Master's degree course in
Conservation Science and Technology for Cultural Heritage

Thesis

The Pigments' Characterization of the 15th Century Bas-relief *"Madonna col bambino, Santa Caterina da Siena e un priore certosino"* by A.G. Amadeo through SEM-EDX and Vibrational Spectroscopic Techniques

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INTRODUCTION

The present study deals with spectroscopic analytical techniques aimed at characterizing pigments placed on the surface of a polychrome terracotta bas-relief, dating back to the 15th century, entitled *"Madonna col bambino, Santa Caterina da Siena e un priore certosino"*. The analyzed work comes from the workshop of Giovanni Antonio Amadeo (Pavia, 1447 - Milan, 1522) and is stored at the Castello Sforzesco in Milan.

The report is organized in six main chapters: the first describes the pigments and their properties; the second chapter describes Italian painting between the 15th and 16th centuries; in the third part there are the most common methods of cleaning the paintings; in the fourth chapter the nature of terracotta is explained, to deepen the knowledge of this material used as a support in painting; in the fifth chapter there are the materials and methods used for scientific analyses and in the sixth part the results and discussion of the latter. The conclusion of the work is dedicated to the final considerations, which summarize what has been said and further specify the reason for the research carried out.

Seven samples were taken in different areas of the work for the characterization of the pigments using analytical techniques such as ATR-FTIR, SEM-EDX, Raman and optical microscopy with 3X magnification.

The results of the analyses performed on the cited samples, obtained by the spectroscopic techniques will be reported. They are organized by dividing them by color. The identification of the pigments was carried out by comparing the results obtained with the data present in the literature.

Thanks to my investigations on these samples, the restorers were able to proceed with the cleaning of the surface of the work of art. Indeed, this terracotta was subjected to a cleaning operation, carried out by Mario Colella and Silvia Marchioron, restorers of the Piccolo Chiostro Study and Conservation Center. This procedure was performed in order to gradually remove the dark patina that obscured the surface of the bas-relief making the colors almost unrecognizable[1], so as to bring back the original ones and the precious materials used by the artist.

As a matter of fact, the cleaning revealed a rich and lively chromatic range: from the bright red of the Madonna's robe and the Child's pillow, to the white of the Carthusian's robe, the veil of Saint Catherine and the Child's robe.

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[1] https://www.finestresullarte.info/arte-antica/milano-restauro-terracotta-giovanni-antonio-amadeo

Moreover, it showed the clear incarnations of the characters and the different expressions of their faces, previously completely lost and which now allow a completely different vision and reading of the work. According to the museum, however, the real surprise was the discovery of the color with which the Virgin's veil is made, i.e., green, an unusual chromatic choice, compared to the traditional blue of the mantle.

From the analyses and measurements carried out on the work, the restorers discovered that the pigments used were the original ones, used precisely in the Lombard artistic workshops of the 16th century, and it was therefore possible to ascertain that the work almost entirely preserves the ancient original polychrome project.

1. PIGMENTS

The pigments are fine colored powders, insoluble in the dispersing medium forming a more or less dense mixture, which manifests its covering power once applied as a pictorial layer. Inorganic pigments are used in painting as they are, while organic dyes generally require a substrate to support them, giving rise to a lacquer that stands out for its partial transparency. The inorganic pigments have a mostly mineral origin, among which oxides, carbonates, sulphides, sulphates[2].

1.1 Chemical properties

From a chemical point of view, it is appropriate to distinguish between organic and inorganic pigments. The first are essentially composed of carbon and hydrogen. In the classic palette there are no real organic pigments, but rather organic dyes fixed on a semi-transparent inorganic support mostly consisting of hydrated aluminum oxide. Examples are the various types of lacquers and the various colors deriving from tar. The origin is both vegetable and animal[3]. The fundamental properties that a pigment must possess are insolubility in the medium and in general in most solvents, chemical stability, and inertia towards the substances with which it must be mixed. The properties and composition of a pigment can be modified by the action, single or combined, of light, air, and pollutants.

The inorganic pigments, many of which of mineral origin, consist of the oxides, carbonates, sulphides, sulphates of various metals. They generally have a crystalline structure.

Pigments containing organic substances, for example, are not very stable to the action of light with a tendency to discolor. On the other hand, the inorganic ones are less sensitive to this phenomenon, but can undergo degradative effects due to a chemical reaction caused by pollutants present in the atmosphere or by inappropriate restoration interventions.

Light, humidity, and air can act concomitantly on the pigments causing either a darkening or, on the contrary, a loss of color or, more generally, a chromatic alteration.

The action of light is generally more marked if the constituent radiations have more energy, the most dangerous are therefore the UV radiations, which cause some pigments to become dark. In museums, the effects of light are usually considered by appropriately shielding the lighting sources[4].

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[2] Campanella L., Casoli A., Colombini M.P., Marini Bettolo R., Matteini M., Migneco L.M., Montenero A., Nodari L., Picciolo C., Plossi Zappalà M., Portalone G., Russo U., Sammartino M.P., *Chimica per l'Arte*, Zanichelli, Bologna, 2011.

[3] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, Nardini, 2007.

[4] Ivi, pp. 20-21.

UV radiation is one of the most probable causes that make the so-called "verdigris" dark[5].

The action of air is due to the oxygen, but also to the compounds present in the atmosphere such as CO_2, H_2S, SO_2, and SO_3 in the form of impurities to which some pigments are very sensitive. The action of these agents, however, is slowed down by the presence of the pictorial binder which, enveloping every single particle of the pigment, protects it from contact with these agents and separates it from the particles of the other pigments[6].

Oxygen combines with some pigments, modifying their composition by oxidation and causing them to brown organic pigments, but also inorganic pigments. Among the inorganic mineral pigments, we can cite as examples of oxidation those of lead white and lead dioxide, dark brown, which occur in wall paintings.

Carbon dioxide, (CO_2), associated with humidity, is involved in complex reactions that are not completely elucidated involving oxides and carbonates; azurite, for example, transforms into different hydrated copper salts of a green color[7].

Some pigments are subject to the action of hydrogen sulphide, (H_2S), which alters their nature by transforming them into dark-colored sulphides.

Moreover, hydrogen sulphide, interacts with all the pigments containing metals with which it forms black sulphides, such as lead presents in lead white, silver leaf, etc. Furthermore, they can occur between chromates and organic compounds with photocatalyzed formation of green chromium oxide (Cr_2O_3), but also mechanical processes as in the case of other pigments, such as bitumen, which by not drying completely cause the reticulation of the pictorial surface with their movement, also involving the adjacent pictorial layers. In particular, the action of acid oxides such as SO_2 and SO_3 present in the air, combined with water, give rise to strong acids which in turn cause sulphation.

Humidity is not in itself an aggressive agent, however associated with others it enhances its action both because it facilitates reactions by bringing the substances into solution, and because it can autonomously give rise to hydrolysis phenomena. It has been pointed out that the composition of the pigment is not the only factor that determines its stability, which also depends on the medium used.

The action of atmospheric agents is usually very slowed down by the presence of both the protective varnish and the pictorial binder.

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[5] Gargano M., Bonizzoni L., Grifoni E., Melada J., Guglielmi V., Bruni S., Ludwig N., *Multi-analytical investigation of panel, pigments and varnish of The Martyirdom of St. Catherine by Gaudenzio Ferrari (16th century)*, "Journal of Cultural Heritage" 46 (2020), pp. 289–297.
[6] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit.
[7] Campanella L., *op. cit.*, pp. 112-113.

While carrying out a protective action, it should be remembered that even mediums can interact negatively with pigments[8]; in addition to the influence on the optical properties, in some cases there is a real chemical incompatibility between binder and pigment, so much to involve the specific use of each pigment for a specific technique[9].

Chromates can oxidize various organic pigments (reaction catalyzed by light) causing them to lose color and transforming themselves into chromium oxide green (Cr_2O_3).

Other pigments such as bitumens, as they never dry completely, cause with their movement and contractions the reticulation of the pictorial surface with large cracks, sometimes involving also the adjacent pictorial layers[10].

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[8] Recommended reading: Clark R.J.H., *Pigment identification by spectroscopic means: an arts/science interface,* "C. R. Chimie" 5 (2002), pp. 7-20.
[9] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit. pp. 20-21.
[10] Gargano M., *op.cit*.

1.3 Pictorial film

Let is consider the effect of the incident light on a pictorial film, that is on a thin layer of chromatic material spread over a support. The pictorial layers are essentially composed of colored materials in the form of fine powder (pigments) dispersed in a homogeneous transparent binder (medium), all applied in the form of thin layers (a few tens of microns) over a white background (preparation) or also colored. The set of layers can possibly be covered with further protective films of transparent resinous substances (paints). Among these materials the one that determines the color to a greater extent is the pigment as the paint and medium are transparent and almost colorless[11].

The color of the pigment derives from its specific absorption coefficients of white light which act selectively on the various wavelengths. Furthermore, given the subdivision of the pigment into powder, the phenomena of diffuse reflection and refraction also take on great importance in determining the overall tonality. It is these parameters that combine to produce the opacity or hiding power of the pictorial film. The diffusion or "scattering" of light is directly linked to the granulation of the pigment, so the more it is ground, the greater the diffusion. However, this also depends on the ratio between the refractive index of the pigment and that of the medium: the higher this ratio, the opaquer the film. Therefore, the more a pigment is ground and the greater its refractive index than that of the medium, the greater the ability of the pictorial film to cover the surface on which it is spread, that is the preparation base.

It can be said that the hiding power of a pigment depends on its refractive index with respect to the medium, on the average size of its particles and on the tonality of its color[12].

For light pigments it is above all the refractive index and granulation that determine the hiding power. On the other hand, for dark pigments it is selective absorption, whereas for normal colored pigments the three factors act simultaneously.

In any case an important role is also attributed to the concentration of the pigment in the medium[13]. Normally the artists used preparations of white tone, however in many cases a further background of colored preparations was spread over the top (primers, background backgrounds) which served to give a particular result to the pictorial film by contrast or to confer specific intonations by exploiting the selective absorption of the substrate.

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[11] D'Anna G., Marconi S., Merucci C., Papini M.L., *Preparazione e finitura delle opere pittoriche. Materiali e metodi*, a cura di Maltese C., Mursia, Milano, 1993.

[12] Diodato S.P., *I buoni colori di una volta: ricettario fotografico per conoscere e fabbricare pigmenti, leganti, vernici e materiali artistici antichi, direttamente dai trattati medievali*, Menabò, 2010.

[13] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit. p. 14.

The technique of painting the models is based on the same principle by means of "glazes" of a semi-transparent colored substance applied on a layer of covering pigment[14].

The varnish, in addition to having the primary function of protecting the painting, acts optically on the pictorial layer strongly attenuating its scattering as it varies the refractive index of the pigment. The effect is to decrease or eliminate the whitish diffusion and to better appreciate the color in each pigment[15].

However, this involves a slight lowering of the reflection intensity, commonly called "tonal lowering", due to the slightly filtering effect of the paint so that the colors are moderately darker than the unvarnished painting[16].

In conclusion, by analyzing the path of white light that strikes a painted surface it can be observed that:

a) part of the beam is mirrored by the paint surface;

b) the other fraction passes through the paint layer and undergoes refraction;

c) this portion reaching the pictorial layer can be partly diffused, partly selectively absorbed;

d) any fraction that crosses the pictorial layer meets the preparation from which it can still be diffused or absorbed;

e) all the components that have been reflected in this path return to the eye and determine the global effect of perception.

At this point one can well understand how complicated the mechanism that leads to the definitive formation of the image of the painting that is observed is. It should also be borne in mind that for some colored pigments made up of very transparent granules a too fine grinding would increase the hiding power but would lead to a loss of color, as the scattering of white light would become predominant over selective absorption. In these cases, it is necessary to control the granulation in order to reach a compromise[17,18]. Some pigments can also interact with each other if the binder is not sufficiently protective. For example, pigments containing sulphides, except for vermilion (HgS is insoluble and therefore stable), tend to react with lead and copper-based pigments to form dark-colored sulphides[19].

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[14] Cfr. Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit. pp. 19-20.
[15] McLaren K., *The Color Science of Dyes and Pigments*, Hilger A. Ltd., Boston, 1986.
[16] Gargano M., *op.cit.*
[17] Campanella L., *op.cit.*, pp. 112-113.
[18] D'Anna G., *op.cit.*
[19] Recommended reading: Church A.H., *The chemistry of paints and painting*, Seeley & C., London, 1890.

Chromates can oxidize various organic pigments (reaction catalyzed by light) causing them to lose color and transforming themselves into chromium oxide green (Cr_2O_3).

Other pigments such as bitumen, as they never dry completely, cause with their movement and contractions the reticulation of the pictorial surface with large cracks, sometimes involving also the adjacent pictorial layers[20].

1.4 Other properties of pigments

Among the properties of the pigments, those related to their interaction with the binder deserve attention. The pigments, to be used, must be mixed with an adhesive medium to form an easily spreadable paste with it. The characteristics of this paste depend both on the nature of the pigment and on that of the binder. Each pigment generally requires specific quantities of a certain binder[21]. It should be borne in mind that the medium, with aging and the consequent alterations, can yellow and change the chromatic aspect of the pigment dispersed in it. These cases occur especially if the binder is linseed oil, a substance with a marked tendency to yellow. some pigments show a close affinity for a particular binder; others are almost incompatible. This has consolidated the prevalent use of each pigment for a specific pictorial technique. In this sense there are pigments typical of the oil technique, others typical of the tempera or water techniques in general[22].

The type of medium influences the tone of the pigments with its refractive index, making some of them more transparent and therefore less reflective and darker than others that are more reflective and brilliant. This is for example the case of the Green Earth which is more transparent in oil than in tempera.

In addition to physical incompatibilities sometimes also chemical incompatibilities with the binder occur, as in the case of "wet" painting in which the alkaline medium (calcium hydroxide) excludes the use of many alkali-sensitive pigments.

In fact, the pigments used in this technique are above all stable mineral oxides (Terre and Ochre) or other inert inorganic substances, such as silicates (Green Earth, Enamel, etc.), black based on Carbon, Calcium carbonate (Bianco di San Giovanni) and others[23].

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[20] Gargano M., *op.cit.*
[21] D'Anna G., *op.cit.*
[22] Gettens R.J., Stout G.L., *Painting materials: A short encyclopedia.* Dover Publications Inc., New York, 1966.
[23] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., pp. 21-22.

1.5 Classification of pigments

The pigments are fine colored powders, insoluble in the dispersing medium with which they form a more or less dense mixture, which manifests its covering power once applied as a pictorial layer. Inorganic pigments are used in painting as they are, while organic dyes generally require a substrate to support them, resulting in a lacquer that stands out for its partial transparency.

1.5.1 White pigments

- Calcite and marble dust – $CaCO_3$

Calcite is the name of the most common mineral form of calcium carbonate. Marble is metamorphic limestone, a recrystallized calcite, formed following the transformation of carbonate rocks under the action of external agents such as pressure and temperature. Calcium carbonate is the pigment of inorganic and mineral origin, known since prehistoric times and subsequently used in various eras, from the Roman to the entire medieval period[24]. From the grinding of marble and travertine a very fine powder is obtained, insoluble in water and with poor covering power, for these characteristics it was widely used in the glazing of the frescoes. It is also used in the preparation of Venetian plaster and it is stable to light and humidity. Moreover, this pigment is applied in tempera and it is not recommended for the oil technique[25].

- San Giovanni white – $CaCO_3$

San Giovanni white is a natural mineral and artificial pigment: from the calcination of a limestone, calcium oxide (CaO) is obtained, which by adding excess water forms, $Ca(OH)_2$, which by prolonged exposure to air with carbon dioxide combines to reform calcium carbonate, $CaCO_3$[26]. San Giovanni white, as Cennini reports, is dried and powdered slaked lime that is immersed in water for eight days, the water must be changed by stirring every day[27].

Then small loaves are made which are left to dry in the sun. Afterwards San Giovanni white is finely ground, dissolves in acids and by calcination it becomes calcium oxide. In addition, it is stable to light and humidity, it has a more or less white color, depending on the granulation and the impurities present. Moreover, this pigment has good hiding properties only in the wall painting technique and is quite resistant to normal atmospheric agents, except for acidic ones.

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[24] Ivi, p. 23.
[25] Campanella L., *op.cit.*, pp. 113-114.
[26] Diodato S.P., *op.cit.*
[27] Rinaldi S., *La fabbrica dei colori, pigmenti e coloranti nella pittura e nella tintoria,* Bagatto Libri, Roma, 1995.

Furthermore, it is still considered the white par excellence in fresco painting, it is also used in tempera but is not recommended in oil techniques. As inert it can be found in preparations, instead of plaster, in paintings of northern Europe.

- Lime white – $Ca(OH)_2$

This pigment is of artificial origin obtained from the calcination of a limestone with the formation of calcium oxide, which by adding excess water forms, $Ca(OH)_2$. Calcium hydroxide, drying in the air, is transformed into calcium carbonate. Lime white was known since prehistoric times and by almost all ancient civilizations, it was used in fresco as a pigment for the preparation of plaster and in tempera painting. Due to its optical properties and poor hiding power, this pigment is often replaced with other white pigments in oil paints. Moreover, it is stable to light and humidity.

- Plaster – $CaSO_4 \cdot 2H_2O$

Plaster is a material of natural, mineral origin, a calcium sulphate dihydrate. From the chemical point of view, it is not very soluble in water, but quite soluble in a solution of ammonium salts or alkaline carbonates. Calcium sulphate exists in a semi-hydrated form, called "gypsum" capable of setting when mixed with water. Thus, this pigment is transformed into common plaster and it is used above all for the preparation of tables and canvases, mixed with animal glue[28].

- Lead white (*biacca*) – $2PbCO_3 \cdot Pb(OH)_2$

Biacca is of inorganic, mineral and artificial origin. It is a basic lead carbonate, one of the most used whites since the 4th century BC[29]. It was used by the Greeks and Romans, in the Renaissance up to the 19th century, replaced, due to its high toxicity, first by zinc white and then by titanium white. Besides, this pigment has a high hiding power; it is insoluble in water but soluble in acids and, when it dissolves in them, this gives rise to efflorescence. Through calcination it first becomes yellow (massicot) and then red (minio). Lead white tends to darken due to the action of hydrogen sulphide, turning into black lead sulphide, PbS. In wall paint, this pigment often tends to form the oxidized form, PbO_2, brown in color, in lean binders and in the presence of moisture. In the oil technique, it is compatible with all pigments[30].

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[28] Gettens R.J., Mrose M.E., *Calcium Sulphate Minerals in the Grounds of Italian Paintings*, "Studies in Conservation", 1:4 (1954), pp. 174-189.
[29] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., pp. 23-24.
[30] Campanella L., *op.cit.*, p. 115.

Moreover, it was mainly used in egg tempera by artists; mixed with linseed oil, which dries quickly, it forms a very compact and hard pictorial film[31].

- Solid white – $BaSO_4$

Barium sulphate has an artificial origin. It is produced by reacting sodium sulphate with a solution of barium chloride. It is a transparent white and for this reason used above all as an additive filler for other pigments and for glazes. It is an inert material both to chemical agents and to light and heat. This pigment is used in fresco, tempera and oil painting[32]. Due to its transparency in oil, since the mid-19th century, it has been widely used as an additive filler for other pigments and as a support for the preparation of lacquers. It is compatible with all pigments even if it seems to accelerate the discoloration of some synthetic organic pigments. Solid white is used in different techniques such as: oil, tempera, and watercolor.

- Tin white – SnO_2

Pigment of inorganic, mineral, and artificial origin, it is a tin oxide. This pigment is obtained by calcining stannic acid and tin oxalate. It was used in Europe especially between the 16th and 17th centuries. Tin white has an excellent hiding power, quite stable to light and humidity, it is used both in the tempera technique and in oil painting.

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[31] Bazzi M., *Abecedario Pittorico*, Longanesi & C., Milano, 1956.
[32] McLaren K., *op.cit*.

1.5.2 Blue pigments

The cultural choice of blue as the dominant color of the new course of society, from the mid-Middle Ages onwards, evidently has a meaning deeply rooted in the pervasive theocratic vision of the world, as evidenced by its close relationship with the dominant gold. The luster, that was typical of the material, was transmitted to the color and evidently succeeded in giving the sacred spaces and the artistic furnishings contained therein a symbolism, and an evocative power that could not be reached by other means.

Even the concept of a "color of the sky" seems, from linguistic studies, to be quite recent compared to the descriptions of the classical era and it is certainly no coincidence that in the epochs preceding the definition of blue as the color of the sky, the latter was defined as "the color of gold". Just as it is particularly interesting that, for symmetry, the first words that define the color of the sky use the specification, below, of "the color of lapis lazuli". The color of the precious stone and therefore, consequently, the pigment obtained from it, contain, experientially but also conceptually, the sense of "brilliance" and also in the history of Indo-European languages are related to gold[33]. The preciousness of these materials therefore derived not only from their intrinsic value and from their scarce accessibility and production cost, but also from the aesthetic and conceptual qualities that they conveyed. To complement and almost compete with gold (of the mosaics, liturgical goldsmiths, framing and gold backgrounds of the altarpieces), even the choice of blue had to be equally precious in terms of color rendering; it had to be the bearer of aesthetic values only lapis lazuli blue could transmit, in the wide choice of possibilities offered to artists. In fact, there were many pigments and dyes that made it possible to create the blue color, available at the time[34]. Among them, the oldest and most widely used, still up to the early Middle Ages, given the material attestations available to us, was the so-called Egyptian blue. It was certainly not second to him azurite, widely used and attested since ancient times, a splendid blue pigment that was obtained by grinding and purifying the mineral bearing the same name, the element of which is mainly copper, which is extracted from the mines of silver. This pigment is sometimes referred to as *lapis armenius*, but better known as *blue of the Magna* (elsewhere also called "Tuscan blue" or "Italic blue")[35].

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[33] Diodato S.P., *op.cit.*
[34] Bazzi M., *op.cit.*
[35] Cennini thus mentions azurite in chap. LX: «Azzurro della Magna è un colore naturale, el quale sta intorno e circunda la vena dell'ariento. Nasce molto in nella Magna, e ancora in quel di Siena. Ben è vero che con arte, o ver pastello, si vuole ridurre a perfezione».

- Azurite – $2CuCO_3 \cdot Cu(OH)_2$

Azurite is of natural mineral origin. It is basic copper carbonate and has an intense blue color if not too finely ground, otherwise it loses color and covering power. It has been known since the time of the Egyptians and many ancient civilizations, used until the 17th century.

Under normal environmental conditions this pigment is rather stable but tends to become stable in wall paints under the action of humidity and other atmospheric agents, transforming into hydroxide-sulphate or hydroxide-chloride. It is stable even in weak acids.

In ancient times, Azurite was used in tempera on a wall over a red base of morellone or black vine, not being compatible with the fresco technique[36]. Moreover, it has been used in all techniques on a mobile support, such as tempera on wood.

The market offers many blue pigments and dyes, as an alternative to using only ultramarine blue obtained from lapis lazuli[37], and it would be too simplistic to state, as we often read, that the choice made by the various artists or clients was due exclusively to considerations of economic type or demonstrative of a *status*. The use of azurite in past ages occurred frequently, in fact there are many examples of paintings also of very high commission in which another pigment is preferred to ultramarine blue. There were therefore also aesthetic or even technical evaluations that could direct the choice: among all the possible examples, see the splendid and extremely refined "*Madonna Stoclet*", by Duccio di Boninsegna, today at the Metropolitan Museum of Art in New York, in which the mantle of the Virgin is qualified for a dark draft of a deep shade of azurite, which can only be reached using this pigment[38].

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[36] Bazzi M., *op.cit.*

[37] Frison G. & Brun G., *Lapis lazuli, lazurite, ultramarine 'blue', and the colour term 'azure' up to the 13th century,* "Journal of the International Colour Association" 16 (2016), pp. 41-55.

[38] Recommended reading: Maltese C., *I supporti nelle arti pittoriche. Storia, tecnica, restauro*, Mursia, Milano, 1990.

- Vivianite (blue ocher) – $Fe_3(PO_4)_2 \cdot 8H_2O$

Pigment of natural mineral origin, with a greenish blue color, was known by the Greeks in the classical age and it is obtained by grinding the base material. Vivianite is light stable and moisture stable enough. It has a fair covering power and has been used in all painting techniques.

- Natural ultramarine blue (lapis lazuli) – $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$

The descriptive term for the blue color and the lapis lazuli material is attested in the western area, since the Greek world, since one of the three terms used to describe color is precisely κυάνεος, a word that also indicates lapis lazuli as a stone[39]. «Il blu più bello è ricavato da una pietra, e proviene da terre al di là dei mari, ed è perciò detto oltremare»[40].

Its presence in the classical world was considered limited to stone and exclusively linked to precious decorations. The ever-increasing possibility of analytically investigating material survivals has instead made it possible to trace the use of lapis lazuli as a pigment in painted decorations, both murals of objects, in increasingly ancient periods[41]. Then, expanding to consider the countries of the neo-eastern Mediterranean, again for the ancient era, we encounter considerable evidence of the use of lapis lazuli blue, in a privileged environment, in Egypt. Blue combined with white, for the representation of the gods and the pharaoh's family, is well known. Even for the Babylonian and Jewish populations, lapis lazuli was a sacred color, often in combination with the other great material-color connected to the representation of the divine: gold. The ultramarine blue therefore allowed saturation without paint and hue almost without the need for mixing. However, it is undeniable that the use of the oily *medium* constituted a challenge to the supremacy of the ultramarine blue, who was partly losing precisely those characteristics that had made him appreciated above any other choice, despite the cost. The granulometry of the mineral pigment in fact made slippage of the pictorial surface very frequent during the polymerization phase of the binder, that is, thickening in islands created by the strong *craquelure*[42]. To regain a completely saturated blue, the painters who used it were forced to add lead white, thus compromising the purity of the pigment.

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[39] Ibidem.

[40] Averlino A. (Filarete), *Trattato di architettura*, a cura di Finoli A.M., & Grassi L., Il Polifilo, Milano, 1972.

[41] Among the new discoveries, most important for dating examples from the ancient world, it is recommended this reading: Brecoulaki H. *"Precious colours" in ancient Greek polychromy and painting: material aspect and symbolic values*, "Revue Archéologique" 1 (2014), pp. 3-35.

[42] Wallert A., Hermens E., Peek M., *Historical Painting Techniques, Materials and Studio Practice*. J. Paul Getty Trust, The Uninted States of America, 1995.

«Azzurro oltremarino si è un colore nobile, bello, perfettissimo oltre tutti i colori, del quale non se ne potrebbe né dire né fare quello che non ne sia più. E per la sua eccellenza ne voglio parlare largo e dimostrarti a pieno come si fa. E attendici bene, però che ne porterai grande onore e utile. E di quel colore, con l'oro insieme (il quale fiorisce tutti i lavori, di nostra arte), vuoi in muro o vuoi in tavola in ogni cosa risprende».

Cennino Cennini defines it in this way, singing her praises and giving us proof of the absolute consideration, he enjoyed not only among the various blues, but also all the colors available in the palette of the artists of the time[43].

Lapis lazuli is a precious pigment, of mineral and natural origin. It is s a sodium and aluminum silicate containing sulphides and traces of pyrite, obtained from a stone, lazurite, which is washed, purified and ground[44]. Chemically it is the most complex of all mineral pigments: the proportions between Al, Si and O are fixed in the alumino-silicate lattice, while the quantities of the other elements present such as cations and anions are variable. Various recipes are known, including that of Cennino Cennini which describes the method of extraction.

Natural ultramarine blue, from blue tending to violet, can vary in shades from light to dark. It appears brighter in tempera than in oils and is often mixed with a white pigment. In the late Middle Ages, it was reserved for the Virgin's mantle, and its use was described separately in the contract signed by the painter[45]. This pigment is stable to normal atmospheric agents; it decomposes and discolors with acids. Furthermore, it has a fair covering power and can be used in fresco, tempera, oil.

In the countries of Northern Europe, starting from the 16th century there was a sort of crisis in the supplies of the finest blue pigment, which became more and more linked to works of great prestige. This pigment crossed the entire history of art up to the 18th century and was then replaced starting in 1827 by its artificial version, known as artificial ultramarine[46].

The examples of the use of ultramarine blue range from precious objects among the Egyptians to medieval illuminated manuscripts, to the Impressionists (Monet, Pissarro, Renoir).

Raffaello was another artist who used ultramarine blue, see the example of the *"Madonna del Cardellino"* (figure 1)[47].

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[43] Cennini C., *Il libro dell'Arte*, a cura di Fabio Frezzato, Neri Pozza Editore, 2003.
[44] Rinaldi S., *op.cit*.
[45] Frosinini C., *L'oltremare. Il blu dei santi e dei re*, "Lapislazzuli magia del blu", catalogo della mostra, a cura di Sframeli M., Conticelli V., Gennaioli R., e Parodi G.C., Firenze, 2015, pp. 123-133.
[46] Gettens R.J, Stout G.L., *op.cit*.
[47] AA.VV., *Galleria degli Uffizi*, collana *I Grandi Musei del Mondo*, Gruppo Editoriale L'Espresso, Roma 2003.

Even an artist like Vermeer made a wide and refined use of it, in almost all of his paintings, exploiting the brightness of the pigment to achieve its luministic effects. In his painting perhaps more famous than him, la *"Ragazza col Turbante"* (figure 2), he used an ultramarine, very intense but clear, in overlapping layers applied one on top of the other while the one below was still fresh, to obtain an effect of impasto directly on the canvas and not in the palette.

Figure 1, 2: Raffaello Sanzio, Madonna del Cardellino, (1506), oil painting on board, 107x77 cm, Florence, Galleria degli Uffizi; Jan Vermeer, Ragazza col turbante, (1665-1666), oil painting on canvas, 44.5×39 cm, Mauritshuis L'Aia.

- Egyptian blue – $CaCuSi_4O_{10}$

Pigment of inorganic, artificial origin, also known as Pompeian blue, is probably the oldest artificial pigment (3100 BC). Above all thanks to the Romans, we are aware of some important details, in fact, within the *"De Architectura"*[48] of Vitruvius in which the Egyptian blue is called *caeruleum*[49], there is a description of the procedure and the ingredients to prepare it.

Its invention, perhaps given by the need to obtain a more stable blue pigment than Azurite, is surprising for the synthesis process and the quality of the product. Many finds decorated with Egyptian blue, dating back to more than 3000 years ago, still maintain their color unaltered.

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[48] Latin treatise written by Marco Vitruvius Pollio around 15 BC. It is the only text on architecture that has come intact from antiquity and became the theoretical foundation of Western architecture, from the Renaissance to the end of the 19th century.

[49] The Greek Theophrastus as well as the Latins Vitruvius and Pliny also speak of the Egyptian blue and its manufacture. Egyptian blue could be considered the first "artificial" product in the history of artisanal production, not being obtained directly from natural substances, but from a cooking process of some components.

It is obtained by melting around 850 °C a calcium compound such as marble or limestone dust, a copper-containing mineral such as malachite, a silica sand, and a flux such as sodium carbonate. The pigment obtained may contain variable quantities of quartz, calcium silicates, and copper oxides, depending on the raw materials and the production technique[50].

- *Smaltino*, potassium glass – CoO, SiO_2, K_2O, Al_2O_3

It is the most ancient of cobalt pigments of artificial origin, it was already known at the time of the Egyptians, not as a pigment but as glass, only in the Renaissance it begins to be used as a pigment: probably from before the 15th century, particularly between the 17th and 18th centuries. Besides, in the 19th century it was replaced by cobalt blue and artificial ultramarine. It has poor hiding power, with a color ranging from blue purple to light blue, depending on the starting mineral, and is coarsely ground to maintain the color[51]. The vitreous and conchoidal structure of the particles allows them to be recognized under an optical microscope even at low magnifications. *Smaltino* is resistant to atmospheric agents and is used in all techniques, in the fresco used in tempera and oil painting, it tends to lose hiding power and color saturation due to its low refractive index. However, it can catalyze oxidative processes of organic binders.

- Prussian Blue – $Fe_4[Fe(CN)_6]_3$

This pigment, of inorganic and synthetic origin, was invented in Germany by Diesbach in 1704 and used throughout the 18th century. It is obtained from the hot reaction between a ferric salt, generally ferric chloride or ferric nitrate, with potassium hexacyanoferrate in an acid solution. Prussian Blue is an intense blue color with shades tending to violet. This pigment has a low covering power and a granulation so fine that it can look like a dye. It is resistant to diluted acids and is decomposed by alkalis which transform it into brown ferric hydroxide. For this reason, it is not used in fresco, but widely used in oil painting. Besides, Prussian Blue is used between the 18th and 19th centuries for repainting and restoration work.

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[50] Aramini F., Sidoti G., Santopadre P., *L'identificazione del blu egiziano nelle sezioni stratigrafiche mediante fotoluminescenza*, "Bollettino ICR", 27 (2013), pp. 20-24.
[51] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., p. 29.

1.5.3 Green pigments

- Green Earth, silico-aluminates of Fe(II), Fe(III), Mg e K

Pigment of inorganic origin, mineral was known by the Greeks and Romans, used during the Middle Ages and the Renaissance, until the 19th century. In the Middle Ages it is remembered by Cennino Cennini as a component of some preparations or, in place of the red bole, as a base for gilding (green bole). It is made up of ferrous and ferric silico-aluminates of potassium and magnesium. The green color is due to the interaction of the Fe (II) and Fe (III) chromophores. Fe (II) contributes with the blue color, while Fe (III) with the yellow component.

Its color varies greatly depending on the area of origin and the content of other minerals (oxides and hydroxides): from opaque green with blue undertones to yellowish green. Green Earth is obtained by grinding the minerals glauconite and celadonite. The most valuable qualities were the land of Verona (Verona land) and lands from central-northern Europe (Bohemian green and Alemagna green). This pigment has a fair covering power, it does not change into alkalis and acids, and when calcined, it takes on a red-brown hue. Besides, Green Earth is stable to light and humidity, so it has been used in all painting techniques.

Given the low cost of obtaining it, the best quality varieties were also used as a substitute for malachite green[52].

- Malachite – $CuCO_3 \cdot Cu(OH)_2$

Malachite is a quite pure and widespread mineral based on basic copper carbonate[53]. It can be found associated with other copper minerals, including chrysocolla. The pigment is obtained by grinding malachite, similar in composition to azurite. Among the green pigments, it is the most used: its use is known by the ancient Egyptians, Greeks, Romans and Byzantines, up to the 19th century. Malachite has a bottle green color and a poor hiding power. Furthermore, like azurite, this pigment is stable to the action of light, but not to atmospheric agents. In fact, it alters and blackens by strong or mild heating in the presence of alkali, providing tenorite (CuO). It decomposes into acids and tends to darken when mixed with pigments containing sulphides. Besides, malachite has been used in all painting techniques, except in fresco painting. In ancient times it was used in tempera on a wall over a red base of morellone or black vine. The best pictorial results were obtained in the tempera technique.

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[52] Campanella L., *op.cit*., p. 119.
[53] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., p. 32.

- Chrysocolla – $CuSiO_3 \cdot nH_2O$

The pigment of natural origin, mineral, was already known to the Egyptians, the Greeks, and the Romans. Chrysocolla, a hydrated copper silicate, is an almost amorphous mineral. In nature, the pigment is found as a solidified hydrogel in a cryptocrystalline phase. Sometimes instead of malachite chrysocolla was used, described by Plinio, in the *"Naturalis Historia"*, as «a liquid that flows in wells and gold mines [which] in winter condenses to the hardness of pumice». It is opaque, stable to light and humidity. Besides, it is presented to be used in all painting techniques and has shades ranging from bluish green to blue, in relation to the deposit of origin[54].

- Verdigris – $Cu(CH_3COO)_2 \cdot xCu(OH)_2 \cdot nH_2O$

This inorganic pigment of artificial origin was known since the time of the Egyptians, Greeks, and Romans. Verdigris is a copper hydroxide-acetate, which is obtained by exposing copper plates to vinegar vapors. Its color varies from bright green to blue. It is soluble in water and in acids, while it alters in alkali. It is poorly stable to light and humidity. Furthermore, this pigment has a poor covering power, for this reason it is not recommended for frescoes but is used in tempera, in oil painting, in illuminated works[55].

- Copper resinate

The copper resinate is an artificial organic pigment, with a warm and transparent green color. It has been used in the oil technique for superficial glazes, certainly starting from the Renaissance. Uncertainties still exist in the interpretation of ancient documents relating to the composition of this pigment, which was obtained by reacting copper salts with rosin or Venetian turpentine[56]. Since abietic acid is the main component of rosin and Venetian turpentine, the chemical composition of the copper resinate is sometimes indicated in the literature with the formula $Cu(C_{19}H_{29}COO)_2$. This formula is questionable as the coniferous resins, used for its preparation, are poorly stable mixtures of many diterpenoid acids with abietadiene and pimaradienic structure. Therefore, the final product of the preparation is a mixture of cupric compounds containing diterpenoid acids and their oxidation products.

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[54] Ivi, p. 36.
[55] Campanella L., *op.cit.*, p. 120.
[56] Ibidem.

According to some medieval treatises, pigments analogous to copper resinate were prepared by reacting copper acetates with soap. In this case, the result was a mixture of copper acetate and cupric salts of fatty acids.

Currently the copper resinate is no longer available on the market in the form and with the chemical and optical characteristics with which it is present in ancient polychromies. In fact, it is a pigment that has long been disused, due to the ease and rapidity with which it tends to darken, a characteristic known since ancient times and cited in numerous ancient treatises and manuscripts[57].

The reference to copper resinate for transparent green pigments used in miniatures, in some cases could be traced back to verdigris or to a partial reaction of copper salts with organic binders of different nature[58].

Two examples of the use of the green pigment are: painting of Tiziano Vicellio[59] *"Giovane donna con cappello piumato"*, and painting of Paolo Veronese *"Lucrezia"* (figure 3, 4).

Figure 3, 4. Tiziano Vicellio, *Giovane donna con cappello piumato*, (1534-1536), oil on canvas, 75x96 cm, San Pietroburgo, Ermitage Museum; Paolo Veronese, *Lucrezia*, (1585), 109x90.5 cm, Vienna, Kunsthistorisches Museum.

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[57] Diodato S.P., *op.cit.*

[58] Recommended reading: Kühn H., *Verdigris and copper resinate*, "Studies in Conservation", 15 (1970), pp. 12-36. The updated version of the article was reprinted in the book: Roy A., *Artists' pigments, a handbook of their history and characteristics*, vol. II, Oxford University Press, 1994.

[59] Tiziano Vecellio (Pieve di Cadore, about 1490 - Venice, 1576), one of the greatest artists of the 16th century and of the entire history of art. he was able to renew the Venetian tonal painting, starting from the conquests of Giovanni Bellini and Giorgione, to bring it to levels of strength and vigor never seen in Venice. He was also a master of tonalism with Giorgione and the renewal of the painting of which he was the author is based precisely on the very personal use of color.

1.5.4 Yellow pigments

- Yellow ochres, silico-aluminates colored by hydrated iron oxides

Ocher is the yellow color par excellence, the oldest and most used since prehistoric times which is widespread throughout the planet. It is a pigment of mineral origin, it is a natural earth, of an opaque yellow color of different shades (light, medium, dark, golden and orange) depending on the source material. Limonite ($Fe_2O_3 \cdot nH_2O$) represents the most common ocher, turns red by calcination, evidence of this phenomenon can be found in the wall paintings of the Vesuvian area, Pompeii and Herculaneum, in which the yellow backgrounds often turn red in many areas. It has good hiding power and is very resistant to all atmospheric agents. Besides, this pigment is stable to light and humidity, for this reason it can be used for all painting techniques[60].

- Massicot – PbO

Artificial yellow pigment, poisonous, not very intense in color. Known by ancient civilizations such as the Greek and Roman ones, massicot is a lead oxide obtained from the direct oxidation of metal or lead white at about 300 °C. For further heating, around 400 °C, it turns into litharge and at 480 °C into red lead. The calcination process determines the various shades ranging from lemon yellow, to peach yellow, to greenish yellow[61].
According to Plinio it would have been discovered by chance after the fire of Piraeus, with the discovery of Massicot inside vases originally containing cerussa (lead white). Massicot blackens in contact with sulphides. Besides, it has an excellent hiding power, a solubility in nitric and acetic acid, and it a remarkable stability to light and humidity. This pigment is particularly used in tempera and oil techniques.

- Naples Yellow – $Pb_2Sb_2O_7$

This is a pigment of inorganic, artificial origin, which can be obtained by calcination of litharge, ammonium salts, alum, and potassium antimoniate. Naples Yellow is essentially made up of lead antimoniate. It was known since the time of the Egyptians and Assyrians. It has been widely used in all pictorial techniques for the brilliance of color, since the end of the Middle Ages, as evidenced by Cennino Cennini who speaks of it underlining its qualities in its use in fresco.

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[60] Campanella L., *op.cit.*, p. 124.
[61] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., p. 37.

This pigment had a moment of fortune between 1740 and 1850. It has various shades: lemon, orange, greenish, pink, and it tends to blacken to sulphide vapors. Other characteristics of this pigment are excellent hiding power, stability to light, and humidity.

- Lead-tin yellow – Pb_2SnO_4 (type I), $PbSn_2SiO_7$ (type II)

It is an inorganic pigment of artificial origin. Its discovery dates to the late Middle Ages, Cennino Cennini gives news of it. Two varieties of lead yellow and tin are known, denominated I and II. The first compound is a stannate of lead, differentiable from the yellow lead and tin type II which also has silicon in the chemical formula. It alters and blackens in contact with sulphides[62]. It is soluble in nitric acid and is characterized by an excellent hiding power. Moreover, this pigment is stable to light and humidity, for this reason it is used in fresco, tempera, and oil techniques.

- Orpiment – As_2S_3

It is of natural mineral origin but can be artificially prepared. The synthetic pigment was introduced starting from the 18th century. It is arsenic trisulphide and is obtained by sublimating the sulphur with arsenic oxide As_2O_3. The pigment known to the Egyptians, the Greeks and the Romans was mainly used in the 12th and 17th centuries, abandoned in the 19th century due to its toxicity. This pigment has a bright golden yellow color, it was used to simulate gilding. It presents an incompatibility with lead and copper-based pigments with which it reacts forming black sulphides. Orpiment is not very light stable and it is used in the tempera technique as it is not suitable for fresco painting due to its instability towards lime and humidity[63]. During the Middle Ages it was used in the painting of illuminated manuscripts.

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[62] Campanella L., *op.cit.*, p. 122.
[63] Ivi, p. 123.

1.5.5 Red and orange pigments

- Red ocher – $Fe_2O_3 \cdot nH_2O$

Known since prehistoric times and used by all ancient civilizations, this pigment has mineral origins and a composition similar to yellow ocher: it consists mainly of iron oxides mixed with clay silicates and impurities that vary according to the origin, for this reason, it is known by various denominations. *Sinopia red* is probably known since prehistoric times, used to trace the preliminary drawing on the arriccio before the final drafting of the plaster in the fresco technique[64]. *Morellone* is also from the same family, which still today finds conflicting opinions on its composition: some consider it a mixture of hematite with pyrulisite, MnO_2, gray black in color; others believe it is red earth darkened by carbon black. Red ocher can have various shades from red to brown and it is stable to light and humidity. Moreover, this pigment has a high hiding power, for this reason it has been used in all techniques.

- Red bolus – $Fe_2O_3 + Al_2O_3 \cdot SiO_2$

It is a pigment of natural inorganic origin, known since ancient times, coming from certain areas of Middle Eastern Europe and the Middle East. It has a dense and greasy appearance to the touch and an excellent covering power. It is stable to light, but not to humidity. Due to its very fine grain it was used as a base for gilding.

- Vermilion (cinnabar) – HgS

It is a pigment of inorganic origin, a mineral which in Europe is found in the deposits of Monte Amiata in Tuscany, Istria and Spain. It was obtained from the cinnabar mines near Belgrade as early as the third millennium BC: it is found in frescoes and decorations in Persia (first millennium BC), in Palestine and in numerous Roman sites. Its color is brighter than red ocher, considered a pigment of greater value and moderate durability. Vermilion is mercury sulphide, which can also be prepared artificially[65]. It is believed that the discoverer of artificial cinnabar was a famous Arab alchemist of the eighth century, to whom we owe its introduction in Europe; it is also said that the Arabs learned from the Chinese the process of artificially preparing it.

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[64] Wallert A., *op.cit*.
[65] Diodato S.P., *op.cit.,* p. 364.

The method of preparation was already known at the time of Cennino Cennini, in the 15th century, Venice became an important center to produce of vermilion[66]. This pigment is obtained artificially by mixing one part of sulfur and five parts of mercury and heating up to bright red powder. It has varying shades: light, dark, purple, and violet. Furthermore, vermilion has a fine and homogeneous appearance and excellent hiding power. It is stable to light, and resistant to atmospheric agents. Besides, this pigment was commonly used with lead white for skin tones, without noticing the formation of lead sulphide, black, and it has been used in all techniques[67].

- Litharge – PbO

An inorganic pigment of artificial origin with an orange color, it is obtained from the direct oxidation of solid yellow at 400 °C. Litharge was used by both the Egyptians and the Greeks of the classical period and well known by ancient civilizations. It has a high covering power and a solubility in nitric and acetic acid. It blackens in contact with sulphides and at 480 °C becomes red lead. Moreover, litharge is very stable to light, but not as stable to humidity. This pigment is used in tempera and oil techniques.

- Minium – Pb_3O_4

Already used by the Greeks and Romans, it is a lead tetroxide that is found in limited quantities even in the natural state. Minium is artificially obtained by heating lead salts (for example, litharge) to 480 °C or by calcining lead white (basic lead carbonate). Orange in color tending to red, it has good hiding power. Usually, the characteristics of the pigment vary according to the preparation. Minium is soluble in acids and remains unaltered in alkali. It is altered by hydrogen sulphide for the formation of lead sulphide (PbS, black), and it is not very stable in light and air. In humid climates, it is often found oxidized to PbO_2 brown in color. Besides, this pigment has been used in all techniques.

- Realgar – As_4S_4

Realgar is an inorganic mineral pigment, with an orange-red hue, and it is an arsenic sulphide. It was already known at the time of the Egyptians and presents a high hiding power.

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[66] Campanella L., *op.cit.*, p.125.
[67] Liberti S., *Ricerche sulla natura e sull'origine delle alterazioni del cinabro*, "Bollettino dell'Istituto Centrale del Restauro", 3-4 (1950), pp. 45-46.

This pigment is not very stable to light and humidity, moreover it is attacked by acids. Realgar was generally used mixed with orpiment, in tempera, compatible with fresco and oil techniques.

We can cite as example of using the red pigment, probably cinnabar, the painting, *"Madonna col Bambino, Santa Elisabetta e San Giovanni Battista"*, by Jacopino Del Conte[68], this is particularly evident in the making of the Virgin's mantle (figure 5). Another example is *"Ritratto di Giulio II"* by Raffaello Sanzio (figure 6).

Figure 5, 6. Jacopino Del Conte*, Madonna col Bambino, Santa Elisabetta e San Giovanni Battista*, (1535), oil on panel, 161.3x119 cm, London, National Gallery. Raffello Sanzio, *Ritratto di Giulio II*, (1511), oil on panel, 108.7x80 cm, London, National Gallery.

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[68] Jacopino Del Conte, (Florence, 1515- Rome, 1598), an important pupil and collaborator of the Florentine painter Andrea del Sarto (1486-1531), he was a mannerist painter who worked in Florence and Rome. His style developed under the guidance of Sarto but became more personal after the latter's death in 1531. Conte embellished his works with monumental figures, in the style of Michelangelo (1475-1564).

1.5.6 Brown pigments

- *Terra di Siena* – $Fe_2O_3 \cdot nH_2O + Al_2O_3 + MnO_2$

Known since prehistoric times, this yellow-brown-orange pigment of natural mineral origin is a compound of iron oxides, clay silicates and various impurities. *Terra di Siena* is a natural ocher with a characteristic color due to the presence of hydrated ferrous oxides and manganese dioxide, whose name indicates the territory in Tuscany where an excellent quality ocher is extracted. By heating it is possible to darken the color. When there is a high content of manganese oxide, the color tends to greenish brown and the pigment is called umber. It is light stable and moisture stable enough. Moreover, this pigment is used in all techniques and has been used for pictorial glazing.

- Brown manganese – MnO_2 e Mn_2O_7

The pigment can be of both natural and artificial origin, in the first case it derives from the grinding of the mineral pyrolusite (MnO_2). It was synthesized in the mid-19th century: manganese dioxide and manganese peroxide are obtained by precipitation from a solution of manganese sulphate with soda. It is stable to light and humidity. Moreover, this pigment is used in fresco, tempera, watercolor and oil, but it is not recommended for encaustic[69].

- Bruno Van Dyke – organic pigment

Known from both the 16th century in England and Holland, it is an organic pigment of natural origin, composed mainly of unique substances found in soil and peat bogs. Bruno Van Dyke has a brown-red color tending to purple, with poor covering power. It is an acid pigment due to the presence of humic acids and dissolves in alkaline solutions. Like all organic materials, it oxidizes on exposure to light and tends to discolor[70]. It does not present incompatibility problems, except for alkaline environments, therefore it cannot be used in fresh techniques and in modern ones with polymeric dyes in emulsion with ammonia.

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[69] Gargano M., *op.cit.*

[70] Eastaugh N., Walsh V., Chaplin T., Siddall R., *Pigment Compendium: A dictionary of historical pigments,* Elsevier Butterworth-Heinemann Linacre House, Jordan Hill, Oxford, 2004.

- Bistro

Used to illustrate manuscripts in the 14th century it remained in use until the 19th century, this pigment is of artificial origin and derives from the tarry material produced by burnt beech wood.

It is possible to observe the use of brown pigments in painting of Leonardo da Vinci[71], *"Dama con l'ermellino"* (figure 7), in particular on the young woman's hair and partly on the dress in which an iron oxide or iron sulphate belonging to this family could have been used, also the so-called *Terre di Siena*, very ancient pigments and the most used in that historical period[72].

Figure 7. Leonardo da Vinci, *Dama con l'ermellino*, (1488-1490), oil on panel, 54x40 cm, Cracovia, Czartoryski museum.

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[71] Leonardo da Vinci (Anchiano, April 15, 1452 - Amboise, May 2, 1519), was an Italian scientist, inventor, and artist. A man of genius and universal talent of the Renaissance considered one of the greatest geniuses of humanity. Among his pupils there were names who would become the great masters of the next generation, such as Sandro Botticelli, Perugino, Domenico Ghirlandaio and Lorenzo di Credi, and the workshop carried out a multifaceted activity, from painting to various sculptural techniques up to the "minor" arts. Above all, the practice of drawing was stimulated, leading all collaborators to an almost common language, so much so that even today it can be very difficult to attribute the works that came out of the workshop to the hand of the master or to a specific student.
[72] Magnano M., *Leonardo*, collana *I Geni dell'arte*, Mondadori Electa, Milano 2008.

1.5.7 Black Pigments

- Carbon black - amorphous carbon

Known since ancient times, it is a pigment of organic, natural, and vegetable origin, consisting mainly of coal, formed naturally by the carbonization of organic materials and collected in the form of soot. Carbon black has a fair covering power. It is stable to light and humidity. This pigment can be used with any technique in various eras[73].

- Vine Black - amorphous carbon

Known since the time of the Greeks, Vine Black has organic, natural, and vegetable origin, is obtained from the calcination of wine lees, which results in a pure carbon with small quantities of potassium and sodium salts. This pigment is a very light powder, with bluish undertones, it has an excellent covering power. Moreover, it is stable to light and humidity, so it can be used in fresco, tempera and oil.

- Ivory black – $[Ca_3(PO_4)_2]$ + $CaCO_3$ + amorphous carbon

Ivory black is a pigment of organic, natural, and animal origin. It is used since ancient times, known by the Greeks in the classical age. This pigment is obtained by calcining, in the absence of air, fragments of ivory. It is made up of 84% calcium phosphate, 6% calcium carbonate, 10% amorphous carbon. Furthermore, Ivory black looks fine, opaque and transparent at the same time. It has a fair covering power and partially solubility in acids. It is usually confused with animal black. Besides, this pigment is stable to light and humidity, so it can be used in fresco, tempera, encaustic and oil.

- Graphite - crystalline carbon

Graphite is a pigment of inorganic, natural, and mineral origin, known since the Middle Ages. It is a mineral composed of carbon in crystalline form, silica, iron oxide, lime. Moreover, it is extracted and then ground, purified, and washed[74]. This particular pigment is greasy to the touch and insoluble in water and acids. Besides, graphite is light stable and it is mainly used for writing and drawing.

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[73] Campanella L., *op.cit.*, p. 128.
[74] Rinaldi S., *op.cit.*

1.6 Metals used in painting

To enrich the medium and add materials with exceptional optical characteristics to the classic palette, some precious metals were used in painting.

- Gold

This noble metal was used pure in very thin leaf (in the order of tens of μm) or in powder form, to create backgrounds and details (gilding and decorations), and had an important role in tempera, frescoes, and manuscripts before the advent of oil painting[75]. It has a high covering power and it is unalterable. Powder is used in fresco, tempera, encaustic, and oil[76]; leaf is used in gilding on various supports. This metal is very stable to light and humidity. Sometimes, it has been replaced by purple powder (stannic sulphide, SnS_2).

An example of the use of gold is Giovanni Antonio Boltraffio's[77] work of art, "*Madonna con Bambino*", for the color of the saint's dress (figure 8). The decorative floral design is superimposed on the gold highlights. In the highly calibrated register of colors, the white petals of the jasmine that the Virgin plucks from a vase and the red rose towards which the Child leans on take particular prominence. Even the flowers, and in particular the jasmines that are picked by the Madonna and which are a flower often associated with her figure, are described in a realistic way: this way of approaching reality derived from Boltraffio's lesson from the great Leonardo.

Figure 8. Giovanni Antonio Boltraffio, *Madonna con Bambino*, (1485-1490), tempera on wood, 36.5x46.5 cm, Milan, Poldi Pezzoli museum.

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[75] Diodato S.P., *op.cit.*

[76] Gargano M., *op.cit.*

[77] Giovanni Antonio Boltraffio or also Beltraffio (Milan, 1467 - Milan, 1516) was an Italian painter of the early Renaissance, one of the first pupils of Leonardo da Vinci. A genre in which Boltraffio was particularly well versed was that of portraiture, in which the portrait figure (which often stood out on a black background) was transfigured into the image of a saint (San Giorgio, Santa Lucia, San Sebastiano).

- Mosaic gold – SnS_2

This compound was used starting from the 13th century and especially in the 14th century, in the form of bronze powders which, however, did not completely imitate the appearance of gold. Another expedient was to use other less expensive white metals, such as silver and tin, and cover them with a layer of paint colored with organic yellows such as saffron and aloe. If the superficial layer, which also had a protective action, was lost, the metal tended to blacken[78].

- Silver

For purposes like those of gold, silver in leaf or powder was used, albeit less widely. It appears in painting for the most part in the medieval period, but it is little used because by reaction with hydrogen sulphide it is easy to blacken. Tin and, later, aluminum were used as substitutes for silver in ancient times[79].

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[78] Diodato S.P., *op.cit.*, p. 389.
[79] Campanella L., *op.cit.*, p. 128.

2. ITALIAN PAINTING BETWEEN THE 15th-16th CENTURIES

The art of the Renaissance was born in Florence but spreads very quickly in the noble courts of other Italian cities, often wrongly considered of lesser importance such as Rimini, Urbino, Perugia, where the interest in the patronage of the great lords requires the search for new oriented artistic forms towards the recovery of the classical Greek and Roman forms, that reproduce, for example, the correct shape and proportion of the human figure, giving it a central role in expression[80]. It is no coincidence that this period is characterized by the "portraiture" of the face with the underlining of the details and shades produced by the expressions, but also a greater attention is rediscovered of the dimensions of nature that surrounds man with his landscapes, the pictorial description of the flora and fauna, which in many works becomes predominant, and where many artists begin to introduce in their works the use of perspective and techniques not used until then, such as oil painting[81]. Painting therefore begins its path of renewal or "rebirth" towards a new expressive model.

The culture of the Renaissance bases its possibilities of becoming Art, in the various communication methods, exclusively on the relationship with *Nature* and with a canon of the shape of bodies that makes them perfect and "beauty"[82].

This culture of Nature reappropriates itself in structural terms of the lesson of the Ancients, in particular of their fundamental theoretical and normative texts (of poetics, rhetoric, architecture, painting: Aristotele, Orazio, Cicerone, Quintiliano, Vitruvio, Plinio), because all the arts they work the same way[83].

2.1 Painting technique in the Renaissance

Painting is considered the "art of addition", in the sense that adding color to an inexpressive surface actually produces a form of language that the artist wishes to give through his color and his techniques. The same thing happens for sculpture, the so-called "art of removing", which "levers" from what already exists in its consistency to create new forms (marble, wood, stone, etc.). Both are the result of communication models that determine a state of mind, identify a historical period and represent a subject and his condition[84].

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[80] AA.VV., La Nuova Enciclopedia dell'Arte Garzanti, Garzanti, Firenze, 1986.
[81] Cennini C., *op.cit.*
[82] Bernardini M.G., *I grandi Maestri del Rinascimento*, Franco Cosimo Panini, Modena, 2008.
[83] Pilo G.M., *Pittura Veneziana - dal Quattrocento al Settecento,* Arsenale, Verona, 1999.
[84] Nezzo M., Tomasella G., *Dire l'Arte. Percorsi critici dall'antichità al primo Novecento*, collana Biblioteca di Arte, Il Poligrafo, 2020.

Regarding painting, there are countless research and new paths that art has taught us to recognize through the thoughts and hands of its artists, who have determined, often only with the creation of a work, a concentration of experimentation that is such as to recognize it as a "reference painting" both by the artist and representative of a style and an era[85].

By tempera we mean the pictorial technique that uses water to dissolve the natural pigments prepared in powder and composed of vegetable resins, stones, and earths of different colors (brown, red, brown, etc.). The pigments are also amalgamated by mixing egg white, isinglass, and often Arabic gum, all to allow you to create a real emulsion with water[86].

This technique allows you to obtain a liquid or semi-liquid mixture according to the artist's needs and according to the support on which you intend to paint, whether paper, stone, wood or canvas[87]. The use of free canvas on loom was introduced by the Venetians at the end of the 15th century. Made of cotton or linen, the supports were prepared with a preparation made from a light coat of glue (starch glue and sugar). The next day a layer of plaster and glue was passed, and after a few hours, another layer passed in an orthogonal direction. The white background could annoy the artist and therefore, as Vasari himself suggests, a red or brown tint could be applied to make it more neutral.

The colors were prepared in the laboratory through patient work: natural or calcined earths, animal or vegetable residues and extracts, were ground and mixed on a granite or glass plate with a little oil. The oils were those of walnut, flax, poppy. Essential oils, such as the essence of turpentine, were also added to the mixture, useful for giving greater transparency to the colors.

In painting on wood, the painting was built in depth. Antonello da Messina, for example, first spread a patina on the board prepared with hard plaster, then on a coat of cooked oil he spread the colors, and still used oil to obtain a light fusion; he let it dry and finished it in a definitive form, using the essence of turpentine as a diluent[88].

The technique adopted by Leonardo was different. In the "*S. Anna*" and the "*Mona Lisa*", a blue preparation was observed at the top, red at the bottom and umber for the faces. The artist started from medium lights towards darker and lighter tones, subsequently working for transparency and using cooked walnut oil.

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[85] Baccheschi E., Dufour Bozzo C., Franchini Guelfi F., Gallo Colonni G., Gavazza E., Giubbini G., Leva Pistoi M., Parma Armani E., Pesenti F.R., Sborgi F., *Le tecniche artistiche*, a cura di Maltese C., Mursia, 2009.
[86] Maltese C., *op.cit*.
[87] Clark R.J.H., *op.cit.* pp. 7-20.
[88] https://www.leonardodavinci-italy.it/pittura/none

In his paintings there is no trace of the brushstroke and thin lacquers can be observed under the microscope. In the paintings on canvas, the brushstrokes were faster and more fluid. The light preparation welcomed dense and full-bodied colors.

The great protagonist of Renaissance painting was Tiziano, who brought about an artistic revolution made up of innovations that surpassed the Michelangelo's schemes typical of the Tuscan school. These were based on the use of the preliminary drawing for the realization of the work, Tiziano on the contrary perfected the tonal painting, where by now the drawing was outdated, painting the shapes and contours through color, taking care of the work in the smallest details.

Usually, the layers of paint were very light and were prepared with an emulsion generally composed of a ratio of 1:10, which was equivalent to one part of albumen with ten parts of water which guaranteed a mixture that could be spread without difficulty[89]. Once spread, the drying process was immediate, and the paint had to be continuous to prevent the color from drying out. In cases of greater color intensity, the amount of water was reduced, and a second time was passed on the detail that had to stand out from the whole drawing.

The transition with color made with a brush had to be precise, without hesitation, in order to avoid ripples or tonal errors. To make a glaze, it was better to moisten the surface first to let the color flow smoothly and without streaks. Soft and delicate tempered surfaces did not darken over time as with oils, although the oil-egg emulsion did[90].

2.2 Late Renaissance

The expression "late Renaissance" usually indicates a short period from the beginning of the 16th century, in which art achieved results of great harmony, clarity and expressiveness, thanks to figures such as Leonardo, Michelangelo, and Raffaello[91].

These artists shared the commitment with which they dedicated themselves to the study of human anatomy (in order to be able to portray the figures in probable positions and attitudes) and they deepened the perspective research started in the 15th century[92].

They interpreted the naturalism of the early Renaissance, combining it with more idealized and monumental forms: their essential works earned the applause of their contemporaries, who judged them superior even to those of the masters of ancient art[93].

[89] Ibidem.
[90] AA.VV., La Nuova Enciclopedia dell'arte Garzanti, cit.
[91] Previati G., Zeri F., Storia dell'Arte Italiana, II, Dal Medioevo al Novecento, 5, Dal Medioevo al Quattrocento, Einaudi, Torino, 1983.
[92] Pilo G.M., *op.cit*.
[93] Bernardini M.G., *op.cit.*

2.3 Oil painting on canvas

In oil painting on canvas, the type of canvas is of fundamental importance to identify the historical period of realization of the work of art. Before the 16th century, hemp or linen canvases glued to the boards were used, so it was possible to create large paintings that were easily transportable, in fact the canvas could be rolled up and reinserted once it reached its destination. The canvas was pulled and fixed on the frame, then it had to be prepared for painting. For this purpose, the primer technique was used which made it waterproof, so the color did not spread on the fabric[94]. The finer the canvas, the more it allows to obtain a smooth painting. The preparation of the canvas varies according to the school and the time, but it was always essential to keep the canvas elastic, so that it would not crumble when drying[95]. For this purpose, a preparation based on lead white and oil was used, there were various recipes to prepare it, which could include various ingredients: Vasari in *"Le Vite"* describes his method as follows:

> «ma per mettere in opera questo lavoro si fa così: quando vogliono cominciare, ciò è ingessato che hanno le tavole o quadri, gli radono, e datovi di dolcissima colla quattro o cinque mani con una spugna, vanno poi macinando i colori con olio di noce o di seme di lino (benché il noce è meglio, perché ingialla meno), e così macinati con questi olii, che è la tempera loro, non bisogna altro, quanto a essi, che di stendergli col pennello. Ma conviene far prima una mestica di colori seccativi, come biacca, giallolino, terre da campane, mescolati tutti in un corpo, et un color solo, e quando la colla è secca, impiastrarla, su per la tavola: il che molti chiamano la imprimatura»[96].

The tint of the primer influences the colors of the painting: the Venetian painters of the 16th century used to insert earths (powder colors) in the primer to have an already colored background. This facilitated the painters in the rendering of the complexion of the figures, as the background was used as a base for the painting[97].

The primer performed by Palma il Vecchio (1480-1528, real name Jacopo Negretti) had ancient origins: the painter had one or more layers of animal glue and plaster adhered to the support[98]. The fine plaster was used to create a grayish base on which to finally start working. Dyes could be applied to the plaster in order to give a certain tonality to the finished result, however this was not the case with Palma il Vecchio, who preferred to work on bases in shades of gray.

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[94] AA.VV., La Nuova Enciclopedia dell'arte Garzanti, cit.
[95] Bazzi M., *op.cit.*
[96] *Vasari G., Le Vite dè più eccellentissimi pittori, scultori ed architetti, Torrentino, Firenze 1550.*
[97] Pilo G.M., *op.cit.*
[98] Bernardini M.G., *op.cit.*

2.3.1 Oil painting by Tiziano

The period between about 1470, when the artist Giovanni Bellini imposes himself on the scene, and about 1540, when the Mannerist[99] novelties brought to Venice by Salviati and Vasari influenced Venetian art and Tiziano himself, who abandoned his harmonious chromatic classicism, is generally defined the golden age of Venetian painting, because Venice never again reached such height in art. In the training years of Tiziano, Venice offered a varied panorama of the various artistic trends, for the presence, between the end of the 15th and early 16th century, of exceptional personalities. In 1494 he had been called to Venice by the Senate Pietro Perugino to paint a canvas for Palazzo Ducale, Lombard artists had arrived in the lagoon city including Andrea Solario and Agostino da Lodi and the most famous Flemish, Albrecht Dürer[100].

In 1508, the event took place around which all of Tiziano's youth revolved. The artistic collaboration with Giorgione, on the occasion of the execution of the ornamental frescoes on the two facades of the Fondaco dei Tedeschi, the emporium of the Nordic merchants, near the Rialto bridge. Giorgione, owner of the contract, took care of the main facade, on the Grand Canal, while Tiziano was assigned the facade towards the haberdashery. Only a few fragments remain of the frescoes.

Unlike other artists, his compositions mostly concern secular topics, dedicated to literary myths, music, love, and nature, full of mysterious meanings, clear only to the small circle of cultured and refined aristocrats to whom they were destined[101].

An example of the artist's oil painting is the *"Madonna zingarella"* of about 1512, (figure 9). This artwork comes from the collections of Archduke Leopoldo Guglielmo of Austria. Radiographs revealed a landscape different from the visible one, relating to a first draft of the work of art. The title is from the 19th century and refers to the dark hair and features of the Madonna, vaguely "gypsy": it is a definition adopted at that time for many other 16th-century female figures by various painters.

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[99] The term Mannerism is traced back to Giorgio Vasari, who around 1550 - believing that perfection in art had been achieved with the works of Michelangelo, Raphael and Leonardo - argued that subsequent artists could not improve what had already been done and should therefore have resigned themselves to imitate the already existing masterpieces: in practice, to paint (or sculpt) in the manner of. Mannerism in art therefore means the repetition of characteristic elements of an artist, an era, or a school, in a sort of imitation but with different execution styles. Mannerists in particular are defined as those painters who, during the 1500s and until the beginning of the following century, followed in the footsteps of the great Renaissance artists, with undoubted personal skills but without the original inspiration and genius that made them immortal and unique in the world the works and artists from which they drew their ideas.

[100] Bernardini M.G., *op.cit.*

[101] Venturi A., *Storia dell'arte italiana*, IX, 3, Milano, 1928; Baccheschi E., *op.cit.*

Figure 9. Tiziano Vicellio, *Madonna zingarella*, (about 1512), oil on canvas, 38.8x83.8 cm, Vienna, Kunsthistorisches Museum.

Often Tiziano did not execute a preparatory drawing, creating the various elements overlapping each other according to the laws of perspective or to his own chromatic taste[102]. In many of his works, the lack of correspondence between the surface color and the underlying one suggests a way of proceeding with continuous adjustments.

On other paintings, however, there are traces of carbon black drawing, justified, as in this case, by the need to limit the overlaps economically, or by the particular conditions of the perspective system[103,104].

The preparation consists of the usual mixture of plaster and animal glue but of such thinness as to barely cover the texture of the fabric[105]. The pictorial surface is already organized in its spaces and in its *chiaroscuro* relationships: this is, in practice, the sketching technique in which the painting grows by overlapping and progressively perfects itself. In fact, Tiziano almost never painted the first draft. These first layers are characterized by a great impetus, without concern for the contours or the drawing: the doughs are loose, and the brushstrokes are free and spontaneous.

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[102] Gibellini C., *Tiziano, I Classici dell'arte*, Rizzoli, Milano, 2003.
[103] https://artenet.it/tiziano-tecnica/
[104] Gettens R.J, Stout G.L., *op.cit.*
[105] Cfr. D'Anna G., *op.cit.*; Previati G., op.cit.

2.4 Tempera painting on wooden panel

Some painters loved to paint on wooden panel more than on canvas, in particular in the 16th century this support was used[106]. The best wood for painting was poplar, because it has a compact texture and few imperfections (such as knots, holes, deformations, which in the case had to be plastered in order not to spoil the painting over time). Poplar was widely used by Italian painters, while the Flemings preferred oak and fir. Even painting on wood required a long and careful preparation of the support[107].

The wooden board at first had to be well sanded, then primed with several layers of animal glue and plaster. The plaster was used to create a uniform base of grayish color, to which dyes could be applied to obtain a colored ground on which to paint. After having done the painting, it was covered with a coat of protective varnish, which preserved the work from decay and served to make the colors shiny and accentuate the contrast between lights and shadows[108].

Panel painting is very suitable for tempera, colors that obtained by mixing the pigments in water with a binder that makes them adhere to the support. Tempera colors require a rather absorbent base for a good yield, for this purpose at the time the panels were prepared with a plaster-based primer and glue.

Depending on the binder used, lean tempera or greasy tempera were obtained. For the former, a binder of animal origin was used, such as egg, milk casein, animal glues, or a vegetable such as gum[109] and flour. For the greasy tempera oils and resins were also added as binders[110].

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[106] http://www.antiques-magazine.com/le-tecniche-pittoriche-dei-dipinti-antichi.html

[107] Cennini C., *op.*cit; Nezzo M., *op.cit.*

[108] FitzHugh E.W. *Artists' Pigments, A Handbook of Their History and Characteristics*; National Gallery of Art: Washington, DC, USA, Volume 3, 2012.

[109] Vegetable gums are amorphous materials contained in some species of plants chemically belonging to the class of polysaccharides. they have a characteristic solubility in water and insolubility in organic solvents, which differentiates them from other plant exudates. this characteristic is the distinctive element between rubbers and natural resins (the latter insoluble in water but soluble in organic solvents). The most common vegetable gums are Arabic gum, tragacanth and cherry gum. The gums have also been used to form emulsions and blends with oils, egg and casein.

[110] Wallert A., *op.cit*.

2.4.1 Painting on panel by Antonello da Messina

Antonello da Messina[111] was able to instill on the subjects portrayed a psychological analysis that has no equal in all the painting of the 15th century. It is precisely in the portrait that one of the most original and interesting lines of this artist can be appreciated.

The journey into Antonellian portraiture could begin with the "*Ritratto d'uomo*" from around 1465, which is located in the Mandralisca Museum in Cefalù. An important aspect to consider is the study of volumes, that represents the typically Italian component of Antonello's portraiture and this is one of the reasons why his portraits are so interesting and appear so realistic: this very solid volume derives from the study of the works of Piero della Francesca.

Figure 10. Antonello da Messina, *Annunciata*, (1476), oil on panel, 45x34.5 cm, Palermo, Abatellis Palace, Regional Gallery.

One of Antonello's most interesting works is the "*Annunciata*" (figure 10), of the Regional Gallery of Abatellis Palace in Palermo. It is a half-length portrait that emerges from the dark background, with a figure characterized by Pierfranciscan volumes, but it is interesting to note the gesture of the left hand, very natural, which holds the veil at the height of the breast, while the other hand it would seem to address the viewer, perhaps a gesture of surprise towards the archangel Gabriel that the viewer does not see, but who may have arrived in Maria's room[112]. Therefore, the position of the hands suggests a movement, an element that gives dynamism to a work that without this detail perhaps would not have the same innovative meaning[113].

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[111] Antonello da Messina (Messina, c. 1430 - 1479) was probably the greatest portrait painter of the 15th century. After leaving his homeland, Sicily, he studied in Naples in the workshop of Colantonio (Niccolò Antonio; about 1420 - Naples, after 1460), where he was able to meet Provencal and Flemish painting, from which he regained his attention to detail and naturalism. To these characteristics he combined the volumes and rigor of Piero della Francesca and, after a trip to Venice in 1475, also the delicacy of Venetian colors.

[112] Lucco M., *Antonello da Messina*, 24 Ore Cultura, 2011.

[113] Ibidem.

2.5 Fresco technique

Fresco technique was known to all civilizations of the Near East. It was then developed by the Greeks, Etruscans, and Romans. After the barbarian oblivion, it returns to the early Middle Ages with maximum diffusion between the 13th and 16th centuries. Later, the fresco technique continued to be used, often with "dry" additions[114].

The preparation of the substrate consisted in the drafting of several layers on the wall such as:

S*upport*, in stone or brick;

Arriccio, mortar composed of lime or mastic, sand or, in some cases, pozzolan and water;

Sinopia, preparation drawing;

Palster (or *tonachino*) is the most important element of the whole fresco. It is composed of a mixture of fine sand, sifted marble or pozzolan powder, lime, and water;

Paint layer, on which colors must be applied to the still damp plaster (hence the name fresco).

Figure 11. Schematic section of fresco's layers.

In the 13th century the *"buon fresco"* technique matured, this process was marked by the passage from the *"pontate"* to the *"giornate"* of plaster[115].

Since ancient times, various techniques and expedients have been devised to facilitate the work, for example by creating a drawing with a red sinopia on the curl (from Sinope, a place on the Dead Sea where this red was collected), which will then be hidden by the plaster. Sinopia is the design that is imprinted on the *arriccio* by means of dusting.

The development of the fresco became the result of meticulous planning by the workers who had to decide which part to perform and evaluate its feasibility during the day before spreading the plaster (to guarantee the execution *"buon fresco"*).

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[114] Cuní J., *What do we know of Roman wall painting technique? Potential confounding factors in ancient paint media analysis*, "Heritage Science", 4, 44 (2016).
[115] Trenti Antonelli M.G. *L'Affresco. Tecniche e Materiali*, Sillabe, 2005.

During the Renaissance the fresco had its moment of maximum diffusion. In central Italy the use of sinopia was abandoned (which was instead used in other areas until the end of the 16th century) and the use of the preparatory cartoon was introduced[116].

Usually the lines that made up the figures of the preparatory drawing were perforated. Once the cardboard was placed on the fresh plaster, it was dusted with a pad soaked in very fine charcoal powder. In this way the powder, passing through the small holes, left a trace to be followed for brush application. This technique is called *spolvero* and over time it has been used exclusively for the parts of the painting that required greater precision in the execution of the details (such as the hands, the faces, or some details of the clothes).

2.5.1 Fresco technique by Michelangelo

Michelangelo[117], together with the great talent he showed as a child, was also a free and rebellious spirit, eager to identify his own expressive capacity outside the guidelines imposed by the customs of his time. His interiority emerged from the very beginning in his works, and probably the studies of the Bible and Dante instilled in him that sense of the glorious and heroic that transpires in all his works. Although Michelangelo considered himself mainly a sculptor, he painted numerous masterpieces with the technique of oil painting and fresco, of which he was absolute master[118]. Michelangelo painter begins his work with the first brilliant signs that in 1506 with the work of art *"La Deposizione"*, *"La Madonna di Manchester"*, *"La Sacra Famiglia dei Doni"* at the Uffizi. Moreover, he developed until reached the highest levels with the prodigious frescoes of the vault of the Sistine Chapel and the *"Giudizio Universale"*, painted for Pope Julius II, who admired the great genius of Michelangelo. The *"Giudizio Universale"*, as part of the frescoes painted by the artist in the Sistine Chapel, is located on the wall behind the altar. This is a location desired by Pope Clement VII (Giulio de' Medici 1523-1534), who commissioned the work, who explicitly chose that position, although this theme was usually reserved for the facade or counter-facade of sacred buildings.

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[116] The cartoon in the artistic field is a sketch, a preparatory study for the realization of a fresco. Usually, the cardboard is made of the same size with which the painting will be made.

[117] Michelangelo Buonarroti (Caprese, 1475- Rome, 1564) was Italian sculptor, painter, architect, and poet. Belonging to a family of minor nobility, Michelangelo had the opportunity to attend the school of Domenico Ghirlandaio with whom, however, he never got along. The activity of the workshop did not correspond to the character of Michelangelo who always worked in solitude, it is in this period in which he studied the 15th-century Florentine culture and in particular painters such as Filippo Lippi, Gentile da Fabriano, Verrocchio, Pollaiolo and above all Masaccio. From 1489 he frequented the Medici gardens of San Marco, to study ancient sculptures and modern cartoons and learn the techniques of sculpture under the guidance of Bertoldo di Giovanni, a pupil and collaborator of Donatello.

[118] Ducan P.R., *Michelangelo and Leonardo. The frescoes for the Palazzo Vecchio*, Graduate Student Theses, Dissertations, & Professional Papers, 2974, (2004).

Michelangelo carried out this second intervention inside the Sistine Chapel (after the grandiose frescoes previously painted on the vault) in the years ranging from 1533 to 1541, and it was completed, after a long and troubled preparatory phase, under the pontificate of Pope Paul III (Alessandro Farnese 1534-1549) successor of Clement VII. To carry out the Last Judgment, Michelangelo first asked for a brick lining to be made, which provided the artist with a very different base from the tuff of the Sistine vault.

Regarding this aspect, we have a testimony of Vasari: «Fece dunque Michelangelo fare, che non vi era prima, una scarpa di mattoni, ben murati e scelti e ben cotti, alla facciata di detta cappella, e volse che pendesse dalla sommità di sopra un mezzo braccio, perché né polvere né altra bruttura si potesse fermare sopra»[119]. Vasari states that the inclination desired by Michelangelo was for reasons of conservation of the fresco, but studies on the artist's work rather suggest that it was a strategy linked to reasons of an optical nature.

As on the vault of the Sistine Chapel, the layer of the *arriccio* is followed by the plaster, white or whitish layer, while the sky is often prepared with a slight haze of red ocher, very clear, which at times appears pink.

The technique that Michelangelo uses is that of *"buon fresco"* even if the pictorial procedure is different, both in the preparation of the plaster base, and in the use of "dry" in the operative phase. The oil color is used only in the lower part of the demons to obtain certain metallic shades of green and blue, impossible to obtain both in fresco or tempera.

In the fresco of "*Giudizio Universale"*, which as it is known was painted by Michelangelo twenty-three years after the central vault of the Sistine Chapel, there is a different technique.

In particular, the sketch of the figures is with a gray-brown preparation and not perfect and nuanced as it was in the central vault. The sketch is also executed in "half spot" in brown for the shadows and in gray for the parts in light, with well-defined masses.

Moreover, above this preparation, color of the meat was given, for parts in light with a "full body" color by insisting a lot in the modeling to give them a plastic sense also through subsequent overlapping of color, and in the last veiling with diluted brown, or blending the colors with water only.

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[119] Vasari G., op. cit.

It is also observed, in *"Giudizio Universale"*, the shadows and lights were often made with a series of crossed hatches, as did masters of the caliber of Tiziano[120], Veronese and others. Besides, it is known that for his compositions, Michelangelo sometimes used small figures modeled in clay, wax or other material, as did Veronese, Tintoretto, Daumier, Poussin, up to Degas.

Furthermore, the palette of colors that Michelangelo uses in this artwork it presents some variations with respect to that used on the vault of the Sistine Chapel. Some colors such as Mars yellow, brown, lead orange and ivory black are no longer used.

Figure 12. Michelangelo Buonarroti, *Giudizio Universale,* (1536-41), fresco painting detail, 1370x1200 cm, Rome, Vatican museums, Sistine Chapel.

[120] Mancinelli F., Colalucci G., Gabrielli N., *Michelangelo. Il Giudizio Universale*, Giunti, 1994.

Among the blues, enamel disappear, which are completely replaced by lapis lazuli blue, and by small quantities of azurite.

Red lacquer, *giallorino* and orpiment appear on Michelangelo's palette, pigments used mainly dry and little in fresco[121].

For the rest, the pigments used by Michelangelo are the same ones already used by the artist in painting the vault: the whites are made up of the white San Giovanni, the yellows and reds are mainly ocher.

Among the browns appear the umber and the burnt Sienna; the blacks are instead constituted by the vine black and the greens by the green earth, while, limited to the dress of Santa Caterina, painted not by Michelangelo but by Daniele di Volterra, Malachite green is used[122].

2.6 Gold background technique

Since ancient times, gold was used to give images greater prominence and brilliant chromatic effects due to its texture. In fact, this type of metal contains a series of so-called "bright" minerals that give it a series of qualities such as ductility, malleability, hardness, essentially due to the absorption of the blue wavelengths from light. Furthermore, gold is not affected by air or by most chemical reagents.

Besides, gold has always been considered a symbol of power and synonymous with royalty, ancient populations have extensively exploited its brilliance and incorruptibility to represent the gods and the world of the divine. Depending on the work and the historical period, this element was shredded and applied as a pigment, combined with glass to create mosaic tiles, cast, and chiseled to produce wonderful goldsmith objects. A typical feature frequently found in medieval table paintings is the presence of portions of this precious mineral. The most common gilding technique was that of the gold leaf, also known as "a gouache", which involved the application of the gold layer before the colors, on the specially treated table[123,124]. This background technique, despite the new perspectives of change, is still used in the archaic world and in the areas considered more peripheral than the great feudal and ducal cities, for that taste of preciousness and aura of spirituality that the effect reproduces on the images.

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[121] Cennini C., *op.cit.* In this book there are suggestions and explanations on the composition and use of these colors, as regards red and yellow.
[122] Mancinelli F., *op.cit.*
[123] Cennini C., *op.cit.*
[124] https://artenet.it/cennino-cennini/

In the historical period of the Renaissance around 1438, there are some artists who abandon this technique, in particular used to create the altarpiece and for the first time there is evidence that there are works considered "free from gold". Among the artists who first abandoned this technique are Beato Angelico, Filippo Lippi and Domenico Veneziano, with works dating back to the thirties-forties of the 15th century.

The use of the pigments document Michelangelo's increased ability and experience with painting techniques, most likely also due to his frequentation with another great painter Sebastiano del Piombo, mentioned in the work "*Le Vite*" by Vasari.

2.6.1 Processing on the table

The first intervention was the smoothing, then the impregnation which involves the spreading of "clove glue" obtained by boiling and shrinking scraps of animal skin. The table was wrapped in a "cloth bandage", often made of hemp and jute which they wrapped and then covered, only on one side or on both sides, depending on the artist, by at least two layers of plaster:

- *the first layer*: rough and consistent bottom then leveled to fortify the canvas;
- *the second layer*: finely worked to accommodate the pictorial base.

Once the table was painted, the part to be gilded was proceeded with the "spread of Armenian bolus", which consisted of a thin layer of reddish clay from the territories of central Armenia that was kneaded and made almost liquid with the addition of water and egg white to create what has been called "the red preparation", which gives the gold leaf a very warm and bright hue[125]. Several coatings of bolus were required, usually four, at different concentrations, in order to obtain an adequate surface to accommodate the gilding. At the end of the procedure, after allowing the surface to dry completely, it was smoothed and burnished with agate stone to make it as compact as possible. So ready, the surface was moistened again with water and egg white to prepare it to finally welcome the gold leaf.

It was preferred to apply this gold leaf in small rectangles which, placed on the surface of the painting, were blown, made to adhere delicately to the surface since they were of very fine and light material, positioned with the help of a brush with which a small pressure was applied. In this way the gold leaf was "impressed" on the table and the smoothing proceeded.

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[125] Trenti Antonelli M.G., *La pittura su tavola*, Sillabe, 2003.

Due to the high cost and difficulty of obtaining, the thin gold leaf was spread only on the necessary parts of the painting, taking great care to cut out the excess parts and reuse them for subsequent processing and drafts. The other parts were then painted with tempera or oil colors. After having dried the table, the gold parts were burnished, which were thus polished and allowed to affix decorations by engraving or impression, which could have a significant influence on the final effect of the painting[126,127].

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[126] Ibidem.
[127] Cennini C., *op.cit*.

3. THE CLEANING OF THE PAINTINGS

The cleaning of the paintings is one of the most critical and consequently more specific operations of the restoration. It consists in the selective removal of materials, mostly present on the surface, which are considered negative for the physical preservation of the artefact, or which alter or falsify the aesthetics, the expressive message.

The varnish, which dulls over time and thus tends to yellow, is removed so that it is possible to highlight the original colors by bringing them to higher brightness values[128].

Stephen Rees Jones notes:

> «In general, the paint will consist of a layer of homogeneous substance (...) and consequently the response to the solvents will be uniform. The same cannot be said of painting, which is increasingly complex even when the binder is only a drying oil, without the presence of wax or resin; the action of the solvent will change from zone to zone and it is not exceptional to find lower resistance in a section of black or umber rather than in a section of the same coat painted with lead white»[129].

The surface of a painting is not so regular: the surface texture due to the mixture, the texture of the canvas, the brush strokes. Over time it has been discovered that the non-perfected cleaning technique of the past could not avoid the abrasions of some more prominent parts[130].

There are extreme cases in which it is necessary to remove glazes or to damage the enamel of the color, this requires a particularly coarse intervention. While it would be easier to brush a painting, degreasing the color and leaving a depleted film[131].

When cleaning it is important to keep in mind the material effect that the clean painting assumes[132].

An interesting case is offered by Giovanni Bellini's *"Pietà Donà delle Rose"*, where an essay was carried out to remove the seriously oily paint that covered it, an essay with which the tablet was exhibited in one of the Giorgione's exhibitions of 1978[133].

The color turns out to be dull and severely depleted due to cleaning with alkaline substances.

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[128]A noteworthy balance of the difficulties and problems encountered in cleaning the paintings are drawn by Stephen Rees Jones, 1962.

[129] Jones S.R., *Science and the art of picture cleaning*, " The Burlington magazine", 104 (1962), pp. 60-62.

[130] Brandi C., *Teoria del restauro*, Einaudi, Torino, 2016.

[131] Campanella L., *op.cit.*, pp. 139-140.

[132] Conti A., *Manuale di restauro,* Torino, Einaudi, 1996, pp. 180-182.

[133] Augusti Ruggeri A. Fantelli P.L, *Giorgione a Venezia: Venezia, Gallerie dell'Accademia*, Mondadori Electa, Milano, 1978.

In Italian restoration, the boundary between what must be removed and what must be preserved is even more critical than elsewhere. Not everything that is foreign, in fact, requires elimination. There may be "material presences" to which an acquired historical value is attributed, for example some natural patinas, some slightly yellowed paints, some retouching or repainting, or even "historicized" renovations. The operation can thus be even more complex.

Often, in fact, it is necessary to remove, but only partially. Selectivity therefore becomes not only qualitative, but also quantitative (in the sense of reducing a thickness, for example thinning a very yellowed original paint). On the contrary, in the past we have not acted as cautiously: with the frequent use of caustic alkalis, not only paints and patinas, but original glazes and even pictorial layers have been removed.

Today, therefore, in order to have a capacity for discrimination, the finest in cleaning interventions, all possible ways are used: chemical-physical (solvents, surfactants), chemical (reactive solvents), physical (traditionally scalpel, today laser) and biological (enzymes). Each of these different approaches is based on specific principles, makes use of particular materials (or tools), and it is carried out following defined protocols.

We will now examine the main methods of cleaning polychrome works, including both those in use for paintings on a mobile support and those more specific for murals.

3.1 Cleaning with aqueous solutions

Cleaning with water alone may be ineffective in some cases. In fact, the materials to be removed can be:

- hydrophobic in nature such as resinous paints, oil repainting, etc., possibly cross-linked, but which may present a certain solubility in water due to the presence of acid species due to oxidation reactions that occur during aging;
- relatively hydrophilic in nature (such as casein and egg), but with a polymeric structure, and therefore, in any case, almost insoluble;
- saline in nature with relatively low solubility products, and therefore insoluble in water alone.

It must also be considered that water could be dangerous for the pictorial preparations of the panels (consisting mainly of gypsum and animal glue, both partially soluble in water) and also for the supports (wood and canvas) which, if reached by water, they could suffer from it. Therefore, water alone would be ineffective and potentially dangerous in the painting of this category of paintings.

Different is the case of water in supported form (gel) and with the addition of substances that vary its pH, such as weakly acidic and, better still, weakly alkaline substances; or with the addition of complexing agents or surfactants. In this case the aqueous solution can also interact effectively with the materials mentioned above and which often must be removed from the surface of the paintings[134].

To operate in a controlled manner with respect to pH, so-called buffer systems are necessary, consisting mostly of the mixture of a weak base, together with its salt. Buffers suitable for cleaning paints can be prepared by advantageously exploiting the properties of some amines. With the prolonged contact allowed by the gel, the protein materials thus begin to swell, soften and can be removed with a mild mechanical action exerted by the operator.

Cleaning usually consists in removing surface dirt, or deposits, of poorly soluble saline substances, just think of gypsum, mixed with other components, such as fats, proteins, and silicates. In this case, complexing agents, or chelating agents, can be added to the water, which capture the cations of organic substances and therefore dissolve them and weaken the "structure" of the dirt, facilitating its removal.

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[134] Campanella L., *op.cit.*, pp. 140-141.

Among these we can mention citric acid and EDTA (ethylenediaminetetraacetic acid), both of acidic nature, which however can be brought to the safe pH value by neutralization with one of the above amines.

As far as wall paintings are concerned, their cleaning is carried out mainly on a water basis, more often, by means of aqueous solutions. In wall paints, gypsum mortars are porous and often contain water-soluble or partially water-soluble salts that can be easily removed. Furthermore, their supports, plasters, are made up of calcium carbonate and silicates, insoluble materials both in water and in moderately alkaline solutions. On the contrary, they do not tolerate the acidic environment, since already at pH 4.5 the carbonate decomposes considerably, to give carbon dioxide as the final product. Removal of soluble salts.

The cleaning of the wall paintings, for what has been said above, therefore also provides for the removal of soluble salts. If these are sufficiently soluble, they can be removed by means of extractive compresses with only water dispersed in cellulose powder as a support. The compress is placed in contact with the pictorial surface by interposing a sheet of Japanese paper. In the first phase, the water dissolves the salts and brings them back to the mortar. In the second, the cellulose acts as a sponge and absorbs the saline solutions that crystallize in the pack through the capillarity of the plaster. The compress is removed and repeated several times. This is one of the few systems available to obtain a partial elimination of salts from plasters. The method is moderately effective because at most it can involve a few millimeters of plaster thickness, while the salts often permeate thicknesses of tens of centimeters.

Plaster removal

Due to widespread of gypsum and the damage it causes, it is certainly the most dangerous salt for frescoes and murals. The phenomenon of disintegration of the pictorial surfaces caused by gypsum takes the name of sulphation[135]. The action is due to its solubility in water which facilitates the cyclic crystallization and accumulation on the surface, just below the pictorial layers or inside them, where it determines the formation of sub-florescences and micro-lifts. It is important to consider that water is not enough to dissolve the plaster[136].

It would take a lot with the risk of moving other salts. It is necessary to use alkaline solutions among which the most suitable is that of *ammonium carbonate*.

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[135] Ibidem.
[136] Cfr. Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit., p.99.

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$$
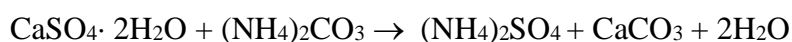
The ammonium carbonate, applied as a compress on the surface for no less than two hours, causes the transformation of the gypsum into soluble ammonium sulphate which is dispersed in the compress and plaster, and in insoluble and harmless calcium carbonate. The advantage of ammonium carbonate over other alkaline reactive solvents is due to its spontaneous decomposition, with the formation of only gaseous products, which therefore do not remain in the mortar:

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$

Other advantages are given by the moderate alkalinity of the product, however sufficient to dissolve (by partial saponification) deposits of greasy dirt, to soften, allowing their removal, film of protein fixatives and repainting performed with protein binders that are often found on frescoes and tempera.

However, a useful alternative to remove the gypsum are *ion exchange resins* which have the advantage of not softening the binders in tempera or attacking the copper pigments, and the disadvantage of being effective only against gypsum on the surface.

Thanks to the use of gels, it has been possible to use controlled aqueous solutions, moderately alkaline, slightly acidic or complexing, so-called reactive solvents, also for cleaning paintings on wood and canvas, such as ammonia, diluted acetic acid, chelating agents. The gels, in fact, exert a strong retention of aqueous solutions and prevent them from migrating inside, towards painted and prepared layers, allowing only a superficial action. Obviously, these reactive solvents are used in limited concentrations and only when they are indispensable.

3.2 Cleaning with organic solvents

For several years the use of organic solvents has been exceptionally successful in cleaning paintings on canvas and wood, while their use for wall paintings has been rare, limited to the removal of acrylic, vinyl, or otherwise synthetic polymer fixatives, applied in restorations to starting from the 1960s. The reason for this success is to be found in the great effectiveness of many of these solvents, especially for the removal of yellowed paints, in the ease of use (applied by brush), in their volatility, in the possibility of forming binary mixtures with great ease ternary or more complex with specific behaviors. A first criticism on the use of these solvents came when it was ascertained their washing effect towards some natural plasticizers present in the paint binders.

The solvents, washing them off, make the layers less flexible, more prone to cracking.

A second important downsizing came when it was realized that some of these solvents underwent a very marked retention by some pictorial materials.

Retention occurs when a liquid, in contact with certain materials, establishes strong chemical bonds with them that prevent their removal. The solvent, despite its volatility, remains in the paint, helping to soften the layers and cause yellowing or other damage. They were mainly amines, to undergo strong retention.

These amine solvents, already in the seventies, were recognized as very toxic, therefore, retention and toxicity quickly convinced them to prohibit their use as they were harmful both to the paintings and to the operators. In the following decades it became clear that many other solvents, besides amines, were highly toxic. Occupational medicine put into effect ever greater restrictions on the use of organic solvents in workplaces and not only in those of restoration[137]. However, laboratories needed to be equipped with effective suction systems to minimize exposure to solvent vapors, whatever they were. These strong restrictions and the awareness that the free use of organic solvents was still invasive for paintings, led, in the 1980s and 1990s, to seek alternative and less invasive solutions, from which the new classes of emulsions and solvents originated. Gels, resin soaps, enzymes and then laser methodologies, without supplanting the use of organic solvents, but significantly limiting their use[138,139].

Principles of organic solvents' action

The mechanism of action on which organic solvents are based is the breaking of the intermolecular bonds of the substances to be dissolved, to bring them into solution without altering their chemical identity. On the other hand, the reactive organic solvents act by transforming insoluble species into soluble species.

A general principle states: "like dissolves like", this now means that the solvent and the potential solute must have "similar intermolecular bonds".

This similarity is characterized and quantified based on three types of intermolecular bonds:

- The dipole-dipole interactions f_P;
- The forces of dispersion or bonds between non-polar molecules f_d;
- The hydrogen bonds f_h.

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[137] Cfr. Stulik D., Miller D., Khanjian H., Khandekar N., Wolbers R., Carlson J., and Peterson W.C., *Solvent Gels for the Cleaning of Works of Art*, editor Dorge V., Getty Publications, Los Angeles, 2004.

[138] Cremonesi P., *L'uso degli enzimi nella pittura di opere policrome*, Padova, Il Prato, 2002.

[139] Campanella L., *op.cit.*, p. 143.

Several studies were carried out in the 1970s on the solubility parameters for each liquid-solvent. It was thus possible to uniquely represent each potential solvent with a point in a triangular diagram (*triangle of solvents*, shown in figure 13), thus acquiring an immediate and visual perception of its solvent properties. These properties are additive, for example, by mixing three liquids with equal properties together, a mixture is obtained which is placed in the diagram in the center of gravity of the triangle, whose vertices are the positions of the three liquids. In the triangle of solvents, *areas of solubility* can be delineated, areas within which only solvents of a given substance are found, while outside, non-solvent liquids.

Figure 13. Ternary diagram of solvents.

The cleaning process is simple, the operator passes on the surface to be cleaned a brush or a small wet swab in the solvent or the suitable mixture. When you notice that something begins to be removed, you check the action by applying a pad soaked in a non-solvent liquid, usually a White Spirits mixture.

For convenience, it is advisable to construct a sequence of solvents with increasing polarity with which to carry out preliminary tests on very small areas to understand which mixture to orient towards. This also allows to highlight the possibility that no solvent or mixture is effective and, consequently, it is necessary to resort to other procedures, from solvent gels, resin soaps, enzymes, etc. In order to obtain a solvent-test sequence with regularly increasing polarity, in addition to pure solvents, suitable mixtures must also be used. In fact, even if we have the suitable pure solvent as regards the solvent power, this too could be toxic or too volatile or subject to retention therefore, ultimately, not suitable.

For this reason, the use of mixtures is almost always more satisfactory than the single solvent.

Feller's solubility test uses a sequence of solvents with increasing polarity, then with decreasing f_d, where one gradually passes from almost apolar mixtures (high f_d solubility parameter) to more polar mixtures (low f_d). In this way it is possible to obtain all the shades to carry out orientation tests on very small areas, before choosing which one to use.

3.3 Cleaning with surfactants

The first system to support the solvents used in cleaning was that of *wax / water emulsions*. They allow the action of the solvent to be confined to the surface, to maintain a more prolonged contact with the materials to be dissolved, to control the cleaning action from the color they take: the emulsions are in fact white and when they begin to act, they "get dirty" more and more of the dissolved material.

Surfactants are composed by molecules with different ends: one with polar-hydrophilic characteristics while the other apolar-hydrophobic. Introduced into a heterogeneous system of two immiscible liquids (in practice two liquids separated in two superimposed layers such as water and oil or melted wax) they tend to distribute themselves not homogeneously, at the separation interface between the two phases, they orient their hydrophobic end in the hydrophobic liquid (oil / wax) and the other in the hydrophilic liquid (water).

The *interfacial tension* between the two liquids thus strongly decreases, a tension that keeps them separate, so that, even with a weak energy (for example through moderate agitation) one phase rapidly disperses into the other and forms a stable *emulsion*. One of the two phases, such as water, acts as a *dispersing phase*, while the other, such as oil or wax, is the dispersed phase in the form of microscopic droplets, stabilized by the surfactant (*emulsifier*). In this case the emulsion is called O / W (*oil in water*). As the micro-drops scatter white light, the appearance of the emulsions is generally white or clear mayonnaise, egg yolk and Vinavil are emulsions.

Principles of surfactants' action and their surface properties

At low concentration the surfactants in solution lower the surface tension of liquid and show only the surface properties: greater wetting power, less diffusion vertical below the surface, or less capillary rise. Instead, at a higher concentration in solution, aggregates of surfactant molecules are formed, called Micelles, which impart emulsifying, detergent and solubilizing properties to the solution. There, the quantity of surfactant necessary for this situation to occur is called precisely Critical Micellar Concentration, or CMC, and is characteristic for each surfactant.

We could define the use of surfactants as wetting agents[140]. It is important to consider that with suitable surfactants it is possible to prepare lean emulsions (or oil in water) or greasy (or water in oil). For both, you can vary the volume of the internal phase (that dispersed) according to the desired properties of the emulsion, that is allow concentration of dispersed phase.

The emulsion will be fluid, basically with the characteristics of the dispersing phase, while at higher concentration it will be possible to obtain more and more emulsions viscous, up to dense pastes. The emulsions in themselves are not solvents for paintings, but are supports, that is, means of dispersion and support for solvents.

Besides, the emulsions retain the liquid-solvents in the two phases. If the solvent is polar-hydrophilic it disperses in the aqueous phase, if it is hydrophobic it goes into the hydrophilic phase (oil, wax). This allows the emulsions to host at the same time also solvents that are immiscible to each other such as ammonia and the essence of turpentine, with the advantage of a synergistic action. By dispersing and supporting the solvents, the emulsion hinders their migration towards the interior of the painting, that is, it contains their action on the surface: cleaning thus becomes less invasive[141].

As the emulsion inhibits the evaporation of the solvents, they are kept in contact with the surface of the painting for prolonged times. During application, the emulsion is gently stirred in order to allow a more effective action.

The main disadvantage of this type of cleaning is that at the end of the action it is necessary to quantitatively remove the "charged" emulsion of the removed material. This is not always easy, but still possible through the removal of the main part, mechanically, with the buffer, and finally, of the residues, using non-solvent liquids that dissolve and disperse the wax.

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[140] Meloni M., *La pulitura delle opere policrome: metodi a confronto. Solventi contro tensioattivi-chelanti,* Roma, Università La Sapienza, 2004, pp. 18-19.
[141] Recommended reading: Horie C.V., *Materials and Conservation. Organic Consolidants, Adhesives and Coating*, Butterworth Heinemann 1987.

3.4 Cleaning with resin soap

Principles resin soap's action

I would like to deepen some characteristics of surfactants and their practical use in painting cleaning operations. Surfactants are generally classified into three categories: anionic (such as common soaps) characterized by a hydrophilic end of the anionic type, often a carboxylate ion, cationic (such as some quaternary ammonium salts) which have a hydrophilic end of the cationic type, and non-ionic, whose hydrophilic ends. The latter are less influenced by what has an ionic nature, such as metal cations or salts.

An important parameter in the classification of surfactants is the hydrophilic / lipophilic balance (HLB). Different values of this parameter are indicative of the intended use of the surfactants. For low values (HLB 4-6) we have surfactants suitable to act as W / O emulsifiers; increasing in value (HLB 7-9) they become useful as wetting agents, which facilitate the uniform distribution of a liquid or solution on a surface; with higher values, O / W (HLB 8-18), they become useful as emulsifiers, detergents (HLB 13-15) and finally with solubilizing action (HLB 15-18 and beyond). The HLB parameter also changes with the type of surfactant: for the non-ionic ones it does not exceed the value of 20, while it can also assume a double value for the ionic ones[142].

Critical Micellar Concentration or CMC is also an important parameter to consider, as once a certain concentration of a surfactant in a certain solvent, for example water, has been exceeded, the surfactant molecules tend to associate in micelles, concentrically joining together the apolar ends and turning towards the outside of their hydrophilic ends.

The opposite occurs if the solvent liquid is apolar. Since the CMC is influenced by various parameters, such as pH, temperature, etc., for safety we operate at surfactant concentrations up to 10 times higher than the CMC. The micelles can easily incorporate and subsequently disperse particles of a different nature and this property focuses on the usefulness of surfactants, and of some types of them, in cleaning operations[143]. A very useful action that surfactants can perform, which among other things we make daily use at home, is the *cleansing effect*. This is nothing more than a particular application of the emulsifying function.

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[142] Ivi, p. 147.
[143] Ibidem.

Therefore, the removal of the emulsion formed between water and a fatty substance carries out the *detergent action*. The greasy dirt, thanks to the soap, enters the aqueous emulsion in the micelles which are then removed with running water: the overall effect is a cleaning action.

Regarding the painting, it is important to consider that fat deposits from the anthropogenic environment of conservation often accumulate on the surface of a painting. Their removal, instead of being carried out with a solvent for non-polar fatty substances, can be advantageously dealt with using surfactants. Since the surfaces of paintings on mobile supports are generally hydrophobic, greasy dirt will be removed more easily with a water-based surfactant, rather than with an apolar solvent, which, once the solution is formed, would rather tend to diffuse it into the porosity of the painting impregnating it with dirt[144].

Different, for example, is the case of a mural covered with deposits of lampblack from candles. If a solvent were used, it would dissolve the fatty components of the deposit and drag the whole (grease and carbon black particles) into the porosity. Even with the cleansing effect, however, the result would be negative. The substrate, in fact, in this case is hydrophilic and the emulsion would enter the porosities by affinity. Although it may seem strange, the best solution for this problem is water alone, supported by a sheet of Japanese paper applied to the surface. In fact, by removing the sheet, most of the greasy and inconsistent carbon black deposits remain attached to the sheet thanks to the forces of adhesion/ interfacial tension.

The most common cleaning case concerns the removal of old yellowed resinous paints: these can be dissolved with a solvent or emulsified and subsequently removed with a swab[145]. Since these solid, aging-hardened materials are particularly resistant to forming an emulsion, it is necessary to use a surfactant whose hydrophobic end is chemically like that of the resin.

This surfactant in aqueous solution is a resin soap, therefore it is an anionic surfactant. A kind of softener is added which allows the swelling of the paint and therefore a more effective elimination of the same. With the pad, then, the emulsion is removed from the place of formation, carrying out a cleaning action. In addition, it is recommended to add a thickener to the emulsion to support the surfactant solution in the form of a gel.

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[144] Ivi, p. 148.
[145] Ibidem.

3.5 Cleaning with solvent gel

The use of solvent gels today represents an appropriate way, in the effective, precise, and minimally invasive sense, to clean up the paintings. I add that this approach offers a very flexible procedure, that is, capable of being really calibrated to the specific case of cleaning in question. Basically, the system consists of using a cleaning agent supported by a gel containing a thickener, a surfactant, and a buffer for pH control. The gel reduces the capillary flow of the solvent and allows the cleaning agent to carry out its action gradually. In this sense, the successful use of these systems relies heavily on the awareness of the identity of what we want to remove. In other words, the intervention will be more effective if the preliminary diagnostic analyses have provided indications on the composition of the organic materials to be removed. The gel, at this point, can be formulated with greater precision. For aqueous gels it will be possible to adjust the pH, the presence or absence of chelating agents, surfactants, etc. For non-aqueous gels it will be possible to calibrate the solvent power according to the criterion of the solubility parameters. Among the most used solvents, dimethyl sulfoxide (DMSO), triethanolamine, benzyl alcohol, ethyl alcohol, acetone, ethyl acetate, xylene, ligroin etc., are to be considered. The gel application technique exploits the prolonged contact times allowed by the gel; these can be decreased by even tens of minutes and, certainly, moderate agitation of the gel on the surface considerably facilitates removal[146].

Principles of solvent gels' action

The principles of action of the solvent gels are like those already explained in the paragraph on emulsions. Gels are above all systems of *dispersion* and *retention* of solvents, that is, those that are defined as adjuvants. In this case the adjuvant effect, unlike the emulsions, is based on the very nature of the gelling agent[147].

The advantages of working by supporting the solvents with gels are evident. There are some minor difficulties, for instance, it is not entirely easy, at the end of the operation, to eliminate the residues of the gel: effect depending on the type of gelling agent chosen and the solvents[148].

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[146] Ivi, p. 149.

[147] The latter can consist of a system composed of a substance rich in *hydrogen bridge bonds*, i.e., capable of retaining very high percentages of water, with a thickening effect, or even of a particular polymer, which combined with certain organic solvents, however, creates a heavily dense system. These systems can host, dispersed within them, various potential solvents to remove various materials from paintings on mobile supports and murals, as well as other types of artefacts.

[148] Campanella L., *op.cit.*, p. 150.

The use of gels is even more important when it is necessary to resort to the use of reactive agents. Their incorporation into a solvent gel system allows them to take full advantage of their properties, without running the risk of their penetration inside the pictorial film with consequent action on the original components of the painting. Since these solvents do not have an intrinsic selectivity, if used free, they would risk penetrating inside and act on the original components of the painting, for this the use of solvent gels is crucial in these cases.

3.6 Enzymatic cleaning

Enzymes are proteins, substances developed by living organisms, whose basic action is to catalyze a huge number of chemical reactions essential to the metabolic processes of organisms. The specialty of enzymes, which is responsible for their extraordinary effectiveness, is linked to their three-dimensional shape (the so-called tertiary and quaternary structures of proteins). They join in a complementary way (form a sort of complex) with the active sites of the substrate of which they are specific, determining the lowering of the reaction potentials to such an extent that this is possible under mild conditions. Otherwise, prohibitive conditions would be required for organisms, such as heat, acidic or basic pH, etc.

In the biological environment, all this takes place mainly inside the cells, in the homogeneous phase, i.e., in an aqueous solution. Enzymes can therefore be defined as *biological catalysts* with very high specificity.

In recent decades the attention of conservation science has turned to these substances, which in the meantime technology had been able to extract from living organisms, to evaluate them as potential agents capable of breaking down complex molecules, i.e., in cleaning operations[149]. The high specificity of the enzymes, a determining factor for the cleaning of the paintings, was promising, as well as the possibility of operating in a much less invasive way than the reactive solvents used in cleaning and in conditions of harmlessness for the operator: the enzymes are in fact not volatile like solvents and act in an aqueous environment.

Principles enzymatic cleaning's action

To work at their best, enzymes require specific conditions of use such as a certain temperature range, characteristic of each enzyme. The right temperature must be reached with quality thermostatic systems to avoid possible denaturation of the enzyme. Obviously in the applications on the paintings only enzymes capable of operating at temperatures close to the ambient one or slightly higher than it is tolerated.

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[149] Ivi, p. 151.

It is also necessary to operate within a certain pH range, for which it is usually necessary to add a suitable buffer to the formulation, to prevent the materials of the support themselves, if acidic, from altering the optimal value.

Sometimes it is also necessary to add activators (some metal ions) to promote the catalytic effect. We must not forget that in a paint, the same material can coexist in different layers. If such a situation is assumed, it is necessary to confine the action of the enzyme to the surface, supporting it with suitable gelling agents. A further reason for the enzyme's support is that it acts in an aqueous environment: water that must not come into contact with the pictorial layers sensitive to it, such as plasterboard preparations and glue plates. Therefore, it is necessary to act with caution and support the enzymatic formulation in the best possible way to avoid, in these cases, inducing damage to the hydrophilic materials of the painting.

It may be necessary to use an inhibitor to block the action of the enzyme. Sometimes an inhibitory effect arises from ionic components (heavy metals) present in the same pigments and other materials of the painting.

Finally, to remove the enzyme and auxiliary substances that have been added to the formulation, as well as the demolition products of the materials "attacked" by the enzyme, it is necessary to use a surfactant, also chosen in such a way as not to be aggressive for the enzyme. The enzyme is still a "reactive agent", even if extremely specific[150].

Today enzymes, and sometimes enzymatic formulations, already more or less ready to use, are available, capable of cleaving common molecules in the field of restoration such as oils, protein materials, starches, etc. Among the proteases can be found enzymes useful for hydrolyzing casein, sometimes used as a binder for repainting, as an adhesive and as a surface fixative, as well as egg, itself very frequent in the past as a restorative fixative both in wood and in painted walls[151,152].

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[150] Ivi, p. 152.

[151] Amylases, on the other hand, can be useful for the removal of starch, for example present in the "glue-glue" adhesives of the linings, and of other substances of a polysaccharide nature. Natural and synthetic saliva should also be mentioned among the enzymatic formulations. The first was known by the restorers of a few decades ago who, perhaps unwittingly, realized the solvent power of this natural liquid in whose composition enzymes also enter, mainly of the amylase type.

[152] Cremonesi P., *op.cit.*

3.7 Cleaning with ion exchange resins

In the thirties of the last century polymers containing small side chains capable of giving rise to ion exchange were implemented. Ion exchangers were already known as natural substances, such as some types of silicates, glass, etc., but now we have specially constructed molecules, organic polymers (resins) insoluble both in water and in most organic solvents, which, placed in contact with electrolyte solutions, they can sequester the one (cation exchange resins) the cations of the electrolyte, the others (anion exchange resins) the anions of the electrolyte. If we make sure that the cation and anion that are exchanged are, respectively, H^+ and OH^-, we have the classic and best-known ion exchange resins used to prepare *deionized water*, free of ions, but slightly impure of traces of the resins themselves. This water is certainly the most widespread in the world of restoration and is used in several operations[153].

- *Cationic resin* $\quad \text{Resin} -SO_3^- H^+ + M^+ \rightarrow \text{Resin} - SO_3^- M^+ + H^+$
- *Anionic resin* $\quad \text{Resin} -NR_3^+ OH^- + A^- \rightarrow \text{Resin} -NR_3^+ A^- + OH^-$

These find an important use in the restoration, especially for the "desalination" of stone materials, even in wall paintings. But it has been shown that while cationic resins are difficult to apply, since the acidity developed with the exchange uncontrollably attacks calcium carbonate, anionic resins are a valuable agent available for restoration.

Principle of ion exchange resins' action

In the restoration of wall paintings, anionic resins are used above all for the removal of gypsum: they are in fact defined as desulfating resins. The resins, marketed in the form of microspheres, are mixed with water and applied with a spatula on the painted surface, preferably without interposing the Japanese paper, to exert a more direct action[154]. All the anions of the salts present on the surface can be sequestered but only the gypsum accumulates on the surface while the other salts, due to their greater solubility, are more homogeneously distributed inside and for this reason they are unreachable by the action of the resin. In addition, the water in the mixture dissolves them and draws them back further. The resin, therefore, is a surface desulfating agent.

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[153] The cationic resins in the H^+ form, used alone, as they exchange tend to acidify the solutions, while the anionic ones in the OH^- form make them more alkaline.

[154] Campanella L., *op.cit.*, pp. 152-153.

The gypsum contained inside cannot be eliminated, in this case it is possible to remove it by using ammonium carbonate. However, anion resins have great advantages over the latter. By exerting only a superficial action, they do not attack the binders of the paintings (egg, casein and possibly also oil) as does ammonium carbonate, nor do they attack the copper pigments. They are therefore a very useful alternative for the desulfation of tempera and areas painted in azurite, malachite, verdigris, copper resinate. Finally, the alkalinity developed by the resins in their exchange makes them an excellent detergent for greasy "dirt", old protein fixatives and similar substances[155].

3.8 Cleaning with laser techniques

To complete the picture of procedures currently in use for cleaning paintings, at least one mention should be made of laser cleaning, although it is part of the physical techniques[156]. Lasers are systems capable of coherent radiation, which means that the beams of the beam are in phase agreement with each other. For about ten years they have been used for cleaning stone artefacts, and also of metal, such as gilded bronzes, coins, etc[157].

The use of the laser to clean a painting has always been considered with great caution due to the poly-materiality of the polychromies: the many and different pigments, the binders, the multiple very thin layers that overlap in a few hundred microns to form the pictorial surfaces. However, there has been a lot of progress in this area over the years.

Lasers interact with matter causing its ablation, which is the transformation into plasma (ionic gas) due to the very high energy that develops through impulses of infinitesimal duration (of the order of nano or microseconds) and can be concentrated on an area, within certain limits. In restoration, the laser could therefore be defined as a thermophysical method for the punctual removal of portions of matter from the surfaces of the works.

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[155] Ibidem.
[156] Ivi, pp. 153-154.
[157] The use of lasers for the restoration of works began in the 1970s, but the technique began to grow in the late 1990s when scientific studies validated the effectiveness of using a laser beam for cleaning masterpieces. The laser emission parameters have also been optimized to ensure safe and efficient cleaning of different substrates. Moreover, laser ablation offers many advantages over traditional mechanical and chemical methods in terms of graduality, self-termination, selectivity, environmental impact and safeguarding the so-called "patina of time". The laser has been widely used for cleaning frescoes and murals even in very particular and extreme environments such as the catacombs.

Principle of laser's action for paintings

Lasers for stone artefacts, mainly of the Nd:YAG type, operate in the near infrared, $\lambda = 1.064$ µm, and cause the removal of what is dark, such as black crusts, safeguarding what is light, as in the case of marble and other stones, light patinas[158]. Paint lasers must clearly be based on different principles. A first category of lasers, the so-called excimers, operates in the ultraviolet region.

These lasers, with a relatively rich energy beam, can remove most paint materials, so they are not selective. Furthermore, they would hardly be controllable by an operator, they must therefore be entrusted to robotic management.

A second category of lasers, Er:YAG lasers, called *erbium lasers*, again operate with an infrared beam, but at $\lambda = 2.94$ µm, a region in which the radiation is absorbed mainly by the −OH groups, present, for example, in water and alcohols. However, also many aged organic substances (especially natural resins but also oils) possess, as a result of oxidation and photo-oxidation, hydroxyl groups, so that they can be ablated by the laser.

In the absence of −OH groups, wetting the surface with water and alcohols can "sensitize" the material to the action of the laser. The portable devices allow a very simple use of the instrument, with terminals that can be gripped like a pencil and that can be maneuvered like a scalpel at a distance of about ten centimeters from the painting. They are a valid alternative in all those cases in which chemical and chemical-physical methods are unsuccessful and which are the most difficult to solve in the cleaning of paints, just think of highly cross-linked organic fixatives, oxalate patinas, or resistant repainting.

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[158] Ibidem.

4. PAINTING SUPPORT: TERRACOTTA

4.1 Raw Materials

4.1.1 Clays

When we talk about the material with which ceramic artifacts are manufactured, in common parlance we refer generically to *clay*. The term used in this way is too general and does not provide any indication of the properties of the raw materials that make up the ceramics. The purpose of this paragraph is to understand what a clay is, what its properties are and what characteristics it imparts to the finished ceramic product.

Definition and origin

From a mineralogical or lithological point of view a clay is a rock originated by the alteration of other rocks or minerals. According to the type of alteration, the original material and the place of discovery compared to that of formation, clays can be divided into *primary clays* and *secondary clays*. The first originates from in situ alteration of minerals; this type of alteration, generally hydrothermal, produces a rock with a chemical composition practically unaltered compared to that of the parent rock. Secondary clays, on the other hand, are sedimentary rocks whose deposits are formed in places other than the place of alteration due to natural transport (hydrological and atmospheric phenomena). Moreover, atmospheric phenomena can degrade the same source rock in different ways.

Therefore, there can be a *mechanical degradation*, also called physical, due to the growth of ice or salt crystals in the cracks or pores of the rocks. The formation of ice, as well as that of salts, leads to an increase in volume inside the cavities and a consequent disintegration of the host material. In a similar way the sudden changes in temperature and the effects of abrasions caused by impact, for example of dust or sand carried by the wind, act in a similar way.

A second type of deterioration is *chemical degradation*, which is the decomposition of the rock due to chemical reactions and mineralogical transformations that occur under the spit of new thermodynamic contexts with the consequent formation of new minerals. This occurs because these rocks were formed inside the mantle, in conditions of temperature and pressure drastically different from those found on the earth's surface, so that they become thermodynamically unstable when in contact with the atmosphere. Climate, oxidizing atmosphere, vegetation growth and biological activity favor degradation through chemical processes. It is also important to remember that all these factors act simultaneously and with a synergistic effect on all the transformations that occur in the various minerals.

The solubility of the mineral due to the action of water, for example, depends on some physical parameters such as temperature, pressure, availability of oxygen and chemicals such as pH. The latter is fundamental in the degradation of rocks; when the source rock meets acid solutions following the presence of atmospheric CO_2 or other acids dissolved in the water itself, an exchange can take place between the metal cations present in the minerals and the H_3O^+ groups. Oxygen dissolved in water can act as an oxidant thus varying the global charge of the mineral. To cancel this charge variation, and thus return to electroneutrality, the composition of the mineral must undergo variations that can lead to the formation of new phases[159].

From the chemical point of view, clays can therefore be considered as the product of a reaction between the mother rock, containing various minerals, and water, in which various chemical species are dissolved. Clay minerals are essentially phyllosilicates, while non-clay minerals can be other silicates, oxides or hydroxides such as hematite and quartz, salts such as sulphides, sulphates, titanate phosphates, and sometimes organic compounds.

The minerals from which the clay is composed usually have very small dimensions, of the order of micrometers. After understanding the origin and the different types of clay, we want to understand what the optimal particle sizes for a set of minerals are to be defined as clay. This is important because depending on the applications and disciplines that study clay minerals, the dimensional limit can vary from 4 µm for sedimentology to 2 µm for geology and petrology, and finally to 1 µm for colloidal chemistry.

The nature and definition of clay itself is therefore quite complex and can have various meanings depending on the discipline that studies it. A clay is defined as follows:

> «a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic with adequate water content and hardens when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or cooked. The associated phases in clay can include materials that do not impart plasticity and organic matter»[160].

From this definition the main characteristics of a clay material are the ability to become plastic, and therefore easily moldable, by adding suitable quantities of water and rigid once dried and fired. According to the definition cited above, clay is therefore made up of two intimately mixed portions: a skeleton and a matrix.

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[159] Campanella L., *op.cit.*, p. 224.
[160] This is the definition of this rock which contains all the information necessary to understand its physical nature. according to AIPEA (Association International Pour l'Étude des Argiles) and CMS (Clay Mineral Society).

The skeleton is made up of fragments of crystals of various kinds of whose dimensions can reach up to 4 µm. On the other hand, the matrix containing crystals with dimensions lower than 4 µm and it is made up of real clay minerals.

The plastic component consisting of clay materials, the inert component mainly consisting of silica, veiling, and melting component are part of the mixture. These are essentially mixtures of carbonates and feldspar. *Inert*, *leaning* and *melting* substances are added to the clay to obtain the product with the desired characteristics.

4.1.2 Clay minerals

The plasticity of clay derives from the nature of the clay minerals it contains, these belong to the phyllosilicate family. The four main groups of clay minerals are: kaolinites, illites, vermiculites, and smectites. Kaolinites include kaolinite, dickite, nacrite and halloysite; illites include illite, hydrated micas, glauconite and celadonite; smectites include montmorillonite, while vermiculite forms a group of its own[161].

The chemical composition of these minerals can vary considerably depending on the degree of substitution of silicon, aluminum, magnesium with other cations, the nature and quantity of interlayer cations, in the case of micas, and the water content. In the classification of clay minerals and silicates used for the manufacture of ceramics, particular attention is paid to both the cations present and the chemical-physical properties of the minerals themselves. The metal cations, and especially the divalent and trivalent iron, act as chromophores both in the raw material and in the baked product. Their concentration and their oxidation state are responsible for the coloring of the raw material and of the product, while the chemical reactions and phase transformations control the color variation during the firing processes[162].

- Kaolinite

One of the most important groups is that of kaolinite, the main member cu is the kaolinite itself with formula $Al_4[Si_4O_{10}]$ $(OH)_8$: some other minerals belonging to this group are dickite and nacrite, rare polymorphic forms of kaolinite itself, and halloysite, a hydrated kaolinite, which in any case are not of particular interest in ceramic bodies.

Kaolin indicates a clay rich in kaolinite and the term derives from Kau-Ling, toponym of a place located near the Yellow River from which this clay was extracted[163].

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[161] Campanella L., *op.cit.*, pp. 226-227.

[162] Cfr. Sersale R., *I Materiali Ceramici*, Casa Editrice Ambrosiana, Milano, 1975.

[163] Recommended reading: Fioravanti I., *Terrecotte policrome*, Gavioli L. curatore, Marsilio, Venezia, 2003.

This mineral is generally white in color although sometimes it can take on reddish, brown, or bluish shades depending on the origin, as kaolinite is subject to small variations in its chemical composition.

There are some cations such as iron, chrome, titanium, magnesium and potassium, in very small percentages as impurities, in the form of oxides and hydroxides, of the mineral itself. Dickite and nacrite are chemically identical to kaolinite but differ in the packing sequence of the layers. The main sources of kaolinite are the primary deposits formed by the degradation or hydrothermal alteration of feldspar, muscovite or other aluminum-rich silicates contained in acidic rocks such as granites and quartz diorites. Kaolinite is also found in secondary deposits where the mineral itself or the source rocks have been transported by natural phenomena.

- Illite

Structurally, the minerals belonging to this group are very similar to micas; in fact, most of the illites are like the Muscovite, not a dioctahedral, while others may be similar to biotite, a trioctahedral mica. Illite can be represented by the formula $K_yAl_4(Si_8-yAl_y)O_{20}(OH)_4$, with y generally less than 2 and usually 1.5. The potassium content can be variable and depends on the composition of the source rock. In illite the octahedral layer contains 4 atoms of aluminum per unit of formula as in muscovite and the excess charge with respect to the tetrahedral components is compensated by the lack of potassium ions between the layers with respect to the muscovite configuration[164]. The rocks from which this group of clay minerals derives can be muscovite, kaolinite and feldspar, or their formation can be due to processes of metamorphism, called sepulchral metamorphism, which occurred in the smectites. This process involves a transformation of the layers of the mineral from smectite to an illite / smectite system and finally to illite.

- Smectite

Smectites are widely used in the ceramic and brick industry and, due to some of their chemical-physical properties, as filtering agents and catalysts in hydrogenation and other chemical reactions. The smectite component provides excellent plasticity and its addition in the dough improves the rheological characteristics during the realization of the products[165]. The general formula that represents the family of dioctahedral smectites, of which montmorillonite is part, $Al_4[Si_8O_{20}](OH)_4$, like to that of pyrophyllite.

[164] Johnsen O., *Minerali del Mondo*, a cura di Trossarelli C. & Costa E., Zanichelli, Bologna, 2006, p. 338.
[165] Campanella L., *op.cit.*, p. 228.

The chemical composition of pyrophyllite may vary slightly from that mentioned above due to small substitutions of silicon with aluminum and of hexacoordinated aluminum with Mg^{2+}, Fe^{2+}, Fe^{3+}, and titanium more rarely with calcium, sodium, potassium.

Smectites are generally white, yellow or greenish in color. They are very common constituents of sedimentary rocks in which they were formed by hydrothermal processes. These processes can involve the transformation of a clay or non-clay precursor (mother rock) or the neoformation from a colloidal solution. One of the minerals present in clay is chlorite, a phyllosilicate whose structure is like that of micas. This mineral occurs in small flakes or aggregates of lamellae that are mostly green (hence the name chlorite from the Greek indicates green), but also white, yellowish, brown, red or pink. The variety of coloring depends on the quantity and type of metal cations contained in the octahedral sites of the mineral itself.

The chlorite formula, $(Mg, Fe^{2+}, Fe^{3+}, Mn, Al)_{12}[(Si, Al)_8 O_{20}](OH)_{16}$.

4.1.3 Properties of clays

As mentioned, clays are mixtures of clay and non-clay minerals, consequently the chemical-physical properties of these mixtures derive from those of the constituents[166]. Clay minerals give the clays the most important properties for ceramic applications. Taking into consideration the characteristics of *colloidal systems*, i.e., the presence of surface ceramics, the ability to absorb water molecules or ions and the ion exchange capacity, properties that play a fundamental role in the preparation of the mixtures, therefore in the manufacture of ceramic[167]. The stability of these systems is due to the balance between Brownian motion, i.e., thermal energy, weight, i.e., gravitational energy, and electrostatic interactions, i.e., electrical energy. The particles in colloidal suspension, which represent the dispersed phase, cannot be separated by normal filtration and to be separated from the dispersing medium they must be subjected to ultrafiltration or precipitated by adding an electrolyte that alters the electrostatic interactions. The colloidal particles have a large surface compared to the volume and this surface is rich in electrical charges due to isomorphic substitutions in the structural units of the clay minerals, of Si^{4+} of tetrahedral units with Al^{3+}, or of Al^{3+} with Mg^{2+} in the octahedra.

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[166] Ivi, p. 230.
[167] A colloidal arrangement is a viscous heterogeneous system that does not sediment and is subject to Brownian motion due to the thermal excitation of the particles.

These substitutions involve an excess of negative charges on the oxygen bound to the central cation; these are present on the faces of the particles and are compensated by the presence of hydrated cations in the space between the various layers, and which do not become part of the crystalline structure. Depending on the type of clay mineral, the thickness of the layer of water molecules can vary and with it the plasticity and cohesion of the material itself.

For instance, the water layer on a kaolinite micelle is not very thick, as the surface charges present on the micelle itself are distributed very evenly and in this way the water dipoles disturb each other. The macroscopic consequence of this fact is the decrease in the plasticity and cohesion of kaolinite compared to other clay minerals such as illite and chlorite[168].

The arrangement of the clay particles is mainly influenced by the concentration of the electrolytes. In electrolyte-rich systems the clay particles tend to arrange themselves in such a way as to neutralize the overall charge, so the preferred arrangement will be that which puts the flat face of the particle (rich in negative charges) in contact with the edge (rich in positive charges). The system thus composed leads to the formation of large aggregates in whose cavity the liquid remains trapped. Clays can be considered as electrolytes. This consideration led to the definition of clays as "argillic acids" and this implies that the fixation of the cations does not occur only through an adsorption process, but also through a chemical ionic bond. If clay can be considered an acid, then the pH of an aqueous suspension can be measured accordingly. While clay minerals behave as very weak acids and their pH falls in the range between 5 and 7, clays, mixtures of clay and non-clay minerals, behave more complex and the pH of their suspension can vary between 3 and 9 and can be modified by the possible presence of organic components. Even clays of the same type can show differences in the pH values, therefore in the ion exchange capacity, since these are mixtures of different minerals with different acidity. In general, it can be said that clays with a high basicity contain in large quantities basic soluble salts, such as carbonates and bicarbonates[169]. The pH of these clays is between 8 and 9 and they are sometimes defined as marly clays or illitic clays. Neutral or very little basic clays, with pH between 6 and 7.5 owe their acidity to soluble salts or humic acids. Soluble salts such as sulphates and chlorides finally make the clay very acidic, with a pH between 3 and 5.5.

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[168] Campanella L., *op.cit.*, pp. 232-234.
[169] Buys S., Oakley V., *Conservation and Restoration of Ceramics*, Routledge, 1996.

4.2 FIRING

Principles

The ancient art of ceramics, whose origins date back to the first stable settlements of farmers in the transition from the Mesolithic to the Neolithic age, includes various techniques for the production of clay objects subjected to one or more firings. The term, which also distinguishes the same ceramic products, is derived from the Greek *Keramos,* but came into current use only in the 19th century[170].

The different clays are classified according to their use and not according to the technique used. Below it is reported a simple technological sheet of porous and compact clays.

- *Red clay* is fired at 980 °C - 1050 °C, orange and red in color depending on the iron oxide contained within the dough, after the first firing its body is porous (permeable);
- *Refractory* is composed by mixing various raw materials (kaolin, feldspar, alumina, quartz, etc.) with the addition of different granulometry 1000 °C - 1350 °C. This clay after firing has a porous body;
- *Terraglia* is a white clay divided into two groups, soft and hard, it is characterized by a white mixture, due to the lack of iron oxide and derivatives, and the presence of kaolin in addition to the other raw materials. For the tender cooking it is similar to red clay for the hard 1120 °C. This clay after firing has a porous body;
- *Gres* is a white or colored clay obtained from silicon-rich sedimentary rock clays, it is divided into three groups, klinker, ball clay, fire clay. Widely used for coverings (tiles) and sanitary ware, today used a lot in artistic ceramics. The cooking is around 1250 °C - 1400 °C. This clay after firing has a compact body (waterproof vitrified). The main features are resistance to acids, frost and scratches;
- *Porcelain* is a white clay, characterized by a mixture of few raw materials where feldspar and kaolin are in large percentages. It is divided into two soft and hard groups, the first vitrifies at 1220 °C reaching translucency (similar to opaque satin glass), the second (hard) can reach 1400 °C. This clay after firing has a compact body (waterproof vitrified). The main characteristics are resistance to acids, frost and scratches and the soft porcelain is translucent.

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[170] Ivi, p. 242

Since porous clays absorb liquids, the product requires a waterproofing coating. There have been glass roofs since ancient times; a paint composed of silica sand and lead oxide (lead glaze), or a lead compound in tune with tin (tin glaze), or with a veil of white earth[171].

The techniques that can be applied on all clays are different including:

- Etruscan technique: bucchero;
- Roman / Greek technique: sealed terracotta;
- Roman technique: simple terracotta and glazed terracotta;
- Medieval / Renaissance technique: glazed terracotta, majolica;

Furnaces

Traditional clay firing methods can be grouped into two categories: the first in which the artifacts are in intimate contact with the fuel and the other in which fuel and artifacts are physically separated. The first firing is called *open firing* because it does not require any fixed structure that contains the fuel and the artifacts. The artifacts themselves are placed in the ground, sometimes in a hole, *pit firing*, and covered with fuel.

Firing is carried out by setting the fuel on fire and waiting for it to run out. Once the fuel is exhausted, the incinerated residues and the ashes are removed, thus extracting the cooked product. It is a very primitive cooking method, but it requires skill and experience for its execution, and is still used by some primitive cultures of Oceania, North America, and the Middle East. This type of firing is characterized by non-homogeneous heating, during which the temperature rises rapidly, but discontinuously, creating hot spots in which 1000 °C can be reached. Open firings are never completely oxidizing processes due to the positioning of the fuel before ignition, which if done incorrectly inhibits a good passage of air[172].

Pit firing, a variant of open firing, allows you to create a decidedly reducing atmosphere and to easily obtain black or dark gray ceramic artefacts. This is because the deposition of the raw products in a depression in the ground limits the circulation of air during cooking.

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[171] Taylor J.R, Bull A.C., *Ceramics Glaze Technology*, Institute of Ceramics & Pergamon Press, 1986.
[172] Campanella L., *op.cit.*, p. 245.

The ovens, masonry structures, guarantee, thanks to their construction technique, a better control of the temperature and of the cooking atmosphere because the heating of the artifacts can take place by radiation.

A kiln for ceramic materials can be schematized as a construction consisting of a combustion chamber and a firing chamber. The two chambers are separated by a septum that allows the flow of heat and fumes thus avoiding direct contact between the fuel and the product. Depending on how much air enters, a completely oxidizing or completely reducing atmosphere can be obtained.

In addition to the high control of the atmosphere in the oven, kiln firing has the advantage of being able to reach very high temperatures, up to 1300 °C and being able to effectively control the heating rate[173].

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[173] Ibidem.

5. EXPERIMENTAL MATERIALS AND METHODS

5.1 Bas-relief by Giovanni Antonio Amadeo

5.1.1 Executive technique of the analyzed bas-relief

"Madonna col Bambino, Santa Caterina da Siena e un priore certosino", by Giovanni Antonio Amadeo (1447 - 1522), is in cold painted and gilded terracotta. The bas-relief shows portions executed in the round like the child's left arm and almost entirely the head. It portrays a traditional subject of Renaissance painting of the Carthusian area, with particular reference to one of the corbels on the north side of the large cloister of the Certosa di Pavia. According to the traditional bibliography, the young Carthusian monk portrayed could be San Bruno or, due to the absence of the halo, Blessed Stefano Maconi, former prior of the Pavia convent.

The observation under the microscope of the gaps and fracture points, carried out by the restorers[174], seems to indicate how the dress was cold painted in the traditional Dominican color with different techniques. The white veil was made with a thick clear preparation, while the black robe is rendered with a transparent veil of pigment spread apparently with an oily mission. A close iconographic example for the analysis of pigments, always coming from the environment of the Certosa di Pavia, could be the small tempera on panel by Bergognone (Ambrogio da Fossano, 1453 - 1523) today in the Pinacoteca in Brera and dated between 1488 and 1494 then performed during the first period of the artist's activity at the abbey.

Furthermore, analyzes carried out by the restorers have been able to define that the thick light-colored preparation seems to be common to all the white backgrounds, as well as the monk's habit with the characteristic central U-shaped buttonhole identifying the Carthusian tunic. The observation of the first cleaning tests suggested how, under the heavy and dark application of glue and the drying oil, the white tone of the light tunic has now partially absorbed the dirt carried by the protective agents applied in the old restorations.

According to part of the bibliography at the Museum of the Certosa di Pavia there is a plaster cast of this precious terracotta[175]. It is therefore likely that before transferring the work to the Castle's collections a copy was made for the rich Gipsoteca Pavese. Forming operation that could justify the presence of rabbit glue and drying oil[176].

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[174] Marchioron S., Colella M., *Santa Caterina da Siena presenta un monaco certosino (San Bruno?) alla madonna in trono con bambino (terracotta dipinta e dorata). Attribuita a Giovanni Antonio Amadeo (1447-1522) e/o sua bottega*, Milano.

[175] Righi N., in *Ambrogio da Fossano detto il Bergognone*, 1998, catalogo della mostra, p. 198.

[176] Cavazzini L., *Il giovane Amadeo e la terracotta*, in Albertini Ottolenghi M.G. e Basso L. (a cura di), *Terracotte del Ducato di Milano*, Milano, 2011, p. 68.

According to the restorers, before the casting of the plaster and animal gelatin matrix, an attempt was made to re-establish a sufficient degree of cohesion both in the color and in the preparation of the terracotta.

In fact, terracotta presents areas of compromise of the microstructure. As a practice for the casts, to avoid tearing the polychromy during the demolding, they may have applied a drying oil along the surface, noticed in the diagnostic phase, to make the terracotta more hydrophobic and therefore facilitate the operations of detaching the gelatin or plaster.

The terracotta appears compact, has slight radial firing fractures at the head of the Virgin and mainly horizontal in the rest of the relief: presumably indicating the junction of several raw clay loaves. The work appears to be made up of a single clay plate (terracotta) by layering two distinct blocks of raw clay before firing. According to careful studies, the restorers maintain that this precious work in terracotta was made with a mixed technique; or with the indirect method and the subsequent adhesion in raw clay of the elements worked in the round.

The work is therefore a bas-relief made with a main shaping and completed with the modeling of some main elements. The thicknesses of the terracotta are irregular, you can see the classic signs in the direction of the removal of excess clay pressed with *stagge* and *mirette*.

In some places the terracotta appears to be covered with a thin layer of white preparation. Recurring preparation in many painted and gilded terracotta both in Lombard and in the more general Renaissance context.

This white preparation was observed under a digital microscope by the restorers, in particular, in the vicinity of the chromatic gaps of the figure of the Carthusian, along the robe of Saint Catherine, along the veil of the Madonna and the Child's hair where XRF examination and microscopic observation identified the use of gouache gilding[177].

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[177] Among the techniques used for the gilding of a surface, gouache gilding, or bolus gilding, is the most widespread and appreciated so much that it is identified with gilding *tout court*. The procedure is fully described by Cennino Cennini (late 14th century) and essentially consists in the application of one or more coats of Armenian bole cast by jet on the previously plastered and well-polished surface. Once the surface is perfectly smoothed with a linen cloth, the gold is applied: the gold leaf is cut with a special knife to bring it to the necessary measurements. Wet the small area to be gilded with beaten egg white and water, take the leaf using the electricity of the brush and gently place the gold leaf on it. The gold is made to adhere perfectly by pressing lightly. Once the gilding is completed, the surface is subsequently smoothed, or burnished, and possibly enriched with further pictorial interventions.

5.1.2 Main forms of decay present on terracotta

Relief of the work (figure 14) showing the stuccoes and repaintings of a previous restoration. During the insertion of the rear support bracket of the work, probably inserted for the preparation of an exhibition, the work suffered damage to a portion at the top and the consequent plastering with chalky resin, which in compliance with the principle of minimum intervention, was not removed at this stage.

Figure 14. Plastering and repainting of ancient restorations.

The following are the main images (figures 15, 16) relating to the terracotta being restored taken in visible light and in ultraviolet light with the aid of a Wood lamp. The camera used for shooting is a Nikon D70 modified with the removal of the IR and UV Cut with the help of Kodak Wratten 2 filter for UV and High pass 780 for IR. The use of this technique made it possible to identify compositional inhomogeneities due to subsequent interventions, it was also possible to reconstruct the conservation story of the work.

In general, the immediate observation of strong absorption of ultraviolet radiation and the consequent dark appearance of the terracotta also in UV immediately confirmed the suspicion of the presence along the entire surface of a dull oily varnish, referable to an old maintenance.

The different luminosities that can be observed in UV vary according to the time that has elapsed since these materials were applied, for this reason it is possible to differentiate the repainting from the original painting where the less ancient materials are in fact darker.

The image in UV light, (figure 16), highlights numerous darker areas with the exception of the cleaning pads A and B and the upper part of the veil of Santa Caterina where the lowering of the oily varnish immediately highlighted a more intense fluorescence[178].

Figure 15. Observation under IR light shows that the removal pads of the restoration paints A and B reveal an ocher yellow underlying repaint which emits a more intense fluorescence.

Figure 16. Observation in UV light reveals that the removal pads of the restoration varnishes in points A and C show an underlying yellow ocher repaint that emits a more intense fluorescence. The lowering at point B of the varnish based on pre-consolidating agent with natural glues is gradually bringing to the surface the white lead draft of the veil of Santa Caterina. It is therefore also assumed here the presence of an oily overpainting mixed with animal glue (pre-consolidating agent from a previous restoration).

The high absorption of fluorescence seems to exclude the presence of a restorative pre-consolidating agent composed of linseed oil, but there is a more complex mixture, consisting mainly of a natural glue. Natural materials such as Arabic gum, casein or animal glue do not normally show fluorescence. On the other hand, the oils (flax, poppy, stand oil) have an intense yellow fluorescence. Even shellac sometimes used in 19th century restorations has an intense yellow-brown fluorescence[179].

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[178] Ivi, p. 10.
[179] Ibidem.

5.2 Description of samples

Seven samples, collected from the polychrome terracotta bas-relief datable between the 15th-16th centuries, were analyzed with spectroscopic techniques.

As already announced in the introduction of this written paper, these samples belong to an important Lombard Renaissance terracotta, present in the Castello Sforzesco in Milan, *"Madonna col bambino, Santa Caterina da Siena e un priore certosino"* (about 1470), attributed to an Italian sculptor, engineer and architect, Giovanni Antonio Amadeo (Pavia, 1447 - Milan, 1522).

Figure 17. Giovanni Antonio Amadeo, *Madonna col bambino Santa Caterina da Siena e un priore certosino*, (1470), bas-relief in polychrome terracotta, 59x46 cm, Milan, Catello Sforzesco. Before and after the cleaning operation. 1) sampling of the Carthusian priest's white robe; 2) sampling of blue mantle of the Madonna; 3) sampling of the Madonna's robe; 4,5,6) sampling of the bottom of the work of art; 7) sampling of the Madonna's red arm.

Figure 18. Detail of the sampling areas on the polychrome terracotta bas-relief.

Table 1. Presentation of the 7 samples taken from the bas-relief of polychrome terracotta.

Sample 1

Sample 1 was taken from the white habit of the Carthusian priest visible on the left side of the work, particularly in the area near the gap, visible in detail 1) of figure 18. It is composed of two larger whitish fragments of 0.3 cm and of a sample powder of the same color. Macroscopic observation shows that sampling also removed part of the underlying substrate, a condition that often occurs at this stage, as we will see in subsequent cases. Moreover, sample was also observed using a stereomicroscope with 3X magnification (Table 1).

Sample 2

Sample 2 was taken from the Madonna's mantle, oriented towards the right side of the work as shown in the detail 2) of the figure 18. It is a sample composed of intense blue fragments of 0.6 cm. The surface of sample appearances on one side blue and light colored on the other side due to the underlying substrate also taken during the sampling phase.

Besides, sample was also observed using a stereomicroscope with 3X magnification, (Table 1), to be able to have a better understanding of their morphology and color, given that they are samples of limited size.

Sample 3

Sample 3 was taken from the lower area of the Madonna's robe placed on the right side of the work. It is visible in the detail 3) of the figure 18. The sample is made up of three more evident fragments and two more little, their dimension is around 0.3-0.4 cm and all of them appear in homogeneous dark blue color, an apparently duller shade than the previous sample.
As previously indicated, this sample shows one side of an intense blue color and the other a whitish hue like the support from which it was taken.
Also in this case the samples were studied using a stereomicroscope with 3X magnification to better evaluate their morphology and color (Table 1).

Sample 4

Sample 4 was taken from the background patina of the work, in particular near the head of the Madonna, to the upper right part of the bas-relief, it is visible in detail 4) of the figure 18. This sample is composed of small and numerous dust-like fragments of about 0.1 cm. The color of this sample is a dull ocher color. While the underlying part has a whitish color due to the presence of sampled substrate. In this case, the morphological observation under the stereomicroscope was not possible due to the scarcity of the sample available.

Sample 5

Sample 5 was taken from shoulder of Madonna, this particular area is visible in detail 5) of the figure 18. Moreover, the sample is composed of several fragments of about 0.2 cm, each of an ocher color, while the underlying part has a whitish color due to the presence of sampled substrate. As in the previous case, the samples were studied using a stereomicroscope with 3X magnification to better evaluate their morphology and color (Table1).

Sample 6

Sample 6 was taken from the gold leaf of the bottom of the work from which this precious mineral emerged. In particular, the extraction point is located to the right part of bas-relief, it is visible in the detail 6) in figure 18. The sample is composed of several fragments of about 0.1 cm, their color is intense gold. As in the previous case, the samples were studied using a stereomicroscope with 3X magnification to better evaluate their morphology and color (Table1).

Sample 7

Sample 7 was taken from the red arm of Madonna, the sampling area is visible in detail 7) of figure 18. The sample is composed of two fragments of about 0.4 cm and is of an intense red color, while the underlying part has a whitish color due to the presence of sampled substrate. Moreover, also in this case it was possible to proceed with the investigation using a stereomicroscope with 3X magnification to observe its morphology and color with greater precision (Table1).

5.3 Methods of scientific investigation for works of art

It is now well known that the restoration and conservation of works of art can no longer be separated from the cognitive contribution offered by science today.

For artistic artefacts, various and sophisticated methodologies must be progressively used for the acquisition of preliminary data for the restoration intervention. In this way it is possible to know in depth the material nature of the work and above all its current state of conservation, the "diseases" in progress, the transformations it has undergone, similarly to medical diagnostics. These investigations constitute the indispensable premise for any serious restoration and conservation discourse that one wishes to program, for this reason, it is necessary that those who work in this sector must be informed about what science is implementing.

The figurative work of art exists as constituted by matter and its "life" is nothing but a spontaneous or forced transformation of this. Chemistry and related sciences investigate the matter, therefore, a considerable help can come from them to get to know in depth an important aspect of the work, its material nature. Furthermore, it is precisely from the scientific disciplines that indications can be obtained to prolong its existence with the most correct methods. The object may not consist only of the work but also of the environment in which it is preserved and also of the materials used for its restoration and conservation.

A fundamental aspect, which concerns the investigation methodologies applied to cultural heritage, is the concept of the destructiveness of the method to be used for the diagnostic analysis of the work of art.

The diagnostic techniques used can be classified into:

- *non-invasive investigations*: no sampling is required;
- *invasive investigations*: they require the taking of a sample and often its preparation to make it suitable for analysis[180].

Compared to the sample, invasive investigations can be:
- *destructive*: the sample undergoes strong changes following the analysis;
- *micro-destructive analyses*: the area affected by the analysis is very limited and practically invisible except under strong magnification;
- *non-destructive*: the analysis does not cause any modification of the sample allowing the execution of multiple investigations on the same sample.

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[180] Aldrovandi A., Picollo M., *Metodi di documentazione e di indagini non invasive sui dipinti,* Il Prato, Padova, 2007.

The diagnostic analyses, used in the present work for the characterization of the samples, are both non-destructive and micro-destructive invasive.

To perform the scanning electron microscope analyses, thanks to the already small size of the samples available, no type of treatment of the fragments was performed.

The analysis using FTIR spectroscopy does not require particular treatments, although in order to have a better contact between the sample and the crystal of the instrument and, therefore, a better signal / noise ratio, it is often necessary to grind the sample.

Raman analyses were performed directly on the sampled surface without any treatment.

5.4 Methods of characterization of pigments

The characterization of the pigments involves analysis using non-invasive techniques, as the investigations can be performed in different points of the same paint and be replicated even after the conservative treatments. In this way it is possible to monitor the different phases of intervention. The tools used can be portable and therefore also allow in situ analyses, very useful when dealing with large or non-removable paintings, as in the case of wall paintings.

Spectroscopic diagnostics of a painting can be performed using image techniques such as color reflectography, IR reflectography, UV fluorescence, X-ray radiography.

About diagnostic imaging, the most used instrumental investigation is represented by infrared reflectography, which is carried out with a video camera equipped with a Vidicon tube and connected to a monitor.

While the X-ray fluorescence spectrometry (XRF) allows to obtain information on the chemical elements, thanks to which it is possible to trace the pigments used on the analyzed surface.

Additional techniques used for the analysis of pigments are reflectance spectroscopy with optical fibers (FORS) and fluorescence spectroscopy with optical fibers, which allow to obtain a considerable amount of information on the electronic and vibrational states of the materials of the polychrome work as well as of the pigments used on it[181].

When performing micro-sampling, microscopy is used as a preliminary to instrumental investigations. Optical microscopy is used on the sample as it is or incorporated in the resin, cut transversely and polished, it is a stratigraphic section.

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[181] FitzHugh E.W., *op.cit.*

For a detailed morphological analysis, it is necessary to resort to scanning electron microscopy with X-ray Microanalysis (SEM-EDX) which also allows to highlight imperfections and alterations. X-ray microscopy allows to perform qualitative and quantitative elementary analyses on selected areas of the sample and to obtain information on individual elements.

This information is also obtained by X-ray fluorescence spectrometry and X-ray photoemission spectroscopy (XPS), while the X-ray diffraction (XRD) allows to obtain information on the crystalline structure of solid substances.

Fourier transformed infrared spectroscopy (FTIR) and Raman spectroscopy, used for the determination of organic and inorganic substances, are widely used to define the compound under investigation[182].

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[182] Campanella L., *op.cit.*, p. 129.

5.4.1 Scanning electron microscopy with energy dispersion X-ray analysis (SEM-EDX)

Basic principle

This type of microscope is always based on the use of electronic waves instead of light waves and therefore on the use of electromagnetic optics.

The scanning electron microscope (at most 1000.000x but in reality, about 20.000x effective) has had a much wide development and diffusion[183].

This derives from the fact that the SEM, unlike other types of microscopes such as the optical microscope, is able to provide very realistic images of an object characterized by a very high degree of definition and which recall its three-dimensional shape, ultimately therefore images much more similar to those we are familiar with (figure 19). The grayscale image obtained as a product of the interaction between radiation and matter, goes beyond reporting the real coloration of the analyte[184].

Figure 19. SEM micrograph of a small surface area of a sample taken from the painted terracotta bas-relief, "*Madonna col bambino Santa Caterina da Siena e un priore certosino*".

[183] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, Nardini, Firenze, 1984.
[184] Holler J.F., Crouch S.R., *Fondamenti di chimica analitica*. Edises, 2015.

Two signals are mainly produced in the scanning electron microscope:

- *secondary electrons*: they originate from an inelastic surface interaction between the primary electron beam and the sample. Secondary electrons provide predominantly morphological information through the creation of topographic images;

- *backscattered electrons*: they come from the interaction with the nuclei of the sample atoms and provide mainly compositional information. Large atoms scatter more electrons towards the detector than smaller atoms producing a greater signal and, consequently, appear clearer on the SEM image. The contrast in the images is therefore directly proportional to the atomic number (the average atomic number is considered in the case of a compound).

The image is formed not by electrons passing through the sample but by secondary electrons emitted point by point from the surface of the object which is hit by a very thin beam of (primary) electrons.

In the SEM the image is formed from a temporary sequence of effects in a similar way to what happens in television. A very thin focused beam of electrons systematically scans the sample at low speed[185]. The secondary electrons emitted in temporal sequence from each point explore the sample, even if not flat, are collected by a suitable collector. The signal is amplified and sent to a cathode ray tube through which the enlarged image of the object that can be photographically recorded is returned on a fluorescent screen.

Sample preparation in the case of the scanning electron microscope is not very complex. In fact, the object may not be perfectly flat, i.e., there are no such limiting depth-of-field problems as in the case of optical and transmission electron microscopy.

Each point of the object, on the basis of the secondary emission to which it gives rise, is characterized in the image without this depending on the coplanarity with the other points.

On the other hand, so that the secondary emission to occur according to the right modalities, it is necessary that the investigated surface is all at constant electric potential. This requires the surface to be electrically conductive.

If the sample contains materials that do not conduct electricity, the surface must be made conductive by covering it with a very thin film of conductive material (usually gold or carbon vaporized and deposited in a thin film under vacuum)[186].

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[185] Recommended reading: Moll S., *Scanning electron microscopy: a versatile analytical tool. Technology and Conservation*, Spring, 1975.
[186] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, cit.

The secondary emission of the surface hit by accelerated electrons may also consist of (secondary) electrons responsible in most cases for the formation of the image, or even by X-rays, capable of making elementary analysis of the surface possible as well as providing an image. The emission of X-rays characteristic of the atoms contained in the sample (X-ray fluorescence) comes from areas of the sample that are deeper and the phenomenon is caused by the excitation due to the incident electron beam.

Therefore, the electron microscope, conceived mainly to produce three-dimensional images, if equipped with a detector capable of detecting the characteristic X-rays emitted by the sample (in our case an EDX detector, or Energy Dispersive X-ray detector), allows to obtain the elementary analysis of the sample itself by measuring the intensity and energy of the characteristic X emission for each element. The technique is called electron microscopy coupled with energy dispersion X-ray fluorescence analysis / spectroscopy (SEM-EDX or SEM-EDS)[187].

Types of investigations that can be carried out

Semi-quantitative analyses, which use the energy dispersion detector, can be carried out on an area of different sizes or on a specific point on the surface, and measure the intensity of the X radiation generated by the electron beam incident on the sample.

The purpose of the quantitative analysis is to find the correlation between the intensity of the characteristic radiation of the elements under examination and their concentration. For this purpose, the intensities of the X-rays emitted by the sample are compared with those emitted by the reference standards for which the concentrations of the elements to be measured are known. This analysis is limited by the matrix effect that identifies all those phenomena of attenuation of the beam caused by the presence of different phases within the analyte. A correction is then made on the final calculated value and this correction depends on the fact that:

a) the mass penetrated by the different elements is not constant (*stopping power* correction);

b) part of the incident electrons escapes from the sample surface after being deflected, and therefore are not detected (*backscattering* correction);

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[187] Moropoulou A., Zendri E., Ortiz P., Delegou E.T., Ntoutsi I., Balliana E., Becerra J. and Ortiz R., *Scanning Microscopy Techniques as an Assessment Tool of Materials and Interventions for the Protection of Built Cultural Heritage*, "Hindawi Scanning", 20 (2019).

c) the X-rays are attenuated after having crossed the sample for a certain depth (correction by absorption);

d) the intensity of the X-rays is increased due to the fluorescence of other X-rays generated in the sample (fluorescence correction).

The qualitative analysis, on the other hand, involves the identification of the characteristic spectrum lines, since the final purpose is to instantly identify the elements present in the unknown sample. Chemical elements having an atomic number greater than or equal to that of beryllium can be detected.

Once the EDX analysis is finished, the standard deviation and the relative error (ratio between the standard deviation and the mean) are calculated with the data obtained to allow you to estimate the accuracy of the analyses. The lower their value, the greater the precision. Sometimes, in some studies, the calculation of accuracy is also required, which represents how much the measured value approaches the known one. It is evaluated by calculating R^2, which is the sum of the squares of the differences between the average measured value and the known one. Also in this case, the lower this value, the greater the accuracy of the analyses.

By means of SEM-EDX analysis, samples of any shape can be analyzed, however, having relatively small dimensions so that they can be inserted into a chamber that must work under vacuum. The sample must theoretically be an electrical conductor therefore, for non-conductive materials, a conductive surface coating is applied by vacuum deposition to allow electrons to travel through the sample. The coating materials used are gold or carbon in the form of graphite. Some instruments, however, do not require the metallization of the sample as they can operate in low vacuum with equally satisfactory results, as in the case of the instruments used in this work.

The measurements were carried out using two different scanning microscopes, both equipped with an electronic microprobe. The first, Hitachi TM-1000 is equipped with an electronic microprobe operating at an excitation voltage of 15 kV and a detector for backscattered electrons. It was mainly used for the elementary analysis of sample areas, always maintaining the same area.

The second scanning microscope is a Hitachi TM-4000 instrument, equipped with an EDX microprobe and with detectors for backscattered and secondary electrons. The instrument was used both to conduct morphological investigations of some details of the samples, to be able to observe them in detail and to be able to perform maps relating to the distributions of the elements.

The elementary microanalyses were carried out by means of the electronic microprobe EDX Oxford-AztecOne, operating with an excitation voltage of 5kV, 10 kV and 15kV in high vacuum conditions.

5.4.2 Fourier transform infrared spectroscopy in attenuated total reflection (ATR-FTIR)

Basic principle

Qualitative IR spectroscopy is a valuable analytical tool that allows for the identification of organic and inorganic materials. Each compound's IR spectrum contains a substantial amount of information. This information, along with some patience, skill, and knowledge about a sample's background, can be used to determine molecular structures successfully, as well as to characterize unknown materials[188].

Similarly to what happens for ultraviolet and visible radiation, also the radiations of the infrared field can be selectively absorbed following the crossing of a substance. The electrons of the covalent and covalent-polar bonds of the molecules possess quantized energies not only in relation to their possession with respect to the nuclei (potential energies) but also in relation to the vibrational and rotation movements of the bonds and atoms (vibrational and rotational energies). The quantum leap of these types of energy can easily be caused by exciting the electrons with radiation from the infrared zone. For this purpose, radiations with a wavelength varying between 3-25 µm (vibrational spectra and greater than 25 µm up to over 200 µm (rotational spectra) are used.

In this way, an absorption spectrophotometry in the infrared is also possible. Almost all substances give absorption spectra in this radiation field. These spectra are characteristic of the complex of bonds that a molecule possesses and therefore of the same molecule.

This technique is of great importance in analytic chemistry, especially qualitative. In the zone ranging from 2.5 µm to 16-25 µm there are absorption spectra of all organic and inorganic substances containing polyatomic anions.

On the other hand, many binary inorganic substances absorb only in the far infrared. Also, the hydration water contained in salts, hydroxides etc., it can be revealed in a characteristic way[189].

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[188] Cfr. Derrick M.R., Stulik D.C., Landry J.M., *Scientific Tools for Conservation. Infrared spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, 1999.
[189] Holler J.F., Crouch S.R., *op.cit.*

Types of investigations that can be carried out

Infrared spectrophotometry allows the identification of the functional groups that characterize both organic and inorganic compounds. It is used it is used for the identification of many substances. In the field of works of art, it is therefore of great help for the analysis of paints, adhesives, binders, many pigments, polluting salts, and materials used in the restoration, in all states of aggregation and also in solution (figure 20).

Figure 20. IR absorption spectrum of a pigment sample taken from the polychrome terracotta bas-relief, "*Madonna col bambino Santa Caterina da Siena e un priore certosino*".

The wavelengths of the absorption bands depend on the bonds present in the molecule and are characteristic of each substance or group of similar substances, so that each IR absorption spectrum provides information on the functional groups and *fingerprints* of the molecules. It was found, however, that this analysis hardly allows to distinguish between the various materials belonging to the same class, especially since the materials to be analyzed are in the form of complex heterogeneous mixtures that aging has made even more complicated[190]. For this reason, when infrared spectroscopy is not satisfactory, it is often integrated with other suitable analyses. The analysis is based on the property, which almost all compounds possess, of absorbing infrared radiation in a different and unmistakable way, to produce a characteristic IR spectrum for each substance examined[191].

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[190] Campanella L., *op.cit.*
[191] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, cit.

Specifically, vibration spectroscopy is based on the interaction between infrared radiation and the sample. When a molecule is hit by IR radiation, part of the energy given to it by the radiation is absorbed and converted into vibrational energy. The absorption of radiation, as a function of the wavelength, corresponds to the stimulation of the different energy levels of the molecule.

In order to determine at what wavelength the vibrational transitions in the molecules present in the sample are induced, the transmitted light is detected and analyzed using a spectrometer, obtaining a band spectrum.

Most of the spectra are realized in transmission (or transmittance T) generally as a function of the wavenumber ($\bar{\nu}$ in cm^{-1}) or of the wavelength (λ in μm) or of the frequency (ν in s^{-1}).

In the analysis of the bands of a spectrum, the acquired spectra are compared with the known ones of the reference materials. The recognition of the compound is accomplished through the identification of three parameters of the bands, which are:

- The *position*: it indicates which functional groups are present in the molecule. In particular, the region of functional groups is located between 4000 and 1300 cm^{-1}. Between 1300 and 650 cm^{-1} is the so-called *fingerprint* zone, characteristic of each substance;

- The *shape*: it provides information on the functional groups and the purity of the material. The observation of asymmetrical bands indicates either the presence of another superimposed band, or the existence of a component with a lower concentration, or it is caused by changes in the material;

- The *intensity*: it provides, with respect to the intensity of the other bands, information on the quantity of the specific functional group within the molecule[192].

Like most modern instrumentation, Fourier transform technology is used which enjoys good spectral resolution even with minimal quantities of powdered sample and significantly optimizes measurement times.

Another very useful support, especially when solid and massive samples are examined, is the ATR. An FTIR instrument associated with this support allows you to perform a completely non-destructive analysis and therefore does not require a particular pre-treatment of the sample. This technique exploits the attenuated total reflection of the IR ray inside the sample, considering that in order to have a good spectrum, and therefore a good signal / noise ratio, it is necessary to have an excellent contact between the crystal of the instrument and the sample.

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[192] Adrover G.I., *Applicazioni della spettrofotometria IR allo studio dei beni culturali*, Il Prato, Padova, 2001.

Often this can be achieved by bringing the instrument as close as possible to the sample.

When treating samples such as those examined in this work, as well as minerals, rocks, mortars, etc., it is necessary to fragment and grind it into a powder[193].

The instrument used to carry out the analyses is a portable PerkinElmer Spectrum Two spectrophotometer equipped with ATR (UATR Two).

The spectra were acquired in percentage transmittance in a range between 4000 and 400 cm^{-1}.

5.4.3 Raman spectroscopy

Another molecular spectroscopy technique, complementary to the IR technique, is Raman spectroscopy. This technique is widely used in the identification of pigments on works of art, above all thanks to its non-destructiveness, the possibility of being applied in situ, the excellent spatial and spectral resolution, the excellent sensitivity and specificity, finally the ability to not suffer interference from adjacent materials[194].

Furthermore, the high selectivity of this technique allows to identify different chemical species in the molecular structure and not only in the composition.

The Raman technique exploits a physical phenomenon discovered in 1928 by the Indian physicist and Nobel laureate Chandrasekhara Venkata Raman (1888-1970). He discovered that a small part of the radiation scattered by certain molecules had different energy from that of the incident radiation, and that the difference in energy was related to the chemical structure of the molecules responsible for the scattering.

The principle on which the Raman technique is based is the diffusion of a monochromatic radiation incident on the sample. Considering the radiation-matter interaction in terms of particles, we can think of a collision between the photons and the molecules that make up the sample. When this interaction occurs, in addition to the normal phenomena of reflection, transmission and absorption, two effects of diffusion of the radiation by the molecules are also produced.

The first, called "Rayleigh scattering", is the most frequent event, it is of an elastic nature and does not involve any exchange of energy between the molecules and the incident photons; in fact, scattered photons have the same energy as incident ones.

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[193] Recommended reading: Chalmin E., Castets G., Delannoy J-J., David B., Barker B., Lamb L., Soufi F., Pairis S., Cersoy S., Martinetto P., Geneste J.M., Hoerle S., Richards T., & Gunn R., *Geochemical analysis of the painted panels at the "Genyornis" rock art site*, Arnhem Land, "Quaternary International", 430 (2017) pp. 60–80.
[194] FitzHugh E.W., *op.cit*.

The other effect is of an inelastic type and is called the "Raman effect". It involves a transfer of energy that excites the vibrational energy levels of the molecule[195].

The frequency shift, which may be due to the loss or gain of energy, depends on the final energy of the particular energy level concerned and is independent of the radiating frequency.

Therefore, since most molecules have more than one Raman vibrational level active, there will be a frequency range in the diffuse beam capable of forming two specular spectra around the radiating frequency ("Stokes" and "anti-Stokes" bands) which make up the Raman spectrum of the molecule involved in the energy exchange described[196].

The Stokes lines are linked to the functional groups of the sample molecules and their vibration modes and are used for diagnostic purposes for the qualitative identification of the compounds present within the sample.

The anti-Stokes lines, on the other hand, have very low intensities to be detected and are used only to estimate the temperature of the sample based on the relationship with the intensity of the Stokes lines.

In general, the Raman effect is in most cases so weak that it requires very intense sources to be able to collect significant signals. The latter are possible to obtain with laser sources.

One of the negative aspects of this technique is constituted by the presence of the fluorescence that is generated when a sample is excited in the vicinity of one of its electronic absorption bands. It is generally much more intense than the Raman signal, so much so that at times it prevents the observation of the spectrum.

The fluorescence that originates from the same materials to be analyzed or from impurities contained in them can be reduced or eliminated by changing the wavelength of the exciter source, or using FT-Raman instrumentation, often chosen also to obtain a higher spatial resolution. This high spatial resolution makes micro-Raman spectroscopy particularly suitable for the identification of inhomogeneous mixtures and samples[197,198].

Raman analyses were performed using a portable BWTek i-Raman plus spectrometer equipped with a microscope with a 40x objective and equipped with a solid-state laser with 785 nm excitation emission and a CCD detector.

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[195] Doménech-Carbó M.T., Oeste-Cortina L., *Another beauty of analytical chemistry: chemical analysis of inorganic pigments of art and archaeological objects,* "ChemTexts" 2 (2016).
[196] Campanella L., *op.cit.*, pp. 26-27.
[197] Iidem.
[198] Doménech-Carbó M.T., *op.cit.*

6. RESULTS AND DISCUSSION

6.1 Diagnostic study of pictorial pigments

The results of the analyses performed on the cited samples, obtained by the analytical techniques presented in the previous chapter, will be reported below. The results are organized by dividing them by color of the pigment corresponding to the sample analyzed. The identification of the pigments was carried out by comparing the results obtained with the data in the literature.

6.1.1 White pigment, Sample 1

The first analysis performed on sample 1, and on all the other samples, was the SEM-EDX one in order to have an initial approach on the elemental chemical composition of the white pigment. Sample 1 is composed of two larger fragments, both used for SEM analysis. The figures 21a and 21b show the morphology of the two fragments.

The SEM-EDX investigations were carried out on different areas of the sample surface, we consider two of these. Morphologically, the parts analyzed do not appear homogeneous with respect to the entire surface of the sample under analysis.

Figure 21a and 21b. SEM micrograph respectively of the first and the second fragment of the sample 1.

The morphological analysis of the image shows the sample with clear and dark areas evident in various parts of the surface, this condition is visible in both fragments of sample 1.

Three parts of both fragments were analyzed by SEM as shown in the following images (figures 22-24).

Figure 22. SEM photomicrograph of the area relative to the first fragment of the sample 1 (area relating to the analysis 1 in the table 2).

Figure 23. SEM photomicrograph of the homogeneous area relative to the second fragment of the sample 1 (area relating to the analysis 2 presents in the table 2).

Figure 24. SEM photomicrograph of the organic particles relative to the second fragment of the sample 1.

The semi-quantitative EDX analysis obtained on two of the examined areas, detects the presence of chemical elements in different percentages of weight. By way of example, one of the EDX spectra obtained from the analysis is shown (figure 25).

Table 2 therefore shows the percentages of oxides (the data obtained directly from the instrument) of the elements detected at each analysis performed on a specific area of the sample.

Table 2. Semi-quantitative EDX analyses performed on the sample 1 (percentages by weight)[199].

N° analysis	CaO	SiO$_2$	Cl	SO$_2$	FeO	PbO$_2$	Br$_2$O	K$_2$O
1	1.7	-	3.6	-	-	90.7	-	-
2	8.9	18.5	3.2	6.0	5.7	47.7	7.7	2.4

The most abundant element is lead, whose presence is attributable to the use of lead white, the so-called *biacca,* 2PbCO$_3$·Pb(OH)$_2$. Moreover, the presence of calcium suggests the presence of calcite, CaCO$_3$. Besides lead and calcium, there is aluminum, element that can be considered, not being a chromophore element, as an integral part of the substrate composed by terracotta. Sulfur could be associated with the presence of gypsum, CaSO$_4$·2H$_2$O, that can be used as a preparation for the artefact before applying the paint film. Other elements such as silicon, chlorine, bromine, iron, and potassium are related to the material of substrate.

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[199] The data are expressed in oxides. In order to have the data expressed in elements available, the average in elements was calculated. By "element average", in fact, we mean the average referred to the single elements obtained by dividing the "oxide average" (in turn obtained from the oxide data obtained directly from the instrument) by the ratio between the atomic weight of the oxide and that of the element. In this case, the sum of the averages of the elements obtained will not close at 100, but at a number which, if subtracted from the total, allows to obtain the sum of oxygen and carbon not calculated as a percentage.

Using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 26).

O	Si	Ca	Pb	Cl	Fe	K	Al	P	Na	Mg	S
12.29	1.27	3.06	77.31	1.98	0.67	0.45	0.51	0.27	0.37	0.35	1.47

Figure 26. SEM-EDX analysis of sample 1. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of Pb; e) SEM-EDX map in false colors of C; f) SEM-EDX map in false colors of O; g) SEM-EDX map in false colors of Ca; h) SEM-EDX map in false colors of Si; i) SEM-EDX map in false colors of Cl; l) SEM-EDX map in false colors of Al; m) SEM-EDX map in false colors of P; n) SEM-EDX map in false colors of K; o) SEM-EDX map in false colors of Mg; p) SEM-EDX map in false colors of Na; q) SEM-EDX map in false colors of Fe.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 27) which highlighted the presence of several components.

Figure 27. ATR-FTIR spectrum of sample 1.

This analysis brought to light several substances, in particular the proteinaceous binder of the paint and the presence of the lead white pigment, $2PbCO_3 \cdot Pb(OH)_2$[200,201,202,203]. Furthermore, the presence of gypsum, $CaSO_4 \cdot 2H_2O$, is probable following the analytical results[204,205]. In particular, gypsum has its bands around 778, 602, and 461 cm^{-1} [206, 207], it was probably used as a preparatory basis for painting as was the case in many paintings of the time[208]. The characteristic bands of lead white visible in the analysis are around 1400 cm^{-1}, 1042 cm^{-1}, and 678 cm^{-1} [209].

The other bands like those in 3300 (br), 2920, 2849, 1651, and 1538 cm^{-1} can be associated with organic proteinaceous products[210,211].

[200] Turco A., *Nuovissimo ricettario chimico*, Volume 1, Hoepli Editore, 1990.

[201] Bevilacqua N., Borgioli L., Adrover G.I., *I pigmenti nell'arte dalla preistoria alla rivoluzione industriale*, collana *I Talenti*, Il Prato, Padova, 2010.

[202] Stuart B.H., Analytical Techniques in Material Conservation, Wiley USA, 2007.

[203] Zhao Y., Berns R.S., Taplin L.A., Coddington J., *An investigation of multispectral imaging for the mapping of pigments in paintings,* Computer Image Analysis in the Study of Art, "Spie digital library", 6810 (2008).

[204] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, cit.

[205] Lebon M., Gallet X., Bondetti M., Pont S., Mauran G., Walter P., Bellot-Gurlet L., Puaud S., Zazzo A., Forestier H., Auetrakulvit P., Zeitoun V., *Characterization of painting pigments and ochres associated with the Hoabinhian archaeological context at the rock-shelter site of Doi Pha Kan (Thailand)*. "Journal of Archaeological Science: Reports", 26 (2019), pp. 11-14.

[206] Chukanov N.V., *Infrared spectra of mineral species*, Springer, Berlino, 2014.

[207] Stuart B.H., op.cit.

[208] D'Errico F., Bouillot L.D., García-Diez M., Martí A.P., Pimentel D.G., Zilhão J., *The technology of the earliest European cave paintings: El Castillo Cave, Spain*. "Journal of Archaeological Science", 70 (2016), pp. 48–65.

[209] Database of pigments: https://spectra.chem.ut.ee/paint/pigments/

[210] Feller R.L. *Artists' Pigments, A Handbook of Their History and Characteristics*; National Gallery of Art: Washington, DC, USA, Volume 1, 2012.

[211] ATR-FT-IR database spectra of materials: https://spectra.chem.ut.ee/paint/binders/

The analysis performed on the Carthusian's sleeve by Raman spectroscopy investigation confirmed the presence of lead white, *biacca,* (figure 28)[212,213,214,215,216], because of the band at 1050 cm^{-1}. It is also visible the strong peak at 1080 cm^{-1} due to calcite[217], probably present in the preparatory layer.

[212] Fuster-López L., Izzo F.C., Piovesan M., Yusá-Marco D.J., Sperni L., Zendri E., *Study of the chemical composition and the mechanical behaviour of 20th century commercial artists' oil paints containing manganese-based pigments,* "Microchemical Journal", 124 (2016), pp. 962-973.

[213] Turco A., *op.cit.*

[214] Bevilacqua N., *op.cit.*

[215] Beninatto R., De Lucchi O., Chimica organica per artisti e restauratori: sostanze naturali, CreateSpace Independent Publishing Platform, 2016.

[216] Recommended reading: García-Bucio M.A., Casanova-González E., Ruvalcaba-Sil J.L., Arroyo-Lemus E., Mitrani-Viggiano A., *Spectroscopic characterization of sixteenth century panel painting references using Raman, surface-enhanced Raman spectroscopy and helium-Raman system for in situ analysis of Ibero-American Colonial paintings*, "The Royal Society Publishing", 374 (2016).

[217] Smith G.D. & Clark R.J.H., *Raman microscopy in art history and conservation science*, "Reviews in Conservation", 2 (2001), pp. 96-106; Chaplin T.D. & Clark R.J.H., *Raman microscopy techniques for the characterization of pigments*, In Focus, (2006).

Blue pigment, Sample 2

Sample 2 is composed of four larger fragments used for analysis by SEM. It is possible to see the surface of sample in the following image (figure 29).

Figure 29. SEM micrograph of the sample 2 of polychrome terracotta in dark blue tones.

The SEM-EDX investigations were carried out on different areas of the sample surface, we consider three of these. Morphologically, the image shows the homogeneous granular surface of the sample except for lighter and darker spots (organic particles) that characterize it.

Figure 30a and 30b. SEM micrograph referring to the detail of the granular surface of the sample 2.

Three parts of these fragments were analyzed by SEM as shown in the following images (figures 31-33).

Figure 31. SEM micrograph of the area of interest taken on the lower part of the sample 2, visible in figure 29 (area relating to analysis 3 presents in the table 3).

Figure 32. SEM micrograph of the area of interest taken on the left side of the sample 2, visible in figure 29 (area relating to analysis 1 presents in the table 3).

Figure 33. SEM micrograph of the area of interest taken on bottom of sample 2, visible in figure 20 (area relating to the analysis 2 presents in the table 3).

The semi-quantitative EDX analysis of the three areas examined, detects the presence of chemical elements in different percentages of weight. By way of example, one of the EDX spectra obtained from the analysis is shown (figure 34).

Figure 34. EDX spectrum obtained on sample 2 of the respective SEM micrograph in the figure 32.

Table 3 therefore shows the percentages of oxides (the data obtained directly from the instrument) of the elements detected at each analysis performed on a specific area of the sample.

Table 3. Semi-quantitative EDX analyses performed on the sample 2.

The most abundant element in analyses 1 and 2 is lead, attributable to the use of lead white (table 3), the so-called *biacca*, $2PbCO_3 \cdot Pb(OH)_2$, pigment presents on the surface of the analyzed sample. Silicon can be considered, not being a chromophore element, as an integral part of the substrate composed by terracotta. Sulfur and calcium may indicate the presence of gypsum, $CaSO_4 \cdot 2H_2O$, that could be used as a preparation for the artefact before applying the painting film. Finally, it is worth noting the high percentage of iron in analysis 3 that is possibly related to the substrate.

By using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 35).

Figure 35: SEM-EDX analysis of sample 2. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of Si; e) SEM-EDX map in false colors of O; f) SEM-EDX map in false colors of C; g) SEM-EDX map in false colors of Pb; h) SEM-EDX map in false colors of K; i) SEM-EDX map in false colors of S; l) SEM-EDX map in false colors of Ca; m) SEM-EDX map in false colors of Al; n) SEM-EDX map in false colors of Na; o) SEM-EDX map in false colors of Mg; p) SEM-EDX map in false colors of Fe; q) SEM-EDX map in false colors of Cu; r) SEM-EDX map in false colors of Co; s) SEM-EDX map in false colors of Ni.

The presence of copper, (figure 35), could be associated with the use of azurite, $2CuCO_3 \cdot Cu(OH)_2$, as a pigment mixed with lead white. The contemporary presence of copper, calcium and silicon may also suggest the use of Egyptian blue, $CaOCuO(SiO_2)_4$, in the sample. Furthermore, the presence of cobalt could indicate the use of *smaltino*, a blue pigment based on cobalt, which use started in the Renaissance.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 36) which highlighted the presence of several components and in particular of lead white pigment, $2PbCO_3 \cdot Pb(OH)_2$ and azurite, $2CuCO_3Cu(OH)_2$.

Figure 36. ATR-FTIR spectrum of sample 2.

Furthermore, the presence of gypsum, $CaSO_4 \cdot 2H_2O$, is indicated by bands around 668 and 600 cm^{-1} [218,219,220,221], probably used as a preparatory basis for painting as was the case in many paintings of the time. The characteristic bands of lead white, *biacca*, $2PbCO_3 \cdot Pb(OH)_2$, visible in the analysis are around 1400 cm^{-1} and 680 cm^{-1}, whereas the characteristic bands of azurite are placed at 3420, 1400 (overlapped to *biacca*), 1092, 952, 833, 815, 740, and 446 cm^{-1} [222,223,224], so it is possible to confirm the presence of this blue pigment in the sample instead of Egyptian blue as previously supposed from the SEM-EDX analysis. In the FTIR spectrum are evident the very strong bands at 2080 and 602 cm^{-1}, indicating the presence of Prussian blue, $Fe_4[Fe(CN)_6]_3$. This result is probably correlated to the high presence of iron as previously detected with EDX analysis 3. Other bands like those in 3300 (br), 2920, 2849, 1650, and 1538 cm^{-1} can be associated with organic products, but, because of the bad signal to noise ratio of the spectrum, it is not possible to attribute them to a particular substance[225,226,227].

[218] Adrover G.I., *op.cit*.

[219] Lebon M., *op.cit*.

[220] Database of pigments: https://spectra.chem.ut.ee/paint/pigments/

[221] Chukanov N.V., *op.cit*.

[222] D'Errico F., Bouillot L.D., García-Diez M., Martí A.P., Pimentel D.G., Zilhão J., *The technology of the earliest European cave paintings: El Castillo Cave, Spain*. "Journal of Archaeological Science", cit.

[223] ATR-FT-IR database spectra of materials: https://spectra.chem.ut.ee/paint/binders/

[224] Fuster-López L., Izzo F.C., Piovesan M., Yusá-Marco D.J., Sperni L., Zendri E., *Study of the chemical composition and the mechanical behaviour of 20th century commercial artists' oil paints containing manganese-based pigments,* "Microchemical Journal", cit.

[225] Macchia A., Schuberthan L.M., Ferro D., Colasanti I.A., Montorsi S., Biribicchi C., Barbaccia F.I., La Russa M.F., *Analytical Investigations of XIX–XX Century Paints: The Study of Two Vehicles from the Museum for Communications of Frankfurt*, "Molecules" 28, 2197 (2023).

[226] Bevilacqua N., *op.cit*.

[227] Beninatto R., *op.cit*.

6.1.3 Blue pigment, Sample 3

The sample 3 is composed of three larger fragments used for analysis by SEM. The figures 37a, 37b show the morphology of the three fragments.

Figure 37a and 37b. SEM micrograph of the three blue fragments relating to sample 3 of the polychrome terracotta.

The SEM-EDX investigations were carried out on different areas of the sample surface, we consider three of these. Morphologically, the image shows the surfaces are granular with light and dark spots evenly distributed over the entire sample area. Three parts of both fragments were analyzed by SEM as shown in the following images (figures 38-40).

Figure 38. SEM micrograph of the granular area relating to the sample 3 (area relating to the analysis 1 presents in the table 4).

Figure 39. SEM micrograph of the detail relating to the sample 3 (area relating to the analysis 2 presents in the table 4).

Figure 40. SEM micrograph of the detail relating to the sample 3 (area relating to analysis 3 presents in the table 4).

The semi-quantitative EDX analysis of the three areas examined detects the presence of multiple chemical elements in different percentages of weight. By way of example, the EDX spectrum obtained from the analysis is shown (figure 41).

Figure 41. EDX spectrum obtained on sample 3 of the respective SEM micrograph in the figure 40.

Table 4 therefore shows the percentages of oxides (the data obtained directly from the instrument) of the elements detected at each analysis performed on a specific area of the sample.

Table 4. Semi-quantitative EDX analyses performed on the sample 3.

The most abundant element is copper that may suggest the use of azurite, copper-based pigment, $2CuCO_3 \cdot Cu(OH)_2$, on the surface of the sample (figure 50). Another element is barium found only in analysis one, it is attributable to the use of barium sulphate, the so-called barite, $BaSO_4$, white pigment of artificial origin presents probably mixed with azurite. Indeed, given its low covering power, it has been used above all as an additive filler for other pigments or as a support for preparing lacquers. Sulfur may suggest, together with barium, the use of barite as a white pigment. Other elements such as potassium, calcium, silicon, present in all the three analyses, could be related to the material of substrate, the presence of calcite and gypsum can be probably[228].

On the other hand, it could be possible that calcium, silicon and copper indicate the use of Egyptian blue, $CaOCuO(SiO_2)_4$, and not azurite on the sample, pigment known by Egyptians, Etruscans, Greeks and Romans and was also used in the Middle Ages and the Renaissance.

Using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 42).

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[228] Bevilacqua N., *op.cit.*

Figure 42. SEM-EDX analysis of sample 3. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of O; e) SEM-EDX map in false colors of Cu; f) SEM-EDX map in false colors of C; g) SEM-EDX map in false colors of Pb; h) SEM-EDX map in false colors of S; i) SEM-EDX map in false colors of Si; l) SEM-EDX map in false colors of Ca; m) SEM-EDX map in false colors of K; n) SEM-EDX map in false colors of Ba; o) SEM-EDX map in false colors of Mg; p) SEM-EDX map in false colors of Al; q) SEM-EDX map in false colors of Fe; r) SEM-EDX map in false colors of Cl.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 43) which highlighted the presence of several components.

Figure 43. ATR-FTIR spectrum of sample 3.

This analysis brought to light several compounds, in particular the presence of azurite, $2CuCO_3Cu(OH)_2$, and barite $BaSO_4$. Characteristic bands of azurite are visible at 3425, 1492, 1463, 1412, 952, 833, 815, 769, 740, 490 and 446 cm^{-1} [229], so it is possible to confirm the presence of this specific pigment and not of the Egyptian blue, as it was previously supposed by the observation of the SEM-EDX analyses. The presence of barite could be hypothesized because of the bands at 1185, 1080, 635, and 603 cm^{-1} [230]. Other bands like those at 2922, 2850, 1642 and 1394 cm^{-1} can be associated with organic binders [231,232,233,234,235,236].

Finally, the presence of the strong band at 1637 cm^{-1} and the peak at 1318 cm^{-1} is typical of calcium oxalate.

It was not possible to recognize the blue pigment by Raman spectroscopy because of the high fluorescence signal.

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[229] Database of pigments: https://spectra.chem.ut.ee/paint/pigments/
[230] Chukanov N.V., *op.cit.*
[231] Rinaldi S., *op.cit.*
[232] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, cit.
[233] ATR-FT-IR database spectra of materials: https://spectra.chem.ut.ee/paint/binders/
[234] Fuster-López L., *op.cit.*
[235] Stuart B.H., op.cit.
[236] Learner T.J.S., Analysis of Modern Paints, Getty Conservation Institute, Los Angeles, CA, USA, 2004.

6.1.4 Light ocher pigment, Sample 4

The sample 4 is composed of dust of grainy material, as there was not enough sample, it was not possible to carry out an accurate analysis with the SEM-EDX for this reason, only the ATR-FTIR and Raman analysis were carried out for the characterization of the pigment in question. According to the observation with the naked eye it is possible to state that the pigment used in the area where the material was sampled is most likely ocher.

The analysis was performed on the sample using ATR-FTIR (figure 44) which highlighted the presence of several components.

Figure 44. ATR-FTIR spectrum of sample 4.

According to the ATR-FTIR spectrum it is possible to indicate the presence of lead white and of an organic binder. Characteristic bands of lead white, $2PbCO_3 \cdot Pb(OH)_2$, are visible at 1393 and 672 cm^{-1} [237]. The use of a proteinaceous binder could be hypnotized because of the bands at 3340, 2920, 2849, 1651, and 1537 cm^{-1} [238]. The bands at about 3520, 3400, 1460, 667, and 595 cm^{-1} should be ascribed to gypsum, whereas the ones at 1030, 525, and 470 cm^{-1} are probably due to the presence of a silicate containing iron oxide.

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[237] Database of pigments: https://spectra.chem.ut.ee/paint/pigments/
[238] ATR-FT-IR database spectra of materials: https://spectra.chem.ut.ee/paint/binders/

No Raman spectrum was obtained on this sample because of the high fluorescence signal[239,240].

6.1.5 Dark ocher pigment, Sample 5

The sample 5 is composed of several fragments that are of ocher color and used for analysis by SEM. The figures 45 and 46 show the morphology of the two fragments.

The SEM-EDX investigations were carried out on different areas of the sample surface, we consider three of these.

Figure 45. SEM micrographs of the first ocher fragment of the sample 5.

Figure 46. SEM micrographs of the second ocher fragment of the sample 5.

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[239] García-Bucio M.A., *op.cit.*

[240] Franquelo M.L. Duran A., Herrera L.K., Jimenez de Haro M.C., Perez-Rodrigez J.L., *Comaprison between micro-Raman and micro-FTIR spectroscopy techniques for the characterization of pigments from Southern Spain Cultural Heritage,* "Journal of Molecular Structure", 924-926 (2009), pp. 404-412;
Catillejo M., Martìn M., Silva D., Stratoudaki T., Anglos D., Burgio L., Clark R.J.K., *Analysis of pigments in polychromes by use of laser induced breakdown spectroscopy and Raman microscopy*, "Science Direct", Volumes 550–551, (2000), pp. 191-198.

From the morphological analysis the sample surface is quite homogeneous with evident lighter spots well distributed over the whole sample under analysis. Three parts of both fragments were analyzed by SEM as shown in the following images (figures 47-49).

Figure 47. SEM micrograph of the light area detail relating to the first fragment of the sample 5, visible in figure 45 (area relating to the analysis 1 in the table 5).

Figure 48. SEM micrograph of the dark area detail relating to the first fragment of the sample 5, visible in figure 45 (area relating to the analysis 2 in the table 5).

Figure 49. SEM micrograph of the light area detail relating to the second fragment of the sample 5, visible in figure 46 (area relating to the analysis 3 in the table 5).

The semi-quantitative EDX analysis of the three areas examined detects the presence of multiple chemical elements in different percentages of weight. By way of example, the EDX spectrum obtained from the analysis is shown (figure 50).

Figure 50. EDX spectrum obtained on sample 5 of the respective SEM micrograph in the figure 49.

Table 5 therefore shows the percentages of oxides (the data obtained directly from the instrument) of the elements detected at each analysis performed on a specific area of the sample.

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Table 5. Semi-quantitative EDX analyses performed on the sample 5.

The most abundant element is lead which is probably attributable to the pigment on the pictorial layer indeed, it is visible in all three analyses (table 5). Calcium is attributable to the underlying substrate and also this element is present in all three analyses. Sulfur is always associated with the presence of gypsum commonly used as a preparation for the artefact before applying the paint film. Moreover, silicon could be associated either to the substrate or more possibly to the ochre pigment of the pictorial layer.

On the other hand, iron can be considered as an integral part of the pigment, probably given by the presence of ocher, which would prove the color of the sample. The last elements that emerged in the analysis are potassium and aluminum probably regarding the sample substrate.

Using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 51).

Figure 51. SEM-EDX analysis of sample 5. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of C; e) SEM-EDX map in false colors of Si; f) SEM-EDX map in false colors of O; g) SEM-EDX map in false colors of Pb; h) SEM-EDX map in false colors of Al; i) SEM-EDX map in false colors of Ca; l) SEM-EDX map in false colors of S; m) SEM-EDX map in false colors of K; n) SEM-EDX map in false colors of Fe; o) SEM-EDX map in false colors of Mg; p) SEM-EDX map in false colors of Na; q) SEM-EDX map in false colors of Ba; r) SEM-EDX map in false colors of Cu.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 52) which highlighted the presence of several components.

Figure 52. ATR-FTIR spectrum of sample 5.

The main components of sample 5 were basically the same of sample 4.

This analysis brought to light several components, in particular lead white, basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, gypsum, $CaSO_4 \cdot 2H_2O$, proteinaceous substances, calcium oxalate and silicates[241,242,243,244,245].

Besides, the bands at about 1088, 1032, 913, 798, 779, 530, and 470 cm^{-1} should be ascribed to the presence of silicate containing iron oxide. The whole spectrum is relating to goethite, i.e., an iron oxyhydroxide, mixed with quartz and other silicates[246]. Thanks to the elemental analysis which indicates iron as the only possible chromophore, and because of the just mentioned bands of yellow iron oxide, the pigment was recognized as yellow/brown ocher[247].

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[241] Gonzalez V., Hageraats S., Wallez G. Eveno M., Ravaus E., Réfrégieres M., Thoury M., Menu M. & Gourier D., *Microchemical analysis of Leonardo da Vinci's lead white paints reveals knowledge and control over pigment scattering properties*, "Scientific Reports" 10, 21715 (2020).

[242] Zhao Y., Berns R.S., Taplin L.A., Coddington J., *An investigation of multispectral imaging for the mapping of pigments in paintings,* Computer Image Analysis in the Study of Art, "Spie digital library", 6810 (2008).

[243] Spring M., Ricci C., Peggie D.A. & Kazarian S.G., *ATR-FTIR imaging for the analysis of organic materials in paint cross sections: case studies on paint samples from the National Gallery, London*, "Analytical and Bioanalytical Chemistry" 392 (2008), pp.37-45

[244] https://spectra.chem.ut.ee/oil_color/lead-white-linseed-oil/

[245] Cosentino A., *Identification of pigments by multispectral imaging; a flowchart method,* "Cosentino Heritage Science" 2 (2014).

[246] Guglielmi V., Lombardi C.A., Fiocco G., Comite V., Bergomi A., Borelli M., Azzarone M., Malagoni M., Colella M., & Fermo P., *Multi-Analytical Investigation on a Renaissance Polychrome Earthenware Attributed to Giovanni Antonio Amadeo*, "Applied Sciences", 13, 394, (2023).

[247] Ibidem.

The presence of gypsum could also be suggested by the features at 3525, 3400, 1460, 667, and 598 cm^{-1}, and traces of calcite, whose characteristic bands stand at 874 and 713 cm^{-1}. Probably they were used as a preparatory basis for painting as was the case in many paintings of that time[248,249,250,251,252,253,254].

No Raman spectrum was obtained on this sample because of the high fluorescence signal[255,].

[248] Spring M., Ricci C., Peggie D.A. & Kazarian S.G., *op.cit.*

[249] Chukanov N.V., *op.cit.*

[250] Matteini M., Moles A., *Scienza e Restauro. Metodi di indagine*, cit.

[251] Stuart B.H., *op.cit.*

[252] Learner T.J.S., op.cit.

[253] García-Bucio M.A., *op.cit.*

[254] Franquelo M.L., *op.cit.*

[255] Recommended reading: Marucci G., Beeby A., Parker A.W., & Nicholson C.E., *Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts*, "Analytical Methods", 10 (2018).

6.1.6 Gold-colored pigment, Sample 6

The sample 6 is composed of two larger fragments, both used for analysis by SEM-EDX. The figures 53 and 54 show the morphology of the two fragments.

Figure 53. SEM micrograph of first fragment from the sample 6, gold-colored pigment of polychrome terracotta.

Figure 54. SEM micrograph of second fragment from the sample 6, gold-colored pigment of polychrome terracotta.

A first morphological analysis carried out by electron microscopy suggests the use of gold leaf. The SEM investigations were carried out on three different areas of the sample surface, as shown in the following images (figure 55-57).

Figures 55. SEM micrograph surface detail relating to the first fragment of the sample 6, visible in figure 53 (area relating to the analysis 2 presents in the table 6).

Figures 56. SEM micrograph of a ruined part of the surface. The detail relates to the first fragment of the sample 6, visible in figure 53.

Figures 57. SEM micrograph surface detail relating to the second fragment of the sample 6, visible in figure 54 (area relating to the analysis 1 presents in the following table 6).

The semi-quantitative EDX analysis of the two areas examined detects the presence of multiple chemical elements in different percentages of weight. By way of example, the EDX spectrum obtained from the analysis is shown (figure 58).

Figure 58. EDX spectrum obtained on sample 6 of the respective SEM micrograph in the figure 55.

Table 6 therefore shows the percentages of oxides (the data obtained directly from the instrument) of the elements detected at each analysis performed on a specific area of the sample.

Table 6. Semi-quantitative EDX analyses performed on the sample 6.

The most abundant element is gold which is attributable to the golden surface of the pictorial layer. In fact, this noble metal is usually used in the artistic field in very thin leaf or in powder form, to create backgrounds and details (gilding and decorations). It has a high covering power and it is unalterable. Powder is used in fresco, tempera, encaustic, and oil; leaf is used in gilding on various supports. Moreover, gold is very stable to light and humidity.

The morphological analysis carried out by electron microscopy suggests the use of gold leaf in this case. Lead may indicate the presence of lead white, *biacca*, in the area of the bottom from which the sample under examination was taken. Other elements are calcium that could refer to the sample substrate as well as silicon, iron, and aluminum.

Using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 59).

Figure 59. SEM-EDX analysis of sample 6. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of Au; e) SEM-EDX map in false colors of C; f) SEM-EDX map in false colors of Pb; g) SEM-EDX map in false colors of O; h) SEM-EDX map in false colors of Si; i) SEM-EDX map in false colors of Ca; l) SEM-EDX map in false colors of S; m) SEM-EDX map in false colors of Al; n) SEM-EDX map in false colors of P; o) SEM-EDX map in false colors of Na; p) SEM-EDX map in false colors of K; q) SEM-EDX map in false colors of Fe; r) SEM-EDX map in false colors of Cl; s) SEM-EDX map in false colors of Mg; t) SEM-EDX map in false colors of Ba; u) SEM-EDX in false colors of Cu.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 60), which highlighted the presence of several components.

Figure 60. ATR-FTIR spectrum of sample 6.

The ATR-FTIR spectrum is very similar to the one of sample 5: in fact, besides *biacca*, just gypsum, silicates and organic components are visible[256,257,258,259,260].

The presence of calcite is hypothesized as it emerges from the SEM-EDX analyses but also in this case no characteristic bands are found in the ATR-FTIR spectrum that can confirm it. Furthermore, in the elemental analysis the presence of gold emerges, visible also to the naked eye on the sample, but from this spectrum it is not possible to confirm it.

No Raman spectrum was obtained on this sample because of the high fluorescence signal[261,262,263].

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[256] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit.

[257] Campanella L., *op.cit.*

[258] Bevilacqua N., *op.cit.*

[259] Derrick M.R., *op.cit.*

[260] Learner T.J.S., op.cit.

[261] Clark R.J.H, *op.cit.*

[262] Vandenabeele P., *Raman Spectroscopy in art and archaeology*, "Journal of Raman Spectroscopy", 35 (2004) pp. 607 – 609.

[263] Edwards H.G.M., Farwell D.W., Rozenberg S., *Raman spectroscopic study of red pigment and fresco fragments from King Herod's Palace at Jericho*, "Journal of Raman Spectroscopy" 30 (1999), pp. 361-366.

6.1.7 Red Pigment, Sample 7

The sample 7 is composed of two larger fragments, both used for analysis by SEM. The figures 61 and 62 show the morphology of the two fragments.

The SEM-EDX investigations were carried out on different areas of the sample surface, we consider three of these.

Figure 61. SEM micrograph of the first fragment of sample 7 of reddish hue.

Figure 62. SEM micrograph of the second fragment of sample 7 of reddish hue.

According to a first morphological analysis it is possible to say that in both cases the image shows the surface of the sample divided into two macro areas, one visibly light and the other darker with more intense, well-distributed spots. It is possible to see in figure 63 and 64 below, a detail of the apparently brightest areas of the sample surface.

Figure 63. SEM micrograph relating to the clear detail of the sample surface 7.

Figure 64. SEM micrograph relating to light grain detail of the sample surface 7.

Three parts of both fragments were analyzed by SEM keeping as shown in the following images (figures 65-67).

Figure 65. SEM micrograph relating detail of the first fragment sample surface 7 (area relating to the analysis 1 presents in the following table 7).

Figure 66. SEM micrograph relating detail of the first fragment sample surface 7 (area relating to the analysis 2 presents in the table 7).

Figure 67. SEM micrograph relating detail of
the first fragment sample surface 7 (area relating
to the analysis 3 presents in the table 7).

The semi-quantitative EDX analysis of the three areas examined detects the presence of
multiple chemical elements in different percentages of weight. By way of example, the EDX
spectrum obtained from the analysis is shown (figure 68).

Figure 68. EDX spectrum obtained on sample 7 of the respective SEM micrograph in the figure 65.

Table 7 therefore shows the percentages of oxides (the data obtained directly from the
instrument) of the elements detected at each analysis performed on a specific area of the
sample.

Table 7. Semi-quantitative EDX analyses performed on the sample 7.

The most abundant element is lead which is probably attributable to the lead white pigment, $2PbCO_3 \cdot Pb(OH)_2$, on the pictorial layer. Moreover, there are calcium probably is referred to the sample substrate as well as silicon, aluminum, iron, potassium.

Using the SEM-EDX Hitachi TM-4000 instrument it was possible to map the elements present in the sample and consequently understand where they are distributed (figure 69).

Figure 69. SEM-EDX analysis of sample 7. a) BSE image; b) SEM-EDX map in false colors obtained from the analysis of the sample surface; c) EDX spectrum obtained from the analysis of the sample surface and relative table with the percentage weight of the detected elements; d) SEM-EDX map in false colors of C; e) SEM-EDX map in false colors of Si; f) SEM-EDX map in false colors of O; g) SEM-EDX map in false colors of Pb; h) SEM-EDX map in false colors of S; i) SEM-EDX map in false colors of Al; l) SEM-EDX map in false colors of Ca; m) SEM-EDX map in false colors of Hg; n) SEM-EDX map in false colors of K; o) SEM-EDX map in false colors of Fe; p) SEM-EDX map in false colors of Mg; q) SEM-EDX map in false colors of Na; r) SEM-EDX map in false colors of P; s) SEM-EDX map in false colors of Cl; t) SEM-EDX map in false colors of Ba.

Other elements that emerged from the analysis are sulfur which can refer to cinnabar, HgS, used as a red pigment, in fact Hg is present as an element (figure 69). This pigment would explain the deep red color of the analyzed sample.

Subsequently, the analysis was performed on the sample using ATR-FTIR (figure 70) which highlighted the presence of several components.

Figure 70. ATR-FTIR spectrum of sample 7.

Characterization by elemental analysis revealed in particular the presence of lead white in addition to the presence of organic products as possible binders. In this case the red pigment could be given by cinnabar, widely used among the artists of the Renaissance period, as the chemical elements from which it is composed emerged from the SEM-EDX analyses. Unfortunately, however, this cannot be stated with certainty as there are no indicative characteristic bands from the IR analyses. Furthermore, the presence of calcite is hypothesized as it emerges from the SEM-EDX analyses but also in this case there is no finding of characteristic bands in the IR spectrum that can confirm it.

Lead white can be associated to the preparatory basis of the painting layer[264,265,266]. This pigment is evident according to the bands around 1400 and 678 cm^{-1} [267]. Other characteristic bands including 2919, 1462, and 1392 cm^{-1} they may indicate the presence of organic material, probably waxes, on the sample, while characteristic absorption bands around 1650,1633, 1614, 1556, 1537, and 1519 cm^{-1}, associated with organic materials, can make us think of proteins and therefore of binders used in painting[268,269,270].

It was not possible to recognize the red pigment by Raman spectroscopy because of the high fluorescence signal.

[264] Bevilacqua N., *op.cit.*

[265] Stuart B.H., op.cit.

[266] Cosentino A., *op.cit.*

[267] Database of pigments: https://spectra.chem.ut.ee/paint/pigments/

268 Derrick M.R., *op.cit.*

[269] Stuart B.H., op.cit.

[270] Learner T.J.S, *op.cit.*

6.2 Comparison of the results obtained

The final interpretations made following the comparison of the information obtained from all the techniques used are summarized below.

Table 8. Pigments analysis sheet.

Sample	Color	SEM-EDX (elements)	ATR-FTIR (bands, cm^1)	Raman (bands, cm^{-1})	Pigment
1	White	O, Si, Ca, Pb, Cl, Fe, K, Al, P, Na, Mg, S	3300 (br), 2920, 2849, 1651, 1538, 1400, 1042, 778, 678, 602, 461	1080, 1050	Lead white, Gypsum, Calcite
2	Blue	O, Si, S, K, Ca, Fe, Pb, Co, Ni, Cu, Mg, Na, Al	3420, 3300 (br), 2920, 2849, 2080,1650, 1538, 1400, 1092, 952, 833, 815, 740, 680, 668, 602, 600, 446	Not detectable	Azurite, Prussian Blue, *Smaltino*, Gypsum, Lead white
3	Blue	O, S, K, Ca, Cu, Ba, Pb, Fe, Al, Mg, Si, Cl	3425, 2922, 2850, 1642, 1637, 1492, 1463, 1412, 1394, 1318, 1185, 1080, 952, 833, 815 769, 740, 635, 603, 490, 446	Not detectable	Azurite, Barite
4	Light Ocher	The analysis could not be performed	3520, 3400, 3340, 2920, 2849, 1651, 1537, 1460, 1393, 1030, 672, 667, 595, 525, 470	Not detectable	Silicates, Lead white, Gypsum
5	Dark Ocher	O, Pb, Al, Si, S, Ca, Fe, K, Ba	3525, 3400, 1460, 1088, 1032, 913, 874, 798, 779, 713, 667, 598, 530, 470	Not detectable	Silicates, Lead white, Gypsum
6	Gold	O, Ca, Au, Pb, Fe, K, Cu, Ba, Cl, Al, Si, Na, S	3525, 3400, 1460, 1088, 1032, 913, 874, 798, 779, 713, 667, 598, 530, 470	Not detectable	Gilding, Lead white, Calcite?, Gypsum
7	Red	O, Mg, Al, Si, S, K, Ca, Fe, Pb, Na, Hg, Ba, P	2919, 1650, 1633, 1614, 1556, 1537, 1519, 1462, 1400, 1392, 678	Not detectable	Cinnabar, Lead white, Calcite

Thanks to the data obtained, it was possible to characterize the pigments present on the polychrome bas-relief and to find that most of these are contemporary with the work of art analyzed, except for Prussian blue and barium sulphate (table 9).

As regards the latter, it is a pigment of artificial origin used above all as an additive filler for other pigments or as a support for preparing lacquers[271].

Table 9. Pigments data sheet.

Pigment	Composition	Origin	Use
Calcite	Calcium carbonate: $CaCO_3$	Natural mineral	Since prehistoric times and subsequently, calcite has used in various periods, from the Roman one to the whole Middle Ages up to the present day.
Gypsum	Calcium sulphate hydrate: $CaSO_4 \cdot nH_2O$	Natural mineral	From antiquity to the present day, gypsum has used as inert.
Lead white, *biacca*	Basic lead carbonate: $2Pb(CO_3) \cdot Pb(OH)_2$	Inorganic, mineral and artificial	Since ancient times to the 19th century, lead white has mainly used for oil paintings and was incompatible with frescoes.
Solid white, barite	Barium Sulphate: $BaSO_4$	Artificial	Since the mid-19th century, barite has widely used as an additive filler for other pigments and as a support for the preparation of lacquers.
Azurite	Basic copper carbonate: $2CuCO_3 \cdot Cu(OH)_2$	Natural mineral	Since the time of the Egyptians and many ancient civilizations, azurite has used until the 17th century.
Prussian Blue	Ferric hexacyanoferrate: $Fe_4[Fe(CN)_6]_3$	Inorganic, artificial	Prussian blue began to be produced in Germany by Diesbach in 1704 and used throughout the 18th century. It is usually obtained from the hot reaction between a ferric salt and potassium hexacyanoferrate in an acid solution.
Smaltino	Cobalt (II) oxide aluminum oxide or cobalt (II) aluminate, $CoAl_2O_4$	Inorganic, artificial	*Smaltino* was already known to the Egyptians, but as glass and not as a pigment. It is an inorganic pigment, a double silicate of potassium and cobalt with metal oxides. Since the Renaissance *smaltino* has used as a pigment in painting.
Cinnabar	Mercury sulphide: HgS	Inorganic, mineral	Cinnabar was obtained in the cinnabar mines near Belgrade as early as the third millennium BC; it is usually found in frescoes and decorations in Perisa and in numerous Roman sites.
Gilding	Gold: Au	Noble metal	Since ancient time gold has had an important role in tempera, frescoes and manuscripts before the advent of oil painting.

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[271] Matteini M., Moles A., *La Chimica nel Restauro. I materiali dell'Arte Pittorica*, cit.

6.3 Characterization of the repainting

The repainting of the work come from a previous conservative restoration carried out in modern times; the restorers believe it is after 1850.

In the digital microscope observation some main paints have been identified. One is more external, and therefore more recent, very thin and easily removable present on all surfaces. The solubilization tests have probably indicated a complex mixture composed of natural glue, applied in the second half of the twentieth century and which has progressively absorbed particles, smog and unburned hydrocarbons.

The observation of the first cleaning tests and the first progress of the diagnostic campaign suggested that the glue was also applied as a pre-consolidator of the pictorial film before the application of the oily release agent for the poured gelatin[272]. The drafting of the polychromies could have involved the pre-consolidation of the color with the traditional drafting of rabbit glue, a widespread practice in the conservation of works painted on canvas and wood.

During the preliminary stages of the conservative intervention, several tests with reagents were also performed on a micro-sample of the old darkened and aged protective, verifying the certain presence of an animal protein, thus confirming the hypothesis of glue.

When the cleaning was almost complete, a series of observations with a polarized light microscope of the pictorial surface were carried out. In particular, the sequence of pictorial layers of the veil of Santa Caterina. At this point, subsequent Raman measurements, in situ analysis, confirmed the hypothesis made in the preliminary observation phase of a color spread in two layers of lead white.

Following the general cleaning, a series of solvent-gel tests were carried out to best remove the glue residues (old protective or consolidating) that had penetrated into the roughest and most porous areas. The solvent-gel mixture has created a reaction which gives rise to the formation of the compound with thickener and emulsifier characteristics, the latter due to the surfactant properties. With the addition of the organic solvent and water, a viscous gel is formed with a density similar to that of jam. The compound obtained therefore has the fundamental characteristics, given its viscosity, of a "gel", thus effectively repressing the ability of the solvent to penetrate the subsoil.

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[272] Marchioron S., Colella M., *op.cit.* pp. 6-7.

Furthermore, the combined action of the solvent power with the detergent capacity allows for effective, gradual, and controlled cleaning.

Studies and analyzes conducted by the team of researchers and restorers coordinated by Wolbers and the Getty Conservation Institute (GCI) in California, show that: solvent gels residues are inert and degrade without creating interference.

During the first cleaning tests carried out by the restorers, the oil immediately demonstrated good sensitivity to tests with non-ionic surfactants. In particular, the tests with Tween 20 (2% volume / volume) or Brige L23 (2% weight / volume) solutions ensured excellent detergent / emulsifying power and good water solubility. For an even more effective and localized action, the solutions, once prepared, were applied thickened with methylcellulose, forming gels.

In the subsequent observation, after reducing the drying oil, in the terracotta the presence of a second, more tenacious surface paint, applied only on the back, deeply darkened and browned, was evident. On the painted and gilded areas, the paint appears thicker and more tenacious and with a rubbery and still elastic consistency[273]. To tackle the scientific laboratory diagnostics phase, a digital microscope observation campaign and solubilization tests were carried out on the restoration paints (figure 71). Subsequently, non-destructive measurements were performed along the surface with a digital colorimeter, FTIR, XRF and Raman. In the restoration paint removal tests, samples of the paints alone were collected by applying cotton swabs soaked in demineralized water and cotton swabs soaked in non-ionic surfactant (Tween 20) at 5% in demineralized water. In the hypothesis a brown pre-consolidating agent was applied, therefore with a hydrophilic character (such as oily fat), 3% Tween 20 was excluded due to a slight tendency to yellowing and a tendency to form peroxides. Therefore, tests with non-ionic surfactants such as Brige L23 have been proposed.

Figure 71. Solubilization test of the restoration varnish based on rabbit glue and drying oils.

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[273] Ivi, p. 8.

6.4 Application technique of gold leaf

The microscopic investigation seems to indicate the presence of a plaster preparation bound to animal glue with an Armenian bole under the child's hair and in the locks of the Madonna's hair. A further non-destructive diagnostic examination with micro-Raman spectroscopy was performed along these areas. The restorers assumed that the artist used the traditional gouache gilding method in shaping the terracotta for these areas only.

The observation of the removal pads of the ocher repainting of the bottom did not indicate the presence of a plaster preparation. It is therefore assumed that the background was made by applying the lamina with an oily medium, and subsequently a mission gilding[274].

Figure 72. Child hair cleaning gusset. The piece highlights an underlying gold foil applied in gouache. It is therefore assumed that the artist used the traditional method of gouache gilding for these areas.

According to the restorers, there could also be the hypothesis of the use of the mission gilding technique, because it was assumed that the artist applied the gold foil more quickly for the background using this gilding. Indeed, mission gilding is a much simpler technique to perform than gouache gilding but less common on terracotta. In fact, mission gilding makes it possible to apply gold leaf on many surfaces as long as they are not particularly porous.

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[274] The "mission" or "mordant" gilding technique appears to have already been described by Cennino Cennini and widely used in painting between the 14th and 15th centuries.
Compared to the more well-known and appreciated gouache gilding, the technique involves the use of a "mordant", that is, a rather dense oleo-resinous adhesive instead of the Armenian bolus.
The mordant is applied with a brush on the areas where the gold must be adhered, the leaf is placed on these and lightly pressed after the adhesive has started to be sticky. The excess gold leaf is then easily removed by dusting the surface.

Traditionally in Lombard Renaissance modeling it was used on stucco, wood, metal, and stone, less commonly on terracotta[275]. In the mission technique, it is not necessary to prepare the base with Bologna plaster[276] and not even to apply a bolus.

The microscope observation of the surface of the terracotta, in the areas where the gold foil has fallen from the bottom, does not seem to have identified traces of varnish for gilding (varnish mission) or, more generally, the darkening due to the application of any oily medium (oil mission).

It is assumed, pending further verification with portable FTIR instrumentation, that the gilding of the bottom was performed by applying the gold leaf with a simple water mission. Reason that could justify the general poor conservation conditions compared to the areas treated with the more tenacious gouache gilding. Probably the artist chose this technique because it is suitable for easy application on a smooth and flat surface such as this background, also exploiting the characteristics of lower light reflection of the pure gold foil applied with water mission, compared to the much brighter and warmer gilding with oily varnish.

The mission gilding with oily paint gives a greater brilliance to the work of art and greater resistance over time, for example always in the Lombardy area, this technique appears in the gilding of the marble sculpture also intended for the open environment, already from the 14th century to the whole of the 16th century[277].

The ground in gold foil of the terracotta appears enriched with a freehand punching decoration using a small punch with a circular tip. In fact, a singular geometric decoration is evident, made with many small holes of 1.5 mm in diameter placed to draw a rhomboid motif.

Observation of the decorative holes showed how they were made, that is, in the wet clay and not afterwards mechanically in the dry or baked clay. From the set of applied techniques, it was therefore possible to highlight the presence of the common plaster preparation only in the area of the child's hair. The thickness of this preparation, which on terracotta works also had the purpose of masking small cooking defects, leveling them, varies from area to area depending on the type of gilding.

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[275] Ivi, p. 14.
[276] Bologna plaster is hydrated calcium sulphate. It has a unique softness to the touch, given by the fineness of the grain of which it is composed and is used in the gilding to prepare the amination, a specific base for the preparation of the surface to be decorated with gold leaf. It is also useful in the preparation of stucco to be used on various occasions and generally in the creation of high-quality decorations.
[277] Ivi, p. 15.

Figure 73. Digital microscope image 100x observation of the pure gold foil decoration of the background in the terracotta bas-relief. At the top center, the image still highlights the presence of the amber and browned restoration paint (probably a diluted animal glue) that covered the entire work. As evident in the image, the gold foil appears applied directly to the terracotta without a chalky preparation. It is assumed that the gilding of the background was performed by applying the pure gold leaf with a simple water mission.

The observation of the Child's hair shows that the gold leaf is applied on a layer of red bole spread on a thin plaster preparation (about 1 mm).

6.5 Conservation state of color

The polychromies of the relief is generally well preserved and intact for at least 95% of the surface. The removal of dirt and old protective materials (restoration glue) highlighted some lack of preparation and color, even if in a minimal way compared to other contemporary specimens always coming from the Certosa di Pavia[278]. This is an indication that the work has probably always enjoyed fair conditions of conservation in a protected environment and not directly exposed to atmospheric agents.

Figure 74. The Virgin's mantle seems to have been made with two overlapping coats of blue pigment, a first (1) with a less brilliant and lighter appearance and a second (2) more full-bodied and dense. Observation of these gaps with a digital microscope does not seem to indicate the presence of a white preparation as for the veil.

Figure 75. Detail of the drapery of the Madonna. The removal of dirt and old protective materials has highlighted some deficiencies in preparation and coloring integrated in an old restoration with hasty repainting, (R) performed without stucco and with glazes based on very bright and harmonious synthetic colors.

After the lowering of the oily overpainting with animal glue (old restoration), many coarse repainting appear more evident, carried out with hasty glazes made with very bright synthetic colors and shades.

The most important and evident damage is represented by a series of breaks around the halo of the Madonna. Further material deficiencies are found in the Carthusian robe at the height of the folds, while the Virgin's halo also has a large integrated break.

The polychrome surface highlights *craquelure* and there are also more important gaps, such as in the lower edge of the base, the point of greatest mechanical stress during movement. The biggest gap in the polychromy is concentrated in the pictorial drafting of the blue robe of the Madonna, towards the outer edge behind the Child.

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[278] Ivi, p. 31.

6.6 Cleaning intervention

The work presented an opaque pictorial surface, obscured by the progressive sedimentation of the dust largely penetrated into the unstable restoration paint.

The atmospheric deposits present on the work were of greater intensity in the light complexions while in the drapery of the painted and gilded garments, they covered the original color.

The cleaning carried out by the restorers who took care of the intervention, Mario Colella and Silvia Marchioron of the Small Cloister Studies and Conservation Center, allowed to gradually remove the patina that had deposited on the surface of the terracotta, bringing to light the clear incarnations of the characters and the expressions of their faces, previously completely lost and which now allow a different vision and reading of the work. This intervention thus revealed a rich and lively chromatic range: from the bright red of the Madonna's robe and the Child's pillow, to the white of the Carthusian's robe, the veil of Saint Catherine and the Child's robe. According to the museum, however, the real surprise was the discovery of the color with which the Virgin's veil is made, that is green, an unusual chromatic choice, combined with the traditional blue of the mantle. Besides, thanks to the cleaning it was also possible to admire the decoration in pure gold foil in the background, where the still legible cartouches stand out.

The first operation performed was therefore the lowering of the oil painting mixed with animal glue. Specifically, following preliminary tests to determine the choice of the most suitable products and concentrations, all surfaces were cleaned with a 2% non-ionic surfactant in deionized water, applied and rinsed with a cotton swab. At the end of the consolidant removal operations, the work had a surface pH equal to 7. To remove the ocher repainting, tests were carried out with specific soaps (anionic surfactants) for the removal of paints based on natural terpene resins such as Mastic, Dammar, Rosin, Turpentine, Copal etc., used in gelled solution at alkaline pH (pH 8-9). Specifically, the resin soaps based on ABA-TEA with moderate polarity Resin Soap 1295 and Resin Soap 1194 by Bresciani s.r.l. were used[279].

The final cleaning of the paint film now underway is trying to gradually thin out the altered surface film-forming materials, in order to make the aesthetic values readable while respecting the natural aging of the constituent materials.

Moreover, from the analyses and measurements carried out on the work, the restorers discovered that the pigments used were the original ones, coming from the Lombard artistic workshops of the 16th century, and it allowed to ascertain that the work almost entirely preserves all the original polychromies.

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[279] Ivi, p. 33.

Finally, during the next inspection, the restorers will evaluate with the Superintendency how to treat the gaps in the pictorial layers: whether to leave them in their current state or to resort to a traditional plastering with Bologna plaster and rabbit glue and subsequently brought to the level of the original surface. The pictorial integration of the gaps will possibly be evaluated later.

Figure 76. Observation of the ocher repainting on the halo of Saint Catherine. a) The repainting in addition to covering the gold foil residues has filled the marks of the punches and the incision in the raw clay; b) The disassembly of the repainting with Resin soap 1295 by Bresciani s.r.l. The heavy ocher repainting of the restoration, as well as having entirely covered the gilded background, has filled all the decoration of the terracotta with a large punch (P) and small punch (S) as well as the fine lines executed with a stylus.

Figure 77. Details of artwork after the conservative intervention has been completed: a) detail of Madonna's face; b) detail of child; c) detail of Santa Caterina; d) detail of Carthusian priest.

CONCLUSIONS

As mentioned at the beginning, this thesis was born with the aim of characterizing the pigments present in each sample using the following techniques: SEM-EDX, ATR-FTIR, Raman and optical microscopy with 3X magnification. The choice of these tools was dictated by their effectiveness in the field of diagnostics of cultural heritage. From the obtained results it was possible to have useful information in order to identify the elements, in particular the chromophores and in general the compounds that make up the samples examined. By means of the analytical results it was possible to define the presence of pigments used by the artist on the polychrome terracotta surface, such as white, red, blue, ocher, and of gildings.

In particular, in the white sample lead white was recognized, in the blue samples predominantly azurite, in the light ocher sample, lead white, in the dark ocher one goethite (based on iron) with lead white. Moreover, in the gold-colored sample gold leaf was found, while in the red sample cinnabar mixed with lead white were identified.

In addition, the use of organic binders to apply the pigments on the artifact was highlighted. The study carried out on the artwork also allowed us to deduce that the pictorial palette used by the artist on this work was consistent with the data provided by the literature. The only investigation that did not bring useful results was that using Raman technique, which unfortunately provided an unsatisfactory spectrum for the identification of the pigments due to the high fluorescence emitted by the sample during the investigation. This problem occurred for most of the tested samples.

Some of the hypotheses discussed in this thesis work could be further expanded and possibly validated with subsequent studies. As regards the binders that emerged from the analyzed samples, it is possible to deepen their nature through further investigations with specific analytical techniques such as gas chromatography coupled with mass spectrometry (GC-MS) or high-performance liquid chromatography (HPLC). In this way it will also be possible to understand the nature of the organic compounds present in the sample.

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