka et al., 2014).
- 2) Lead elements from lead carboxylates can migrate to the surface of the paint layer without aggregation, which then interact with air pollution to crystallise or precipitate as lead sulfates and carbonates, causing white crusts on the surface (Klaassen et al., 2019; Van Loon et al., 2019).

The aggregation and crusts resulting from the lead affect the physical properties and aesthetic values of the paintings, leading to irreversible damage such as losses and potentially cracks (Izzo et al., 2021). Therefore, identification and characterisation of metal carboxylates and white crusts are crucial to enable conservators to effectively conserve these oil paintings. Extensive research has characterised white crusts and has suggested their correlation to metal carboxylates explained by possible degradation processes (Klaassen et al., 2019; Rosi, Cartechini, Monico, et al., 2019). However, these explanations are not clear in the absence of distribution information of white crusts and metal carboxylates in paint cross sections. Micro ATR-FTIR spectroscopic imaging was demonstrated for the first time to identify metal carboxylates and obtain their distribution information in chemical images of two paint cross-sections from the National Gallery, London (Spring et al., 2008). This micro ATR-FTIR spectroscopic imaging technique has been utilised extensively to study delamination resulting from zinc carboxylates (Hageraats et al., 2019; Raven et al., 2019), and surface white crusts containing oxalates (Klaassen et al., 2019). Lead sulfates as another regularly identified white crusts on the surface of oil paintings have also been studied (Loon et al., 2011; Wingel et al., 2019), but little attention was paid to mechanisms for the diffusion of lead from the ground to the surface of paintings.

4.2.2 Experimental setting up

This section aims to investigate the white crusts found on the cartoons painted by Edward Poynter from the Parliamentary Art Collection at UK Parliament. Micro ATR-FTIR spectroscopic imaging with a high spatial resolution ($\sim 3\text{--}4\ \mu\text{m}$) was utilised to investigate the complex stratigraphy of the Edward Poynter cartoons for the first time regarding the characterisation of white crusts, metal carboxylates, and materials such as pigments and fillers used by the artist. Information about the distribution of substances provided by ATR-FTIR images allowed us to reveal the heterogeneity of white crusts and better understand migration processes of materials from the ground to the surface of paintings.

Paint samples were taken from the following 5 locations of the 3 cartoon paintings: St George, St David and Harmony, as summarised in Table 4.5 and Figure 4.19. These samples were mounted as paint cross-sections in a polyester resin (Clear Casting AM, Tiranti) with liquid hardener Methyl ethyl Ketone Peroxide 33% in Dimethyl Phthalate (Butanox M50, Tiranti). The paint cross-sections were polished with micromesh cloths (from 6000 to 12000 mesh) before being examined using a combination of LM, SEM-EDX and micro ATR-FTIR spectroscopic imaging.

A Meiji LM with 200–400 magnification was used to examine the paint cross-sections with halogen and ultraviolet light. SEM imaging and EDX analysis were performed using a Zeiss SigmaTM VP SEM fitted with a field emission electron source, with TEAMTM EDAX Enhanced Version: V4.4. quantitative software. The fragment specimens were mounted in aluminium pin stubs, (12.5 mm dia), using conductive carbon aluminium adhesive tabs. All SEM imaging and X-ray analysis was performed at variable pressure mode (~ 13.5 Pascals) in order to avoid any charging effect using backscattered electron mode. Samples were subjected to analysis at between 30 kV, with the working distance between 5–6 mm. Micro ATR-FTIR spectra were collected with $8\ \text{cm}^{-1}$ spectral resolution in the range $3,900\text{--}750\ \text{cm}^{-1}$ using 64 scans.

Table 4.5 List of samples analysed

Sample No.	Sample area	Painting	Surface condition
470	St George's ankle	WOA 7680 St George 2951×1292mm c. 1869	No white crust
472	St David's cloak	WOA 7674 St David 2981×1323mm c. 1897	A layer of white crust
479	Harmony's hair	WOA 7673 Harmony 2982×1088mm c. 1897	A layer of white crust
482 and 481	Harmony's cloak		A localised small dot of white crust
483	Harmony's harp		A darkened area and a white crust



Figure 4.19 Three cartoons: from left to right, Harmony (WOA 7673), St David (WOA 7674) and St George (WOA 7680) before conservation treatment. The numbers are related to the locations where cross-sectional samples were taken.

4.2.3 Characterisation of original materials and degradation products in Edward Poynter cartoons

4.2.3.1 ATR-FTIR spectroscopic imaging of detected compounds

The ATR-FTIR spectroscopic images of components in the cross-sections of the oil paintings were acquired by plotting the distribution of integrated spectral bands of interest as a function of all pixels. The components that can be detected in the cross-sections vary depending on what degradation affecting the oil paintings and what materials used in the artist's palette. Throughout the four case studies in this research, all the cross-sectional samples contain calcium carbonate, lead white, lead carboxylates, aliphatic compounds, fatty acids and resin that was used to mount the samples. To avoid repetition, the spectra of these substances are summarised in Figure 4.20a, rather than discussed in the different sections of each case study. Figure 4.20a also illustrates how the wavenumber ranges are used for integrations of spectral bands that were used to generate the chemical images in this section. These representative spectra to explain the integrated spectral bands were extracted from single pixels of the FPA detector corresponding to the locations in chemical images of different samples, as illustrated in Figure 4.20b. Firstly, the ground layers of the 4 case studies comprise lead white and calcium carbonate. Lead white is a mixture of large fraction of basic lead carbonate (hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and a small amount of lead carbonate (cerussite, PbCO_3) (Welcomme et al., 2007). The spectrum of $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ has a strong absorbance band at 1392 cm^{-1} of $\nu_{\text{as}}(\text{CO}_3^{2-})$ and relatively weak absorbance bands at 1045 cm^{-1} and 3540 cm^{-1} of $\nu_{\text{sy}}(\text{CO}_3^{2-})$ and $\nu(\text{OH})$, respectively, while the spectrum of PbCO_3 shows the absorbance band of $\nu_{\text{as}}(\text{CO}_3^{2-})$ at lower wavenumbers at 1365 cm^{-1} and absence of $\nu_{\text{sy}}(\text{CO}_3^{2-})$ and $\nu(\text{OH})$ (Possenti et al., 2021a). Because the absorbance band of $\nu_{\text{as}}(\text{CO}_3^{2-})$ at 1392 cm^{-1} is overlapped with $\nu_{\text{as}}(\text{CO}_3^{2-})$ of calcium carbonate, spectroscopic images of lead white were obtained by plotting the integrated absorbance of the band centred at 1045 cm^{-1} .

Secondly, the spectrum of the calcium carbonate in the ground layers shows two absorbance bands at 1400 cm^{-1} of $\nu_{\text{as}}(\text{CO}_3^{2-})$ and at 872 cm^{-1} of $\delta_{\text{out-of-plane}}(\text{CO}_3^{2-})$. The band at 872 cm^{-1} is characteristic for calcite (Badou et al., 2022; Myszkka et al., 2019) and was selected to produce chemical images of calcium carbonate (calcite) by plotting its integrated absorbance. Thirdly, metal carboxylates have strong spectral bands of $\nu_{\text{as}}(\text{COO}^-)$ between $1500\text{--}1600\text{ cm}^{-1}$. The position of these bands for metal carboxylates depends on the type of metal ions. In the case of lead carboxylates in this study, the position of the spectral band is at around $1508\text{--}1512\text{ cm}^{-1}$, which is in agreement with the spectra band of pure synthesised lead carboxylates (J. Hermans et al., 2014). However, the other spectral band of $\nu_{\text{as}}(\text{COO}^-)$ attributed to lead carboxylates which can be found at 1540 cm^{-1} in the literature (Izzo et al., 2021; Mazzeo et al., 2008) is not apparently shown in this study. The absence of the absorbance at 1540 cm^{-1} may be due to the different coordination structures of lead carboxylates (Hermans et al., 2021). In addition, it is not feasible to specify types of lead carboxylates (palmitate, stearate, oleate and azelate) from the ATR-FTIR spectra. It is because these types of lead carboxylates may co-exist in the samples, and because the other characteristic bands such as the progression bands caused by

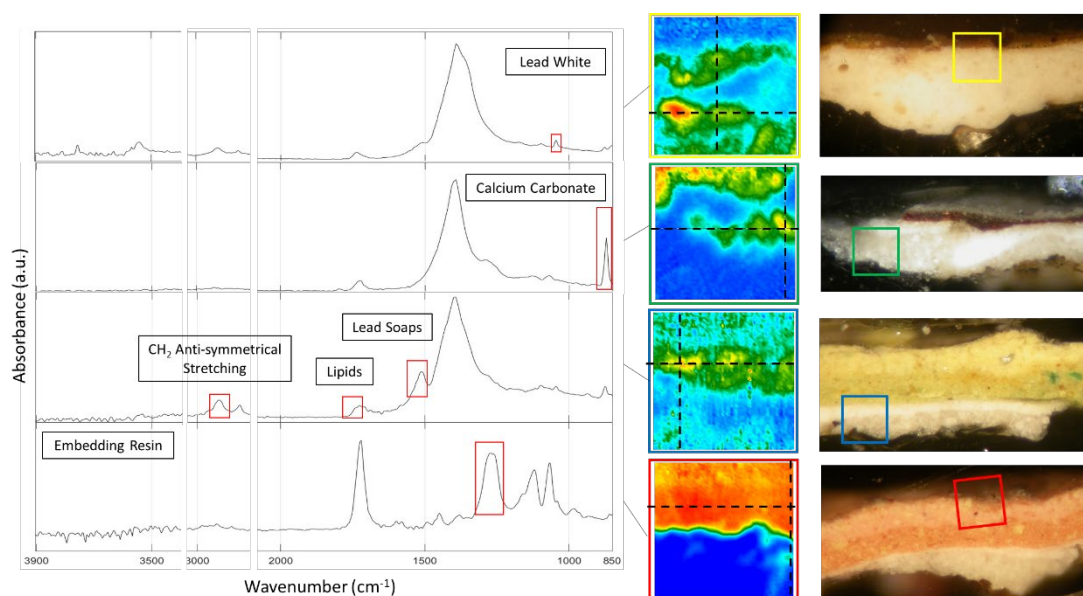


Figure 4.20 Micro ATR-FTIR spectra of substances detected in the chemical images. The red rectangles indicate the integrated bands used to generate chemical images for lead white, calcium carbonate, lead carboxylates, lipidic binders, aliphatic compounds and embedding resin.

wagging and twisting of CH₂ long chains (Catalano et al., 2019) are in the wavenumber region between 1150 and 1350 cm⁻¹ that overlaps with the spectral bands of other components detected. In some spectra of the compounds detected, two spectral bands at around 2924 cm⁻¹ (ν_{as}(CH₂)) and 2853 cm⁻¹ (ν_{sy}(CH₂)) can be seen. These two bands are attributed to CH₂ aliphatic chains, which are functional groups in aliphatic compounds that can be assigned to many organic substances such as metal carboxylates and lipids (e.g. lipidic binders). To generate exclusive spectroscopic images of lipidic binders, the absorbance band at 1730 cm⁻¹ of ν(C=O) was selected. Although the ν(C=O) of lipidic binders is overlapped with the ν(C=O) of the embedding resin, the band of lipidic binders is usually at higher wavenumbers (5–10 cm⁻¹ higher). As a result, the range of higher wavenumbers between 1720–1780 cm⁻¹ was chosen for integrating the absorbance band of ν(C=O) of lipidic binders. Finally, spectroscopic images of the embedding resin were also produced to locate the boundaries of the cross sections of the samples. The spectrum of the embedding resin has four strong characteristic bands of ester functionality (Nishikida & Coates, 2003; Socrates, 2004): 1725 cm⁻¹ ν(C=O), 1270 cm⁻¹ ν(C–O) and a doublet at 1126 cm⁻¹ and 1099 cm⁻¹ ν(C–O). Because the band at 1725 cm⁻¹ of ν(C=O) overlaps with that of lipids, the spectroscopic images of resin were obtained by spatially plotting the integrated absorbance of the bands at 1270 cm⁻¹. The spectroscopic images of the embedding resin of the 5 samples are provided in Figure 4.21, showing that there is not much

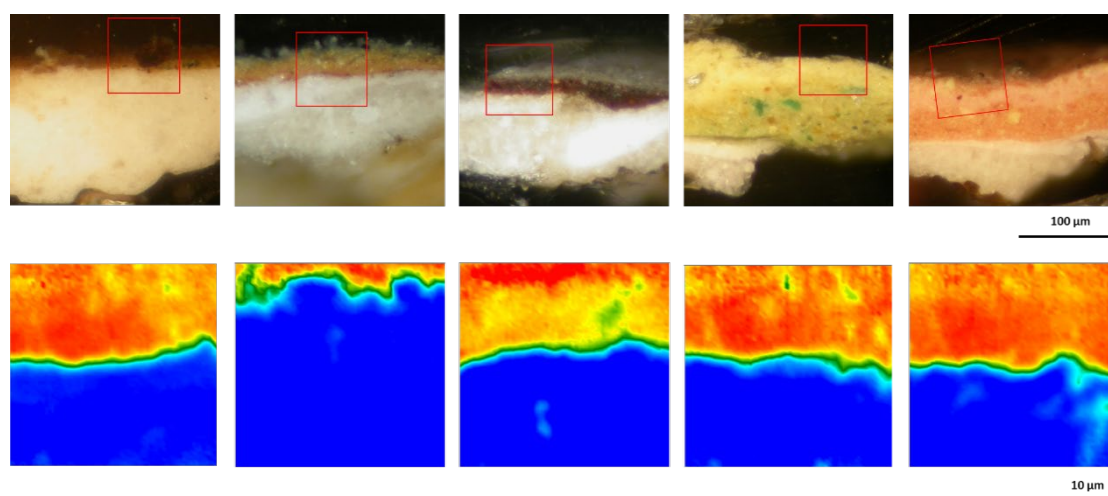


Figure 4.21 ATR-FTIR spectroscopic images of resin of the 5 samples (from left to right: 470, 472, 479, 482, 483) showing the boundaries between resin and cross-sectional samples

ingress of the embedding resin into the cross sections and thus its potential adverse influence on the results would be minor.

4.2.3.2 Case study: paint cross section of St David's cloak – 472

A cross-section photomicrograph from an area of St David's cloak shows the clearly defined white crust, brown paint layer and ground layer (Figure 4.22a). The main constituents of each layer are summarised in Table 4.6. For all ATR-FTIR spectroscopic images in Figure 4.22, the location of the white crust was highlighted using with a dotted white line, and the boundary between the paint and ground layers was indicated using a dotted black line. In the white crust, oxalates (Figure 4.22b and c) were detected by assigning the spectral bands at 1628 cm^{-1} ($\nu_{\text{as}}(\text{C=O})$), 1304 cm^{-1} ($\nu_{\text{as}}(\text{C-O})$) and 1396 cm^{-1} ($\nu_{\text{sy}}(\text{C-O})$ and $\nu(\text{C-C})$ combination mode), as shown in the spectrum of pixel (P1) in Figure 4.23.

Table 4.6 List of main components in each layer of sample 472

Layers	Main components
White crust	Deterioration Products: Lead sulfate, metal oxalates
Paint layer	Iron-based earth Deterioration Products: Unspecified metal carboxylates
Ground layer	Lead white, calcium carbonate, barium sulfate Deterioration Products: Lead carboxylates

These oxalates in the white crust which are circled with a dotted white line may be either Pb or Ca based. This was then confirmed by SEM-EDX analysis (Figure 4.24) as Pb and Ca were detected in the white crust. Other metal elements such as Mg, Al and Fe were also detected in the white crust with lower atomic percentages compared to Pb and Ca. Calcium oxalate has previously been identified as a deterioration product on wall paintings (Egel & Simon, 2013) and polychromed mineral sculptures (Castro et al., 2008). The formation of calcium oxalate is associated with the attack of oxalic acid on pigments or fillers which contain calcium carbonate. The source of oxalic acid can be various (Van Loon et al., 2019) and is still being debated (Klaassen et al., 2019; Spring & Higgitt, 2006) and depends on the environment, including the concentration

of atmosphere aerosols (Kawamura & Bikkina, 2016; Ray & McDow, 2005) and the materials that artists used, such as oil binding media or protective coating agents (Arbizzani et al., 2004; Poli et al., 2019). Apart from the materials applied to the painting, other sources of oxalic acid can be the atmosphere itself, where high level of dicarboxylic acids have been detected in atmospheric aerosols (Kawamura & Bikkina, 2016; Ray & McDow, 2005). In addition to the oxalates, sulfates were discovered in the white crust by assigning the spectral band at 1065 cm^{-1} . The detection of metal oxalates together with sulfates as deterioration products has been reported in art works (Bordignon et al., 2008; Klaassen et al., 2019), including polychrome sculpted stone (Casadio et al., 2005) and wall paintings (Pérez-Alonso et al., 2004).

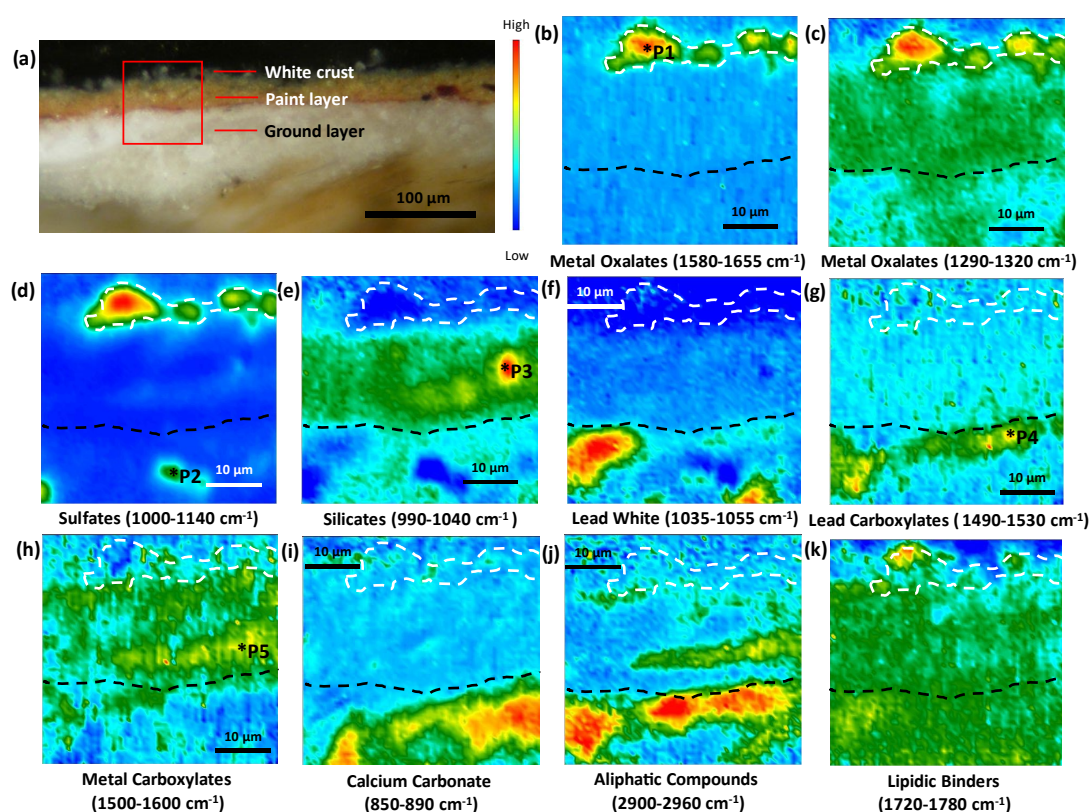


Figure 4.22 St David's cloak sample 472: (a) Photomicrograph of the polished cross section. A red square indicates the measuring area (ca. $70\text{ }\mu\text{m}\times 70\text{ }\mu\text{m}$) by micro ATR-FTIR spectroscopic imaging. Micro ATR-FTIR images showing the distribution of (b) oxalates ($1580\text{--}1655\text{ cm}^{-1}$); (c) oxalates ($1290\text{--}1320\text{ cm}^{-1}$); (d) sulfates ($1000\text{--}1140\text{ cm}^{-1}$); (e) silicates mixed with iron-based earth ($950\text{--}1040\text{ cm}^{-1}$); (f) lead white ($1035\text{--}1055\text{ cm}^{-1}$); (g) lead carboxylates ($1490\text{--}1530\text{ cm}^{-1}$); (h) unspecified metal carboxylates ($1500\text{--}1600\text{ cm}^{-1}$); (i) calcium carbonate ($850\text{--}890\text{ cm}^{-1}$); (j) aliphatic compounds ($2900\text{--}2960\text{ cm}^{-1}$). (k) lipidic binders ($1720\text{--}1780\text{ cm}^{-1}$).

In the paint layer, the spectrum taken from the pixel labelled P3 from the ATR-FTIR image (Figure 4.22e) suggests the presence of iron-based earth. An intensive absorbance at around 1030 cm^{-1} (Getty Conservation Institute, 2022) is attributed to silicates (most likely kaolinite) in mixture with the iron-based minerals (Figure 4.23). This distribution of silicates mixed with iron-based earth on the ATR-FTIR image matches well with the SEM-EDX map where iron (Fe) is revealed in the paint layer (Figure 4.24). It is worth noticing that in the white crust, the ATR-FTIR image (Figure 4.22e) reveals no iron-based earth. This result may imply that the degradation products (oxalates and sulfates) do not penetrate the paint layers but accumulates on top of it.

The ground layer contains lead white (Figure 4.22f), lead carboxylates (Figure 4.22g) and calcium carbonate (Figure 4.22i). Unassigned metal carboxylates with absorption bands in the region of $1500\text{--}1600\text{ cm}^{-1}$ were mostly found in the paint layer (Figure 4.22h). Compared to the spectrum of lead carboxylates, a broader absorbance of $\nu_{\text{as}}(\text{COO}^-)$ appears in the spectrum for this type of unassigned metal carboxylates.

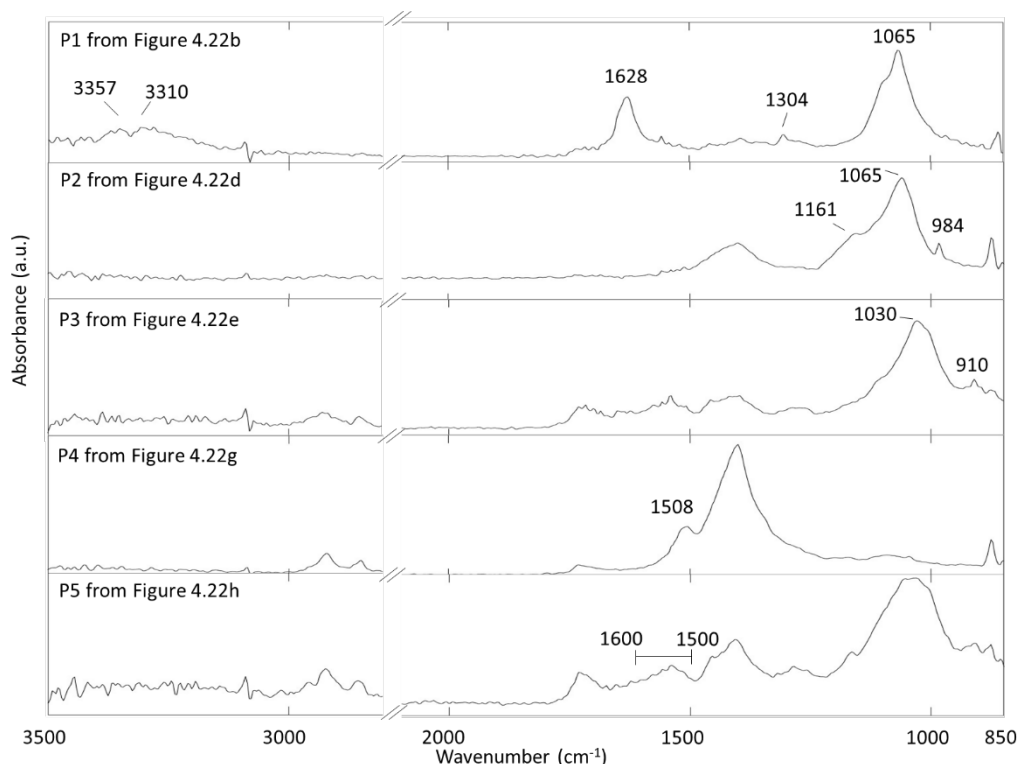


Figure 4.23 ATR-FTIR spectra extracted from pixels (P1–P5) in Figure 4.22b, d, e, g and h respectively. The wide range of $\nu_{\text{as}}(\text{COO}^-)$ band between $1500\text{--}1600\text{ cm}^{-1}$ is indicated by a bar in the spectrum of P5. The white crust is circled with a dotted white line and the paint and ground layers are divided with a dotted black line.

Lead and calcium may have been migrating from the ground layer to the surface of the painting via this type of unassigned metal carboxylates. Some pixels such as P2 (Figure 4.22d) in the ground layer shows spectrum of barium sulfate (BaSO_4) which has three spectral bands at 984 cm^{-1} , 1065 cm^{-1} , 1161 cm^{-1} ($\nu(\text{SO}_4^{2-})$) (Figure 4.23). This type of the sulfate (P2) acts as a paint extender (BaSO_4) in the ground layer and so should be differentiated from the sulfate (P1) which is a degradation product (PbSO_4) in the white crust.

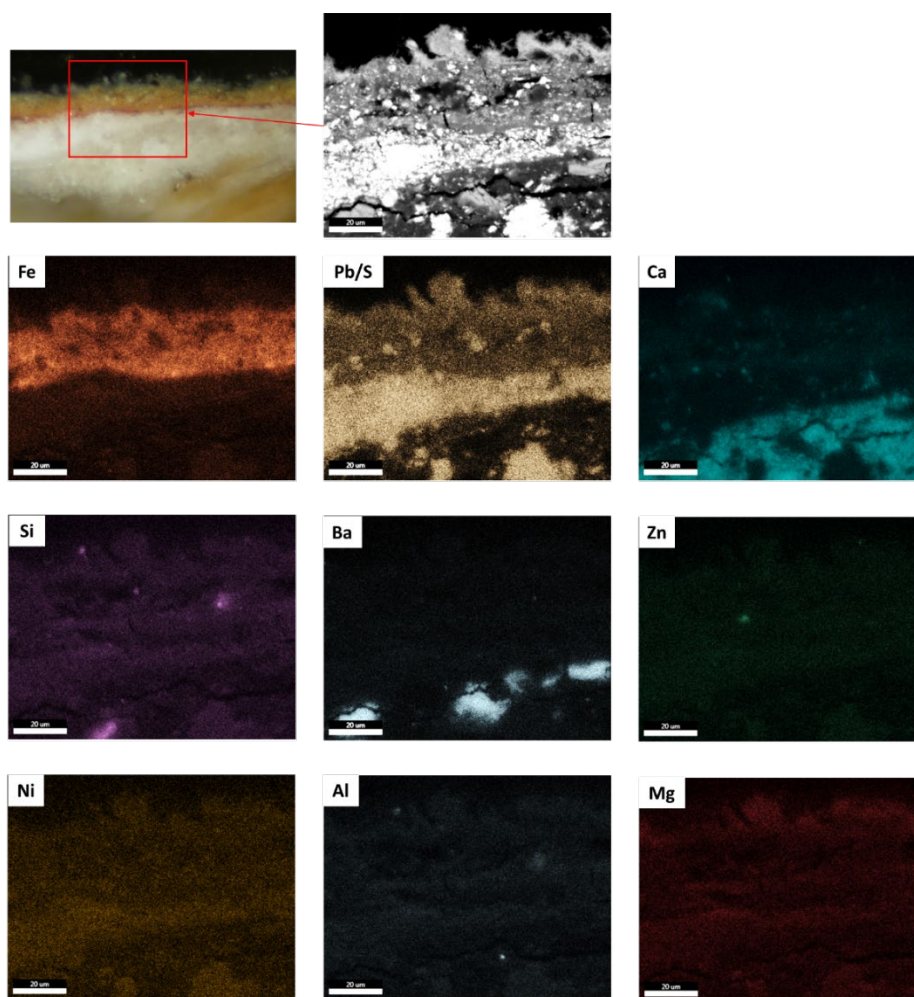


Figure 4.24 St David's cloak sample 472: EDX single element distribution maps

4.2.3.3 Case study: paint cross section of Harmony's hair – 479

Figure 4.25a displays a cross-section from an area of Harmony's hair. In order from the top, there are a white crust, a brown paint layer and a ground layer. The main constituents of each layer are summarised in Table 4.7. In the white crust, sulfates (P1,

Figure 4.25b) were detected. The sulfates in the white crust circled by a dotted white line are deterioration products which exhibit spectral bands at 964 cm^{-1} , 1041 cm^{-1} and 1161 cm^{-1} ($\nu(\text{SO}_4^{2-})$), as shown in Figure 4.26. These three spectral bands could be assigned to lead sulfate as the SEM-EDX map shows the distribution of Pb element in the area (Figure 4.27). The lead sulfate in the white crust may be due to migration of lead ions that precipitated and crystallised on the surface of the paint layer to form lead sulfate (Loon, 2008) by reacting with atmospheric sulfur, such as, sulfur dioxide (SO_2) (Osmond, 2014). In addition to lead sulfate, calcium carbonate (P3, Figure 4.25d) was also found in the white crust. The spectrum of P3 shows a spectral band located at 872 cm^{-1} (Figure 4.26), which is characteristic for calcium carbonate and cannot be found in the spectrum of lead carbonate. SEM-EDX map also shows identification of calcium and confirms the absence of lead in this area (Figure 4.27). As a result, it is possible to exclude the presence of lead carbonate and determine calcium carbonate in P3 in the white crust. These findings, confirming that the white crust of Harmony's hair is mainly lead sulfate with smaller amounts of calcium carbonate present.

Table 4.7 List of main components in each layer of sample 479

Layers	Main components
White crust	Iron-based earth Deterioration Products: Lead sulfate
Paint layer	Iron-based earth Deterioration Products: Unspecified metal carboxylates
Ground layer	Lead white, calcium carbonate, barium sulfate Deterioration Products: Lead carboxylates

Sulfates can be detected in the white crusts and the ground layers of samples 472 and 479. The position of the $\nu_1(\text{SO}_4^{2-})$ band of sulfates can be used as a reference to study whether the detected substances are degradation products (i.e. lead sulfate, PbSO_4) or original painting materials (barium sulfate, BaSO_4). These two types of sulfates have absorptions of $\nu(\text{SO}_4^{2-})$ in the spectra that are slightly different. Between $950\text{--}1200\text{ cm}^{-1}$, two modes of $\nu(\text{SO}_4^{2-})$ can be observed, the anti-symmetric stretch (ν_3) and symmetric stretch (ν_1) (Lane, 2007). Both of PbSO_4 and BaSO_4 have spectral bands of $\nu_3(\text{SO}_4^{2-})$ at around 1068 cm^{-1} . However, $\nu_1(\text{SO}_4^{2-})$ of PbSO_4 is centred at

964 cm^{-1} , while $\nu_1(\text{SO}_4^{2-})$ of BaSO_4 has a peak at 984 cm^{-1} , as indicated in Figure 4.28. It is conceivable from the ATR-FTIR spectra that the sulfates in the white crusts are PbSO_4 , whereas the sulfates in the ground layers are BaSO_4 that was used as an extender.

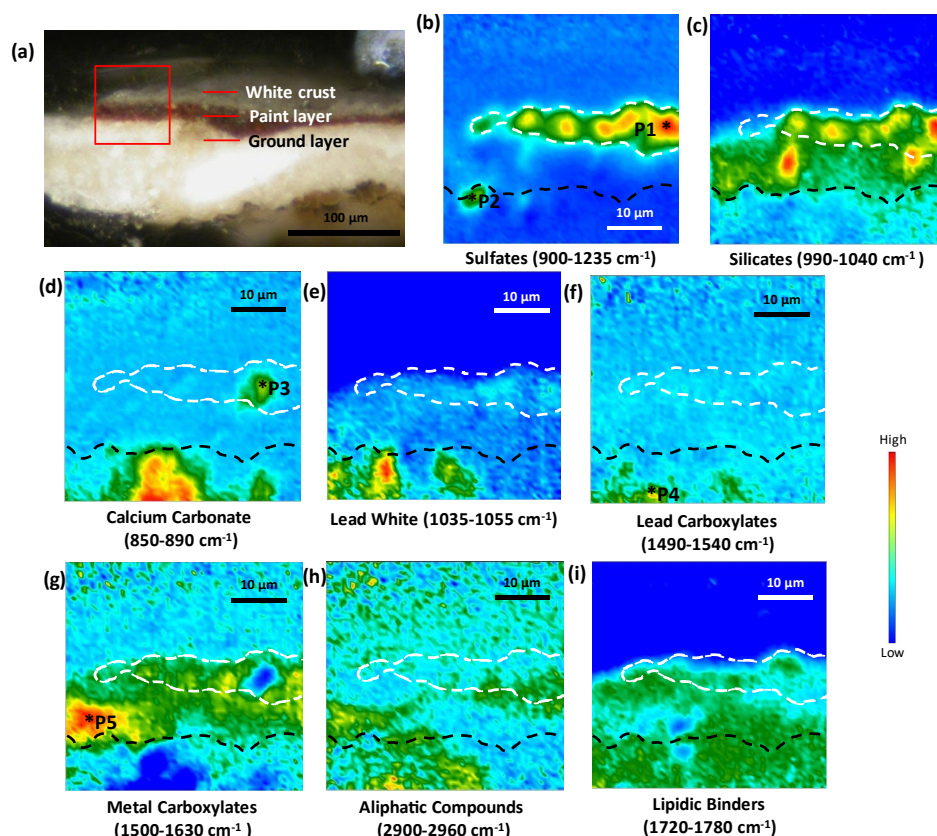


Figure 4.25 Harmony's hair sample 479: (a) Photomicrograph of the polished cross section. A red square indicates the measuring area (ca. 70 $\mu\text{m} \times 70 \mu\text{m}$) by micro ATR-FTIR spectroscopic imaging. Micro ATR-FTIR images showing the distribution of (b) sulfates (900–1235 cm^{-1}); (c) silicates mixed with iron-based earth (990–1040 cm^{-1}); (d) calcium carbonate (850–890 cm^{-1}); (e) lead white (1035–1055 cm^{-1}); (f) lead carboxylates (1490–1560 cm^{-1}); (g) unspecified metal carboxylates (1500–1630 cm^{-1}); (h) aliphatic compounds (2900–2960 cm^{-1}); (i) lipidic binders (2900–2960 cm^{-1}).

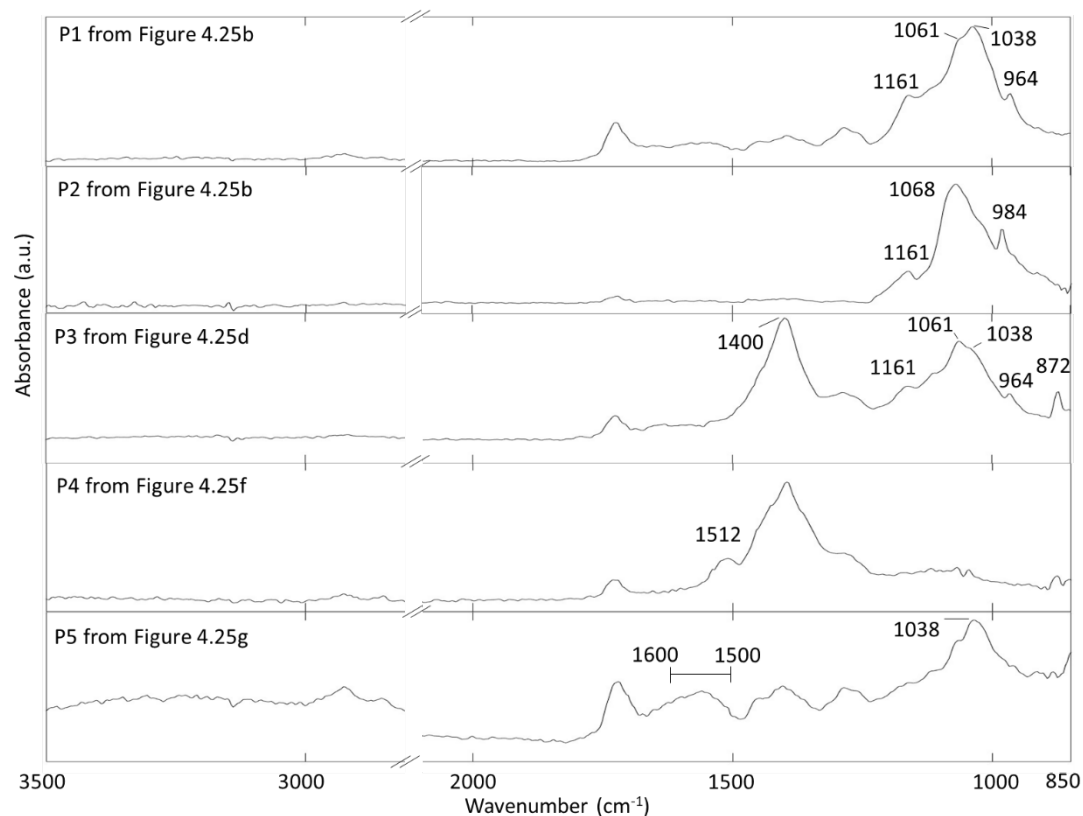


Figure 4.26 ATR-FTIR spectra extracted from pixels (P1–P5) in Figure 4.25 The white crust is circled by a dotted white line and the paint and ground layers are divided by a black dotted line.

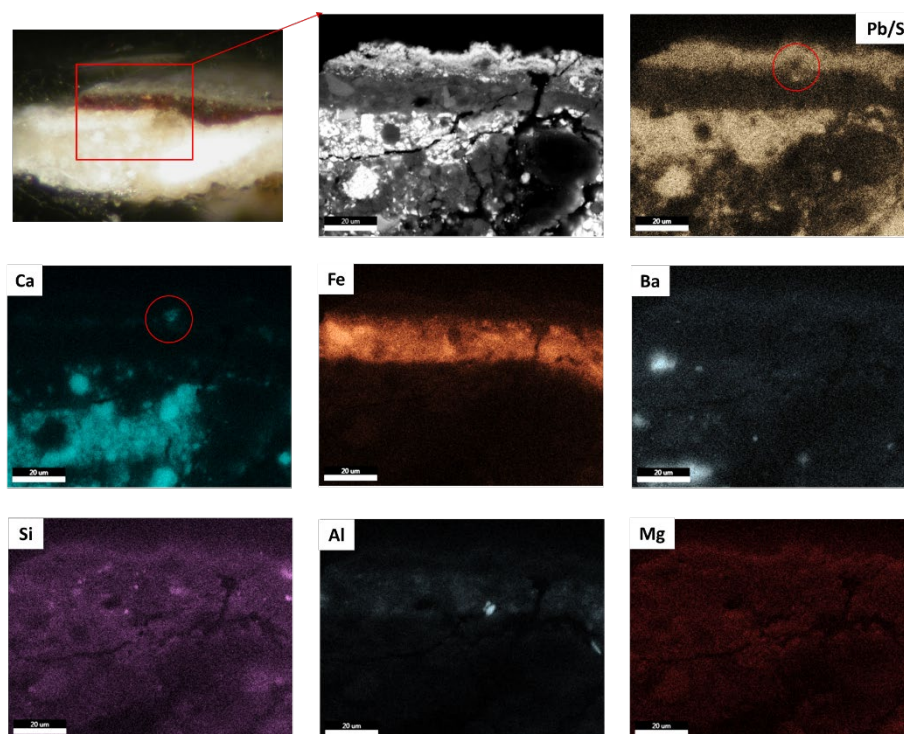


Figure 4.27 EDX single element distribution maps

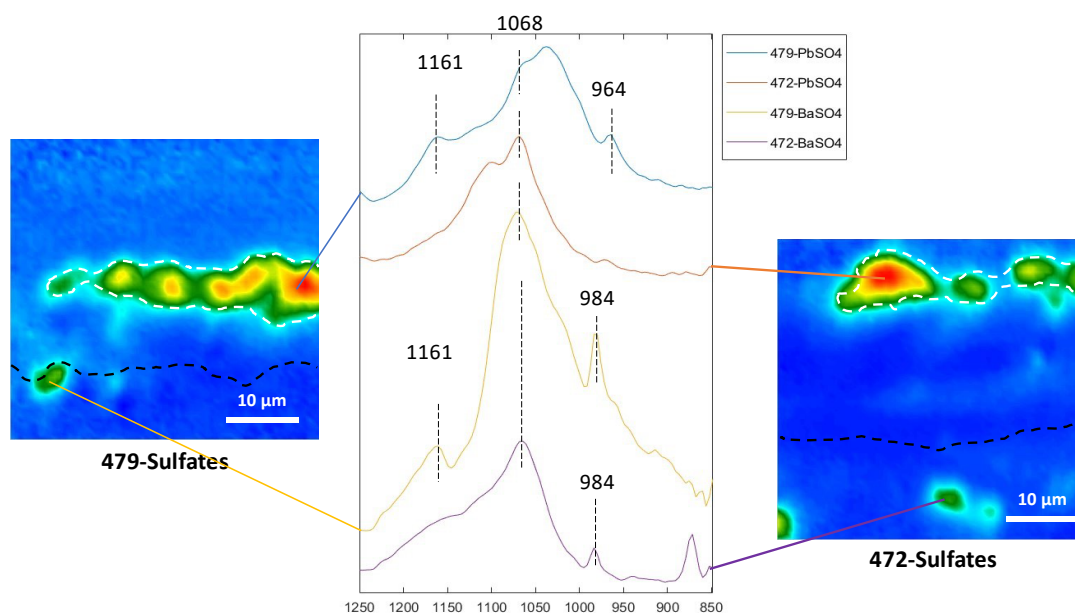


Figure 4.28 Comparison of the ATR-FTIR spectra of PbSO_4 and BaSO_4 found in sample 472 and 479.

The integrated absorbance of the spectral range between 990 and 1040 cm^{-1} represents the distribution of silicates mixed with iron-based earth, as shown in Figure 4.25c. The silicates mixed with iron-based earth can be detected in the paint layer as well as the white crust. This observation is different from the results of sample 472 where silicates mixed with iron-based earth was not detected in the white crust. The distribution of silicates mixed with iron-based earth of sample 479 may imply that the deterioration products (lead sulfate and calcium carbonate) have started to form within the paint layer, resulting in a thicker more developed white crust compared to the other areas as shown in Figure 4.22. It is also possible to hypothesise that the white crust of sample 479 has been migrating into the paint layer from the surface, while the white crust of sample 472 has accumulating on the surface of the paint layer. However, SEM-EDX results (Figure 4.27) show lower concentration of Fe-rich elements in the white crust compared to the paint layer. Future study should investigate in which part did the conversion of lead from metal carboxylates to lead sulfates in white crusts occur. It would also be of interest to study the growth rate of white crusts.

Lead carboxylates (P4, Figure 4.25f) were mostly found in the ground layer, while unspecified metal carboxylates with broad absorbance of $\nu_{\text{as}}(\text{COO}^-)$ were found in the paint layer (P5, Figure 4.25g). As mentioned in Section 4.2.3.2, the migration of lead

ions from the ground layer may be attributed to the presence of these unspecified metal carboxylates with a broad $\nu_{\text{as}}(\text{COO}^-)$ band. A dotted black line was used to mark the edge of the paint layer and the ground layer. Calcium carbonate and lead white were mostly detected in the ground layer as shown in Figure 4.25d and e. The ground layer can be divided into upper and lower ground layers with no significant chemical compositional difference between the two layers except the presence of proteins found in the lower ground layer, as shown in Figure 4.29.

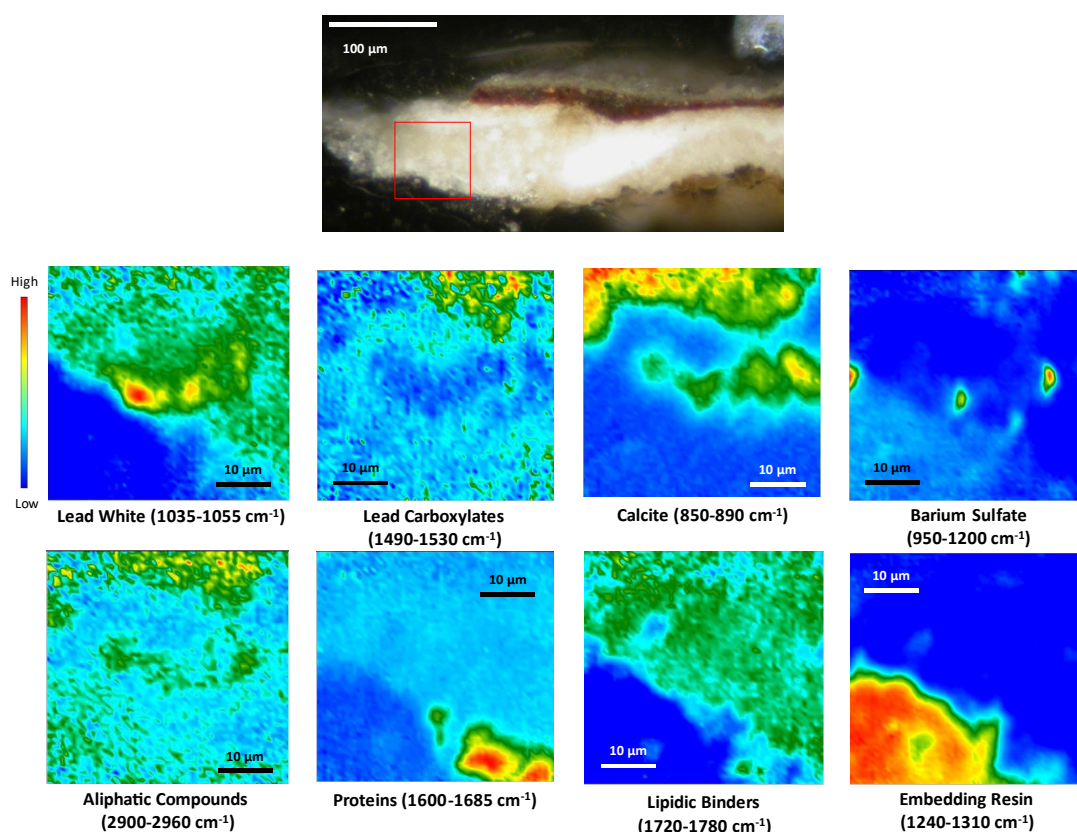


Figure 4.29 ATR-FTIR chemical images of the ground layer of sample

4.2.3.4 Case study: paint cross section of Harmony's cloak – 482 and 481

Cross sectional analysis of Harmony's cloak can be viewed in Figure 4.30a: a white crust, upper and lower paint layers, and a ground layer. The main constituents of each layer are summarised in Table 4.8. Unlike sample 472 and sample 479 where the white crust layers are apparent and continuous on the surface of the paint layers, the white

crust of sample 482 is localised. A white crust with 10 μm in length was selected to investigate, as shown in a red square in Figure 4.30a. Calcium carbonate was identified in this white crust (P1, Figure 4.30b) from the band at 876 cm^{-1} of $\delta_{\text{out-of-plane}}(\text{CO}_3^{2-})$ (Figure 4.31). Though lead carbonate, which is the main components of lead white, shows identical bands to calcium carbonate at around 1400 cm^{-1} of $\nu_{\text{as}}(\text{CO}_3^{2-})$ (Figure 4.31), lead carbonate would not show a band at 876 cm^{-1} . However, it is possible that the white crust contains both calcium carbonate and lead carbonate because SEM-EDX confirmed the presence of both calcium and lead elements (Figure 4.32).

Table 4.8 List of main components in each layer of sample 482

Layers	Main components
White crust	Deterioration Products: Calcium carbonate
Upper paint layer	Naples yellow, kaolinite, quartz, hydromagnesite, chrome green, barium sulfate or lithopone (only in the lower paint layer), zinc white (from the SEM-EDX results) Deterioration Product: Zinc carboxylates
Lower paint layer	
Ground layer	Lead white, calcium carbonate Deterioration Products: Lead carboxylates

Two layers of paint can be seen in the photomicrograph of sample 482 (Figure 4.30a). The upper paint layer shows distributions of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) (P2, Figure 4.30c) and zinc carboxylates (P3, Figure 4.30d) by plotting the integrated absorbance of $\nu_{\text{as}}(\text{CO}_3^{2-})$ and $\nu_{\text{as}}(\text{COO}^-)$, respectively. SEM-EDX results confirmed the presence of Mg and Zn, and their distributions are provided in Figure 4.32. The bands of $\nu_{\text{as}}(\text{CO}_3^{2-})$ of hydromagnesite show two absorbances at 1419 cm^{-1} and 1481 cm^{-1} , which are different to one single peak of $\nu_{\text{as}}(\text{CO}_3^{2-})$ of lead white at around 1400 cm^{-1} . The bands of $\nu_{\text{as}}(\text{COO}^-)$ of zinc carboxylates show a split doublet at 1527 cm^{-1} and 1539 cm^{-1} , which is also different to one single peak of $\nu_{\text{as}}(\text{COO}^-)$ of lead carboxylates at lower wavenumber of around 1512 cm^{-1} . The potential origin of Zn can be attributed to the presence of zinc white (ZnO) in the upper paint layer. Additionally, in the lower paint layer, lithopone, a mixture of barium sulfate (BaSO_4) and zinc sulfide (ZnS), cannot be disregarded as a potential source of Zn. This is supported by the detection

of Zn and BaSO₄, as depicted in Figure 4.32 and 4.33, respectively. The peak at around 1034 cm⁻¹ is due to kaolinite or silicates mixed with iron-based earth (P4, Figure 4.30e) which is overlapping with the bands of quartz in the wavenumber region of around 1000–1100 cm⁻¹. Quartz, used as a filler, was detected in upper paint layer (P5, Figure 4.30f) as well as in the lower paint layer (Figure 4.33) of sample 482. Lead carboxylates were observed in the ground layer of sample 482 where lead white was identified to have been used in the painting (Figure 4.30).

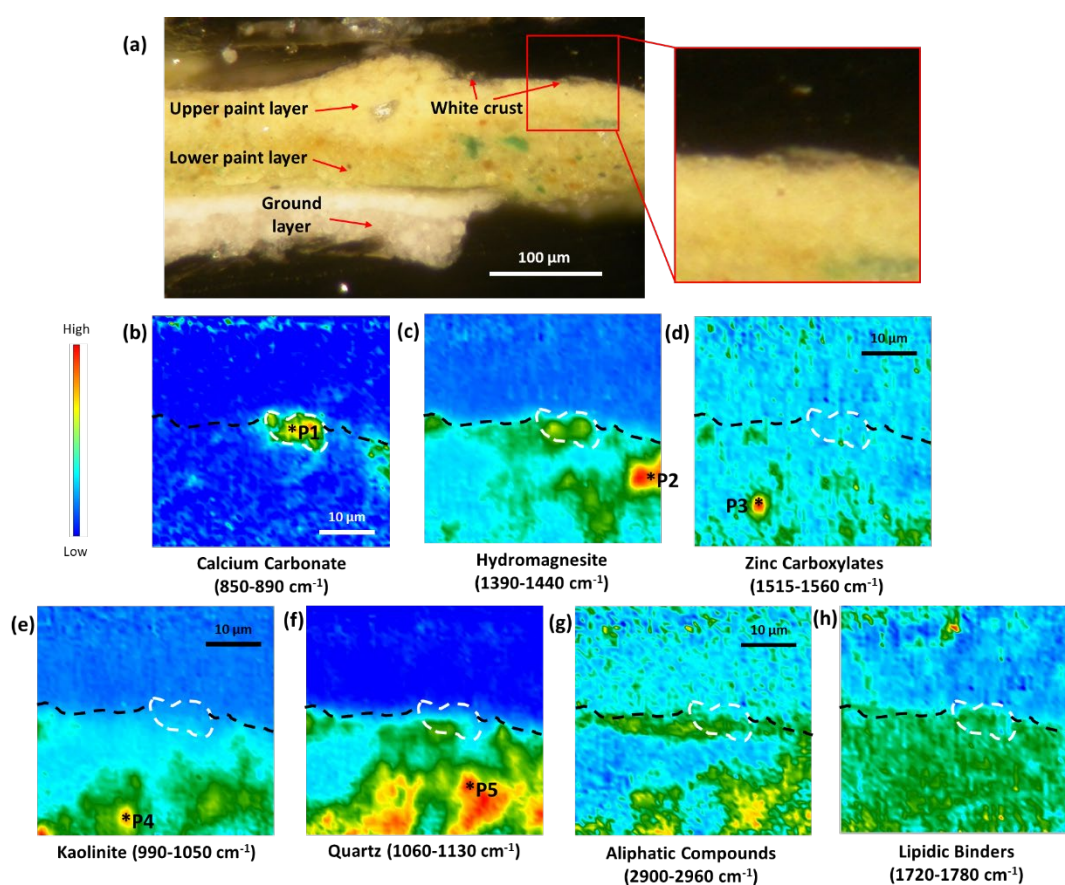


Figure 4.30 Harmony's cloak sample 482. (a) Photomicrograph of the polished cross section. A red square indicates the measuring area (ca. 70 μm×70 μm) by micro ATR-FTIR spectroscopic imaging. Micro ATR-FTIR images showing the distribution of (b) calcium carbonate (850–890 cm⁻¹); (c) hydromagnesite (1390–1440 cm⁻¹); (d) zinc carboxylates (1515–1560 cm⁻¹); (e) kaolinite (990–1050 cm⁻¹); (f) quartz (1060–1130 cm⁻¹); (g) aliphatic compounds (2900–2960 cm⁻¹); (h) lipidic binders (1720–1780 cm⁻¹).

SEM-EDX results (Figure 4.32) identified the presence of lead and antimony, the elements constituting Naples yellow, or lead antimonate yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7$). Naples yellow, a pigment unusual to find at this late date, is lead-based and prone to degradation because of its sensitivity to environmental factors such as light, pollutants, rain, CO_2 and microbial damage (Coccato et al., 2017). As a result, a wide variety of degradation products such as PbSO_4 , PbCO_3 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and PbS may be formed (Pérez-Rodríguez et al., 1998). As mentioned above, the white crust on samples 482 may consist of calcium carbonate and lead carbonate. This assertion is supported by the results of SEM spot analysis of the white crust, as illustrated in Figure 4.34. In contrast to the white crust of sample 472 and 479 where the lead elements

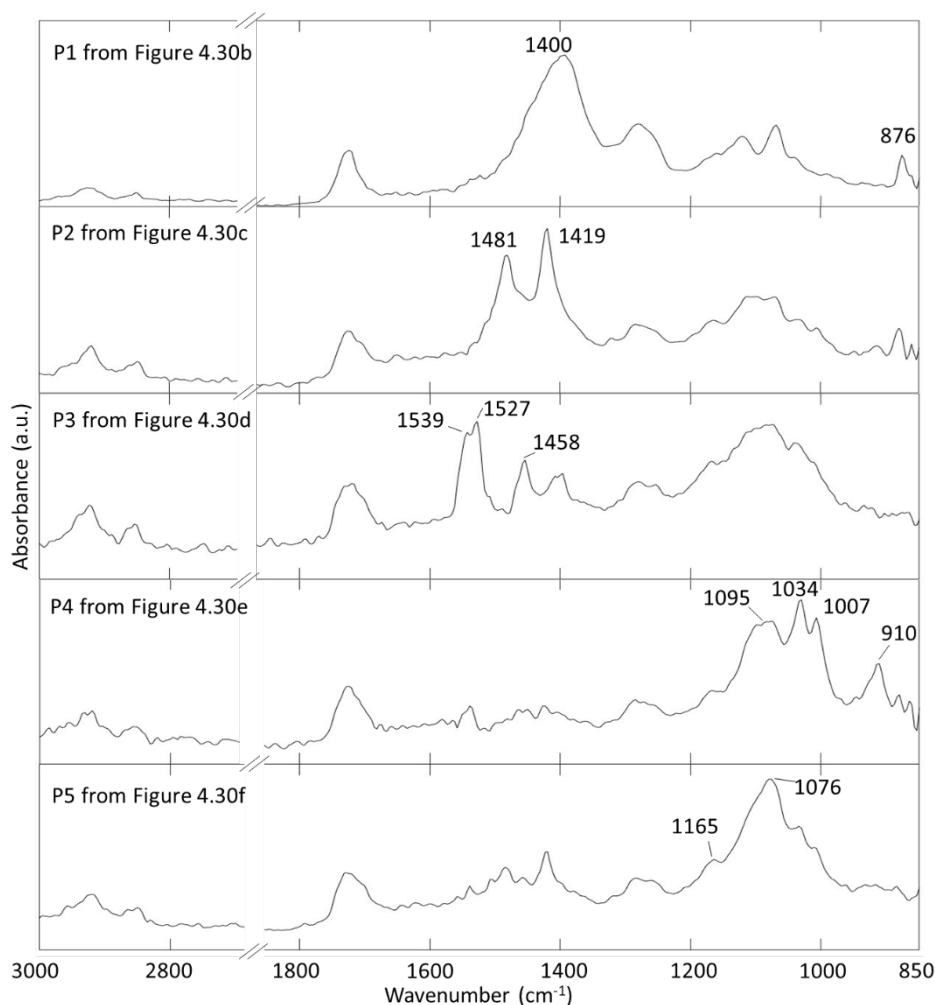


Figure 4.31 ATR-FTIR spectra extracted pixels (P1–P5) from the ATR-FTIR images of sample 482. The location of the white crust in the upper paint layer is circled with a dotted white line. The boundary between the upper paint layer and the embedding resin is indicated using a dotted black line.

were derived from the ground layers with the help of migration of metal carboxylates, the white crust of sample 482 was formed on the paint layer that is abundant in lead elements. This hypothesis can be supported by the fact that the zinc carboxylates are the only type of metal carboxylates detected in the paint layer of sample 482, as shown in Figure 4.30 and Figure 4.33. These ATR-FTIR spectroscopic images of sample 482 do not show any presence of unspecified metal carboxylates with a broad $\nu_{as}(\text{COO}^-)$ band that have been detected in sample 472 and 479. In addition to lead antimonate yellow, iron-based earth and chrome yellow were also characterised in the paint layers, as illustrated in SEM-EDX maps and ATR-FTIR chemical images, as shown in Figure

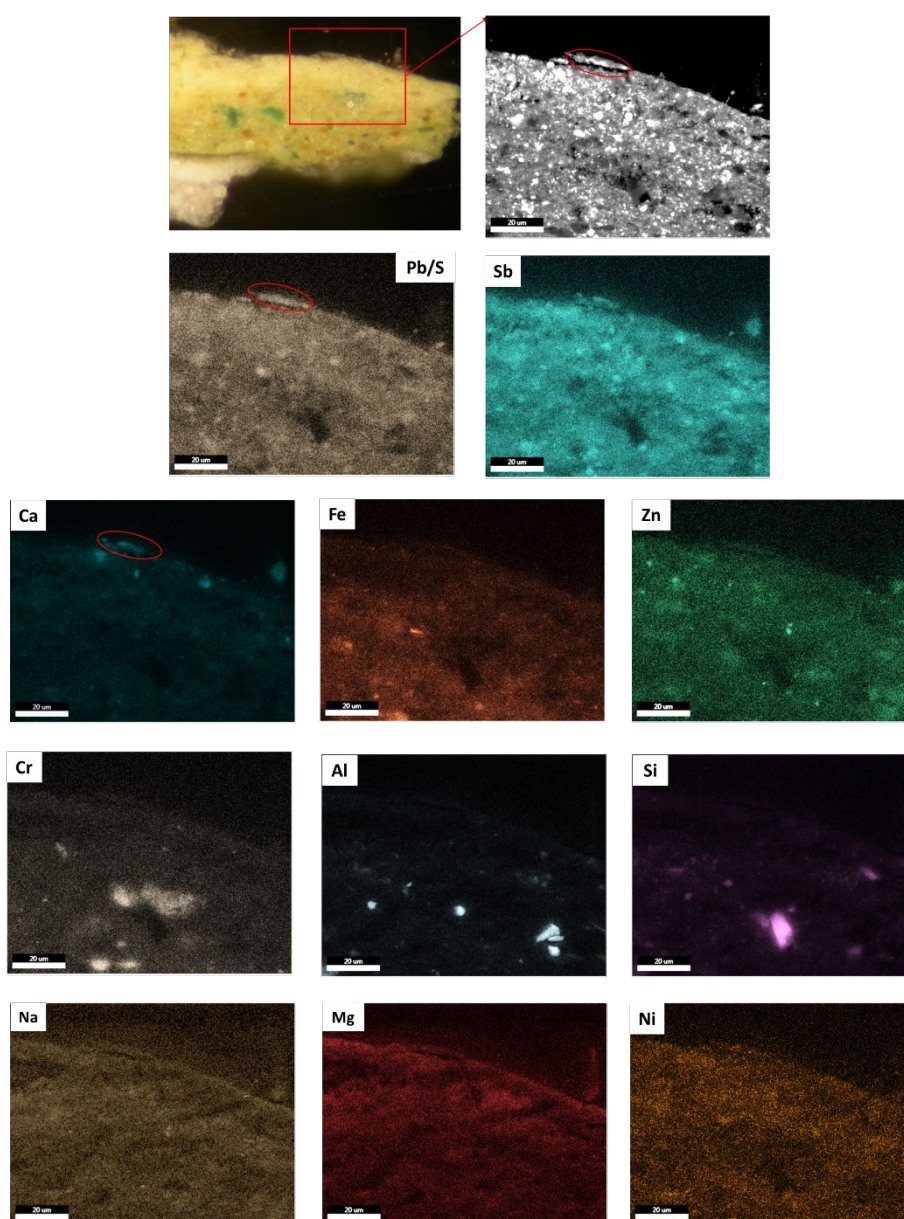


Figure 4.32 SEM-EDX single element distribution maps of sample 482

4.32 and Figure 4.33, respectively.

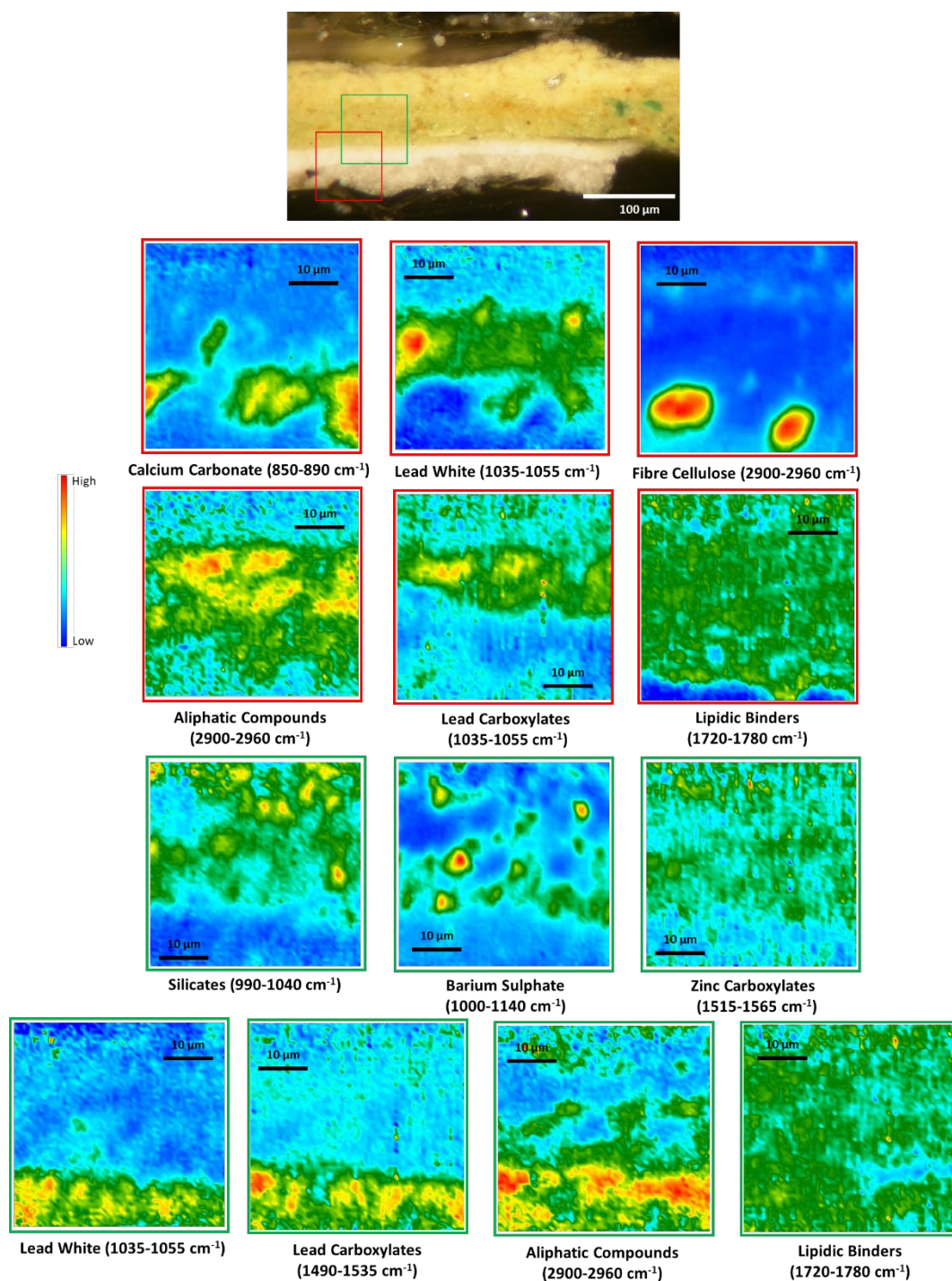


Figure 4.33 ATR-FTIR chemical images of the ground and lower paint layer of sample 482

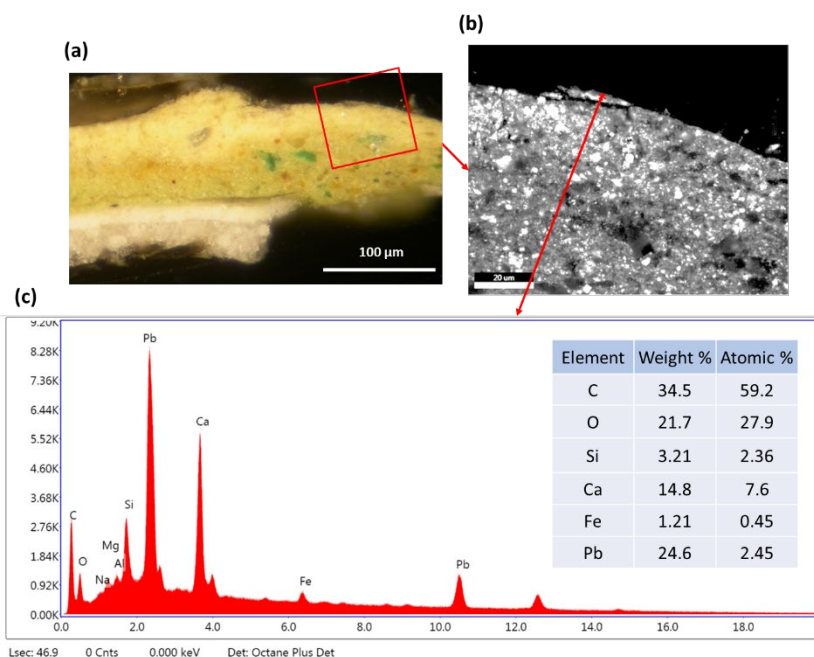


Figure 4.34 Spot analysis of the white crust of the cross-sectional sample 482: (a) Photomicrograph where a red square indicates the measuring area of (b) SEM image of the white crust and upper paint layer. (c) Weight and atomic of chemical elements detected in the pixel in the white crust. The values are derived from the EDX spectrum and only elements of which weight percentages >1% are shown. The location of the white crust of sample 482 is highlighted using a red oval in Pb/S and Ca maps.

The other area of Harmony's cloak was also analysed. Sample 481 was taken from the location near where sample 482 was extracted, as displayed in Figure 4.35. The compositions in each layer of sample 481 (Table 4.9) are slightly different to sample 482. In addition, the micrograph of cross-sectional sample 481 (Figure 4.35a) shows a thicker ground layer and a thinner paint layer compared to sample 482. In the white crust of sample 481, lead white and lead carboxylates were identified, as shown in Figure 4.35–4.37. It is likely that this lead white in the white crust was remineralised where the lead element was from Naples yellow. The remineralised lead white has then reacted with the binding medium to form lead carboxylates in the white crust. The remineralisation of lead white and the formation of lead carboxylates in lead-containing oil paint layers, such as Naples yellow, has been observed and discussed in other case studies in the literature (Boon et al., 2002; Keune & Boon, 2007). It should be noted that metal carboxylates with the $\nu_{as}(\text{COO}^-)$ band shifted to higher wavenumbers at

around 1531 cm^{-1} (P3, Figure 4.36) were detected in the ground layer (Figure 4.35f). These metal carboxylates mainly distributed in the upper ground layer and were not detected in the lower ground layer of sample 481, as indicated in Figure 4.38.

Table 4.9 List of main components in each layer of sample 481

Layers	Main components
White crust	Deterioration Products: Lead carboxylates
Paint layer	Naples yellow, kaolinite, quartz, hydromagnesite (from the SEM-EDX results)
Ground layer	Lead white Deterioration Products: Lead carboxylates, amorphous metal carboxylates

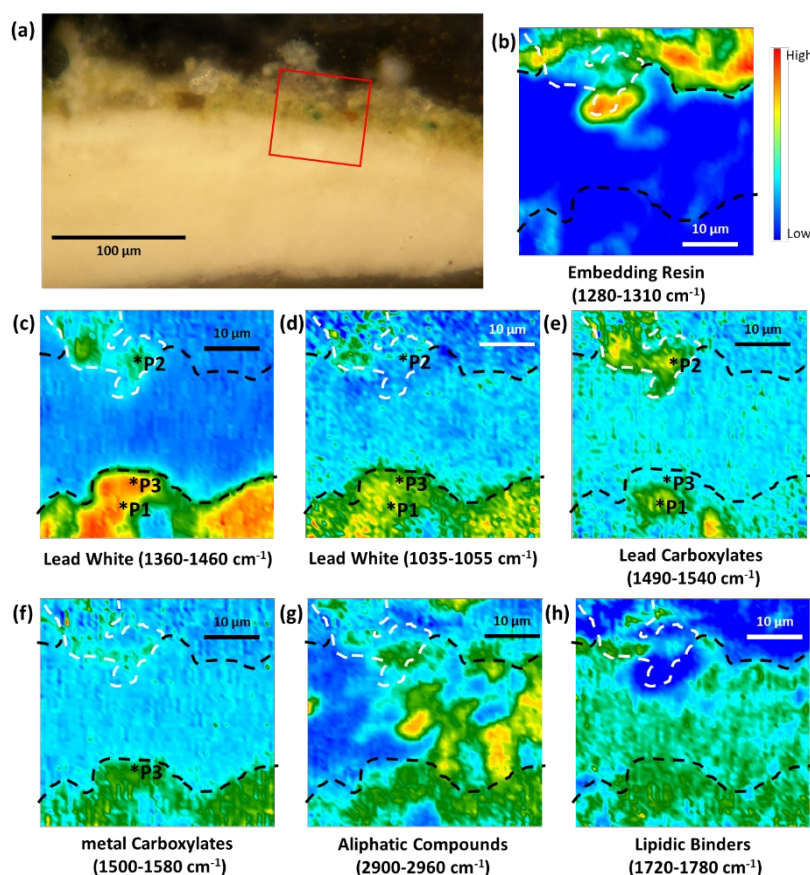


Figure 4.35 Harmony's cloak sample 481. (a) Photomicrograph of the polished cross section. A red square indicates the measuring area (ca. 70 $\mu\text{m} \times 70 \mu\text{m}$) by micro ATR-FTIR spectroscopic imaging. Micro ATR-FTIR images showing the distribution of (b) embedding resin (1280–1310 cm^{-1}); (c) lead white (1360–1460 cm^{-1}); (d) lead white (1035–1055 cm^{-1}); (e) lead carboxylates (1490–1540 cm^{-1}); (f) metal carboxylates (1500–1580 cm^{-1}); (g) aliphatic compounds (2900–2960 cm^{-1}); (h) lipidic binders (1720–1780 cm^{-1})

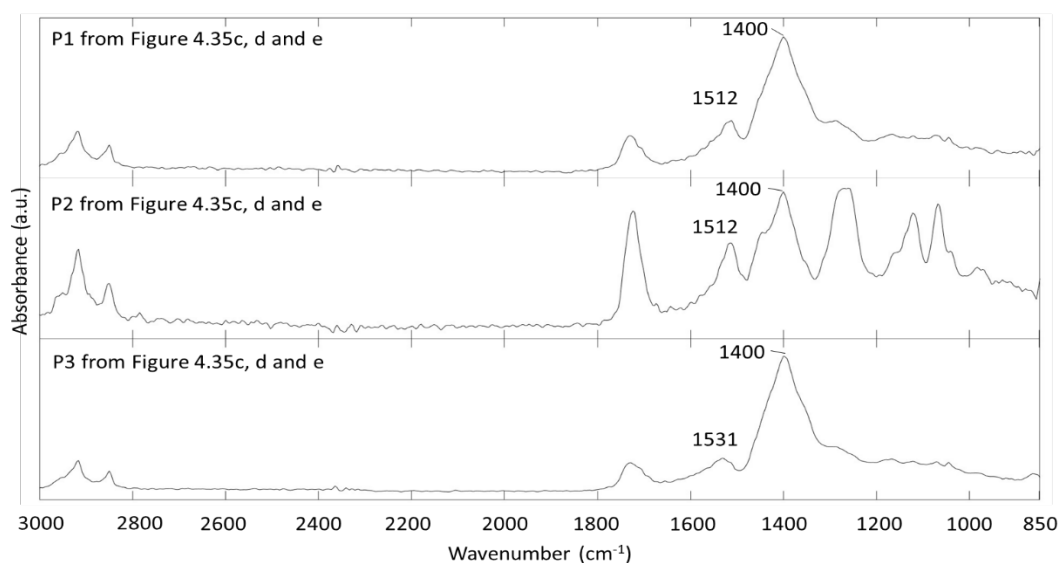


Figure 4.36 ATR-FTIR spectra extracted pixels from the ATR-FTIR images of sample 481

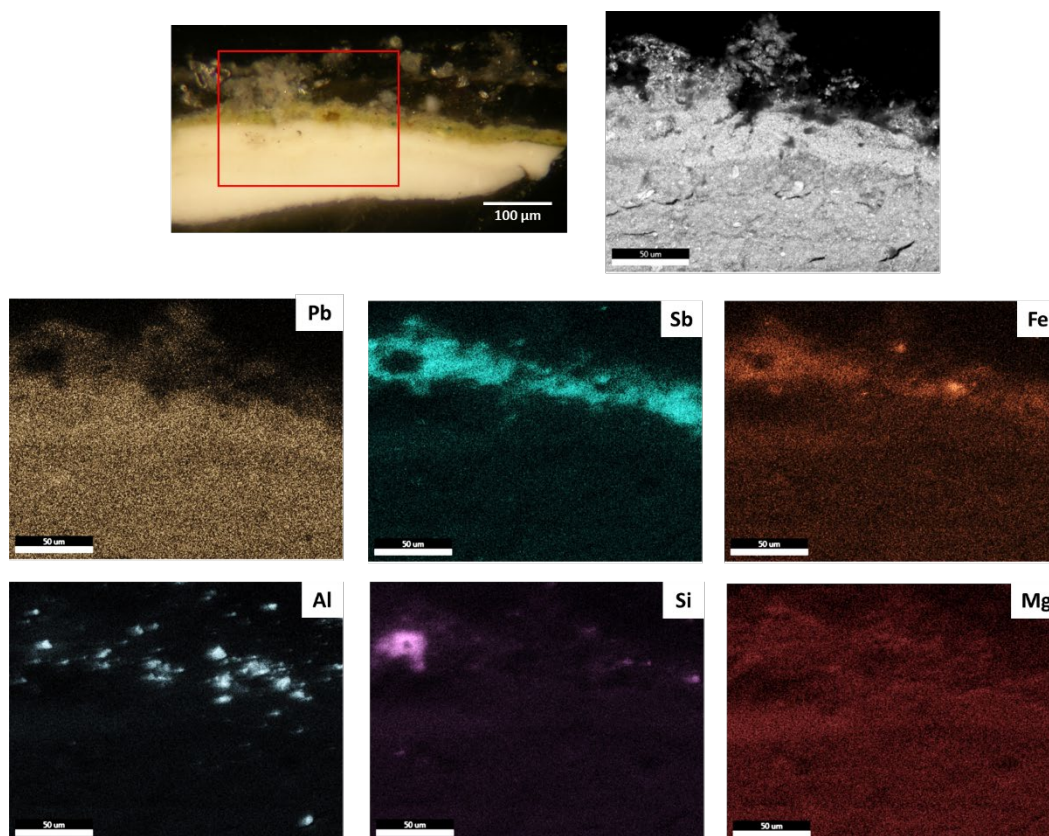


Figure 4.37 SEM-EDX single element distribution maps of sample 481

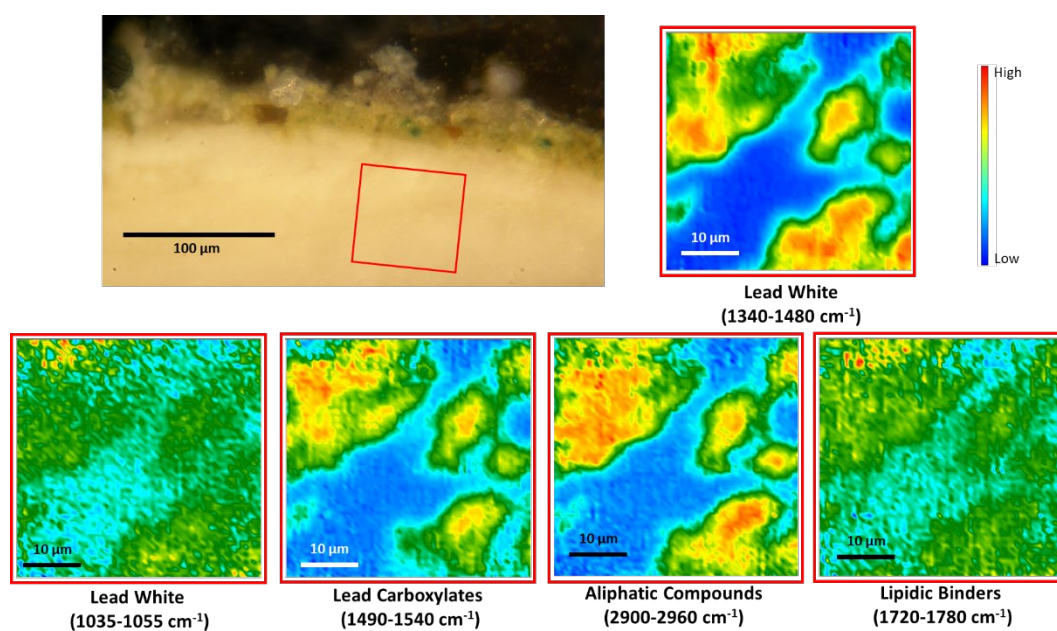


Figure 4.38 ATR-FTIR chemical images of the ground of sample 481

4.2.3.5 Case study: paint cross section of Harmony's harp – 483

The paint cross-section taken from an area of Harmony's harp (Figure 4.39a) identified: a white crust; an upper paint layer; a lower paint layer and a ground layer. The main constituents of each layer are summarised in Table 4.10.

Table 4.10 List of main components in each layer of sample 483

Layers	Main components
White crust	Deterioration Products: Lead sulfate, lead sulfide, calcium carbonate, metal oxalates, gypsum
Upper paint layer	Deterioration Products (only in the darkened area of the upper paint layer): Lead sulfide, lead sulfate
Lower paint layer	Naples yellow, lead white (only in the upper paint layer), barium sulfate or lithopone (only in the lower paint layer), zinc white (from the SEM-EDX results) Deterioration Products: Zinc carboxylates
Ground layer	Lead white, calcium carbonate Deterioration Products: Lead carboxylates

The major difference between the upper and the lower paint layers is that lead white was used in the upper layer while barium sulfate (BaSO_4) as a paint extender was used in the lower paint layer (Figure 4.41 and 4.42). The detection of Zn and BaSO_4 also indicates the possible presence of lithopone ($\text{BaSO}_4 + \text{ZnS}$) or a combination of BaSO_4 and zinc white (ZnO) in the lower paint layer. However, in the upper paint layer, the absence of BaSO_4 suggests that ZnO is the likely source of Zn. Lead white may explain why the upper paint layer shows whiter colour than the lower paint layer. In the upper paint layer, a darkened area which shows similar colour to the lower paint layer can be seen (Figure 4.39a). This darkened area of the upper paint layer was characterised to contain high levels of lead sulfide (PbS) and lead sulfate (PbSO_4). This was identified by assigning a broad spectral band at 872 cm^{-1} (Pb-S bonding) (John Wiley & Sons; Mozafari et al., 2011) and a weak band at 964 cm^{-1} ($\nu(\text{SO}_4^{2-})$), as shown in the spectra of P1 and P2 (Figure 4.39c, d and Figure 4.40). SEM-EDX results confirmed the presence of lead and sulfur elements (Figure 4.41). The chemical images for spectral bands between $800\text{--}930\text{ cm}^{-1}$ (Figure 4.39b) and $1000\text{--}1225\text{ cm}^{-1}$ (Figure 4.39c)

represent spatial distributions of PbS and PbSO₄, respectively. PbS and PbSO₄ are only located at the top of the upper paint layer, suggesting that these are likely to be deterioration products rather than original materials used in the painting. The source of Pb can be either from Naples yellow as Sb is confirmed with the SEM-EDX results (Figure 4.41), or from lead white used in the upper paint layer. In the upper part of PbS and PbSO₄ is the white crust consisting of a thin layer of oxalates and a spot of carbonates as shown in P3 in Figure 4.39d and P4 in Figure 4.39e, respectively. The oxalates in the white crust show spectral bands at 1643 and 1315 cm⁻¹, which could

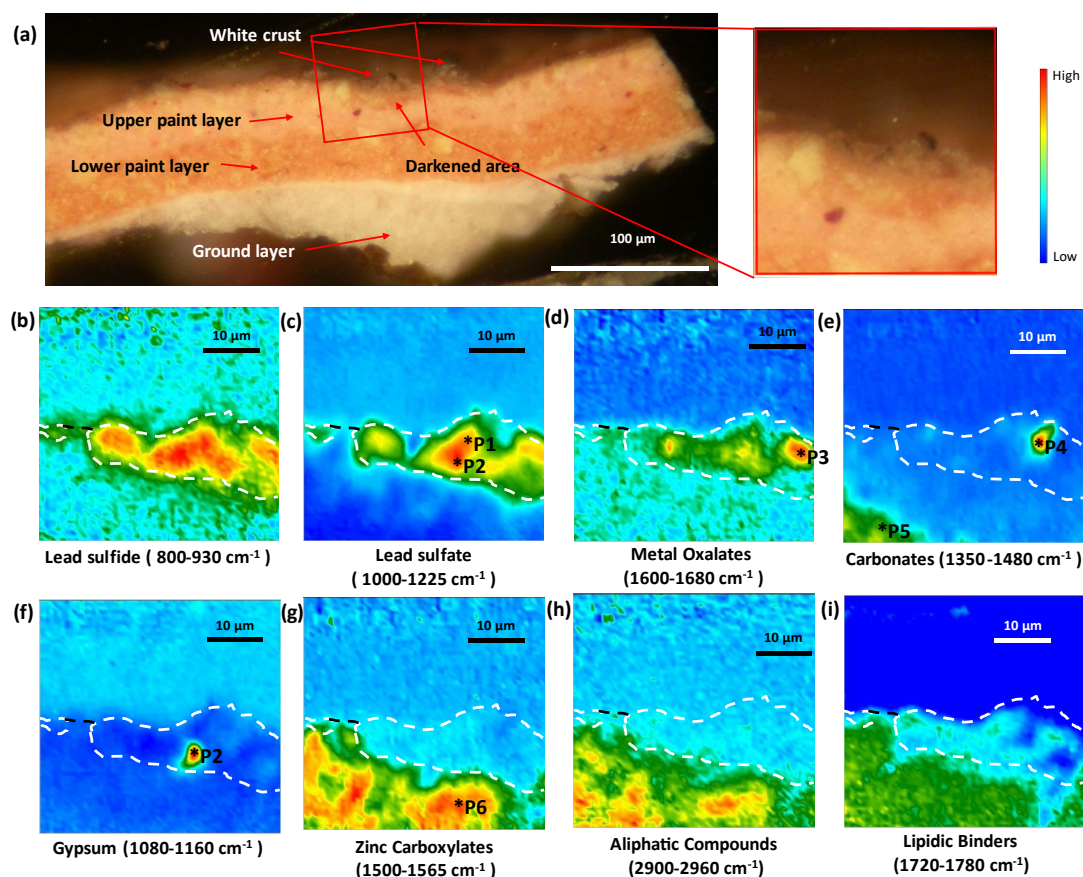


Figure 4.39 Harmony's harp sample 483: (a) Photomicrograph the polished cross section. A red square indicates the measuring area (ca. 70 μm $\times$ 70 μm) by micro ATR-FTIR spectroscopic imaging. Micro ATR-FTIR images showing the distribution of (b) lead sulfide (800–930 cm^{-1}); (c) lead sulfate (1000–1225 cm^{-1}); (d) metal oxalates (1600–1680 cm^{-1}); (e) calcium carbonate and lead white (1350–1480 cm^{-1}); (f) gypsum (1080–1160 cm^{-1}); (g) zinc carboxylates (1500–1565 cm^{-1}); (h) aliphatic compounds (2900–2960 cm^{-1}); (i) lipidic binders (1720–1780 cm^{-1}). The location of the white crust as well as the darkened area in the upper paint layer is highlighted using with a dotted white line, and the boundary between the upper paint layer and the embedding resin is indicated using a dotted black line.

be assigned to calcium oxalate. The carbonate in the white crust shows 1400 and 876 cm^{-1} which are characteristic for calcium carbonate, while the carbonates detected in the paint layer (P5, Figure 4.39e) should be lead white due to the absence of the spectral band at 872 cm^{-1} . Gypsum (P2 in Figure 4.39f) was detected with absorption bands at 1107 cm^{-1} . This gypsum is more likely to be degradation products because it was found in the darkened area which contains PbS and PbSO₄. In addition, there is no detection of gypsum in any other areas of the sample including the paint and the

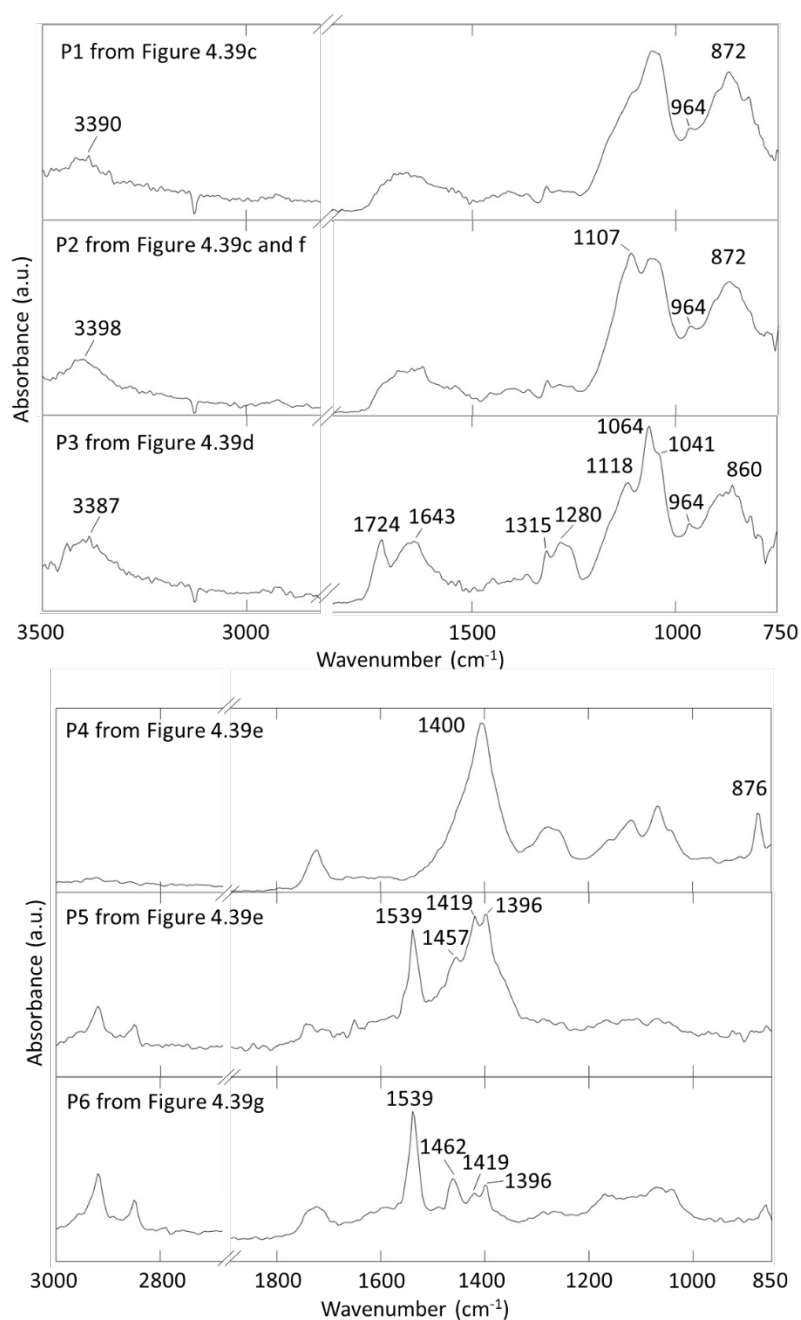


Figure 4.40 ATR-FTIR spectra extracted from pixels (P1–P6) in Figure 4.39

ground layers. Gypsum has been reported as a common deterioration product found in wall paintings and manuscripts (Coccato et al., 2017; Deneckere et al., 2011), where calcium carbonate was used as the original materials. The degradation of calcium carbonate due to SO₂ pollution in the environment results in the formation of gypsum. In the case of sample 483, gypsum may have been derived from the degradation of calcium carbonate, the substance which is also found in the white crust as a deterioration product (Klaassen et al., 2019). The source of calcium in the white crust can be from the calcium carbonate used in the ground layer of sample 483 (Figure 4.42). The calcium ion can migrate from the ground layer to the surface of the painting with the help of mobile calcium carboxylate (Higgs & Burnstock, 2019), but calcium carboxylates were not detected in the sample of 483. The source of calcium in the white crust is more likely to be linked to calcium-containing dust, which has also been suggested in other cases in the literature (Klaassen et al., 2019; Kontozova-Deutsch

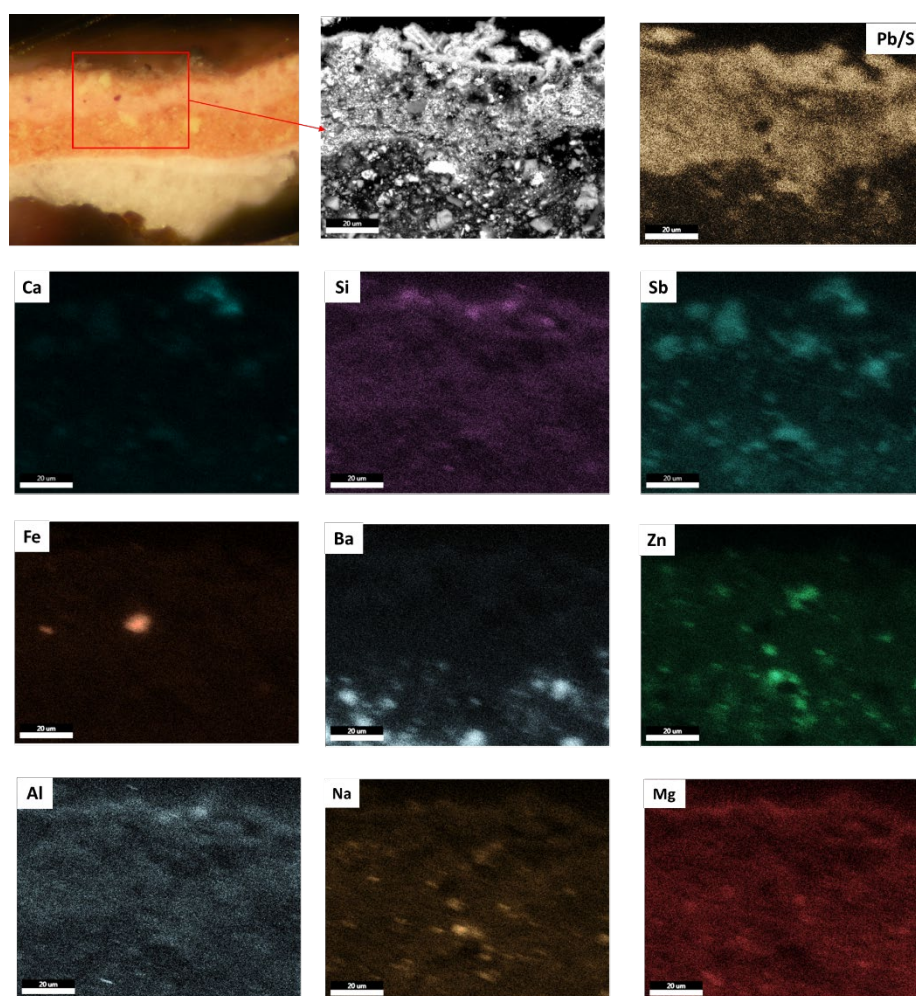


Figure 4.41 SEM-EDX single element distribution maps of sample 483

et al., 2011). This explanation could also be used to explain the source of calcium that formed calcium carbonate in the white crust of sample 482. In the paint layer of sample 482, no calcium carboxylates were detected. The spectrum of the metal carboxylates detected in the paint layer of sample 483 (P5, P6 in Figure 4.40) indicates the metal cation may be zinc, which has a spectral band at around 1539 cm^{-1} . It is worth noticing that the zinc carboxylates in sample 483 have a single peak centred at 1539 cm^{-1} , which is different to the zinc carboxylates in 482 consisting of a doublet at 1527 and 1539 cm^{-1} (P3 in Figure 4.31). This may be due to the different symmetry of the components between the zinc carboxylates (Helwig et al., 2014) in 482 and 483.

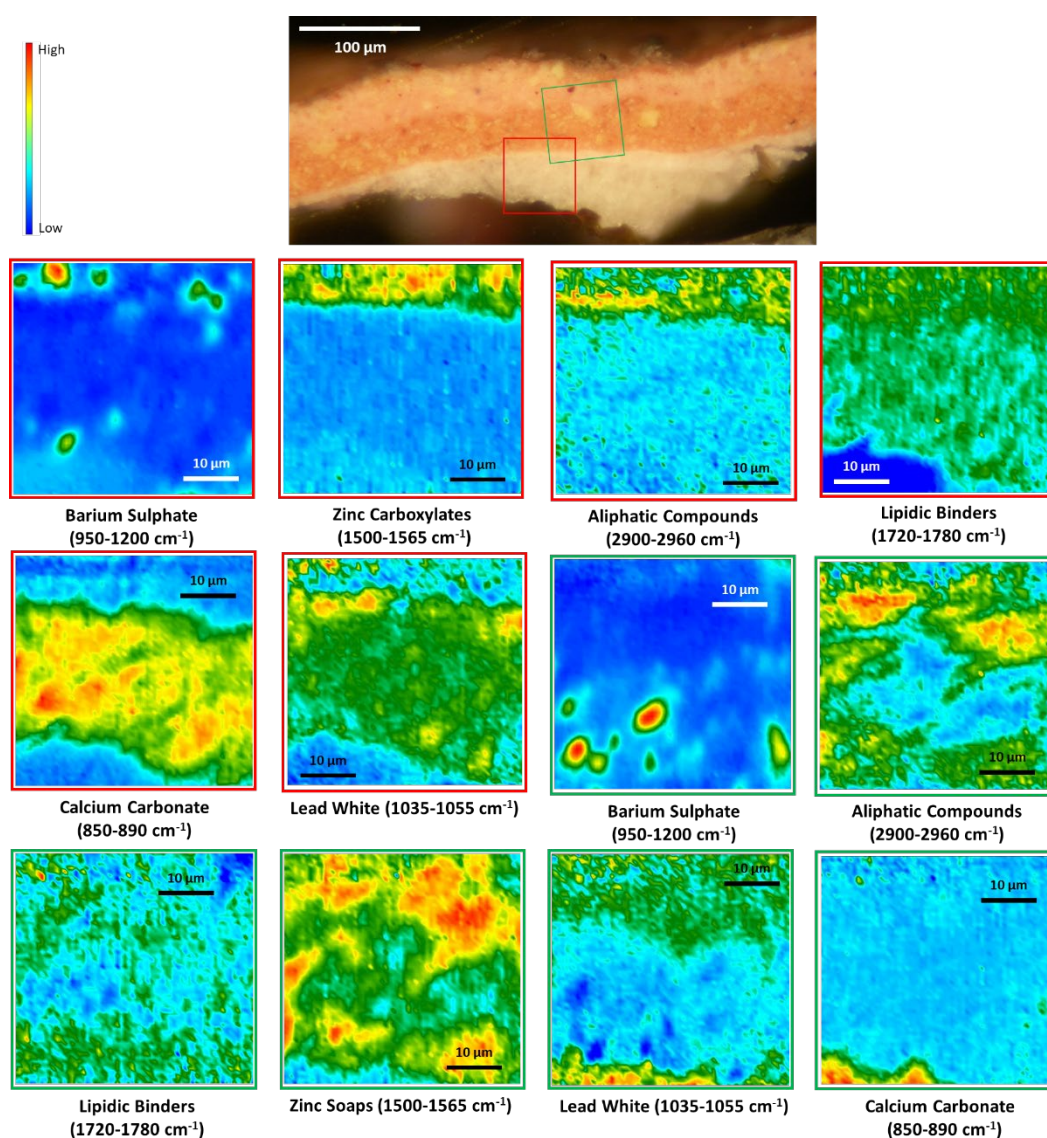


Figure 4.42 ATR-FTIR chemical images of the ground and lower paint layers of sample 483

4.2.4 Studies of the formation of substances in the white crusts

4.2.4.1 Diffusion of lead via amorphous metal carboxylates to form lead sulfate and metal oxalate in the white crusts

In the paint layers of samples 472 and 479, the metal carboxylates show a broad band in the range of 1500–1650 cm^{-1} in FTIR spectra, as displayed in Figure 4.23 (spectrum P5) and Figure 4.27 (spectrum P5). These metal carboxylates featuring the broad spectral band of $\nu_{\text{as}}(\text{COO}^-)$, which can be commonly seen in lead and zinc carboxylates in paint samples, have been reported in previous research (Gabrieli et al., 2017; Garrappa et al., 2020; Hermans, Keune, van Loon, et al., 2016; Hermans et al., 2015; MacDonald et al., 2016). Hermans et al. (Hermans, Keune, van Loon, et al., 2016) have suggested that broad bands are linked to amorphous metal carboxylates, while sharp bands are linked to crystalline metal carboxylates of saturated fatty acids. Figure 4.43 shows spectra of six pixels extracted from sample 472 and spectra of five pixels extracted from sample 479. It can be seen that in the ground layers where lead carboxylates are formed, a sharp $\nu_{\text{as}}(\text{COO}^-)$ occurs in the spectra at 1512 cm^{-1} (P5 in 4.43a) and at 1508 cm^{-1} (P5 in Figure 4.43b). The spectral bands of $\nu_{\text{as}}(\text{COO}^-)$ attributed to metal carboxylates in the paint layers are shifted to the higher wavenumbers and become broader at 1524 cm^{-1} , 1539 cm^{-1} , 1562 cm^{-1} (P4, P3, P2 in Figure 4.43a, respectively) and at 1540/1558 cm^{-1} , 1562 cm^{-1} (P4, P3 in Figure 4.43b, respectively). In the region of the white crusts where oxalates and sulfates are identified, the intensity of $\nu_{\text{as}}(\text{COO}^-)$ decreases in the spectra (P2, P1 in Figure 4.43a and P2, P1 in Figure 4.43b). The amorphous metal carboxylates with broad $\nu_{\text{as}}(\text{COO}^-)$ band appear to be abundant in the paint layers of sample 472 and 479. A possible explanation for the presence of these amorphous metal carboxylates is the formation of ionomers neutralised by free metal ions (Hermans, Keune, van Loon, et al., 2016). Another hypothesis for the presence of the amorphous metal carboxylates in the paint layers is that these amorphous metal carboxylates might have been derived from the crystallised lead carboxylates in the ground layers. The crystallised lead carboxylates

became the amorphous metal carboxylates when migrating through paint layers to the surface of the paintings. Nevertheless, this hypothesis is not possible because the crystallisation of metal carboxylates is irreversible, as illustrated in the chemical model proposed by Eumelen et al. (Eumelen et al., 2023; Eumelen et al., 2019). Our results also reveal that these pure and crystallised lead carboxylates with a sharp spectral band of $\nu_{as}(\text{COO}^-)$ at around 1508/1512 cm^{-1} are mainly distributed in the ground layers where abundant lead white was used. These pure and crystallised lead

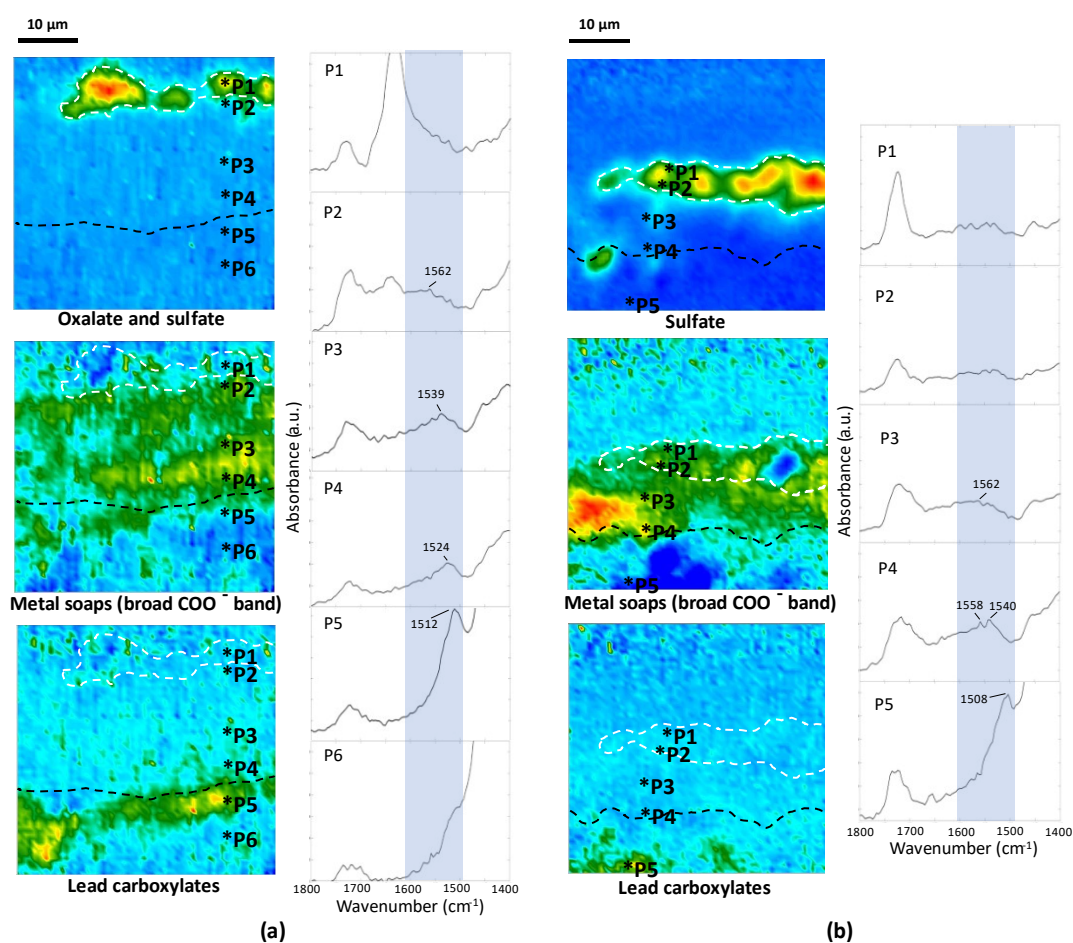


Figure 4.43 (a) Chemical image of sample 472 showing the distribution of oxalates/sulfates, metal carboxylates with broad COO^- band and lead carboxylates (from top to bottom), and ATR-FTIR spectra collected from the white crust (P1, P2), the paint layer (P3, P4), and the ground layer (P5, P6); (b) Chemical image of sample 479 showing the distribution of sulfates, metal carboxylates with broad COO^- band and lead carboxylates (from top to bottom), and ATR-FTIR spectra collected from the white crust (P1, P2), the paint layer (P3, P4), and the ground layer (P5). The blue bands indicate the absorption region attributed to metal carboxylates. In each ATR-FTIR spectroscopic image, the white crust is circled with a dotted white line and the paint and ground layers are divided with a dotted black line.

carboxylates are not shown in the paint layers. It is worth noticing that lead carboxylates with a broad spectral band of $\nu_{as}(\text{COO}^-)$ at 1540 cm^{-1} was found in a lead white paint sample from *Portrait of a Man* painted by Thomas de Keyser (J. Hermans et al., 2014). Hermans et al. has explained that this broad $\nu_{as}(\text{COO}^-)$ band of lead carboxylates is due to multiple overlapping spectral bands resulting from heterogeneous molecular species in aged oil paint. This explanation also illustrates the amorphous form of metal carboxylates found in the lead white paint sample. Lead carboxylates were previously hypothesised to be the form in which lead elements diffuse to the surface (Sawicka et al., 2014). However, it has been proven that lead carboxylates can easily crystallise and are insoluble in oil, so this is not possible (Hermans, Keune, Loon, et al., 2016). It is more likely that lead elements diffuse from the ground layers to upper paint layers through a mechanism known as ion hopping via the amorphous metal carboxylates in the paint layers (Hermans et al., 2015). Of particular interest is the fact that these amorphous metal carboxylates were also detected in the paint layer of sample 470 (Figure 6.3 in Appendices), the sample which was extracted from St George's ankle where no visible white crust was observed. Other unknown factors in the paintings need to be explored to figure out why paintings that have experienced a similar environment show differences in terms of the presence or absence of white crust. Novel approaches may also be applied to investigate heterogeneity and evolution of metal carboxylates in chemically complex systems with higher spatial resolution ($\sim 500\text{ nm}$), such as using Optical Photothermal Infrared (OPTIR) or Photothermal-Induced Resonance (PTIR) Spectroscopy (Ma et al., 2022). Furthermore, the white crusts appear thicker in Harmony's hair (sample 479) than any other areas of the paintings. The fact that the hair is dark brown also enhances the contrast between the paint and the white crust. There is a possible connection between the white crust and the presence of excess medium used. Additional quantitative analysis using Gas Chromatography-Mass Spectrometry (GC-MS) (Tammekivi et al., 2021) would be of great interest and value in understanding the correlation between the amounts of white crust and medium used in the paintings.

4.2.4.2 Studies of the formation of calcium carbonate

The progressive formation of CaCO_3 in the white crusts within sample 479 was investigated by reviewing the different spectral positions of the $\nu_{\text{as}}(\text{CO}_3^{2-})$, which is illustrated in Figure 4.44. The chemical image shown in Figure 4.44a is from Figure 4.25d, where spectra were extracted from fourteen locations of CaCO_3 in the white crusts. As described in literature, crystallised CaCO_3 show strong absorbance (ν_3) in the vibrational region $1390\text{--}1410\text{ cm}^{-1}$ (Farhadi Khouzani et al., 2015; La Russa et al., 2009; Salter et al., 2019), while amorphous CaCO_3 shows a split doublet (ν_4) in the wavenumber region $1400\text{--}1470\text{ cm}^{-1}$ (Farhadi Khouzani et al., 2015; La Russa et al., 2009). Apart from different spectral bands of ν_3 and ν_4 , crystallised CaCO_3 shows absorbance (ν_2) at 872 cm^{-1} , while amorphous CaCO_3 displays absorbance (ν_2) to lower wavenumber at 863 cm^{-1} (Farhadi Khouzani et al., 2015). Recent crystallisation studies (Farhadi Khouzani et al., 2015) have illustrated that during crystallisation processes, ν_2 bands at 863 cm^{-1} vanished and ν_2 bands at 872 cm^{-1} developed. Furthermore, the split doublet (ν_4) became a singlet and the peak of ν_4 shifted to lower wavenumbers. In a slowly controlled crystallisation experiment of CaCO_3 , a peak shift of ν_2 bands was observed from larger wavenumbers to 872 cm^{-1} during the development of the ν_2 bands. In this research, the ATR-FTIR spectra revealed that the $\nu_4(\text{CO}_3^{2-})$ bands are shifted to the larger wavenumber regions by 4 cm^{-1} or 8 cm^{-1} when obtaining the ATR-FTIR spectra of the CaCO_3 precipitates from the upper parts to the lower parts (Figure 4.44b), from the core to the left parts (Figure 4.44c), and from the core to the right parts (Figure 4.44d). In addition, $\nu_2(\text{CO}_3^{2-})$ bands are also found to be shifted to the higher wavenumber at 876 cm^{-1} at the leftmost and rightmost datapoints of CaCO_3 precipitates. The peak shifts toward higher wavenumbers can be explained by the variation from crystalline CaCO_3 to its amorphous or disordered form. It may also be inferred that the crystallisation direction of CaCO_3 is from the upper to the lower domains, and from core outwards.

Previous studies have demonstrated that ATR-FTIR spectroscopic imaging can provide not only spatial information but also quantitative information by collecting ATR-

FTIR spectra that offer a detailed analysis of the composition and heterogeneity of the

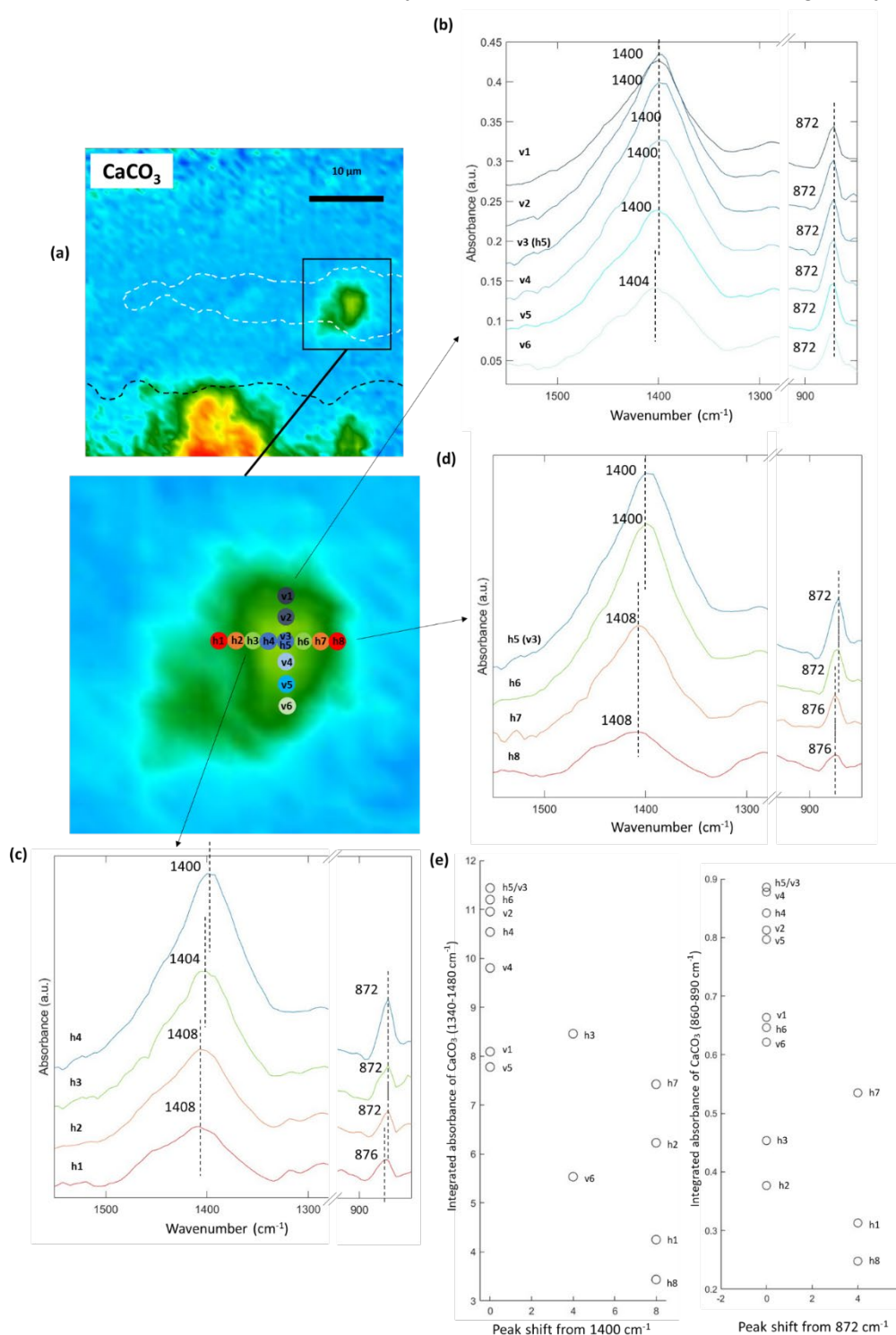


Figure 4.44 (a) Chemical image of cross section of sample 479 displaying the CaCO_3 precipitate in the white crust. ATR-FTIR spectra of $\nu_{\text{as}}(\text{CO}_3^{2-})$ bands as extracted from a single pixel of the chemical image of the CaCO_3 precipitate in (b) vertical and (c) (d) horizontal directions. (e) Graphs showing the integrated absorbance of the $\nu_{\text{as}}(\text{CO}_3^{2-})$ of CaCO_3 in the range 1340–1480 cm^{-1} and 860–890 cm^{-1} versus the peak shift. Each point represents a single pixel of the ATR-FTIR image of the CaCO_3 precipitate.

sample. Possenti et al. identified the correlation between the peak shift of the $\nu_{as}(\text{CO}_3^{2-})$ band of lead white and a decrease in its quantity (Possenti et al., 2021a). These findings explain the advanced decay of lead white in different region of the sample. In the case of our research, a similar approach was adopted to investigate the formation of the deterioration products, CaCO_3 . Figure 4.44e illustrates that the peak shift is negatively correlated to integrated absorbance of the $\nu_{as}(\text{CO}_3^{2-})$ which represents the amount of CaCO_3 . The core of CaCO_3 (v3/h5) shows the best crystallinity and highest quantity, while the left (h1) and the right (h8) show it was poorly crystallised and in lower amounts. In the future, it would be of interest to investigate crystallisation kinetics of CaCO_3 in the white crusts on the surface of paintings.

4.2.5 Summary

ATR-FTIR imaging facilitated the identification of paint materials and components within the white crusts of 19th century cartoons in oil on canvas. The chemical distribution of various types of metal carboxylates, implicated in the formation of white crusts on painted surfaces, was also characterised. Particularly, unspecified amorphous metal carboxylates exhibiting a broad band between 1500–1630 cm^{-1} in the paint layers may elucidate the migration of lead and calcium ions from the ground layers, resulting in the formation of white crusts on painting surfaces. Lead was found to play a pivotal role in the formation of these studied white crusts. Augmented by SEM-EDX mapping results, the micro ATR-FTIR spectroscopic imaging results confirmed the presence of abundant lead white, lead carboxylates in the ground layers, and lead-containing Naples yellow in the paint layers. The crystallinity and formation directions of CaCO_3 surrounded by PbSO_4 in the white crust of sample 479 were determined through quantitative and qualitative analysis, involving the evaluation of peak shifts and calculation of integrated absorbance in the ATR-FTIR spectra, respectively. These findings offer comprehensive insights into the heterogeneity and composition of the white crusts.

4.3 ATR-FTIR spectroscopic imaging of black and white antique photographs

This section is adapted from: Liu, G. L., Chen, T. C., & Kazarian, S. G. (2024). Identification of black and white antique photographs via non-destructive microscopic and spectroscopic techniques coupled with chemometric approaches. *Microchemical Journal*, 200, 110297. (Liu et al., 2024)

4.3.1 Background

Before 1960s when colour photographs were expensive, black and white photographs were the most common media to capture and record images (Stulik & Kaplan, 2013). These black and white photographs utilised silver compounds exposed to light creating images on glass or paper. A combination of materials such as organic binders and inorganic baryte can also be found on the historical black and white photographs depending on photographic techniques employed. Due to the complexity of the materials used in the manufacture of the historical antique photographs, different storage conditions and restoration procedures are required for photographic conservation (Oravec et al., 2019). As a result, structural and compositional identification of these antique photographs is fundamental and essential for the purpose of establishing suitable and adequate conservation and prevention strategies (Casoli & Fornaciari, 2014; Nieto-Villena et al., 2019).

A wide variety of techniques utilised to produce black and white photographs have been invented since William Henry Fox Talbot (1800–1877) first applied photography to a paper substrate in around 1835 (Crawford, 1979; Schaaf, 1992). This photographic process invented by Talbot is salt print, which is the earliest type of photography on paper. The process of creating a salt print (Schaaf, 1996; Schaaf, 2000) involves sensitising handmade or mould-made watercolour paper by soaking it in a salt solution which may consist of sodium chloride, sodium citrate or ammonium chloride, 4% by

weight. This sensitised paper is then coated with a 12% solution of silver nitrate, which sometimes contains a small amount of citric acid, and is dried in darkness or subdued light. The paper is exposed to ultraviolet (UV) light using a negative until the image is darker than required, typically for around 10 minutes in bright sunlight. The paper is then washed in several rinses of water to remove any excess silver nitrate, optionally toned with gold toner, fixed in a 5% solution of sodium thiosulfate or dilute print fixer, and finally washed for an hour in water to remove any remaining chemicals from the paper. The salt print process was dominant until the middle of the 1850s when its successor, albumen print process, became the most common technique for manufacturing black and white photographs.

The albumen process, invented by Louis Blanquart-Evrard (1802–1872), almost replaced salt print process in around 1855, and was dominant black and white photographic printing until 1890. The recipes for albumen photo production (Lavédrine, 2009; Nadeau, 1994; Ricci et al., 2007) vary in terms of different paper substrates, different chemical components and their percentages, but the general procedures are almost similar. The essential albumen process includes selecting the paper substrate, separating egg white from egg yolk, adding sodium chloride or ammonium chloride to the egg white, liquefying the froth overnight, straining and aging the resulting suspension, coating the paper substrate by floating it on the suspension to coat the paper substrate, hanging the paper substrate to dry and to cure, sensitising the paper substrate by floating it on a solution of silver nitrate with the coated side facing down. Due to the use of the albumen coating on the paper substrate, albumen photographs are glossy compared to their predecessor salt prints, and higher concentration of albumen used in the coating process results in glossier appearance of the albumen photographs (Reilly, 2012).

The albumen process gradually become less dominant after 1890s and was surviving in different albumen variants into the late 1920s. The collodion and gelatine print photographs became dominant after 1890s. The collodion print process was almost completely replaced by silver gelatine print process after 1930. Both collodion and gelatine photographs used baryta-coated paper substrates, resulting in a structure

of multi-layers. In this study, collodion photographs were not investigated but gelatine photographs were focused due to the longer and more dominating period of silver photographs. Silver gelatine photographs have become the most used black and white photography on paper substrate since 1890s and were prominent throughout the 20th century (Lavédrine, 2009). Unlike the salt print and albumen print processes, the invention of the silver gelatine print process cannot be attributed to any one individual. The development and research of various types of silver gelatine photographs can be attributed to several inventors, namely José Martinez-Sanchez, Jean Laurent, Peter Mawdsley, Josef Marie Eder, Giuseppe Pizzighelli, and Sir William de Wiveleslie Abney, who made significant contributions to its advancement (Stulik & Kaplan, 2013). There are two types of silver gelatine prints: printing-out paper (POP) and developing-out paper (DOP), which do not have apparent difference in their internal chemical structure. POP process utilises light to develop a visible image, whereas DOP process employs chemical development to create the complete image. Salt prints and albumen photographs are also classified as POP, of which the only procedures are washing, toning, and fixing. This study does not discuss methods for distinguishing silver gelatine POP and DOP, but explores the chemical structure of silver gelatine photographs.

Due to the complexity and diversity of chemical structures of those black and white antique photographs, detailed understanding and characterisation of the antique photographs are of importance for the long-term conservation of the antique photographs. At a photograph conservation meeting where conservation scientists, curators, photography art historians participated (Stulik & Kaplan, 2013), a conclusion has been drawn that only 75% of identification questions can be answered by visual and microscopic investigation of antique photographs. The remaining 25% of the identification questions may be crucial and can only be answered by additional diagnostic techniques. The most commonly used diagnostic technique to examine chemical components of those antique photographs is Fourier Transform Infrared (FTIR) spectroscopy, especially Attenuated Total Reflection (ATR) (Casoli & Fornaciari, 2014; Eldeeb et al., 2022; Oravec et al., 2019; Stulik & Kaplan, 2013). Coupled with

FTIR spectroscopy, Raman spectroscopy and XRF have also been utilised to investigate photographs (Vila & Centeno, 2013).

As far as we are aware, there is only one documented use of micro ATR-FTIR spectroscopic imaging for analysing antique photographs in the literature (Ricci et al., 2007), where a research question about the correlation between amounts of metallic silver elements and proteinaceous binders present in different regions of antique photographs needs to be further explored. The purpose of the present work is to characterise and differentiate three types of antique photographs created in different years between 19th and 20th centuries into distinct groups. The novelty of this work is applying ATR-FTIR imaging coupled with the chemometric analysis to the identification of antique photographs which have heterogenous compositions. It is hoped that the knowledge advancement of ATR-FTIR imaging techniques coupled with chemometric analysis demonstrated in this work can aid in identification of various types of antique photographs that have different manufacturing processes.

4.3.2 Experimental set-up

Materials studied include three types of antique photographs dating back to different eras, as shown in Figure 4.45. Table 4.11 summarises the production years and providers of these three antique photographs. Six locations, including the black and white areas of the three photographs, were first investigated using conventional ATR-FTIR spectroscopy and macro ATR-FTIR spectroscopic imaging. The conventional ATR-FTIR spectra were acquired in the mid IR range of 3900–900 cm⁻¹ with a 4 cm⁻¹ resolution and with 64 co-added scans, while the macro ATR-FTIR spectroscopic data were collected in the mid IR range from 3900 cm⁻¹ to 900 cm⁻¹, at 8 cm⁻¹ resolution and with 64 co-added scans.

PCA was subsequently applied on the macro ATR-FTIR spectroscopic data of each sample for dimensionality reduction processed with Matlab R2022b (MathWorks, Inc., USA). PCA analysis was performed by projecting the ATR-FTIR spectra onto a PCA score plot. The first Principal Component (PC) explained the majority of the data variance, while subsequent PCs captured the residual variance. The scores,

representing the projection of the ATR-FTIR spectra onto the PCs, were plotted in a three-dimensional space to validate the differences among the spectral data.

These six locations investigated were then removed from the photographs by being cut into 10 mm × 10 mm square samples. These six square samples were then examined using a benchtop XRF for chemical elemental characterisation. After the six square samples were examined with XRF, they were located in plastic clips, had their

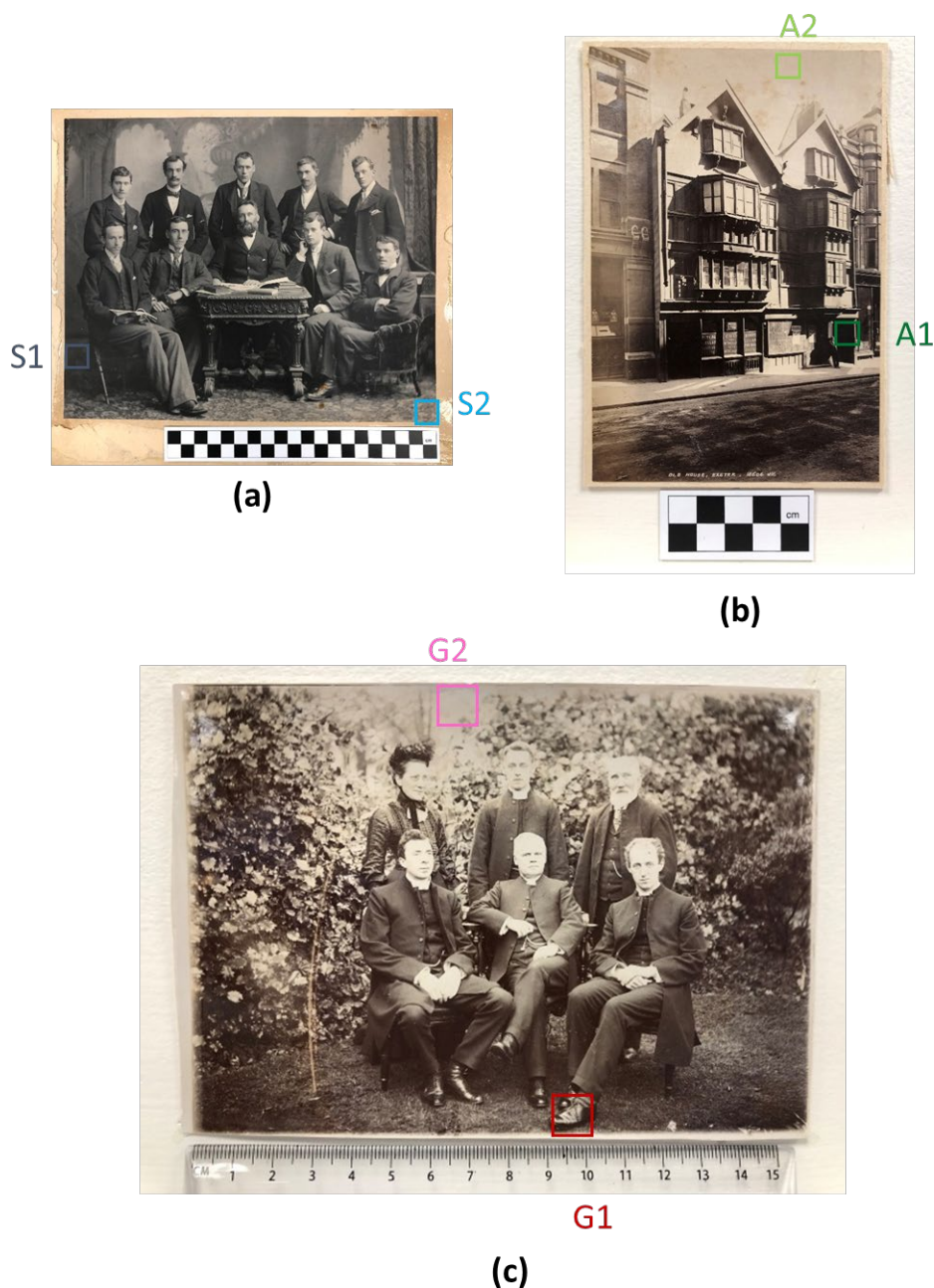


Figure 4.45 (a) Salt print, (b) albumen photograph, (c) silver gelatine photograph, with approximate sample locations of black and white areas marked. Black areas: S1, A1, G1; white areas: S2, A2, G2 (See Table 4.11).

positions recorded, and were mounted as cross-sections in 30 ml epoxy resin with liquid hardener (Cheng E Chemical Raw Material, Taiwan) in a ratio of 3:1. These cross-sections were polished with micromesh cloths (from 800 to 2000 mesh) before being investigated using a combination of confocal laser and light microscopy, micro ATR-FTIR spectroscopic imaging, and SEM-EDX. The cross-sectional morphologies of the photograph samples were examined using a LEXT OLS4000 (Olympus Inc., Japan) confocal microscope. The microscope was equipped with a white Light-Emitting Diode (LED) and a 405 nm semiconductor laser source. Light images of the samples were obtained using a single-panel charge-coupled device, while laser intensity images were captured using a photomultiplier. Micrographs of the samples were taken at a magnification of 50x and were displayed in both light mode and laser intensity mode. The micro ATR-FTIR spectroscopic measurements were conducted in the mid IR range from 3900 cm^{-1} to 900 cm^{-1} , at 8 cm^{-1} resolution and with 64 co-added scans. A JEM-7100F SEM (JEOL Ltd., Japan) operated at an accelerating voltage of 10 kV was utilised to analyse the layered structure of the photograph samples. Elemental distributions along the cross section of the samples were obtained by an X-Max 80mm² EDX (Oxford Instruments PLC., UK), which was attached to the SEM. The EDX was operated at the same accelerating voltage as the secondary electron mode, and the spectrum acquisition time was set at 120 seconds.

Table 4.11 Details of photograph samples

Sample (Colour)	Type	Name	Production Year	Provider
S1 (black)	Salt print	Ten Men in a Conference	1850	Imperial College Archives, UK
S2 (white)				
A1 (black)	Albumen photograph	Old House in Exeter	1880	Ephemeral Treasures, UK
A2 (white)				
G1 (black)	Silver gelatine photograph	Victorian Lady & Clergymen in the Garden	1900	Pictorial Past, Kilbowie Park Ltd, UK
G2 (white)				

K-means clustering with Matlab R2022b was implemented to process the spectral data to determine the natural grouping of the spectral data. Savitzky-Golay (SG) smoothing algorithm with 15 smoothing points was applied to the spectral data processed when using k-means clustering. Through the application of this unsupervised k-means clustering technique, clusters were formed that exhibited maximum variance among clusters while minimising variance within each cluster.

4.3.3 Surface characterisation

The IR spectra collected using the conventional ATR-FTIR spectroscopy on selected locations of the antique photographs as shown in Figure 4.45 are provided in Figure 4.46. To understand if there is any structural or chemical discrepancy between black and white areas, two locations of each sample were chosen to be investigated. In the FTIR spectra of the photograph samples, it appears that the spectral absorbance of the black areas is higher than that of white areas. These results may imply that the concentration of materials used in the photographs such as gelatine and albumen is higher in the black areas which contain more silver elements compared to the white areas. Nevertheless, additional measurements of twelve locations from two gelatine photographs and two albumen photographs indicate that no correlation was found between the amount of silver elements and the concentration of binders (albumen and gelatine). The results of these additional measurements are summarised in the Figure 6.4 in Appendices. The evident differences among the three types of antique photographs are that albumen photographs and gelatine photographs have absorbance peaks for amide I and amide II, while salt prints have peaks for cellulose in the FTIR spectra. The dominant spectral contribution from the salt print photograph is the substrate, while in the other samples, it is the binders. The absorbance peaks and their vibrational modes of the corresponding molecules in the three types of photographs are summarised in Table 4.12.

The result of XRF analysis on the surface of the unmounted photographs, as presented in Table 4.13, shows the presence of different concentrations of silver (Ag), which is the imaging element used for the black and white photography (Baines & Garrett, 1959). The XRF results obtained on the salt print sample reveal high counts of platinum (Pt). It should be noted that the penetration depth of the XRF beam can range from a few micrometres to over 50 micrometres (Ardebili et al., 2019), depending on the types of metal elements measured. Therefore, the XRF results may contain elemental information contributed from the substrate. The detection of Pt indicates that this salt print may have been toned with platinum. Platinum toning was performed with the intention of changing the print's colour and improving its longevity by substituting a

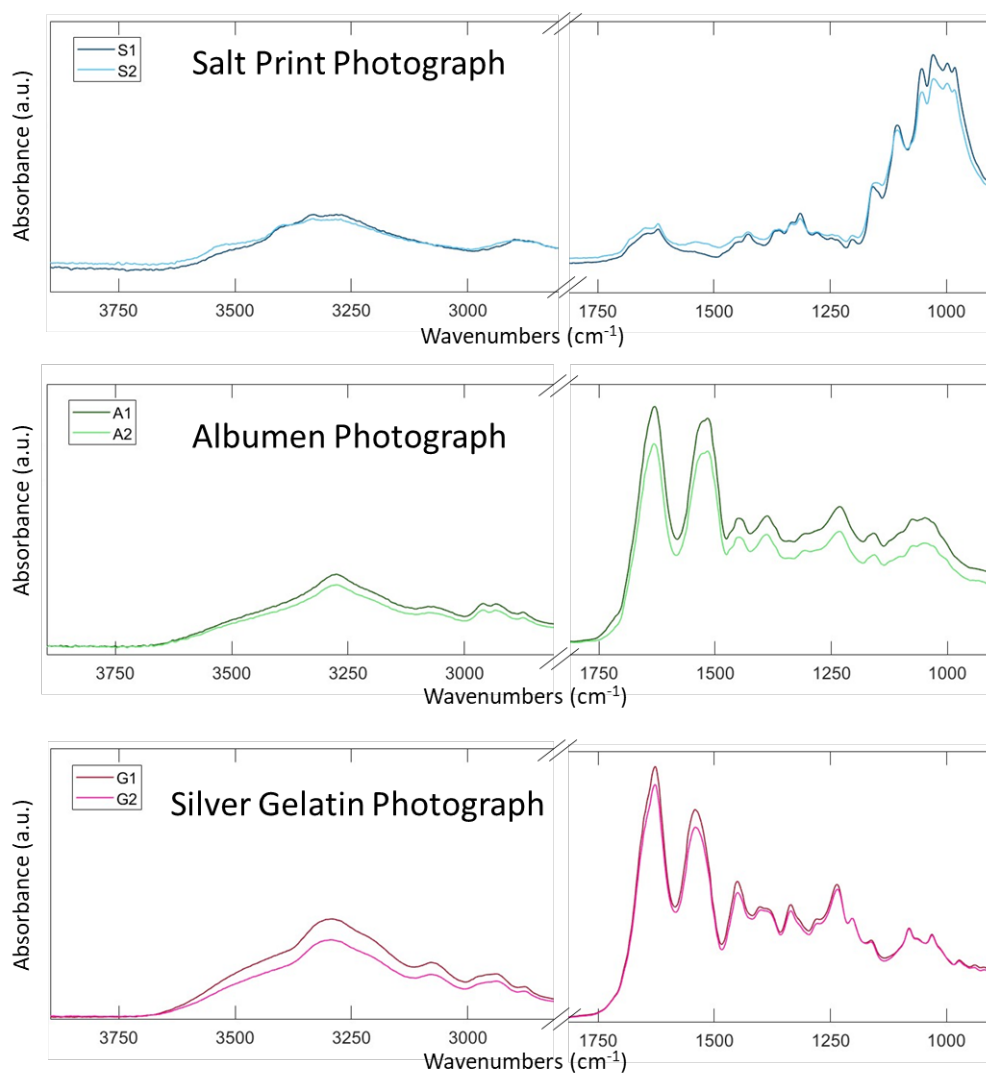


Figure 4.46 Conventional ATR-FTIR spectra of the detected areas on the antique photographs from Figure 4.45

Table 4.12 Band assignment in the spectral region 1000-1700 cm⁻¹

Spectral band assignment	Peak wavenumber (cm ⁻¹)			
	Salt print	Albumen photo	Silver photo	gelatine
C–OH stretching (Bhagia et al., 2022)	997			
C–O stretching (Barth, 2007; Bhagia et al., 2022; Jeevithan et al., 2014)	1024, 1053 and 1159	1030, 1076	1032, 1080	
Ring stretching (Bhagia et al., 2022)	1109			
CO–O–C anti-symmetric stretching (Barth, 2007; Jeevithan et al., 2014)		1158	1162	
C–OH bending (Bhagia et al., 2022)	1202			
C–OH in plane bending (Bhagia et al., 2022)	1230			
Amide III: N–H in-plane bending coupled with a C–N stretching (Barth, 2007; Jeevithan et al., 2014)		1232	1235	
C–H bending (Bhagia et al., 2022)	1280			
C–H ₂ wagging (Barth, 2007; Bhagia et al., 2022; Jeevithan et al., 2014)	1314	1335	1339	
C–OH in plane bending (Bhagia et al., 2022)	1334			
C–H bending (Bhagia et al., 2022)	1370			
C–H ₂ bending (Barth, 2007; Bhagia et al., 2022; Jeevithan et al., 2014)	1427	1450, 1388	1450, 1401/1387	
Amide II: N–H bending (40%–60%) coupled with a C–N (18%–40%) and C–C stretching vibrations (Barth, 2007; Jeevithan et al., 2014)		1515/1525	1541	
Amide I: C=O stretching (70%–85%) with C–N stretching (10%–20%) (Barth, 2007; Jeevithan et al., 2014)		1630	1627	
Conjugated C=O with absorbed water (Bhagia et al., 2022)	1646			

portion of the silver image (Walker & Namde, 2020). Traces of calcium (Ca) and iron (Fe) may be attributed from the paper substrate, which is in agreement with results from the literature (Stulik & Kaplan, 2013). The XRF analysis of the albumen photograph sample shows the presence of Ag and gold (Au). The results of the XRF analysis clearly indicate that gold toning was used for this albumen photograph. According to the literature (Stulik & Kaplan, 2013), gold toning was widely adopted as

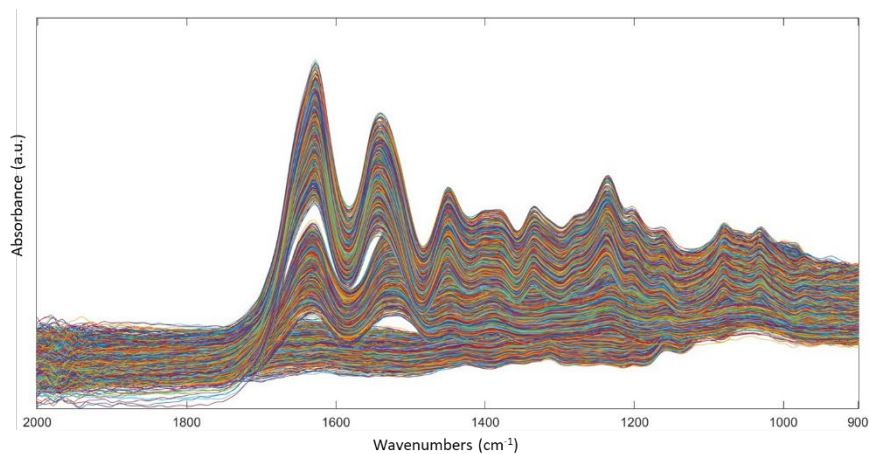
the primary approach for toning albumen photographs. Detection of sulfur (S) on the surface of the albumen photograph sample confirms the identification of albumen binder. Similar to the albumen photograph sample, Ag and S were also detected on the surface of the gelatine photograph sample, confirming the identification of silver pigment and gelatine binder, respectively. Furthermore, the XRF results of the silver gelatine photograph's surface indicate the presence of a baryta layer, as evidenced by the detection of barium (Ba) and strontium (Sr) and titanium (Ti) (Stulik & Kaplan, 2013). The baryta layer utilised in a gelatine photograph mainly contains barium sulfate (BaSO_4) with small amounts of strontium sulfate (SrSO_4) and titanium dioxide (TiO_2). It is worth noticing that the detection of S on the surface of the silver gelatine photograph is also attributed from the BaSO_4 and SrSO_4 composing the baryta layer.

Table 4.13 XRF results for chemical elemental characterisation on the surface of photographs

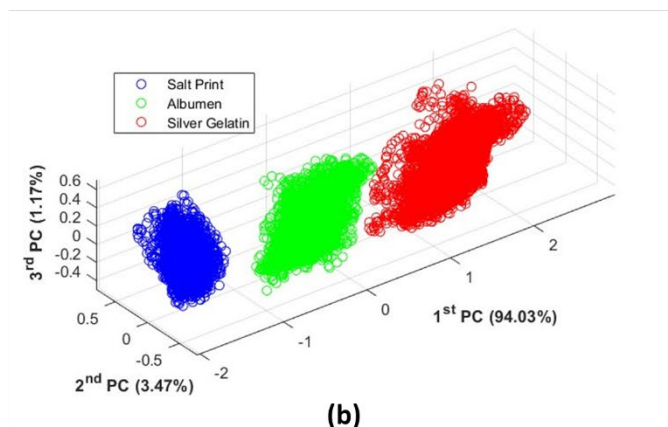
Salt print		Albumen photo		Silver gelatine photo	
Element	Amount (wt%)	Element	Amount (wt%)	Element	Amount (wt%)
Ca	41.892	Ca	30.826	S	38.316
Pt	21.019	S	24.346	Ba	35.772
Ag	20.675	Ag	20.054	Cl	6.126
Fe	13.134	Cl	8.954	Ag	5.496
Al	1.6	Fe	4.207	Al	4.939
Cu	1.087	Au	2.94	Si	2.639
Cl	0.592	Ce	1.817	Ca	1.861
		Ti	1.799	Ti	1.499
		Si	1.706	Sr	1.358

The 4096 IR spectra obtained simultaneously from one measurement using macro ATR-FTIR spectroscopic imaging for each sample are displayed in Figure 4.47a. Spectroscopic data between 900 cm^{-1} and 2000 cm^{-1} were selected for PCA analysis. The data are projected onto the first three principal components (PCs) that account for 94.03%, 3.47%, and 1.17% of the variance, respectively, as plotted in Figure 4.47b. In this PCA score plot, the scores are oriented primarily in the direction of PC1 with a range of -2.1 to 3.0, followed by PC2 with a range of -0.8 to 0.8 and PC3 with a range of -0.5 to 0.7. Spectroscopic data from three different types of photograph samples are well discriminated into the groups on this 3-dimensional plot. Important spectral

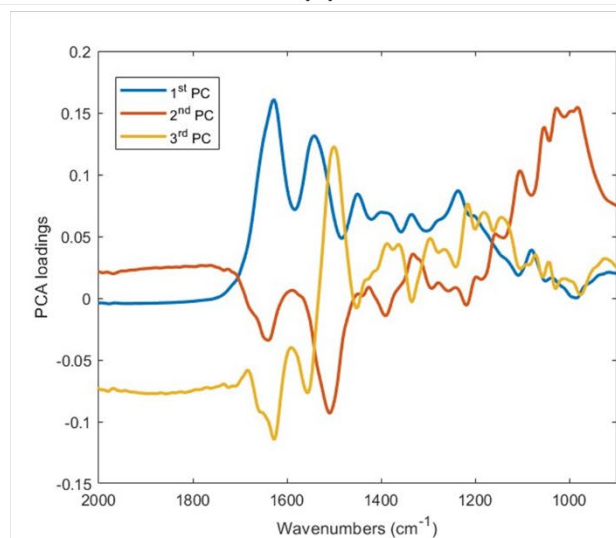
features are identified from the PCA loading plot, as indicated in Figure 4.47c. PC1 shows positive correlation of amide I and amide II bands, whereas PC2 shows positive correlation of cellulose bands such as C–OH stretching, C–O stretching, Ring



(a)



(b)



(c)

Figure 4.47 (a) The raw spectra of 4096 pixels each extracted from salt print, albumen photograph and silver gelatine photograph, and the (b) PCA score plot and (c) loading plot.

stretching and C–OH bending. PC1 and PC2 successfully distinguish albumen photograph and silver gelatine photograph from the salt print as shown in Figure 4.48. A close inspection of PC3 shows that the most prominent spectral feature is the loading peak at 1500 cm^{-1} , which is between the band of amide II and the band of CH_2 bending (at around 1450 cm^{-1}). PC3 coupled with PC1 can distinguish the albumen photograph

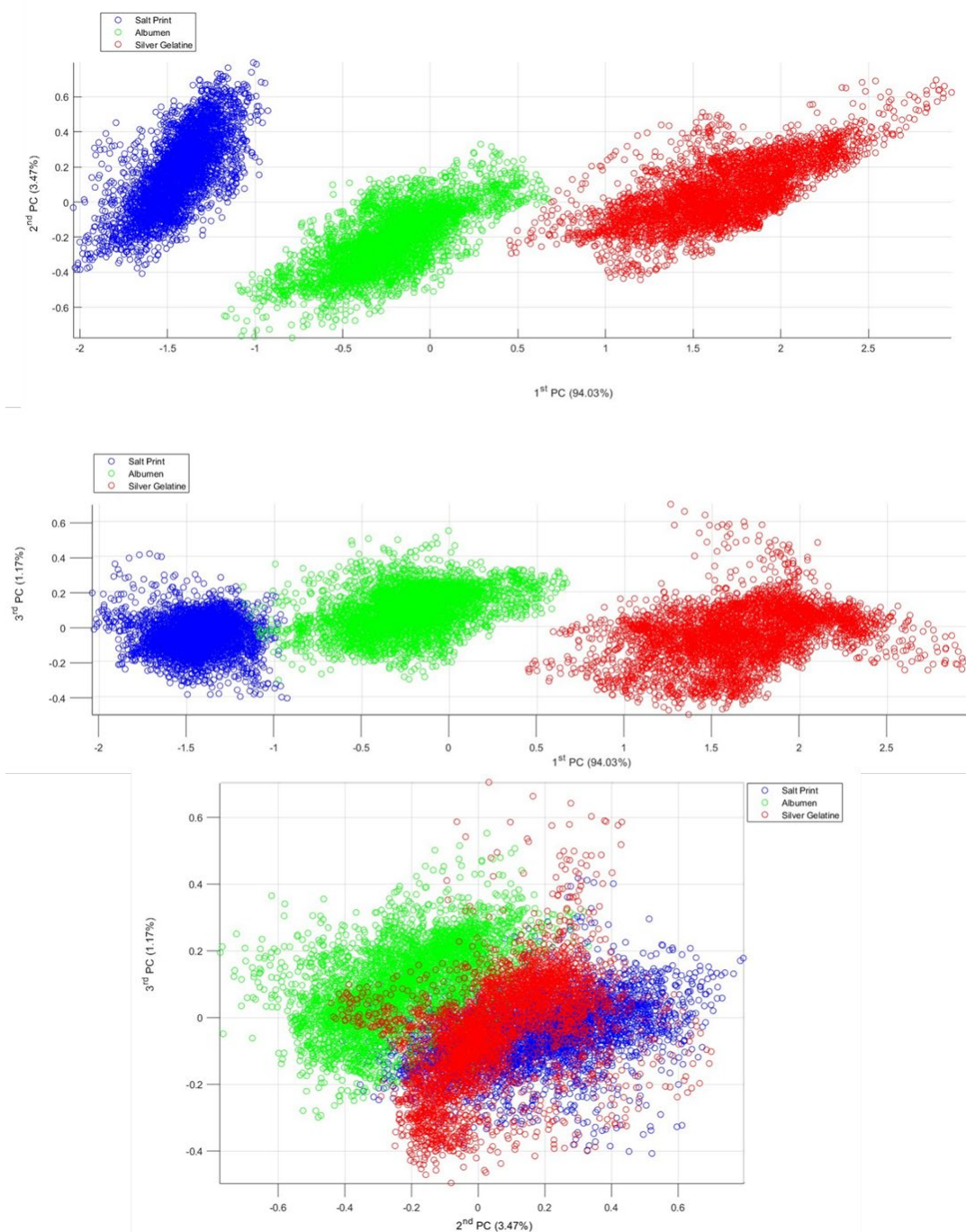


Figure 4.48 Two-dimensional PCA score plots: PC1 vs PC2 (upper row), PC1 vs PC3 (middle row), and PC2 vs PC3 (lower row)

and the silver gelatine photograph, as shown in Figure 4.48. The absorbance of the amide II band of the albumen photograph is at a lower wavenumber position at around 1515–1525 cm^{-1} compared to that of the silver gelatine photograph which is at a higher wavenumber position at 1541 cm^{-1} , as illustrated in Figure 4.46 and Table 4.12. Furthermore, the spectra of the albumen photograph show that the intensities of the two spectral bands of CH_2 bending at 1450 cm^{-1} and 1388 cm^{-1} are similar, while the spectra of the silver gelatine photograph show that the intensities of these spectral bands are apparently different, with the band at 1450 cm^{-1} higher than the band at 1387–1401 cm^{-1} . PC3 utilises these spectral features assisting in the distinction between the albumen photograph and silver gelatine photograph. This experiment employing macro ATR-FTIR imaging combined with PCA can be expanded in the future to investigate more samples with complex structures and manufacturing processes such as photographs varnished with beeswax, paraffin, shellac or collodion. This future work may establish a reliable and non-destructive framework on identification of black and white photographs that have similar appearance. Furthermore, this application has the potential to be entirely automated through the use of simple programming.

4.3.4 Cross-section characterisation

The confocal light and laser intensity micrographs of samples extracted from black areas of the three types of antique photographs are displayed in Figure 4.49. The micrographs show that salt print, albumen photograph and silver gelatine photograph are 1-layered, 2-layered and 3-layered structures, respectively. To further investigate these different structural features, the same samples of these three types of antique photographs were examined using ATR-FTIR spectroscopic imaging and SEM-EDX. The concentrations of the proteinaceous layers including albumen and gelatine layers should not be related to the amounts of Ag regarding whether the sample is a black or white end, as suggested by our data in Section 4.3.3. Therefore, in this section only the results of the black area samples are shown, with the results of the white area samples presented in Figure 6.5–6.7 in Appendices.

ATR-FTIR spectroscopic imaging as shown in Figure 4.50 illustrates distributions of organic components of the cross-sectional samples. Firstly, chemical images of the embedding resin were produced by spatially plotting the integrated absorbance of the bands between 1240–1310 cm^{-1} for locating the boundaries of the cross sections of the samples. The spectra extracted from the resin areas show characteristic absorptions of $\nu(\text{C}-\text{O}-\text{C})$ and $\nu(\text{C}-\text{C})$ of the aromatic ring and at around 1240 and 1580 cm^{-1} , respectively (Ramírez-Herrera et al., 2021), as shown in the spectra of p1, p3 and p6. Secondly, chemical images of the paper substrates of the three antique photographs were obtained by plotting the integrated absorbance between 950 and 1180 cm^{-1} , including absorptions of $\nu(\text{C}-\text{O})$ and aromatic ring vibration from cellulose as indicated in Table 4.12. These absorptions of cellulose are illustrated in the spectra p2, p5 and p9, which were extracted from the paper substrates of the three types of antique photograph. Thirdly, proteinaceous binders are present in albumen and gelatine photographs, and their chemical images were produced using absorbance of

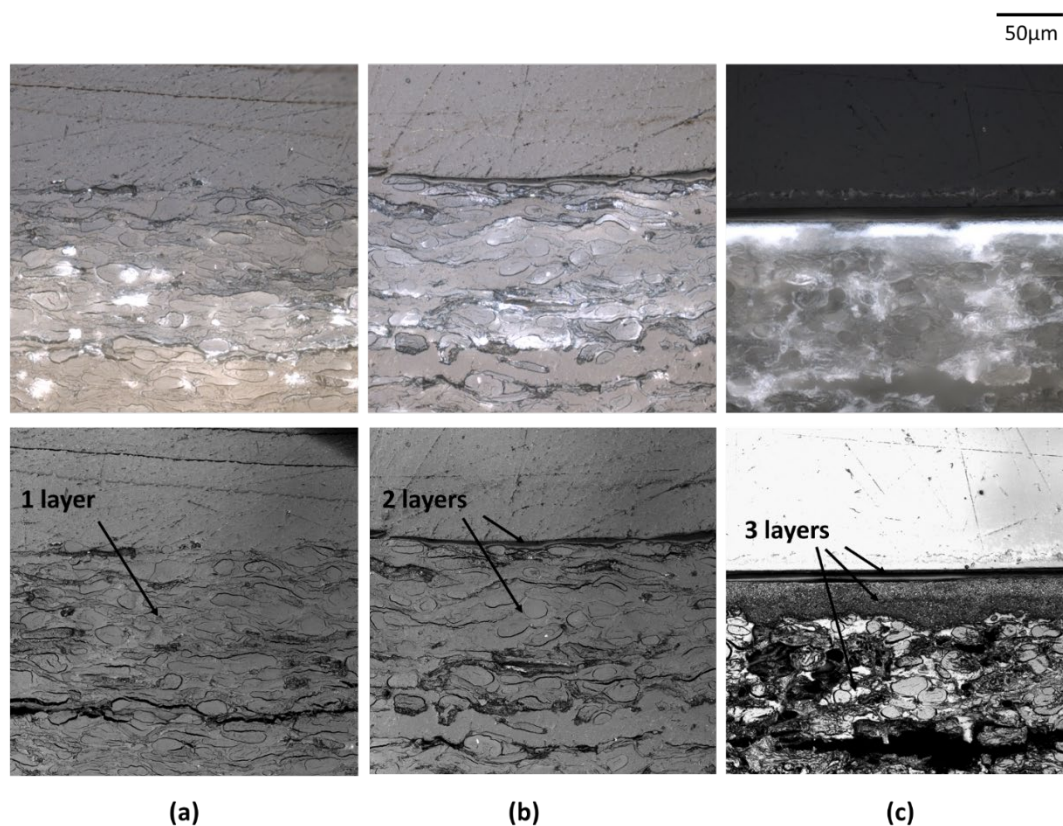


Figure 4.49 Confocal light (upper row) and laser intensity (lower row) micrographs (50 $\times$) of (a) salt print, (b) albumen photograph and (c) silver gelatine photograph

amide I in the wavenumber region of $1600\text{--}1680\text{ cm}^{-1}$. Spectra of p4 and p7 extracted from these proteinaceous binder layers identify albumen and gelatine, respectively. In the cross-section of silver gelatine photograph, a baryta layer composed of barium sulfate (BaSO_4) which is underneath the gelatine layer was imaged by plotting the integrated absorbance between $1170\text{--}1220\text{ cm}^{-1}$, including three spectral bands at

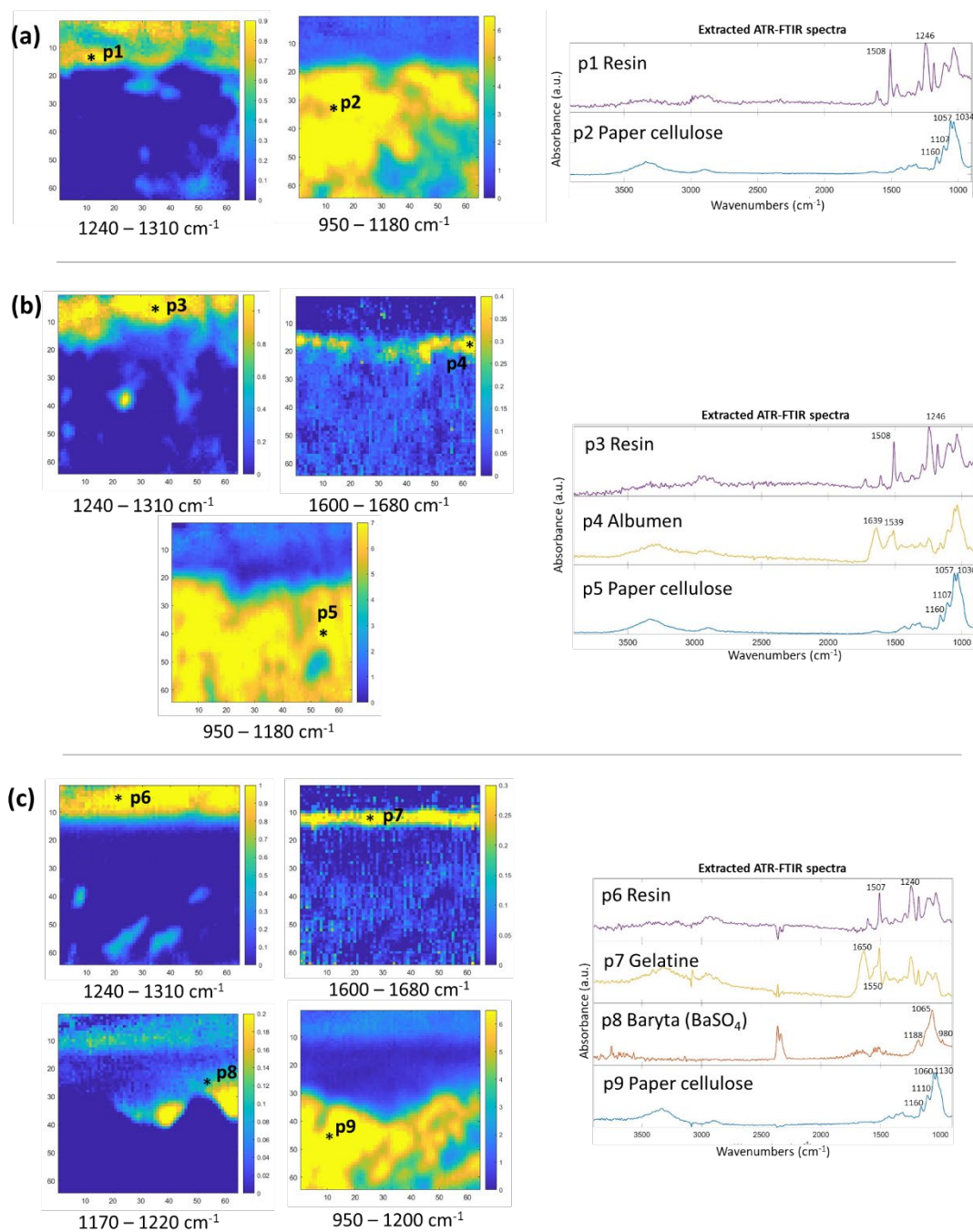


Figure 4.50 Chemical images of cross-sectional samples of (a) salt print, (b) albumen photograph and (c) silver gelatine photograph. The FTIR spectra extracted from 9 pixels of the samples are provided next to the chemical images. The size of each image is $70 \times 70\text{ }\mu\text{m}^2$.

980 cm^{-1} , 1065 cm^{-1} , 1188 cm^{-1} assigned to $\nu(\text{SO}_4^{2-})$, as shown in the spectrum p8. The thickness of the baryta layer of the silver gelatine photograph is around 30 μm . It is worth noting that the album layer displays discontinuity while the gelatine layer appears more complete without any breaks. This feature can also be observed from the results of the white areas of the samples (Figure 6.5 in Appendices). The micro ATR-FTIR imaging results of the cross-sectional samples are in line with the previous research (Ricci et al., 2007) that the typical surface of albumen photographs exhibit cracking, which is the most typical signature of albumen photographs (Messier & Vitale, 1993; Stulik & Kaplan, 2013). The occurrence of cracking in albumen photographs might be attributed to excessive physical handling and manipulation, such as aqueous treatment that aimed to decrease photograph yellowing (Messier & Vitale, 1994). Low humidity may worsen the cracking of albumen photographs. As a result, remote moistening and humidity control have been guided methods for preserving albumen photographs (Lavédrine, 2003). The silver gelatine photograph sample does not show the presence of cracking, possibly because of the baryta support that prevents physical damages on the silver gelatine photograph.

To categorise the ATR-FTIR spectroscopic imaging data with similar features of the cross-sectional samples, unsupervised k-means clustering is employed. Through an iterative algorithm, cluster centres are randomly assigned until distinct boundaries between clusters are obtained. This method assigns a class membership to each spectrum. Based on the layered structure features, the numbers of clusters designated are 2, 3, 4 for the salt print, albumen photograph and silver gelatine photographs, respectively, to match the regions intended for identification. Figure 4.51 displays pseudo-colour images organised in 2-dimensional spatial coordinates, where each cluster is visually represented by a colour. Through this representation, the layers present in each antique photograph sample can be clearly defined.

For additional information about the layered structures, SEM-EDX elemental mapping was performed on the cross-section samples after investigated with ATR-FTIR spectroscopic imaging. SEM images and individual element maps are shown in Figure 4.52. For each SEM image, a red dotted line was used to mark the boundary

between embedding resin and the sample. Lines with different colours including green and blue were also used to mark the boundaries between different layers for albumen sample and silver gelatine sample. The results of SEM-EDX can be supplemented to the XRF results to discuss the chemical elements detected in the antique photographs.

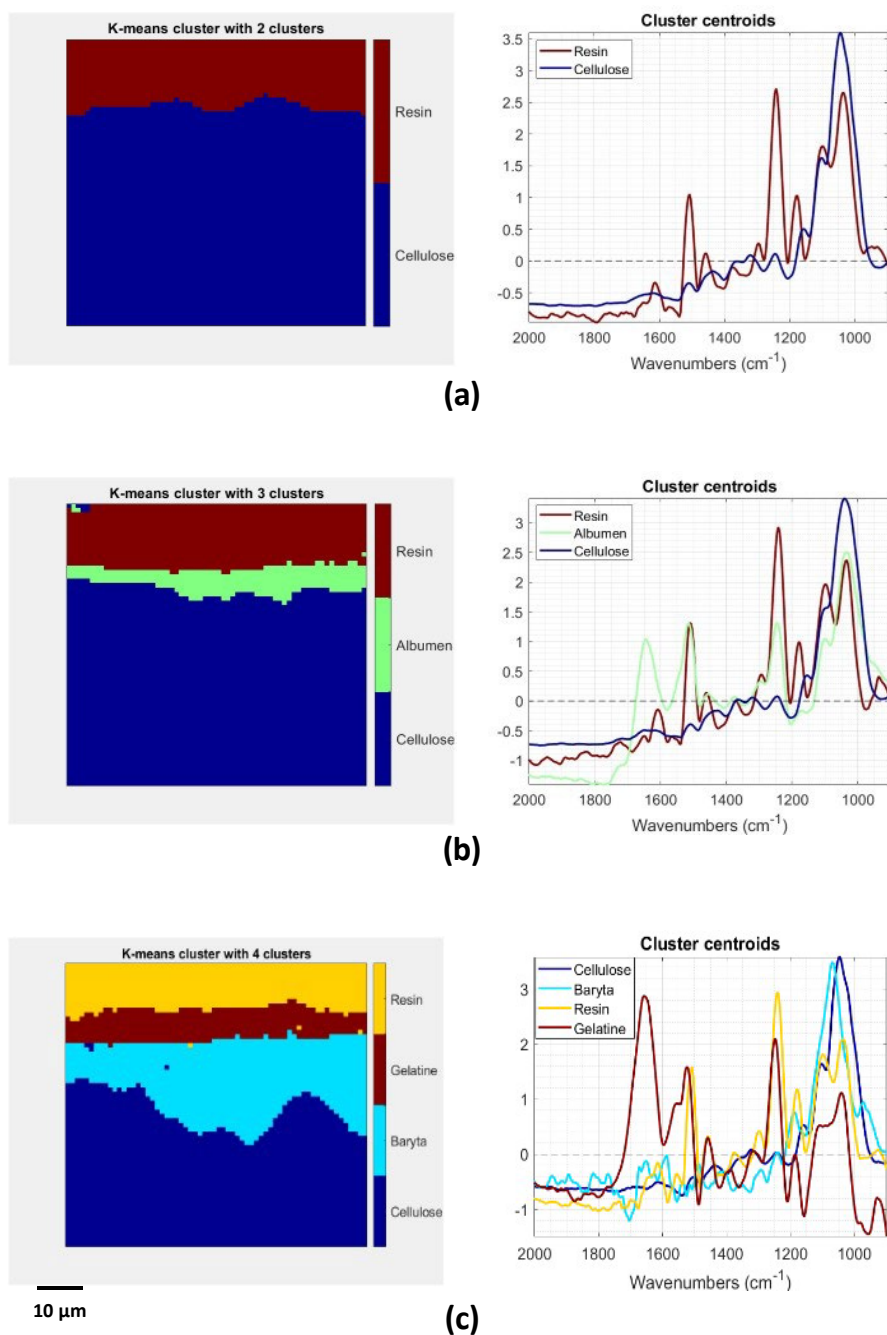


Figure 4.51 Left: False colour k-means clustering images of cross-sectional samples of (a) salt print, (b) albumen photograph and (c) silver gelatine photograph obtained by mapping from stitched images. Each of the chemical images has a size of $70 \times 70 \mu\text{m}^2$. Right: Mean spectra for each cluster shown for each spectral region

XRF results can only provide the chemical element information for antique photographs as a whole, whereas SEM-EDX results are capable of visually displaying the distribution of these elements in the stratigraphic samples of antique photographs. Overall, the SEM-EDX results are in good agreement with the XRF results, except that K and Si detected in the salt print and Al detected in the albumen photograph using SEM-EDX were not detected in the XRF results. This discrepancy may be due to the limitations of XRF in detecting light elements. The presence of Al and Si detected using SEM-EDX and/or XRF suggests that fine particles of kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), a commonly used additive in the production of glossy paper (Bundy & Ishley, 1991), can be found in the paper substrates of the three antique photograph samples. Figure 4.52a shows the elemental maps of salt print. The embedding resin contain Cl and Pt was deposited on the non-conductive sample for elemental mapping, so Cl and Pt were detected in the whole measured areas, including the embedding resin areas. Other elements such as Ag, Ca, Fe and K appear to be throughout the paper substrate of the sample. Figure 4.52b shows the elemental maps of albumen photograph. Ag and S were detected abundantly in the albumen layer. The presence of S should be attributed from albumen as the binder. The distribution of Ag and S suggests that Ag be localised in the albumen layer. Figure 4.52c shows the elemental maps of silver gelatine photograph. The presence of Ba and S confirmed the baryta layer (BaSO_4). It should be noted that all the elements detected in the silver gelatine photograph are at high concentration in the baryta layer. The gelatine layer which is highlighted with a dotted red line and a dotted green line shows high amount of Ag, while it shows no noticeable concentration of S which is the main component of gelatine. This outcome can be attributed to the considerably high signal intensity of S in the baryta layer, posing challenges in mapping the comparatively weaker S signal in the gelatine layer in relation to the baryta layer. In addition, when comparing the Ag maps of the black and white areas (Figure 6.7 in the Appendices) of the silver gelatine photograph, it is evident that the gelatine layer in the white area exhibits a lower Ag signal. The observed difference in Ag concentration within the gelatine layers between the black and white areas is expected, considering that Ag is the element responsible for

imparting the characteristic colour to silver gelatine photographs. The elemental maps of Ag and Cl in the silver gelatine photograph indicate the utilisation of silver chloride (AgCl) in the emulsion during its production. Upon exposure to light, a chemical reduction process occurred, leading to the formation of Ag pigment from the AgCl

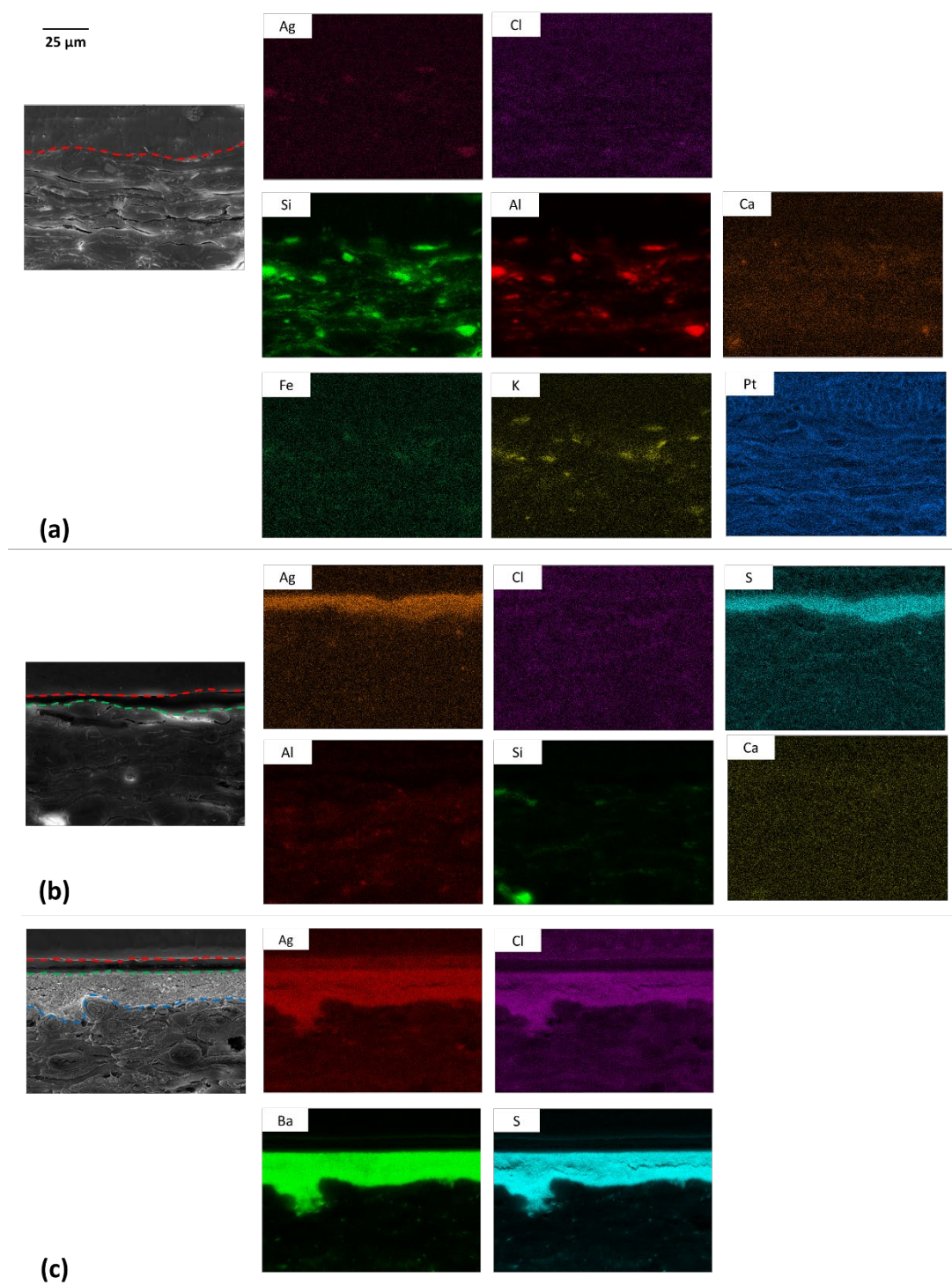


Figure 4.52 SEM images and EDX elemental maps of cross-sectional samples of (a) salt print, (b) albumen photograph and (c) silver gelatine photograph.

within the gelatine layer. Subsequently, the unexposed AgCl was removed from the gelatine layer. Our SEM-EDX results show that AgCl was absorbed within the baryta layer and was not totally removed from the baryta layer.

4.3.5 Summary

In this section, both macro and micro ATR-FTIR spectroscopy, along with other non-destructive techniques such as confocal light and laser microscopy, XRF, and SEM-EDX, were employed to investigate three types of black and white antique photographs: salt prints, albumen photographs, and silver gelatine photographs. It is the first time that macro ATR-FTIR imaging combined with PCA was utilised for differentiating antique photographs into groups. Furthermore, the application of micro ATR-FTIR imaging was extended from albumen photographs to encompass salt prints and silver gelatine photographs. K-means clustering, another chemometric tool utilised in this study, was applied to analyse micro ATR-FTIR spectroscopic data obtained from cross-sectional samples, allowing the characterisation of different layers within each antique photograph, as observed through confocal light and laser microscopy. Micrographs and micro ATR-FTIR images disclosed that salt prints, albumen photographs, and silver gelatine photographs exhibit 1-layered (paper cellulose), 2-layered (albumen and paper cellulose), and 3-layered (gelatine, baryte, and paper cellulose) structures, respectively. XRF was employed to gather elemental information from the surface of these three photographs, and SEM-EDX elemental mapping was utilised to gain further insights into the elemental distribution in the cross-sections. The elemental data, in conjunction with ATR-FTIR spectroscopic imaging data, are essential for in-depth investigations of antique photographs with complex structures.

4.4 Depth profiling of antique photographs using macro and micro ATR-FTIR spectroscopic imaging

4.4.1 Background

Using an ATR crystal for FTIR spectroscopic imaging provides a higher spatial resolution in comparison to the transmission mode (Kazarian & Chan, 2010a). This proves especially beneficial when examining small areas of interest within the sample. For instance, when analysing cross-sectional samples of oil paintings (Liu et al., 2023; Spring et al., 2008) and antique photographs (Ricci et al., 2007), it becomes possible to investigate the distribution of chemical components within different layers in detail. Moreover, the applicability of ATR-FTIR spectroscopic imaging has also been demonstrated in examining the crystallisation kinetics of infrared-active reaction products originating from conservation treatments administered to cultural heritage stone objects using water-based solutions (Possenti et al., 2021b). This is attributed to the shallow penetration depth of ATR, which mitigates the potential interference from water spectra (Song & Kazarian, 2019). Nevertheless, in an ATR measurement, anomalous dispersion can occur, resulting in spectral distortions and band shifts, as mentioned in Section 2.2.2. This is particularly significant for samples with a high refractive index.

Changing the angle of incidence of the IR light on the surface of IRE provides the means to probe different depths in the sample, as discussed in Section 2.2.2, thus enabling the acquisition of 3-dimensional (3D) profiling information. This 3D profiling approach using variable angles of incidence has been demonstrated couple with macro and micro ATR-FTIR spectroscopic imaging on polymer (Chan & Kazarian, 2007; Frosch et al., 2010; Wrobel et al., 2015) and biological samples (Chan & Kazarian, 2007; Song & Kazarian, 2019). An additional crucial aspect is that by increasing the angle of incidence, it becomes possible to decrease or even prevent spectral distortions and band shifts caused by anomalous dispersion, as elucidated in

preceding studies (Kazarian & Chan, 2013; Tay & Kazarian, 2009). These findings shed light on the potential of extending this approach of variable angles to examine the structure and exterior conditions of cultural heritage objects, offering potential applications in heritage conservation. This section explores the utilisation of micro and macro ATR-FTIR spectroscopic imaging techniques using variable angles to investigate the surface of antique photographs at different probing depths. Additionally, it aims to analyse the acquired ATR-FTIR images qualitatively and semi-quantitatively.

4.4.2 Experimental setting up and design of the apertures

The materials under investigation encompass three distinct types of antique photographs. The detailed characterisation of both surface and cross-sectional aspects of these antique photographs can be found in Section 4.3. For the current study, six specific locations, encompassing black and white regions across the three photographs, as indicted in Figure 4.45, were selected for comprehensive analysis through micro and macro spectroscopic imaging, employing variable angles of incidence.

The micro ATR-FTIR spectroscopic imaging system encompasses a Cary 620 FTIR microscope, coupled with an Agilent Varian 670 spectrometer (Agilent Technologies, Inc., USA), was employed. The microscope was equipped with a slide-on ATR accessory attached to the 15 $\times$ -Cassegrain objective. A germanium (Ge) crystal with a refractive index of 4 was utilised as the Internal Reflection Element (IRE) for ATR. A liquid nitrogen cooled 64 $\times$ 64-pixel Focal Plane Array (FPA) detector (Santa Barbara Focalplane, USA.) was employed for the simultaneous acquisition of 4096 FTIR spectral data. All measurements were executed within the mid IR range, spanning 3900 cm^{-1} to 900 cm^{-1} , at 8 cm^{-1} resolution and with 64 co-added scans. The estimated size of the chemical images acquired using this setup is 70 $\times$ 70 μm^2 . For the macro ATR-FTIR spectroscopic depth profiling experiments, a Tensor FTIR spectrometer (Bruker Corp., USA) in conjunction with a 64 $\times$ 64 Focal Plane Array (FPA) detector (Santa Barbara Focalplane, USA) and a diamond Golden Gate™ ATR accessory

(Specac, UK), was utilised. This accessory has a Field Of View (FOV) measuring 0.6 mm × 0.55 mm, featuring a spatial resolution of ca. 10–15 μm , and enables the simultaneous capture of 4096 ATR-FTIR spectra. The macro ATR-FTIR spectral data were obtained in the mid IR range from 3900 cm^{-1} to 900 cm^{-1} , at 8 cm^{-1} resolution and with 64 co-added scans. Principal Component Analysis (PCA) was then applied on the 4096 ATR-FTIR spectral data of each sample for dimensionality reduction processed with Matlab R2022b (MathWorks, Inc., USA). PCA analysis was performed by projecting the macro ATR-FTIR spectral data onto a PCA score plot. The first Principal Component (PC) elucidated the majority of data variance, while the second PC captured the remaining variance. These scores, denoting the projection of ATR-FTIR spectra onto the PCs, were graphed to validate disparities among the spectral data.

Three apertures designed by Wrobel et al. (Wrobel et al., 2015), each with a circular slit on the illumination side, were used to explore multiple depths of penetration into the sample for the micro ATR-FTIR spectroscopic depth profiling study. The width of the circular slit was consistently set at 3 mm. These apertures were constructed from 2 mm thick transparent acrylic, coated with 0.5 mm white paper, as depicted in Figure 6.8 in the Appendices. It is important to note that a portion of the IR light is blocked when an aperture is inserted, leading to a significant reduction in the signal-to-noise ratio. As a result, a circular shape was chosen for the apertures to maximise the amount of light passing through and thus achieve a reasonable signal-to-noise ratio. The primary function of these apertures is to select a portion of the cone of IR light entering the crystal, with the design ensuring that only part of the light on the illumination side is blocked. The collection side of the objective remained unobstructed, as illustrated in Figure 4.53a. The set-up of the apertures positioned between the Ge accessory and the objective is depicted in Figure 4.53b.

The apertures employed in the macro ATR-FTIR spectroscopic depth profiling study were initially designed by Chan (Chan et al., 2008), and later by Frosch (Frosch et al., 2010) and Vichi (Vichi, 2018). Each of these apertures consists of either a circular or a square hole located at varying distances from the central point of the illuminating

lens of the Golden Gate, as depicted in Figure 4.54. This design enables the selection of the angle of incidence through a single circular or square hole. Two sets of apertures are available: line-apertures and rotating-apertures. Each of the four line-apertures features a square hole measuring 5x5 mm² and can be positioned on the illuminating lens with the square hole vertically aligned with the lens's centre, referred to as the first position (e.g., A1, A2, A3). By rotating the aperture by 180 degrees, it is placed in the opposite orientation (i.e., A7, A6, A5). This repositioning limits a different portion of the IR light passing through the lens, thereby facilitating the selection of a second angle of incidence, as shown in Figure 4.54a. This approach (Vichi, 2018) to preparing apertures offers significant flexibility in terms of the number of angles and, consequently, penetration depths that can be achieved. The rotating-aperture is comprised of two parts that fit one over the other. The bottom part of the aperture

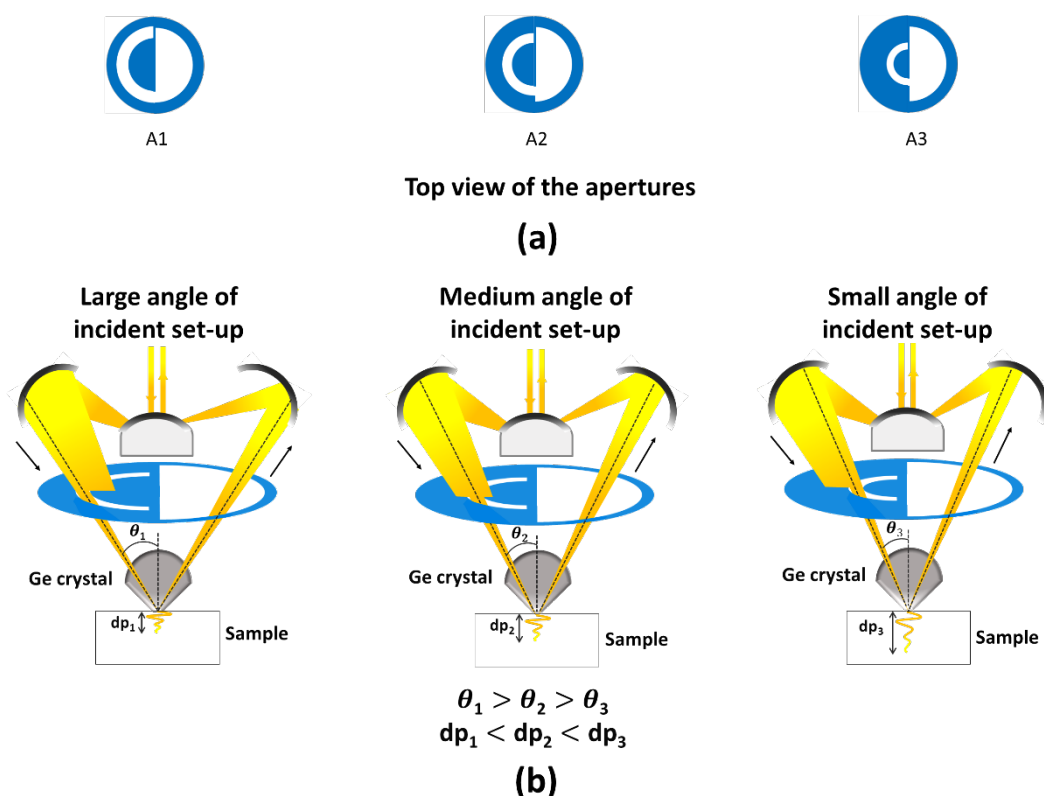


Figure 4.53 Schematic depiction illustrating the placement of three custom-designed apertures in the micro ATR-FTIR setup to investigate sample penetration depths (dp) through the adjustment of incident angles (θ) for the IR light beam, adapted from (Wrobel et al., 2015) with the permission from Applied Spectroscopy. The apertures partially obstruct the illumination side of the light cone, while the collection side remains unobstructed. Please note that this depiction is not to scale.

features four circular holes with a diameter of 4.5 mm, positioned at various locations relative to the lens's centre. The top part of the aperture has a single circular hole, which, through a simple manual rotation, allows selection of one of the four holes on the bottom part of the aperture, as shown in Figure 4.54a. Both the line- and rotating-apertures were fabricated by laser cutting 0.5 mm thick cardboard. The set-up of the apertures positioned on illuminating lens of the Golden Gate is depicted in Figure 4.54b.

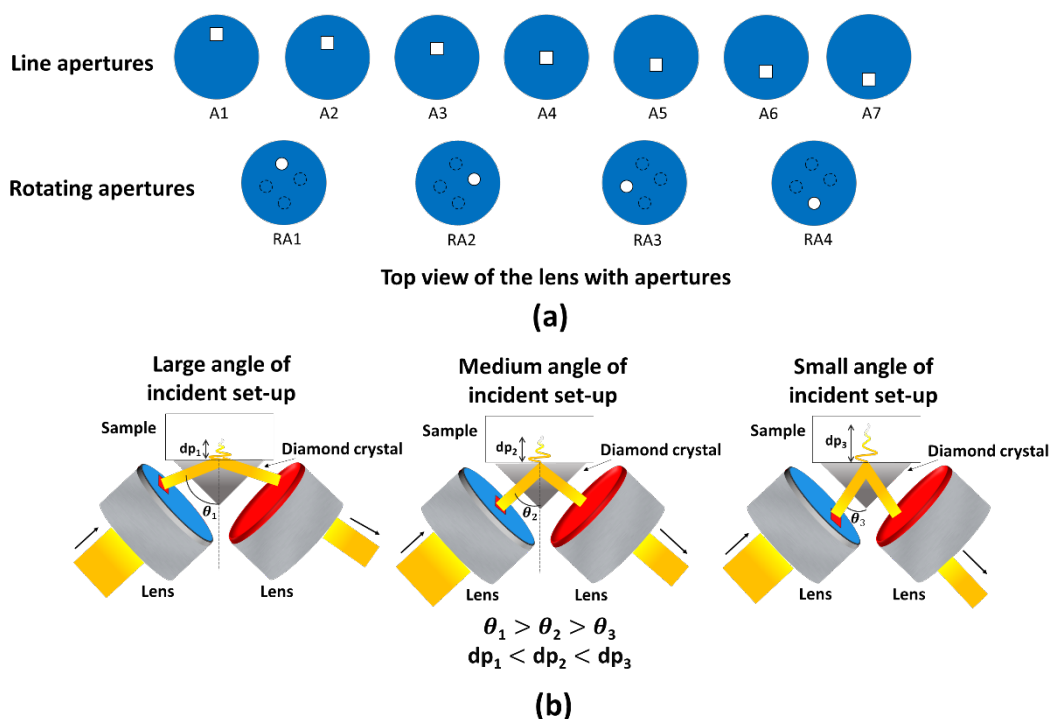


Figure 4.54 Schematic depiction illustrating the positioning of line- and rotating-apertures within the macro ATR-FTIR setup for the exploration of sample penetration depths (dp) by adjusting the incident angles (θ) of the IR light beam. The apertures partially block the illuminating lens, located on the left (depicted in blue), while the collection and focusing lens is situated on the right (depicted in red).

4.4.3 Calibration of the angles of incidence of the IR light

The calibration of the angles of incidence of the IR light beam with apertures was performed by measuring deionised water, used as a reference sample. To determine the angles of incidence, the concept of effective path length or effective thickness, denoted as de and discussed in Section 2.2.2, was applied. The value of de is

influenced by the polarisation of the light beam, the angle of incidence, and the refractive indices of the IRE (n_1) and the sample (n_2). de , as defined in Equation 2.10–2.12, quantifies the sample thickness required to produce an equivalent absorbance in a theoretical transmission experiment (Kazarian & Chan, 2010a). By applying Beer-Lambert's Law (Equation 2.7), which states that de is directly proportional to the absorbance of a spectral band obtained through ATR measurements, the value of de can be determined. In this calibration process, where these equations were used, n_1 represents the refractive index of the IRE, such as Ge ($n_1 = 4.00$) or diamond ($n_1 = 2.42$), and n_2 is the refractive index of the sample, such as water ($n_2 = 1.33$).

Figure 4.55a displays the calibration results of FTIR spectra acquired through the averaging of 4096 pixels from a 64×64-FPA in the micro ATR-FTIR spectroscopic imaging system equipped with a Ge crystal. These spectra were obtained with three apertures (A1–A3), as well as without an aperture (denoted as A0). The angles of incidence for each aperture were subsequently calculated using the absorbance band at 1640 cm^{-1} , which is attributed to the bending mode of H_2O . In this context, the effective path length (de) for each aperture was determined by dividing the absorbance values of the band at 1640 cm^{-1} (A) by the molar absorptivity (ε) and the molar concentration (c) of water, in accordance with Lambert-Beer's law, as expressed in Equation 2.7. The values of ε and c of water were obtained from the literature (Venjaminov & Prendergast, 1997), ε of water = $21.8\text{ M}^{-1}\text{cm}^{-1}$ and c of water = 55.5 M . Once the values of de were determined, calculations were made for the angles of incidence (θ) for the three apertures (A1–A3), as well as for the configuration without an aperture (A0), by using Equation 2.10–2.12. Furthermore, values for the depth of penetration (dp) at 1640 cm^{-1} for deionised water were determined by using Equation 2.9. Table 4.14 summarised the measured absorbance at 1640 cm^{-1} (A) and the estimated de , θ , and dp .

Figure 4.55b illustrates the correlation between the depth of penetration (dp) and wavenumbers spanning from 900 cm^{-1} to 4000 cm^{-1} in water ($n = 1.33$) using different apertures. It is evident that the dp values demonstrate an increase of approximately $1\text{--}1.5\text{ }\mu\text{m}$ when comparing 900 cm^{-1} to 4000 cm^{-1} , depending on the angle of incidence

under examination. As stated in Section 2.2.2, when $\frac{n_{21} \cos \theta}{(1-n_{21}^2)} \left(1 + \frac{2 \sin^2 \theta - n_{21}^2}{(1+n_{21}^2) \sin^2 \theta - n_{21}^2}\right)$ approaches 1, regardless of the wavelength of the illuminating beam, the value of dp converges toward that of de . Figure 4.55c illustrates the curves of dp and de values in water as functions of wavenumbers and angles of incidence, demonstrating that these values converge at approximately 32°.

Table 4.14 Summary of the calibration of the angles of incidence, along with the measured absorbance of water at 1640 cm⁻¹, calculated effective path lengths, and calculated depths of penetration for the FTIR microscope (Agilent) in micro ATR mode with the same IRE (Ge) using with three apertures and without an aperture

	Absorbance at 1640 cm ⁻¹	Estimated Effective path length (μm)	Estimated Angle of incidence (°)	Estimated Depth of penetration (μm)
A1	0.053	0.44	36.6	0.48
A2	0.070	0.58	32	0.57
A0	0.067	0.55	32.5	0.56
A3	0.093	0.77	28.4	0.69

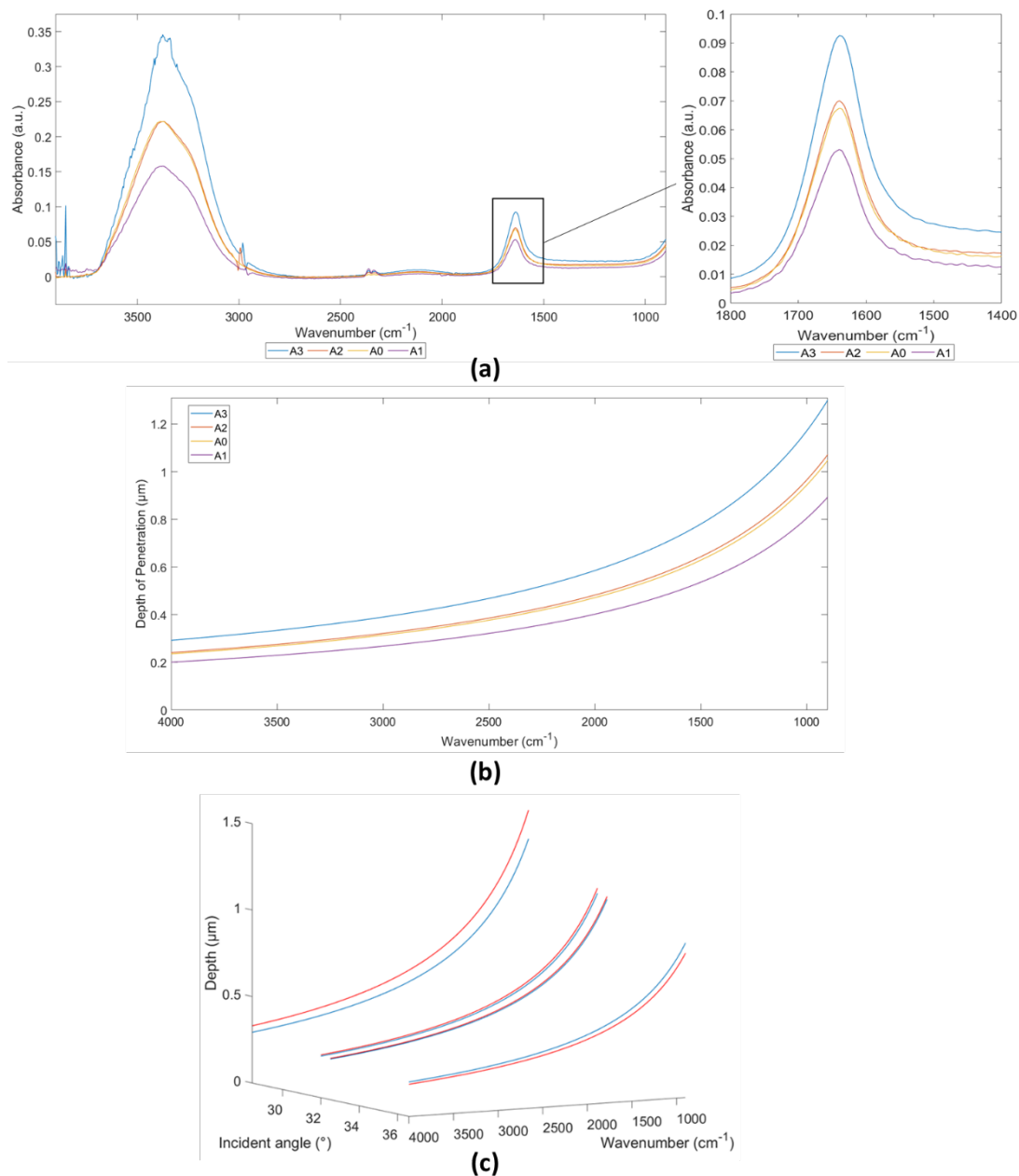


Figure 4.55 Results of calibrating the apertures using water for micro ATR-FTIR spectroscopic imaging with the same IRE (Ge). (a) FTIR spectra obtained with three apertures and without an aperture, acquired by averaging the 4096 pixels of the FPA array, considering FTIR spectra in the region of 1400–1800 cm^{-1} . (b) Plot of the calculated depths of penetration against wavenumbers for various angles of incidence. (c) Plot of depths into water as a function of angles of incidence and wavenumbers, where the red line represents de , and the blue line represents dp .

Following the aforementioned procedure, absorbance values of the band at 1640 cm^{-1} , corresponding to the bending mode of H_2O , were used to determine the angles of incidence for line-apertures and rotating-apertures in the macro ATR-FTIR spectroscopic imaging system equipped with a diamond crystal, as illustrated in Figure 4.56 (line-apertures) and Figure 4.57 (rotating-apertures). The measured absorbance at 1640 cm^{-1} (A) and the estimated de , θ , and dp values are summarised in Table 4.15 (line-apertures) and Table 4.16 (rotating-apertures). It is noteworthy that the estimated angles of incidence with water, without an aperture, from the two sets of measurements for line-apertures and rotating-apertures show a difference of 0.1° , as indicated by A0 in Table 4.15 and RA0 in Table 4.16. This suggests that the accessory maintained consistent alignment during calibration, demonstrating the reliability of the calibration method. The differences in dp and de values in water decrease with increasing angles of incidence, as illustrated in Figure 4.56c.

Table 4.15 Summary of the calibration of the angles of incidence, along with the measured absorbance of water at 1640 cm^{-1} , calculated effective path lengths, and calculated depths of penetration for the macro ATR-FTIR spectroscopic imaging system equipped with a diamond crystal in the ATR accessory of the Imaging Golden Gate (Specac, UK), using with seven line-apertures and without an aperture

	Absorbance at 1640 cm^{-1}	Estimated Effective pathlength (μm)	Estimated Angle of incidence ($^\circ$)	Estimated Depth of penetration (μm)
A1	0.1381	1.14	49.3	0.77
A2	0.14453	1.19	48.3	0.79
A3	0.1643	1.35	46.5	0.85
A4	0.1847	1.52	44.8	0.91
A0	0.19136	1.58	44.2	0.94
A5	0.217	1.79	42.7	1.01
A6	0.2506	2.07	41	1.12
A7	0.2734	2.25	40.3	1.17

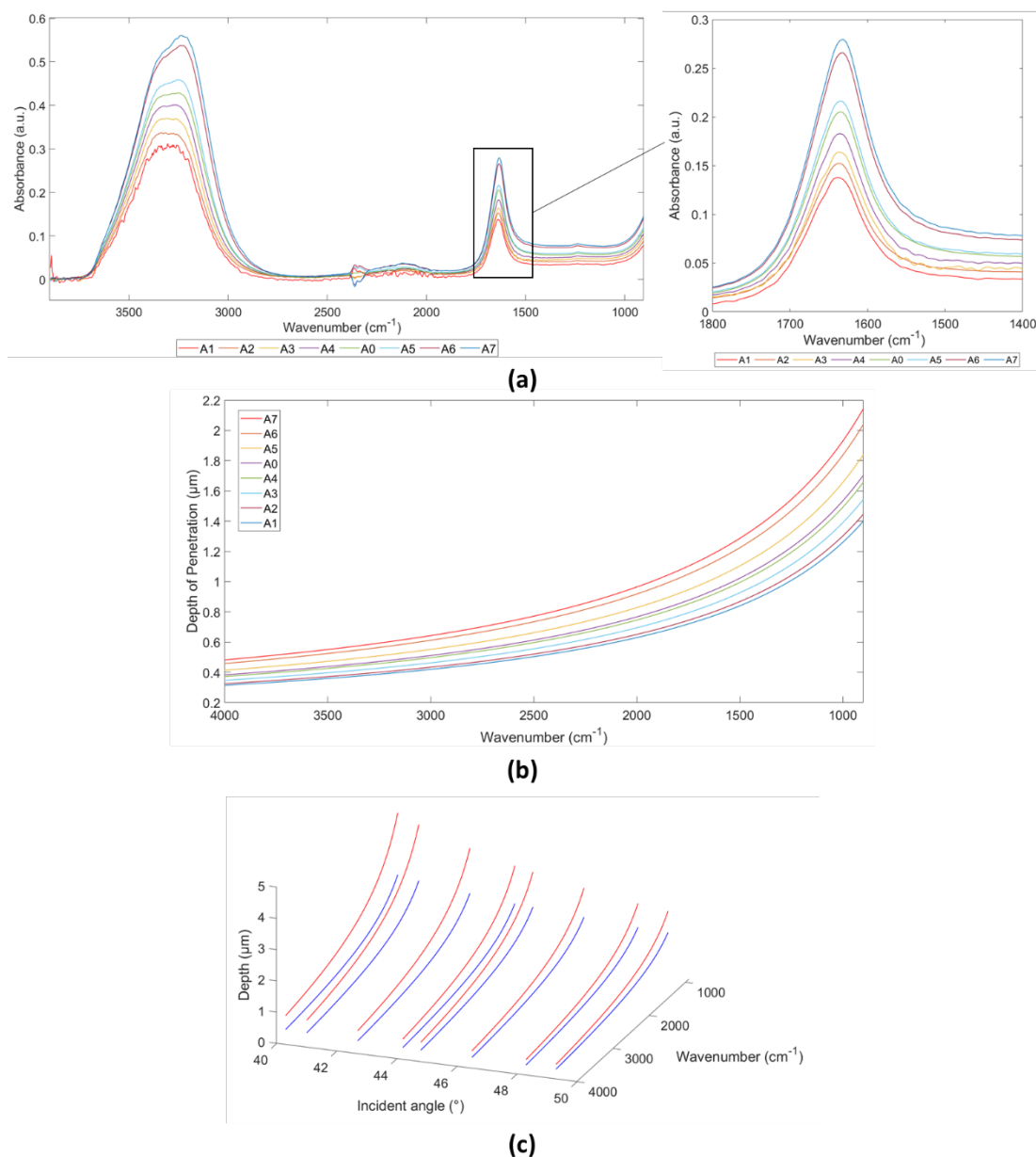


Figure 4.56 Results of calibrating the line-apertures using water for macro ATR-FTIR spectroscopic imaging with the same IRE (diamond). (a) FTIR spectra obtained with seven apertures and without an aperture, acquired by averaging the 4096 pixels of the FPA array, considering FTIR spectra in the region of 1400–1800 cm^{-1} . (b) Plot of the calculated depths of penetration against wavenumbers for various angles of incidence. (c) Plot of depths into water as a function of angles of incidence and wavenumbers, where the red line represents d_e , and the blue line represents d_p .

Table 4.16 Summary of the calibration of the angles of incidence for the macro ATR-FTIR spectroscopic imaging system equipped with a diamond crystal in the ATR accessory of the Imaging Golden Gate (Specac, UK), using with four rotating-apertures and without an aperture

	Absorbance at 1640 cm^{-1}	Estimated Effective pathlength (μm)	Estimated Angle of incidence ($^\circ$)	Estimated Depth of penetration (μm)
RA1	0.14817	1.22	48.2	0.80
RA2	0.16814	1.39	46.2	0.86
RA0	0.1957	1.62	44.1	0.94
RA3	0.20628	1.70	43.4	0.97
RA4	0.24811	2.05	41.3	1.10

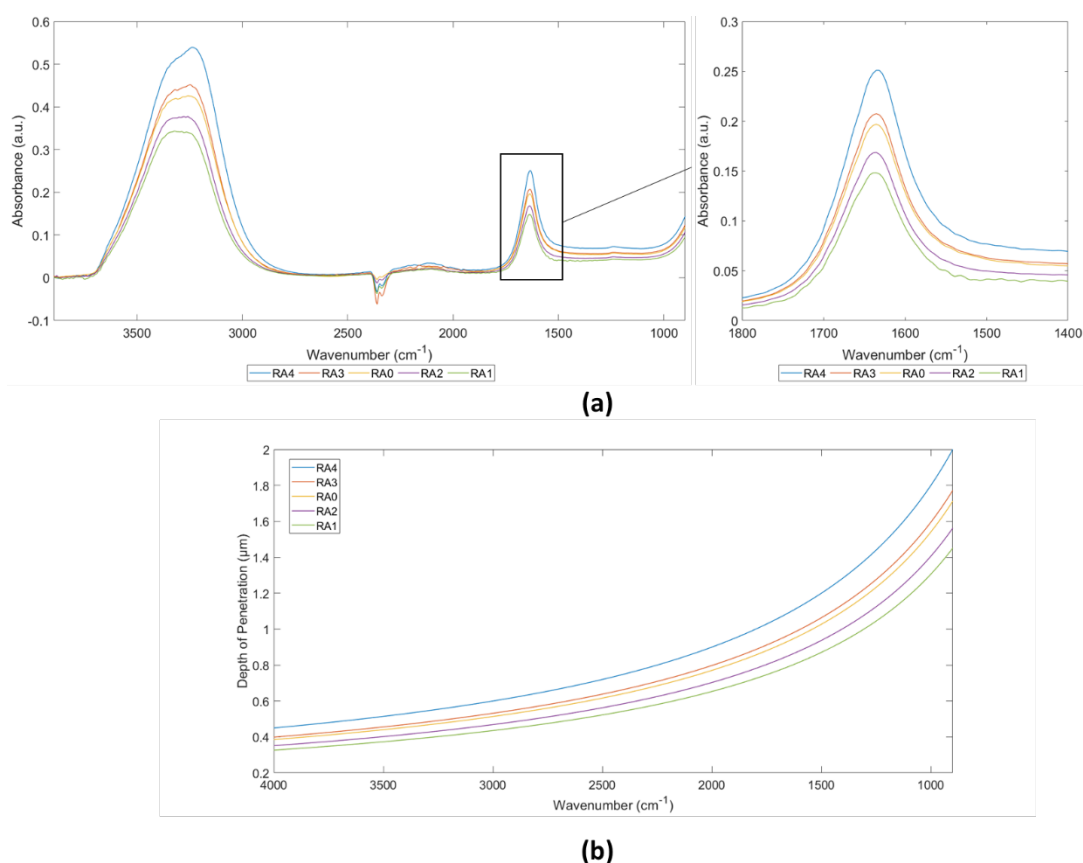


Figure 4.57 Results of calibrating the rotating-apertures using water for macro ATR-FTIR spectroscopic imaging with the same IRE (diamond). (a) FTIR spectra obtained with four apertures and without an aperture, acquired by averaging the 4096 pixels of the FPA array, considering FTIR spectra in the region of 1400–1800 cm^{-1} . (b) Plot of the calculated depths of penetration against wavenumbers for various angles of incidence. (c) Plot of depths into water as a function of angles of incidence and wavenumbers, where the red line represents d_e , and the blue line represents d_p .

4.4.4 Depth profiling with micro ATR-FTIR spectroscopic imaging of three types of antique photograph samples

Depth profiling measurements were conducted on three types of antique photographs with variable angles of incidence using a Ge crystal in contact with the black area on the surface of the sample at a constant pressure. Figures 4.58, 4.59 and 4.60 present the results of depth profiling with micro ATR-FTIR spectroscopic imaging of the silver gelatine photo, the albumen photo, and the salt print, respectively. Chemical images were generated by plotting the integrated absorbance between 1600 and 1680 cm^{-1} for every pixel, corresponding to the spectral band of amide (primarily the C=O stretching mode), as illustrated in Figure 4.58a (gelatine photograph) and Figure 4.59a (albumen photograph). For the salt print sample, chemical images were generated by plotting the integrated absorbance between 950 and 1180 cm^{-1} , representing the spectral bands of paper cellulose (comprising $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$), and the gypsum band ($\nu(\text{SO}_4^{2-})$), as depicted in Figure 4.60a.

As discussed above, the depth of penetration (dp) depends on the wavelength (λ), the refractive index (n) and the angle of incidence (θ). The refractive indexes used to calculate dp are roughly 1.5 (gelatine) (Calixto et al., 2018), 1.35 (albumen) (Romanoff & Sullivan, 1937) and 1.55 (paper cellulose and gypsum) (Long et al., 1993; Niskanen et al., 2019). The results of dp are summarised in the captions of Figure 4.58–4.60. It is evident that as the angle of incidence decreases, approaching the critical angle, greater depth into the sample can be measured. However, band shifts due to anomalous dispersion, as discussed in Section 2.2.2, can also be observed when the angle of incidence decreases. Figure 4.58b (silver gelatine photograph) and Figure 4.59b (albumen photograph) display the average spectra calculated from the entire FPA pixel array obtained with each aperture (A1–A3) and without an aperture (A0). Table 4.17 and 4.18 summarise the band shifts of amide A, amide I and amide II for gelatine and albumen photographs, respectively. Notably, the average spectrum collected using the aperture that has the smallest angle of incidence (A3) exhibited the most significant distortions because its angle of incidence approached the critical angle.

For the silver gelatine photograph, the band shifts of amide A, amide I, and amide II with A1 to A3 are 23 cm^{-1} , 12 cm^{-1} , and 8 cm^{-1} , respectively. In contrast, for the albumen photograph, the band shifts are 12 cm^{-1} , 8 cm^{-1} , and 4 cm^{-1} for amide A, amide I, and amide II, respectively. Overall, amide A exhibits the most significant band shift among the three amide bands, and for each amide band, the silver gelatine photograph displays more pronounced band shifts than the albumen photograph as the angle of incidence increases from 36.6° to 28.4°.

Figure 4.60a displays chemical images of paper cellulose and gypsum with varying depths of penetration probed. Three points on the surface of the salt print (P1–P3) were selected for investigation, and their spectra are provided in Figure 4.60b. P1 reveals the identification of paper cellulose exclusively, while P2 and P3 detect gypsum with varying thickness on paper cellulose, as illustrated in the chemical images acquired without an aperture (A0) in Figure 4.60b. Estimated dp values for gypsum are 1.30 μm (A3), 0.99 μm (A2), 0.96 μm (A0), and 0.79 μm (A1), based on the utilisation of absorbance at 1110 cm^{-1} . By examining the spectra of P2 and P3, it can be inferred that the thickness of gypsum in P2 may exceed 1.3 μm , while the thickness of gypsum in P3 may range between 0.79 μm and 0.96 μm . It is important to note that the sampling depth can surpass the estimated depth of penetration values (Mirabella, 1983). Consequently, the presence of the bands at 1034 cm^{-1} ($\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$) and 1057 cm^{-1} ($\nu(\text{C}-\text{C})$) indicate that paper cellulose was also detected in P3 with and without apertures. Nonetheless, by comparing the spectra of P2 and P3, it is possible to determine the relative thickness of gypsum, which appears to be around a micrometre. This capability, with the apertures for micro ATR-FTIR spectroscopic imaging to probe depths below one micrometre, for identifying components with different thicknesses can also complement results obtained using confocal Raman microscopy, where the z-direction spatial resolution exceeds 2–3 μm (Everall, 2009).

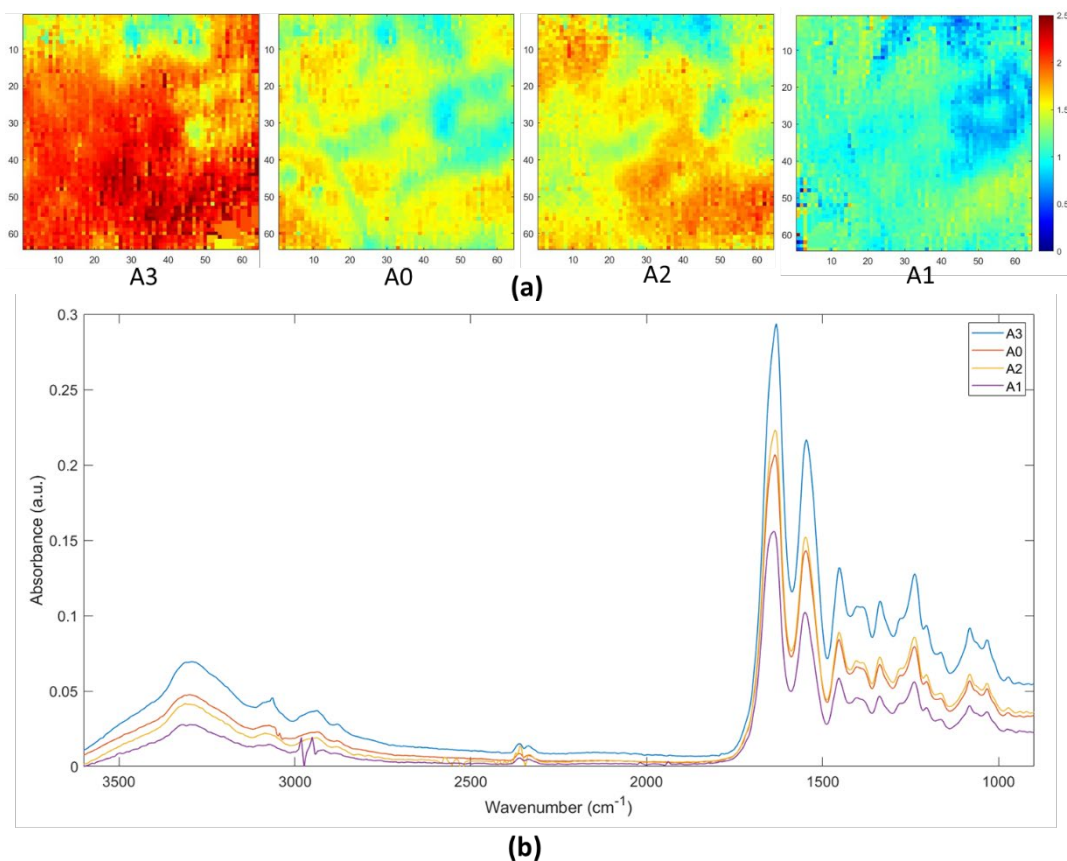


Figure 4.58 (a) Chemical images of the surface of silver gelatine photograph obtained with micro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of amide I between 1600 and 1680 cm^{-1} . $dp = 0.83 \mu\text{m}$ (A3), $0.63 \mu\text{m}$ (A0), $0.65 \mu\text{m}$ (A2), and $0.52 \mu\text{m}$ (A1). The size of each image is $70 \times 70 \mu\text{m}^2$. (b) FTIR spectra in the range 900–3700 cm^{-1} obtained with four apertures and without an aperture (A0), acquired by averaging the 4096 pixels of the FPA array.

Table 4.17 Spectral absorbance positions for Amide A, I, and II bands on the surface of the silver gelatine photograph, using a micro ATR spectroscopic imaging accessory with a Ge crystal and three apertures

Aperture and angle of incidence	Amide A (νNH) band (cm^{-1})	Amide I band (cm^{-1})	Amide II band (cm^{-1})
A3	3294	1631	1543
A2	3317	1639	1547
A1	3317	1643	1551

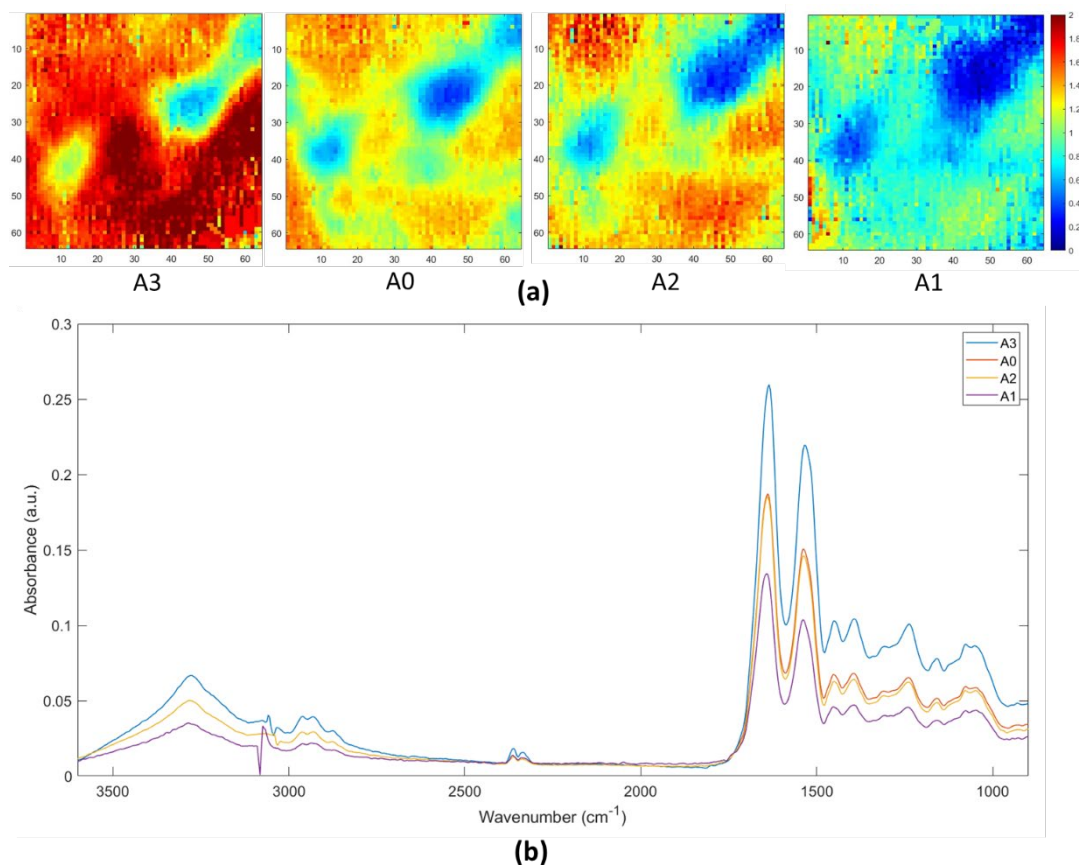


Figure 4.59 (a) Chemical images of the surface of albumen photograph obtained with micro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of amide I between 1600 and 1680 cm^{-1} . $dp = 0.72 \mu\text{m}$ (A3), $0.58 \mu\text{m}$ (A0), $0.59 \mu\text{m}$ (A2), and $0.49 \mu\text{m}$ (A1). The size of each image is $70 \times 70 \mu\text{m}^2$. (b) FTIR spectra in the range 900–3700 cm^{-1} obtained with four apertures and without an aperture (A0), acquired by averaging the 4096 pixels of the FPA array.

Table 4.18 Spectral absorbance positions for Amide A, I, and II bands on the surface of the albumen photograph, using a micro ATR spectroscopic imaging accessory with a Ge crystal and four apertures

Aperture and angle of incidence	Amide A (νNH) band (cm^{-1})	Amide I band (cm^{-1})	Amide II band (cm^{-1})
A3	3278	1635	1535
A2	3282	1639	1539
A1	3286	1643	1539

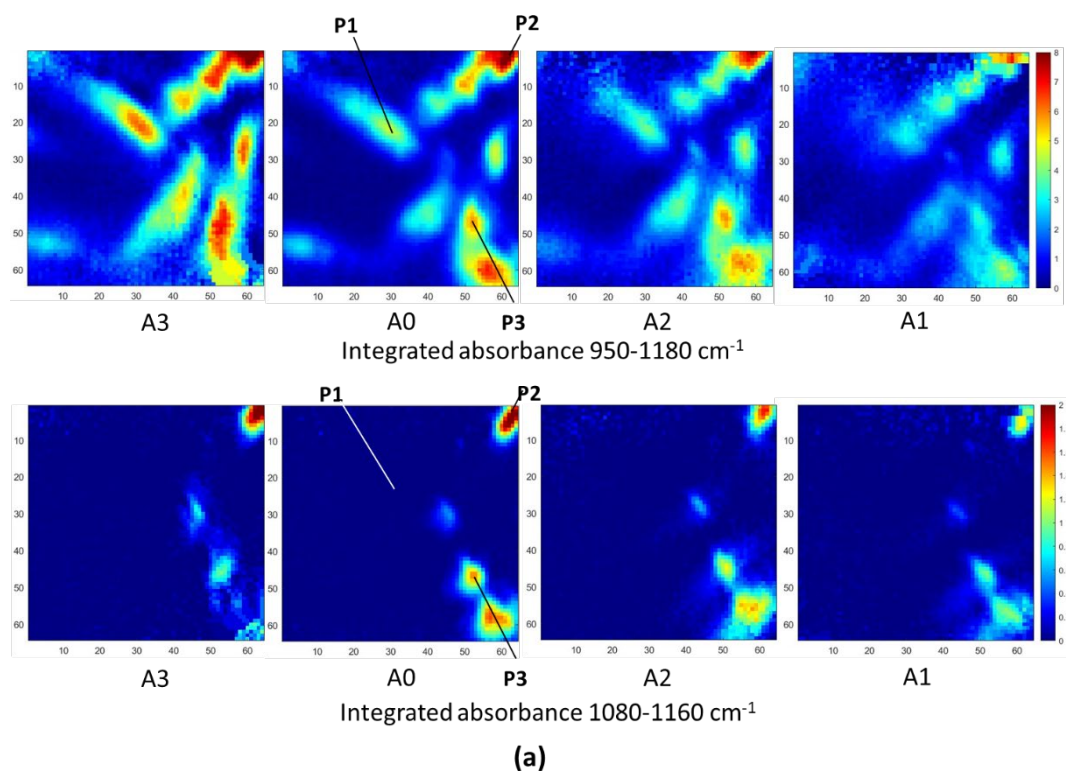


Figure 4.60 (a) Chemical images of the surface of albumen photograph obtained with micro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of paper cellulose between 950 and 1180 cm^{-1} , and the spectral band of gypsum between 1080 and 1160 cm^{-1} . $dp = 1.22\text{--}1.52\text{ }\mu\text{m}$ (A3), $0.90\text{--}1.13\text{ }\mu\text{m}$ (A0), $0.94\text{--}1.16\text{ }\mu\text{m}$ (A2), and $0.75\text{--}0.92\text{ }\mu\text{m}$ (A1). The size of each image is $70 \times 70\text{ }\mu\text{m}^2$.

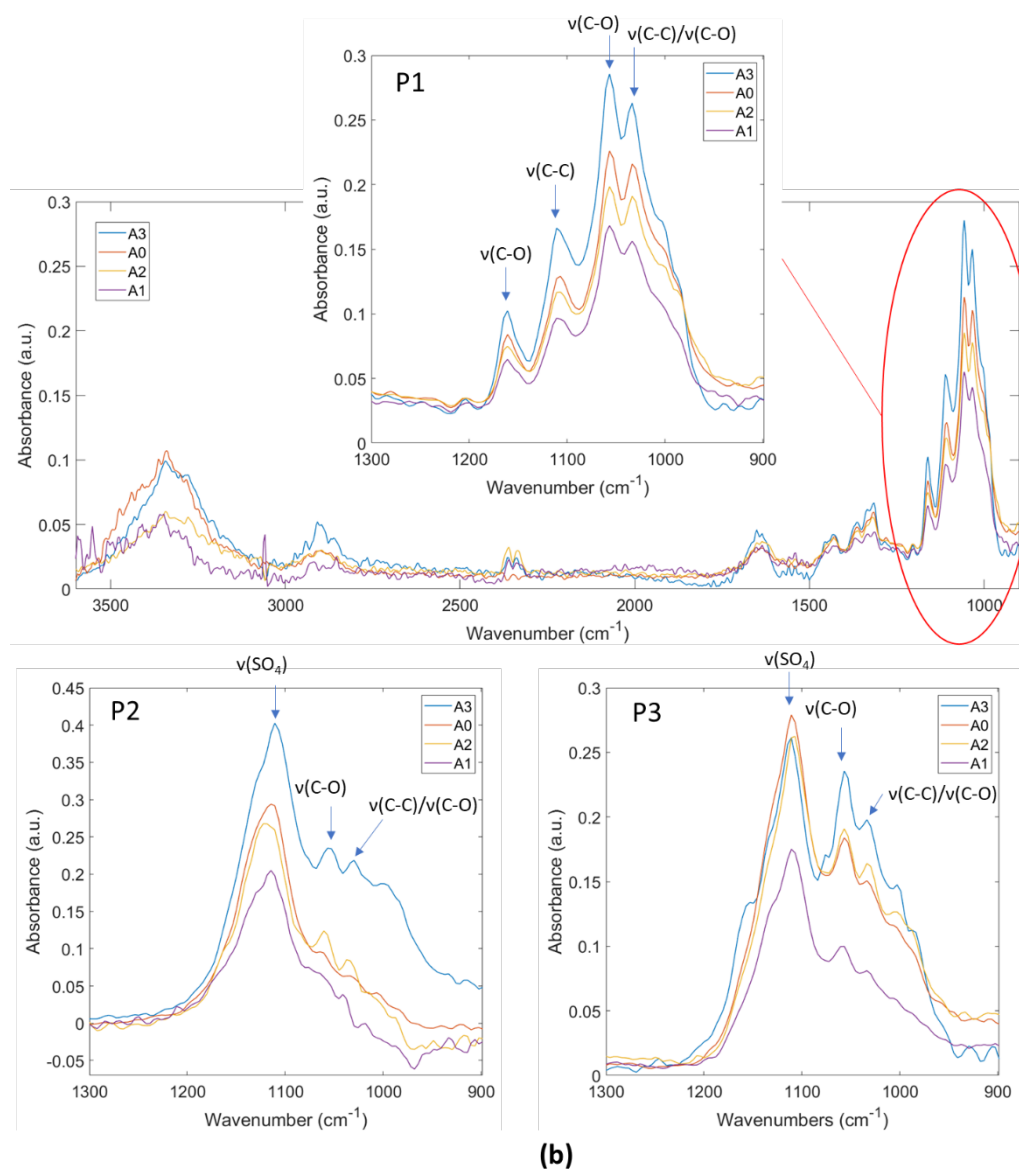


Figure 4.60 (b) FTIR spectra of the three points (P1–P3) extracted from the chemical images in Figure 4.60a obtained with four apertures and without an aperture (A0), acquired by averaging the 4096 pixels of the FPA array. The region of interest in the spectra is between 900–1300 cm⁻¹.

4.4.5 Depth profiling with macro ATR-FTIR spectroscopic imaging of three types of antique photograph samples

As deduced from Equations 2.9–2.12, both dp and de increase when utilising the ATR crystal with a smaller refractive index, as demonstrated in Figures 4.55 and 4.56. Depth profiling measurements of antique photographs with varying angles of incidence were performed using the micro ATR-FTIR spectroscopic imaging system with the Ge crystal ($n = 4.0$) in Section 4.4.4. In Section 4.4.5, depth profiling measurements of the same antique photographs were conducted using the macro ATR-FTIR spectroscopic imaging system with the diamond crystal ($n = 2.42$). It is expected that the sample penetration depth can be probed deeper with the diamond crystal.

Figure 4.61a presents chemical images of the amide I on the surface of the silver gelatine photograph, obtained by plotting the integrated absorbance between 1600 and 1680 cm^{-1} using seven line-apertures (A1–A7). One notable advantage of this line-aperture design in the macro ATR-FTIR spectroscopic imaging technique is the broad range of selectable angles of incidence, ranging from 49.3° to 40.3° , resulting in eight depth profiling spectral datasets, as illustrated in Figure 4.61b. Nevertheless, this design comes with certain limitations. Notably, every time the apertures are changed for a measurement at a different angle of incidence, it requires temporarily lifting and repositioning the top-plate where the ATR diamond crystal sits. Consequently, achieving consistent measurements of the same sample area may prove challenging due to potential sample displacement caused by top-plate movement. To address this issue, rotating-apertures have been devised, allowing angle selection without requiring the displacement of the sample situated on the top-plate. In this section, we discuss in further detail the depth profiling of the three types of photographs performed using the rotating-apertures (Figure 4.62–4.64), while the depth profiling measurements using the line-apertures were exclusively conducted on the silver gelatine photograph (Figure 4.61).

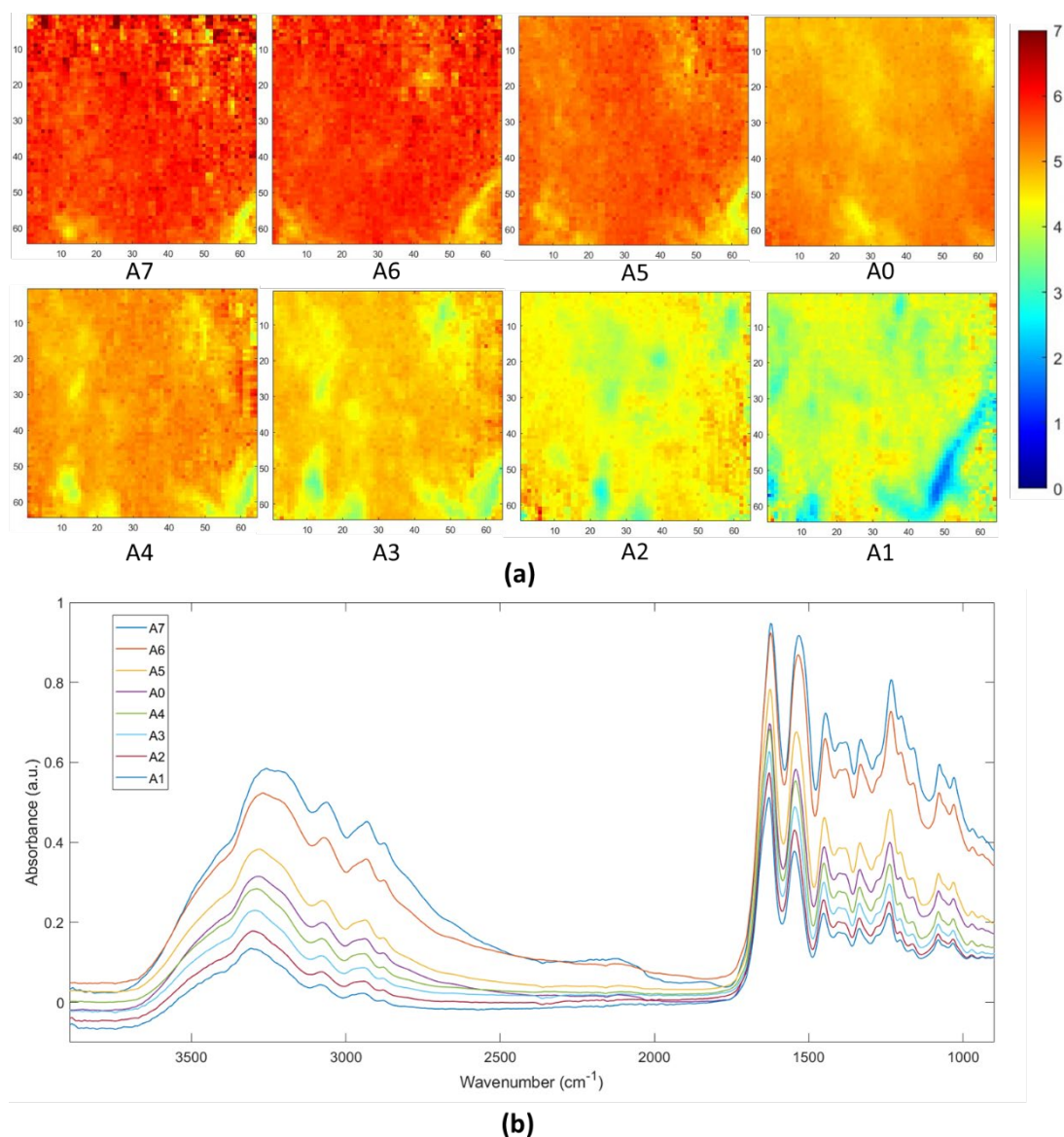


Figure 4.61 (a) Chemical images of the surface of silver gelatine photograph obtained with the line-apertures in macro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of amide I between 1600 and 1680 cm^{-1} . $dp = 2.17 \text{ } \mu\text{m}$ (A7), $1.87 \text{ } \mu\text{m}$ (A6), $1.46 \text{ } \mu\text{m}$ (A5), $1.26 \text{ } \mu\text{m}$ (A0), $1.20 \text{ } \mu\text{m}$ (A4), $1.06 \text{ } \mu\text{m}$ (A3), $0.96 \text{ } \mu\text{m}$ (A2), and $0.92 \text{ } \mu\text{m}$ (A1). The size of each image is $600 \times 550 \text{ } \mu\text{m}^2$. (b) FTIR spectra in the range $900\text{--}3900 \text{ cm}^{-1}$ obtained with the seven line-apertures and without an aperture (A0), acquired by averaging the 4096 pixels of the FPA array.

The average spectra of the silver gelatine photograph (Figure 4.62b) and the albumen photograph (Figure 4.63b) exhibit the same spectral bands as those detected in the average spectra acquired using the micro ATR-FTIR imaging system with the Ge crystal in Section 4.4.4. However, the average spectra of the salt print (Figure 4.64b) do not show any absorption of gypsum. Additionally, no chemical image of gypsum in the salt print can be obtained using the macro ATR-FTIR spectroscopic imaging system with the diamond crystal. These results may be attributed to the greater depth of penetration probed in macro ATR-FTIR measurements, which results in a higher signal collection from paper cellulose, particularly in the wavenumber region around 950–1180 cm^{-1} . In addition to the raw average spectra of the three types of the photographs, second derivative spectra were obtained by differentiating the raw spectra twice to correct the baseline shift and to determine the positions of the absorbance peaks, as illustrated in Figure 4.62c (silver gelatine photograph), Figure 4.63c (albumen photograph) and Figure 4.64c (salt print). Since the second derivatives tend to introduce unavoidable noise, Savitzky-Golay (SG) smoothing algorithm with 13 smoothing points was employed to obtain the smoothed second derivative spectra. The position of the amide A, I and II bands of silver gelatine and albumen photograph observed are listed in Table 4.19 and 4.20, respectively. By comparing the positions of these bands, as summarised in Table 4.17–4.20, spectral distortions and band shifts are found to be more pronounced in macro ATR-FTIR measurements due to the deeper depth of penetration. It is worth noting that the amide II of the albumen photograph is distorted the most, shifting from 1539 cm^{-1} (A1, $dp = 0.49 \mu\text{m}$) to 1508 cm^{-1} (RA4, $dp = 1.14 \mu\text{m}$), as indicated in Table 4.18 (micro ATR-FTIR measurements) and 4.20 (macro ATR-FTIR measurements), respectively.

In addition to the shifted positions of absorbance peaks, the absorbance values of amide II with respect to amide I on the surface of the albumen photograph were found to decrease with less depth of penetration probed, as shown in Figure 4.63b. The ratios of amide II/ amide I of the albumen photographs acquired by using the absorbance values at the peaks listed in Table 4.20 are 1.083 (RA4, $dp = 1.14 \mu\text{m}$), 0.988 (RA3, $dp = 1.00 \mu\text{m}$), 0.977 (RA2, $dp = 0.88 \mu\text{m}$), 0.893 (RA1, $dp = 0.81 \mu\text{m}$). Amide I

contains information about protein secondary structure, such as α -helices and β -sheets. Studies on human fibroblasts have employed the IR absorbance ratio of amide II/ amide I as an index of the formation of fibrils to investigate human physiological aging (Magalhães et al., 2022; Martins et al., 2023). In these studies, the ratios of amide II/amide I decreased with increasing age. The results of decreased ratios of amide II/amide I with less depth of penetration probed in the present study can be explained by the fact that the surface of the albumen on the photograph may exhibit more signs of aging due to more exposure to ultraviolet (UV) radiation compared to the interior of the albumen on the photograph. This is in agreement with the results of the silver gelatine photograph with depth profiling measurements where the ratios of amide II/amide I are 0.968 (A7, $dp = 2.17 \mu\text{m}$) and 0.739 (A1, $dp = 0.92 \mu\text{m}$), as derived from Figure 4.61b, and 0.937 (RA4, $dp = 1.77 \mu\text{m}$) and 0.742 (RA1, $dp = 0.97 \mu\text{m}$), as derived from Figure 4.62b.

The band shift due to anomalous dispersion was not apparent in the depth profiling results of salt print, as shown in Figure 4.64b and c. Nevertheless, the spectral band of C–OH bending (Bhagia et al., 2022) at 984 cm^{-1} (RA1–RA3) or 980 cm^{-1} (RA4) became more pronounced as more depth of penetration was probed, as indicated in Figure 4.64b. This band of C–OH bending is related to intermolecular hydrogen bonds of cellulose (Bhagia et al., 2022; Maréchal & Chanzy, 2000) and was not apparent in the results of salt print in micro ATR-FTIR measurement (Figure 4.60) where the depth of penetration was around $1 \mu\text{m}$. In the future, it would be of interest to investigate the hydrogen bonding network of cellulose at various depth within $1\text{--}4 \mu\text{m}$.

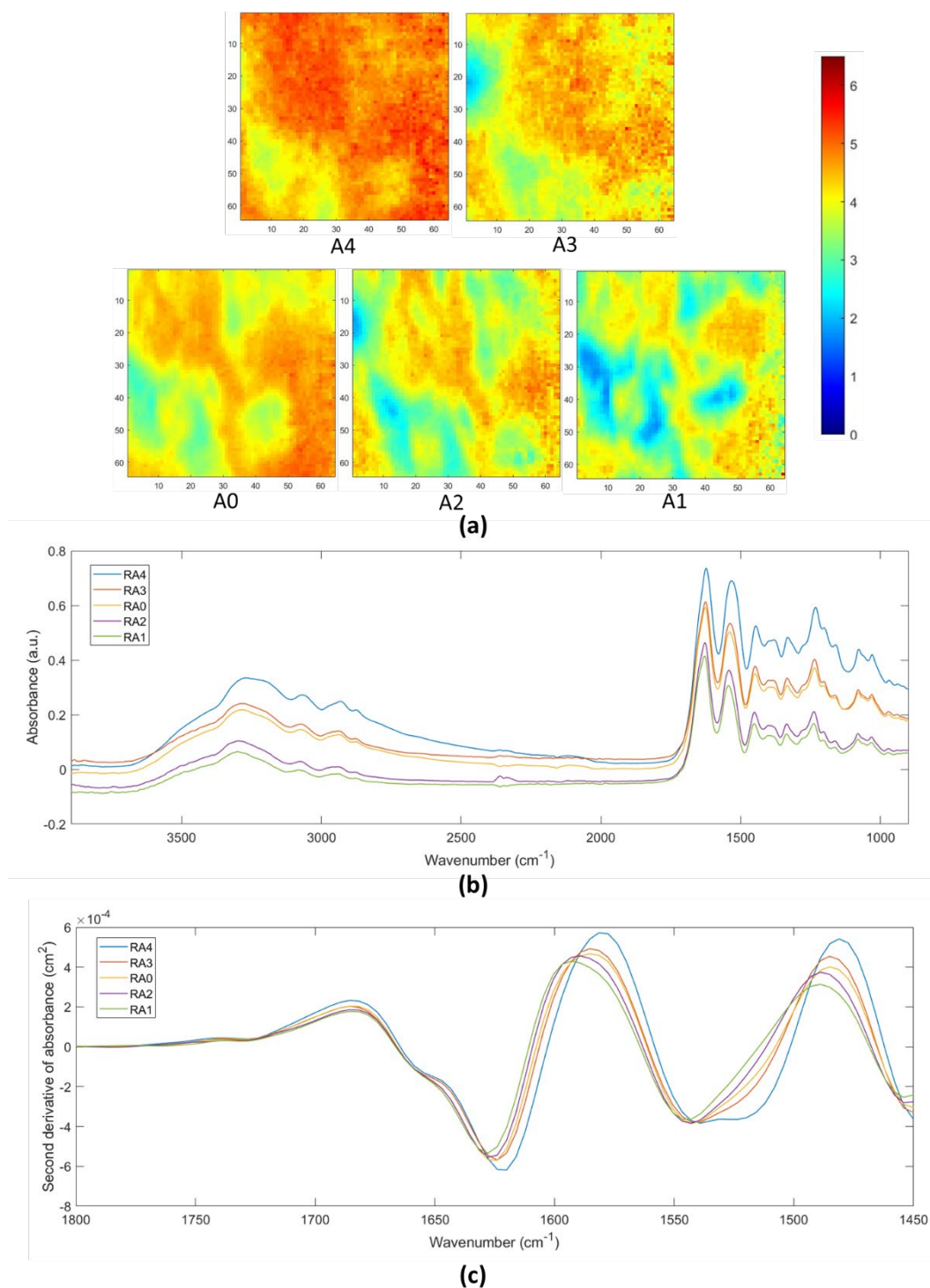


Figure 4.62 (a) Chemical images of the surface of silver gelatine photograph obtained with the rotating-apertures in macro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of amide I between 1600 and 1680 cm^{-1} . $dp = 1.77 \mu\text{m}$ (RA4), $1.35 \mu\text{m}$ (RA3), $1.27 \mu\text{m}$ (RA0), $1.08 \mu\text{m}$ (RA2), and $0.97 \mu\text{m}$ (RA1). The size of each image is $600 \times 550 \mu\text{m}^2$. (b) The average FTIR spectra in the range $900\text{--}3900 \text{ cm}^{-1}$ and (c) the average second derivative spectra in the range $1450\text{--}1800 \text{ cm}^{-1}$ measured with the four rotating-apertures and without an aperture (RA0).

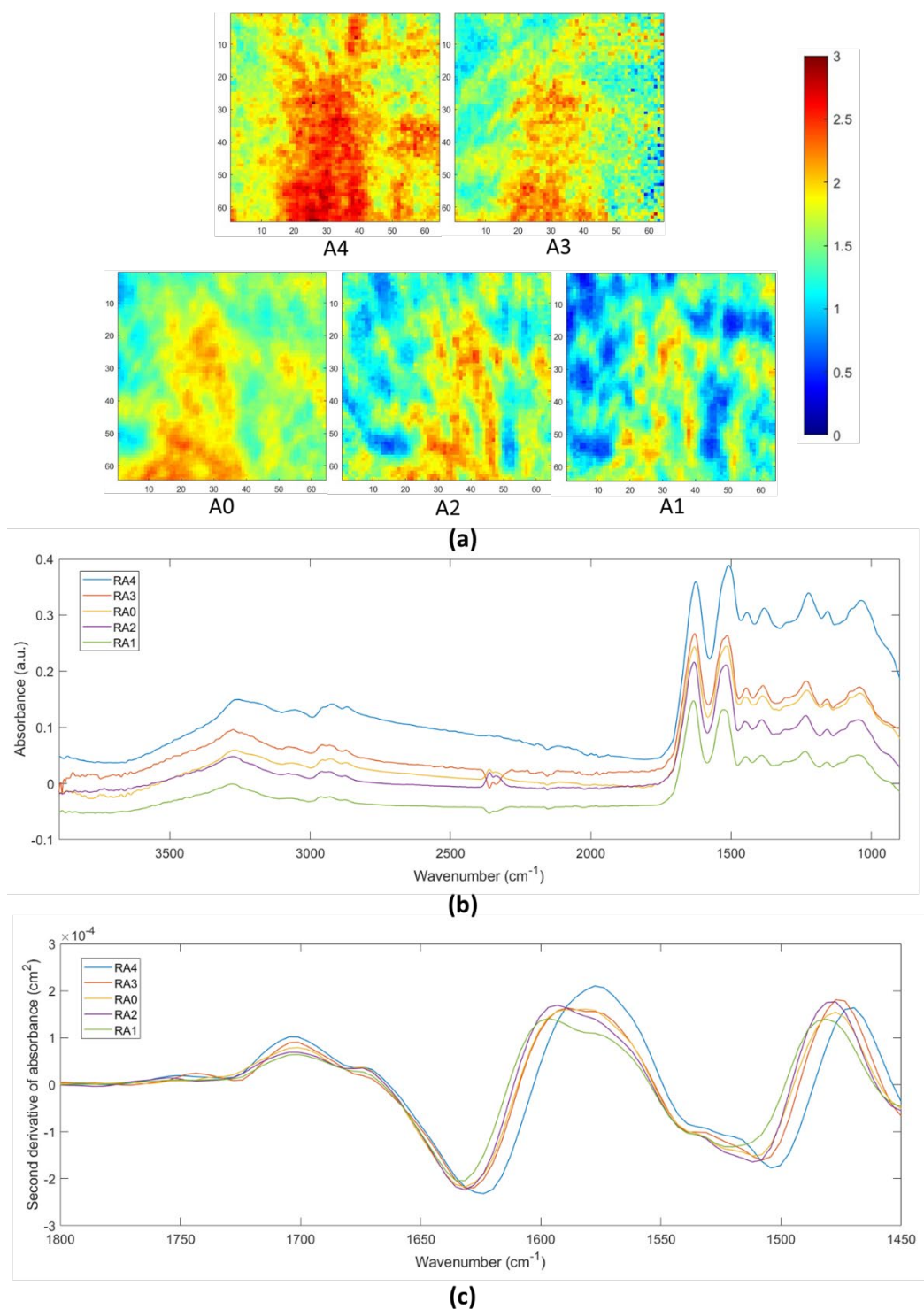


Figure 4.63 (a) Chemical images of the surface of albumen photograph obtained with the rotating-apertures in macro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of amide I between 1600 and 1680 cm^{-1} . $dp = 1.14 \mu\text{m}$ (RA4), $1.00 \mu\text{m}$ (RA3), $0.96 \mu\text{m}$ (RA0), $0.88 \mu\text{m}$ (RA2), and $0.81 \mu\text{m}$ (RA1). The size of each image is $600 \times 550 \mu\text{m}^2$. (b) The average FTIR spectra in the range 900–3900 cm^{-1} and (c) the average second derivative spectra in the range 1450–1800 cm^{-1} measured with the four rotating-apertures and without an aperture (RA0).

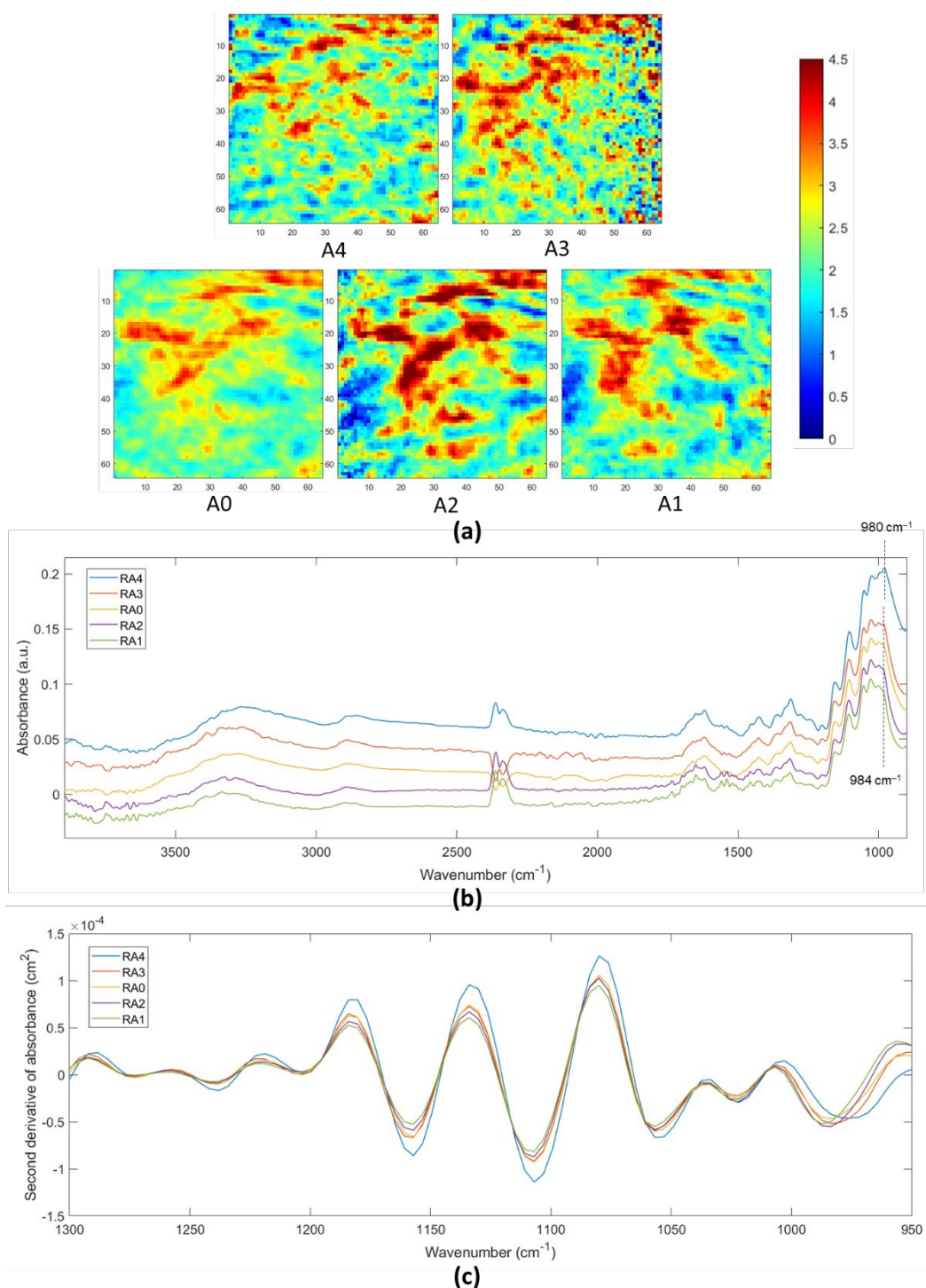


Figure 4.64 (a) Chemical images of the surface of salt print obtained with the rotating-apertures in macro ATR-FTIR spectroscopic imaging, produced by plotting the integrated absorbance of the spectral band of paper cellulose between 950 and 1180 cm^{-1} . $dp = 3.49\text{--}4.35\text{ }\mu\text{m}$ (RA4), $2.24\text{--}2.78\text{ }\mu\text{m}$ (RA3), $2.05\text{--}2.54\text{ }\mu\text{m}$ (RA0), $1.68\text{--}2.08\text{ }\mu\text{m}$ (RA2), and $1.46\text{--}1.81\text{ }\mu\text{m}$ (RA1). The size of each image is $600 \times 550\text{ }\mu\text{m}^2$. (b) The average FTIR spectra in the range 900–3900 cm^{-1} and (c) the average second derivative spectra in the range 950–1300 cm^{-1} measured with the four rotating-apertures and without an aperture (A0).

Table 4.19 Spectral absorbance positions for Amide A, I, and II bands on the surface of the silver gelatine photograph, using a macro ATR spectroscopic imaging accessory with a diamond crystal and four rotating-apertures

Aperture and angle of incidence	Amide A (ν NH) band (cm^{-1})	Amide I band (cm^{-1})	Amide II band (cm^{-1})
RA4	3271	1624	1531
RA3	3290	1628	1539
RA2	3282	1628	1539
RA1	3298	1628	1543

Table 4.20 Spectral absorbance positions for Amide A, I, and II bands on the surface of the albumen photograph, using a macro ATR spectroscopic imaging accessory with a diamond crystal and four rotating-apertures

Aperture and angle of incidence	Amide A (ν NH) band (cm^{-1})	Amide I band (cm^{-1})	Amide II band (cm^{-1})
RA4	3255	1624	1508
RA3	3275	1632	1516
RA2	3271	1632	1520
RA1	3279	1635	1527

4.4.6 Differentiation of antique photographs with macro ATR-FTIR spectroscopic imaging

This section investigates how penetration depth influences the application of PCA chemometrics in discriminating spectra within the wave number range of 900–2000 cm^{-1} acquired from the three types of photographs in macro ATR-FTIR measurements with the rotating-apertures. Figure 4.65 displays the PCA score plots at various angles of incidence. The variance explained by the first two PCs (PC1 and PC2) for the different rotating-apertures is as follows: 94.86% (RA1), 95.85% (RA2), 98.56% (RA0), 97.39% (RA3), and 98.34% (RA4). Following PCA, the classification of data using PC1 and PC2 underwent further examination. This involved fitting the data to a Linear Discriminant Analysis (LDA) classifier in Matlab (The MathWorks, 2023), a supervised

classification model incorporating a 10-fold cross-validation approach. Classification loss, which represents the mean squared error between the true responses and the predicted values, specifically for the three types of photographs, was used to assess the predictive performance of each LDA model. The cross-validation loss for each aperture is reported as follows: 0.0517 (RA1), 0.02 (RA2), 0.0069 (RA0), 0.0127 (RA3), and 0.0032 (RA4). Lower loss values represent a more accurate LDA model, indicating better data separation. The results show that RA4 has the lowest loss, while RA1 has the highest loss. It is therefore reasonable to suppose that by probing the samples at

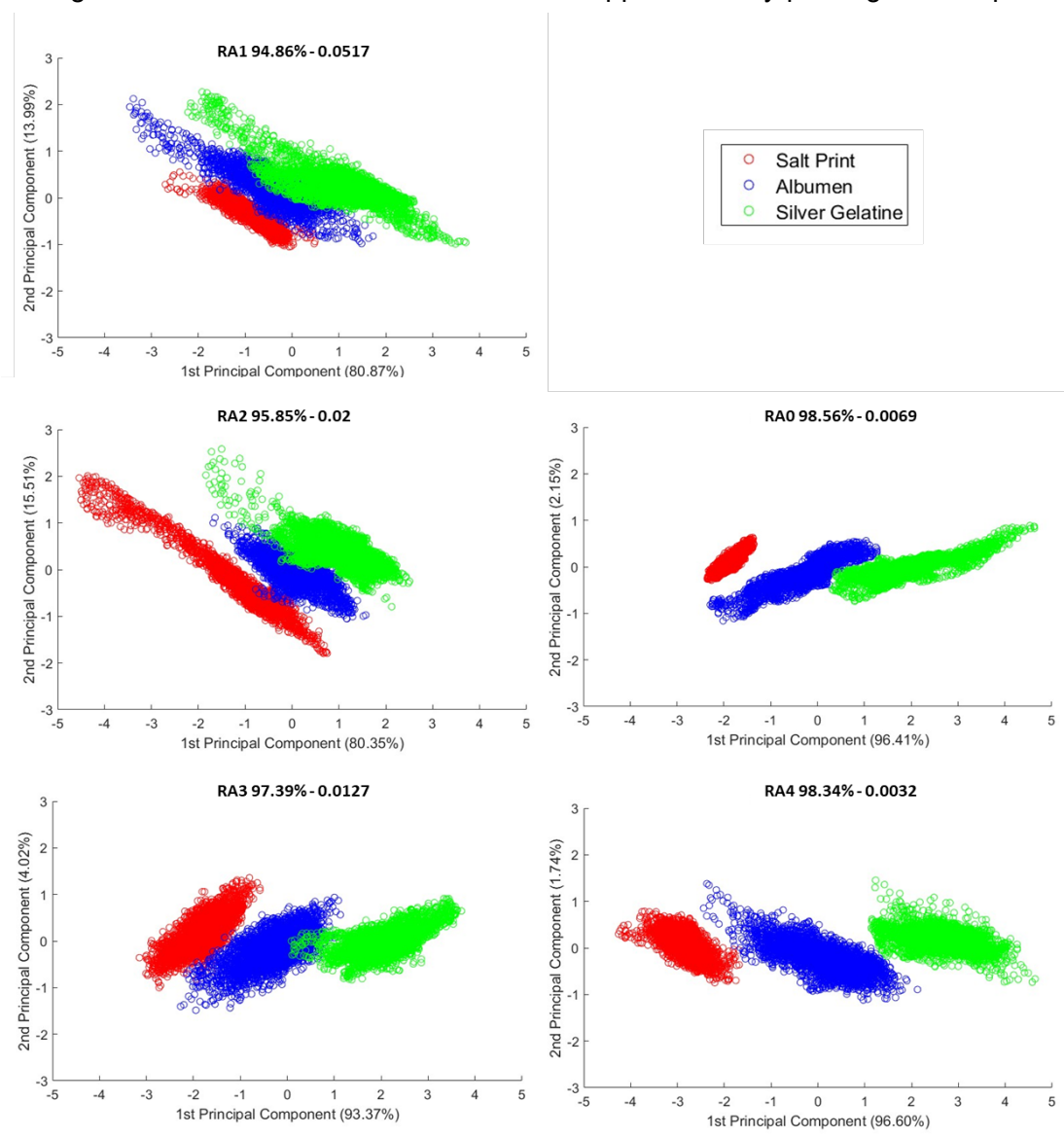


Figure 4.65 PCA score plots of spectra extracted from the results of macro ATR-FTIR spectroscopic imaging measurements in the wavenumber region of 900–2000 cm^{-1} at different angles of incidence using the rotating-apertures. The variance explained by the first two PCs and the classification loss of the LDA classifier are labelled on top of each PCA score plot.

a deeper depth of penetration the discrimination among the three types of photographs may be more reliable and significant.

4.4.7 Summary

This section presents a depth profiling approach for macro and micro ATR-FTIR spectroscopic imaging measurements achieved by manipulating the angles of incidence of infrared (IR) light using custom-made apertures. This depth profiling approach, featuring variable angles of incidence, facilitates the acquisition of three-dimensional (3D) profiling information. This approach has been applied to investigate both polymer and biological samples. Notably, this present study marks the first demonstration of the application of this depth profiling approach to the analysis of three types of antique photographs. To implement this approach, two sets of apertures (line and rotating) were installed on the macro ATR-FTIR spectroscopic imaging system, which employs a diamond crystal with a lower refractive index. Another set of apertures was used with the micro ATR-FTIR spectroscopic imaging system, utilising a Ge crystal with a higher refractive index. By varying the angles of incidence (θ), the refractive index of the IRE crystals (n_1), the refractive index of the samples being analysed (n_2), and observing different wavenumbers (different λ), we were able to determine the penetration depth (dp) ranging from 0.49 μm to 4.35 μm . Furthermore, as we probed more extensively into the sample, the performance of PCA chemometrics improved, allowing for better differentiation of the three types of photographs analysed.

4.5 Micro ATR-FTIR spectroscopic imaging investigation of Donatello's Virgin and Child sculpture

4.5.1 Background

This section explores the application of micro ATR-FTIR spectroscopic imaging to examine four cross-sectional samples of Donatello's Virgin and Child, provided by the Victoria and Albert (V&A) Museum. Before being sent to our lab for micro ATR-FTIR spectroscopic imaging analysis, the stratigraphy of the samples was investigated using Raman spectroscopy (not shown here) and SEM-EDX (refer to Figure 6.8 in the Appendices). The advantage of using the FTIR technique over Raman spectroscopy and SEM-EDX is its capability of identifying proteinaceous and/or lipidic binders used in painted artwork. In addition to the conventional FTIR measurements, polarised FTIR measurements were explored for the application to cultural heritage objects. Polarised FTIR spectroscopy is a technique that utilises different linear polarisations of incident light to gather different chemical information from the detected sample. The incident light can be polarised as p-polarised or s-polarised, as introduced in Section 2.2.2. Polarised ATR-FTIR spectroscopic measurements have been conducted to investigate a wide variety of materials, ranging from polymers (Hikima et al., 2019; Ishige et al., 2021; Perret et al., 2021), biological tissues (Chrabaszc et al., 2021; Koziol et al., 2020), clay (Grégoire et al., 2020; Ras et al., 2003), to food (Kaneko et al., 2021). The results of polarised ATR-FTIR measurements include the acquisition of molecular orientation of the detected materials and/or their degradation condition. However, little attention has been paid to the investigation of cultural heritage objects using polarised micro ATR-FTIR measurements, which could serve as a potential non-destructive method for identifying degradation conditions in these objects, simply determined by examining different polarisation behaviours. This section illuminates how micro ATR-FTIR spectroscopic analysis can augment the interpretation of results obtained from

other techniques, while also demonstrating the pioneering application of polarised micro ATR-FTIR measurements to cultural heritage objects.

4.5.2 Experimental set-up

Four cross-sectional samples, embedded in resin and displaying stratigraphic features of Donatello's sculpture, *Virgin and Child*, were prepared and provided by the V&A Museum. The locations from which these samples were extracted from Donatello's *Virgin and Child* are illustrated in Figure 6.9 in the Appendices. To ensure consistency, the samples are named in accordance with the V&A Museum's previous, as-yet-unpublished report on Raman spectroscopy and SEM results, identified as samples 9-12.

Firstly, samples 9-12 were investigated using a non-polarised micro ATR-FTIR spectroscopic imaging system, the Cary 620 FTIR microscope connected to the Agilent Varian 670 spectrometer (Agilent Technologies, Inc.). The aim of the non-polarised micro ATR-FTIR spectroscopic measurements is to identify and characterise chemical components within the stratigraphy of the cross-sectional samples. After obtaining chemical information about the components, polarised micro ATR-FTIR spectroscopic measurements were conducted with the same micro ATR-FTIR spectroscopic imaging system to examine the areas analogous to those investigated with non-polarised measurements. Both non-polarised and polarised micro ATR-FTIR spectroscopic measurements were conducted in the mid-IR range from 3900 cm^{-1} to 850 cm^{-1} , at 8 cm^{-1} resolution, and with 64 co-added scans. Spectral data were processed with Matlab R2023a (MathWorks, Inc., USA) to produce chemical images and the corresponding spectra. Each chemical image is composed of 64×64 pixels with a $1.1\text{ }\mu\text{m}$ projected pixel size, giving a measured area of $70\times 70\text{ }\mu\text{m}$.

Polarised ATR-FTIR spectroscopic measurements were carried out by inserting a rotatable IR polariser (Agilent Technologies, Inc.) above the objective lens. By changing the degree ($0\sim 360^\circ$) on the polariser, the direction of the electric field of the IR beam can be determined, leading to a polarised IR beam. Two types of polarisations

were employed in this study, s-polarisation (90° on the polariser) and p-polarisation (0° on the polariser). S-polarisation is defined as the IR beam whose electric field is perpendicular to the scattering plane, while p-polarisation is defined as the IR beam whose electric field is parallel to the scattering plane, as illustrated in Figure 4.66. The scattering plane is defined as a plane where the incident and reflected IR beams are located.

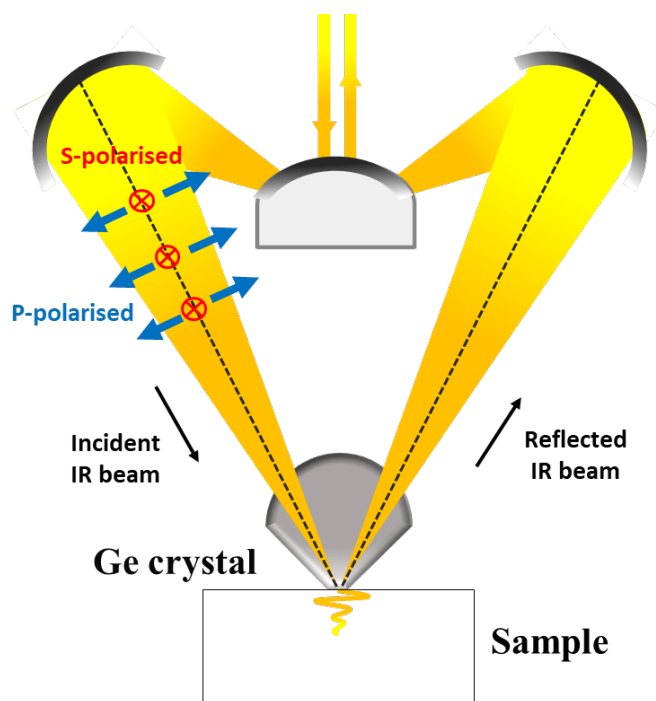


Figure 4.66 Schematic depiction illustrating the set-up of micro ATR-FTIR spectroscopic imaging system for polarisation analysis.

4.5.3 Non-polarised ATR-FTIR spectroscopic imaging results

Figure 4.67a shows the micrograph of cross-sectional sample 9 extracted from the Virgin's cloak. The picture of this sample collection was supplemented in Figure 6.9 in Appendices. Components identified using SEM-EDX, optical microscopy and Raman spectroscopy are azurite, ultramarine blue, lead white, and gypsum in the ground layer, with their elemental distribution indicated in Figure 6.8a in Appendices. Micro ATR-FTIR spectroscopic imaging has confirmed the presence of these components and provided their chemical images in 4.67b. Spectral bands assigned to produce the chemical images of these detected components are $900\text{--}960\text{ cm}^{-1}$ ($\delta_{\text{out-of-plane}}(\text{O-H})$)

and $1450\text{--}1470\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{CO}_3^{2-})$) for azurite, $900\text{--}1040\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{O--Si--O})$) for ultramarine blue, $1300\text{--}1480\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{CO}_3^{2-})$) for lead white, and $1060\text{--}1160\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{SO}_4^{2-})$) for gypsum, as illustrated in Figure 4.68. It is important to note that the spectral band for lead white overlapped with that of azurite. This issue of overlapping spectral bands of lead white and azurite can be resolved by examining their spectra, which indicate that the $\nu_{\text{as}}(\text{CO}_3^{2-})$ band of azurite shows a split doublet at 1400 cm^{-1} and 1462 cm^{-1} . Besides these components, the presence of protein was also identified by assigning amide I ($1600\text{--}1680\text{ cm}^{-1}$) and amide II ($1500\text{--}1580\text{ cm}^{-1}$), suggesting the use of proteinaceous binders. The micro ATR-FTIR images of the proteinaceous binders show a higher concentration at the top of the layer and as isolated and

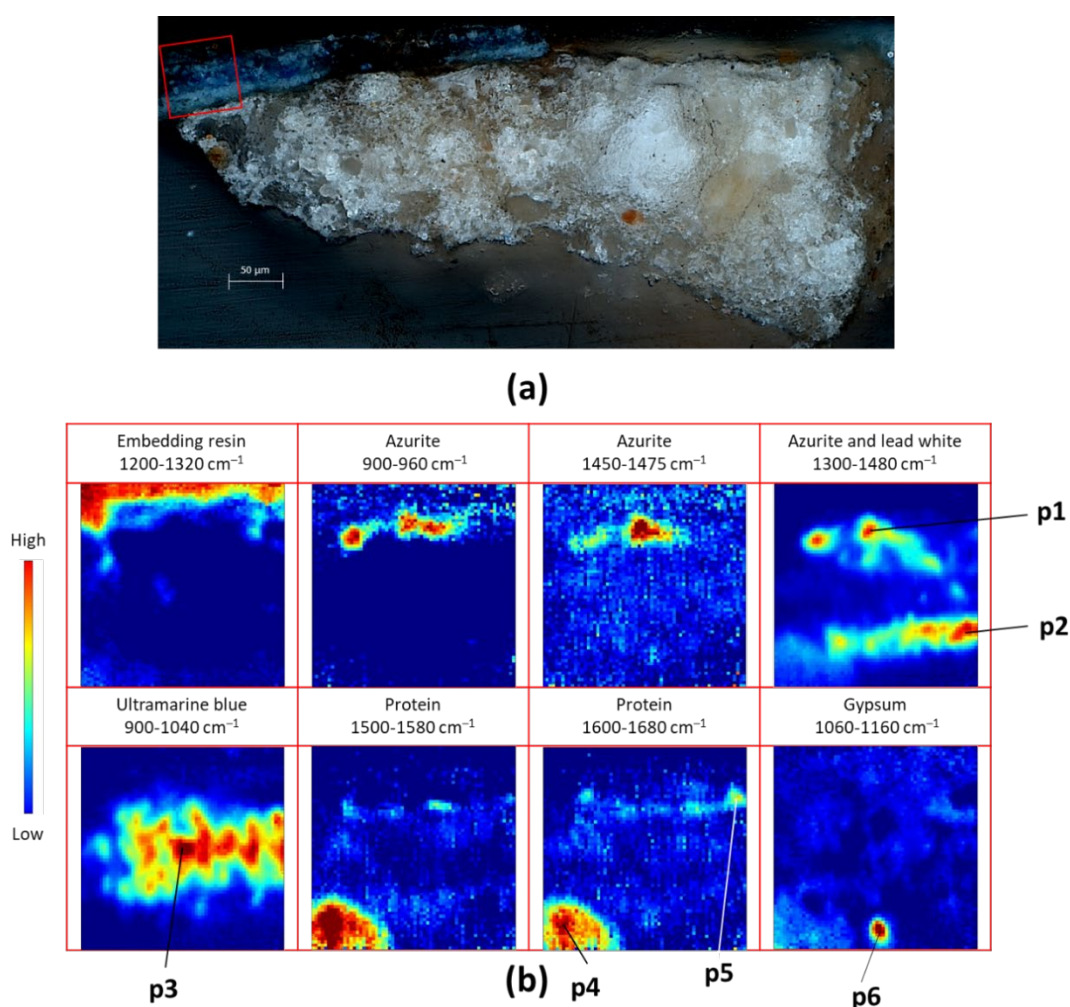


Figure 4.67 (a) Photomicrograph of sample 9. A red square indicates the measuring area (ca. $70\text{ }\mu\text{m}\times 70\text{ }\mu\text{m}$) by micro ATR-FTIR spectroscopic imaging. Reprinted with permission, copyright © V&A Museum. (b) Micro ATR-FTIR images showing the distribution of chemical components identified.

localised occurrences within the layer, as illustrated in Figure 4.67b. This can be explained by the sedimentation of solid particulates within a layer, causing the top to

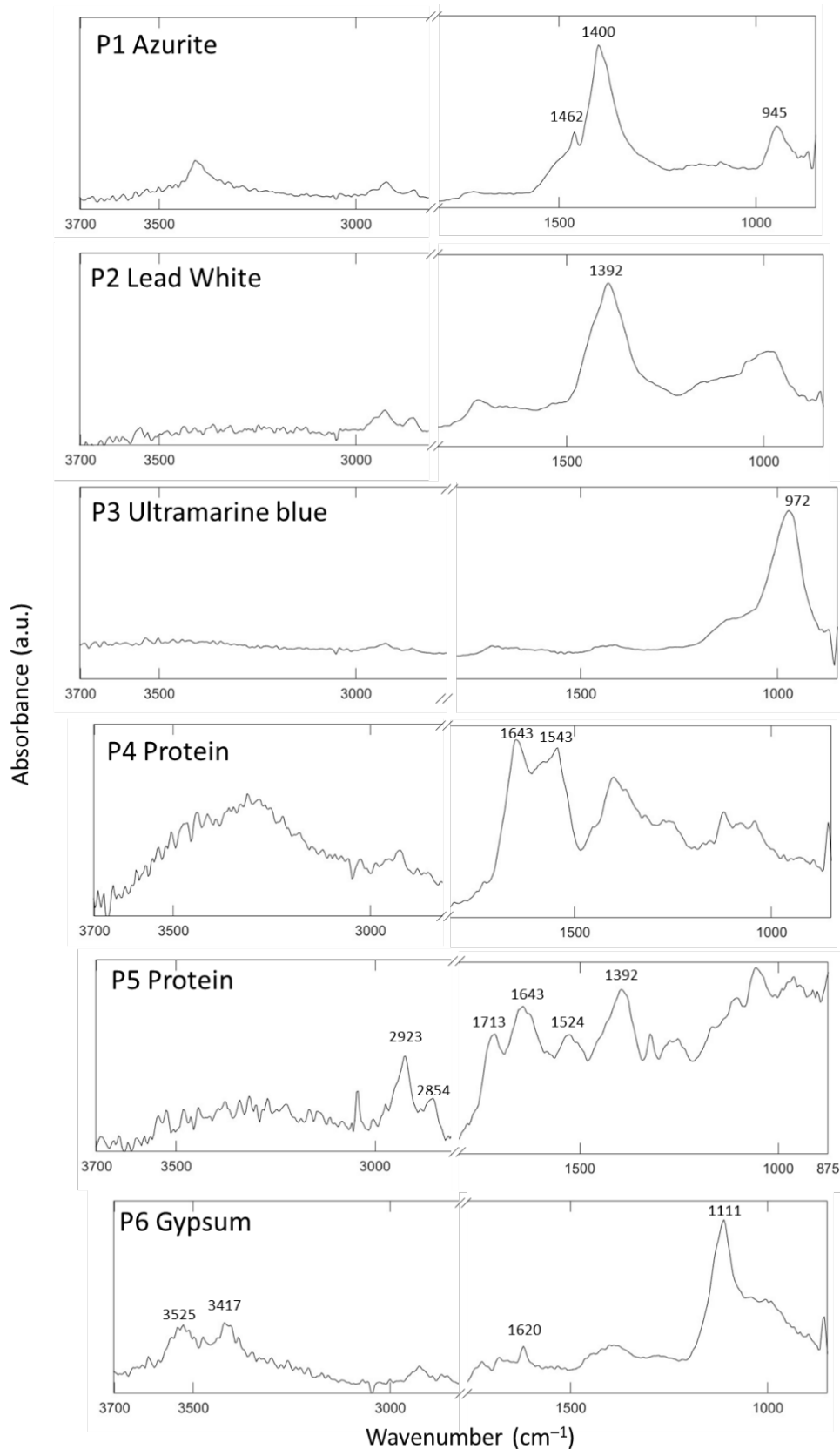


Figure 4.68 ATR-FTIR spectra extracted from pixels (p1–p6) in Figure 4.67b

be richer in binders and the bottom richer in particulates due to gravity.

Figure 4.69a shows the micrograph of cross-sectional sample 10 taken from the Virgin's cloak. The picture of this sample collection was supplemented in Figure 6.9 in the Appendices. The results of ATR-FTIR spectroscopic imaging are summarised in Figure 4.69b and Figure 4.70. Unlike sample 9, where azurite and ultramarine were used, only azurite was identified in the blue paint layer of sample 10. Other components such as clay and calcium carbonate were detected in this blue paint layer. Underneath this blue paint layer is a yellow layer. As SEM-EDX results (Figure 6.8b in the Appendices) indicate, this yellow paint layer mainly contains lead tin yellow (Pb_2SnO_4), which has been confirmed using Raman spectroscopy (not shown here). The results of ATR-FTIR spectroscopic imaging show a chemical image acquired by plotting integrated absorbance of a broad spectral band between 990 cm^{-1} and 1160 cm^{-1} , as indicated in p3 in Figure 4.69b and the spectrum of p3 in Figure 4.70. This ATR-FTIR chemical image shows the possible distribution of Pb_2SnO_4 , which has an identical distribution to Pb_2SnO_4 from the SEM-EDX image. Consequently, the ATR-FTIR spectrum of p3 may be attributed to Pb_2SnO_4 . However, limited literature discusses the FTIR spectrum of Pb_2SnO_4 due to the numerous overlapping spectral bands in this wavenumber region around 1068 cm^{-1} . The most frequently used techniques to identify Pb_2SnO_4 are Raman spectroscopy (Sandalinas & Ruiz-Moreno, 2004; Šefců et al., 2015), SEM-EDX (Sandalinas & Ruiz-Moreno, 2004) or FTIR spectroscopy in far-infrared region (Nodari & Ricciardi, 2019). In addition to these original materials, degradation products, including metal carboxylates and metal oxalates, were also identified in the yellow paint layer and the top of the blue paint layer, respectively. The metal oxalates exhibit spectral bands at 1323 cm^{-1} and 1639 cm^{-1} (refers to the spectrum of oxalates of p6 in Figure 4.70), while the metal carboxylates show a broad spectral band at around $1570\text{--}1600\text{ cm}^{-1}$ (refers to the spectrum of Pb_2SnO_4 of p3 in Figure 4.70). These metal oxalates may be calcium-based, as suggested by findings in the literature, indicating that calcium oxalate is one of the most common oxalates associated with the attack of oxalic acid on pigments or fillers containing calcium carbonate (Egel & Simon, 2013). Our ATR-FTIR

spectroscopic results show the presence of calcium carbonate, which may be the source of the calcium oxalate.

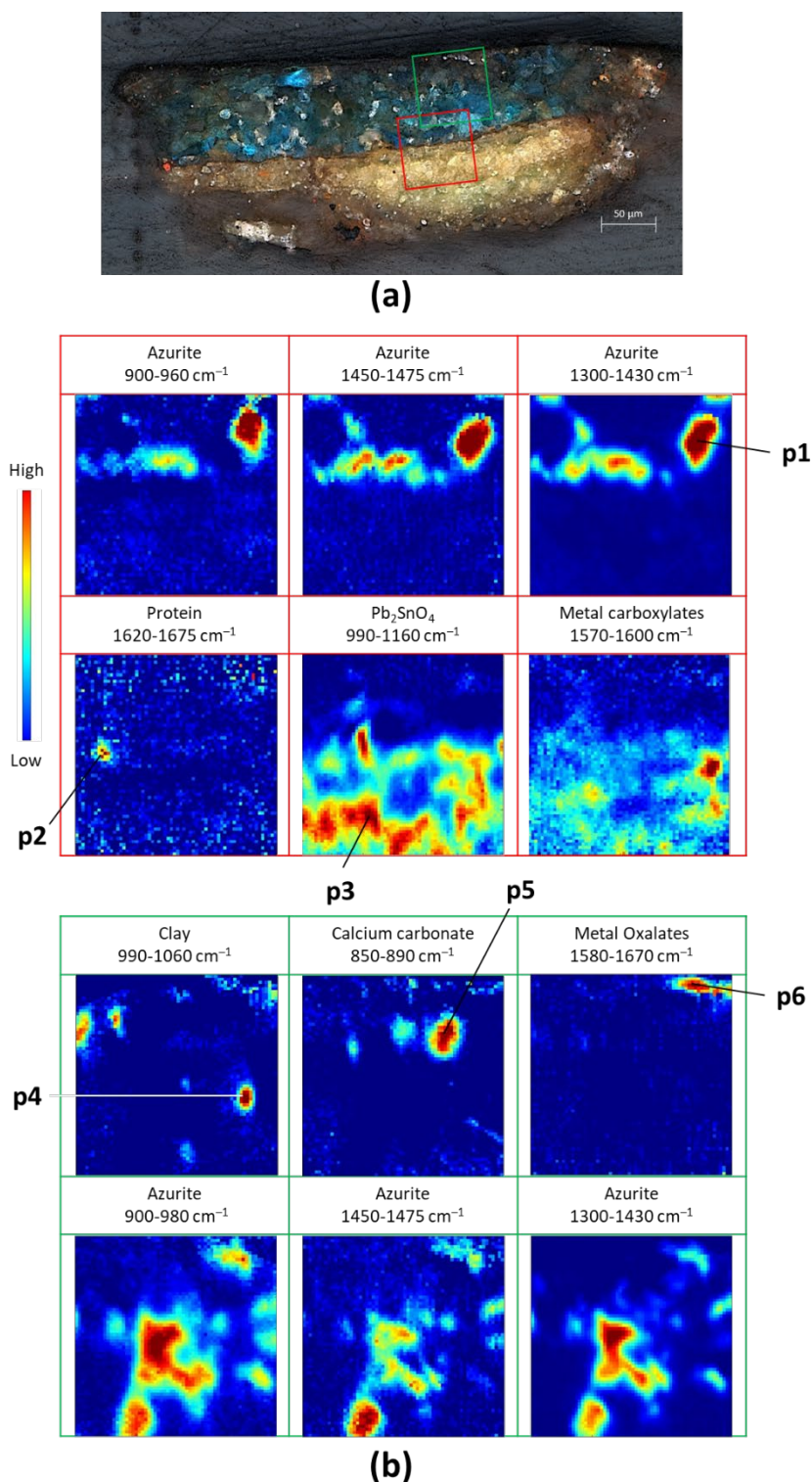


Figure 4.69 (a) Photomicrograph of sample 10. Red and green squares indicate the measuring areas (ca. 70 $\mu\text{m} \times 70 \mu\text{m}$) by micro ATR-FTIR spectroscopic imaging. Reprinted with permission, copyright © V&A Museum. (b) Micro ATR-FTIR images showing the distribution of chemical components identified.

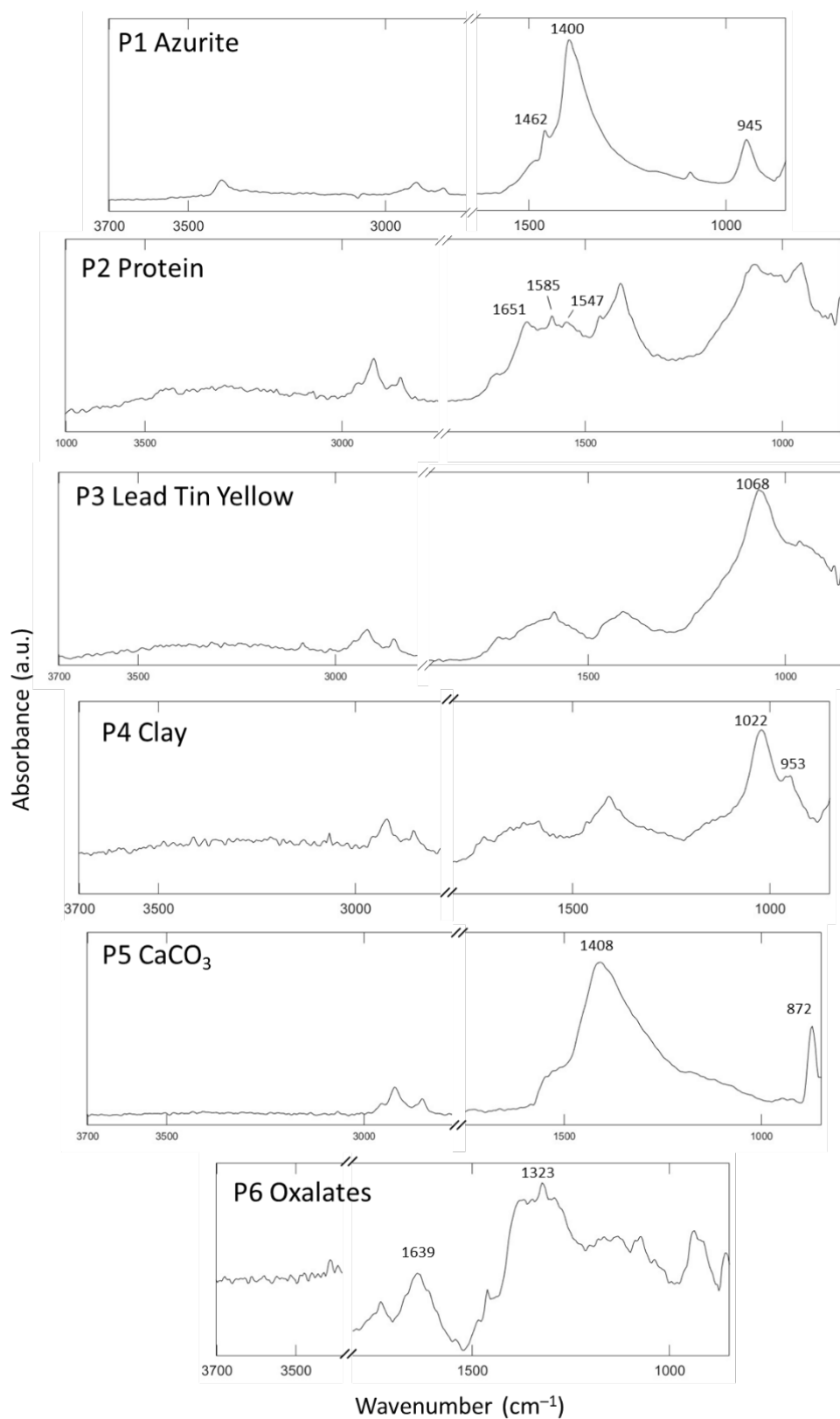


Figure 4.70 ATR-FTIR spectra extracted from pixels (p1–p6) in Figure 4.69b

Figure 4.71a shows the micrograph of cross-sectional sample 11 taken from the floor in Donatello's Virgin and Child. The picture of this sample collection was supplemented in Figure 6.9 in the Appendices. The presence of silicates, as displayed in Figure 4.71b,

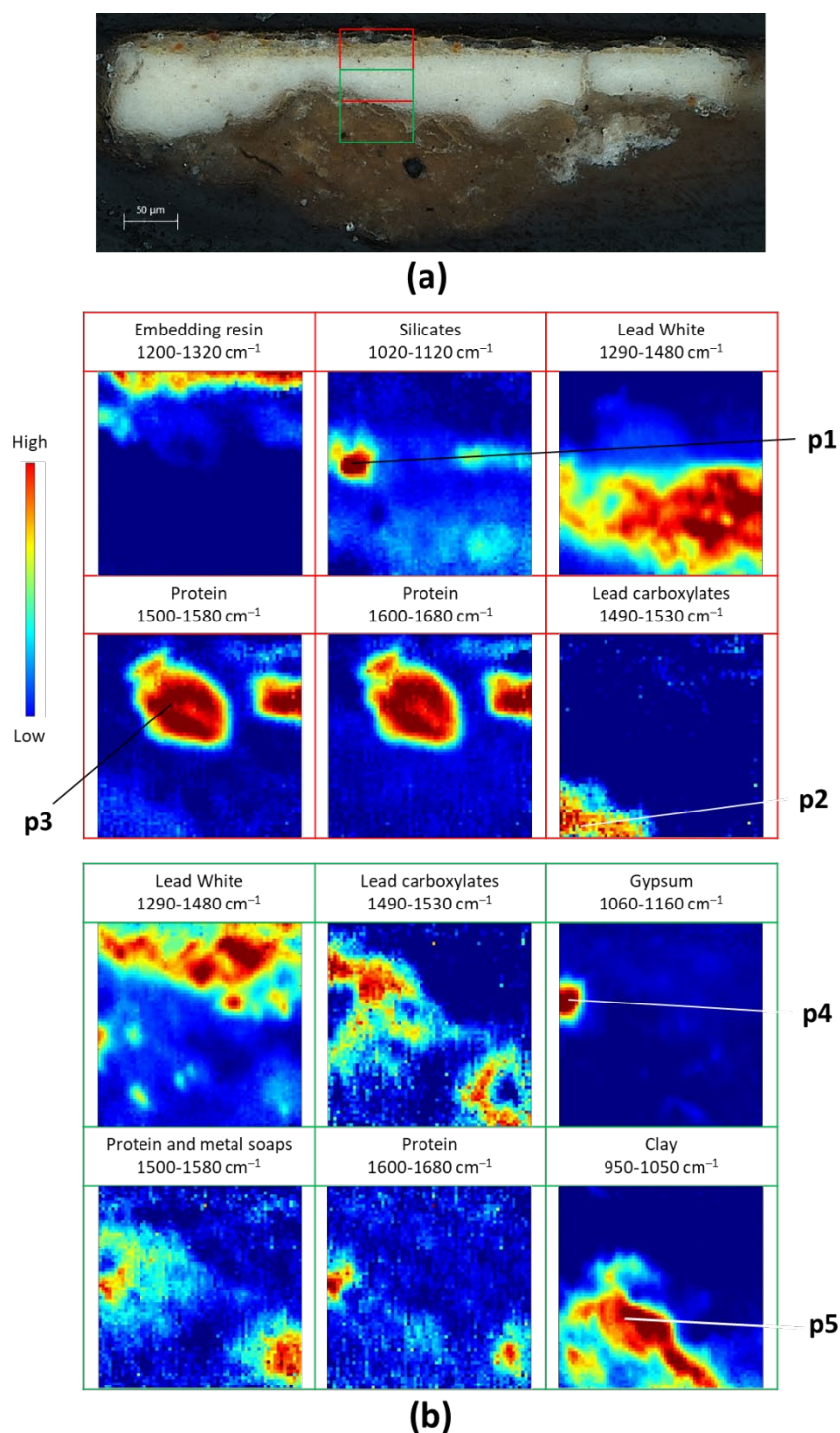


Figure 4.71 (a) Photomicrograph of sample 11. Red and green squares indicate the measuring areas (ca. 70 μm ×70 μm) by micro ATR-FTIR spectroscopic imaging. Reprinted with permission, copyright © V&A Museum. (b) Micro ATR-FTIR images showing the distribution of chemical components identified.

was identified by assigning a spectral band at 1061 cm^{-1} , as revealed in the spectrum of p1 in Figure 4.72. The identification of silicates may imply the utilisation of red iron oxide (Fe_2O_3) which has been identified with SEM-EDX (Figure 6.8c in the Appendices). Silicates are often in mixture with the iron-based minerals, which has also been observed from the results in Section 4.2. In addition, ATR-FTIR imaging results show identification and distributions of lead white and clay, further confirming the results of SEM-EDX (Figure 6.8c in the Appendices) and Raman spectroscopy (not shown here). It is of importance to note that CaCO_3 was assumed to be identified by the detection of Ca from the SEM results. However, ATR-FTIR spectroscopic results suggest these Ca-based components should be gypsum, as illustrated by assigning the spectral band at 1107 cm^{-1} in the chemical image (Figure 4.71b) and spectrum (Figure 4.72) of gypsum in p4. Proteins were also detected in the lead white layer and in the clay-containing ground layer. Apart from the original materials, lead carboxylates were also detected at the boundaries of the lead white layer and the clay-containing ground layer. Lead carboxylates show an apparent $\nu_{\text{as}}(\text{COO}^-)$ band at 1508 cm^{-1} , as shown in p2 in Figure 4.72, which is distinct from other metal carboxylates.

Figure 4.73a shows the micrograph of cross-sectional sample 12, extracted from the robe of Jesus. The picture of this sample collection was supplemented in Figure 6.9 in the Appendices. Clay was identified in the bottom layer, while azurite was identified in the blue paint layer, as revealed in Figure 4.73b. It is worth noting that this clay appears to be kaolinite due to the adsorption of inner-surface OH in-plane bending at 914 cm^{-1} , as indicated in the spectrum of p1 in Figure 4.74. These findings are consistent with the SEM-EDX results, as supplemented in Figure 6.8d in the Appendices. From the SEM-EDX results, gilding can be observed between the paint layer and the clay layer, with the detection of gold (Au). Although there is no spectral band of gold in the wavenumber region of $900\text{--}3900\text{ cm}^{-1}$, an overall higher absorbance value can be observed from pixels in the gilding area (not shown here), possibly due to the high optical reflection of gold. SEM-EDX has detected barium (Ba), implying the presence of barite (BaSO_4) impurity in the azurite blue layer. Micro ATR-FTIR spectroscopic imaging results have further supported these findings by assigning the bands of

$\nu(\text{SO}_4^{2-})$ at 984 cm^{-1} , 1057 cm^{-1} , 1184 cm^{-1} , as illustrated in the spectrum of p6 in Figure 4.74. Resin was also identified in the blue layer by assigning bands at 1724 cm^{-1} ($\nu(\text{C}=\text{O})$), 1273 cm^{-1} ($\nu(\text{C}-\text{O})$), and a doublet at 1122 cm^{-1} and 1068 cm^{-1} ($\nu(\text{C}-\text{O})$), which are analogous to the spectral bands that show in the ATR-FTIR spectrum of the embedding polyester resin. The source of the resin detected in the azurite blue layer is not clear. It is reasonable to assume that the polyester resin has penetrated

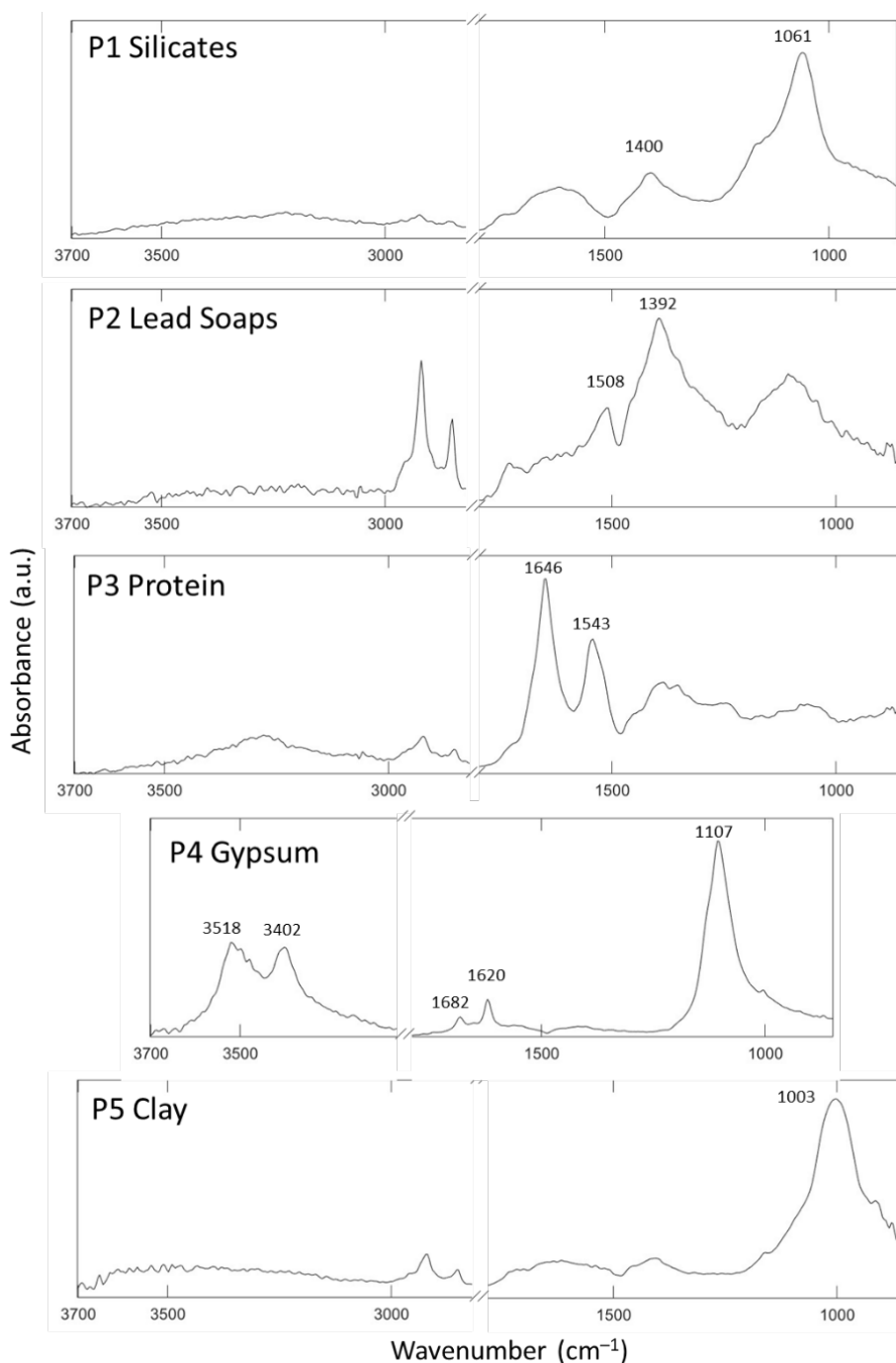


Figure 4.72 ATR-FTIR spectra extracted from pixels (p1–p5) in Figure 4.71b

the azurite blue layer during the embedding procedure, or the polishing was not sufficient to remove the residual embedded polyester resin.

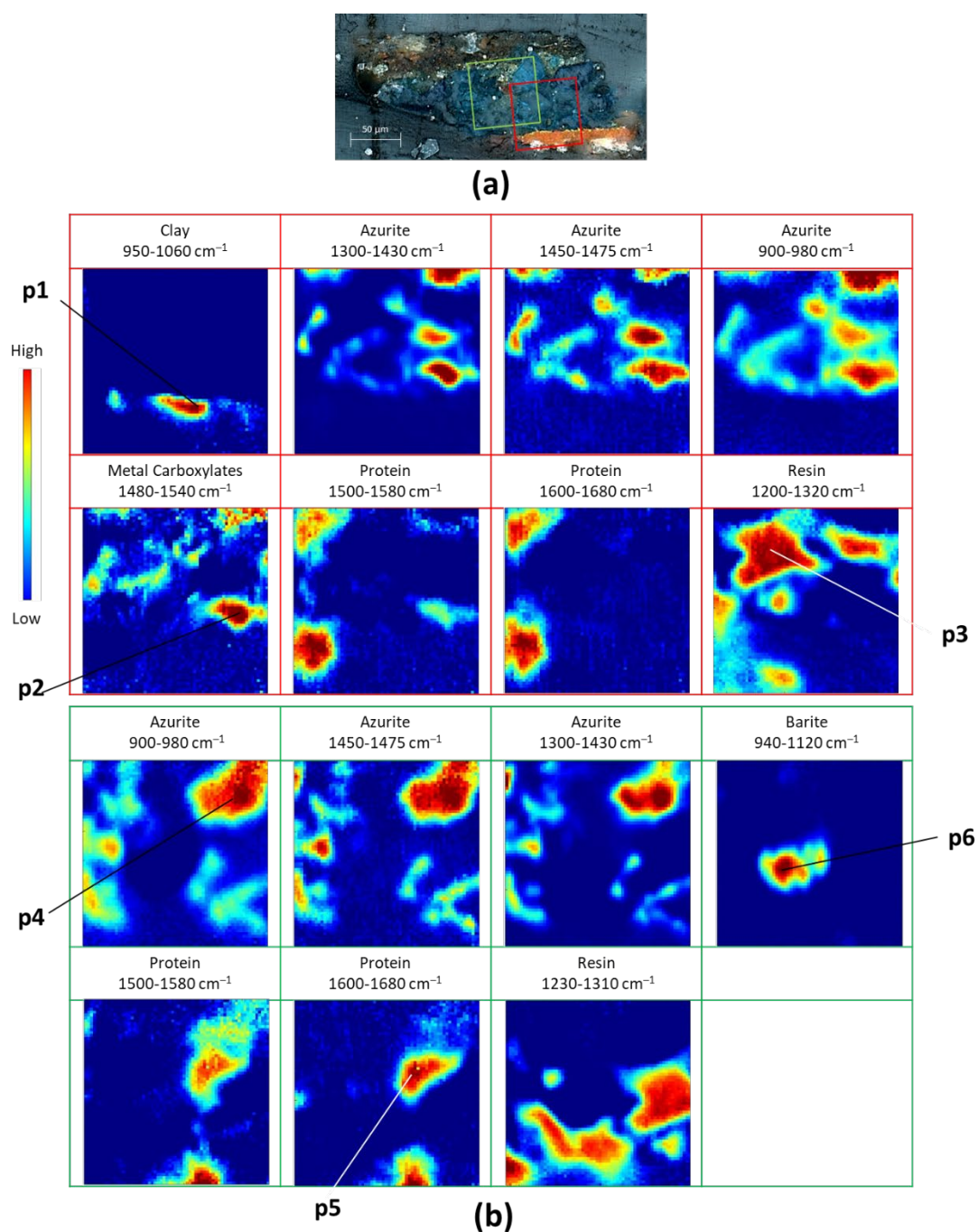


Figure 4.73 (a) Photomicrograph of sample 12. Red and green squares indicate the measuring areas (ca. 70 μm $\times$ 70 μm) by micro ATR-FTIR spectroscopic imaging. Reprinted with permission, copyright © V&A Museum. (b) Micro ATR-FTIR images showing the distribution of chemical components identified.

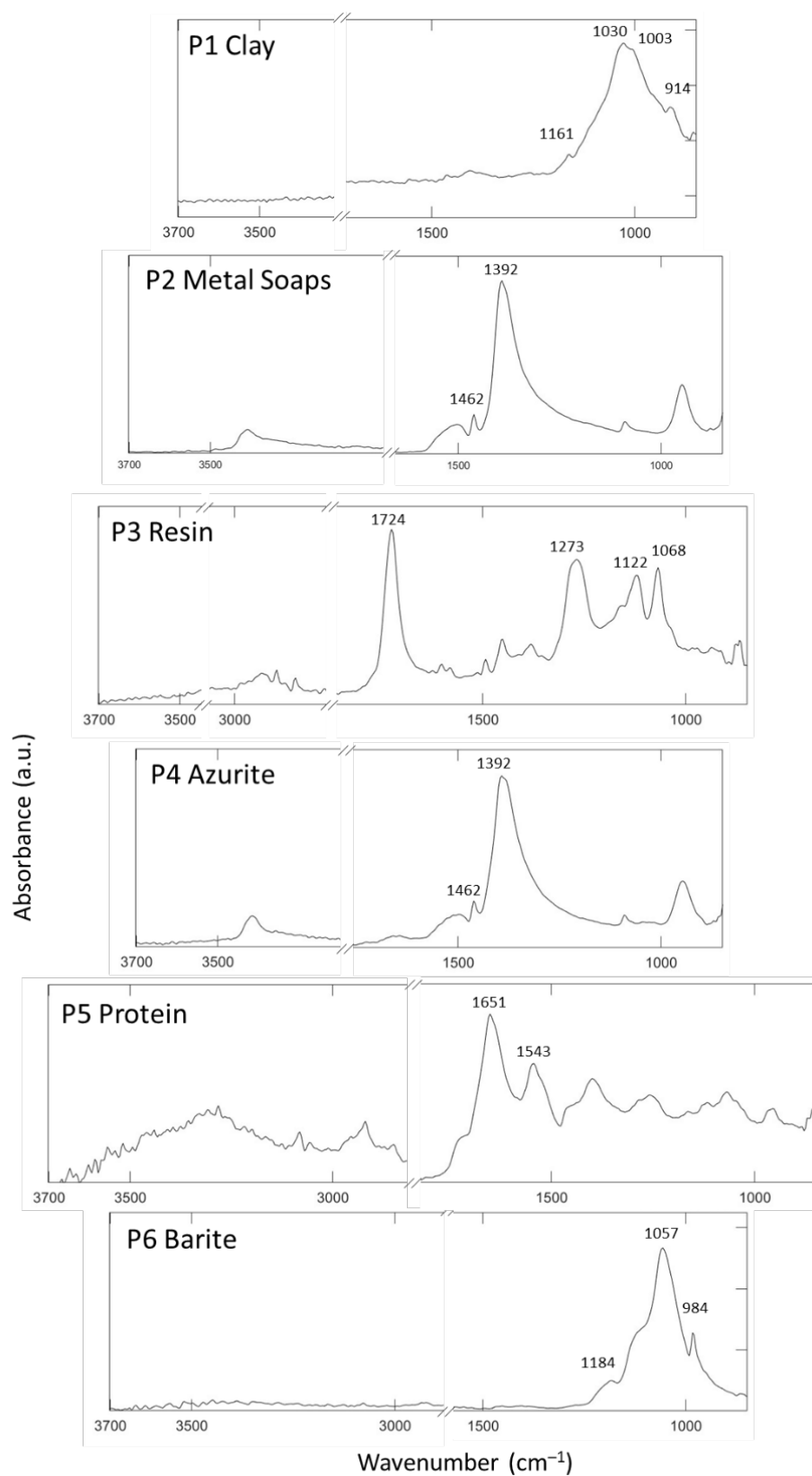


Figure 4.74 ATR-FTIR spectra extracted from pixels (p1–p6) in Figure 4.73b

4.5.4 Polarised micro ATR-FTIR spectroscopic imaging of clay and azurite in the samples

Polarised ATR-FTIR spectroscopic results are analysed and discussed in this section. Azurite and clay were chosen to study polarisation behaviours and structural inhomogeneity using p- and s-polarisation methods because they were abundantly identified in sample 9–12, as reported in Section 4.5.3. Figure 4.75 shows the polarised ATR-FTIR spectroscopic results of azurite in sample 9. Chemical images were acquired by plotting integrated absorbance of $\delta_{\text{out-of-plane}}(\text{O-H})$ ($900\text{--}980\text{ cm}^{-1}$) and $\nu_{\text{as}}(\text{CO}_3^{2-})$ ($1300\text{--}1430\text{ cm}^{-1}$, $1450\text{--}1470\text{ cm}^{-1}$, and $1480\text{--}1540\text{ cm}^{-1}$) for azurite, as illustrated in Figure 4.75b. These $\nu_{\text{as}}(\text{CO}_3^{2-})$ bands are classified into the third band of $\nu(\text{CO}_3^{2-})$. Carbonate group consists of four modes: the symmetric stretching (ν_1), the symmetric bending (ν_2), the anti-symmetric stretch (ν_3), and the anti-symmetric bending (ν_4) (Buzgar & Cuza, 2009; White, 1974). As a result, $\nu_{\text{as}}(\text{CO}_3^{2-})$ can also be denoted as $\nu_3(\text{CO}_3^{2-})$. The vibration mode of $\nu_{\text{as}}(\text{CO}_3^{2-})$ is schematised in Figure 4.76. In this section, $\nu_{\text{as1}}(\text{CO}_3^{2-})$, $\nu_{\text{as2}}(\text{CO}_3^{2-})$, and $\nu_{\text{as3}}(\text{CO}_3^{2-})$ are employed to stand for the three bands of $\nu_{\text{as}}(\text{CO}_3^{2-})$ at the wavenumber regions of $1300\text{--}1430\text{ cm}^{-1}$, $1450\text{--}1470\text{ cm}^{-1}$, and $1480\text{--}1540\text{ cm}^{-1}$, respectively.

Three points on the 64×64 -pixel-image were selected to investigate their polarised ATR-FTIR spectra, (5, 26), (20, 22), (31, 24), as labelled in the chemical image produced by plotting the integrated absorbance between $1300\text{--}1430\text{ cm}^{-1}$ with the non-polarised measurement. The $\nu_{\text{as3}}(\text{CO}_3^{2-})$ was detected at the points of (5, 26) and (31, 24) with non-polarised and p-polarised measurements, but was not identified with s-polarised measurement, as indicated in Figure 4.75b and c. In the spectrum of (20, 22), the point where $\nu_{\text{as3}}(\text{CO}_3^{2-})$ was not apparently detected with non-polarised and polarised measurements, the relative absorbance intensities of the $\nu_{\text{as1}}(\text{CO}_3^{2-})$ and $\nu_{\text{as2}}(\text{CO}_3^{2-})$ are unidentical. In other words, the $\nu_{\text{as1}}(\text{CO}_3^{2-})$ between $1300\text{--}1430\text{ cm}^{-1}$ are more active in the s-polarisation, while the $\nu_{\text{as2}}(\text{CO}_3^{2-})$ between are more active in the p-polarisation. In addition, the vibrations of $\delta_{\text{out-of-plane}}(\text{O-H})$ between $900\text{--}960\text{ cm}^{-1}$ are not active in p-polarisation at the points of (5, 26) and (31, 24).

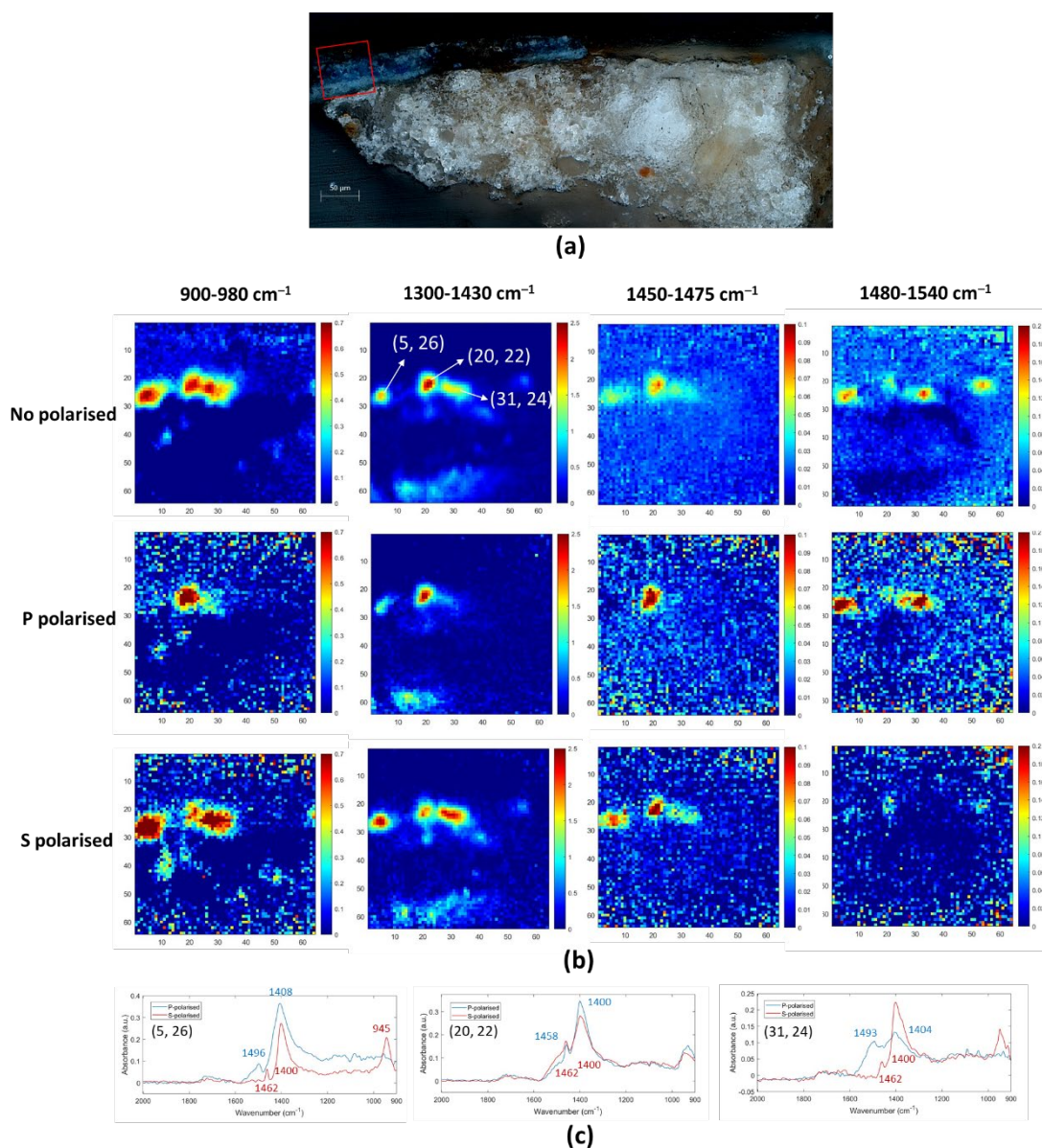


Figure 4.75 (a) Photomicrograph of sample 9, with a red square indicating the measuring area for polarisation investigation. Reprinted with permission, copyright © V&A Museum. (b) Polarised and non-polarised micro ATR-FTIR images produced by plotting integrated absorbance between 1300–1430 cm^{-1} , 1450–1470 cm^{-1} , 1480–1540 cm^{-1} , and 900–980 cm^{-1} (from left to right). (c) Polarised spectra of the pixels extracted from the micro ATR-FTIR images, with blue for p-polarisation and red for s-polarisation.

The $\nu_{\text{as3}}(\text{CO}_3^{2-})$ detected in sample 10 exhibit similar polarisation behaviour as that in sample 9. The $\nu_{\text{as3}}(\text{CO}_3^{2-})$ is less active in the s-polarisation, as indicated in the chemical image produced by plotting the integrated absorbance between 1480–1540 cm^{-1} in Figure 4.77b. The spectral bands of $\nu_{\text{as}}(\text{CO}_3^{2-})$ and $\delta_{\text{out-of-plane}}(\text{O-H})$ of azurite

show different polarisation behaviours within sample 10. Dichroic ratio (D) is defined as the A_p/A_s , where A_p and A_s represent the absorbance values for p-polarisation and s-polarisation, respectively. When A_p is larger than A_s , $D > 1$; when A_p is smaller than A_s , $D < 1$. It can be observed in Figure 4.77c that the dichroic ratio of absorbance between 1300–1430 cm^{-1} is smaller than 1 at the points of (24, 33), (50, 28), and (13, 35) from the polarised ATR-FTIR spectroscopic results in Figure 4.77b. However, the dichroic ratio of absorbance between 1300–1430 cm^{-1} is smaller than 1 at (50, 28) and is larger than 1 at (24, 33) and (13, 35), while the dichroic ratio of absorbance between 900–980 cm^{-1} is smaller than 1 at (24, 33) and (13, 35) and is larger than 1 at (50, 28), which shows the opposite polarisation behaviour.

The polarised ATR-FTIR results of azurite in sample 12 are summarised in Figure 4.78. The absorbance of $\delta_{\text{out-of-plane}}(\text{O-H})$ between 900–960 cm^{-1} indicate different polarisation behaviours. The dichroic ratio of absorbance between 900–960 cm^{-1} is smaller than 1 at the point of (30, 21), but is larger than 1 at (35, 31), as illustrated in Figure 4.78b and c. Different polarisation behaviours are also observed for the spectral bands of $\nu_{\text{as1}}(\text{CO}_3^{2-})$ between 1300–1430 cm^{-1} , and of $\nu_{\text{as2}}(\text{CO}_3^{2-})$ between 1450–1470 cm^{-1} , revealed from the chemical image with non-, s-, and p-polarisation in Figure 4.78b. The absorbance of $\nu_{\text{as3}}(\text{CO}_3^{2-})$ between 1480–1540 cm^{-1} appears to show similar polarisation behaviour. It is worth noticing that the $\nu_{\text{as2}}(\text{CO}_3^{2-})$ between 1450–

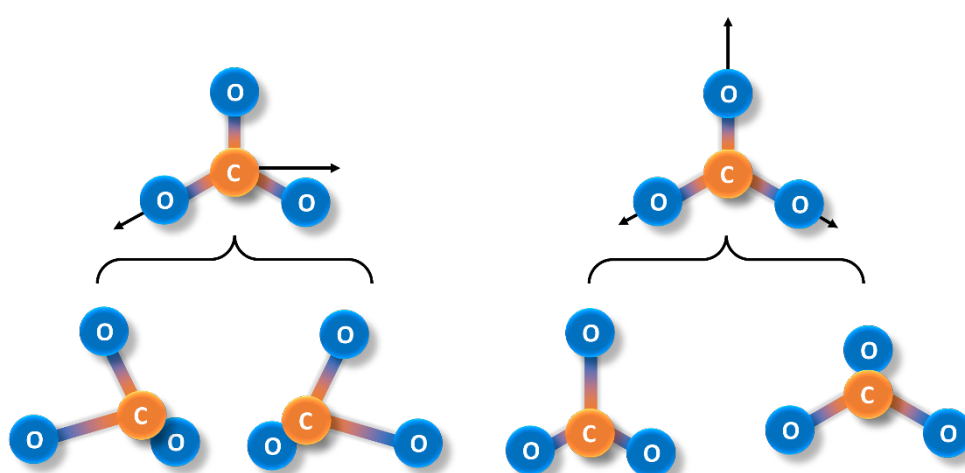


Figure 4.76 Schematic illustration of anti-symmetric stretching mode of $\nu(\text{CO}_3^{2-})$, with arrows representing the vibration displacement vectors (top row). Possible configurations of the atoms undergoing the vibrations (bottom row).

1470 cm^{-1} in the spectrum of the point (30, 21) has an elevated baseline from 0 a.u. to around 0.4 a.u. when comparing the s-polarisation and p-polarisation measurements. This elevated baseline of the $\nu_{\text{as}2}(\text{CO}_3^{2-})$ with s-polarisation might be correlated the influence of the $\nu_{\text{as}1}(\text{CO}_3^{2-})$ and the $\nu_{\text{as}3}(\text{CO}_3^{2-})$, which needs to be further studied.

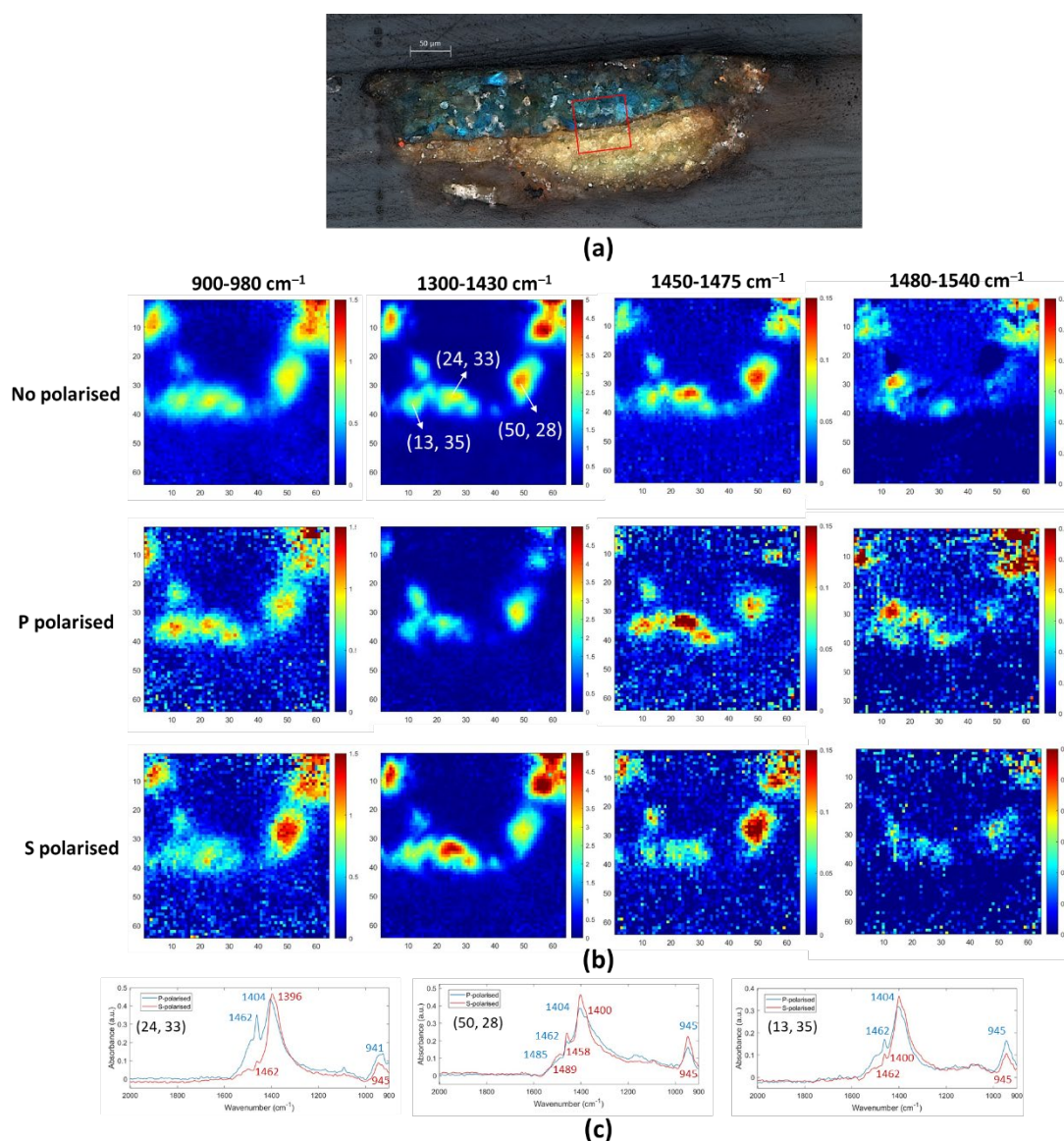


Figure 4.77 (a) Photomicrograph of sample 10, with a red square indicating the measuring area for polarisation investigation. Reprinted with permission, copyright © V&A Museum. (b) Polarised and non-polarised micro ATR-FTIR images produced by plotting integrated absorbance between 1300–1430 cm^{-1} , 1450–1470 cm^{-1} , 1480–1540 cm^{-1} , and 900–980 cm^{-1} (from left to right). (c) Polarised spectra of the pixels extracted from the micro ATR-FTIR images, with blue for p-polarisation and red for s-polarisation.

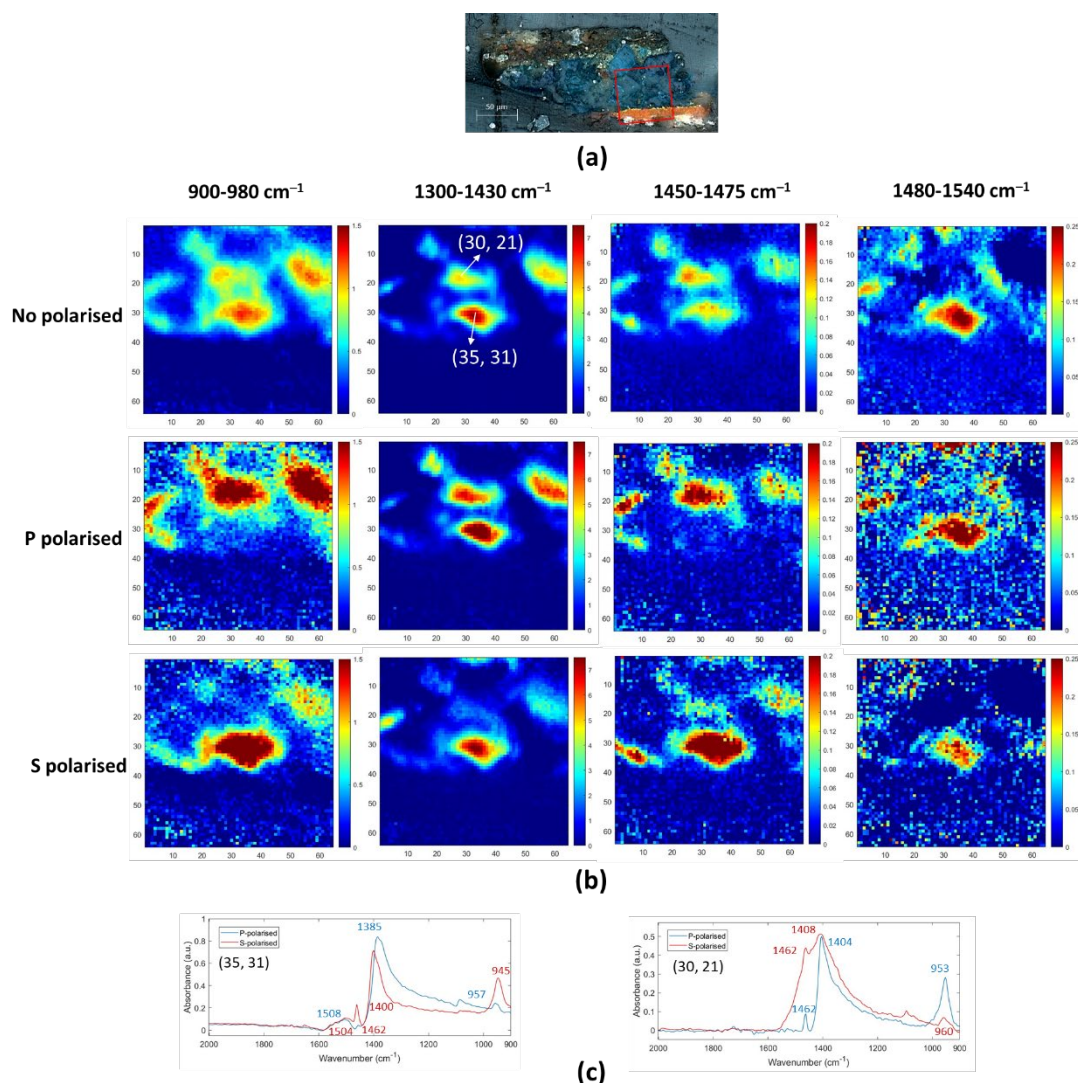


Figure 4.78 (a) Photomicrograph of sample 12, with a red square indicating the measuring area for polarisation investigation. Reprinted with permission, copyright © V&A Museum. (b) Polarised and non-polarised micro ATR-FTIR images produced by plotting integrated absorbance between 1300–1430 cm^{-1} , 1450–1470 cm^{-1} , 1480–1540 cm^{-1} , and 900–980 cm^{-1} (from left to right). (c) Polarised spectra of the pixels extracted from the micro ATR-FTIR images, with blue for p-polarisation and red for s-polarisation.

Figures 4.79 and 4.80 show the polarised ATR-FTIR results of clay in sample 11 and 12, respectively. The absorbance attributed to the clay identified in sample 11 and 12 is a broad band in the wavenumber region of 950–1050 cm^{-1} , peaked at around 1005 cm^{-1} . This broad spectral band is assigned to equatorial Si-O bond anti-symmetric stretching. The chemical images of clay with different polarisation measurements may appear similar, as displayed in Figures 4.79b and 4.80b. Nevertheless, the difference

can be observed from ATR-FTIR images of the dichroic ratio, as indicated in Figure 4.79c and 4.80c. These ATR-FTIR images of dichroic ratio were obtained by plotting the dichroic ratios between integrated absorbance in the region of 950–1050 cm^{-1} for p-polarisation and those for s-polarisation. The approach of using dichroic ratio acquired by integrated area of absorbance (method B) can enhance the quality of results because it eliminates the influence of baseline variation among pixels, compared to using dichroic ratio by the value of absorbance (method P), as elucidated in Section 3.2.1.

The ATR-FTIR images of dichroic ratio between 950–1050 cm^{-1} of the clay in sample 11 show various polarisation behaviours, with the dichroic ratio value around 2 at (10, 47), 1.8 at (20, 20), 1.2 at (35, 47), and 0.8 at (45, 45), as illustrated in Figure 4.79c. In contrast, the ATR-FTIR images of dichroic ratio in the wavenumber region of 950–1050 cm^{-1} of the clay in sample 12 show similar polarisation behaviours, with the dichroic ratio value close to 1 at (58, 45), (17, 43), and (22, 44), as illustrated in Figure 4.80c. The results of polarisation measurements suggest the clay in sample 11 is more structurally inhomogeneous. More information, such as the orientation of the equatorial Si–O bond anti-symmetric stretching mode within the samples, can be acquired but is not discussed in this thesis due to plenty of complex algorithms needed to achieve this, which may be out of focus. Furthermore, the implications of polarised ATR-FTIR spectroscopic techniques on clay components in sculptures are currently in progress and being explored. The aim of this section is to demonstrate the polarisation measurements using ATR-FTIR spectroscopic imaging on cross-sectional samples of cultural heritage objects. In the future, it would be of interest to focus on orientation analysis of the components that commonly show in the objects of cultural heritage.

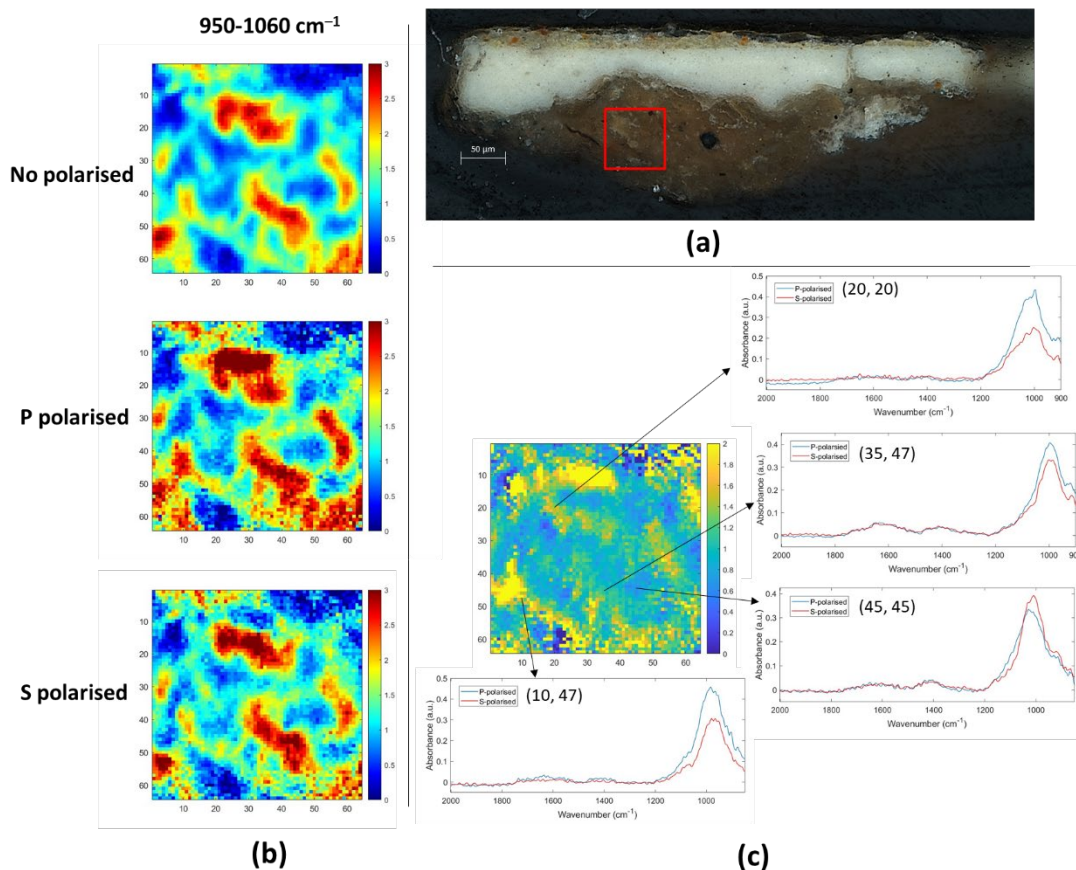


Figure 4.79 (a) Photomicrograph of sample 11, with a red square indicating the measuring area for polarisation investigation. Reprinted with permission, copyright © V&A Museum. (b) Polarised and non-polarised micro ATR-FTIR images produced by plotting integrated absorbance between 950–1060 cm⁻¹ (from top to bottom). (c) ATR-FTIR images of dichroic ratio and extracted polarised spectra.

4.5.5 Summary

This section clearly demonstrates the usefulness and capability of micro ATR-FTIR spectroscopic imaging technology in augmenting data acquired through other analytical techniques, including SEM and Raman spectroscopy. Four cross-sectional samples of Donatello's Virgin and Child, provided by the V&A Museum, have been examined using the micro ATR-FTIR spectroscopic imaging system. This section reveals that the results obtained from micro ATR-FTIR spectroscopic imaging, such as the identification of gypsum and barium sulfate, can either support or enhance the findings from SEM and Raman spectroscopy. Additionally, polarisation measurements on azurite and clay were implemented in this section, paving the way for the potential

application of polarised ATR-FTIR spectroscopic analysis to heritage objects from museums.

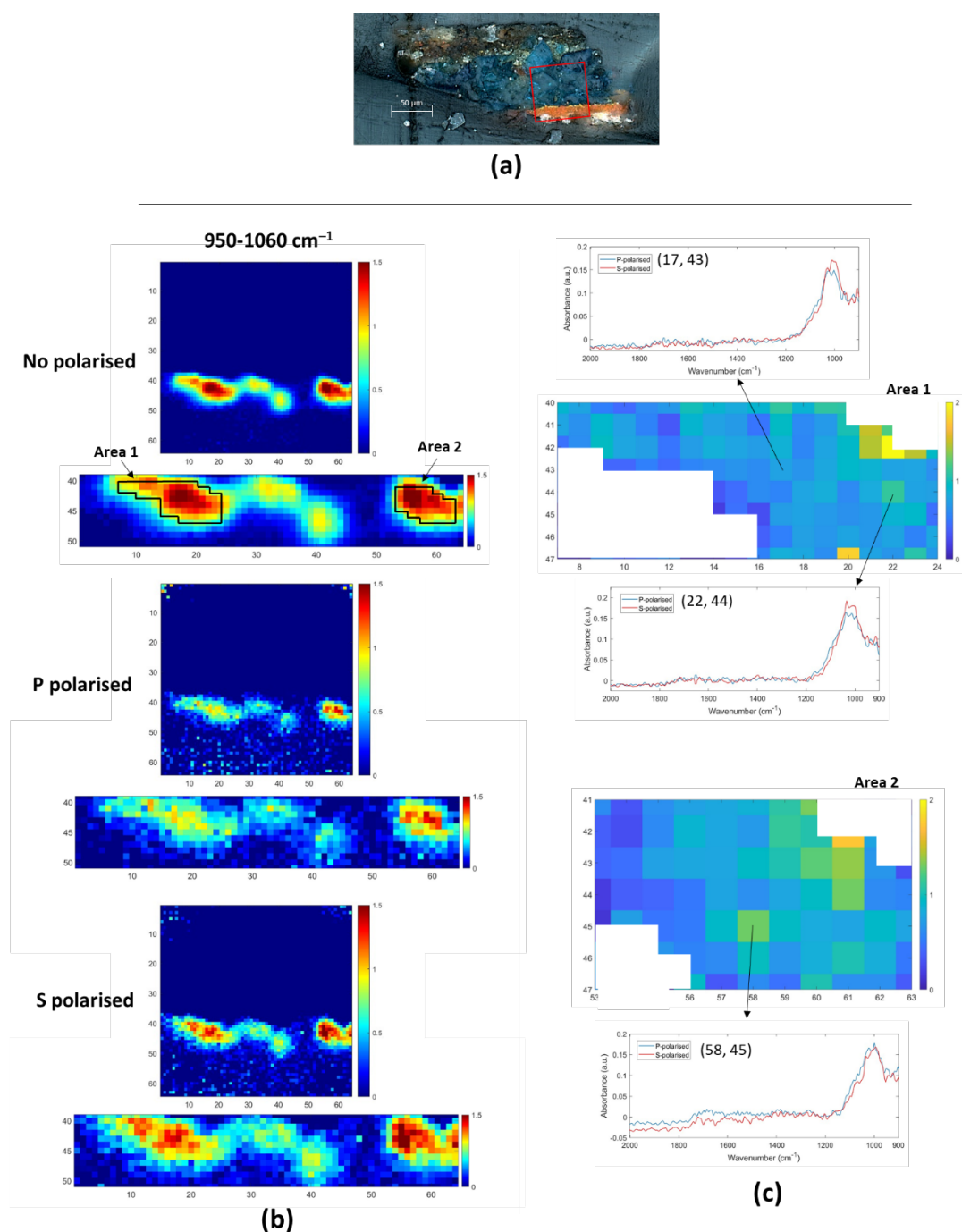


Figure 4.80 (a) Photomicrograph of sample 12, with a red square indicating the measuring area for polarisation investigation. Reprinted with permission, copyright © V&A Museum. (b) Polarised and non-polarised micro ATR-FTIR images produced by plotting integrated absorbance between 950–1060 cm^{-1} (from top to bottom). (c) ATR-FTIR images of dichroic ratio and extracted polarised spectra.

5 Conclusions and Outlooks

5.1 General conclusions

This thesis aimed to explore innovative methods for scientific examination of cultural heritage objects using macro and micro ATR-FTIR spectroscopic imaging. The research initiated with investigation of the pigments used by Martiros Sarian in five of his paintings created in 1900s–1940s (Liu & Kazarian, 2023), as addressed in Section 4.1. Through the application of micro ATR-FTIR spectroscopic imaging in conjunction with XRF, the successful identification and characterisation of the extracted blue, green, yellow/brown, and red/orange pigments were accomplished, offering insights into the palette of Martiros Sarian. The analysis revealed the presence of several different pigments commonly used by Sarian, aligning with those utilised by his influential predecessors, Henri Matisse and Paul Gauguin. Ultramarine blue was identified in earlier paintings (1900s–1910s), while cobalt-containing blue pigments, including cerulean blue and cobalt blue, were present in later works (1920s–1940s). Chromium-containing green pigments, including viridian and chromium oxide were identified in the five paintings, which were used with slight variations in combination. Yellow/brown and red/orange pigments were examined and discussed together, with the results showing that chrome yellow was found in *Morning in Stavrino* (1900s), red ochre in *Arabian Dancer* (1910s), *Caravan* (1920s), and *Kirovakan* (1940s). Erbium was identified using XRF; however, its presence is not convincing due to the lack of literature on the application of erbium red in oil paintings. It was noted that Prussian blue, one of the most commonly used blue pigments from the early 18th century to the late 20th century, was not detected from the examined five paintings. Further research on additional paintings by Sarian would help determine if Prussian blue was absent from his palette.

Section 4.1 also explored the formation of degradation products within the pigments, including metal carboxylates and metal oxalates. A significant role in the development

of these compounds was attributed to calcium carbonate. The identification of zinc and lead carboxylates as crystalline structure carboxylates was based on the distinct presence of the sharp band of $\nu_{as}(\text{COO}^-)$. Conversely, other amorphous metal carboxylates displayed broad $\nu_{as}(\text{COO}^-)$ bands in the ATR-FTIR spectra.

Results from Section 4.1 enrich our understanding of Martiros Sarian's artistic techniques and materials. The findings contribute to the preservation and conservation of his artworks, providing valuable insights for art historians, conservators, and curators. However, there are some limitations in this investigation that utilised micro ATR-FTIR spectroscopic imaging in conjunction with XRF. Since XRF used in this study is a semi-quantitative technique, the amount of sample needed for effective quantitative analysis is 2 to 3 grams. The extracted pigment samples, each weighing only around 200 mg, resulted in the inability to quantify sodium, an essential element in ultramarine blue. Additionally, all micro ATR-FTIR spectroscopic measurements were conducted on the pigment surfaces. Although 2D chemical ATR-FTIR images have suggested potential correlations between the formation of metal carboxylates/metal oxalates and calcium within the pigments, the influences of substances from ground layers were not examined. This information could be obtained by investigating sample stratigraphy through cross-sections.

To explore and advance the high chemical specificity and high spatial resolution capabilities of micro ATR-FTIR spectroscopic imaging, complex stratigraphy samples extracted from 19th century cartoons in oil on canvas that suffer from a degradation issue of white crusts were embedded in resin and were investigated, as described in Section 4.2 (Liu et al., 2023). Chemical distribution of paint materials and the components of the white crusts in the stratigraphic samples were determined. The chemical distribution of different types of metal carboxylates which may cause the appearance of white crusts on surface paintings were also characterised. Lead carboxylates were present in the ground layers of St George's ankle (samples 470), St David's cloak (sample 472), Harmony's hair (sample 479), Harmony's cloak (sample 481 and 482) and Harmony's harp (sample 483), whereas zinc carboxylates were identified in the paint layer samples 482 and 483. Unspecified amorphous metal

carboxylates featuring a broad band between 1500–1630 cm^{-1} in the paint layers of samples 472 and 479 may explain how lead and calcium ions have migrated from the ground layers, to form white crusts on the surface of paintings.

Lead plays a crucial role in the formation of the white crusts, as discussed in Section 4.2. The lead elements in the white crusts from samples 472 and 479 are likely to have migrated from the ground layers where abundant lead white and lead carboxylates were identified. The paint layers of samples 482 and 483 contain abundant lead elements due to Naples yellow identified. The upper paint layer of 483 also contains lead white that contributes to the amount of lead elements identified.

The micro ATR-FTIR spectroscopic imaging results supplemented with SEM-EDX mapping show that white crusts of sample 472 consisted of oxalates and sulfates, while that of sample 479 comprised major amounts of lead sulfate and minor amounts of calcium carbonate. The minor amounts of calcium carbonate were also observed in the white crusts of sample 482 and sample 483. A thin layer of oxalates together with a spot of gypsum were also discovered in the white crusts of sample 483. The remineralisation of lead white and the formation of lead carboxylates can be found in the white crust of Harmony's cloak sample 481. Crystallinity and the formation directions of the CaCO_3 surrounded by PbSO_4 in the white crust of sample 479 were acquired using the quantitative and qualitative analysis by evaluating the peak shift and calculating the integrated absorbance in the ATR-FTIR spectra, respectively. This information provides more in-depth insights into the heterogeneity and composition of the white crusts. Overall, the findings in Section 4.2 may facilitate novel practices and ideas for developing responsible and effective conservation strategies for oil paintings in the future.

The applications of micro and macro ATR-FTIR spectroscopic imaging approach to scientific investigation of objects of cultural heritage, in combination with other effective non-destructive techniques, were adopted next in Section 4.3. The focus shifted from oil paintings to black and white antique photographs that were produced in the late 19th –early 20th century. Three types of black and white antique photographs, salt print, albumen photographs, and silver gelatine photograph, were investigated. While the

identification of these three antique photographs using ATR-FTIR spectroscopy has been well-documented, this is the first instance, to our knowledge, of classifying these photographs using macro ATR-FTIR imaging coupled with PCA. Additionally, this section expanded the use of micro ATR-FTIR imaging from albumen photographs (Ricci et al., 2007) to salt print and silver gelatine photographs.

K-means clustering was implemented to analyse the micro ATR-FTIR data collected from the cross-sectional samples, enabling the characterisation of different layers within each antique photograph, as observed under confocal light and laser microscopy. The micrographs and micro ATR-FTIR images revealed that the salt print, albumen photograph, and silver gelatine photograph exhibit 1-layered (paper cellulose), 2-layered (albumen and paper cellulose), and 3-layered (gelatine, baryte, and paper cellulose) structures, respectively. XRF was employed to acquire elemental information from the surface of these three photographs, and SEM-EDX elemental mapping was utilised to further understand the elemental distribution in the cross-sections. The elemental data, in conjunction with micro ATR-FTIR spectroscopic imaging data, are essential for in-depth investigations of antique photographs with complex structures. The results suggest that the concentrations of the proteinaceous layers including albumen and gelatine layers should not be related to the amounts of Ag regarding whether the sample is a black or white end.

Extended from section 4.3, a depth profiling approach for macro and micro ATR-FTIR spectroscopic imaging measurements (Chan et al., 2008; Vichi, 2018), achieved by manipulating the angles of incident infrared (IR) light using custom-made apertures, was applied to the investigation of three antique photographs in Section 4.4. This depth profiling approach, featuring variable angles of incident IR light, facilitates the acquisition of 3D profiling information. Section 4.4 marks the first demonstration of the application of this depth profiling approach to the analysis of three types of antique photographs. To implement this approach, two sets of apertures (line and rotating) were installed on the macro ATR-FTIR spectroscopic imaging system, which employs a diamond crystal with a lower refractive index. Another set of apertures was used with the micro ATR-FTIR spectroscopic imaging system, utilising a Ge crystal with a higher refractive index. By varying the angles of incident IR light (θ), the refractive index of the IRE crystals (n_1), the refractive index of the samples being analysed (n_2), and

observing different wavenumbers (different λ), the penetration depth (dp) were determined, ranging from 0.49 μm to 4.35 μm in Section 4.4.

The results of depth profiling with micro ATR-FTIR spectroscopic imaging show that the relative thickness of gypsum on the surface of salt print photograph may be roughly a micrometre. This demonstration validates the usefulness of variable angle approach installed onto micro ATR-FTIR spectroscopic imaging which has an advantage of good z-direction spatial resolution, compared to confocal Raman microscopy, where the z-direction spatial resolution exceeds 2-3 μm . The results of depth profiling with both micro and macro ATR-FTIR spectroscopic imaging reveal that by increasing the angle of incident IR light, the distortion of spectral band attributed from the effect of anomalous dispersion can be reduced. On the contrary, by decreasing the angle of incident IR light, the performance of PCA chemometrics improved, allowing for better differentiation of the three types of photographs analysed.

Although the micro ATR-FTIR spectroscopic imaging technique has been employed for scientific investigations of cultural heritage objects for fifteen years, and its usefulness and capabilities have been validated and demonstrated, it is still not as commonly used in museums or cultural heritage institutions compared to other non-destructive equipment such as SEM and Raman spectroscopy. Section 4.5 delves into the utilisation of micro ATR-FTIR spectroscopy to investigate four cross-sectional samples of Donatello's Virgin and Child, provided by the V&A Museum. This section reveals that the results obtained from micro ATR-FTIR spectroscopic imaging, including the identification of gypsum and barium sulfate, can either support or enhance the findings from SEM and Raman spectroscopy. In addition, polarisation measurements on azurite and clay within the cross-sectional samples were implemented. Different polarisation behaviours were observed for the spectral bands of $\nu_{\text{as}}(\text{Si-O})$ for clay and $\delta_{\text{out-of-plane}}(\text{O-H})$ (900–980 cm^{-1}) and $\nu_{\text{as}}(\text{CO}_3^{2-})$ (1300–1430 cm^{-1} , 1450–1470 cm^{-1} , and 1480–1540 cm^{-1}) for azurite. Dichroic ratios were employed to display various polarisation behaviours and structural inhomogeneity using p- and s-polarisation methods. However, how these polarisation behaviours correlate with degradation conditions of the sculpture objects was not within the scope

of this study and should be explored in the future.

To sum up, the objectives of this thesis were achieved through a series of conducted experiments. Identification and characterisation of original materials and degradation products of various cultural heritage objects studied in this thesis have been successfully undertaken, and the results have contributed to cultural heritage conservation. Novel implementations, such as the variable angle approach and polarisation method, have been incorporated into the ATR-FTIR spectroscopic imaging system to investigate objects of cultural heritage. As often the case, there is additional work that can be carried out to further advance research in this field, and these prospects of future work are briefly outlined in the next section.

5.2 Future work

The experiments detailed in this thesis centred on advancing ATR-FTIR spectroscopic methods and unveiling new discoveries. Chemometrics was also adopted for spectroscopic data analysis on objects of cultural heritage. The results obtained highlight significant research and practical prospects for the ATR-FTIR spectroscopic imaging technique. These findings represent an initial step in establishing a comprehensive processing framework and demonstration for the proficient and impactful ATR-FTIR spectroscopic examination of cultural heritage objects. To progress toward this objective, further research is imperative in the following areas.

5.2.1 Enhancing the current ATR-FTIR spectroscopic findings of oil paintings in this thesis.

The creation years of the investigated paintings produced by Martiros Sarian are the 1900s–1940s. Some interesting findings include the absence of Prussian blue, and a significantly larger amount of lead identified in *Caravan*, which was created in the 1920s. To understand the choice of Sarian's palette, more paintings created in the 1920s should be explored. It is important to extend this research to investigate Martiros Sarian's paintings created in the 1950s–1970s, which is one final piece of the puzzle. In addition, for some micro ATR-FTIR spectroscopic results showing the presence of ultramarine blue containing sodium, while XRF results failed to detect sodium, it is necessary to use other techniques, such as Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), to confirm the presence of sodium. Given that this research has offered significant guidance in the first step towards characterisation of Martiros Sarian's paintings, further investigations, such as the preparation of cross-sectional samples and the utilisation of SEM-EDX, should also be considered.

Although the investigation of cartoon paintings created by Edward Poynter in the Heritage Collections at the UK Parliament is quite comprehensive, there are still some

intriguing research questions to be addressed. One such question is the location of the conversion of lead from metal carboxylates to lead sulfates in white crusts. Does this conversion take place in the paint layers, at the surface of the paintings, or either? Another question involves the crystallisation kinetics of calcium carbonate in the white crusts. These questions can be explored by using mock-up samples of metal carboxylates (Garrappa et al., 2020; J. J. Hermans et al., 2014) and white crusts containing lead sulfate and/or calcium carbonate. The final question arising from this research concerns the conservation treatment solution that removes the white crusts. Because this research focuses on the characterisation and identification of the paintings, conservation treatments were not discussed. After this research, conservators have applied Ethylenediaminetetraacetic acid (EDTA), a lead chelator, for the removal of the white crusts. However, it remains unclear how long this EDTA solution should be applied to the paintings before being washed away and what concentration of this solution is optimal—information crucial for understanding the conservation process. The pH of EDTA for the removal of a lead-based white crust has been discussed using SEM-EDX in the literature (Shah et al., 2023). It would be of interest to explore the proper duration and concentration of this EDTA solution using macro ATR-FTIR spectroscopic imaging system.

5.2.2 Developing a reliable model using an extensive database of antique photographs.

Despite the successful classification of the three types of antique photographs using chemometrics, including PCA and k-means clustering for macro and micro ATR-FTIR spectroscopic data, some identification difficulties still exist. For instance, beeswax might have been varnished onto albumen photographs, or gelatine might be used as an internal binder in the paper substrate for albumen photographs (Stulik & Kaplan, 2013), complicating the identification and categorisation of photographs. The photograph samples used in Section 4.3 have relatively simple structures compared to the types mentioned above. The prospective application of the ATR-FTIR

spectroscopic imaging technique, along with PCA and k-means clustering, holds the potential to analyse a broader range of 19th–20th century antique photograph samples with intricate structures and diverse manufacturing processes. Furthermore, the depth profiling using a variable angle approach demonstrated in Section 4.4 can readily be applied to ATR-FTIR spectroscopic measurements of various types of antique photographs, facilitating non-destructive 3D investigation without sampling. It is necessary to seek collaboration with institutions that archive and conserve photographs to build a reliable model from their database for this prospective ATR-FTIR spectroscopic application.

5.2.3 Conducting experiments involving IR polarisation measurements.

Azurite and clay in the samples of Donatello's Virgin and Child sculpture have exhibited different polarisation behaviours and structural inhomogeneity, the results obtained using p- and s-polarisation methods. These results may be attributed to varying degradation conditions corresponding to dissimilar molecular orientations. However, interpretations of the polarised ATR-FTIR spectroscopic data require further verification. The spectral bands of interest for investigating polarisation behaviours are $\nu_{\text{as}}(\text{Si-O})$ for clay and $\delta_{\text{out-of-plane}}(\text{O-H})$ (900–980 cm^{-1}) and $\nu_{\text{as}}(\text{CO}_3^{2-})$ (1300–1430 cm^{-1} , 1450–1470 cm^{-1} , and 1480–1540 cm^{-1}) for azurite. The utilisation of mock-up samples and artificial aging experiments can enhance the work presented in this thesis.

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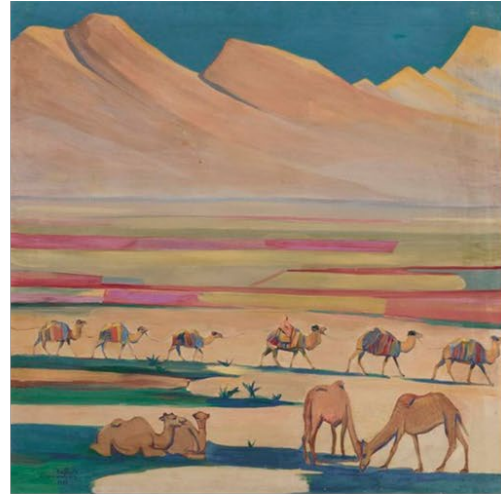
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6 Appendices



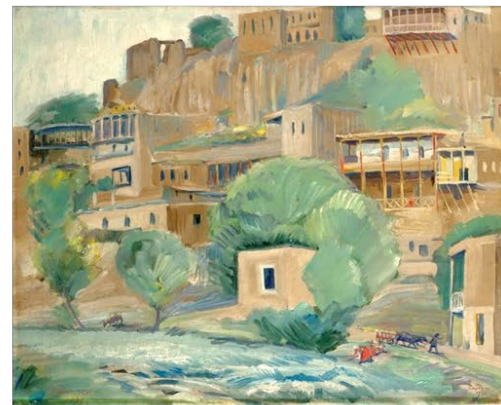
(a)



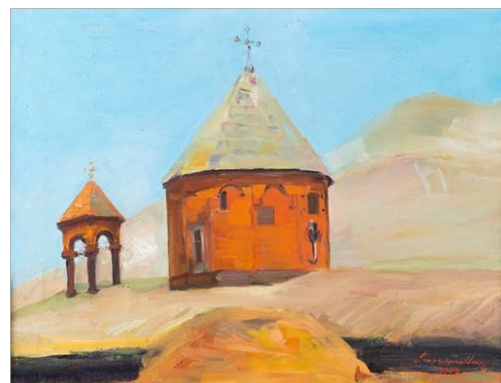
(c)



(b)



(d)



(e)

Figure 6.1 Five paintings housed at the Martiros Sarian House-Museum in Armenia: (a) *Morning in Stavrino* (1909), (b) *Arabian Dancer* (1913), (c) *Caravan* (1926), (d) *Yerevan Zangu River* (1931), and (e) *Kirovakan* (1948). Those pictures of the paintings are provided by Sophie Sarian, the Chief Curator at Martiros Sarian House-Museum.

Table 6.1 XRF data of the blue and the light blue pigments³

Colour Painting	Blue								Light blue	
	<i>Morning in Stavrino</i> (1909)		<i>Arabian dancer</i> (1913)		<i>Caravan (1926)</i>		<i>Yerevan Zangu River</i> (1931)		<i>Kirovakan (1948)</i>	
Quality/ Quantity	Zn	41.475 %	Zn	70.761 %	Pb	62.298 %	Zn	45.931 %	Zn	90.243 %
	Ca	18.057 %	Si	6.478 %	Ca	13.065 %	Sn	27.969 %	Ca	3.597 %
	S	9.69 %	S	5.27 %	Co	5.647 %	Co	13.582 %	Sn	1.911 %
	Si	7.504 %	Al	4.711 %	Al	4.862 %	Si	3.953 %	Co	1.658 %
	Cr	6.499 %	Ca	3.769 %	Fe	3.895 %	Ca	3.805 %	Si	0.993 %
	Al	5.213 %	Pb	2.574 %	Zn	3.839 %	Fe	1.873 %	S	0.706 %
	Pb	3.69 %	Fe	2.534 %	S	3.606 %	Cl	1.694 %	Cl	0.402 %
	Cl	2.715 %	K	0.951 %	Cd	1.42 %	Cr	1.027 %	Fe	0.209 %
	Fe	2.268 %	Cl	0.761 %	Cl	0.869 %	As	0.167 %	Cu	965.8 ppm
	Ti	0.763 %	P	0.575 %	Cr	0.209 %			As	914.8 ppm
	Cu	0.538 %	Cd	0.467 %	V	0.121 %			Cr	460.7 ppm
	As	0.484 %	Cr	0.381 %	Sr	859.5 ppm			P	456.7 ppm
	P	0.364 %	As	0.211 %	Ga	828.1 ppm				
	Cd	0.227 %	Ga	0.147 %						
	Co	0.22 %	Co	0.131 %						
	Mn	917.6 ppm	Cu	0.107 %						
	Ga	789.1 ppm	Ti	988.7 ppm						
	Ni	674.9 ppm	Mn	527.8 ppm						
	Sr	544.2 ppm	V	199.7 ppm						

Table 6.2 XRF data of the green and the blue green pigments

Colour	Green								Blue green	
Painting	Morning in Stavrino (1909)		Arabian dancer (1913)		Yerevan Zangu River (1931)		Caravan (1926)		Caravan (1926)	
Quality/ Quantity	Ca	72.222 %	Zn	64.572 %	Zn	54.605 %	Pb	75.037 %	Pb	73.932 %
	Cr	7.424 %	Na	8.699 %	Pb	14.551 %	Ca	9.221 %	As	9.722 %
	Si	3.865 %	S	6.005 %	Si	9.074 %	Cr	7.785 %	Cu	7.015 %
	S	3.552 %	Si	4.28 %	Ca	6.237 %	Mg	3.855 %	Ca	5.173 %
	Al	3.359 %	Ca	4.131 %	Al	4.801 %	Fe	1.284 %	Co	2.143 %
	Fe	3.228 %	Al	2.94 %	Fe	2.801 %	Zn	1.086 %	Zn	0.841 %
	Zn	2.794 %	Cr	2.331 %	S	1.84 %	Cd	0.764 %	Fe	0.451 %
	Cl	1.217 %	Fe	2.106 %	Cl	1.816 %	Cl	0.714 %	Cl	0.311 %
	P	1.08 %	Pb	1.578 %	Cr	1.369 %	Ti	0.116 %	Sn	0.174 %
	Pb	0.418 %	Ti	1.505 %	Co	1.246 %	Sr	690.2 ppm	Sr	863.2 ppm
	Co	0.399 %	P	0.683 %	As	0.756 %	Mn	502.5 ppm	Cr	757.2 ppm
	Ti	0.2 %	Cl	0.418 %	Er	0.598 %	Zr	195.8 ppm	Ti	655 ppm
	Cu	0.127 %	Co	0.296 %	V	0.124 %			Zr	105.3 ppm
	As	649.7 ppm	Cd	0.2 %	Ga	0.107 %				
	Mn	505.8 ppm	Sn	913 ppm	Mn	747.8 ppm				
			As	868.2 ppm						
		Sr	790.6 ppm							

³ In the obtained XRF results, specific elements are observed to exhibit a concentration of 0 ppm. This occurrence stems from the fact that while these elements were detected during the qualitative analysis phase, their corresponding signals were of insufficient strength to facilitate accurate quantification in the subsequent quantitative analysis.

Table 6.3 XRF data of the yellow and the brown pigments

Colour Painting	Yellow				Brown	
	<i>Morning in Stavrino (1909)</i>		<i>Caravan (1926)</i>		<i>Caravan (1926)</i>	
Quality/ Quantity	Si	24.419 %	Pb	87.827 %	Pb	92.339 %
	Ca	21.482 %	Ca	4.994 %	Ca	3.044 %
	Zn	14.826 %	Cd	2.742 %	Cd	2.339 %
	Cl	8.94 %	Ti	1.219 %	Zn	1.055 %
	Pb	7.658 %	Cl	1.063 %	Al	0.346 %
	S	7.583 %	Fe	0.851 %	Fe	0.305 %
	Fe	7.213 %	Zn	0.737 %	Cr	0.193 %
	Cr	2.975 %	V	0.253 %	Co	0.16 %
	Sn	2.479 %	Cr	0.211 %	Sr	777.8 ppm
	Ti	2.041 %	Sr	828.5 %	Ti	632.3 ppm
	As	0.383 %	Zr	208.9 %	Cu	446 ppm
					Zr	320.7 ppm
					Rb	20.5 ppm

Table 6.4 XRF data of the red and the orange pigments

Colour Painting	Red				Orange	
	<i>Arabian dancer (1913)</i>		<i>Caravan (1926)</i>		<i>Kirovakan (1948)</i>	
Quality/ Quantity	Zn	63.831 %	Pb	45.645 %	Zn	67.757 %
	Na	12.947 %	Cl	19.636 %	Si	12.517 %
	S	9.227 %	Co	10 %	Ca	10.242 %
	Ca	3.384 %	Ca	9.61 %	Fe	3.999 %
	Al	2.512 %	P	6.532 %	Cl	2.117 %
	Si	2.181 %	Fe	3.648 %	S	2.085 %
	Cd	1.433 %	Zn	2.52 %	Ti	0.389 %
	Fe	1.242 %	Er	1.841 %	Cr	0.341 %
	P	1.187 %	Cr	0.56 %	V	0.207 %
	Cl	0.612 %	Ga	87.5 ppm	As	0.128 %
	K	0.427 %			Co	0.119 %
	As	0.399 %				
	Cr	0.372 %				
	Ti	0.106 %				
	Co	920.1 ppm				
	Mn	474.2 ppm				

Harmony's hair



Figure 6.2 Detail photo of the investigated surface oil cartoons affected by the white crusts.

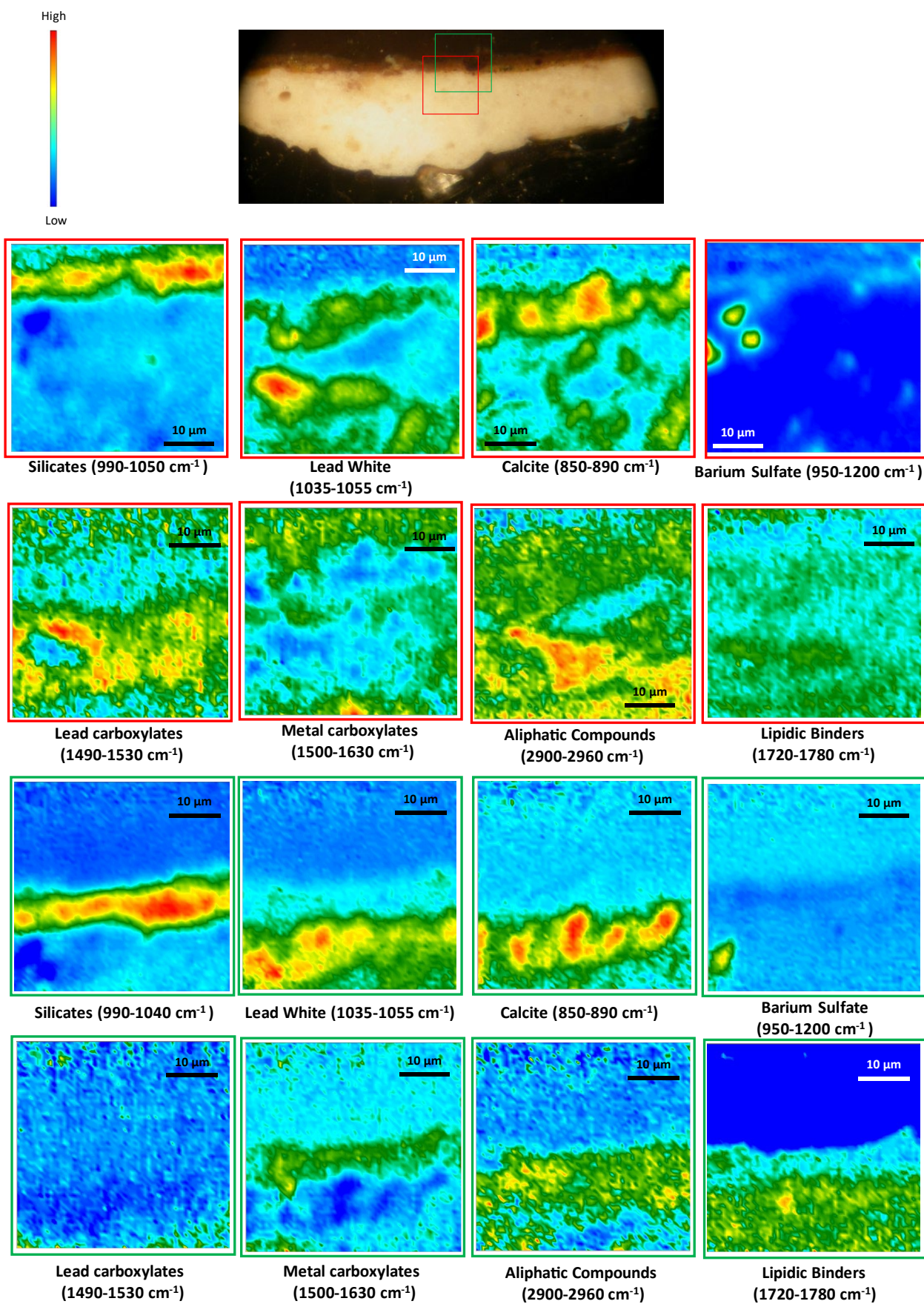


Figure 6.3 ATR-FTIR chemical images of the ground and lower paint layer of sample 470

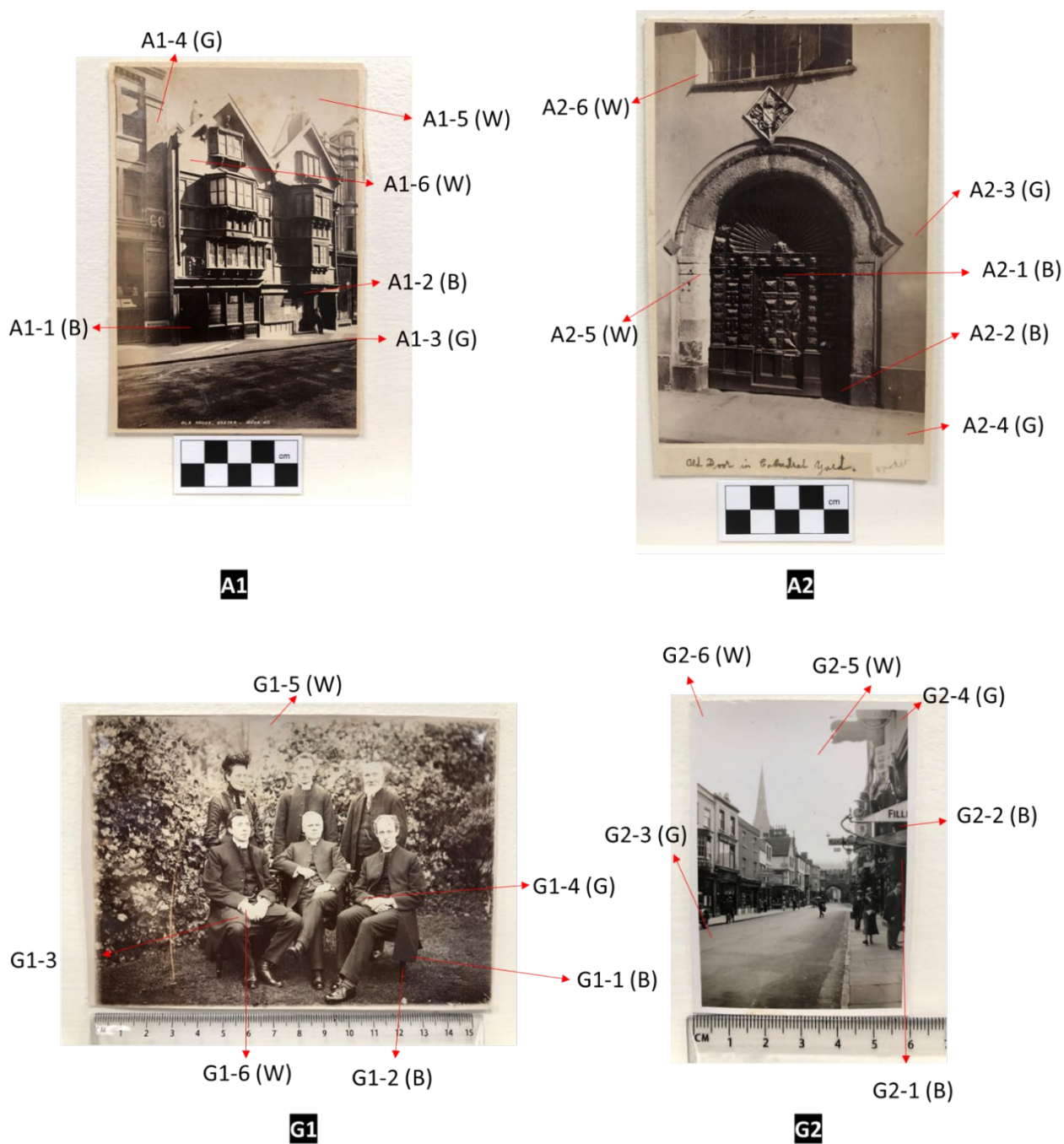


Figure 6.4-1 Two albumen photographs (A1 and A2) and two silver gelatine photographs (G1 and G2) for the experiment regarding the correlation between the amount of silver elements and the concentration of binders (albumen and gelatine), with approximate sample locations of black and white areas marked. W stands for white; G stands for grey and B stands for black.

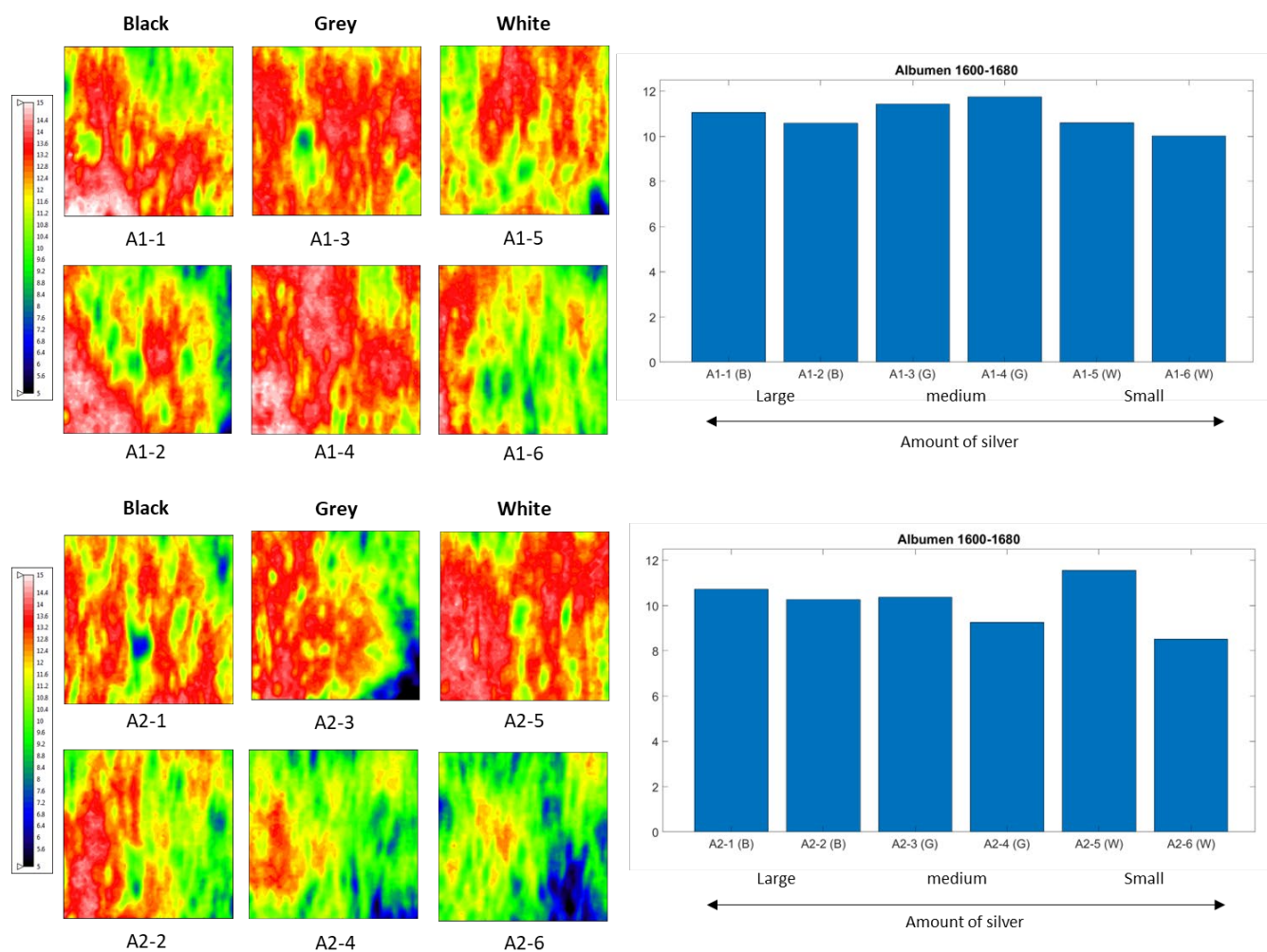


Figure 6.4-2 IR images of albumen photographs (A1 and A2) produced by plotting the integrated absorbance between 1500 and 1580 cm^{-1} (Amide II) using macro ATR-FTIR spectroscopic imaging (left). The values of integrated absorbance between 1500 and 1580 cm^{-1} vs the amount of silver elements in different areas of the albumen photographs (right).

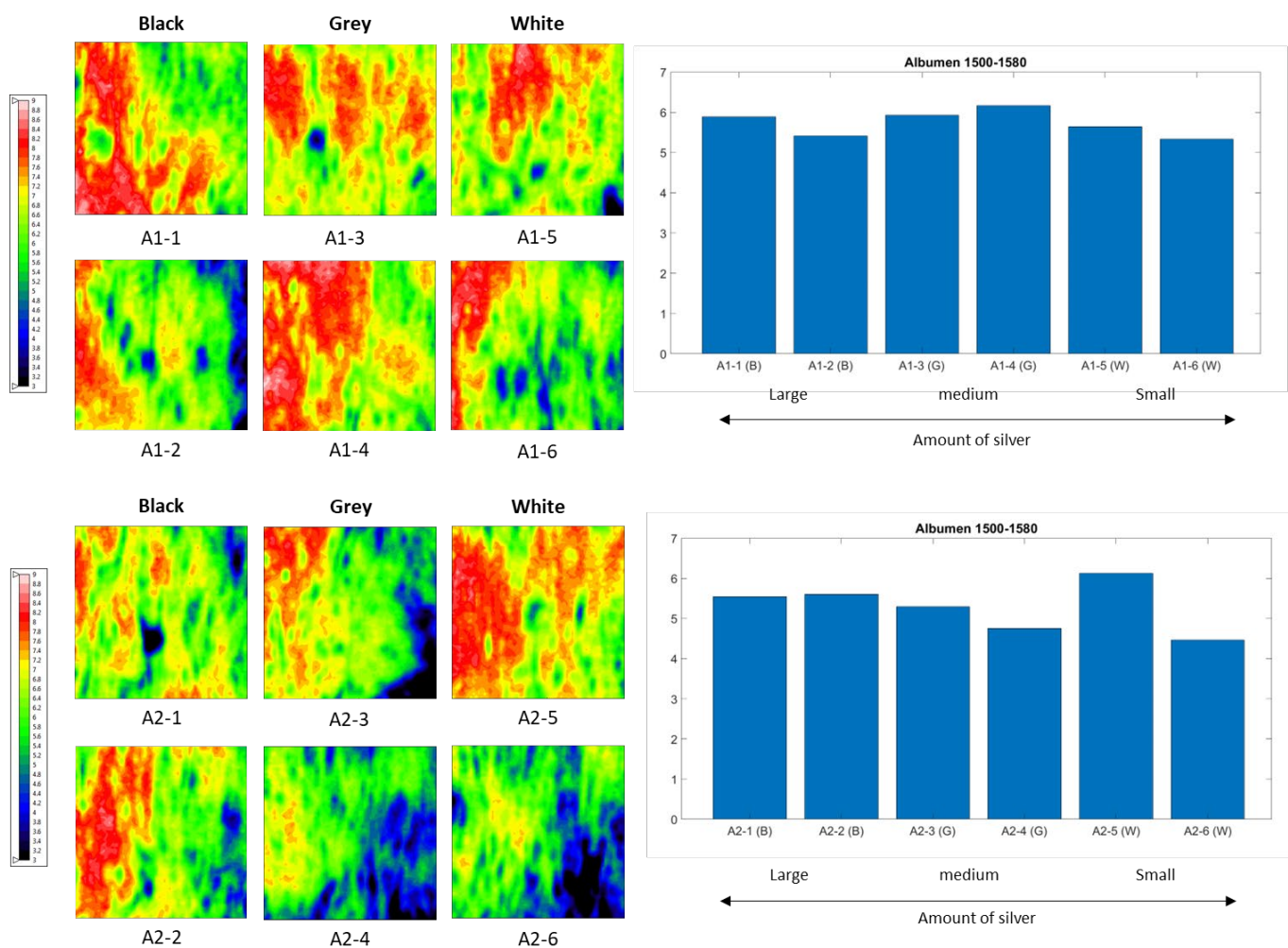


Figure 6.4-3 IR images of albumen photographs (A1 and A2) produced by plotting the integrated absorbance between 1600 and 1680 cm^{-1} (amide I) using macro ATR-FTIR spectroscopic imaging (left). The values of integrated absorbance between 1600 and 1680 cm^{-1} vs the amount of silver elements in different areas of the albumen photographs (right).

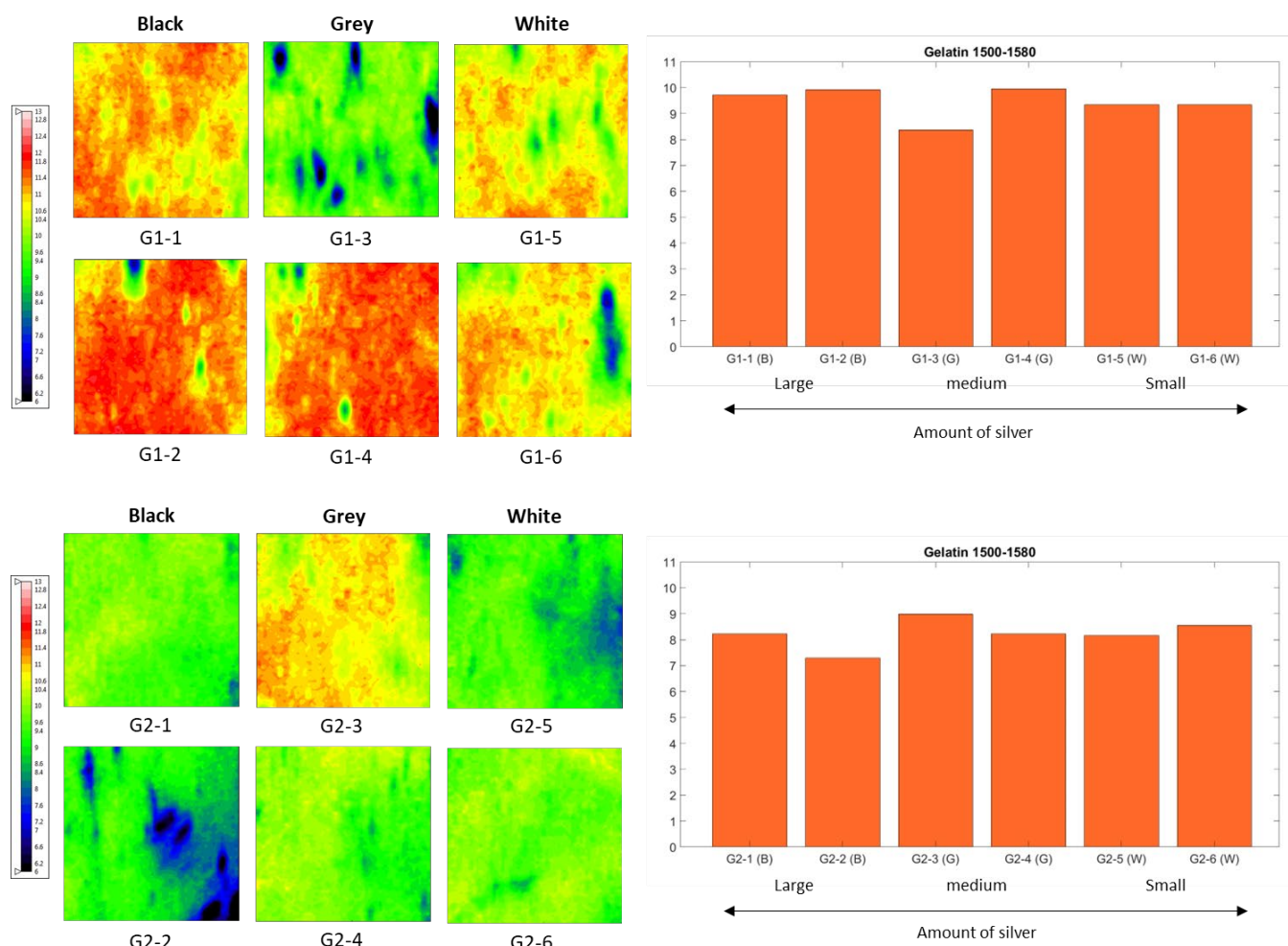


Figure 6.4-4 IR images of silver gelatine photographs (G1 and G2) produced by plotting the integrated absorbance between 1500 and 1580 cm^{-1} (Amide II) using macro ATR-FTIR spectroscopic imaging (left). The values of integrated absorbance between 1500 and 1580 cm^{-1} vs the amount of silver elements in different areas of the silver gelatine photographs (right).

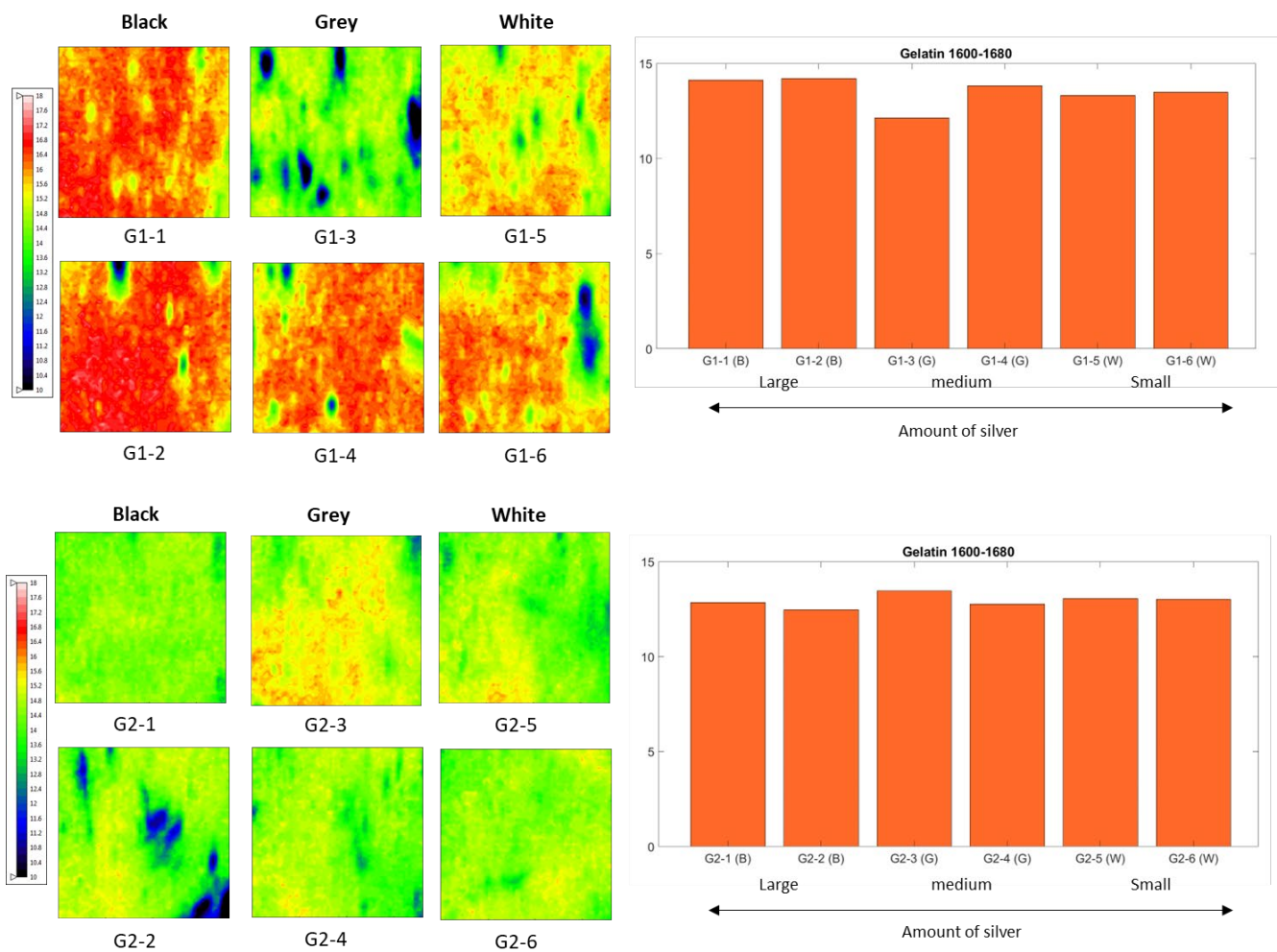


Figure 6.4-5 IR images of silver gelatine photographs (G1 and G2) produced by plotting the integrated absorbance between 1600 and 1680 cm^{-1} (Amide I) using macro ATR-FTIR spectroscopic imaging (left). The values of integrated absorbance between 1600 and 1680 cm^{-1} vs the amount of silver elements in different areas of the silver gelatine photographs (right).

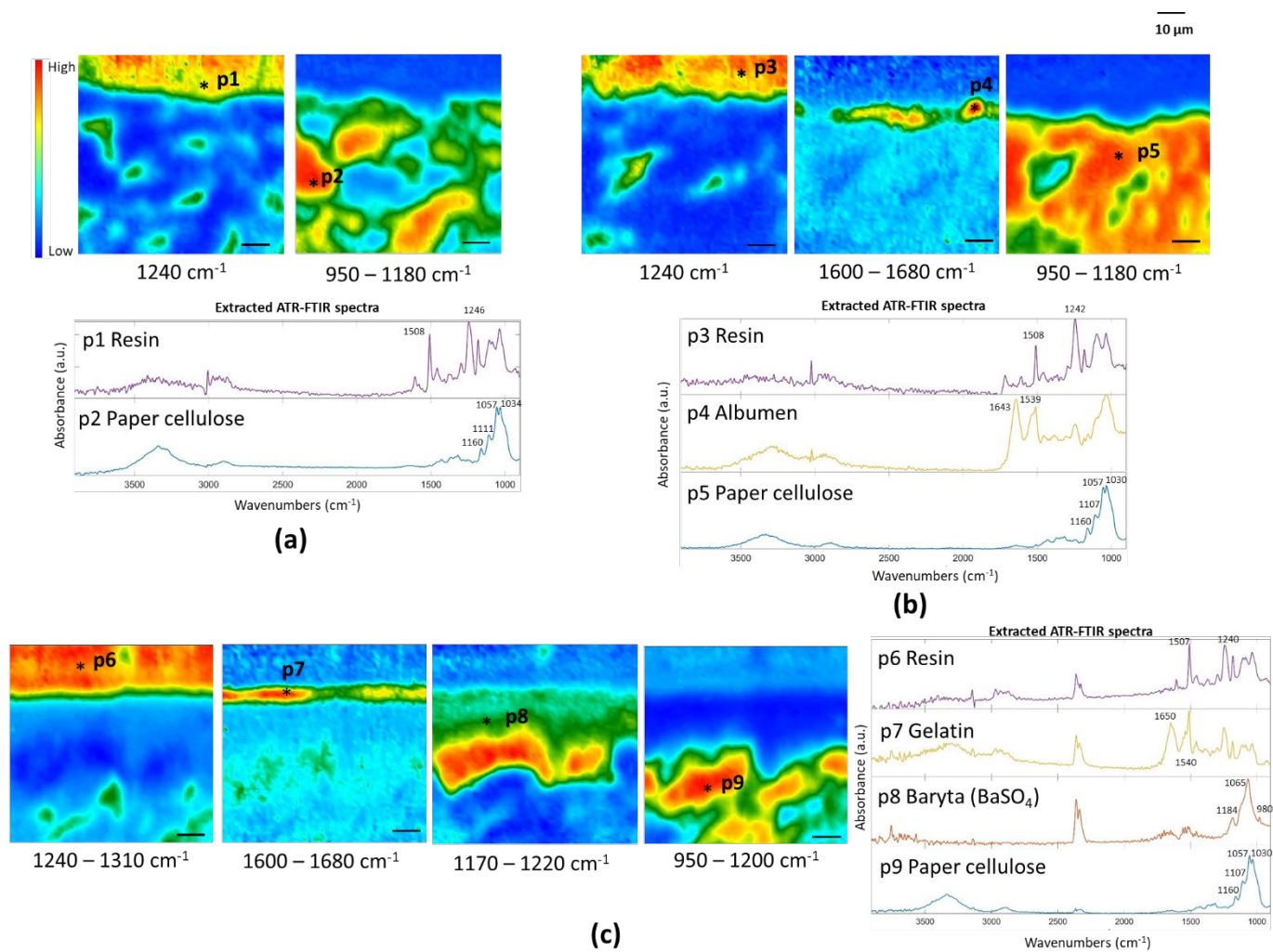


Figure 6.5 Chemical images of white area cross-sectional samples of (a) salt print, (b) albumen photograph and (c) silver gelatine photograph. The FTIR spectra extracted from 9 pixels of the samples are provided next to the chemical images.

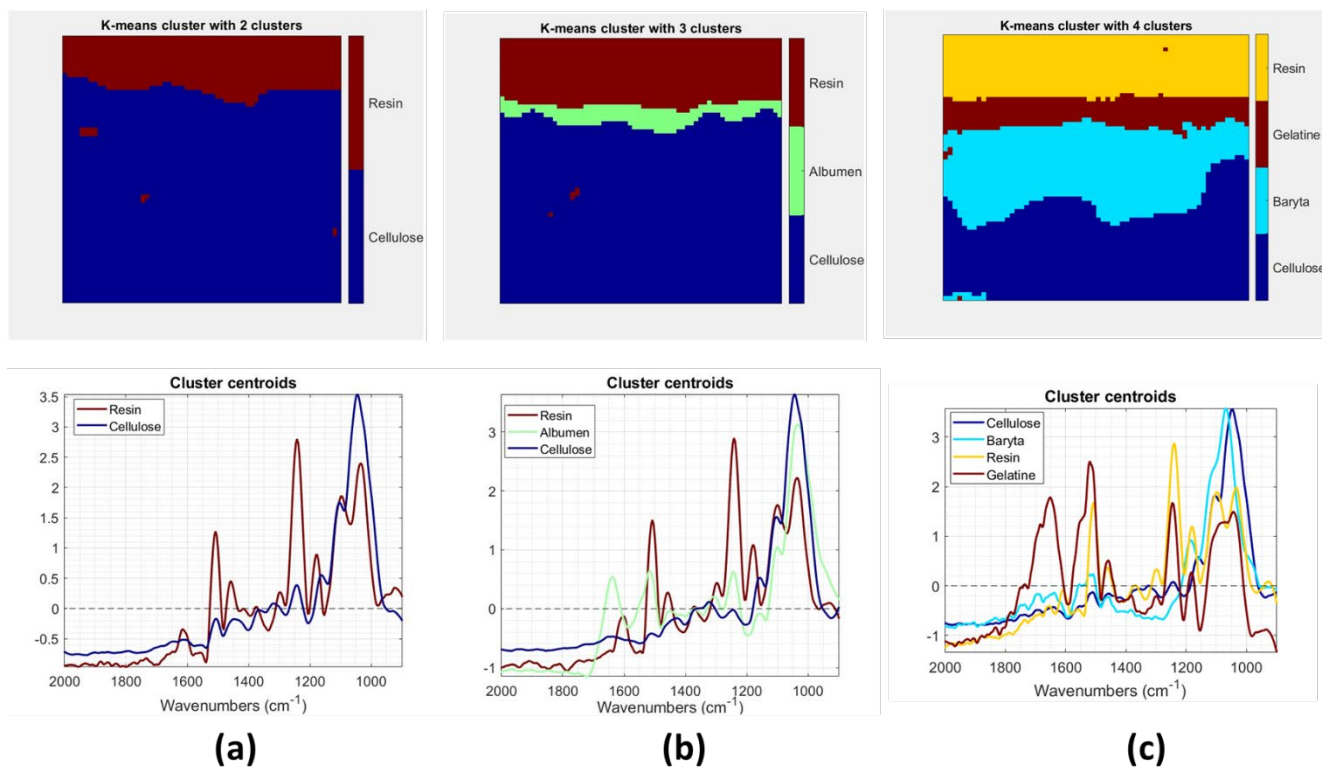
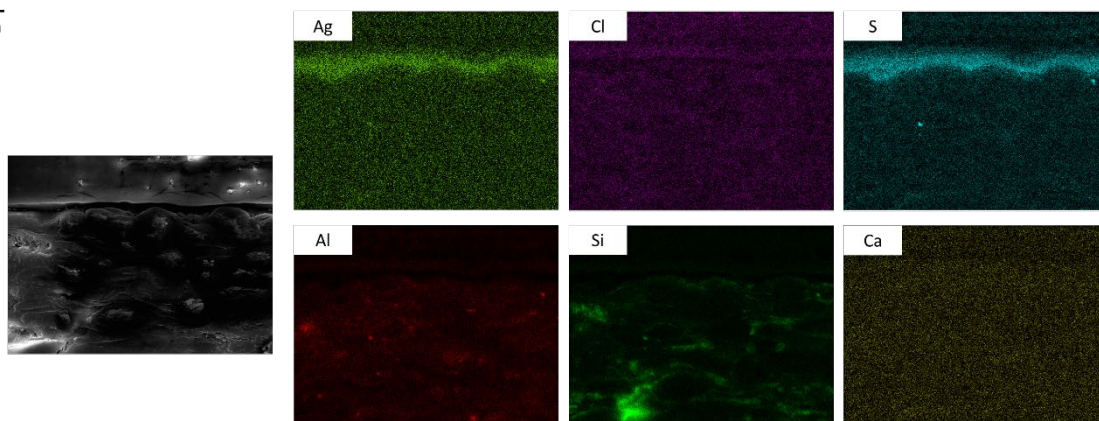
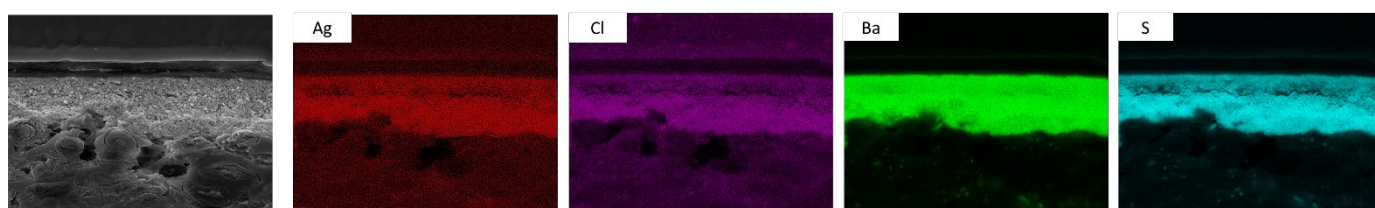


Figure 6.6 K-means clustering results of the white areas of the antique photographs: (a) salt print, (b) albumen photograph and (c) silver gelatine photograph.

25 μm

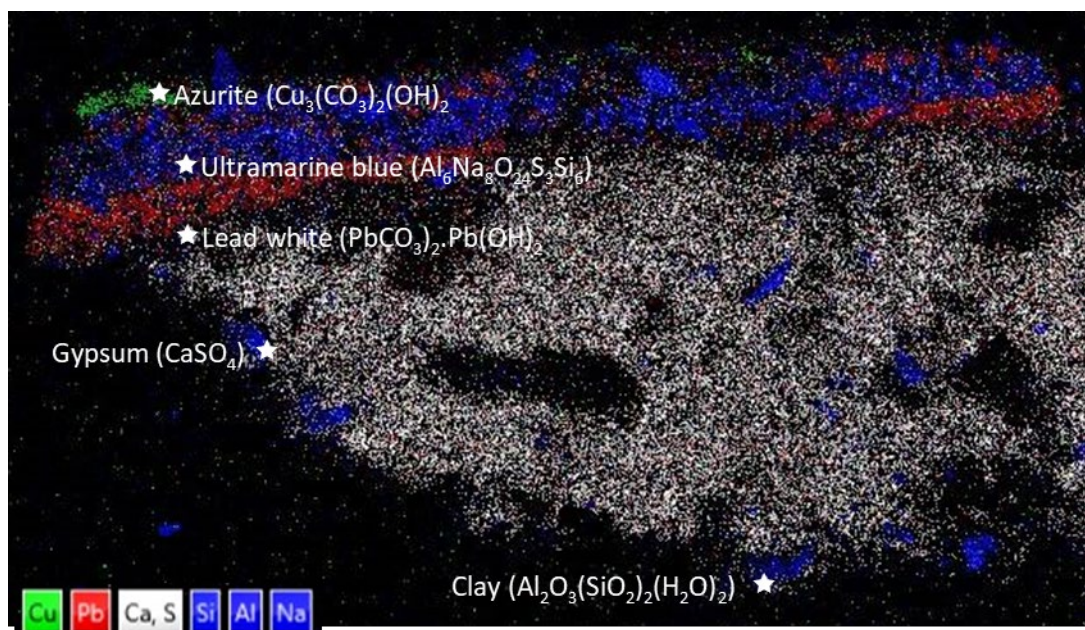


(a)

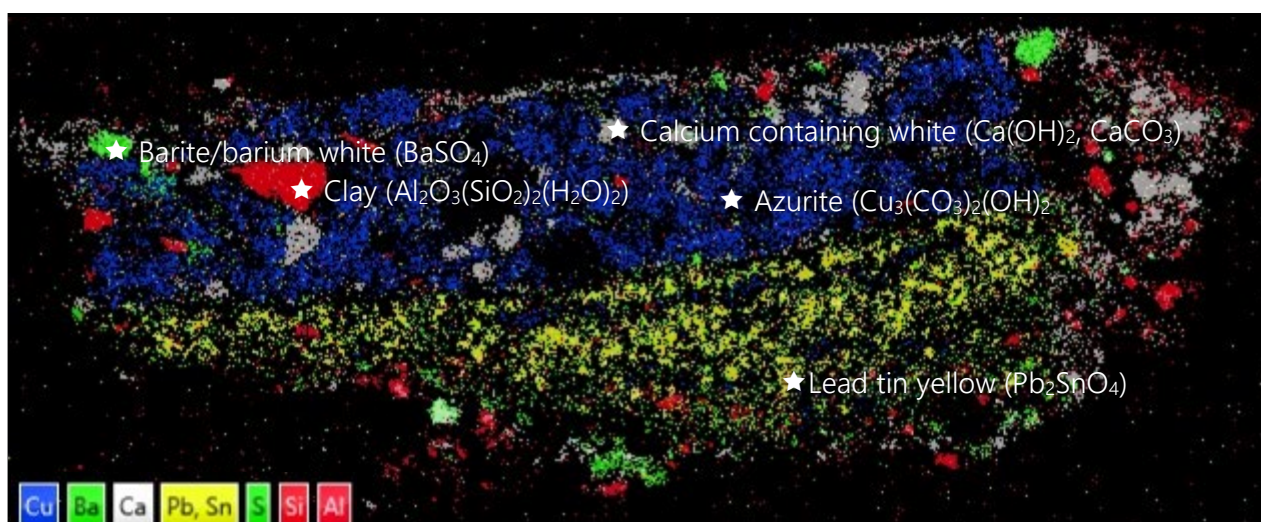


(b)

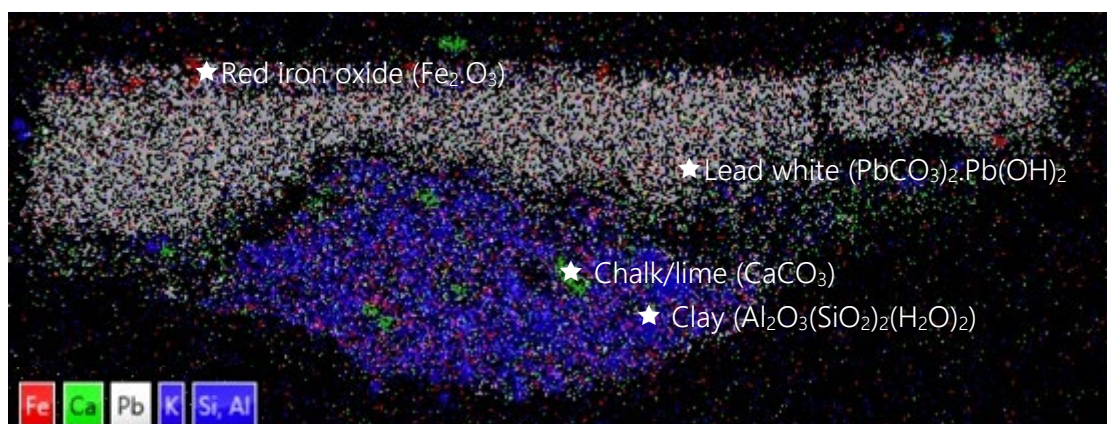
Figure 6.7 SEM-EDX results of the white areas of the antique photographs: (a) albumen photograph and (b) silver gelatine photograph.



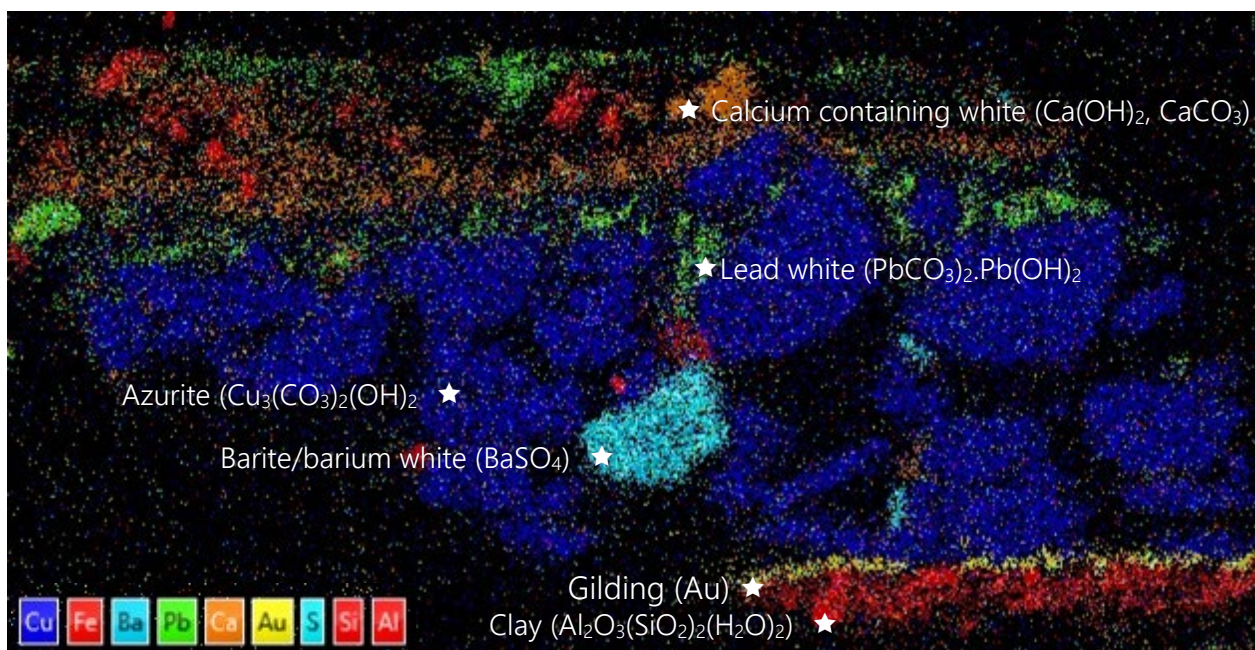
(a)



(b)



(c)



(d)

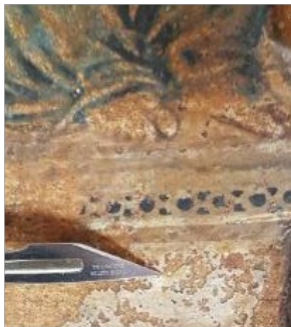
Figure 6.8 SEM-EDX results of cross-sectional samples extracted from Donatello's Virgin and Child: (a) sample 9, (b) sample 10, (c) sample 11, and (d) sample 12. It is noted that the SEM-EDX image of sample 9 is upside down and left-to-right compared to the micrograph of sample 12. Reprinted with permission, copyright © V&A Museum.



Sample 9 from the Virgin's cloak



Sample 10 from the musician's sleeve



Sample 11 from the floor



Sample 12 from the robe of Jesus

Figure 6.9 Locations of the extracted samples of Donatello's Virgin and Child. Reprinted with permission, copyright © V&A Museum.