

BOOK OF ABSTRACTS

# COLOURS 2015

BRIDGING SCIENCE WITH ART



[WWW.COLOURS2015.UEVORA.PT](http://WWW.COLOURS2015.UEVORA.PT)

24-26 SEPTEMBER 2015

ÉVORA UNIVERSITY

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ISBN -989-20-5862-7

ORGANIZED BY:



COLOURS2015 is organized within the framework of project FCT PTDC/CPC-EAT/4769/2012 entitled *PRIM'ART\_Portugal Rediscovering Mural Art: Historical and scientific study of Évora Archepiscopate (1516-1615)*

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## WELCOME TO COLOURS2015

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Dear Colleagues,

We are very pleased to welcome you to the second edition of the international conference on colour research, COLOURS2015: Bridging Science with Art, hosted by the University of Évora and organized by HERCULES laboratory with two goals. First to celebrate the UNESCO International Year of light and light-based technologies and the second to celebrate the closure of Project FCT PTDC/CPCEAT/4769/2012 entitled PRIMA'RT\_Portugal Rediscovering Mural Art.

In the next 3 days, it is going to be all about COLOURS in its wide perspective in cultural heritage and conservation science.

The scope of COLOURS2015 to promote a forum between several specialists and scientists is already fulfilled and we would like to thank the participants for their contributions and our sponsors for their help in making this meeting a success. A special note of thanks is also extended to Fundação Para a Ciência e Tecnologia (FCT), as well to the students and administrative staff who have worked to make this meeting possible.

We wish you all a pleasant journey in Évora.

On behalf of the Organization Committee,

Milene Gil and António Candeias ( main-chairs)

## ABOUT PROJÉT PRIM'ART

Since the first quarter of the sixteenth century until the early seventeenth century, the best Portuguese and European Art Masters have passed by Évora, combining the values of the Renaissance with the tradition of Christian spirituality. Their presence promoted by the permanence of the Royal court in the city, launched bases for the development of Culture and Art, both regionally and nationally. Among them, was the Mural Paintings which in this period reached its maximum splendor. The stylistic, technical and material corpus of the Évora's easel painters has been studied, as well as the artist's who worked in other nucleus that radiated from here (like Montemor-o-novo and Vila Viçosa). The same analysis was carried out over 2 years by projet PRIM'ART for the region's mural painters that have worked for the Évora Archdiocese between 1515-1615.

PRIM' ART main goals were:

- To assess the extent to which artists were influenced by the Évora's cultural environment;
- To identify contact points between mural and other art expressions at the level of formal elements and building compositions, the use of materials and color palette, in order to clarify authorship;
- To characterize from the technical and material point of view. To what extent painters followed the practice of buon fresco emphasized by Art theorists, like the Portuguese Francisco de Holanda? and if not, which techniques did they use?
- To relate and compare several painting nucleus in the region with testimonies in the centre and North Portugal and abroad.

The research plan consists of three approaches:

- Research of History and Art History with collecting and evaluating documentation, its integration with the results of material and surface characterization, allowing a critical analysis of the art works and its context with the mentality of the time;
- Surface analysis of the paintings through the detailed examination by visible (Vis) and raking light (RAK); photography of UV fluorescence induced in the Vis and Infrared (IR);
- Material characterization by combining in situ non invasive methodologies ( X-ray fluorescence spectrometry and visible spectrophotometry) with laboratory analytical techniques (micro-Raman, micro FT-IR and GC-MS) and microscopic techniques ( bright and dark field microscopy; scanning electron microscopy).

Projet PRIM'ART was based on the synergy of a strong collaboration between HERCULES laboratory, History Department (University of Évora), the Department of Art History, Faculty of Humanities and Centre for Atomic Physics of the University of Lisbon and the Regional Department of Culture of Alentejo, integrating a multidisciplinary team that constitute the Local organizing Committee of COLOURS2015. For more informations, please visit in the near future the website of the projet, host in HERCULES Laboratory.



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Nuno Carriço Lab. HERCULES, Universidade de Évora, Portugal



Detail of a 16th century Fresco Painting  
(Ermida de São Pedro da ribeira,  
Montemor-o-Novo, Southern Portugal)  
Case study of Projet PRIM'ART

# DAY 1

[conference program]

**THURSDAY, 24 SEPTEMBER 2015**

08:00 Registration and check in at Colégio do Espírito Santo (auditorium until 10:00 / room A after 10:00)  
09:30

09:30 Opening ceremony  
10:00

10:00 Plenary Lecturer 1 (auditorium) - COLOUR: reality, perception and evolution - Michel Ratureau  
10:35

10:35  
11:30 Coffee break and poster session

**ROOM A 131**

S1: Colour History and symbolism/Painters and workshop practices

11:30 Color as an element in cultural communication between social elites during the iberian period. Maria Belén Ruiz Ruiz, Julio Romero Noguera, Luis Emilio Vallejo Delgado, Fernando C. Bolívar Galiano  
11:50

11:50 Artists, materials and techniques of 17th century mural paintings in Alentejo. Patricia Monteiro  
12:10

12:10 What are the colors of Portuguese Noble House façades? Contributions to their chromatic study. Ana Veiga and José Aguiar  
12:30

**ROOM B 124**

S2: Colour materials origin/reproduction/ painting techniques

Natural Fe-Based geomaterials from the Lessini Mountain (Venetto Italy: a review). Giovanni Cavallo, Maria Pia Riccardi, Roberto Zorzin  
05

Madder: from the plant to the museum objects. Carole Mathe, Jean-Baptiste Mazzitelli, Cathy Viellascazes  
06

The technique of blue paint layers in Gdansk paintings from the mid-sixteenth to the end of the eighteenth century. Justyna Olszewska-Swietlik and Bozena Szmelter-Fauzek  
07

12:30 12:50	The birth of a painter: Estevão Tomás and the great works of the Manueline/Johannine period in Évora. <b>Antónia Conde e Vítor Serrão</b>	04	Yellow pigments based on lead, tin and antimony: synthesis, characterization and hue choice in artworks. <b>C.Pelosi, G.Agresti, P.Baraldi and U.Santamaria</b>	08
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12:50  
14:30 Lunch

14:30 14:50	Reconstruting Ferdinand Bauer's 18th century colour chart. <b>Richard Mulholland and David Howell</b>	09	Smalt production and Colour Analisis: <b>Leonor Ferrão, Agnès Le Gac, Márcia Vilarigues, António Candeias</b>	011
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14:50 15:10	All the Colours of Keith Haring. <b>Vincenzo Palleschi, E.Grifoni, S.Legnaioli, G.Lorenzetti, L.Marras and S.Pagnotta</b>	010	The importance of original historic reference materials. <b>W.Vetter and M.Schreiner</b>	012
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S3: Colour History and symbolism/Painters and workshop practices I

S4: Colour analysis, authorship and date attribution studies

15:10 15:30	Pigments from a paint box from the atelier of the Portuguese painter of the early twentieth century, Aurélia de Sousa. <b>Maria Aguiar, Ana Calvo, António João Cruz, António Candeias and José Mirão</b>	013	Shimmering colours. Coloured glazes on silvering in portuguese altarpieces and sculptures. <b>Tiago Dias, Elsa Murta, Cristina Dias, Vítor Serrão</b>	016
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15:30 15:40	Decorative surface finishes: bronzing, patina-Antiqua, Verd-Antique in NY Furniture 1810-1830: New -York workshops practices 1810-1830. <b>Pascale Patris</b>	014	Colour and colourants in illuminated manuscripts. <b>Paola Ricciardi and Stella Panayotova</b>	017
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15:40 16:00	Colour and fantasy in an eighteenth century ceiling. <b>Margarida Donas Boto</b>	015	From the painted colours to the discovered colour. <b>E.Grifoni, G.Piachi, P.Palleschi, M.Salvini, S.Legnaioli, G.Lorenzetti, L.Marras, S.Pagnotta and V.Palleschi</b>	018
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16:00  
16:30 Coffee break

16:30 Plenary Lecturer 2 ( ROOM A) - Light and COLOUR: from theory to practice. José Aguiar and João  
17:00 Pernão

17:00  
17:35

Poster Session

19:00 Alentejo de honra with music (welcome cocktail) Teather Garcia de Resende (19th century)



General view of the 17<sup>th</sup> century mural paintings at the vault of the low-choir of Convento da Saudação (Montemor-o-Novo, Southern Portugal). Case study of Projet PRIM'ART

# DAY 2

[conference program]

## FRIDAY, 25 SEPTEMBER 2015

09:00 Plenary Lecturer 3 (ROOM A) - The use of black pigments in the decoration of architectural surfaces in north western Italy. A comparison of different cases study. **Marco Zerbinatti**  
09:35

## ROOM A 131

S5: Colour analysis, authorship and date attribution studies I

09:35 "Hidden evidence": Color in Modern Italian architecture from contemporary journal leafing through. **Anna Frangipane** 019  
09:55

09:55 Colour of Algarve exterior stucco ornaments. **Marta Santos, João Pernão, José Aguiar and Miguel Reimão Costa** 020  
10:15

10:15 Technical Examination of Polychromy of St Reinhold Altarpiece from National Museum in Warsaw. **Lućja Brzozowska and Justyna Inga Olszewska-Swietlik** 021  
10:35

10:35 Tracking the old colours and the new: Technical and material study of the José de Escovar workshop - mural paintings from the Évora Cathedral. **Yigit Helvacı, Marta Manso, Luis Dias, Ana Cardoso, António Candeias and Milene Gil** 022  
10:55

## ROOM B 12

S6: Diagnosis and colour alteration studies in conservation-restauration

An Exercise in Fugitivity: investigating the fading of red lake pigments. **Daniela R. Leonard** 023

Understanding the (in)stability of semiconducting pigments via electrochemistry. **Karolien De Wael** 024

Measuring Degradation: The evaluation of Colour Change in Objects with Spectrophotometry. **Tania Desloge** 025

Changes in Colour of some pigment mixtures used in restoration of paintings. **Elzbieta Szmit-Naud** 026

10:55

11:30

Coffee break and poster session

11:30 Multi-technical characterization of the pictorial palette of 16th century frescoes from Ribeira Sacra (NW Spain). **Lucía Pereira-Pardo, Beatriz Prieto, Milene Gil, Manuel Ribeiro and Benita Silva** 027  
11:45

The colour of the granite that built the city of São Paulo, Brazil. **Eliane Aparecida Del Lama, Lauro Kazumi Dehira, Danielle Grossi and Luciane Kuzmickas** 034



15:10

15:45

## Coffee break and poster session

	Session 10: Colour documentation and management		Session 11: Science and technology applied to colour heritage I	
15:45	Precise reproduction of colours in cultural heritage digitization. <b>Agnieszka Olejnik-Krugly and Przemyslaw Korytkowski</b>	039	A new hyperspectral imager for studying Egyptian coffins. <b>Tiziana Cavalerieri, M.Pisani and M.Zucco</b>	044
15:55				
15:55	Color accurate photography of cross-sections of paint samples at the Rijksmuseum in Amsterdam. <b>Susan Smelt, Lizzy Jongma, Carola van Wijk, Henni van Beek, Rick Klein Gothink and Robert Erdmann</b>	040	Reflectography analysis on some paintings at the Pinoteca of Ascoli Piceno. <b>Graziella Roselli, Valeria Corradetti, Marcello Melis, M.Minicucci, G.Di Girolami, M.Miccoli and M.Martelli</b>	045
16:15				
16:15	Colour management applied to photographic documentation in the restoration of scientific collections: anatomical wax models. <b>Alicia Sanchez Ortiz, Luis Castelo Sardina</b>	041	Hyperspectral imaging applied to the study of paintings. <b>Luis Bravo</b>	046
16:35				
16:35	Computer match pigment selection for ceramic glaze restoration. <b>Norman H. Tennent, Isabelle Garachon, Bodill Lamain, James H. Nobbs</b>	050	The study of pigments by Diffusive Reflectance Spectroscopy (DRS). Applications to restoration and fine arts. <b>Andrei Hrib, Felicia Iacomi, Carmen Măta, Octaviana Marincas and Mihai Hrib</b>	055
16:55				
16:55	Colour essay for characterization of losses for the chromatic reintegration process of cultural heritage. <b>Ana Bailão, Frederico Henriques, Susana Mendes, Alexandre Gonçalves</b>	051	Colorimetric measurements of different variants of verdigris: powder and bound pigments. <b>Margarita San Andrés, N.Nancho, S.Santos, J.M. de La Roja</b>	056
17:15				
17:15	Plenary Lecturer 4 (ROOM A) - Innovative and Sustainable Technical Art Examination and Color Documentation. <b>Antonino Cosentino</b>			

19:00

21:00

## Guided visit to the Museum of Évora colourful collection

# DAY 3

[conference program]

**SATURDAY, 26 SEPTEMBER 2015**

09:00 Plenary Lecturer 5 (ROOM A) - Analytical Archaeometry: trends and prospects. **Peter Vandenaabeele and Luc Moens**

09:35

**ROOM A 131**

S12: Colour physics and virtual reconstructions

09:35 LED Museum Lighting: Colour Quality and Artwork Preservation. **Ferenc Szabo, Zs.Wierdl, P.Csuti** 049

09:55

09:55 Implement lighting policy for vulnerable artwork. **Christel Pesme** 050

10:15

10:15 Coffee break and poster session 051

10:45

10:45 A new online tool to detect colour misconceptions. **Francisco Luis Naranjo Correa, G.Martínez, A.L.Pérez, M.I.Suero and P.J.Pardo** 052

10:55

10:55 Reconstruction of Wall Paintings at Herculaneum. **Katelin Fallon, Cindie Kehlet, Philippe Zarrazin and Elenora Del Frederico**

11:30

11:45 Closing session 061

12:05

12:05 Lunch

13:30

14:00 Guiding Visit to Casas Pintadas and Paço de São Miguel (16th-17th century)

18:00



Observations in VIS-RACK light  
Capela do Lourenço, Sé de Évora, Portugal  
16th mural painting (lime fresco?)  
Case study of PRIM'ART Project

# DAY 1

[oral communication]

**(PLENARY LECTURER 1)****LA COULEUR: RÉALITÉ, PERCEPTION ET ÉVOLUTION**

Michel Ratureau

Enseignant chercheur retraité de l'Université d'Orléans, 1966-2000

Comment admettre le concept de couleur sans prendre en compte l'ambiguïté des notions essentielles mises en cause : la réalité d'un phénomène physique et la perception de ce phénomène. Que serait la couleur sans le verbe et la parole ?

En d'autres termes, le physicien doit exploiter un phénomène électromagnétique, assez bien connu mais complexe et dans le même temps transférer cette notion en la modélisant pour que le spectateur soit en accord avec ses explications...

La couleur est partout, même la nuit dans les rêves où parfois elle se décline souvent en noir et blanc ; le cerveau reproduisant le cycle de la vision stricto sensu !

Pour aborder la connaissance de la couleur d'un objet, il est nécessaire de considérer un trio indissociable : {source de lumière - cible - observateur}. L'absence ou la défaillance d'un seul de ces trois acteurs rompt le mécanisme générateur de la couleur.

Très rapidement l'homme a cherché à reproduire ce qu'il voyait, d'abord par le dessin qui dépend de sa main, puis par la photographie qui automatise la capture d'une scène. Le remplissage de la forme imposée par le trait a exigé rapidement l'usage de produits (encres ou pigments) générateurs de couleurs. Tout aurait pu rester en cet état mais la société a besoin de diffuser ses travaux et l'étape de la mesure est arrivée au XVIIIème siècle grâce à la comparaison avec des zones colorées répertoriées dans un album (par exemple de Chevreul ou de Munsell). Puis sont apparues progressivement les nombreuses méthodes instrumentales des physiciens qui permettent une « mesure » mais qui restent en marge de la perception physiologique.

Ce dernier point fait l'objet de recherches et la neuro physiologie dévoile progressivement les mécanismes complexes de la vision ; en particulier le problème de la comparaison des couleurs et celui de leur mémorisation.

Pour se rapprocher du sujet de notre colloque, nous donnerons quelques exemples de couleurs naturelles (argiles quartziques des Eyzies, silicates hydratés à pseudo-feuillets, ôcres...) et de couleurs maîtrisées par une action sur une structure cristalline (talc). Ce dernier exemple permet d'aborder le délicat problème de la stabilité de la couleur.

Au contact d'un objet cible, l'interaction entre la lumière d'une source et cet objet est subordonnée à la permanence des caractéristiques du rayonnement incident mais aussi à l'état de cet objet. C'est là que l'on rejoint les préoccupations des conservateurs et restaurateurs pour qui la durée est une donnée fondamentale. D'innombrables exemples peuvent être étudiés

1. Evolution par mélange
  - i. Argile et eau (humidité)
  - ii. Action du temps, coloration par diffusion : reptation des nano particules
2. Rôle de la température.

Enfin nous pourrions évoquer la possibilité de réversibilité.

[01]

## COLOR AS AN ELEMENT IN CULTURAL COMMUNICATION BETWEEN SOCIAL ELITES DURING THE IBERIAN PERIOD

María Belén Ruiz Ruiz(1), Julio Romero Noguera(2), Luis Emilio Vallejo Delgado(3), Fernando C. Bolívar Galiano(1)

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(2) Departamento de Pintura, Universidad de Sevilla. Laraña 3, 41005 Sevilla, España

(3) Museo Arqueológico Municipal de Obulco. C/José Moreno Torres, s/n. 23790 Porcuna, España

The legacy of the Iberian culture allows showing up the fact that the use of color in sculptures has not, in the cultural and sepulchral field, a realistic pretension but a symbolic one. This communication studies the importance of color in the Iberian period as an element of cultural communication between social elites.

The prevalent color in Iberian sculpture is red, raising features and attributes of warriors and zoomorphic, as in the case of archaeological ensembles of Cerrillo Blanco, in Porcuna (Spain), where the social position of this ancient aristocracy is reaffirmed. Particularly, female sculptures employed a wider variety of colors, using polychromy in her jewelry and clothes to show her wealth and social status.

This communication deals with the issue of the importance of color in Iberian society in the s. V a.C. by means of the study of Cerrillo Blanco's heritage. Technically it is considered one of the best sculptural examples of pre-roman West, and up to now there are no studies on the polychromy of the pieces in relation to the dominating social class of that time and its cultural meaning.

[1] Mielke, D. P. Die Polychromie iberischer Skulpturen, *Madridrer Mitteilungen* 52, 2011, 306-332. La traducción al español fue realizada por Teresa Piñel, 2013.

(02)

## ARTISTS, MATERIALS AND TECHNIQUES OF 17<sup>TH</sup> CENTURY MURAL PAINTING IN ALENTEJO

Patrícia Monteiro(1)

(1) Artis-Instituto de História da Arte da FLUL

At the end of the 16<sup>th</sup> century and until the first quarter of the 17<sup>th</sup>, there was a slow but inexorable social movement that separated the painters from the bonds of the medieval mechanical trades. Gradually painters assumed their individuality amongst the artistic production accepting, at the same time, multiple functions, in order to respond effectively to the increasing demands of their patrons. At the centre of the relation between patrons and artists was the contract, a regulatory instrument of all parameters related to the artistic activity that left little room for any creative freedom. The standards required by the contracts remained virtually unchanged for centuries, making these documents the most rigid and stable instrument of regulating the working activity. At the same time, they give us, still today, precious elements regarding to the artists working methods and materials used by them. With a few exceptions, the artists' activity in Évora's Archiepiscopate in the late 16<sup>th</sup> century remains, in many ways, unknown. On the other hand, for the following century we have a larger number of data available, which allows us to identify some changes at the features of the painters' working methods.

We conclude, for example, that in the 17<sup>th</sup> century the figure of the painter-gilder emerged, activity that was not strange to most artists, and that increased to the same extent that multiplied the orders for gilded altarpieces by brotherhoods. Slowly, the painter-gilder wins a major role, finally exceeding the fresco painter, previously considered as the most noble and prestigious amongst artists.

Perhaps one of the last performers of fresco painting working in the Évora region was José de Escovar, a prolific painter whose work made the transition between the 16<sup>th</sup> to the 17<sup>th</sup> century. The multifaceted nature of the painter is visible in the contract signed in 1610 with the bailiff Rui de Brito for the painting of the church in the Santa Clara's convent (Elvas). Escovar should run some parts of the painting with fresh oil inks, and others with fresco, showing the existence of some hierarchy of importance between the fresco regarding the other painting genres. The fresco was reserved (almost) exclusively for those spaces that were considered of a higher symbolic relevance within the building.

This differentiation (spatial and material) between the fresco and the oil technique will be progressively diluting as we move forward in the 17<sup>th</sup> century. Although the expression "fresco painting" does not disappear completely from the documentation, its correct use is, from now on, questionable. In most cases, the paintings described in the documents correspond, actually, to secco paintings, executed with very specific materials: plaster; gold; mordant; oil; egg-based paint; varnish; glue; siccativo.

Regarding the documentation reviewed, the boundaries between the fresco and the oil painting are unclear, and often the two concepts were mixed, so the frontier between the two techniques began to dim. In order to present some answers to these questions was created the project PRIM'ART\_ Redescoberta da ARTE Mural em Portugal: Estudo Histórico e Científico do Arquiepiscopado de Évora (1516-1615) (PTDC/CPCEAT/ 4769/2012).

[03]

## WHAT ARE THE COLORS OF PORTUGUESE NOBLE HOUSE FAÇADES? CONTRIBUTIONS TO THEIR CHROMATIC STUDY.

Ana Motta Veiga<sup>(1)</sup> and José Aguiar<sup>(2)</sup><sup>(1)</sup> Faculdade de Arquitectura da Universidade de Lisboa<sup>(2)</sup> Faculdade de Arquitectura da Universidade de Lisboa

A question that usually arises around the history, conservation and restoration of Portuguese Noble House is the original color - or the color of, artistic and historically most significant periods - of their façades. The absence of this information in this period iconography, historical descriptions, projects and even in personal correspondence, deepens this unknowledge. Directly related with color, is its materialization (façade materials or the existence of coatings and paints).

By studying these Houses we are faced with the interrogation of three chromatic moments of its façades: what are the current colors; which colors may have been the original ones; which colors changed throughout their existence. Also important, is to know the support of color, that in this architectural type is found most often in the form of two solutions: the faced stone and the lime arts. And it's precisely with the dialogue between them, the study of the finishing and their possible overlap, or in the existence of joints, that we will find clues that indicate the original solutions and the possibility of another existing color.

The main issues of this research are to try understand how Noble House façades are currently coated and in which colors are they painted, how much has evolved the way they are shown and presented, what's their materiality (between stone and lime), and how they could have strengthen or limited the architectural use of color on their outside.

For the initial object of this study, we chose as a documental base the pioneering work of Carlos de Azevedo "Portuguese Manors: introduction to the study of the Noble House ", conducted and published in the 60's. This work involves the comparative analysis of about 120 manors located from north to south of Portugal, and where we can find the listing of the most significant examples of Portuguese erudite residential architecture, from the robust fifteenth medieval tower to the exquisite neoclassical palace and its figurations.

From the analysis of this documentation and its images we made this comparison with current images (by direct visit or access to updated information) extracting those correlations. It is intended to continue the study of Carlos de Azevedo by coloring it, taking a step further in a topic yet to start: the colors of these houses!

It's expected the beginning of a sistematization of the cromatic knowledge of its façades, with immediate practical application as part of its conservation and revival. In order to find answers we launch new questions that will launch new hypotheses of a heritage with more colors yet to discover.

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(04)

## THE BIRTH OF A PAINTER: ESTÊVÃO TOMÁS AND THE GREAT WORKS OF THE MANUELINE/JOHANNINE PERIOD IN ÉVORA

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The documentary surveys conducted by the Primar't Project (PTDC/CPC-EAT/4769/2012) lead to the discovery of documents regarding a painter whose artistic activity was hitherto unknown: Estêvão Tomás who, according to the historic sources, was already dead in 1534. However, these same sources reveal the work he made for Évora's female Cistercian monastery, the monastery of S. Bento de Cástris – an unfinished altarpiece. The then Manager (*Regedora*) of that Cistercian House, D. Violante da Silveira, came into possession of two finished paintings, the *Annunciation* and the *Birth of Jesus*, which were meant to be placed on an altarpiece that was being painted in the cenoby at the time, most likely to decorate the primitive chance's back wall.

So, the artist, whose identity was completely unknown, can now be reliably identified and associated with a solid artistic knowledge, which may allow finding new connections to the various *nebulous* Johannine works by the so-called «Ferreirim masters» whose authors remain unknown. The detailed study of the *Annunciation* preserved at the Évora Museum (inv. no. 1543) – a work that has now been ascribed to Estêvão Tomás – opens possibilities of comparisons with other paintings from the same period with a similar style, which may be the subjects of new research works.

### Acknowledgement

The authors acknowledge Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program

[05]

## NATURAL FE-BASED GEOMATERIALS FROM THE LESSINI MOUNTAINS (VENETO, ITALY): A REVIEW

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The paper intends to assess the state of art concerning the knowledge of Fe-based geomaterials occurring in different geological environments in Lessini Mountains (Veneto, NE Italy) locally known as colouring earths (terre coloranti). Red, yellow, green and black earths will be discussed; among these, green earth from Monte Baldo near Verona is very famous and mentioned for the first time in 1574 [1]. The yellow and red natural earth are mentioned in the 1815 Catalogue by Barelli as reported in [2].

The industrial exploitation and processing of the materials reached the top during the early and middle of the 20<sup>th</sup> c. as demonstrated by the presence of numerous local paint factories; in that time Veneto region was most probably the principal district in northern Italy for natural earths exploitation and processing.

All the available scientific literature was consulted since the end of the 19<sup>th</sup> c. to date. The pioneer work was carried out by Nicolis in 1898 [3] and later by other authors such as Federici [4], Forlati [5], Corrà [6]; all these contributions are limited to the hills around the city of Verona. These works were aimed at describing the morphologies of the palaeokarst caves, the geology and in some cases the origin of the infilling sediments.

The researches carried out at the end of the 20<sup>th</sup> c. and at the beginning of the 21<sup>st</sup> c. allowed to include new caves and deposits, establish chronologies also based on biological evidences (pollen analysis), propose models indicating the evolution of the karst system [7-8], characterize the geological occurrences [9-10]. These data will be discussed in the light of the recent evidences coming from analysis based on optical microscopy (PLM), X-ray Diffraction (XRD) and geochemistry (ICP-MS).

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[06]

**MADDER: FROM THE PLANT TO THE MUSEUM OBJECTS**

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*Rubia tinctorum*, also called madder, is a tinctorial plant belonging to the Rubiaceae family. Madder was employed since the ancient times: painters used madder lacquer as a medium for their paintings [1, 2]. Moreover, this natural substance was also used for dyeing textiles in many parts of the world [3–6]. Madder roots contain dyes with an anthraquinonic (anthracene-9,10-dione) skeleton corresponding to heterosidic and aglycone molecules. The heterosidic dyes are composed by molecules with an anthraquinonic part (aglycone) and a primeverose one (6-O- $\beta$ -D-xylopyranosyl- $\beta$ -D-glucose). The major heterosidic dyes are lucidin primeveroside, ruberythric acid (alizarin primeveroside), galiosin (pseudopurpurin primeveroside) and rubiadin primeveroside. The aglycone compounds are alizarin, purpurin, pseudopurpurin, lucidin, xanthopurpurin and rubiadin.

These colored compounds are secondary metabolites and it is possible to increase their proportion in the plant by abiotic stresses applications. Several types of stress were tested: use of UVc, spray of eliciting molecules (methyl jasmonate)... The aim of this study is to optimize the production of anthraquinonic compounds and the experiments concern the natural heritage.

Nowadays, the classical extraction method of madder dyes is a reflux of roots with a water–alcohol mixture during more than one hour [7, 8]. An extraction method of *Rubia tinctorum* roots dyes using ultrasounds was established and optimized to obtain the original chemical composition [9, 10]. This ultrasonic process permits to reduce extraction time and energy cost, to give a better yield and to preserve the dyes population by using soft extraction parameters values. Liquid chromatographic analyses were performed in order to characterize madder dyes from the plant... to museum objects.

All of these experimental conditions were applied to the analysis of samples from cultural heritage. Ancient materials belonging to the collection of the Roure Museum in Avignon (France) and dating from the nineteenth century were analysed [11]. Madder roots from the Sainte Marthe pharmacy of Avignon (XVIIIth century) and ancient red colored textiles were also studied.

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[07]

## THE TECHNIQUE OF BLUE PAINTING LAYERS IN GDAŃSK PAINTINGS FROM THE MID-SIXTEENTH TO THE END OF THE EIGHTEENTH CENTURY

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The technique of blue painting layers was analyzed on the example of selected 27 panel paintings made in Gdańsk workshops and origin from the churches and the museums of Gdańsk, Pelplin and Poznań (Poland).

The general aim of this work was to analyze and systematize of how the technique and the technology of painting the blue layers had been changing from the mid-sixteenth to the end of the eighteenth century. The commonly used blue pigments were natural azurite, natural ultramarine and smalt, and since the beginning of the eighteenth century the only one blue pigment was organic indigo.

The results show the correlation between the time of dating of paintings and the sort of the used pigments. Blues were developed in different intensities and hues [1]. The color was dependent on the used pigment and the size of the grains of minerals and glass particles of cobalt and from admixtures of such pigments like lead white, lead-tin yellow and organic red. The important role was played by the color of the imprimatura and the ground layer as well as the underpainting, which sometimes created halftones and shadows. The white, gray, yellow and pink ground layer and white and brown imprimatura were used in the Gdańsk School of Painting. There was a dominant of white and gray underpainting under the blue painting layer.

The performed analysis is a database on ways of developing the blue painting layers in Gdańsk School of Painting and it will be helpful when comparing with other works both schools of Gdańsk, as well as the other European schools.

Acknowledgment

The painting workshop of the Gdańsk artists was a subject of interdisciplinary research supported by the Polish National Science Center of the Ministry of Science and Higher Education (Grants No. N N105 430940 and N N204 370340 to J.O.-Ś.).

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(08)

## YELLOW PIGMENTS BASED ON LEAD, TIN AND ANTIMONY: SYNTHESIS, CHARACTERIZATION AND HUE CHOICE IN ARTWORKS

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The aim of this study is to investigate the yellow pigments based on lead, tin and antimony produced according to ancient treatises, recipe books and literary sources, starting from our previous research devoted to the synthesis of these materials based on the stoichiometric ratio of the final compounds [1-2]. A relevant part of the work was spent in studying and interpreting the old treatises in order to select the most diffused and repeated recipes in different times and geographic areas [3]. The pigments considered in the present study are lead/tin yellow type I ( $\text{Pb}_2\text{SnO}_4$ ), lead/tin yellow type II ( $\text{PbSnO}_3$ ), lead antimonate or Naples yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ) and lead/tin/antimony yellow ( $\text{Pb}_2\text{SnSbO}_{6,5}$ ).

Colour was measured by a X-Rite reflectance spectrophotometer to investigate the chromatic characteristics of the produced pigments in relation to the recipes. The pigments were chemically characterized by XRF, SEM-EDS and micro-Raman analysis in order to investigate the influence of reagents, temperature and melting modalities in the compositions of the produced powders. Lastly, a part of the work was devoted to the study on the use of yellow pigments, based on lead, tin and antimony, in the art history especially concerning the *modus pingendi* of Italian artists between 14<sup>th</sup> and 19<sup>th</sup> century.

The results of this work highlighted the possibility to obtain pigments with different colours and composition according to the reagents, to the temperature, to the melting modality (single or double melting). Generally the pigments prepared according to the ancient recipes are mixtures of different compounds. Lead/tin yellows often contain excess of lead oxide and/or tin oxide. Lead antimonate yellows are always made of different compound with variable stoichiometry (such as *rosiaite*,  $\text{PbSb}_2\text{O}_6$ ). Lead/tin/antimony yellow, prepared according to the *Danzica manuscript*, contains an excess of lead. The study on the use of these pigments by artists highlighted that the choice of one specific pigment was strictly linked to its peculiar shade for obtaining the exact desired colour. In fact, the lead/tin yellows are characterized by brilliant colours whereas lead antimonate and lead/tin/antimony yellows show warm hues.

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**RECONSTRUCTING FERDINAND BAUER'S 18TH CENTURY COLOUR CHART**

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Outside of the natural sciences, the work of Ferdinand Bauer (1760-1826), the pre-eminent eighteenth century natural history painter is little known. However, his botanical paintings on paper are considered to be among the finest in the world. Of particular interest is the unusual drawing and painting technique he utilised, recording colour information about specimens by annotating preliminary pencil field sketches with simple numerical colour codes to be were painted in full colour at a much later stage, by referring directly to a painted colour chart.

Late eighteenth-century Oxford formed the backdrop for two ambitious and ground breaking botanical expeditions (1786-87 and 1794-95) to Greece and the Levant inspired and led by third Professor of Botany at Oxford University, John Sibthorp (1758-1796). The results of this expedition were published as the ten-volume *Flora Graeca* (1806-40), regarded by many as the most beautiful botanical work ever produced.

Ferdinand Bauer was Sibthorp's chosen artist for preserving and documenting the flora discovered during the expedition, and also for creating the almost one thousand painted watercolour illustrations for the *Flora Graeca*. Moving from place to place rapidly, Bauer only had the time to record the basic structure of specimens using brief pencil sketches. Crucial colour information was recorded on these sketches solely by means of a numerical code, which could be used by Bauer to reproduce these colours accurately in paint at a much later stage. Bauer's accomplishment with the *Flora Graeca* watercolours is characterised not only by his attention to detail and the speed at which he worked (each full scale watercolour was completed in about 1¼ days), but also by his astonishing ability to reproduce colour on the page with great accuracy.

The Bodleian Library at Oxford University holds the entirety of Bauer's original watercolours and annotated field sketches for the *Flora Graeca*. However, the crucial key to his technique, the colour chart of some 300 numbered colours is lost. This paper will discuss new research at the Bodleian Conservation Research department to understand Bauer's working methods, and to identify his 18th century colour palette. Using Raman spectroscopy and Hyperspectral imaging to positively identify pigments used by Bauer and cross-referencing these results with the numerical codes, the aim of the project is to create a historically accurate reconstruction of Bauer's lost colour chart.

This will highlight the fact that if Bauer's paintings were created using only this simple colour reference system, and that they were painted several years after seeing the original living specimens, and furthermore that they are highly regarded even today for their visual and scientific accuracy, it speaks to his expertise as an artist and his astonishing memory for colour.

(010)

**ALL THE COLOURS OF KEITH HARING**

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The murals of Keith Haring are important pieces of contemporary art scattered in the most important cities of the world (New York City, Paris, Rio de Janeiro, Sidney, Melbourne). However, the last public work of the Artist, ‘Tuttomondo’, was painted in 1989 in Pisa, Italy, on the side wall of the church of Sant’Antonio Abate, near the local railway station. In 2011, thanks to the contribution of the Haring Foundation and with the support of the Municipality of Pisa, the ‘Tuttomondo’ mural was restored by Will Shank and Antonio Rava, with the intention of bringing back to life the brilliant colors that were fading out after more than 20 years of exposition to weather and urban pollution. The Laboratory of Applied and Laser Spectroscopy of CNR, in Pisa, participated to the complex diagnostic process that allowed the identification of all the pigments used by Keith Haring in ‘Tuttomondo’ through the application of advanced scientific methods as multispectral imaging techniques, micro-Raman spectroscopy, Laser-Induced Breakdown Spectroscopy (LIBS) and X-Ray Fluorescence. The precise determination of the nature of the colours used in ‘Tuttomondo’ was fundamental for its restoration. The same in-depth study was performed by our Laboratory on the degraded pigments of the Collingwood mural in Melbourne, another masterpiece of Keith Haring that was brought back to the original brilliance by the same Antonio Rava in 2013.

In this communication, we will present the main results of the scientific procedure that allowed us to precisely determine the nature of the colours used by Keith Haring in the ‘Tuttomondo’ and Collingwood murals, and the kind of degradation products that were responsible of the fading of the painted surfaces.



Figure 1 – The ‘Tuttomondo’ mural in Pisa

[011]

## SMALT PRODUCTION AND COLOUR ANALYSIS

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Blue smalt pigment, as a cobalt-doped glass ( $\text{SiO}_2(\text{vit})\text{Cox}$ ), was widely used in Europe during the 16th and 17th century as a substitute from azurite and lapis-lazuli [1]. There are several treatises and recipes describing how to produce raw smalt and how to obtain the blue smalt pigment [1,2].

Because a 1685-blue smalt paint was extensively applied to the Main Altarpiece of the Coimbra Old Cathedral and is no longer displayed for having been later covered by a Prussian-blue containing overpaint [3], the current research sought to reproduce the smalt pigment: 1) to better assess its original grade colours, and 2) to distinguish them from any discoloration phenomenon known to be influenced by the paint medium.

On the basis of analyses carried out on several altarpiece cross-sections putting in evidence smalt particles of different sizes and shades of blue [4], and recipes found in treatises on glassmaking [1], two smalt pigments were produced in the laboratory, in order to study their optical and chromatic characteristics at the different stages of production. A three-step procedure was followed:

1) Two batches of cobalt-based glasses, S1 and S2, were heated and melted in alumina crucibles, the former containing 6,0% of cobalt oxide, and the latter, 2,1%. After 10 hours in the oven at a temperature of 1,400 °C, the crucibles were plunged into distilled water at room temperature, breaking and resulting in a glass frit.

2) As particle size was said to be hugely influential to the final colour and smalt was indeed sold in size grades [2,5], both batches of smalt were ground manual and mechanically, in an attempt to obtain the same particles sizes as the ones found in the altarpiece samples cross-sections (<5-65>  $\mu\text{m}$ ). Mechanical grinding was performed with distilled water and the particles were sifted by means of meshes with 63  $\mu\text{m}$ , 45  $\mu\text{m}$  and 25  $\mu\text{m}$  openings for obtaining the respective grade particles.

3) As recipes stated that specific vehicles employed during grinding, such as milk or o mixture of egg-yolk and honey, would avoid a loss of colour, normally occurring with traditional grinding with water, manual grinding was performed as well using these substances for each batch of smalt.

At each step, examination were performed by optical microscopy and SEM imaging, and analysis were carried out by SEM-EDS. Finally, every grade colour of ground smalt pigment, from the palest powder blue to the deepest violet-blue, was applied with funori glue over a white ground, in order to quantify and describe their human colour perception by means of Colorimetry.

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012)

## THE IMPORTANCE OF ORIGINAL HISTORIC REFERENCE MATERIALS

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The particular properties of materials available for an artist strongly influence the painting technique as well as the artistic possibilities. From this view, it is highly desirable to obtain analytical information from historic paint materials. We had the possibility to investigate a case with original watercolors of the Austrian painter Moritz Michael Daffinger (1790-1849) by using FTIR- and UV/Vis-spectroscopy as well as XRF with the aim to build databases for the identification of artist materials.

The analysis of the watercolor cakes and fragments in the case allowed the identification of two mixed purples (cobalt blue & carmine, indigo & red colorant), two mixed greens (Hooker's green: Prussian blue & gamboge, emerald green & Prussian blue, Fig.1), viridian, chrome yellow, carmine and umber. Arabic gum was identified in several cases of the materials listed. Three different types of red colorants could be characterized, but not clearly identified. Additionally, ultramarine and Indian yellow were detected in small particles found on the leather lining of the case and lead white in a white paint splash.

The result that 4 out of 13 materials were mixtures of different pigments shows that the suppliers of painting materials in the 19th century provided colorants with specifically adjusted purple and green color shades, which probably met the demands of the artists. This information could hardly be derived from the analysis of paintings, as pigments often were mixed by artists themselves during the painting process. With regard to the mixtures identified in our study, the frequent use of Hooker's green is well documented in the literature, whereas only few has been reported about other mixed colorants. Indian yellow was highly valued by artists for its vivid hue which is caused by a yellow fluorescence. Nevertheless, it was not produced after the 19th century for reasons of animal protection, as it was manufactured from the urine of cows as a result of a pathogenic metabolism. However, as a natural product with variable contents of magnesium euxanthate and euxanthone, it could potentially be used for authentication of artworks. Similarly, differing manufacturing processes and raw materials lead to variable products in case of cobalt blue pigments, e.g. with differing nickel contents.

We conclude from our results, that the analysis of historic references offers several advantages compared to contemporary reference materials, as some materials are hardly available nowadays and some modern formulations or manufacturing processes differ remarkably from historic ones. Furthermore, the use of customized pigment mixtures by artists in history can hardly be proven by other means.

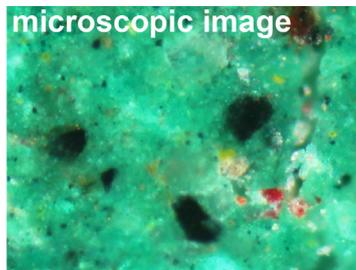


Fig.1: Inclusions of Prussian blue particles in a matrix of emerald green and Arabic gum.

[013]

## PIGMENTS FROM A PAINT BOX FROM THE ATELIER OF THE PORTUGUESE PAINTER OF THE EARLY TWENTIETH CENTURY, AURÉLIA DE SOUSA

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Painting materials can provide relevant information about the availability offered to artists within specific periods of time and particular geographical locations, contributing to understand painter's choices, preferences and limitations. The nineteenth century was, by far, the moment where an unprecedented diversity on pigments and lakes occurred, due the discovery of new metals and the huge advances on inorganic chemistry and on the synthesis of artificial dyestuffs.

A painting box containing 36 oil tubes was recovered by the family of the Portuguese painter, Aurélia (1866-1922) atelier, at Quinta da China, Porto. The atelier was shared with her sister, Sofia de Sousa (1870-1960), who ceased painting when Aurélia died. They both studied at the Academia Portuense de Belas Artes, at Porto and later, at the turnover of the 19th century, at the Academie Julian, in Paris.

It was intended to identify the inorganic constituents of the paints, namely pigments, fillers, extenders and lake substrates, through SEM-EDS, in order to know the painting materials actually used in Portugal, in general, and, in particular, to complement the knowledge of Aurelia's palette previously determined through the study of her paintings.

The cardboard painting box has an embossed lid with the Lefranc & Cia mark as used from 1880 onwards [1] and on its interior contains oil colours, mainly from this well-known artist's materials supplier and from two others: Winsor & Newton and Talens & Son. Characterization of particular tube features and labels revealed that some were produced after 1912 while others, possibly, after 1910, corresponding to the last decade of Aurelia's life. The majority of inorganic colours of the painting box have been found on Aurélia's works, namely iron oxide pigments, lead white, Prussian blue, cobalt blue and chrome and cadmium pigments. Titanium white has not been found at the box neither on works while zinc white and vermilion are absent from the box but not from the paintings. Analysis to paint tubes revealed several adulterations made by the suppliers to imitate expensive colours based on cadmium, cobalt and antimony.

[1] CONSTANTIN, S., The Barbizon painters: a guide to their suppliers. *Studies in Conservation*, nº 46, 2001, p. 49-67

(014)

**DECORATIVE SURFACE FINISHES: BRONZING, PATINA-ANTIQUA, VERD-ANTIQUÉ IN NY FURNITURE 1810 – 1830: NEW-YORK WORKSHOPS PRACTICES 1810- 1830**

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In Europe during the late 18<sup>th</sup> century, neo-classical style had a great influence in architecture and furniture design. A large repertoire of forms were easily accessible through sources reference, such as publications and engravings. Excavated archeological bronze furniture from the first century A.D provided abundant examples of antique decorative elements with their oxidized surfaces. This furniture that reflected an archeological reference led furniture makers to replicate in their design the tonalities, colors and patinas of the deteriorated surfaces by means of artificial processes. A comparative study of samples taken from the decorative surfaces of furniture in the collection of the Metropolitan Museum of Art, as well as in diverse private or American museums collections, led to a better understanding in workshops practices of the most influential cabinetmakers working in New York from 1810 to 1830.

The layering techniques were examined using reflected light microscopy. After extensive research it is now possible to draw conclusions about the methods in use. These methods always based on similar concept of superposition of pigmented paint layers and transparent resin coatings, embedded brass particles, or gold powder and glazing.

It also confirms great disparities and variations in the workshop practices.

The decorative faux bronze patinas, often lost due to their complex chemical composition deteriorated over time. Often disturbed and concealed by misguided restoration attempts, they can be observed relatively untouched in a few examples. These well preserved faux-bronze finishes are representative of specific verd-antique variations. It provides case studies from which benchmark examples can be compared to other furniture of the period, and can contribute to attribution to workshops.



[015]

**COLOUR AND FANTASY IN AN EIGHTEENTH CENTURY CEILING**

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The purpose of the presentation is to reveal a decorated wooden ceiling of an eighteenth century house in the southern village of Messejana, Portugal, where a variety of nautical and fantastic themes are presented in a narrow but effective palette of colours. The originality and variety of the decoration, where mermaids, several different types of ships and architectural elements mix together in a naïf but interesting composition is even more unusual if we consider that Messejana is a quite an interior village, where connections with the sea were scarce. Yet, this was an important land, still housing a significant set of civil and religious buildings.

This paper will try to disclose the story of the house - a property of Misericórdia of Messejana - and to recognize the social and economical context of the time when it was built, in Messejana and Southern Alentejo. It will try to establish some parallels for this curious ceiling decoration, comparing it to some other wooden ceilings of the same period; it also aims to introduce the colours and materials used in the composition, as well as understanding its iconography.

Finally, and to not focus only in the object itself, it will show a larger perspective on the use of colour and its meaning in architectural context.

[016]

## SHIMMERING COLOURS. COLOURED GLAZES ON SILVERING IN PORTUGUESE ALTARPIECES AND SCULPTURES

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Portuguese guilders alike their European counterparts had at their disposal a vast array of techniques when creating polychromy programs. Alongside with plain gilding and silvering, the use of coloured glazes over the metallic leaves was an artistic resource that could further embellish altarpieces and sculptures. Red, green and blue glazes could be used on gilded and silvered surfaces, in drapery areas to mimic luxurious high gloss fabrics like silk satin. These coloured varnishes are also referred as appropriate for making faux precious gems, in historic art technical treatises [1].

In several of the objects under study, special care has been taken to apply the coloured glazes over silver leaf, while the rest of the surface is gilded and/or polychromed. Although this could be attributed to a cost-effective material management, there should also have been aesthetic reasons to this decision, since a different metallic base layer will result in different colours as is referred in the technical literature [2]. Among the colored glazes, the “gold varnish” presents a different purpose. As multiple references attest, this varnish was part of a specific technique to create a gilded appearance using silver leafs instead of gold, resulting in a much more inexpensive procedure, that still allowed for estofado techniques to be used [3]. There are multiple examples where this practice, silver leaf gilding, has been used in entire altarpieces. The presentation of several examples will draw attention to the implementation and development of these techniques in Portuguese altarpieces and sculptures, supported with the presentation of relevant results from the ongoing multi-analytical approach to case-studies, which should allow to a better understanding of their material nature.



Fig. 1 – Polychromed sculpture with a red glaze over silvered cap, St. John the Evangelist’s processional litter. Museu Rainha D. Leonor, Beja.

[1] E. Emmerling, M. Kühenthal, M. Richter (eds). *Lüsterfassungen Des Barock Und Rokoko - Coloured Glazes on Metal Leaf from the Baroque and Rococo Period*. München: Siegl, 2013.

[2] J. D. Portell, “Colored glazes on silver-gilded surfaces,” 1992, pp. 116–118.

[3] F. Pacheco, *Arte de la pintvra, sv antigvedad, y grandezas : descrivense los hombres eminentes que ha auido en ella, assi antiguos como modernos, del dibujo, y colorido, del pintar al temple, al olio, de la iluminacion, y estofado, del pintar al fresco, de las encarn.* En Sevilla : por Simon Faxardo, 1649.

[017]

## COLOURS AND COLOURANTS IN ILLUMINATED MANUSCRIPTS

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This paper will examine the evolution and expansion of the Western illuminator's palette during the Middle Ages and the Renaissance. The discussion of the increasing range of both colours and colourants will be based mainly on the cross-disciplinary study of approximately one hundred illuminated manuscripts from the Fitzwilliam Museum in Cambridge.

Art-historical, palaeographical and codicological analyses are being undertaken along with extensive technical examination with a range of non-invasive imaging and spectroscopic methods, as part of the MINIARE research project ([www.miniare.org](http://www.miniare.org)). The increased availability in recent years of non-invasive analytical methods is allowing more specificity in the identification of painting materials, supporting a more nuanced description of artists' palette. For example, one can now often distinguish between different categories of organic red dyes (plant- vs. insect-based), or between different types of verdigris, without the need for sampling. Much of the analytical instrumentation is portable, allowing for rapid in-situ surveys of entire collections which yields statistically more significant information.

Selected examples will be chosen to illustrate the main trends which have emerged from the cross-disciplinary study, as well as individual cases in which 'unusual' pigments and mixtures have been identified.

Left:  
MS 45-1980, fol. 87v  
France  
9th c.



Right:  
MS 300, fol. 70v  
France, Paris  
c. 1260-1270



Left:  
MS 6-1954, fol. 160v  
Italy, Siena  
c. 1446-1450



Right:  
Marlay Cutting It40  
Italy, Venice  
c. 1567-1572



[018]

**FROM THE PAINTED COLOUR TO THE DISCOVERED COLOUR**

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The bright colors characteristic of the paintings of ancient sepultures are the vivid symbol of the desire of men and women of the times to participate to the cycle of light, which defeats the dark of the night as the new life of the deceased would come back to the light after the darkness of the death. In the Etruscan region of Tuscany and upper Latium, many painted tombs were discovered in XVIII and XIX century, in Tarquinia, Cerveteri, Vulci (the famous François Tomb) as well as in Chiusi, where several tombs in the necropolis of Poggio Renzo show examples of relatively well preserved coloured paintings. However, in Archaeology the information about the painted colour is often substituted by the knowledge of the discovered colour, which is the result of the injuries of the time, sometimes made more dramatic, in the past, by the mistakes and negligence of the persons in charge of their conservation. The current methods of archaeometric analysis, however, are capable of giving information that could be correlated to the original colours used for some representations. One example is given by the red figures in the front room of the Tomb of the Monkey (Necropolis of Poggio Renzo, Chiusi (Siena) Italy) which appear as fuzzy red stains at naked eye, but became again readable when observed in the IR reflection band.

This communication deals with the reconstruction of the painted colour of the wall pictures of some of the tombs of the Poggio Renzo necropolis in Chiusi, starting from the information recovered from the discovered colours. Most of the tombs show decoration in just two colours, black (made of carbonaceous pigments) and red (ochres), sometimes the whites are present (made of calcium carbonate). In the Tomb of the Monkey, the vegetation and some details of the Monkey are painted in blue colour, which resulted made with Egyptian blue (an ancient calcium copper silicate synthetic pigment). The multispectral, infrared, and UV-visible fluorescence imaging techniques, supported by the results of X-Ray Fluorescence and Laboratory chemical analysis, allowed a complete reconstruction of the painted colours used by the unknown Etruscan artists who decorated the tombs of the Poggio Renzo necropolis.



Fig. 1 – Acquisition of colour information at the Tomb of the Monkey, in Chiusi.

**(PLENARY LECTURER 2)****LIGHT AND COLOUR: FROM THEORY TO PRACTICE! EIGHT YEARS OF INQUIETUDE AND FINDINGS (2007 – 2015)**

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We address concerns and dramas of Light and Colour (which still intrigue us): the chromatic pollution derived from the excessive use of glaring white; the forgetfulness that architecture had colour and that ornament was not a crime; the importance of colour as a matter - with its interplay between gloss and matte surfaces- which (con) forms the space; the necessary realization that the night is not the day, the lights are not all the same and that less light is better than too much light. We describe the research works and the pedagogical effort concerning the subject of light and colour in the Faculty of Architecture, throughout the ArchC-3D research group's activity and the MEDCROMA module of the CIAUD-FA Colour Lab, presenting both the in-depth research projects and the applied research, already developed and on going.

We want to reinforce the critical need to move from theory to praxis, discussing participatory urban projects where the colour issues played a major role. To this goal we present projects of urban requalification in which we were involved: “Green Quarter”, or Bairro das Alagoas, Régua; Rua das Mães de Água / Alto do Zambujal, Amadora; Bairro das Descobertas / Bairro do FFH, Moita; and Bairro das Amendoeiras, Marvila, Lisbon.

We also present conservation, restoration and rehabilitation projects with special emphasis on the issues of light and colour, like the interventions in heritage sites as Palácio de Queluz, Terreiro do Paço and in the Arch of Rua Augusta, in Lisbon; the restoration of Colégio de Jesus, in Coimbra; and the conservation of Chafariz dos Canos, in Torres Vedras; as well as the requalification of hospital spaces I for the Centro Hospitalar de Leiria.

Finally we describe some collaborations with some architectural offices, namely with Atelier da Baixa; Atelier LGLS; Atelier CVDB and Atelier José Neves, where we could test the findings of our continuous research from the design process to the working site.

We believe that the only way to study, teach, and operate in this field of knowledge is throughout this circular path from theory to practice.



Technical photography  
Mural paintings at the Charola of the  
Convento de Cristo em Tomar  
16th century mural paintings (secco technique)  
Case study of Projet PRIM'ART

# DAY 2

[oral communication]

**(PLENARY LECTURER 3)****THE USE OF BLACK PIGMENTS IN THE DECORATION OF ARCHITECTURAL SURFACES IN NORTH WESTERN ITALY. A COMPARISON OF DIFFERENT CASES STUDY**

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In many different periods the decoration of historic architectural surfaces has been influenced by the use of black pigments. In mural paintings (made with fresco technics, mezzo fresco or temper), in sgraffiti and in smooth external plasters, the use of black pigments contributed to connote paints and surface decorations according to the taste of different historical-artistic periods, sometimes even determining the quality of the job and the final result.

This contribution makes reference to previous studies on black pigments used for the same purposes and it focuses the attention, particularly:

- on the nature of black pigments widely used for the architectural surfaces taken as example,
- on the employment of the black in structuring perspective effects, chiaroscuro effects or simulation of space depth on flat surfaces.

This study analyzed many paintings of artistic interest located in the north western Italy, and got analytical and instrumental data. This allowed the research group to delineate a way of critical interpretation, which is open to further developments and analyses of research.

[019]

## THE “HIDDEN EVIDENCE”: COLOUR IN MODERN ITALIAN ARCHITECTURE FROM CONTEMPORARY JOURNAL LEAFING THROUGH

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Despite the black and white appearance of Modern architectures, passed on by contemporary pictures, as put in evidence by Bruno Reichlin [1], colours marked their early stages. Such a circumstance is emerging with force in recent years, due to the increasing attention paid to listed Modern architectures preservation, introducing in Modern contexts the application of common investigation methods used in ancient buildings, mainly stratigraphy of painting coats.

However, this is just a “hidden evidence”: when leafing through the first issues of the most famous contemporary Italian journals of architecture, as Casabella and Domus are, dating the late ‘20thies, colour description is often part of the black and white pictures captions. Such an evidence reminds “The Purloined Letter” by Edgar Allan Poe [2] left on the desk and, therefore, too visible to be considered the looked for one.

Having in mind such a fascinating reference, the research carried on is aimed in finding a path of knowledge through the pages of the early issues of contemporary journals, looking for visible, but forgotten, footprints, joining the description to the direct link to advertising material for facade and interior coloured paintings.

These new reading lens, as it is the case of the green spectacles worn by detective C. Auguste Dupin, allow finding the “hidden evidence” of colour in black and white picture, constituting the starting point of further investigation in the field of preservation of Modern architecture.

[1] Bruno Reichlin, L’uso del colore nell’architettura del XX secolo. Una griglia di lettura in funzione della salvaguardia, in Giacinta Jean, La conservazione delle policromie nell’architettura del XX secolo | Conservation of colour in 20th Century architecture, SUPSI, Lugano (CH) and Nardini Editore, Florence (I), 2014.

[2] Edgar Allan Poe, The Purloined Letter, Carey & Hart, Philadelphia (US), 1844.

(020)

**COLOURS OF ALGARVE EXTERIOR STUCCO ORNAMENTS**

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This paper will discuss preliminary results of an ongoing research , which aims to address the lack of knowledge concerning traditional exterior stucco and other architectonic surfaces (traditional techniques of lime coating mortars and renders, such as fresco paintings with simulation of stone patterns and sgraffito) present in the Algarve region, in Southern of Portugal, which represent an important heritage value of the regions vernacular architecture.

This study, of the chromatic aspects of traditional architectural surfaces, has been most important to the aesthetic interpretation of these building coatings and reinforces the concept that colour is dependent of architectural design and facade building composition.

This research has contributed to the understanding of the praxis of techniques and materials used in making these coatings, giving us the possibility to understand the influence of the craftsmen expertise and their building owners.

The progression of this research has been supported by the development of a comprehensive survey, indexed on a geo-referenced database platform. At the present time this survey as identified 2510 buildings of 35 historic centers, which are distributed across the 16 municipalities of Algarve region.

In this survey a set of classification categories was considered in order to allow the interpretation of the key factors of building colour (inherent color and perceived color, physical and visual texture, brightness level, hue harmony, harmony saturation and value of harmony). This paper presents and discusses some preliminary results of this survey.

The analysis of these preliminary results allow us to considerer that the chromatic perception of traditional architectural coatings should be considered in the context of architectural design and building, specifically in esthetical composition of building facades. These preliminary results also confirmed that the defined classification categories of the survey are suitable for the interpretation of colour perception on facade building coatings. This study also contributes to access and classify some of the chromatic identity proprieties of traditional architectural coatings of the Algarve region.



Fig.1, 2 and 3 - Some examples in the Algarve region (Olhão, Tunes and Moncarapacho).

[1] PhD research in Architecture, Conservation and Restoration, olded by Faculty of Architecture of Lisbon University entitle “Conservation of architectural surfaces of the Algarve region: The ornaments in relief and mass work”, with the supervision of Prof. João Pernão, Prof. José Aguiar and Prof. Miguel Reimão Costa. FCT (SFRH / BD / 88732/2012).

[021]

## TECHNICAL EXAMINATION OF POLYCHROMY OF ST REINHOLD ALTARPIECE FROM NATIONAL MUSEUM IN WARSAW

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The original optical aspect of historical paint layers is one of the main concerns of most restoration projects that deal with polychromy treatment. The aim of modern conservation procedures is to keep what is preserved, not to return to the original chromatic effect. Aging processes cause advanced changes in paint layers, modifying its hue, opaqueness and lightness. Therefore, our perception of old masters' techniques is hugely influenced by materials' state of preservation.

In this study we present the results of an interdisciplinary collaboration project between Nicolai Copernicus University of Toruń and the National Museum of Warsaw. A technical examination of polychromy was performed in order to define layered structures and colour effects used by Antwerp workshops. Paint samples reproducing original brilliance of gold and colours were created for selected areas of the medieval altarpiece, produced by XVI century members of Antwerp Guild of St Luke.

A technical examination of the altarpiece was performed to identify the composition and layering of polychromy. The aim was to establish which pigments, natural dyes and binding mediums were used, as well as, to evaluate the coarseness and shape of pigment particles (the amount of grinding time) and the rate of intended transparency. Test samples were prepared in accordance with the results of the technical examination and used as a visual reference for defining approximate original colour effects.

We demonstrate a detailed description and documentation of colouring materials and optical effect of paint, typical for XVI century Antwerp studio practices. The results were combined into a digital simulation of the original colour brilliancy, displaying the detailed imaging of the selection of painted panels and polychrome sculptures. This simulation also aims to improve the understanding of the original aesthetics of Antwerp masters' works of art from the late Middle Ages period.

**(022)****TRACKING OLD AND NEW COLOURS: TECHNICAL AND MATERIAL STUDY OF JOSÉ DE ESCOVAR WORKSHOP - MURAL PAINTINGS FROM THE ÉVORA CATHEDRAL**

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This paper describes a study carried out on late 16th century mural paintings from Évora Cathedral, one of the prominent monuments that has influenced the culture, history and urban fabric of Évora (Portugal). Arranged in five panels, these paintings were laid out to decorate the vault of the cathedral's northern chapel and are artistically attributed to the Portuguese artist José de Escovar, whose painting workshop has been remarkably active in Alentejo (the southern-central part of Portugal) at the time. As the mural paintings in question are yet to be systematically investigated to date, this study aims to reconstruct their life story through a materials science perspective by focusing on their execution techniques (stratigraphy, binders, etc.), pigment characterization and later alterations that they are likely to have undergone.

The investigation was carried out through a multi analytical methodology that consisted of both in-situ and laboratory work. The in-situ and non-invasive examination was carried out through a setup consisting of technical photography in visible (Vis), racking (Vis-RAK), Infrared (IR), Ultraviolet reflectance and visible induced fluorescence (UVR and UVF) ; visible spectrophotometry and portable X-ray fluorescence (EDXRF). Further detailed investigation of collected samples was undertaken in the laboratory with an analytical setup comprising dark field optical microscopy (OM), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), micro X-ray diffraction ( $\mu$ -XRD) and micro Fourier transform infrared spectroscopy ( $\mu$ -FT-IR). The preliminary results point out that, the paintings were mainly executed with a fresco technique, using a chromatic palette consisting of red and yellow ochre's, cinnabar and copper green pigments. Finger nails to control the right moment to start painting are clearly seen by racking light. The analytical setup, in situ and in vitro, also allowed to identify several later mimetic retouches with earth pigments and extensive repaints in the sky backgrounds with white zinc, white lead and Prussian blue. Another discovery was in the lime stuccos that frame the paintings. Analysis of cross sections revealed that the first decorative campaign of these stuccos was made with a gold and silver alloy which have been later covered with layers of lead white, white zinc and lead-chrome yellow.

**Acknowledgement**

The present research is a part of an ARMCHAT ERASMUS MUNDUS MASTER thesis. The authors acknowledge Sr. Cónego Eduardo Pereira da Silva from the Diocese de Évora and DRCAleat for allowing this study; Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPHTypology 4.1, co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP).

[023]

## AN EXERCISE IN FUGITIVITY: INVESTIGATING THE FADING OF RED LAKE PIGMENTS

Daniela R. Leonard

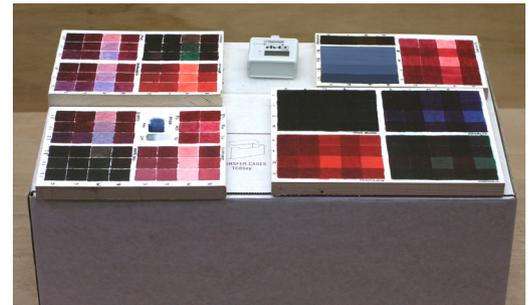
The Art Institute of Chicago, 111 S. Michigan Ave., Chicago, IL 60603, USA

Fading and other light-induced damage of paint is of interest to conservators because the most basic act of displaying an artwork can result in alterations to the original composition. An artist's choice of materials and painting technique are integrally linked to the lightfastness of a composition. In 2009, a third-year student project at the Hamilton Kerr Institute, University of Cambridge was undertaken to investigate the initial visual appearance, handling, and effects of light on a selection of red lake pigments (brazilwood, cochineal, lac lake and madder) made from traditional recipes and used in simplified paint systems based on real paintings [1].

Experiments by Johnston-Feller, Saunders and Kirby, and van Eikema Hommes were the primary sources for the design of this project [2]. These and other investigations have tended to focus on the fading of organic pigments in isolation or in mixtures with white paints. This project aimed to expand on the work of others by comparing red lakes used in overlapping layers and in mixtures with a wider variety of inorganic pigments (Figure 1). In conjunction, one sample set was created by more closely mimicking the material and layer structure of a late 17th century painting, Godfried Schalcken's *Self Portrait* from the Fitzwilliam Museum, based on scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) and visual analysis of cross-sections, as well as on color readings taken from the surface of the painting with a Minolta CR-221 colorimeter.

Final results for this study will be presented as part of a discussion of the considerations and concessions involved in the design of the setup, the benefits and limitations of using reconstructions to investigate the complex degradation processes that occur in paintings, as well as the uncertainties involved with the comparison of paint systems that contain a range of pigments with diverse characteristics.

Figure 1. Samples placed in a light box for artificial aging.



[1] D. Leonard, *In Artists' Footsteps: the reconstruction of pigments and paintings*, 2012, 141-149.

[2] R. Johnston-Feller, *Journal of the American Institute of Conservation* 23, 1984, 114-129; D. Saunders, J. Kirby, *National Gallery Technical Bulletin* 15, 1994, 79-97; M. van Eikema Hommes, *Changing Pictures: discoloration in 15th-17th century oil paintings*, 2004.

**(024)****UNDERSTANDING THE (IN)STABILITY OF SEMICONDUCTING PIGMENTS VIA ELECTROCHEMISTRY**

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Several artists' pigments are semiconductors. Examples of such colorful materials are the ancient pigments vermilion ( $\alpha$ -HgS), orpiment ( $As_2S_3$ ) or mosaic gold ( $SnS_2$ ), and the modern pigments cadmium yellow (CdS), cadmium red (CdSe) or titanium dioxide white ( $TiO_2$ ). Some of these materials appear stable over time, whereas others already show remarkable signs of degradation after limited time periods, sometimes triggered by physical or chemical parameters. In this study, the stability of semiconductor pigments is thermodynamically predicted, based on literature data. A starting approach to predict the photostability of semiconductor pigments, is based on thermodynamics. Gerischer [1] already introduced the concept of thermodynamic oxidation and reduction potentials of the semiconductor ( $\phi_{ox}$  and  $\phi_{red}$ ). For several pigment-related materials, the thermodynamic oxidation and reduction potential ( $\phi_{ox}$  and  $\phi_{red}$ ) were determined and evaluated considering the absolute energy positions of the valence and conduction band edges and the water redox potentials. The positions of  $\phi_{ox}$  and  $\phi_{red}$  can be used in a fast screening of the stability of semiconductor pigments towards photoinduced degradation in an aqueous/humid environment. This theoretical approach can be used as a fast and easy screening, and corresponds well to experimental data describing pigment permanence and degradation phenomena. Apart from studying degradation products, a new electrochemical approach is developed for the real-time monitoring of pigment degradation processes and the prediction of (environmental) harmful conditions. In the cell, environmental conditions are mimicked by irradiating the electrode with light of different wavelengths and intensity, while exposing the pigment to an electrolyte compound present in the atmosphere (e.g., an organic acid, water-soluble salts present in airborne particles, etc.). By applying an appropriate electrochemical method such as amperometry or linear sweep voltammetry, details on the degradation process can be gathered in a fast way by providing information on the changes in photocurrent intensity or in the oxidation state of the metal ions present. This work discusses how the sensitivity towards environmental parameters can be estimated for sulfide semiconductor pigments. Experimental results for CdS and  $\alpha$ -HgS are discussed.

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(025)

## MEASURING DEGRADATION: THE EVALUATION OF COLOUR CHANGE IN OBJECTS WITH SPECTROPHOTOMETRY

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Colour change of an object signifies degradation. Spectrophotometry now enables institutions to assign colour and its characteristics—hue, lightness and saturation—quantitative values, with delta E representing the overall colour change. This research focuses on acceptable colour change of objects on display and assesses how different environments, and institutional environmental policies, are helping prevent or contribute to overall colour change of objects. Three collections in three environments were utilised and measured by a Konica Minolta 2600d spectrophotometer: the Lady Douie reference watercolours at the Sherardian Library in Plant Sciences at the University of Oxford, two Eastern works of art on paper on short-term display at the Ashmolean Museum and swatches of conservation materials (leather, textiles, parchment and paper) in the wet room of the Book and Paper Conservation Laboratory at the Bodleian Libraries.

All objects were monitored for approximately four to six months. The Lady Douie watercolours were not accessed throughout the experiment and therefore had 0 lux exposure in an environment of 18-20°C and RH of 45-55%. However, several of the pigments measured had a value of delta E over 0.50, which was deemed as the cut-off for acceptable colour change for objects on short-term display. The change was attributed to the unspecified rag paper used for the watercolours and natural degradation of standard 20<sup>th</sup> century British watercolours. Attempts to stop the colour change included interleaving acid-free paper in between the pages to inhibit deterioration due to off-gassing. The two Eastern works of art on display at the Ashmolean were exposed to light levels of 50 lux, 18-20°C and 45-55% RH.

Although two areas had an overall colour change over 0.50, one was ascribed to the density of the pigment in the region, which did not align with the first measurement. Overall the colour change for the Ashmolean works of art was minimal and attributed to natural degradation of the pigments and binder, gum arabic, for the Asian works.

The third experiment focused on several different types of material used by conservators for treatment. A test board was exposed to working light conditions in the wet room of the Book and Paper Conservation laboratory at the Bodleian libraries. Light levels ranged from 430-550 lux, consistent for light levels for working conditions and a temperature range of 16-23°C. A control board was hidden from radiation. All control materials, except for alum-tawed calf, were well under the delta E value of 0.50. Nearly all the materials exposed to light exceeded the acceptable colour change limit. However, aerocotton made by the bindery and archival-quality paper were closer to the delta E value of 0.50, proving the significance of choosing archival-quality materials for conservation treatments. The research presented several collections with varying degrees of success in deterring colour change. Institutions should consistently monitor and measure their collections if possible, as a spectrophotometer can help create a reference database for objects that will be beneficial if tracking their degradation over time.

**(026)****CHANGES IN COLOUR OF SOME PIGMENT MIXTURES USED IN RESTORATION OF PAINTINGS****Elzbieta Szmit-Naud**

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Some pigments or mixtures of pigment used in historic palette are well known as not permanent or are suspected to change colour hue when aged. In the contemporary conservators-restorers palette, they are usually replaced by permanent substitutes, so one doesn't expect any undesirable change of colour of inpainting caused by used pigments.

Some changes like whitening, already remarked by Feller and Marconi 50 years ago<sup>1</sup>, can however still be observed in several retouched parts executed using available paints for retouchings.<sup>2</sup>

In addition some paint layers of inpaintings that contain pigments separately stable in ageing process could more or less change the hue, even when mixed in very stable binders. This paper present the results of examination and analysis done on some case studies in easel paintings and the study of colour changes of samples of paint layers induced by artificial ageing.

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[027]

## MULTI-TECHNICAL CHARACTERIZATION OF THE PICTORIAL PALETTE OF 16<sup>TH</sup> CENTURY FRESCOES FROM RIBEIRA SACRA (NW SPAIN)

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Ribeira Sacra, a region in the North-West of the Iberian Peninsula, is remarkable for its rich natural and cultural Heritage: its steep slopes and canyons are riddled with medieval monasteries and churches, many of which were decorated with wall paintings. By the end of the 16<sup>th</sup> century, these murals were covered with plaster or hidden behind altarpieces, due to a change in aesthetic taste and as a preventive measure facing epidemics, therefore remaining forgotten for centuries. A growing number of frescoes are being discovered and projects to study and preserve this unknown heritage have been launched recently. The present work aims to characterize for the first time the pictorial palette of the 16<sup>th</sup> century wall paintings of Ribeira Sacra, as this knowledge would be interesting both for research in Technical Art History and for future interventions of conservation. A multi-technical approach is proposed for the investigation of the pigments: technical photography (IR, UV, micro-photography) and non-invasive analysis by XRF and VIS-RS were performed on site. When necessary, micro-samples were taken carefully and studied in the laboratory by means of OM, SEM-EDS, MRS,  $\mu$ -XRD and HPLC-ESI-TOF.

The analytical results revealed a basic palette of natural earth pigments, lime white and several varieties of carbon black, the latter were distinguished considering the particle morphology by SEM and the presence of trace elements [1,2]. Flesh tones were painted with a mixture of red ochre and lime white, obtaining different shades by adding vermilion, yellow ochre or carbon black. "Optical blue" was identified in several murals, a mixture of carbon black and lime white that appears bluish to the naked eye, being a common resource for obtaining affordable blue tones [3]. The identification of certain pigments allowed dating some murals and later repaintings: lead-tin yellow, Prussian blue, synthetic ultramarine, titanium white... A chromatic enrichment of the palette is observed from the second half of the 16<sup>th</sup> century: azurite, smalt, malachite, verdigris and a purple dye were identified. Some of the pigments were found altered and the degradation causes and mechanisms were investigated. MRS proved that red lead had been transformed into plattnerite, a dark compound, as this pigment is known to be instable in alkaline environment, thus inadequate for fresco technique. In the church of Fión, the Virgin's mantle was discolored, and the analysis by  $\mu$ -XRD revealed the presence of paratacamite, a common degradation product of azurite in presence of water and chloride [4], which entered the building by water infiltrations from the roof.

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(028)

## PAINTING COLOURS: ORIGINAL VS OVERPAINT

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This abstract aims at the case study of the paintings of the main chapel's retable of Funchal's Cathedral in order to identify the overpainting layers from the original ones through the colours and the different technical characteristics and to understand the decisions taken regarding the material and iconographic alterations. In addition to layers of grime, coatings and materials from previous interventions, overpainting was a common practice during the 16<sup>th</sup> and the 18<sup>th</sup> centuries within the Portuguese context. These interventions, which were trusted to the church and nobility, were most of the time considered a noble activity [1].

The conservator must acknowledge the reasons for these alterations, as well as, their removal. In contemporary conservation, such decisions have no general rules on how to handle later additions and these must be considered case by case [2]. Most often the justification for the removal of an overpaint layer is to recover the painting as closer to its original state [3]. Furthermore, one has to take into consideration if these additions misrepresent and conceal the original 'reading' [4]. During the conservation and restoration intervention of the paintings of the main chapel's retable it was possible to identify different types of overpaint, total or partial application of colours layers, usually motivated by different stylistic trends or iconographic representation or by degradation of the paintings.

At first, conservators already suspected the existence of an overpaint layer in some paintings. Differences such as aesthetic and material characteristics were evident. A closer look showed differences in terms of colour, texture and quality. The composition of the paint layers, craquelure patterns and pigments obtained by scientific examination of microsamples together with x-ray radiography and infrared reflectography exams provided relevant information, crucial for the decision-making. Historical research on primary documental sources also provided important clues about the paintings previous interventions.

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[029]

## PORTUGUESE TIN-GLAZED EARTHENWARE FROM THE 17<sup>TH</sup> CENTURY: A SPECTROSCOPIC CHARACTERIZATION OF PIGMENTS, GLAZES AND PASTES OF THE THREE MAIN PRODUCTION CENTRES

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Sherds representative of the 17<sup>th</sup> century three main Portuguese faience production centres – Lisbon, Coimbra and Vila Nova were studied with the use of non-invasive spectroscopies, namely: micro-Raman, Ground State Diffuse Reflectance Absorption (GSDR), Fourier-Transform Infrared (FT-IR) and Proton Induced X-Ray (PIXE) or X-Ray Fluorescence Emission (XRF). X-Ray Diffraction (XRD) experiments were also performed.



Three plates representative of the 17<sup>th</sup> century Portuguese faience produced in (i) Lisbon - spiders, (ii) Coimbra – laces, and (iii) Vila Nova – armorial decoration, all from the 2<sup>nd</sup> half of the 17<sup>th</sup> century

The obtained results evidence a clear similarity in the pastes of the pottery produced at Vila Nova and some of the ceramic pastes from Lisbon, in accordance with documental sources that described the use of Lisbon clays by Vila Nova potters, at least since mid 17<sup>th</sup> century. Quartz and Gehlenite are the main components of these Lisbon's pastes, but other different ceramic pastes were also detected pointing to the use of different clay sources. The spectroscopic trend exhibited in Coimbra's pottery is remarkably different, Quartz and Diopside being the two major components of these pastes, enabling one to well define a pattern for these ceramic bodies.

The blue pigment from the Lisbon samples is a cobalt oxide that exists in the silicate glassy matrix allowing the formation of detectable cobalt silicate microcrystals in most productions of the second half of the 17<sup>th</sup> century. A less clear micro-Raman cobalt blue signature was detected in the Vila Nova and Coimbra blue glazes, in accordance with lower kiln temperatures in these two production centres, the Co<sup>2+</sup> ions being dispersed in the silicate matrix [1-3]. In all cases the white glaze was obtained with the use of tin oxide. Hausmannite was detected as the manganese oxide mineral used to produce the purple glaze (wine colour or “vinoso”) in Lisbon.

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(030)

## JOSÉ DE ESCOVAR AT CAPELA DAS ALMAS: BETWEEN THE CONTRACT AND THE WORK

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José de Escovar was one of the most productive painters of the fresco technique in the transition between the 16<sup>th</sup> and the 17<sup>th</sup> centuries [1]. A large number of works in Alentejo, particularly, situated around the city of Évora, has been attributed to him. Nevertheless, this attribution has mainly been based on the comparison of the stylistic work, since most of the documentation has not survived [1]. The case of the Capela das Almas (Chapel of Souls), located in the parish church of Vila Nova da Baronia, Alentejo, is particular interesting since the contract for the work, established between the master from Évora, José de Escovar, and the brotherhood of Almas judge is well documented. The work done by Escovar included not only mural paintings but also in wood and gilding of the altarpiece. The fresco technique was used for the walls while oil technique was chosen for the altarpiece. The possibility of comparing different techniques by the same artist, and especially to document the use of oil painting by Escovar, is an unique opportunity to better define the artist's know how. The analytical setup has comprised in situ technical photography (Vis, raking light, IR and UV), digital microscopy and portable X-ray fluorescence spectrometry. Microsampling was done in order to compare painting details in similar figures, the pigments and binders used with techniques as scanning electron microscopy with X ray microanalysis coupled, micro Raman spectroscopy and micro Fourier transform infrared spectroscopy.

### Acknowledgement

The authors acknowledge Sr. Padre Paulo Godinho Reis and Diocese de Beja for allowing this study; Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program.

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[031]

**THE COLOUR OF THE GRANITE THAT BUILT THE CITY OF SÃO PAULO, BRAZIL**

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The city of São Paulo, until the 1900s, was restricted to a small nucleus downtown, also called historic triangle, which concentrated the oldest monuments and buildings of the city. They are built with a few ornamental stones but one was the most important: Itaquera Granite. It is a biotite monzogranite, pale gray, with a slightly oriented structure and inequigranular texture, with variable size, giving the rock a heterogeneous and anisotropic aspect. Currently, it is not explored anymore but its exploration dates back to 1888 [1]. It was replaced by the Gray Mauá Granite after the 1940s, either because the Itaquera Granite quarry was exhausted, or due to better technological characteristics of the Mauá Granite [2].

There are numerous examples of cultural heritage monuments and buildings made with the Itaquera Granite in the city of São Paulo. The ones selected for this study were: the church of Santo Antonio (Saint Anthony Church) (1899-1919 - present façade), A Menina e o Bezerro (The Girl and the Calf) (1911-1913), Nostalgia (1920), Faculdade de Direito (Faculty of Law) of University of São Paulo (1934), Depois do Banho (After the Bath) (1941) and Índio Caçador (Indian Hunter) (1940).

The purpose of this paper is to characterize the Itaquera Granite according to its colourimetric aspects and its colour variation in a range of five years by using a spectrophotometer.

Colourimetric changes in the stone can be caused by many factors, such as cleaning methods, deposition of atmospheric pollutants, biological colonization, leaching of bronze, dissolution and reprecipitation of mortar, or even by natural causes such as the oxidation or alteration of minerals present in the stone.

Measuring the change in color can be useful to monitor the evolution of natural changes, analyze the effectiveness of treatments with repellents and consolidants, and monitor the installation of biological colonization in the monuments. In the long run, these data may aid in the treatment and restoration of these monuments.

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032]

## DARKENING OF LEAD BASED PIGMENTS: THE MICROBIOLOGICAL CONTRIBUTION

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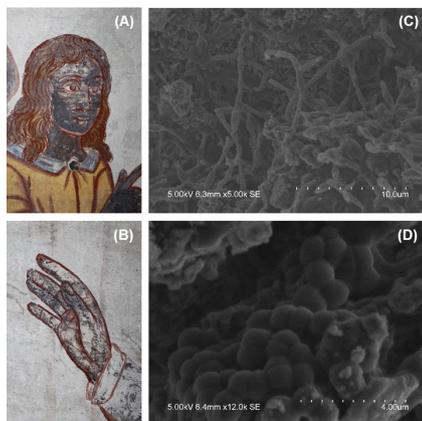
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Santa Clara church (Arraiolos, Southern Portugal), one of the Mannerist exemplars of the region, evidenced by the classic simplicity of the late-sixteenth-century, classified as Monument of Public Interest in 2001, has a set of mural paintings date from 18th century covering the vault, presenting a wide range of religious scenes. Unfortunately, these paintings have suffered degradation/deterioration due to darkening process of some figures represented and salt efflorescences appearance. These alterations affect mainly carnations areas like faces, arms, hands and feet, where it was possible to observe black spots covering particular areas, or, in some cases affecting a broad region. Therefore, it is crucial to identify the phenomena that induced these alterations in the mural paintings, in order to give useful information for a possible intervention-restoration process to avoid the dissemination of the problem.

To find answers for this problem, a set of multidisciplinary methodologies were applied, enabling microbiota identification, products alteration and materials characterisation [1].

The results revealed the presence of plattnerite ( $PbO_2$ ) on darkened areas, where concomitantly was detected high contamination levels, particularly by fungi of the genus *Penicillium*, which seem to be related with the chromatic alteration detected, probably induced by their metabolic activity and excretion products [2, 3].



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[033]

## UV STABILITY OF ULTRAMARINE BLUE PIGMENT IN SYNTHETIC PAINT COLORS: A PRELIMINARY, MULTI-ANALYTICAL STUDY

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A comprehensive study about the stability after different periods of exposure to UV light of synthetic ultramarine blue pigment (Color Index name: PB 29) mixed with two different types of synthetic binders (acrylic and alkyd) widely used in modern and contemporary art has been carried out. For this purpose a multi-analytical approach based on color measurements, Raman spectroscopy, FTIR-ATR, and SEM-EDX has been applied.

Based on sodium alumina-silicate sulfate with the empirical formula ( $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$ ), ultramarine blue is characterized by a sodalite framework where  $\text{S}_3^-$  radical anions are mainly responsible for the blue color of the pigment while  $\text{S}_2^-$  radical anions represent the yellow chromophores. Some indications of the low stability to UV light of the ultramarine blue pigment when mixed with synthetic binding media have been obtained in UV ageing studies of modern paints [1, 2].

For this study, several mock-ups were carefully prepared by mixing pure ultramarine blue pigment with each type of binder, for example acrylic (Plextol® D498, Kremer Pigmente GmbH & Co. KG, Germany), in a mixing ratio of 1:3 and prepared on glass slides obtaining a film thickness of approximately 30-40  $\mu\text{m}$ . Commercial acrylic ultramarine blue paints from four different companies (Liquitex®, Lukas®, Lascaux®, and Rembrandt®) and alkyd from Winsor & Newton® were also considered. The prepared mock-ups were allowed to dry at room temperature and then aged for 31 and 83 days in the UVACUBE SOL 2/400F chamber (Dr. Hönle GmbH UV-Technology, Germany), which provides radiation with wavelengths between 295 and 4000 nm.

After UV ageing, Raman measurements recorded a decrease of the ratio of  $\text{S}_3^-$  and  $\text{S}_2^-$  radical anions in some of the mock-up samples as well as in some commercial blue paints while an increase of the  $\text{S}_3^-/\text{S}_2^-$  was observed in other specimens, indicating a variation of the content of  $\text{S}_3^-$  and  $\text{S}_2^-$  chromophores in the sodalite cage. Additionally, a color change was determined by color measurements showing a shift in the  $a^*$  (redness/greenness) and  $b^*$  (yellowness/blueness) values of the aged samples. An increase in  $L^*$  (lightness/darkness) value of some commercial blue paints was also determined by color measurements, corresponding to a brightening of the samples. On cross-sections of the mock-ups SEM-EDX analyses displayed the formation of cracks through the aged paint film as well as the agglomeration of the ultramarine blue pigment particles on the surface in contrast to the unaged samples. On the other hand the infrared bands of the blue ultramarine detected by FTIR-ATR remained unchanged after UV exposure.

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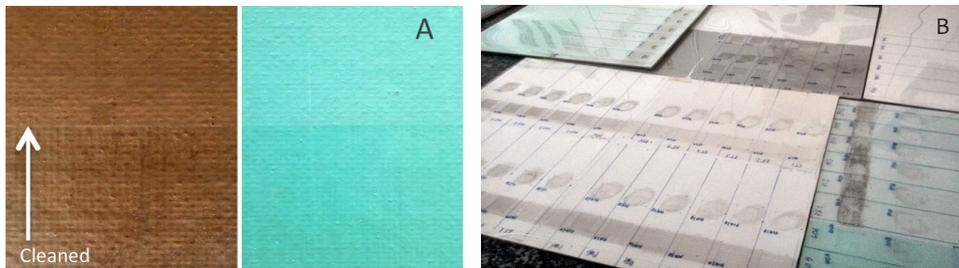
0341

## COLOR CHANGE INDUCED BY DRY CLEANING PROCESS ON PAINTED SURFACES

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In the last few years, dry cleaning process has become a remarkable alternative to solvent or aqueous mixtures in the cleaning of painted surfaces, which allows preventing the soiling of the dirt and its diffusion into the painting structure. The use of this kind of cleaning is especially valuable on contemporary paintings [1] given that it prevents the soiling of some additives such as surfactants contained in polymeric dispersions (e.g. in acrylic and PVAc based paintings).

In addition to some side effects reported that could be caused by dry cleaning process, such changes in the integrity of the paints [2] or the residual materials that could be left on the painting [3] one parameter that should be tested is the colorimetric change experienced on treated surfaces. In some cases, the use of certain dry cleaning materials can increase the gloss of the painted surface, particularly on matte or semi-matte ones [fig. A]. This effect translates into an increase of the saturation and subsequently in a color change of the area treated, especially on dark shades. This contribution evaluates the colorimetric variation of different kinds of painted surfaces induced by dry cleaning process, such as acrylic, gouache, oil-casein and PVAc [fig. B]. The cleaning materials tested include different kinds of sponges, cloths, malleable materials and erasers used in the field of Conservation-Restoration of Heritage. The change in color is measured by the use of a spectrophotometer and the chromatic values processed in a spreadsheet. The colorimetric changes have been calculated by the advanced equation recommended by CIEDE2000 [4] and the chromatic values obtained have been studied following the standard international recommendations [5].



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[035]

## AN UNUSUAL MURAL PAINTING AT THE CHAROLA OF THE CONVENT OF TOMAR (PARTI). TECHNICAL AND ANALYTICAL CHARACTERIZATION OF SIX PAINTED ANGELS

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This paper describes the analytical research conducted in six angels, with 4 x 1.30/40 meters long, holding instruments of the Passion of Christ that were painted in the 16th century in the outside wall of the central drum at the Rotunda of the Convent of Christ in Tomar. The angels painted in front of the triumphal arch, which are the most visible for the viewers entering the Rotunda from the Manueline church, are more refined and richly decorated than the ones in the opposite site, less noticeable from the ground floor. This fact was enhanced by the conservation team during the last conservation-restoration campaign held in 2013.

The analytical setup has comprised in situ technical photography (visible, Vis-raking and infrared) and spectroradiometry complemented with optical (OM) and variable pressure scanning electron microscopy (VP-SEM-EDS); micro-Raman; micro FT-IR spectrometry and pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS).

Results have shown that all the paintings were made directly on the carved limestone surface without the presence of renderings to level out and create a smooth surface to receive the painting. By racking light, the grooves left by cutting tools, the stonemasons' marks and all the irregularities of the rocky surface are clearly visible. All the paintings were produced with a secco technique following the same modus operandi and that the main differences between the six angels rely in the way the pigments were used. Similitudes in the pictorial materials and in the organic binders with the ones found in the easel paintings from the Rotunda are also emphasized.

### Acknowledgments

The authors wish to acknowledge the Consórcio Nova Conservação Lda; the the administration board of the Convent of Christ in Tomar and the Direção Geral do património Cultural ( DGPC) for allowing this study; the Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP).

[036]

## CHROMATIC ANALYSIS APPLIED TO HERITAGE ARCHITECTURE OF A LARGE TOWN: BARCELONA

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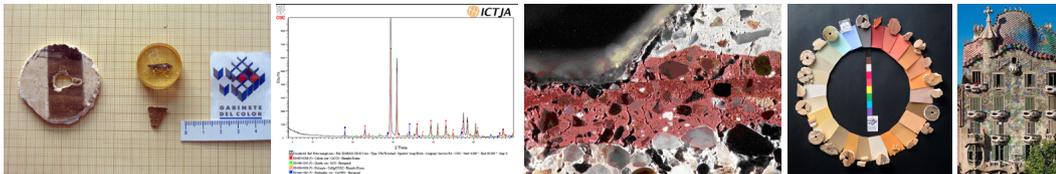
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This work is aimed at showing how the characterization of mortars and original pigments, together with documentary research and experience of the artisan, can serve to define the chromatic patterns and a palette of colours scientifically verified for urban historical center. This multidisciplinary research provides insight into the colour palette and the traditional techniques of painting and ancient coloured mortars of the historic buildings, in order to establish guidelines for restoration and recovery of chromatic and original techniques, as well as antique finishes. Based on the sampling of the façades to deduce the pigments used, several petrographic analyses have been conducted, through X-Ray Diffraction (XRD) as well as observation with optic microscopy (UV-OM) and Scanning Electron Microscopy (SEM/EDX), infrared spectroscopy (FTIR/FTIR-ATR) and gas chromatography (GC-MS). These analyses have then been related to the local construction techniques of each historical center to reach a definition of the façade coatings in each case, according to their colours and their constructive era.

This methodology, initiated more than 25 years ago by the “Gabinete del Color” of Barcelona, brings together the know-how of the classical architecture and restoration with the scientific analysis, resulting in the Colour Plans of several municipalities as Barcelona [1], Girona, Sevilla, Málaga [2], Melilla, Madrid [3], Toledo and other Spanish cities. In each case, all the façades of the historical centers have been inspected, mapped and pinpointed. Taking into account all these features, detailed studies have been performed on the different architectural styles of each era and its original finishes and colours, finally captured in a color chart and chromatic ordinances to restore the original image of the cities and historic centers studied. These chromatic studies performed prior to each restoration give support to curator and conservator works, they help in the conservation of cultural heritage and are also useful for advanced academic research.

### Acknowledgments

Authors are grateful to laboratory personnel from the Institute of Earth Sciences Jaume Almera belonging to the Spanish Council for Scientific Research, ICTJA/CSIC.



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[037]

## COLOUR SPECTROPHOTOMETRY AND HYPERSPECTRAL IMAGING TECHNIQUES TO DETERMINE THE SUITABLE GRAFFITI CLEANING PROCEDURE

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Nowadays, graffiti is one of the most common alteration forms of monuments, when they are applied as a vandalism action on monuments and historic façades. They are an aesthetic problem but also a serious threat to the conservation of built heritage. Cleaning can be expensive and furthermore in some cases, total removal cannot be achieved without damaging the rock substrate, e. g. roughness variations [1], whitening and yellowing [2], chemical and physical alterations of minerals [3]. Different procedures are used to remove graffiti, such as mechanical techniques (hydro pneumatic cleaning, low pressure water projection, low pressure water spray, etc.), chemical products (acids) and recently, laser application. It is well-known that sometimes the same cleaning procedure has different results attending to the stone and the deposits to be cleaned. Therefore, an analytical technique to in situ discriminate among the possible cleaning procedures for a particular case of study would be useful. This seems more difficult when the stone has polymineral nature. In this sense, granite was commonly used to build monuments and historic buildings in NW Spain and its inhomogeneous surface composed of quartz, feldspar, plagioclase and biotite crystals affects the assessment of cleaning degree.

The aim of this paper was to in situ evaluate the cleaning of red graffiti on granite by three different procedures: chemical (Wendrox®), mechanical (Hydrogommage®) and physical (using the third harmonic of a Nd:YVO<sub>4</sub> nanosecond laser). The cleaning methods' effectiveness was evaluated on the basis of graffiti extraction rate and damages on the surfaces. The granite surfaces were examined in situ by means of a hyperspectral imaging technique and colour measurements in CIELAB space. The measurements were applied after the cleaning interventions and they were compared with those from the original granite (from the quarry). These techniques were selected because they are non-destructive, on-line, fast and in situ monitoring. Based on the results, a recommendation was carried out to clean red graffiti on the studied granite. Finally, the results of this study contribute to develop a methodology to assess cleaning interventions applied on architectural surfaces.

Keywords: color spectrophotometry, hyperspectral imaging technique, graffiti, granite, cleaning stone.

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**(038)****HYPERSPECTRAL IMAGING ON THREE FRENCH MEDIEVAL ILLUMINATIONS OF THE XVI CENTURY (TREASURY OF BORDEAUX CATHEDRAL, FRANCE)**

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The Marcadé Collection (treasury of the cathedral of Bordeaux) includes forty one illuminations dated from the XIII to the XVI century. Among them, three French medieval illuminations, dated about 1530, never studied before, were a part of the same antiphonal book. Their iconographic and stylistic study, the conservation point of view and the analysis of their materials are discussed. Besides, hyperspectral imaging techniques (HSI) are applied to characterize the pigments.

HSI has proven to be a rapid and non-invasive technique, giving information on the entire image. This technique is used to give a preliminary approach of the materials of the paintings. The comparison of RGB and IRFC images of illuminations to those of reference (a color chart made according to medieval techniques) allows us to hypothesize about the pigments used. Then, the mapping of the repartition of the pigments used on the entire painting is obtained by comparison of the measured reflectance spectra with our database (150 medieval pigments). When, in certain zones, doubts remain, analyses were done by Raman or XRF spectroscopies.

The hyperspectral imaging system provided by SPECIM (Finland) works between 400 to 1000 nm. Spectro-imagery associates reflectance spectra with each pixel of the image and treats the received signal in various wavelengths. The characteristics of the spectral signal in VIS range are used to get rapidly an identification and localization (mapping) of the components (pigments) without sampling and in respect to these fragile artworks.

HSI allows us to identify the palette (more than fifteen pigments). Colours used in highlights are organic pigments as brazil wood lake, buckthorn “nerprun”, bucktooth “bourdaine” and indigo. For the inorganic pigments, azurite, red lead, cinnabar, yellow ochre, lead tin yellow, lead white, malachite, salt green and salts of copper were identified, ... The gilding is a shell gold technique. The palette used for these three illuminations is varied and typical of the XVI century in France and compared with the treatment of colours to Flemish or Italian illuminations of the same collection previously published.

[039]

**PRECISE REPRODUCTION OF COLOURS IN CULTURAL HERITAGE DIGITIZATION**

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Photography is nowadays the preferred method in digitizing cultural heritage materials for both flat and volumetric objects. The digitization process encompasses: shooting scene arrangements, image illumination, sensor and lens testing, camera settings, digital image processing, colour management and image post-processing. The aim of the image capturing workflow is to obtain a close digital representation of the original object. Two well-known guidelines are in use in cultural heritage: FADGI (Federal Agencies Digitization Guidelines Initiative) from the US [1] and Metamorfoze from the Netherlands [2]. They both provide measures to assess the quality of digital images and are mostly focused on optical image quality (i.e. sharpness, resolution, geometry, colour misregistration). Although they mention the importance of good colour management, images taken using the guidelines are not sufficient to achieve a high quality and precise reproduction of colours. Both FADGI and Metamorfoze uses delta E 2000 as a measure of colour quality. In the case of FADGI the best reproduction of colour quality is when the average colour difference in the image is lower than 3 and the maximum colour difference from a measured set of patches is lower than 6. In this paper we make a step-by-step investigation of the procedures and factors affecting the reproduction of colours in the digitizing cultural heritage materials workflow. Our aim is to describe and better understand the registration and transformation of colours in the digitization process and analyse what could be done in order to achieve as close a reproduction of colours as possible in a given environment.

In this research we take into account: shooting scene illumination, relative spectral power distribution; RAW to TIFF transformation, RGB to CIE L\*a\*b\* transformation; transformation from 12-bits or 14-bits to 16-bits per colour channel; standard colour spaces: AdobeRGB, ProPhoto, sRGB; custom ICC profile spaces etc.

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**(040)****COLOR ACCURATE PHOTOGRAPHY OF CROSS-SECTIONS OF PAINT SAMPLES AT THE RIJKSMUSEUM IN AMSTERDAM**

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The Rijksmuseum Amsterdam (The Netherlands) recently developed a web based paint sample database; one of the first in it's kind in the world. The museum aims to digitize all paint sample documentation currently on paper. And all existing embedded paint samples will be digitally photographed. The Rijksmuseum is one of the pioneering museums in the field of online, digital heritage (Rijks Studio, Rijksmuseum Open Data). The Image Department of the museum is currently developing color accurate photography of paintings and cultural objects. With the paint sample database project the Rijksmuseum saw an opportunity to color accurately photograph the museums' collection of cross-sections: it is considered vitally important that the museum maintains high standards of quality in every respect.

A team of photographers, a paintings conservator and a research scientist developed a userfriendly system to gain color accurate photographs of cross-sections, while maintaining the scientific integrity of the images. The embedded cross-sections are photographed under a research microscope with reflected light (bright field with crossed polarizing filters, dark field and ultraviolet fluorescence) at between 25x and 1000x magnification. The influence on the color quality of the images of the objective (e.g. magnification), exposure time and the type of reference color chart is taken into account. To our knowledge no other institution records its' cross-sections scientifically controlled and color accurately.

It is important to make use of color accurate images of cross-sections during research to improve consistency and to gain objective scientific results. The color of the image of a crosssection is influenced by several factors, like the source of light, filters, and the software of the microscope, e.g. the white balance. Color accurate photography makes it possible to compare pictures of different cross-sections even taken with different microscopes with different types of lamps. The standards for digital recording in the paint sample project will result in a system that can be easily adopted by other institutions. In this presentation we will talk about our experiences and share our (first) results in the field of true color digitization of cross-sections.

[041]

## COLOUR MANAGEMENT APPLIED TO PHOTOGRAPHIC DOCUMENTATION IN THE RESTORATION OF SCIENTIFIC COLLECTIONS: ANATOMICAL WAX MODELS

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Actually, the systematic use of digital devices as cameras and scanners for the capture of images requires our consideration about the use of instruments that provides us the guarantee consistency of colour throughout the restoration process. The incorporation of standard colour cards is essential to conserve the colour fidelity of what we are restoring. In the world of graphic arts and photography this point is also so critical. The colour management, the lighting with chromatic stability professional sources, the use of specific colour profiles and good photographic equipment, and the correct digital development of RAW archives, give us the accurate work flow and the objective reference of that we are recording.

This proposal shows the work done in connection with the award of two Research and Development I+D Projects to stablish the conservation and restoration methodologies focused to the formal and technical characteristics features of two wax anatomical models collections: one of human specimens and the other of animals, that complain and important historic and artistic heritage of the Complutense University of Madrid. At the time of its creation- 18<sup>th</sup>, 19<sup>th</sup> centuries –, this kind of artifacts were an authentic technical revolution, because they allowed a high fidelity and realism reproduction in wax of the anatomical texture and chromaticism of real specimens. Although this artisans, looked to maximize the accuracy of their figurative representations, the pass of time attached to inappropriate conditions of exhibition and the natural aging processes of constructive materials, have caused a significant aesthetic transformation that distances these objects to their original intentionality and function. The photographic record to document the execution techniques of each piece, its conservation and restoration processes, has supposed specific challenges in their photographic reproduction, because their surfaces had very different aspects as the result of their construction techniques, as shiny or matte finishes and impairments that distort subjacent original colours. We'll make a tour around the use of different light sources and the photographs obtained with them, and we'll show its results that have enabled to have a visual documentation essential for the conservation of this objects.

[042]

**COMPUTER MATCH PIGMENT SELECTION FOR CERAMIC GLAZE RESTORATION**

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This paper will report the practical implementation of computer match pigment selection (CMPS) for the restoration of ceramic glazes. During the reinstatement of missing glazes, metamerism is a common troublesome feature faced by conservators. Under certain lighting conditions, a mismatch occurs between the ceramic glaze colour and those areas in-filled using a pigmented polymer medium. This often results in a colour match which is imperceptible in the lighting of the conservation studio but very discordant in the different lighting set-ups used for museum display. Blue glazes most frequently give problems (Fig.1) but virtually invisible repairs can be achieved when metamerism is overcome (Fig.2).



Fig.1 A metameric pigment match (top left) for the Dutch blue tile design



Fig.2 Chinese blue & white bowl before (top) and after (bottom) conservation

Previous studies by the authors have demonstrated the potential of CMPS to provide non-metameric pigment combinations which match original glazes for all light sources [1]. In particular, the colour variations of blue designs and the neutral 'white' background of a range of ten Dutch tiles have been recorded and recipes selected by means of a unique computer database for non-metameric glaze colour matching [2]. Similarly, colour measurements and non-metameric pigment matches have been reported for blue and white Chinese ceramics [3].

In this paper, practical experiences of CMPS for implementation of visually optimal reinstatement of missing tile glazes with pigment/polymer recipes will be described and discussed. Particular attention will be given to the difficulty of colour measurement of small, non-planar areas of glaze colour and the formulation, by eye, of the computer-generated pigment percentages to produce a perfect colour match during conservation.

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[043]

## CHROMATIC ESSAY FOR CHARACTERIZATION OF LOSSES FOR THE CHROMATIC REINTEGRATION PROCESS OF CULTURAL HERITAGE

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The study presented here was conducted in the framework of the doctoral program in Cultural Heritage, specialization in Painting, which took place at the Catholic University of Portugal, with the theme of quality in chromatic reintegration. The aim of this study is to propose a system for the characterization of the losses in the pictorial surface, so that conservator-restorer can have access to qualitative and quantitative accurate information before, during and after the intervention. We used photographic images of a panel painting from the (XVI) century and a geographical information system software, used in the processing of spatial data, the QGIS open source program.

Keyword: characterization, losses, chromatic reintegration, GIS, QGIS.

[044]

## A NEW HYPERSPECTRAL IMAGER FOR STUDYING EGYPTIAN COFFINS

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The study of artworks' constitutive materials is essential, as it can reveal precious information about history, provenience and conservative condition, identifying original and superimposed materials. Exhibition lightening also is fundamental for enhancing the artworks' beauty: light interacts differently with different materials, thus the choice of the lamp can be crucial.

For identifying pictorial materials, the use of noninvasive techniques is always preferred: in particular, UV-Vis-NIR reflectance spectroscopy is a noninvasive punctual technique based on the selective light-absorption principle [1]. The obtained spectral information can represent a diagnostic tool, a colour measure suitable for monitoring chromatic variations [2], and a basis for colour rendering elaborations, useful for addressing illumination choices.



Fig. 1. Picture of the set during a hyperspectral video acquisition on Coffin of Hor (Egyptian Museum, Turin).

Besides reflectance spectroscopy, hyperspectral imaging techniques (HSI) are lately spreading [3]: they provide images combined with the spectral information of each pixel, with evident advantages if compared to punctual analyses. The National Institute of Metrological Research of Turin recently realized a new hyperspectral imager based on a Fabry-Perot interferometer, inserted in an optical set-up: while the optical path delay between the mirrors is varied, a sequence of images is recorded on a CCD camera. The spectrum for each pixel is then calculated using a Fourier transform-based algorithm and it is finally stored in a dataset called 'hyperspectral cube': a 3D matrix formed by a 2D image and the spectral composition of each pixel along the third dimension. The analysis is particularly quick because, differently by classical hyperspectral devices, it does not need any mechanical scanning system.

Thanks to a fruitful collaboration, we used this prototype at Centro Conservazione e Restauro La Venaria Reale for studying three Egyptian coffins coming from the Egyptian Museum of Turin. Once we acquired hyperspectral cubes on different regions of the coffins, we successfully validated hyperspectral data comparing them with spectra acquired by an Ocean Optics HR2000+ES spectrophotometer, so identifying the authorial Egyptian pigment palette. Moreover, we used those data for color rendering elaborations: here we present some images of the coffins, as they would appear under different kinds of illumination.

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[045]

**REFLECTOGRAPHIC ANALYSIS ON SOME PAINTINGS AT THE PINACOTECA OF ASCOLI PICENO**

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A series of diagnostic tests on some paintings preserved at the Pinacoteca of Ascoli Piceno have been performed. These analysis were made possible through the use of totally non-invasive devices, which can provide useful information in a complex and heterogeneous situation of studies currently conducted on Cultural Heritage. In particular, numerous investigations have been executed, as IR Reflectography and other types of analysis, including X-ray Fluorescence and infrared Thermography, to acquire new analytical data concerning: the identification of pigments and materials used, the detection of any products of alteration and degradation, the understanding of modus operandis of an artist, to making them available to scholars. The analysis performed on Crivelli's panels have confirmed previous investigations already made. Reading reflectograms however it is not easy to interpret, because of the strong correlation between underdrawings and painted surface. We detected that the paintings investigated were drawn with extreme precision in every detail. The dual use of, both brush and dry graphic medium, such as charcoal, is here confirmed, as it has already been found in numerous other works previously studied.

We were also able to make more clearly legible many details that otherwise appeared confused in the visible or almost completely lost in the naked eye.

We also made at the Pinacoteca new studies on some panels by Pietro Alemanno, Crivelli's pupil, to discover, by comparing certain details, the different pictorial construction by the two artists.

A further important data was obtained by analysis of X fluorescence . This survey is able to identify some chemical elements present in the color fields of painting, which allows us to trace the type of pigment used. Beside the already mentioned diagnosis techniques, we followed a further non invasive approach making use of the Hypercolorimetric Multispectral Imaging (HMI). This approach is based on the measurement of the spectral reflectance, evenly sampled every 100 nanometers, derived as an optimization of the standard colorimetry expanded to a wider spectral range (300-1000 nanometers) and to 7 linear matching functions. This system, allowing to record pixel by pixel an absolute spectral reflectance, was able to discover even little pigment variations (or similarities) not visible to the naked eye. The viewer of the system has been used also to integrate the other imaging analysis achieving large amount of data for the single pixel. This has been the basis for spectral and spatial statistical analysis and correlations to improve the identification of the pigments. The protection of cultural heritage has become the convergence point of different professionals: humanities (historians, architects, archaeologists), scientific (chemists, physicists, geologists, etc.), and operational (restorers, conservators). Therefore we want to give our contribution by providing our scientific expertise and innovative information for an ever deeper knowledge of a cultural heritage that belongs to us all and that it is our duty to preserve for future generations.

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## HYPERSPECTRAL IMAGING APPLIED TO THE STUDY OF PAINTINGS

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The spread of digital photographic cameras (predominantly of D SLR type) during the last decade has opened new possibilities to the investigators of work of arts, having now a tool not only to document the conservation state of a work of art but also to examine in the invisible spectrum (such as in Infrared or Ultraviolet) or to collect and analyze information in the visible spectrum in new ways [1]. This is the case of the present work, which presents some results obtained on building, calibrating and testing a system using a commercial digital camera (a Nikon D300 D SLR) that showed to be possible, entirely on the visible spectrum, to capture hyperspectral images composed of 28 bands, between 420 nm and 690 nm, in steps of 10 nm (22 bands are directly captured with the system and 6 are interpolated), a number of bands superior to many other multispectral and hyperspectral imaging systems built with more complex and expensive hardware.

Compared to a reference spectroradiometer (Photoresearch PR650) using a standard 24 color chart *ColorChecker X Rite*, the proposed system showed good results, indicating that it presents an accuracy good enough to many of the new and promising uses in hyperspectral imaging.

It showed average values for RMSE (Root Mean Square Error) of 3,4% and 99,3% for GFC (Goodness of Fit Coefficient); the colorimetric precision of the system presented values for color differences equations of 6,0968 units for  $\Delta E^*_{ab}$ , 3,8228 units for  $\Delta E^*_{94}$  and 3,6794 units for  $\Delta E^*_{00}$ ; the tested metameric indices showed values of 1,1457, 1,2410, 0,8078 and 0,7777 for illuminant pairs “D65,A” and “D65,F2”, all quantified in terms of color differences equations  $\Delta E^*_{ab}$  and  $\Delta E_{00}$ , respectively.

The possibility of capturing images in more bands than the traditional three channels color models (the RGB model, commonly used on digital camera’s sensors), opens new possibilities, because this type of data contains reflectance values (data independent of the type of illuminant) and in an higher number of wavelength bands. This type of data is more colour accurate than conventional photography and it is not susceptible to colours metamerism, a frequent problem with trichromatic reproduction systems [2].

With the present work we have shown some of the possible applications of hyperspectral imaging. In a practical case using a XVI Century painting (*Triptico de Pentecostes de Miragaia*, Porto) and a XX Century work of Art (*O Cabouqueiro*, by Julio Pomar) observing and analyzing individual isolated bands in certain wavelengths of the visible spectrum, allowed us to detect alterations in paintings, areas with repainting, reintegration, under drawings and other type of information, traditionally only possible to obtain using invisible radiation imagery. Using adequate software programs it was possible to virtually test the appearance of the work of art in different types of illuminants or light sources, preventing more time consuming experiences or, in both situations, avoiding submitting the work of art to unnecessary stress or more destructive radiations.

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[047]

## THE STUDY OF PIGMENTS BY DIFFUSIVE REFLECTANCE SPECTROSCOPY (DRS). APPLICATIONS TO RESTORATION AND FINE ARTS

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Use diffuse reflection spectroscopy (DRS) is one suitable radiation in the visible, near IR and UV (UV-VIS-NIR domain). Are analyzed the pigments who are put in work and those used in the operation for color retouching. It brings out the phenomenon of metamerism, phenomenon minimized under restoration and start point in arts.

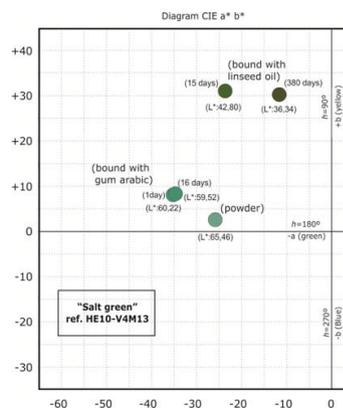
048)

## COLORIMETRIC MEASUREMENTS OF DIFFERENT VARIANTS OF VERDIGRIS: POWDER AND BOUND PIGMENTS

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There exists plenty of different recipes to prepare the historical pigment verdigris. Obviously, its composition is depending on the recipe and process for obtaining. All of them produce compounds derived from the corrosion of copper. The most important varieties are copper(II) acetate monohydrate and several copper(II) hydroxyacetates hydrated [1]. They are also significant the varieties consist of copper(II) hydroxychlorides mixed with other substances [2,3]. Obviously these diversity of compounds produce pigments with different colorimetric characteristics [4]. On the other hand, the type of medium used in applying it also affect these properties [5]. In this paper are presented the results corresponding to the colorimetric measurements of different varieties of verdigris obtained in our laboratory. All of them have been previously analyzed to identify its chemical composition. The relationship between the color of painting and the medium used have been also established. The varieties studied have been: neutral verdigris  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ , two types of basic verdigris  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$  and  $[\text{xCu}(\text{CH}_3\text{COO})_2 \cdot \text{yCu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$ , and "salt green", consists of copper(II) hydroxychlorides.

As an example of our results, in this figure are shown the colorimetric measurements corresponding to "salt green" obtained from recipe XXXVIII of Ms. Heraclius (10<sup>th</sup> - 13<sup>th</sup> C.). The sample studied is a mixture of atacamite and clinoatacamite. The powder pigment has a green color ( $h_{ab}^* = 175^\circ$ ) but this property changes attending to the medium used to be applied in pictorial layers. These changes are not significant when this pigment is bound with gum arabic ( $h_{ab}^* = 169^\circ$ ), however, they are very important when it is bound with linseed oil. Paint layer obtained with this last medium has a green-yellowish color. Moreover, in this case the drying time of the paint has a clear influence, after 15 days  $h_{ab}^* = 134^\circ$  and after 380 days  $h_{ab}^* = 119^\circ$ .



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## (PLENARY LECTURER 4)

**INNOVATIVE AND SUSTAINABLE TECHNICAL ART EXAMINATION  
AND COLOR DOCUMENTATION**

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(1) Cultural Heritage Science Open Source, Piazza Cantarella 11, Aci Sant'Antonio, Italy

Scientific examination and documentation of art is expensive. The most important and recognizable works of art from prestigious museums get extensive scientific studies, unfeasible for the vast majority of cultural heritage objects, existing in local communities since they lack comparable financial resources. Typically larger museums have budgets sufficient for scientific departments equipped with cutting-edge technologies. In contrast, small to medium sized cultural institutions have relatively limited access to the same science and technology.

Cultural Heritage Science Open Source (CHSOS) was launched in 2012 to bridge this technological divide, to develop and disseminate affordable and sustainable methodologies for art examination that can reach a much larger audience of cultural institutions. CHSOS disseminates methods for art examination in three significant ways, focusing specifically on the low-cost technical solutions: its popular blog, publications and training programs. The CHSOS blog has attracted a growing network of art conservation professionals interested in introducing Cultural Heritage Science concepts into their workflow.

CHSOS has developed and disseminated low-cost technical solutions for panoramic infrared reflectography [1], technical photography [2,3], reflectance transformation imaging [4] and reflectance spectroscopy [5]. This paper discusses the development of a low-cost multispectral imaging [6] system for art and archaeology realized thanks to the first ever crowdfunding project in art conservation science.

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[2] A. Cosentino "Identification of pigments by multispectral imaging a flowchart method" Heritage Science, 2:8, 2014.

[3] A. Cosentino "A practical guide to Panoramic Multispectral Imaging" e-conservation Magazine, 25, 2013, 64-73.

[4] A. Cosentino "Macro Photography for Reflectance Transformation Imaging: A Practical Guide to the Highlights Method" e-conservation Journal 1, 2013, 70-85.

[5] A. Cosentino "FORS spectral database of historical pigments in different binders" e-conservation Journal 2, 57-68, 2014.

[6] A. Cosentino "Multispectral imaging and the art expert" Spectroscopy Europe, 27 (2) 2015.



EDXRF analysis in loco  
Capela do Lourenço, Sé de Évora, Portugal  
16th mural painting (lime fresco?)  
Case study of PRIM'ART Project

# DAY 3

[oral communication]

**(PLENARY LECTURER 5)****ANALYTICAL ARCHAEOLOGY: TRENDS AND PROSPECTS**

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Archaeometry is the research area where methods from natural sciences are used to help research questions in archaeology or art history. On the other hand, these questions also inspire scientists to optimise and develop new techniques. This research field encompasses a broad field of expertise, including dating techniques, methods of visualisation, identification of materials, prospection techniques, conservation science, etc. Analytical archaeometry[1] is the sub-domain that evolves developing and optimising techniques for the analysis of objects and materials.

An important issue in analytical archaeometry is that people should try to maximise the amount of information that is obtained, while minimising the (risk on) damage on the artefact. A first approach to reach this goal, is to minimise the sample size by using sensitive analytical techniques. Moreover, if several complimentary non-destructive investigations can take place on the same sample, the information that is extracted from the object is maximised. This goal can also be achieved by using non-destructive analytical techniques that can be applied during in situ examinations. For these, sensitive mobile instrumentation should be used.

During this presentation, these approaches will be illustrated with several examples from daily lab life. Typically a research campaign might start with close examination with visual and UV light, eventually completed with high-resolution microscopy. In a second stage, analytical techniques are used for the analysis, and we typically focuss our investigations on the optimisation of Raman spectroscopy and different X-ray fluorescence (XRF) approaches, such as handheld XRF (hXRF), micro-XRF( $\mu$ XRF), and total-reflection XRF (TXRF).

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[049]

**LED MUSEUM LIGHTING: COLOUR QUALITY AND ARTWORK PRESERVATION**

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(2) ICOMOS Mural Painting Scientific Committee, Budapest, Hungary

The failure of the current CIE Colour Rendering Index (CRI) for modern (especially LED based) light sources has been demonstrated during the past decade. Experience has shown that the current CRI based ranking of a set of light sources containing white LED light sources contradicts the visual ranking. Various attempts have been made to clarify the possible reasons and to improve the CRI, but no internationally adoptable solution has been found. As the application area of LEDs significantly expanded, new criteria have been defined for LED lighting to be fulfilled.

The objects exhibited in museums are artworks from different art periods. As different materials were available during the different centuries of the history of art, different raw materials have been used for producing pigments. Artists of different epochs used different materials as pigments, which resulted in different reflection properties of the painted surface. This fact enables new challenges to the description of colour rendering of light sources by CIE Colour Rendering Index. The definition of colour quality in case of museum lighting needs special attention and carefully tailored light spectrum in case of paintings from different art periods. Pigments produced from minerals or organic components are sensitive against optical radiation in various extent.

Artists used different painting technologies (aquarelle, tempera, oil, secco, fresco) and different binding materials (gum Arabic, egg, glue, casein, linseed oil, lime), which resulted in different reflection properties of the surface and different sensitivity against optical radiation. Reflectance curves of pigments used with five different binding materials have been compared in order to reveal the possible differences caused by the different binding materials.

Based on the pigment sets, the optimization of light spectral power distribution was carried out with the help of two different mathematical algorithms. One is a modified version of the CIE colour rendering index (CRI) and the other is the corresponding colour colour rendering (CCCR). A set of LED spectra has been used as basic set and composite spectra have been optimized by changing the current values of the separate LED chains (meaning emissions at different wavelengths) in order to fulfil the criteria for important colorimetric parameters such as colour fidelity, CCT and duv.

Preservation of art is at least as important factor in museum lighting as the appearance of paintings. According to a recent DOE study, the majority (48%) of the museum community members prefer light sources with lower damage potential in first place. Improved colour quality is at the second place, while energy usage and maintenance, inconspicuous transition to state-of-the-art technology were at least half as much a concern than damage. In order to describe the damage potential of LED based light compared to traditional light sources and theoretical illuminants, another series of mathematical calculations were carried out. UPAN would like to find the barriers of optimization according to damage index and colour quality parameters, which will lead to a reasonable compromise between the achievable colour quality parameters of light and damage index of LED based museum lighting.

(050)

**IMPLEMENT LIGHTING POLICY FOR VULNERABLE ARTWORKS**

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Light exposure constitutes an important risk for cultural heritage collection items and identifying vulnerable colors on cultural property is of considerable importance for informing collection lighting decisions. In preventive conservation color change is often used as an indicator for light induced degradation: light sensitivity of a material is assessed by measuring its Dose-Response Function, in other words, by plotting the color change (in  $\Delta E$ ) induced on the material by increasing total exposure (in lux.hour). The traditional way to estimate light sensitivity of a given cultural item is to use results obtained by testing lab samples mimicking artwork material composition in accelerated light aging chambers [1]. However such method is not always reliable: first of all, it is challenging to visually assess material composition of an item; in addition, sample lab surface rarely models accurately collection item surface behavior to light exposure as light sensitivity is a complex phenomenon that depends on multiple parameters. Therefore microfadotesting offers an interesting alternative testing method: microfader permits assessing the Dose-Response Function of a collection item while taking its surface complexity into account as it allows in situ accelerated light ageing on a sub millimeter spot of the item surface [2]. A brief description of the main microfader design options will be presented along with mention of the main technique limitations [3,4]. Methodological approach related to lighting decision making and to best use of MFT results will then be discussed. Concepts already developed in preventive conservation field - such as Accessible Value, Damage Function, Color-Value Function and Preservation Target - will be defined in the specific context of lighting policy implementation [5,6]. Adapting previous work on solid-state lighting engine for artwork-specific illumination with controlled photochemical safety [7], an exploratory concept called Referrent Rendering will be proposed to complete lighting decision making framework for vulnerable artworks. Such rendering could be defined as the one presenting best value(s) of the artwork on display: selecting it would require collaboration with curator and could further help in assessing quality of the light source used for exhibition. Integrating MFT results in such completed framework for lighting policy decision would allow conservator to select lighting scenario for which value(s) of artwork on display are best presented and that also minimizes risks of value loss by aligning with the light-dose set by the collection item's preservation target.

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[051]

## A NEW ONLINE TOOL TO DETECT COLOUR MISCONCEPTIONS

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In previous studies, our research group designed and implemented a test to determine misconceptions about concepts of optics in general. One of our findings was that over 80% of the individuals tested had misconceptions concerning the concept of colour. From early age, most individuals arrive spontaneously to a type of “subconscious explanation” about how the perception of colour works, which in turn leads to the creation of misconceptions. In most cases, these misconceptions persist throughout life. Even at the highest level of university, sometimes instruction is not enough to make misconceptions about colour disappear.

As an evaluation instrument, we designed an online test, which is aimed at obtaining information about the misconceptions people have concerning colour. To obviate the influence that the interpretation of textual language may have in inducing specific erroneous responses, we invented a purpose-designed set of symbols. Using this set of symbols, we created a 9-item test. On every item, the scene statements were presented using figures: an apple of one of the three primary colours was illuminated by a light bulb of one of those primary colours. The overall scenes are illuminated by a white light lamp, which will be turned off. The question asked in the test is always the same: “What colour will the apple look once the white light lamp is turned off?” From the responses to our test, we found out that the misconceptions were structured in the form of authentic implicit theories: the vast majority of incorrect response patterns on our test corresponded to just four sequences, reflecting the existence of four respective mini-theories about colour, with a high internal consistency. The detected misconceptions about colour were as follows:

1. Colour is a property of bodies (similar to their mass)—a body ‘is’ a certain colour and will always be perceived as that colour. The normal use of the verb “to be” to describe the colour of an object adds greatly to this misconception.
2. The colour that an object appears to be depends only on the light that illuminates it. Objects behave in a ‘neutral’ fashion with respect to how they reflect the light that reaches them and will always be seen to have the colour of the illuminant.
3. Bodies ‘emit’ their colour, which reaches the eye of the observer together with the colour of the light from the illuminant, so that the colour finally perceived by the observer is the sum of the two.
4. When the space surrounding an object is “full” of the colour of the illuminant, and an object of that same colour is located within that space, then that object will not be seen, because of the lack of contrast. This misconception can coexist with any of the previous three misconceptions.

We found a clear example of the first misconception in a viral photo, which recently became popular over the Internet. It showed a washed-out photograph of a two-colour dress, with the question “What colour is the dress?” There is an on-going dispute over whether the dress pictured is blue and black, or white and gold, but few people realize that it is the question that is wrong. The dress cannot “be” of one colour or other. It is a matter of perception, and the right question should be “What colour do you see the dress?” The best thing about this question is that there is not a right or wrong answer, as every individual will perceive the colours differently.

**(052)****RECONSTRUCTION OF WALL PAINTINGS AT HERCULANEUM**

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In 79 AD the eruption of Mount Vesuvius covered the ancient city of Herculaneum with magna and mud preserving a small part of the ancient world for posterity. In the early 20th century Amedeo Maiuri performed excavations at the site and his findings were written down and documented. Since its excavation the city has undergone severe deterioration and most of the wall paintings on-site are no longer intact. Furthermore, deposits of salts hide the scenery of the paintings in many places. However, utilizing Maiuri's texts, on-site visual examinations and Infrared Photography it is possible to reconstruct some of the wall paintings. Here we present the visual reconstruction of the garden scene wall painting in the summer triclinium at the House of Neptune and Amphitrite. Visible Induced Luminescence (VIL) revealed the presence of Egyptian Blue uncovering birds, a water fountain and flowers. Handheld X-Ray Fluorescence (XRF) allowed the determination of the elemental composition of applied pigments. In addition, the reconstruction was aided by comparison with similar garden scenes of wall paintings at Pompeii and Oplontis. A wall painting located at the tablinium of the same house was also reconstructed. In this case in addition to visual examination, XRF and VIL, the well-preserved wall paintings at the house of Marcus Lucretius Fronto in Pompeii proved to be an extremely helpful guidance in the reconstruction.

The work presented in this abstract has taken place in the context of the Herculaneum Conservation Project's collaborative program for scientific research and site trials that address the conservation challenges at the archaeological site of Herculaneum, Italy.

**POSTERS**

(P 01)

## WHO WERE THE MAN'S BEHIND THE WORK OF ARTS? A BIBLIOGRAPHIC SURVEY OF PAINTERS THAT LIVED AND WORKED IN ÉVORA IN THE 16<sup>TH</sup>-17<sup>TH</sup> CENTURY

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There is no doubt about the importance of documentation research for studies in History of Art, for Conservation and Restoration and for Conservation Science. With the obtained data, it can be possible to ascertain pertinent facts, including validating the date of a masterpiece, confirmation of authorship and acknowledgement or dismissal of historical theories relating to the art in question. The start point is usually the work of art and not the man behind it.

In the framework of project PRIM'ART, a bibliographic survey was conducted into the lives

of 70 painters who lived and worked in Évora over 400 years ago in the 16th and 17th centuries.

This poster shows that it is possible to reconcile the computer language of today and the language of notaries and witnesses of the “De genere” inquiry process from that period.

This research has led to the discovery of some documents, so far unknown, as some “genere inquiry process” such as the will of the painter Francisco Lopes that reveals interesting details of the painter's everyday life and the discovery of the authorship of the paintings of the dome of the Church of N. Sra. Da Esperança in Vila Viçosa.

### Acknowledgments

The authors wish to acknowledge the District Archive of Évora and the technicians Paulina Araujo and Célia Caeiro; the Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP).

(P 02)

## PRE-HISPANIC PIGMENTS AND ITALIAN RENAISSANCE DESIGNS AT SPANISH COLONIAL MISSIONS CHURCHES IN NORTHERN MEXICO

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It is well known that cochinitilla and indigo were used to produce carmine and Mayan blue (respectively) during the Prehispanic period at central and south of Mexico. At soon as Spaniards learned about the good qualities and properties of these pigments, they reached a great value at the European commercial trade. [1] However in Northern Mexico, most of the decorations in ceramics and wall decorative surfaces are based on iron oxide pigments colors being blue and carmine not common in the chromatic palette of the natives from this region.



Previous studies have determined the presence of Mayan blue and carmine [2], among others, at the decorative surfaces of a 17th century Spanish Colonial Mission church, Asunción de Santa María de Cuevas, at the Northern Mexican State of Chihuahua.

The painting decoration is governed by the most representative European Renaissance canons patterned by the head missionary, who was Sicilian. The use of the pigments discussed above, were probably introduced by the painter Domingo Guerra, who signed at the bottom of the Jesuits monogram IHS at the upper frieze of the presbytery in 1700 [3].

Seven other Jesuit missions located in the Alta Tarahumara region present polychrome decoration on their wooden ceilings and choirs such as Santa María. All of them appear to share same technique but have been executed with different qualities of hand skills. Thanks to a grant awarded by the Mexican federal institution, Consejo Nacional de Ciencia y Tecnología – CONACYT (National Council of Science and Technology), the technical examination of the decorative surfaces found in these eight churches is being carried out. An international and interdisciplinary project led by the non-profit Misiones Coloniales de Chihuahua has been organized. At a more specific level, the project has the goal to identify the presence of indigo and cochinitilla (not commonly found in Chihuahua) among other natural materials around this region.

[1] Roquero Anna, *Del Carmesi a la Escarlata, Rojo Mexicano*, Coloquio Internacional sobre la Grana Cochinilla en el Arte, del 11 al 14 de noviembre 2014, Palacio de Bellas Artes. Mexico D.f. conferencia en YouTube.

[2] Primary technical Studies were done at the Smithsonian Museum Conservation Institute in Washington D.C. Recently, Marcello Piccollo Phd and Giovanni Batrolozzi Phd from IFAC-CNR in Firenze, Italy have determined by the technique FORS the pink red pigment as carmine from cochinitilla.

[3] This mission church was founded by the Jesuits in 1687. Its decorative surface has been identified as the earliest figurative painting in northern Mexico and the southwest United State. Muñoz Alcocer Karla et al, Project Planning Report, J. Paul Getty Grant Program, Chihuahua, Mexico 2003. Unpublished.



(P 04)

**COLOURATION CAPABILITIES IN COVER AND FLOOR TILES FOR ANCIENT MATERIALS´ REHABILITATION: TRADITIONAL AND WASTE SOURCES**

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The colour in ceramics (tiles for roof and floor coverings) for rehabilitation can be induced in bulk or in surface by using a wide range of processing and raw materials (traditional and nowadays from some waste recycling). Vitreous compositions can be applied both in surface as glazes and in bulk as coloured glassy phase designed from the own composition and/or introduced as dispersed phase favorize better sintering of the final material [1]. With respect the ration and effect of colouration strongly depends of the vitreous composition is phase separated or if the final material is a conventional clayed product (less vitrified material) and/or a glass-ceramic or porcelain-stoneware (all highly vitrified materials). Usually since years, the color basis principle has been widely considered in glasses and in ceramics by the direct introduction of pigments or colouration oxides and is being widely investigated in ancient art and architectural materials [2] as was exposed in previous Colours 2008 congress [3]. They are shown the scientific aspects of color in both the crystalline and glassy phases and the own experimental results by using the addition of some oxides which operate also as nucleating agents for the crystal growth. These include transition oxides from the 4th period of the Periodic Table and which can give interesting functionalities to the final glass-ceramics containing iron, titanium, vanadium, chromium, manganese, iron and even some rare earth oxides [1][4][5].

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(P 05)

## THE ROLE OF UNDERLAYERS IN THE 1685-SMALT COATING OF THE MAIN ALTARPIECE OF THE COIMBRA OLD CATHEDRAL

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Ex Libris artwork of Flemish Art in Portugal, the main altarpiece of the Coimbra Old Cathedral dedicated to the Assumption of the Virgin Mary dates back to the early 16<sup>th</sup> century (1499-1502). Its original polychromy by the Flemish painter Jean d'Ypres and his team could not better match the Flamboyant Gothic style by profusely combining water gilding, oil gilding and tempera azurite blue paint [1].

Although a new polychromy applied at the Baroque time, dating from 1685, sought to perpetuate the original color scheme, subtle shades, textures and shiny effects were required in the contract signed by the painter Manuel da Costa Pereira [2], by using different materials and techniques: burnished gilding was the soil technique to be used and smalt in oil, which should also be burnished, was the blue paint to be applied.

While the blue smalt pigment was in vogue at that time, and known for having replaced the expensive azurite in Painting [3], its use in the altarpiece revealed an unusual type of implementation, by the previous application of two colored underlayers - pink and blue -, and the further use of smalt pigments of different grades mixed with colorless glass [4], perfectly observed in several samples cross-sections.

The underlayers were examined and analyzed by several techniques, namely by means of Optical Microscopy (OM), Scanning Electron Microscopy (SEM) imaging, Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), micro-Fourier Transform Infrared Spectrometry ( $\mu$ -FTIR) and Gas Chromatography/Mass Spectrometry (GC/MS).

On the basis of the gathered data, the unwonted use of smalt pigment in great amounts in a Portuguese monumental three-dimensional artwork at the end of the 17<sup>th</sup> century, the degree of brightness then required for its execution and the variations in blue resulting from the application of different colored underlayers will be discussed from an artistic, aesthetic and iconographic point of view.

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(P 06)

**SYNTHESIS OF YELLOW AND RED OCHRE:  
RECIPES AND RECOGNITION TECHNIQUES IN WORKS OF ART**

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Red and yellow ochre are in artists' palette from Prehistory. This is due to aesthetic preference for these hues, as testified by the first examples of paintings in Art History. Another reason is their easy availability. Conservation science has also adduced a third evidence for the red: man has soon learnt to synthesize red ochre by simple heating of the yellow one. This is what Pomiès reported in 1999 for the Paleolithic site of Troubat, France [1]. However, his work is the only one in works of art. Here we present the beginning of a systematic study to define the best, less invasive methodology in the discrimination of synthetic and natural red ochres.

First, goethite – the main component of yellow ochre - has been synthesized from a solution of KOH and  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ . Four samples of natural yellow ochre have been chosen for comparison. All of them have been heated to synthesize red ochre, namely hematite, through two different pathways: at 300°C for 18 hours and at 700°C for 1 hour. The complete set of samples has been then analyzed by scanning electron microscopy (SEM-EDAX), X-ray powder diffraction (XRPD), micro-IR spectroscopy ( $\mu$ -FTIR) and differential thermal analysis (DTA and TG).

SEM secondary electron images have been used to study the morphology of the synthesized samples. They showed that well-developed acicular crystals of goethite can be found only when this has synthetic origin. The length and shape of these crystals is preserved when hematite is obtained from its heating. SEM-EDAX gave elemental composition of all samples.  $\mu$ -FTIR has been used to better characterize the synthetic products. It evidenced the retention of water from the parent compound when red ochre is synthesized from goethite. X-ray powder diffraction has been used to characterize natural and synthetic products. Calcite, gypsum, kaolinite, montmorillonite, hornblende, clinocllore and anatase have been identified as accessory phases. It also ensured purity for the synthetic goethite and for the red ochres obtained from it. Thermal analysis was used to describe the synthesis and to add information for the precursor of synthesized red ochres. It showed that synthesized goethite has a mass loss, and consequently an excess of OH groups, corresponding to ideal goethite [2]. This allows us to exclude goethite presence in  $\mu$ -FTIR spectra from synthetic red ochre. Thus, OH group vibrations in the Functional Group Region are only due to water retention in synthetic hematite. This leads to a preliminary conclusion:  $\mu$ -FTIR spectroscopy could be a good, fast and micro-destructive technique to distinguish natural red ochre from the heated one.

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(P 07)

## COLOUR MATERIAL IDENTIFICATION HELPING ON DATING ISSUES – A POST-BYZANTINE ICON FROM THE MUSEUM OF ÉVORA

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This study aimed to identify the materials used in the production of a post-byzantine orthodox icon that belonged to the private collection of the Archbishop Friar Manuel do Cenáculo and is now part of the Évora Museum collection. The icon, representing the Emperor Constantine and his mother Helen holding a cross, was part of the “Exposição Ornamental Portuguesa e Espanhola” (Portuguese and Spanish ornamental art exposition) held in 1881/1882, where was described as being from the 10th century, date that until today has not been revoked. This might be explained, we suppose, due to the low level of knowledge about this kind of art - orthodox iconography - in the region and also because it is a unique piece of its kind in this museum, and also in the Portuguese museum’s collections. The fact that the production of icons is an unbroken tradition with more than 1500 years [1] makes difficult the attribution to schools of production and of a supposed date. Therefore, in order to identify the materials used by the artist, we searched for materials or techniques that were only used after the 10th century and compared them with other technical studies about icons. Were used multiple spectroscopic techniques, nondestructively as possible [2]. The UV light photography to identify possible restorations, the Radiography to access the inner structure and painting composition and the IR reflectography to reveal possible preparatory drawings were used as area analysis. In situ XRF was made for a first approach to the elementary composition of materials, and then micro samples were taken for cross-section complementary analysis by OM, SEM-EDS, and LC-DAD-MS and PY-GS-MS.

Taking into consideration the results obtained using this integrated approach we can now say that it is probably a Greek-origin icon made after the 16th century.

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(P 08)

## THE “PENTECOST” OF MUSEU NACIONAL DE ARTE ANTIGA THE ISSUE OF COLOUR OF VIRGIN MANTLE

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Within the traineeship of a Master’s degree in Conservation and Restauration at the Instituto Politécnico de Tomar, to happen with the Laboratório José de Figueiredo/Direcção-Geral do Património Cultural, is in development the study, Conservation, Restauration and intervention of the easel painting “Pentecost” of the Museu Nacional de Arte Antiga [1]. It is an oil painting in Baltic Oak support [2], allocated to the Portuguese School [1] and dating from around 1530 [2]. The pictorial composition illustrates the descent of the Holy Spirit in the form of tongues of fire, the Virgin Mary being the central figure of the composition.

The study of this portuguese painting, sustained by the various methods of examination and analysis, concluded the presence of overpainting on the pictorial surface. One covers the entire mantle of the Virgin, that is, an originally mantle of blue appeared to be black. In identifying this overpainting, the use of the portable optical microscope (Dino- Lite® Pro AM- 413T) allowed us to observe the existence of two overlapping layers, verifying also the interruption of cracks to the original blue layer and its ground layer. This was also confirmed by observation under an optical microscope (Leitz Wetzlar, coupled to a digital camera Leica DC500) the cross-section [3]. For Fourier transform infrared microspectroscopy (Continuum™ microscope coupled to a Thermo Nicolet® IR spectrometer Nexus 670 FTIR™ Thermo Nicolet®) it was detected on the original blue mantle, a mixture of white lead and azurite bonded in oil, and on the overpainting a lead white layer also bonded in oil, but it has not been possible to detect the material responsible for the black color [4].

During the intervention it was possible to verify the actual wear the repainted layer making clear the true mantle of the Virgin color, blue. After the survey repaint, it was evident the change of color values in the composition, restoring it to its original state.

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[3] L. Esteves. Estudo biológico da pintura “Pentecostes” do Museu Nacional de Arte Antiga (85-14), relatório do Laboratório José de Figueiredo/Direcção-Geral do Património Cultural, Lisboa, 2015.

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[4] A. Oliveira. Relatório de micro- FTIR da pintura “Pentecostes” do Museu Nacional de Arte Antiga (85-14), relatório do Laboratório José de Figueiredo/Direcção-Geral do Património Cultural, Lisboa, 2014.

**(P 09)****19<sup>TH</sup> C. COLOURED STUCCOS AND PLASTERS FROM GRILLO'S CHURCH (OPORTO, PORTUGAL): MATERIALS AND TECHNIQUES EMPLOYED**

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The Oporto's St. Lourenço Church of the Jesuit College is locally known, since the St. Augustin Barefooted Eremites occupation (1779/80), as Grillo's Church. The Oporto's siege laid by D. Pedro and D. Miguel (1832/33) succeed in the college abandonment by Grillo's Friars. Throughout Augustin Friars presence period, the white plasters of the nave (end of 18th c.) were executed and it was constructed the Holly Sacrament Chapel (beginning of 19th c.) with neoclassic coloured stuccos and plasters, influenced by Robert Adam, Luigi Chiari and Teixeira Barreto ornamental motives. Pigments were added to the external layer to imitate the marble and to achieve the "base" colour of the panels.

This study of the blue, rose and white stuccos and plasters of H.S. Chapel of Grillo's Church allows to carry out useful database on the original mortars composition by the use of different analytical techniques, important to select the most adequate solutions for restoration interventions. Optical microscopy, XRD, DSC-TGA, SEM-EDS and XRF analysis results were considered to identify the composition of different layers and to provide mineralogical, microstructural and chemical characterization of the mortars components and paint layers and to quantify the percentage of binder in those mortars. These results were compared with collected information on compositions from other sources. This study allowed the identification of the decay causes of the decorative stuccos and plaster suggesting that water retention in the masonries and wooden laths structure of the dome of the chapel is the main factor.

(P 10)

**SHEDDING LIGHT ON GREGÓRIO LOPES' PALETTE: A MULTI-ANALYTICAL APPROACH FOR THE CHARACTERIZATION OF PAINTING MATERIALS USED IN THE 'RESSURREIÇÃO DO MANCEBO'**

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Gregório Lopes (A.D. circa 480-1551) is one of the most representative painter of Portuguese Renaissance period. The large painting 'Ressurreição do Mancebo' now belonging from the Évora Sacred Art Museum, was once part of an alterpiece from the Évora Cathedral [1].

The work presented here aims to chemically characterize both the inorganic and organic fillers and painting materials used in the artwork using a multi analytical approach. The use of non-destructive and micro-destructive techniques, as Optical Microscope (OM), Scanning Electron Microscopy (SEM), micro Fourier Transform Infrared spectroscopy ( $\mu$ -FT-IR),  $\mu$ -Raman spectroscopy and pyrolysis gas chromatographic-mass-spectrometric (Py-GC/MS), allows us the determination of the pigments and organic binders preventing the waste of sample. The combination of spectroscopic and mass-spectrometric techniques provided us the exhaustive characterization and the stratigraphy distribution of the painting materials used by the artist requiring only few amount of sample.

The results achieved have been fundamental to outline the artist's palette and painting technique allowing the comparison with other artworks of Gregório Lopes and of his Portuguese contemporaries. In conclusion, the complementary interpretation of the data obtained with all the different techniques applied on micro heterogeneous samples, has provided for the first time the chemical characterization of the material used in the 'Discovery of the cross' shading light on the painting technique of one of the Portuguese greatest artist of XVI century.

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(P 11)

## THE COLOUR OF “GOLDEN” LEAF - A NEW INSIGHT INTO THE CONDITION AND COLORIMETRIC PARAMETERS OF GILDED COMPOSITES DURING AGEING

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The poster presents preliminary data on an experimental study using gilded composites reconstructed in laboratory according ancient gilding recipes and monitored during natural and artificial ageing using optical microscopy (OM), scanning electron microscopy (SEM) and CIE  $L^*a^*b^*$  colorimetry.

This study is part of a research project funded by the Portuguese Foundation for Science and Technology ([www.gilt-teller.pt](http://www.gilt-teller.pt)) and aims to better understand the evolution of the conservation state of the gilded composites and of the colorimetric parameters of the gold and silver leaves used to gild properly prepared wooden supports.

Two water gilding and two mordant gilding recipes were appropriately chosen from the treatises written by the Portuguese Philippe Nunes (1615) [1] and José Lopes Baptista de Almada (1749) [2] as being representative for Baroque époque. After the completion of gilding, the samples' surfaces were divided into areas and on each different finishing layers (wax, animal size, shellac, sandarac resin) and decorations (punching, “esgrafitado”, “estofado”) were applied.

The model samples were subject to both natural and artificial ageing. The natural ageing was performed in laboratory between July 2014 and May 2015 for water gilded samples, while the mordant gilded samples underwent this ageing between November 2014 and May 2015.

The artificial ageing was performed in a climatic chamber with cycles of relative humidity (RH) at constant temperature to imitate the variations between day and night.

The preliminary results point on the comparison in the behavior of gilding layers with and without protection and between naturally and artificially aged samples. Thus the microscopic techniques complement themselves in the characterization of the surfaces and interfaces, while the colorimetry gives an estimate of the variation of the main chromatic parameters

( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ , delta E) of the gilded surfaces in the attempt to evaluate the effectiveness of artificial ageing against the natural one.

### Aknowledgements

This work has been supported by Fundação para a Ciência e a Tecnologia through grant no. PTDC/EAT-EAT/116700/2010. The support of IMAGOS – Inovative Methodologies in Archaeology, Archaeometry and Geophysics – Optimizing Strategies X APOLLO - Archaeological and Physical On-site Laboratory – Lifting Outputs, n. ALENT-07-0224-FEDER-001760, funded by INALENTEJO programme through FEDER. Project is also kindly aknowledged.

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[2] J. Lopes de Baptista Almada, Prendas da Adolescência, ou adolescência prendada com as prendas, artes, e curiosidades mais úteis, deliciosas, e estimadas em todo o mundo, Lisboa, Off. de Francisco da Silva, 1749

**CHROMATIC CHARACTERIZATION OF THE CODEx BORBONICUS**

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The Codex Borbonicus is a mesoamerican codex held at the library of the French parliament. It is a 14 meters long screen-folded band of a fibrous material that forms 36 pages painted on one side only. The colors are very well preserved for a document painted five centuries ago. This manuscript details divinatory and solar calendars used by the Aztecs and different religious ceremonies. From a stylistic point of view, we can consider that the codex is made of two distinct parts which have likely been executed by at least two different scribes. A simple visual observation also suggests that although there is a similar global set of color categories in both parts (blue, red, pink, orange, green, yellow and brown), the shades used in each part look different. For example, the colors in the second part seem to be more saturated.



Page 9 (Part I) and page 30 (Part II) of the Codex Borbonicus

The aim of the present work is to characterize the chromatic features of the codex palettes in order to underline the differences between the two parts. To avoid bias resulting from visual observations that are very subject dependent, this study is based on the colorimetric coordinates of digital photographs of the different pages. The colorimetric space and the graphical display is chosen to visualize as well as possible these differences. The purpose is setting-up a methodology quite simple that could be used by non-specialists without using expensive equipment.

To validate this methodology, the previous results will be compared to those obtained from hyperspectral images in the visible range (400-800 nm) that gives the reflectance spectra in each pixel of the document with a very good resolution. From these images, calibrated colorimetric coordinates can be extracted that can be used as references.

**(P 13)****NEW INSIGHTS INTO THE RED AND GREEN PIGMENTS IN THE ILLUMINATED FORAL CHARTER OF SETUBAL (1515-PORTUGAL) BY COMBINED USE OF MICRO-XRF AND MICRO-RAMAN**

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The magnificently decorated foral charter attributed by D. Manuel I of Portugal, in 1515, to the village of Setubal, was studied using Energy Dispersive X-ray Fluorescence spectrometry and Raman micro-spectroscopies. A complete characterization of the pictorial materials used in the production of this masterpiece showed a very different pigment pallet choice when compared to other Manueline charters. The red and green pigments are particularly puzzling, as the widely used vermilion and malachite were not found in the illuminated frontispiece. Instead, the cheaper lead based pigment minium was used in the king's flag, while a combination of antlerite, brochantite, posnjakite and langite were found by means of micro Raman spectroscopy. While the use of minium appears to be a choice of the miniaturist, albeit uncommon, the green color gives rise to many questions. We can conclude that the green pigment is a copper sulfate with various hydration degrees, but we are not able to say if this was knowingly used or if it's the result of the degradation/hydration of the original pigment [1].

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(P 14)

## COLOUR AND PARCHMENT DEGRADATION IN A 15<sup>TH</sup> CENTURY BOOK OF HOURS: THE CASE STUDY OF COFRE NO. 31 FROM PALÁCIO NACIONAL DE MAFRA

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The “Cofre no.31” is a French 15th century book of hours from the Palácio Nacional de Mafra (PNM), in Portugal. This prayer book, composed by illuminations and devotional texts, is in a bad condition due mainly to the rebinding done between 18th - 19th centuries.

As an aid tool for the diagnostic of its conservation state, it was used the IDAP protocol (Improved Damage Assessment of Parchment) [1]. In a set of selected folios, the main damage signs were observed: surface contamination, deformation and discoloration of the parchment, damages in the illuminations and text. In an overall analysis, 78% of folios were slightly damaged and 17% damaged. For colour analysis, it was used colorimetry on different areas of the folios, showing considerable differences between the most and least handled areas due to the deposit of dirt and grime.

The pigments and other materials, such as gold and silver, are in consonance with the materials used in the 15th century [2, 3]. Some pigments are heavily degraded, such as minium and silver, having darkened and migrated to the back of the parchment; other colours, like copper blues and greens, present a light migration. Another visible type of degradation occurs with the blue used in the decoration outside the illuminations, which has suffered partial or total detachment in most of the folios, as well as the green and white colours.

The current binding, suitable for books on paper, is inadequate to a parchment support and has contributed to its deterioration, allowing the free movement of the skin according to humidity and temperature variations, which promotes detachment of the pigments; another consequence is the free entrance of air content into the manuscript, allowing the contact with humidity, oxygen and atmospheric pollutants, such as hydrogen sulphide, which reacts with the silver, producing Ag<sub>2</sub>S [4]. For these reasons, a full diagnosis was done and main results will be presented, as well as the full conservation / restoration treatment of this codex, allowing that the binding functionality is recovered, but without removing any trace of its history and promoting the preservation of this single art work from cultural heritage.

[1] R. Larsen, ed. Improved Damage Assessment of Parchment (IDAP). Assessment, Data Collection and Sharing of Knowledge. (Research Report No. 18), EU-Directorate-General for Research, Luxembourg, 2007

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[3] A. Lemos, R. Araújo, C. Casanova, M.J. Melo, V.S. F. Muralha. Regards croisés des historiens de l'art et des chimistes sur deux livres d'Heures de la Bibliothèque Nationale du Portugal, les mss IL15 et IL19. In: Portuguese Studies on Medieval Illuminated Manuscripts. Edited by M.A. Miranda and A. Miguélez Cavero, Barcelona-Madrid, 2014, pp. 145-168

[4] Guerra M., Manso M., Pessanha S., Le Gac A., Longelin S., Guilherme A., Gil M., Carvalho M. L.. X-ray Fluorescence Spectrometry as a Diagnostic Tool in Conservation of Illuminated Manuscripts, in Piero Frediani (ed.), Cultural Heritage: Protection, Developments and International Perspectives, New York: Nova Science Publishers, 2013, Chapter 9, pp. 235-256

(P 15)

## ATTEMPTS IN ENZYMATIC DEGRADATION OF THE PIGMENTATION PRODUCED BY FUNGI ISOLATED FROM PORTUGUESE WALL PAINTINGS

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Wall paintings are prone to different types of deterioration, including of biological origin. Our study focuses on the chromatic alterations of the paintings' surfaces related to the presence and growth of microorganisms.

The removal of the dark coloured stains from wall paintings is extremely difficult. Although treatment with biocides can eliminate microorganisms, these compounds are ineffective in cleaning the black pigmentation resulting of their growth. Therefore, it is necessary to understand which organisms are present, the characteristics of the compounds they generate, and in which conditions they produce it.

The aim of this study was to isolate the pigment that is the source of the black stains in the studied wall paintings in order to, in a broader scope, eliminate or attenuate their visual impact.

Wall paintings presenting black stains from three case studies – Igreja de Santa Eulália/Igreja de São Salvador de Arnoso (V.N. Famalicão), Igreja Paroquial de Valadares (Baião) and Igreja de Santa Cristina de Serzedelo (Guimarães) were dully studied from the conservation point of view.

Fungi were isolated from selected areas that displayed dark pigmentation of the pictorial layer. Samples were collected with wet swabs and grown on solid culture medium, e.g. Potato Dextrose Agar (PDA). Isolates were further identified by classical and molecular biology methodologies.

Three fungal isolates were selected for further studies due to their pigmentation and growth characteristics, mainly: blackening of solid culture media, dark or black hyphae growth, or a presence of black exudates produced by colourless hyphae.

Enzymatic degradation of pigmentation resulting from a selected fungal isolates was attempted both in solution and on solid support and tested with fungal versatile peroxidase from *Bjerkandera adusta*. Changes in colour were detected by UV-Vis spectrophotometry and with a CIE L\*a\*b system colorimeter.

**DEVELOPMENT OF HYPERREALISTIC SIMULATIONS TO TEACH CONCEPTS ABOUT COLOURS**G. Martínez<sup>(1)</sup>, F.L. Naranjo<sup>(1)</sup>, A.L. Pérez<sup>(1)</sup> and M.I. Suero<sup>(1)</sup><sup>(1)</sup> University of Extremadura, Avda. de Elvas s/n, 06006 Badajoz, Spain

In this work we have created a set of computer simulations that exhibit greater realism than traditional simulations, which we call hyperrealistic simulations [1]. The purpose of these simulations is to show the student concepts related to colour generation and mixing. For the programming and development of these simulations we used computer tools specifically designed for rendering photorealistic graphics environments, such as the POV-Ray software, an open-source ray-tracer [2]. Our choice of this program was determined by our need for a technique capable of imitating faithfully the optical system in a manner that was consistent with the theoretical models involved. POV-Ray (Persistence Of Vision Raytracer) uses a geometrical optics-based ray-tracing technique that synthesizes images with great realism [3].

The software models the light's path by following the rays as they interact with optical surfaces, yielding accurate simulations of optical phenomena. These simulations emerge as a natural result of the combined use of the ray-tracing algorithm and a specific Monte Carlo algorithm for the synthesis of three dimensional images with perspective.

The program implements additional algorithms, such as photon mapping, which add realism to the overall illumination of the scene. In addition, the program is open-source and available for almost all computer platforms. It allows the user to represent objects internally with mathematical functions using a scene description language. This is a major advantage; the user then only has to be concerned with the geometric description of the optical system (light source, object and observer) because all of the underlying optics already form part of the program's source code.

To qualitatively validate our simulations, we compared the results with those predicted by the theory and photographs of real systems. Students using the simulations are able to relate them without difficulty with their real counterpart, noting that sometimes are virtually indistinguishable. In conclusion, appropriately designed hyper-realistic computer simulations are very effective teaching tools in certain educational contexts, such as e-learning teaching platforms.

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[2] <http://www.povray.org>

[3] G. Dolling, M. Wegener, S. Linden, and C. Hormann, Photorealistic images of objects in effective negative-index materials. Optic Express 14 (5), 2006, Pages 1842.

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**COLOUR-BASED AUTOMATIC DETECTION OF WORN OUT VARNISHES ON STRADIVARI VIOLINS**

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UV fluorescence photography is widely used in the study of artworks, in particular for the analysis of historical musical instruments (e.g. violins). This technique allows seeing important details which cannot be observed with visible light, such as retouching, different paints coats or worn areas of the superficial varnishes. However, interpretation of UV photos may be very complex and is strictly related to the preservation state: the more alterations, the wider range of colors that are detected by the technique. Recent studies on Stradivari violins have shown four main layers of materials on the surface of the instruments: wood, wood filler, transparent paint coat and colored paint coat [1]. The aim of this work is the development of a new tool able to automatically detect the presence of colours related to the worn areas on the back plates of violins. The study was performed on UV images of Stradivari violins of the historical collection held in the "Museo del Violino" in Cremona. Although paint coats of the examined instruments display considerably different colours, the analysis of the acquired data shows that all the worn areas (where the wood and the wood filler are more evident) are always characterised by the same colour hue, with a different level of saturation directly proportional to the level of wear. The system developed in the present work can automatically select these surface areas analysing the histogram of the images in HSV colour space. Our algorithm works even when worn areas cannot be directly detected by looking at the original photos due to perception illusion (e.g. very low level of wear and/or worn areas hidden by nearest paint coats). During the computation, the fraction of the worn areas respect to the entire surface of the back plate is also computed. The detected areas are highlighted with three different levels of wear: high in red, medium in orange, low in yellow (see Figure 1).

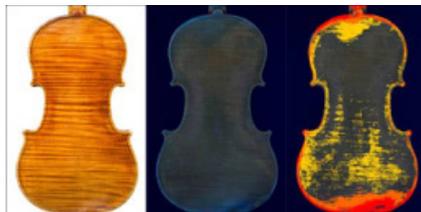


Figure 1: Example of the application on the back of Antonio Stradivari "Cremonese" violin(1715). From left to right: visible, UV fluorescence, final result.

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(P 18)

## AS WHITE AS THE LIGHT- THE BRIGHT EFFECTS ON WHITE CHALK GROUND LAYERS OF THE 15<sup>TH</sup> AND 16<sup>TH</sup> CENTURIES PAINTINGS

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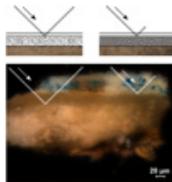
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The phenomenon of reflection of light by chalk material, provided largely by calcareous (mainly coccoliths and calcispheres) is well known since 15<sup>th</sup> century. Its excellent workability comes from its fineness and softness. This is afforded by the rounded shapes of microfossil limestone, which facilitates the sliding in the application, thereby increasing the speed of handling. The fast application of the chalk as a painting ground layer allows its homogenization before drying, thus facilitates the aggregation of particles and their subsequent flattening. Concerning the grain size of the material and its coloring power, the thinner material gives the best color effect. These characteristics have been used to optimize the pictorial technique [1]. In addition to the fineness and smoothness characteristics chalk has a special feature required and explored by the artists who used it - a particular light reflection. The mixture of chalk and animal glue has refractive index characteristics of surface light, since the chalk constituent elements remain suspended in adhesive bonds, causing the light to penetrate in depth and reflecting mainly in the surface. The oil mixed with chalk provides the phenomenon of deep light, since the slow-drying oil oxidation polymerization encapsulates the particles. This factor allows light to penetrate deeply, but being partially absorbed [1].

In this perspective, it is justified the existence of a characteristic painting ground layer stratigraphy containing a proteic binder in the lower region and in the upper region an oily binder.



a) diagram of the reflection surface light on white background, giving brightness and luminosity to the pictorial layer, equivalent to the bottom of chalk and glue; b) diagram of the reflection light on the deep translucent background, reducing the amount of reflection and the brightness of the color layer, adapted diagram from [2]; c) sample 10-07C-1 of painting Christ before Pilate, of the Altarpiece of the Esporão Chapel (ME) where we observe the reflection scheme surface light, the bottom proteic ground layer and deep light in the oil binder top layer of the chalk ground.

[1] Nicolaus, K., Manual de restauración de cuadros. 1999, Köln: Konemann, p.266.

[2] Mayer, R., Manual do artista de técnicas e materiais. 1999, São Paulo: Martins Fontes., p.174.

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## COLOR SPACE PATH ANALYSES OF PAPER COLOR

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**Abstract:** Cellulose paper conservation is quite important to those responsible for library collections and historic documents in museums. The color changing of paper is a known aesthetical problem that can become a mechanical instability one. However a carefully made study of the course of paper color in a color space can reveal new information.

Discolored paper can be caused by many factors, nevertheless, this work has tried to address isolated light effects on paper color. In particular, artificial ageing procedure using photo-oxidation under UV-C lamp was performed on ordinary printing and Whatman paper samples [1].

These samples were aged by exposing them to a UV-C light source in a home-made irradiator box assembled during 30 days. Temperature and relative humidity were kept in a narrow range around 25°C and 50%, respectively. The UV source, a Philips TUV 30W T8 lamp, emits 12 W in a narrow line at wave length of 253,7 nm. Irradiance and spectral irradiance were approximately 40 W/m<sup>2</sup> and 4 W/m<sup>2</sup>.nm, respectively.

A chroma meter (colorimeter) Konica Minolta CR-400 was used to measure the color departure from non-aged paper samples as function of time exposure. L\*a\*b\* color space with illuminate C was selected. Euclidean distances  $\Delta E^*$  were calculated using non-aged paper color as reference ( $L_0^*$ ,  $a_0^*$ ,  $b_0^*$ ).

Time evolution of paper color were plotted on the tridimensional representation on the L\*a\*b\* color space. In addition to that two new color degradation indexes were calculated:

$$\Delta E_R^* = \sqrt{\left(\frac{\Delta L^*}{L_0^*}\right)^2 + \left(\frac{\Delta a^*}{a_0^*}\right)^2 + \left(\frac{\Delta b^*}{b_0^*}\right)^2} \quad \text{and} \quad \Delta S_R^* = \sum_{i=1}^N \Delta S_i^* \quad \text{where}$$

$$\Delta S_i^* = \sqrt{\left(\frac{\Delta L_i^*}{L_0^*}\right)^2 + \left(\frac{\Delta a_i^*}{a_0^*}\right)^2 + \left(\frac{\Delta b_i^*}{b_0^*}\right)^2} \quad \text{whit} \quad \Delta L_i^* = L_i^* - L_{i-1}^* \quad \Delta a_i^* = a_i^* - a_{i-1}^* \quad \Delta b_i^* = b_i^* - b_{i-1}^*$$

The 3D-plot indicates a fast change of color quadrants while a relatively small change in lightness within the first seven days of irradiation. After this initial period, 3D-plot shows small color changes and some reversibility on color course. Time evolution of the  $\Delta E_R^*$  acknowledges the color reversibility. Relationship between  $\Delta E_R^*$  and  $\Delta S_R^*$  will be discussed still.

[1] M. Cocca, L. D'Arienzo, and L. D'Orazio, International Scholarly Research Network, 2011, Article ID 863083

## COLORIMETRIC RESEARCH OF VARIOUS OLD LITHIC MATERIALS TREATED WITH HYDROPHOBIC PELLICLE, IN VIEW OF THEIR RESTORATION AND CONSOLIDATION

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The purpose of the paper is to evaluate the chromatic and aesthetic impact of hydrophobic and consolidation treatments done on old indigenous lithic materials, from the XVII - XIX-th centuries, materials that were used in building of two historical monuments, that are undergoing restoration. During the preservation and stripping processes, different porous or fragile lithic surfaces were identified, alongside with several ornamental terracotta and limestone, kept by degraded traditional mortar. The paper wants to identify hydrophobic consolidation methods, done by applying a pellicle, that are less aggressive and more efficient from a technological point of view, all respecting the modern principles of scientific conservation [1,2]. During research, different chemical products, part of the hydrophobic additives group and available in commerce, were used. The tests were done in laboratory conditions, in order to show the chromatic interaction between surface and product in different environments. CIE  $L^*a^*b^*$  [3,4], OM and exposure to UV radiation in laboratory condition were implemented as analysis techniques during the study of optimizing these pellicle disperse systems. The obtained results will be analyzed, transmitted and discussed through direct correlation, in order to propose the most efficient solutions, taking into consideration the chromatic deviation in rapport with the hydrophobic degree, the capacity to be applied as a pellicle and the capacity to consolidate. The researches will include the characterization of the lithic surfaces undergoing preservation from a chromatic point of view, both before and after the proposed chemical treatment. Keywords: CIE  $L^*a^*b^*$  colorimetry, OM, UV radiation, lithic materials, geomaterials, hydrophobic pellicle.

### Acknowledgement

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[2] I. Sandu, V. Vasilache, F.A. Tencariu, V. Cotiugă, The scientific conservation of ceramic artifacts (Conservarea științifică a artefactelor din ceramică), University Publishing „Al.I.Cuza”, Iași, 2010.

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**(P 21)****ANALYSES OF ALFREDO VOLPI'S PAINTINGS WITH EDXRF, SPECTROPHOTOMETER AND MULTISPECTRAL IMAGING**

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Painter Alfredo Volpi (1896 - 1988) is one of the most important contemporary Brazilian artists. His extensive work, mostly characterised by chromatic compositions and geometric abstractions is technically unique. The artist attributed great importance to craft and materials, developing his own systematic way of working. From the mounting of the canvas to the paints, made with natural earth pigments.

It is understood that these elements are important keys to a deeper understanding of his work, both technically and artistically. The present investigation was carried making use of non-destructive complementary analytical techniques. The aim was to study the chromatic and chemical composition characteristics of his paintings and gather information on the technical procedures the artist may have used.

Among the paintings analyzed were temperas belonging to the Museum of Contemporary Art-USP. The selection focused on the time the artist's work underwent a major transformation, from figuration to abstraction, from the use of industrial oil-based paints to the medieval technique of tempera. This technique, known for its opacity, colour saturation and material presence of pigments on the canvas became as important as the colour itself in the shaping of the artist's new spatial relation.

The spectrophotometer was used to measure the colour based on the spectral curves and numerical reference coordinates within a uniform colour space. Techniques of visual examination from imaging visible light, visible fluorescence by ultraviolet radiation and near infrared reflectography were used to gather information about the artist's creative process. These techniques also helped detect restoration patches and identify pigments. Spectroscopy EDXRF (Energy Dispersive X-Ray Fluorescence) is important for chemical characterization of materials.

From the integration of these techniques it was possible to identify a part of the rich palette of Volpi's paintings; document the present aspects of the colours; recognize or give indications of pigment compositions and shed light on parts of each of the works stories, such as the presence of graphite sketches, covered earlier paintings and brushstrokes as well as document its current condition.

The tools used have proven useful in characterizing the paintings, revealing new information about the work of the artist and raised new questions. The information obtained may be the beginning of a database on his oeuvre.

## VISIBLE AND FALSE-COLOR INFRARED IMAGES FOR PIGMENT IDENTIFICATION IN ARTWORKS

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In this work is presented a simple preliminary method that can be used to identify pigments, based on the images in visible (VIS) and false color infrared (IRFC). Although this method was used for painting analysis at macro scale, the novelty of this approach is that images through microscope in visible and infrared are used for pigment identification. The advantage is that mixture of pigments could be identified.

Images captured with a portable microscope in visible and infrared light were used to create a database of pigments applied with gum Arabic on paper. The proposed method consists first in computing the average color of the Color Checker patches viewed through the microscope, then creating a color profile of the microscope to correct images and finally comparing the images. Using Matlab software, images obtained for the unknown pigments were transformed into L, a and b parameters and compared to values from the pigments in the database. To determine the color difference, the delta E parameter, calculated with the formula CIEDE2000, was used.

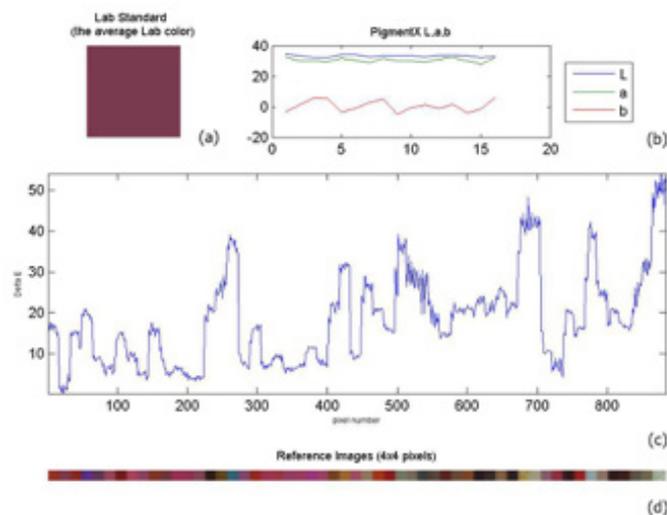


Figure 1 IRFC image for an unknown pigment (a) with Lab parameters (b) and the delta E calculated for every pixel in the reference images (c); the matching color in this case is the second color (d), corresponding to Egyptian blue.

**(P 23)****“DIFFERENT METHODS OF OIL ANALYSIS IN OIL PAINTS”**

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The oil as binder consists mainly of triglycerides (TAG's), esters of different fatty acids (FA) with glycerol, this composition will alter with drying, ageing and maturing and we aim at a better understanding of these molecular changes (in chemical drying of the oil and subsequent stages).

Paint ageing can be observed by several techniques. oil standards, of Linseed, Poppy, Walnut, Hemp, Perilla, and Safflower with known effective age, can be analysed from the start of the process of drying, to characterise the chemical composition of the initial oil and its oxidation products/drying products/hydrolysis products, throughout maturing and ageing.

Historically this was achieved with peroxide value determination, drying index weight changes, or Gas Chromatography- Mass Spectrometry (GC/MS). But GC-MS gives only a FA profile i.e. the composition in FA's present in each oil. This is because TAG's are not volatile and cannot be analysed without prior derivatisation which consists of hydrolysis of the esters to each components FA's and analyse as methyl esters(FAMES) or silylated. This will give a detailed FA profile with C16 or C18 carbon chains, position and number of double bonds.

Nowadays, with the availability of different instrumental methods of analysis it is possible to identify or quantitatively describe the “state” of drying. If we use Fourier Transform Infrared (FTIR) microspectroscopy we are able to detect the amount of double bonds present in the FA's; and their isomeric state - cis or trans; as well as being able to assess the carbonyl function in its Free FA form, ester bound (TAG) or bound as metal soaps (with metal from pigments).

With the aim of monitoring change, in oil, Mass spectrometry (MS) is a valuable technique, and with the help of soft Electrospray Ionization (ESI) it is possible to monitor samples as liquids, oil samples in solvents (or extracts of Paints). ESI-MS can give very informative composition on the actual oil TAG's, but also we can detect diglycerides (DAG's) and monoglycerides (MAG's) as well as some FFA. So ESI-MS is able to “see” how the FA are bound in TAG form, but also it gives a very important picture on how this changes molecularly, so we can see the presence of other moieties( OH/ OOH/ dimers/ trimers ) that indicate the state of oil or paint.

ESI-MS on a triple quadrupole instrument can add a closer look for monitoring, for example, the loss of the know previously FA with Neutral Loss Scanning (NLS) or selectively monitor known TAG's with Molecular Reaction Monitoring (MRM)

Also Liquid chromatography (LC) can also add separation of different compounds that can be detected coupled to MS in LC-MS or LC- MSMS experiments, that confirm each component and subsequent changes. The appearance of oxidation products of TAG's (also known as TAGOX) and attribution.

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## EXPLORING THE POTENTIALITIES OF PORTABLE MICROSCOPY IN TECHNICAL AND MATERIAL STUDIES IN MURAL PAINTINGS. AN AFFORDABLE TOOL FOR CONSERVATORS-RESTORERS

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Optical microscopy is one of the oldest tools available for conservation science in the laboratory but for in situ research the use of bulky equipment can have some restrictions. In the past few years the development of affordable digital microscopes, small and light enough to be easily handled, has offer new potentialities for unveiling technical and material details in the field of mural paintings. This paper reports three cases studies in Southern Portugal in which optical microscopy carried out with Dino-lite premier AD3713TB with x20 and Dino-lite ProX AM4000 series with x435 magnification have allow to gather data on the painter's craft and to identify pigments deterioration.



Fig.1. Three images examples of portable digital microscopy for technical studies (x20x) and for diagnosis (small pigment at 435x)

### Acknowledgments

The authors wish to acknowledge Santa Casa da Misericórdia de Montemor-o-Novo; A Fundação da Casa de Bragança; The Director of the Major Seminary of Évora; Pe Herminio Rico; DRCAIent and DGPC for allowing this study; the Fundação para a Ciência e Tecnologia for financial support (Post-doc grant SFRH/BPD/63552/2009) through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP).

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## AESTHETIC AND TECHNICAL CONSIDERATIONS ON CONSERVATION OF THE DECORATIVE REGISTRY FROM THE ROMANIAN FOLK POTTERY

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Pottery remains one of the most suitable ways of materializing artistic qualities. Above all, folk pottery stands out as spectacles of shapes, color and decors of the most aesthetically refined. Traditional pottery of all kinds brought together aside the practical role, a series of artistic virtues arising from skills and imagination of the craftsman.

An inappropriate microclimate, incorrect handling, improper treatments can cause damage to the ceramic items. [1] The scientific approach to stabilize enamel objects provides the assumption of a correct reconstruction of the decorative registry, ensuring the sustainability of the interventions. The work presents some of the important aspects of the technological process of restoration and preservation of ceramic objects from ethnographic collections, emphasizing the importance of studying their glaze degradation factors and the nature of colours used by craftsmen.

The technological process of conservation-restoration involves the use of substances and materials that are in an incontestable dynamic, generating ongoing debates, studies and different attitudes of specialists in the field. [2] An example in this regard is the choice of adhesive and consolidant to be used in the technological process of restoration-conservation of a particular piece.

Optical Microscopy (OM), Scanning Electron Microscopy/Energy Diffraction X-ray (SEM/EDX) were used to find the nature of colours and also for the validation of the conservation treatment.

Restoration and conservation of ethnographic heritage ceramic objects generates, besides saving and preserving in due time the items, the readability of the folk ornaments, of the plastic representations which identify a traditional way of life.

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(P 26)

## CHEMICAL AND TEXTURAL CHARACTERIZATION OF CERAMIC TILES FROM TALAVERA DE LA REINA PRODUCTION IN ÉVORA

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Majolica ceramics are among the most characteristic tableware from the Medieval and Renaissance times in Europe, evidencing a very high technological and artistic flourish in Spain during the Renaissance. As a ceramic artefact, majolica is earthenware characterised by a ceramic creamy buff-light colour body and a white tin-opacified lead glaze coating the whole outer surface of the vessel. However, the most characteristic feature of majolica pottery perhaps lies in its decoration. In that sense, decorations, which are made of metallic oxides, usually applied on top of the opaque white glaze coat, have been profusely studied by Art historians. Seville is one of the most important majolica production centres in Spain [1]. In the 16th century, Talavera de la Reina (Toledo) would become one of the main majolica ceramic production centres in the Iberian Peninsula. Due to its fineness and wholesome status, the monarchy and the aristocracy would become the most important customers [2]. The beginning of 1600's is a time of transition in the history of tiles in Portugal, attending to the slow decline of Seville, and the rise of the "new" production centres of Lisbon and Talavera de la Reina. This new emergence is accompanied by an appearance of figurative tile panels and polychrome patterns in Mannerist style.

The aim of this work is the study of the chemical and mineralogical composition of the ceramic body and the evaluation of the glaze-ceramic interface of ceramic tiles attributed to Talavera de la Reina production centre and nowadays belonging to Museu de Évora and Convento dos Remédios (Évora). These samples have been analysed through variable pressure scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (VP-SEM-EDS), micro-X-ray diffraction ( $\mu$ -XRD) and micro-Raman spectroscopy in order to compare the glaze and the ceramic body technology.

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(P 27)

## HPLC-DAD-MS AND LDI-MS STRATEGIES FOR ANTHRAQUINOID LAKES IDENTIFICATION IN PAINT SAMPLES

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Lakes are artificial pigments obtained from one or more organic natural dyes, extracted from roots, plants, or shellfish, and fixed by absorption or complexation on an insoluble and inorganic material. Red anthraquinoid lakes, such as madder lake, kermes lake, cochineal lake and Indian lac, have been the most important and widely used for painting purposes and some great examples of lakes used as glazes are exhibited in European paintings since XIV century [1].

From an analytical point of view, identifying the lakes in paint samples is challenging because of the high amount of binding media in which they are dispersed and the simultaneous presence of several organic materials and non-original compounds as consequence of ageing and environmental contamination. In addition, the low percentage of dyes used in traditional lakes (1-3 % w/w) and the difficult extraction of dyes from the matrix further complicate the analysis [2]. Thus, the interference in the analyses of the lakes possibly caused by the presence of the binders has to be investigated and an analytical procedure able to detect anthraquinoid dyes at very low concentration avoiding matrix effect has to be developed.

This study deals with the optimization of methods for the detection of the anthraquinoid dyes achieved through the analysis of reference materials and paint model systems evaluating the role played by the binders by means of chromatographic and mass spectrometric techniques, such as High Performance Liquid Chromatograph with Diode Array and Mass Spectrometric detector (HPLC-DAD-MS) and Laser Desorption Ionization - Mass Spectrometry (LDI-MS).

The procedures developed aim at identifying organic dyes by these different techniques maximizing the information achievable while minimizing the amount of sample needed. Different solvents of extraction and injection and experimental set ups have been tested in order to build up the most efficient strategies.

The most significant results for reference materials, paint model systems and relevant samples from Greek mural paintings will be presented.

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**PROTEIC BINDERS IN ART: APPROACHES FOR IMMUNODETECTION**

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Mural or easel paintings contain a variety of components, such as support materials, binding agents and emulsifiers, that are easily degraded by microorganisms causing structural and aesthetic damage, like discoloration, stains or biofilms on the surface, degradation of the support and adhesive polymers, resulting in cracking and detachment of the layers ink [1]. Binding materials are commonly proteins (e.g.: egg, milk, animal glues) that promote adherent films with variable elasticity and durability [2]. The correct identification of these materials, including its characterization, is an important step in understanding the technique used by the artist, also providing relevant information for conservation and restoration processes. Immunological techniques for protein identification in artworks show unique advantages over others: selectivity regarding the biological source, ability to resolve complex mixtures of proteins and high specificity of antibody-antigen binding, detecting protein at low quantities [3].

In this study, immunological approaches were carried out for the identification of several proteic binders used in easel paintings. The immunoassays were performed using monoclonal and polyclonal antibodies (Ab) such as Anti-Chicken Egg Albumin (ovalbumin), Anti-Collagen type I and Anti-Casein as primary antibodies and Anti-Mouse IgG (for monoclonal Ab) or Anti-Rabbit IgG (for polyclonal Ab) enzyme alkaline phosphatase conjugates as secondary antibodies (all from Sigma-Aldrich). In the first step antibodies titrations have been determined by dilution of the commercial standards (ovalbumin, collagen and casein - Sigma-Aldrich), and the ELISA protocol has been optimized testing different temperatures and incubation times for a detection signal increase. These optimized assay conditions were used in the establishment of a linear range for the protein quantification in microsamples. In the second step a selectivity study for each antibody was performed using several proteins usually found as binders in paintings (sheepskin, rabbit skin, rabbit bones, fish, egg yolk and white, bovine milk and commercial BSA, casein, collagen and gelatin from cold water fish skin). The procedure was then used in paint models microsamples, enabling the optimization of the antigen (protein) extraction efficiency, and the development of a methodology that allowed the detection and quantification of low quantities of proteins with high specificity.

**Acknowledgments**

This work has been financially supported by FCT, FEDER and INALENTEJO under the projects ON FINARTS (PTDC/EAT-HAT/115692/2009) through program COMPETE and IMAGOS X LARES (ALENT-07-0224-FEDER-001761, 11BI/LARES/2014).

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**(P 29)****AN UNUSUAL MURAL PAINTINGS AT THE CHAROLA OF THE CONVENT OF TOMAR (PART II).  
RED LAKES AND ORGANIC BINDERS**

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The Convent of Christ is one of the most emblematic monuments of the town of Tomar that received the classification of World Heritage by UNESCO. The oldest building of the Convent is the Charola, dated from the 12<sup>th</sup> century. The Charola is a central-plan Romanesque construction that has eight sides on its central drum and sixteen on the outer walls, similarly to the Holy Sepulchre of the Mosque of Omar in Jerusalem. Over the centuries, this space has undergone several architectural renovations. The most significant was promoted by King Manuel I, presumably between 1510 and 1525 [1]. The iconographic enrichment includes sculptures, oil paintings on wood and on leather, stucco work and mural paintings. The mural paintings are particularly important because they are the only example in Portugal of a monumental pictorial cycle made exclusively with organic binders, known to date.

This work presents the analysis of the organic materials (binders and red lakes) from the flesh tones, wings and vests of the angels. Fourier transform infrared microscopy and spectroscopy ( $\mu$ -FTIR) was used for pre-screening of binding media and pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) was selected for the identification of binders. Optical microscopy with UV light was used for examination of the samples' cross sections.

First results reveal that linseed oil was the main binder used by the painters, although the presence of protein was also suggested by  $\mu$ -FTIR. Madder lake was detected in the red paint layers. Alizarin and purpurin, the main chromophores in *Rubia* spp., were identified using LC/MS. Lakes prepared in laboratory following historical recipes were also injected in the LC/MS system for comparison. The obtained chromatographic profiles will serve as database for future work.

**Acknowledgments**

The authors wish to acknowledge Consórcio Nova Conservação Lda; Administration board of the Convent of Christ in Tomar and Direcção Geral do Património Cultural (DGPC) for allowing this study; Fundação para a Ciência e Tecnologia, for financial support (Post-doc grant SFRH/BPD/63552/2009), through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund and Project PRIM'ART PTDC/CPC-EAT/4769/2012, funded by financed by national funds through the FCT/MEC and co-financed by the European Regional Development Fund (ERDF) through the COMPETE - Competitiveness Factors Operational Program (CFOP).

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**RESTORATION: SURFACE AND COLOUR**

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The painting with three-dimensional composition “Lily and Woman” was made by famous Lithuanian artist Petras Repsys in 1968. The artist creates in different fields of art – graphic, fresco, sculpture, applied art, book illustration. This painting consists of gilded and painted parts. Painter has told he made ground and paints for this work by himself.

The picture was brought to restoration workshop to restore some flaking parts of paint and ground layers. The main focus of restoration was how to consolidate damaged places that traces of restoration would be less visible. The layer of paint was very friable and matt, lost binding media. The colour of background of paint was palish.

Places with crumbling layers of ground and paint were consolidated with hide glue. Later all surface of paint was strengthened with cellulose derivative in special way.

The paint’s layer became homogeneous, colour hue recovered and revealed itself.



Painting “Lily and Woman” after restoration

**(P 31)****CHARACTERIZATION OF 19TH CENTURY PHOTOGRAPHIC MATERIALS BY NON-INVASIVE ANALYTICAL TECHNIQUES**

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The characterization of the conservation status of photographic materials is usually assessed through visual analysis or optical microscopy. However, many of these materials cannot be completely characterized by a simple visual-optical evaluation and need more non-invasive multi-analytical techniques [1]. Most importantly, these techniques need to be safe, non-contact and non-destructive and well suited for in situ analysis of cultural heritage objects and especially for the extremely vulnerable daguerreotype photographs.

Daguerreotypes were the first successful photographic images presented to the world in Paris, 1839. This first form of photography was an instant success, and for over 15 years it was the dominant photographic process. Although millions were made during this period of great experimentation, the extreme vulnerability of the image recorded directly on a polished silver plate led to the loss of many of them in a few short years. Those that survive are often deteriorated, often with a highly coloured and obscuring corrosion products on their surface, and still remain highly vulnerable [2]. The most common form of deterioration found on daguerreotypes is a surface tarnish exhibiting interference colours. Previous analyses have identified the typical tarnish as consisting of silver sulfide, commonly referred as ‘silver mirroring’. In most cases the colour of silver mirroring appears blue under reflected light. Degradation in terms of formation of a hazy, spread out white surface layer and white spots obstructing the images has also been previously reported [3].

In this work, examples of the application of in situ, non-invasive and non-destructive multi-analytical instrumental techniques used to study the morphology and degradation status of daguerreotypes are presented. This is in order to cross-check information about the production processes and the degradation status of the studied items with the conservators and art historians’ analysis.

The analytical techniques used for the morphological and chemical characterization include technical photography, optical microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), micro X-ray diffraction ( $\mu$ -XRD), micro-Fourier transform infrared spectroscopy ( $\mu$ -FTIR) and micro-Raman spectroscopy.

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(P 32)

**BEHIND THE GLASS: ANALYTICAL AND MICROBIOLOGICAL STUDY OF PHOTOGRAPHIC GLASS PLATES**

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Photography helps to construct the past as well as reveal it, evoking memories and evidencing stories and thereby, a relevant part of our cultural heritage. The adoption of glass as a negative support marked the beginning of a new era in the negative technology. Photographic glass plates negatives consist of a light sensitive emulsion fixed to a glass plate base with a binder. The gelatine glass negatives process reports that the emulsion was composed by gelatine and silver salts which after exposure form image substance [1]. This was a technical innovation in the history of photography and it was developed in 1871 by Richard Leach Maddox being widely used until the 20th century [2]. These negatives are subject to various types of deterioration due to their fragile physical format and highly varied chemical properties influenced by extrinsic and intrinsic factors. Physical pathologies as colour fading (yellowing and browning) as well as breakage and cracking are common occurrences. The delamination of gelatine layer can succeed by the improperly manufacturer, the poor quality of the glass (that affects the gelatine-glass bond) and the exposure to extreme temperature fluctuations as well as humidity, atmospheric pollutants and mould attack. Oxidative deterioration can also occur and can cause fading of the image, gelatine layer yellowing and silver mirroring which results in a bluish metallic sheen on the image [3, 4].

In this work morphological, chemical and microbiological characterization of gelatine glass negatives belonging to the Municipal Archive of Évora and dated from 1916 to 1940 was done. Tones, colour fading, gaps and detached emulsions evaluation was carried out by technical photography and optical microscopy. Scanning electron microscopy coupled with energy dispersive X ray spectroscopy (VP-SEM-EDS) was used to evaluate the morphology and the elemental composition of the glass plate and the materials used in the manufacturing and micro-Fourier transform infrared spectroscopy ( $\mu$ -FTIR) was used for binder analysis. Microbiological studies were carried out in order to evaluate the influence of biotic attack in these samples.

The authors acknowledge the Municipal Archive of Évora for the glass plates and Joana Duarte and Susana Cunha for selection and description of pathologies.

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## INVESTIGATION ON THE MATERIALS AND DEGRADATION OF CELLULOSE ACETATE NEGATIVES

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For the past thirty years, the interest for the preservation of photographic materials has intensified. The knowledge of the structure and composition of these artefacts is essential to design appropriate approaches for their preservation and conservation [1]. Cellulose acetate film is composed of four layers: gelatine emulsion (top layer), subbing cellulose nitrate (subbing for gelatine emulsion), cellulose acetate film (support layer) and gelatin (bottom anti-curl layer to provide dimensional stability). The bottom gelatine anti-curl layer contain anti-halation (anti-halo) dyes to prevent the exposure of the silver salts from light bouncing off the support. This dye was removed or bleached out during the negative image processing but the compound remained in a “leuco” (i.e., invisible) state [2, 3]. Cellulose acetate negatives are susceptible to various types of degradation which can be grouped into three major categories: physical, chemical and biological. A common degradation process is the “vinegar syndrome.” This syndrome is a slow form of chemical deterioration which affects the plastic support, eventually causing it to become acidic, to shrink, and to give off an odour of acetic acid (vinegar) [4]. The regeneration of anti-halo dyes present in the anti-curl layer is prompted by the acetic acid released by the film support and the consequent pH decrease of the gelatine layer. Pink colors are found in some black & white Kodak films, while blue colors are found in some black & white Agfa and, Ansco films [3].

In this work, acetate negatives belonging to a private collection were studied. Photography and detailed macro-photography were done under transmitted light, UV radiation and raking light. Morphological aspects were also evaluated by optical microscopy and variable pressure scanning electron microscopy with energy dispersive X-ray spectrometry coupled (VP-SEM/EDS). Elemental composition was also obtained by X-ray fluorescence (XRF) spectroscopy and Fourier transform infrared spectroscopy in attenuated total reflexion (ATR-FT-IR) mode and micro-Fourier-transformed infrared ( $\mu$ -FT-IR) supplied important information about the emulsion and plasticizers used in the production of the negatives. Biological colonization was also studied in order to evaluate the influence of biodeterioration.

### Acknowledgements

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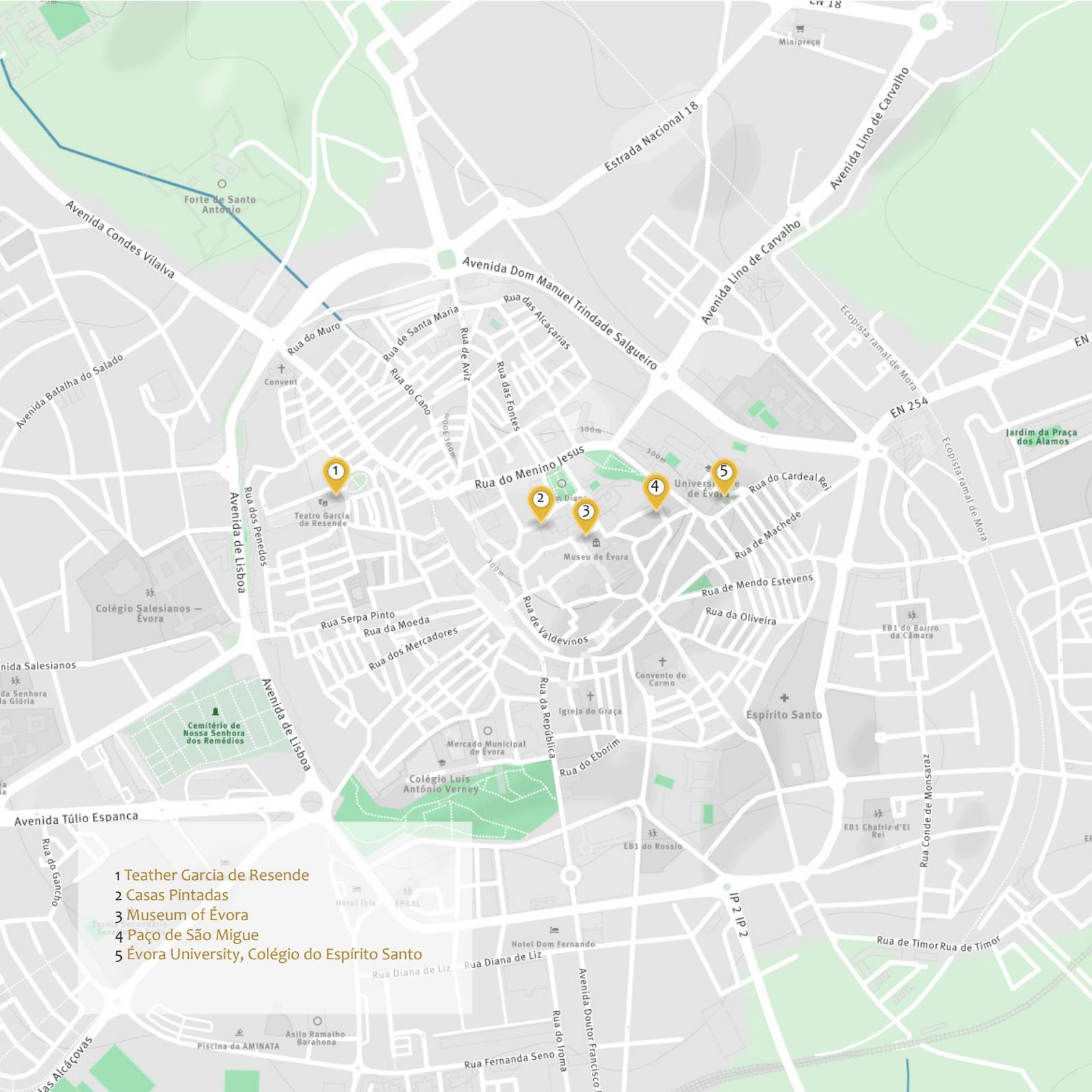
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**COLOR WATCH – MONITORING CHANGE OF COLOR APPEARANCE OF MEDIEVAL MOSAIC**

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The contribution presents an experimental method and a device developed for monitoring state of mosaic surface. Medieval mosaic of the Last Judgement on St. Vitus Cathedral in Prague was created in 14th century. Tesserae are made from easy to melt glass that is prone to weathering, thus a special coating was applied to stop degradation. But the coating itself has to be selected to withstand environmental attack and also not to block visibility of original beauty of the mosaic. It was found that degradation of the coating is associated with increase of occurrence of internal flaws and surface roughness. The two defects types cause loss of transparency and add foggy layer to appearance of mosaic pieces, decreasing color saturation at the same time. Accumulation of defects translates into change of surface reflectivity, measurement of which is a basis for monitoring to be regularly applied during inspection of coating state. The method can detect degradation process before it gets apparent to human eye and therefore precautions can be taken.



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