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Historical Reconstructions of Raw Materials based on a Blue Smalt coating applied to a seventeenth-century Altarpiece

Dissertação para obtenção do Grau de Mestre em

Conservação e Restauro

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UNIVERSIDADE NOVA DE LISBOA

Dezembro de 2015

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Acknowledgments

Firstly, I would like to thank my supervisor Professor Agnès Le Gac for the opportunity to write this thesis. It wasn't easy to do it, but she stood by my side all the time, not allowing me to give up. I couldn't ask for a better supervisor for this thesis, so I thank her from deep inside my hearth for everything.

I also want to thank to the people in Laboratório Hércules, in Évora, especially to my co-supervisor, Dr. António Candeias, and also to Dr. Luís Dias for the SEM-EDS analysis and to Dr. Ana Margarida Cardoso for the μ-FTIR analysis.

To the people in Instituto Super Técnico, in Lisbon, with a special acknowledgement to Dr. Isabel Nogueira for the SEM-EDS analysis, Dr. Manuel Pereira for the mechanical grinding and sieving of the smalt and also for the X-Ray CT, and to Dr. Pedro Nolasco for the help with the Vickers Indentation Test.

From FCT-UNL, I want to thank to Professor Sara Fragoso for allowing me to conduct experiments in her lab and giving me a place to work (and a friendly shoulder), to professor Leslie Carlyle for all the amazing help with the smalt research, by allowing me to download scientific articles, and for the pressing of the walnut oil, and also to Professor Maria João Melo, for giving me the opportunity to take this master's degree. In Vicarte, I really want to thank to Professor Márcia Vilarigues, Professor António Pires de Matos and Dr. Andreia Machado for all the help in creating the three smalts and for always being available when I had questions and suggestions.

In my personal life, I owe all the support during this thesis to some very important people. First of all, my family - parents, brothers, grandparents – who, even when they were away or sick, didn't stop calling me, giving me strength and encouraging me. I can never thank you enough for this.

From my course, I want say a big thank you for the people on my class, especially to Raquel Fernandes, Leonor Oliveira, Rosa Vidigal, Sara Sá and Gonçalo Paiva for all the conversations and support during these five years. Also to my godfather Nuno Campos, for helping through my way at university.

I also want to say thank you to my best friends Ana Beatriz Luís, Diana Ramos, Diana Mateus, Laura Roque, Inês Leitão, Tomás Brandão, Teresa Cristina and Rodrigo Gama for all the support, the long conversations, the time we spent together and all the laughs.

To the *Liga Steampunk de Lisboa e Províncias Ultramarinas,* especially to Pedro Guerra, David Claudino, Vanda Adão, Tixa Guerreiro, Anna Ildefonso, Filipe Saint and Alexandra Rolo for all the laughs, the amazing events and all of our geeky conversations at dinner. Also to Luís Gregório (Jack) for all the chat conversations while I was analyzing spectrums and writing, that helped me to stay awake.

To Vítor Pinto, from the bar *O Arranca-Corações,* for letting me relax and sometimes work in the bar, while spoiling me with lime mousse and tea.

Last but not least, to my lovely boyfriend Gonçalo Ogando, for being there for me at all times and supporting me even at my worse days.

Thank you!

Abstract

Based on samples cross-sections from the Main Altarpiece of the Coimbra Old Cathedral, where a blue coating performed in 1685 is observed (that was partly covered with a Prussian blue-containing overpaint), the raw materials present in this coating were reproduced and studied.

Blue areas were painted with smalt in oil, according to the contract signed by Manoel da Costa Pereira in 1684 and the analysis by Le Gac in 2009. Based on these, three batches of cobalt-based glasses (S1, S2 and S3) were heated and melted in alumina crucibles in the kiln. S1 contained 6.03 % of cobalt oxide, S2 contained 2.10 %, with the addition of 1.49 % of magnesium oxide, and S3 contained 6.82 % of cobalt oxide, with the addition of 4.63% of antimony trioxide. These batches were ground mechanically with water and manually with different vehicles stated in recipes. The results were studied by means of OM, SEM-EDS, X-Ray CT, Colorimetry and Vickers HT.

Different binders were also produced and analyzed by means of μ-FTIR, in order to perform their characterization and obtain Standard Spectra. Since anhydrite was identified in the ground layers, gypsum from Óbidos was also characterized by XRD.

The main goal of this thesis was to study all the raw materials present in the 1685-blue coating, in order to allow the historically accurate reconstruction of the layers build-up in the next future.

Keywords: smalt, reconstruction, pigment, binder, vehicles

Resumo

Baseado em análises de cortes transversais do Altar-Mor da Sé Velha de Coimbra, onde uma policromia executada em 1685 pode ser observada (que foi parcialmente coberta por uma camada de azul da Prússia), as matérias-primas presentes nesta policromia foram reproduzidas e estudadas.

A policromia foi executada com esmalte em óleo, segundo o contracto assinado por Manoel da Costa Pereira e as análises feitas por Le Gac em 2009. Com base nestas informações, três fornadas de vidro de cobalto (S1, S2 e S3) foram aquecidas e derretidas em cadinhos de alumina no forno. S1 contém 6,03% de óxido de cobalto, S2 contém 2,10%, com a adição de 1,49% de óxido de magnésio, e S3 contém 6,82% de óxido de cobalto, com a adição de 4,63% de trióxido de antimónio. Estas fornadas foram moídas mecanicamente com água e manualmente com diferentes veículos descritos em receitas. Os resultados foram analisados por Microscopia Ótica, SEM-EDS, Tomografia de Raio-X, Colorimetria e Teste de Dureza de Vickers.

Os diferentes ligantes também foram produzidos e analisados por μ-FTIR, para fazer a sua caracterização e obter Espectros Padrão. Como a anidrite foi identificada nas camadas de preparação, gesso de Óbidos foi também caracterizado por Difração de Raios-X.

O objetivo desta tese foi o de estudar todas as matérias-primas presentes na policromia de 1685, de modo a se poder fazer uma reconstrução histórica das camadas no futuro.

Termos-chave: esmalte, reconstrução, pigmento, ligante, veículos

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Symbols and abbreviations

BSE – Backscattered Electrons

μ-FTIR – Micro-Fourier Transform Infrared Spectroscopy

Grind. – Grinding

OM – Optical Microscopy

SEM-EDS – Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy

SM – Stereomicroscopy

Vickers HT – Vickers Hardness Test

μ-CT – X-ray Computed Tomography

XRD – X-Ray Diffraction

1. Introduction

1.1. The blue smalt pigment

Between the 15th and the 17th century, smalt was widely used as a pigment in Europe, for both easel painting and polychrome sculpture [1]. It was mainly used by Venetian glass-makers since the 15th century [2-3] , since painters used superior quality blue pigments such as azurite ($2CuCO_3 \cdot Cu(OH)_2$) and lapis-lazuli ($((Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)_{1-2}$). Those were two main sources for the blue color in that era, who were also very expensive [1, 2, 4]. These pigments became scarce in the 17th century, and smalt was employed as a substitute [2]. Although it was less satisfactory as a pigment, it was also less expensive. Until the discovery of Prussian blue at the beginning of the 18th century, this was the most common blue pigment [1].

The smalt pigment is a moderately finely to coarsely ground potassium glass of blue color, easily recognized at low magnifications. The particles show conchoidal fracture and typical thin sharp edges of glass splinters. Small air bubbles can also be observed within the particles through microscopic observation [2, 4]

The blue color of smalt was obtained by the addition of a cobalt oxide to the potash during the manufacturing. In the Middle-Ages, the main source for cobalt was the mineral smaltite ($[Co,Ni]As_{3-2}$), and in the 17th and 18th centuries the minerals erythrite ($[Co,Ni]_3[AsO_4]_3 \cdot 8H_2O$] and cobaltite (CoAsS) were also employed [1, 2]. In the recipes it is mentioned that the cobalt ore was roasted for purification [1, 5], in order to remove contaminants such as arsenic, which is often found associated with the cobalt ore [6-7], but some artists would skip this step because the arsenic could be used as an opacifier for the smalt particles, making them less transparent and the color more intense [5, 9]. After it was produced in the kiln, while it was still warm, the compound was dropped into water, making the smalt break into a glass frit [4, 8].

The blue color of smalt come from the Co^{2+} ions that are coordinated in a tetrahedral form by oxygen atoms and when the K^+ ions leach from the potash and are replaced by H_2O or H_3O^+ molecules, this tetrahedral coordination can become octahedral and the Co2+ will no longer exhibit specific absorption in the visual range, thus making the blue color of the pigment to fade [7, 9].

Particle size was said to be hugely influential to the final color and smalt was sold in size grades [10-12].

1.2. The Main Altarpiece of the Coimbra Old Cathedral

Produced in 1499-1502, the Main Altarpiece of the Coimbra Old Cathedral, located in Portugal, already comprises five interventions, all registered in historical records. The third intervention, a new polychromy performed in 1685, is registered in a contract signed by the painter Manoel da Costa Pereira [10, 13-14]. It stipulated that the blue areas should be painted with smalt in oil and "burnished", apparently with the view to obtain a polished effect similar to the gilded areas [14]. The blue areas were covered in 1900 by a Prussian blue-containing overpaint, so now the smalt coating can only be observed on samples cross-sections [10-14]. From the contract we can take

some key information regarding the pigment (smalt) and the binder (oil) used for the final effect (burnished) required. More details about the Main Altarpiece studies can be found in chapter VI from the thesis by Le Gac [14].

The main goal for this work was to perform a historically accurate reconstruction of the smalt layer applied in 1685, including the preparation layers and the desired burnished effect, in order to see what was the real color observed at the time and how it was applied, since there are not many recipes that state how to apply the blue smalt pigment to a tridimensional figure.

Fig. 1 – Detail from the Main Altarpiece, where the blue background is visible. ©A. Le Gac

1.3. The importance of historically accurate technical reconstructions

Reconstructions of the artist's techniques from the past has been explored by many scholars to answer specific questions during their research, mainly to investigate how the materials act in different conditions, how they degrade and how to treat or prevent their degradation [15]. Due to modern materials being different from the ones used in the past, it can be hard, but not impossible, to reach an accurate historical reconstruction.

Modern day's raw materials have different properties from the ones used in the past. In the past, these were treated and produced mainly by local artists and artisans, following different recipes left by the artists. Since the Industrial Revolution, most of the raw materials used in art started to be produced and treated industrially, by machines and on a larger scale. For example, before the 18th century, the cobalt ore was bought in the raw by the artists, who would then proceed to purify its blue color to produce the smalt pigment, following specific recipes. After the 18th century, even though smalt was less used in painting, the artist would buy smalt produced industrially.

For these reasons, among other, like the air becoming more polluted with different chemicals throughout the decades, the characteristics of these raw materials have become different. So, it was important to make sure that the materials used for this thesis were historically accurate, by reading articles and studying old recipes, and also to analyze and characterize every material used.

2. Experimental design

2.1. Sources

2.1.1. *Case-Study:* The Main Altarpiece

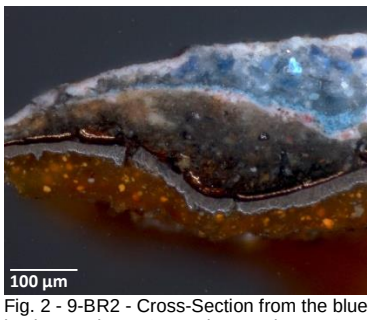


Fig. 2 - 9-BR2 - Cross-Section from the blue background – OM micrograph x110 – interferential contrast – scale bar: 100 µm. ©A. Le Gac

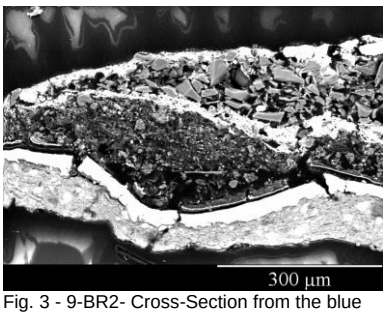


Fig. 3 - 9-BR2- Cross-Section from the blue background – SEM record (BSE) – x150, 25 kV – scale bar: 300 µm. ©A. Le Gac

Analyses performed by means of OM revealed smalt particles with an average size of 20-45 µm (<5-63 µm>), with the typical conchoidal fracture and colors ranging from a dark cobalt blue to a light blue, mixed with colorless particles [10, 14].

As for the chemical constitution, the results obtained by SEM-EDS showed the presence of the following elements, in weight percentage: SiO_2 (61.9-89.0w%), K_2O (0.4-18.2w%), CoO (1.8-9.9w%), As_2O_5 (0.4-7.5w%) and Fe_2O_3 (1.1-11.9w%), with some traces of Al_2O_3 (1.1-15.8w%), MgO (1.5-7.1w%), CaO (0.4-3.6w%), PbO (2.7-37.6w%) and Bi_2O_3 (>2.0w%). It was verified that the blue particles with the higher amount of Co have the darkest hue [10, 14]. The presence of arsenic oxide (As_2O_5) and bismuth oxide (Bi_2O_3) as contaminants seems to originate from the cobalt ore used in the pigment synthesis, although, as it was mentioned before, it could be intentionally used as an opacifier [5], which would explain the higher amounts of As_2O_5 in some particles. PbO is believed to originate from the preparation layers laying under the smalt layer, which have lead white in their constitution, and may also be assumed as a form of contamination. The Al_2O_3 would probably come from the alumina crucibles used to place the smalt composition in the kiln. These impurities are known to influence the chemical stability, shade and intensity of the blue color, also depending on the binding medium employed [1, 10, 14].

As for binders, micro-chemical tests carried out on the samples cross-sections showed the presence of a mixture of both proteinaceous (e.g. animal glue) and oil binding media [14].

The ground layer is mainly composed of Anhydrite. Regarding the layers over which the smalt coating was applied, two superimposed underlayers were found: one of a pink color, the coloring matter of which was not already identified; and a second one of a light blue color, likely made with a mixture of Indigo ($C_{16}H_{10}N_2O_2$) and Lead White ($2PbCO_3 \cdot Pb(OH)_2$) bound with oil [10, 14].

This information was of major importance for the reconstruction of 1685-the blue coating.

2.1.2. Historical recipes

In addition to a compilation of historical recipes from Portugal, recipes from other countries of Europe were also collected, mainly from Italy and Germany. Although the Altarpiece was produced in Portugal, it was important to know how the blue smalt pigment was produced and applied, considering that knowledge would often come from other countries [16].

Taking into account that the date of application of the blue smalt pigment to the Main Altarpiece was known – 1685 - recipes from the same time period were obviously considered. However, a research for recipes from before and after 17th century was also done, since some of the knowledge from the painters could come from earlier manuscripts/treatises, and also because later artists would sometimes register the knowledge that they learnt from their predecessors – so, a treatise dated from the 18th and 19th century could contain knowledge from the 16th and 17th centuries [16]. According to the book of recipes, treatises and more recent sources consulted, the recipes found were divided into four tables:

1) Recipes containing references to the cobalt ore [1, 4, 17-18] (Table A.13 in Appendix II.2);
2) Recipes for producing the smalt pigment [1, 4, 17- 18] (Table A.14 in Appendix II.2);
3) Recipes for maintaining the blue color of smalt during the grinding process [17, 19] (Table A.15 in Appendix II.2);
4) Recipes for obtaining the smalt blue paint [1, 10, 13-14, 18, 20] (Table A.16 in the Appendix II.2).

Based on the investigation by Le Gac [14] and Hommes [18], the different media recommended for binding the smalt pigment were also compiled, in order to better determine the binder used for the 1685-smalt coating and to achieve the desired burnished effect (Table A.4 in Appendix II.2 and Appendix II.3)

As for vegetable oils, it was found that linseed, walnut, lavender and poppy oil were used in the past [14, 18], with the first two being the most indicated for smalt and other blue pigments. For glues, references were found to gloves glue [14, 21]. The recipes can be found in Appendix II.3.

The oils and glues marketed at present are produced industrially and do not have the same characteristics as the ones produced in the 17th century. It was necessary to produce new binders, following old recipes and using biologically produced materials. Walnut oil was cold pressed. Animal glue was also produced from edible gelatin of an animal origin, produced industrially. Gloves glue was made by following the recipe from Filipe Nunes (1615) and using a tawed leather produced in Portugal from a sheep skin, based on the work carried out by Le Gac on the Bolognese Manuscript recommendations and on subsequent technical sources [14, 21].

To obtain the desired burnished effect, hypothesis were studied on the basis of the issues rose by Le Gac [10]: water mixed with glue, like fish glue, based on recipes by Helmreich (1574), Van Dyck (1632) and Symmons (1649-1651) [12]; “untreated oil” or “floating oil”, based on a recipe by De Mayerne referenced by Hommes [18] in which smalt mixed with untreated linseed oil would gather and “deposit”, creating a floating oil layer which would create a shining “layer

similar to glass"; and "Vernix", referred in several recipes by De Mayerne (1620-1640), Latombe (1620-1649) and Portman (1620-1640) in the De Mayerne manuscript, compiled by Le Gac [14], quoted in Table A.16 (Appendix II.2). The so called "Vernix" could be a mixture of different ingredients, for example Aspic or Oil of turpentine and Sandarac, according to Pacheco [14]. It is supposed to give a final "shiny" appearance to the paint layer.

While the treatises and recipes are dated, their content must be analyzed carefully. For example, the smalt recipes in the manuscript *A far littere de oro*, were mistakenly attributed to Savonarola, and since this discovery the recipes are credited to a "Pseudo-Savonarola" author [1]. Also, in the article by Rica Jones, it is explained that most of the information contained in the De Mayerne Manuscript was obtained by oral interviews that he made to the artists, and "most of the topics of conversation are instigated by De Mayerne, not by the artist or craftsman, and that the material under discussion is not necessarily one used by that artist" [22]. Since recipes in treatises were compiled by authors, and few records of painting techniques were published before the mid-eighteenth century, with some of the recipes being translations from Latin or Italian from earlier painters [16], all the treatises should be read carefully, as the information being passed majorly in "secrecy" and orally could have gotten some changes throughout over time.

2.2. Smalt production

The elements obtained by SEM-EDS analysis from the samples cross-section of the altarpiece were converted into oxides, since every glass is composed by silicon-oxide connections, and the metal oxides are known to give color to the glass. Special attention was given to the cobalt oxide, which is responsible for the blue color of the smalt pigment.

The average amount of cobalt oxide present in the particles is about 4.46%, since this oxide is ranging from 2% to 6% in most particles. Among 20 particles, 9 have values of about 2% and 8 have values of about 6% [14]. From these results, three well-represented particles were chosen as a basis for the production of three different batches designed as S1, S2 and S3.

Smalt 1 (S1) – Addition of 6.03 % of CoO, along with 82.71% of SiO_2, 6.35% of K_2O and 4.90% of Fe_2O_3.

Smalt 2 (S2) – Addition of 2.10% of CoO, along with 77.05% of SiO_2, 15.76% of K_2O and 2.43% of Fe_2O_3. Besides these oxides, common to S1, 1.49% of MgO was added, which was present in some of the particles (among 24 particles, 4 put in evidence the presence of MgO) and always associated to a 2% quantity of cobalt oxide.

Smalt 3 (S3) – In this smalt, As_2O_5, was supposed to be part of the constituents since this oxide is present in several particles in a significant quantity (between 0.4% and 7.5%, in an average of 4.21%). It was important that this smalt, produced after S1 and S2, would have characteristics that would allow a direct comparison between the batches of smalt. Since S2 contains MgO, and in none of the particles MgO appears at the same time as As_2O_5, the composition chosen to be the basis for smalt S3 could allow a direct comparison with smal 1. Since As_2O_5 is highly toxic, and the main interest was to evaluate whether this oxide would alter the smalt characteristics

(less bubbles, more opacification, etc), antimonium (III) trioxide (Sb_2O_3) was used. It is a modern substitute for arsenic, which is known to have the same influence on the final glass properties (opacity and as a fining agent for glass) and to be less toxic [8, 23]. So, this batch of smalt contains 6.82% of CoO, along with 72.06% of SiO_2, 11.20% of K_2O and 5.31% of Fe_2O_3 and the addition of 4.63% of Sb_2O_3, a value closer to the average amount of As_2O_5 present in the particles.

The raw materials were mixed into a red powder (the color being due to iron in the composition) and placed in alumina crucibles. For the batches of smalt S1 and S2, the crucibles were positioned in the kiln for 10 hours at a temperature of 1.400º C. For S3, the crucible was positioned in the kiln for 6 hours at a temperature of 1.400 ºC (due to being produced later and to lack of time). After that time, the crucibles were removed from the kiln and, while it was still warm, the crucibles were dropped into a container with cold distilled water, in order to break it and obtain a blue glass frit [4].

The kiln had several impurities which could influence the final smalt. Some particles with contamination were found and later analyzed.

The size of the particles of smalt is a matter of interest because it was known that the size of the smalt pigment would influence the final color [10-12]. For this characteristic to match that of the smalt particles found in the Coimbra Main Altarpiece, and test grinding recipes, both manual and mechanical grinding were carried out on the batches of smalt, with different vehicles.

After the mechanical grinding was performed with water, in a Retsch Mortar Grinder at the speed of 50 Hz, smalt was place in several sieves, with the following openings: 63µm, 45µm and 25µm. An additional size, called Ultra-Fine, was added, since some smalt particles were so small that they did not decant and continued to float in water. This was made in order to separate the smalt particles by sizes and grades of color, as it was made in the past, and analyze the influence of the smalt particle size on the final color.

The manual grinding was performed with distilled water, milk alone and a mixture of egg-yolk and honey. It was important that the egg-yolk, honey and milk came from biological sources, in order to have a more accurate reconstruction of the materials – since the vehicles used in the past were from biological production. Recipes stated that these vehicles would prevent the smalt blue color to fade [10-12].

> ***MS2265 (14th century) [19]***
>
> *How to pulverize blue smalt so that it can [be] painted without losing its color. Take the smalt and finely pulverize it and then grind it on a porphyry slab with egg yolk together with a small amount of honey. Grind it finely as you know it and when it dries add a little water. And when it is ground then wash the honey and egg yolk out with water and it will remain a beautiful color.*

Pseudo-Savonarola (1535), Smalt with a beautiful color [17]

Take smalt and grind it with milk and when it is well ground wash it with water and let the coarse [particles] sink to the ground. When the water is cloudy pour it into another vessel and let it sink to the ground and do this repeatedly. Do not make more than three grades [smalt], each more beautiful than the last.

When ground with milk alone and the mixture of egg-yolk and honey, the smalt particles were washed with distilled water (a minerals and microorganisms water free, hence a cleaner water than tap water). Each lot was washed 7 times, in order to obtain a clear water once the smalt precipitate has settled. It was interesting to notice that, in the case of smalt ground with milk, the first water would always become cloudy; and in the case of smalt ground with the mixture of egg-yolk and honey, the first water would come out green, since the light in the yellow color of the egg-yolk used as a vehicle and present in the blue smalt surface reflected as green, only then it would become cloudy until it is completely clean.

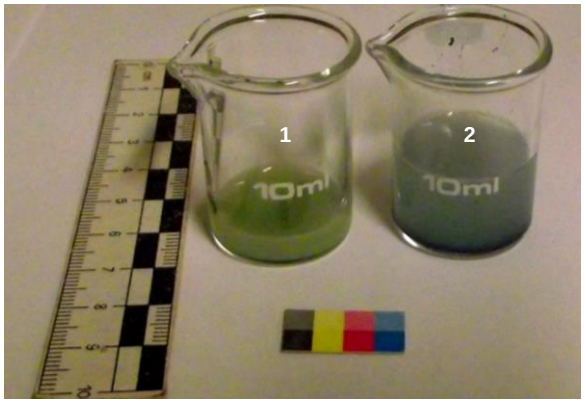


Fig. 4 – Washing of the smalt ground with the mixture of egg-yolk and honey: first water (**1)** came out green, and the next water (**2**) comes out cloudy.

2.3. Protocols

The particles were studied by means of OM, SEM-EDS, Colorimetry, Vickers HT and X-Ray CT.

2.3.1. Optical Microscopy (OM)

OM was used in the different stages of the smalt production, in order to evaluate the particles as for their shape, size, color, fracture and the presence of visible bubbles. Cross-polarization illumination, where the sample contrast comes from the rotation of polarized light through the sample, was not used because glass materials, such as smalt, are isotropic and simply preserve the polarization of a wave but do not differentiate between polarization states [23].

It was important to observe whether if the amount of cobalt oxide in the raw material would have any influence on the final color of the smalt and also on its opacity. The opacity was important since it defines the impenetrability to radiation, in this case, visible light. When light strikes the smalt interface, the light is reflected, refracted and transmitted, since it is

a glass. So, the main goal was to verify if a higher amount of cobalt oxide would make the smalt more or less opaque, by observing the smalt in both incident and transmitted light.

Ultra-violet light was not used because a smalt, being a glass, even if transparent will always be opaque in UV-light, since glass passes about 90% of the light above 350 nm, but blocks over 90% of the light below 300 nm (and UV is from 10 to 400 nm) [24].

2.3.2. SEM-EDS

SEM imaging allows to obtain records of a higher resolution from the smalt particles, because of the small diameter of the primary electron beam. BSE records give a greatest amount of information and are “reflected” from the atoms in the solid, producing a readily interpretable image of the surface. The contrast is determined by the atomic number of the elements in the sample, so the final image will show the distribution of different chemical phases in the sample [25].

The interaction of the primary beam with the atoms in the sample causes the emission of an X-ray, which has an energy characteristic of the parent element. EDS detects and measures the energy and can provide quantitative analysis of elemental composition. The X-rays can also be used for elemental mapping in order to show the elemental distribution in a sample.

2.3.3. X-Ray Computed Tomography (µ-CT)

X-Ray CT makes use of computer-processed combinations of several X-Ray images taken from different angles to obtain a tomographic image of specific areas of a scanned object. Digital geometry processing is used to generate a three-dimensional image of the object and its inside from several two-dimensional radiographic images taken around a single axis of rotation, making it possible to see inside of the object without cutting [26].

This technique was used to see the inside of some particles from the three batches of smalt, in order to evaluate the presence of bubbles.

2.3.4. Colorimetry

Colorimetry is the science and technology used to quantify and describe physically the human color perception [27]. The measurements were made using the CIELAB Color Space (*L*a*b** model), which describes all the colors visible to the human eye. It has three coordinates that can be arranged in a three-dimensional model. The *L** stands for the lightness of color, with the value 0 for black and 100 for diffuse light, the *a** stands for the positon between red and green, negative values indicating green and positive values indicating red, and *b** stands for the position between yellow and blue, negative values indicating blue and positive values indicating yellow. This technique was

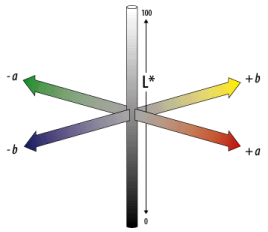


Fig. 5 - Three-dimensional CIELAB color space

used in order to have a correct quantification of the blue color after the different grindings processes were performed.

2.3.5. Vickers Hardness test (Vickers HT)

The Vickers HT measures the hardness of a material in Vickers Pyramid Number (HV) [28], which can be converted to GigaPascal (GPa) by multiplying the HV value by 0.009807 [29]. The indentation is made by pyramidal diamond indenter, which produces a pyramidal shape in the sample and, by measuring the diagonals, allows to obtain the HV value.

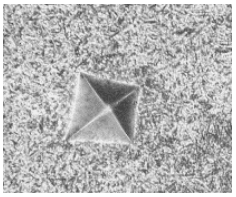


Fig. 6 - Pyramid shape made by the indenter

This technique was used to obtain a value of hardness for each smalt, because S2 revealed to be much harder to grind than S1 and S3 - when grinding this smalt, a higher strength was required. Six particles were selected from each smalt and three indentations were made in each particle. An average value was obtained from the three indentations, later converted for GPa.

2.3.6. X-Ray Diffraction (XRD)

XRD consists in X-Rays that diffuse in just one space direction, without altering its wavelength. This was used to characterize anhydrite in several stages of production, based on a gypsum from Óbidos, Portugal, the area from where the anhydrite present in the preparation layers from the Main Altarpiece might have been sourced.

2.4. Binder production

Based on the importance of using the most accurate raw materials, a walnut oil and gloves glue binders were produced. Along with other binders and vehicles, gloves glue was analyzed by means of µ-FTIR. Because the walnut oil had little time to decant, and subsequently dry, it was not possible to do carry out the µ-FTIR analysis.

2.4.1. Walnut oil

This experiment was carried out in order to produce walnut oil that could be used in a further historically accurate reconstructions of the 1685 smalt coating of the Main Altarpiece, taking into account that modern industrial oils are expected to have distinct characteristics comparing to the ones used in the past. Most of the recipes that were found indicated walnut oil as the best binding medium for blue pigments such as smalt [14].

There was a concern in using walnuts produced biologically, without any fertilizers or pesticides. Walnut meats were pressed at room temperature, by using a mechanical method

only, with no chemical treatment, in order to obtain an extra virgin walnut oil. The unit SIMPLEX from the HART project was used for this purpose, with the collaboration of Dr. Leslie Carlyle. Two Lots were produced, one with walnuts ground for 15 seconds and another with walnuts ground for 10 seconds. The description of the experimental process can be found in Appendix III.1.

2.4.2. Gloves glue

The recommendations from the Bolognese manuscript [31] were crucial to produce historically accurate tawed leather, and afterwards, to produce gloves glue as well [21], which is a glue indicated for preparation layers. The recipes chosen were found in treatises by Felipe Nunes (1615) and Pacheco (1649), as shown below [21, 31-33].

> ***Felipe Nunes (1615), Cola de Pele de Luvas [32]***
>
> *You will use glue made of baldreu, which is leather from which gloves are made; clippings of gloves are to be perfectly cooked; the water that remains after they are dissolved is the glue itself; it cannot be too strong; apply two layers over the panel with it; when it [the glue] is dry, take ground gesso and with the glue, make a wash or watercolor and apply another layer. When it is dry, apply another layer containing more gesso.*
>
> ***Pacheco (1649), Cola o engrudo de tajadas [33]***
>
> *Glue used to distemper these colors [glue tempera] was made on a very common way: cheap cuts glue were soaked in water, when turned soft, they were boiled adding enough water so that the glue was neither strong nor weak. Glue made of cooked and filtered gloves clippings may also be employed but it gives some trouble.*

A tawed leather made from sheep skin was used. 43.70 g of leather clippings were soaked for 24 hours in distilled water until the clippings became curled, weighing 110.49 g. After this, the skin clippings were boiled, with the same distilled water at a concentration of 23%, at 100ºC for 4 hours and left to dry for 3 days at the temperature and relative humidity present in the lab, without ventilation and without a natural source of light. Since the first experiment resulted in a dark-brown glue, and what was expected was a lighter-brown glue, a new experiment was made. 12.32 g of leather clippings were soaked in distilled water, weighing 29.80 g. This time, the glue was boiled in the same distilled water at a concentration of 23%, but at a temperature of 65 ºC, and was left to dry for 3 days at the temperature and relative humidity present in the lab, without ventilation and without a natural source of light. This resulted in a lighter-brown glue, still far from what was expected.

A more detailed description of the process can be found in Appendix III.2.

This was produced and studied to be used in a future reconstruction of the preparation layers from the Main Altarpiece.

3. Results and Discussion

3.1. Optical Microscopy (OM)

After the smalt was produced, well representative particles from the raw material were selected and recorded by OM in both incident and transmitted light, except for S3, which was only photographed in incident light.

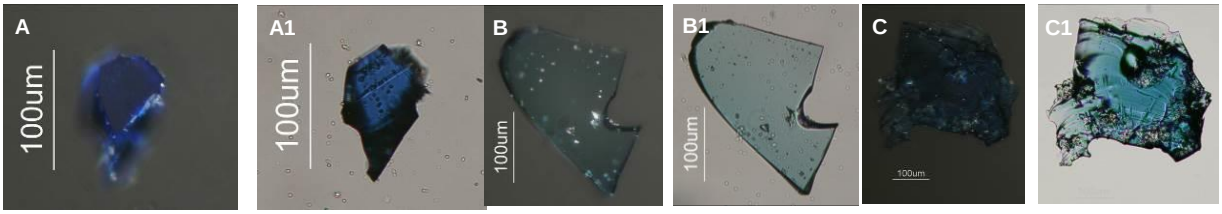


Fig. 7 – Raw smalt 1 (after it came from the kiln, before grinding) - OM micrograph x20 – interferential contrast – scale bar: 100 µm – **A)** Smalt particle of a darker color; **A1)** Smalt particle of a darker color in transmitted light; **B)** Smalt particle of a lighter color; **B1)** Smalt particle of a lighter color in transmitted light; **C)** Smalt particle where the presence of bubbles can be observed; **C1)** Smalt particle where the presence of bubbles can be observed in transmitted light..

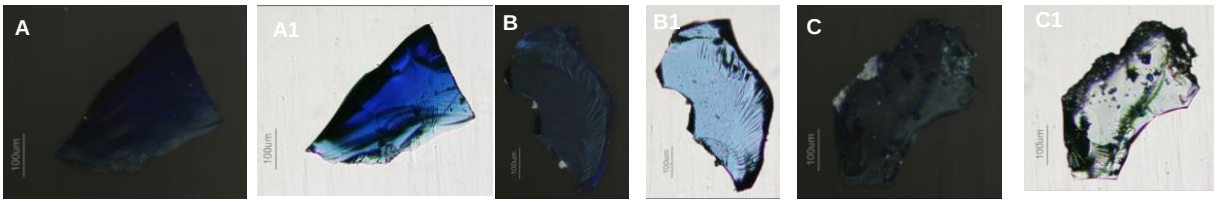


Fig. 8 – Raw smalt 2 rawhide (after it came from the kiln, before grinding) - OM micrograph x20 – interferential contrast – scale bar: 100 µm – **A)** Smalt particle of a darker color; **A1)** Smalt particle of a darker color in transmitted light; **B)** Smalt particle of a lighter color; **B1)** Smalt particle of a lighter color in transmitted light; **C)** Smalt particle where the presence of bubbles can be observed; **C1)** Smalt particle where the presence of bubbles can be observed in transmitted light.

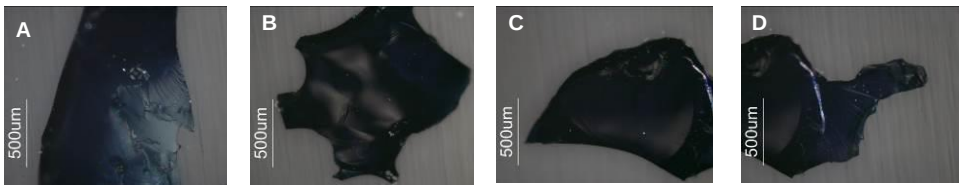


Fig. 9 – Raw Smalt 3 rawhide (after it came from the kiln, before grinding) - OM micrograph x5 – interferential contrast – scale bar: 500 µm – **A)** Smalt particle of a darker color, with some lighter areas; **B)** Dark blue smalt particle; **C)** Dark blue smalt particle; **D)** Smalt particle of a darker color with a lighter area.

The raw smalt particles showed different colorations and opacities. In S1, the particle that has a darker shade of blue showed to be more opaque, meaning less light passes through it, and the lighter particles appeared to be more transparent in transmitted light. In some particles, it was also possible to see the presence of bubbles. In S2, the particles showed the same results as the particles from S1. In S3, the particles, besides being of a much bigger size, showed to be more opaque and dark, even though it had the same amount of cobalt oxide as S1. Since antimony trioxide was used as an alternative to arsenic oxide, and this was used in the past as an opacifier [5, 9], the presence of this oxide may be the reason for this smalt darkness. The transmitted light images showed the particles to be dark and opaque, but because of a computer problem, these images were lost. New images should be done again soon.

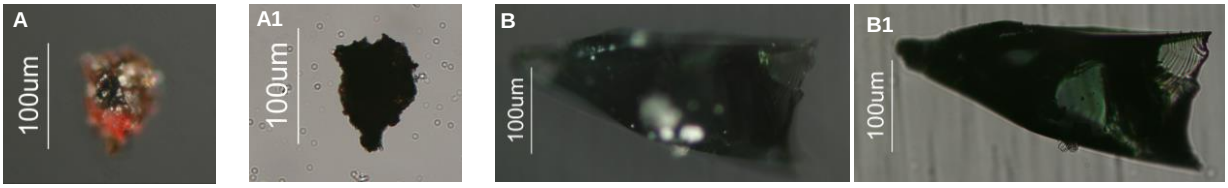


Fig. 10 – Different particles found in the raw smalt material - OM micrograph x20 – interferential contrast – scale bar: 100 µm – **A)** Contamination particle; **A1)** Contamination particle in transmitted light; B**)** Green smalt particle; **B1)** Green smalt particle in transmitted light.

A small particle, opaque and of brownish and red color, was found among the particles of S1. This could be a particle that was in the kiln and contaminated the smalt glass. Also, some dark green particles were found among the particles of S2. This is a result from the reduction of the iron oxide (II), present in the original raw constitution, that occurs in the kiln [34].

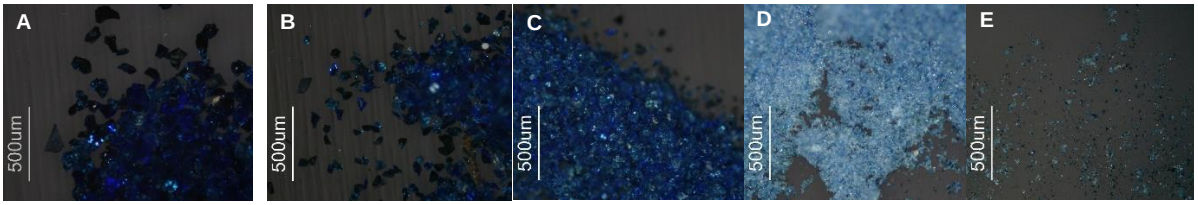


Fig. 11 – Mechanical grinding of Smalt 1- OM micrograph x50 – interferential contrast – scale bar: 500 µm – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine.

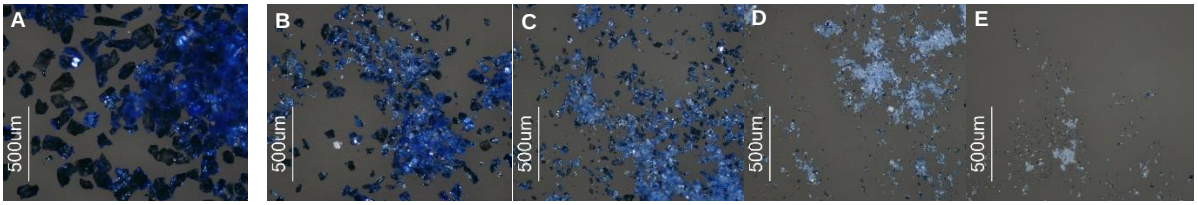


Fig. 12 - Mechanical grinding of Smalt 2- OM micrograph x50 – interferential contrast – scale bar: 500 µm – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine.

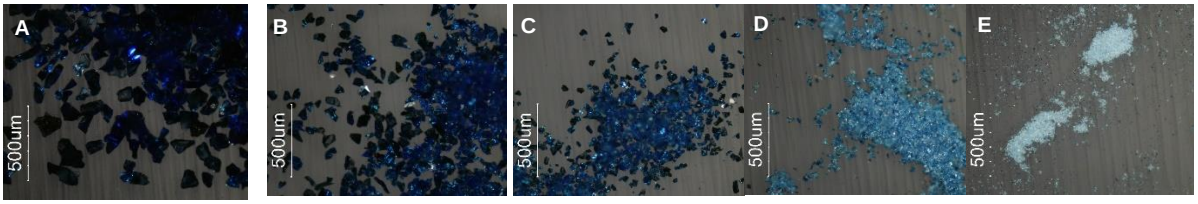


Fig. 13 - Mechanical grinding of Smalt 3- OM micrograph x50 – interferential contrast – scale bar: 500 µm – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine.

Records of the mechanical ground smalt obtained by OM imaging with Filter 3 showed clearly that there is a relation between the smalt particles size and the intensity of the blue color – as the particles get smaller, the blue color of the smalt particles starts to fade.

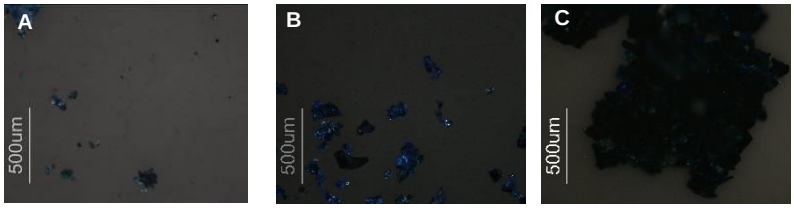


Fig. 14 – Manual grinding with a mixture of egg-yolk and honey - OM micrograph x50 – interferential contrast – scale bar: 500 µm – **A)** Smalt 1 ; **B)** Smalt 2; **C)** Smalt 3.

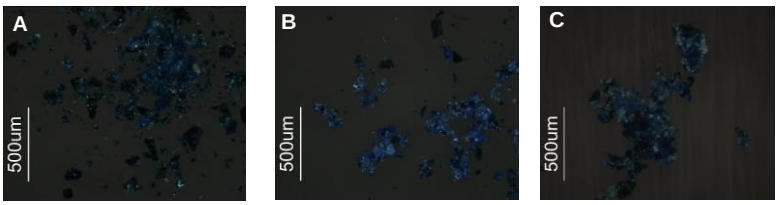


Fig. 15 - Manual grinding with milk - OM micrograph x50 – interferential contrast – scale bar: 500 µm – **A)** Smalt 1 ; **B)** Smalt 2; **C)** Smalt 3

At a first observation, smalt particles ground with a mixture of egg-yolk and honey and milk alone seem to be of a darker blue color. The smalt particles were studied by colorimetry.

3.2. SEM-EDS

Table 1 – Raw smalt 1 particles

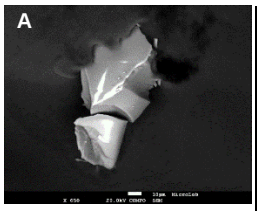
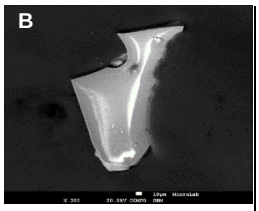
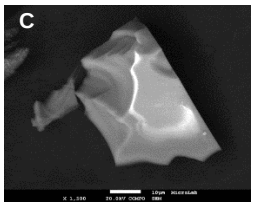
Smalt sample			
Analytical Parameters	x650 Scale bar: 10µm 20.0 kV - BSE	x650 Scale bar: 10µm 20.0 kV - BSE	x1500 Scale bar: 10µm 20.0 kV - BSE
Chemical composition (wt%)	Si 75.41 K 12.90 Fe 4.62 Co 6.11 Al 0.95	Si 77.80 K 9.91 Fe 6.18 Co 5.14 Al 0.98	Si 72.15 K 14.25 Fe 5.46 Co 7.35 Al 0.78

Table 2 – Raw smalt 2 particles

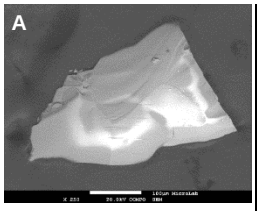
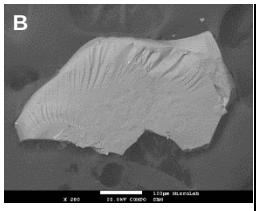
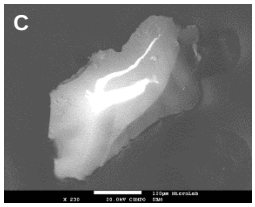
Smalt sample			
Analytical Parameters	x250 Scale bar: 100µm 20.0 kV - BSE	x200 Scale bar: 100µm 20.0 kV - BSE	x230 Scale bar: 100µm 20.0 kV - BSE
Chemical composition (wt%)	Si 66.72 K 19.97 Fe 2.00 Co 8.53 Al 1.33 Mg 1.46	Si 55.22 K 28.74 Fe 1.90 Co 1.43 Al 12.20 Mg 0.75	Si 46.34 K 10.94 Fe 0.84 Co 1.17 Al 32.48 Ca 5.75 Mg 1.62 Na 2.19

Table 3 – Raw smalt 3 particles

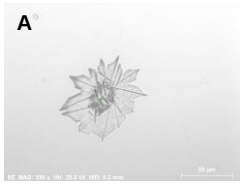
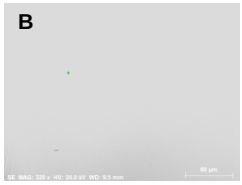
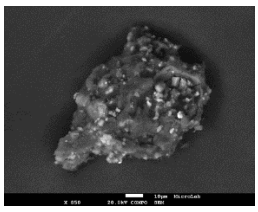
Smalt sample			
Analytical Parameters	x550 Scale bar: 50µm 20.0 kV - SE	x320 Scale bar: 80µm 20.0 kV - SE	x500 Scale bar: 50µm 20.0 kV - SE
Chemical composition (wt%)	Si 68.40 K 9.65 Fe 4.34 Co 10.77 Al 1.51 Sb 5.33	Si 58.05 K 12.79 Fe 9.36 Co 10.33 Al 1.53 Sb 7.97	Si 59.64 K 12.92 Fe 4.99 Co 12.14 Al 1.94 Sb 8.36

Table 4 – Contamination particle found in smalt 1

Smalt sample	
Analytical Parameters	x850 Scale bar: 10µm 20.0 kV - BSE
Chemical composition (wt%)	Si 23.13 K 2.97 Fe 8.68 Al 2.91 Pb 26.41 S 12.17 Ca 37.60 Mg 1.97 Cr 1.88 Br 17.51 Ba 8.48 Na 2.08

The contamination particle showed several elements that were not present in the original mixture for producing the smalt raw material, so it probably came from an older contamination present in the kiln. The green particle, glued to the carbon tape used for the analysis, got lost in the transport from the university to the SEM-EDS.

Table 5 – Smalt 1 particles after mechanical grinding – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine

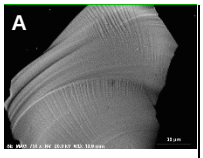
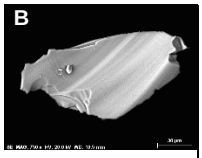
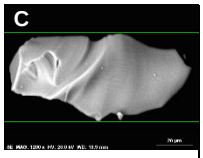
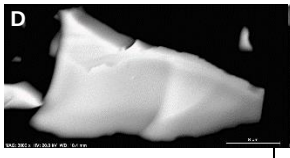
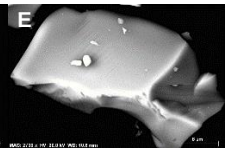
Smalt sample					
Analytical Parameters	x750 Scale bar: 30µm 20.0 kV - BSE	x750 Scale bar: 30µm 20.0 kV - BSE	x1200 Scale bar: 20µm 20.0 kV - BSE	x3000 Scale bar: 8µm 20.0 kV - BSE	x2700 Scale bar: 8µm 20.0 kV - BSE
Chemical composition (wt%)	Si 68.56 K 16.12 Fe 5.31 Co 7.73 Al 0.98 Cu 0.34	Si 68.49 K 13.75 Fe 7.77 Co 8.67 Al 1.19 Cu 0.12	Si 66.40 K 19.17 Fe 5.82 Co 7.37 Al 1.24	Si 65.34 K 11.75 Fe 10.55 Co 10.88 Al 1.01 Cu 0.47	Si 68.22 K 17.28 Fe 6.75 Co 6.29 Al 1.47

Table 6 - Smalt 2 particles after mechanical grinding – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine

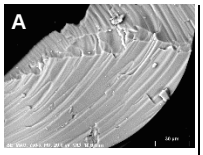
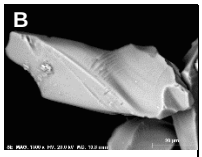
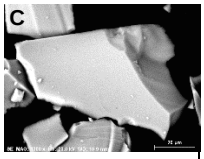
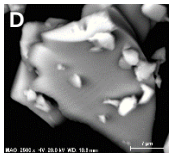
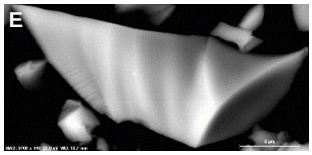
Smalt sample					
Analytical Parameters	x750 Scale bar: 30µm 20.0 kV - BSE	x1300 Scale bar: 20µm 20.0 kV - BSE	x1300 Scale bar: 20µm 20.0 kV - BSE	x2500 Scale bar: 7µm 20.0 kV - BSE	x3700 Scale bar: 6µm 20.0 kV - BSE
Chemical composition (wt%)	Si 64.36 K 26.91 Fe 3.05 Co 2.67 Al 1.02 Cu 0.26 Mg 1.73	Si 63.66 K 27.65 Fe 2.87 Co 2.47 Al 1.20 Cu 0.17 Mg 1.98	Si 62.89 K 28.29 Fe 3.12 Co 2.67 Al 1.06 Cu 0.35 Mg 1.62	Si 62.73 K 28.05 Fe 3.13 Co 2.72 Al 1.17 Cu 0.56 Mg 1.65	Si 59.37 K 28.85 Fe 3.22 Co 5.54 Al 1.74

Table 7 - Smalt 3 particles after mechanical grinding – **A)** After grinding; **B)** Sieve opening: 63 µm; **C)** Sieve opening: 45 µm; **D)** Sieve opening: 25 µm; **E)** Sieve opening: ultra-fine

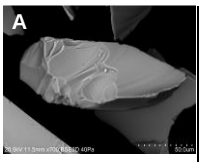
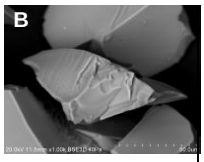
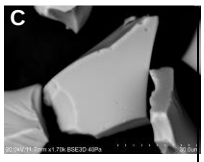
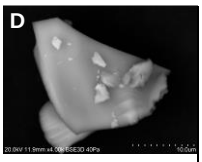
Smalt sample	A 	B 	C 	D 	E 
Analytical Parameters	x700 Scale bar: 50µm 20.0 kV - BSE	x1000 Scale bar: 50µm 20.0 kV - BSE	x1700 Scale bar: 30µm 20.0 kV - BSE	x4000 Scale bar: 10µm 20.0 kV - BSE	x7000 Scale bar: 5µm 20.0 kV - BSE
Chemical composition (wt%)	Si 57.17 K 13.89 Fe 6.11 Co 12.49 Al 2.27 Sb 8.07 Na 0.51	Si 60.95 K 6.88 Fe 2.81 Co 10.30 Al 2.26 Sb 7.95 Na 0.94	Si 60.94 K 13.39 Fe 4.40 Co 9.78 Al 2.31 Sb 7.54 Na 1.63	Si 31.19 K 6.15 Fe 4.79 Co 10.36 Al 2.11 Sb 6.98 Na 1.26	Si 58.35 K 14.00 Fe 5.40 Co 11.34 Al 2.54 Sb 6.79 Na 1.57

Table 8 - Manual grinding with a mixture of egg-yolk and honey – **A)** Smalt 1; **B)** Smalt 2; **C)** Smalt 3

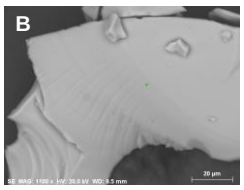
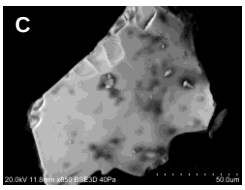
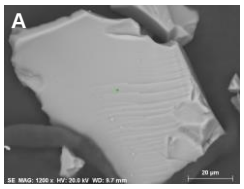
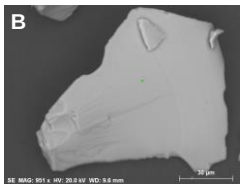
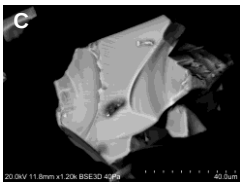
Smalt sample	A 	B 	C 
Analytical Parameters	x1894 Scale bar: 10µm 20.0 kV - SE	x1100 Scale bar: 20µm 20.0 kV - SE	x850 Scale bar: 50µm 20.0 kV - BSE
Chemical composition (wt%)	Si 55.72 K 8.67 Fe 13.60 Co 22.20	Si 58.77 K 31.38 Fe 4.67 Co 3.87 Al 0.50 Mg 0.81	Si 56.48 K 12.92 Fe 6.00 Co 13.39 Al 2.16 Sb 8.87 Na 0.19

Table 9 - Manual grinding with milk – **A)** Smalt 1; **B)** Smalt 2; **C)** Smalt 3

Smalt sample	A 	B 	C 
Analytical Parameters	x1200 Scale bar: 20µm 20.0 kV - SE	x951 Scale bar: 30µm 20.0 kV - SE	x1200 Scale bar: 40µm 20.0 kV - BSE
Chemical composition (wt%)	Si 67.89 K 14.99 Fe 7.66 Co 9.46	Si 60.35 K 27.92 Fe 3.83 Co 3.62 Al 3.17 Mg 1.11	Si 60.86 K 6.16 Fe 4.47 Co 12.65 Al 2.36 Sb 7.41 Na 0.44

A SEM-EDS record was also made for every smalt sieving after the mechanical grinding, in order to observe the size and aspect of the particles in a general view.

Fig. 16 – After 63 µm sieving - x90, scale bar: 500µm, 20.0 kV – BSE

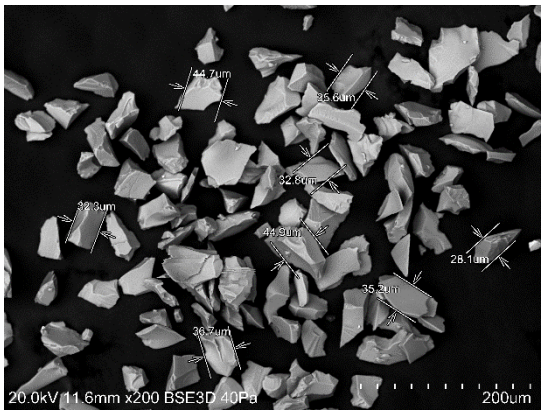


Fig. 17 - After 45 µm sieving – x200, scale bar: 200µm, 20.0 kV – BSE

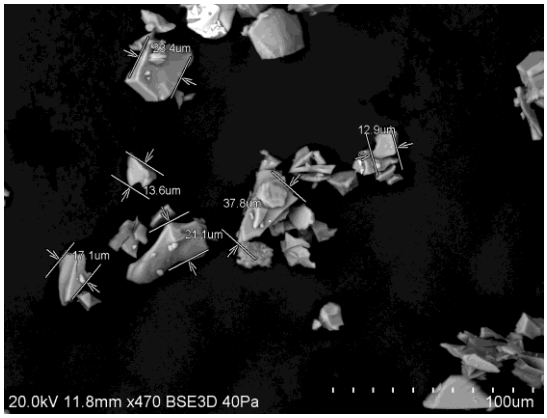


Fig. 18 – After 25 µm sieving – x470, scale bar: 100µm, 20.0 kV – BSE

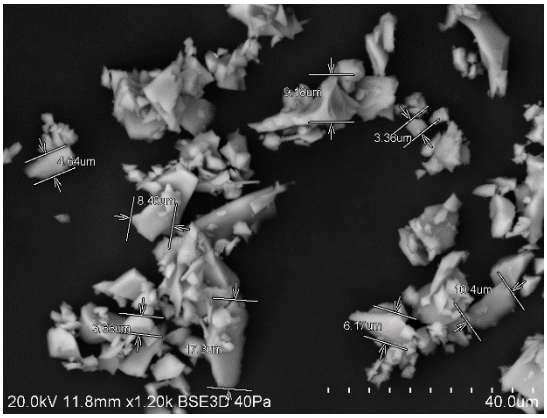


Fig. 19 – Ultra fine – x1200, scale bar: 40µm, 20.0 kV – BSE

The SEM-EDS analysis showed that particles with a lighter color have a lower wt% of cobalt, so it can be concluded that the quantity of cobalt oxide in the smalt constitution influences the intensity of the blue color. As the smalt particles get smaller, the blue color loses intensity but it doesn't lose cobalt in its constitution, so the loss of the blue color that is observed optically is not due to the loss of cobalt in the original constitution, but of the decreasing size of the particles. The lots of smalt ground with a mixture of egg-yolk and honey and milk alone also didn't show a higher amount of cobalt in its constitution.

The mechanical ground particles showed sometimes the presence of copper. This could be a contamination from the sieves used to separate the smalt by sizes.

It also showed that, even though the smalt was divided into different sizes by sieving, some bigger particles still passed through the lower sieve screen, so in a same sample different sizes of particles can be found. Yet, the appearance of the particles seem to be homogeneous and with the typical conchoidal rounder shape.

Due to some darker spots in smalt 3 ground with a mixture of egg-yolk and honey, analysis was carried out with a lower beam energy (10Kv) in order to obtain a better image of the sample surface, as this procedure was applied in [35].

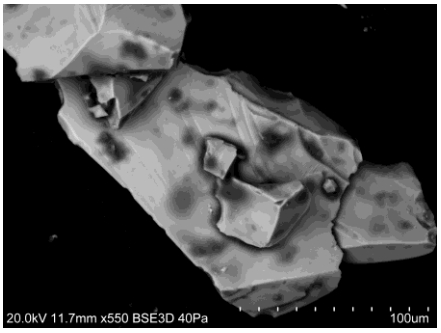


Fig. 20 – Smalt particle ground with a mixture of egg-yolk and honey– x550, scale bar: 100µm, 20.0 kV – BSE

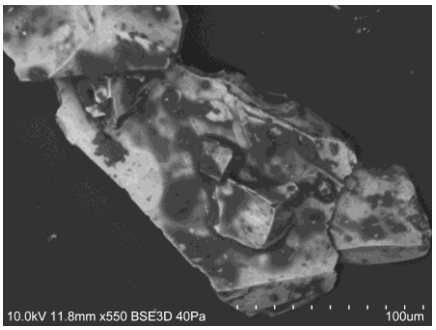


Fig. 21 - Smalt particle ground with a mixture of egg-yolk and honey– x550, scale bar: 100µm, 10.0 kV – BSE

Darker spots already detected at 20.0 kV, which represent lower atomic weight areas and seem to be residual, were better observed by decreasing the beam energy at 10.0kV, since the surface morphology is enhanced [35]. At 10.0 kV, it clearly appears that an organic substance occupies a larger area on the particle. This can be a residue from the egg-yolk vehicle that got fixed to the surface. Further studies on the particles, by means of µ-FTIR, should be done in order to identify the residue.

3.3. X-ray Computed Tomography (µ-CT)

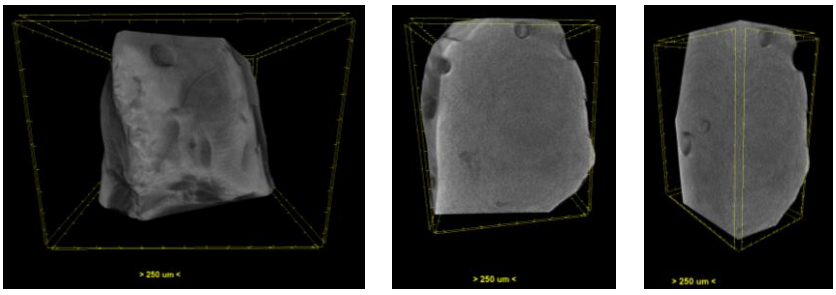


Fig. 22 - Smalt 1 – X-Ray CT; scale bar 250 µm – Different sights, where bubbles are visible on the inside.

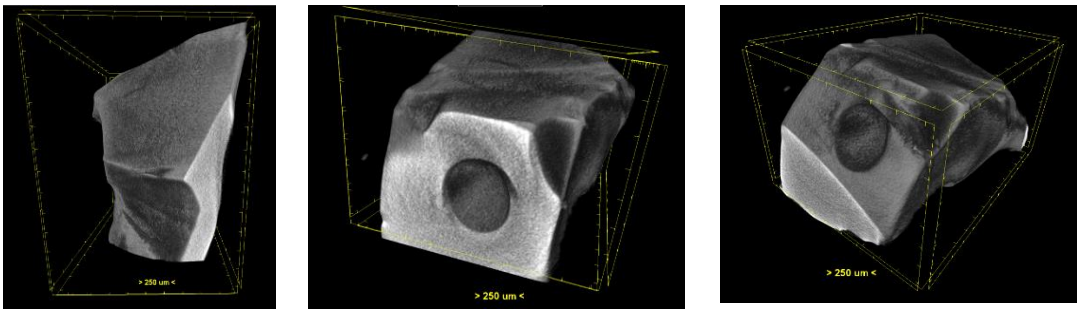


Fig. 23 – Smalt 2 – X-Ray CT; scale bar 250 µm - Different sights, where bubbles are visible on the inside.

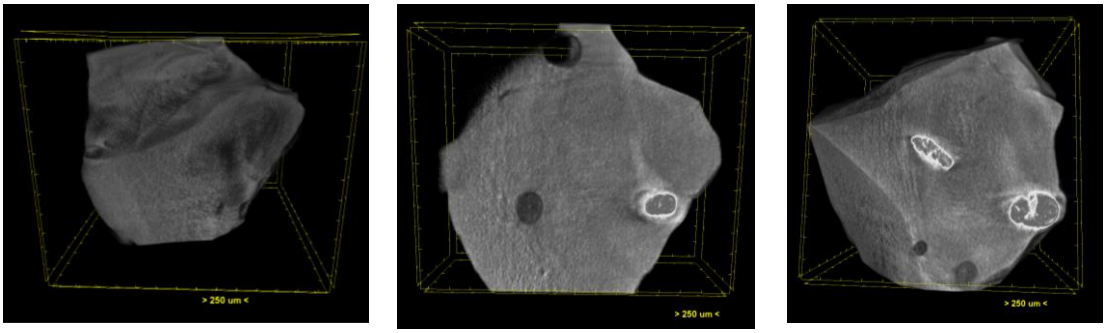


Fig. 24 – Smalt 3 – X-Ray CT; scale bar 250 µm - Different sights, where bubbles are visible on the inside and a contamination is visible in a whiter color.

Observed by means of µ-CT, the batch S3, which was produced with antimony trioxide (III) as an additive in order to avoid the presence of bubbles inside the molten glass, showed the presence of small bubbles, as shown in Fig. 24. This might be due to the fact that this batch of smalt was produced in the kiln for 6 hours instead of 10 hours, thus in conditions rather different than those of the batches S1 and S2. Therefore, the three batches can be hardly compared. A new batch of S3 should be produced in the next future, with the same amount of oxides but with a 10 hour time in the kiln, to verify the impact the time factor may have on the particular bubbles issue. As far as the white areas found in the particle of smalt S3 are concerned, it is noteworthy the fact that the presence of Na was detected by SEM-EDS analysis. It is possible that these areas originated from a contamination with a Na-rich substance from the kiln, during the melting process. This particle was kept in order to analyze and identify the product that appears white in the radiographic records.

3.4. Colorimetry

Every different ground smalt (manual and mechanical) was applied in 1cm squares with a commercial animal glue (commercial gelatine, since it was quick and easy to make and it was transparent, not altering the original color of the smalt and allowing a better analysis) in white gesso surface and photographed by Stereomicroscopy (SM). It was noted that the particles that passed through the 45µm and the 25µm sieve openings were the easier to apply with the brush, and this is the particles sizes that were mainly found in the Main Altarpiece. The newly painted areas were analyzed with the colorimeter.

The tables below show the different results obtained by colorimetry for the different smalt particles size and ground with different vehicles. Higher quality images can be found in Appendix V.

Table 10 – Mechanical grinding of Smalts- SM micrograph x40– scale bar: 400 µm; colorimetry CIELAB color space

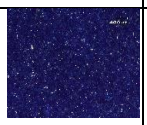
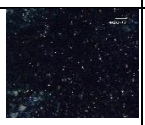
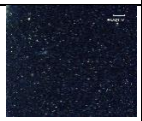
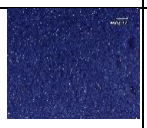
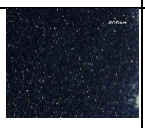
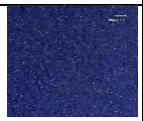
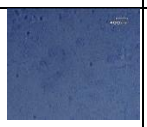
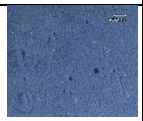
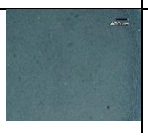
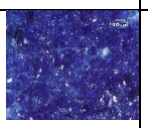
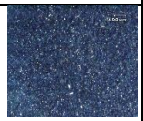
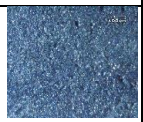
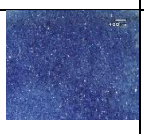
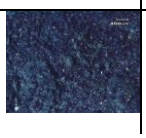
Smalt size	Smalt 1 (SM image)	L*	a*	b*	Smalt 2 (SM image)	L*	a*	b*	Smalt 3 (SM image)	L*	a*	b*
After grind.		25.76	-3.18	-29,11		31.40	-0.55	-61,10		20.85	0.00	-19.37
After 63 µm sieving		26.04	-3.43	-30.76		39.73	-5.53	-54.75		25.36	-2.54	-26.02
After 45 µm sieving		31.23	-5.49	-30.58		42.10	-7.30	-53.36		28.32	-4.70	-28.90
After 25 µm sieving		44.00	-8,47	-30.88		58.63	-8.35	-39.95		39.00	-7.81	-27.88
Ultra fine		48.11	-8.48	-28.66		62.33	-8.77	-36.29		59.43	-7.81	-18.37

Table 11 - Manual grinding of Smalts with different vehicles- SM micrograph x40– scale bar: 400 µm; colorimetry CIELAB color space

Smalt grind. vehicle	Smalt 1 (SM image)	L*	a*	b*	Smalt 2 (SM image)	L*	a*	b*	Smalt 3 (SM image)	L*	a*	b*
Water		26.25	6.17	-20.17		30.77	3.97	-17.40		28.22	-4.80	-27.10
Egg yolk + Honey		29.28	10.43	-30.21		48.57	11.94	-51.74		27.64	3.04	-20.26
Milk		35.27	8.80	-31.97		46.05	15.81	-56.26		31.93	2.05	-24.84

The gathered results showed that, as the particles became smaller, the value of b* became more positive, meaning that the intensity of the blue color became lower, but at the same time the values of a* and L* increased. In some smalts that value of L* increased almost 50% in the smallest group of particles. It is know that, as the particles become smaller, the white light is more scattered (there's less absorption of the color) and this results in the particles appearing less blue, become almost grey. The value of a* also increases, due to the same reason (the amount of red light absorbed is lower and reflects), changing the optical perception of the blue color.

As for the grinding with different vehicles, it was verified that the mixture of egg-yolk and honey and the milk alone indeed maintained the blue color of the smalt pigment, with the values of b* being more negative, especially the smalt ground with milk, but there are not as many differences

in the values of L* and a* as there is in the smalt ground in different particle sizes. Smalt 3 doesn't show the difference in the values of b* that was observed in smalt 1 and smalt 2, so maybe the antimony (III) trioxide that was added could have an influence in the grinding of the blue color. Further studies should be made in the future.

3.5. Vickers Hardness Test (Vickers HT)

Table 12 – HV and GPa values for the three smalts

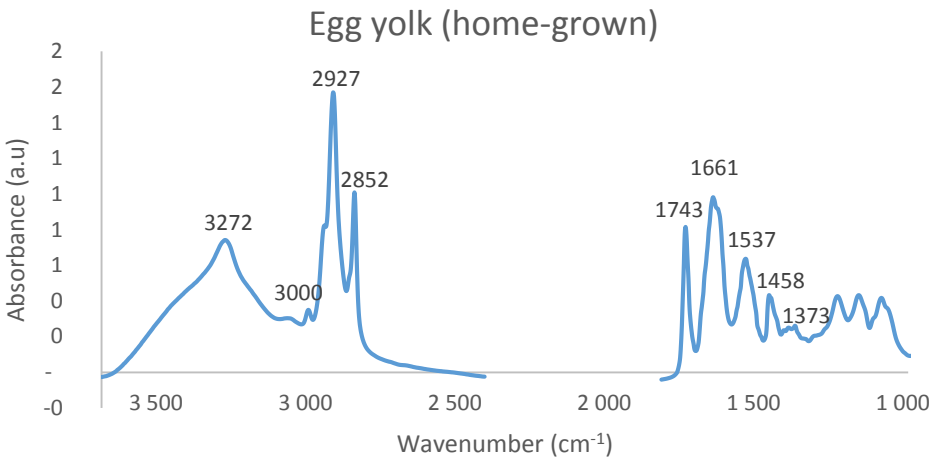
	Smalt 1		**Smalt 2**		**Smalt 3**	
Particles	HV	GPa	HV	GPa	HV	GPa
Particle 1	636	6.234	508	4.985	560	5.492
Particle 2	525	5.152	547	5.364	487	4.776
Particle 3	569	5.580	472	4.629	492	4.825
Particle 4	546	5.354	473	4.639	487	4.776
Particle 5	570	5.590	435	4.269	461	4.521
Particle 6	550	5.394	455	4.462	504	4.943
Average	552	5.414	476	4.673	486	4.768

Regarding the Vickers HT, since S2 had the lower values of HV, followed by S3 and then by S1 (which has the higher hardness number), it was concluded, at this first stage, that the harder the batch of smalt, the easier its grinding.

Indeed, the hardness of the material is only the resistance of the surface to being scratched. In order to study the smalt resistance to fracture, studies for the tenacity, which represents the capacity of a material to fracture or break, should be made in the future.

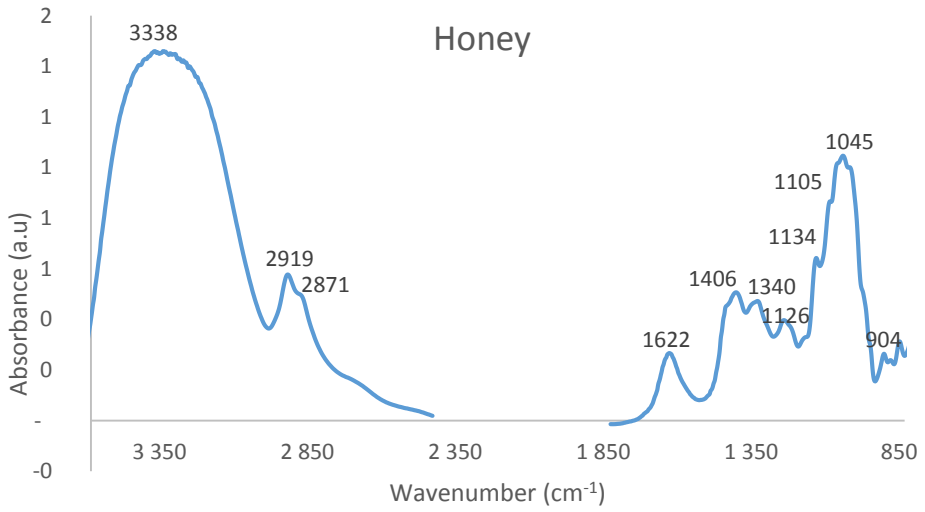
3.6. Micro-Fourier Transform Infrared Spectroscopy (μ-FTIR)

μ-FTIR analysis were carried out to characterize the binders newly produced or the vehicles used during the experiments, in order to create standard spectra as future references.



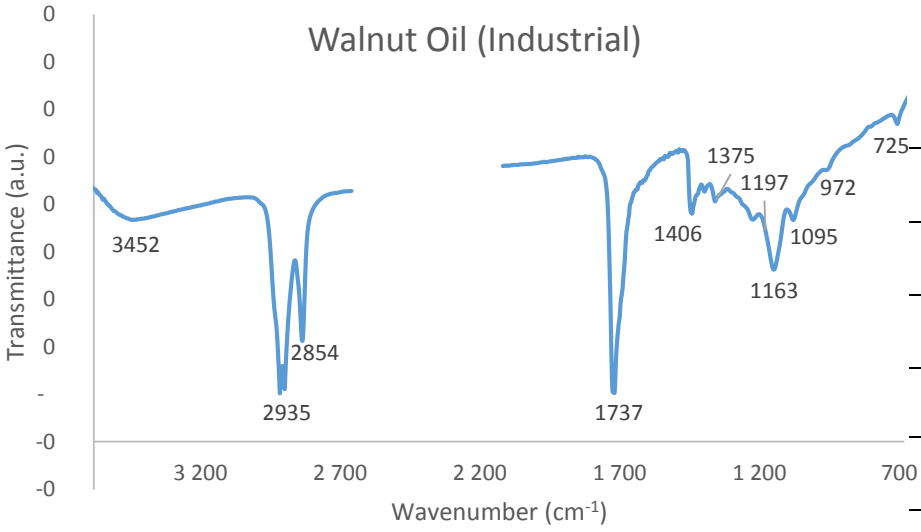
Region	Characteristic IR absorption bands
3400-3200 cm^{-1}	N-H stretching band
3100-2800 cm^{-1}	C-H stretching bands
1750-1600 cm^{-1}	C=O stretching bands
1565-1500 cm^{-1}	C-N-H bending band
1480-1300 cm^{-1}	C-H bending band

Fig. 25 – Egg-yolk used in the smalt manual grinding. It came from a chicken home-grown, to which the feeding and care is known. The information for the table was taken from [36]



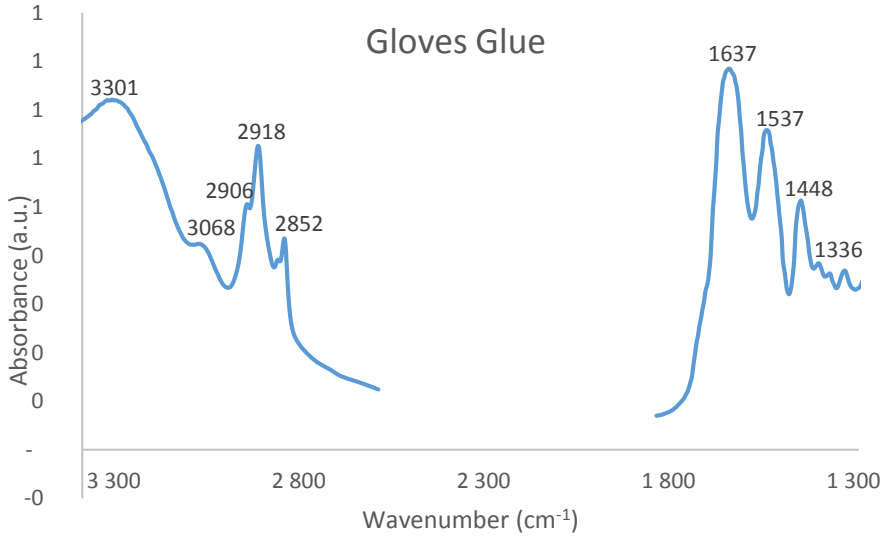
Region	Characteristic IR absorption bands
3600-3200 cm^{-1}	O-H stretching band
3000-2800 cm^{-1}	C-H stretching bands
1650 cm^{-1}	O-H bending band
1480-1300 cm^{-1}	C-H bending band
1300-900 cm^{-1}	C-O stretching bands

Fig. 26 - Honey used in the smalt manual grinding. It came from a biological production of honey. The information for the table was taken from [36]



Region	Characteristic IR absorption bands
3600-3200 cm^{-1}	O-H stretching band
3000-2800 cm^{-1}	C-H stretching bands
1750-1730 cm^{-1}	C=O stretching bands
1480-1300 cm^{-1}	C-H bending band
1300-900 cm^{-1}	C-O stretching bands
750-700 cm^{-1}	C-H torsion band

Fig. 27 – Standard Spectrum for a Walnut Oil produced industrially. The information for the table was taken from [36]



Region	Characteristic IR absorption bands
3400-3200 cm^{-1}	N-H stretching band
3100-2800 cm^{-1}	C-H stretching bands
1660-1600 cm^{-1}	C=O stretching bands
1565-1500 cm^{-1}	C-N-H bending band
1480-1300 cm^{-1}	C-H bending bands

Fig. 28 - Standard Spectrum the Gloves Glue. The information for the table was taken from [36], in the chapter for Gelatin

3.7. X-Ray Diffraction (XRD)

More detailed images from the XRD spectrum can be found in Appendix VI.

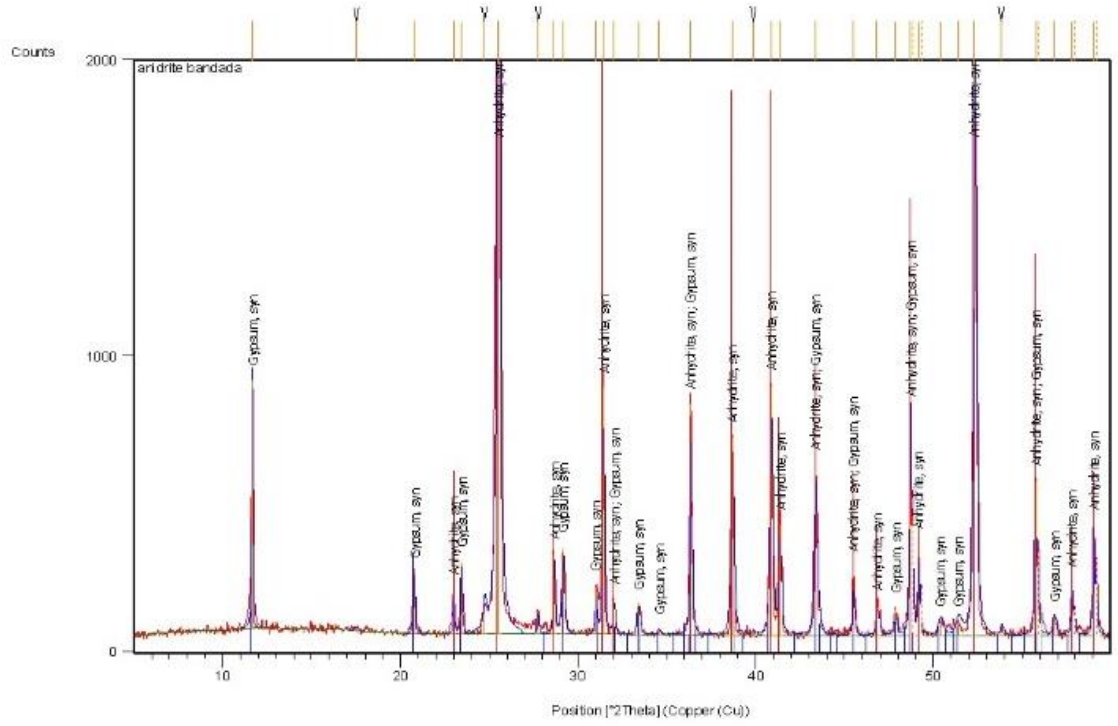


Fig. 29 – XRD spectrum of Anhydrite from Óbidos

4. Conclusions

In this thesis, some positive results were obtained. It was possible to produce the three batches of smalt, although the smalt 3 should have stayed longer in the oven, and to perform several studies with them, such as studies of color, chemical constitution, bubbles, and hardness, among others. It was also possible to produce walnut oil and gloves glue, using only raw materials as similar as the ones used at the time of the Altarpiece, and perform some analysis. A study of natural anhydrite as a possible preparation layer for the 1685-coating was also started.

Comparing all the results obtained, it was noted that the particles that appeared more opaque and of a darker blue color in OM records, have a higher amount of cobalt in their constitution, as this has been supported by SEM-EDS, and a more negative value of b*, which means it is more blue, as it has been supported by the colorimetric measures. The particles that were ground with a mixture of egg-yolk and honey and milk alone also showed to have a more negative value of b* than the particles ground with water, as it has been supported by the colorimetric measures, and also a higher amount of cobalt in its constitution, as it has been supported by SEM-EDS. It is known that the blue color of smalt come from the Co^{2+} ions that are coordinated in a tetrahedral form by oxygen atoms and when the K^{+} ions leach from the potash and are replaced by H_2O or H_3O^{+} molecules, this tetrahedral coordination can become octahedral and the Co2+ will no longer exhibit specific absorption in the visual range, thus making the blue color of the pigment to fade [7, 9].

The μ-Ray CT imaging showed the presence of bubbles on the three different smalts, but since S3 stays a shorter time in the kiln, as would be expected, the presence of bubbles in this very batch may be the result of this particular protocol. Maybe if S3 had stayed 10 hours in the kiln (as the other batches), instead of 6 hours, the bubbles would disappear, as it was supposed to happen with the addition of antimony to the raw material.

The Vickers HT showed that the smalt that was easier to ground was also the one with the higher values of hardness, so maybe it is not the hardness of the material that makes it harder to grind. Further research is needed to better understand the exact relationship existing between the two properties.

The Standard Spectra showed the match with the ones found in the literature.

5. Future Work

Further studies should be done on smalt, such as FORS (Fiber Optics Reflectance Spectra) in order to obtain UV-VIS spectra and new values for the CIELAB color space, to compare the different techniques.

The low atomic residue present in S3 ground with a mixture of egg-yolk and honey should be analyzed by means of µ-FTIR.

The µ-FTIR spectrum of the Walnut Oil produced in the HART project should be done, in order to obtain the standard spectrum.

A study of the binders used to reproduce the "burnished" effect to the 1685-smalt coating should be made, testing the different varnishes/coatings and the possibilities of a floating oil.

The different layers should be reconstructed – preparation layers, pink underlayer, blue underlayer, smalt layer with different binders possibilities and different varnishes/coatings to obtain the "burnished" effect. These layers should be studied and compared with the ones applied to the Main Altarpiece, in order to obtain a historically accurate reconstruction.

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Appendices

Appendix I – Contrato feito sobre o dourar e estofar o retabollo da Capella Mayor da Santa See

1684 – Manoel da Costa Pereira [13] – retranscribed from [10]

28 Novembro 1684 – Coimbra

Contrato feito sobre o dourar e estofar o retabollo da Capella Mayor da Santa See.

Saibam quantos este publico instrumento de contrato e obrigassão ou como em direito milhor dizer se possa virem que no anno do nascimento de Nosso Senhor Jesus Christo de mil e seicentos e outenta e quatro annos e nos vinte e outo dias do mes de Novembro do dito anno nesta cidade de Coimbra e cazas de morada do Senhor D. Nuno Alvres de Portugal thizoureiro mor de Santa See desta cidade onde elle ahy estava prezente e bem asim Manoel da Costa Preira (sic) natural desta cidade pintor e dourador de obras de retabollos e as mais pertencentes a dita arte pelos quais e por cada hum delles foi dito em primeiro lugar pelo dito Senhor D. Nuno Alvres de Portugal que elle tinha poder e comissão particular do illustrissimo Senhor D. João de Mello por merce de Deus e da Santa See Apostolica desta dita cidade Conde de Arganil Senhor de Coja e do concelho de Sua Majestade pera effeito declra impreitada o dourarse e estoffarse o retabollo da Capella Mayor da Santa See desta dita cidade e porquanto se tinha comtratado com o dito Manoel da Costa Pereira pera effeito de fazer a dita obra comforme a trassa e apontamentos que entre sy tinham feito; pelo dito Manoel da Costa Preira (sic) foi dito que elle se obrigava por sua pessoa e bens a fazer a dita obra de dourar e estofar o dito retabollo na forma seguinte comvem a saber: que sera o dito retabollo lavado athe que fique em madeira; sera o dito retabollo dourado de ouro sobido e bem corado o qual ouro ha-de ser bornido e tam dourado nas partes adonde de antes levou ouro de madeira (sic) que se veja senao ouro; serao as partes de onde de antes foi azul tambem de azul que sera de esmalte de olio o qual tambem sera bornido; serao as imagens que estiverem no dito retabollo como tambem as que nelle faltarem que se hao-de mandar fazer todas douradas do ouro assima dito e tam borinas, diguo, e tambem bornidas e as imagens de Nossa Senhora que ouver em passos de paixão de Christo serao estofadas as tuniquas dellas de cor roixa de brocado com alcachofras e bordadduras levantadas, os mantos destas ditas imagens como tambem os de todas as outras de Nossa Senhora que ouver em passos serao de cor azul que sera fuio (sic) de brocado com as mesmas alcachofras e bordaduras assima ditas, os forros destas ditas ropas serão de regraxo caramezim que imite rubis; serao todas as outras imagens vestidas das cores que a noticia andaram no mundo de brocados com alcachofras e bordaduras levantadas; serao os rostos maos e mais partes que se descobrirem carnes destas ditas imagens incarnados a pulimento naturalmente; sera a imagem de Christo Cruxifiquado de encarnassao ao natural as quais encarnassois serao de pulimento por conservar milhor a cor; serao tambem os rostos dos sarafins e anjos assim dos ditos retabollo (sic) como os que estao n'aboboda entre as pernas de aranha que o croam tambem da mesma encarnassao e as azas do ouro assima dito, isto se entendiam em os sarafins mas os anjos hao-de ser as azas estofadas como as vestiduras das mais imagens; sera o vao d'aboboda que de antes era azul do azul assima dito tudo na form ..... [ilégivel] ..... Manoel

da Costa Preira (sic) assinados que fiquam ... Senhor D. Nuno Alvres de portugal e loguo pelo dito Manoel da Costa Preira (sic) foi dito que estava contratado com o dito Senhor pela dita comissao que tinha do dito ilustrissimo Senhor Bispo Conde pera effeito de fazer toda a dita obra atras referida em presso e quantia de dois mil cruzados forros pera elle dito Manoel da Costa Preira (sic) pelo qual foi outossim dito que elle pella dita quantia se obrigava por sua pessoa e bens a fazer a dita obra e a dar principio a ella no principio do mes de Fevereiro do anno que vem de seiscentos e outenta e sinco pera o que serao obriguados os ditos Senhores a darem-lhe a dita Capella livre pera poder trabalhar nella mando-lhe fazer os andaimos necessarios pera a dita obra e assim tambem mandar concertar qualquer obra que do dito retabollo e madeira for necessario a custa do dito ilustrissimo Senhor Bispo Conde e porquanto nesta forma estavam assim contratados se obrigaram assim o dito Senhor Bispo Conde e o dito Manoel da Costa Pereira cada hum pela sua parte a cumprir este instrumento e a nao hir em couza algua contra elle e o dito Manoel da Costa Preira (sic) obrigou mais a que depois de feito e acabado o dito retabollo nao estando elle comforme aos ditos apontamentos atras referidos avendo qualquer falta ou denunciassao que se lhe impute por os mais peritos ofeciais a refazella e reformalla toda a dita falta que se lhe puzer a sua custa e despeza ou a faze elle mesmo de modo com que haja de se asseitar e a cumprir o dito Manoel da Costa o sobredito disse se obrigauva responder pello tocante a este e sua dependencias perante o Reverendo Doutor Vigario Geral ou provisor deste bispado pelo, diguo, pera o que renunciava o Juiz de seu foro e ferias gerais especiaais e as mais que nao forem as que a igreja manda guardar e se sobmetia debaixo das sensuras dellas e aos nao declinar o jurou ao juramento dos Santos Evangelhos que recebeo da mao de mim publico tabaliam e porquanto ao ler e assinar deste lhe foram loguo entregues pelo dito ilustrissimo Senhor Bispo Conde cem mil reis em dinheiro de contado pera comprar o que lhe for nessessario pera dar principio a dita obra ..... [ilegível] ..... por seu fiador e principal pagador a Bento da Costa mestre alfaiate desta cidade e nella morador irmao do dito obriguado pello qual foi dito perante mim tabaliam e das testemunhas deste instrumento ao diante nomeadas e assinadas que elle de sua propria e livre vontade se obriguava como fiador e principal paguador mas tao somente o dito Manoel da Costa Preira (sic) nao fazendo elle a dita obra como dito fiqua a entreguar os ditos cem mil reis mas tambem a elle a fazer na forma em que esta obriguado sobmetendosse tambem debaixo das mesma condissois pennas e obriguassois a que o dito Manoel da Costa Preira esta obriguado e pello dito Senhor D. Nuno Alvres de Portugal foi dito que pella comisao que tinha do dito ilustrissimo Senhor Bispo Conde o obriguava a que comprindo o dito Manoel da Costa Pereira com tudo como dito fiqua a lhe fazer o dito Senhor muito bom paguamento dos ditos dois mil cruzados e lhos ir paguando as paguas comforme o estado da obra e por nesta forma estarem assy contratados de hua e outra parte ourtoguaram ser feito este instrumento nesta notta de mim tabaliam de que pediram e consederam cada hum leu deste theor e os mais que comprirem que eu tabaliam como pessoa publica estipulante e aceitante tudo estipulei e aceitei tanto quanto com direto posso e devo em nome das pessoas ausentes a que tocar possam a que foram testemunhas prezentes que com elles partes ao diante assinados aquy assinaram o Padre Bernardo Gomes de Sao Thiago

assistente em casa delle dito Senhor thizoureiro mor e Joam da Costa notario pay de mim tabaliam e eu Manoel da Costa de Andrade tabaliam o escrevi.

Bento da Costa *Manoel da Costa Pereira*

Appendix II – Historical recipes

Appendix II.1. – Transcription of recipes

The recipes were transcribed from different articles and books [1, 4, 10, 14, 17, 19, 20, 37, 38, 39] often found translated to English. When possible, the original version of the recipe is transcribed, along with the translation.

Appendix II.1.1. – Smalt recipes

Fondaco dei Tedeschi (1328) [1]

Earliest reference to *zaffer* or *safflor,* a cobalt ore that has been purified from arsenic to a large extent, under the name of *caffaranum.*

MS2265 (14th century) [1, 19]

A macinare ismalto azuro che poi pingere in suo colori. Pili ail smalto et rompelo sotile poi macinelo sopra il porfido cun sorro de ovo cun ono pocho di melle. Masinalo sutile como vope et se andasse secondo azonze uno poco de aqua. Et quando e masinato lava fora il mele et lo ovo cun l'aquae remanera cossa bellisima.

MS2265 (14th century) [1]

How to pulverize blue smalt so that it can [be] painted without losing its color. Take the smalt and finely pulverize it and then grind it on a porphyry slab with egg yolk together with a small amount of honey. Grind it finely as you know it and when it dries add a little water. And when it is ground then wash the honey and egg yolk out with water and it will remain a beautiful color.

Peter Månsson (b.1462-1534) [1]

To make smaltum [enamel]. Take a well roasted iron ore and mix one part of it with seven parts of glass as prescribed, and ½ a part of the color grasse (unknown term). The more you add of the color grasse the quicker it flows except for the green color. For this reason you should add only a little. To make green take one weight of copper oxide and mix this with 8 weights of glass. To make blue smalt take a measure of safri [cobalt oxide], 8 measures of glass and ½ of the color. […] The more color you add the faster it melts and when less is added it melts slower. Take 2 pounds of crystal and grind it to a powder. Then take one pound of lead ash grinded with salt and mix the substances together and put on the fire until it melts. After dissolving alum in strong vinegar add crystal powder to soak for 9 days.

Pseudo-Savonarola (1535), A dar color di bello azuro al smalto [1, 17]

Recipe smalto e macinalo cum latte e poi che è bem macinato lavalo cum aqua e lascialo [na] dare al fondo il più grosso, et di quanto l'aqua è torbida votala in uno altro vaso e lascialo andare al fondo e cosi fa più volte et ne faraj di tre sorte una più bella che a'altra.

Pseudo-Savonarola (1535), Smalt with a beautiful color [1]

Take smalt and grind it with milk and when it is well ground wash it with water and the let the coarse [particles] sink to the ground. When the water is cloudy pour it into another vessel and let it sink to the ground and do this repeatedly. Do not make more than three grades [smalt], each more beautiful than the last.

Pseudo-Savonarola (1535), Azuro simile allo oltramarino [1,17]

Recipe cogulum christallium once 3, vitrum optimum bene tritum, misce simul, deinde Recipe zafranum once 5, omnia terre super mármore cum aqua clara, postea pone in crucibulo e coperi et pone ad coquendum ad furnum figolorum, postea terre matteriam super mármore si habebit colorem bonum dimittas, si non pone iterum modicum de vitro e zafrano e terre, e iterum /f. 146/ coque in crusibulo ut supra, postea terre e habebis azurum optimum.

Pseudo-Savonarola (1535), A blue that looks identical to ultramarine [1]

Take three ounces of crystals that have been fused together just as much well-grinded glass of the best quality and 5 ounces of Zafranum *[cobalt oxide]. Grind everything on a marble [slab] with clean water and then put it in a crucible, close it and place it for burning in a potter's kiln. Then grind the [produced] material on a marble [slab]. If it has a good color then leave it, but if not then add more glass and* Zafranum *and grind and burn it one again as done before in a crucible. Then grind if and you will have the best blue.*

Helmreich's (1574), [1, 20]

Blawe Farbe oder Lasur. Nim oblawen Lasur ein Loth in ein vluschel/vnd geus darauff Gummiwasser/rüre es vmb mit einer Feder oder Finger/geus mehr Gumiwasser daran/vnd lege weisse Mirren/so gros als eine Bohne/auch so viel Gummi tragantum darein/Darnach thue es auff einen Reibstein/vnb zerreib es vnter einander/wenn das geschehen/so nim es vom stein in ein Hörlein oder Muschel etc. So du nu damit schreiben wilt/rüre es wol vnter einander rmb/duncke ein die temperirte Feder/Wenn die Blawe dinte schön vnd verne aus der Feder gehet/so ist sie recht vnd wol temperirt. Wo aber nicht/so ist sie zu dicke/vnd thue mehr Gummiwasser daran/das nicht lick ist/vnd rüre es offt vmb/[…].

Helmreich's (1574) [1]

Blue color or lasur. Put one loth of oil blue lasur in a shell/and pour gum water on top/stir this with a feather or a finger/pour more gum water on top/and lay white myrrh/as big as a bean/add just as much gum tragacanth/After this put this mixture on a grinding stone/and grind it together/when this is done/then take it from the stoen and put it in a small horn or shell, etc. So if you want to write with this/mix it well/dip in the tempered feather/When the blue ink flows out of the feather nicely/then it is good and well tempered. If not/then it is too thick/add more gum water/that is not thick/and stir it often/[…].

Rubens (1577-1640) [10, 12]

To turn the smalt more beautiful and clear it is convenient to dilute it with varnish and place it carefully when the color is fresh.

Mayerne (1620-1640) [10, 12]

When working the blue, you need a special brush […] and add Aspic oil or Paraffin oil, and as soon as it is dry, carefully place the Vernix on top.

Latombe (1620-1640) [10, 12]

The blue, can be applied in a tempera with glue over the oil imprimittura (rubbed with garlic juice) and after apply a good vernix subtle and strongly siccative.

Van Dyck (1632) [10, 12]

He proposed that the colors, blue and green, mixed with gum water or diluted animal glue and then varnished are equivalent to those mixed with oil. He told me that, many time, mixes in his paintings the colors with gum water and, when dried, covers with the varnish. But the secret consists in which the two colors connect under the imprimittura which is oil. Which will be done in a reliable way if one covers the imprimittura with onion juice (or garlic).

Johann Kunckel (1679) [1, 37]

[…] but those who want a violet color just have to add some Magnesie [magnesite, $MgCO_3$] or Braunstein [manganese dioxide materials] to the Zaffera […].

Cröker (1736) [1]

This oil-blue is made in Schneeberg [Saxony] with roasted cobalt when it is mixed with a certain amount of sand and potash. Whoever wants pure cobalt has to look for it in Schneeberg and pay a high price.

Darduin (16th century), Recipe LXVIII – a far smalto da muro bello (a smalt for wall painting) [4]

A frit prepared with 300 parts of grepola nera *(uncalcinated raw tartar) and 90 to 110 parts of pulverized quartz was prepared; 200 parts of this frit were mixed with 85 parts of* zaffera che sia buon e ben braseado *(well-calcinated cobalt ore of good quality) and melted at high temperature for one-and-a-half-days. To improve the color, the eventual addition of 1.5 to 2 parts of manganese oxide is also suggested.*

Brunoro (16th century), Recipe B255, smalto de muro [4]

A frit was first prepared with 300 parts of grepola *(tartar) and 100 parts of quartz. A batch of 120 parts of this frit, 25 parts of* colletti de cristallo *and 2 parts of manganese oxide was melted in a crucible. 155 parts of* zaffera *were added to the melt.*

Johann Samuel Halle (1761) – Herstellung von Smalte [1, 38]

Die helblau Smalte (blaue Stärke) wird dem gerösteten giftigen Kobalte [Oxid] mit Potash und Sand zum tiefblauen Glase geschmolzen, zwischen Mühlsteinen fein gemalen, geschlämt, durchgesiebet, und nach der verschiednen Feinheit Verkauft. Mus viele Stunden gerieben warden.

Johann Samuel Halle (1761) – Manufacturing of Smalt [1]

The light blue smalt (blue Stärke) is produced by fusing the roasted, poisonous cobalt [oxide] with potash and sand into a deep blue glass that is finely ground between milestones, elutriated, sieved and sold according to the different grades produced. Needs to be ground for several hours.

Gaetano Milanesi (1864), Recipe XXVII - How to prepare* azzuro di cristallo da dipingere *(preparation of a light-blue pigment for painting) [4, 39]

10 parts of finely ground quartz and 10 parts of sale de tartaro *were calcinated to prepare a frite that was melted in a crucible. The coloring compound called* azuro da vetro *was added to the melt until the desired color was obtained (no precise quantity is reported). Once free of bubbles, the melt was poured in water and finely pulverized with* lescivia *(purified soda or potash used in the recipe as a lubricant).*

Appendix II.2. – Smalt recipes compiled in four tables

Table A.13 – References to the Cobalt Ore

Author	Date	Page	Name	Description
Fondaco dei Tedeschi	1328	?	Caffaranum	Cobalt ore that was purified from Arsenic in a great extension
Peter Månsson	b. 1442-1534	?	Safri	Cobalt oxide
Pseudo-Savonarola	1535	fl. 145v and 146	Zafranum	Cobalt oxide
Johann Kunckel	1670	118	Zaffera	Cobalt oxide
Gaetano Milanesi	1864	?	Azuro da vetro	Another name for zaffera

Table A.14 – For producing the smalt pigment

Author	Date	Page	Description
Peter Månsson	b. 1462-1534	162	To make blue smalt take a measure of safri, 8 measures of glass and ½ of the color grasse [unknown term].
Pseudo-Savonarola	1535	fl. 145r and 146	Three ounces of crystals that have been fused together, three ounces of well-grinded glass of the best quality and 5 ounces of Zafranum. Grind on a marble [slab] with clean water and then put it in a crucible, close it and place it for burning in a potter's kiln.
Darduin	16th Century		Smalt for wall painting – a frit prepared with 300 parts of 'grepola nera' (uncalcinated raw tartar) and 90 to 110 parts of pulverized quartz was prepared; 200 parts of this frit were mixed with 85 parts of 'zaffera che sia buon e ben brusado' (well-calcinated cobalt ore of good quality) and melted at high temperature for one and a half days. To improve the color, the addition of 1.5 to 2 parts of manganese oxide is also suggested.
Brunoro	16th Century		Smalt for wall painting – a frit was prepared with 300 parts of 'grepola' and 100 parts of quartz. A batch of 120 parts of this frit, 25 parts of 'colletti de cristallo' and 2 parts of manganese oxide was melted in a crucible. 155 parts of zaffera was added to the melt.
Johann Kunckel	1670	118	Blue smalt is made with Zaffera with the difference being that the smalt is melted into glass.
Cröker	1736	113	Oil-blue is made with roasted cobalt mixed with a certain amount of sand and potash.
John Samuel Halle	1761	299	Recipe for light blue smalt (blue Stärke). Fusion of poisonous roasted cobalt [oxide] with potash [KOH] and sand into a deep blue glass.
Gaetano Milanesi	1864		10 parts of finely ground quartz and 10 parts of 'sale de tartaro' (potassium bitratrate) were calcinated to prepare a frit that was melted in a crucible. Azuro da vetro (raw cobalt ore) was added to the melt until the desire color was obtained.

Table A.15 - For maintaining the blue color of the smalt during the grinding process

Author	Date	Page	Vehicle	Pigment
Italian Manuscript from Casanatense Library, Rome	14th Century	fl. 88r	A mixture of egg yolk with a small amount of honey	Blue smalt pigment
Pseudo-Savonarola	1535	Folio 145	Milk and, after grinding, wash with water	Blue smalt pigment

Table A.16 - For obtaining the smalt blue paint and applying the finishing touches to the paint layer in order to obtain a shiny surface

Author	Date	Page	Preparation Layers	Binding medium	Pigment	Finishing touches
Helmreich	1574	23		Gum water	Blue pigment ("lasur")	
Rubens in [13]	1577-1640	Folio 150		Dilute with Varnish		
De Mayerne in [13]	1620-1640	Folio 9		Aspic oil	Blue	Vernix
Latombe In De Mayerne [13]	1620-1640	Folio 11	Oil imprimitura - Layer with garlic juice	Tempera with glue	Blue	Vernix
Portman In De Mayerne [13]	1620-1640	Folio 150	Lead white ground with oil	Egg white or fish glue	Crass smalt	Vernix
Van Dyck In De Mayerne [13]	1632	Folio 143	Oil imprimitura Layer with garlic or onion juice	Gum water or diluted fish glue	Blue and Green	Varnish
Pacheco	1649					Aspic Oil+ Sandarac (vernix?)
Richard Symmons	1649-1651			"in guazzo" – gum water	Smalt pigment	
Marco Boschini	1664			Glue made from leather strips	Blue pigment	
André Felibien in [13]	1676					Turpentine oil + Sandarac
Manoel da Costa Pereira	1684			Oil	Blue smalt pigment	"Burnished"

Appendix II.3 – Binders for smalt

De Mayerne (1620-1640) [12, 14]

Color's death is when the oil floating on the surface dries and forms a skin which turns dark in the air. There are a few pigment, such as the smalts, that do not mix easily with oil, and therefore [the pigment particles] will always stick together, and therefore [the color will] easily die, i. e., darken.

Latombe (1620-1640) [14, 18]

Walnut oil is the best [oil] for white, smalt and ash.

Paulus Van Sommer (1620-1640) [18]

Poppy oil is good for [painting] white, and for blue.

Francisco Pacheco (1638) [14, 18]

Purified linseed oil that had been bleached for fifteen days in the sun. At least the blues that I (…) have executed this way have been evenly absorbed, remained brilliant, and kept their color. In the hands of other painters, the blues die. Even when the use walnut oil and lavender oil, the blues die on them. (…) Neither my blues nor my whites are mixed with the walnut oil so revered by all. (…) I have nothing against linseed oil, although there are those who say that blue and white must not have anything to do with it. The blue paint should be applied thinly and it should be allowed to dry slowly in a cool place.

André Felibien (1676) [14, 18]

Those who wish that [the colors of] their paintings remain fresh, use as little oil as they can and keep their colors firmer by mixing them with very little spike oil.

Felipe Nunes (1615), Cola de Pele de Luvas [14, 21]

You will use glue made of baldreu, which is leather from which gloves are made; clippings of gloves are to be perfectly cooked; the water that remains after they are dissolved is the glue itself; it cannot be too strong; apply two layers over the panel with it; when it [the glue] is dry, take ground gesso and with the glue, make a wash or watercolor and apply another layer. When it is dry, apply another layer containing more gesso.

Pacheco (1649), Cola o engrudo de tajadas [14, 21]

Glue used to distemper these colors [glue tempera] was made on a very common way: cheap cuts glue were soaked in water, when turned soft, they were boiled adding enough water so that the glue was neither strong nor weak. Glue made of cooked and filtered gloves clippings may also be employed but it gives some trouble.

Appendix III – Binder production

Appendix III.1. Walnut oil production

Weight of walnuts with shells: 2388.25 g

Weight without shells: 810.22 g

Weight of shells: 1552.14 g

Total number of walnuts: 280

Number of rejected walnuts: 9

Although the walnuts were home storage, there was a low spoilage losses: from 280 walnuts in their shells, 9 walnuts were discarded, which represent only 4.63 g of the total amount of the obtained walnuts kernels, ie 0.57% of spoiled product.

Walnuts meats were shelled, and the partition that separates the two halves of which each walnut kernel is made up was removed as well.

From the initial unprocessed walnuts weighing 2,388.25 g, the shelled walnuts meats weighed up to 810.22 g, corresponding to one third of the initial product.

Walnut preparation

Using a coffee mill, the walnuts meats were ground, for obtaining smaller particles of walnuts. The meats were ground during 15 seconds for a first lot, and during 10 seconds for a second lot, in an attempt to verify until which point the grinding process could produce portions more homogenous and not too small. The visual comparison was not conclusive. The particles of walnuts were then placed in the unit in a vertical position. The first lot of walnuts meats was prepared to fill the press cylinder to the brim. The second lot corresponded to the remaining walnuts meats. In this case, the cylinder was not completely filled up.

Oil pressing

<u>1st Lot:</u>

2 pressings were made for the same amount of walnuts, ground for 15 seconds. The equipment was only designed for linseed oil, which required a pressure of ~200-220 Ba. Therefore, the pressure for the walnut oil was unknown.

In the first pressing, the oil started dripping at about 7 minutes of bombing, at a pressure of about 100-110 Ba. As it reached around 220 Ba, the walnut dough started to come out. In order to avoid the walnuts dough extrusion and oil contamination, the second pressing was performed at a maximum of 120 Ba, and the oil was cloudy and of a yellow color.

In the first lot weighing 493.03 g, the walnuts meats pressing produced the total amount of 180 ml of oil.

2nd Lot:

In an attempt to obtain a higher performance equipment for walnut oil extraction, the nets setting was modified (as previously mentioned in "Preparing the equipment") and pressure levels were readjusted.

The oil pressing started after 11 minutes of bombing, at a low pressure of 40 Ba. The pressure was progressively increased during the next 20 minutes up to 130 Ba. Then pressure was kept between 140 and 170 Ba during the next 20 mn. In fact, when the pressure was getting too high, the pumping was stopped so the pressure grudge went down to lower pressure levels. Although at this stage the oil was still dripping but very slowly, it was decided to stop the process. So the whole procedure lasted 51 minutes and the extraction itself lasted 40 minutes.

The oil obtained was almost clear, with a light yellow color.

In the second lot weighing 314.33 g, the walnuts meats pressing produced the total amount of 100 ml of oil.

Appendix III.2. Gloves glue production

The glue was produced from a white tawed leather, obtained from sheep skin tanned with alum, in 2005 [20]. Small leather strips were cut, weighing of 43.70 g, and soaked in water for 24 hours. The leather strips were supposed to curl, but only a few actually curled. After removing from water, the strips weighed 110.49 g. The glue was then made with the same distilled water at a concentration of 23 % and boiled at 100 ºC (the temperature for water evaporation) for 4 hours, where smell of burned paper was felt, until a glue paste was obtained. This glue was left to dry for 3 days at the temperature and relative humidity present in the lab, without ventilation and without a natural source of light. The result was an extremely dark-brown glue, and what was expected was a lighter brown glue.

Because of this result, a new gloves glue was produced on the 17th of March of 2015, with 19.30 g of leather strips soaked in water for 24 hours. Once again, only a few leather strips curled. After being soaked, the leather strips weighed 19.30 g. This time, they were boiled at a lower temperature of 65 ºC, the temperature used to boil other animal glues in the past, with no smell of burned paper. The glue was left to dry for 3 days at the temperature and relative humidity present in the lab, without ventilation and without a natural source of light. This time, a lighter-brown glue was obtained, but still far from what was expected. This could be because the tawed leather had about 10 years of age and this could influence the final result of the glue.

Appendix IV – Materials analysis

Appendix IV.1. – Equipment information

The optical microscope was an Axioplan 2ie Zeiss microscope equipped with transmitted and incident halogen light illuminator (tungsten light source, HAL 100) and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for micrographs. Samples were analyzed with 10x ocular lenses and 5x, 10x, 20x and 50x objective Epiplan lenses (giving a total optical magnification of 50x, 100x, 200x and 500x). For the incident and transmitted light the samples were analyzed under analyzer filters. The scales for all objectives were calibrated within the Nikon ACT-1 software.

The SEM-EDS analyses were carried out using a FEG-SEM model JSM 7001F by JEOL with an Oxford Si(Li) INCA PentaFet 33 detector. The accelerating voltage was 20 kV and the acquisition time was 60 s. Samples of smalt were only mounted on a double-coated carbon tape. Samples were examined by SEM for high-magnification imaging, using secondary electron (SE) imaging for topographical aspects, and backscattering electron (BSE) imaging for chemical contrast. The chemical composition of the particles was ascertained by SEM-EDS, which enables major element point analysis.

The X-Ray computed tomography consists in a Skyscan1172 scanner. For the S1 batch, the analysis was carried out/performed by means of 383 radiographs, with a source voltage of 79 kV, a source current of 125 uA, image pixel size of 2.53 µm and a rotation step of 0.500º. For S2, 388 radiographs were made, with the same source voltage and current, an image pixel size of 3.98 µm and a rotation step of 0.500º.

The mechanical grinding was executed with a Retsch Mortar Grinder 200, at the speed of 50 Hz: 100 min^{-1}, S1 for 11 minutes and S2 for 7 minutes.

The Vickers Indentation was performed with a Struers Duramin, with the force of 5N (HV 0.5), for 10 seconds in each particle.

The colorimetry was executed using the colorimeter DataColor with iluminant D65/50 at 10º, calibrated with two porcelain pieces, one black and one white.

µ-FTIR analysis was done with a spectrometer Bruker, Tensor 27 model, in the mediam infrared region (MIR). The spectrometer, linked to the mycroscope Hyperion 3000 is controled by the softawere OPUS 7.2, Copyright© Bruker Optik GmbH 2012, has a detector MCT (*Mercury Cadmium Telluride*) which allows the acquisition of spectrums from different points in the sample.

The samples were analyzed in the transmission mode using a 15x objective and a Diamond compression microcell EX'Press 1.6 mm, STJ-0169. The IR spectrums were traced in the 4000-600 cm-1 region, with 64 scans and spectral resolution of 4 cm-1.

Mineralogical composition and crystallinity of the raw and final products were determined by X-ray diffraction (XRD). Prior to any analytical measurements, the samples were air dried and grounded. An XPERT-PRO (PANalytical) diffractometer with CuKα radiation and a X´Celerator detector was used. The measurement conditions were: 40 kV and 35 mA, 0.002 º2θ step size and 10 s of counting time. "High Score Plus" analytical software and PDF2 database were used to identify the phases.

Appendix IV. 2. - Raw materials information

Egg Yolk

Home-grown egg production by Engineer José Carmo Rosa. Chickens grown in the countryside, fed with cabbages and sometimes grain. Eggs sourced in Carvalhal, a small village in the Tomar ridge, Santarém district, Portugal. First egg collected the 12th of March of 2015 and kept stored in the fridge until its use the16th of March of 2015. It was then place in a lamella for 24h to dry, inside a cabinet, and then analyzed by means of µ-FTIR. Second egg collected the 4th of September of 2015 and kept stored in the fridge until its use the 6th of September of 2015.

Honey

Honey of biological production in Castanheiro, with low crystallization. Used in both the 16th of March of 2015 and the 6th of September of 2015. Placed in a lamella and dried for 30 hours inside a cabinet for µ-FTIR analysis.

Milk

The milk used was from the brand Mimosa, since at the time it was used a biological milk could not be found.

Gelatin

The transparent gelatin used for the colorimetric measures was from the brand Jerónimos, it is indicated for alimentary use, and was prepared by dropping the leaves of gelatin for 1 minute in distilled water (on which the initial weight of 1.08g turned to 4.33g), after that they were boiled at 15% concentration and applied with the smalt pigment.

Walnuts

From the producer Mr. Domingos Barros in Raposa, Santo André, Parish of the County of Montalegre (North of Portugal). Supplied by Dr. Agnès Le Gac. Biological production

with neither fertilizers nor pesticides. Collected in the 3rd week of October 2014, acquired in April 2015 (six months of drying).

Walnut oil (industrial production)

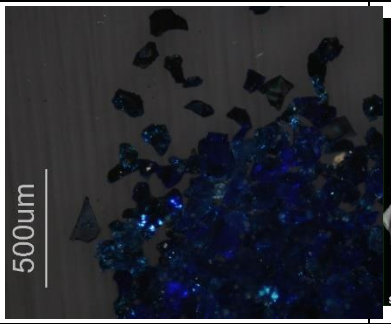
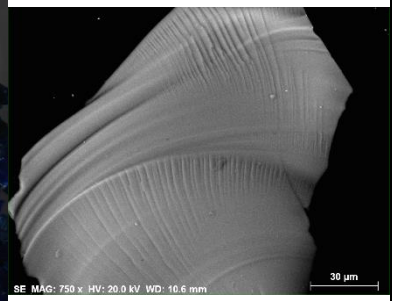
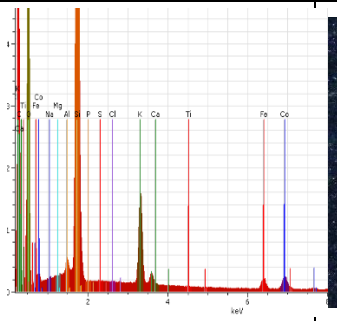
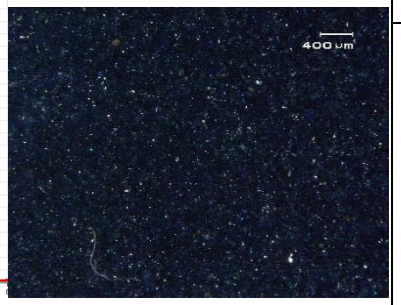
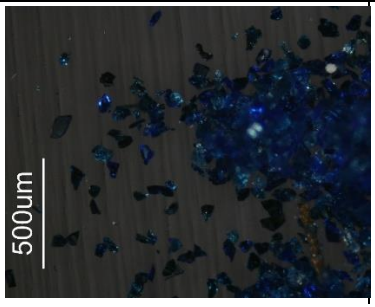
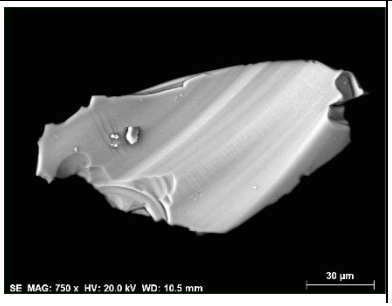
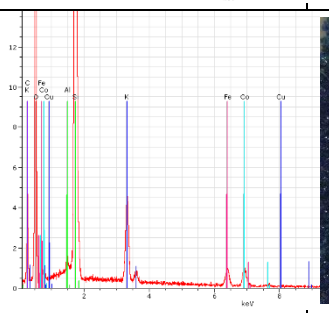
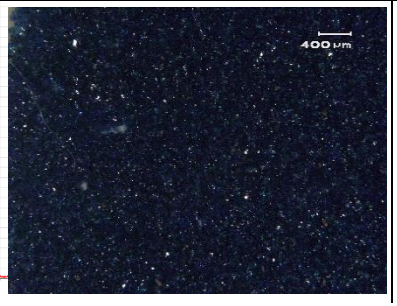
Maimeri (dal 1923), made in Italy-F.lli Maimeri SC. Srl Mediglia (MI), walnut oil for oil painting. Extract from refined walnut seed. Acquired by the DCR FCT-UNL in 2003. Placed in a lamela in June 2014 and dried for 6 months.

Gloves glue

Glue made from a white tawed leather, obtained from a sheep skin tanned with alum in March of 2000 by António Augusto Carvalho Ramos in *Casa das Luvas,* Geifães, Portugal. Supplied by Dr. Agnès Le Gac. The glue was produced according to the procedure described in Appendix III.2 and then left to dry for three days to proceed to μ-FTIR analysis.

Appendix V – Smalt analysis

Table A.17 – Smalt 1 analysis

Sample	Optical Microscopy	SEM imaging	Chemical Composition (wt%)	Spectrum	Stereomicroscope (Paint applied with glue)	Colorimetry		
						L*	a*	b*
After grinding			Si 68.56 K 16.12 Fe 5.31 Co 7.73 Al 0.98 Cu 0.34			25,76	-3,18	-29,11
Sieve opening: 63µm			Si 68.49 K 13.75 Fe 7.77 Co 8.67 Al 1.19 Cu 0.12			26.04	-3.43	-30.76

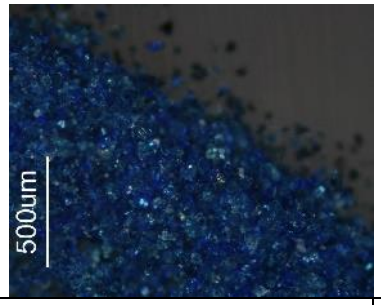
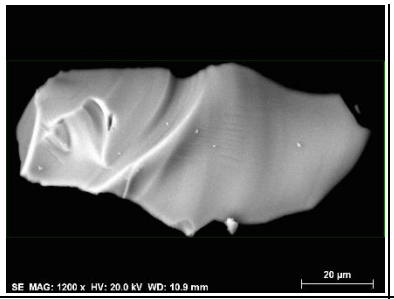
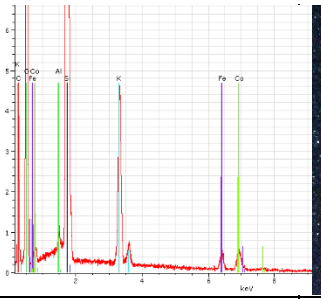
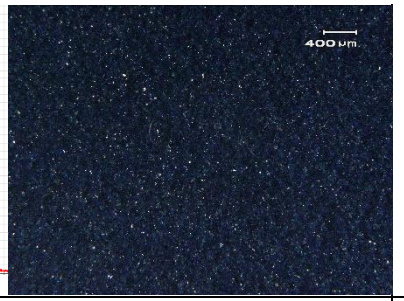
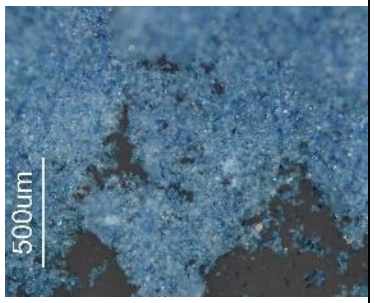
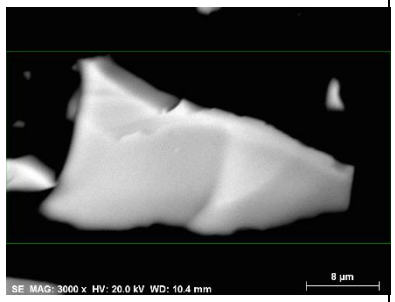
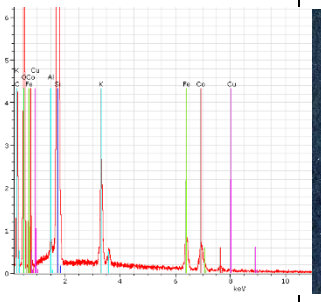
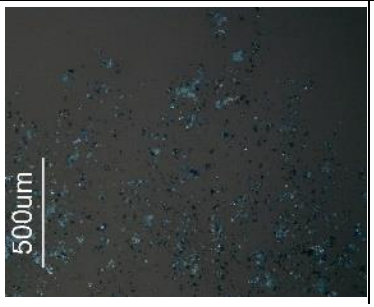
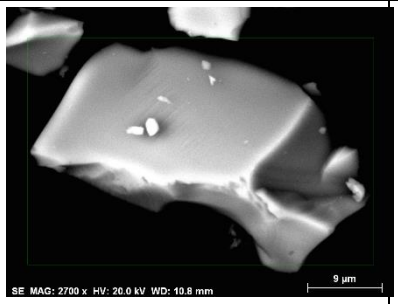
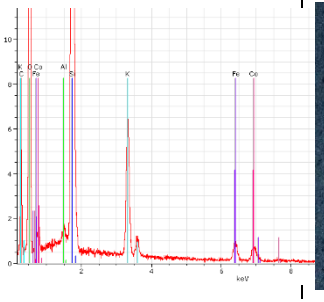
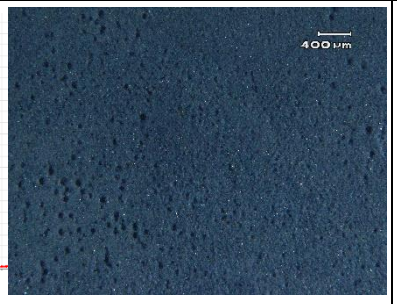
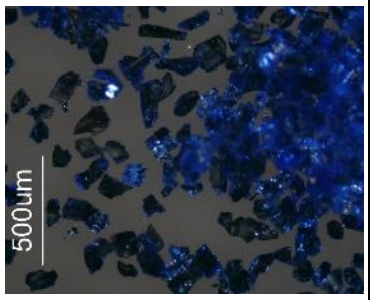
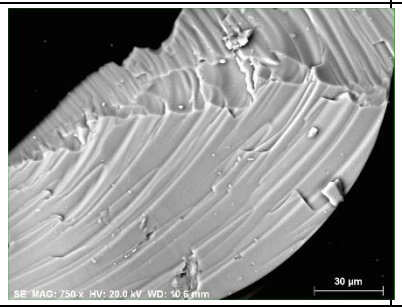
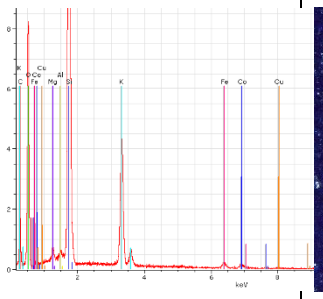
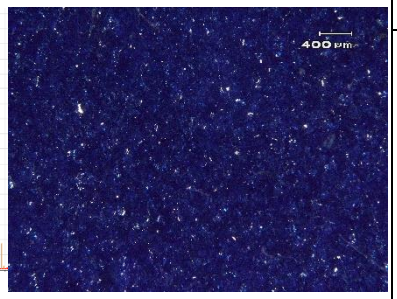
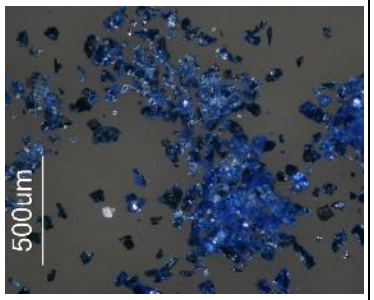
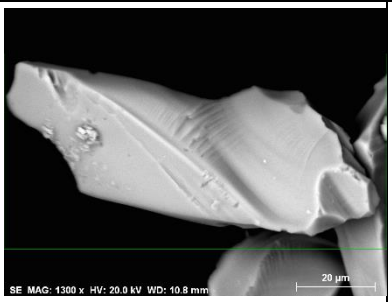
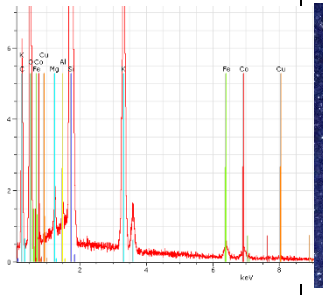
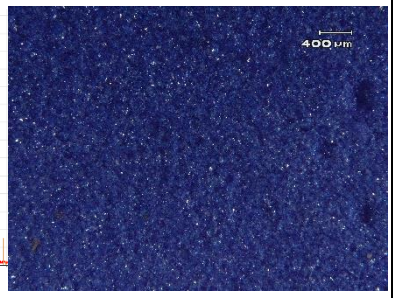
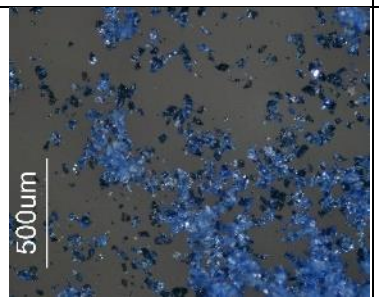
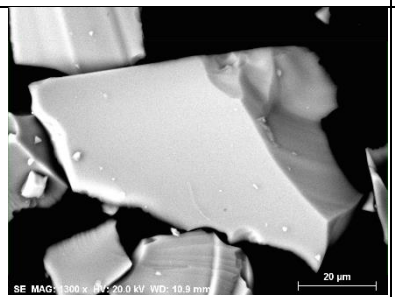
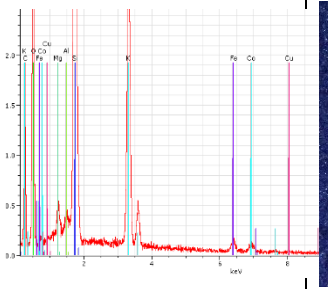
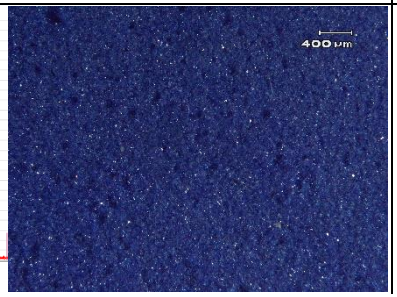
Sieve opening: 45 µm			Si 66.40 K 19.17 Fe 5.82 Co 7.37 Al 1.24			31.23	-5.49	-30.58
Sieve opening: 25 µm			Si 65.34 K 11.75 Fe 10.55 Co 10.88 Al 1.01 Cu 0.47			44.00	-8,47	-30.88
Sieve opening: Ultra Fine			Si 68.22 K 17.28 Fe 6.75 Co 6.29 Al 1.47			48.11	-8.48	-28.66

Table A.18 – Smalt 2 analysis

Sample	Optical Microscopy	SEM imaging	Chemical Composition (wt%)	Spectrum	Stereomicroscope (Paint applied with glue)	Colorimetry		
						L*	a*	b*
After grinding			Si 64.36 K 26.91 Fe 3.05 Co 2.67 Al 1.02 Cu 0.26 Mg 1.73			31.40	-0.55	-61,10
Sieve opening: 63µm			Si 63.66 K 27.65 Fe 2.87 Co 2.47 Al 1.20 Cu 0.17 Mg 1.98			39.73	-5.53	-54.75
Sieve opening: 45 µm			Si 62.89 K 28.29 Fe 3.12 Co 2.67 Al 1.06 Cu 0.35 Mg 1.62			42.10	-7.30	53.36

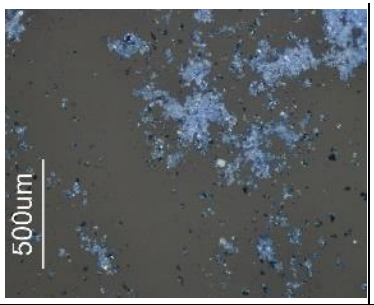
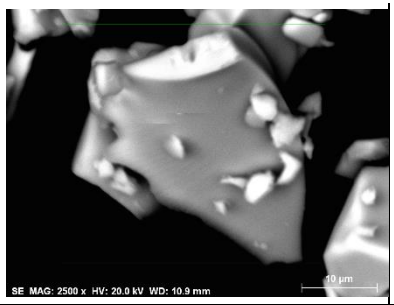
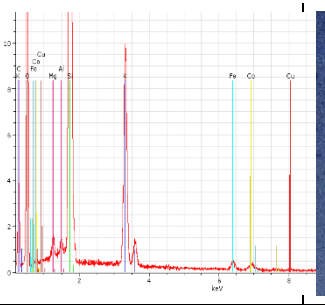
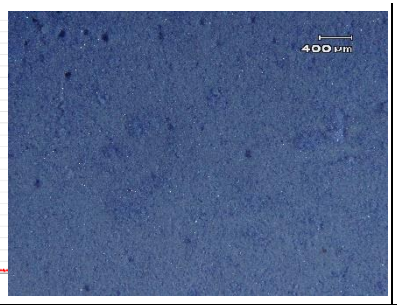
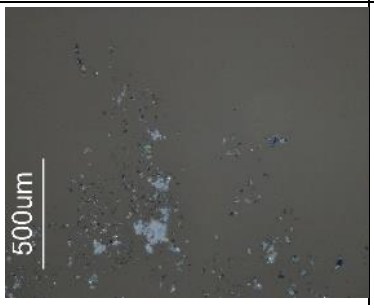
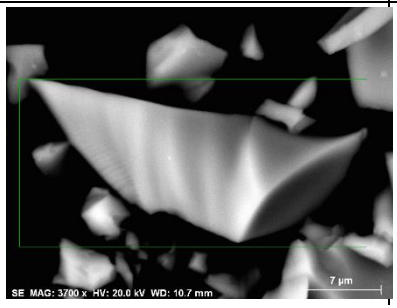
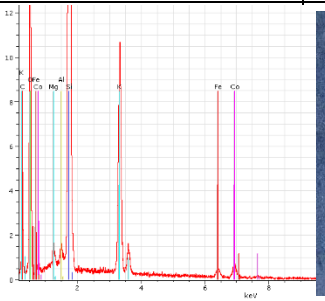
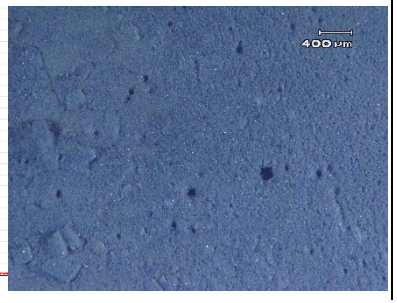
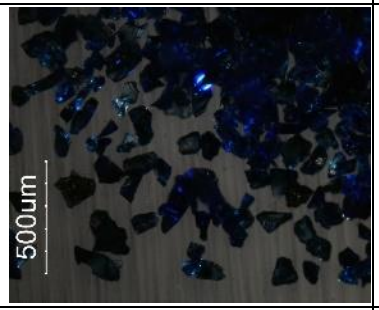
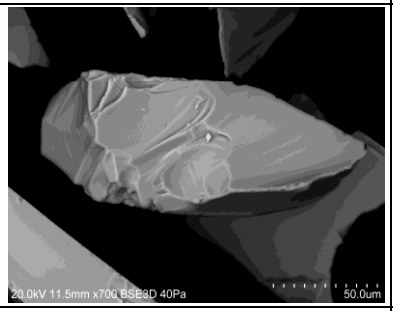
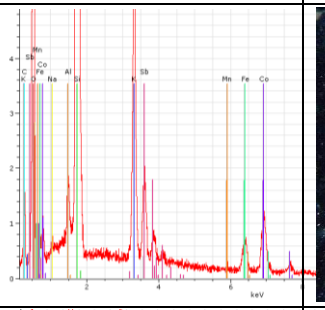
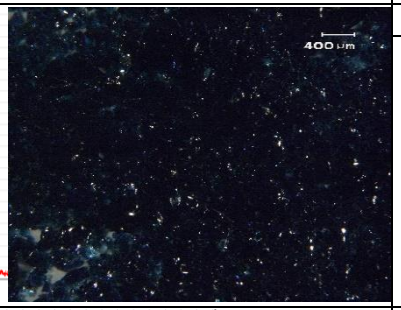
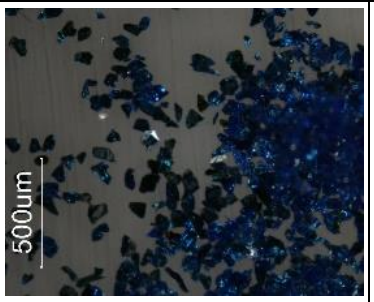
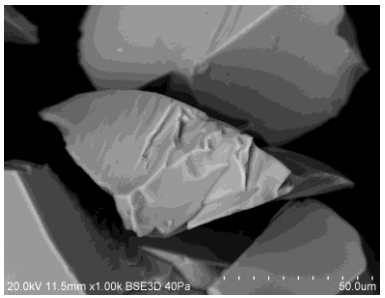
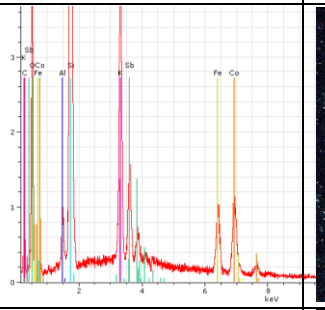
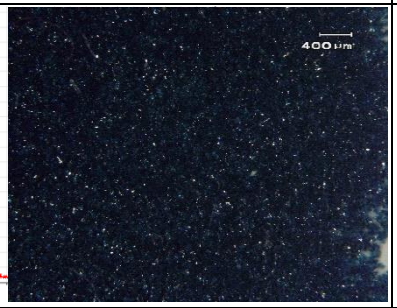
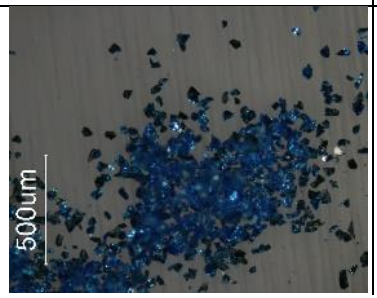
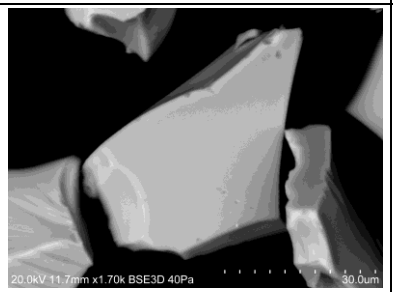
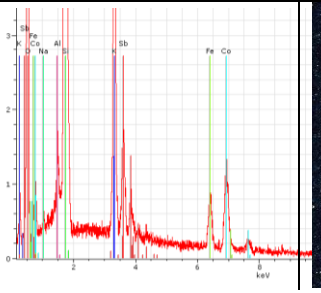
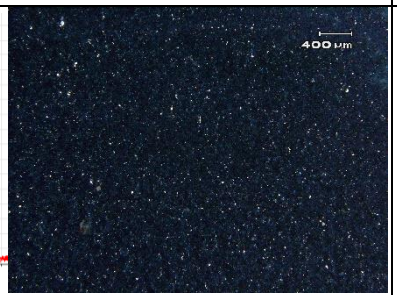
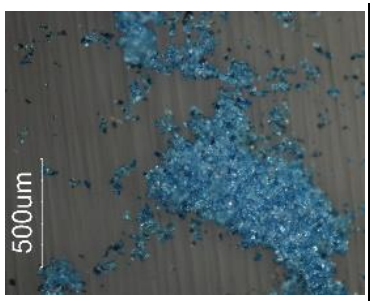
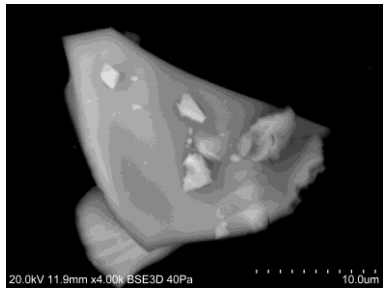
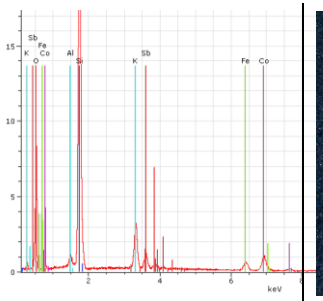
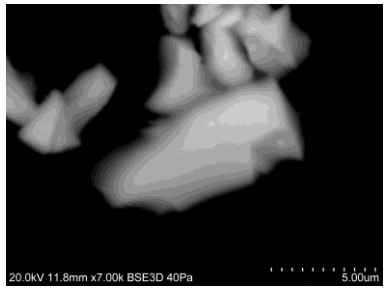
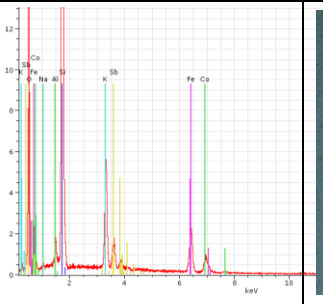
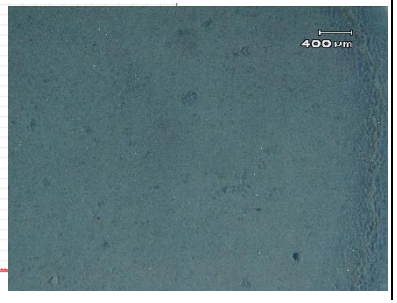
Sieve opening: 25 µm			Si 62.73 K 28.05 Fe 3.13 Co 2.72 Al 1.17 Cu 0.56 Mg 1.65			58.63	-8.35	-39.95
Sieve opening: Ultra Fine			Si 59.37 K 28.85 Fe 3.22 Co 5.54 Al 1.74			62.33	-8.77	-36.29

Table A.19 – Smalt 3 analysis

Smalt 3

Sample	Optical Microscopy	SEM imaging	Chemical Composition (wt%)	Spectrum	Stereomicroscope (Paint applied with glue)	Colorimetry		
						L*	a*	b*
After grinding			Si 57.17 K 13.89 Fe 6.11 Co 12.49 Al 2.27 Sb 8.07 Na 0.51			20.85	0.00	-19.37
Sieve opening: 63µm			Si 60.95 K 6.88 Fe 2.81 Co 10.30 Al 2.26 Sb 7.95 Na 0.94			25.36	-2.54	-26.02
Sieve opening: 45 µm			Si 60.94 K 13.39 Fe 4.40 Co 9.78 Al 2.31 Sb 7.54 Na 1.63			28.32	-4.70	-28.90

Sieve opening: 25 µm			Si 31.19 K 6.15 Fe 4.79 Co 10.36 Al 2.11 Sb 6.98 Na 1.26			39.00	-7.81	-27.88
Sieve opening: Ultra Fine			Si 58.35 K 14.00 Fe 5.40 Co 11.34 Al 2.54 Sb 6.79 Na 1.57			59.43	-7.81	-18.37

Appendix VI – XRD spectrum