The colour of architecture. Physical-chemical analysis of polychromy on stone in a 16th century gothic Portal at the Cathedral of Santo Domingo

To cite this article: Esteban Prieto Vicioso et al 2020 IOP Conf. Ser.: Mater. Sci. Eng. 949 012092

View the article online for updates and enhancements.
The colour of architecture. Physical-chemical analysis of polychromy on stone in a 16th century gothic Portal at the Cathedral of Santo Domingo

Esteban Prieto Vicioso¹, Virginia Flores Sasso²*, Letzai Ruiz Valero², José M. García de Miguel³

¹Universidad Nacional Pedro Henríquez Ureña, Dominican Republic. eprieto@unphu.edu.do
²Pontificia Universidad Católica Madre y Maestra, santo Domingo, Dominican Republic. virginiaflores@pucmm.edu.do, letzairuiz@pucmm.edu.do.
³Universidad Politécnica de Madrid, Spain. jomagar@iies.es

Abstract. Colour always played a role in the human evolutionary process and has been used as a way of expression. But the time, the lack of maintenance and abandonment, the lack of studies related to the presence of polychromy in architecture and the nineteenth-century idea of eliminating building plasters to expose stone and brick have caused many to ignore and forgotten the presence of colour in historical buildings. In most cases disappear leaving only traces of colours. For this reason the aim of this research is study the polychromy on stone of a 16th century gothic Portal in the Cathedral of Santo Domingo. Analyses were performed using non-destructive techniques as Transmission Polarized Light Microscopy (PLM), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy / Energy Dispersive Elemental Analysis X-Ray (SEM/EDX), Gas Chromatography (GC) and X-Ray Diffraction (XRD). To determinate the colour was used a CIELAB System and Munsell Colour System. In conclusion patinas yellow, ochre, red, green and blue colours; and pigmented successive layers of plaster and lime was found. Remains of these layers of polychromies are also spread throughout many areas of the Cathedral.

1. Introduction

The scientific approach began in the 70's with the technology advanced. In Spain one of the pioneers is the chemist José María Cabrera Garrido, who analysed the pictographs of the Altamira Caves in Spain, to find out the nature of the diseases they suffer. The study was published [1] and discovered the components of the dyes used in the paintings of the caves and the support they placed to paint. The samples were made with an optical microscope, subjected to semiquantitative analysis of emission spectrography, X-ray diffraction (XRD), in powder diagrams and by means of oriented aggregate techniques, with ethylene glycol and thermal treatment for clay minerals [2].

A Paleolithic art was study in the decade of the 80s [3], especially the paintings of the caves of Lascaux in France and the components of the polychromy. Later, the cave of Pena Rubia was describes and studies the cave paintings. Also, the natural patina rose-brown covering the external surface on Imperial Roman Marbles was study. This Patina was called 'scialbatura' and is the product of the biochemical activity of encrusting lichens [4].

In France, [5] carried out a study on the preparation of the Magdalenian paintings of the caverns of Ariege, particularly in Niaux, finding the minerals that compose it, determining the different ways of preparing the painting in prehistoric times. In the mid-1990s, Cabrera Garrido [6] presented the paper “Estudios de recubrimientos de fachadas antiguas: la pátina de la piedra y el color de la arquitectura” (Studies of coatings of old facades: the patina of stone and the color of architecture) at the XI Congreso de Conservación y Restauración de Bienes Culturales, in Castellón, Spain.
During the XXVII Reunión de la Sociedad Española de Mineralogía in 2007, several techniques used for the analysis of polychromy in heritage were presented, as optical polarization microscopy, fluorescence microscopy, Scanning Electronic Microscope (SEM), analytical techniques (EDS, electronic microprobe, DRX, FTIR, LIBS, EDFRX, etc.), as well as the characterization of some of its petrophysical properties (water vapour permeability, degree of water repellence, etc.).

The Spanish geologists Maria Carmen Vázquez Calvo and Monica Alvarez de Buergo [7] focuses on studying the patinas, considering the location in façades, height, colours, continuity, etc, as well as the analytical techniques to use for their characterization, mainly microscopic and microanalysis techniques. The mineralogical composition of patinas has been referred by many authors like Kouzeli et al. [8]; Previde Massara & Perego [9]; Polikreti & Maniatis [10], Alessandrini [11], Alvarez 2002, 2004, 2003, 2006. Some of the minerals that may comprise are: calcium carbonates, calcium sulphates, calcium oxalates, calcium phosphates, silicates (quartz, feldspars, etc.), clay minerals and iron oxides and/or hydroxides. But this do not mean that all these minerals are present in one single patina [12].

In 2008, Jorge Rivas López [13] presented his doctoral thesis entitled “Policromías sobre piedra en el contexto de la Europa medieval aspectos históricos y tecnológicos” (Polychromes on stone in the context of medieval Europe, historical and technological aspects) in which he studies the polychrome on stone and its functions, describes the traditional techniques and the chemical composition of the patinas studied, among others. Vazquez et al. [7] used portable energy dispersive X-ray fluorescence spectrometer for the characterization of patinas from the architectural heritage of the Iberian Peninsula. Likewise. Durán et al [14] analyses the gilding techniques used in polychrome stones with micro X-ray diffraction and complementary techniques. Also, Durán et al [15] uses the same technique of X-ray diffraction to analyse polychromy of Pompeian wall paintings.

The Cathedral of Teruel, restored 2008-2009, the researchers De Miguel and Pardo [16] rescued the remains of polychrome of the eaves, allowing the complete reading of the interior-exterior roofing, and the absence of repaintings or signs of intervention was verified on the polychromies of the eaves, which gives a degree of authenticity unique to the whole. To cover the study of polychromies, a formal and stylistic comparison of the elements abroad was performed following the Morellian method and secondary details were studied. In the Cathedral Santa María de Vitoria, Cortázar et al conducted an identification study of the different pictorial stages on the surface of the stone found in the portico of Santa María simultaneously during the restoration work that was being carried out in the church. This study of identification of the different pictorial stages on its surface, is perhaps the most extensive work of these characteristics ever carried out so far. Also, a polychromatic correspondence guide and a graphic polychromic reconstruction were performed.

Pérez Rodríguez et al [17] characterized the polychromy of a wooden Gothic sculpture representing Our Lady Saint Anne, with the Virgin Mary and the Child Jesus. For this, analyzes were carried out with portable FRX, μ-DRX, μ-Raman, μ-FTIR and MEB / EDX, with which the compounds were identified: vermillion, minium, lead white, hematite, red lacquer, gold, brass and plaster, all of them compounds used in the past. It was also possible to identify more recently applied compounds, such as: Titanium oxides (titanium white: rutile, anatase), barium white, zinc white, lithopone, lazurite, and gold.

In 2014, the pigments in illuminated manuscripts was identified and mapped using the imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence [18]. In 2015 Stéphanie Castanetand and Juliette Rollier-Hanselmann1Castanet [19], collected samples of polychromes and gildings from lapidary fragments of different parts from the Romanesque Portal of the abbey-church of Cluny and analysed the pigments and gildings using SEM, EDS and micro-Raman spectrometry. The physicochemical analyses point up the use of relatively expensive materials, such as gold leaves, lapis lazuli or cinnabar. Moreover, some blackish layers were identified as altered leaves of tin. The palette and abundance of metallic leaves should reflect the prestige of the abbots of Cluny [19].

Another study with petrographic and chemical analyses, was doing in the façade of the Scuola Grande di San Marco in Venice, in the sculptural and painted decorations and in the polychrome marbles and the false perspective view between the pilasters of the lower order. In the analysis Antonelli et al. [20] characterized the micro- and macro-morphologies of decay and identify the causes.
and mechanisms of deterioration as well as the nature and application technique of the polychromy, gilding, and patinas present on parts of the monumental Renaissance façade. Likewise, the patina on Modern Bronze Sculpture [21] were studied employing a range of techniques such as colours measurements, scanning electron microscopy with energy dispersive X-ray spectroscopy, and micro-Raman spectroscopy. The collected data revealed the formation of main compounds (cuprite, cassiterite, rouaite, chalcocite, isocubanite, and ferroxyhite) and additional compounds (atacamite and CN-containing compound).

2. Polychromy in architecture

The colours on stone has been used from prehistory to the present day, in all the cultures and civilizations of the world. Colour always played a role in the human evolutionary process and has been used as a way of expression. But with the time, lack of maintenance and abandonment, was forgotten and disappearing little by little, leaving only traces of colours.

In the 18th century, the presence of colour in historic buildings was reported. Between 1751 and 1753, the architects Nicholas Revett and James Stuart explored the ruins of ancient Athens, although they do not mention polychromy, years later, in the 1780s, the antiquarian Richard Chandler reveals the presence of polychromy in buildings. In medieval art, colour was applied to its statuary and sculpted ornamentation, which has been confirmed by the numerous vestiges available. There are also data that confirm that it was customary to carry out maintenance and periodic renewal of said polychromies, especially those exposed to the elements. According to Jorge Rivas López, polychrome on stone had different meanings and functions including: protective function of the stone, didactic-religious function, iconographic and identifying function, reading management function, aesthetic function [13].

The British mineralogist Edward Daniel Clarke (1769-1822) and the archaeologist Edward Dodwell (1767-1832), note in their notebooks first-hand testimonies about the polychromies on stone that they observed on the marbles, like the statues of the Parthenon of Athens. Other English, especially Gell and Gandy, also describe the engraved and painted friezes of the Parthenon (Rivas 2008:120). The use and preference for specific colours in ancient Greek polychromy and painting are determined not only by aesthetic criteria and material availability but also by the function and destination of each artefact, within its specific social and cultural context [22].

The lack of studies related to the presence of polychromy in architecture and the nineteenth-century idea of undressing buildings to leave sight of stone and brick, have caused a void in the study of the colour in historical buildings. The unknowing and ignorance about the polychromy in architecture is one of the main reasons that is causing its disappearance. For this reason, the aims of this research is to analyse the chemical components and physical characteristics of the polychrome on stone of a Gothic Portal in the Cathedral of Santo Domingo, from the beginning of the 16th century, in Hispaniola.

New research has shown that the buildings were not finished until their walls were covered, their surfaces were brushed and their decorative elements were polychrome [23]. It is also proven that it was common to apply patina to the noble parts of stone buildings [24]. This has been possible with the technological advance and the new microscopes that allow us to observe previously unimaginable dimensions. The amount of historical, technological and constructive data we obtain in millimetres is important to better understand the material. Today, it no longer allows a restore to the overlooked building coatings.

Over time, the polychromy applied in architecture, painting and sculpture has been changing both in its composition and origin, it is even very common to find layers on layers of colour, generating a more or less complicated stratigraphy. This polychromy has gone unnoticed by many people. From the second half of the 18th century, the established idea of the immaculate whiteness of ancient sculpture began to change with the archaeological discoveries of Greek art that were being brought to light, where polychromy was observed both in architecture and in the statuary [13].

The first interpretation about the origin of a yellowish patina found on the Parthenon marble of Athens, looking similar to a varnish, was due by the German chemist Justus von Liebig in 1853, assuring that it was due to the effect of the prolonged action of lichens for centuries. The patina that he identified was orange and was called Thierschit and later called whewellite [25]. It was calcium
oxalate monohydrate Ca (C2O4) H2O. However, with technological advances it was determined that the origin of the Patina is a product of different nature applied in past times as aesthetic and/or protective treatments [26].

In modern times, the interest in studying polychrome dates from the late nineteenth century, from the work done by the physician and physicist Giovanni Morelli, who developed the Morellian method, along with the arts expert Bernard Berenson. This method differentiates genuine from false works or, what is the same, distinguishes the original paintings from the copies. The method identifies the artist and workshops by idiosyncrasies or by repeated stylistic details that appear in their works.

Between 1874 and 1876 the German magazine Zeitschrift für bildende Kunst published a series of articles by Morelli under the pseudonym Iván Lermolief, in which he presents the Morellian method, as the most effective methodology for analyzing paintings. In 1890 he wrote his seminal book Della pittura italiana, and in 1893 he published Studi di critica d'arte sulla pittura italiana. In spite of the changes that were generated and the innovation that this methodology was, everything focuses on painting and sculpture, leaving out architecture. In the second half of the 20th century, as a result of the massive restorations that took place after the Second World War and the creation of UNESCO (1945), pigment studies were carried out that provided only approximate interpretations of its composition. In 1959, F. Margival described in a general way the pigments used for the realization of prehistoric painting. Later, Pietsch [27] mentions the contribution of chemistry in the study.

3. The Gothic Portal of the Cathedral of Santo Domingo

The Basilica and Metropolitan Cathedral Our Lady Saint Mary of the Incarnation, of Santo Domingo was built between 1521 and 1540. It is the first cathedral in the new world, located in the Hispaniola Island. Was built during the reign of Emperor Charles V. Is a Gothic Cathedral with a Hallenkirche or saloon plant, with three naves and fourteen chapels between buttresses. The church is covered with ribbed vaults made of Coralina limestone. It oriented east-west, following the astronomical criteria, with the entrance to the west and the altar and polygonal Apse to the east. In the transepts have two portal, one on the south, which led to the bishop's palace and the priest’s houses, was private and therefore less decorated; and other on the north, call the Gothic portal, which is more decorated with vegetable motives and religious sculpture.

The North Portal was finished in 1527 and inside there is a stone on the door that confirms it. In 1615 the Portal was partially mutilated to build the cathedral chapter. The north transept entrance, which was primarily used by the masons, brotherhoods, canons and was the doors where parishioners accessible to church and served as part of the processional route. The Portal is framed within an ogee arch, resembling a curtain, element used in the Spanish tardogothic. The three arches that form the archivolt, are decorate with vegetables motives, pearls and a surbased oval arch framing the tympanum of a portal were are Saint Domingo, Saint Saturnino and Virgin Mary of the Incarnation. A carved limestone vases of lilies between the archivolt and the ogee arch.

During the preservation labours in 2013, paint was located on this portal which were analysed and catalogued. About five different colours of painting were collected and fragments were taken for analysis. The selected fragments are representative of different parts of the portal (vases, jambs, tympanum, and archivolts).

It is important to note that all the masons that work in the Cathedral arrive from Spain, specific from Castile, Cantabria and the Basque Country. Some stonemasons are unknown but in previous investigations was identify that many of these masons were part of the crews of important workshop such as Juan de Álava, Alonso Rodríguez or Juan Gil de Hontañón, to name a few [28].

4. Materials and Methods

The following analysis techniques were used for this investigation: Transmission Polarized Light Microscopy (PLM), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy / Energy Dispersive Elemental Analysis X-Ray (SEM/EDX), Gas Chromatography (GC), Diffraction Rays X (DRX). Also, to determinate a reference of the colour was used Munsell Color System (MCS) and Digital Colorimeter. The samples that have been taken are: ochre: CSD-2, blue: CSD-3, green: CSD-4 and red: CSD-5 (Fig.1).
4.1. *Transmission Polarized Light Microscopy (PLM)*
Technique employs the use of polarizing filters to know the optical property of the observed material. Can be utilized for quantitative and qualitative studies targeted at a wide range of anisotropic specimens. This is a basic technique that allows the study of overlapping layers of paint as well as the preliminary analysis of pigments, binders and varnishes using microchemical and selective coloration layer and oil quenching assays. The microphotographs obtained were performed with reflected light at 300 X and crossed Nicols.

4.2. *Fourier-Transform Infrared Spectroscopy (FTIR)*
Technique to know an infrared spectrum of absorption or emission of a solid, liquid or gas. This study is used mainly in the analysis of the preparations and the components of coatings or varnishes. The analyses are between 4400 cm⁻¹ and 370 cm⁻¹, in an IR-transparent material such as KBr pellets or by surface analysis using UATR (Universal Attenuated Total Reflectance).

4.3. *Scanning Electron Microscopy / Energy Dispersive Elemental Analysis X-Ray (SEM/EDX)*
Technique to know quantitative elemental composition data. Used for elemental analysis of grains of pigments, in order to unequivocally determine the nature thereof. The SEM/EDX is a ZEISS DSM 960, which operates at high vacuum, with secondary electron detectors and backscattered. The microscope has an integrated analysis system Oxford Instruments Analytical-Inca with an X-ray detector of the EDS (energy dispersive) type.

4.4. *Gas Chromatography (GC)*
Analytical chemistry for separating and analysing compounds that can be vaporized without decomposition. The gaseous phase chromatography coupled to mass spectrometry, is used for the determination of lipophilic substances, such as drying oils, resins and waxes; and of hydrophilic substances, such as proteins and gums - polysaccharide (Arabica gum and related products). To analyse lipophilic substances, samples are treated with the Meth-prep II methylation reagent. For carbohydrates and proteins a hydrolysis is carried out with microwave-assisted 6M HCl and a derivatization with BSTFA in pyridine of the resulting fatty acids, amino acids and monosaccharides.
4.5. Diffraction Rays X (DRX)
Technique to identify semi-quantitatively and qualitatively mineralogical composition of the samples, through interference produced when a monochromatic radiation passes through the sample made powder. It was performed with a Philips Analytical X´Pert Diffractometer. For the preparation, the sample was crushed to a powder, a hole was filled in a slide and pressed, subjected to radiation.

4.6. Determination the color by Munsell Colour System (MCS) and Digital Colorimeter
The Munsell Colour System is a set of colour charts with an almost uniform colour representation, make accurate colour specification and matching possible in science and art, by defining a coordinate system for all possible colour perceptions. In the Munsell System every possible colour percept can be described by three variables: hue (red, blue, green, etc.), value (lightness or darkness), and Chroma (purity, or difference from neutral grey). The Portable Digital Colorimeter model FRU WR10, measure the different of colour, used Colour space CIE L*a*b* and Light Source is D65.

5. Results and Discussion
5.1. Transmission Polarized Light Microscopy (PLM)
The sample CSD-2 has 4 layers, the first one is a white base and on it there are ochre and brown. The pigment is from natural earth and as a binder the animal glue was used (Fig.2). The CSD-3 has 2 layers, the first one is a white base and on it there are blue. The pigment is organic blue and as a binder used fatty acids and hydrocarbons (Fig.3). The CSD-4 has 3 layers, the first one is a white base and on it there are one green and other brownish. The pigment of the green colour are from copper chlorides and as a binder used fatty acids and hydrocarbons (Fig.4). The CSD-5 has 3 layers, the first one is a white base and on it there are one red and one grey-brown. The pigment is from natural earth and as a binder used fatty acids and hydrocarbons (Fig.5).
Figure 5. Transmission Polarized light microscopy of Sample CSD-5

5.2. Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR covers a wide range of chemical applications, especially for polymers and organic compounds. A few examples reflecting some of the more important functional groups. When it compare the results can appreciate the subtle differences, comparing frequency, intensity and shape. In sample SDC-2 can see de deformation product of the chemical structures. The first graph is the inner face and the second the outer. It was observed that the chemical composition are quite similar (Fig.6).

Figure 6. Fourier-transform infrared spectroscopy of Sample CSD-2, CSD-3, CSD-4 y CSD-5

5.3. Scanning Electron Microscopy / Energy Dispersive Elemental Analysis X-Ray (SEM/EDX).

The results indicated that all the samples have Calcium and some show Sulphur due to the pollution and dirt that the walls have (Table 1). Also, although in minimal quantities, it appears Aluminium (Al), Silicon (Si), Chlorine (Cl), Iron (Fe), Potassium (K), Sulphur (S), Sodium (Na).

Table 1. Results of the micro SEM

|       | Layer 1 | Layer 2 | Layer 3 | Layer 4 | Layer 1 | Layer 2 | Layer 3 | Layer 4 | Layer 1 | Layer 2 | Layer 3 | Layer 4 | Layer 1 | Layer 2 | Layer 3 | Layer 4 | Layer 1 | Layer 2 | Layer 3 | Layer 4 |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| CSD-2 | Ca (Al, Si) | Ca, S (Na, Al, Si, Cl, Fe) | Ca, S (Al, Si) | Ca, S, Si (Al, K, Fe) | Ca (Al, Si) | Ca, C, S, Ba (Al, Si) | Ca, S, Cu, Cl (Al, Si, Fe) | Ca, S (Na, Si, Cl, K) | Ca, S (Al, Si, Na, K, Cl) |
| CSD-3 | Ca (Al, Si) | Ca, S (Na, Al, Si, Cl, Fe) | Ca, S (Al, Si) | Ca, S, Si (Al, K, Fe) | Ca (Al, Si) | Ca, C, S, Ba (Al, Si) | Ca, S, Cu, Cl (Al, Si, Fe) | Ca, S (Na, Si, Cl, K) | Ca, S (Al, Si, Na, K, Cl) |
| CSD-4 | Ca (Al, Si, S) | Ca, S, Cu, Cl (Al, Si, Fe) | Ca, S (Na, Si, Cl, K) | Ca, S (Al, Si, Na, K, Cl) |
| CDS-5 | Ca, S, Si, Fe (Al, K) | Ca, S, Si, Fe (Al, K) | Ca, S, Si, Fe (Al, K) | Ca, S, Si, Fe (Al, K) |

Elements in parentheses are minority
5.4. Gas Chromatography (GC)

The fatty acid chromatogram of sample CSD-2 indicate that the peak at 22 minute corresponds to animal fat cholesterol. The amino acid and sugar chromatogram of sample CSD-2 indicates peaks at 22 min. The table of compounds of the CSD-2 sample indicates 6 elements and Chromatogram of amino acids and sugars detected more than 70 compound. In the Fatty acid chromatogram of sample CSD-3 can observed five compound. In SCD-4 sample, the amino acid and sugar chromatogram indicates that there are 65 components. In sample SCD-5 present peak at 16,5 min and 18,437 min. The fatty acid chromatogram presents 6 mayor components (Fig.7).

![Figure 7. Gas chromatography of Sample CSD-2, CSD-3, CSD-4 y CSD-5](image)

5.5. Diffraction Rays X (DRX).

Sample CSD-2. This colour is applied directly on the stone. The analysis shows soil as chromatophore, a plaster base as a support and a gum arabic as a binder, perhaps sap of the Opuntia species that abounds on the island Hispaniola. The CSD-2 sample first presents a plaster stucco, pigmented with an earth tempera that also contains animal glue. Gypsum plaster jamb left with yellowish tone. They also have a tempera as an agglutinant and a plaster base. It has been applied over a plaster stucco and its chromatophore is of yellow or ochre earth. As particularities it contains calcium phosphate. This component can come from bone ash, sometimes added to pigments to darken them. Bone black provides a black brown tone, to distinguish it from carbon black, which provided a bluish black tone.

Samples CSD-3, CSD-4, CSD-5. All of them carry a load of plaster and a hardening binder. As for the chromatophore, the blue is organic, the malachite green is copper mineral (copper carbonate) and the earth red. As particularities, the blue polychrome, arrives a load of mineral barite (barium sulphate) to lighten the tone. Barium sulphate was usually synthetic from the 18th century onwards. Since the mineral contained in the sample is mineral, it must be assumed that this pigment predates that century. As for the red polychrome, it shows traces of a synthetic treatment based on polyvinyl. It should be remembered that polyvinyl acetate has been a treatment that became fashionable in a stage of the last century in restoration by what appear to be the remains of a recent treatment.

CSD-3 (blue): This sample shows a very thin layer of blue directly applied to the stone support. The organic blue is possibly indigo. The presence of barium sulphate in the layer attracts attention. Although barium sulphate appears in nature in the form of barite, it has been used in painting since ancient times. The particle size of the pigment confirms that it is a natural pigment. As far as the
technique is concerned, it is a greasy tempera in which the protein has disappeared, transforming itself into oxalates.

CSD-4 (Green): was made with malachite, which is partially altered to chlorine copper carbonates. It is a natural pigment as it is accompanied by small inclusions of ochre soil rich in clays and iron oxides. The green pigment grains are immersed in a gypsum matrix. The binder is fatty (possibly a protein with an abundant fatty component, such as casein or albumin). Traces of palmitic and stearic fatty acids and a trace of azelaic acid are also observed.

CSD-5 (Red): The pigment is red earth, covered by a patina in which plaster, charcoal and a trace of vinyl polymer appear, a sign of protection from a recent restoration. The binder is fatty (possibly a protein with an abundant fatty component, such as casein or albumin).

All three samples present chlorides which is a consequence of their exposure to a saline environment (marine aerosols surely). These chlorides have also had to attack the malachite of the green pigment by generating chlorine copper carbonates. There is also charcoal trapped in the outermost layer which indicates pollution.

5.6. Determination the color by Munsell Color System (MCS) and Digital Colorimeter

In the Munsell system the value is indicated with a number, so for CSD-2 is 10, CSD-3 is 5, CSD-4 is 1 and CSD-5 is 5. Hue is the colour and are given letter codes, i.e. Red (R), Yellow-Red (YR), Green (G), Green-Yellow (GY) and so on. In the Munsell system, Chroma is indicated with a number, typically in the range of 2-14. Each colour is designated with what is referred to as a colour notation. By viewing colours on the charts, we can see how colours related to one another visually.

| Sample | Colour | Photo | Location | Munsell | CIELab | RGB  |
|--------|--------|-------|----------|---------|--------|------|
| CSD-2 (14) | Ochre | Jambs, decorative pearls, walls | 10YR 7/8 | L:73.23 a:10.13 b:36.93 | R:214 G:172 B:112 |
| CSD-3 (17) | Blue | Typanum | 5PB 5/8 | L:44.87 a:-16.13 b:-19.17 | R:49 G:115 B:138 |
| CSD-4 (18) | Green | Typanum and in lilies | GLEY1 3/2 | L:47.99 a:-18.36 b:-0.79 | R:77 G:123 B:112 |
| CSD-5 (19) | Red | Archibolt | 5R 5/8 | L:44.92 a:40.45 b:17.20 | R:170 G:75 B:80 |

Figure 8. Colour of sample in Munsell Colour System, CIELab and RGB

6. Conclusion

The results indicate that four colours were used in the north portal: ochre, blue, green and red. The ochre was identified in two types of applications: one directly on the stone of the walls and the other applied on a base of plaster, in this case appears in the jambs and decorative details. All the colours use the earth as a pigment and polysaccharide rubber as a binder, coming from a fruit tree rubber or the sap of Opuntia. There are also pigments that were used as a very greasy tempera binder of casein or albumin and animal glue probably blood and/or milk.

The types of pigments used were: malachite for green, organic blue for blue, earth for ochre and for red, the same earth but calcined. In singular zones, of the portals, such as the typanum or the archivolts, polychromies were also applied with techniques similar to the general monochromatic tones.
Therefore, the color ochre is a paint of earth with protein binder having been identified animal glue. It is applied on a stucco rich in plaster and calcite. The blue comes from indigo with a degraded protein binder, but with a high fat component, so it could be tempora of casein or albumin, because the egg, blood and milk have a high fat component. Green uses malachite which is a copper mineral with a degraded protein binder, but with a high fat component. The red colours has calcite and red earth with an animal tail binder.

References

[1] Cabrera Garrido, J.M. (1978) “Le matériaux des peintures de la grotte d’Altamira”, en Actes 5, Réunion Triennale de L’INCOM, Zagreb, pp.1-9.
[2] Montes Bernárdez, R. & Cabrera Garrido, J.M. (1991-92) Estudio estratigráfico y componentes pictóricos del arte prehistórico de Murcia (sureste de España). Anales de prehistoria y Arqueología 7-8. Secretariado de publicaciones, Universidad de Murcia.
[3] Leroi-Gourhan, A. (1982) Arqueología de la cueva de Lascaux”, en Investigaciones y Ciencia, agosto, pp.60-70
[4] Del Monte, M. & Sabbioni, C. (1987) A Study of the Patina Called 'Scialbatura' on Imperial Roman Marbles, in Studies in Conservation Vol.32, No.3, pp.114-121, DOI: 10.2307/1506215
[5] Clottes, J., Menu, M., & Walter, Ph. (1990) La préparation des peintures magdaléniennes des cavernes arigéaises, en Bulletin de la Société préhistorique française, 87-6, pp.170-192.
[6] Cabrera Garrido, J.M. (1996) “Informe Técnico”, in Beltrán y San Nicolás. “Las pinturas de las cuevas de Pena Rubia (cehegin, Murcia)”, Caesaraugusta, 64, Zaragoza.
[7] Vázquez-Calvo, M.C., Álvarez de Buergo, M., Fort, R. (2007) Overview of recent knowledge of patinas on Stone monuments: the Spanish experience, in Building Stone Decay: from Diagnosis to Conservation, R. Prikryl, R. y B. Smith (eds.), The Geological Society of London, Special Publications, Vol 271, pp.295-307.
[8] Kouzeli, K., Lazari, C., Economopoulos, A. & Pavlis, C. (1996) Phosphatic Patinas on Greek monuments (Acropolis of Athens and other Ancient and Byzantine monments): General Discussion and Further documentation on the presence of oxalates. In: II International Symposium: The Oxalate Films in the conservation of works of Art; Proceedings, Politecnico di Milano.
[9] Previde Massara, E. & Perego, G. (2000) Study of the colorings of the St. Peter’s Façade (Vatican). In: Fassina, V. (ed) Proceedings of the 9th International Congress on Deterioration and Conservation of Stone. Volume 2, Elsevier. Amsterdam, pp.425-433.
[10] Polikreti, K. & Maniatis, Y. (2003) Micromorphology, composition and origin of the orange patina on the marble surfaces of Propylaea (Acropolis, Athens). The Science of the Total Environment, 308 (1-3), pp.111-119
[11] Alessandrini, G. (2004) Patine su materiali lapidei. In: Tiano, P. & Padrini, C. (eds) Le Patine, Genesi, significato, conservazioni. Nardini Editore, Florence, pp. 15-28
[12] Vázquez-Calvo, M.C., Álvarez de Buergo, M., Fort, R., Varas, M.J. (2007) Characterization of patinas by means of microscopic techniques. Materials Characterization 58 (11-12), pp. 1119-1132.
[13] Rivas López, J. (2008) “Policromías sobre piedra en el contexto de la Europa medieval aspectos históricos y tecnológicos”, tesis doctoral, Universidad Complutense de Madrid, Facultad de Bellas Artes.
[14] Durán, A., Perez-Rodriguez, J.L., Jiménez de Haro, M.C. (2009). “Study of the gilding techniques used in polychromed stones and ceramics by dedicated laboratory made micro X-ray diffraction and complementary techniques”, in Anal Bioanal Chem 394, pp.1671-77.
[15] Durán A, Castaing J, Walter P (2010): X-ray diffraction studies of Pompeian wall paintings using synchrotron radiation and dedicated laboratory made systems, in Appl Phys A 99, 333-40.
[16] De Miguel Alcalá, B. & Pardo Redondo, G. (2011) Estudio histórico-estratigráfico de los muros de la nave central de la Catedral de Teruel y su encuentro con la techumbre, en Revista Arqueología de la Arquitectura, No. 8, pp.121-140.
[17] Pérez Rodríguez, J.L., Durán, A., Arquillo, D., Franquelo, M.L., Castaing, J. (2012) Caracterización de la policromía de una escultura gótica por técnicas de Análisis No Destructivas, en Revista Macla nº 16, Revista de la Sociedad Española de Mineralogía.

[18] Delaney, J.K., Ricciardi, P., Deming Glinsman, L., Facini, M., Thoury, M., Palmer, M. & René de la Rie, E. (2018) Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts, in studies in Conservation, 59:2, pp.91-101, DOI: 10.1179/2047058412Y.0000000078

[19] Castandet, S. & Rollier-Hanselmann, J. (2013) The Romanesque Portal of the abbey-church of Cluny. Study of polychromy, Journal of Archaeometry - Vol. 1, nök1, pp.54-57.

[20] Antonelli, F., Lazzarini, L., Cancelliere S. & Tesser, E. (2016) Study of the deterioration products, gilding, and polychromy of the stones of the Scuola Grande Di San Marco’s façade in Venice, in Studies in Conservation, Vol.61,2,74-85, doi.org/10.1179/2047058415Y.0000000004

[21] Crippa, M., Bongiorno, V., Piccardo, P. & Carnasciali, M.M. (2018) A Characterisation Study on Modern Bronze Sculpture: The Artistic Patinas of Nado Canuti, in Studies in Conservation, Volume 64, 2019 - Issue 1, 19 Jul 2018.

[22] Brecoulaki, H. (2014) “Precious colours” in Ancient Greek polychromy and painting: material aspects and symbolic values” in Dans Revue archéologique 2014/1 (nº 57), Pp. 3-55

[23] Pardo San Gil, D., Ruiz, E., De Arkaute, E., Cortázar, M. & Sanz, D., (2003) Estudio Microestratigráfico de las superficies y aplicación, en arqueología de la arquitectura, 2, 227-234.

[24] García de Miguel, J.N. (2002) Tratamiento y Conservación de la piedra en los monumentos, Colegio Oficial de Aparejadores y Arquitectos Técnicos de Madrid.

[25] Álvarez de Buergo Balleste, M. (2007) Pátinas en el Patrimonio Histórico, MACLA, 7, XXVII Reunión de la Sociedad Española de Mineralogía.

[26] Knoll, H. (1968) Die Trajanssaule, Rep. Instituten fur Anorganische Chemie, Freie Universitat Berlin.

[27] Pietsch, E. (1964). “Altamira y la prehistoria de la tecnología química”, in Patronato de Investigaciones Científicas y Técnicas “Juan de la Cierva”, CSIC, Madrid, 48.

[28] Flores Sasso, V. (2011) "Arquitectura de la Catedral. La Obra de Fábrica" en Basílica Catedral de Santo Domingo, editores Chez Checo, J.; Pérez Montas, E. & Prieto Vicioso, E. Patronato de la Ciudad Colonial de Santo Domingo & CAEHIE Co-editor, Amiga del Hogar, Santo Domingo. Pp. 211-371.

Acknowledgments

This research is part of the ACROFA project "Application of physical-chemical methods for the chromatic characterization of exterior facades. Case: Colonial City of Santo Domingo", Code: 2016-2017-159 funded by FONDOcYT 2016-2017, MESCyT (Ministry of Higher Education Science and Technology). The authors also thanks Oficina de la Obra y Museos de la Catedral de Santo Domingo.