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Unveiling Portuguese Modern Mural Painting | MULTI-ANALYTICAL ANALYSIS OF A PENTECOSTES BY JULIO RESENDE (1917-2011)

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CONTENTS

ABSTRACT

This work is focused on the materials study carried out on the mural painting Pentecostes executed by the Portuguese artist Julio Resende in 1955. The painting depicting Twelve Apostles is covering the altarpiece on the eastern wall of the Igreja da Nossa Senhora da Boa Esperança located in Canaviais, a small village near Évora. This study aimed to characterize the painting from a materials science perspective focusing on its execution techniques and pigment characterization. The investigation was carried out with the use of both in-situ non-destructive and laboratory micro-destructive techniques. In-situ examination included technical photography in visible (Vis), raking (Vis-RAK) and Infrared (IR) light, Ultraviolet induced visible fluorescence (UVF), portable optical microscopy, visible Spectro-photometry and Energy dispersive X-ray fluorescence spectroscopy (EDXRF). Further analysis of the collected powder and cross-section samples was undertaken by means of Dark field optical microscopy (OM), Scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), micro Fourier transform infrared spectroscopy (μ-FTIR) and micro Raman spectroscopy (μ-Raman). According to the acquired data, the mural was mainly executed in a fresco technique, with the possible use of lime painting on a limited scale. Incised drawings and cartoons were used. No organic binder was detected and the analysis of the paint layers and cross-sections revealed the use of Cobalt blue, Red Ochre, Cadmium red, Chromium green and Barium white pigments. The use of Titanium white, Chromium red, and Green earth was hypothesized.

RESUMO

Este trabalho teve como foco o estudo conduzido na pintura Pentecostes, realizada pelo artista Luso Julio Resende em 1955. A pintura representando os doze apóstolos cobre a parede leste do altar da Igreja da Nossa Senhora da Boa Esperança em Canaviais, um pequeno vilarejo nas proximidades de Évora. O estudo conduzido visou caracterizar os métodos de execução da pintura bem como os pigmentos

utilizados numa perspectiva de ciência dos materiais. A investigação envolveu o uso de técnicas não-destrutivas in-situ e técnicas laboratoriais micro-destrutivas. As análises in-situ incluem: fotografias técnicas com luz visível (Vis), rasante (Vis-RAK) e infravermelho (IR), Espectrofotometria no visível e Fluorescência de Raios-X por dispersão de energia (EDXRF). Demais análises dos pós coletados e secções transversais das amostras foram feitas através de Microscopia óptica de campo negro (OM), Microscopia eletrónica de varredura acoplada a um espectrômetro de fluorescência de raios-X por dispersão de energia (SEM-EDS), micro espetroscopia no infravermelho com transformada de Fourier (μ-FT-IR) e micro espectroscopia Raman (μ-Raman). De acordo com os dados obtidos, a pintura foi realizada em sua maior parte com a técnica de frescos com o possível uso de cal em uma escala limitada. Desenhos e cartuns incisos também foram utilizados. Nenhum ligante orgânico foi detectado e a análise das camadas da pintura e das secções transversais revelaram o uso de pigmentos como azul cobalto, ocre vermelho, verde cromo e branco bário. O uso de branco titánio, vermelho cromo e verde terra também foi hipotetizado.

CHAPTER 1. Introduction

1.1 Object of study

This thesis is focused on the material and technical study of a mural painting known as *Pentecostes* sited at *Igreja da Nossa Senhora da Boa Esperança,* in Canaviais, a small village 5km away from Évora. The mural painted at altarpiece on the eastern wall of the church attributed to Julio Resende (1917-2011), one of the leading artists of Portugal in the second half of XX century.

1.2. Research aims

The main aim of the study is to reveal for the first time the painting techniques and pigments used by Julio Resende. The study undertaken can contribute both to understanding of the art practices of Julio Resende and modern mural painting. Despite the fact, that Julio Resende's legacy is formed by the works made in a variety of techniques (including sketching, easel and mural paintings, ceramics and tile painting [1]) none of his works have been subjected to an archaeometric analysis before. The only exception is a conservation study undertaken by C. Aquini et al. The aim of this study was to develop a graphical documentation methodology for a contemporary art object, and a garden bench, created by Julio Resende in Oporto [2]. Therefore, our study is important the first insight into the artist's materials and painting technique. On a broader scale, the study undertaken can complement the existing literature concerning modern mural painting. Although the number of case studies in that field has been done (see Chapter 2.2.), the existing scholarly context of that topic remains limited. Characterization of a mural painting executed by a Portuguese artist will allow further comparison between artistic practices adopted by the modern muralist from all over the world.

To achieve relevant results the following research questions have been formulated:

1. Was the mural executed in *fresco* or *secco* technique?
2. Which pigments were used? Did the artist favor traditional pigments or novel art materials, and what can his pigment choice tell us about his willingness to experiment?
3. What is the role of the pigment selection and the painting technique in the painting current state of conservation?

To answer these questions the research process was divided in three phases. First, a broad context for the artist's work was formed by consultation of bibliographical and archival sources. Next, the mural was analyzed *in-situ* using non-destructive techniques (Colorimetry, Dino-Lite, XRF, Technical photography). That allowed creation of a detailed documentation of the painting, preliminary characterization of the pigments and binder. During this part of the study, the samples for further laboratory analysis were chosen and extracted. The final phase of the study was carried out in laboratory with the use of the following techniques: SEM-EDS, Optical Microscopy, μ-Raman, and μ-FT-IR. That allowed recognition of the pigments, characterization of the mortar and paint layers. Taken together, the research seeks to provide a more comprehensive portrait of Resende as an artist, in addition to contributing data on the still-understudied mural painting methods of Portuguese modern artists.

1.3 Thesis structure

The thesis will be presented in five chapters.
Chapter 1 offers a brief overview of the object of study, the research aims and thesis structure. In doing so, it will provide a reader with the information required for understanding of the research undertaken.

Chapter 2 explores the artist's biography and sources of inspiration. It will also present the artistic context by describing the techniques and materials used in the first half of XX century by artists from Mexico, Italy, Argentina, Great Britain and Greece.

Chapter 3 focuses on the analytical case study of the mural *Pentecostes*, and explains the methodology adopted, its rationale and provides experimental conditions.

Chapter 4 provides the reader with the results and discussion of the data acquired. This chapter consists of three main parts. In the first part, the plaster work and painting technique are discussed. Then the order of paint execution and question of preparatory drawing presence were discussed. The third part addresses the pigments and binders used.

In Chapter 5, the results of the study undertaken were summarized. The interpretation of the results in terms of the research questions is presented. Finally, future avenues of research are proposed.

1.4 List of references

[1] Paz Barroso, E. (2007). JÚLIO RESENDE E A PINTURA, Galeria Cordeiros, Porto, pp.616-630
[2] Alquini, C., Henriques, F., Teixeira, J., & Vieira, E. (2018). Uma metodologia de documentação gráfica para uma obra de arte contemporânea: o banco de jardim de Júlio Resende do edifício Parnaso (Porto). *Conservar Património*, (27), pp. 94-102

CHAPTER 2. The artist Julio Resende (1917-2011)

Julio Resende (1917-2011) remains one of the most acclaimed Portuguese artists of the XX century. His works are very diverse in form, ranging from oil paintings to murals and traditional *azuleju*. Stylistically his art evolved from early Neorealistic works through phases of Neo-cubism and Non-figurativism to Action painting and Neo-figurativism [1]. According to the research undertaken by an art historian L. Castro, paintings executed in a manner close to Cubism constitute a brief in time but distinctive phase in Resende's art, associated with the time he spent in the Alentejo region (central Portugal) [1]. At that time the mural painting on which this study is centered – *O Pentecostes* – was created. For a better understanding of the artistic intentions and traditions behind the piece, this chapter will provide an overview of Julio Resende's biography and place in the history of Portuguese modern art.

2.1 The mural painting art in the XX century

The mural painting technique exists for centuries. It reached its highest sophistication during the Roman period and Renaissance but was relegated to a decorative art during the early modern era [2]. Even in the interior design the position of mural paintings was taken by the wallpapers and textiles [2]. However, with the rise of modernism in the XIX - early XX centuries artists began to search for new means of expression. British art historian and architecture specialist A. Powers defined this process as a "fresco revival", since this long-neglected technique became one of the renewed approaches, and artists eagerly explored its potential [3]. The development of mural art the first half of XX century was not limited to Europe only. The Mexican mural movement associated with the names of Diego Rivera (1886-1957), David Alfaro Siqueiros (1896-1974) and José Clemente Orozco (1883-1949) established a mural tradition in Latin America. British art historian Margaret A. Casey in her PhD thesis described the manner of Mexican muralists as the mixture of European and indigenous art traditions with the left-wing socialist inspirations of Mexican revolution (1911-1917). Such approach allowed to create a new form of visual art [4].

What themes did the artists reflected in their works? Which materials and painting techniques were adopted in different countries? Could the mural movement of the first half of the XX century be described as a solid artistic movement or it rather was a number of an individual art practices? To understand that it is needed to describe and compare several case studies. That, in return, will allow to understand whether Julio Resende's murals were typical or not and what kind of influence he could possibly experience.

The Mexican muralism is possibly the most well-known branch of mural art of the XX century. However, the number of paintings studied by means of analytical techniques is limited. *America tropical* by Siqueiros, is an exception – the mural was subjected to a complex study by Getty Conservation Institute staff [5]. The mural was performed in Los-Angeles in 1932 on exterior wall of El Pueblo de Los Angeles (see Figure 2.1.). The artist was commissioned to depict idyllic scene of old Mexico. However, he painted completely different scene with a strong political message – a crucified body of an indigenous man surmounted by an American eagle, and revolutionaries with rifles crouched on a nearby rooftop. Soon after the controversial mural was whitewashed and remained in vain for decades, until in 1980s Getty Conservation Institute started the conservation project [5].

Figure 2.1. America Tropical soon after execution. (Getty Research Institute, 960094. Photo: Getty Research Institute; mural: © 2012, Artists Rights Society (ARS), New York/Sociedad Mexicana de Autores de las Artes Plásticas (SOMAAP), Mexico City

Getty's research team leading by F. Pique undertook analytical study of the mural materials and painting technique. According to their study, Siqueiros developed his own innovative technique of mural painting consisting of two main features [Piqué et al., 1995]. The first one was the substitution of tradition lime plaster to white cement plaster. However, the cement setting time is quicker than that of the lime, so the second feature was introduced - the use of air brush. That allowed painting large surfaces in a short time [6]. *America tropical* is a fine of this technique implemented. The brick wall was covered with cement plaster and then painted with airbrush. Siqueiros used yellow ochre, raw and burnt sienna, red ochre, chromium green, titanium and zinc oxides, charcoal and gypsum. It was suggested that cellulose nitrate was used as a binder in that mural [6].

In contrary, Diego Rivera represented more traditional approach advocating the use of fresco technique [7]. However, according to M. Casey, the common point between both (who to certain extent were antagonistic to one another) was the use of mural not only as a form of art but also as a political statement. This additional political dimension of mural art became typical for Mexican muralism [4].

An example of how Mexican muralists influenced their foreign colleagues can be found in work of Argentinian artistic group *Taller de Arte Mural* (made up of the artists Castagnino, Spilimbergo, Urruchúa and Colmeiro), who collaborated with Siqueiros [8]. The art group left only one work - a set of murals to cover the dome of the *Galerías Pacífico*. Italian research team led by P. Moretti characterized the murals. The preparation layer was composed of gypsum, and oil was used as a binder. Two types of pigments were used - inorganic (hematite, goethite, zinc yellow, ultramarine blue, titanium white, barium white and carbon black) and synthetic organic dyes (phthalocyanine blue, PR 49:1, PR 166, PY 3 and PY 74) [8].

In Italy, a country renowned for its Roman, Medieval and Renaissance mural paintings, the reappearance of an interest in large wall-paintings could be associated with exhibitions of *Triennale di Milano*, first inaugurated in 1923 [9]. Mosaic and murals were widely presented during these exhibitions, and attracted much public attention during the fifth *Triennale* in 1933. The interest to murals culminated when an artist Giorgio de Chirico created a monumental surrealistic mural painting on a wall of the *Palazzo Dell'Arte* [9]. Italian artists of the first half of the XX century were searching for the inspiration in local mural tradition, thus, at least in theory, desired to work in *buon fresco* technique [10]. Among Italian muralists of the first half of the XX century, the names of Mario Sironi (1885-1961) and Edmondo Bacci (1913-1978) should be mentioned, as their works were subjected to archaeometric study and can provide points of comparison for the work undertaken in this thesis. Both painters executed large politically engaged murals, but in contrast with Mexican muralists, Sironi, Bacci and other Italian artists of the time were hired by their government to make art that glorified the fascist regime [10].

Sironi's *Venezia, l'Italia e gli Studi* adorned the big hall of *Ca' Foscari* in Venice (see figure 2.2.).

Figure 2.2 Venezia, l'Italia e gli Studi, by M. Sironi, 1937. Image taken from [10]

The characterization of the mural performed by Izzo et al. showed that the painting was executed on two-layered plaster, with the internal layer composed of lime and *cocciopesto* (lime mortar with crushed brick fragments), while the outer layer consisted of lime and silicate aggregates. The painting was divided into *giornata*; cartoons and preparatory drawing were used. However, only background areas of the painting were executed in *buon fresco*. The rest of the painting was done in *secco*, with egg yolk and casein as binding agents. The elemental XRF and EDX showed that Sironi had used traditional pigments (such as earth pigments and ochers) as well as modern ones: Titanium white, Chrome green, Chrome red, Chrome yellow, Zinc white and Zinc yellow [10].

The Bacci's mural *I massimi geni della Razza Italiana* was painted in the big hall of a public lyceum (see Figure 2.3.).

Figure 2.3. I massimi geni della Razza Italiana by E. Bacci, 1939. Image taken from [10]

The painting was executed over a single layer of a bright dolomitic lime mixed with a silicate sand. The artist used *secco* technique and chose linseed oil as a binder. Izzo et al. undertook chemical characterization of the pigments. The artist's palette included Chrome yellow, Barium yellow, Lead yellow, Barium sulphate, Zinc white and Titanium white [10].

Although both Italian artists claimed to work in *buon fresco*, the study done by Izzo et al in 2008 showed that in fact the process of painting was more complex and included use of binders, typical for tempera painting [10].

In Great Britain, Mary Sargant Flores, Joseph Southall, John D. Batten and Jack Hastings were key figures in the revival of the English mural painting tradition [3]. Mary Sargant Flores (1857-1954) was an active muralist during 1900-1914 period; she left three main pieces of art, performed in *fresco* technique (The Story of Gareth, which adorned the hall of Oakham School, in Rutland; *Les Aveugles* in hallway of The Lord's Wood and panels in Bourneville Junior School, see Figure 2.4., 2.5.).

Her painting style was described by A. Powers as “transparent washes of color, with considerable freedom of brushwork” [3].

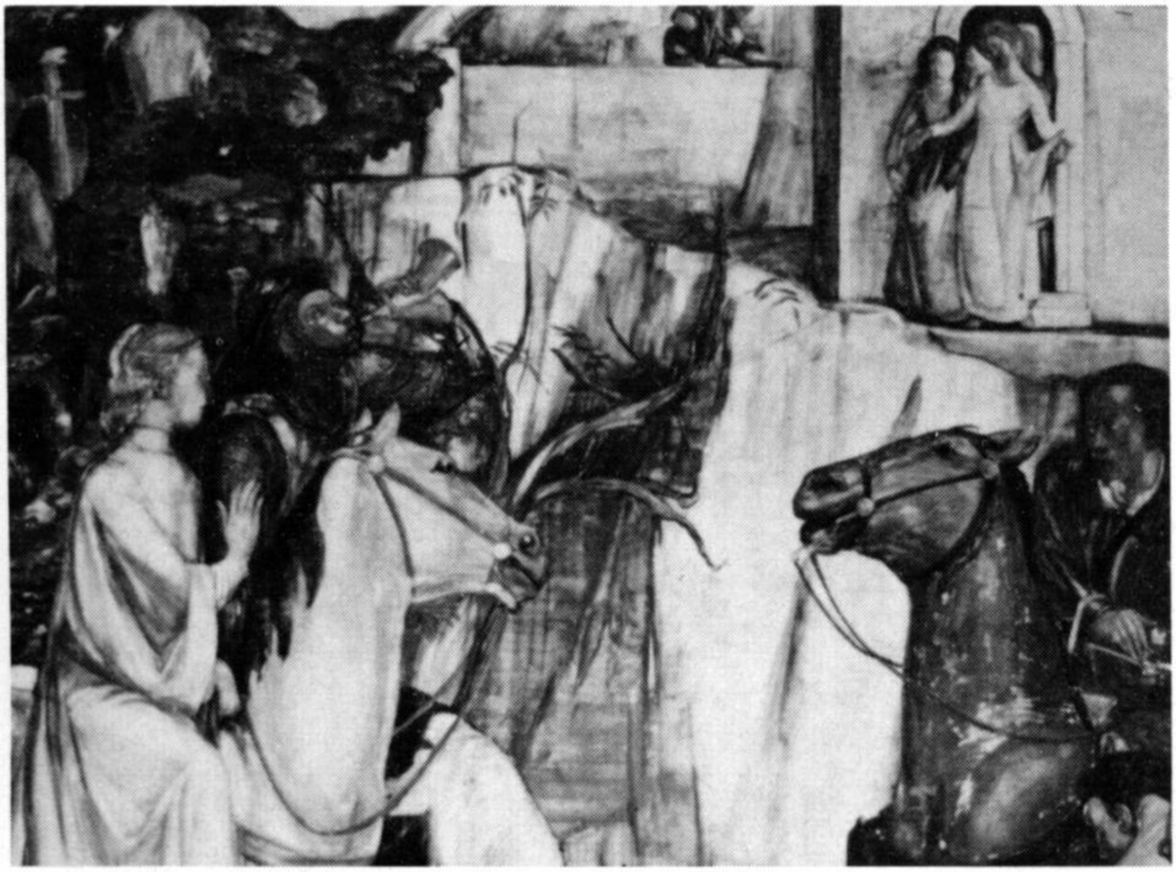

Figure 2.4. The story of Gareth – The Challenge (fragment) by M. S. Flores, circa 1903. Image taken from [3]

Flores outlined her modus operandi in a number of articles published in *Papers of the Society of Mural Decorators* a periodic issue of the same name society. She pointed out the importance of a thoughtfully prepared painting surface and recommended the use of three layers of lime plaster, the final one being the *intonaco* divided by the artist into *giornata*. She also preferred to use detailed cartoons to ensure a free and steady workflow and avoid any later correction or alterations in *secco* technique. Considering fresco paintings “the only form of painting which finds its true place as readily in the light soaring constructions of steel, concrete and glass which we erect today, as on the gigantic heavy walls of earlier architecture," she steadily refused to use oil paints [3].

Figure 2.5. Les Aveugles by M.S. Flores, circa 1903. Image taken from [3].

Another significant example of modern British muralism was Jack Hastings, also known as Francis John Clarence Westenra Plantagenet Hastings, 16th Earl of Huntingdon (1901-1990). A man of noble origin and left-wing political sympathies, Hastings studied mural painting under Diego Rivera's supervision [7]. He met Rivera for the first time in November 1930 and worked as his assistant until September 1932 [7]. His main mural work ("The worker of the future upsetting the economic chaos of the present", see Figure 2.6.) was executed in 1935 in the Marx

Memorial library, and evidenced significant influence from Mexican muralists [3].

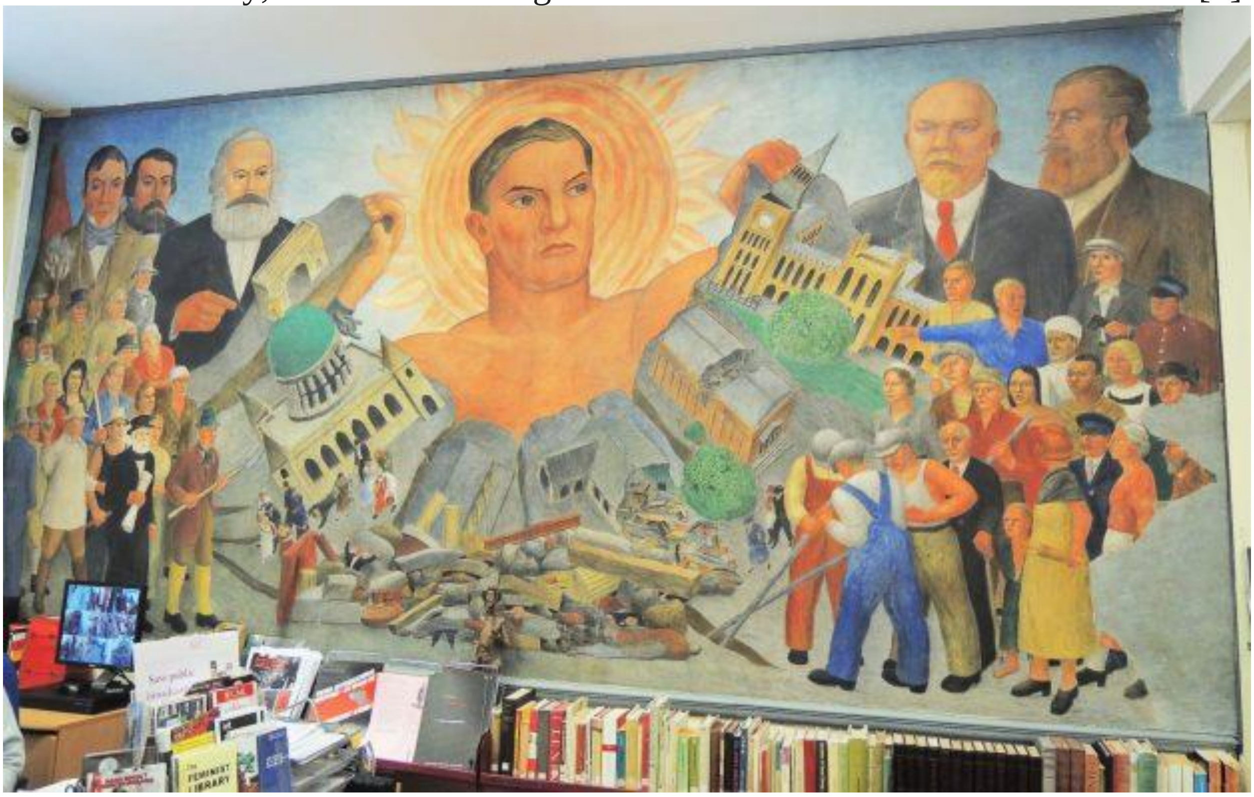

Figure 2.6. The worker of the future upsetting the economic chaos of the present by Jack Hastings, 1935. Photo: credits to Marx Memorial Library & Workers School, London

Unfortunately, none of the artist’s mural paintings has been subjected to material characterization, limiting the comparisons to be drawn with Resende’s work. As his mentor Diego Rivera advocated the use of *buon fresco*, one would expect Hastings to employ this technique. However, A. McClean who studied Hastings’s heritage described at least one case when Hastings adopted quite a different approach. The artist painted the mural with a spray gun on aluminum panels, perhaps showing more similarity with the works of Siqueiros than to Rivera’s [7].

Hans Feibusch observed a significant shift in the idea of how a mural should be made in his book *Mural Painting.* According to Feibusch, 'there is a widespread opinion in this country that *fresco* should be treated like watercolor, and that one should work in transparent tones from light to dark [...] it is by no means necessary to follow this approach; *fresco* can be painted almost like oil, that is to say, in opaque tone’ [3].

Another example of a modernist approach to mural painting can be found in works of a Greek artist Spyros Papaloukas (1892-1957). Liritzis et al. examined his mural paintings in the Amfissa cathedral by means of archaeometry in 2007 [11]. The paintings were made on a single layer of lime mortar applied directly to the wall. A *secco* technique was implemented with lime or casein, egg, animal glue, linseed oil or vegetable gum serving as a binding media. Identified pigments include Ultramarine, Charcoal, Hematite, Yellow ochre, Prussian blue, Lead white, Chrome yellow, and Calcite. The array of incompatible materials and technique used likely explain the work’s current poor conservation state [11]. A key feature of

Papaloukas's painting technique was an extensive use of very detailed preparatory drawings (*anthivolo*) on paper (see Figure 2.7.). Later those drawings meant to be transferred to the walls by piercing a series of small holes with a sharp pointed instrument. The use of *anthivolo* is a tradition of Byzantine art; however, it is close to the use of cartoons and pounced drawing. To achieve desired visual effects, the artist rendered the contour of the figures with an arbitrary thick line and extensive amounts of pigments on particular areas of his compositions [11].

Figure 2.7. An example of anthivolo used by Papaloukas. Image taken from [11]

The mural art of the first half of XX century cannot be characterized as one solid artistic movement. Different techniques were used, ranging from traditional and demanding *buon fresco*, to more convenient *secco*, and the groundbreaking experiments of Siqueiros and Hastings. Different themes were pursued, from traditional religious motifs (Papaloukas, and Julio Resende) to expression of leftist (Siqueiros, Rivera, Hastings) and rightist (Sironi, Bacci) political agendas. However, as Y. Jin pointed it out, what united all these disparate movements was a vision of the mural painting as a way of bringing an idea to the broadest possible audience [9].

2.2. Modern Art in Portugal.

In the beginning of the XX century, the art of Portugal was still dominated by long-lasting traditions of Classicism and naturism. However, a sequence of rapid and dramatic changes (including the assassination of King Carlos II in 1908, the Revolution of 1908, The First World War which Portugal joined in 1916) led to a significant shift in society and, therefore, art [12].

The first steps of Modernism in Portugal were associated with *Orpheum*, a magazine inspired by Italian and French avant-garde artists, which played the role of a manifesto for a new aesthetic. The key figures behind the magazine were the writer Fernando Pessoa, the artist Almada Negreiros and the poet Mario de Sá Carneiro [12]. Although the publications outraged conservatives, they attracted many young and open-minded artists. Despite being short-lived, the journal's influence was so significant that the first generation of Portuguese futurists were named after it, and are known as Orphists [12].

The road toward Futurist painting in Portugal began with the 1915 exhibition of Amadeu de Souza-Cardozo entitled "*Humoristas e Modernistas*" in Oporto [12]. The first generation of Portuguese Modernists included Amadeu de Souza-Cardozo.

Eduardo Viana, Dordio Gomes, and Santa-Rita Pintor. Although diverse, these artists shared a love of Paris. The “first Paris generation” returned to Portugal after the outbreak of the First World War. They brought home not only their works, but also ideas about a new way of painting, influenced by impressionism, cubism, and abstractionism. It took a long time, however, for that seed to take root [12]. Classicist art was well-established, with art schools, exposition halls and government funding. Modernist art, on the other hand, predominantly relied on individual private initiative, since no artistic infrastructure existed to support it. While the new art was more flexible, it was also fragile. After the deaths of two leading luminaries of the movement (Amadeo and Santa-Rita Pintor), the future of the movement was unclear, and its impact on society greatly reduced [13].

The “second Paris generation” was formed after the end of the WWI, when several Portuguese painters (Dordio Gomes, Almada Negreiros, and Jorge Barradas) formed a new artistic diáspora there. This second generation experienced the same problem as the first one - lack of audience, especially in Portugal [12]. They were Portuguese modernists, but there was no modernism in Portugal, especially after the Estado Novo was established. This began to change in the late 1930s, when Antonio Ferro, a state-employed artist, hired modernistic artist when the country was preparing to Portuguese World Exhibition. For Portuguese modern art, it was a significant step towards winning the public’s attention [12].

Julio Resende, together with such painters as Julio Pomar, Fernando Lanhos and many others constitute third (post-war) generation of Portuguese modernist [12]. They were the first painters to build on the artistic experience of previous generations of Portuguese modernists, producing an interesting mixture of modernistic tendencies inspired by Portuguese nature, people and traditional craftsmanship (like painting of pottery and tiles) [12].

In Oporto, modernist art evolved in the same manner, being more a number of personal acts than a solid art movement. The city where Julio Resende made his debut in the world of art played a significant role in development of the country’s fine arts. However, by the time he was a teenager, very little remained of modernism [1] The time of the first futurist expositions of Amadeo and Eduardo had passed and, as Laura Castro described it, in the 1920s, no modernistic societies preserved in the city, and only several artists continued to work in modernistic manner [1]. The 1920s and the 1930s were the time of reaction in art, when naturalism, traditional for Portuguese art of XIX century, had taken back the ground it had lost during its brief confrontation with modernism. At this time not only did the number of modernist exhibitions drop, but also even periodic papers preferred more traditional design [1]. However, some names still can be highlighted (such as Joaquim Lopes and Artur Loureiro, whose exhibitions dominated in 1920s-1930s). A few painters from first two generations of Portuguese modernism become teachers, thus setting the stage for a new wave of modernists. In our case, the most significant of these is Dordio Gomes, who would become Resende's university professor [1].

2.3. Julio Resende's Biography

Julio Resende was born on October 23, in Oporto. His parents were Manuel Martins Dias, a merchant, and Emilia Resende da Silva Dias, a music teacher. He had three siblings. His parents tried to create an artistic environment at home, probably due to Emilia Resende's occupation. At a young age, the future artist took part in some performances of *Radio Clube Infantil* and *Sport Clube de Oporto* [14].

Starting in 1930, Julio Resende was enrolled in the *Academia Silva Oporto*. These years marked Resende's first foray in professional artwork, for it was at this time that he started making illustrations for newspapers (mainly *Jornal de Noticas*, *O Primeiro de Janeiro*, and *O Papagaio*). In 1934, he exhibited his works for the first time at the collective exposition *Grande Exposicao dos Artisas Portugueses* in Oporto. Julio Resende began his higher education in 1937, when he started attending classes at the *Escola de Belas-Artes* in Oporto *(ESBAP)* [14]. Later he referred to his fine arts training as meaningless for a city like Oporto [15]. Students had an opportunity to choose between two professors: Dordio Gomes and Joaquim Lopes. Julio Resende had been familiar with the works of the Gomes one of the numbered modernist painters in Oporto, and chose him as a professor [15]. There he received the first decoration for his work - *Premio Jose Rodrigues Junior* at *ESBAP*. To sustain himself, he used to design advertisements.

The 1940s brought important shifts to Julio Resende's life. He married Maria da Conceicao Moutinho (1943), a sculpture student, and in 1946, his daughter Marta Maria was born. He started to participate in the activities of the *Grupo dos Independentes*, an art group that brought together the students and professors of art, sculpture and architecture of *ESBAP* [14]. *Independentes* had their first exhibition in 1943. The group's informal leader was Fernando Lanhas, one of the most important abstractionists in Portugal. Although the group is sometimes referred to as abstractionist, the reality is more complicated. The name of the group represented two main ideas: the urge to make art institutions less formal and bureaucratized; and need to gather together artists with different training and backgrounds. The last idea allowed the group to create an artistic ethos not dominated by any one particular "-ism" and allowed productive collaboration between dissimilar artists like Julio Pomar, Nadir Afonso, Rui Pimentel, Dordio Gomes, Amandio Silva and, of course, Julio Resende [12]. Participation in the expositions organized by *Independentes* allowed Resende to expand the geography of his expositions – this time his works were presented not only in Oporto but also in Leiria, Coimbra, Braga and Lisbon. He also started his career as a teacher in the *Escola Industrial de Faria Guimarae* (1944) [14]. In 1945 he graduated from ESBAP with honors. By that time, Julio Resende had already garnered acclaim, particularly for his illustrations and his role as the creator of fictional characters *Matulinho e Matulao* (see Figure 2.8.) and *Sr. Arrrepiado* appearing in periodic press [Paz Barroso, 2007].

Figure 2.8. Matulinho e Matulao a periodic comics by Julio Resende published in Primeiro de Janeiro newspaper, 1947
Photo: http://asleiturasdopedro.blogspot.com/2011/09/julio-resende-1917-2011.html

In 1945, he went abroad for the first time. On arriving in Spain, he visited the Prado and set about making copies from the great masters, and met Spanish artist Vasquez

Diaz [14]. A travel grant from the *Instituto da Alta Cultura* (1946) allowed him to continue his tour of major European museums and art centers, heading this time to Paris, where he and his family settled down for a while. While in France, the artist worked in Underseller's studio at the School of Fine Arts in Paris and at the *Grande Chaumiere Academy* as a disciple of Othon Friesz. He also took up fresco painting under the instruction of Duco de la Aix [14]. In addition, of course, Resende regularly appeared at the Louvre, where he was polishing his technique by studying the masters. This period also saw an expansion of the artists professional network; he met and befriended artist from across the world including Mabel Gardner, Pierre Dubois, the Czechoslovak painter Frantisek Emler and the Norwegian artist Oddvard Straume [14]. At that year, he also managed to visit France, Belgium, the Netherlands, England and Italy. In 1948, after brief return to Portugal, he continued his European voyage - returned to Paris, and then relocated to Genoa, Italy. In the end of the journey, he visited Brittany together with painter Pierre Dubois [14].

In Italy, the artist was inspired by the great ornamental compositions created in ancient and medieval times, and he wanted to extend existing mural tradition by applying mosaics and wall paintings to even bigger surfaces [14]. But for Julio Resende, the time of big murals was yet to come.

When the travel grant ended in 1949, Resende faced a return to Portugal and uncertainty about how to continue the activities he'd pursued abroad. Remembering this time, Resende remarked that his main concern was to "…find a solution to allow the maintenance of the family and, at the same time, to continue the artistic life" [15]. For a brief time, he settled down in Braga and started working in Carlos Amarante Industrial and Commercial School, but his plans were halted new opportunity suddenly and serendipitously appeared [15].

Resende's friend Raul David informed him about a vacancy in *Viana do Alenteju*, a small town, 32km south from Evora. The job was offered by a local school, searching for a pottery-painting teacher. Years after, Julio Resende remembered, that he had accepted the offer without any hesitation, because for him it had seemed providential. After the years he spent in splendid Paris, the harsh living conditions of rural Alentejo came as a large contrast, but the artist himself claimed that he enjoyed this change [15].

For the next several years, a small atelier situated in an old palace next to the school became the center of Julio Resende's life and art. Later, he described his meditative working practice there: "sitting in front of a large window, opening the view for a better part of the village and a fountain. On the return from the fieldwork, groups of men and women passed by my providential window, like groups of dancers, moving on a stage. I lived in a mixture of euphoria and expectation, but, physically, in full shape” [14;15]. Such a modus vivendi resulted in several works depicting everyday life of Alentejo (see Figure 2.9.) [14].


Figure 2.9. Paintings by Julio Resende. On the left – Alentejo, watercolor on paper, 1950; on the right – Motivo Alentejano, oil on canvas, 1951. Images taken from [14].

The observations included not only people but also the Alentejo itself – its broad landscape and hot weather, plants and animals [15]. In later memoirs Julio Resende related feelings during that time: “[…] the men's robes, the scarf under the hat, the wrinkles on their faces, the flatness of the landscape, the anatomy of the animals, all seemed to me to have been cut to the knife. It was also 'a principle to be respected, for the organization of the overall framework structure. And, what was not of more importance, I felt in it a fair consonance with what was content. The man predestined to confine himself to the boundless horizon ... The landscape in these paintings was bottomless, and his participation in the discourse would be far from neutral. Men and animals were life within the silhouettes, so supportive, that they were confused. The chromatic gravity, it was a fact that was understood in land fixed and constant coal” [15]. Working in a school also left good memories and allowed the artist to hone his skills of pottery production and painting [14].

Although this period was very tranquil and meditative, the time Julio Resende spent in Alentejo highly contributed the artist’s professional development. In 1951 Julio Resende returned to Oporto. This relocation influenced his work tremendously [14]. As he himself later explained: “From the expectant Alentejan fixity, I was now aware of the dynamic hypotheses of the curved line. The uninterrupted movement of the landscape, the sudden atmospheric changes, the momentary fog, the rhythm of the walking and the talk of the people, all allowed me to witness another universe, so the painting to do now would have to be another, continuing in the be the same. Some permanence on the beaches of Mira and the Torch would accentuate, after all, the tonic that would trigger the said inflection of course” [15].

In 1952, he visited his old friend Oddvard Straume in Norway, and later went to Denmark [15]. One of Resende’s objectives was to establish a link between the Nordic art of Norway and the southern art of Portugal, which at that time were almost unknown to each other. Resende himself found a great aspiration in works of Norwegian expressionist, especially Munch [15].

During that year the artist finally got an opportunity realized an old dream – the creation of a large-scale mural painting. His first work of that kind was done in the canteen of the Technical School Gomes Teixeira in Oporto, and was called *Divertimento Infantile* (see Figure 2.10.) [14;15].

Figure 2.10. Divertimento Infantile by Julio Resende, 1952. Photo:' Fundação Júlio Resende: Lugar do Desenho'

Inspired by his many productive encounters with artists from different nations and backgrounds [15], Resende established the International Missions of Art in 1953. The goal was to create a forum for artists to come together and share ideas. Unfortunately, the idea was short-lived, and only a few meetings took place, but the first one in Evora brought together about 24 artists from 11 countries [15].

1954 found Resende working as a teacher in the Commercial and Industrial School of Póvoa de Varzim. Although he had left Alentejo some years before, he had maintained personal and professional connections there [14].

In 1955 Julio Resende completed the Course of Pedagogical Sciences of the Faculty of Letters of Coimbra (a requirement in order to continue his teaching career). In addition, that year he organized II International Art Mission in Póvoa de Varzim [14]. Then, the artist came back to Evora for a certain time – to create the mural *O Pentecostes*.

Julio Resende lived a long life – he died in 2011 at the age of 93. Since our study is focused on his relatively early work, the information about his following life could be found in Appendix I.

2.4. Julio Resende's style and inspirations

In 1960, João Alves published an article concerning European modern art. There he noted that in case of Portugal, the inherent vice of first Portuguese modernists was the absence of a well-established artistic tradition, rooted in the country's own authenticity. Without this tradition, he argued, Portuguese painters would remain mere provincial copyists of Parisian art [1]. Although quite controversial, that statement is easily applied to example of Julio Resende, who was one of the first modernist painters "rooted" in Portuguese tradition. Although he and his predecessors went to Paris in search of "more innovative artistic practices [...]" that could "serve the country and codify it pictorially" [1], the Paris period for these artists was much more of an internship than an emigration. Julio Resende never cut his ties with homeland and the Portuguese public. His main aspirations throughout the 1950s remained in Portugal [1]. The choice of a life in rural Alentejo is a testament to his attachment to and passion for his country and its art.

To what movement could Resende's midcentury works be assigned? This question is rather confusing, since the artist combined the visual language of several schools. In the 1950s, in Portuguese art there were three dominating tendencies: neo-realism, abstractionism and, only recently introduced, surrealism. The last one was clearly rejected by Resende [1]. Laura Castro explained why: while the art of surrealists was a result of only empathetic reaction to the object, for Resende the reaction combined both empathetic (sensible) and rational ways of reflection [1].

The relationship between Resende and abstractionism is even more confusing. The 1950s became the years of increasing popularity of the abstract art – with many exhibitions, theoretic works and new names [1]. In contrast, describing his artistic style Julio Resende stated: "My painting should not be considered abstract, because I always come from objects, from figures, to extract plastic values from them." [1]. However, the critics not always agree with the performer. Resende's work "*Sobre a Areia*" having rectangular and triangular structures was considered as a bridge from figurative to non-figurative kind of art by the organizers of *I Salao dos Artistas de Hoje* [1]. Roberto Norre (referring to Resende's works of 1950s) notes that although Resende cannot be called an abstractionist, the artist tends not to describe objective reality of things. Thus, his works lean towards abstractionism if not in form, then at least in their idea and spirit [1]. The truth probably lies somewhere in between these two extremes. Julio Resende was highly influenced by abstractionism and occasionally used some of its language, but he applied the abstractionism approach as one tool among many. While abstractionisms hallmarks appear in his works, they do not define him artistically.

Resende himself offers a solution to the quandary of categorization. In his short

Autobiographia he referred to himself as an expressionist [15], connecting himself with artists like Munch. Laura Castro pointed out another source of an inspiration, which Resende could have from both his teacher Dordio Gomes and his personal experience in Paris – Cezanne [1]. That resulted in emergence of para-cubist tendencies in Resende's art. Already visible in his Paris period, they grow and become dominant in early 1950s. He widely using triangular forms, striped areas of color, and dots. At the same time, some expressionist features can be noted both in theme of the paintings and in technique [1]. For example, two-dimensional painting is used, in some cases, faces painted still as masks, it is also affecting the composition in general [1]. The best way to describe Resende's works of the early 1950s is to say that it has a strong expressionist core with geometric way of organizing the space and shape of the painting.

Pentecostes was painted in middle of the 1950s, thus the mural features elements of Julio Resende's style, described above. Although triangular construction was not applied to that mural, the geometric tendencies are clearly visible in colored stripes covering figure's cloaks and color dots, in bi-dimensional "flat" painting, in geometrical organization of the whole composition, like a puzzle divided into geometric figures.

In the end of this section briefly covering Julio Resende's style and inspirations, it is worth mentioning '*Resende. Entre a angustia e a esperanca.*', an essay written by a Portuguese poet Eugenio de Andrade in 1965 [16]. The author tried to understand emotions and mood standing behind the artist's work. He says that the artist is trapped between anxiety and hope, because his works at the same time are filled both with deep despair and remarkable passion to life [16]. One of the reasons for such mood he found in Resende's close connection with ordinary Portuguese people: "peasants of the Alentejo, the fishermen of Mira, the vagabonds of Oporto, the people of the Sargasso or of the Póvoa" [16], and nature. Those connections couldn't be broken even during the artist's experiments with abstraction art. According to Eugenio de Andrade – that was Julio Resende's own way – through national to universal [16].

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CHAPTER 3. The case study | O Pentecostes

3.1. The painting description

Figure 3.1.1. An overall view of Pentecostes by Julio Resende. Photo by Manuel Ribeiro 2018

The painting *Pentecostes* is covering the altarpiece on the eastern wall of the *Igreja da Nossa Senhora da Boa Esperança*. The mural depicts Twelve Apostles. The name of the painting corresponds with the episode described in The Acts of the Apostles. Fiftieth days after the Easter The Apostles were celebrating Feasts of the Week in the Cenacle, when the Holy Spirit descended on them and the other followers of Jesus [1]. In Christian tradition, Pentecost became one of the most important religious feasts. According to "The international standard Bible encyclopedia", Pentecost marks the founding of the Christian church as an institution [1]. The deep religious meaning of this scene justifies its choice for the decoration of an altarpiece.

In the right-bottom corner of the mural, Julio Resende's signature is present (see Figure 3.1.3.). The number '55', presumably indicates the year of the mural execution, 1955. This hypothesis is supported with the archival sources. *Fundação Casa Museu Júlio Resende* was very kind to provide us the photo of Julio Resende executing *Pentecostes*, dated back to 1955 (see Figure 3.1.3.) Unfortunately, the mural has been neglected for a long period of time. The description and picture of *Pentecostes* are missing even in the most recent catalogues of Julio Resende's works [2;3]. The mural was brought back to the public attention only recently. Since 2010 "*Rota da Igrejas d'Évora*" project has been putting an effort to popularize the city's religious heritage. Within the framework of the project, the guided visits to local churches were organized. In 2013, Francisco Bilou and Artur Goulart, an historian and an art historian specialist attended *Igreja da Nossa Senhora da Boa Esperança* and rediscovered the *Pentecostes* [4].

Figure 3.1.2. Detail: Julio Resende's signature. The position of the detail in the painting is marked with the red circle. Photo by Manuel Ribeiro 2018

Figure 3.1.3. Julio Resende is executing Pentecostes. Photo by Virgilio Ferreira, 1955. © Fundação Casa Museu Júlio Resende

3.2. Experimental conditions.

3.2.1. Non-invasive techniques (in-situ examination)

Non-invasive techniques are commonly used as a preliminary step of the investigation of works of art [5]. Such techniques are rapid and repeatable analytic tools which require little or none sample preparation. Non-invasive techniques do not damage the studied object, thus there is no limitation on number and place of the measurements. However, the non-invasive techniques alone may not be sufficient for decisive conclusions on the research questions, like pigments and binder identification [6]. That is why, it is important to support the non-invasive techniques with micro-invasive ones, if it is possible. In the present study, the use of Non-invasive techniques allowed to observe the surface features of the mural painting in details and make the first assumptions on pigment identification, binder characterization and description of the painting technique. The data obtained with the use of these techniques allowed to choose the sampling places and proceed with the laboratory analysis.

3.2.1.1. Photo Documentation.

The primary stage of the research was visual observation and photo documentation of the mural. Visible (Vis) and visible racking light (Vis-RAK) photography were acquired with a Nikon D3200 24Mpx with an objective Nikkor 18-55mm f:3.5-5.6 GII and a Canon SIGMA24-35mm F2 DG HMA015.

The painting overall photography for graphic documentation was achieved by mosaic methodology (see Figure 3.1.1). The number of photos taken was 50 (5 rows with 10 photos each). The photos assembling and edition were made in Adobe Photoshop CS5.5.

Racking light observations of the painting can reveal the presence of incisions, toolmarks, brushstrokes and reveal other surface features which couldn't be noticed in direct Vis illumination [7]. Racking light photography was achieved using an illuminant at an angle of 15-20º from the surface of the painting. The photos were taken from four different surface angles enabling in this way a more complete information about the plaster layering and painting execution technique.

The UV induced visible fluorescence photography (UVF) was also acquired with a Nikon D3200 24Mpx with an objective Nikkor 18-55mm f:3.5-5.6 GII. Unlike UVR, UVF images can be obtain with any digital camera with an UV/IR cut-off filter in front of the sensor to reduce the acquisition of transmitted infrared and ultraviolet radiation. The use of UVF allows detection and preliminary characterization of the surface coatings and fluorescent pigments [8].

The Infrared photography in the near range (NIR) was implemented in order to disclose possible presence of carbon-based underdrawings [9]. The photos were acquired with a Nikon D3100 digital camera modified for full spectrum equipped with 10.0-550mm f/3.5-5.6 lenses and 14.2 Megapixel CMOS sensor. For the NIR images were used three high-pass band filters (X-Nite 780 nm; X-Nite 850 nm and X-Nite 1000nm) (see Figure 3.2.1.).

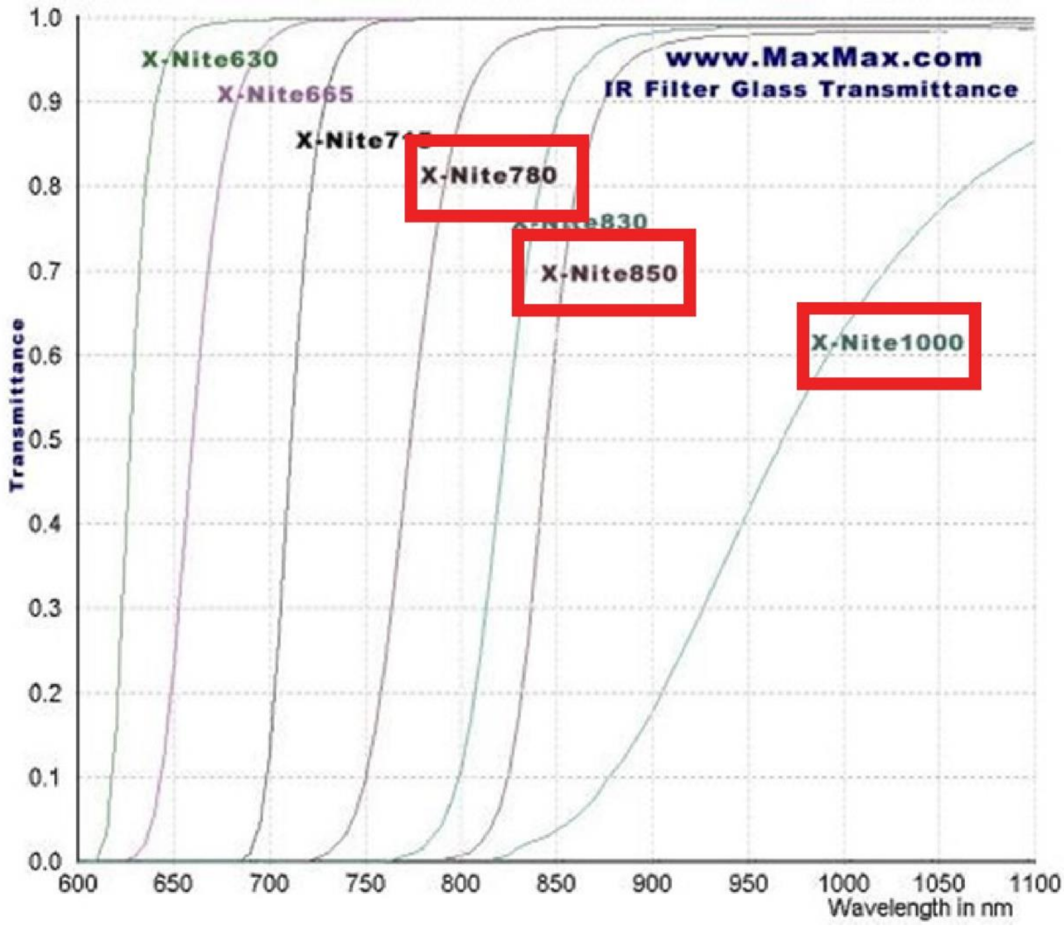

Figure 3.2.1 IR filters transmittance spectra (source of the image www.MaxMax.com). The filters used in the study are marked with red.

Raw image output was used in combination with a reference target QpCard101 v3 and AIC PhD target in order to get a more accurate and comparable color registration. The three patches of target QpCard101 v3 (white, gray and dark gray) are neutral in all lighting conditions with straight spectral response and no fluorescence whitening agents. There are the most suitable for gray balancing and white balancing settings. The CIE Lab values for QpCard101 v3 are: dark grey 35,0,0; Mid gray 48,0,0 and White 95,0,0.

AIC PhD target has the following elements: six-step grayscale, RGBCMY color patches, lighting indicator, size scale, area for date and object identification. The size is 16 x 2 cm. The gray patches are identified by the following designations (for white to black): white; N8; N6.5; N5; N3.5; and black. The red fluorescence emission of the red swatch of the AIC PhD target was used for the exposure correction of UVF images. The photos edition was made in Adobe Photoshop CS5.5.

OSRAM 64575 Halogen lamps 1000W-230V Gx6.35 NAED 58525 (Color temperature: 3400 K) were used for Vis, Vis-RAK and IR photography. UV photography was carried out with a Labino® MPXL UV PS135 (35W PS135 UV Midlight 230V) with a UV filter included (310-400nm and a peak at 365nm); a Midlight distribution angle (beam) of 20º and a start –up time full power after 5-15 sec.

Technical photography was made by a professional photographer (Manuel Ribeiro) within the framework of HERCULES project ‘Unveiling the mural painting art of Almada Negreiros (1938-1956): a scientific study on the painting techniques and pigments as a guide for its future conservation and fruition’.

3.2.1.2. Portable optical microscope (Dino-lite)

For the *in-situ* observations and recording of painting techniques, order of execution, details, and preliminary pigment characterization a portable Dino-lite ProX AM 4000 series with 50x and 430x magnification was used. In addition, portable OM was used to document the measurement spots of Spectro-colorimetry (see Figure 3.2.2.).

3.2.1.3. Spectro-colorimetry

Figure 3.2.2 Map of the colorimetric measurements. Photo by Manuel Ribeiro 2018

In the analysis of the works of art Spectro-colorimetry used for pigment characterization, monitoring of conservation state and evaluating color value of the pigments before and after interventions and deterioration processes [10]. This technique allows to objectively evaluate hues present in the work of art, which is not possible only with the visual observations, due to the differences in color perception [10].

Spectrophotometer, a device used Spectro-colorimetric analysis, measures the manner in which material reflects or transmits light at individual wavelengths of the spectrum. Spectral curves represent reflection or transition as the function of a wavelength in the visible part of spectrum [10].
To objectively represent the current chromatic palette of the painting, in total two hundred fifty-eight color measurements were taken (see Figure 3.2.2). The large number of measurements taken guarantee that all the hues present in the mural were characterized. The large number of colorimetric data allowed to divide the paint layers in groups according to their location on CIE a* b* axis. That, in return, allowed to choose the points of further EDXRF analysis. Data Color Check Plus II (Lawrenceville, NJ), equipped with an integrating sphere was used. The following parameters were used during the colorimetry analysis: diffuse illumination 8 viewing (in accordance with the CIE standard No. 15.2. Colorimetry), SCE and Standard Illuminant / Observer D65 / 10. The aperture size used was USAV (Ø5 mm). The analyzed wavelengths were 360-750 nm with the 10 step between measurements. The measurement spots were documented with the help of portable OM device. The index of correspondence between OM images and Spectro-colorimetry measurements can be found in Appendix II.

The use of Spectrophotometer also allowed preliminary pigment identification in the paint layers studied. The shape of spectral curves is often specific, providing a type of fingerprint characteristic of the chemical nature of the material [5;10]. The data obtained during the survey was compared with reference database of historical pigments in different binders proposed by Antonino Cosentino [11]. However, in general, the use of this technique may be complicated by the possible bad state of conservation and the use of pigment mixtures instead of pure pigments. That is why in the present study Spectro-colorimetry was supported with the use of EDXRF and laboratory techniques.

3.2.1.4. Portable EDXRF

Figure 3.2.3 Map of EDXRF measurements of the paint layers. Photo by Manuel Ribeiro 2018

EDXRF was adopted as a fast *in situ* non-invasive allowing the first recognition of the elemental composition of the paint layers. In EDXRF, all of the elements in the sample are excited simultaneously with the X-ray radiation; than energy dispersive detector in combination with a multi-channel analyzer is used to simultaneously collect the fluorescence radiation emitted from the sample and then separate the different energies of the characteristic radiation from each of the different sample elements [12]. The principal advantages of EDXRF systems are their simplicity and fast operation [12].

The technique also has several limitations. First of all, it does not allow analyses of small spots, so using this technique it is only possible to carry out bulk analyses [13]

Furthermore, the incident X-Ray beam penetrates a few millimeters into the sample's surface [13]. Thus, in case of mural painting study it should be considered that EDXRF data may contain information not only about paint layers but also about the mortar underneath it.

A handheld X-ray fluorescence spectrometer Bruker tracer III SD (Bruker, Germany) was used. The device is equipped with an X-ray tube with a rhodium target and a silicon drift detector. In total, eighty-three paint layers have been measured (see Figure 3.2.3).

3.2.2. Micro-invasive methods.

3.2.2.1. Micro samples and cross sections

Figure 3.2.4. Map of the samples extracted for laboratory analysis. Green: powder samples for μ-FT-IR and μ-Raman examination; red: cross-sections for OM and SEM-EDS examination. In areas marked JR2, 14 and 25 both powder samples and cross-sections were extracted. Photo by Manuel Ribeiro 2018

For laboratory analysis, a total number of twenty-nine microsamples was collected in the form of cross-section and powder micro samples (see Figure 3.2.4.). The samples represent blue, green, red, orange and brown paint layers. The powder micro samples were collected for μ-FT-IR and μ-Raman analysis to prove the presence or absence of organic binder. These samples were collected by slightly scratching the

surface of the painting with a scalpel. Cross-sections of micro samples were supposed to be subjected to OM and SEM-EDS analysis in order to order to reveal paint layers stratigraphy. These samples were collected on the edges of lacunas. In addition, both kinds of micro-samples were used for pigment identification by means of SEM-EDS, μ-FT-IR and μ-Raman. All the samples were collected by Prof. Milene Gil.
Cross-section micro-fragments were embedded in an epoxy fix resin (Epofix Fix, Struers A/S, Ballerup, Denmark) and polished with 6000, 8000 and 12000 sandpapers. During polishing a rotating disc, Drehzal Regler (Jean Wirtz, Dusseldorf, Germany) was used.

3.2.2.2. Optical Microscope (OM)

The optical microscopy observations usually became the first step of a laboratory study of the paint layers. The application of OM in the field of cultural heritage has a long story dating back to 1956 [14]. OM study of cross-sections reveals stratigraphy of the painting micro-samples; it helps to describe pigments and mortar particles. In addition, it may provide information about later retouches [14].

Optical microscopy equipment includes different set-ups determining how is the sample illuminated (dark-field, bright field and polarized). The paint layers cross sections are usually dark-field and bright-field modes are used [14]. In addition. the samples can be observed in UV as well as in visible light. UV observations may reveal presence of binders and fluorescent pigments [14].

In the study presented fifteen embedded cross-sections were studied with a Leica DM2500M reflected light optical microscope in dark field illumination mode. The observations were carried out in 100x, 200x and 500x magnifications. The smaller magnifications were used in order to observe the cross-sections stratigraphy, while the higher ones provided information about the pigment and mortar particles. The observed cross sections were photographed with a Leica MC 170HD digital camera attachment (Leica microsystems, Wetzlar, Germany). The images can be found in Appendix III.

3.2.2.3. SEM-EDS

The twelve paint layers cross sections previously subjected to OM were further analyzed using a scanning electron microscope coupled with energy dispersive X-Ray spectrometry (SEM-EDS) (see Figure 3.2.4.). SEM-EDS has been proved to be an important analytical tool in the study of work of arts. Example of its implementation to the mural paintings study can be found in the case study by M. Gil et al. devoted to mural paintings of *Convent of São* Bento de Cástris. In that case SEM was one of the techniques which allowed detection of carbonation layer, which in return indicates the use of *secco* painting in some areas of the mural [15]. This technique is based on interaction between the electronic beam and the specimen. The electron microscope scans a focused electron beam over a surface to create an image.

The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition [16]. The use of SEM allows acquisition of a high-resolution pictures of the samples in magnification ranging from 20x to 30 000x, thus enabling the researcher to observe micro-morphology and stratigraphy of the paint layers. On the other hand, EDS detector collects and analyses characteristic X rays emitted from the specimen after interaction with the electron beam. That provides the information about abundance of different chemical elements [16]. EDS analysis allows creation of the elemental distribution maps showing spatial distribution of different elements in a paint layer. In addition, EDS can give an elemental composition of both single point and broader area of the sample. Thus, EDS is very useful for pigment and binder identification and characterization of mortar.

Variable Pressure Scanning Electron Microscope HITACHI S-3700N operated with an accelerating voltage of 20kV and chamber pressure 40Pa was used. The use of variable pressure mode conventional in the study of non-conductive specimen allows to analyze the samples without the metal coating. In this mode the pressure can be added into the chamber in order to remove the electron charging artifacts from the images [17;18].

EDS microanalysis was conducted in the same conditions, with the help of Bruker XFlash 5010 Silicon Drift Detector (SDD) with a resolution of 129eV at Mn Kα. Due to the vacuum conditions used; carbon coating of the samples was not required. The SEM images were acquired in backscattering (BSE) mode.

3.2.2.4. μ-FT-IR

Fourier Transform Infrared Spectroscopy (μ-FT-IR) is a powerful tool allowing identification of organic and non-organic compounds [19]. In the study presented the main aim of FT-IR use was identification of binder and pigments chemical composition. Ten powder samples representing the main paint layers were analyzed (see Figure 3.2.4.).

ABruker Tensor 27 Mid-IR (MIR) spectrometer was used for that purpose. The spectrometer is coupled to a HYPERION 3000 microscope and is controlled by OPUS 7.2 software (Copyright© 2012 Bruker Optics and Microanalysis GmbH, Berlin, Germany). It has a MCT (Mercury Cadmium Telluride) detector cooled with liquid nitrogen and allows spectra acquisition at different points of the sample.
The samples were
analyzed in transmission mode using a 15x objective and an EX'Press 1.6 mm diamond compression microcell, STJ-0169. The IR spectra were plotted in the region of 4000-600 cm-1, with 64 scans and 4 cm-1 spectral resolution.

3.2.2.5. μ-Raman.

Raman spectroscopy was used as a technique, complementary to FT-IR for identification of pigments and mortar characterization. The complementary use of XRF and Raman was justified in paper by M. Sawzcak et al. [20] Ten powder micro samples previously subjected to µ-FT-IR analysis were studied (see Figure 3.2.4.). Microspectrometer Raman HORIBA Xplora equipped with a 28mW diode lasers (636nm, 782nm), coupled to an Olympus microscope was used. Raman spectra were acquired in extended mode in the 100–2000 cm-1 region. The laser was focused with an Olympus 50x lens. To achieve better spectra resolution and peak recognition the setup of the equipment was adjusted to each sample individually. Table 3.2.1. presents the parameters used. In addition, reference samples of pure Cobalt blue and Viridian (produced by Kremer) were tested as well to be used as standards. (see Figure 3.2.4.)

Sample	Laser, nm	Exposition, sec	Accumulation, sec	Hole, um	Slit, um	Filter, %
Ref. Co blue dark	782	15	15	300	100	10
Ref. Co blue light	782	15	15	100	50	10
Ref. viridian	782	15	10	100	50	1
JR2a	636	15	10	100	50	10
JR6	782	10	10	300	100	10
JR7	782	15	10	100	50	10
JR14a (green)	782	15	10	300	100	1
JR14a(red)	782	10	15	100	50	10
JR15(green)	636	15	15	300	100	1
JR15(mortar)	636	15	15	300	100	1
JR17(blue)	636	15	15	100	50	1
JR17(green)	636	15	15	300	100	10
JR21(blue)	782	10	5	300	100	10
JR21(mix)	782	10	15	300	100	10
JR25a(mortar)	636	5	5	300	100	10

Table 3.2.1. µ-Raman settings used for analysis of the powder samples

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CHAPTER 4. Results and discussion.

4.1. Plaster work and painting technique.

The first characterization of the support and plaster work was done after *in-situ* observations. The first feature of the plaster revealed with the help of Vis-RAK light was presence of large number of toolmarks. Presumably those marks were left by trowel used to spread the plaster and smoothen the surface of the painting (see Figure 4.1.1.).

Figure 4.1.1. Observable toolmarks. Photo by Manuel Ribeiro 2018

The texture of the plaster surface could be one of the artistic ways of expression. In situ observations shown, that Julio Resende left some areas with coarser surface and intentionally smoothened other ones. The coarser areas are associated with the *giornata 1* (see Figure 4.2.1.) (the presence of *giornata* are explained in section *Preparatory drawings and order of painting* execution below).

The background behind the figure's faces (*giornata 2*) is the smoothest part of the painting (see Figure 4.2.1.). Examples of the different textures used by Julio Resende are shown in Figure 4.1.2.

Figure 4.1.2. Differences in surface smoothness in different areas of the mural. Photos by Manuel Ribeiro 2018

In situ observation of the mural also revealed presence of a large number of nail marks. In some cases, the nails are still present. These nails could be used to fix the cartoon models on the wall (see Figure 4.1.3.).

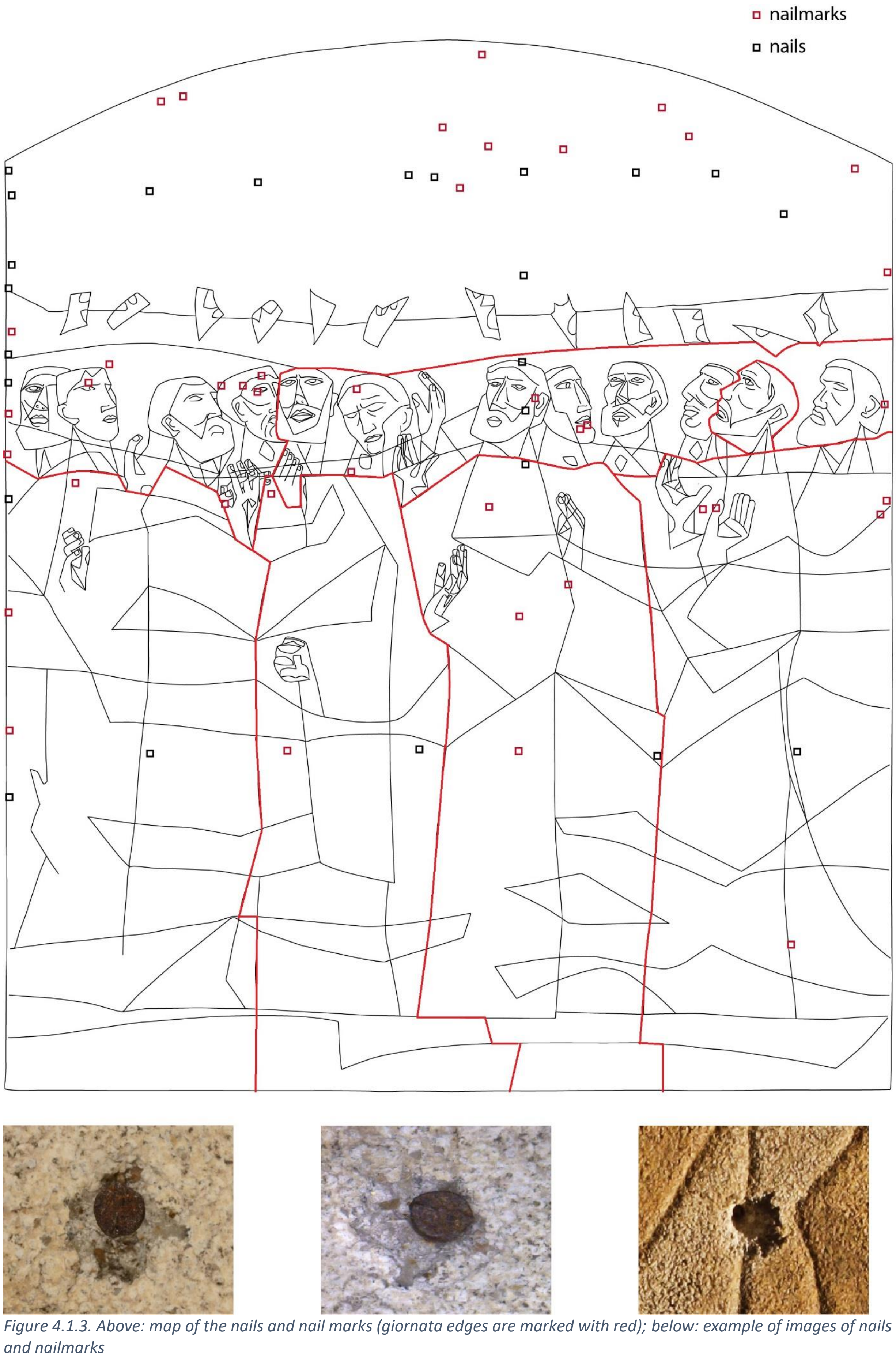
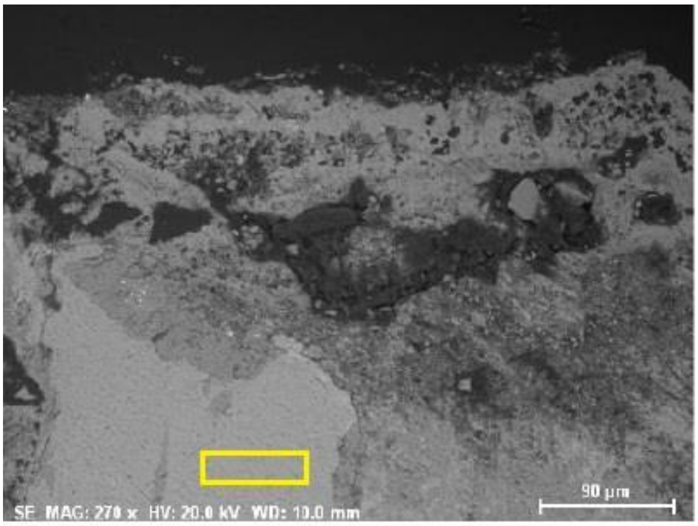


Figure 4.1.3. Above: map of the nails and nail marks (giornata edges are marked with red); below: example of images of nails and nailmarks

The next stage of a plaster examination was characterization of its stratigraphy and chemical composition. In terms of stratigraphy, the two layers of plaster, on which mural paintings are normally executed are known as *ariccio* and *intonaco*. *Ariccio* is usually a relatively coarse support layer applied on the wall. The function of this layer is to level unevenness of the support surface and to retain moisture for the intonaco [1]. Intonaco is an upper layer of plaster usually applied over *ariccio*. In the most cases, it is more fine-grained and thinner than *ariccio*. When the painting is being executed, the pigments mixed with water are applied on the wet intonaco [1].

In case of the *Pentecostes* painting, the lack of deep lacunae and general integrity of the painting did not allow to observe *in situ* the inner layer of the plaster but it was found in three cross-section samples collected from the mural (samples JR13, JR18 and JR19). The cross sections were subjected to OM and SEM-EDS study. Fig.4.1.4 shows the SEM-EDS analysis of the *ariccio* mortar of samples JR13 and JR18.



Element	C atom. [at. %]
Na	2,16
Al	20,51
Si	52,58
S	0,42
Cl	0,46
K	21,87
Ca	2, 00

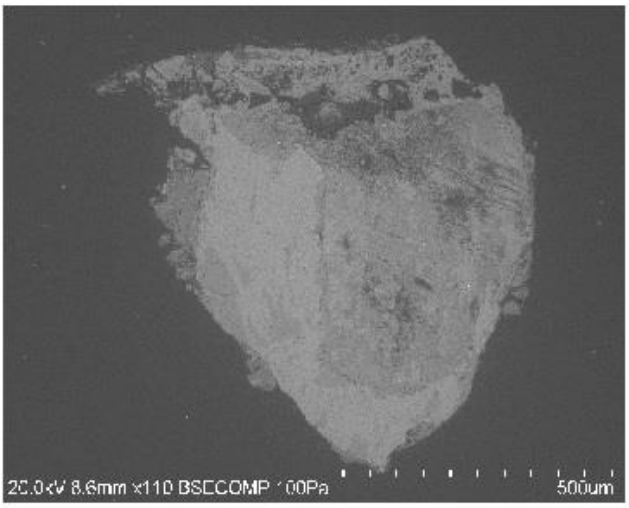
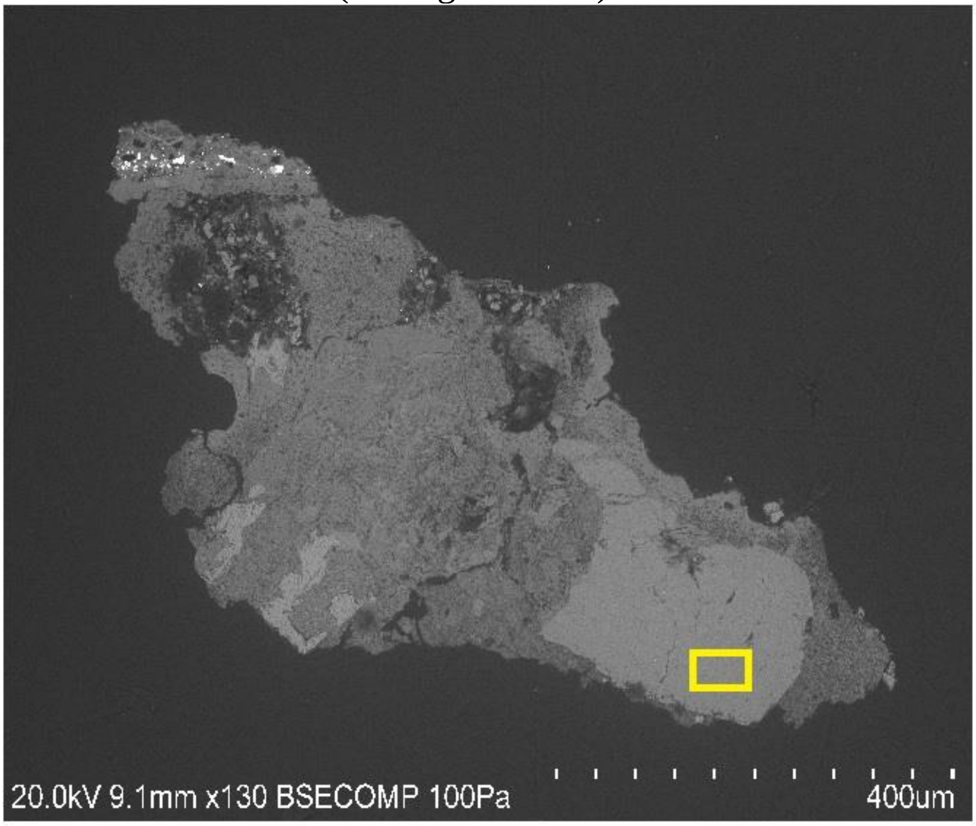


Figure 4.1.4. SEM images of sample JR18 with the table of elemental composition (area analyzed marked with yellow)

The K content found in the area suggest the presence of K-feldspar. Quartz grains were observed in OM (see Figure 4.1.5.).



Element	C. Atom [at. %]
Al	20,61
Si	52,57
S	0,33
Cl	0,57
K	22,72
Ca	2,60
Ba	0,59

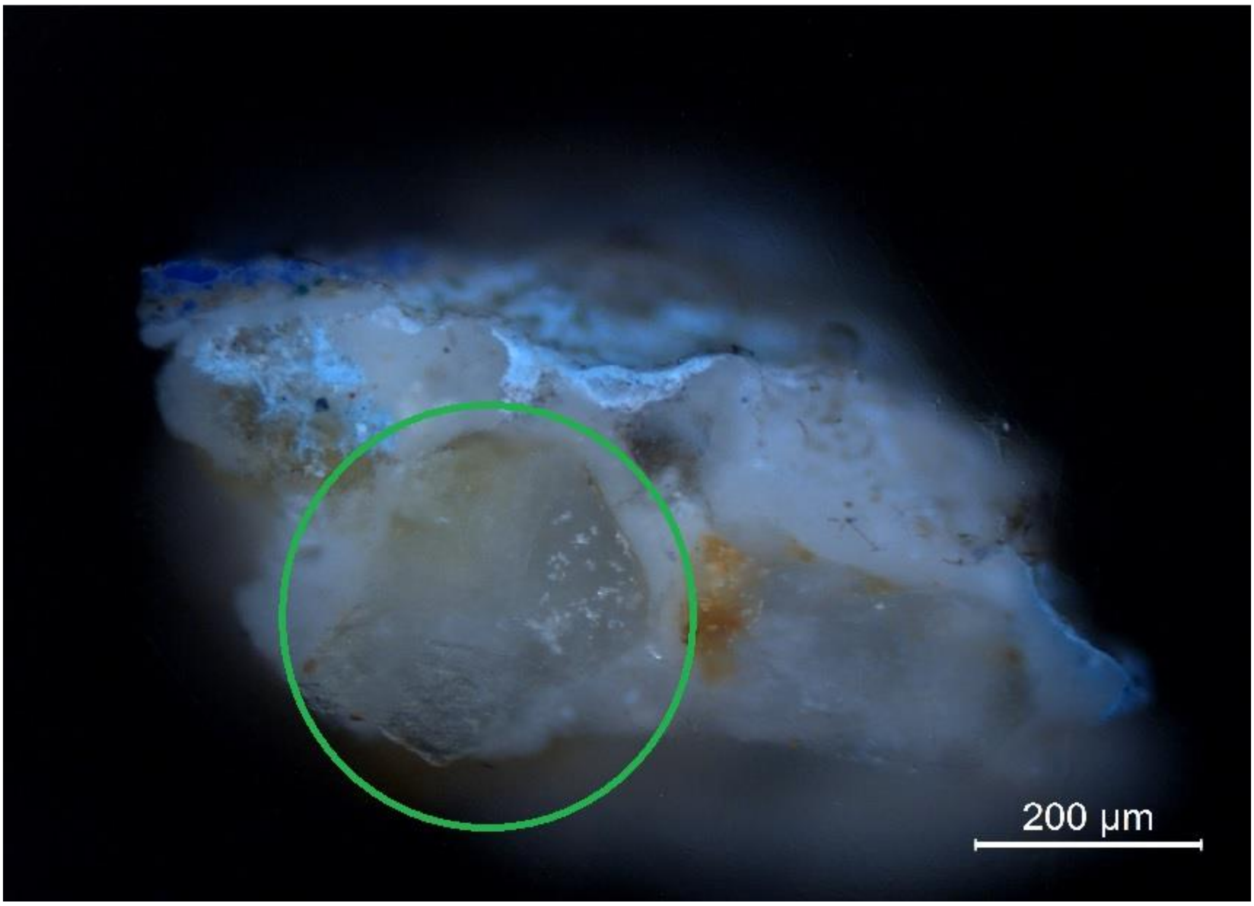
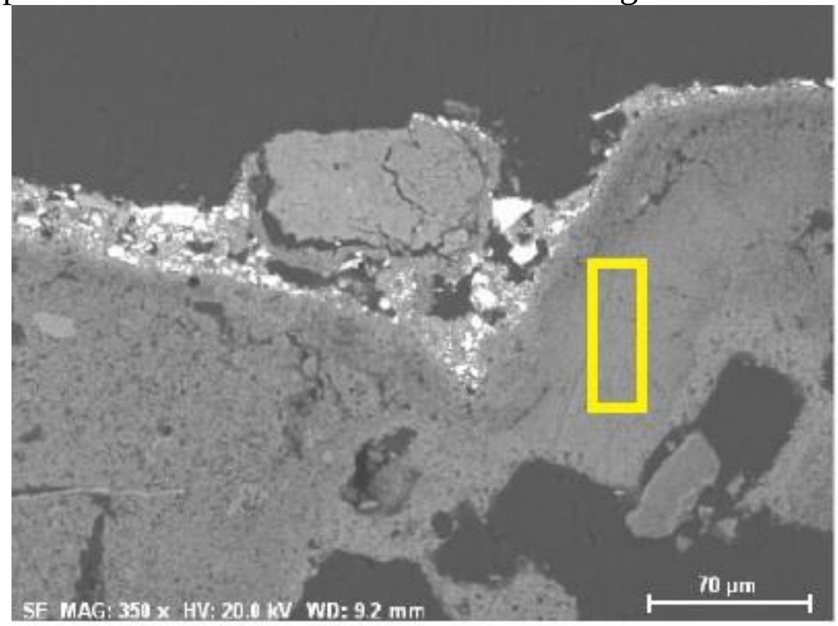


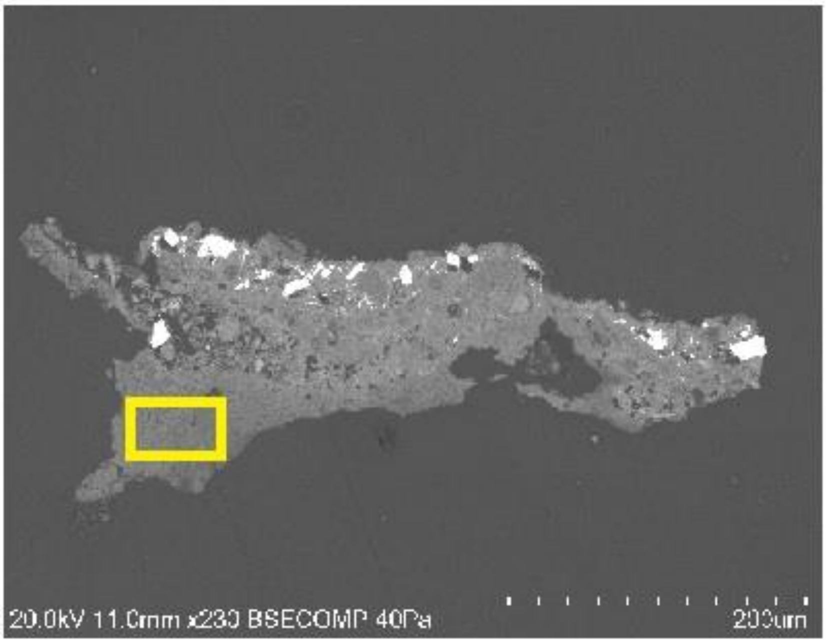
Figure 4.1.5. Cross-section sample JR19. Above: SEM image and table of elemental composition (area analyzed is marked with yellow); below: OM picture at 100x magnification. Green circle marks quartz grain.

More easily accessible *intonaco* layers were examined by OM, SEM-EDS, µ-FT-IR and µRaman. EDS examination of a mortar layer in samples JR10 and JR14 performed in an area mode showed the high concentration of Ca (see Figure 4.1.6.).



Element	C. Atom. [at. %]
O	76,47
Mg	0,17
Si	0,13
S	0,09
Cl	0,13
Ca	22,81
Cr	0,20

JR-10



Element	C. Atom. [at. %]
Mg	0,86
Al	0,83
Si	1,97
P	0,07
S	0,24
Cl	1,51
Ca	91,57
Cr	1,19
Fe	1,77

JR-14

Figure 4.1.6. SEM images and tables of elemental distribution for cross-section samples JR10(above) and JR14 (below). The area analyzed is marked in yellow

The examination of *intonaco* layers with µFT-IR revealed presence of quartz, gypsum, calcite and calcium oxalates (see table 4.1.1).

Sample №	Identified material (mortar)
JR2a	Calcite
JR4	Quartz, Calcite
JR6	Kaolinite, Gypsum, Calcite, calcium oxalates
JR7	Kaolinite, Calcite
JR14a	Kaolinite, Quartz, Gypsum, Calcite

JR14b	Gypsum, Calcite, calcium oxalates
JR15	Quartz, Calcite, calcium oxalates
JR17	Calcite, calcium oxalates
JR21	Kaolinite, Gypsum, Calcite, calcium oxalates
JR25a	Kaolinite, Gypsum, Calcite

Table 4.1.1. µ-FT-IR results of the mortar examination

µRaman analysis of the sample JR21 showed presence of either calcite or anhydrite (peak at 1074 cm^{-1}) Calcium oxalates and anhydrite may be the products of decomposition of calcite and gypsum respectively.

4.2. Preparatory drawings and order of painting execution

There are two main painting techniques used in mural painting:
fresco (or *buon fresco*) is a wall painting technique in which pigments are mixed with clear water and applied to a fresh and still damp lime plaster (*intonaco*); pigments are fixed inside a thin layer of calcium carbonate formed on the plaster surface (carbonation) [1];

secco is a wall painting technique where pigments mixed with an organic binder are applied onto a dry plaster. The use of secco gives an artist more time to execute the painting, and allow to achieve more opaque and soft sheen tones than in buon fresco. In addition, the use of binder allows adverting undesired chemical reaction of pigments (like White lead, Orpiment, Azurite, and Vermillion) with the lime of the plaster [1].

The execution of a large-scale mural painting requires time. However, if the artist is using *fresco* technique the time he has to perform the drawing is strictly limited with the time required for plaster to dry. That is why if the painting is being executed in *fresco* technique it is convenient, to divide the mural into parts known as *giornata*. *Giornata* (in Italian it means ‘a day’s work) is an area of fresh plaster *(intonaco)* applied as one part of a fresco [1]. The use of giornata allows an artist to control his workflow, for example making small giornata in the area where an artist want to make more detailed [1]. In terms of research, presence of giornata provides significant insight into the artist’s modus operandi. First of all, *giornata* itself is an indication of the use of *fresco* technique, since it is barely used in *secco*. In addition, the overlapping edges of *giornata* allow to presume the order of painting execution. In case of *Pentecostes*, the presence of *giornata* was revealed with the use of Vis-RAK light. The mural was divided into 7 *giornata*, see Figure 4.2.1.

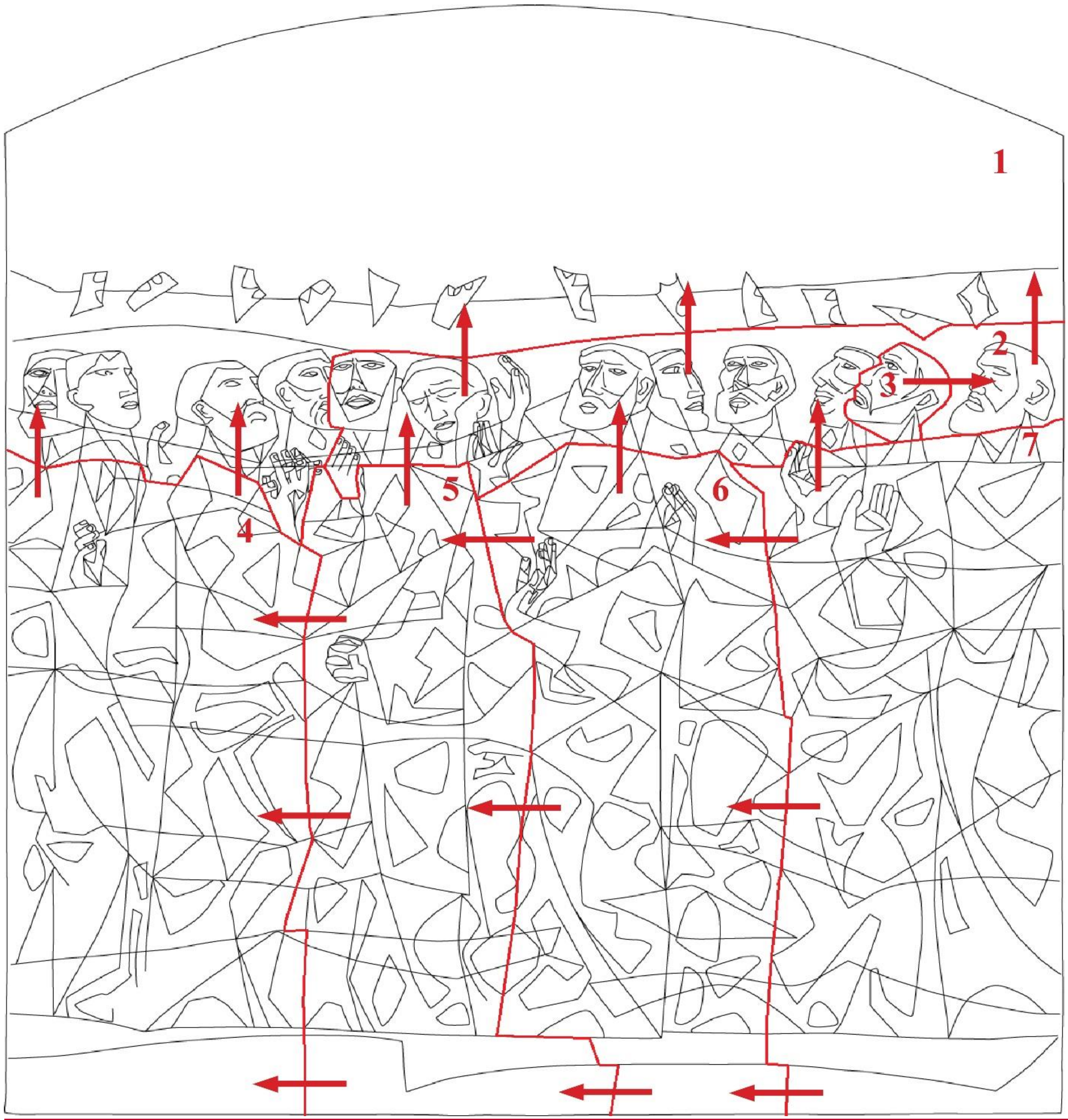


Figure 4.2.1. Map of giornata. Arrows show layers superposition.

Vis-RAK light observation of *giornata 6* revealed presence of finger or round tool marks (see Figure 4.2.2.).

Figure 4.2.2. Round marks visible in RAK-light. Photo by Manuel Ribeiro 2018

That may indicate the use of practice associated with *fresco* technique: an artist was slightly pressing damp intonaco in order to check the surface smoothness and dryness. It is needed to start painting after the surface is hard enough to resist the pressure of the brush, but not too dry, to form a surface carbonate crust. The latter would cause weak physical adherence of the paint layer.

In order to disclose possible presence of preparatory drawings IR-photos were carried out. However, no carbon-based underdrawings were found in the mural.

The final sequence of the mural execution was the application of the paint layers in each *giornata*. Portable OM examination of the painting surface allowed to notice overlaying chromatic layers. That, in its turn, made possibly to hypothesize the order in which the paint layers were applied (see Figure 4.2.3.).

Figure 4.2.3. Order of painting execution. Arrows show layers superposition. Photo by Manuel Ribeiro 2018

The paint layers were applied mostly in two stages. On the first stage, the lighter and more transparent background tones were applied, forming the main volume of the figure's cloaks and faces. Then, on the second stage, the darker tones were applied in more concentrated and opaque layers, forming contours, shadows, horizontal oriented blue stripes, and other details. The most detailed parts of the painting are the faces and the hands of The Apostles. Painting these areas Julio Resende adopted approach that is more complicated. For example, in case of a hand (see figure) he first applied the lighter flesh tones, than darker brown shadows and finally used black paint to contour the hand, fingers and nails. In the faces usually Julio Resende applied flesh tones, then the greyish or white tones of the beards and finally applied shadows and face features (see Figure 4.2.4.).

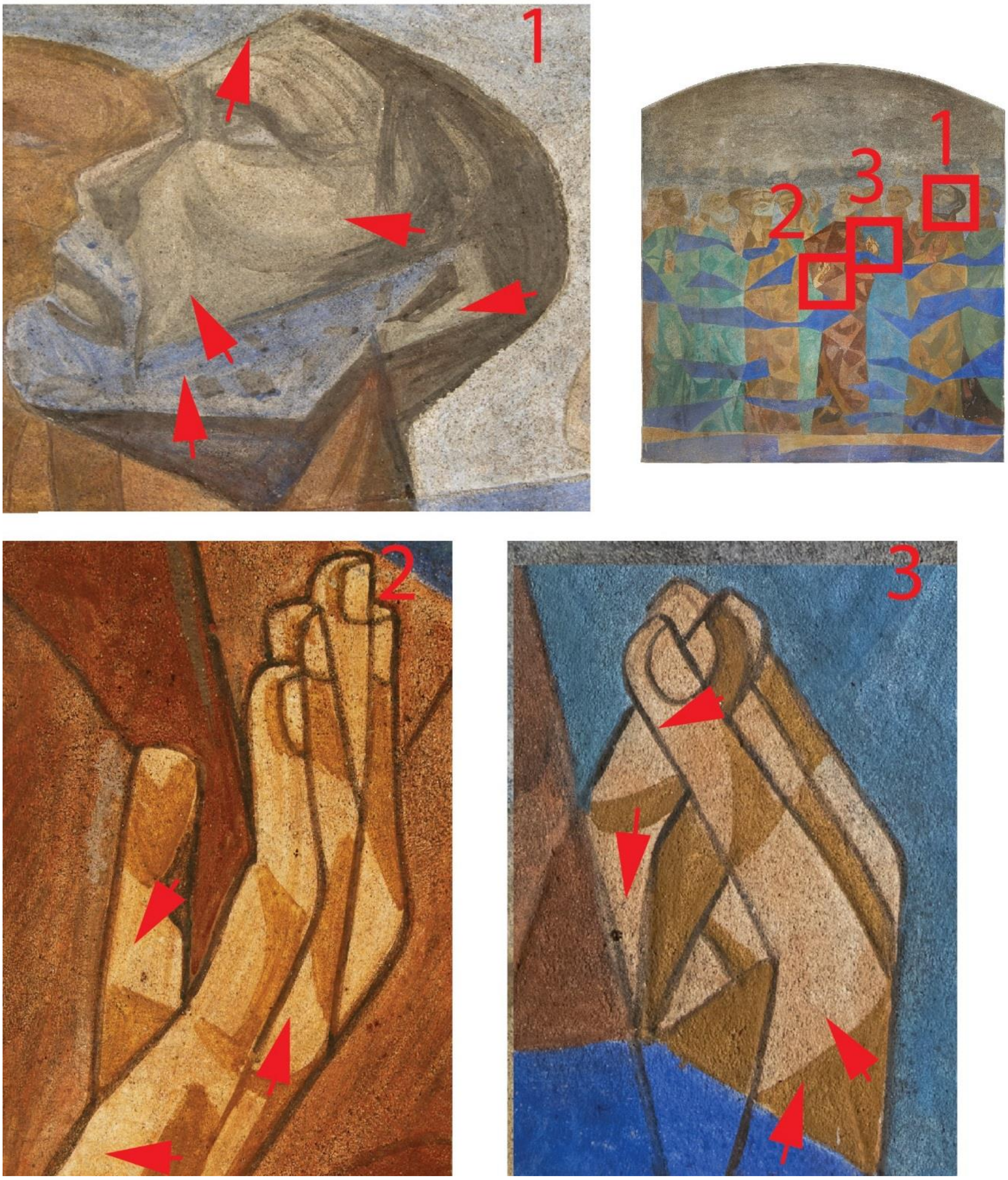


Figure 4.2.4. Order of painting execution. Arrows show layers superposition.

The two-stage pattern of paint layer application is rarely violated. In the one case shown in Figure 4.2.5. it is abandoned, and we may infer that the artist's plan for the color distribution had changed. The darker brown tone overlays the lighter one, the possible explanation could be that the artist's original intention was to paint the whole figure in that color, but later he changed his mind in favor of the lighter brown tone (see Figure 4.2.5.).

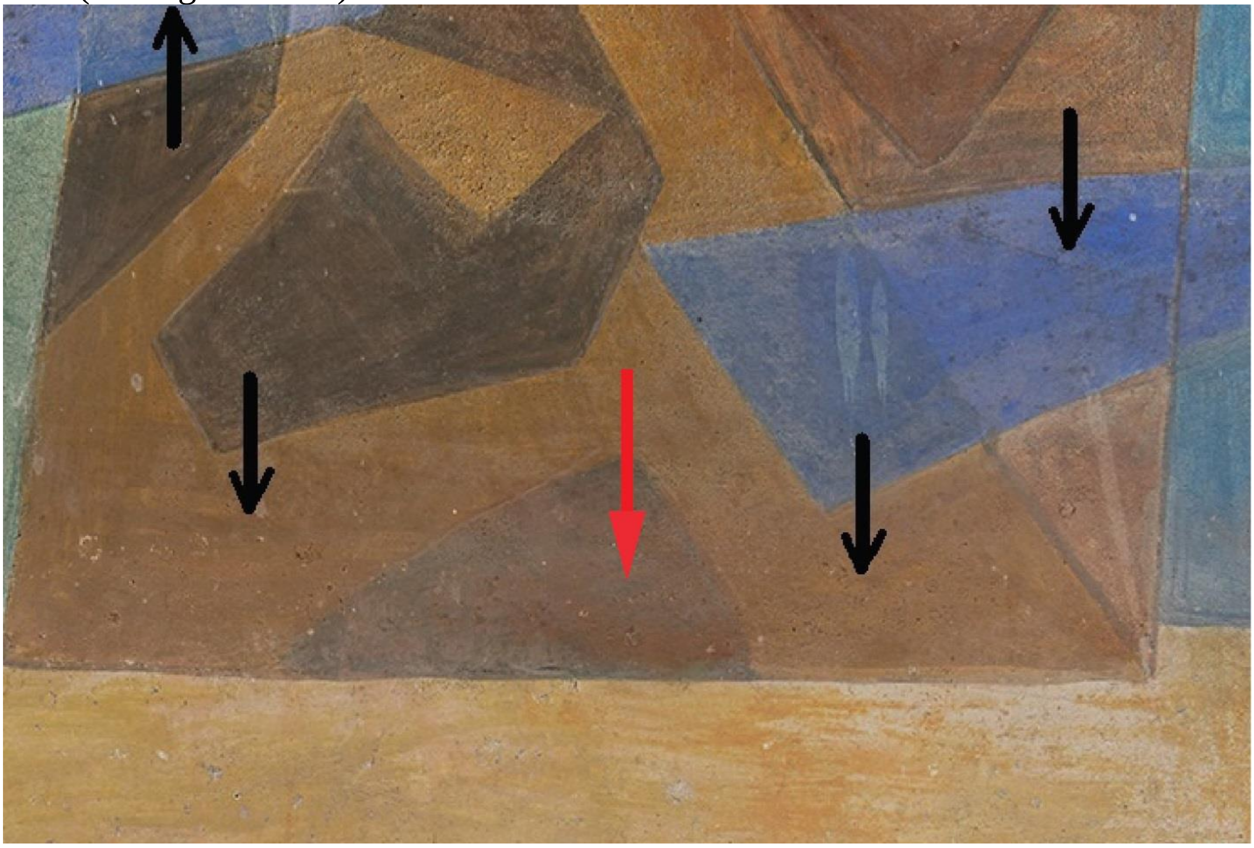


Figure 4.2.5. Order of painting execution. Red arrow indicates unusual case when the detail was painted before background.

In several cases, the artist changed the original color to another one by overpainting it. In the example shown in Figure 4.2.6. a brown paint layer was applied over the original blue one.

Figure 4.2.6. A detail of hand: brown paint layers overlays originally blue one

In many cases the brushstrokes can become the source of information about an artist’s painting technique. However, in this mural painting, the brushstrokes are barely visible. With the use of RAK-light it was possible to detect some of them, mainly in the blue paint layers, where the paint layer is sufficiently thick (see Figure 4.2.7.). All the brushstrokes detected were found in the blue paint layers.

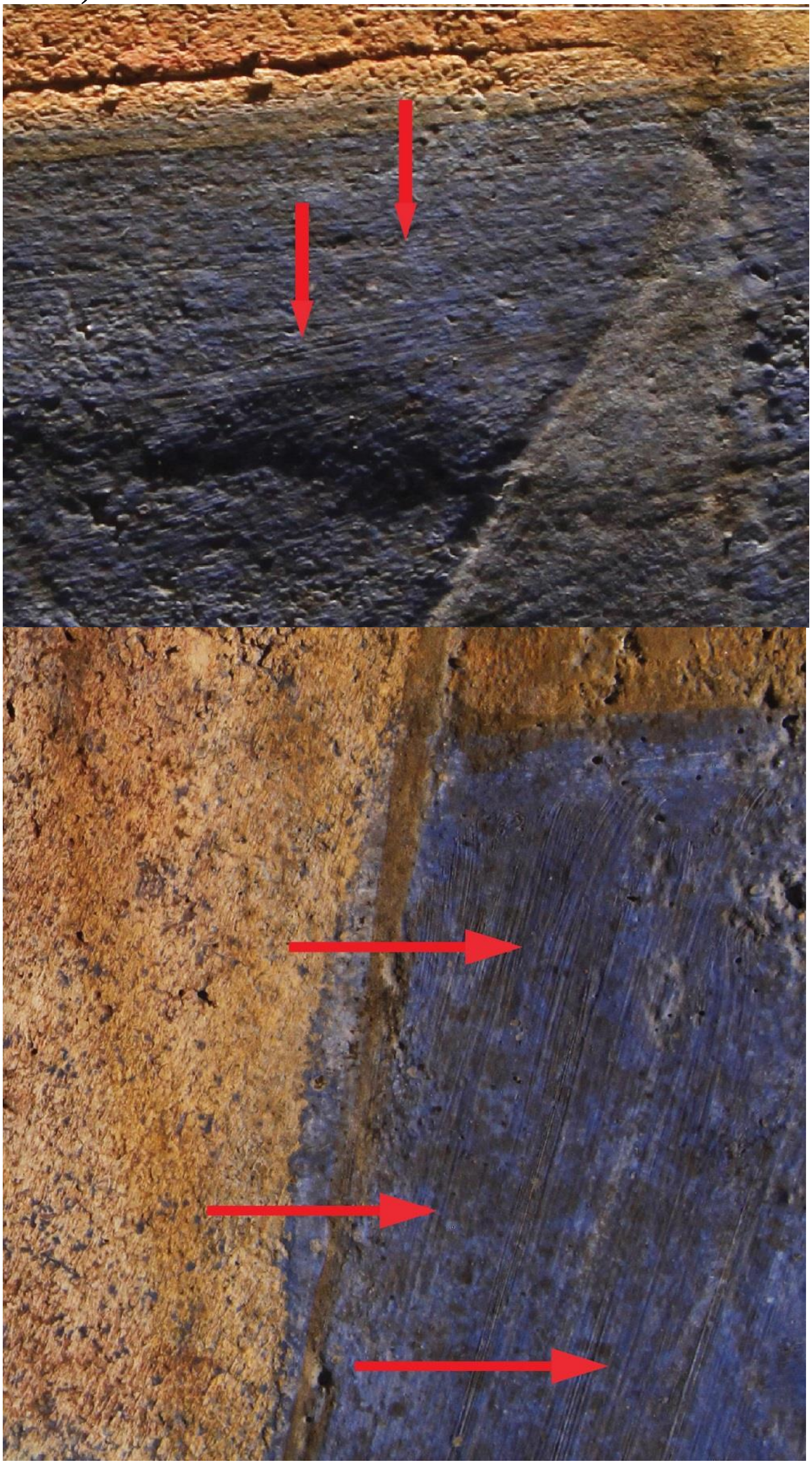


Figure 4.2.7. Brushstrokes details

Another feature of the Pentecostes is presence of *repentimenti* - intentional changes of the composition, presumably executed while the plaster was still wet [1]. The case of possible *repentimenti* when face profile was changed, is shown in Figure 4.2.8.; 4.2.9.)

Figure 4.2.8. Repentimenti. Photo by Manuel Ribeiro 2018

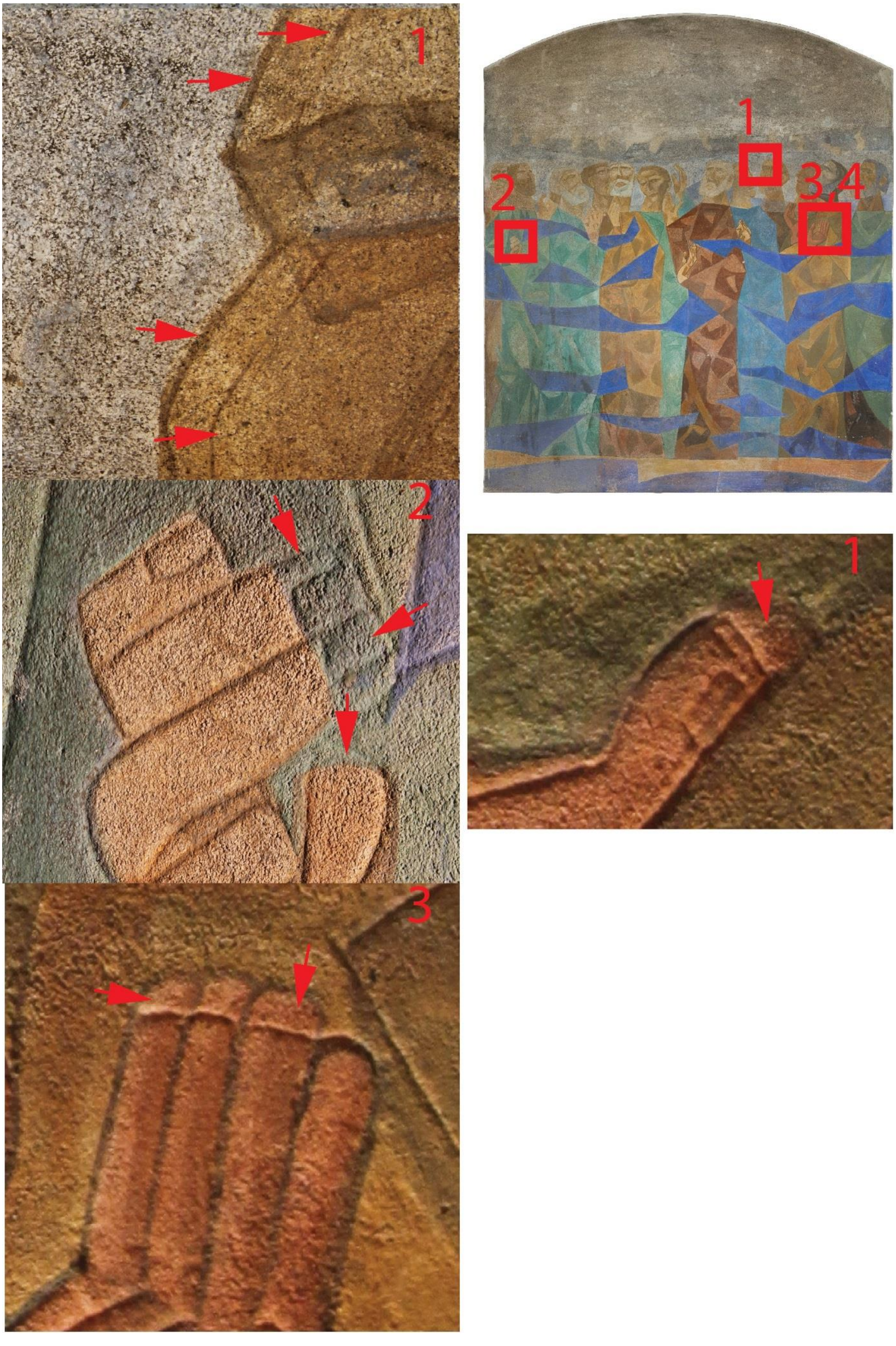


Figure 4.2.9. Ripentimenti

In this mural painting Julio Resende extensively used incised drawing. Two types of such drawings were recognized. The first and the more abundant type is the use rounded groove lines, suggesting that they were made by the pressure of a pointed tool through a cartoon. These lines contour the faces of the figures, their hands as well as subdivide the space and for geometrical figures in the rest of the drawing (see Figure 4.2.10.). Usually but not always, these lines also serve as the division between different colors. The second type of incised drawing used is shallow sketchy lines made with a point tool by free hand (see Figure 4.2.10.). The number of those lines is limited, and it seems that they had an auxiliary assignment. The artist used these incisions after the cartoon ones, when he intended to either slightly alter the previous incisions or add more details. The edges of these incisions have rough shape; sometimes with dried fragments of plaster on it. That allows to hypothesize that these incisions were executed on a later stage of the work when the plaster become slightly drier. The mapping of the two kinds of incisions found is represented in the Figure 4.2.10

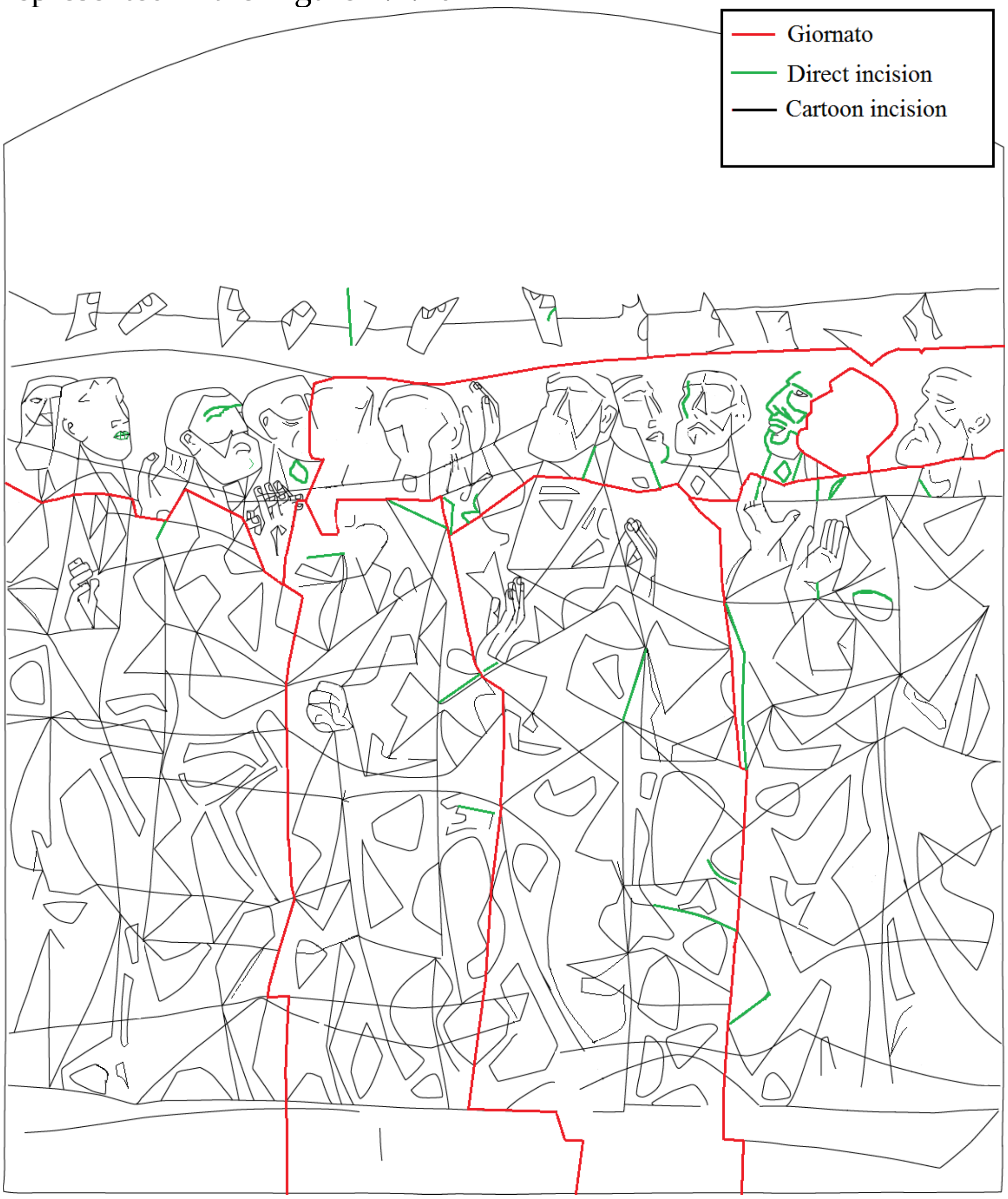


Figure 4.2.10. Distribution of the two kinds of incisions found by Vis-Raking light.

4.3 Paint layers characterization.

Colorimetric measurements were undertaken in-situ in order to objectively evaluate chromatic palette of the painting. Figure 4.3.1. provides the results of the measurements, projected on CIE a*b* color space. In this model only two chromatic coordinates were used: a* (red/green axis) and b* (yellow/blue axis) [2].

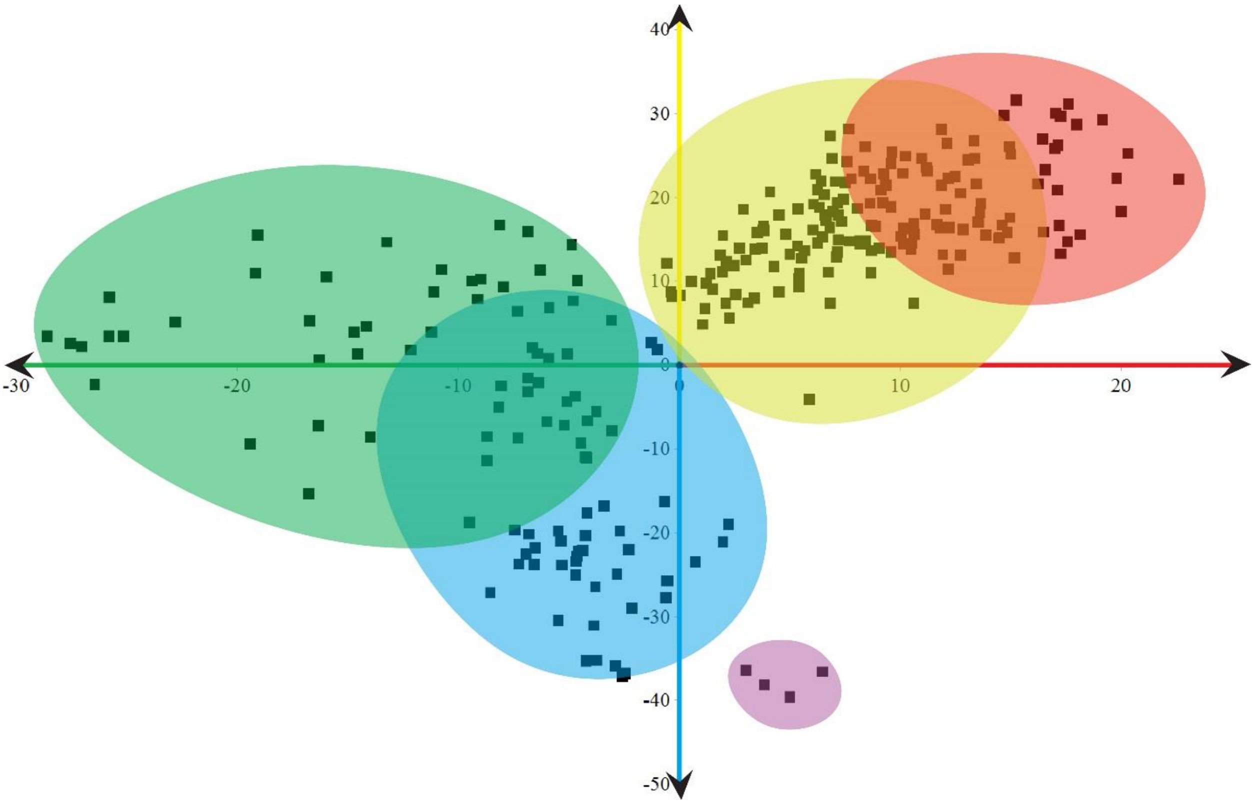


*Figure 4.3.1. Chromatic palette (CIE a*b*)*

From this diagram it can be concluded that the majority of the paint layers analyzed is formed by the paint layers with positive a* and b* and hue ranging from yellowish-brown to reddish brown, red and orange. The green paint layers vary from the ones closer to the ones with the bluish hue to the intense green ones.

The results of Colorimetric measurements allowed to choose the paint layers for an EDXRF analysis. Two kinds of paint layers were chosen – the most average and the most extreme ones of each color.

After the first Diffuse reflectance curves and EDXRF data were collected, it became possible to start preliminary pigment identification. The discussion of that issue is presented in the following paragraph.

4.3.1. Pigment characterization

Blue pigments.

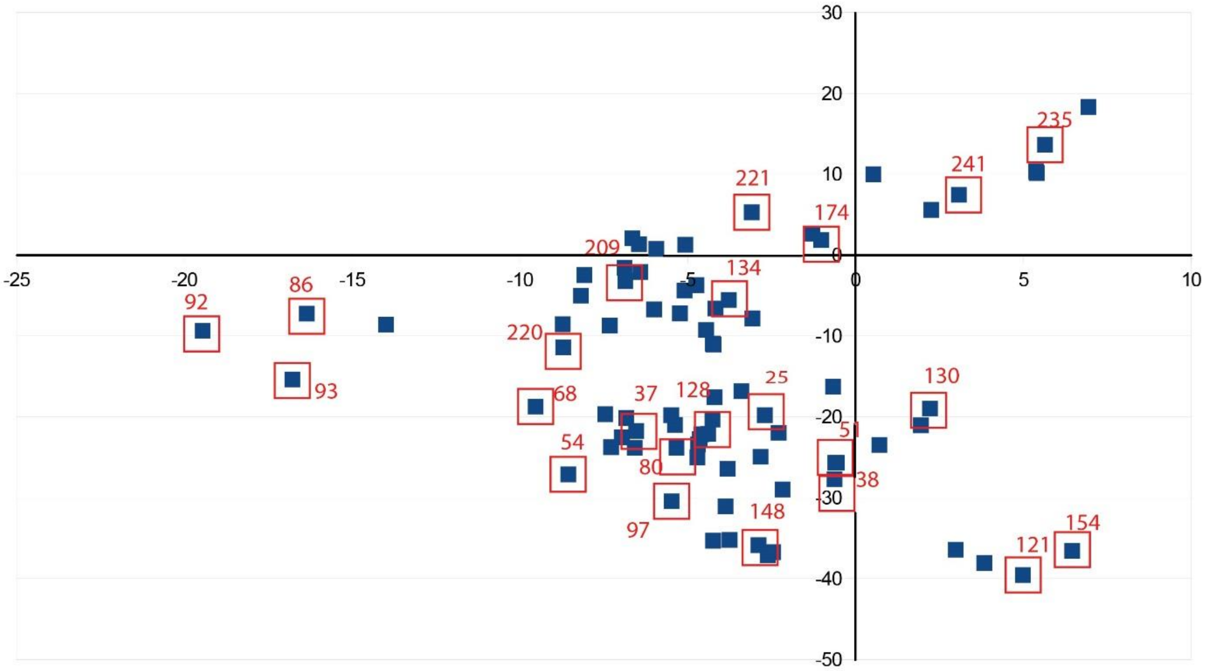


*Figure 4.3.2. Chromatic palette (CIE a*b*) of the blue paint layers. Paint layers subjected to EDXRF analysis are marked with their Jrescol number. (For an index of the areas analyzed, please see Appendix IV)*

Colorimetric results of the seventy-eight blue areas measured was plotted in the CIE a*b* space and showed quite broad spread of the blue shades (see Figure 4.3.2.). There are several hypotheses that can explain this:

a) different pigments were used
b) dirt deposits interference
c) the use of pigment mixtures, with one main pigment and several additives much smaller in their volume.

In case of *Pentecostes*, the last hypothesis seems to be the most reasonable. Portable OM study of the blue paint layers showed the presence of green and white particles (see figure 4.3.3. samples jrescol68 and 92) Unfortunately, the diffuse reflection curves of the blue paint layers did not show any characteristic peaks, suitable for the pigment identification (see Figure 4.3.3.).

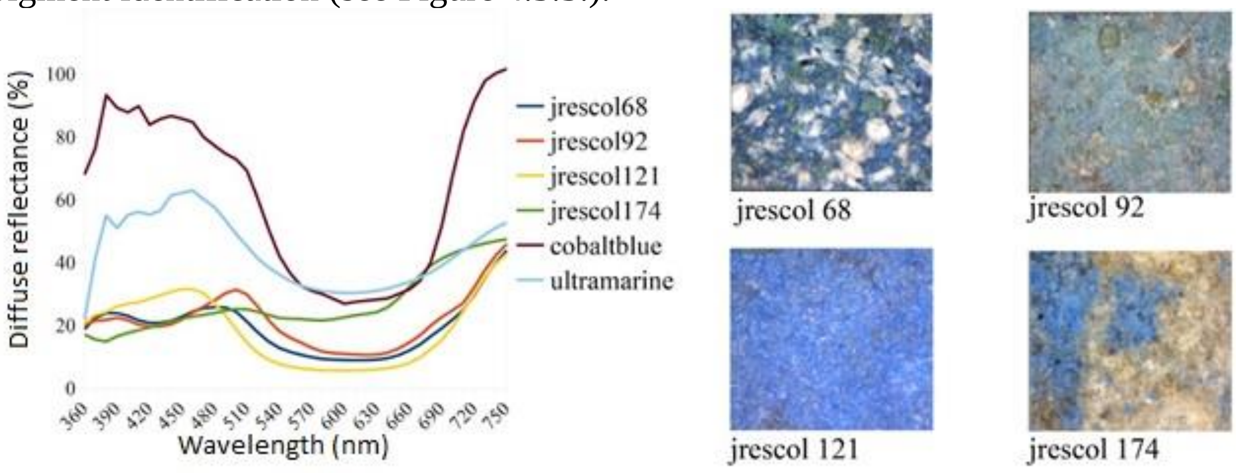


Figure 4.3.3. Diffuse reflectance curves of the blue samples

The analysis of the twenty-three blue paint layers by portable EDXRF has revealed in all the measurements the presence of Co. In a group of samples (Jrescol 68, 80 86, 92, 93 and 94) Cr is present as well (see Figure 4.3.4.) A distinct group is formed by the Ba-rich samples (Jrescol 25, 86, 93, 174, 220, 221 and 235) (see Figure 4.3.4.).

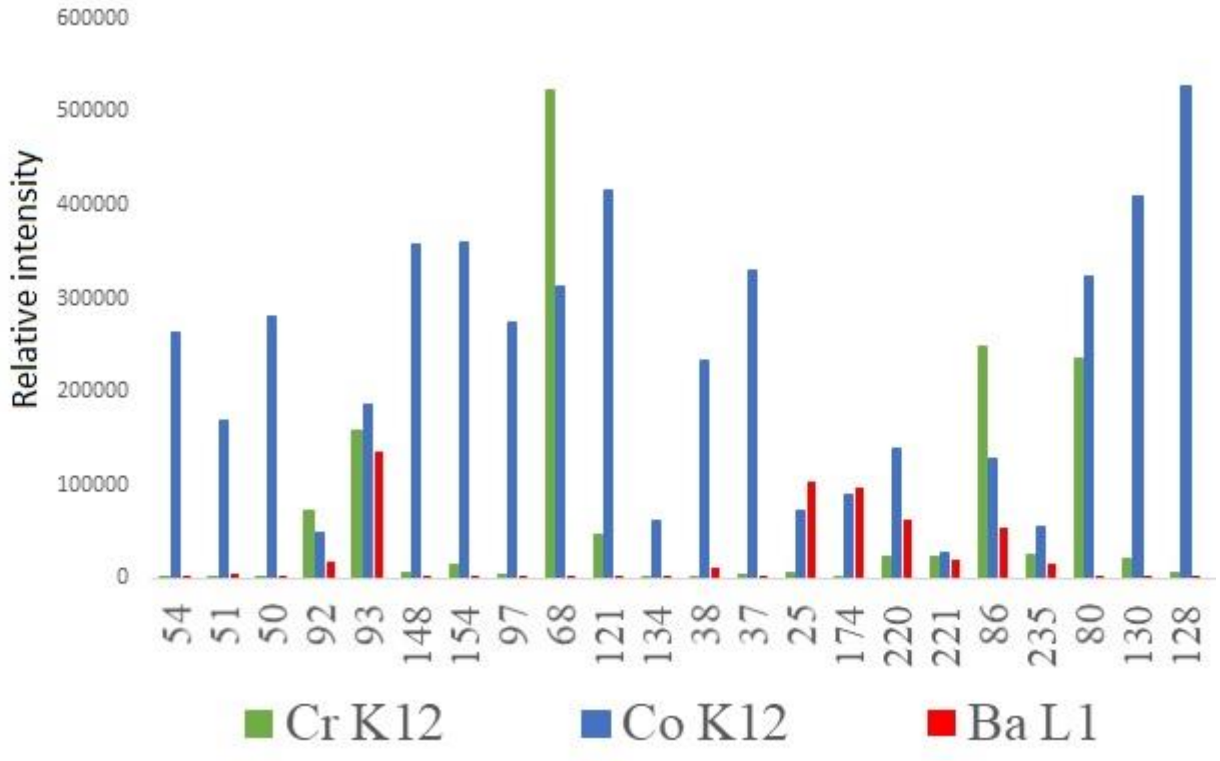


Figure 4.3.4. EDXRF table of the blue paint layers. Relative quantity of Cr, Co and Ba

The use of white pigments and presence of Ba is explained in *White pigments* section below.

The predominance of Co in all the blue samples analyzed by EDXRF rose the hypothesis that Cobalt Blue was used as the base pigment in the blue shades.
Cobalt Blue is a Cobalt (II) oxide-aluminum oxide-based pigment, first introduced in the first decades of the XIX century [4]. The pigment soon gained a recognition from the artists as a cheap and stable substitute of natural ultramarine. Cobalt blue is known as one of the most stable pigments - it is resistant to heating and oxidizing as well as to strong acids and alkalis [4]. However, this pigment was not used in any modern mural painting described in paragraph 2.1.

To confirm the presence of Cobalt blue, additional analysis was undertaken on powder samples from the blue area (JR6, 7, 14b, 17 and 21) FT-IR analysis of the sample JR6 shown presence of calcite, calcium oxalates and presumably Cobalt blue. Results that are more representative were obtained by means of µRaman. A spectrogram of a samples JR6 and JR7 shown well-defined characteristic peaks (at around 205, 415, 522 and 694 cm^{-1}) corresponding both to the reference and table characters (see Figure 4.3.5.).

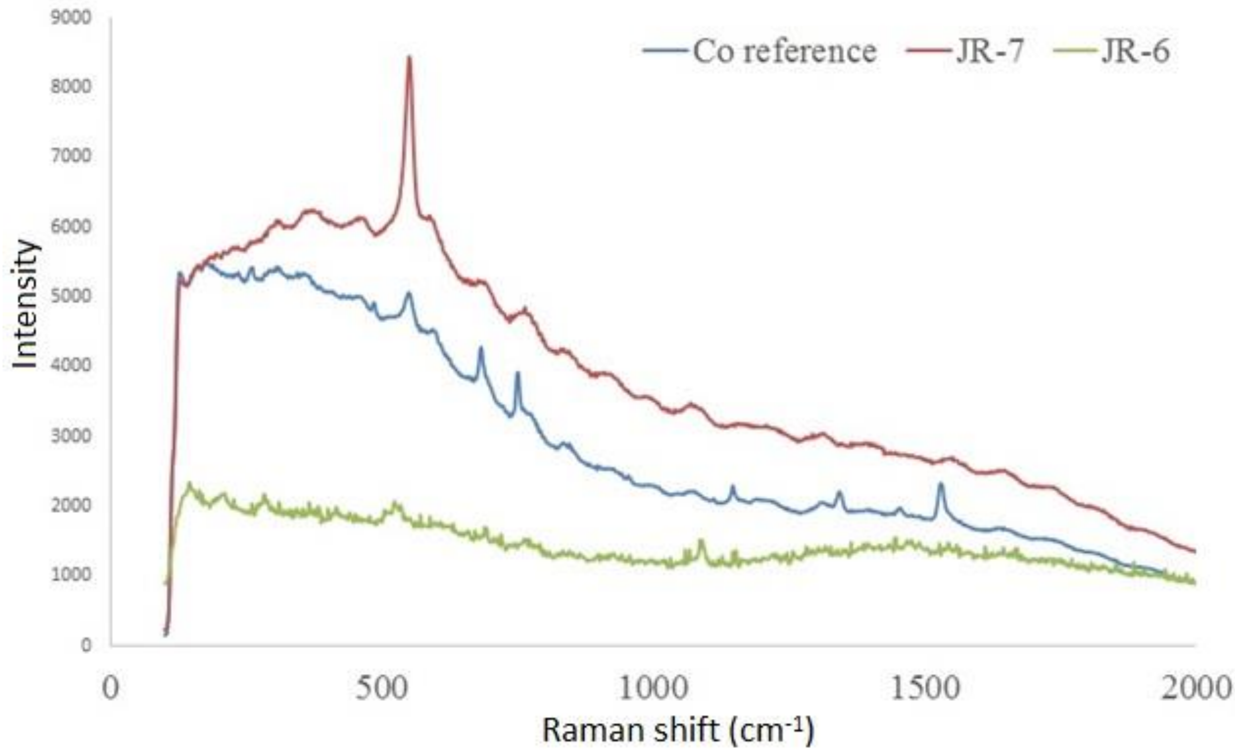
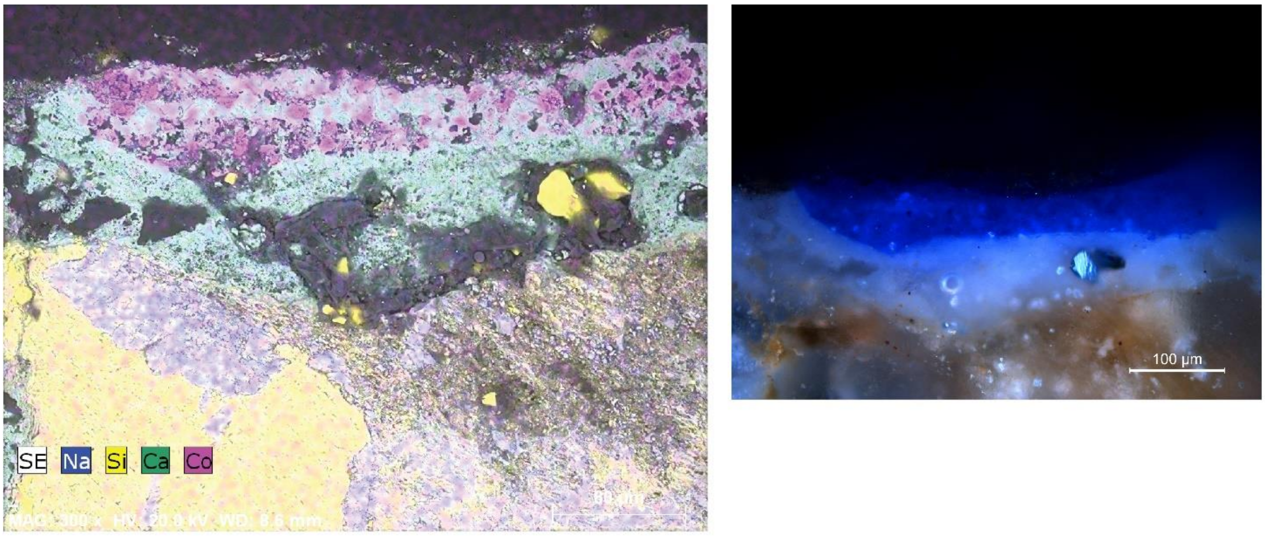
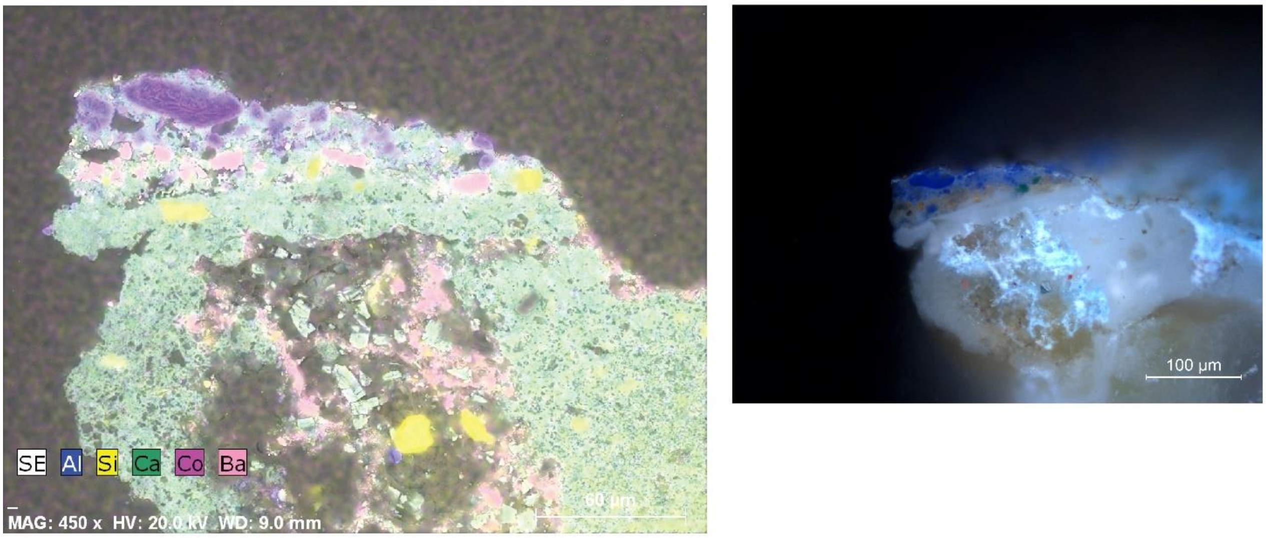


Figure 4.3.5. μ-Raman result for the blue pigment layers. Samples JR6 and JR7

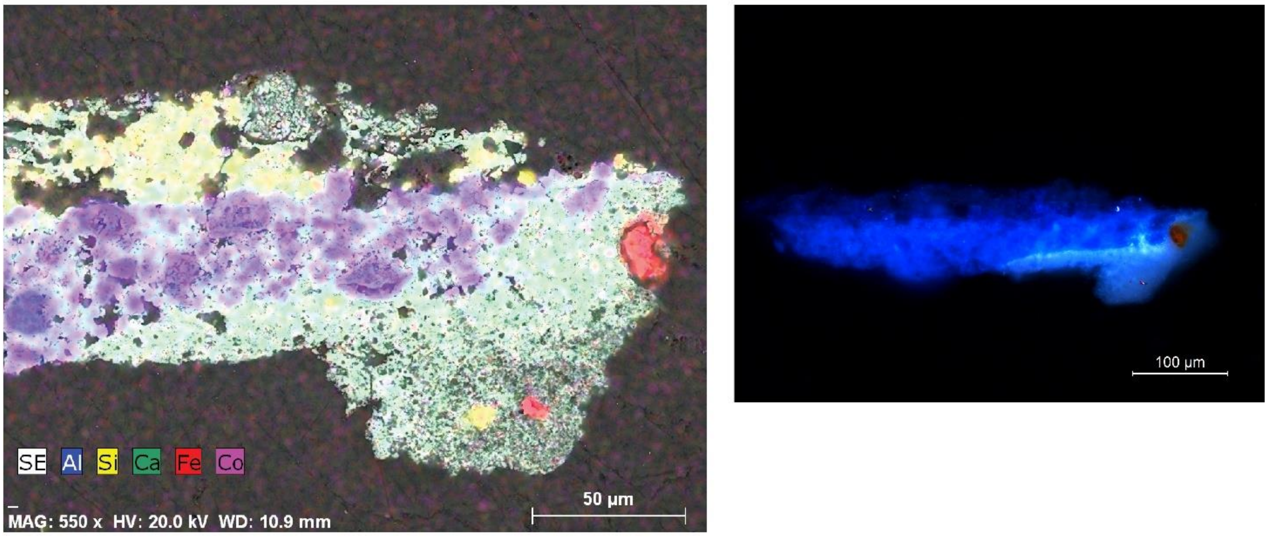
SEM-EDS analysis also have confirmed the previous data. Figure 4.3.6. shows the elemental map of 4 samples where Co and Al were found in all the pigment particles.



JR-18



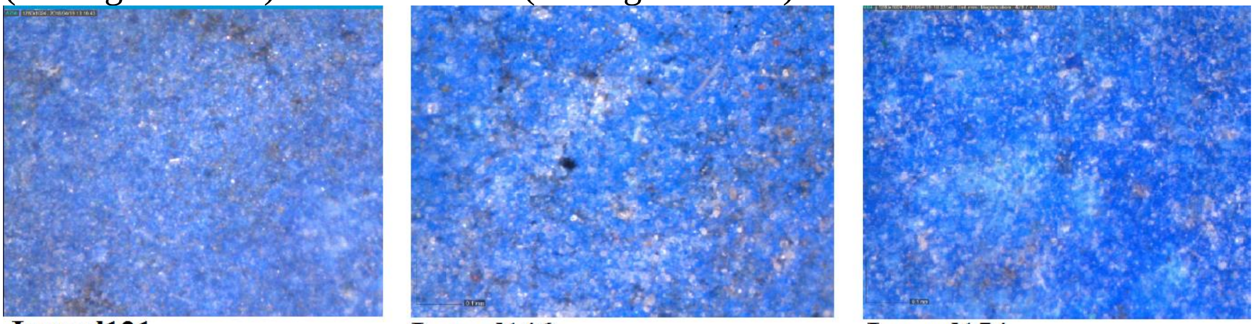
JR-19



JR-22

Figure 4.3.6. Left column: EDS elemental map distribution of Co and Al corresponding with the presence of Cobalt Blue in samples JR-18,19,22; right column: OM images of the same samples with 200x magnification.

A small although distinctive sample group is formed by slightly violet shades Jrescol 121, 146 and 154 (see Figure 4.3.1.). Although they have the same elemental composition as the other blue samples analyzed, their hue is remarkably different (see Figure 4.3.8.) from the others (see Figure 4.3.2.)



Jrescol121 Jrescol146 Jrescol154

Figure 4.3.7. Violet blue samples

A possible explanation was found during SEM-EDS testing of sample JR18, where Co particles are dispersed in thicker Ca matrix (see Figure 4.3.8). That may indicate an intentional mixture of Cobalt blue pigment with lime to achieve a different hue.

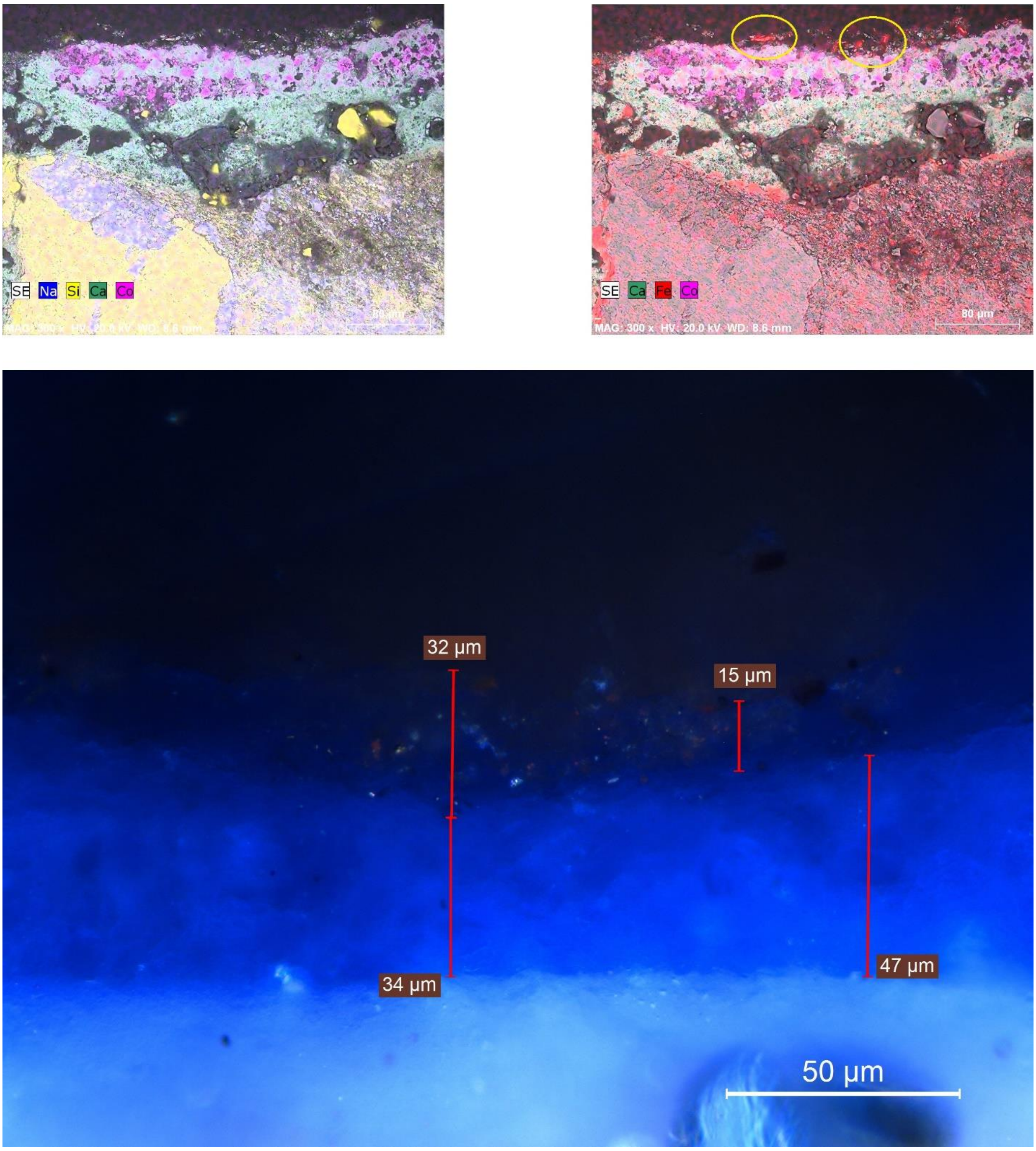


Figure 4.3.8. JR18 cross section. Layer of mixed Co and Ca (with presence of Red Ochre particles). Above on the left: EDS map showing distribution of Ca, Co, Si and Na; above on the right: EDS map showing presence of iron-rich particles (marked with yellow circles); below: OM picture of the cross-section with layer thickness indication.

Green pigments

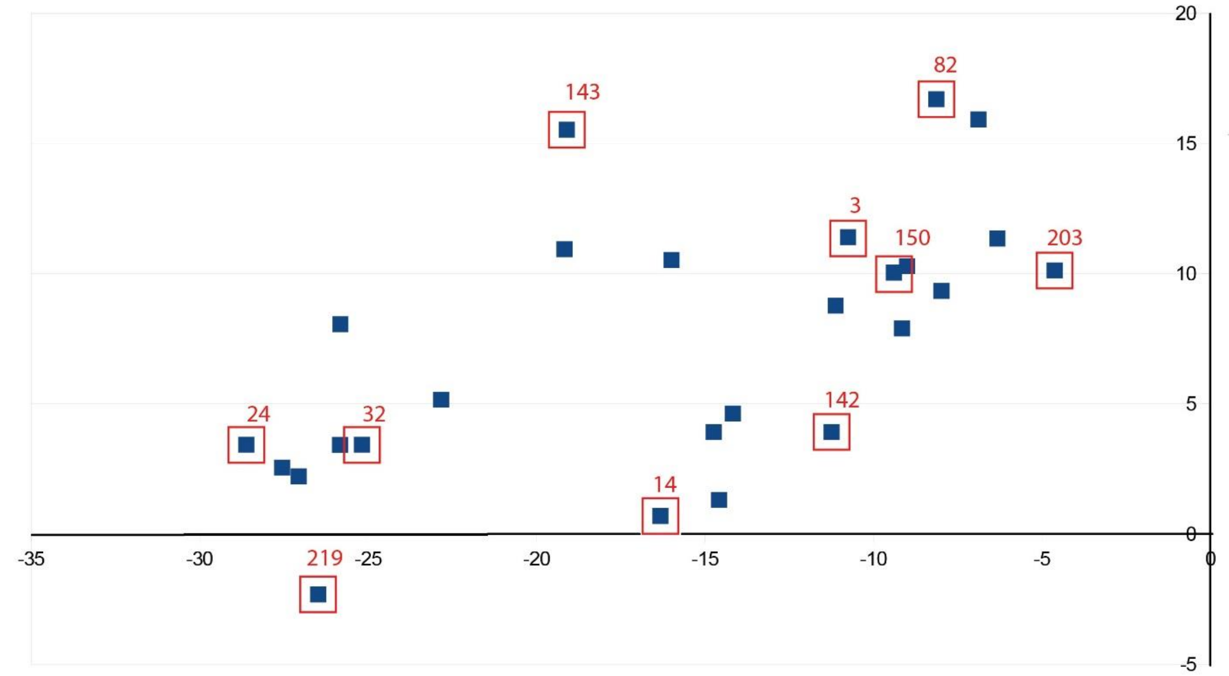


*Figure 4.3.9. Chromatic palette (CIE a*b*) of the green paint layers. Paint layers subjected to EDXRF analysis are marked with their Jrescol number.*

In total twenty-six colorimetric measurements (see Figure 4.3.9.) were taken in green paint layers and 10 points were analyzed by EDXRF (see Figure 4.3.12.). Among the original paint layers two (Jrescol 82 and 143) are supposed to be later stains. Diffuse reflectance spectra of the green paint layers showed a pattern close to reflectance curve of Chromium Green/Viridian (see Figure 4.3.5). Some of the reflectance spectra are shown in the Figure 4.3.10.

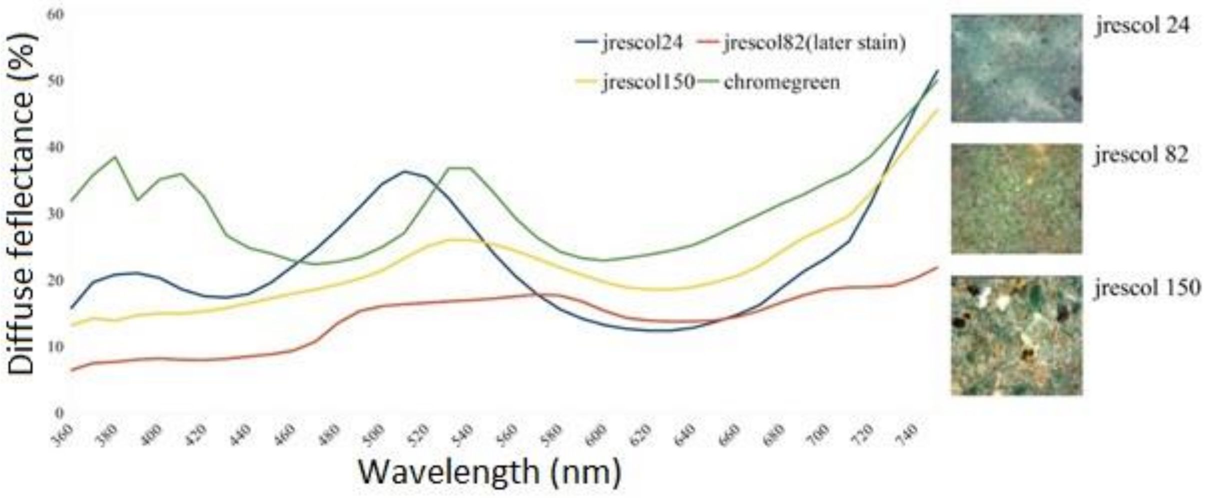


Figure 4.3.10. Diffuse reflectance curves of several green samples (jrescol24, 82 and 150)

EDXRF revealed presence of Cr in the majority of the green paint layers analyzed (see Figure 4.3.12.). In addition, presence of Fe, Ba, Co and Pb was detected.

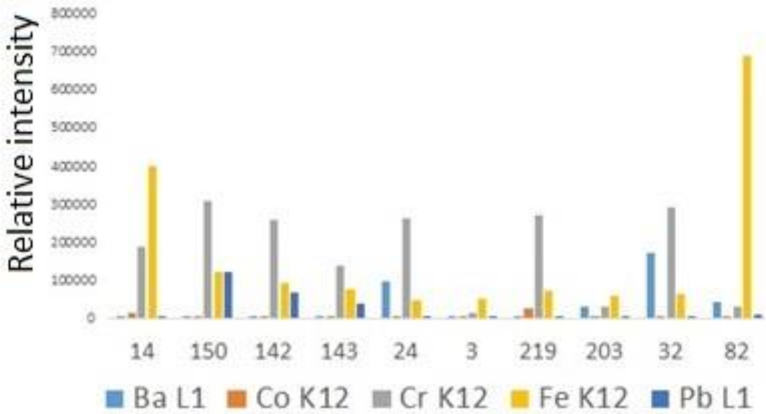


Figure 4.3.12. EDXRF table of the green paint layers. Relative quantity of Ba, Co, Cr, Fe and Pb

Complementary evidence of Cr presence was achieved by SEM-EDS (see Figure 4.3.11.).

Among the artistic pigments there are several chromium-based ones [5]. Before cheap, stable and non-toxic artificial green pigments were introduced, one of the most common ways to achieve green color was to mix Chromium yellow with Prussian blue. In the first half of XIX an alternative was introduced - the use of chromium oxide-based pigments [5].

There are two main kinds of such pigments: chromium oxide (Cr_2O_3) and hydrated chromium oxide ($Cr_2O_3.2H_2O$), also known as Viridian [5].

To verify the hypothesis that Chromium oxide was used as the main green pigment in *Pentecostes* painting, the samples (JR2a, JR4, 14b, 15 and 17) were tested by μ-FT-IR and μ-Raman.

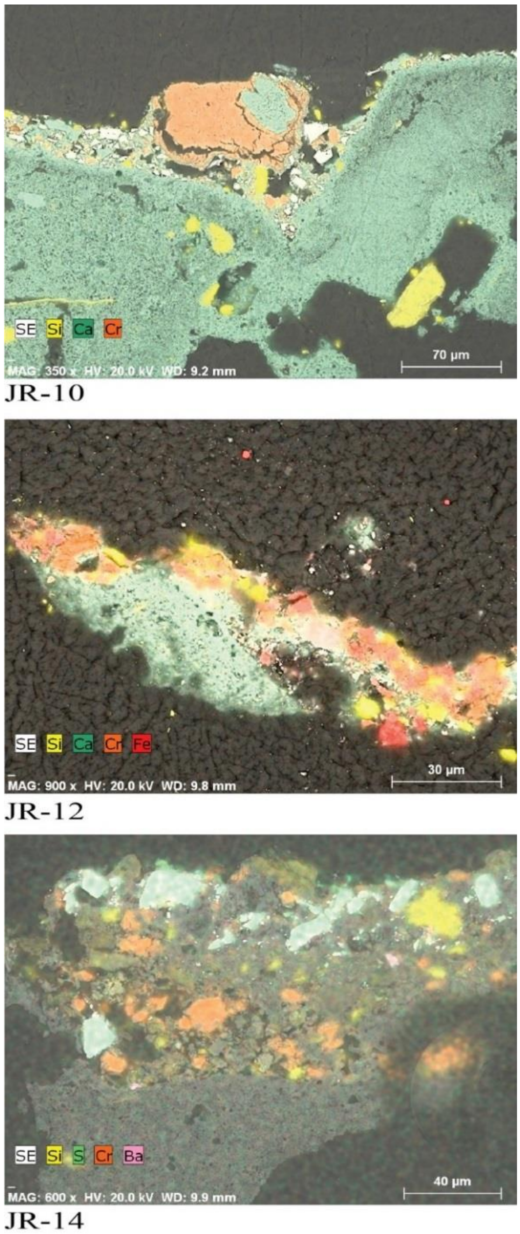


Figure 4.3.11. Distribution of Cr (orange) in three micro sample cross sections(JR10, JR12 and JR14)

Figure 4.3.13. presenting the μ-Raman spectra of sample JR14a showing a correspondence between the sample and Viridian reference. Unfortunately, the rest of the samples tested by μ-Raman did not show any spectra.

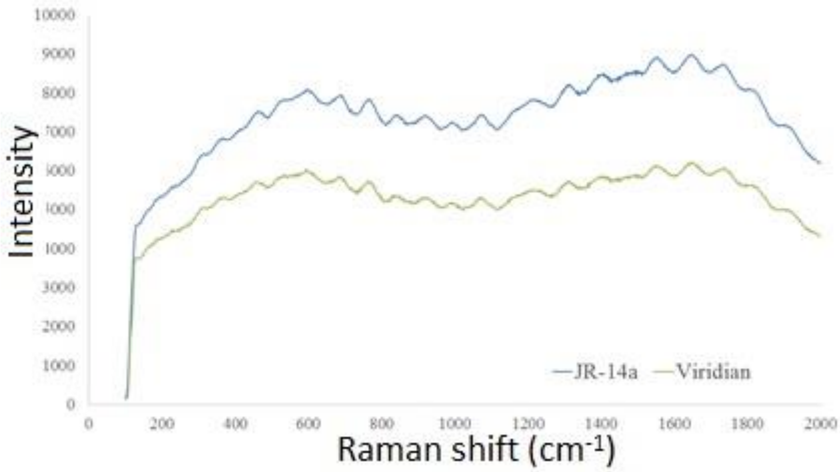
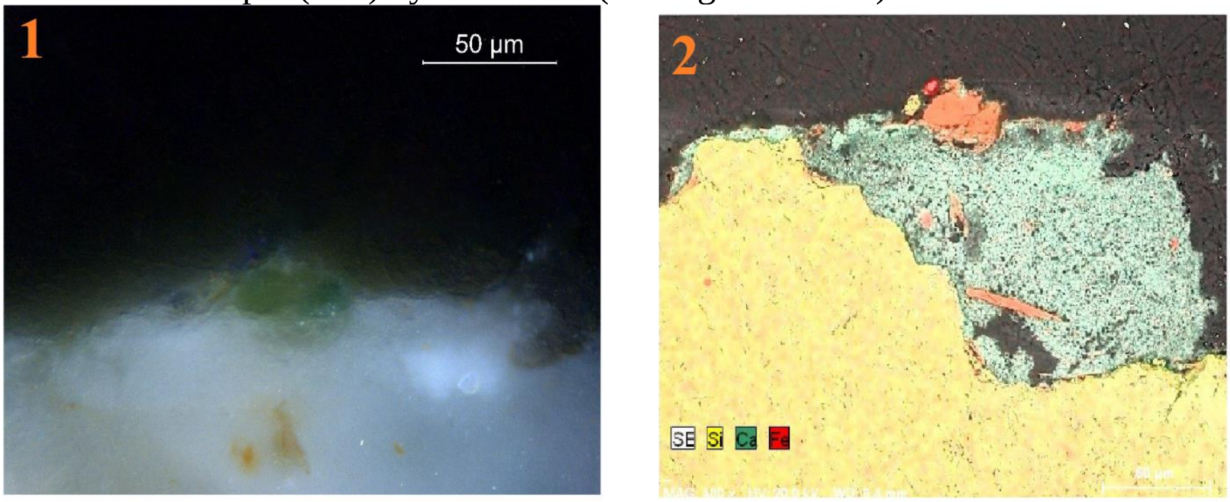


Figure 4.3.13. µ-Raman spectra of sample JR14a in comparison with Viridian reference

Infrared spectroscopy allowed detection of another chromophore. In sample JR2a FT-IR showed the presence of Celadonite. Celadonite is a mica group mineral ($K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$.), one of principal compounds of the Green earth pigment. The Green earth is mainly derived of two minerals: Celadonite and Glauconite, however other minerals are likely to be present. This natural pigment have been used since the ancient times and reached the highest popularity in Medieval ages, when the artists used it for underpainting middle and shadow flesh tones [6]. The presence of Celadonite may correspond to a Fe rich particle revealed in the same sample (JR2) by SEM-EDS(see Figure 4.3.14.).



Element	C Atom. [at.%]
O	62,94
Na	0,79
Mg Al Si	3,64 1,17 17,52
S	0,17
Cl	0,24
K	4,41
Ca	1,27
Fe	7,85

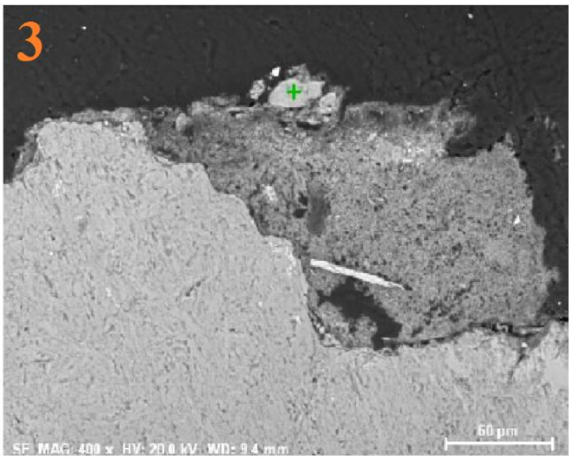


Figure 4.3.14. Detail of the sample JR2. 1. OM picture of JR2 (500x); 2.EDS map of JR2 showing distribution of Si, Ca and Fe; 3. SEM picture of the green particle and its elemental composition (on the left). Minor blue particle corresponds with the presence of Co and Al.

Small green crystals were observed with portable OM in blue paint layers (see Figure 4.3.2., paint layers jrescol68 and 92).

An interesting case of a different use of the green pigments appeared in the cloak of a Figure3. The color of the cloak is different from the other green hues appearing in the painting. IR photography showed that area in much lighter tones, than other green areas in close proximity (see Figure 4.3.15.). The appearance of different pigments in IR-imaging can vary according to their physical and chemical properties. The fact that one green area absorbs more IR than another may indicating the use of two different pigments or pigment mixtures.

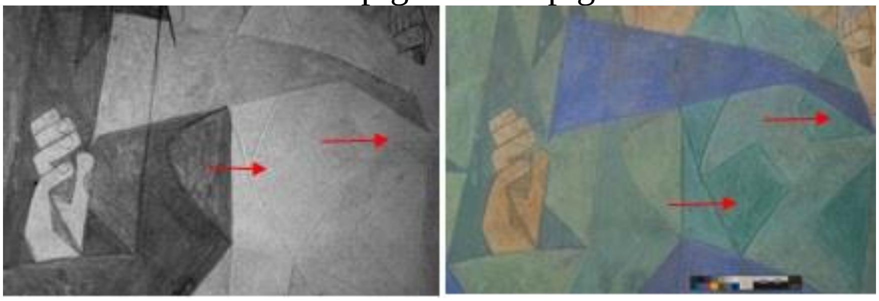


Figure 4.3.15. IR and Vis light pictures of an area

Red and orange pigments

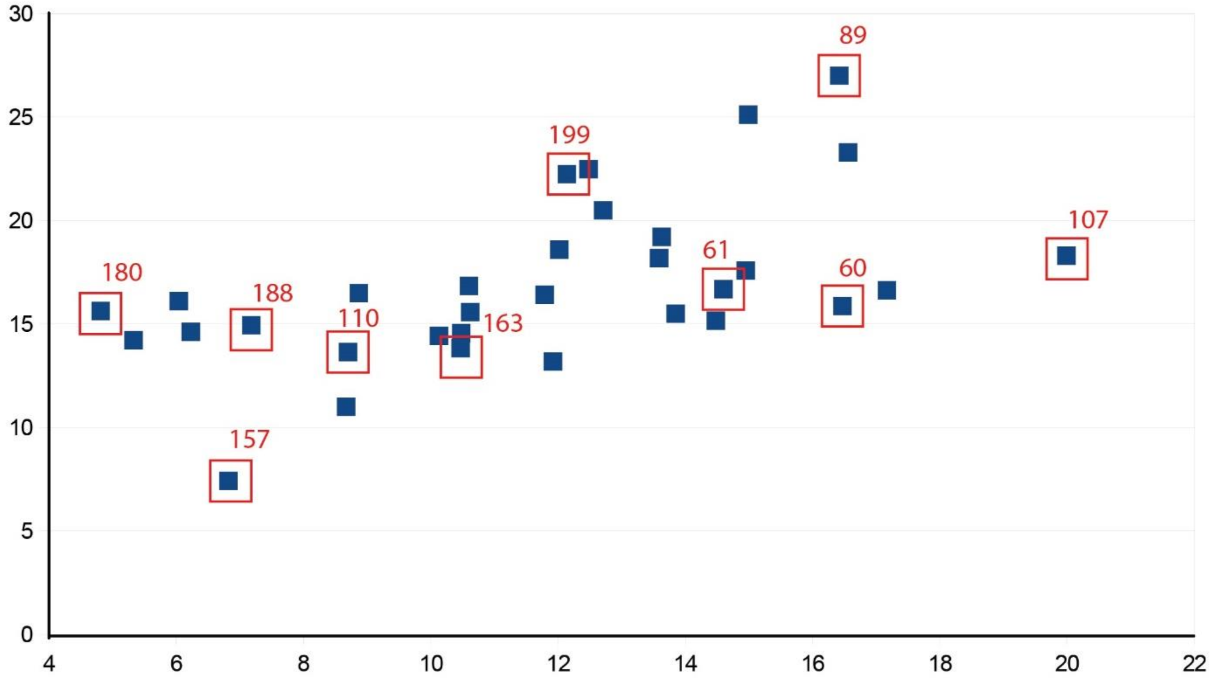


*Figure 4.3.16. Chromatic palette (CIE a*b*) of the red paint layers. Paint layers subjected to EDXRF analysis are marked with their Jrescol number.*

The use of the Red Ochre as the main colorant was presumed after the diffuse reflectance curves were obtained. As shown in Figure 4.3.17. the curves of the red paint layers show resemblance with Red Ochre.

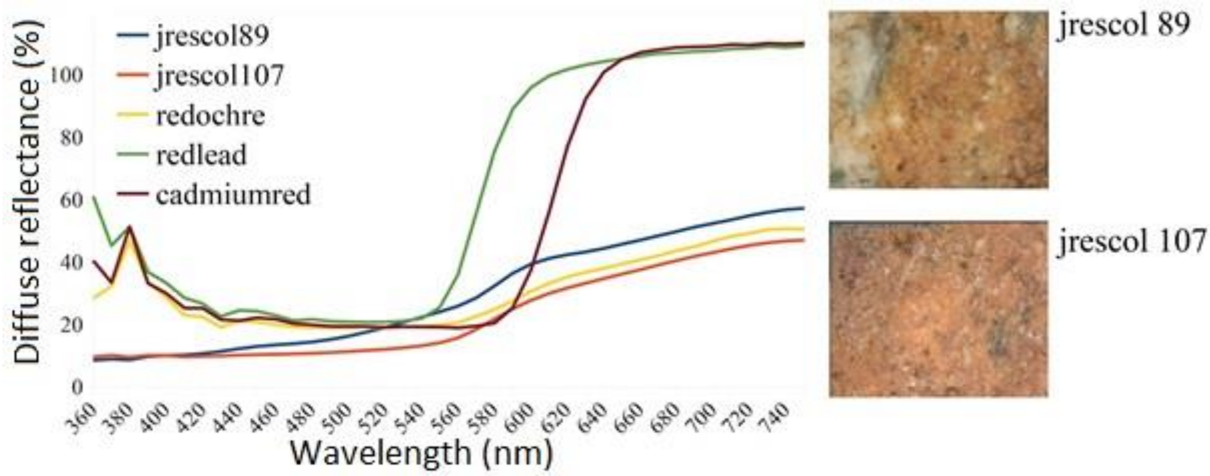


Figure 4.3.17. Diffuse reflectance curves of the red samples

Red Ochers are known as the most ancient pigments, with its use dated back to prehistoric times [7]. The principal component of the Red Ochre is an iron oxide called Hematite (Fe_2O_3), however in natural Red Ochers the presence of other minerals is possible [4]. M. Gil described the extensive use of the earth pigments including Red Ochre in Alentejo region [8]. Local deposits allowed producing pigments of various hues ranging from olive-yellow to dark reddish-brown. The practice of production of homemade limewash and its use for decorative purposes existed in Alentejo until the middle of the XX century [8]. This may have inspired Julio Resende to choose natural Red Ochre rather than industrially produced red pigments. On the other hand, the use of the Red Ochre could be justified by its color only.

Nine red and three orange paint layers were examined by means of EDXRF and Colorimetry. The overall presence of Fe may support the hypothesis of the use of Red Ochre. In addition, presence of Cd, Cr and Pb was detected (see Figure 4.3.18.).

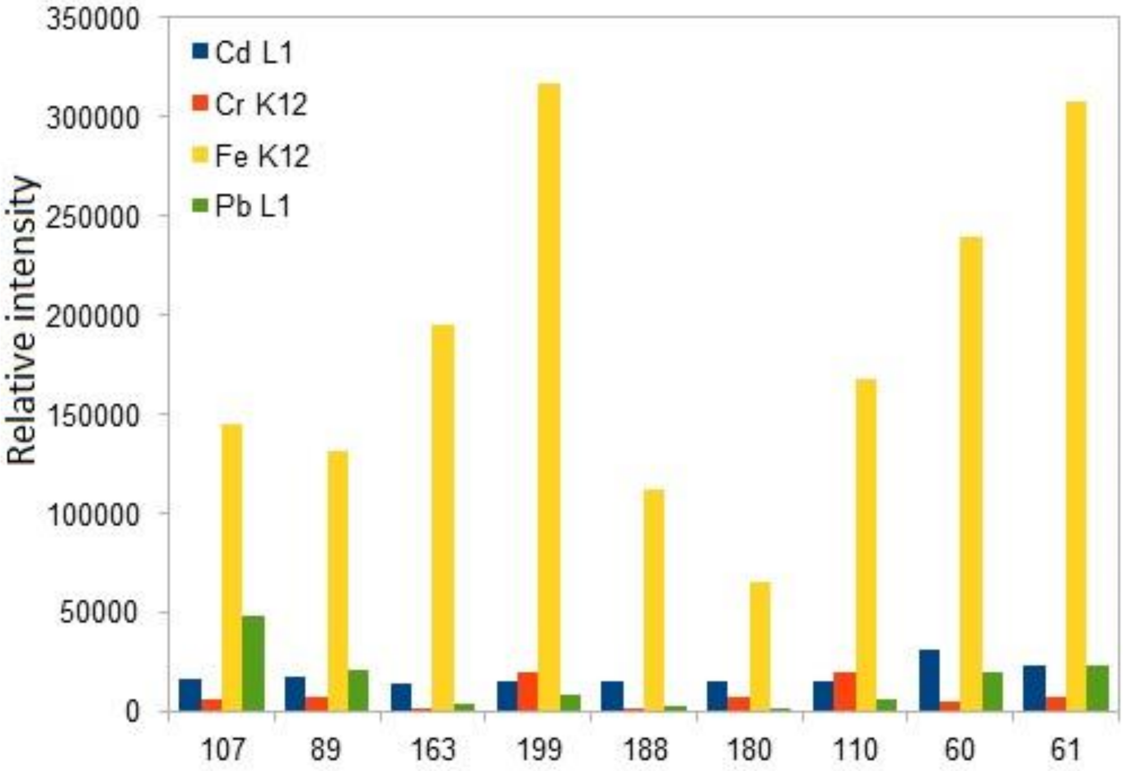


Figure 4.3.18. EDXRF table of the red paint layers. Relative quantity of Fe, Cd, Cr, and Pb

To confirm the use of Red Ochre, the samples were subjected to analysis by means of μ-FT-IR, and μ-Raman. Unfortunately, FT-IR was unable to detect any colorant in both samples studied (JR14a, JR25). However, presence of Hematite was proved in sample JR14a with the help of μRaman (see Figure 4.3.19.).

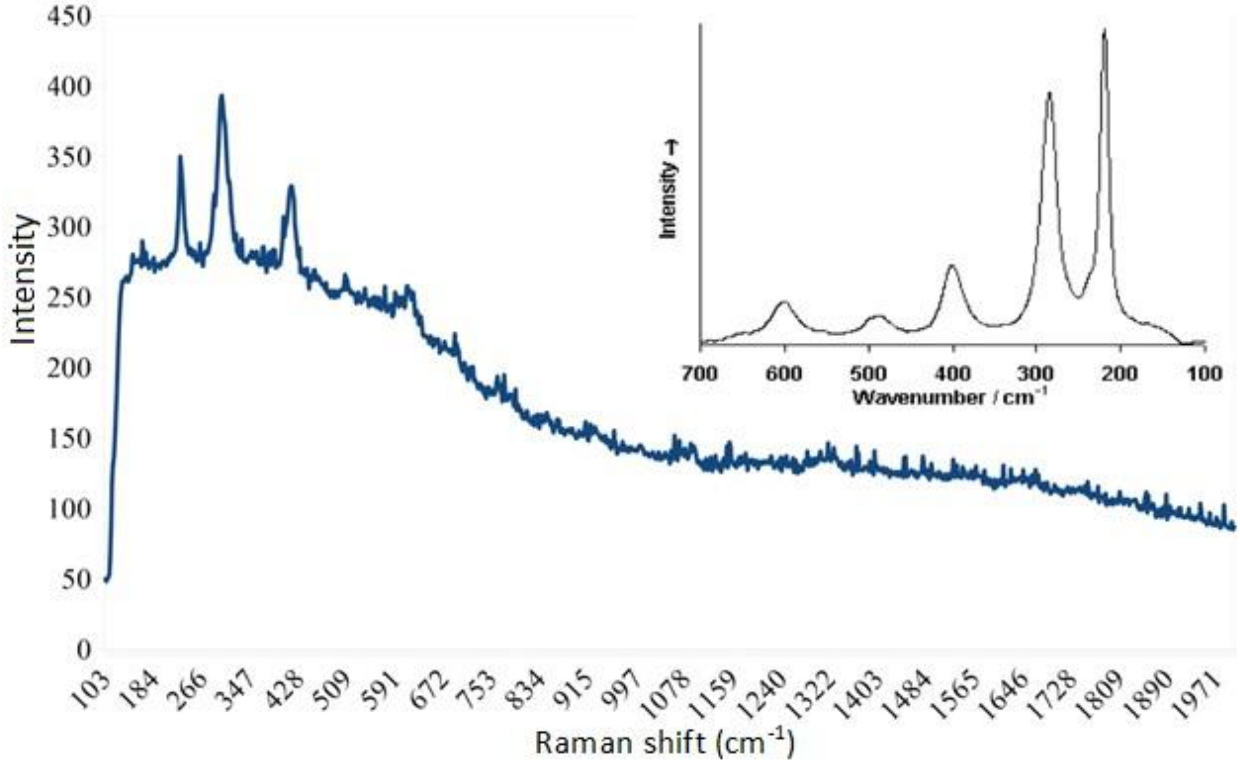


Figure 4.3.19. µ-Raman result for Hematite in sample JR14a with the reference (Reference from RRUF database: http://rruff.info/Hematite/X050102). Characteristic peaks at 225,291,411 cm^{-1}

However, a question remained - did Julio Resende used natural Red Ochre, or pure industrially produced Hematite? SEM-EDS analysis showed predominance of Fe in red paint areas. However, a number of other elements, usually associated with clay minerals (Al, Mg, and Si) was also detected. In samples JR14a and JR25a FT-IR detected clay mineral Kaolinite. That leads to the assumption that the artist used Red Ochre.

Apart from the Red Ochre, it is likely that Julio Resende used another red pigment either cadmium or chromium in the orange paint layers. The presence of these pigments was suggested by the reddish fluorescence in the orange paint layer, visible in UV-lightning (see Figure 4.3.20.).

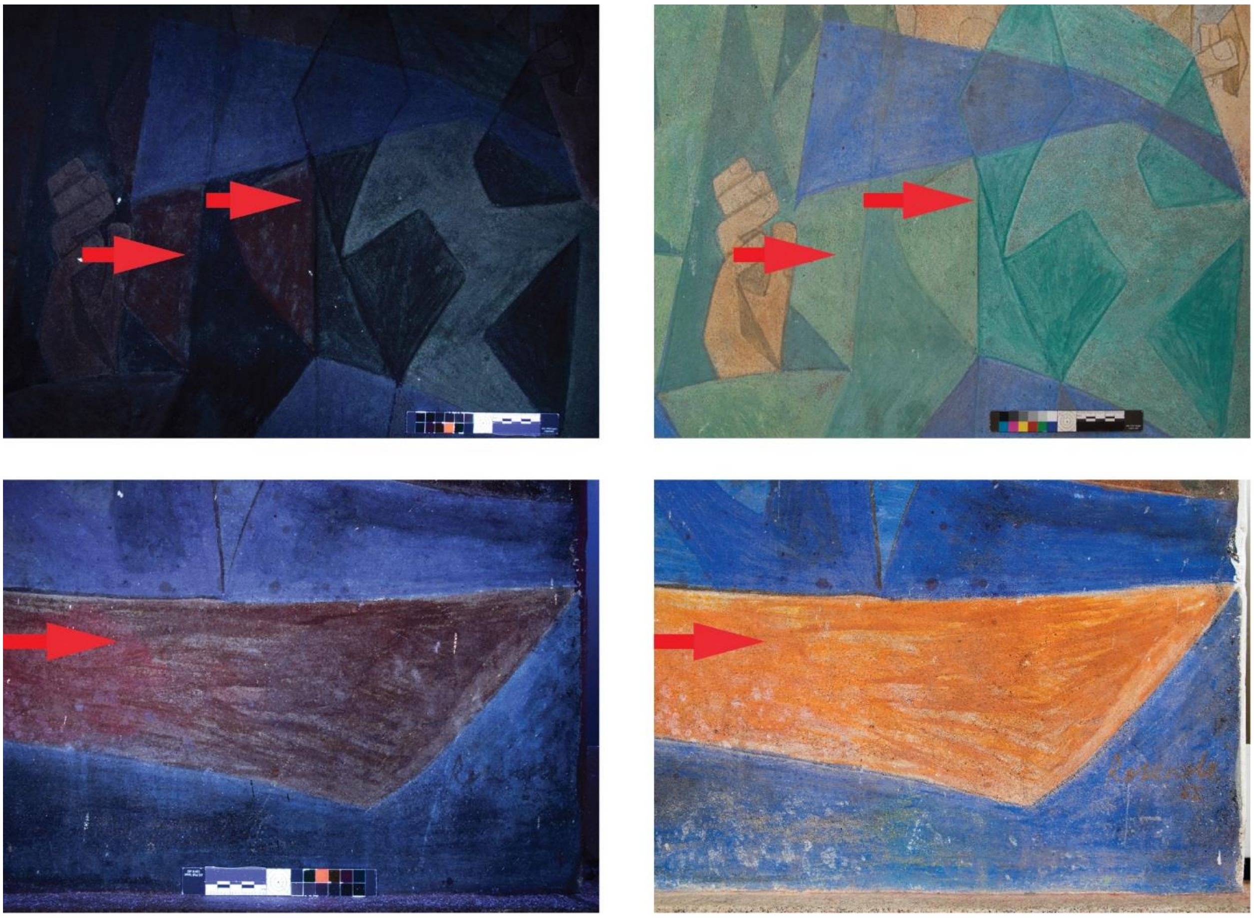


Figure 4.3.20. Details in UFV where fluorescence in the orange paint layer can be seen. Photos by Manuel Ribeiro 2018

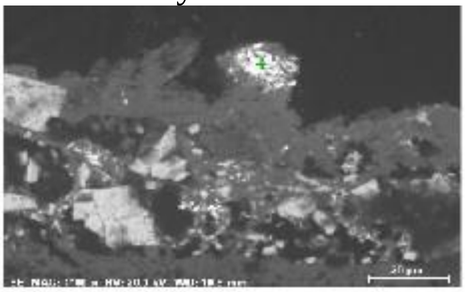
Chromium red basic lead chromate with the chemical formula $PbO \cdot PbCrO_4$. Originally it was introduced in 1797 and came to artistic use since the first quarter of the XIX century. Although the pigment is chemically compatible with all other pigments, it darkens with age. That may be one of the reasons why Chromium Red did not gain much popularity among the artist [6]. Cadmium red is one of the of Cadmium-based pigments, which have different hues. It is a stable pigment with strong red color, consisting of cadmium sulfide (CdS) and cadmium selenide (CdSe) mixed in various proportions. The pigment became available since 1919, but has been used on a limited scale due to its high cost [6].

Both elements (Cr and Cd) were found by SEM-EDS in orange pigment particles of a paint layer cross section taken from this area (JR25).

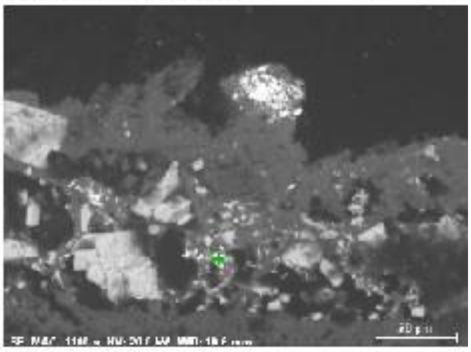
An insight into orange paint layer chemical composition was obtained after sample JR25 was analyzed with SEM-EDS. The sample contains a large 28µm particle of a distinctive bright orange color. Smaller particles of presumably the same origin are dispersed in the paint layer. Results of EDS point analysis are presented in Figure 4.3.21.

The substantial quantities of Pb may indicate the use of Chromium red.

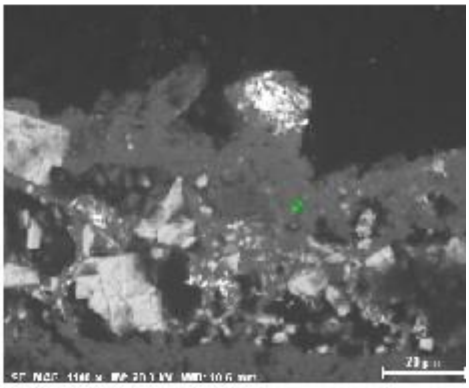
Element	C Atom. [at.%]
Mg	5,76
Al	4,29
Ca	19,72
Cr	20,10
Ba	2,07
Pb	48,03



Element	C Atom. [at.%]
Mg	0,38
Al	0,40
Si	0,92
S	2,49
Cl	0,41
Ca	83,92
Ba	4,51
Pb	6,97



Element	C Atom. [at.%]
Mg	0,13
Al	1,56
Si	4,97
S	3,58
Cl	1,04
Ca	83,51
Fe	1,20
Cd	1,95
Ba	2,05



Element	C Atom. [at.%]
Mg	1,42
Si	0,78
Ca	73,05
Cr	6,48
Sr	0,51
Ba	3,12
Pb	14,64

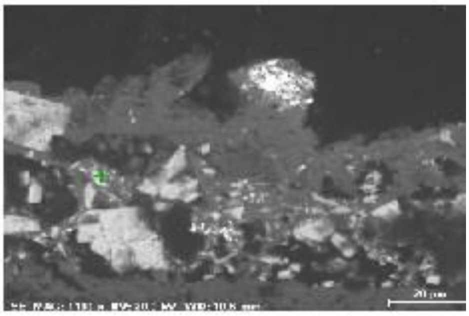


Figure 4.3.21. Results of EDS point analysis in sample JR25 orange paint layer cross section. The points analyzed are marked with green.

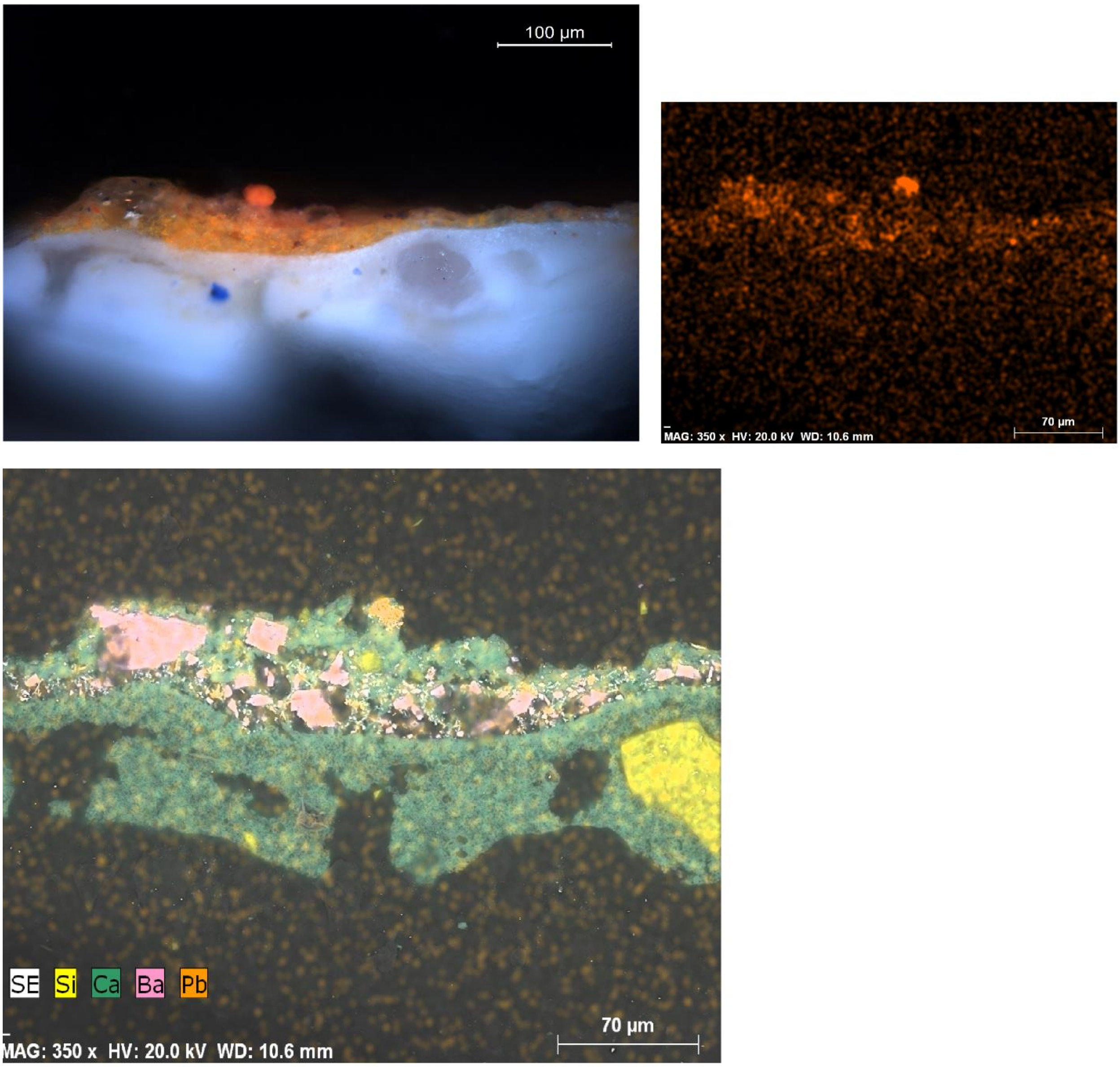


Figure 4.3.22. Detail of the paint layer cross section, sample JR25. On the left: OM picture of JR25 (200x); on the right: EDS map of Cr presence in sample JR25; below: EDS map of sample JR15 showing distribution of Si, Ca, Ba and Pb.

EDS examination of sample JR14 revealed the presence of Cr particles in red paint layer (see Figure 4.3.23.). That supports the hypothesis that Chromium red pigment was used.

Figure 4.3.23. Detail of the cross-section JR14 showing blue layer overlaying brownish one. On the right: sampling area; on the left: OM picture of JR14 (above) and EDS map of JR14 showing distribution of Si, Ca, Cr, Fe and Ba (below).

However, it seems that Cadmium Red was used as well, since EDXRF showed presence of Cd in all nine samples analyzed (see Figure 4.3.18.). OM study of sample JR12 revealed the presence of bright red/orange particles (up to 6 µm in diameter) different from the surrounding red background composed mainly of Fe and Ba. EDS analysis of these particles confirmed that they consist of Cd and the background is Fe and Cr (see Figure 4.3.24.)

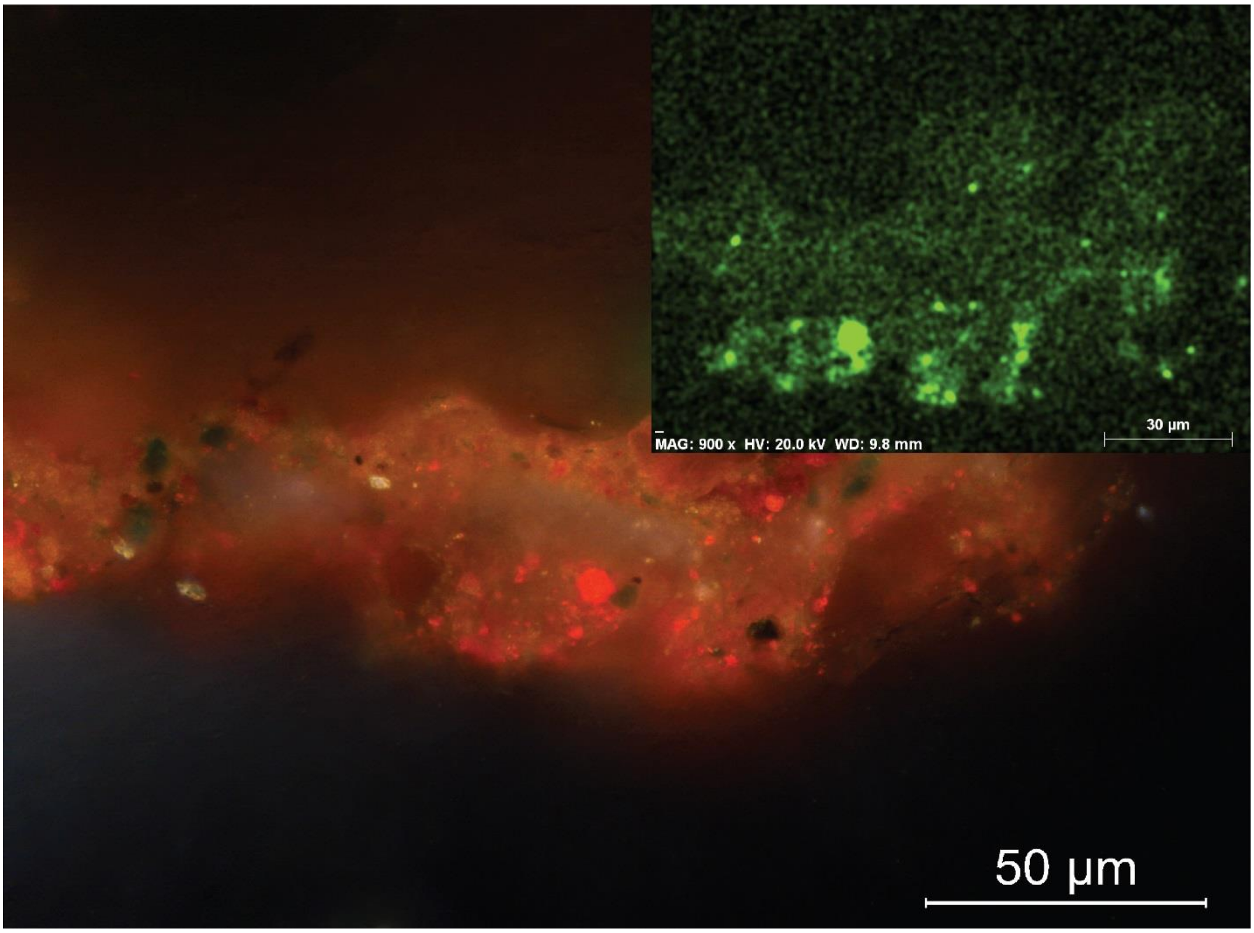


Figure 4.3.24. OM picture of the sample JR12. Right upper corner: EDS map showing distribution of Cd in sample JR12

It seems that Julio Resende intentionally or not mixed Cadmium and Chromium red with the Red Ochre. It seems that both Cr and Cd particles do not form a uniform paint layer; instead, they tend to be dispersed in the Red ochre matrix.

Brown pigments

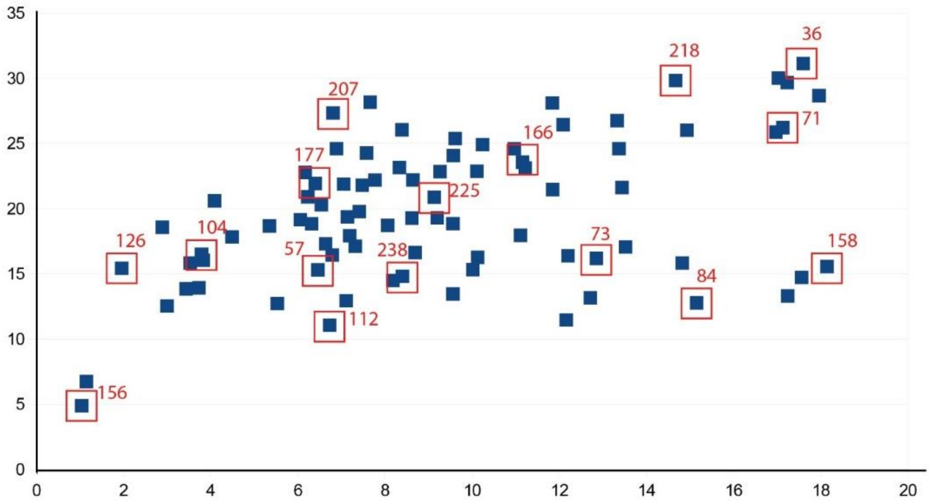


*Figure 4.3.25. Chromatic palette (CIE a*b*) of the brown paint layers. Paint layers subjected to EDXRF analysis are marked with their Jrescol number.*

Portable OM observations of the brown areas revealed inhomogeneous nature of the brown paint layers, with the presence of green, blue and orange particles. Eighty-three colorimetry measurements were taken (see Figure 4.3.25.) and then nineteen paint layers were examined with the portable EDXRF. EDXR analysis showed presence of iron (see Figure 4.3.26.) in all the points studied.

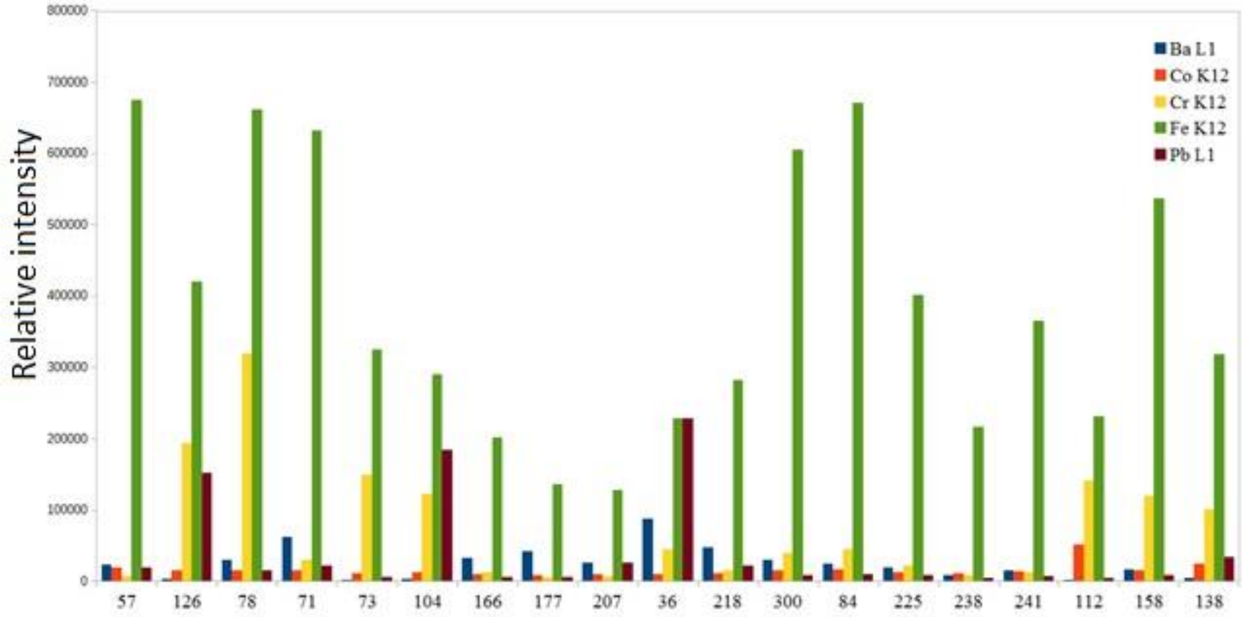


Figure 4.3.26. EDXRF table of the brown paint layers. Relative quantity of Ba, Fe, Cd, Cr, and Pb

According to minor elements present the studied brown paint layers can be divided into five groups:

a) *jrescol57, 166, 177, 238, 241* represent paint layers with predominance of Fe
b) *jrescol36, 104, and 126* are the paint layers with huge relative amounts of Pb. Portable OM revealed the presence of big orange particles, green particles and other minerals in reddish-brown surrounding.
c) *jrescol73, 78* featured presence of Cr and respectively large amounts of green particles in portable OM.
d) *jrescol112, 158*, is similar to the second, but in addition to Cr the paint layers contain Co. Blue particles are visible in portable OM.
e) *jrescol78, 138 156* is the least homogeneous one; the paint layers contain all the elements named above (Cr, Pb and Co) in a high proportion.

Figure 4.3.27 shows examples of the brown paint layers described above.

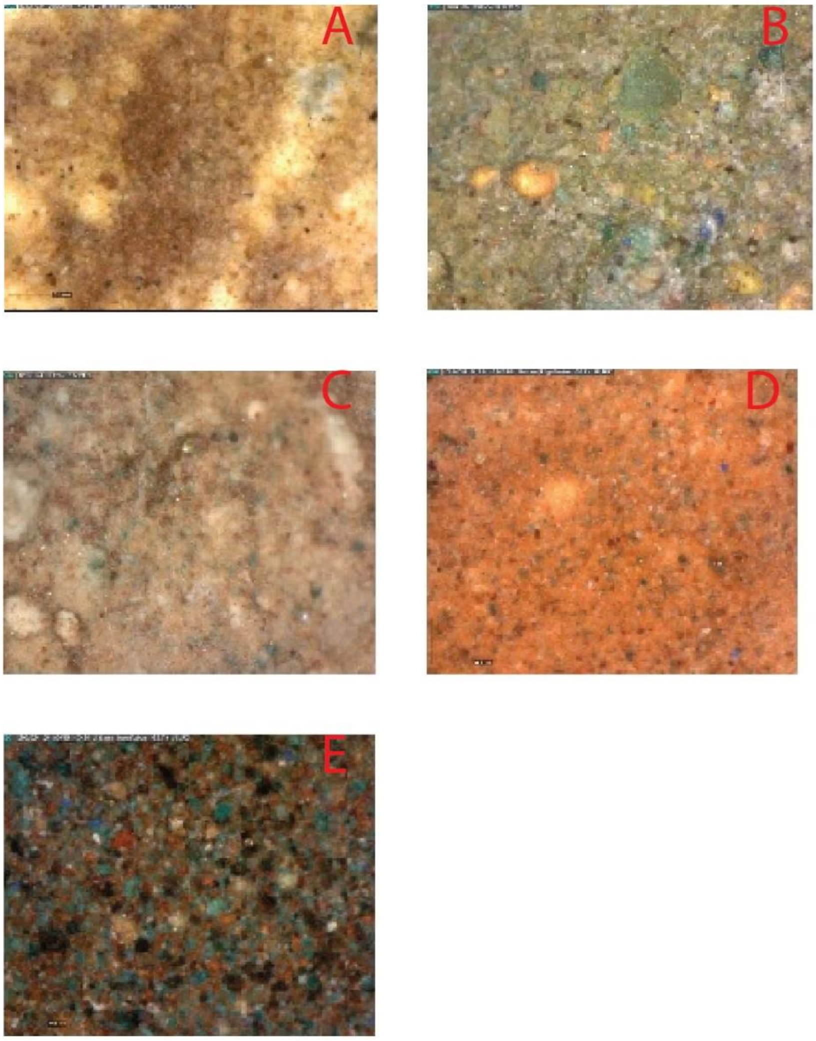


Figure 4.3.27. Optical microscopy photos of the brown paint layers at 430x magnification. A – jrescol166, B – jrescol126, C – Jrescol73, D – jrescol158, E – jrescol156

The fact that brown pigment was mixed with another pigments made identification with the use of diffuse reflectance curves impossible. It was expected to find Mn, one of the principal constituents of Umber; however, only traces of Mn were detected.

For further SEM-EDS analysis two cross-sections of the brown paint layers were extracted (JR12 and JR13).

Sample JR12 has already been addressed in the previous section *Red pigments*. There the presence of Cd particles was noted. However, these particles almost absent in the top layers of the cross-section which constitute its outer brown layer (see Figure 4.3.28.)

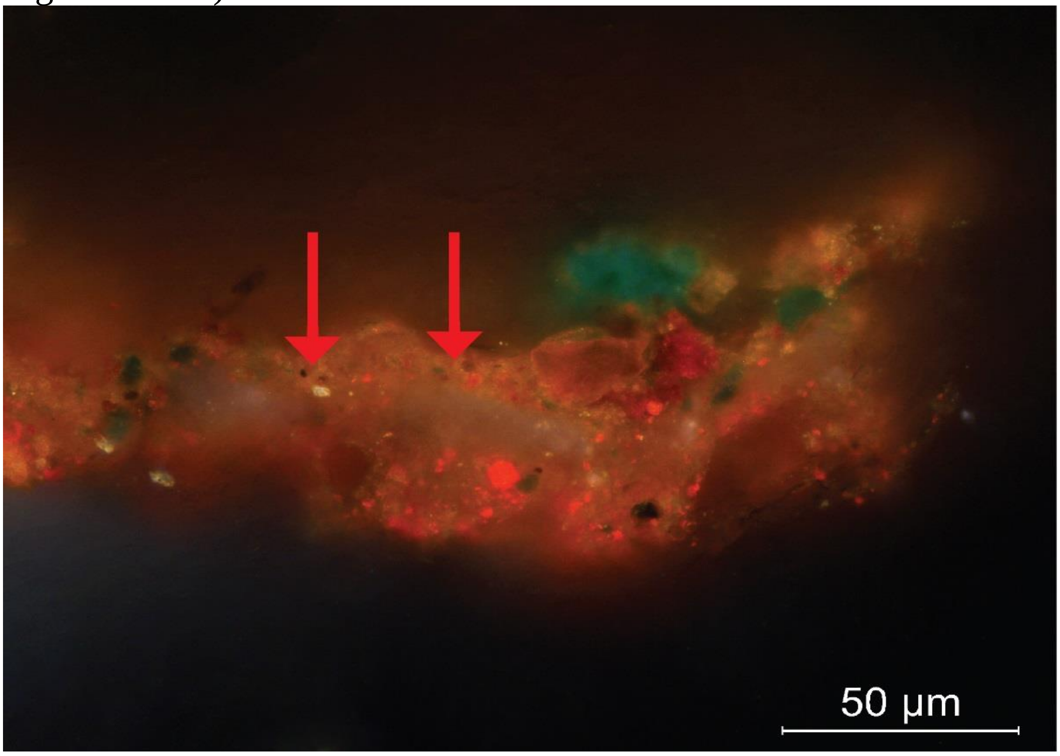


Figure 4.3.28. Detail of sample JR12 cross-section. Red arrows indicate brown paint layer

EDS characterization of this area showed predominance of an iron oxides. The chromium rich area corresponds with the green particle (see figure 4.3.29).

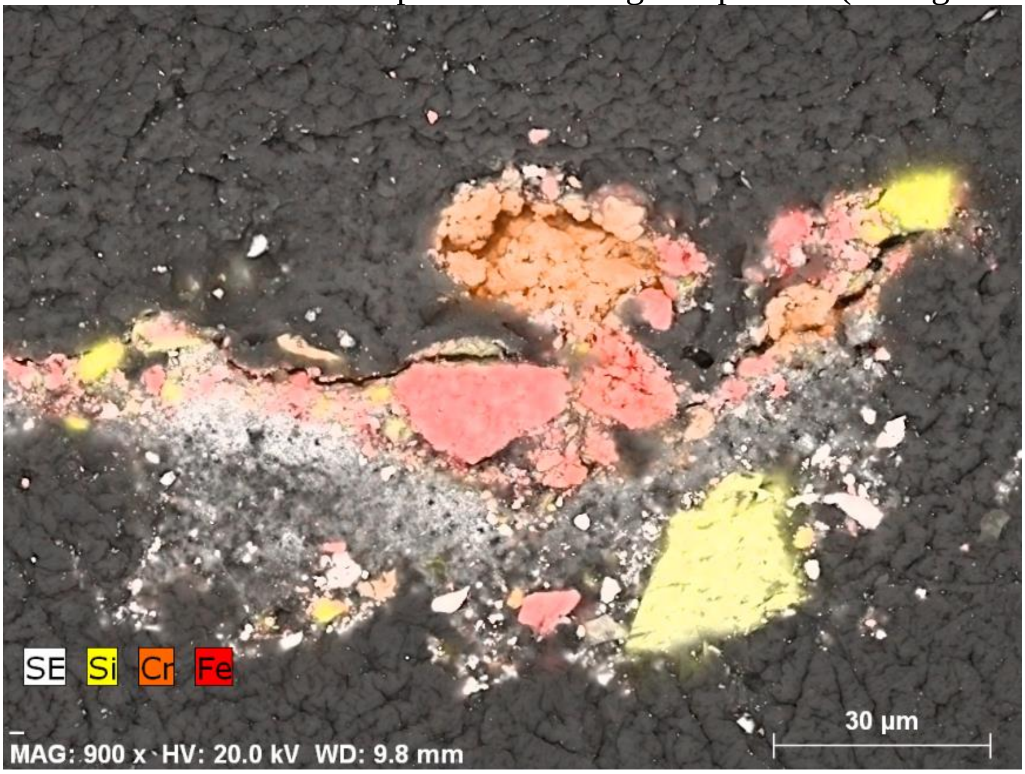


Figure 4.3.29 EDS map of sample JR12 showing presence of Si, Fe and Cr

Element	C Atom. [at.%]
O	70,53
Na	1,10
Mg	1,46
Al	0,81
Si	1,35
P	0,54
S	0,64
Cl	0,20
Ca	7,01
Cr	0,39
Fe	15,71
Cd	0,15
Ba	0,12

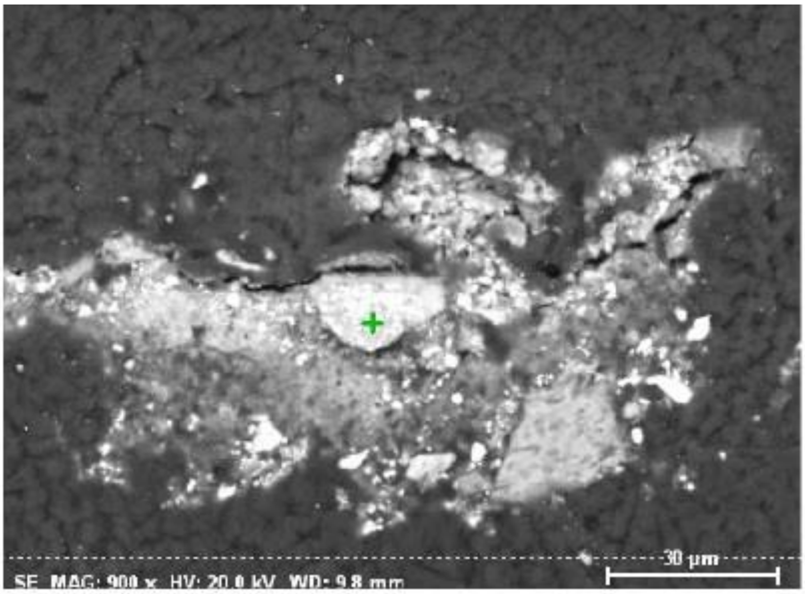


Figure 4.3.30. Sample JR12. Table of elemental distribution and SEM image of an iron oxide particle. The point analyzed is marked with green

Presence of iron oxides allows to hypothesize that earth pigments could been used to form brown paint layers. According to M. Gil, the use of ochers of different composition allows to achieve various hues of the brown color [8].

In sample JR13 only presence of Ba and S and P was detected, suggesting the use of Barium sulphate and apatite. The last could have be intentionally used for darkening the hue. (see Figure 4.3.31. and Figure 4.3.32.).

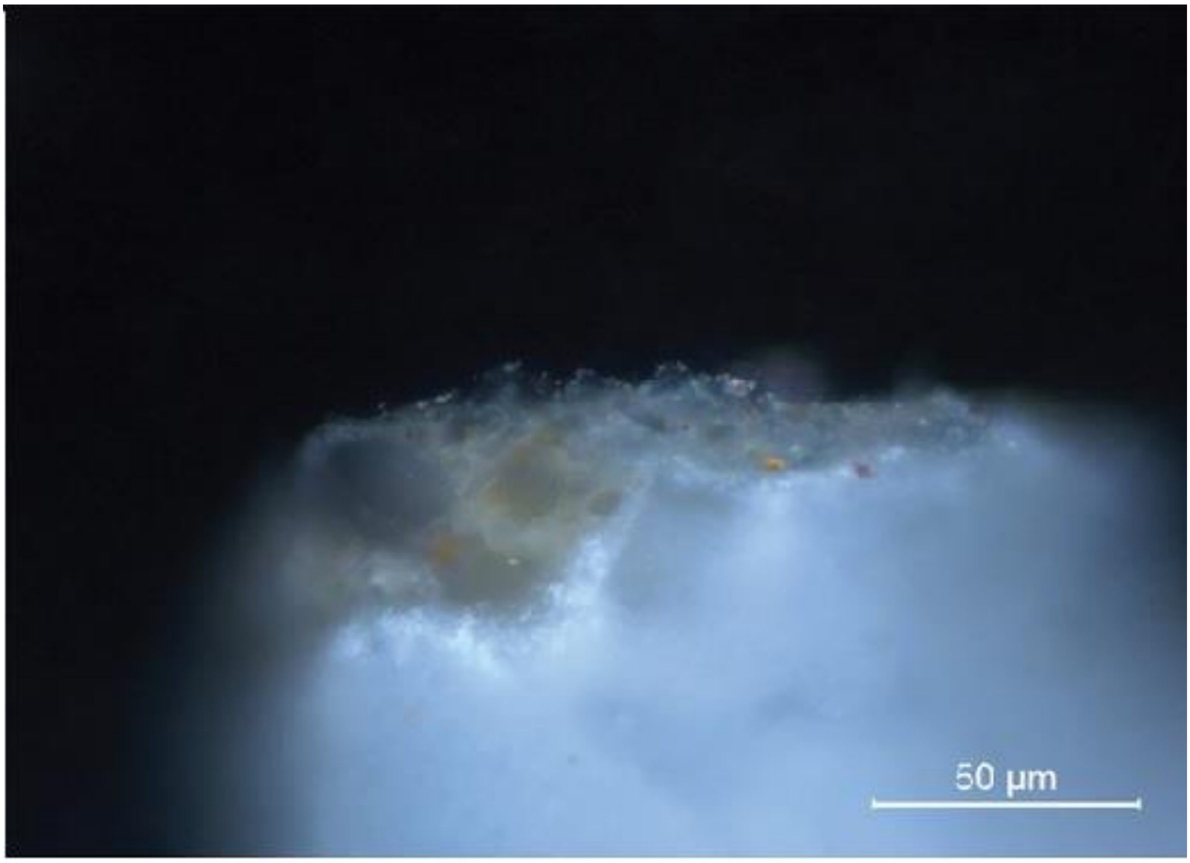


Figure 4.3.31. Part of a sample JR13. On the top: OM picture of the sample at 500x; below – EDS map of the sample showing presence of P, Ca, Ba. P reach area indicating presence of apatite

Element	C Atom. [at.%]
Na	1,22
Mg	2,55
Al	1,35
Si	1,22
P	20,63
S	2,57
Cl	1,87
K	0,62
Ca	66,12
Ba	1,85

Figure 4.3.32. Sample JR13. Table of elemental distribution and SEM image of an apatite particle. The area analyzed is marked with yellow.

White pigments

Although in *Pentecostes* the presence of white color itself is limited, it seems that white pigments were used to create light effects and change the color of the other pigments.

The infrared spectroscopy was used to identify white pigments. In samples JR4, 15, 17 and 25a FT-IR has shown the presence of Barite (see Figure 4.3.33.).

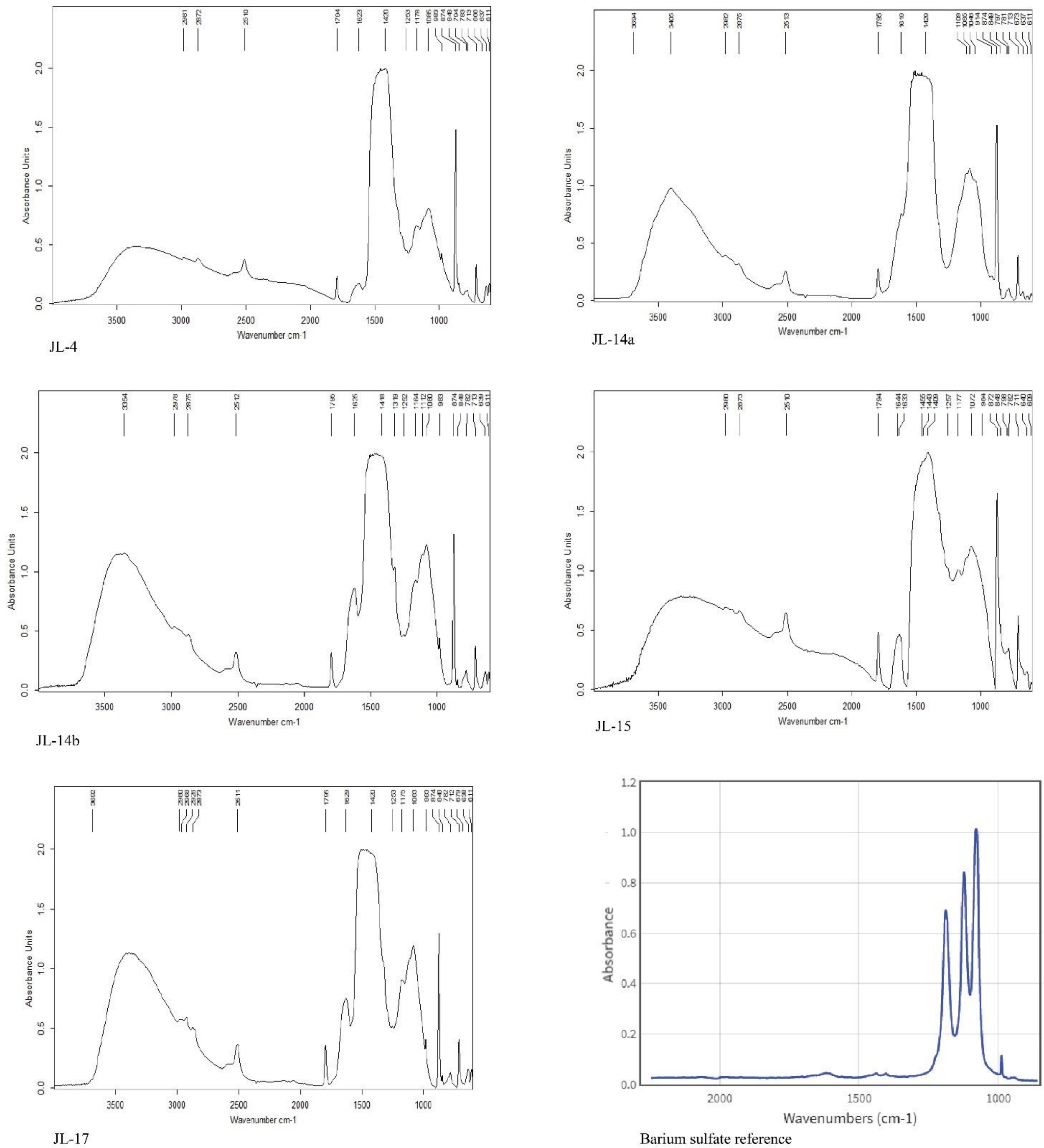


Figure 4.3.33. FT-IR results of the samples containing Barite (characteristic peak at around 1070, 1118, 1172 cm^{-1}). Reference from NIST Chemistry WebBook, SRD 69 (https://webbook.nist.gov/cgi/cbook.cgi?ID=B6004658&Mask=80#IR-Spec) Identification of the other materials in these samples shown in Appendix V

Barite is a mineral consisting of barium sulfate ($BaSO_4$) which is also known as a pigment Barium white. Natural mineral had been used in art since late XVIII century, originally as a substitute to Lead White. In XIX an artificial synthetic Barium Sulfate was introduced, which remains in use for today [6]. However, Barium sulfate has weak covering capacity, in thus in many occasions it is used not as a pigment itself but as a filler in a mixture with the other pigment [6]. By SEM-EDS analysis, the presence of associated Ba and S was also confirmed in the cross-section paint layers of microsamples JR10, 12, 13, 14, 18, 19, 25 and 26 (an example is given in Figure 4.3.34.) The big angular particles of Barium Sulfate are clearly visible in SEM imaging (see Figure 4.3.35.).

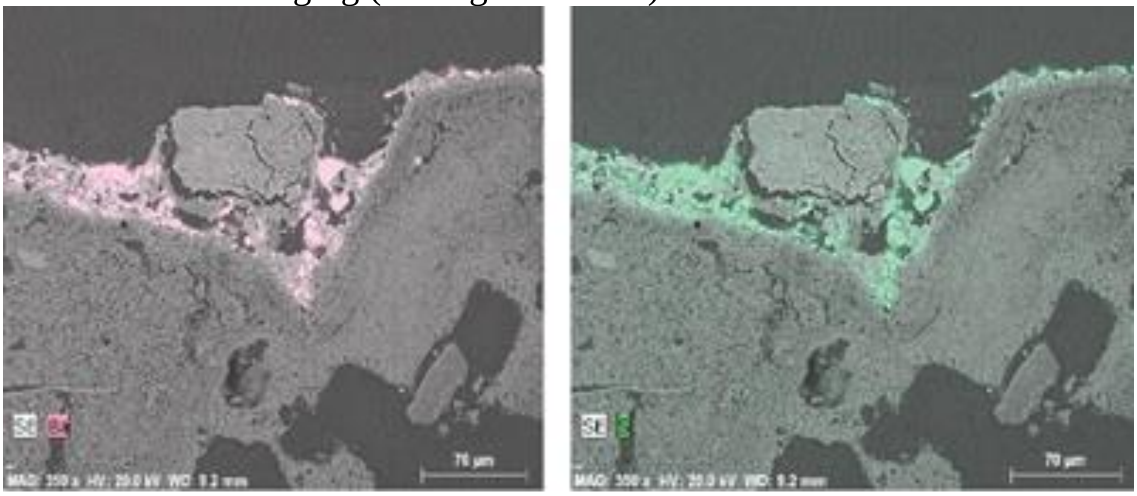


Figure 4.3.34. EDS elemental distribution in sample JR 10. Showing Ba (left) associated with Sulphur (right)

Element	C Atom. [at.%]
Al	1,95
Si	1,93
S	39,40
Cl	1,11
Ca	10,60
Fe	2,52
Sr	1,28
Ba	41,21

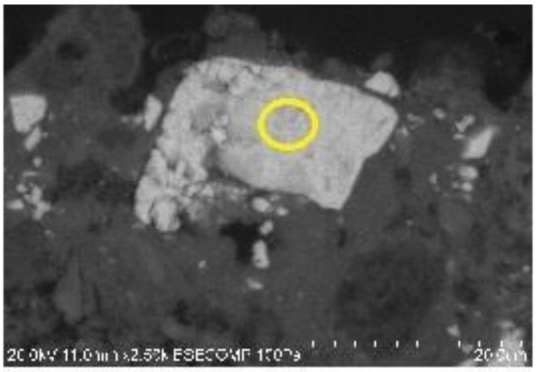


Figure 4.3.35. Table of elemental distribution and SEM image of a Barite particle taken in sample JR14

Presumably, another white pigment present in the painting is Titanium White (TiO_2). Titanium white is a titanium dioxide base pigment, first introduced in 1921. The pigment quickly achieved a great popularity among the artist for its brightness excellent hiding power and chemical stability [6]. Small quantities of Ti were found by EDXRF in a number of samples, however an overlapping with the Ba peak could occur. Traces of Titanium can also be found in ochers. Information that is more straightforward was obtained from the JR19 sample. EDS picture shows both sulfur rich area, which may be associated with the presence of Barium Sulfate and the Ti-rich matrix (see Figure 4.3.36.).

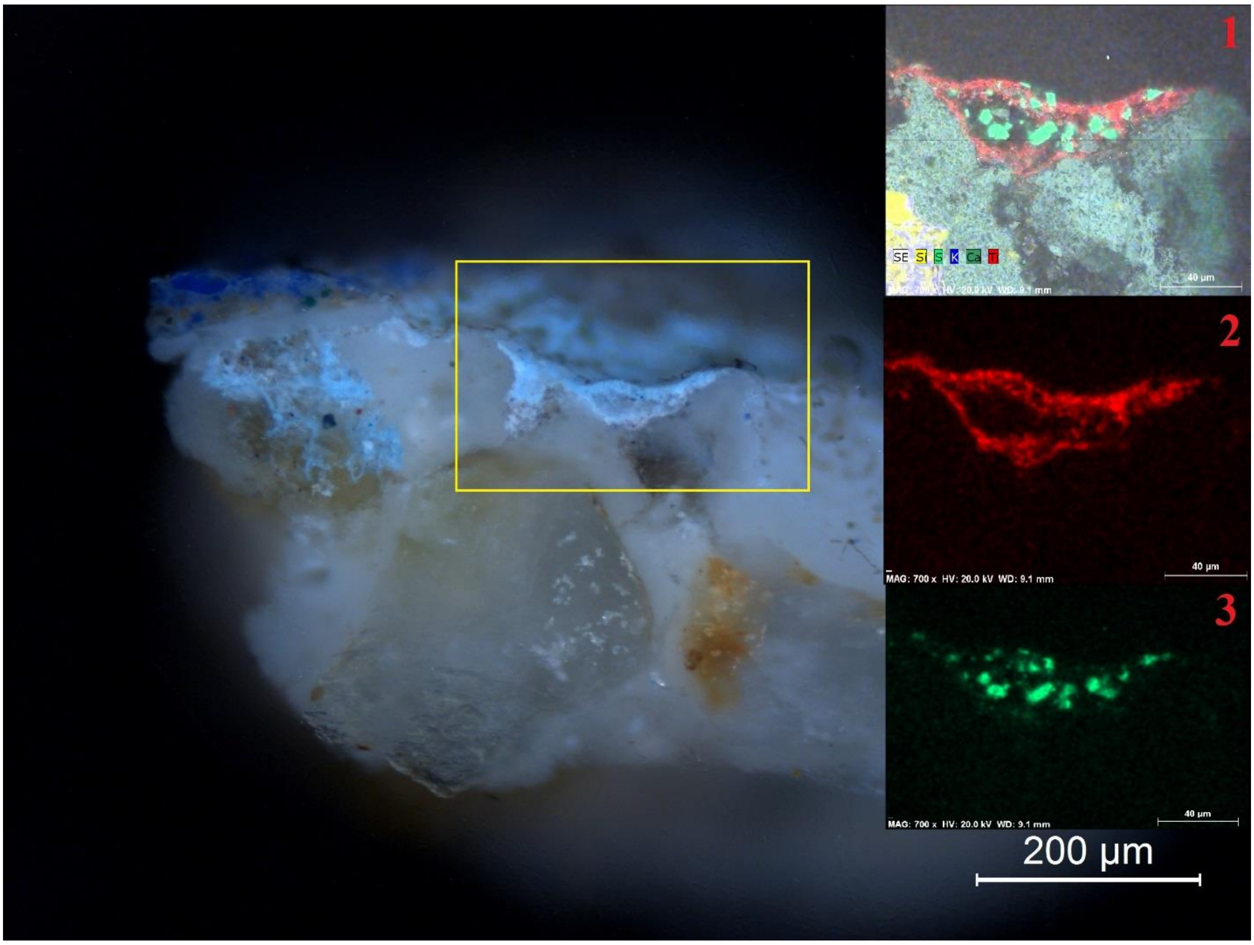


Figure 4.3.36. OM picture of sample JR19 at 200x magnification. The area subjected to SEM-EDS analysis is marked with yellow. On the right: 1. EDS map of the are showing distribution of Si, S, K, Ca, Ti; 2. EDS map of Ti distribution; 3. EDS map of S distribution.

Results of EDS point analysis of presumably Titanium matrix are shown in Figure 4.3.37.

Element	C Atom. [at.%]
Na	4,18
Mg	4,67
Al	4,41
Si	7,13
S	3,04
Cl	1,18
K	1,72
Ca	23,11
Ti	48,77
Fe	1,8

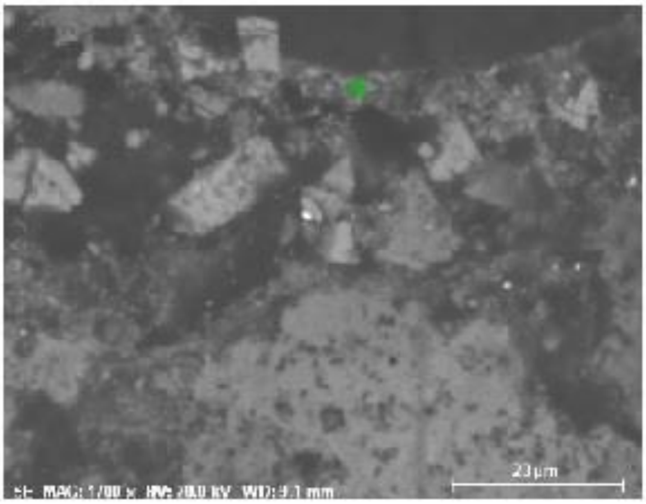


Figure 4.3.37. Sample JR19. Results of EDS performed in point analysis mode. The point analyzed is marked with the green cross

4.3.2. Binder characterization.

OM and SEM-EDS investigations of the chromatic layers have showed that the pigment particles are imbedded in an inorganic crystalline calcium carbonate ($CaCO_3$) matrix.

In several cases (as described in *Blue pigments* section) pigment particles seems to have been mixed with the lime before application. Lack of distinct carbonation crust in the interface of the paint layers and mortar indicates that the pigments were applied on a wet surface. That supports the hypothesis that the painting was executed in *fresco* technique.
UV-light examination could help to detect presence of an organic binder. However, both in-situ and laboratory Optical Microscopy observations performed in UV-light shown lack of fluorescence that could be associated with the binder. FT-IR analysis of samples JR2a(green), JR4(green), JR6(blue), JR7(blue), JR14a(red), JR14b(green-blue), JR15(green), JR17(green), JR21(blue) and JR25a also proved the absence of organic compounds.
It appears from the above that Julio Resende did not used secco technique with an organic binder. However, it remains possible that he could have used lime as a binder, since some of the blue paint layers presenting lack of cohesion. The lack of cohesion has been revealed during preliminary conservation study conducted by Marta Fernández Monforte. The lime could have been used in cases when the plaster became too dry to paint in *buon fresco*. While the presence of *giornata* supports the hypothesis that fresco technique was used, it is possible that the artist also used lime painting on the limited scale.

4.4. List of references

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[2] Gil, M., Serrão, V., Carvalho, M. L., Longelin, S., Dias, L., Cardoso, A., Caldeira, A. T., Rosado, T., Mirão, J.& Candeias, A. E. (2014). Material and diagnostic characterization of 17th century mural paintings by spectra-colorimetry and SEM-EDS: An insight look at José de Escovar Workshop at the CONVENT of Na Sra da Saudação (Southern Portugal). *Color Research & Application*, *39*(3), p.290-293.
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CHAPTER 5. Final Remarks and Future Perspectives.

To summarize the results obtained during the present study it is worth coming back to the main research questions formulated in the Chapter 1:

1. *Was the mural executed in fresco or secco technique*? The division of the mural into seven *giornata*, lack of organic binder and carbonization below the paint layers indicate the use of *buon fresco* as the principle painting technique. However, it should be noted that lack of adhesion observable in several spots allow to presume the use of *lime secco* on a limited scale.
2. *Which pigments were used?* Julio Resende used Red Ochre, Cobalt blue, Chromium green, Cadmium red, and Barium white. There are some evidences of the use of Titanium white, Chromium red, and Green earth however, to make final conclusion, more research is needed. *Did the artist favor traditional pigments or novel art materials, and what can his pigment choice tell us about his willingness to experiment?* Julio Resende used both traditional pigments, like the earth pigments as well as more recent art materials, like Cadmium red. The comparison between painting techniques of Julio Resende and the other modern muralists (described in Chapter 2) allows to conclude the Portuguese artist adopted quite traditional technique. While Siqueiros and Jack Hastings experimented with pigments, binders and even the support of the mural, Julio Resende preferred to work in a more traditional *fresco* technique, like M.S. Florence, and Diego Rivera. It is difficult to compare the works of the modern muralists in terms of materials they used, because of the lack of information. However, it should be noted that Bacci, Sironi, Papaloukas and Julio Resende all used Barium sulfate (presumably as a charger), Chromium red/yellow. Sironi used Chromium green as well as Resende, Papaloukas used pure Hematite, while Resende used the Red Ochre.
3. *What is the role of the pigment selection and the painting technique in the painting current state of conservation?* The case of Papaloukas's paintings of almost the same age as the Resende's work shows, that the poor choice of pigments may lead to quick deterioration of the painting. For example, Papaloukas used Prussian blue, which alterates quickly. The choice of chemically compatible pigments made by Julio Resende, helped to preserve the relatively good conditions of the mural. The use of fresco technique also made the mural more stable.

In conclusion, it is hoped that the data collected within the framework of the present thesis will find its use in future conservation works on Julio Resende's heritage. To understand Julio Resende's artistic manner and intentions on a broader scale, it is recommended to subject his other murals to analytical study as well.

List of illustrations

CHAPTER 2

CHAPTER 3

CHAPTER 4

Appendices

Appendix I. Julio Resende's timeline.

(*Credits to 'Lugar do Desenho. Julio Resende foundation'.* http://www.lugardodesenho.org/002.aspx?dqa=0:0:0:29:8:8:-1:0:0&id=1&ct=8)

1917. Julio Resende born in Oporto, 23rd October
1930/1936. Made his first illustrations and cartoons for newspapers and children's publications. Studied drawing and painting at the Silva Porto Academy.
1937. Attended the Oporto School of Fine Arts. Studied under supervision of Dórdio Gomes.
1943. Founder member of the "Group of Independents". First individual exhibition in the Silva Porto Salon.
1945. Completed Fine Arts course with the painting "Os Fantoches". Visited the Prado Museum. Met Vasquez Diaz while in Madrid. Awarded National Academy and "Armando de Bastos" Prizes.
1946. Awarded a scholarship to study abroad by the "Institute for High Culture". First exhibition in Lisbon.
1947/1948. Studied fresco and engraving techniques at the School of Fine Arts in Paris. Studied under Duco de La Haix. Received lessons from Othon Friesz at the Grande Chaumière Academy. Made copies of the masters in the Louvre. Visited museums in Belgium, The Netherlands, Great Britain and Italy.
1949/1950. Worked as a teacher of ceramics in a school in Viana do Alentejo. Contacts with the writer Virgílio Ferreira and with the artists Júlio and Charrua. Met Almada Negreiros and Eduardo Viana in Lisbon. First trip to Norway as a guest of Oddvard Straume.
1951. In Portugal, moved to Oporto and worked in a secondary school as a teacher. Seafaring folk became the dominant theme in his painting. Special Prize at the S. Paulo Biennial.
1952. Prize-winner at the 7th Contemporary Northern Artists' Exhibition. Second journey to Norway. Painted mural painting Divertimento Infantile at the Gomes Teixeira School in Oporto. Researched into children's drawing.
1953. Created the "International Art Missions".
1954. Taught in secondary school in Póvoa de Varzim.
1955. Promoted the 2nd "International Art Mission" in Póvoa de Varzim. O Pentecostes mural painting was executed.
1956. Collective work with an architect João Andersen for the "Mar Novo" project in Sagres, which won the First Prize in international competition. "Artists of Today" Prize, Lisbon. Completed the Pedagogical Science course at the University of Coimbra.
1957. Organized the "4 Portuguese Artists" exhibition in Oslo and Helsinki. 2nd Prize for Painting from the Calouste Gulbenkian Foundation, Lisbon.
1958. Completed a panel for the "Brussels Exhibition". "Columbano" Prize from Almada City Council. Organized the 3rd "International Art Mission" in Évora. Guest

teacher at the Fine Arts School in Oporto. Made various tile panels for the frontier station in Vilar Formoso.
1959. Received Honorable Mention at the 5th S. Paulo Biennial. Made ceramic panels for S. João Hospital, Oporto. Made eight tile panels for the Miranda do Douro Pousada.
1960. "Diogo de Macedo" Prize at the SNBA Modern Art Salon, Lisbon. Ceramic panel for the Pousada in Bragança.
1962. Applied to join the teaching staff of the Higher School of Fine Arts in Oporto (ESBAP). Executed mural at the Oporto Courts of Justice.
1964. Made five ceramic panels for architectural works.
1965. Designed the sets and costumes for "Auto da Índia" by Gil Vicente, directed by Carlos Avilez for Teatro Experimental do Porto (TEP).
1966. Made a fresco for the Courthouse in Anadia.
1967. Designed the sets and costumes for "Phèdre" by Racine, directed by Carlos Avilez for Teatro Experimental de Cascais.
1968. Illustrated "Aparição" by Virgílio Ferreira. Designed the sets and costumes for the ballet "Judas", choreographed by Agueda Sena and the Company of the Calouste Gulbenkian Foundation, Lisbon.
1969. "Graphic Arts" Prize at the S. Paulo Arts Biennial, with illustrations for the novel "Aparição". Designed the sets and costumes for "Auto da Alma" by Gil Vicente, at TEP, Oporto. Made six sandstone panels for the Courts of Justice in Lisbon.
1970. Supervised the visual aesthetic for the Portugal Stand at the World Exhibition in Osaka. Designed the sets and costumes for "Antígona" at the Teatro Experimental de Cascais.
1971. First journey to Brazil, where he met Jorge Amado and Mário Cravo Filho.
1972. Nominated a Member of the Royal Belgian Academy of Sciences, Letters and Fine Arts, in Brussels, where he presented a paper.
1973. Illustrated the work of Fernando Namora in "Retalhos da Vida de um Médico". Second trip to Brazil. Made a Member of the Order of Santiago da Espada.
1974. Began management work at ESBAP. Designed the set for the film "Cântico Final" by Manuel Guimarães, adapted from the novel by Virgílio Ferreira.
1975/1976. Joined the management of ESBAP full-time.
1977. Journeyed to Northwest Brazil. Met the artists Sérgio Lemos and Francisco Brennand.
1978. Designed the sets and costumes for the ballet "Canto de Amor e Morte", with choreography by Patrick Hurde, inspired by the music of Lopes Graça, for the National Ballet Company. Visited Spanish Fine Arts Faculties.
1981. Made the stained glass windows for Our Lady of Boavista in Oporto. Journey to Pernambuco and Baía. Gave a speech at the Joaquim Nabuco Foundation in Recife.
1982. Received the regalia of Comendador of the "Mérito Civil de Espanha", awarded by the King of Spain.
1984. Created the mural panel "Ribeira Negra".

1985. Awarded the AICA Prize.
1986. Made the grand sandstone mural “Ribeira Negra” in Oporto.
1987. Gave his last class at ESBAP.
1989. Retrospective exhibition at the Calouste Gulbenkian Foundation in Lisbon.
1992. Travelled to S. Vicente and Stº Antão (Cape Verde).
1993. “Lugar do Desenho – The Júlio Resende Foundation” is created.
1994/1995. Made ceramic panels for the Sete Rios Metro Stration in Lisbon.
1996. Travelled to Goa
1997. Travelled to Santiago and Fogo (Cape-Verde). Received the Grand Cross of the Order of Infante D. Henrique. Designed the decorative tiles for the Sete Rios Metro Stration in Lisbon.
1999. Travelled to Mozambique Island.
2000. Travelled to Recife, Brazil.
2001. Retrospective exhibition, Galeria Nave dos Paços do Concelho, Matosinhos.
2007. Alfândega do Porto, anthological exhibition of his 90 years attended by the President of the Republic, Professor Aníbal Cavaco Silva. Honored at the XIV edition of the Art Biennial of Cerveira.
2009. Divorced his wife Maria Zita Leão.
2010. Was granted a permanent location to the tile panel Ribeira Negra at Alfândega do Porto.
2011. On September 21st Julio Resende died at home in Valbom, Gondomar, aged 93.

Appendix II Correspondence between Spectro-colorimetry and OM images acquired *in-situ*.

jrescol#	OM 20x	OM 430x
1	A092	A095
2	A097	A111
3	A114	A119
4	A112	A131
5	A133	A139
6	A144	A149; A146
7	A148	A157
8	A158	A167
9	A182	A187
10	A189	A190
5,1	A191	A193
7,1	A194	A199
11	A201	A205
12	A210	A213
12,1	A217	A221
13	A229	A227
14	A225	A226
15	A231	A233
16	A237	A240
17	A247	A250
18	A256	A263
18,1	A267	A270
19	A273	A278;
19,1	A281	A282
19,2	A284	A287
20	A289	A297
21, 21.1	A299	A300
22	A308	A310
23	A311	A312
24	A314	A316
25	A318	A322
26	A323	A326
27	A327	A329
28	A331	A332
29	A333	A336
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31	A343	A345
32	A347	A350
33	A355	A356
34	A359	A361

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36	A366	A368
37	A371	A372
38	A377	A378
39	A379	A380
40	A385	A386
41	A389	A390
42	A392	A393
43	A396	A397
44	A398	A399
45	A401	A402
46	A403	A404
47	A405	A407
48	A408	A409
49	A410	A411
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51	A418	A419
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53	A422	A423
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70	A474	A475
71	A476	A478
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73	A481	A482
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75	A486	A488
76	A489	A490
77	A492	A493

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81	A505	A507
82	A509	A511
83	A513	A515
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94	A675	A673
95	A676	A684
96	A685	A687
97	A691	A690
98	A692	A696
99	A627	A702
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101	A709	A711
102	A710	A712
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104	A714	A717
105	A720	A718
106	A721	A719
107	A722	A724
108	A723	A725
109	A727	A729
110	A728	A730
111	A731	A735
112	A732	A736
113	A733	A737
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140	A847	A838
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156	A876	A886
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158	A878	A888
159	A879	A891
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161	A893	A904
162	A894	A905
163	895	A906

164	A896	A907
165	A897	A908
166	A898	A909
167	A899	A910
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183	A940	A951
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187	A955	A978
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213	B005	B011
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249	A619	A620

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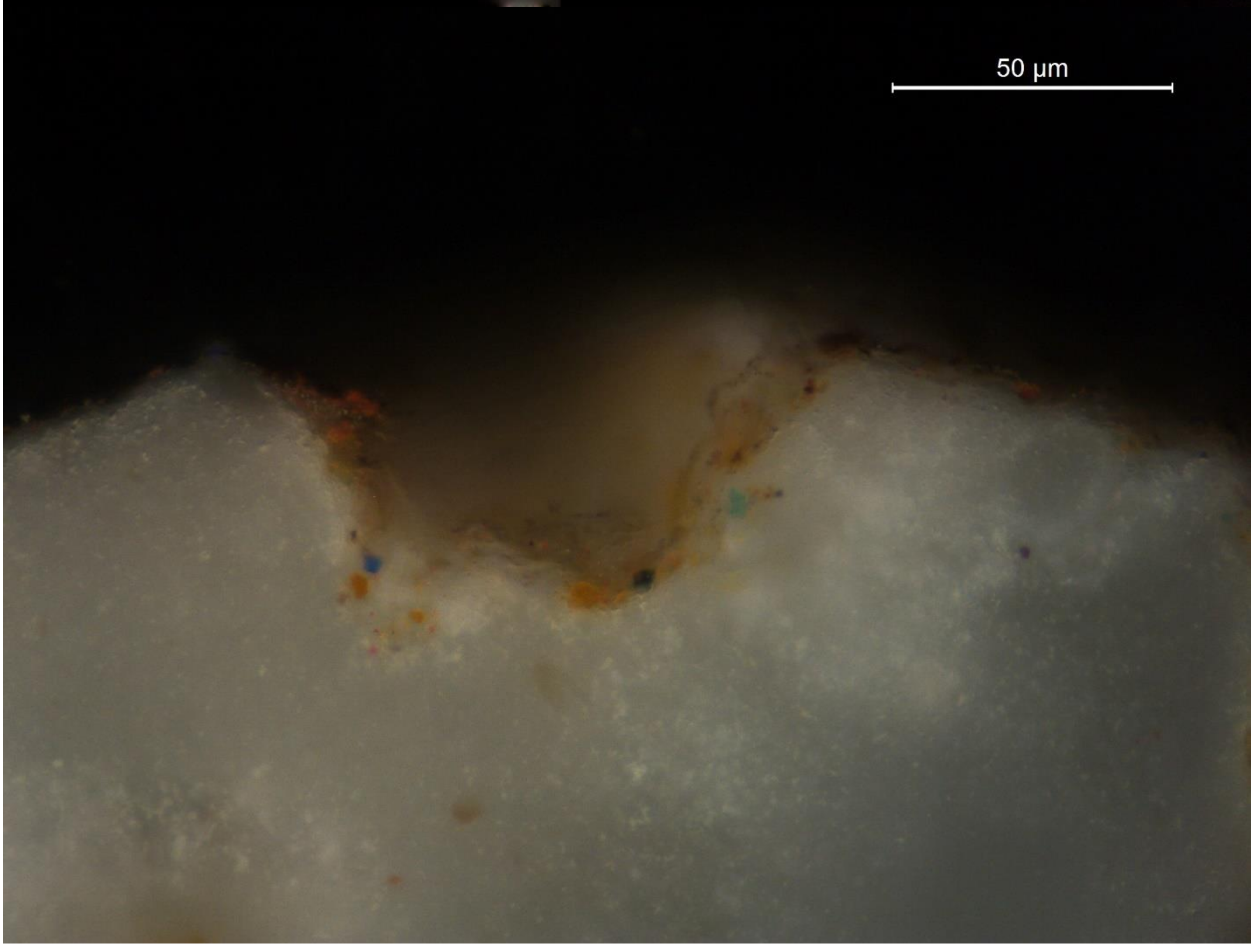
252	A628	A627
253	A629	A630
254	A633	A631
255	B014	B019
256	B015	B020
257	B016	B021
258	B017	B022
259	B018	B023

Appendix III. Optical microscopy images.

JR1 (100x, 200x, 500x):


100 µm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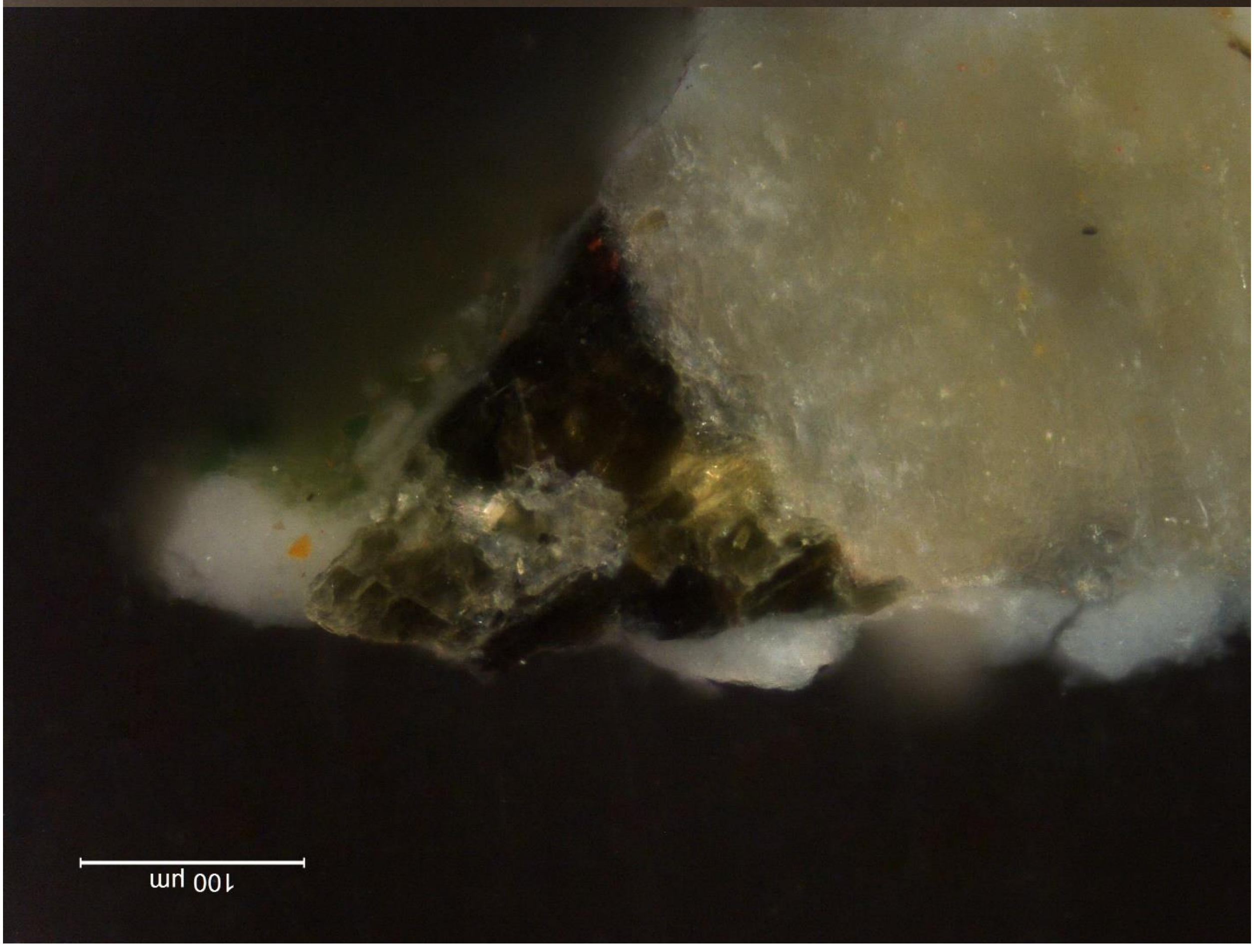

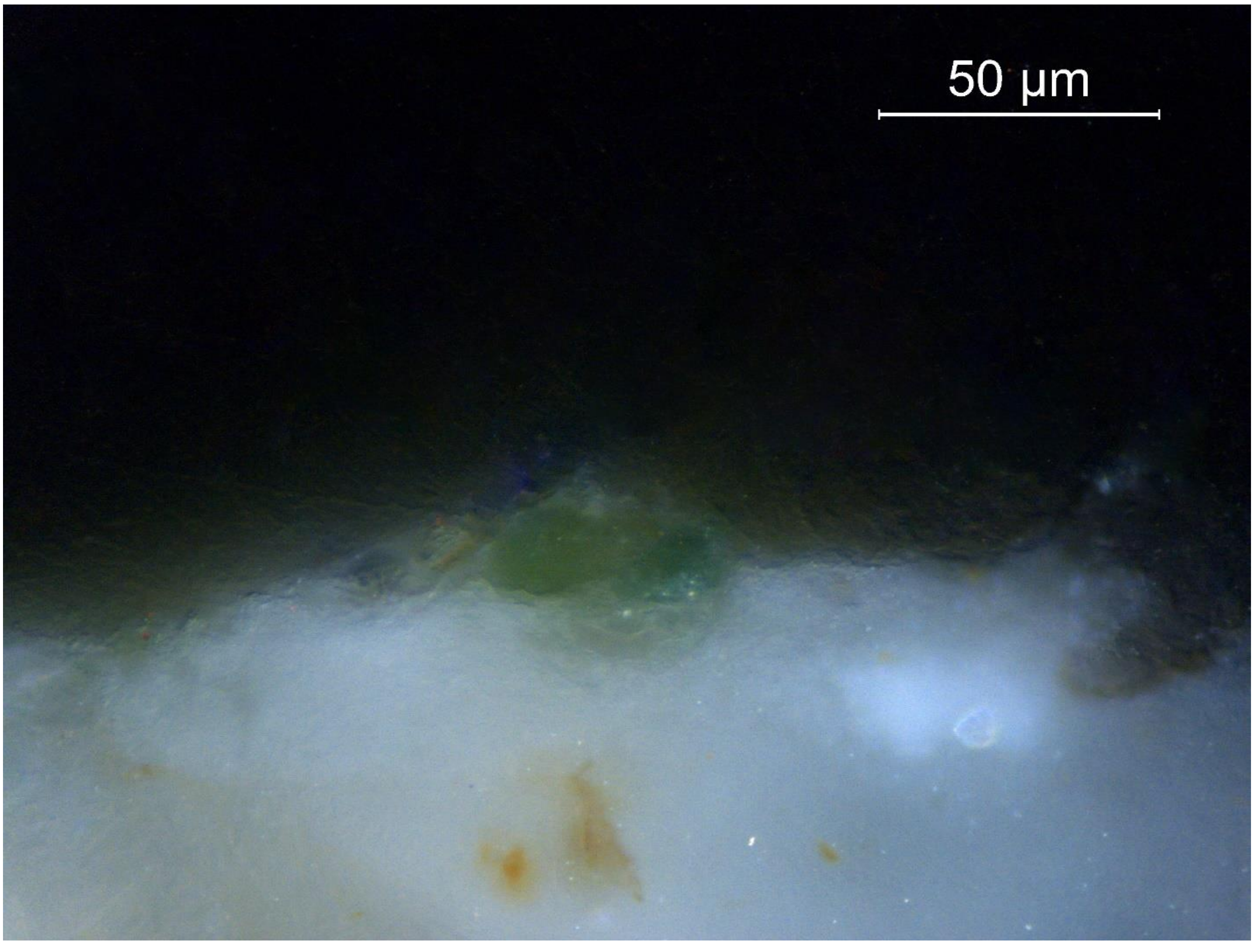

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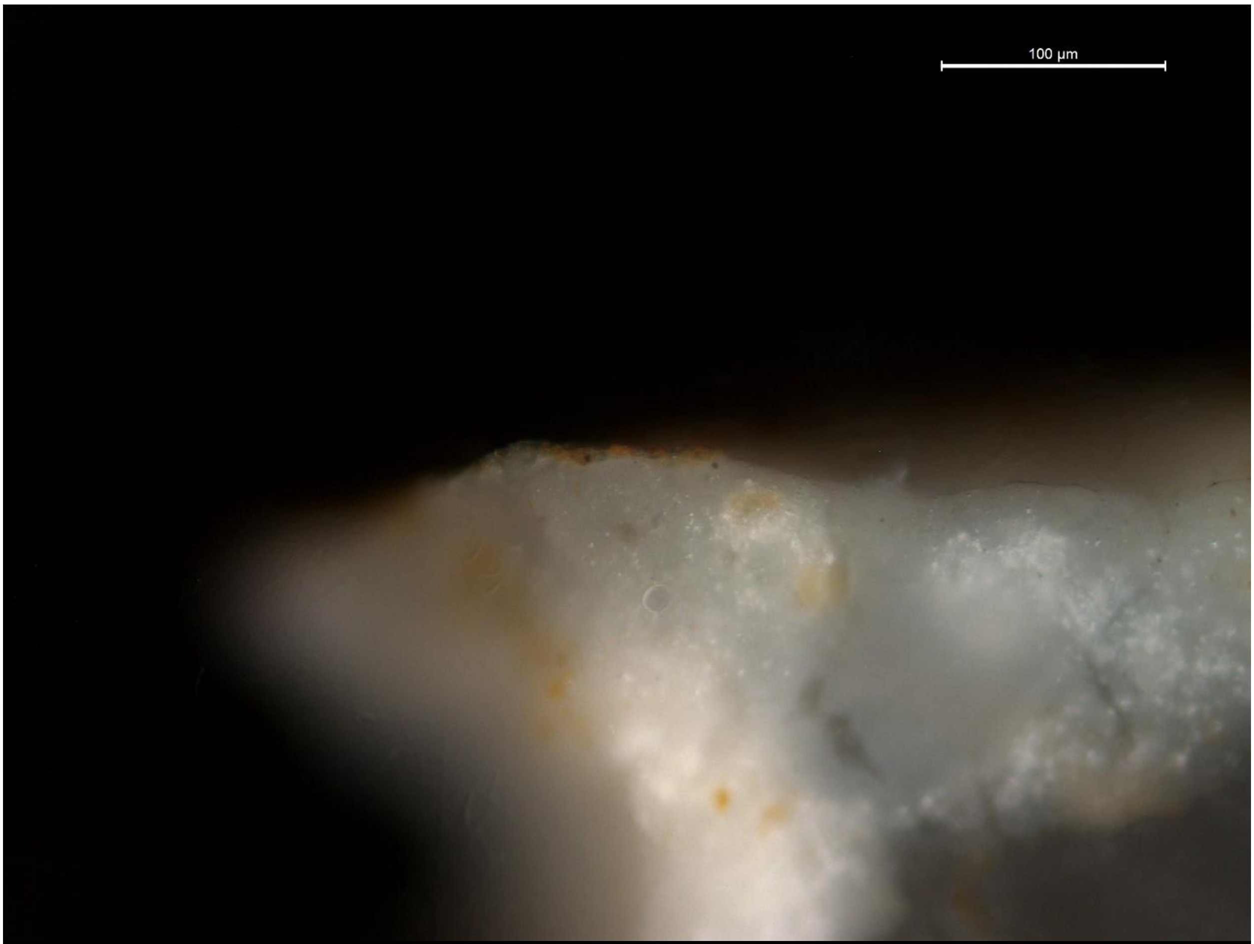
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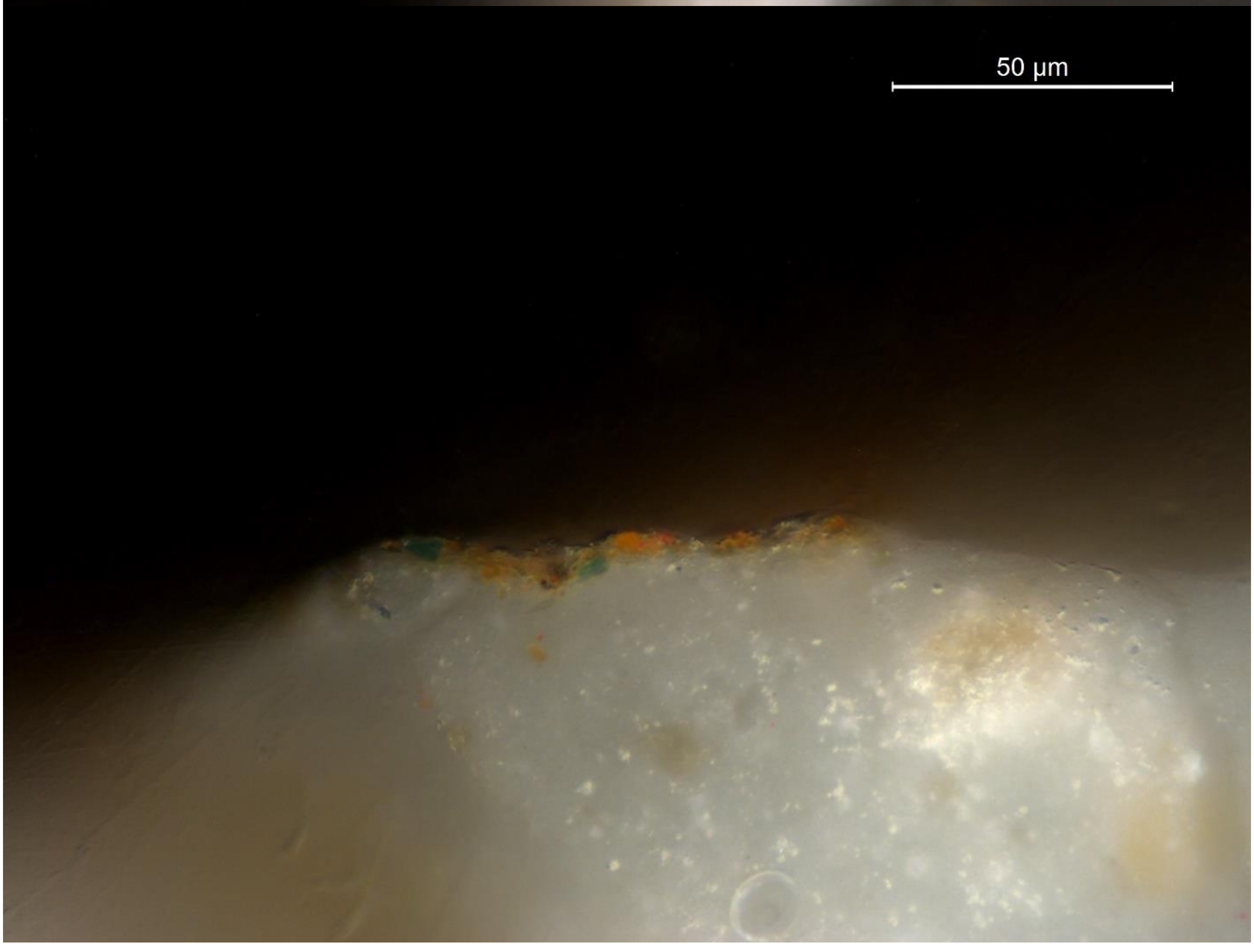
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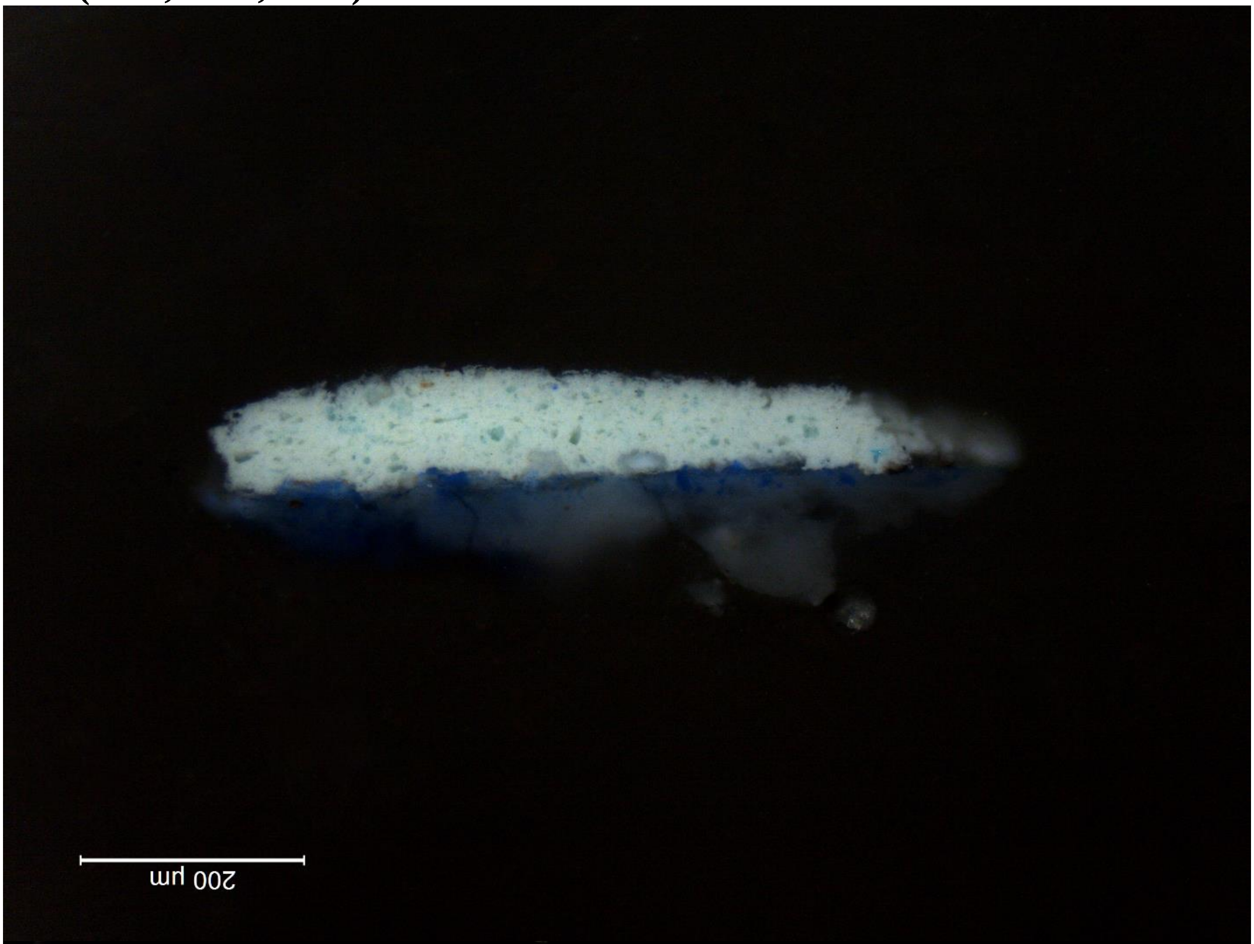

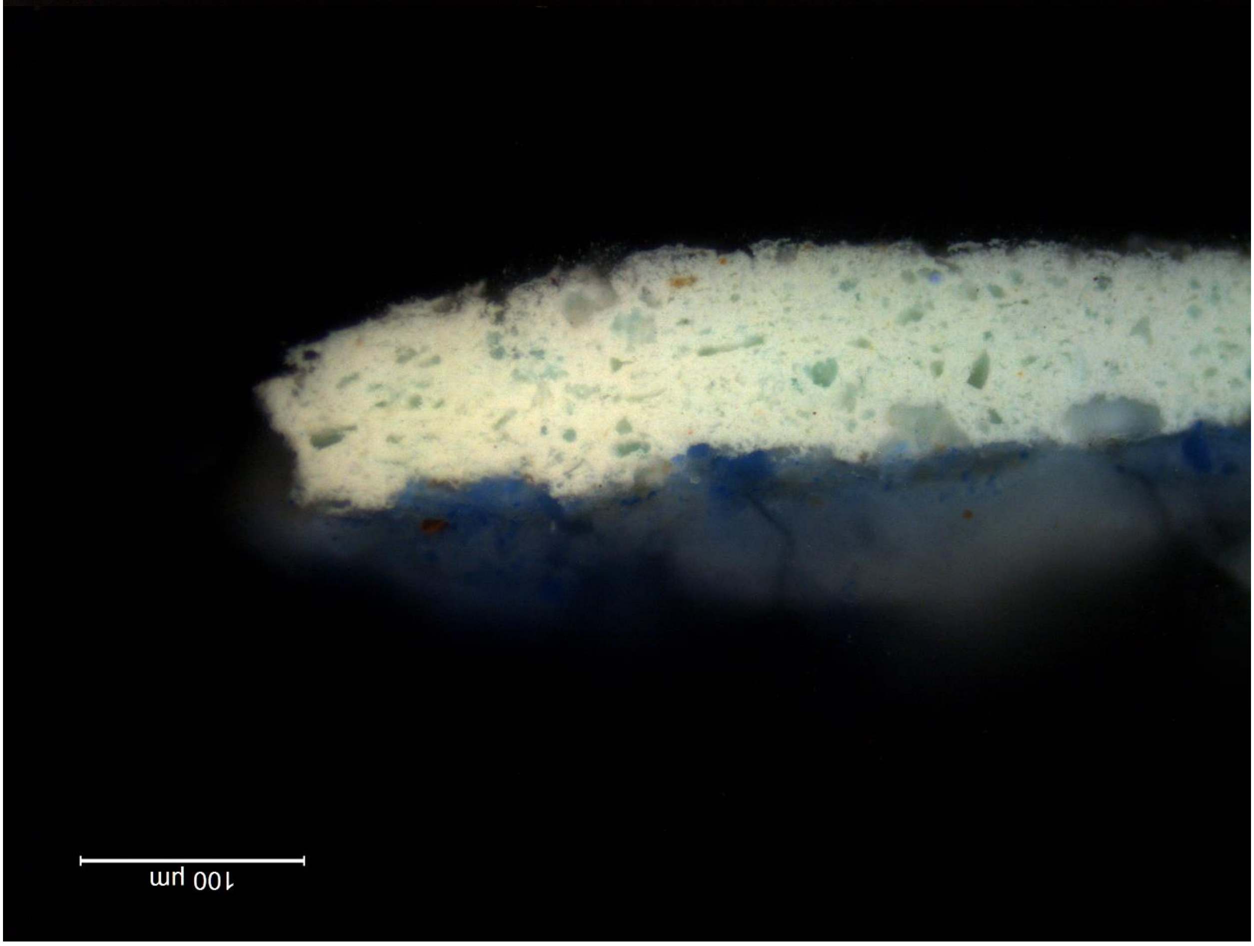

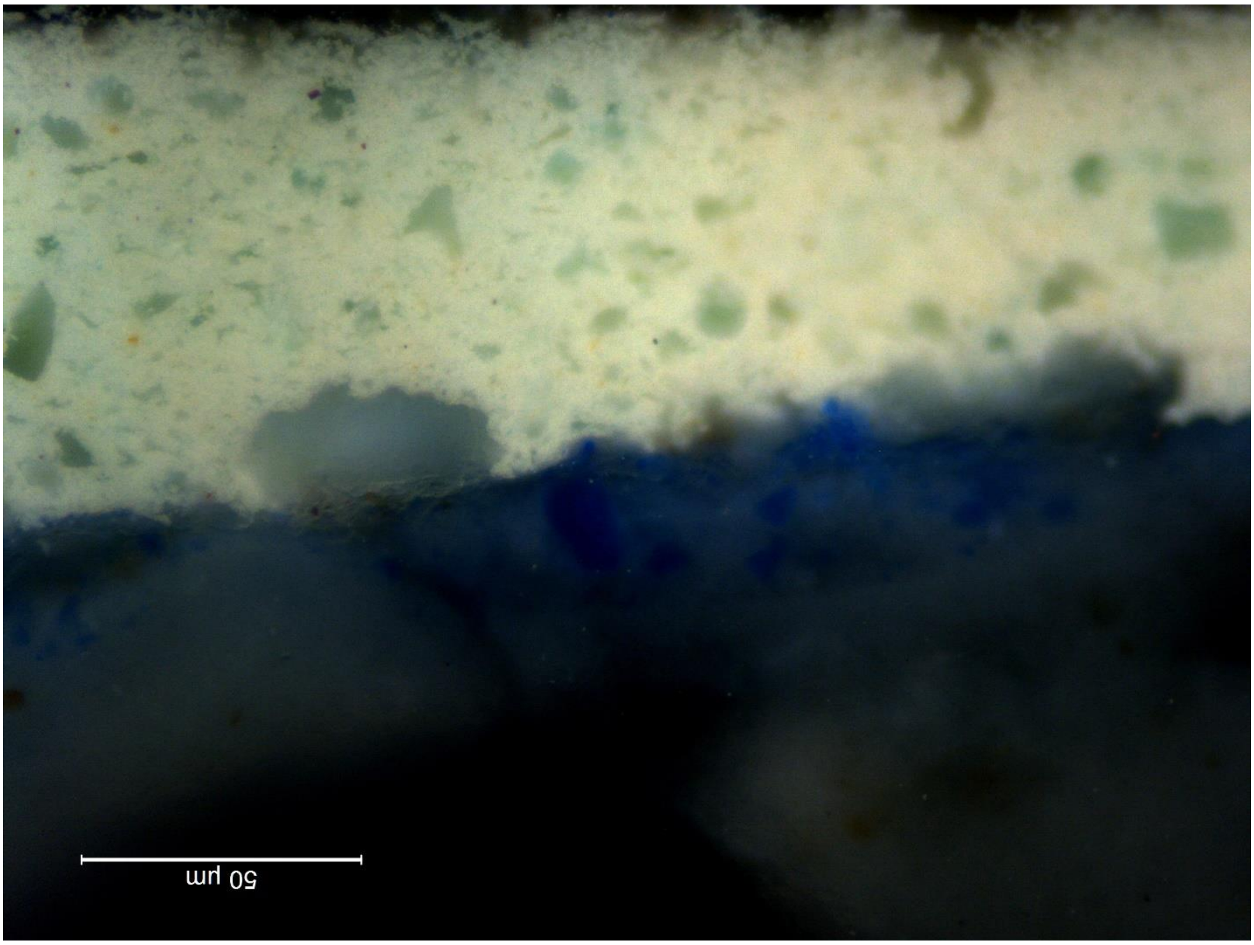

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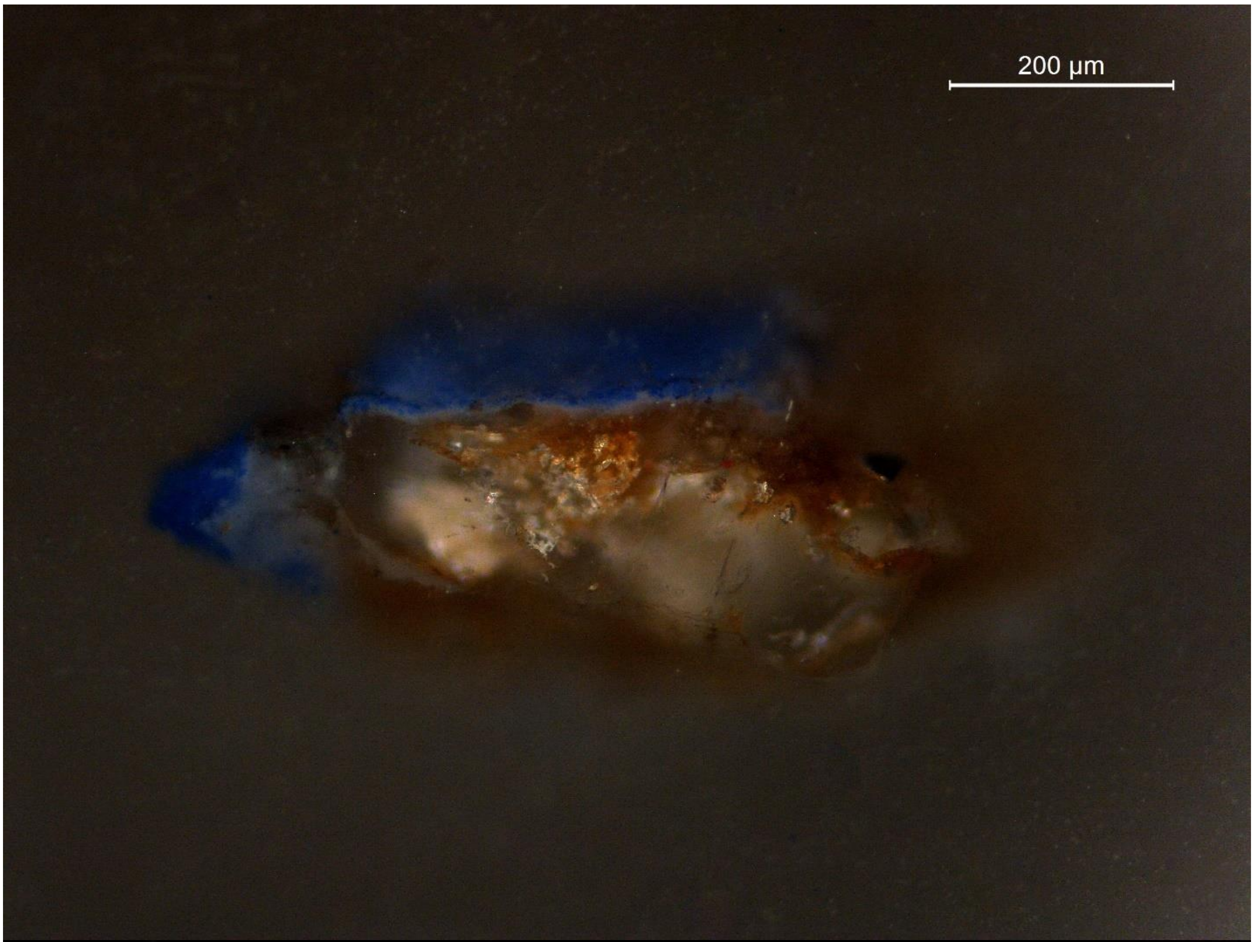
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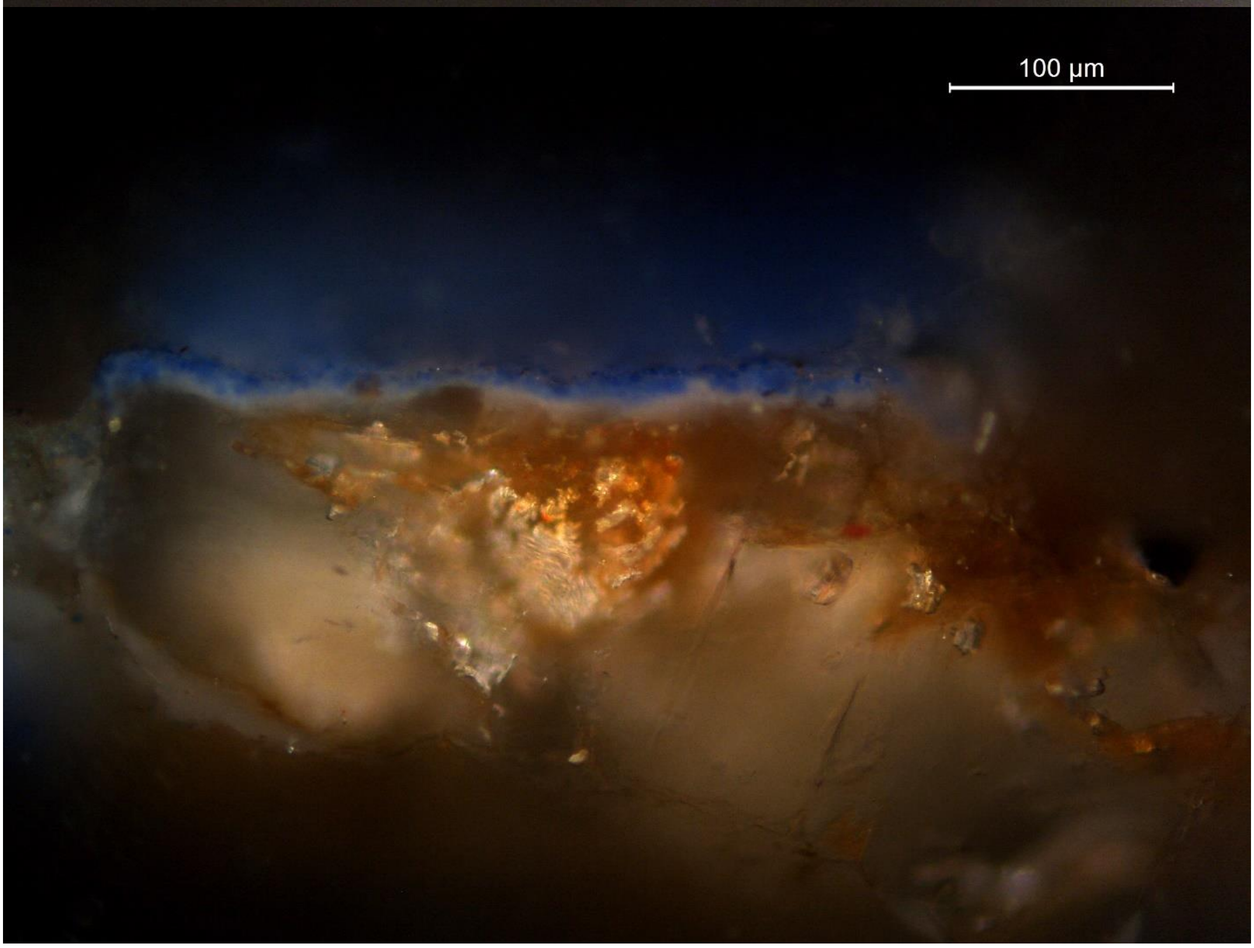
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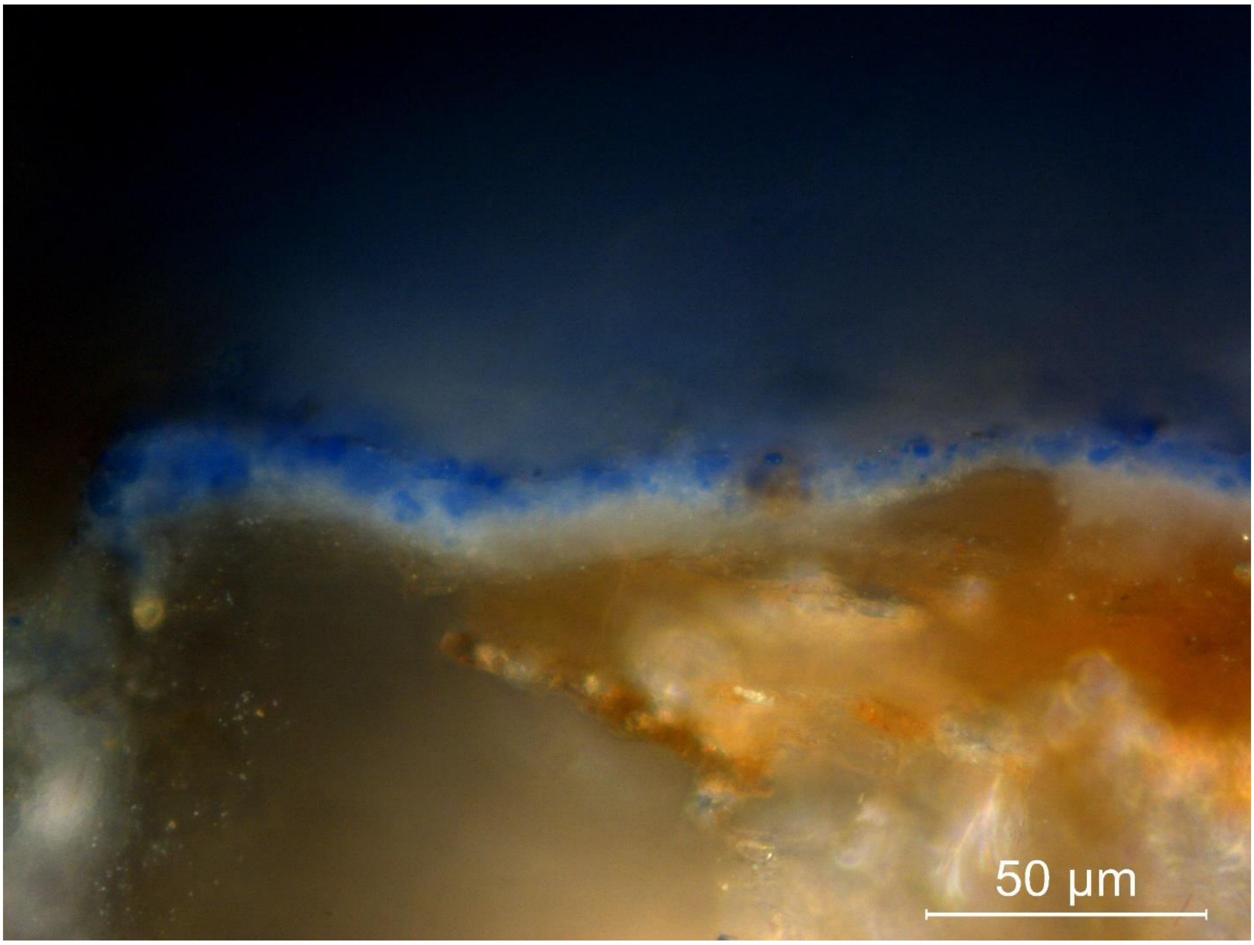

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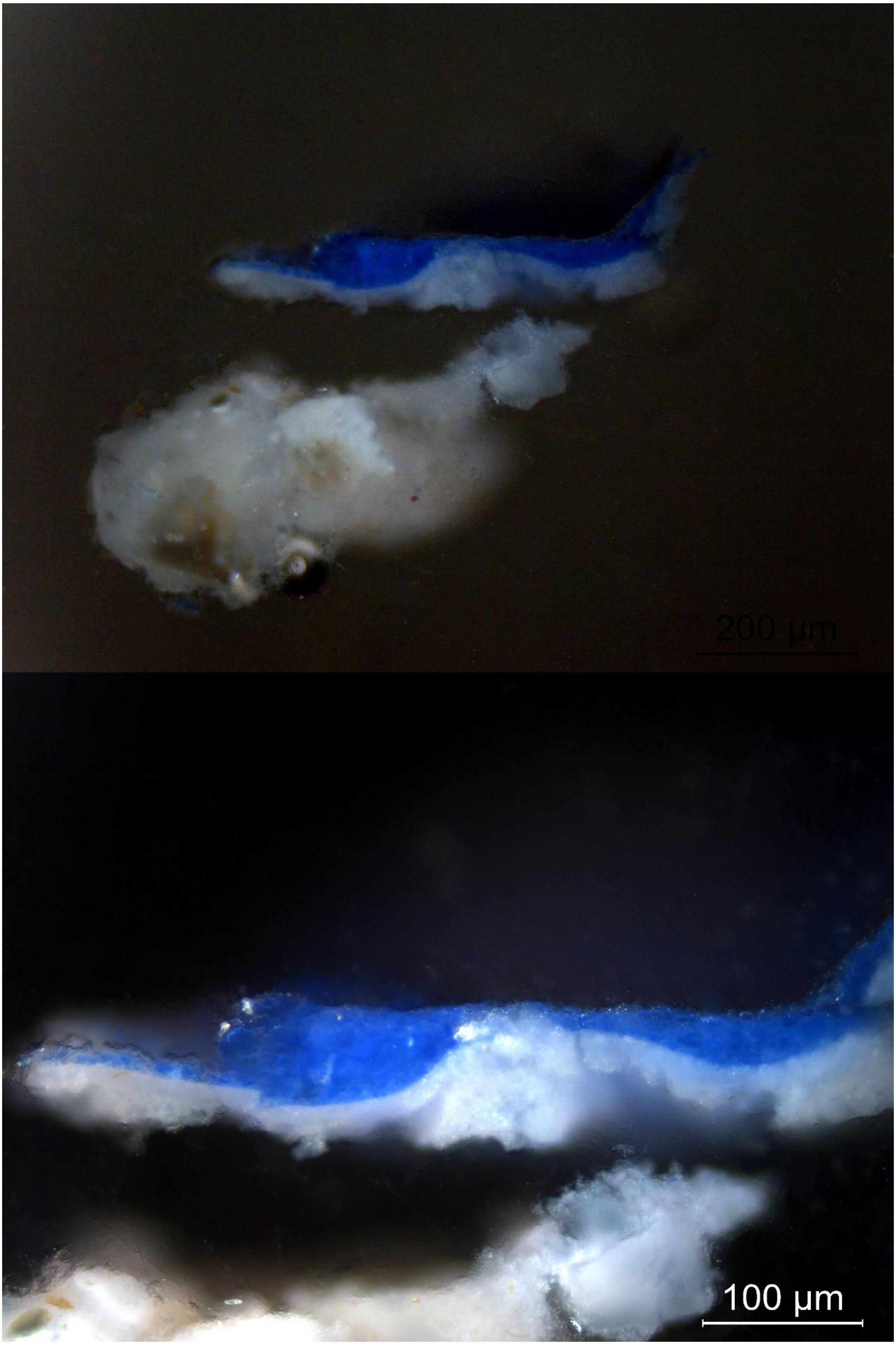
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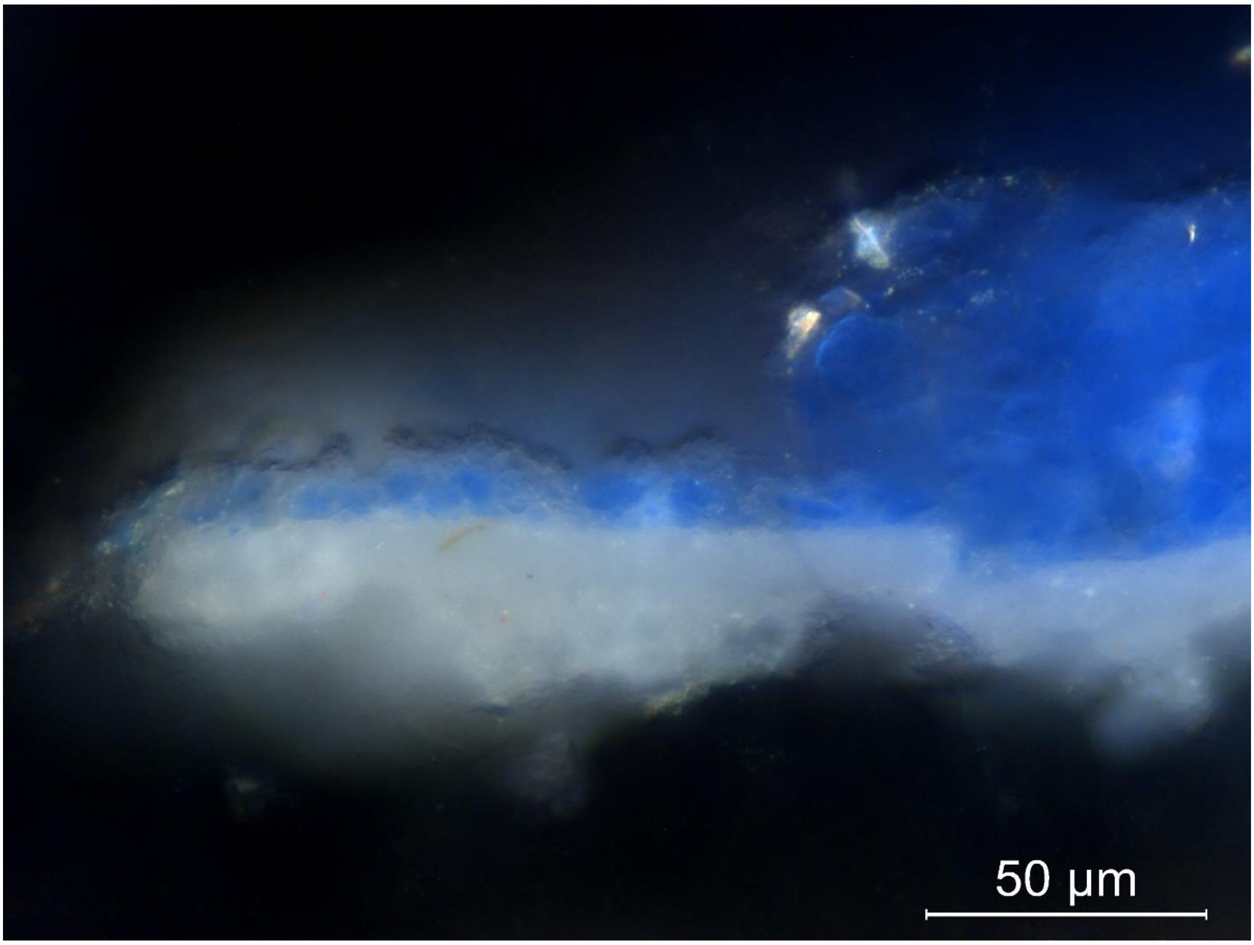
100 µm



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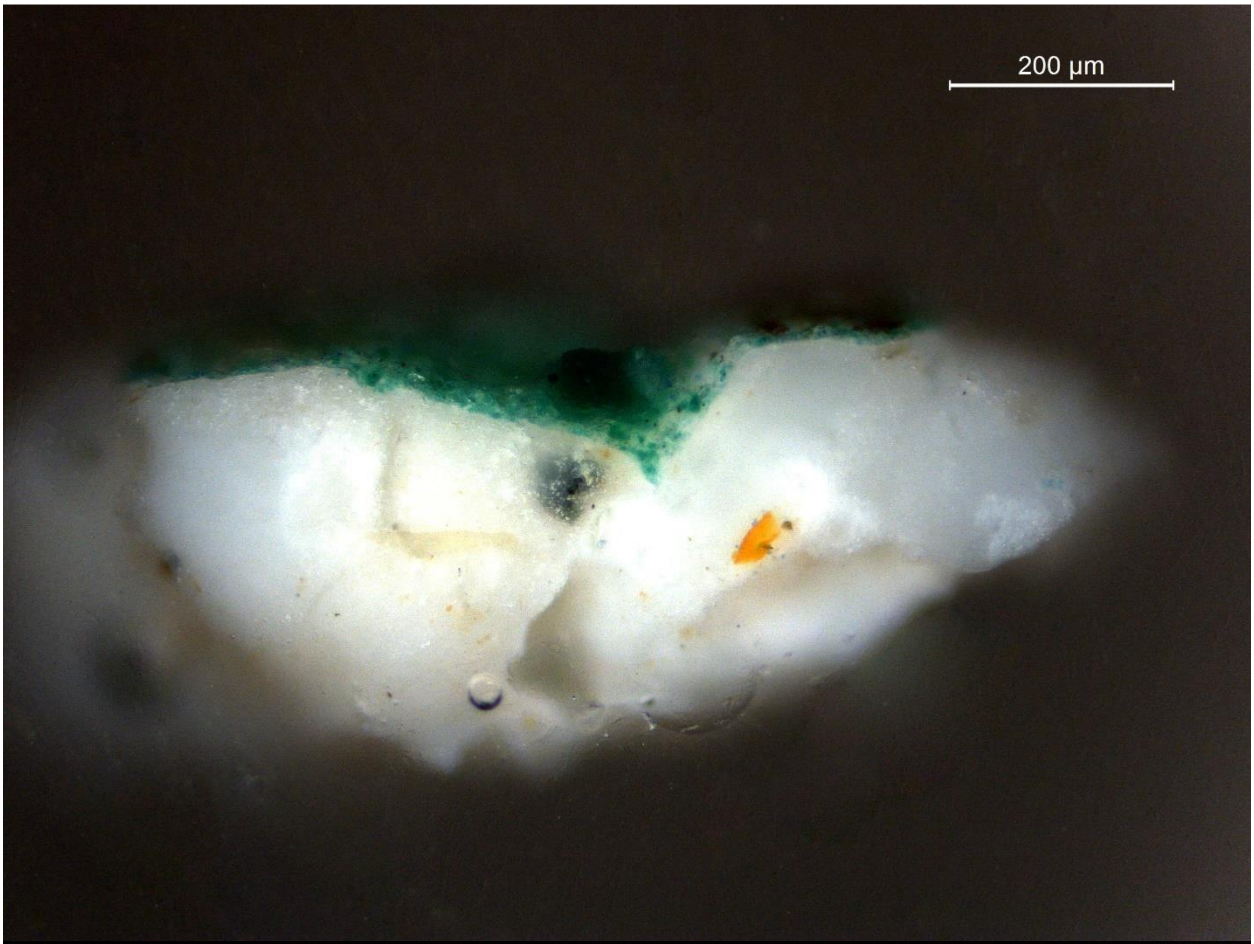
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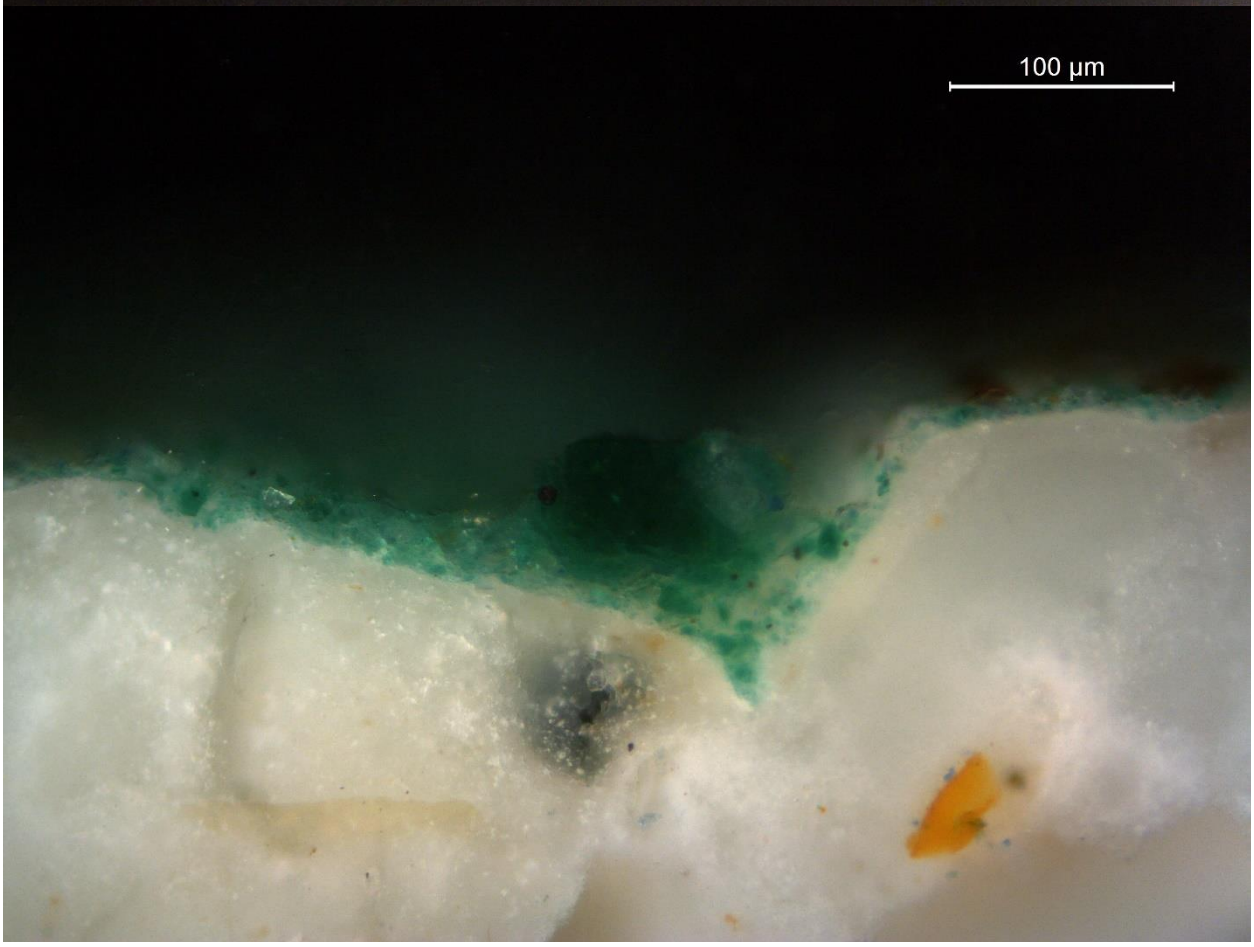
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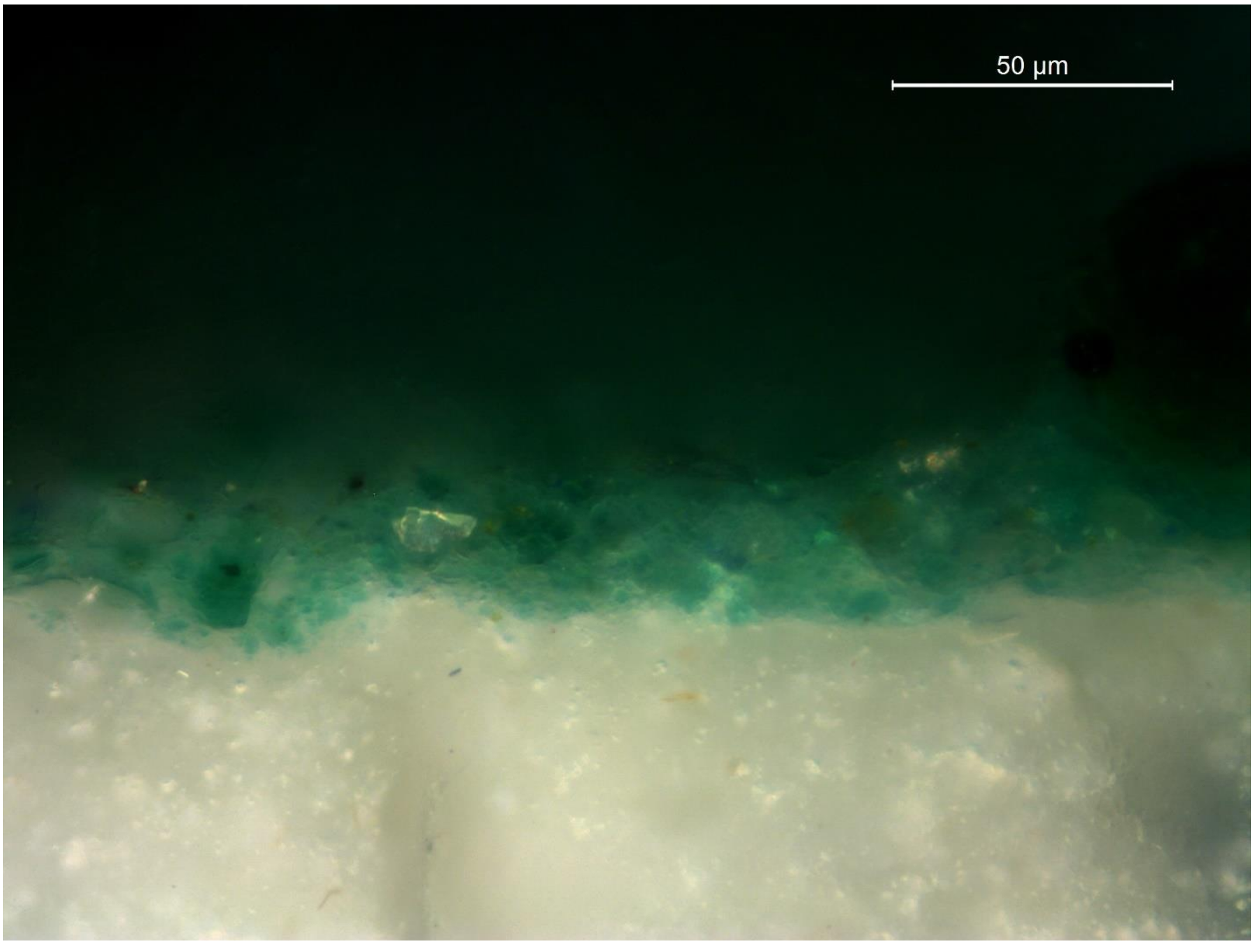

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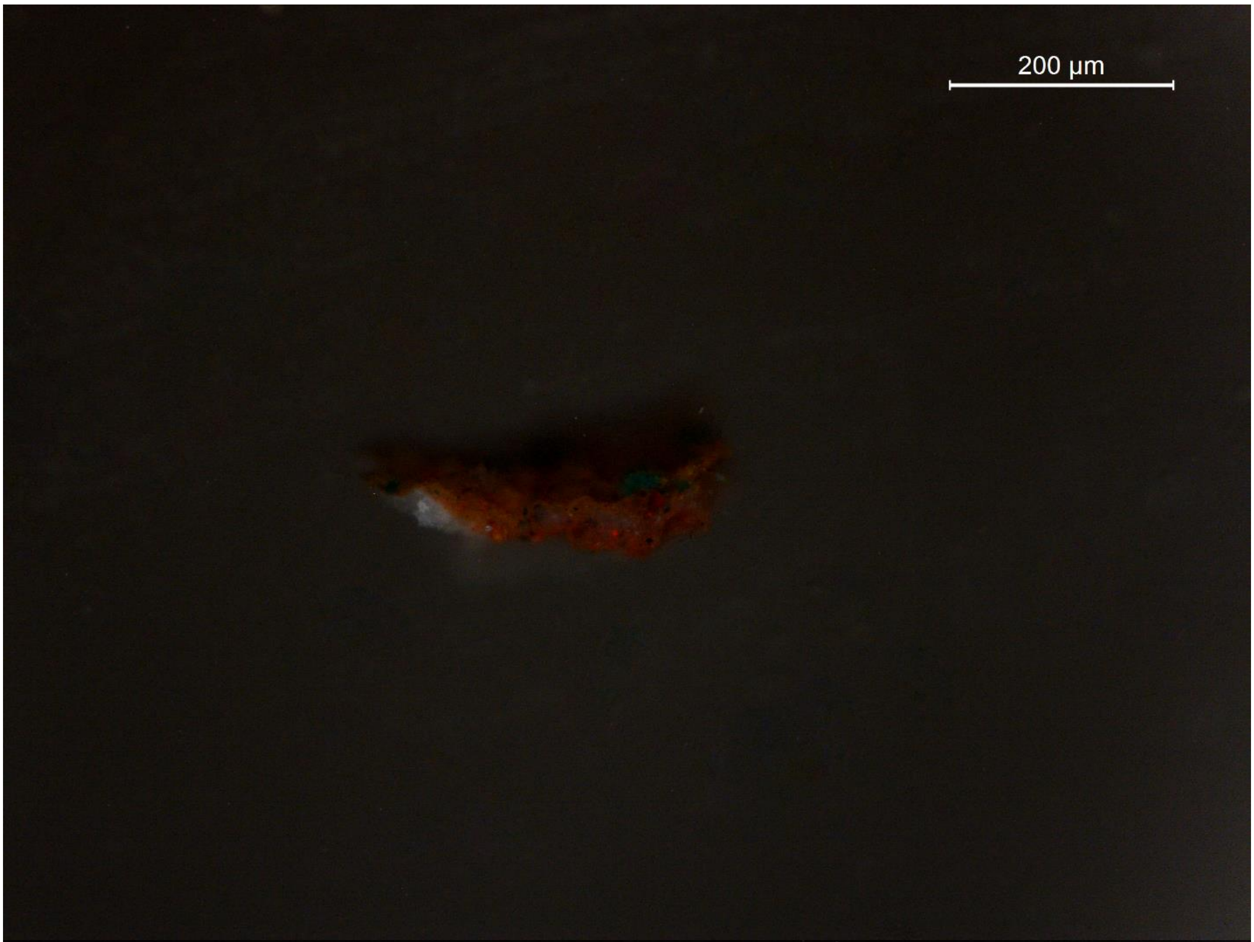
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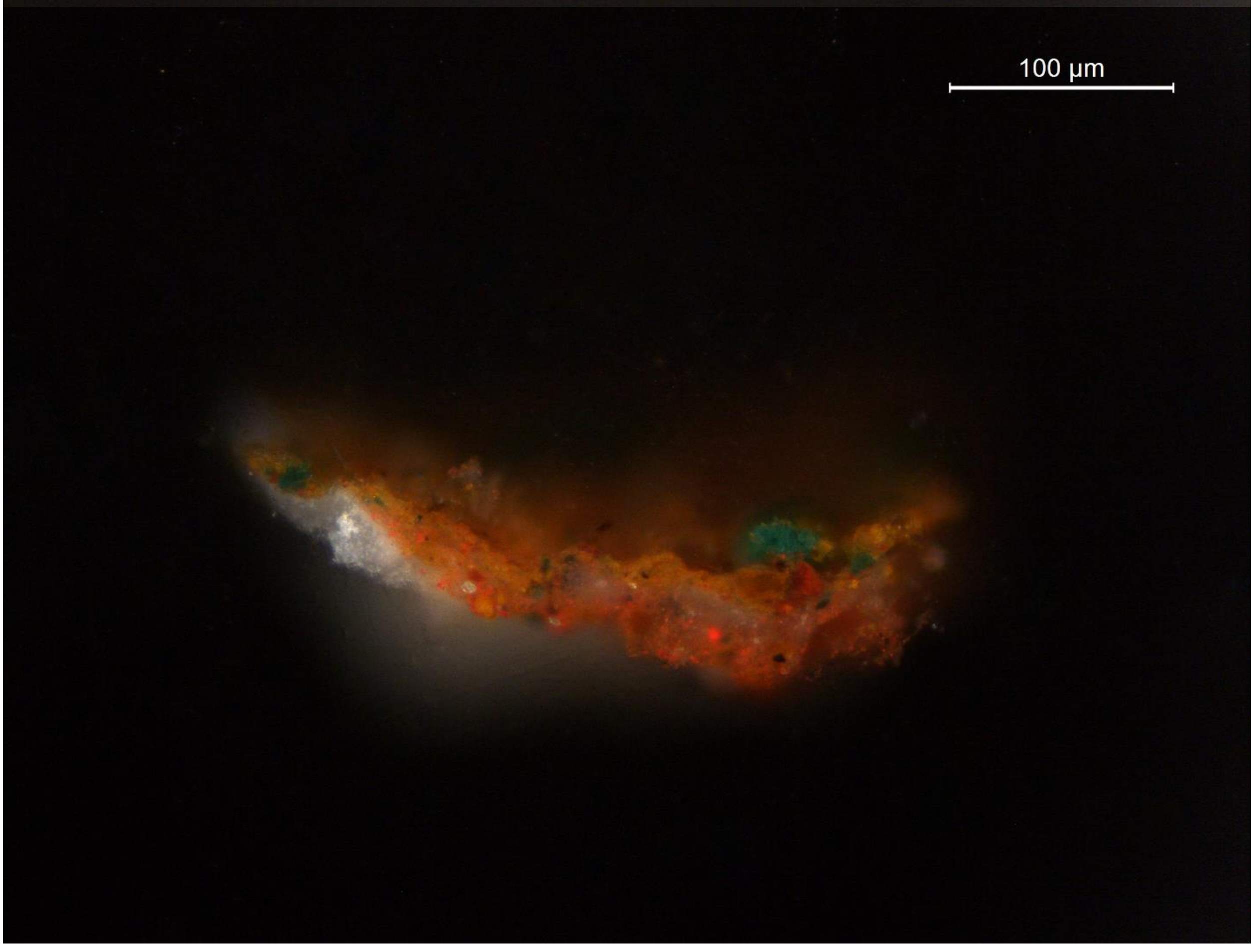
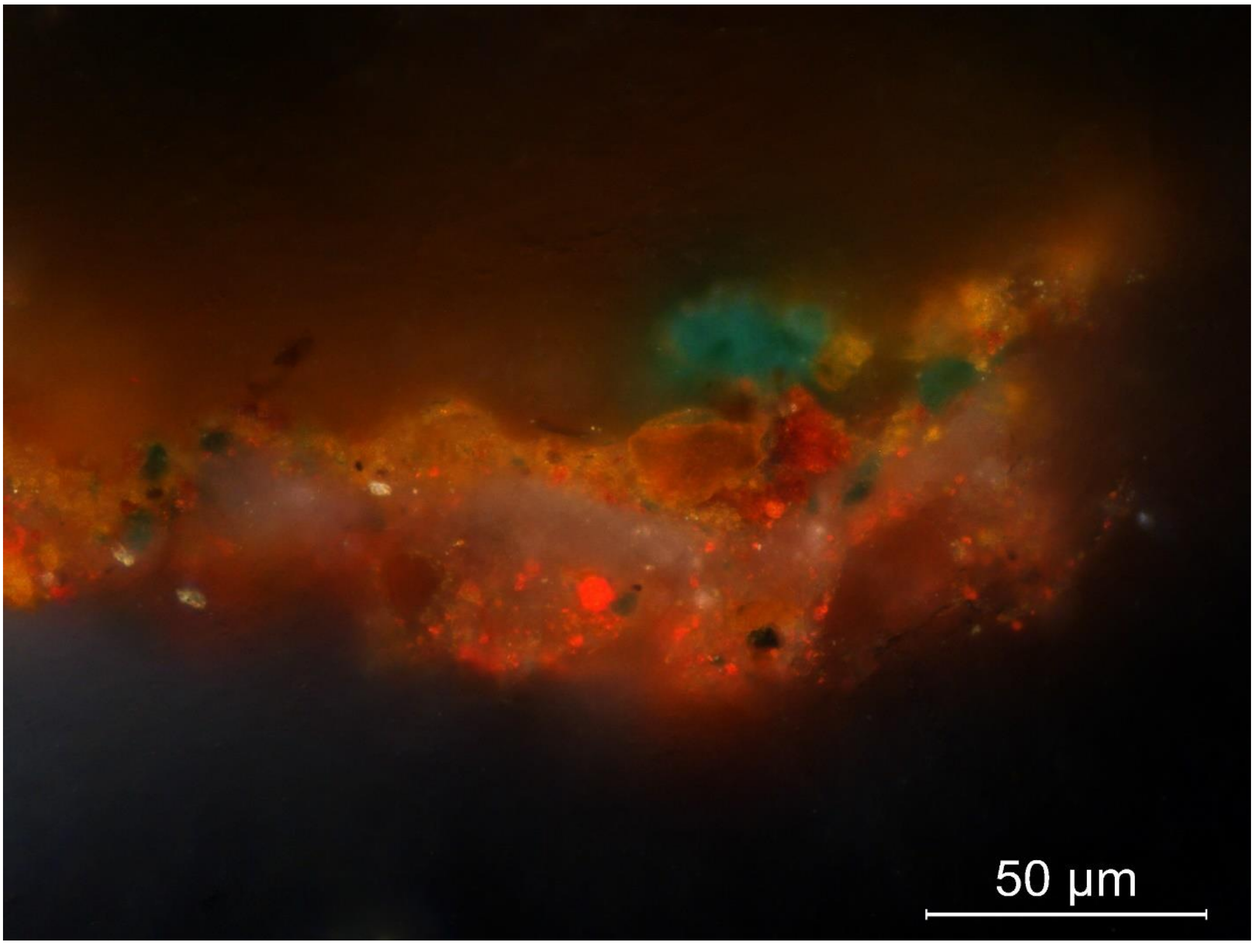
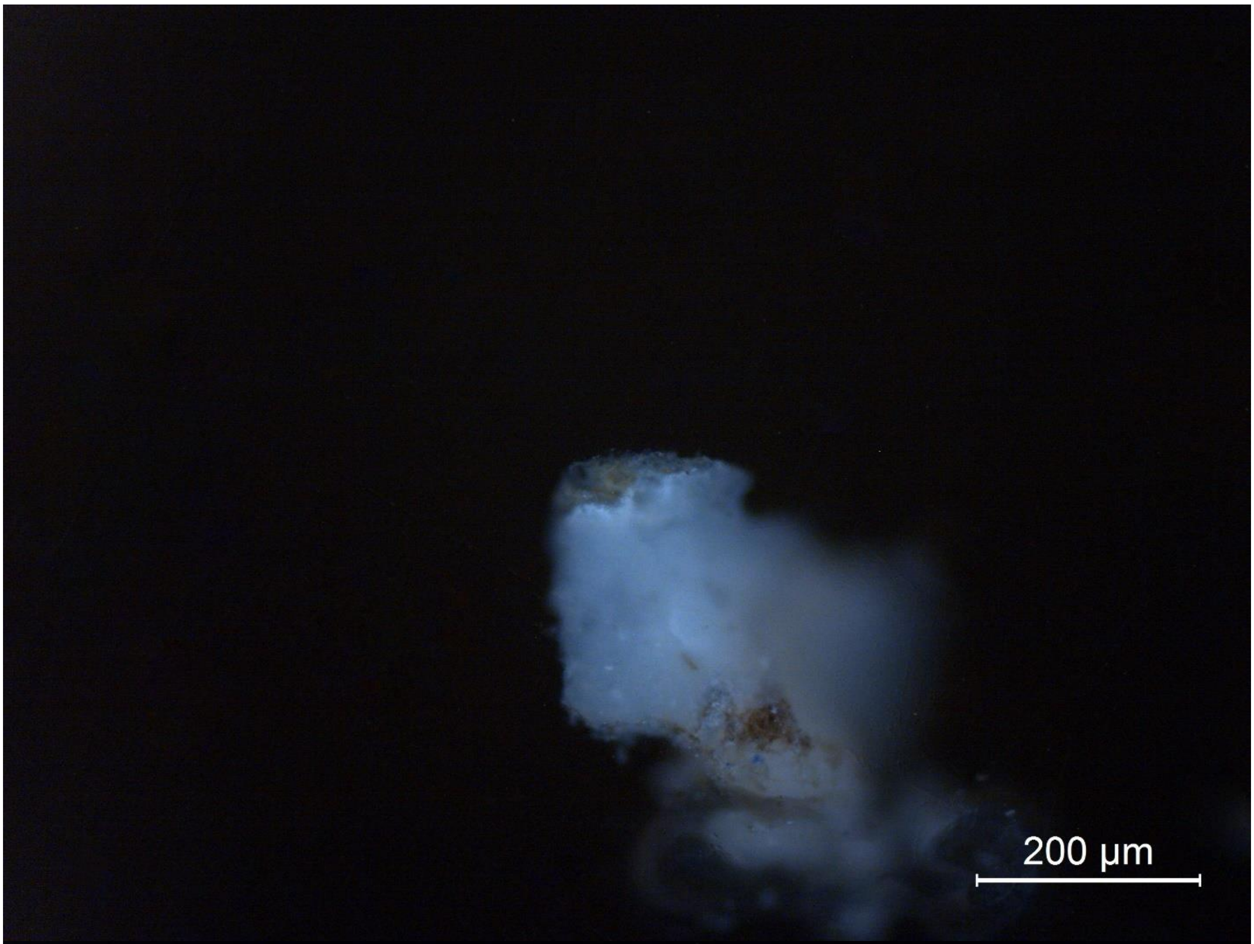
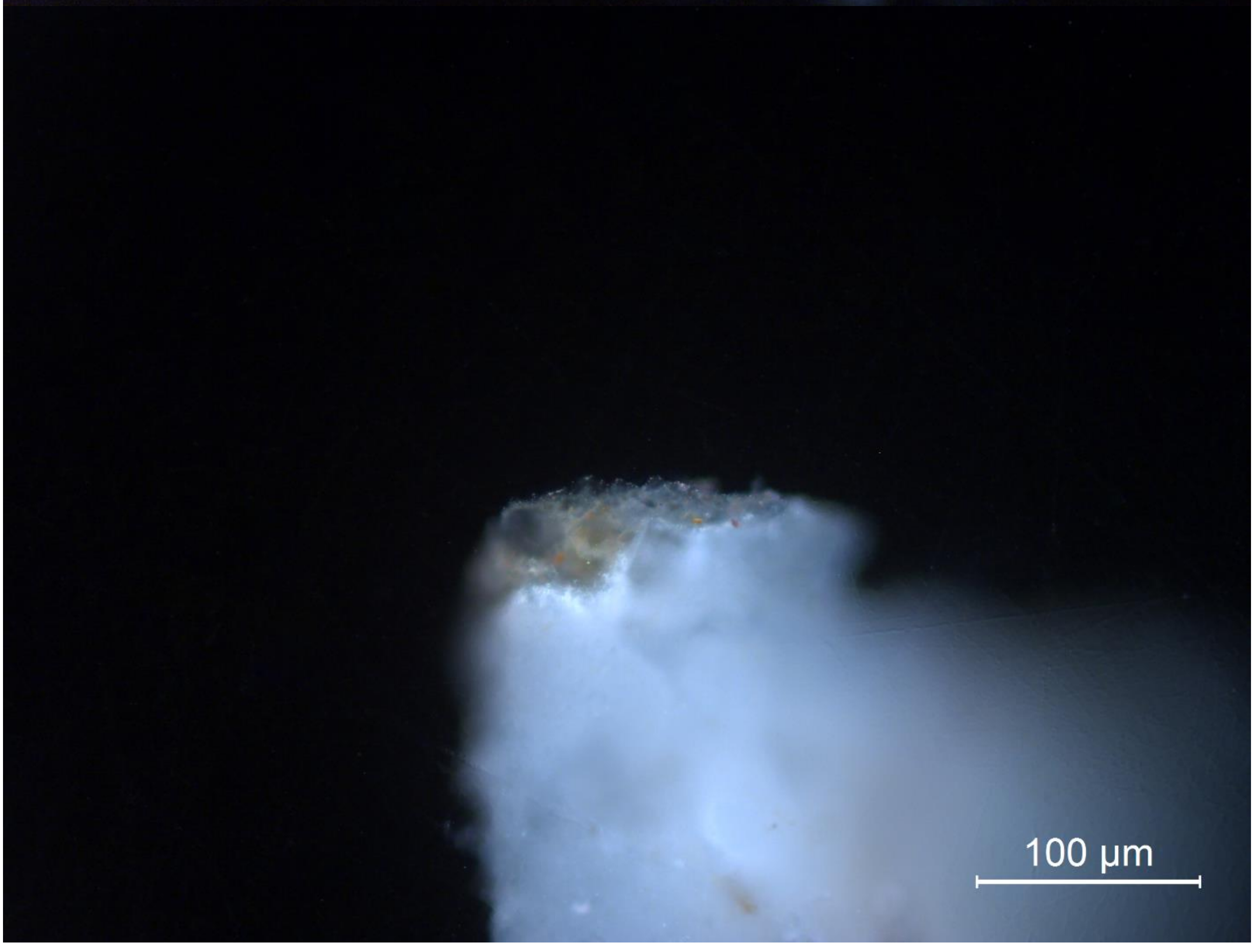
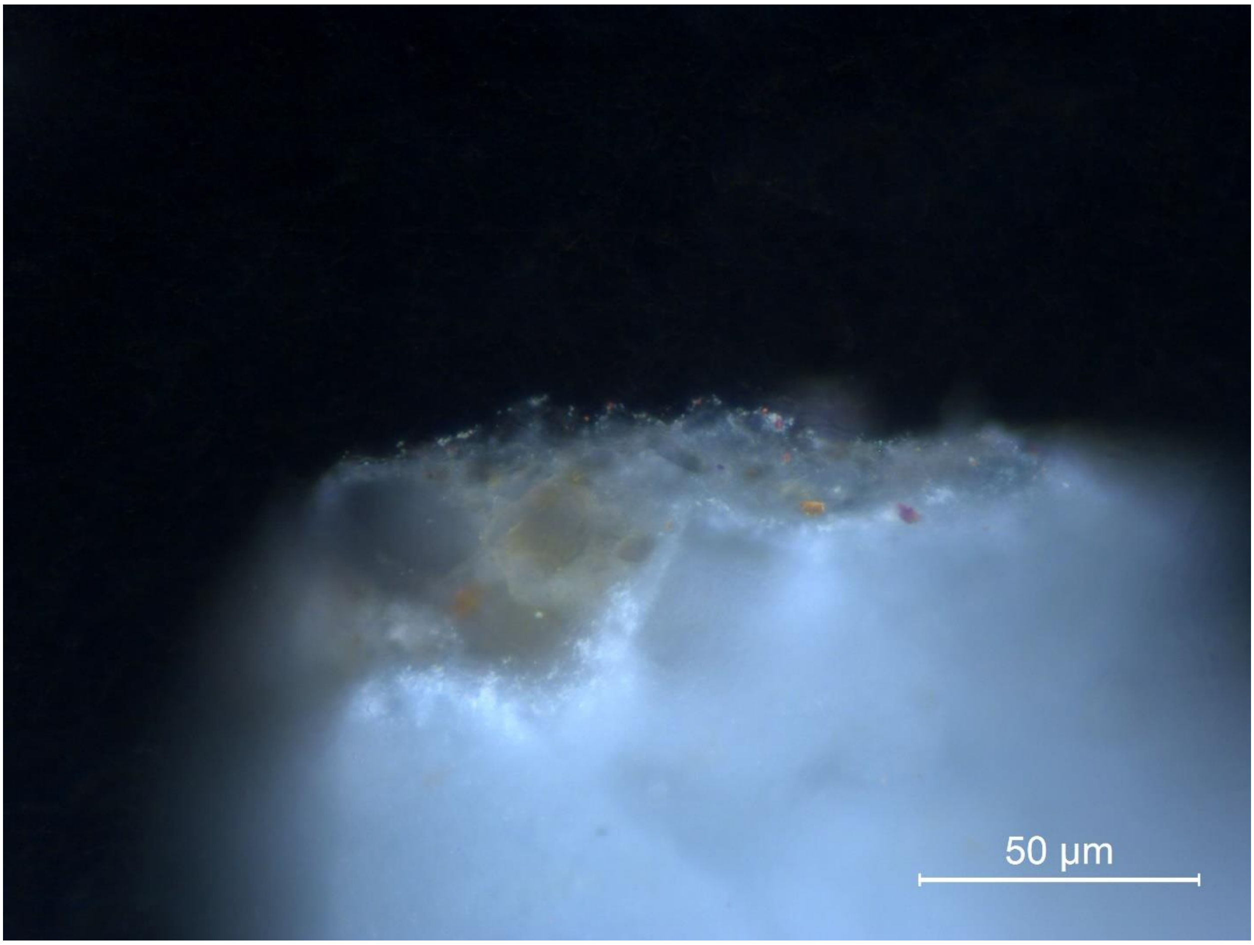

100 µm



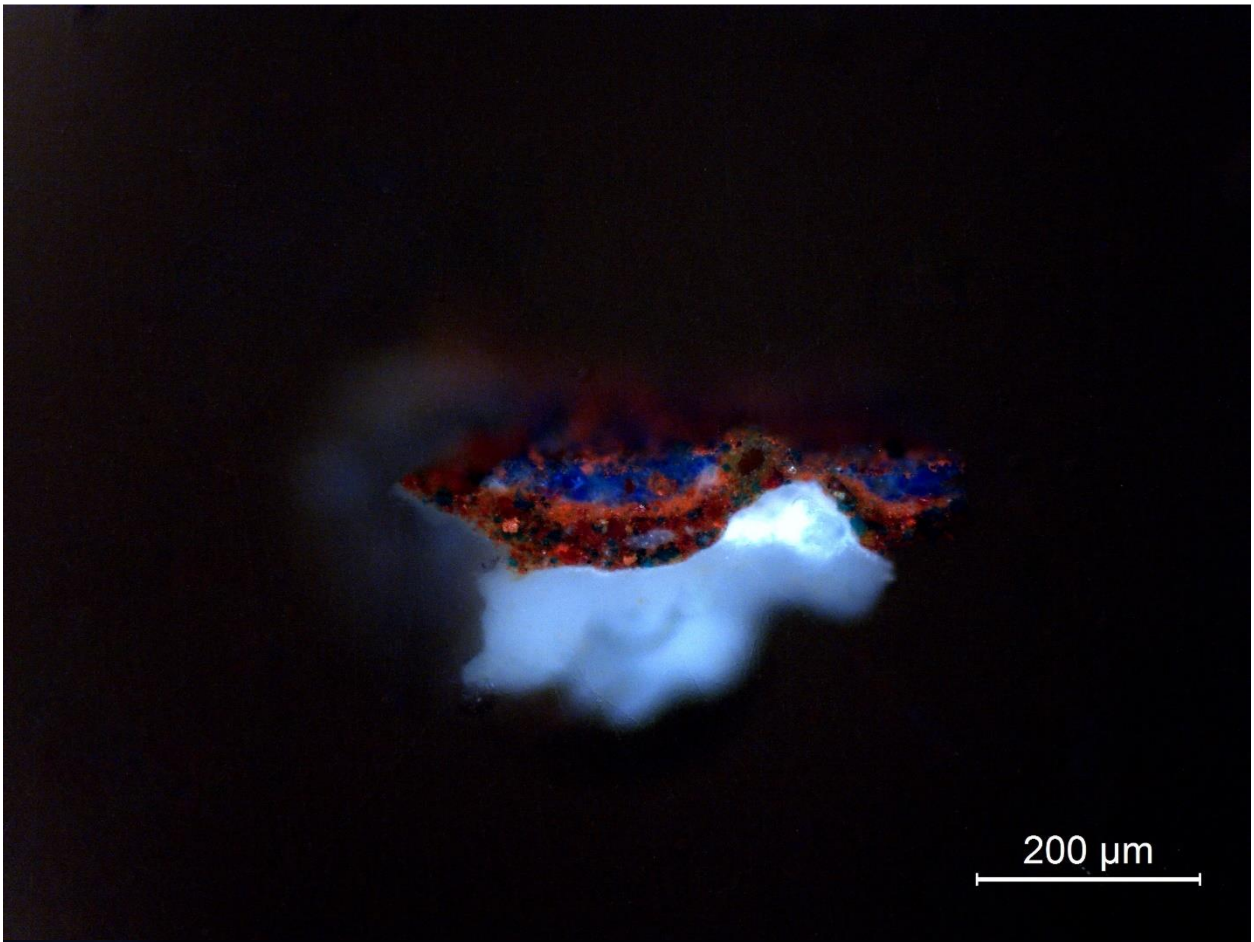
JR13 (100x, 200x, 500x):

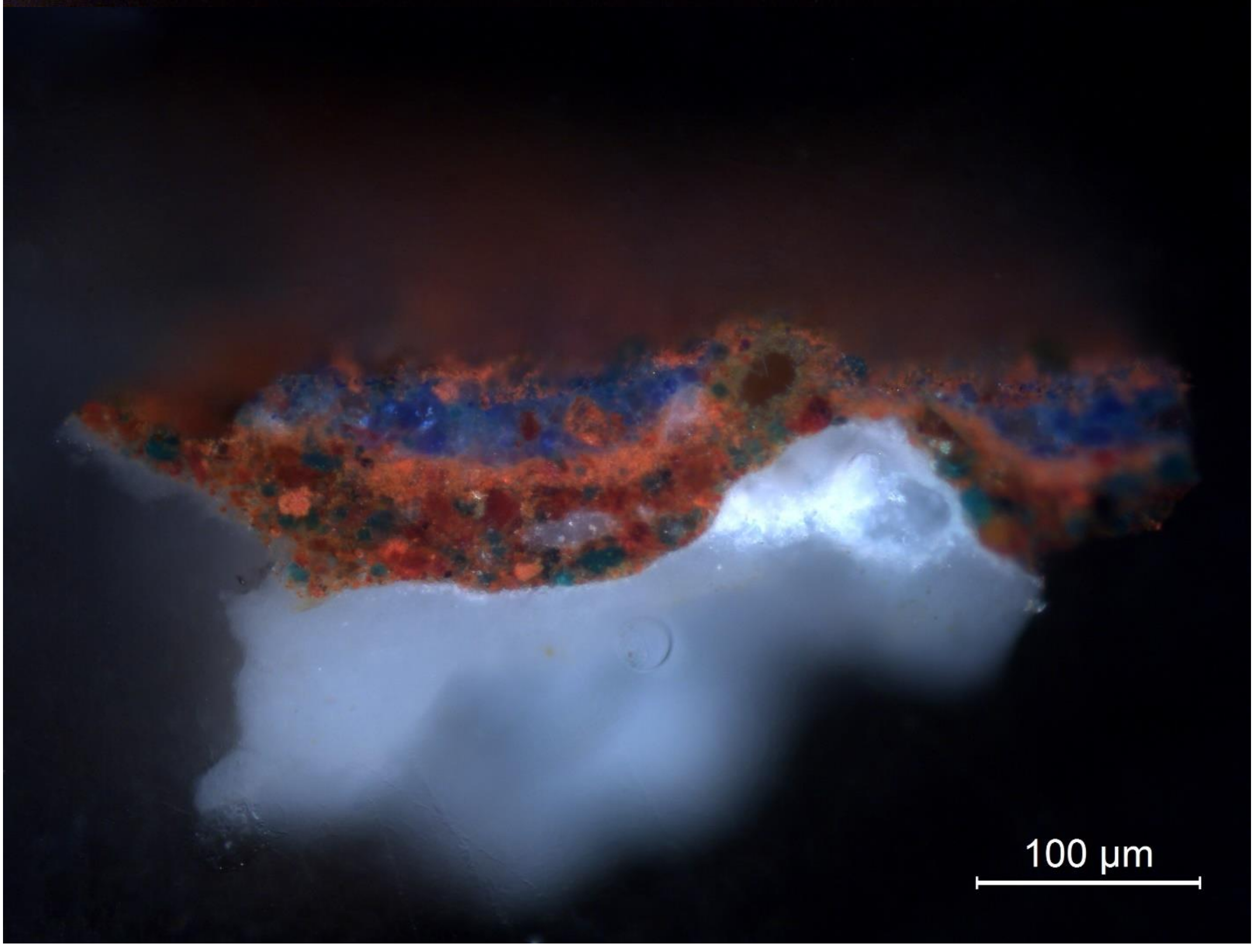

200 µm

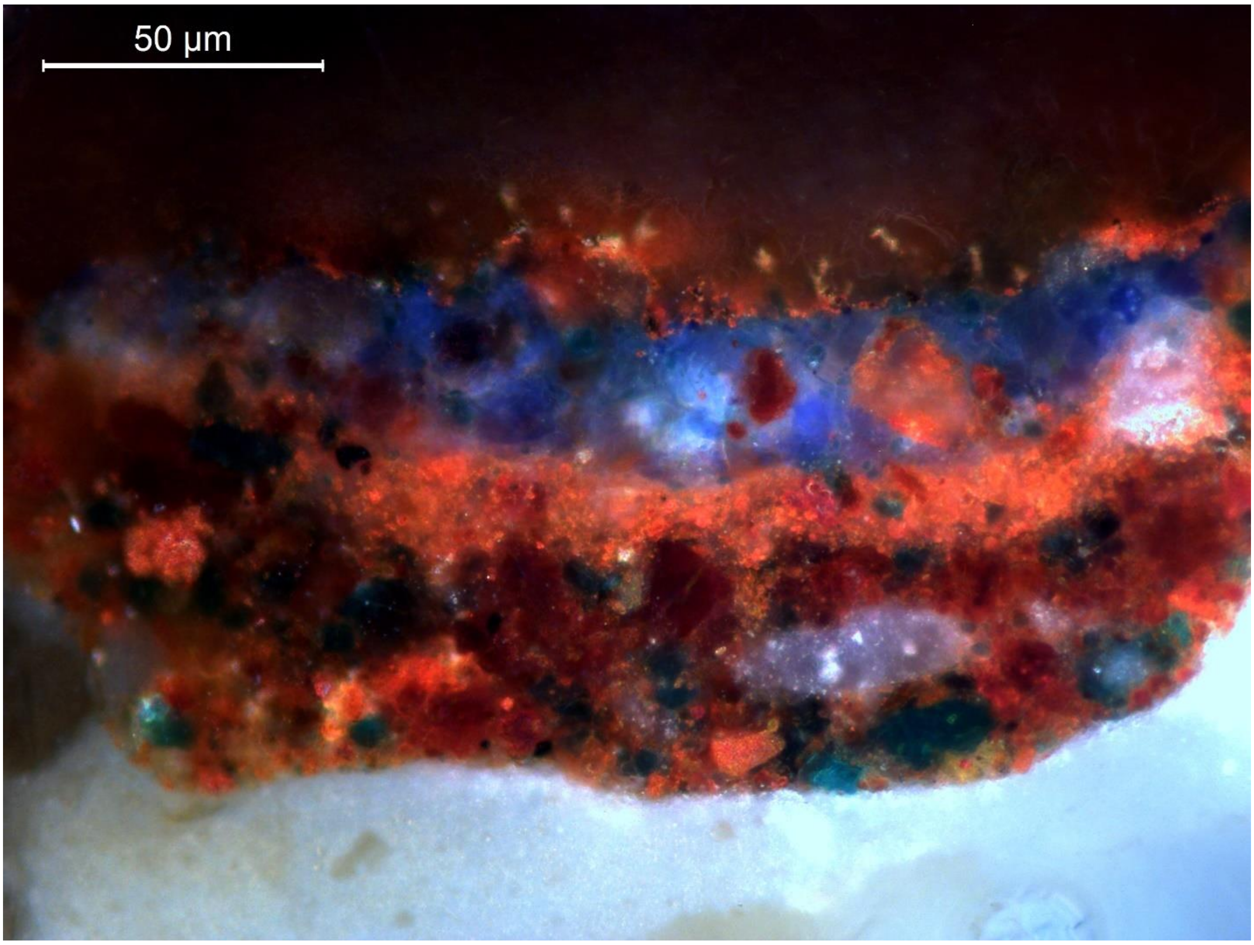

100 µm



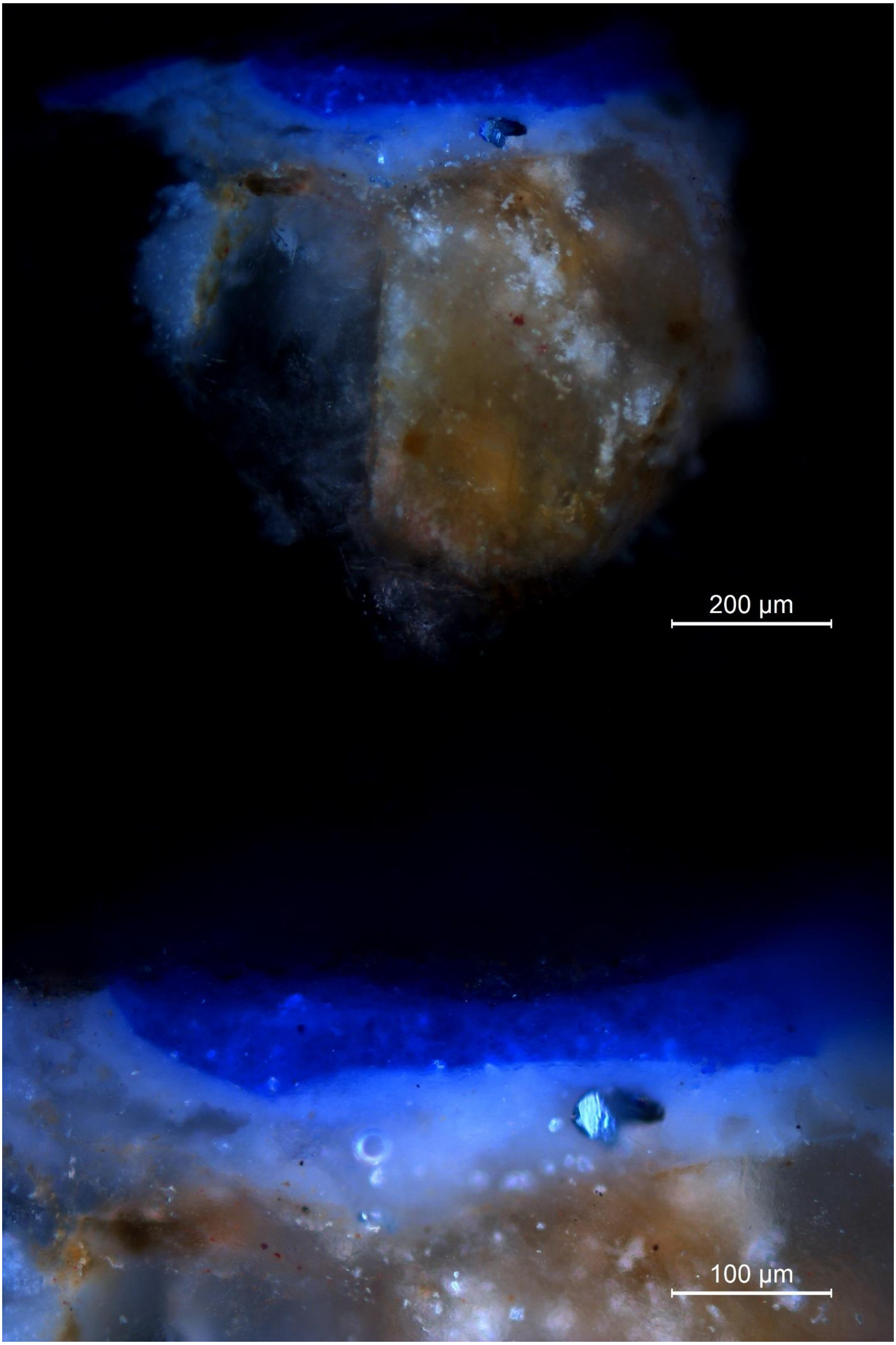
JR14 (100x, 200x, 500x):

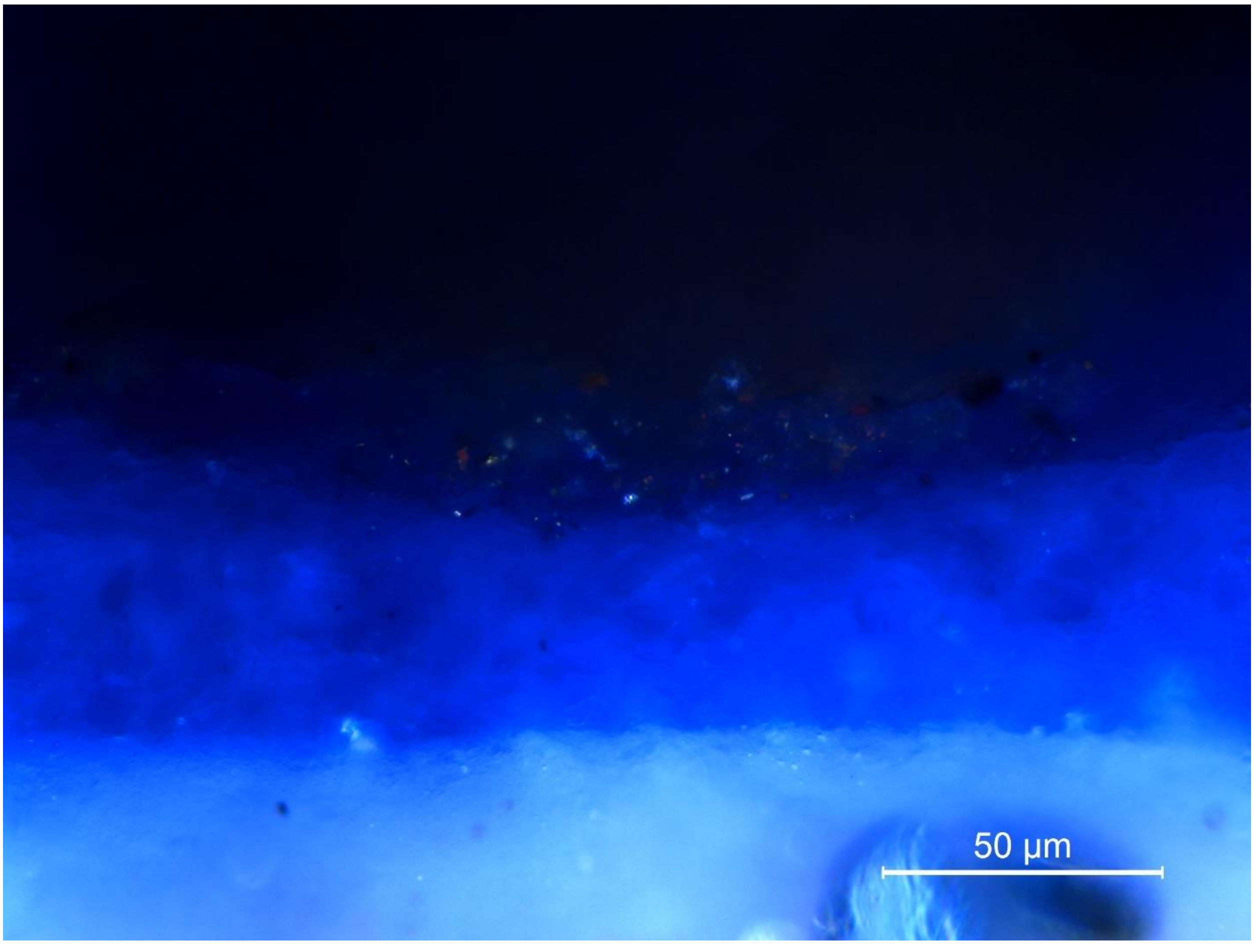

200 µm


100 µm

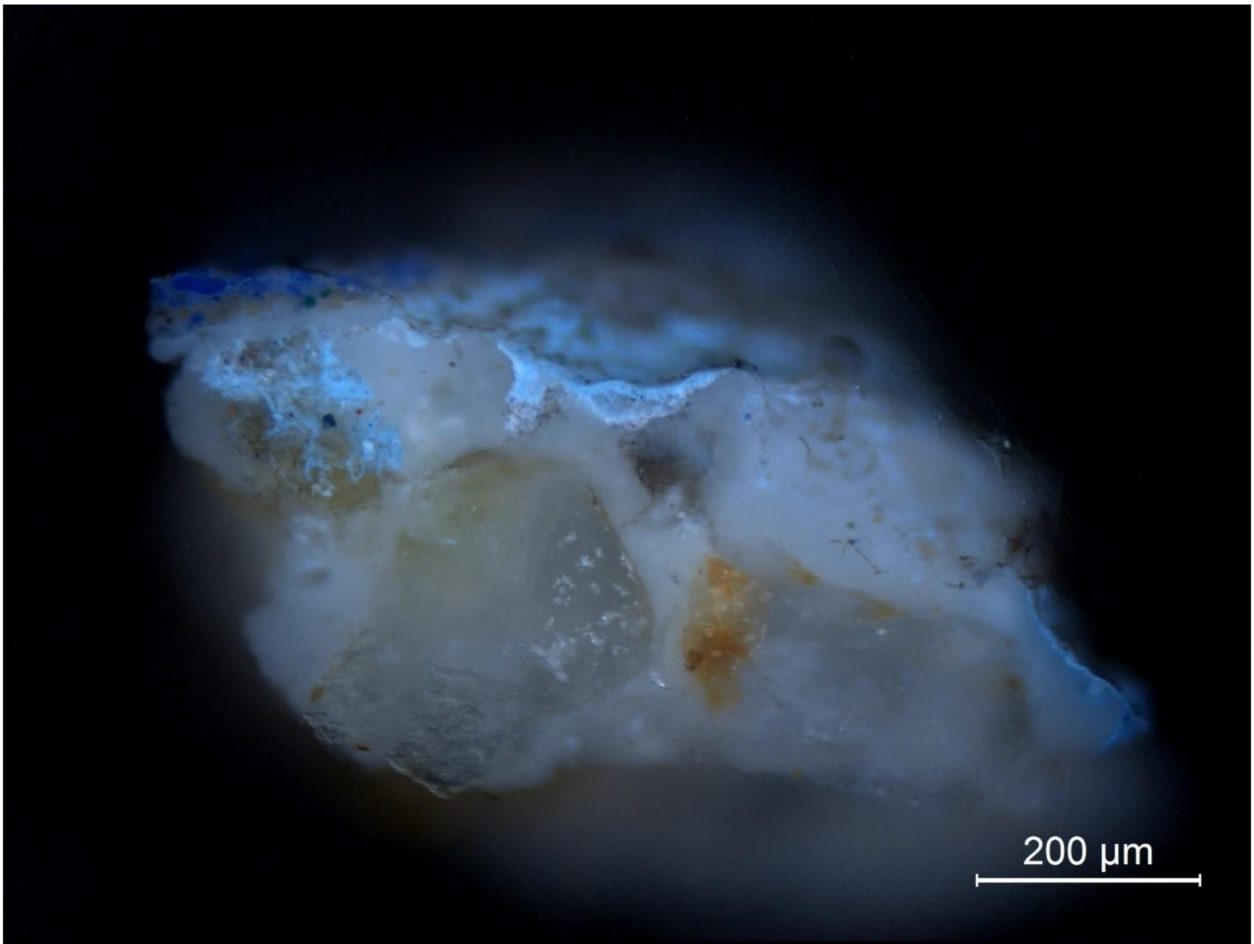


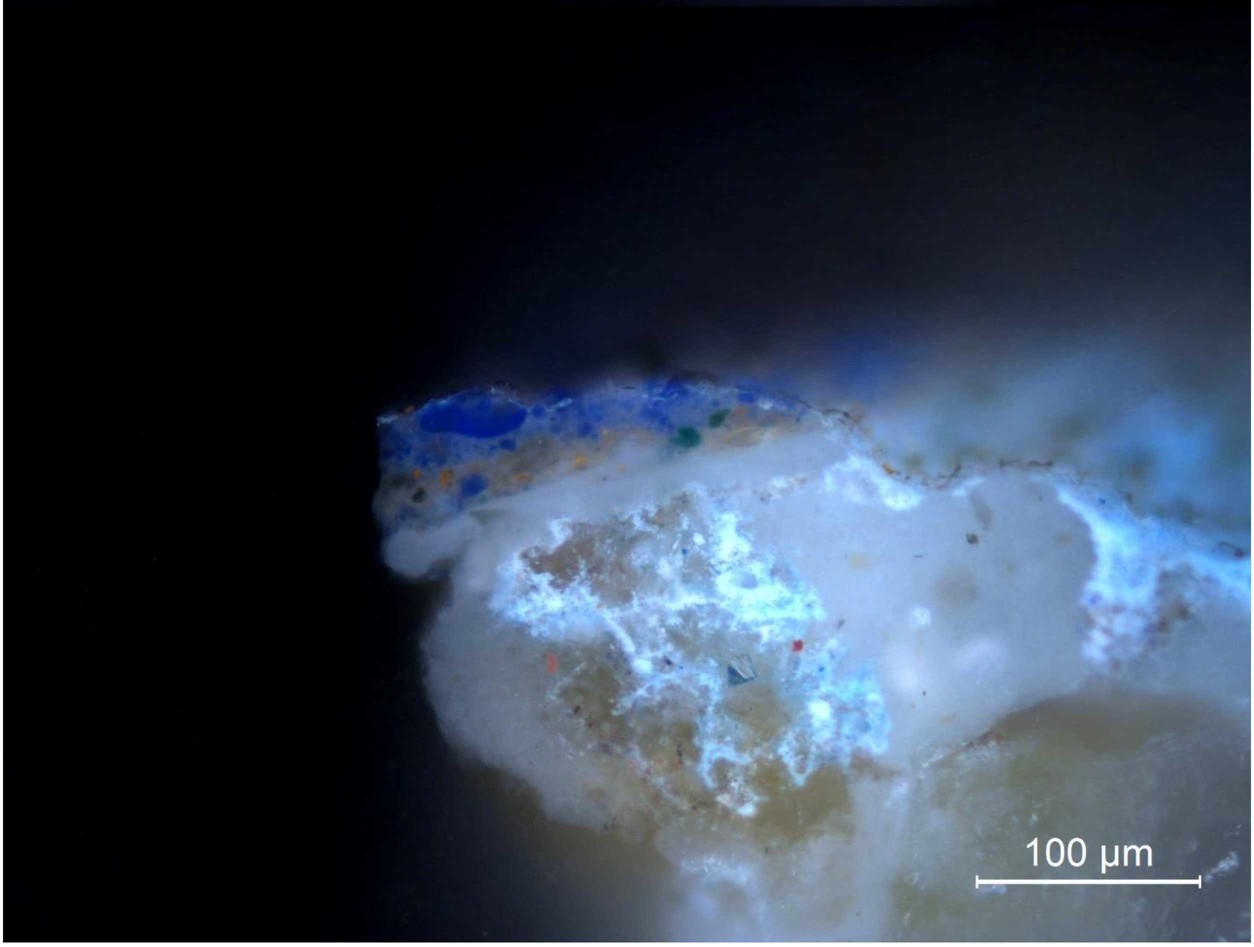
JR18 (100x, 200x, 500x):


200 µm
100 µm

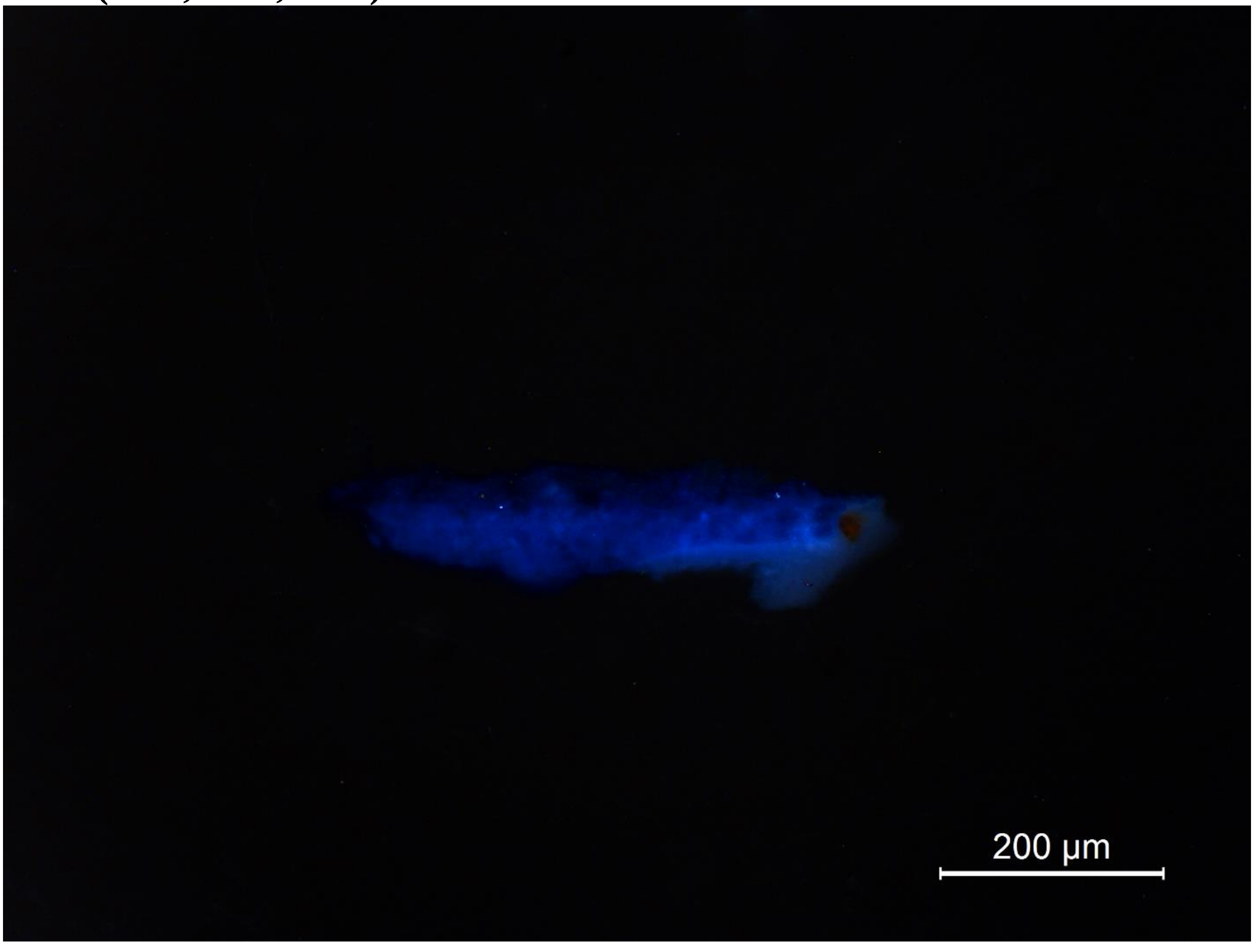


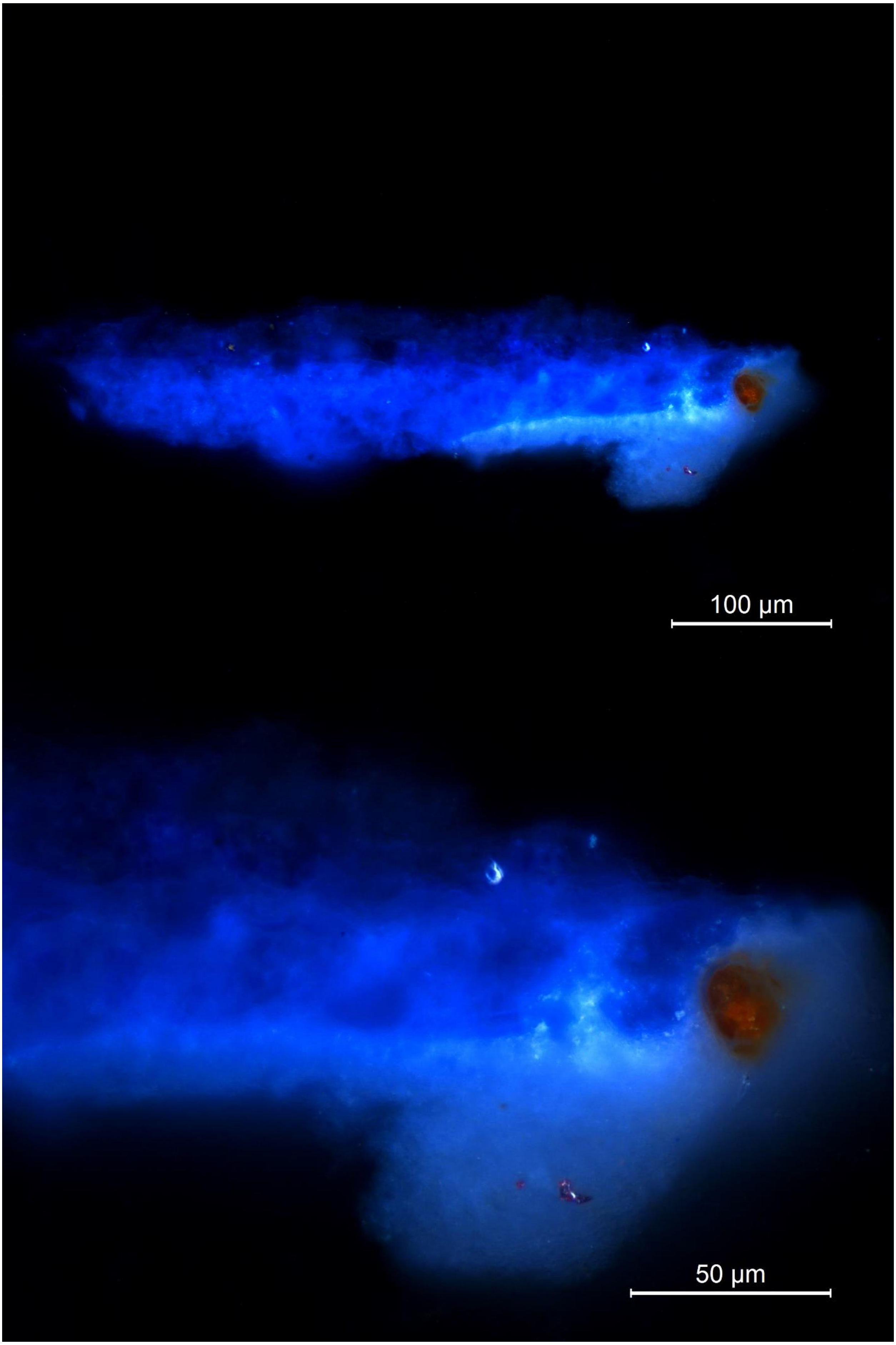
JR19 (100x, 200x):


200 µm

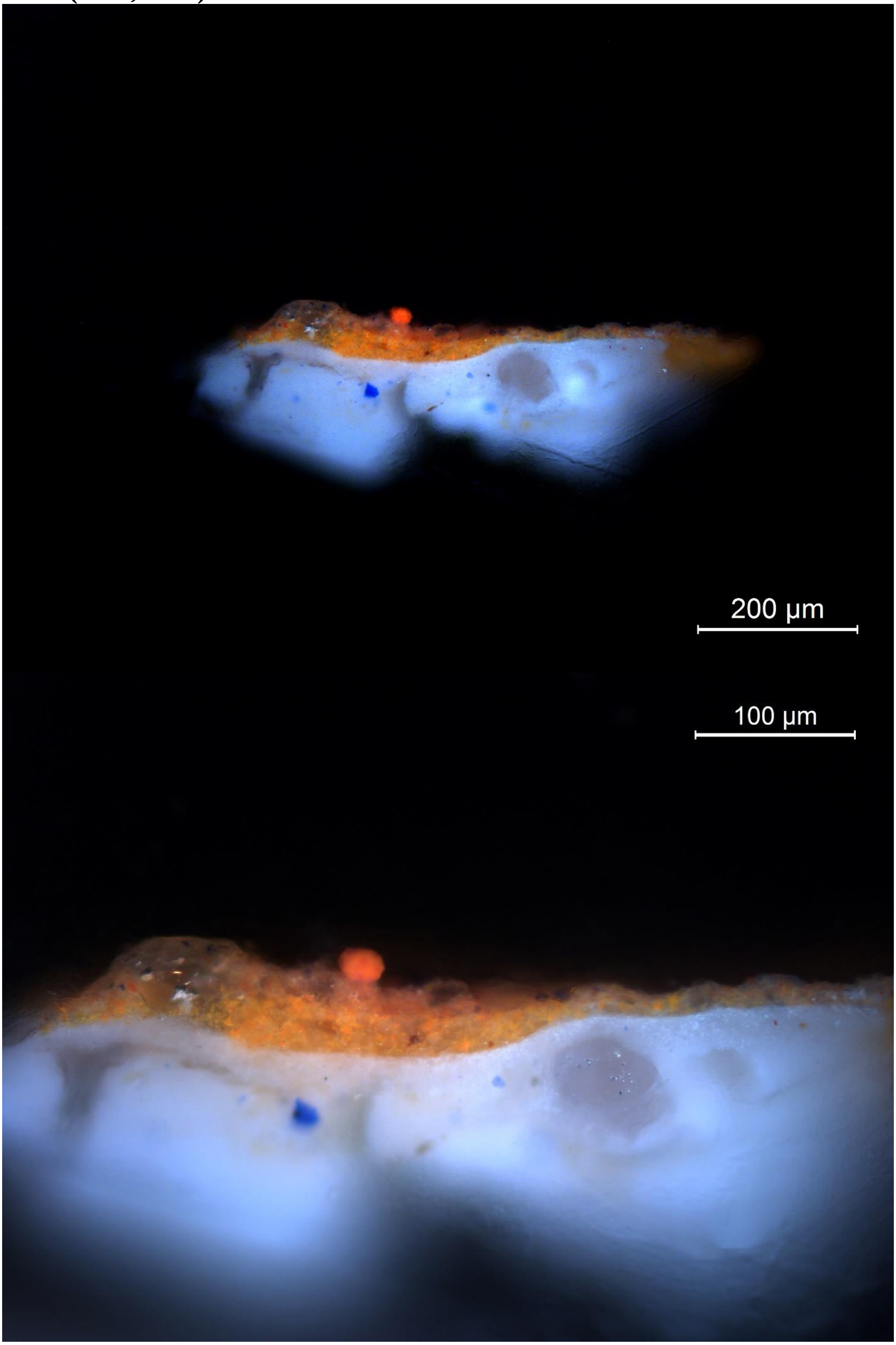

100 µm

JR22 (100x, 200x, 500x):

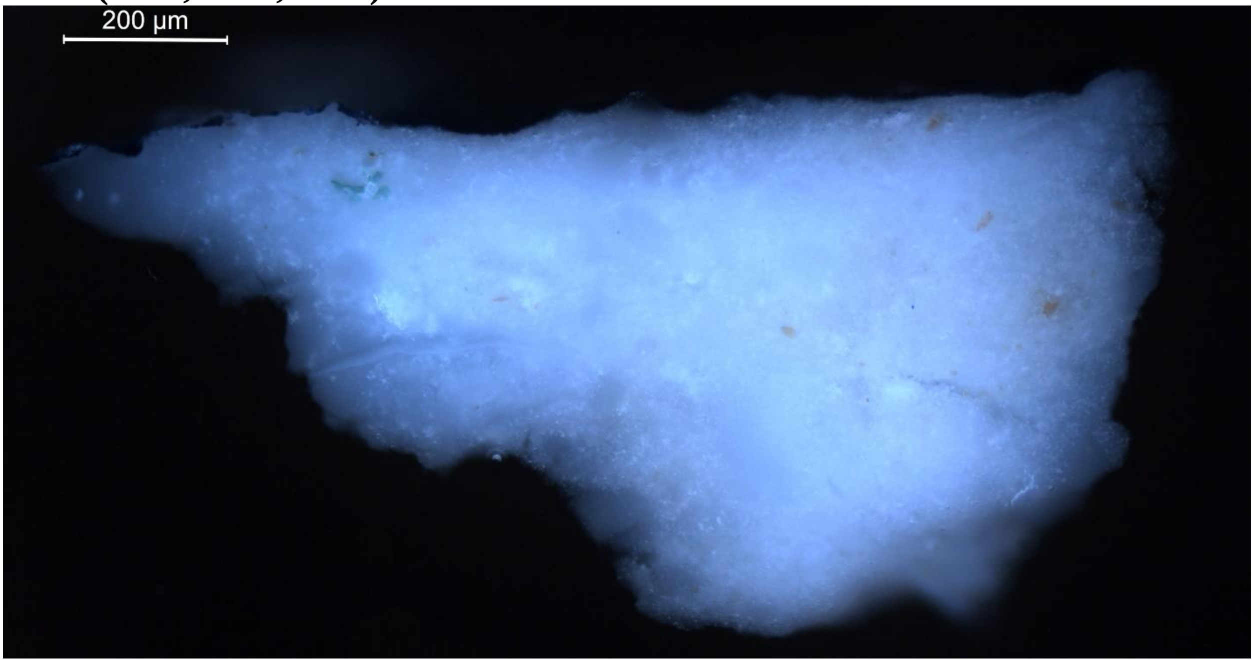


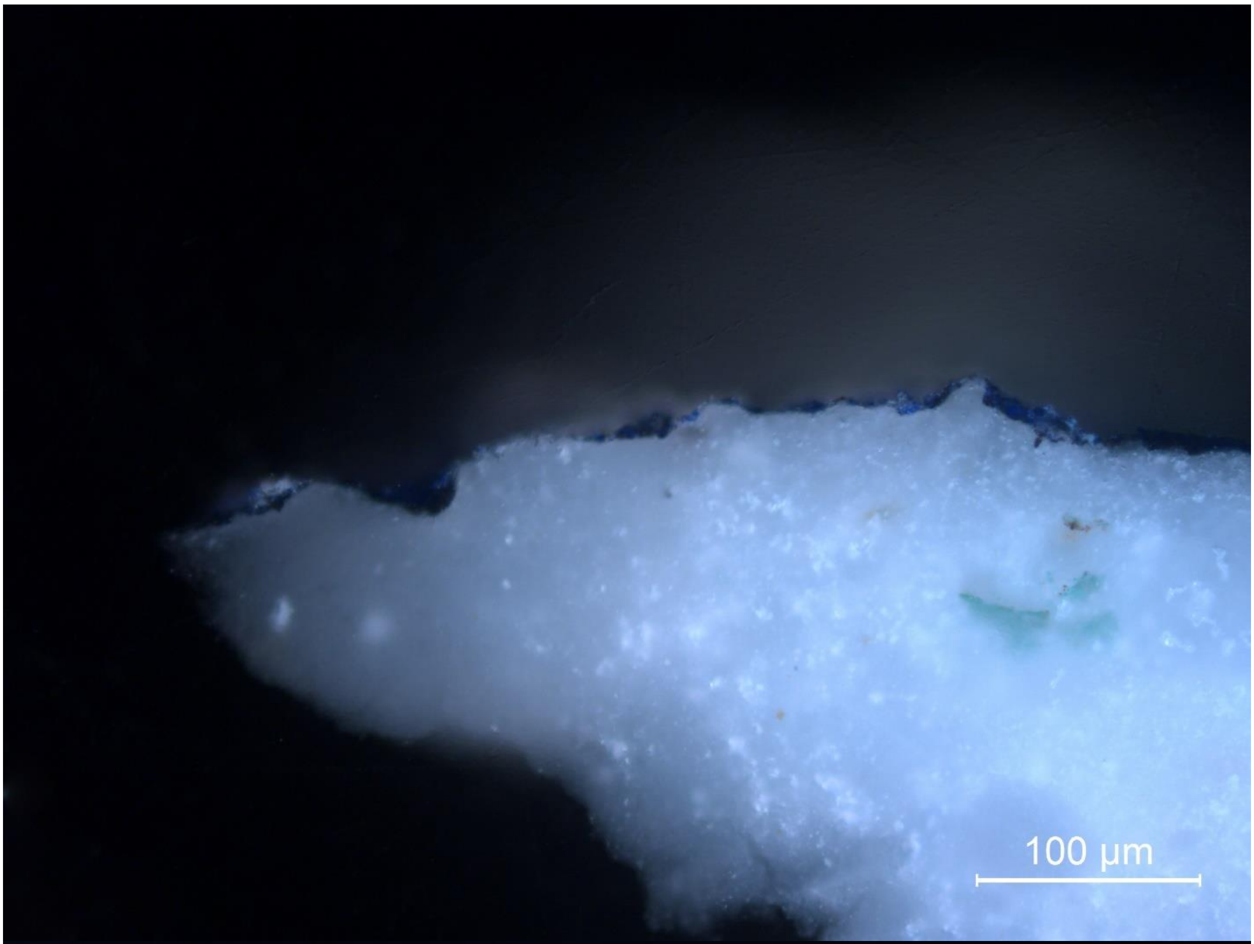

100 µm
50 µm

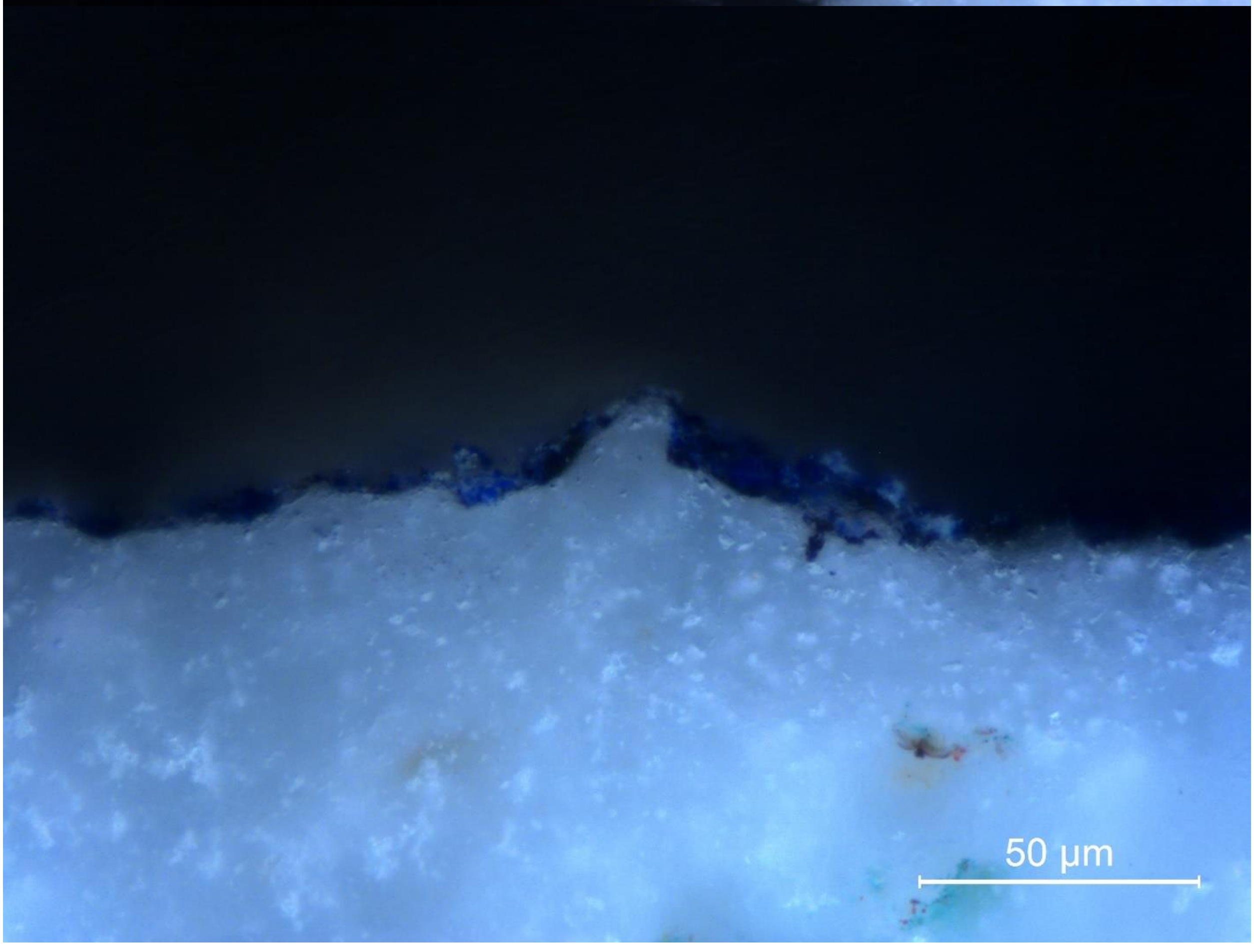
JR25 (100x, 200x):



JR26 (100x, 200x, 500x):




100 µm


50 µm

Appendix IV. Correspondence between Spectro-colorimetry and EDXRF measurements.

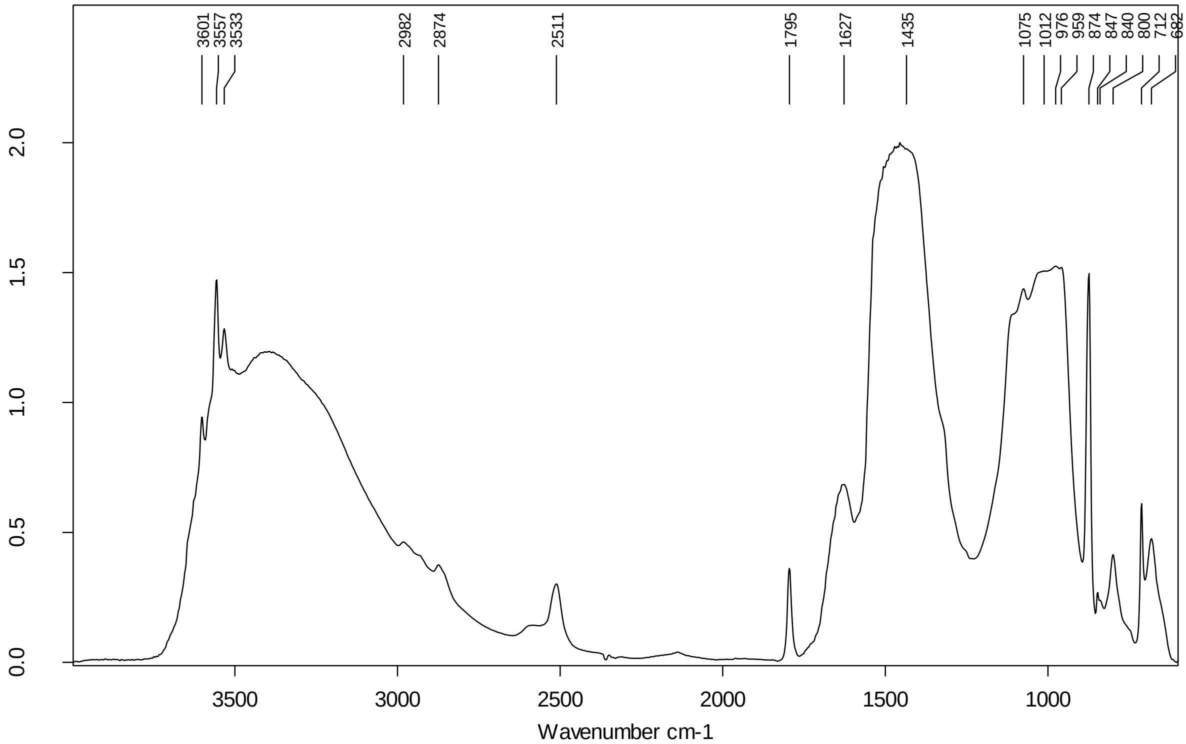
Spectro-colorimetry	XRF	Color
Jrescol3	31	green
Jrescol6	30	dark
Jrescol14	JL3	green
Jrescol24	JL29	green
Jrescol25	JL32	blue
Jrescol32	JL65	green
Jrescol36	JL38	brown
Jrescol37	JL28	blue
Jrescol38	JL27	blue
Jrescol50	JL5	blue
Jrescol51	JL4	blue
Jrescol54	JL2	blue
Jrescol57	JL1	brownn
Jrescol60	JL66	red
Jrescol61	JL67	red
Jrescol68	JL17	blue
Jrescol71	JL14	brown
Jrescol73	JL16	brown
Jrescol78	JL13	brown
Jrescol80	JL68	blue
Jrescol82	JL69	green/orange
Jrescol84	JL53	brown
Jrescol86	JL54	blue
Jrescol89	JL26	red
Jrescol92	JL6	blue
Jrescol93	JL7	blue
Jrescol97	JL12	blue
Jrescol102	JL61	dark
Jrescol104	JL23	brown
Jrescol107	JL24	red
Jrescol108	JL25	dark
Jrescol110	JL62	red
Jrescol112	JL63	brown
Jrescol121	JL18	blue
Jrescol126	JL11	brown
Jrescol128	JL71	blue
Jrescol130	JL70	blue
Jrescol131	JL72	pink
Jrescol133	JL74	pink
Jrescol134	JL22	blue
Jrescol138	JL81	brown
Jrescol142	JL20	green
Jrescol143	JL21	green
Jrescol147	JL19	yellow/green
Jrescol148	JL8	blue
Jrescol150	JL9	green
Jrescol154	JL10	blue
Jrescol156	JL79	dark
Jrescol157	JL78	dark

Jrescol158	JL77	brown
Jrescol159	JL75	orange
Jrescol160	JL80	white
Jrescol163	JL34	red
Jrescol166	JL33	brown
Jrescol174	JL35	blue
Jrescol177	JL36	brown
Jrescol179	JL51	grey
Jrescol180	JL52	red
Jrescol188	JL50	red
Jrescol199	JL48	red
Jrescol203	JL47	green
Jrescol204	JL49	white
Jrescol207	JL37	brown
Jrescol209	JL39	blue
Jrescol214	JL46	dark
Jrescol217	JL40	orange
Jrescol218	JL41	brown
Jrescol219	JL43	green
Jrescol220	JL44	blue
Jrescol221	JL45	blue
Jrescol225	JL57	brown
Jrescol230	JL56	white
Jrescol231	JL55	orange
Jrescol235	JL60	blue
Jrescol238	JL58	brown
Jrescol241	JL59	brown
Jrescol252	JL64	grey
Jrescol256	JL82	white
Jrescol259	JL83	white

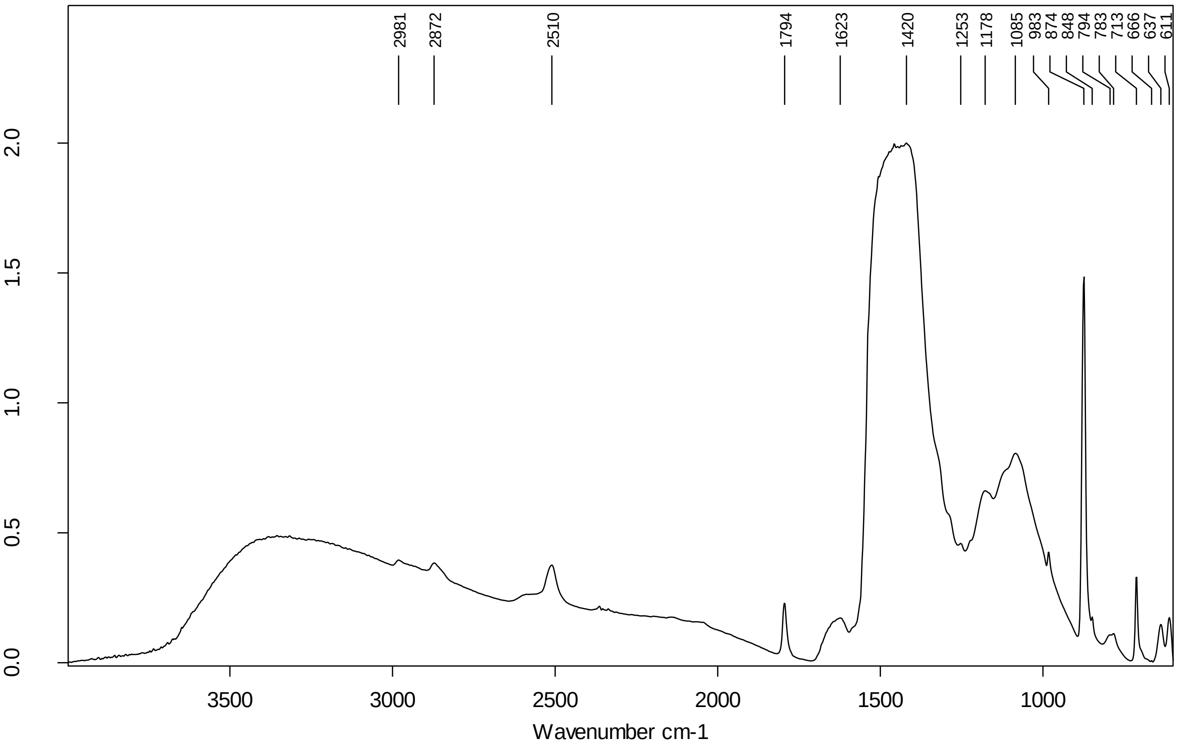
Appendix V. µ-FT-IR results

Sample	Color	Identified materials
JR2a	green	Celadonite + Calcite
JR4	green	Barite + Quartz + Calcite
JR6	blue	Cobalt blue + Kaolinite + Gypsum + Calcite + calcium oxalates
JR7	blue	Kaolinite + Gypsum + Calcite
JR14a	red	Kaolinite + Barite + Quartz + Gypsum + Calcite
JR14b	green/blue	Barite + Gypsum (traces) + Calcite + calcium oxalates
JR15	green	Barite + Quartz + Calcite + calcium oxalates
JR17	green/blue	Barite + Calcite + calcium oxalates
JR21	blue	Kaolinite + Gypsum + Calcite + calcium oxalates
JR25a	orange	Kaolinite + Barite + Gypsum + Calcite

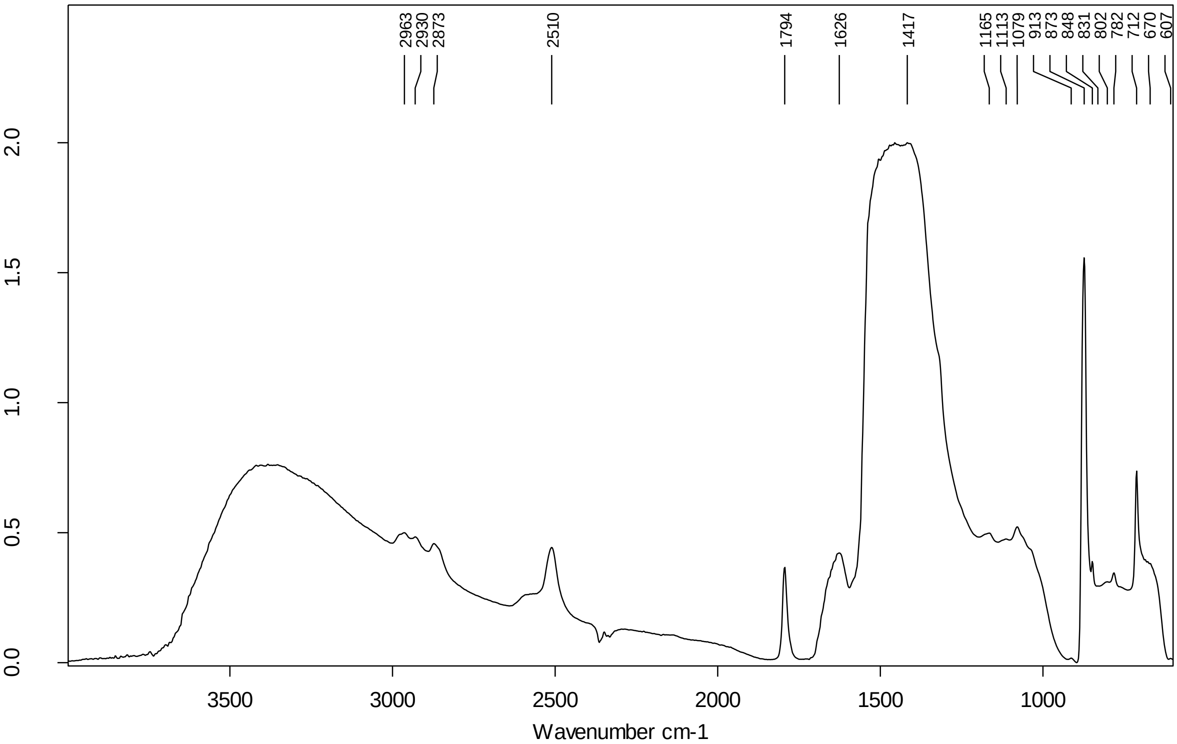
JR2a: (green):



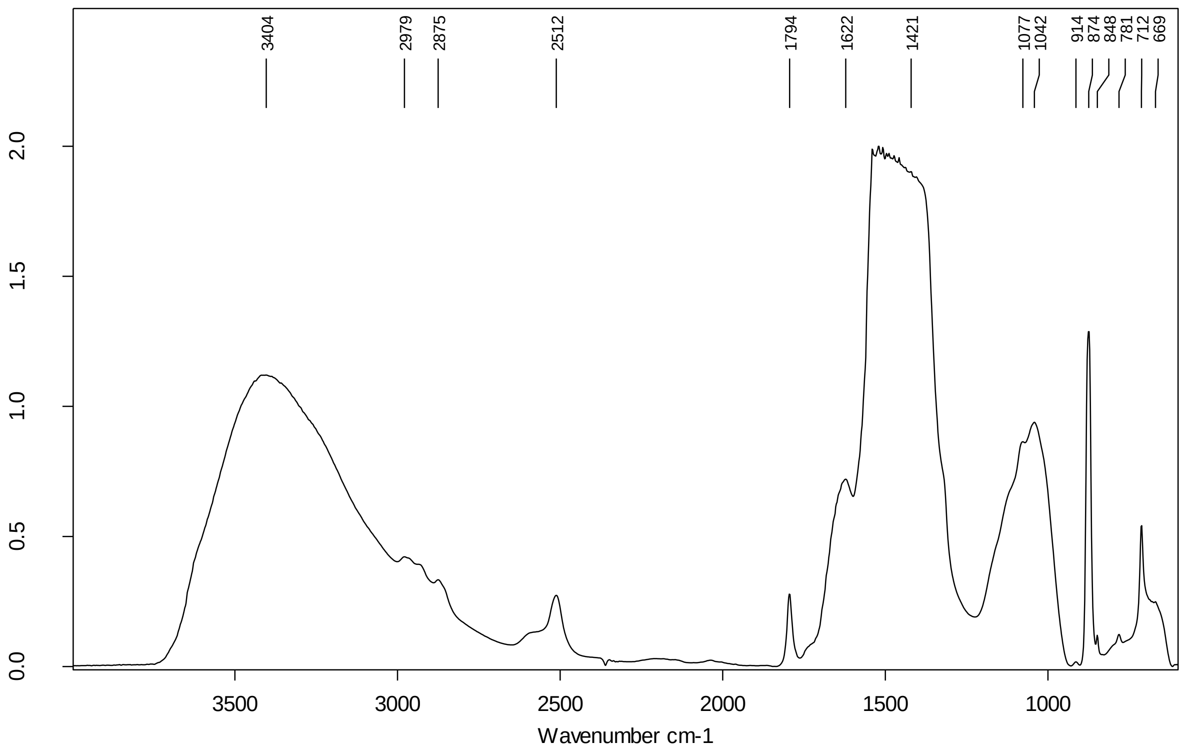
JR4:


2981
2872
2510
1794
1623
1420
1253
1178
1085
983
874
848
794
783
713
666
637
611
2.0
1.5
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

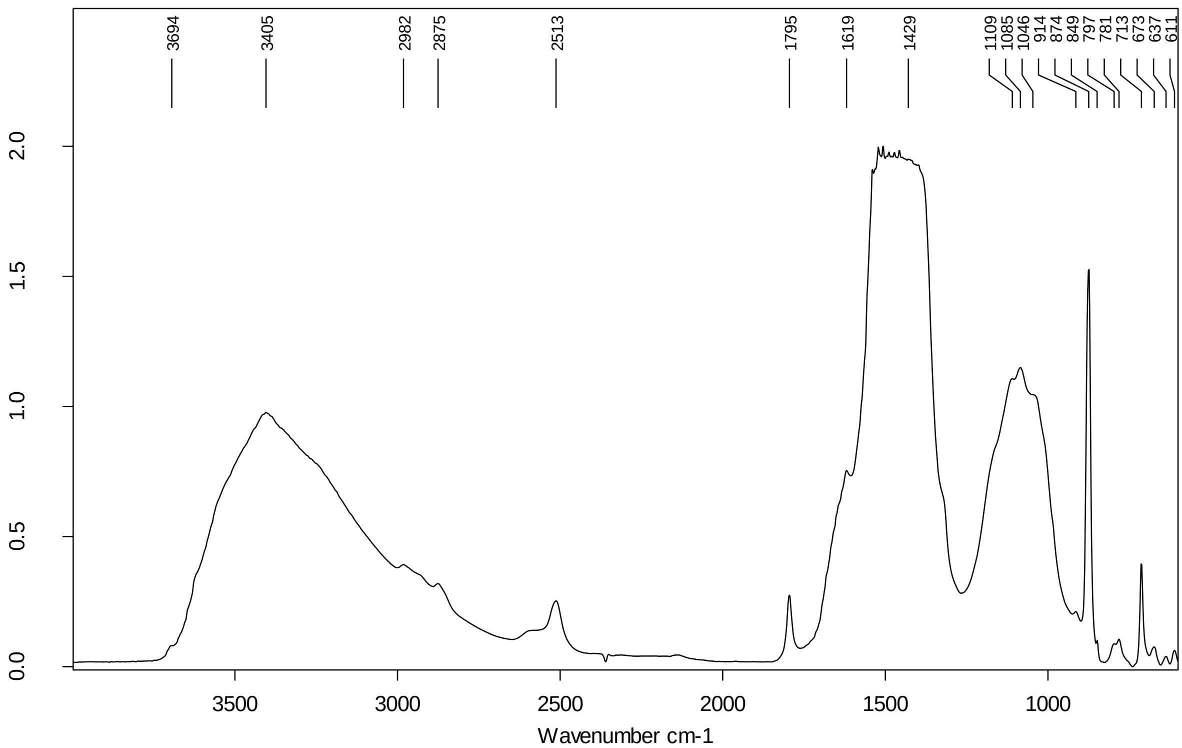
JR6:


2963
2930
2873
2510
1794
1626
1417
1165
1113
1079
913
873
848
831
802
782
712
670
607
2.0
1.5
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

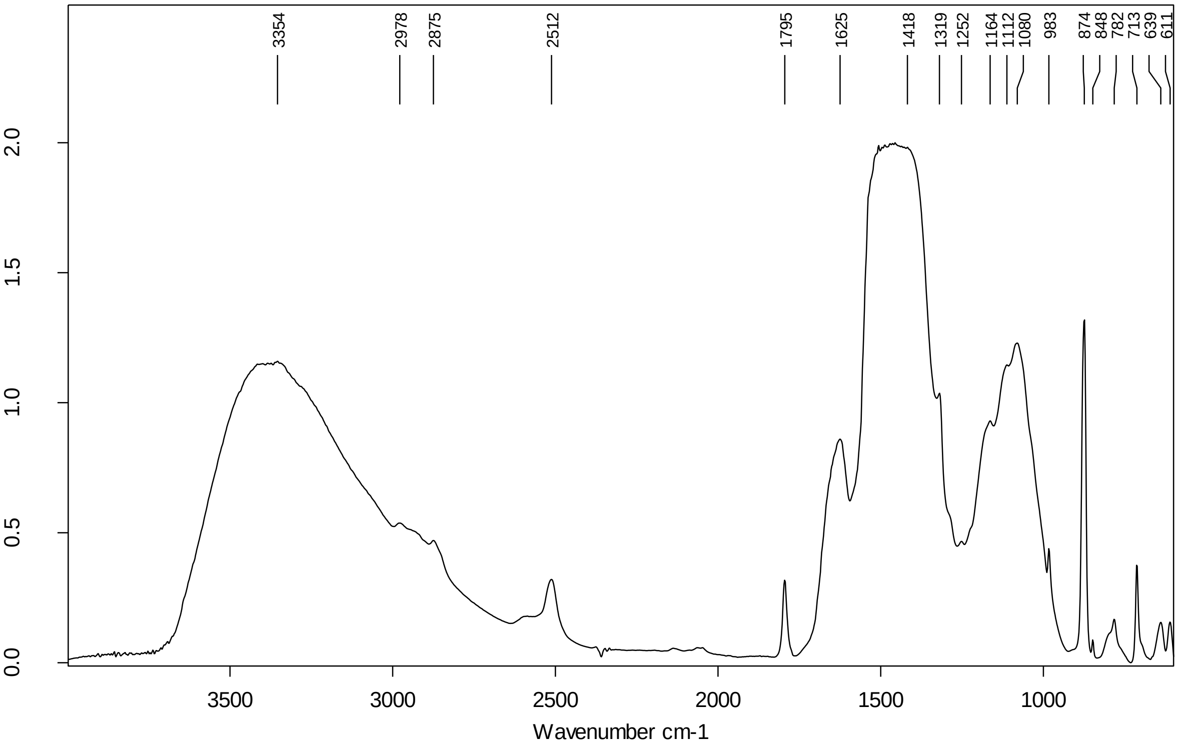
JR7:



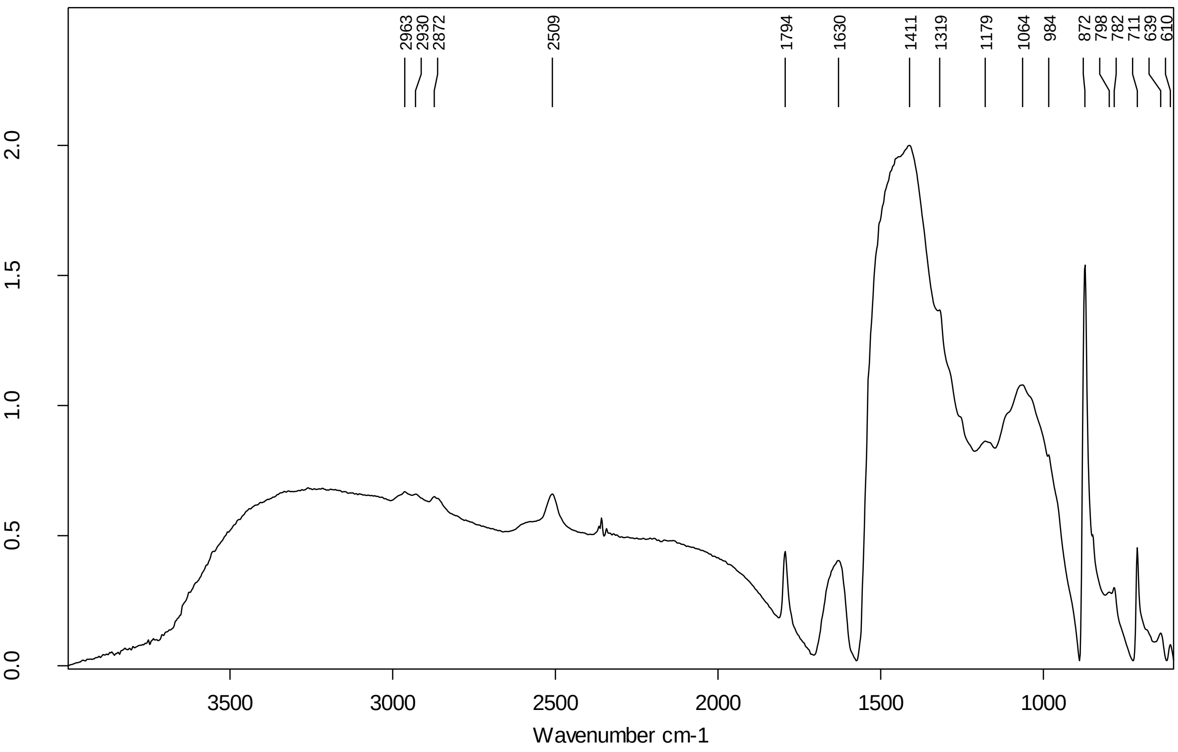
JR14a (red):



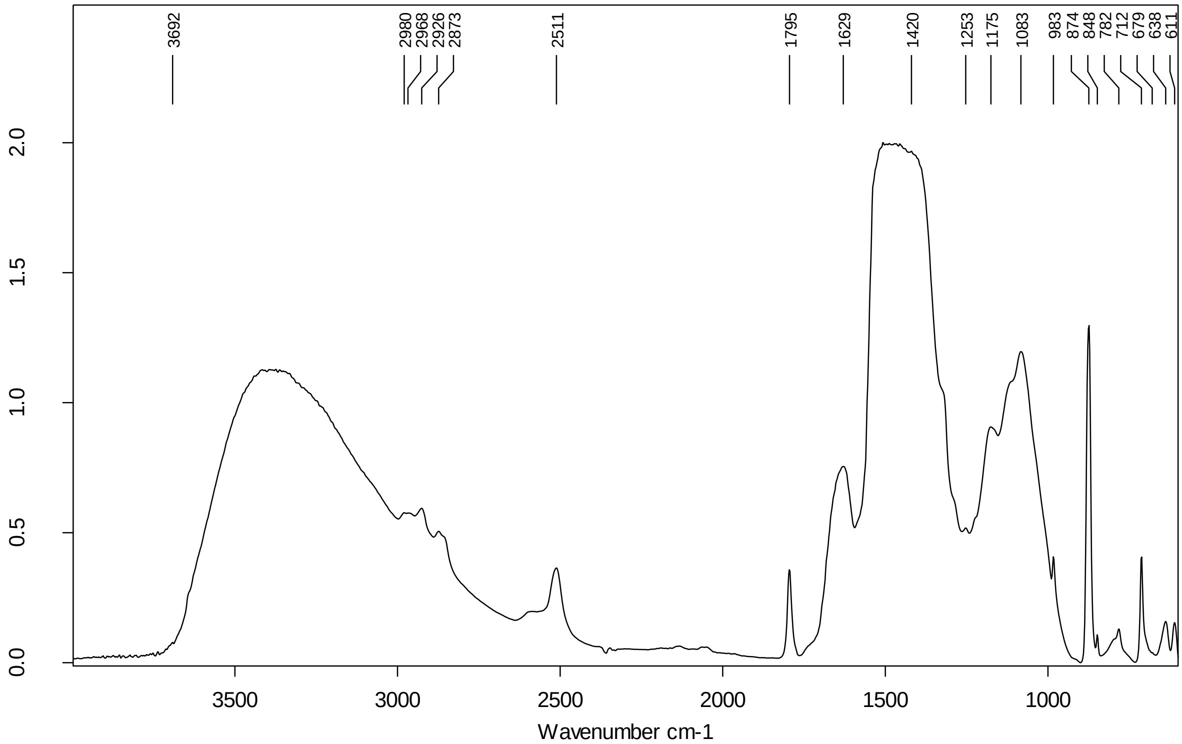
JR14b (green-blue):


3354
2978
2875
2512
1795
1625
1418
1319
1252
1164
1112
1080
983
874
848
782
713
639
611
0.0
0.5
1.0
1.5
2.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

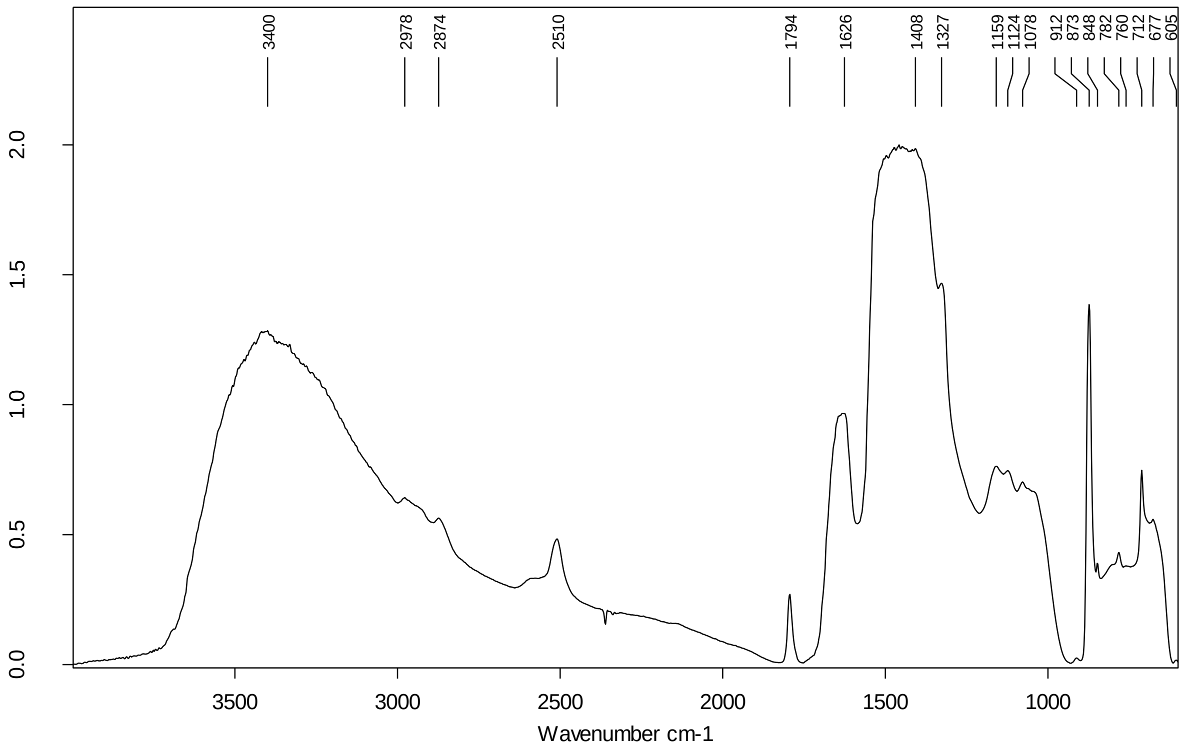
JR15:


2963
2930
2872
2509
1794
1630
1411
1319
1179
1064
984
872
798
782
711
639
610
0.0
0.5
1.0
1.5
2.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

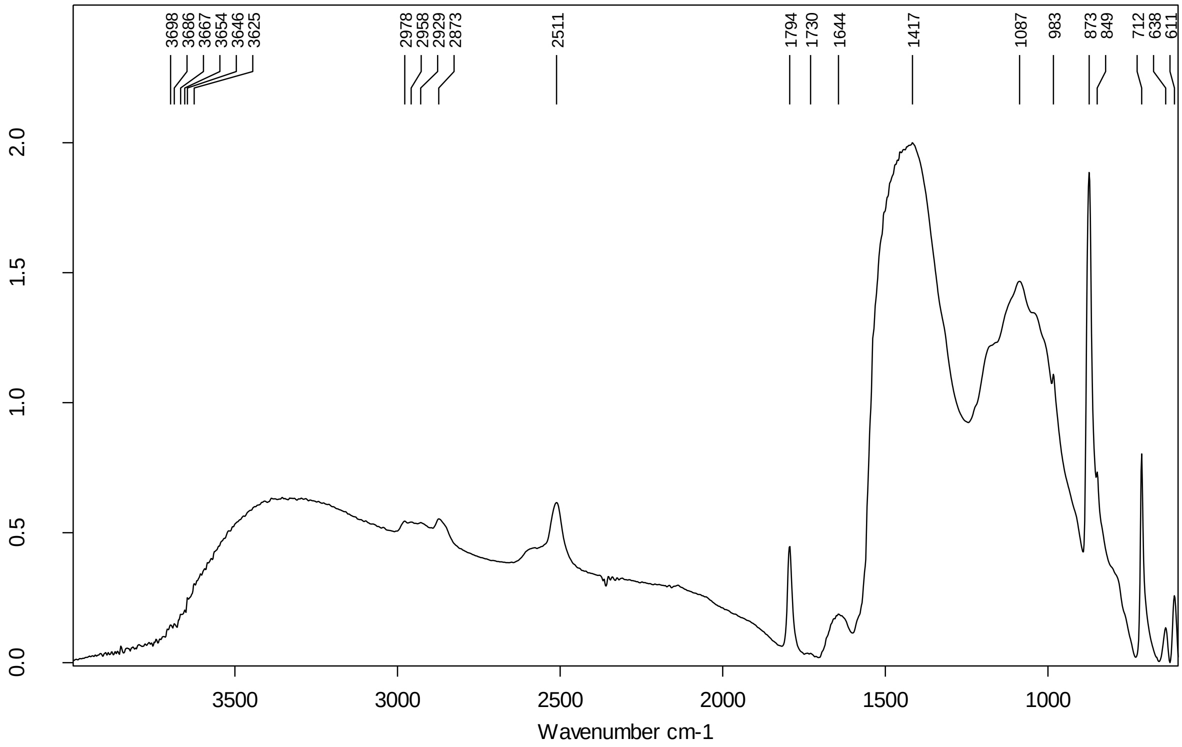
JR17:


3692
2980
2968
2926
2873
2511
1795
1629
1420
1253
1175
1083
983
874
848
782
712
679
638
611
0.0
0.5
1.0
1.5
2.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

JR21:


3400
2978
2874
2510
1794
1626
1408
1327
1159
1124
1078
912
873
848
782
760
712
677
605
0.0
0.5
1.0
1.5
2.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

JR25a:


3698
3686
3667
3654
3646
3625
2978
2958
2929
2873
2511
1794
1730
1644
1417
1087
983
873
849
712
638
611
2.0
1.5
1.0
0.5
0.0
3500
3000
2500
2000
1500
1000
Wavenumber cm-1