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Conservar Património

20

ARP • Associação Profissional de
Conservadores-Restauradores de Portugal

Dezembro | December **2014**

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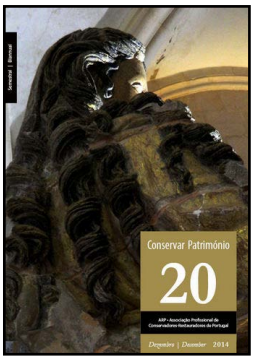

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Editorial

Editorial

A Conservar Património, *com a edição deste número, completa dez anos de publicação ininterrupta.*

A criação da revista em 2005 decorreu da necessidade de divulgação de trabalhos técnicos e científicos produzidos por Conservadores-restauradores, e também por outros profissionais que trabalham a par destes na área da preservação e conservação do Património Cultural em Portugal, entre outros, Historiadores da Arte, Arqueólogos, Museólogos, Químicos, Físicos e Biólogos.

O aparecimento da Conservar Património *subscreveu desde o seu início os princípios éticos fundamentais dos Conservadores-restauradores. Com o seu crescimento, a revista passou por algumas transformações mas manteve-se permanentemente ligada aos propósitos e ideais da profissão de Conservador-restaurador, assim como às boas práticas das intervenções em Património Cultural.*

Hoje, após dez anos de publicação contínua, podemos afirmar que a Conservar Património *já alcançou qualidade e prestígio, e está presente cada vez mais, junto de todos os profissionais ligados às questões de preservação e conservação do Património Cultural. Com este propósito, a revista adoptou desde 2013 um suporte digital, tendo-se disponibilizado na Internet um acesso livre a todos os leitores.*

Em consequência dos avanços da Conservação e Restauro e da crescente visibilidade desta área, continua a sentir-se a

Conservar Património *completes ten years of uninterrupted publication with the release of this number.*

The beginning of its publication in 2005 arose from the need to disseminate technical and scientific papers produced by Conservator-restorers, and also by other professionals working alongside these in the field of preservation and conservation of Cultural Heritage in Portugal, namely Art Historians, Archaeologists, Museum experts, Chemists, Physicists and Biologists.

The advent of the Conservar Património *subscribed since its beginning the fundamental ethical principles of Conservators-restorers. With its growth the journal has undergone some changes but remained permanently connected to the purposes and ideals of the Conservator-restorer profession, as well as to the good practices of interventions in Cultural Heritage.*

Today after ten years of continuous publication, we can say that the Conservar Património *has achieved quality and prestige, and it is increasingly present amongst all professionals related to the preservation issues and conservation of cultural heritage. For this purpose, the journal adopted since 2013 a digital support that is available on the Internet as a free access to all readers.*

As a result of the advances in the Conservation-Restoration field and the increasing visibility of this area, we continue to feel the need to have a publication of

necessidade da existência de um meio de divulgação nacional que dê voz às contribuições de especialistas, quer nacionais como estrangeiros, e ambiciona-se assim que a Conservar Património *ao melhorar continuamente o seu nível de qualidade possa alcançar um prestígio similar às revistas internacionais.*

Neste décimo aniversário, saudamos o contributo inexcedível desde o primeiro momento para com a Conservar Património*, do seu Director António João Cruz. A sua procura permanente em elevar o nível de qualidade das contribuições, e o objectivo constante de melhoria da selecção dos trabalhos apresentados, constituem uma garantia de qualidade dos números da* Conservar Património*, e reflectem a consistência de um trabalho realizado sempre com o desígnio de obter o prestígio que pretendemos para a revista.*

Esta vontade de alcançar uma relevância e notoriedade reconhecidas no meio nacional e internacional, bem como o esforço de produzir uma revista de reconhecido valor, constituem permanentemente a determinação da Direcção e do Conselho Editorial da Conservar Património*, sendo por isso o alicerce desta publicação como uma referência na área da Conservação e Restauro.*

Uma palavra de agradecimento também para o contributo importante e imprescindível de todos os referees*, que anonimamente têm validado o interesse dos trabalhos apresentados e contribuído através das suas críticas e sugestões para o desenvolvimento e manutenção do nível de qualidade da* Conservar Património.

Para o futuro, acreditamos que a Conservar Património *irá continuar um percurso em prol do desenvolvimento científico da Conservação e Restauro em Portugal, preservando os valores que a têm caracterizado desde a sua criação.*

Rui Câmara Borges
Presidente da ARP

national diffusion that gives voice to the contributions of specialists, both national and foreigner, and we aim therefore through the continuous improvement of the quality level of Conservar Património *to reach a prestigious similar to its congenerous international journals.*

In this tenth anniversary, we recognize the unsurpassed contribution from the beginning towards Conservar Património*, from its Director António João Cruz. His constant quest to raise the level of quality of the contributions, and constant aim to improve the selection of the submitted papers, constitutes a guarantee of quality of the numbers of* Conservar Património *and reflects the consistency of a work continuously developed with the purpose of obtaining the prestige we want for the journal.*

This determination to achieve nationally and internationally a recognized relevance and reputation, as well as the effort to produce a journal with a recognized interest, have been the permanent determination of the Board and the Editorial Board of Conservar Património *and are therefore the basis of this publication as a reference in the field of Conservation-Restoration.*

A word of gratitude is also needed to the important and indispensable contribution of all the referees, who have anonymously validated the interest of the papers presented and contributed through their comments and suggestions for the development and maintenance of the quality level of the Conservar Património.

For the future, we believe that the journal Conservar Património *will continue its path towards the scientific development of the Conservation-Restoration in Portugal, preserving the values which characterized it from the beginning.*

Rui Câmara Borges
President of ARP

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Article / Artigo

Colorimetric evaluation of three adhesives used in the consolidation of contemporary matte paint after artificial ageing

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Abstract
Of all the problems associated to contemporary painting, the most complex is probably that which concerns powdering matte surfaces, both for their technical characteristics and optical properties and for the aesthetic significance associated to these types of finishes. These pictorial surfaces are technically complex due to the high risk of irreversible alterations associated to the appearance of the treated surface and the potential for streaking, tide lines, changes in colour, darkening, added gloss and changes in texture during the treatment process. For this study, a colorimetric analysis was performed to evaluate the behaviour of three adhesives commonly used in the consolidation of these types of painted surfaces, to determine the effect of ageing on the adhesives and quantify their stability as a function of adhesive type, concentration, and application method. Of all the adhesives, funori did not result in significant changes when aged using this method.

Keywords
Adhesives
Ageing
Colour change
Powdery paintings
Contemporary art

Avaliação colorimétrica de três adesivos utilizados na consolidação de tintas mate submetidas a envelhecimento artificial

Resumo
Dentro do heterogéneo grupo de problemas associados à pintura contemporânea, o caso de superfícies mate pulverulentas apresenta uma complexidade particular, tanto pelas suas características técnicas e propriedades ópticas, como pela significância estética deste tipo de acabamentos. Estas superfícies pictóricas são tecnicamente complexas, dado o elevado risco de alteração irreversível da aparência da superfície tratada e o possível aparecimento de riscos, linhas de maré, alterações da cor e/ou da textura, escurecimento e brilho durante o processo de intervenção. Neste estudo foi feita uma análise colorimétrica para avaliar o comportamento de três adesivos comummente usados na consolidação deste tipo de superfícies pictóricas, para determinar os efeitos do envelhecimento e a fim de quantificar a sua estabilidade em função da natureza, concentração e método de aplicação da substância adesiva. De todos os adesivos, apenas o funori não registou mudanças significativas após envelhecimento.

Palavras-chave
Adesivos
Envelhecimento
Alterações cromáticas
Pinturas pulverulentas
Arte Contemporânea

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Research aims

The aim of this study is to qualitatively and quantitatively describe the colorimetric stability of the three adhesives typically used in the consolidation of contemporary works of art featuring powdery matte surfaces. After undergoing accelerated ageing cycles using ultraviolet radiation and varying humidity and temperature, funori, Acril 33 and Gelvatol were evaluated for changes in colour as well as any effects upon the painted surfaces. The aim here was to compare changes in colour stability of these adhesives as a function of concentration and application method. The following application methods were used: consolidation using a paintbrush combined with controlled suction; consolidation using ultrasonic mister, and consolidation using ultrasonic mister and controlled suction. The effect of different methods of application will also be studied.

Introduction

The greater focus on concept-based art which began in the 1960s is responsible for the special relationships that exist between an idea, the transmitter of message, and the materials chosen by the artist to convey the intended message in a particular work of art. The materials chosen by the artist hold a particular aesthetic and ideology, which are directly related to his/her philosophical concerns and artistic discourse. It is important to understand the conceptual load contained both in these materials and their aesthetic effect, and how these relate to the comprehension of the artistic message to understand the specific issues associated to a given work — a task which must be undertaken in the evaluation of the material and conceptual deterioration of a given work of art and its requirements in terms of the conservation and treatment [1].

In the case of monochromatic works, the pictorial space depends solely on the surface qualities of the work itself; as these works do not feature representations alluding to the personal or the particular. In these works, pure feeling is expressed by colour alone; no representational elements or anything associated to subjective meanings are used by the artist at all. The chromatic values of the work take on a dimension and a presence that lie somewhere between the spiritual and experiential [2-3]. This search for tangible representation through colour intensity led artists to investigate the artistic properties of raw pigment and the methods by which said pigment could be adhered to the support media without losing its vibrant powdery appearance. This enabled artists to produce matte and velvety surfaces in which the low binder-to-pigment ratio of the paint created subtle fields of ethereal colour. Yet these surfaces are continually at risk of loss of material due to the detachment of pigment particles with the slightest of movements.

Maintaining the coherent transmission of the concept behind this kind of monochromatic work depends upon a conservation process that does not alter the powdery surface of the painting. There are a number of options available to the conservator. The works can be displayed within a glass case, which ensures that any loose particles will be protected from the effects of vibration from both the building itself and the environment. Another option involves the consolidation of the pigment layer. The first option is ethically undesirable given that, for this type of work, the space in which the work is displayed is just as important as the work itself; many artists who make use of this artistic discourse are quite concerned with the displaying of their works, seeing the monochromatic painting as part of an installation in which the gallery and the rest of the his/her works stimulate the spectator in some way [2]. A display case would interfere with the concept of the work as an ethereal object within the gallery space. Yet the second option may endanger the technical properties of the work as it may easily and irreversibly alter the pictorial surface, and its monochromatic properties in turn [4].

Feller and Kunz [5], who pioneered the study of powdery surfaces, investigated the physical properties of porous matte paint in order to establish the physical parameters that would help identify the best method for their consolidation. Their studies mainly showed that the darkening of these surfaces was primarily due to the action of the adhesive on the surface, which eliminated the air-pigment interface. They conducted a battery of tests on paints with varying pigment concentrations using polymers with differing refractive indices, showing that the darkening effects were similar, regardless of the polymer used. Colour saturation occurred when the addition of the adhesive to a porous surface reduced the volume of void spaces, changing the pigment volume concentration (% PVC), which in turn decreases the solid-to-air interfaces which work to disperse the light. Colour perception depends on the PVC of a dry film; it can therefore be described as the result of a physiological effect arising from the interaction of light within a system with the system components (pigment, binder and interstitial air). This interaction is determined by the selective absorption and reflection of different wavelengths that make up white light. Reflection of light from a smooth surface produces specular reflection, which is perceived as glossy or shiny. If the surface has imperfections or defects, the light rays hit the interstices formed by said imperfections and are reflected in different directions and angles, giving the surface a matte appearance due to the diffuse reflection of the light rays [5-6].

The most common problem seen in this type of treatment is poor adhesive penetration. This occurs when the adhesive is too viscous to penetrate the small voids between pigment particles, or when the solvent evaporates before the solution has an opportunity to penetrate these spaces.

Consolidation in an atmosphere that is saturated with the solvent used to dissolve the adhesive is a technique that was developed to prevent the darkening of the surface

and the appearance of tide lines [7]. Used on laboratory samples of wooden supports and ethnographic objects, this treatment showed good results using both fast and slow-evaporating solvents.

Michalski [8-9] focused on resin particle size, using an ultrasonic mister in the consolidation of powdery paint on ethnographic artefacts, both on samples without supports and actual paintings on wooden supports.

Nevertheless, research on the treatment of powdery surfaces created using contemporary paints [10] has shown that these treatments may cause colour saturation formed by the collapse and compaction of pigment particles during the adhesive curing phase, and not due to the formation of a solid film in the interstitial spaces between the particles. This process may also produce tide lines caused by an inadequate regulation of the velocity at which the mist is applied.

In addition to application methods, researchers have also studied the resins employed in the consolidation of powdery paint. Of these, the most noteworthy was the study conducted in the Australian Museum [11], a comprehensive and detailed investigation into the various types of resins, in both liquid and dissolved form, used in the treatment of ethnographic objects.

In recent years, numerous studies have dealt with the consolidation of contemporary matte paint, both on surfaces with good binder properties and those with powdery paint [12].

The current study is framed within another, larger work [13-14] on the consolidation of powdery surfaces of contemporary art works on canvas and the specific requirements and issues these works pose for the conservator. Initial results focused on the study of colour changes produced during the consolidation process, using three different water-based adhesives and several application methods. This experiment yielded interesting conclusions concerning consolidation treatments and provided valuable guidelines for the conservator.

The second part of this study is centred on the characterisation of colour changes arising from these same experimental models, after undergoing various cycles of accelerated aging.

Experimental design

Materials and methods

Artist´s materials

Special attention was paid to contemporary artistic production to prepare samples whose characteristics closely matched those of contemporary artworks on canvas; samples were produced after interviewing contemporary artists, with the materials indicated by them [1]. Commercial canvases (Lienzos Levante) were selected as supports (46 cm × 38 cm.). These contained cotton (60 %), polyester (26 %) and viscose (14 %) with a thread count of 12 × 12 threads per square centimetre. They were further prepared using animal glue sizing and alkyd primer for oil paint.

The paint film was created by mixing 7 % No. 170 acrylic cobalt blue paint (Liquitex), 93 % No. 93 ultramarine blue pigment (Microgiraltin: Agroquímica del Vallès) and deionised water

Consolidation models

Three adhesives typically used in the restoration of contemporary paintings were selected, bearing in mind their aqueous properties to ensure a suitable operation of the mister: Acril 33 (acrylic resin in aqueous dispersion), funori (polysaccharide) and Gelvatol (polyvinyl alcohol). The adhesives were dissolved in deionised water at different concentrations (by weight), according to type (Table 1). Vinyl and acrylic resins were prepared at low proportions to prevent the formation of gloss on the painted surface and to ensure correct operation of the mister, which may not work at high concentrations of adhesive. funori concentrations were higher since, unlike the other adhesives, this product does not hamper the work of the mister or affect the colour of the painted surface [15]. The various concentrations of funori were obtained by using a base solution: 1 gram of algae was soaked in 120 ml of deionised water for 24 hours. The solution was then stirred at 1200 rpm and a temperature of 40ºC for 60 minutes, and then filtered. A drop of Biotin N biocide (Tributyltin naphthenate and quaternary ammonium salts) was then added to the solution.

Table 1
Concentration (by weight) of adhesives versus application method

	Concentration (%)											
	Ultrasonic mister				Ultrasonic mister + low pressure				Paintbrush + low pressure			
Gelvatol	0.5	1.5	2.5	5	0.5	1.5	2.5	5	0.5	1.5	2.5	5
Acril33	0.5	1.5	2.5	5	0.5	1.5	2.5	5	0.5	1.5	2.5	5
Funori	0.2	2	4	6	0.2	2	4	6	0.2	2	4	6

The four different concentrations of the adhesives were applied to the facsimiles using three different application methods: ultrasonic misting (Becker Preservotec AGS 2000, at a particle size of 5 µm), low-pressure ultrasonic misting (micro-table model CTS NSD 11; suction was set at 4999.57 Pa) and application using a paintbrush on Japanese paper at low pressure. The atmospheric parameters during the application processes were measured with a TESTO 608-H1 thermo-hygrometer, which registered a relative humidity of 65-70 % and a temperature of 28-30 ºC.

The application procedure involving the mister was standardised using the following procedure: before application, the mister was placed at the centre of a template at a distance of 10 cm from the surface to be treated. The surface was sprayed for 60 seconds and left to dry during another 60 seconds. In cases where the suction table was used, the micro-perforated plate was placed under the canvas [13-14].

For the artificial accelerated ageing tests, three samples of equal size (5 cm × 2.5 cm) were extracted from each of the samples treated with adhesives. Blank commercial canvases and painted untreated samples were also extracted for artificial accelerated ageing tests.

Accelerated ageing treatments

Artificially accelerated photoageing was performed by way of ultraviolet radiation; the samples were exposed to ultraviolet light for a total of 400 hours in a QUV-Basic weathering chamber, at a constant temperature of 45ºC. This unit contains fluorescent UV lamps (QUVB-313EL), maximum emission at 295 nm.

For the artificially accelerated ageing process involving varying humidity and temperature, i.e. thermal ageing, the samples were exposed to 270 hours of treatment in an environmental chamber (Dycometal DI-100), equivalent to four cold-dry cycles (6 ºC, 30 % HR) and four warm-humid cycles (40 ºC, 80 % HR).

Instrumentation

Microscope

Specimens were studied using a Leica DMR optical microscope with an incident/transmitted light system and polarization system in all cases.

Colorimetric analysis

The measurements were taken with a Minolta CM-2600d spectrophotometer using CIE standard illuminant D65 (daylight colour temperature 6500 K) and a 10º standard observer. Colorimetric measurements were obtained through repeated measurement of the selected areas of the test specimens in order to obtain the standard deviation value and by performing a minimum of three consecutive measurements, using the SCI mode (specular component included). The colour spaces used were CIELAB and CIELCH. The former enabled the calculation of the total chromatic difference between the two stimuli and the latter made information regarding lightness (L*), saturation (C*) and hue (h*) more easily attainable. Both SCI (Specular Component Included) and SCE (Specular Component Excluded) values were measured in order to obtain the gloss difference.

Results and discussion

It was observed that the simultaneous use of misting and suction produces a more localised application of the adhesive, an effect which may be desirable for application to specific areas of an art work. Furthermore, when an application is combined with controlled suction, adhesive penetration was found to improve, as did the drying time [12-13].

Thermal ageing

Table 2 shows the difference in colour and lightness for the samples that underwent humidity and temperature ageing. Our results were based on data provided by Melgosa, who established a suprathreshold colour difference of 1.75 CIELAB units [16]. The results obtained do not exceed this suprathreshold value in any of the samples, regardless of adhesive or application method.

Analysis of the differences in lightness values (ΔL*) of all samples revealed that these were very low and negligible for all adhesives, save for those applied with a paintbrush. In these cases, the surfaces showed some darkening, which was imperceptible to the human eye, as in the values obtained for hue (h*).

Breaking down the obtained results, it was shown that, at low concentrations, funori (Figure 1) is a stable adhesive as it did not underwent a great change in colour with respect to the control. The remaining samples generally obtained ΔE* values that were lower than 0.45.

Acril 33 (Figure 2) seemed to remain stable at low concentrations with a ΔE* value of 0.07-0.29 CIELAB units at these concentrations, regardless of the method of application, and resulted in the greatest colour difference for all three application methods at its highest concentration (5 %) both in terms of total colour values (ΔE*=0.32 with the mister, ΔE*=0.52 using mister and suction, and ΔE*=0.47 for the application using a paintbrush and suction) and lightness, causing the most darkening when applied using a paintbrush.

Gelvatol (Figure 3) produced a difference in colour that was generally like Acril 33, and similar at all concentrations. Note that the largest deviation can be seen for the 1.5 % concentration applied with the brush (ΔE*=0.47).

The variation in gloss produced by the adhesives applied on colour films was found to be almost nil. The

Table 2
Lightness (ΔL*), saturation (ΔC*) and hue (Δh*) before (1) and after (2) thermal ageing for the consolidated samples and its colour (ΔE*) and gloss change (ΔG) (UM: ultrasonic mister; LP: low pressure; B: paintbrush)

Sample	L*(1)	L*(2)	ΔL*	C*(1)	C*(2)	ΔC*	h*(1)	h*(2)	Δh*	ΔE*	ΔG
Gelvatol 0.5 % - UM	44.10	44.17	0.07	41.89	41.91	0.02	244.52	244.25	-0.27	0.21	0.00
Gelvatol 1.5 % - UM	43.69	43.66	-0.03	42.31	42.34	0.03	244.45	244.26	-0.19	0.14	-0.01
Gelvatol 2.5 % - UM	43.17	43.05	-0.12	41.90	42.12	0.21	245.06	244.92	-0.14	0.26	0.00
Gelvatol 5 % - UM	45.85	45.92	0.07	41.36	41.60	0.24	244.12	243.84	-0.29	0.32	0.02
Gelvatol 0.5 % - UM + LP	44.27	44.19	-0.08	42.25	42.20	-0.05	244.04	243.86	-0.18	0.16	0.00
Gelvatol 1.5 % - UM + LP	43.91	43.89	-0.02	42.03	42.15	0.12	244.48	244.16	-0.32	0.27	0.03
Gelvatol 2.5 % - UM + LP	43.85	43.78	-0.08	42.29	42.44	0.14	244.33	244.08	-0.25	0.25	0.03
Gelvatol 5 % - UM + LP	44.83	44.90	0.06	42.51	42.41	-0.10	243.91	243.76	-0.15	0.16	0.02
Gelvatol 0.5 % - B + LP	44.16	44.16	0.00	41.61	41.60	-0.01	244.23	244.02	-0.21	0.15	0.02
Gelvatol 1.5 % - B + LP	42.89	42.42	-0.46	42.06	42.09	0.03	244.80	244.91	0.12	0.47	-0.02
Gelvatol 2.5 % - B + LP	40.88	40.80	-0.08	42.89	42.83	-0.07	245.46	245.37	-0.09	0.13	0.03
Gelvatol 5 % - B + LP	41.18	41.10	-0.05	42.25	42.22	-0.03	244.87	244.80	-0.10	0.10	0.01
Funori 0.2 % - UM	40.20	40.40	0.20	44.33	44.14	-0.19	246.24	246.10	-0.14	0.30	-0.03
Funori 2 % - UM	40.54	40.24	-0.30	44.29	44.29	0.00	245.95	246.02	0.07	0.31	0.01
Funori 4 % - UM	41.90	41.75	-0.15	44.22	44.16	-0.05	245.04	244.94	-0.10	0.18	-0.02
Funori 6 % - UM	41.84	41.40	-0.44	44.16	44.21	0.05	245.04	245.09	0.05	0.44	-0.01
Funori 0.2 % - UM + LP	40.95	41.03	0.07	43.95	43.97	0.02	245.82	245.64	-0.18	0.16	0.01
Funori 2 % - UM + LP	38.95	39.02	0.07	44.82	44.82	0.00	246.47	246.41	-0.06	0.09	0.01
Funori 4 % - UM + LP	39.33	39.28	-0.05	45.32	45.36	0.04	246.27	246.35	0.08	0.09	0.03
Funori 6 % - UM + LP	41.26	41.06	-0.20	44.27	44.31	0.04	245.23	245.26	0.03	0.21	0.00
Funori 0.2 % - B + LP	42.44	42.55	0.11	43.03	42.99	-0.04	244.74	244.67	-0.07	0.12	0.02
Funori 2 % - B + LP	40.72	39.98	-0.74	44.06	44.24	0.18	245.81	245.87	0.06	0.76	-0.03
Funori 4 % - B + LP	40.94	41.07	0.13	43.92	43.93	0.01	245.42	245.30	-0.12	0.16	-0.01
Funori 6 % - B + LP	41.33	41.27	-0.07	44.63	44.64	0.02	245.43	245.39	-0.04	0.08	-0.01
Acril 0.5 % - UM	40.77	40.73	-0.04	45.81	45.76	-0.05	244.38	244.33	-0.04	0.07	0.04
Acril 1.5 % - UM	41.63	41.53	-0.10	45.32	45.35	0.03	244.01	244.05	0.04	0.11	0.01
Acril 2.5 % - UM	42.04	41.98	-0.06	45.58	45.51	-0.07	243.39	243.40	0.00	0.09	-0.02
Acril 5 %- UM	42.15	41.83	-0.32	45.29	45.30	0.01	242.99	243.04	0.06	0.32	-0.01
Acril 0.5 % - UM + LP	39.70	39.60	-0.10	45.12	45.17	0.05	245.35	245.39	0.04	0.11	0.01
Acril 1.5 % - UM + LP	41.11	40.99	-0.12	45.29	45.21	-0.08	244.29	244.33	0.04	0.15	-0.03
Acril 2.5 % - UM + LP	41.26	41.30	0.01	45.44	45.32	-0.12	244.52	244.43	-0.09	0.14	0.00
Acril 5 % - UM + LP	41.51	41.60	0.09	44.77	44.65	-0.12	244.51	244.60	0.09	0.52	-0.15
Acril 0.5 % - B + LP	40.62	40.87	0.25	44.19	44.14	-0.05	245.09	244.92	-0.18	0.29	-0.01
Acril 1.5 % - B + LP	39.09	39.10	-0.02	44.95	45.15	0.19	245.79	245.73	-0.06	0.20	0.02
Acril 2.5 % - B + LP	38.19	38.08	-0.11	44.86	44.77	-0.09	246.29	246.17	-0.11	0.17	0.00
Acril 5 % - B + LP	38.12	37.67	-0.45	44.77	44.89	0.12	245.90	245.82	-0.07	0.47	-0.01

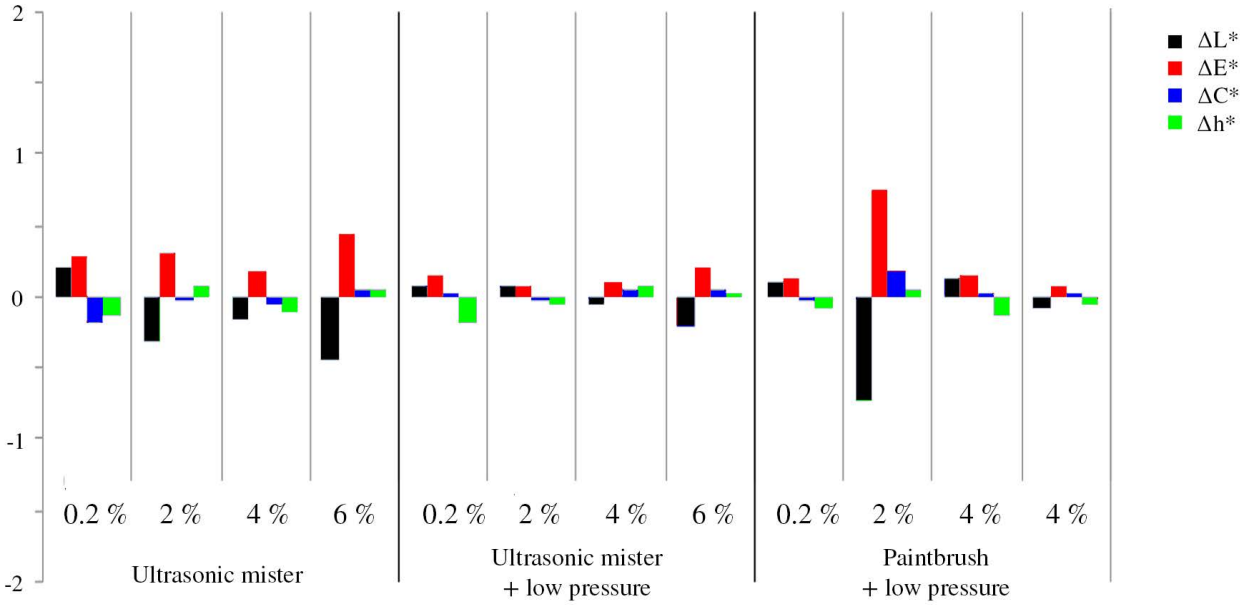

Figure 1. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after thermal aging for the samples consolidated with funori.

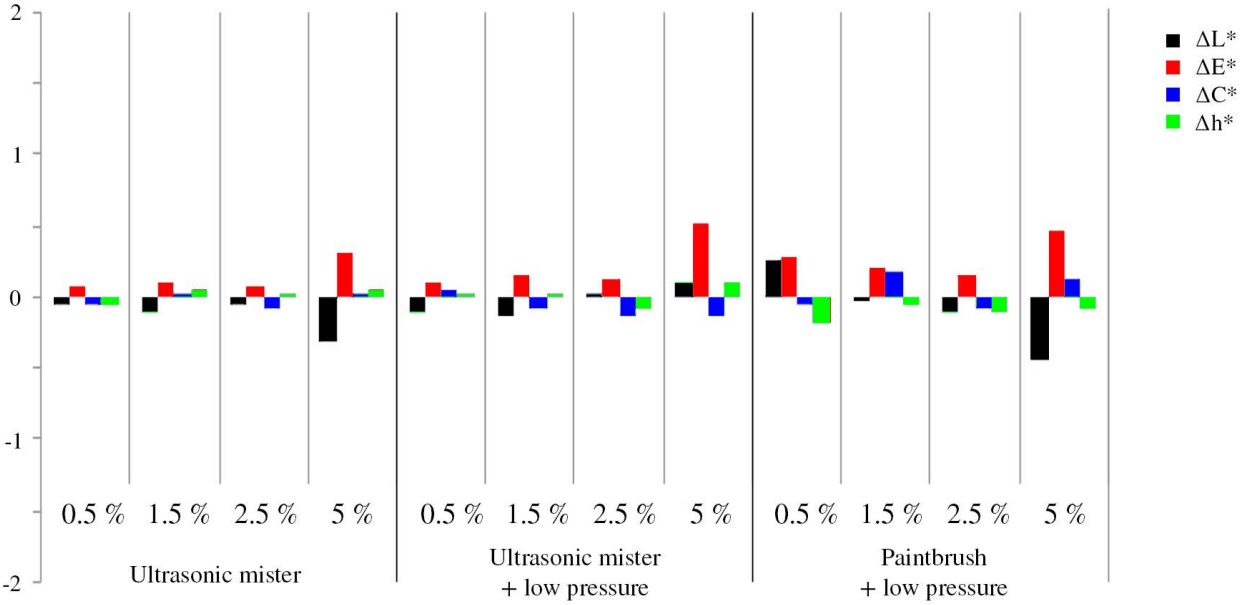

Figure 2. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after thermal aging for the samples consolidated with Acril 33.

average gloss difference in the case of funori was 0, while for Gelvatol and Acril 33 this average gloss difference was found to be 0.01 and -0.01 respectively. The average change in gloss as a function of application method is 0 for all methods.

Photoageing

When the samples were artificially aged using ultraviolet radiation, a change in the overall parameters of all samples was observed, except for the blank commercial canvas sample. Measurements taken from unconsolidated samples showed that this significant difference was mostly attributable to the ageing of the painted surface itself, and not the consolidants. Given that the aim of the present study is to analyse the behaviour of the adhesives and not of the acrylic paints, the average of chromatic variations was calculated for unconsolidated samples, both artificially aged and not (ΔE*=6.33; ΔL*=3.75; ΔC*=-3.04; Δh*=4.98). This average was compared to the consolidated samples in order to obtain the variation caused by adhesive. The

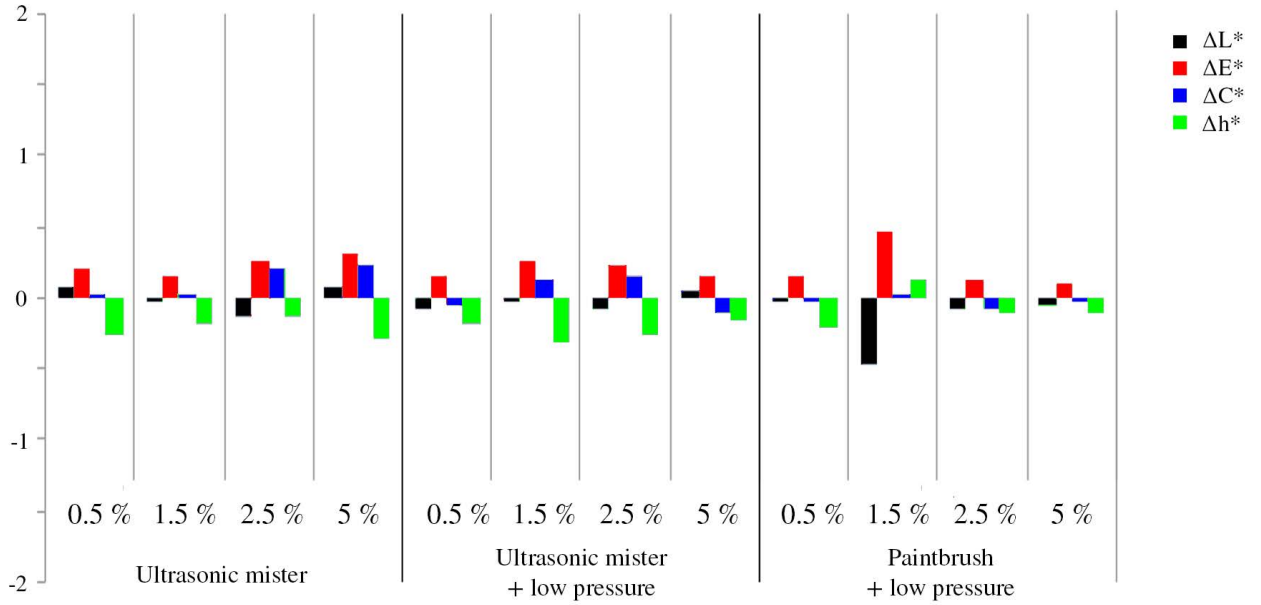

Figure 3. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after thermal aging for the samples consolidated with Gelvatol.

values of colour and gloss variation of the consolidants without the changes to the painted film are provided in Table 3.

Funori (Figure 4) fared the best under the ultraviolet radiation treatment, yielding ΔE* values that were lower than one, except for those samples which received consolidation treatment using higher concentrations of adhesive applied with the paintbrush (4 % and 6 %) and ultrasonic mister under low pressure (4 %). The highest change was found in the sample where the adhesive was applied with paintbrush at the highest concentration, 6 % (ΔE*=1.18).

Gelvatol (Figure 5) was also shown to be sensitive to ultraviolet radiation. Some of the samples were observed to have ΔE* values greater than 1 CIELAB unit. Nevertheless, the changes observed with Gelvatol were not as acute as with Acril 33. Similarly to the funori samples, the samples treated with higher Gelvatol concentrations showed some darkening (negative ΔL* values).

Acril 33 (Figure 6) was found to be the most sensitive to ultraviolet radiation, resulting in the

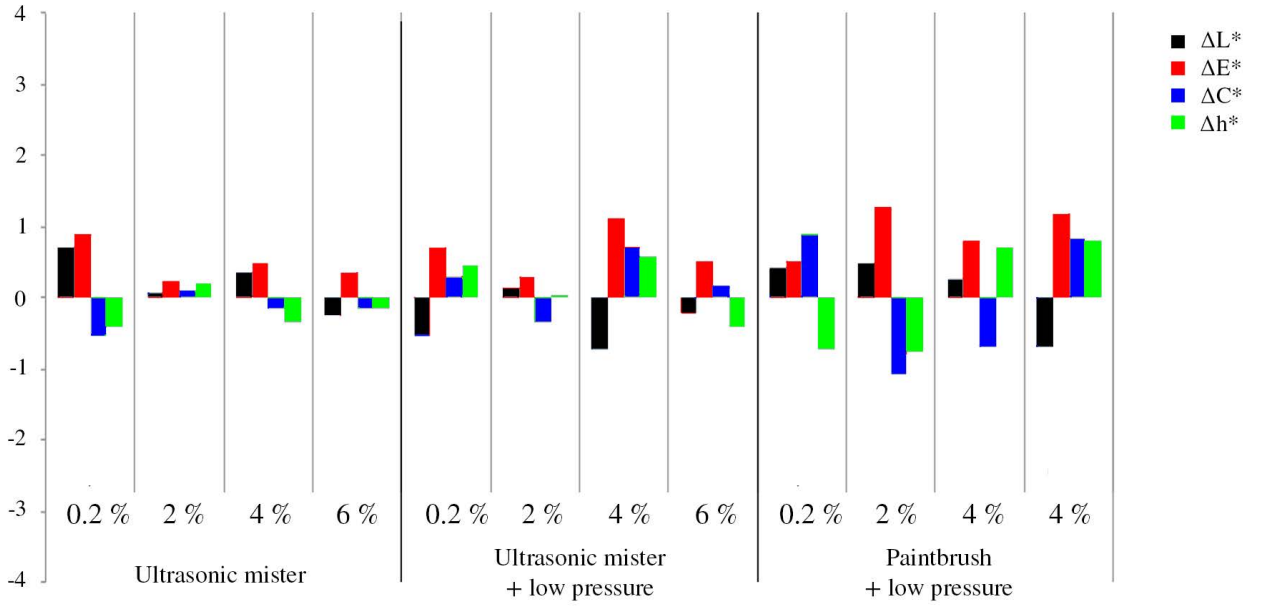

Figure 4. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after photoageing for the samples consolidated with funori.

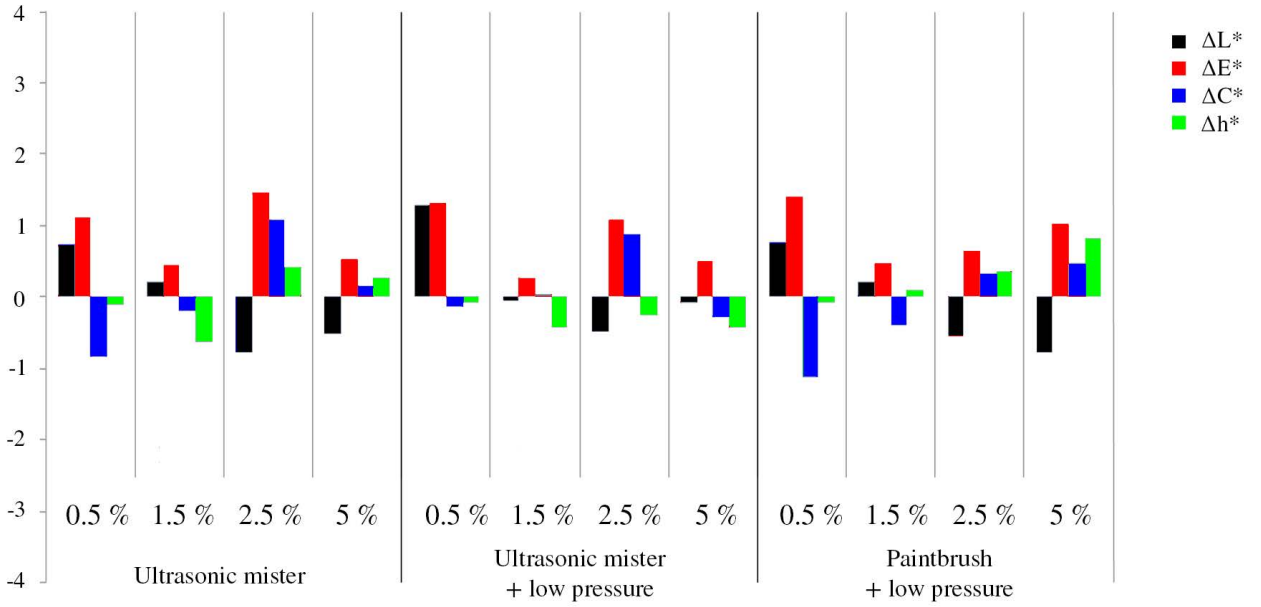

Figure 5. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after photoageing for the samples consolidated with Gelvatol.

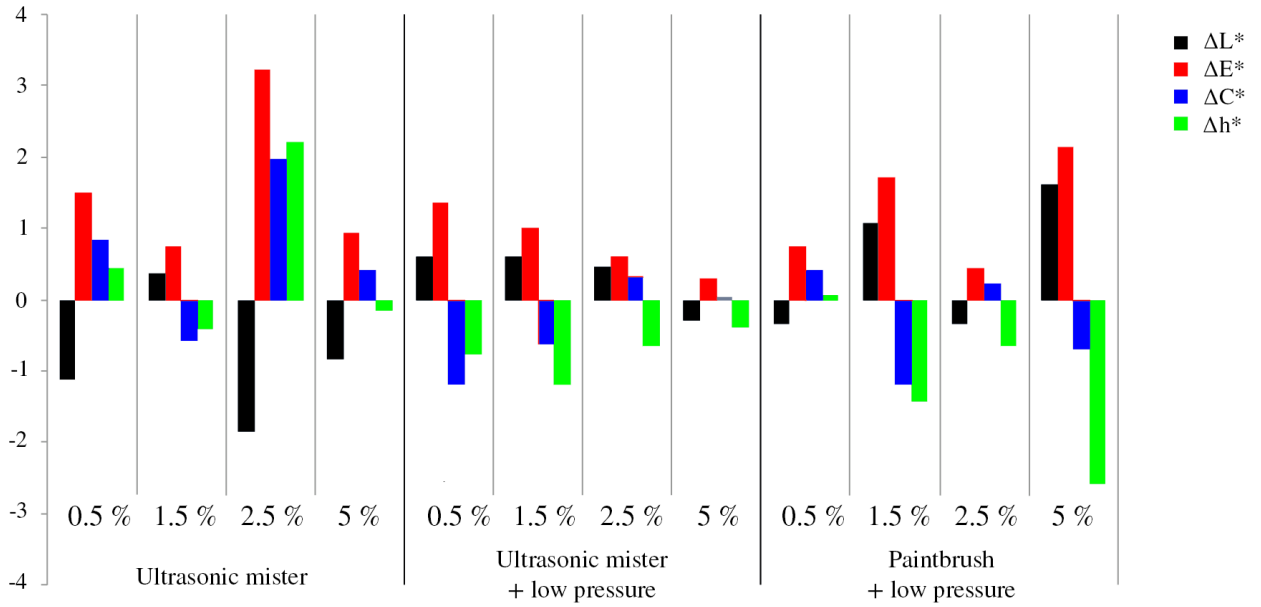

Figure 6. Change in lightness (ΔL*), colour (ΔE*), saturation (ΔC*) and hue (Δh*) after photoageing for the samples consolidated with Acril 33.

greatest differences. Half of the ΔE* values were greater than 1, with the highest found at a concentration of 2.5 % using the mister, which resulted in a ΔE* value of 3.23 CIELAB units. The samples treated with concentrations of 2.5 % and 5 % using a paintbrush produced a ΔE* value of 1.70 and 2.14 CIELAB units respectively.

The influence of the gloss produced by the application of adhesives on the pigment layer after artificial aging was found to be nil. The average difference in the case of funori is -0.02, the value for Gelvatol was found to be -0.03 and for Acril 33 the average difference in gloss was -0.01. In terms of gloss difference as a function of application method, a value of -0.02 was found for all methods.

Conclusions

Thermal ageing hardly produces chromatic variations on any of the three cases. Changes are most noticeable with photoageing.

Table 3
Corrected values of lightness (ΔL*), saturation (ΔC*) and hue (Δh*) before (1) and after (2) thermal ageing for the consolidated samples and its colour (ΔE*) and gloss change (ΔG) (UM: ultrasonic mister; LP: low pressure; B: paintbrush)

Sample	L*(1)	L*(2)	ΔL*	C*(1)	C*(2)	ΔC*	h*(1)	h*(2)	Δh*	ΔE*	ΔG
Gelvatol 0.5 % - UM	43.40	44.14	0.73	39.13	38.29	-0.85	242.69	242.59	-0.10	1.12	-0.03
Gelvatol 1.5 % - UM	41.85	42.05	0.21	38.93	38.72	-0.20	243.51	242.87	-0.64	0.44	0.02
Gelvatol 2.5 % - UM	41.35	40.57	-0.78	38.18	39.26	1.08	243.90	244.32	0.42	1.45	-0.10
Gelvatol 5 % - UM	44.64	44.13	-0.51	39.91	40.07	0.16	242.22	242.48	0.26	0.54	0.02
Gelvatol 0.5 % - UM + LP	44.56	45.85	1.29	38.89	38.77	-0.13	241.60	241.51	-0.09	1.30	-0.04
Gelvatol 1.5 % - UM + LP	42.01	41.96	-0.05	39.23	39.24	0.01	243.27	242.85	-0.42	0.26	0.01
Gelvatol 2.5 % - UM + LP	40.94	40.45	-0.49	38.88	39.77	0.89	243.80	243.56	-0.24	1.08	-0.10
Gelvatol 5 % - UM + LP	44.23	44.17	-0.07	40.13	39.84	-0.28	242.05	241.62	-0.43	0.51	-0.02
Gelvatol 0.5 % - B + LP	45.69	46.44	0.75	39.29	38.17	-1.11	241.13	241.06	-0.07	1.41	-0.10
Gelvatol 1.5 % - B + LP	44.24	44.45	0.21	38.87	38.48	-0.39	242.02	242.10	0.08	0.47	-0.04
Gelvatol 2.5 % - B + LP	43.72	43.18	-0.55	39.50	39.82	0.32	242.32	242.68	0.36	0.66	-0.01
Gelvatol 5 % - B + LP	44.34	43.55	-0.78	39.20	39.67	0.48	241.65	242.48	0.83	1.03	0.01
Funori 0.2 % - UM	41.66	42.37	0.70	41.20	40.66	-0.54	243.25	242.83	-0.41	0.89	0.03
Funori 2 % - UM	42.03	42.11	0.08	41.14	41.22	0.09	243.11	243.32	0.21	0.23	0.01
Funori 4 % - UM	42.18	42.52	0.35	41.31	41.17	-0.15	242.82	242.48	-0.34	0.47	-0.03
Funori 6 % - UM	42.86	42.60	-0.26	41.35	41.19	-0.16	242.16	242.00	-0.16	0.37	-0.02
Funori 0.2 % - UM + LP	42.40	41.87	-0.53	40.92	41.21	0.29	242.80	243.25	0.45	0.70	0.00
Funori 2 % - UM + LP	42.44	42.56	0.12	40.88	40.54	-0.34	242.88	242.90	0.02	0.29	-0.02
Funori 4 % - UM + LP	41.84	41.12	-0.72	41.48	42.18	0.70	243.05	243.63	0.59	1.13	-0.02
Funori 6 % - UM + LP	41.77	41.55	-0.22	41.85	42.00	0.16	242.92	242.52	-0.40	0.52	-0.05
Funori 0.2 % - B + LP	43.13	43.55	0.42	40.67	41.56	0.89	242.08	241.36	-0.72	0.51	-0.05
Funori 2 % - B + LP	43.18	43.67	0.49	40.98	39.91	-1.06	242.42	241.66	-0.76	1.27	-0.04
Funori 4 % - B + LP	42.84	43.09	0.26	41.61	40.93	-0.68	242.10	242.81	0.72	0.79	-0.03
Funori 6 % - B + LP	42.76	42.08	-0.68	41.80	42.63	0.83	242.20	242.99	0.79	1.18	0.00
Acril 0.5 % - UM	41.68	40.57	-1.12	42.93	43.77	0.84	241.77	242.22	0.45	1.50	-0.05
Acril 1.5 % - UM	42.89	43.25	0.36	42.63	42.05	-0.57	241.00	240.59	-0.41	0.74	-0.06
Acril 2.5 % - UM	43.23	41.38	-1.85	42.46	44.44	1.98	240.68	242.89	2.21	3.23	0.02
Acril 5 %- UM	41.88	41.06	-0.83	41.17	41.58	0.41	241.22	241.08	-0.14	0.93	-0.02
Acril 0.5 % - UM + LP	41.33	41.94	0.61	42.44	41.25	-1.18	241.89	241.12	-0.77	1.37	-0.01
Acril 1.5 % - UM + LP	40.81	41.41	0.60	42.29	41.67	-0.62	242.38	241.18	-1.19	1.01	0.00
Acril 2.5 % - UM + LP	40.22	40.69	0.47	42.32	42.65	0.33	242.73	242.08	-0.65	0.61	0.00
Acril 5 % - UM + LP	43.52	43.24	-0.29	42.41	42.44	0.03	241.36	240.97	-0.38	0.29	0.03
Acril 0.5 % - B + LP	42.12	41.78	-0.34	41.04	41.46	0.42	242.50	242.56	0.06	0.75	0.02
Acril 1.5 % - B + LP	41.73	42.81	1.08	41.82	40.64	-1.18	242.56	241.13	-1.43	1.70	-0.03
Acril 2.5 % - B + LP	41.50	41.17	-0.34	42.18	42.41	0.23	242.63	241.99	-0.64	0.45	-0.02
Acril 5 % - B + LP	39.62	41.23	1.62	41.01	40.33	-0.69	243.84	241.26	-2.58	2.14	0.02

Upon evaluation of the differences observed in colour after consolidant application and ageing tests, funori applied with the mister (with and without suction) yielded the best results for the type of paint used in this study. As an adhesive, funori was shown to behave favourably even at high concentrations, allowing for surface consolidation using the mister regardless of whether it is employed at a low pressure or not, thus providing various treatment options based on the specific characteristics of the work. The synthetic adhesives used in this study showed greater sensitivity to ultraviolet light in the ageing treatment used.

As far as the addition of gloss is concerned, after the consolidation treatment and accelerated artificial aging processes were applied, no changes in gloss were observed on the painted surfaces for any adhesives at the concentrations employed or application methods used in this study.

Using low concentrations of film-forming substances aids penetration through the poorly cohesive pigment particles; consequently the picture surface is not altered and no brightness conditions change.

Although it was found that added gloss resulting from consolidation is not a problem with the parameters used in this study, there still may be issues associated to the saturation of the powdery pigment surface due to compaction of pigment particles.

Funori and Gelvatol have a better resistance to photoageing and remain within the ranges that advise their use. Acril 33 would not be as suitable for this particular problem because in some cases it induces changes perceptible to the human eye.

List of suppliers

Cotton canvases: Manufactured by Lienzos Levante – Artículos para Bellas Artes, Carretera Cocentaina km. 144, Muro Alcoy, Alicante, Spain (Tel.: 965530251 / e-mail: lienzos_1@infonegocio.com); and purchased by Viguer S.L. – Material para Bellas Artes, Camino de Vera, 46071 Valencia, Spain (Tel.: 00 34 963 919 054 / e-mail: info@viguer.com).

Pigment Blue Microgiraltin num. 93 and Cobalt Blue "Liquitex": purchased by Viguer S.L. – Material para Bellas Artes, Camino de Vera, 46071 Valencia, Spain (Tel.: 00 34 963 919 054 / e-mail: info@viguer.com).

Acril 33, Gelvatol, funori and Biotin: Purchased by CTS España Productos y Equipos para la Restauración S.L., C/ Monturiol, 9, Polígono Industrial San Marcos, Getafe, Madrid, Spain (Tel. +34 916011640 / e-mail: cts.espana@ctseurope.com).

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Technical photography for mural paintings: the newly discovered frescoes in Aci Sant'Antonio (Sicily, Italy)

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Abstract
A cycle of 18th century frescoes, depicting the last days of Christ on earth, were recently discovered in Aci Sant'Antonio (Sicily, Italy). The paintings survive along the corners of an originally square chapel that was altered in the early 20th century, acquiring the current octagonal plan. This paper presents the results of the technical photography documentation of these wall paintings and illustrates the methodological challenges that were posed during their examination. Raking light photography was used to reveal the paintings' state of conservation, details of the plaster work and painting techniques. Ultraviolet fluorescence and infrared false color photography were also performed to evaluate areas of interest for further analytical and diagnostic studies. The first striking feature is the lack of *giornate*. Only *pontate* are clearly seen in all the scenes thus indicating that in the larger paint areas, a mixed of fresco and secco technique would have been used.

Keywords
Panoramic photography
Infrared photography
Ultraviolet photography
Raking light photography
Infrared false color
Mural paintings

Fotografia técnica de pinturas murais: os frescos redescobertos em Aci Sant' Antonio (Sicília, Itália)

Resumo
Um ciclo de pinturas murais setecentistas, retratando os últimos dias de Cristo, foram descobertas recentemente em Aci Sant' Antonio (Sicilia, Itália). As pinturas localizam-se nos cantos de uma capela originalmente quadrada que foi alterada para uma planta octogonal nos inícios do século XX. Este artigo apresenta os resultados da documentação técnica dessas pinturas e ilustra os desafios metodológicos que foram colocados durante o seu exame. Fotografia de luz rasante foi usada para revelar o estado de conservação dos murais, detalhes da aplicação das argamassas e da técnica pictórica. Fotografias de fluorescência de ultravioleta e de falsa cor no infravermelho foram também realizadas para avaliar áreas de interesse para posteriores estudos analíticos e de diagnóstico. A primeira característica que se realça é a falta de *giornatas*. Apenas *pontatas* são claramente perceptíveis em todas as cenas, indiciando nas áreas de maiores dimensões o emprego de uma técnica mista (fresco e seco).

Palavras-chave
Fotografia panorâmica
Fotografia de infravermelho
Fotografia de fluorescência de ultravioleta
Fotografia de luz rasante
Falsa cor no infravermelho
Pinturas murais

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Introduction

This paper illustrates the application of technical photography (TP) [1-3] for the documentation and examination of a series of 18th century frescoes. TP represents a collection of broadband spectral images realized with a modified full spectrum digital camera and using different lighting sources and filters to acquire images useful for art diagnostics, such as ultraviolet fluorescence and infrared false color photos. This study reports on the TP examination of a fresco cycle recently discovered in Sicily, while presenting an example of the capability that TP provides in the conservation and study of wall paintings.

The examined frescoes were revealed during maintenance works carried out in 2012 in the Crucifix chapel of the Mother Church in Aci Sant'Antonio (Sicily). This church was originally built in 1566 and dedicated to Sant'Antonio. Soon after the destructive earthquake, which struck the south-east part of Sicily in 1693, the church was rebuilt with a Latin cross scheme composed of three naves, a transept and five chapels. The church preserves significant works of art, of which the most celebrated, the frescoes by Pietro Paolo Vasta (1697-1760), can be found decorating the apse. The Crucifix Chapel is located on the left of the transept and has an octagonal floor plan dated to the beginning of the 20th century which has been realized within the original square plan (Figure 1). The

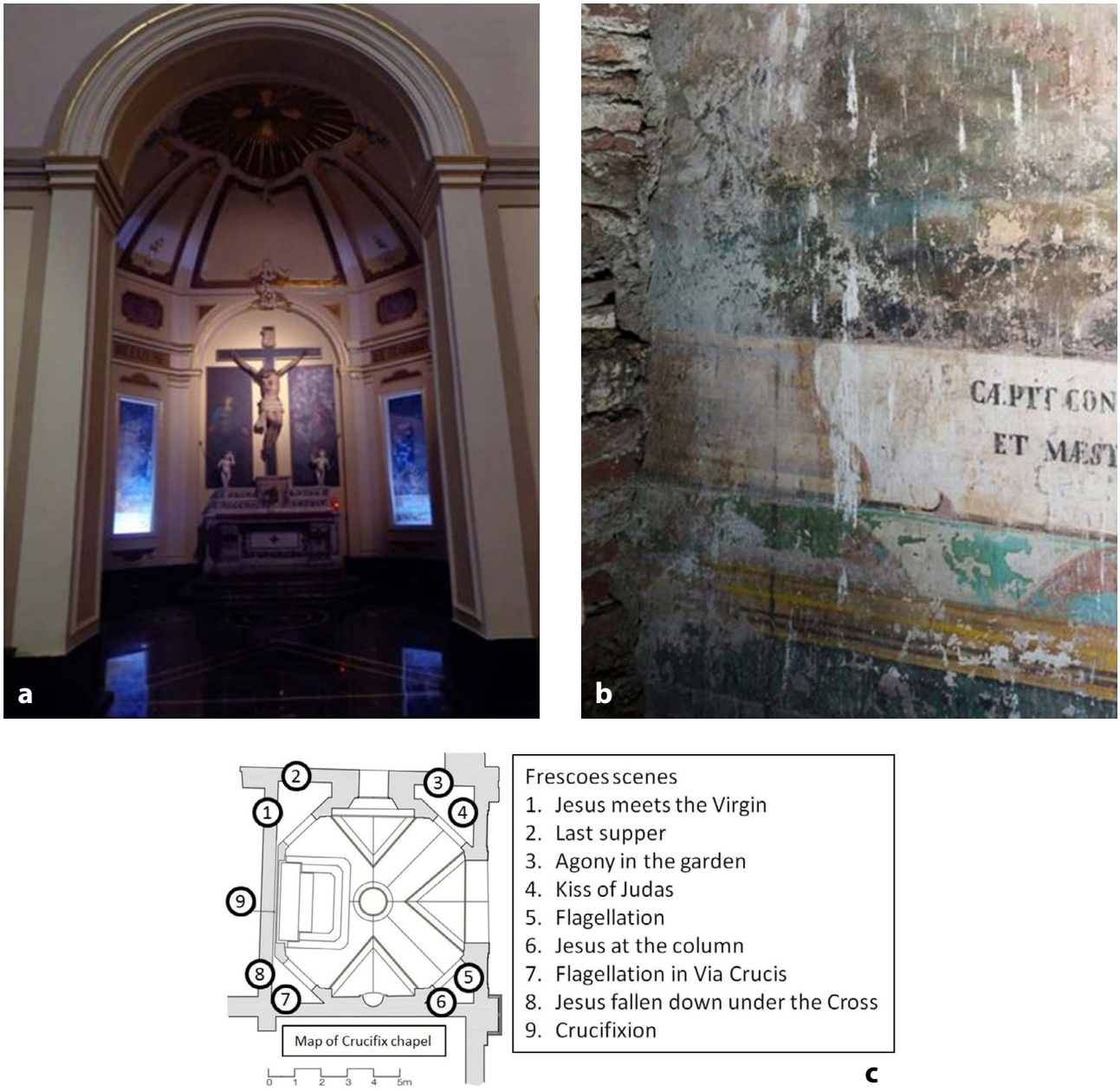

Figure 1. Crucifix Chapel, Mother Church, Aci Sant'Antonio (Sicily): *a)* photo of the chapel from the transept after the renovation; the frescoes are visible through the windows on the walls facing the four corners; *b)* border of the third scene, Agony in the garden; the original plaster was taken down in order to anchor the new wall; *c)* floor plan with the description of the scenes.

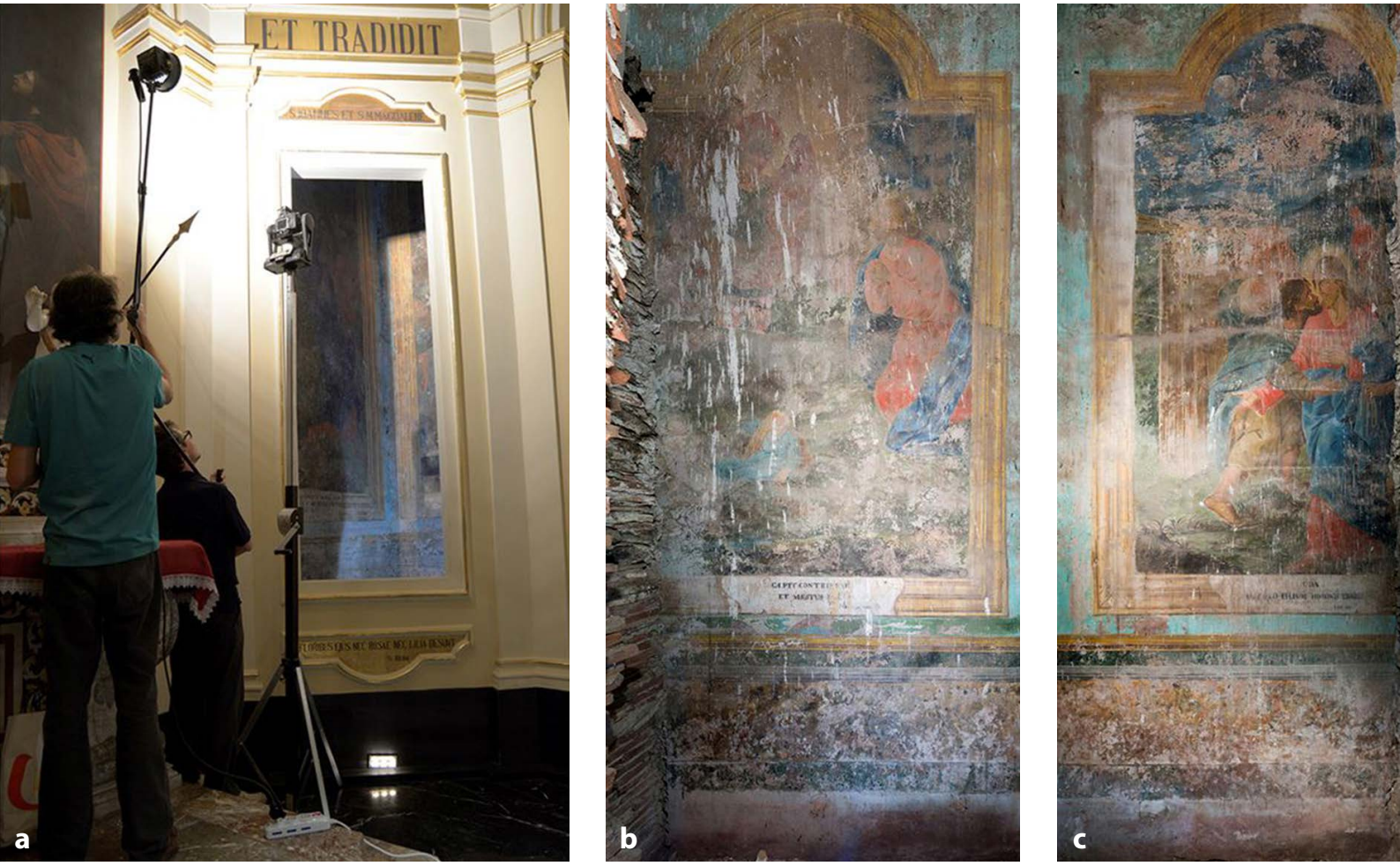

Figure 2. Crucifix chapel: *a)* NW corner. The early 20th century octagonal addition allows only a restricted field of view from outside. The camera was mounted on a telescopic pole and the documentation of the mural paintings was achieved with the mosaic method after shooting a stripe of vertical images; *b)* and *c)* SE corner, documentation of the frescoes realized with the panoramic method from inside the enclosure.

newly discovered mural paintings were preserved along the four corners of the original walls, while other sections of the fresco cycle have been irremediably lost, since new walls were added to the original ones to form the current octagonal plan. The inspection of the interface between the original walls and the later additions shows that no effort was made to preserve the original decorations (Figure 1). There are eight scenes which were preserved and they represent themes of the last days of earthly Christ: Last Supper; Jesus meets the Virgin; Agony in the garden; Kiss of Judas; Flagellation; Jesus at the column; Flagellation in Via Crucis; and Jesus fallen down under the Cross and Crucifixion.

From the examination of the account book of the Mother Church for the period between 1768 and 1792 [4] it was possible to attribute this cycle to the hand of Giuseppe Grasso Naso, pupil of Pietro Paolo Vasta. This paper adds to the sparse literature on the fresco technique used by this important workshop of mural painters in Sicily [5]. The most important figure was Pietro Paolo Vasta who opened his workshop in Acireale in 1734 and formed his apprentices, Michele Vecchio, Alessandro Vasta (his son), and Giuseppe Grasso Naso. The present study deepens a preliminary study of these mural paintings [4] carried out in 2013 with portable X-ray fluorescence spectroscopy, fiber optics fluorescence spectroscopy and technical photography on two of the murals (4 and 5).

Experimental

Technical photography was performed in two spectral bands: visible (400-780 nm, VIS) and infrared (780-1100 nm, IR). The photographic methods implemented were: visible (VIS), raking light (RAK), infrared (IR), raking with infrared light (IR-RAK), ultraviolet fluorescence (UVF) and infrared false color (IRFC). The photos were acquired with a Nikon D800 DSLR (36 MP, CMOS sensor) digital camera modified "full spectrum" for ultraviolet-visible-infrared photography (extended sensitivity between about 360 and 1100 nm). The filters used were: *a)* VIS and RAK photography: X-NiteCC1 filter; *b)* UVF photography: B+W 420 coupled with the X-NiteCC1; *c)* IR and IR-RAK: Heliopan RG1000. Two

1000 W halogen lamps were used for VIS, RAK, IR-RAK and IR photography; for ultraviolet (UV) photography, one high-flux 365 nm LED lamp was sufficient.

Results and discussion

Photographic documentation

After their discovery in 2012, the decision was made to preserve the early 20th century octagonal shape of the chapel and make the frescoes in the corners visible by way of large windows (Figure 2). While this solution is appealing for the visitors, since it provides an understanding of the modifications undergone by the chapel, it makes the photographic documentation of the paintings problematic because of the restrained field of view offered by the windows. The photographic documentation of all the murals is essential in order to formulate the plan for a conservation intervention to clean and consolidate the art works. On the first examination campaign [4], two of the paintings were documented using the panoramic photographic method. The camera was located outside the windows and at 5 m from the murals. The images were taken with a 200 mm lens and a panoramic head. While the quality of the images was satisfactory, the previous panoramic approach resulted in the documentation of only a narrow stripe of each painted wall since the window was substantially restraining the view.

During this study, the photographic documentation of the entirety of the wall paintings was achieved using the panoramic method. However, positioning the camera on a pole at 2.5 m (half the height of the fresco cycle) and inside the enclosure between the original walls and the 20th century additions provided for an increased field of view. The camera photographed the opposite wall mounting a Nikon Nikkor 20 mm f3.5 lens and shooting a vertical sequence of five photos. This method provided a complete documentation of the corners. The stitched image was spatially calibrated using the *Set Measurement Scale* tool in Photoshop [6]. The *Measurement Log* tool provides any other measure needed such as calculation of areas, feature particularly useful to estimate the conservation intervention costs and time. The other technical photos, RAK, UVF, IR and IR-RAK, were realized from outside the windows with a mosaicking method. The camera was applied on a telescope pole and five photos covering the frescoes from the bottom to the top were shot, as allowed by the windows' frame (Figure 2). This solution does not allow the documentation of the entirety of the surface for each scene but just the stripe accessible through the window. Nonetheless, it was chosen because the documentation of the stripe was sufficient to the study of the paintings and the complete documentation would have been extremely difficult and lengthy.

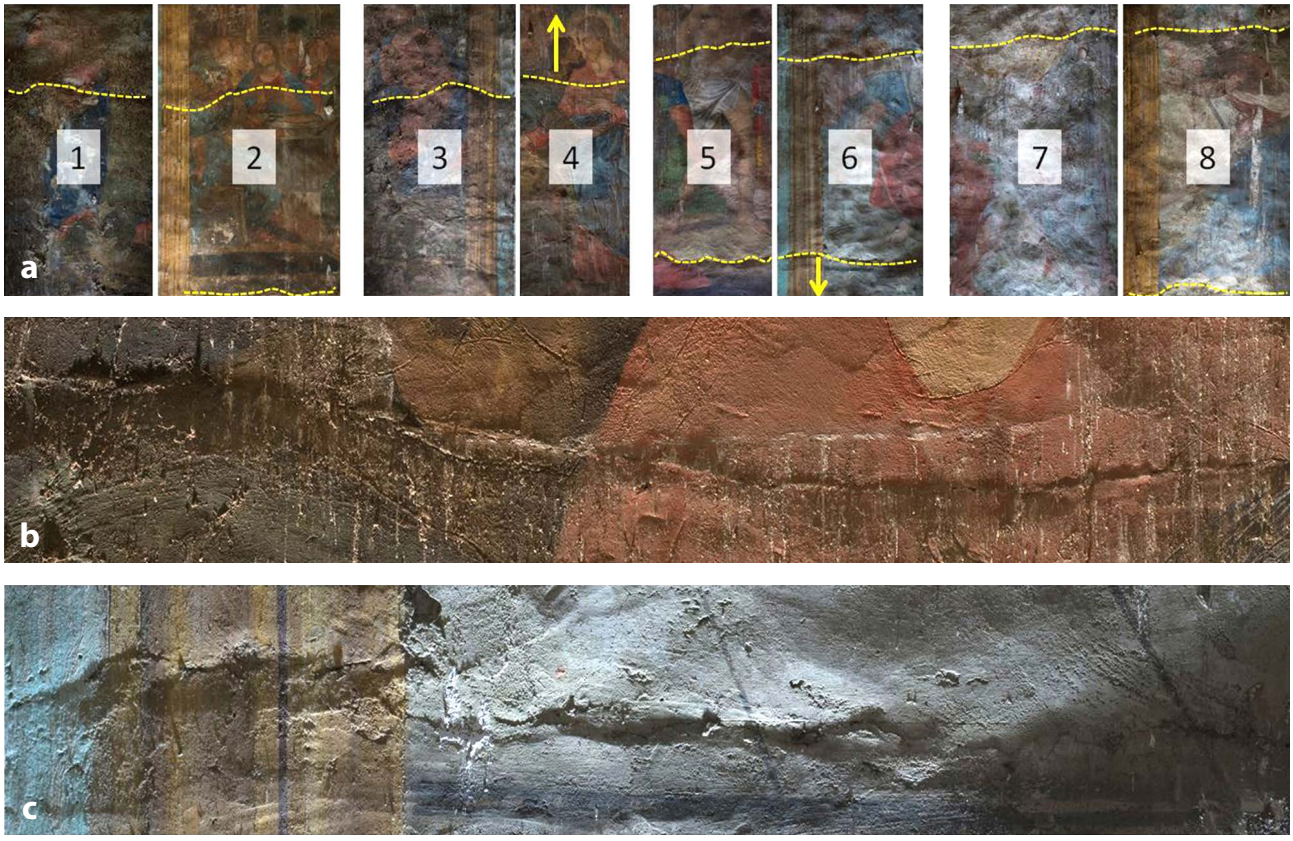

Figure 3. Maps of the pontate on the eight scenes *(a)* and two details of pontate in scene 4 *(b)* and 6 *(c)*.

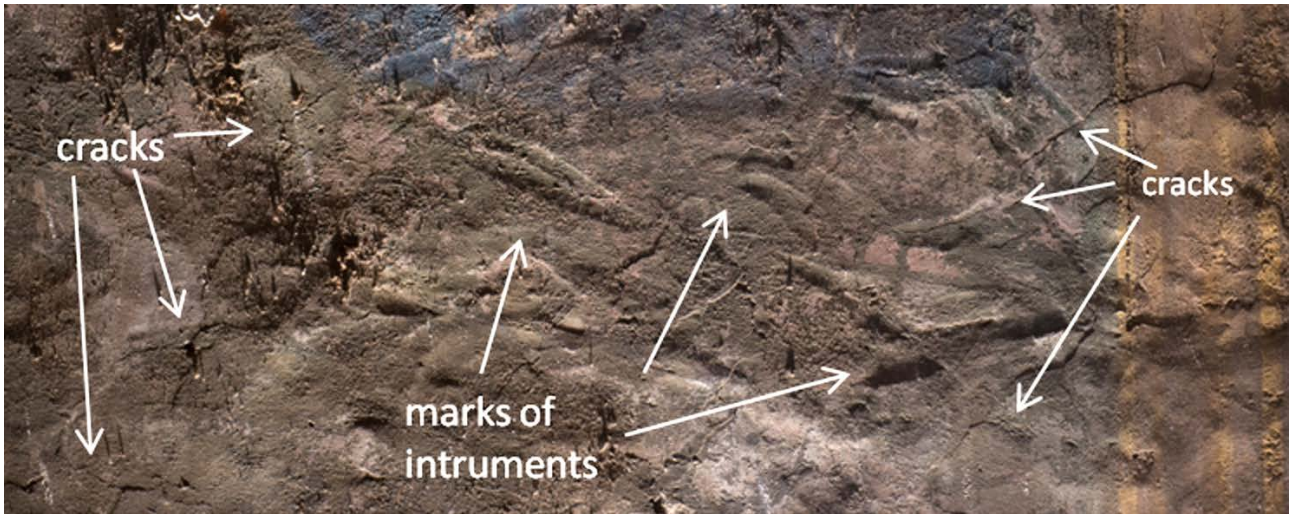

Figure 4. Scene 3, *Agony in the Garden*, detail. Cracks and marks of tools in the plaster.

The paintings on the north wall display the highest degree of deterioration. Rain had been infiltrating though this wall from the roof causing localized detachments in the plaster. Furthermore, pigeons have found their way through the roof and the north wall is soiled with excrements. The upper part of the painted area is overall better preserved than the decorative frames on the bottom, which are in bad condition and seem to have been refashioned several times over the centuries. In addition to these damages, we also observed drippings from a lime wash, abrasions and holes resulting from the octagonal chapel construction.

Plaster work and paintings technique

RAK photos, of the eight scenes were acquired in order to document the plaster layering method. RAK photos revealed that the plaster was laid inside the chapel walls, from left to right, by *pontate* rather than *giornate*. The Italian term *giornata* means "a day's work" and the term is used to describe the amount of *fresco* painting that is done in a single day. The last layer of plaster is applied daily to the wall in restricted areas, often following the outline of a figure. On the other hand, with the *pontata* method (*ponte*, Italian for scaffolding), the plaster is laid in wide horizontal bands corresponding to successively lower stages of the scaffolding. The only joins visible after the execution will be horizontal ones. Unlike *giornate*, *pontate* are not always synonymous of *fresco* technique especially in the case of large areas of paint. In this method the painter has sufficient time just to do the under drawings and to apply background or base colors on the fresh plaster. Once the plaster has dried, the painting is usually refined adding paint *a secco* with a binder.

In the RAK photos, *pontate* are clearly visible in most of the scenes by the slight overlapping of the plaster on the pontate joints (Figure 3). At least two pontate are identified in scene 2, 5, 6 and 8 resulting in three horizontal painting registers. On scenes 1, 3, 4, and 7 only one plaster joint was clearly observed. This could be due to the actual lack of the other pontata or, more likely, the joint was worked particularly smooth and consequently it could not be noticed on such an irregular and dirty surface. Overall, the surface of the *pontate*, even those close to the ground, is completed with coarse plaster. It is not as smooth as it would be expected, in particular, for the paintings on the bottom, nearest to the viewer. It is known that rough *intonaci* (outer plaster layer) were common in Baroque mural paintings to create textural effects [7] but this does not seem to apply for this case since it is not used for "effects" but rather without intention everywhere.

Indeed, several marks from trowels and tools used to spread the plaster can be identified, as well as cracks formed during the hardening of the *intonaci,* suggesting a fast execution (Figure 4).

Preparatory drawings

RAK photos also document the methods used to transfer the composition. The outlines of all of the figures revealed simply shallow lines engraved in the plaster. Curiously, only scene 4, Kiss of Judas, features a different incised drawing method on the lower *pontata* (Figure 5). The contour lines of the hands of Jesus and Judas are rounded groove, suggesting that they were made by the pressure of a pointed tool through a *cartoon*. On the other hand, the upper *pontata* with the faces of Christ and Judas shows just shallow incisions, such as the remaining scenes. Indeed, there are a number of lines indicating a free hand sketching for the contours (Figure 6). In general, the incised lines are sketchy and in some points have a grainy aspect which suggests that the plaster was almost dry. There are not substantial differences between the incised drawings and the final paintings except few small areas. While the *cartoon* traced with a point is immediately identified in the RAK light photo, the shallow incised lines are more difficult to identify, especially in the scenes on the north wall which are much more affected by salts,

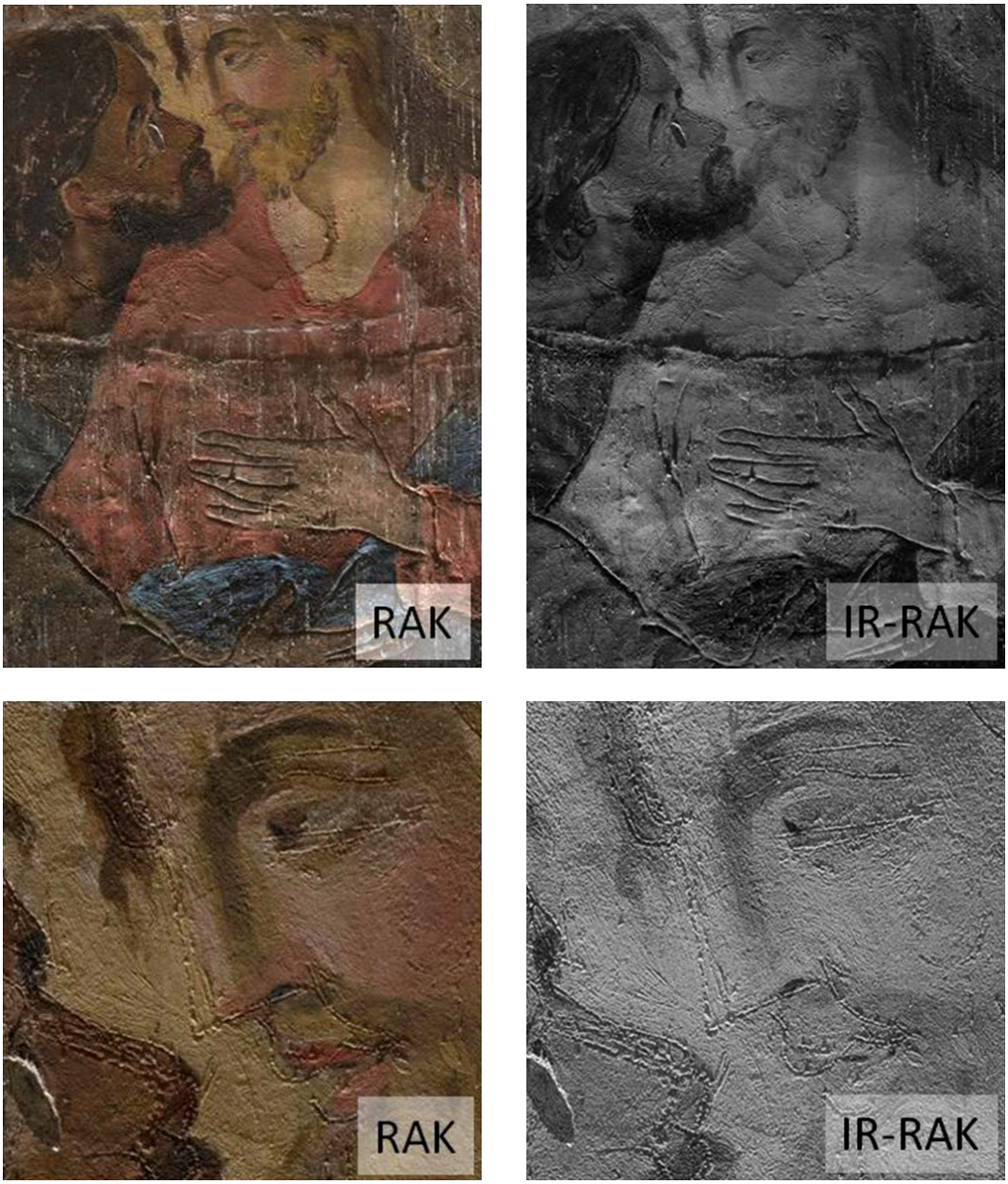

Figure 5. Scene 4, *Kiss of Judas*. Raking photo reveals the two types of incised drawing on the lower and upper pontata. Raking photography in the infrared (IR-RAK) increases the reading of the shallow incisions made with a pointed tool.

pigment detachments, and dirt. Thus, these scenes have also been photographed in IR-RAK. These photos can render better the incisions since the contrast between the shadow of the lines and the ground is increased thanks to the transparency of the ocher pigments (Figure 5).

Paint layers

According to Paolo and Laura Mora analysis of painting treatises from the seventeenth and eighteenth centuries, another characteristic of baroque murals was the method of applying pigments [7]. Pigments were no longer laid down in a thin almost translucent layer such as in *buon fresco,* but rather as an opaque mass to allow impastos of varying thickness in a manner analogous to that of oil painting. This feature is described by Andrea Pozzo in *sezione decima* of *Perspectiva Pictorium and Architectorum,* published by the first time in 1692 and re-edited during the eighteenth century [8]. These mural paintings seem to follow this aesthetic and painting method. Thick brushstrokes are visible in all the scenes, especially on the blue clothing modeling (Figure 6). It is impossible to reach this effect only applying pigments mixed with water (*buon fresco* technique). The addition of a binder to the pigments, such as lime or an organic substance, was necessary. The technique of lime fresco was well known from the Byzantine and Romanesque ages and it also allowed the execution time to be extended beyond that of the *buon fresco* technique [8]. The application of

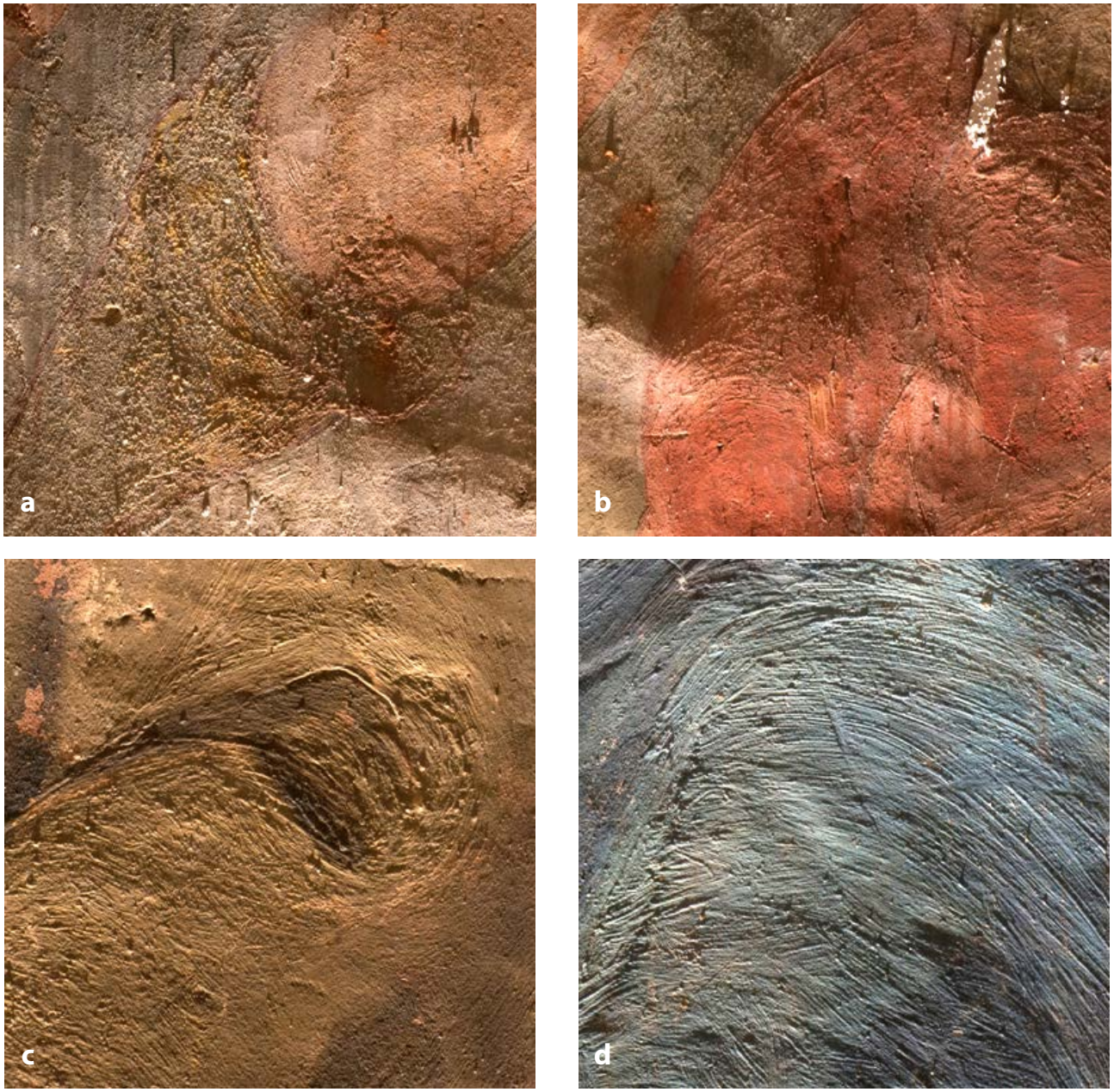

Figure 6. Scene 4 and 6, details. Raking photos document the application of thick brushstrokes of paint.

lime fresco could explain the lack of *giornate* in these paintings. Another hypothesis, suggested by the strong UV fluorescence of some paints (Figure 7), could be the additional use of an organic binder. Further analytical research is needed to confirm either hypothesis; however, the technical photographic documentation in both raking and UV light corroborated the use of mixed techniques in the execution of the mural paintings.

IRFC is used in art examination to distinguish retouches and to provide a tentative pigment identification. The method is not conclusive but it is recognized as a valid tool to select areas of interest for further analytical studies. The IRFC images are usually created by processing VIS and IR photos of the same scene [9]. This paper also presents the false color images acquired with the XNite BP1 filter, indicated with the acronym BP1. This filter was chosen because we required a method faster than traditional IRFC to document the mural paintings. This filter transmits visible light in the range 350-660 nm and infrared after 800 nm and can be used as an alternative to the IRFC method, however not without significant limitations. The Nikon D800, like most digital color cameras, features a CMOS imaging detector whose photosensors cannot distinguish the wavelength of the incoming light. The photosensors are covered with a CFA (color filter array) composed of tiny color filters placed over the photosensors to select only red, green or blue light. The CFA on the Nikon D800, as on the majority of digital cameras, implements the Bayer CFA scheme. Each two-by-two cell contains two green, one blue and

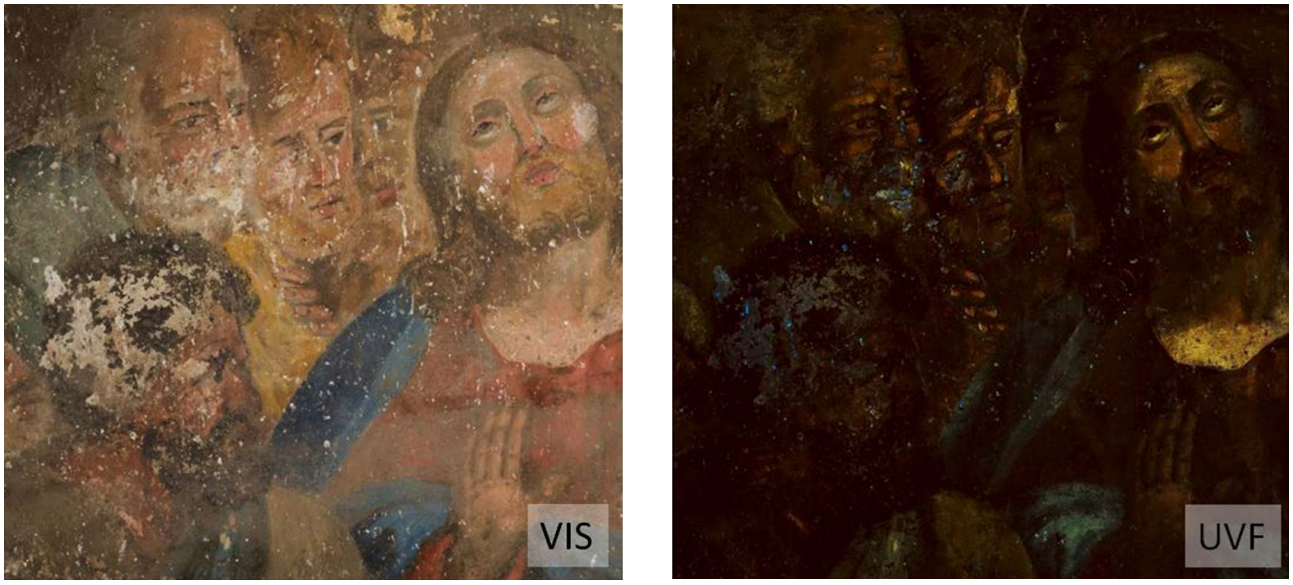

Figure 7. Scene 2, *Last Supper*, detail. Technical photography. The UVF photo shows strong fluorescence which could be assigned to an organic binder.

one red filter. The CFA color filters are transparent to the infrared transmitted by the XNite BP1, and, consequently, this infrared light is almost equally detected by all the photosensors. The photo that is obtained with XNite BP1 would have the infrared light contributing more to the red channel, since the far red has been cut out by the filter itself and the infrared light is the only one that can contribute to the red channel. This filter provides images that are analogous to the IRFC because the infrared and visible lights are blended together through the RGB filters of the CFA, and thus the BP1 is capable of distinguishing paints with different infrared reflectance profiles.

Compared to IRFC, BP1 is less effective since the infrared is also detected by the blue and green photosensors and the capacity to render pigments with different false color is reduced. The advantage of BP1 over IRFC is that no post-processing or editing is needed. Therefore, this method is much faster and it is particularly useful for the study of large artworks, such as mural paintings, since their documentation with IRFC would require the laborious editing of numerous VIS and IR images. Another issue with the BP1 filter is that the images obtained will always be a little bit blurred, the actual amount depending on overall exposure parameters (aperture and distance). A normal lens can focus only one spectral range at a time, visible or infrared. Therefore, if focusing is fine in the visible range, the infrared would be out of focus. This issue could be solved using an expensive apochromatic lens, but for the examination of objects at a long distance and sufficient illumination, a small aperture can minimize the blurring. The filter has been tested on a collection of 54 historical pigments laid with egg tempera (Figure 8). The method differentiates pigments with different infrared behavior, such as malachite and verdigris (both absorb infrared) from the other greens (reflect the infrared) (Figure 9). BP1 seems therefore a valid method to distinguish retouches over the two historical green pigments. The IRFC and BP1 images from the Kiss of Judas scene are shown as an example (Figure 10). Both of the images do not show any retouches. A preliminary identification of the pigments with non-destructive methods has been realized [4] and the IRFC confirmed the results. The red vest of Jesus was indeed realized with vermilion (HgS) and the green background is green earth, while ocher was used for the brown and yellows. Further study is needed to determine the blue pigment used for the mantle of Christ.

Conclusions

Technical photography has been used for the documentation and examination of the newly discovered *frescoes* in the Crucifix chapel in Aci Sant'Antonio. This paper illustrated the solutions that technical photography can provide to pursue important tasks for both the documentation of state of conservation and the study of the technique used to execute these mural paintings. The most challenging part of the examination was the actual photographic documentation of the remaining portions of the fresco cycle. The results were achieved using the mosaic and panoramic methods, a wide-angle lens, and a telescopic pole. Raking light photography in both the visible and infrared range allowed for unique insights into the 18th century painter's workshop. All the plaster work in the Crucifix Chapel was realized by large *pontate*, suggesting that a mixed painting technique was used. Raking light also revealed the methods used to outline the figures, which were mostly sketch lines incised on the wet, and in some cases, nearly dry plaster. Surprisingly, in one scene, we found the painter had used another kind of incised preparatory drawing, a *cartoon*.

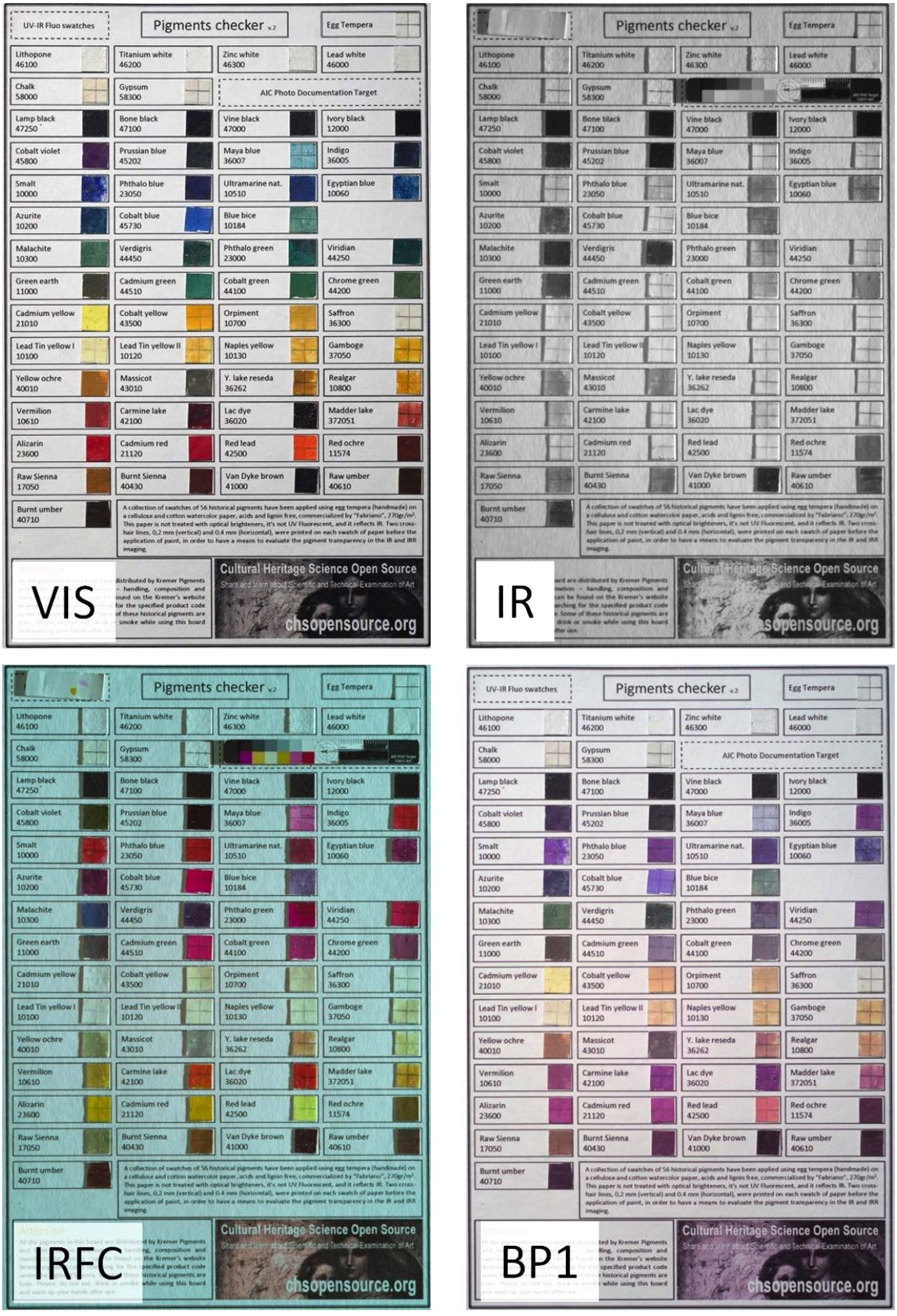

Figure 8. Pigments checker collection of 54 historical pigments laid with egg tempera and tested with the BP1 filter for infrared false color.

Figure 9. Malachite, verdigris, phthalo green and viridian. Both IRFC and BP1 can differentiate the two historical green pigments (malachite and verdigris) from the modern phthalo green and viridian.

Raking photography using infrared light was shown to be an effective method to document the sketch lines. Infrared false color was applied to identify potential retouches completed before the final closure of the mural paintings behind the early 20th century walls, and a new filter was tested to accelerate the process of acquiring infrared false color images.

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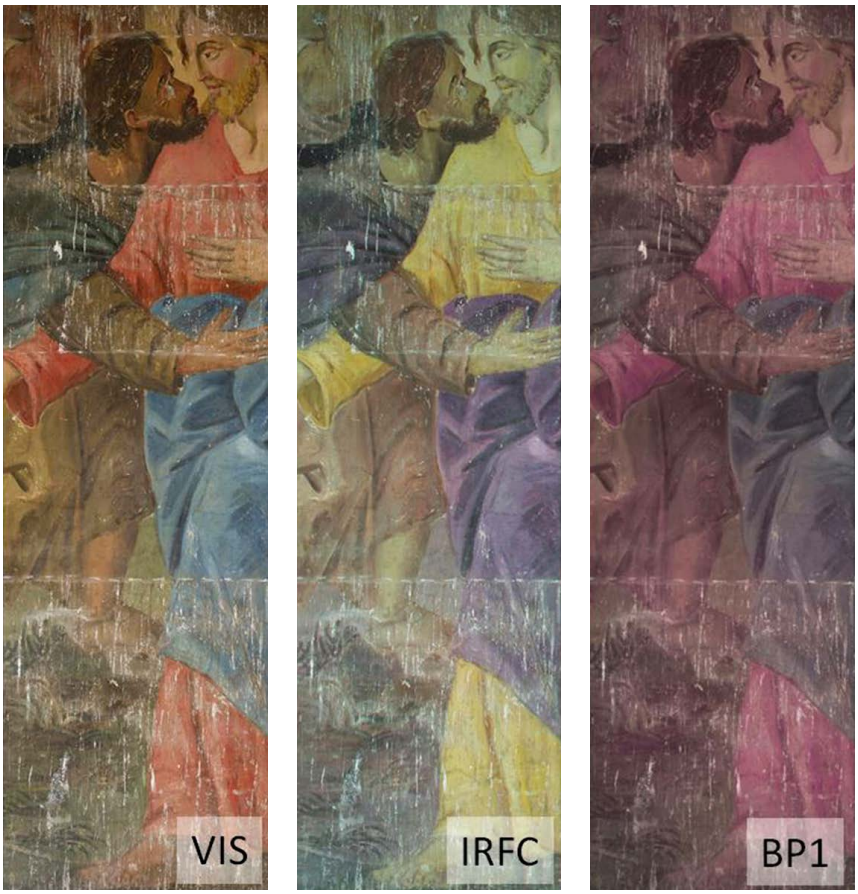

Figure 10. Scene 4, *Kiss of Judas*. IRFC and BP1 confirm the pigments attributions provided by previous non-invasive analysis.

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Application of energy dispersive X-ray fluorescence spectrometry to polychrome terracotta sculptures from the Alcobaça Monastery, Portugal

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Abstract
Portable energy dispersive X-ray fluorescence spectrometry (EDXRF) was used in the Alcobaça Monastery, in order to study the chromatic coatings applied to terracotta statues that belong to two seventeenth-century monumental groupings. The main goal of this scientific approach consisted in determining the elemental composition of the constitutive layers and in trying to reconstitute the existing polychromy, taking into account the technical aspects observed at naked eye. The measurements carried out by EDXRF allowed a first material characterization of these artworks. By comparing the results obtained in each statue, it was possible to attest the application of a seventeenth-century coating to each one and at least a subsequent intervention in the form of a refurbishment or a new polychromy. According to the materials employed in their production, it appears that the refurbishment is likely dated from the 19th century while the new polychromy is still dated from the 18th century.

Keywords
EDXRF
Sculpture
Polychromy
Pigments
Terracotta
Cultural Heritage

Aplicação da fluorescência de raios X dispersiva em energia a esculturas em terracota policromada do Mosteiro de Alcobaça, Portugal

Resumo
A técnica portátil e não invasiva de fluorescência de raios X dispersiva em energia (EDXRF) foi utilizada no Mosteiro de Alcobaça. Foi aplicada ao estudo científico dos revestimentos cromáticos de estátuas em terracota pertencentes a dois conjuntos escultóricos datados do século XVII. Tratou-se de determinar a composição elementar dos estratos constituintes e tentar reconstituir os tipos de policromia aplicados com base em exames prévios feitos à vista desarmada. As medições efectuadas por EDXRF permitiram contribuir para uma primeira caracterização material destas obras. Comparando entre si os resultados obtidos, comprovou-se a presença de policromias seiscentistas e de pelo menos uma intervenção posterior à manufactura das esculturas. Chegou-se à conclusão que a datação do estrato superficial que visava o conserto ou a repolicromia das peças poderia ser datado do século XVIII numa obra e do século XIX na outra, pelo tipo de materiais empregues nas suas realizações.

Palavras-chave
EDXRF
Escultura
Policromia
Pigmentos
Terracota
Património Cultural

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Conservar Património **20** (2014) 35-51 | doi:10.14568/cp2014008
ARP - Associação Profissional de Conservadores-Restauradores de Portugal
http://revista.arp.org.pt

Introduction

As the parent complex of the Cistercian community in Portugal, the Royal Abbey of Saint Mary of Alcobaça (hereinafter referred as Alcobaça Monastery) goes on holding several sets of monumental polychrome terracotta statues mostly produced by the monks during the 17th century [1].

Two of these sets are especially relevant for the present study: *1)* the composition of thirteen sculptures depicting the *Delivery of the Keys* (also called the *Apostleship*, in which Christ is giving the key of the kingdom of heaven to St. Peter), intended for the former Chapel of Saint Peter and known as the early work of the 17th century; and *2)* the set of sixteen sculptures the Abbot Friar Sebastian de Sottomayor commissioned during one of his three-yearly mandate (1675-1678) for the reredos of the presbytery, completed by the statues of *St. Gabriel* and the *Virgin Mary* depicting *The Annunciation*, which overhanged the choir on either side of the main chapel.

Figure 1. Statue of the *Virgin Mary* which was part of the set of monumental terracotta statues commissioned by the Abbot Friar Sebastian de Sottomayor during his three-yearly mandate (1675-1678) for the choir of the Alcobaça Monastery.

These two groupings were dismantled in the 1930s. The former is actually housed in the storage space available at the abbey, where most of the constitutive sections (*tacelos*) of the disassembled statues were stored separately, and not piled up to avoid more extensive damage to the set. The latter is displayed in the chapter house along the four walls, each sculpture having been reassembled. In this new arrangement, *St. Gabriel* and the *Virgin Mary* are flanking the entry of the chapter house as they originally flanked the chancel of the church.

In the framework of the three-years national project *TACELO - Studies for the conservation of monumental terracotta sculptures from Alcobaça monastery* (PTDC/CTE-GIX/111825/2009), the current study focuses on the application of portable energy dispersive X-ray fluorescence (EDXRF) spectrometry to the polychromy of two terracotta statues belonging to the aforesaid ensembles.

Energy dispersive X-ray Fluorescence (EDXRF) spectrometry is a non-invasive technique that provides information on the elemental composition of the constituent materials of the objects under study.

The portable instrument was designed at the Atomic Physics Center of the University of Lisbon to provide on-site analysis in the better condition of measurement, taking into consideration the spatial geometry of each sculpture. The technique is totally non destructive since it does not require any sampling.

Methodology

The methodology adopted in this study took into consideration several aspects:

Apostles' polychromy

According to *1)* the manufacture of the *Apostles'* ceramic body, divided into sections to facilitate the drying of the clay, the firing procedure and the permanent reassembling of the figures in their resting place [2], and *2)* the final coating applied to give them a more realistic appearance matching the Baroque taste, the upper section consisting of the bust and head is the most representative of the palette used for each statue. This section comprises as much the polychromy applied to the garment as the one rendering the hair and flesh, and moreover, any layers that may have been added in subsequent intervention(s). It should be noted that the face was always the main focus and object of worship, and could be refurbished over time independently of the other parts of the image. Given this factual situation, the upper section (*tacelo*) corresponding

to the bust of an *Apostle* (still not identified and designated as *Apostle 2*) was selected in order to assess the elemental composition of the distinct polychrome areas by in situ EDXRF analysis.

Virgin's polychromy

The sculptures of the choir were entirely painted white, probably in the late 18th century or the early 19th century to bring them into fashion according to the Neoclassic style then in force. Even though the set goes on exhibiting this monochrome overpaint, the *Virgin Mary*, from the pair of statues depicting *The Annunciation*, gave rise to the removal of this outer coating to reveal the polychromy underneath. This earlier polychromy applied to the entire figure (only partially preserved nowadays) is giving evidence of an abundant use of gilded surfaces and a larger palette of colors.

This polychromy presents similar features to the ones of the selected *Apostle* and the other statues of the same set, and is believed to be the original coating achieved in the last quarter of the 17th century. It was also studied by EDXRF and further compared to the *Apostle'* finishes.

Primary sources and other references

The polychrome coatings actually visible on the two statues under consideration are imitating golden brocade fabrics to achieve the surfaces of the clothing, by evidencing paint layers which were applied over gilding and stripped off according to specific patterns to expose the shiny gold beneath. These characteristics readily refer to the seventeenth-century treatises by Filipe Nunes [3] and Francisco Pacheco [4], and more specifically to the technique of *sgraffito* (*estofado* in Portuguese) well described by these authors. Therefore their works were considered of primary importance to further interpret the EDXRF spectra, besides other treatises deemed relevant in this research. Portuguese contracts of polychromy were also consulted as valuable art technological sources for the additional information they provide. Moreover, any study on Portuguese polychrome sculpture with similar features and recent findings on the materials used in sculpture and painting were also taken into account, to verify whether the elemental composition of the different matrices analyzed are pertinent to the material and technical particulars from the 17th century or expected in latter times.

Layers build-up

In research involving pictorial layers on three-dimensional artworks, special attention has to be paid to the fact that, from one area to another, the number of layers may vary considerably: either because certain final optical effects may require a more complex build-up than others [5], or because, as already mentioned, some areas would have been the subject of occasional interventions when

Figure 2. Detail of the statue of the *Virgin Mary*'s back showing the seventeenth-century original polychromy actually visible after subsequent interventions have been removed.

others would have remained untouched. An inventory of areas of interest was made. Wherever possible, when some losses within the polychrome surface allowed the analysis of an underlaying ground, metal coating or paint, its measurement was performed individually to better understand its contribution within the spectra.

Experimental procedure / Analytical protocol

The EDXRF equipment used in this study for elemental analysis consists on the Amptek XR-100SDD, thermoelectrically cooled and the X-ray generator Amptek ECLIPSE IV with Rh anode. For collimating the beam an acrylic and brass support with a 2 mm pinhole in Ta was used. The components are assembled on an aluminum structure in a 45º geometry. A macroscopic screening of the statues was made, and 11 measurements were performed *in situ* for the upper section of the *Apostle*, and 15 for the statue of the *Virgin Mary*. All spectra were

acquired during 150 s under working conditions of 40 kV and 40 μA.

Results and discussion

Tables 1 and 2 provide the potential interpretation of the overall data gathered in the areas analyzed by EDXRF technique on the *Virgin Mary* and the *Apostle 2*, respectively.

Virgin's polychromy

The statue of the *Virgin Mary* was studied first since the ground layer, the bole layer, gilding, the colored surfaces and other potential superficial finishes examined in several areas could be analyzed separately (Figures 1 and 2). The EDXRF measurements were carried out in this specific order to better assess the elemental composition of each layer.

Black substance

A black layer remained visible in the mortise made in the *Virgin*'s left wrist and on the surface of the sleeve as well, where this black substance seems to have run over.

The spectrum of this black layer (Figure 3) provides essentially the elemental composition of the ceramic body itself, since the main elements detected were Fe, Ca, K, Mn, Sr, Rb and Zr. The elements Mg, Al and Si, also specific to clay, have very low energy fluorescence lines and are strongly attenuated in the air path to the detector, so their detection was not expected by EDXRF. This composition is especially consistent with calcium-rich clay mineralogy as described by Coroado and co-workers in a research carried out on monumental terracotta sculptures from Alcobaça Monastery [6]. The study was done by X-ray diffraction and showed the presence of quartz, calcite, gehlenite and alumino-silicates as moscovite and feldspars phases. It should be noted that these phases, in particular the presence of calcite and gehlenite together, allowed to estimate the firing temperature round about 850 ºC [6].

Because of the specific location of the black substance in what was a tenon-and-mortise joint, this substance likely refers to the wax-based mixture used to fix the hand in place. Although basically composed of wax and natural resin(s), this kind of organic cement (called *betume* in Portuguese) could contain inorganic additives, such as a mineral powder [2, 7] and sometimes an earth pigment [8], to increase its viscosity, strength and chemical compatibility with the terracotta elements that were to be assembled [9-10]. In case a mineral was added to the cement, it is expected to be either powdered bricks or crushed recovered fired pottery, thus of the same nature as terracotta, or powdered marble or lime, thus calcium-rich materials. All of them are hardly distinguishable from the ceramic body itself. The same can be expected from earth pigments. This could explain why no other elements have been found. On the other hand, the search for a black pigment, able to justify the color observed, is not

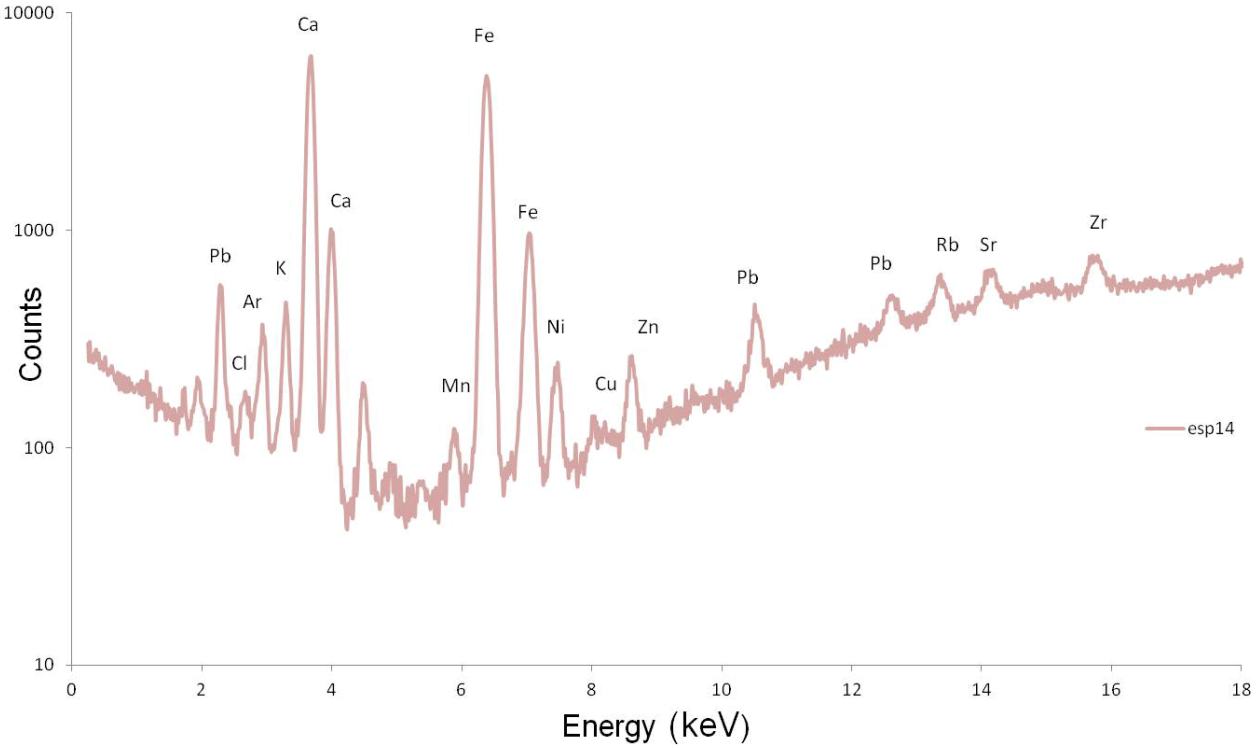

Figure 3. EDXRF spectrum of the black substance observed on the *Virgin*'s sleeve.

Table 1
Virgin Mary — Potential interpretation of the overall data obtained by EDXRF

EDXRF spectra	Detected elements	Interpretation
All spectra (Priming) 05 - Original ground layers 06 - Original ground layers (2) 11 - Overpaint ground layer	Ca / S (?)	Chalk / Calcite: $CaCO_3$ One or more phases of calcium sulfate: Anhydrite / *Gesso grosso*: $CaSO_4$ Dihydrate or synthetic gypsum / *Gesso mate*: $CaSO_4 \cdot 2H_2O$
09 - Pink layer 13 - Flesh tone (hand) 10 - White overpaint	Pb	One or more phases of white lead: Plumbonacrite: $Pb_3O(OH)_2(CO_3)_3$ Hydrocerussite: $2PbCO_3 \cdot Pb(OH)_2$ Cerussite: $PbCO_3$
All spectra (with *estofo*) 04 - Bole	Fe	Bole / Kaolinite / Fine clays + iron oxide (II): $Al_2Si_2O_5(OH)_4 + FeO$
04 - Bole 13 - Flesh tone (hand) 15 - Red sleeve 03 - Black hair	Pb	Red lead: Pb_3O_4
04 - Bole 13 - Flesh tone (hand) 09 - Pink layer – *estofo* 15 - Red sleeve – *estofo* 03 - Black hair	Fe	Hematite: Fe_2O_3
15 - Red sleeve 13 - Flesh tone (hand)	Hg	Vermilion: HgS
All spectra (with *estofo*) 04 - Bole 03 - Black hair / gilding 14 - Black layer (wist)	Fe	Goethite / Ocher – Earth pigments containing Fe: FeO(OH)
04 - Black hair / gilding	Mn	Manganese dioxide (IV): MnO_2
03 - Black hair / gilding 14 - Black layer (wist)		Carbon black: C Bone black (containing hydroxiapatite): $C + Ca_5(OH)(PO_4)_3$
07 - Blue	Co / Ni / Fe / Ca / K	Smaltite: $(Co, Ni)As_{3-2}$ Cobaltite: (Co, Fe)AsS
07 - Blue 08 - Blue 2	Cu	Azurite: $Cu_3(CO_3)_2(OH)_2$
07 - Blue 08 - Blue 2	Ca	Indigo – blue organic dyestuff Precipitated over calcite?
15 - Red sleeve – *estofo* 09 - Pink layer – *estofo* 07 - Blue – *estofo* 12 - Bole – *estofo* 03 - Black hair / gilding	Au	Gold leaf – precious metal Gold alloy or pure gold? The composition should be analyzed by other methods

conclusive. A carbon black of an uncertain origin, called *pó de sapatos* (literally "black from shoes") remains obviously under the limit of detection; it was a synthetic pigment widely used in Portugal, obtained by combustion of vegetable matters by collecting the resulting soot [11]. The presence of phosphorus specific to an animal carbon black containing hydroxiapatite, with the formula $Ca_5(OH)(PO_4)_3$, is challenging, since the Kα peak of P at 1.94 keV overlaps with the existing Ca escape peak at 1.92 keV. Finally, a black earth, such as the one designated as *terra preta* in the account books of the Tibães Monastery [12], only confuses matters for it is expected to contain calcium carbonate, iron, manganese and silica [13].

Ground layer

Besides the elemental composition specific to the ceramic body, in which Ca, Fe and Sr were mostly identified, the EDXRF spectrum characterizing the white ground layer (Figure 4, red line) put in evidence three elements which may relate to the inert — or inerts — employed at the priming stage: Ca, eventually related with a calcium-based material; S, which may be associated to Ca in case calcium sulfate-based layers were applied; and Pb, referring to a white lead-based ground. In the 17th century, in Portugal, a whiting — thus made of chalk ($CaCO_3$) — is very unlikely because it was more specific to the northern region of Europe, while a ground made

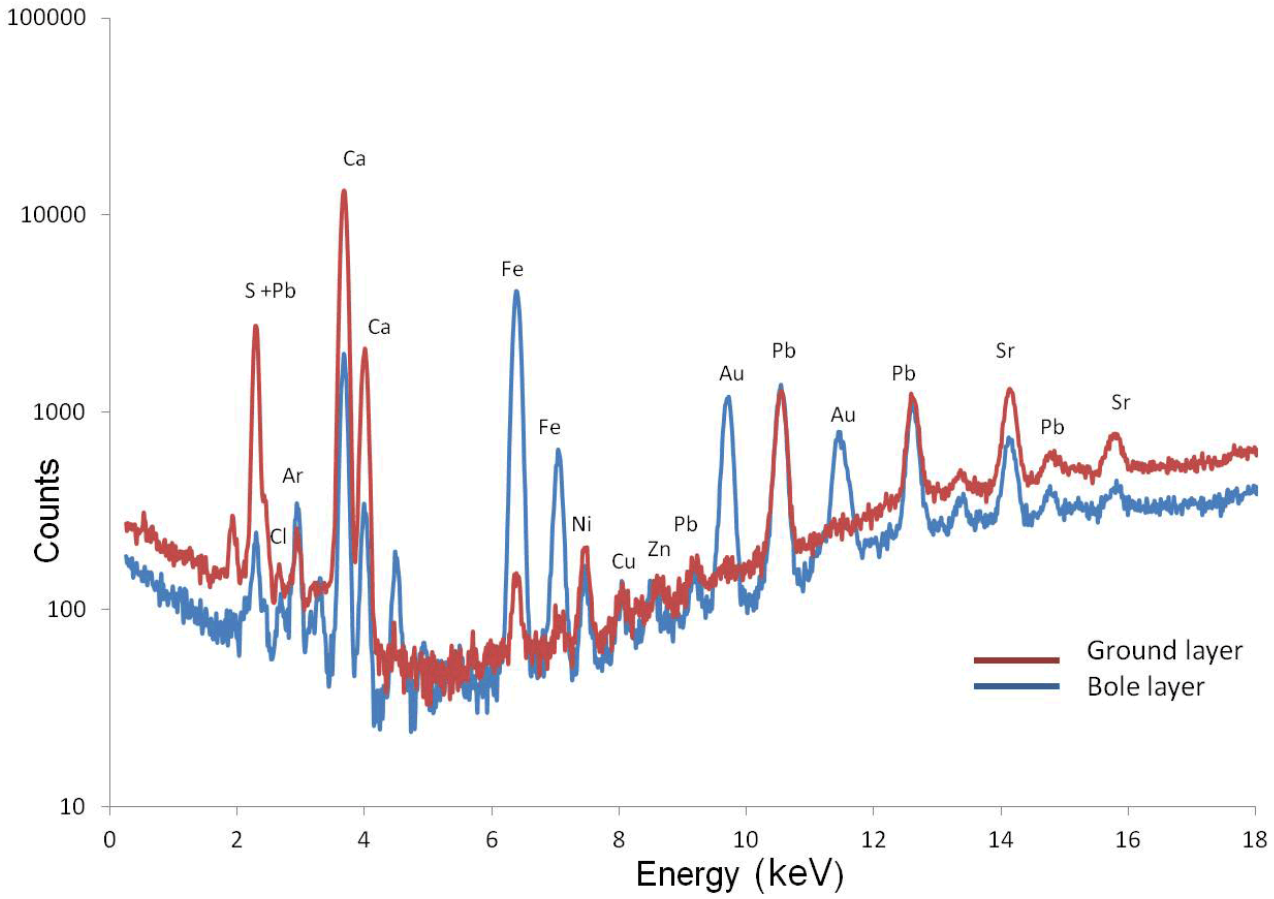

Figure 4. Comparison between the EDXRF spectra of the original ground layer and the bole layer observed on the statue of the *Virgin Mary*.

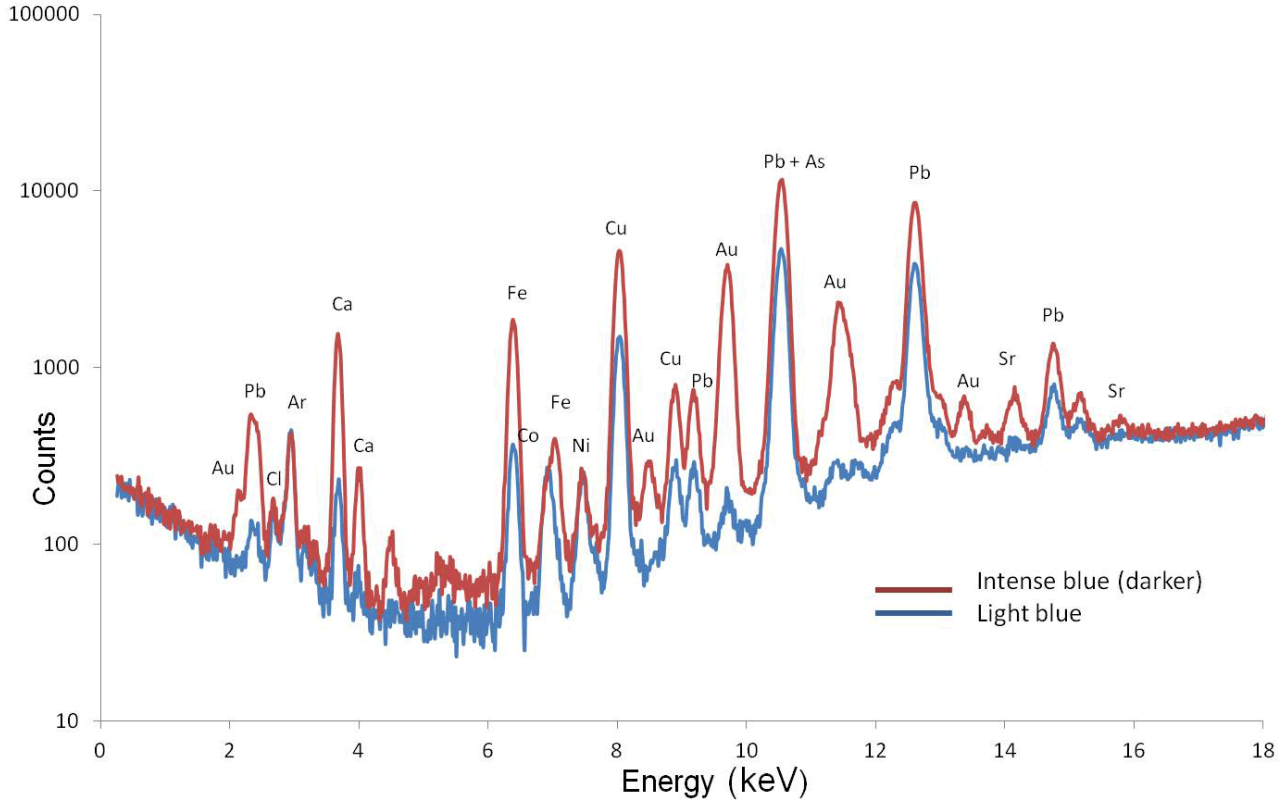

Figure 5. Comparison between the EDXRF spectra of the darker blue paint and the lighter blue paint observed on the *Virgin*'s cloak.

of gypsum ($CaSO_4 \cdot 2H_2O$) perfectly fits the material most available in southern Europe and the practices then involved in sculpture. A double ground implying a base layer of *gesso grosso* consisting of synthetic anhydrite ($CaSO_4$) and a top layer of *gesso mate* consisting of synthetic dihydrate or gypsum ($CaSO_4 \cdot 2H_2O$), as mentioned by Nunes [3] and Pacheco [4], was, in fact, the most in usage in water gilding and *sgraffito* technique performed on Baroque wooden images [9, 14-20] and terracotta statues as well [18, 21]. Its use is attested within the materials purchased by the Benedictine monks in 1682 for the terracotta monumental grouping displayed in the sacristy of the Tibães Monastery [12]. Even though a lead-based priming was far from being habitual, it is not excluded. This kind of ground layer was already identified in other Portuguese wooden or terracotta sculptures produced during the 17th century [18, 22]. It should be noted however that, in the statues from Alcobaça, the presence of Pb may be rather justified by the subsequent application of the white and monochrome overpaint branded with the Neoclassic style (discussed below). The recurrent detection of Pb in all spectra irrespective of the material to be analyzed, likely due to particles of white lead trapped within the damaged original polychrome coating, seems to validate this latter explanation.

Bole layer

A reddish bole was systematically observed in many losses of the gilded surfaces. The comparison between both spectra of the ground layer and this bole layer (Figure 4, blue line) stresses the fact that the main detection of Fe within the bole is directly related to the iron oxide typical of the earthy clay, precisely red, employed as the base for the gold leaf. Even though the bole was native from Armenia as Vasari referred to it [9, 23] — thus its name 'Armenian bole' already employed over time and in Portuguese contracts of polychromy [14-17] — nothing is less certain that, in Portugal, this material ever came from this region in the last quarter of the 17th century [9]. Further analysis, by means of X-ray diffraction for example, should be carried out to distinguish the true quality of this bole: whether it is the Portuguese fine ocher Cennino Cennini spoke highly of [24], the color of which has been reinforced by the addition of red iron oxide for example [9], or one of the famous boles then sourced in Spain [4], as the one called *bolo de Llanes* from Castilla [25-26].

Gilding

The detection of Au in the spectrum of the bole layer (Figure 4, blue line) aided the shiny yellow metal coating to be readily identified as the most precious metal, here laid on the statue in the form of hand-beaten gold leaf. Neither Ag nor Cu was detected. This suggests that the gold was not alloyed, or that Ag and/or Cu present in very low amount remained under the limit of detection, all the more because the metal leaf is extremely thin, expected to be less than 1 micron thick [27]. The deep hue of this gold and its bright appearance are in agreement with a high-grade gold, certainly pure, therefore non-corrosive, and in usage to transmit both the symbolisms of perfection and transcendence of the Virgin Mary. Gold leaves were place side by side (and slightly overlapped on the edges) until covering the whole surface of the garment prior to the application of specific colors to reinforce the iconography of the Virgin.

Blue cloak

While the color blue symbolizes virginity, two superposed shades of blue were observed on the *Virgin*'s cloak, in the depressions of the volumes where the color paints were better preserved over time.

Darker blue paint

The blue color paint in close contact with gilding, and supposedly applied over it immediately after the gold coating was burnished, to obtain the intricate design of a blue brocade fabric, is the more intense one. Marked in red color in Figure 5, the EDXRF spectrum of this darker blue paint shows a complex elemental composition resulting from the combination of the bole, gilding and blue constituents. Given that Pb present peaks of a more significant expression than in the aforesaid spectra, one wonders to which topographic level within the layered structure a lead-based pigment should correspond: whether *1)* to a high reflective underlayer of the blue color, made of white lead as Pacheco recommended it in his treatise "in order to lay the color in a more appropriate manner"? [4]; or *2)* to an admixture of white lead within the blue pigment to produce a lighter tone?; or *3)* to the eighteenth- or nineteenth-century monochrome overpaint already removed but remaining everywhere in the cracks of the original polychromy? Only a cross-section of the blue areas under consideration would shed further light on this question. Whatever the answer, the clear detection of Cu, not to be confused with the tiny Cu peak originating from the collimator (Figure 4), suggests the use of the blue basic copper carbonate mineral known as azurite or fine blue, with the formula $2CuCO_3 \cdot Cu(OH)_2$. In Baroque Portuguese sculpture, this pigment was considered as the most appropriate to depict the *Virgin Mary*'s blue garments and was quite indispensable to express her transcendental nature. The recurrent use of azurite in three-dimension artworks during the 17th and 18th century appears to have lasted longer than in painting [18, 28-29].

Lighter blue paint

Regarding the other blue color, of a paler shade, the EDXRF analysis (Figure 5, blue line) put in evidence the elements Co, Ni (accusing here a greater intensity) and As, besides Cu already found in the underlaying

blue paint, and Pb as well. The presence of Co, Ni and As suggests the use of smaltite with the formula $(Co, Ni)As_{3-2}$, member of the cobalt iron nickel arsenide minerals sourced from Saxonia, or erytrite with the formula $(Co,Ni)_3(AsO_4)_2 \cdot 8(H_2O)$. Both are consistent with the blue smalt pigment, a potassium glass colored with cobalt oxide. The simultaneous use of cobaltite, (Co, Fe)AsS, sourced from Sweden [30-31], is not excluded. Whether all these compounds were present in the pigment should be further studied in order to better define whether the marketed product was of one or more origins. Even though blue smalt was far from being the pigment reference in Portuguese polychrome sculpture during the 17th [9, 32] and 18th century [17], it was widely used in painting since the 16th century onwards [33-34] and also in wall painting, in the chapel over which altarpieces were set to make a handsome contribution to the whole decoration [15, 17]. In this case study, the use of smalt allows at least the identification of a new coating, different from a material viewpoint but respectful of the original color scheme from an iconographic perspective.

Black hair

The same cannot be said with regard to the *Virgin*'s hair. It is mostly black but with gold areas amid the dominant color. Even with a microscopic examination, it proved difficult to determine whether the hair was first entirely gilded, with oil gilding over mordant according to Nunes and Pacheco's treatises [3-4] and then painted black in a subsequent intervention corresponding to the smalt blue paint of the cloak; or originally painted black with glints of gold applied over the color, according to the technique of *peleado* Pacheco fully described [4].

The EDXRF spectrum of the black hair (Figure 6, blue line) put in evidence three elements: Pb, which may relate to the mordant (or *mordente* Nunes referred to [3]), an oily substance made dryer by adding lead-based metallic oxides in it and used to attach the gold leaf in the gilding process [3-4]; Au, which fits the gold coating (either totally or partially laid over the hair); and Cu. The presence of this latter element corresponds perhaps to a low-grade gold, in this case a binary alloy containing a certain amount of copper (Au+Cu); unless it results from the influence of a blue adjacent area of the cloak painted blue with azurite. The fact that the color black is characterized by no element in particular, not even by the presence of P typical of a black pigment of an animal origin (such as bone black), implies that the coloring agent was either pure carbon, of an organic source (like the aforesaid *pós de sapatos*), or a mineral matter (the already mentioned *terra preta* or black earth pigment [12]), the elements of which may be misleading with the underlaying ceramic body and ground layer.

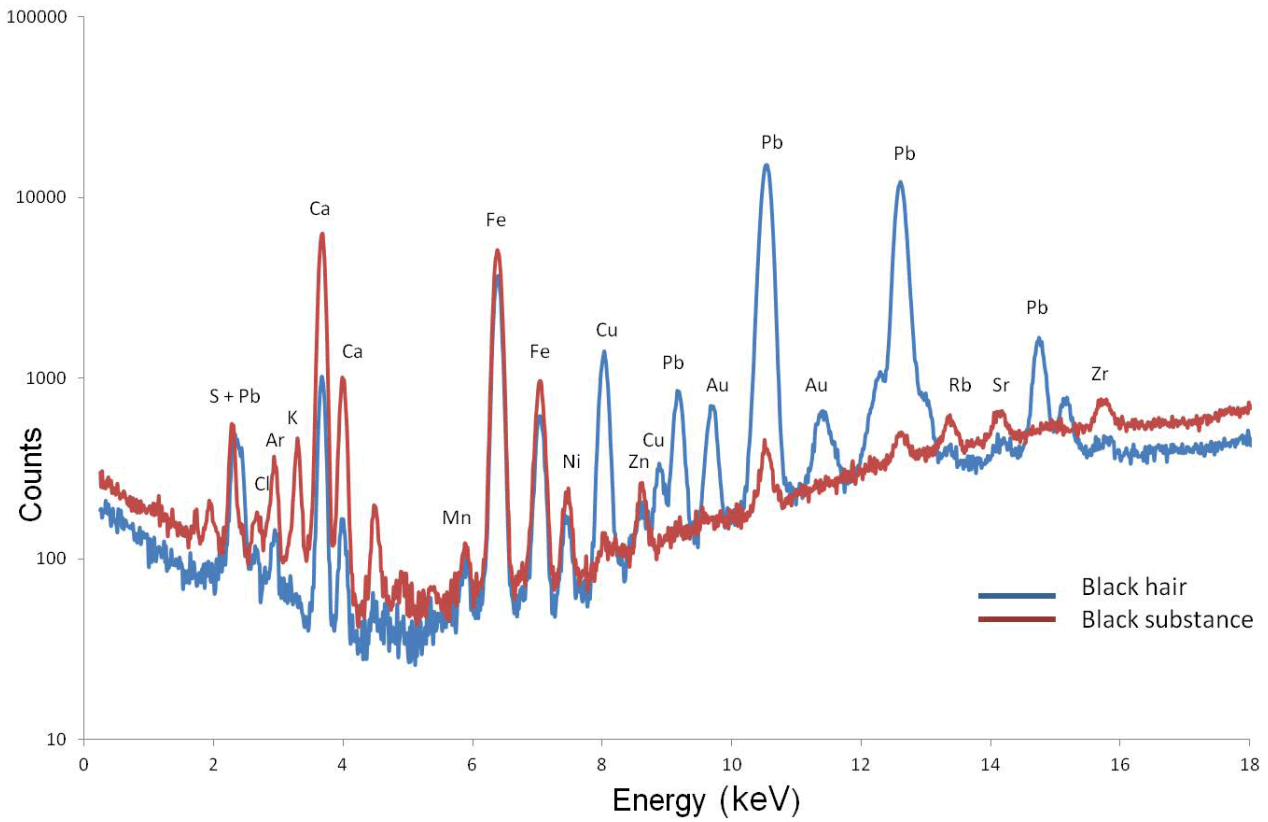

Figure 6. Comparison between the EDXRF spectra of the black paint of the *Virgin*'s hair and the black substance observed on her left sleeve.

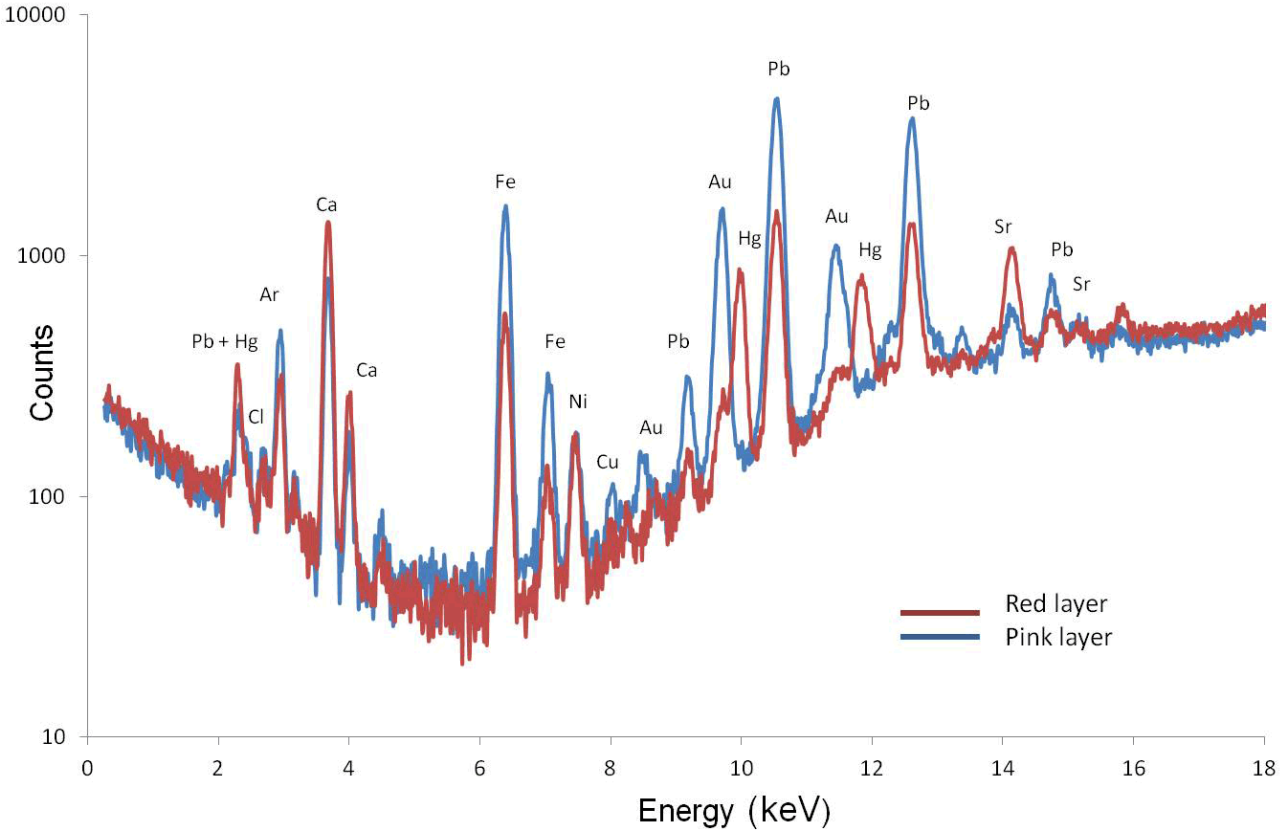

Figure 7. Comparison between the EDXRF spectra of the red paint and the pink paint observed on the *Virgin*'s dress.

Dress of a warm color — red and pink

Regarding the *Virgin*'s dress, it was painted twice over: first red, then pink. This scheme remained visible on her right sleeve.

Red layer

In the red layer applied over gilding, Hg, Au and Pb were detected besides other elements characteristic of the underlaying substrates (Figure 7, red line). The presence of Hg refers undoubtedly to vermilion or mercuric sulfide with the formula HgS, an opaque and costly pigment of a brilliant hue, very often labeled fine (*vermilhão fino*) in Portuguese lists of painting materials [12, 16]; and Au, to the gold coating applied beneath. Pb arose the same considerations as the ones already drawn regarding the blue paints, because it proved difficult to determine, only on the basis of the EDXRF measurement, the material and layer this element matches with.

Pink layer

By comparison of this spectrum with that of the pink color (Figure 7, blue line), the increase of Fe and Pb suggests a mixture containing red iron oxide (Fe_2O_3), also designated as hematite and called *almagre* in Portuguese, and white lead, the so-called *alvaiade* in Portuguese, without excluding red lead (Pb_3O_4), the so-called *zarcão* or *azarcão* [12, 16]. As for the blue paints, this second intervention on the dress conformed to the chromatic relation first established, in accordance with the iconography of the Virgin Mary in which the warm hue symbolizes the Passion of Christ. In this case, the pink color of the dress was probably in keeping with the blue cloak covered with smalt, thus betting on the harmony of two paler shades branded with the Rococo style, typical of the 18th century. In any case, the detection of Pb, as resulting from the Neoclassic white general overpaint, cannot be discarded either.

Flesh tone

The EDXRF analysis of the flesh tone preserved on the *Virgin*'s right hand (Figure 8) showed a specific relationship between the elements Ca, S, Fe, Pb and Hg. Taking into account the recipes by Nunes [3] and Pacheco [4] to render a flesh tone in the 17th century, Pb and Hg make sense. These elements reinforce the idea that white lead was mixed with vermilion to obtain a bright pink color. The two pigments were the most employed for depicting a splendorous completion, especially well adapted to a female character and even more to a dogmatic figure. In this case, Ca and S likely refer to the ground layer already studied, and as much Ca, as Fe and Sr, to the terracotta underneath. The decreased intensity

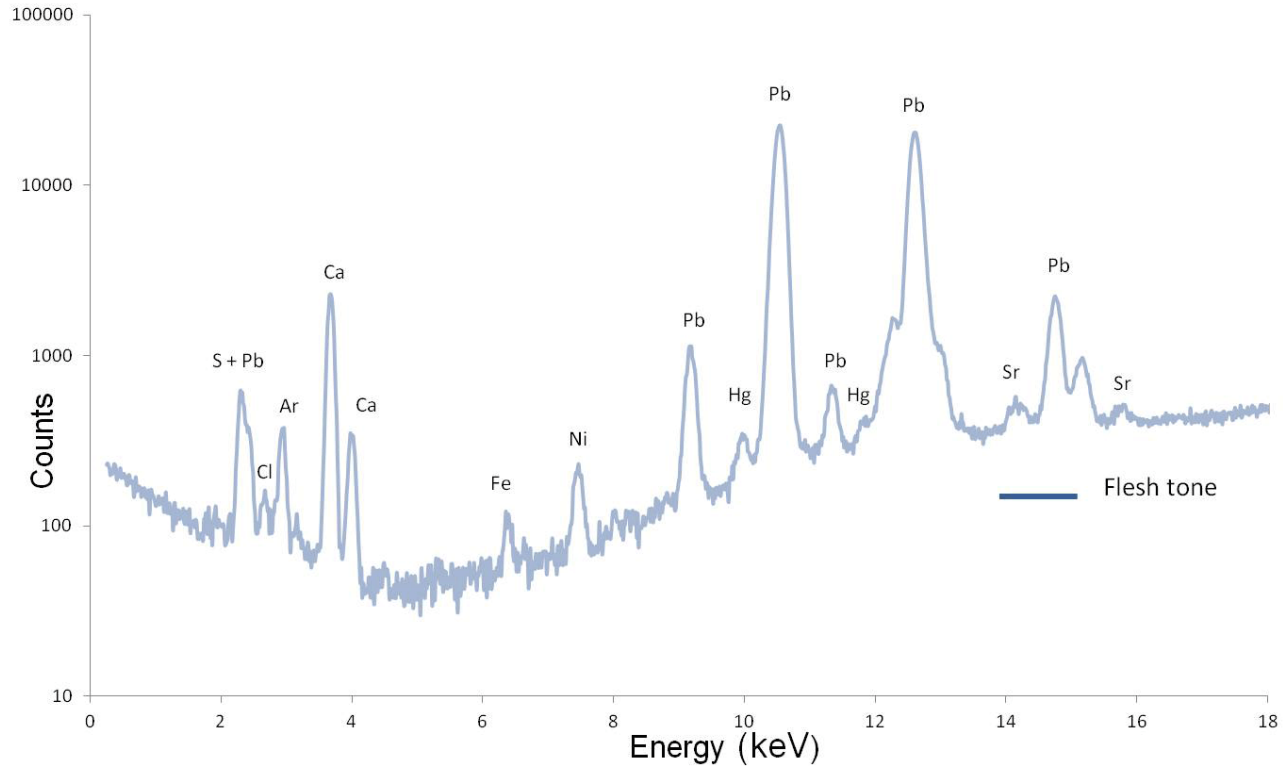

Figure 8. EDXRF spectrum of the flesh tone observed on the *Virgin*'s right hand.

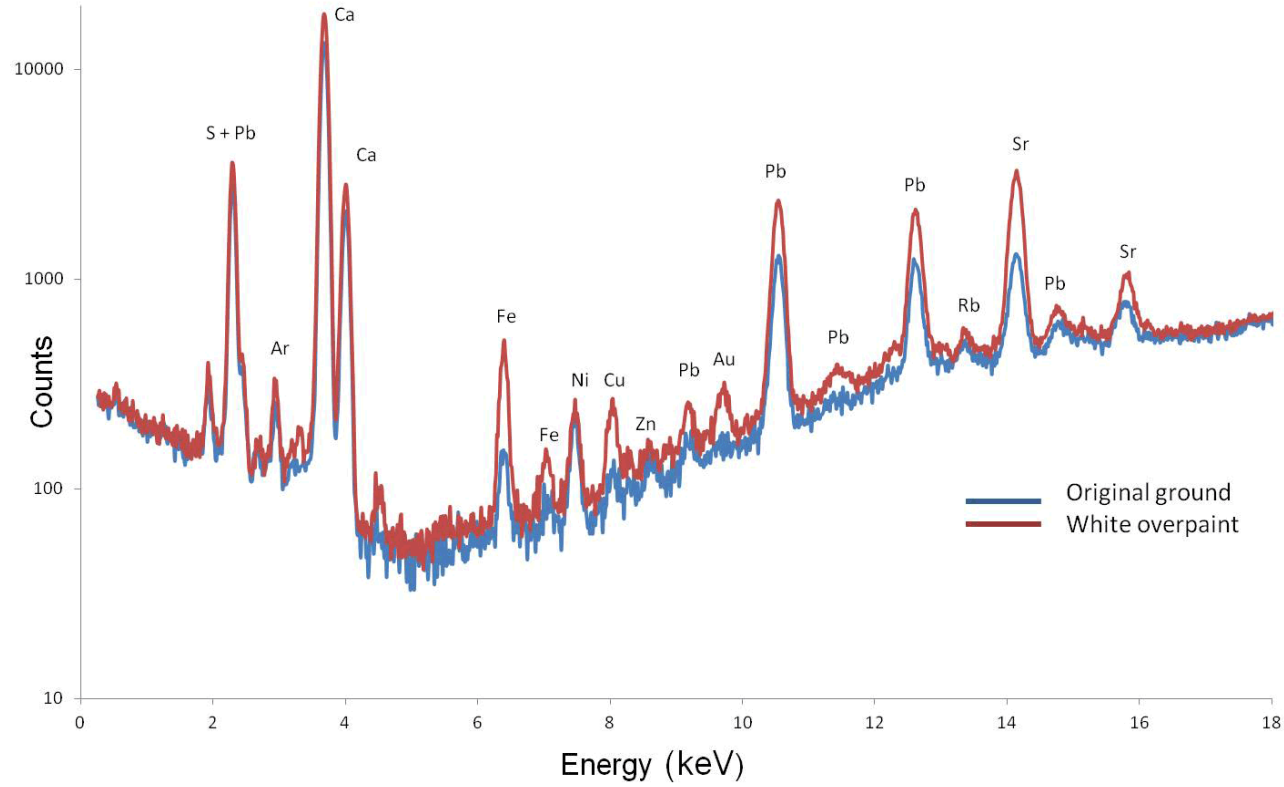

Figure 9. Comparison between the EDXRF spectra of the Baroque original ground and the Neoclassic white overpaint observed on the *Virgin*'s statue.

of these three elements relates to the attenuation effect of the superposed layers. Again, the element Pb may be also considered as being part of the intervention performed afterwards, as described below.

White overpaint

Figure 9 shows the spectrum of the latest intervention of a Neoclassic style applied to the statue (red line) with the spectrum of the original ground layer applied at the Baroque time (blue line). Thanks to this comparison, the detection of the element Pb from the Neoclassic overpaint appears clearly, the other elements belonging to the different layers underneath. Because of the color white analyzed on the surface, white lead is obviously the main constituent expected, even though it is not possible to assess the lead phases – the more basic carbonate plumbonacrite ($Pb_5O(OH)_2(CO_3)_3$) [35], hydrocerussite ($2PbCO_3{\cdot}Pb(OH)_2$) [36] or/and cerussite ($PbCO_3$) — in which *alvaiade* was employed, and the specific conditions in which the pigment was produced [37-39]. On the basis of the readings only, it proves also difficult to be definite on whether a ground layer specific to the monochrome overpaint was applied or not. The detection of both S and Ca may refer either to the original priming or a new gesso ground, and eventually to a *gesso-cré* preparation (supposedly a mixture of both gypsum and chalk, available as a marketed product in Portugal from 1780 onwards [12]), given that the layer build-up and the sate of conservation of the earlier coatings, which remain hidden, are unpredictable.

Apostle 2

On the selected sculpture depicting an *Apostle*, losses within the color paint of the bust are very few or difficult of access for the EDXRF equipment (Figure 10). That is why the measurements were carried out at the very surface of the bust in only five areas: the beard of a darker brown color, the face of a chalky aspect, the cloak of a light blue shade, the tunic of a mauve color and the flowers painted over this latter tone.

Dark brown beard

Although the color of the beard of a darker brown hue seems to have not changed over time on the Apostle, a parallelism between the spectrum of an earlier paint layer still visible in a loss (Figure 11, blue line) and that of an overpaint (Figure 11, red line) readily shows the main differences between what may be assumed as two different coatings: the high intensity of the elements K, Mn, Fe and Hg for the earlier polychromy, and the clear detection of the element Ba and Zn in the overpaint, besides the more significant intensity for the elements S and Sr in this latter intervention.

Figure 10. Top section of the statue of the *Apostle 2*, dated from the 17th century. The lower quality of certain paint layers observed at the very surface let suppose that the statue and the set to which it belongs were overpainted afterwards. Photo: Sónia Tavares.

Beard earlier coating

In the earlier coating (Figure 11, blue line), Mn is probably related with manganese-containing raw or burnt umber (MnO_2), Hg with vermilion (HgS) and Fe with earth pigments like ochers composed of oxides and hydroxides of iron. Among those, the registration of four pigments was recurring in the account books of the Tibães Monastery [12]: two varieties of goethite with the formula FeOOH, of a light and a darker yellow shade labeled *ocre claro* and *ocar escura* respectively; red iron oxide with the formula Fe_2O_3, labeled *almagre*; Cologne earth, a brownish black pigment composed of humic matters, fine clay and hematite Fe_2O_3, compared or equated to Vandyke brown [40] and labeled *sombra de colónia*. It may be assumed that these pigments, amongst the cheapest, were also in usage in the Alcobaça Monastery. The additional use of a black pigment, which could have remained under the limit of detection, is not excluded.

Beard overpaint

In the latter coating (Figure 11, red line), Ba may refer to the synthetic barium sulfate with the formula $BaSO_4$, used as a pigment (commonly called *blanc fixe* or constant white, and barium white) and extender; and Zn, to zinc(II) oxide with the formula ZnO, also manufactured as a white pigment called zinc white or Chinese white. Noteworthy is the fact that both pigments were materials processed at the end of the 18th century (barium white has been invented in 1780 and zinc white was already claimed as the best replacement for white lead in 1782) but were only truly established as marketed products to be used as watercolour and in oil by the 1830s [13]. It should be

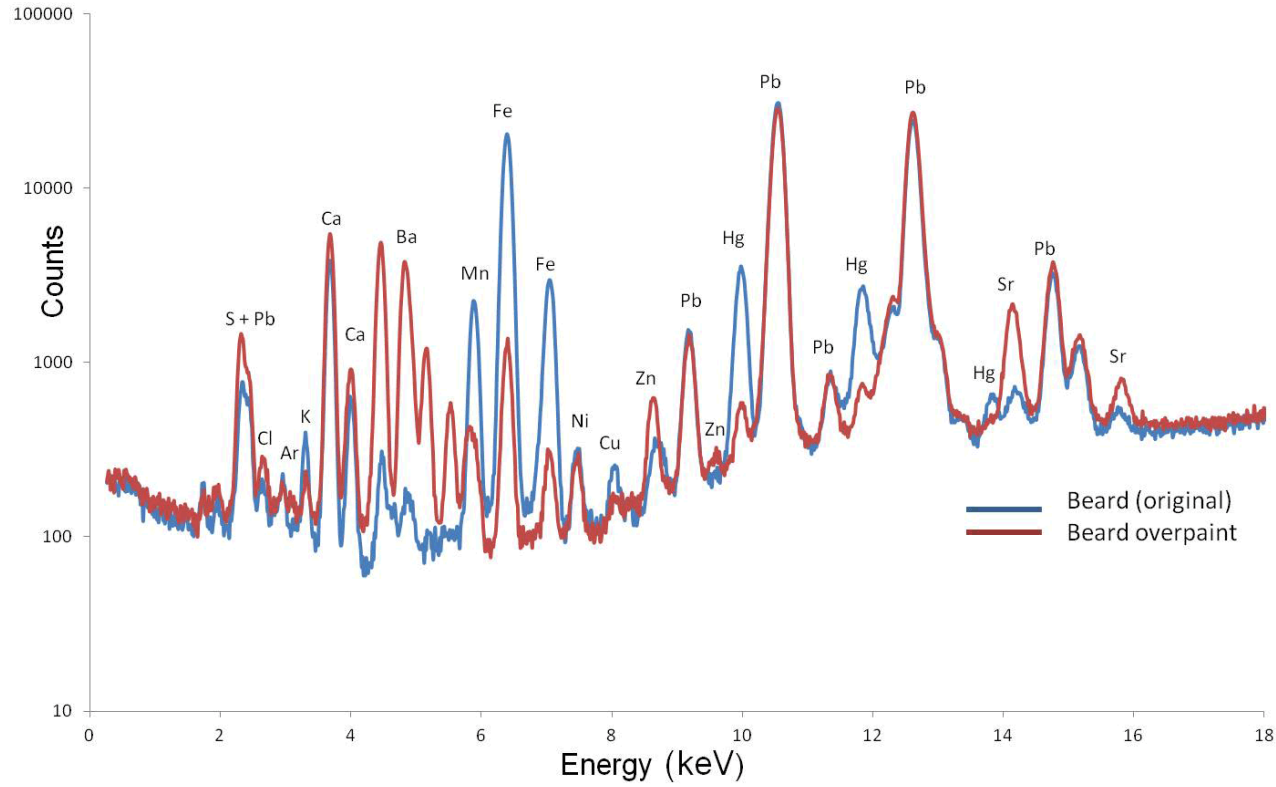

Figure 11. Comparison between the EDXRF spectra of the earlier coating and the subsequent intervention observed on the *Apostle*'s beard.

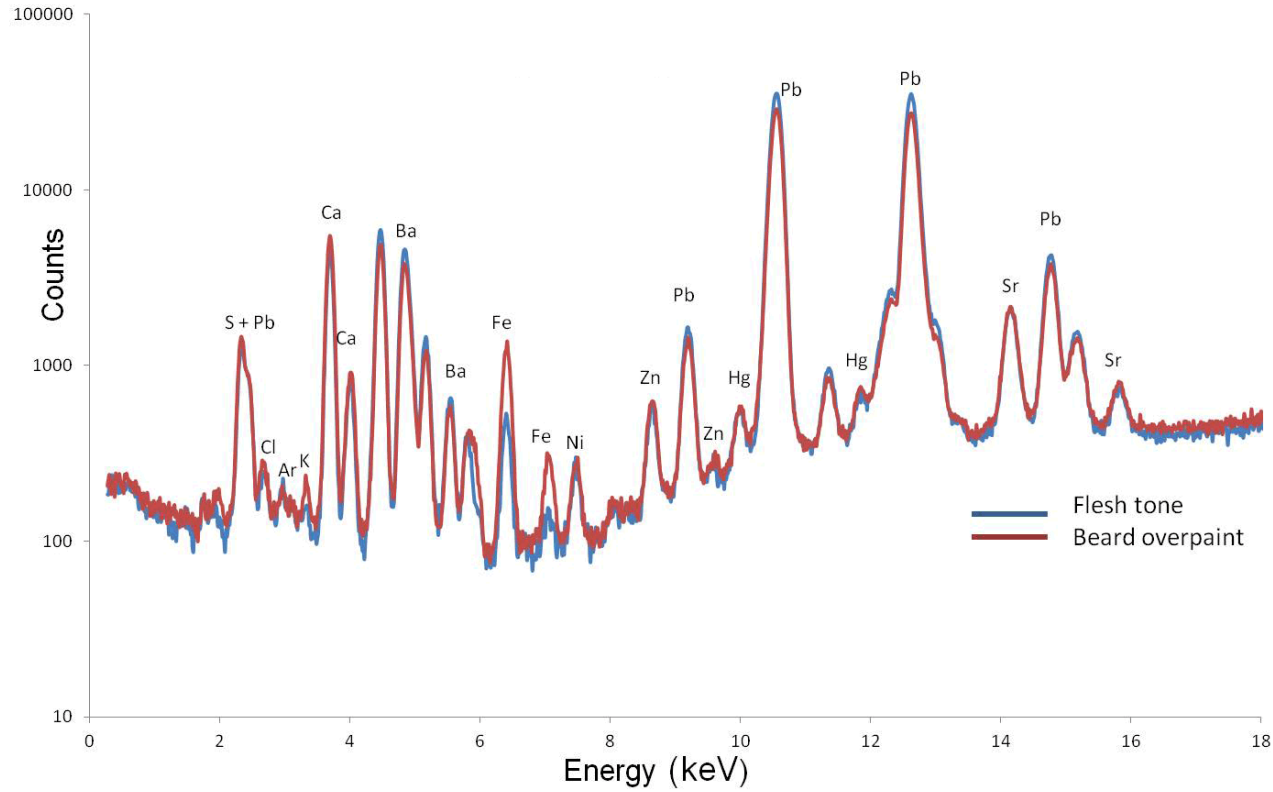

Figure 12. Comparison between the EDXRF spectra of the *Apostle*'s beard overpaint and the flesh tone observed in the adjacent area, on his face.

Tabela 2
Apostle 2 — Potential interpretation of the overall data obtained by EDXRF

EDXRF spectra	Detected elements	Interpretation
All spectra (priming)	Ca / S (?)	Chalk / Calcite: $CaCO_3$ One or more phases of calcium sulfate: Anhydrite / *Gesso grosso*: $CaSO_4$ Dihydrate or synthetic gypsum / *Gesso mate*: $CaSO_4 \cdot 2H_2O$
16 - Mauve cloth 22 - Original flesh tone	Pb	One or more phases of lead white: Plumbonacrite: $Pb_5O(OH)_2(CO_3)_3$ Hydrocerussite: $2PbCO_3 \cdot Pb(OH)_2$ Cerussite: $PbCO_3$
21 - Original beard 23 - Beard overpaint	Pb	Red lead: Pb_3O_4
All spectra (with *estofo*)	Fe	Bole / Kaolinite / Fine clays + iron oxide (II): $Al_2Si_2O_5(OH)_4 + FeO$
21 - Original beard 22 - Original flesh tone 23 - Beard overpaint 24 - Flesh tone overpaint	Fe	Hematite: Fe_2O_3 Goethite / Ocher – Earth pigments containing Fe: $FeO(OH)$ Cologne earth: humic matters + fine clay + hematite Fe_2O_3
22 - Original flesh tone 21 - Original beard 23 - Beard overpaint	Hg	Vermilion: HgS
21 - Original beard	Mn	Manganese dioxide (IV): MnO_2
21 - Original beard 23 - Beard overpaint		Carbon black: C Bone black (containing hydroxiapatite): $C + Ca_5(OH)(PO_4)_3$
16 - Mauve cloth 17 - Blue flowers 18 - Blue cloth	Ca	Indigo – blue organic dyestuff Precipitated over calcite?
16 - Mauve cloth 17 - Blue flowers 18 - Blue cloth	Au	Gold leaf – precious metal Gold alloy or pure gold? The composition should be analyzed by other methods
17 - Blue flowers 18 - Blue cloth	Fe	Azul da Prússia (from 18th century onwards): $Fe_4[Fe(CN)_6]3 \cdot xH_2O$
23 - Beard overpaint 24 - Flesh tone overpaint	Zn	Zinc white / Permanent white / Chinese white (from 18-19th century onwards): ZnO
23 - Beard overpaint 24 - Flesh tone overpaint	Ba / S	Barium sulfate: $BaSO_4$

stressed that Barium sulfate also occurs as a component phase in various co-precipitated pigments, such as the compound known as lithopone, a synthetic pigment formed through co-precipitation of zinc sulfide and barium sulfate. Lithopone is said to have been discovered by G. F. de Doubet around 1850 and first produced on a large scale by J. B. Orr in 1874, hence its alternative name of Orr's zinc white [13]. Whatever the compound(s) employed, it appears that their widespread use during the 19th century objectively constitutes a *terminus post quem* and can assist dating the outermost coating, the application of which has definitely not occurred on the *Apostle* in the 18th century. With regard to the elements S, Ca, Pb and Sr, they may be related with the terracotta substrate and a ground layer, according to the layer build-up existing in the measured area. The importance Sr assumes in this spectrum may rely on two explanations: on one hand, high Sr levels can be associated with Ba minerals, e.g., barite and witherite, due to preferential substitution for the larger Ba^{2+} ion; on the other hand, it may fit the white pigment strontium sulfate, with the formula $SrSO_4$ [13].

Anyway, none of the white matters already referred can explain the dark color of the beard under study. Pigments ranging from yellow to black were certainly part of the palette. Those most commonly used in the paint trades since earlier times were the aforementioned ochers and carbon-based pigments. However, other pigments of a yellow, red and brown shade were manufactured in the 19th century, the formula of which could give rise to the results gathered by EDXRF. Their elemental composition could also reveal the presence of Fe (such as the Mars pigments [13] and Prussian brown [41]), or Ca and Pb (such as brown calcium plumbate Ca_2PbO_4 or lead brown composed of PbO_2), and even K or P (such

as permanganate of potassium $KMnO_4$, or brown iron phosphate with the formula $(NH_4)_6{\cdot}Fe(P_2O_7)_2{\cdot}2H_2O{\cdot}Fe_2O_3$, containing also zinc yellow [41]).

Flesh tone

The analysis of the two coatings existing on the beard (Figure 11) allowed a better reading of the flesh tone actually visible on the *Apostle*'s face. In Figure 12, it appears clearly that this superficial layer (blue line) of a dull chalky aspect, more beige than pink, is contemporaneous of the brown overpaint already identified on the beard (red line), since Ba and Zn have been also detected on the face. Given the high intensity of Fe, the barium and zinc-based compounds were perhaps associated to ochers, or some of the already referred nineteenth-century yellow or brown pigments. On the other hand, it seems that the elements Pb and Hg go on related with the expected white lead and vermilion used to imitate a skin of a warmer tone; unless these elements were part of an underlaying flesh layer, this one counterfeiting the brighter and transfigurated pink completion expected for a saint.

Mauve and blue garments

The *Apostle*'s garments are well differentiated. The tunic is of a mauve color and the cloak, of a light blue one. Both paint layers were applied over water gilding. The colors are even, only decorated from place to place with two different floral patterns. The larger one was obtained by stripping off the colored layers for golden flowers to take shape through the gilding underneath. The smaller design was painted over the colored coating, of an intense blue shade on the tunic and of a very light shade (quite white) on the cloak.

Once again, the comparison between the gathered results of theses layers (Figure 13) shows that the blue coating of the cloak (blue line) is part of the barium-containing latter intervention, while the mauve coating of the tunic (red line) seems of an earlier period and to have remained untouched, for its elemental composition is not including Ba peaks.

Because previous measurements of the layers beneath the superficial colors were not performed, the further interpretation of the spectra showed in Figure 13 is far from being straightforward. Most of the detected elements may refer to the terracotta support, a gesso ground layer, an iron-rich bole layer and gilding as well, as already stressed regarding the *Virgin*'s polychromy.

Mauve paint layer

With regard to the mauve paint layer (Figure 13, red line), it is expected to have been obtained by mixing

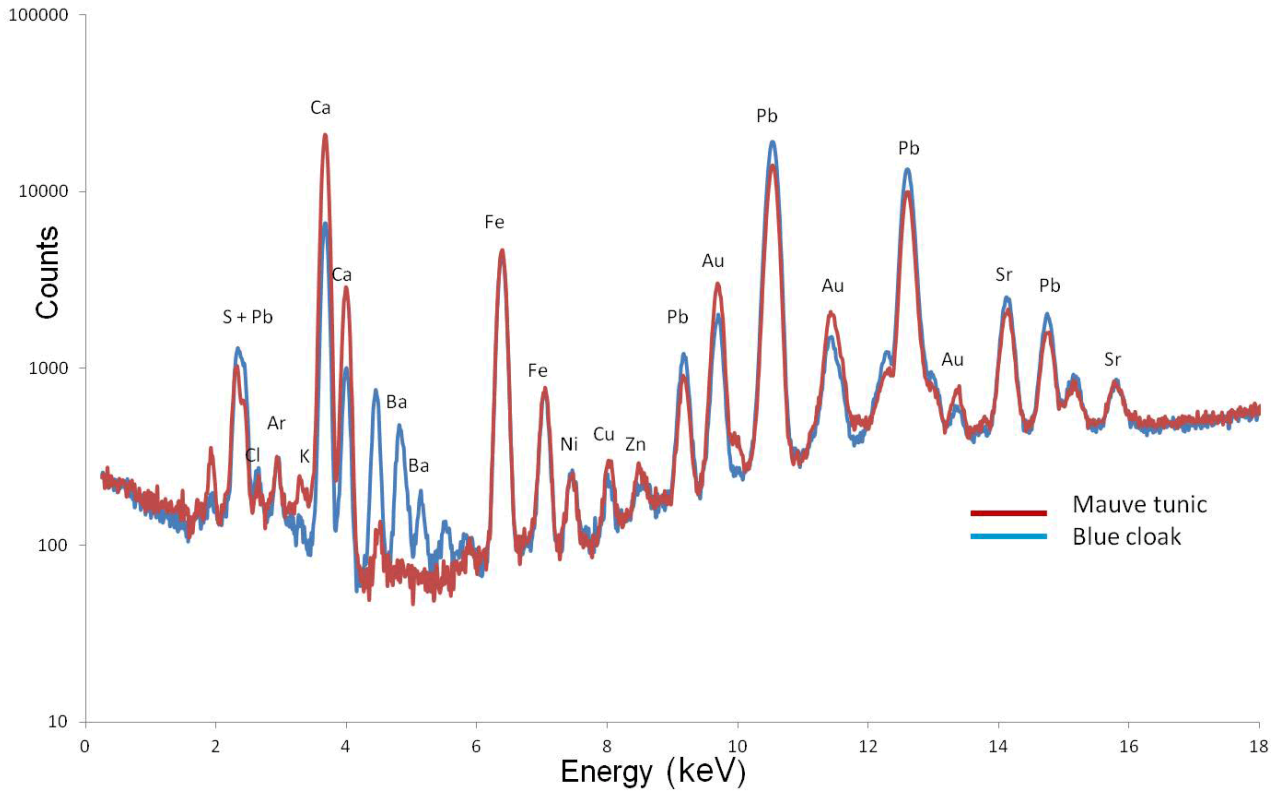

Figure 13. Comparison between the EDXRF spectra of the mauve paint observed on the *Apostle*'s tunic and the blue paint observed on his cloak.

white, blue and red pigments. White lead may obviously be assumed since it was the only white pigment available in the 17th century. Among the red pigments then in usage, red lead and hematite could make sense, except vermilion since no mercury-based pigment has been detected. Although the organic nature of other red colorants prevents to detect them by EDXRF, they may also be considered, taking into consideration the increase intensity of Ca in the spectrum. Indeed, calcium carbonate-based substances were, alone or in admixture with white lead, among the mineral substrates used to precipitate the extract of dyestuffs [42-46]. Many were the red dyes available since earlier times [42-48] and in Portugal in particular [48-50], but without proper analysis, it is impossible to determine whether one of them was employed and if so, which one. Regarding the blue pigments, used either to produce the mauve color or the blue floral design painted above, the spectrum shows that Cu was hardly detected, casting doubt on the use of azurite. The amount of azurite could be quite low or not used at all. In case azurite was not part of the color palette, only indigo as an organic coloring matter can be envisaged on the sculpture during the 17th century. The intensity of Ca in the spectrum may, again, justify the use of a blue dyestuff. The account books of the Tibães Monastery showed that several grade of indigo, called *anil*, could be purchased during the 17h and 18th century, allowing the creation of a very wide range of quality paint layers and blue shades [12].

Blue paint layer

As far as the blue color is concerned in the cloak paint layer (Figure 13, blue line), the question of which coloring matter was used is harder to solve only on the basis of the EDXRF measurement. The spectrum of this layer presents a similar elemental composition than that of the mauve layer, hence the similar considerations that should be drawn for both of them regarding azurite and indigo. However, for a coating dated from the 19th century, thanks to the detection of a barium-based substance in it (either in the color itself or a previous priming), it is more than legitimate to ponder the use of Prussian blue in the overpaint: because of the presence of Fe in its formula, and for being a pigment discovered between 1704 and 1707 and widely employed in Europe since the midst-18th century onwards [7-9, 18, 52]. Prussian blue is an umbrella term for the blue hexacyanoferrate(II) pigments (compounds based around $[Fe(II)(CN)_6]^{4-}$) which also contain Fe(III), and have different composition, method of production and adulteration. To such a point that Prussian blue can contain alumina, chalk, starch, sulfate of lime and baryta, magnesia, zinc oxide, etc. [13]. Noteworthy is the fact that the composition of these adulterants, namely of the inorganic chemical compounds, may also be consistent with the elements detected in the current spectrum, which sets strong limits of identification by the EDXRF technique alone.

Conclusion

The EDXRF technique was useful to have a first non destructive and non invasive approach on the materials potentially used over time on the sculptures of the Alcobaça Monastery. However, the technique itself is limited because several elements are not detectable or have very high detection limits, such as C, Al, Si, Na; and because each spectrum presents the information obtained from superposed layers (terracotta included). In such condition, it proves difficult to relate the elemental composition to the specific constituents of each layer. Furthermore, spectrum interpretation may also be hindered by the overlapping of characteristic peaks, escape peaks and sum peaks, or peaks originating from materials used in the experimental setup.

Anyway, the elements detected in the coatings supposedly applied in the 17th century to the two selected statues seem consistent with the pigments used at that time [53]. These coatings are very alike from a technical and artistic perspective regarding the range of tones and design. However, by comparing the obtained results, namely with regard to the color blue employed in each statue, it appears that the painter-gilders made different material choices and sought to diversify the final effects. These options seem to be consistent with the specific iconography and worship of each figure.

Thanks to the detection of Ba and Zn on the *Apostle*, the EDXRF technique allowed the latter intervention on the grouping depicting the *Delivery of the Keys* to be dated from the 19th century. With regard to the *Virgin Mary* and, by analogy, to the *Angel Gabriel* with which it forms a pair, only white lead was found on the outermost coating. Taking into account that this pigment was not replaced by white zinc, which was used as an alternative to the toxic white lead from the 1780s onwards, the Neoclassic monochromy applied to the *Annunciation* can be still dated from the 18th century.

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Estudo químico e mineralógico e datação por luminescência de altos-relevos miniaturais em terracota

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Resumo

Altos-relevos miniaturais em terracota policromada constituindo dois ciclos narrativos e pertencentes ao Museu Nacional de Arte Antiga (Lisboa) foram estudados. Pouco se sabe da sua autoria, contexto histórico-artístico e técnicas de produção. Perante a sua aparente semelhança formal e material, esta investigação procurou compreender as relações existentes entre estas obras em termos materiais, de fabrico e datação. A composição química dos corpos cerâmicos foi determinada pela análise por activação neutrónica e a composição mineral por difracção de raios X. Os aspectos cronológicos foram estudados por luminescência. Este estudo permitiu elucidar questões de cronologia, proveniência e de produção tecnológica quanto às matérias-primas e as temperaturas de cozedura usadas. Os resultados composicionais permitiram apontar para o recurso a matérias-primas distintas para os ciclos da *Vida de São Francisco* e da *Paixão de Cristo* e temperaturas de cozedura baixas. Os resultados de luminescência apontam para uma produção dos três altos-relevos analisados na segunda metade do século XVIII, em harmonia com os estudos de história de arte.

Palavras-chave
AAN
DRX
TL/OSL
Terracota
Escultura
Património Cultural

Chemical and mineralogical patterns, and luminescence dating of miniature terracotta high-reliefs

Abstract

Polychrome terracotta high-reliefs representing two narrative cycles and belonging to the Museu Nacional de Arte Antiga (Lisbon) were studied. The authorship, historical-artistic context and technological aspects of these artworks are still unknown. Considering the apparent similarity of materials and features of both sets, this research sought to contribute to the establishment of possible relationships between the objects and their workshops in terms of production technology and chronology. The chemical composition of terracotta paste was determined by instrumental neutron activation analysis. The mineralogical composition was acquired by X-ray diffraction. Chronological issues were studied by luminescence. This study enables elucidation of questions related with chronology, provenance and production technology, particularly raw materials and firing temperatures. Compositional results point to the use of distinct raw materials for the cycle of *Saint Francis' Life* and that of *The Passion of Christ*, and low firing temperatures. The luminescence results point to a production of the high-reliefs in the second half of the 18th century, in accordance with art-historical studies.

Keywords
INAA
XRD
TL/OSL
Terracotta
Sculpture
Cultural Heritage

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Introdução

Entre as peças mais delicadas do seu acervo escultórico, o Museu Nacional de Arte Antiga, em Lisboa, conta dois conjuntos miniaturais de altos-relevos em barro cozido policromado, com provável execução no século XVIII dado o seu marcado estilo Rococó. O primeiro conjunto é constituído por dois episódios da *Vida de São Francisco de Assis*, com números de Inventário E242-E243 (Figura 1), e o segundo, por sete cenas da *Paixão de Cristo*, com números de inventário E244-E250 (Figura 2) [1].

Apesar destas obras comporem dois ciclos narrativos deveras distintos pelo tema, são muito parecidas quanto ao seu tamanho — os seus elementos constituintes têm uma altura média de 27,5 cm —, à sua modelação em barro e ao seu acabamento polícromo. A decoração final segue o mesmo princípio estético, com o recurso a materiais muitos diversos, além dos da pintura — finos tecidos, arames, partículas de vidro, areia, verniz, fibras vegetais, etc. — para imitar uma pluralidade de efeitos tácteis condicentes com os materiais imitados — flora, silvas, rochas, reboco de fachadas, mármore polido, lã grosseira, etc. Por isso encara-se a hipótese dos dois conjuntos terem sido manufacturados no mesmo âmbito oficinal e numa faixa temporal relativamente restrita. Com este trabalho pretende-se contribuir para o esclarecimento de algumas destas questões, já que, por estas obras terem sido desmanteladas e se encontrarem sem vínculo documental, nada se sabe sobre a sua encomenda e autoria, o seu local de produção, os processos tecnológicos que lhes deram forma, os espaços sagrados a que estavam originalmente destinados e a sua datação precisa.

Localização original

Aquando da incorporação dos dois conjuntos no museu, em Novembro de 1912, registou-se apenas os locais donde provinham em Lisboa: a Igreja de São Nicolau, para o par de episódios da *Vida de São Francisco de Assis*, e o Convento do Santíssimo Salvador das Irmãs Oblatas, para o ciclo da *Paixão de Cristo* [2]. No primeiro caso, a devoção a São Francisco de Assis numa igreja dedicada a São Nicolau não faz muito sentido. No segundo caso, a encomenda de uma composição escultórica hoje julgada setecentista por uma congregação fundada somente em 1827, é igualmente incongruente. Estas proveniências necessariamente consequentes de uma reafectação dos dois ciclos levaram a seguir duas pistas de investigação quanto à sua localização original: *1)* o Convento de São Francisco da Cidade, em Lisboa, para o ciclo franciscano, porque parte do espólio artístico daquele convento foi transferido para a Igreja de São Nicolau após a extinção das ordens religiosas em 1834 [3]; *2)* o Convento da Boa Morte (fundado em Lisboa em 1736), para o ciclo crístico, tendo em conta que parte dos edifícios foi cedida às religiosas franciscanas missionárias de Maria a partir de 1840 e que o mobiliário e outras peças móveis deram entrada no Tesouro Nacional sob a Primeira República, em 1910 [4]. Para efeito educacional,

Figura 1. Ciclo da *Vida de São Francisco de Assis* composto por dois episódios, com vistas gerais de frente em luz directa: *a) São Francisco Abraçando o Cristo Crucificado* (alt. 275 mm × larg. 220 mm × prof. 55 mm), N.º Inv. MNAA 242; *b) A Tentação de São Francisco* (alt. 273 mm × larg. 228 mm × prof. 55 mm), N.º Inv. MNAA 243.

Figura 2. Ciclo da *Paixão de Cristo* composto por sete cenas, com a vista geral de frente em luz directa: *a) Cristo no Horto* (alt. 276 mm × larg. 217 mm × prof. 57 mm), N.º Inv. MNAA 244; *b) O Beijo de Judas* (alt. 275 mm × larg. 210 mm × prof. 55 mm), N.º Inv. MNAA 245; *c) O Coroamento de Espinhos* (alt. 276 mm × larg. 212 mm × prof. 57 mm), N.º Inv. MNAA 246; *d) Ecce Homo* (alt. 276 mm × larg. 212 mm × prof. 57 mm), N.º Inv. MNAA 247.

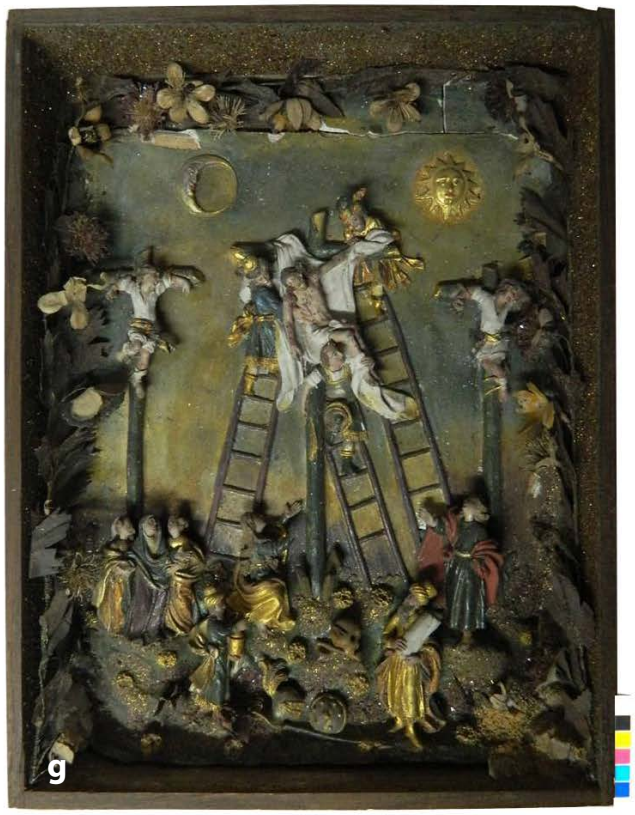

Figura 2 (continuação). Ciclo da *Paixão de Cristo* composto por sete cenas, com a vista geral de frente em luz directa: *e) A Subida da Cruz* (alt. 275 mm × larg. 212 mm × prof. 57 mm), N.º Inv. MNAA 248; *f) A Crucifixão* (alt. 275 mm × larg. 212 mm × prof. 55 mm), N.º Inv. MNAA 249; *g) A Descida da Cruz* (alt. 279 mm × larg. 210 mm × prof. 57 mm), N.º Inv. MNAA 250.

as Irmãs Oblatas tinham entrado na posse do ciclo da *Paixão de Cristo*.

Estes acontecimentos sugerem que ambos os conjuntos estavam destinados a cenóbios lisboetas; o que potencia novas investigações sobre oficinas exercendo actividade no espaço geográfico da capital ou nos seus arredores. Estes acontecimentos mostram sobretudo que o rasto dos bens em análises, na posse dos ramos masculino e feminino da Ordem franciscana em determinado momento, era ainda documentado no início do século

XX mas em fontes dispersas. O valor destas miniaturas era conhecido o suficiente para tornar possível a sua incorporação na mesma altura e no mesmo museu, com números de inventário consecutivos.

Processo tecnológico

Uma observação atenta dos diferentes elementos à vista desarmada e ao microscópio estereoscópico portátil Zeiss com ampliação de 25× permitiu estabelecer o seguinte: tal como chegou ao MNAA em 1912, cada cena está fixa dentro de numa caixa de madeira envidraçada, que circunscreve os limites da representação e lhe serve de expositor. Embora esta montagem comum aos nove elementos inventariados confira uma grande unidade formal a cada conjunto e aos dois conjuntos quando reunidos, a verdade é que a elaboração material das cenas é diferente nos dois ciclos. Com base em argila, a manufactura dos episódios da *Vida de São Francisco* envolveu uma modelação à parte de cada personagem (com altura máxima de *c.* 15 cm) e a sua disposição posterior em chão de cortiça pintada, no meio de flores artificiais em tecido. As cenas da *Paixão de Cristo,* com figuração numerosa (com personagens com metade da altura e até menos), requereu o fabrico prévio de uma placa de barro servindo de fundo sobre a qual foram directamente modelados, em baixo e alto-relevo, tanto as paisagens envolventes com a sua flora e construções, como as figuras. Como se vê, o princípio construtivo inicial dos dois ciclos não é idêntico. Ficou por entender até que ponto estes dispositivos podiam reflectir práticas específicas de modelar com barro — com placa ou sem, e portanto a personalidade de escultores distintos — ou se resultaram apenas de uma gestão sábia, pelo mesmo barrista, das escalas diferentes que exigiam as diferentes representações.

Objectivos

A presente investigação visa compreender as relações existentes entre os dois ciclos narrativos em termos materiais, de fabrico e de datação, para o que se deu particular atenção aos seguintes aspectos:

Figura 3. Amostragem do corpo cerâmico da figura de S. Francisco (comprimento: 15 cm). Amostragem micro-invasiva e não visível na exposição do alto-relevo (amostra #243).

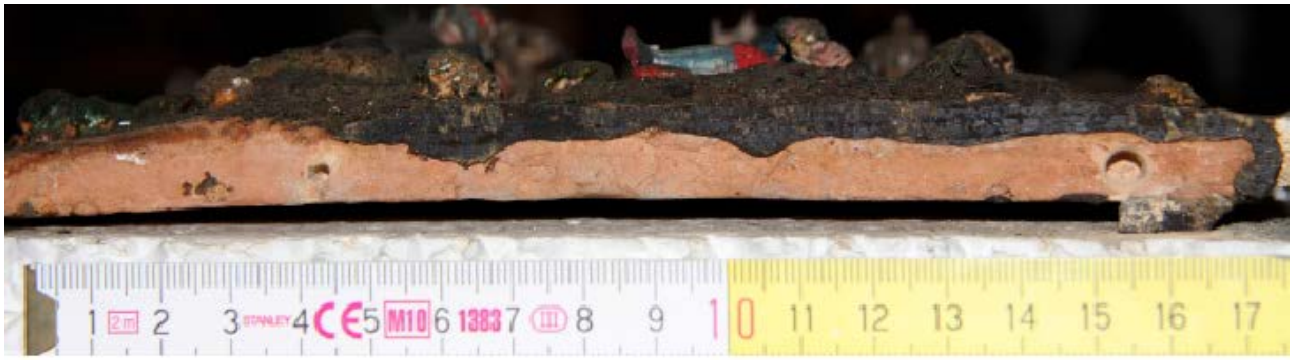

Figura 4. Amostragem ao corpo cerâmico na base do alto-relevo correspondente à Figura 2b. Amostragem micro-invasiva e não visível na exposição do alto-relevo (amostra #245).

1) uma concepção material com variantes significativas, assente, contudo, sobre uma produção por processo aditivo de barro e a sua posterior cozedura para dar resistência e durabilidade aos suportes. Para melhor avaliar às diferentes práticas observadas e examinar a questão subjacente do número de artistas ou oficinas envolvidos, a análise da composição química e da composição mineralógica dos corpos cerâmicos poderia elucidar questões de proveniência e de produção tecnológica, nomeadamente no tocante às matérias-primas empregues e as temperaturas de cozedura alcançadas.

2) O percurso algo conturbado dos dois conjuntos. A questão dos locais pelos quais passaram as obras não é somente importante para retraçar a sua história dentro de um contexto cultural específico. Tem aqui especial relevância na medida em que um estudo direccionado para a datação das peças é corolário do estudo do seu entorno imediato, e do nível de radioactividade que tiveram (ou ainda têm) os materiais arquitectónicos envolvidos no seu percurso. Acontece que as dependências do Convento de São Francisco da Cidade foram reconvertidas no que actualmente corresponde à Faculdade de Belas Artes da Universidade de Lisboa e ao Museu do Chiado, os edifícios tendo sido sujeitos a grandes remodelações. Quanto ao Convento dito "da Boa Morte" (da então Congregação do Senhor Jesus da Boa Morte e Caridade), foi demolido. Ambas situações impossibilitam o estudo ambiental destes espaços, ficando essencialmente as reservas do MNAA o entorno de referência para a última centúria.

Metodologia e protocolo analítico

Para a amostragem, seleccionou-se locais menos visíveis e menos invasivos em três altos-relevos: *A tentação de São Francisco*, do ciclo da *Vida de São Francisco* (Figura 3); *Beijo de Judas* e *Coroação de Espinhos*, do ciclo da *Paixão de Cristo* (Figuras 4 e 5). Esta amostragem foi realizada com o auxílio de uma peça revestida a carboneto de tungsténio para "raspar" o material constituinte, ou noutros casos uma broca de diamante de pequeno diâmetro (< 4 mm) para perfurar e obter pequena amostra, sem contaminar as amostras com elementos traço. Em qualquer dos casos o critério principal foi afectar o mínimo possível o alto-relevo, bem como garantir a invisibilidade da amostragem.

As amostras foram recolhidas e imediatamente seladas em papel de alumínio para minimizar a exposição à luz de faces não expostas, para não interferir com as medidas de luminescência a efectuar em laboratório.

Estas amostras para análise química e mineralógica foram moídas em almofariz de ágata e reduzidas a pó.

A composição mineralógica foi obtida por difracção de raios-X (DRX) na amostra total que foi preparada como

Figura 5. Amostragem ao corpo cerâmico na parte de trás do alto-relevo correspondente à Figura 2c. Amostragem micro-invasiva e não visível na exposição do alto-relevo (amostra #247).

Tabela 1
Associações mineralógicas das amostras estudadas dos altos-relevos miniaturais

Alto-relevo	Amostra	Associação mineralógica
São Francisco	# 243	Quartzo > Feldspatos-K > Filossilicatos > Plagioclases > Anatase
Beijo de Judas	# 245	Quartzo > Feldspatos-K > Calcite > Plagioclases > Filossilicatos > Anatase
Coroação de Espinhos	# 247	Quartzo > Feldspatos-K > Calcite > Plagioclases > Filossilicatos > Anatase

agregado não orientado, utilizando um difractómetro Philips Pro Analytical com radiação CuKα, a 45 e 40 mA, com 1° 2θ/min de 2° a 70° 2θ.

As análises químicas da amostra total foram realizadas pelo método instrumental de análise por activação com neutrões térmicos (AAN), usando o Reactor Português de Investigação (RPI, CTN, Sacavém) como fonte de neutrões.

As amostras de pós foram secas e pesadas e ~200 mg foram embalados e fechados dentro de frascos de polietileno de alta densidade e irradiados durante 6 horas no RPI, com fluxo térmico de $3{,}96\times10^{12}$ n cm^{-2} s^{-1}, $\Phi_{epi}/\Phi_{th} = 1{,}03$ %, $\Phi_{th}/\Phi_{fast} = 29{,}77$. Dois padrões (GSD9, GSS4) foram irradiados numa geometria idêntica para calibração. A amostra e os padrões foram então analisados por espectrometria gama de alta resolução. Detalhes do método encontram-se em Dias e Prudêncio [5]. Este método de análise baseia-se na medição de taxas de contagem de nuclidos radioactivos que são produzidos a partir dos elementos químicos, através de reacções nucleares apropriadas promovidas pelo bombardeamento da amostra com um feixe de neutrões. O decaimento desses radionuclidos é medido num espectrómetro de radiação gama, constituído por um detector de germânio hiperpuro associado a um pré-amplificador, um amplificador e um analisador multicanal, onde o número de decaimentos de cada radionuclido é proporcional à concentração do "elemento-mãe" na amostra. Este método é comparativo, ou seja utilizam-se padrões internacionais de referência, obtendo-se de uma forma precisa e exacta a concentração de uma gama vasta de elementos químicos, nomeadamente elementos traço, que sãos os melhores indicadores geoquímicos. No caso das amostras em estudo os elementos determinados foram: Na, K, Ca, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, U.

Refira-se ainda que este método foi muito útil, quer para o estabelecimento do perfil geoquímico das amostras, quer para obter as concentrações de radionuclidos nos ambientes de deposição das amostras. Destaca-se em particular os teores de K, Th e U fundamentais para a datação por luminescência.

A datação por luminescência baseia-se no relacionamento:

$$Idade = Dose\ Absorvida\ (\mathbf{D}) \,/\, Taxa\ de\ Dose\ (\dot{\mathbf{D}})$$

O protocolo laboratorial das amostras para luminescência incluiu a limpeza dos grãos por ataques ácidos (HCl a 10 % e HF a 10 %) seguidos de lavagem, e posterior separação granulométrica (por deposição segundo a lei de Stokes) da fracção enriquecida em quartzo de dimensão 11-30 µm. As medições foram efectuadas num aparelho Risø, primeiro com um teste inicial para comparar os diferentes possíveis sinais

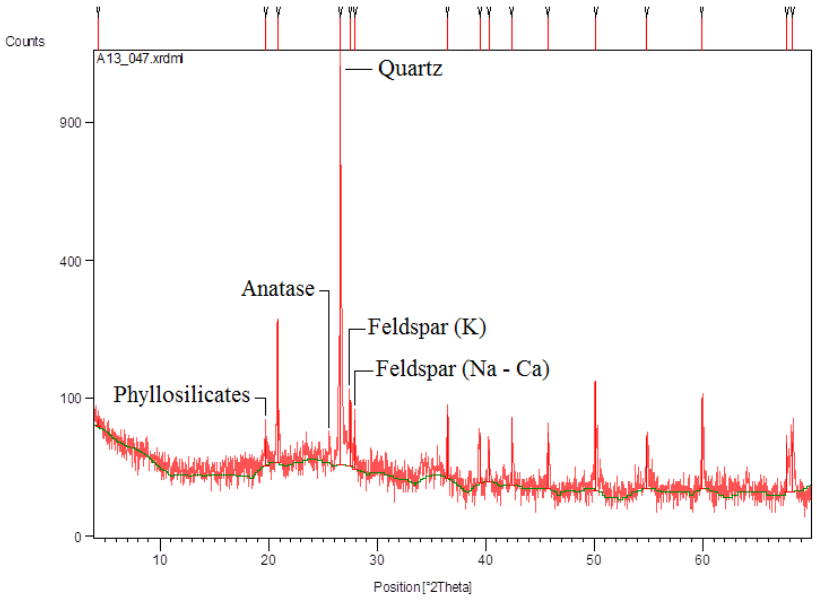

Figura 6. Difractograma da amostra #243 com os principais minerais identificados por DRX.

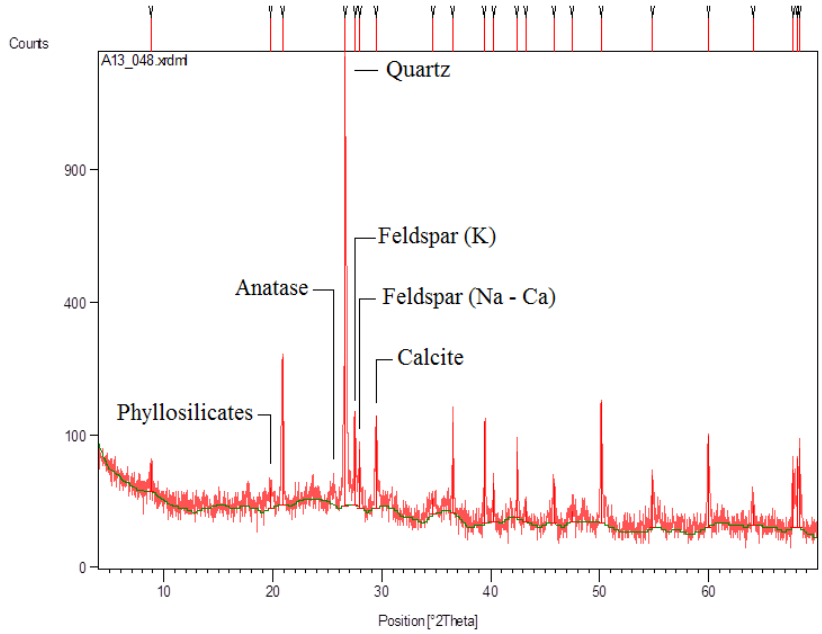

Figura 7. Difractograma da amostra #245 com os principais minerais identificados por DRX.

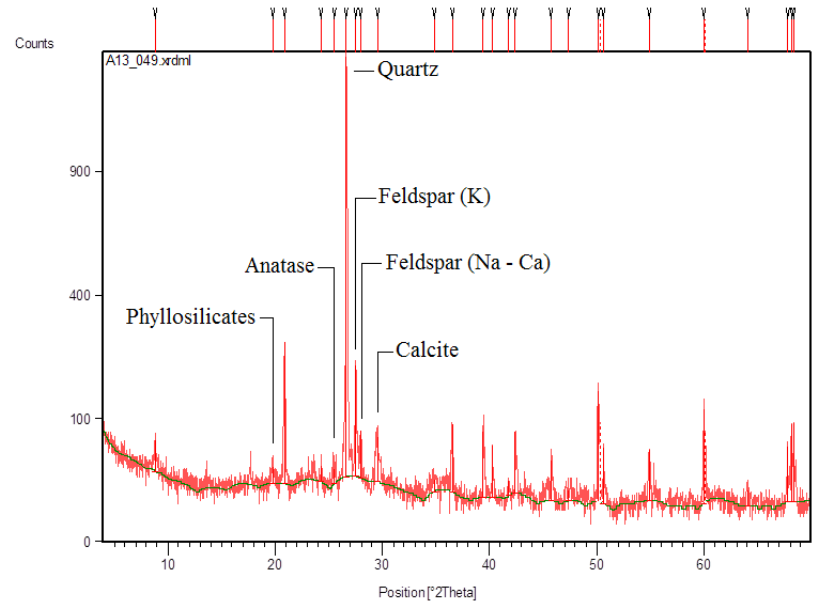

Figura 8. Difractograma da amostra #247 com os principais minerais identificados por DRX.

(IRSL, OSL, TSL), e posteriormente com o protocolo "Single Aliquot Regenerative" (SAR). As estimativas da taxa de dose foram avaliadas com base em medições de Espectrometria Gama do Campo com detetor NaI 3″ × 3″ em diferentes locais dentro do museu, e por AAN no material das amostras em laboratório. Uma descrição mais detalhada sobre métodos de preparação e medição pode ser encontrada em Burbidge *et al.* [6-7].

Tendo como variáveis as concentrações obtidas para elementos químicos seleccionados (pouco alteráveis nos processos de manufactura, cozedura, uso e pós-deposicionais), foram utilizados métodos de análise estatística, nomeadamente gráficos binários de razões entre elementos traço. O tratamento estatístico foi efectuado recorrendo-se ao programa *Statistica* [8].

Resultados e discussão

As três amostras estudadas apresentam diferentes associações mineralógicas (Tabela 1) e os respectivos difractogramas com principais minerais identificados por DRX encontram-se nas Figuras 6, 7 e 8. Será importante realçar que a amostra #243 destaca-se pela ausência de calcite, enquanto as outras duas (#245 e #247) apresentam o mesmo tipo de associação mineralógica, predominando o quartzo associado a feldspatos potássicos, calcite, plagióclases, filossilicatos e anatase. Nestas duas amostras e do ponto de vista mineralógico, será de realçar a presença de filossilicatos, particularmente micas, e a ausência de fases de alta temperatura da calcite. Deste modo, e para as três amostras, aponta-se temperaturas de

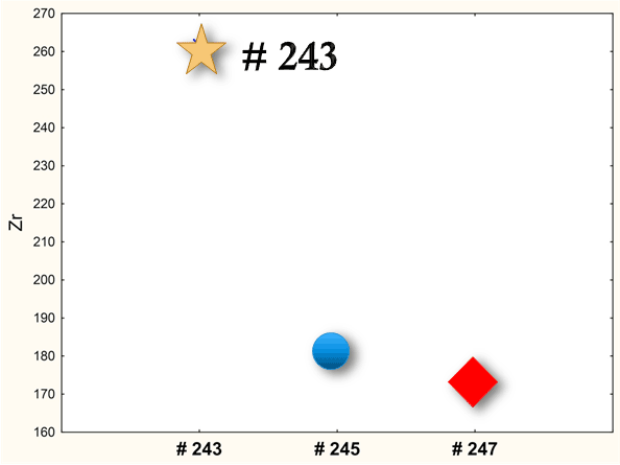

Figura 9. Concentração (µg/g) do elemento químico Zr nas três amostras estudadas. Destaca-se o maior teor de Zr na amostra #243.

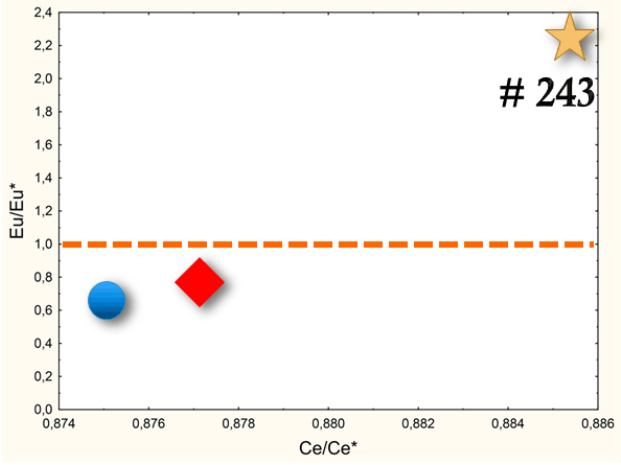

Figura 10. Gráfico binário da anomalia do európio versus a anomalia do cério para as 3 amostras estudadas. Destacam-se as anomalias mais elevadas de Ce e Eu (anomalia positiva de Eu) na amostra #243

cozedura inferiores a 800 ºC, podendo mesmo ter sido muito mais baixas.

Após uma análise detalhada da concentração dos elementos químicos obtidos por AAN, verificou-se que alguns elementos tais como o Co, o As, o Sb, etc., não deveriam ser contemplados no estudo, pois estariam associados aos materiais do revestimento polícromo das peças dos altos-relevos, pelo que contaminaram a composição da pasta cerâmica inicial. Verificou-se assim, que as terras raras constituíram os melhores elementos traço para diferenciar as amostras, embora a amostra #243 se destaque também noutros elementos, apresentando maiores teores de zircónio por exemplo (Figura 9). Esta amostra apresenta também maiores anomalias de cério e európio, tendo mesmo uma anomalia positiva do európio muito acentuada, contrariamente à anomalia negativa do európio que as duas outras amostras #245 e #247 evidenciam (Figuras 10 e 11), bem como um somatório de terras raras mais elevado (Figura 12). Realça-se que as amostras #245 e #247 apresentam também um padrão de terras raras muito similar (Figura 11) e anomalias negativas de cério e európio.

Os resultados de luminescência, ainda que provisórios, são já muito promissores. Na Figura 13 apresenta-se os resultados obtidos para a taxa de dose gama externa calculada com base na espectrometria gama *in situ*. As curvas obtidas em testes iniciais com diferentes condições de estimulação encontram-se na Figura 14. O sinal mais elevado das amostras foi o de OSL, com o qual se determinou a dose absorvida. Apresenta-se, na Tabela 2, estimativas preliminares obtidas para a datação por luminescência destas três peças de alto-relevo miniaturais, obtidas com as medidas no laboratório com o protocolo OSL medido no quartzo (cálculo da dose absorvida), com o de AAN (K, Th e U) (cálculo da taxa de dose nos altos-relevos), e com o de espectrometria gama no museu (taxa de dose do ambiente onde estavam os altos-relevos no museu).

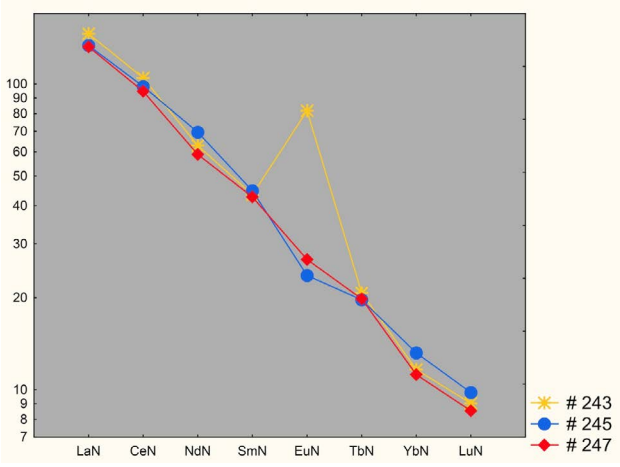

Figura 11. Padrões das terras raras (normalizadas aos condritos) para as 3 amostras estudadas. Realça-se a anomalia positiva da amostra #243 e os padrões similares das amostras #245 e #247.

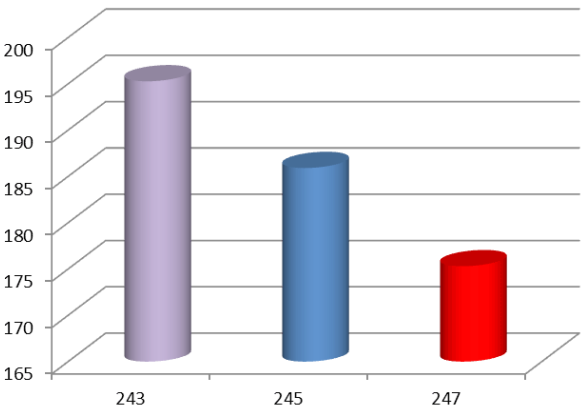

Figura 12. Somatório das terras raras para as 3 amostras estudadas. Destaca-se novamente a amostra #243 das restantes.

Tabela 2
Datação por Luminescência para os três altos-relevos

Amostra	*S. Francisco* #243	*Beijo de Judas* #245	*Coroação de Espinhos* #247
Datação Preliminar (AD)	1772	1796	1788
Interpretação	Segunda metade do século XVIII		

Conclusões

Dados os resultados mineralógicos e químicos obtidos para as pastas cerâmicas dos três altos-relevos, pode destacar-se que a mistura de argila empregue no corpo cerâmico da peça figurativa da amostra #243 difere da usada nas outras duas amostras de altos-relevos. Na amostra #243, nem a calcite nem elevados teores de terras raras (especialmente as leves) foram detectados, mas uma anomalia positiva do európio, bem como elevados teores de Zr foram encontrados.

As amostras #245 e #247 têm composições mineralógicas e químicas similares. Os teores mais elevados de terras raras (especialmente as leves e médias), juntamente com a anomalia positiva do európio encontrados para a amostra #243, não poderão dever-se à presença de plagioclase e/ou calcite ou fases minerais de alta temperatura associadas, pois não foram detectados nesta amostra; pelo que muito provavelmente a micro-amostra recolhida inclui minerais pesados enriquecidos nestes elementos químicos, como por exemplo monazite. Este estudo composicional permitiu distinguir os três altos-relevos miniaturais analisados, apontando para o recurso a dois tipos de matérias-primas: argilas carbonatadas para as amostras #245 e #247 e não carbonatadas para a #243. Para todas as amostras, aponta-se temperaturas de cozedura baixas.

Pela sua coerência, os resultados similares das amostras #245 e #247 reforçam a ideia do ciclo da *Paixão de Cristo*, pelo menos, ter sido produzido na mesma altura e pelo mesmo barrista, com base num projecto iconográfico perfeitamente delineado.

Embora os resultados sugiram o recurso a diferentes matérias-primas para os dois conjuntos (ciclo da *Vida de São Francisco* e ciclo da *Paixão de Cristo*), deverá ter-se em consideração na interpretação que, no primeiro caso, a amostra foi recolhida numa peça figurativa do alto-relevo, enquanto nos outros dois casos foram recolhidas na base de suporte dos altos-relevos. Deste modo, para melhor esclarecer esta fonte diversa, dever-se-iam amostrar também figuras do alto-relevo do ciclo da *Paixão de Cristo*, pois não se sabe até que ponto poderão ter sido usadas diferentes matérias-primas para a base do suporte e para as peças figurativas que constituem estes altos-relevos.

Para a datação dos três altos-relevos analisados, os resultados de luminescência apontam para a segunda metade do século XVIII. Procurando conjugar as datas que fornecem os cálculos com os dados históricos conhecidos, verifica-se que o enquadramento histórico proposto tem toda a legitimidade atendendo a algumas datas especialmente relevantes:

O ano de 1736, correspondente à fundação do Convento da Boa Morte em Lisboa, constitui objectivamente um

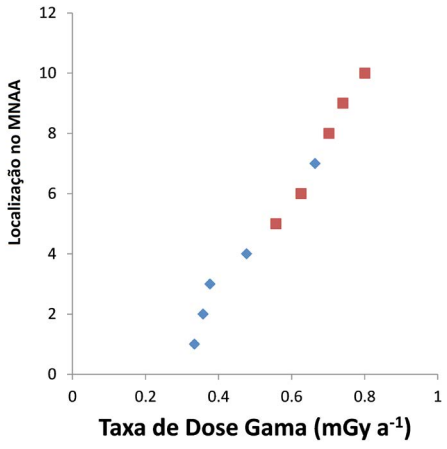

Figura 13. Taxa de dose gama medida com detector NaI 3″ × 3″ em diferentes locais dentro do Museu Nacional de Arte Antiga. Diamantes azuis: locais do MNAA indicados como construção original e mais antiga. Quadrados vermelhos: locais do MNAA indicados como construção mais moderna.

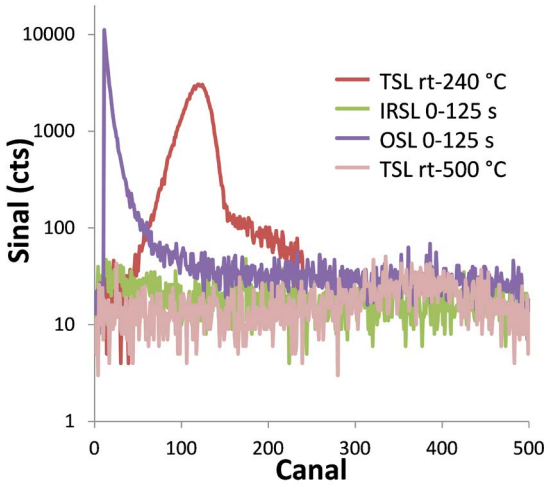

Figura 14. Exemplos de sinais de luminescência estimulada opticamente e termicamente (IRSL, OSL, TSL) do teste inicial, em resposta a 4 Gy de radiação β.

terminus post quem, já que a criação de um ciclo narrativo sobre à *Paixão de Cristo* tendo pertencido àquele cenóbio não faria sentido antes.

Dado que tanto a igreja como as dependências do Convento de São Francisco da Cidade de Lisboa arderam como consequência directa do terramoto de 1 de Novembro de 1755, em que tudo se perdeu [9], entende-se que o ano de 1755 e os imediatamente posteriores representam outros limites temporais a considerar para a feitoria dos episódios da *Vida de São Francisco*.

Obviamente que a "Reforma geral eclesiástica" empreendida pelo Ministro e Secretário de Estado, Joaquim António de Aguiar, pelo Decreto de 30 de Maio de 1834, e a consequente reafectação dos dois ciclos noutros edifícios, constituem por sua vez o *terminus ante quem* das obras em estudo.

O período que sugere as análises também está em consonância com o estilo Rococó então vigente em Portugal nos dois últimos terços do século XVIII, e mais especialmente em obras móveis, com o carácter intimista próprio de peças de interior, a forte teatralização dada aqui às várias cenas numa escala miniatural, a criação de pequenos universos fantasiosos sem por isso se ter renunciado a um realismo exacerbado das matérias.

Este estudo interdisciplinar contribuiu sem dúvida para a reconstrução material e histórica da produção dos altos-relevos do Museu Nacional de Arte Antiga, justificando o alargamento desta abordagem metodológica a peças e problemas similares.

Agradecimentos

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Estudo tecnológico de um presépio em barro do século XVIII

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Resumo
O presépio em barro pertencente ao Santuário de Nossa Senhora dos Remédios, em Lamego (Portugal), é um precioso exemplar da escultura portuguesa em barro do século XVIII. O conjunto é composto por mais de 60 esculturas em barro policromado, com alturas entre os 10 e os 18 cm. As principais figuras evidenciam pormenores e técnicas semelhantes à escultura em madeira do mesmo período: olhos de vidro, rendas, lantejoulas, coroas, vernizes e aplicação de folha metálica. O presépio encontra-se numa maquineta em madeira. Foram efectuados diversos exames laboratoriais de forma a permitir uma caracterização física e química dos materiais e a análise tecnológica do conjunto. A análise qualitativa e semi-quantitativa dos pigmentos foi realizada por microscopia óptica e por microscopia electrónica de varrimento com espectrometria de raios X por dispersão de energia. O estudo tecnológico precedeu a intervenção de conservação e restauro do conjunto.

Palavras-chave
Escultura em barro
Presépio
Microscopia óptica
Microscopia electrónica de varrimento com espectrometria de raios X

Technical study of an eighteenth century clay Nativity scene

Abstract
The Nativity scene (*presépio*), from the Santuário de Nossa Senhora dos Remédios, in Lamego (Portugal), is a rare and precious example of Portuguese clay sculpture from the eighteenth century. This Nativity scene presents more than 60 polychrome clay sculptures, with heights between 10 and 18 cm. The main figures show rich details and techniques, similar to the wooden sculpture decorative motives from the same century: glass eyes, lace, sequins, silver halos, glazes and metallic leafs. The *presépio* is contained within a wooden polychrome structure - a reliquary. Several analytical techniques were carried out in order to characterise some of the physical and chemical features of the materials. The qualitative and semi-quantitative analyses of the pigments were performed by optical microscopy and by scanning electron microscopy coupled with energy dispersive X-ray spectrometry. The technical investigation preceded the conservation and restoration of the sculptures.

Keywords
Clay sculpture
Nativity scene
Optical microscopy
Scanning electron microscopy coupled with energy dispersive X-ray spectrometry

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Introdução

A palavra "presépio" tem a sua origem no latim *præspium* (estábulo) or *præsæpe* (manjedoura). As primeiras referências documentais relativas à descrição de presépios datam de início do século XVI; no entanto, a dramatização de peças durante a época de Natal, com representações do nascimento de Jesus, são executadas desde a Idade Média [1]. Tendo por base os Evangelhos segundo São Mateus e São Lucas, estas representações assumiram diferentes formas, tendo sofrido diversas alterações ao longo dos séculos, aproximando-se de uma representação mais popular e ingénua, combinando características locais e o gosto pela alegoria [2]. As diferentes cenas e cenários captavam o olhar fidalgo para as gentes do campo e da cidade, felizes no seu labor idealizado; no entanto, estas esculturas de género — fonte de imagens e de figuras —, nem sempre foram aceites de bom grado pela Igreja, dado o carácter pagão de algumas cenas representadas [3]. Estas representações estão imbuídas de um carácter dual: o popular e o erudito, o clássico e o anticlássico, o sagrado e o profano [4]. No panorama artístico português do século XVIII, os presépios assumiram o lugar de forma de arte peculiar, recorrendo a poucas influências externas e a inúmeras inspirações internas, nomeadamente na tradição de trabalhar o barro [2].

O presépio do Santuário de Nossa Senhora dos Remédios, em Lamego (Figura 1), é um desses exemplares onde os opostos se unem numa cenografia homogénea, rica e preenchida. A atenção do espectador é imediatamente atraída para a cena principal — a Natividade —; no entanto, o elevado número de imagens — mais de 60 — compele a que o olhar vagueie pelo cenário e pelas suas diferentes representações. O observador obriga-se a parar e a observar cada cena individualmente, de forma a absorver todos os detalhes.

Presépio

Cenografia

O presépio do Santuário dos Remédios, é um precioso exemplar da escultura em barro do século XVIII. As suas características históricas, artísticas e estéticas, tornam-

Figura 1. Presépio após a intervenção de conservação e restauro.

no numa obra de grande interesse. A sua estrutura expositiva divide-se em três planos: o primeiro é o da zona inferior onde se encontra representada a cena principal (*Natividade*), o segundo corresponde à geografia montanhosa que contorna o estábulo e o terceiro é definido pelas muralhas da cidade na zona superior. A leitura poderá ser efectuada no sentido dos ponteiros do relógio, começando no topo superior direito com a *Anunciação aos Pastores* (Figura 2), onde uma delicada figura de um anjo, ricamente vestido, surge num abrigo de madeira onde se encontram três pastores surpreendidos. A acompanhar esta cena, numa zona mais central e deslocando-se do plano superior para o inferior, estão representados os Três Reis Magos com a sua comitiva (Figura 3). Esta representação assume um carácter exótico conferido pela riqueza de cores e acessórios das personagens; os Três Magos surgem montados num cavalo branco, num elefante e num camelo e cada um dos criados traz outro animal idêntico. Tal como referido, esta cena desenvolve-se do plano superior para o inferior, dirigindo o olhar do espectador para a *Adoração dos Pastores* e, por último, para o tema principal — a *Natividade* (Figura 4). A *Natividade* encontra-se na zona central do plano inferior e é composta por três figuras principais: o Menino Jesus, Nossa Senhora e São José. No plano secundário estão representados a vaca e o burro. Todas a figuras se encontram no interior de um estábulo. Do lado esquerdo, ainda na zona inferior, está representada a *Fuga para o Egipto* (Figura 5) e por último, novamente no plano superior, mas sobre a esquerda, o *Massacre dos Inocentes* (Figura 6). Trata-se de uma representação dramática, onde os corpos das crianças estão sobre o chão e onde se distingue claramente a crueldade nos rostos dos soldados e a dor no rosto das mães, enquanto o rei Herodes assiste pacificamente à cena, ladeado pelos seus guardas.

A acompanhar estes cenários e personagens, surgem inúmeros outros como cantores, músicos, personagens a lutar ou a tirar água, pastores, ovelhas e anjos a tocar instrumentos musicais.

O presépio não se encontra completo; algumas das figuras desapareceram total ou parcialmente. Antes do restauro, muitos dos pormenores descritos não eram visíveis, muitas figuras estavam partidas, algumas mal colocadas e outras ocultas sob o cenário. Após o restauro foi possível verificar a inexistência de algumas personagens, identificáveis apenas pela presença dos pés no cenário.

Escultura

As mais de 60 esculturas que compõem o presépio, têm entre 10 e 18 cm de altura e revelam diferente qualidade de tratamento da sua policromia. Estas diferenças estão directamente relacionadas com a sua posição no panorama geral. A Sagrada Família e os Três Reis Magos evidenciam detalhes ricos nas suas vestes, similares aos existentes na escultura em madeira do mesmo período: cordões, lantejoulas e rendas. Diversos

Figura 2. *Anunciação aos Pastores*.

Figura 3. *Reis Magos*.

Figura 4. *Natividade* e *Adoração dos Pastores*.

pormenores são dourados e, embora a transparência inicial se tenha perdido, é possível identificar a presença de vernizes sobre a folha metálica, nomeadamente no azul dos mantos de Nossa Senhora e São José. As rendas que rematam os mantos dos Três Reis terão sido modeladas utilizando uma mistura de cera-resina que permite que os fios mantenham a sua forma. A comitiva dos Reis também

Figura 5. *Fuga para o Egipto*.

Figura 6. *Massacre dos inocentes*.

apresenta roupas ricas e exóticas, assumindo o papel de personagens mais coloridas de toda a composição. Nossa Senhora, São José e os Três Reis Magos têm olhos de vidro. Outro grupo com apontamentos de cores metálicas nas vestes é o do Massacre dos Inocentes, onde o rei e os soldados apresentam pormenores dourados.

O uso de decoração tridimensional nas esculturas cria um sistema decorativo complexo e heterogéneo. Antes da intervenção de conservação e restauro, muitos destes elementos estavam destacados ou partidos, tendo sido possível recuperar a sua quase totalidade. Estes elementos, juntamente com a quantidade de detalhes, o seu posicionamento e a localização específica de cada um, conferem particular relevo na composição final das esculturas, culminando no sentido da total percepção plástica do conjunto.

As restantes figuras possuem uma paleta de cores mais limitada, onde predominam o vermelho e o verde escuros, o castanho, o preto e o branco. Algumas destas esculturas têm uma das peças de vestuário — casaco ou chapéu — com um acabamento aveludado, o que confere mais detalhe e textura às obras.

As três figuras que se encontram nas ameias da muralha apenas possuem meio corpo, revelando a intenção do artista de as colocar naquele preciso local.

Outros materiais complementam o conjunto escultórico: asas dos anjos músicos em papel pintado e alguns detalhes dos instrumentos musicais em madeira, filactera em papel nas mãos do anjo da *Anunciação aos Pastores* e flores em papel, aplicadas em diversos pontos do cenário. São José e Nossa Senhora têm um halo e uma coroa em prata.

Cenário

Para além da madeira utilizada na estrutura da maquineta, o principal material que compõe e estrutura o cenário é a cortiça. A cortiça foi aplicada em placas para execução de relevos, formando rochas, pequenos montes e abrigos; as placas foram coladas, pintadas e cobertas com musgo, plantas secas e flores de papel. Durante a intervenção foi decidido não se colocar novamente musgo ou outros elementos de origem vegetal, tendo sido aplicado o mesmo critério ao "céu" que se encontrava coberto com algodão. Identifica-se ainda a presença de paus e palha utilizados para construir o abrigo dos pastores, criando uma arquitectura mais realista. As muralhas da cidade e as fontes mimetizam a pedra na sua cor e textura através da aplicação de areia e tinta sobre o cartão.

Procedimentos experimentais

Com o objectivo de se proceder a um estudo mais aprofundado dos materiais e técnicas utilizados no conjunto, procedeu-se à análise laboratorial de micro-amostras previamente seleccionadas. Foram recolhidas 12 amostras: seis encontravam-se destacadas, junto às esculturas e outras seis foram retiradas de locais discretos mas representativos. As amostras foram englobadas em resina poliéster (Bylapox 3085A e B – 2:1) e polidas numa lixadora circular (Struers Planopol-V).

Microscopia óptica (OM)

A observação dos cortes estratigráficos foi efectuada através de um microscópio óptico Zeiss Stemi 2000-C, com luz polarizada e reflectida, proveniente de um sistema externo Zeiss KL 1500 LCD. A aquisição das imagens foi realizada com uma câmara AxioCam MRcS e um equipamento de aquisição e tratamento de imagem Axio Vs 40 V4.4 Carl Zeiss Vision GmbH. A montagem e observação das amostras seguiram os procedimentos aplicados na análise de pintura e escultura policromada [5]. O estudo da estratigrafia permite analisar o número de camadas, espessura, cor, textura e ouros aspectos físicos das amostras, nomeadamente a coesão entre camadas, a forma, organização e dimensão das partículas e a presença de repintes [6].

Microscopia electrónica de varrimento com espectrometria de raios X por dispersão de energia (SEM-EDS)

A análise das amostras através de SEM-EDS foi efectuada com um microscópio electrónico de varrimento SU-70 UHR Schottky FESEM (Hitachi) com um sistema Quantax 400 EDS (Bruker AXS – Xflash Silicon Drift Detector). Foi aplicada uma diferença de potencial de 15 kV e intensidade de corrente de 32 μA. Os espectros EDS foram adquiridos em áreas de 1 μm^2, com tempo de aquisição de 60 s e ampliação de 8000×. As amostras foram revestidas com carbono. Os resultados semi-quantitativos foram obtidos após três medições e normalizados para 100 %.

Resultados e discussão

A análise por OM e SEM-EDS permitiu um estudo mais detalhado das características tecnológicas, físicas e químicas dos materiais utilizados no conjunto.

A observação dos cortes estratigráficos por OM permitiu diferenciar dois grupos de amostras: no primeiro grupo distinguem-se duas camadas (preparação e policromia) e no segundo grupo três camadas (preparação, camada intermédia e policromia). O primeiro grupo engloba as amostras recolhidas nas carnações e o segundo as amostras recolhidas nas restantes zonas, nomeadamente em áreas com folha metálica, como o manto e túnica de São José e de Nossa Senhora. A preparação apresenta cor branca com diversas partículas alaranjadas, de diferentes dimensões, distribuídas heterogeneamente por toda a camada. Na camada intermédia, de cor castanha e mais homogénea, identificam-se pontualmente pequenas partículas de cor preta e de um castanho mais escuro (Figura 7). Na amostra recolhida no lençol do Menino apenas se identificou a presença de uma camada de cor branca, de características físicas distintas das restantes quanto à cor e homogeneidade.

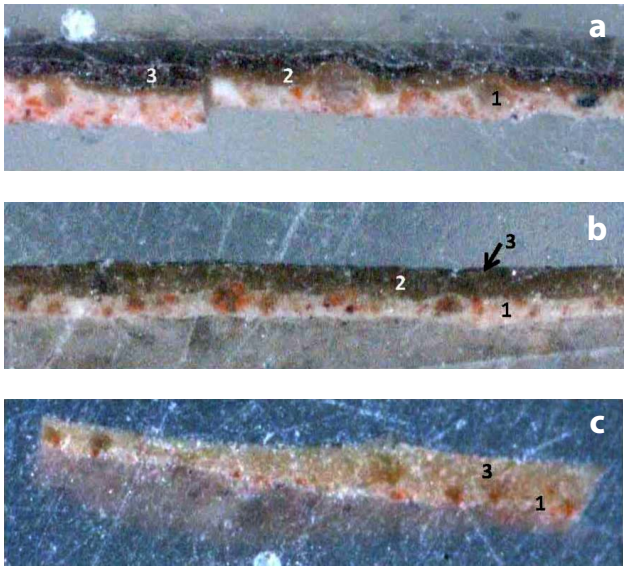

Figura 7. Estratigrafias (OM, 100×): *a)* cor vermelha (túnica de Nossa Senhora); *b)* cor azul (manto de Nossa Senhora); *c)* carnação (Anjo Músico). 1: camada de preparação; 2: camada intermédia; 3: policromia.

A análise por SEM-EDS auxiliou a interpretação da observação das estratigrafias. Identificou-se a presença de diversos elementos, como alumínio, chumbo e silício em todas as amostras; apenas na amostra de cor branca (número 4, Menino Jesus), não se detectou a presença de cálcio. Em algumas amostras foi identificada a presença de prata (Tabela 1). O chumbo apresenta uma concentração mais elevada sendo o elemento principal da camada de preparação, onde se detecta ainda uma presença constante e homogénea de ferro. Na camada de preparação surgem agregados de dimensões variáveis compostos de cálcio, alumínio e silício.

Através de SEM-EDS não foi possível distinguir física ou quimicamente a camada intermédia presente

Tabela 1
Elementos detectados através de análise por SEM-EDS. O número de marcas é proporcional à concentração.

Amostra	Cor	Ag	Al	Ba	Ca	Fe	Mg	Pb	Si	Zn
1 – Nossa Senhora	Azul	++	+		+	++		++	+	
2 – Nossa Senhora	Azul metálico	+	+		++	++		++	+	
3 – Nossa Senhora	Vermelho	++	+		+	++		++	+	
4 – Menino Jesus	Branco		+	++				++	+	++
5 – São José	Azul	+	+		+		+	++	+	
6 – Anjo	Carnação		+		++	+		++	+	
7 – Burro	Castanho		+		+	+	+	++	+	
8 – Elefante	Cinzento		+		+	+		++	+	
9 – Elefante	Preto		+		++	+	+	++	+	+

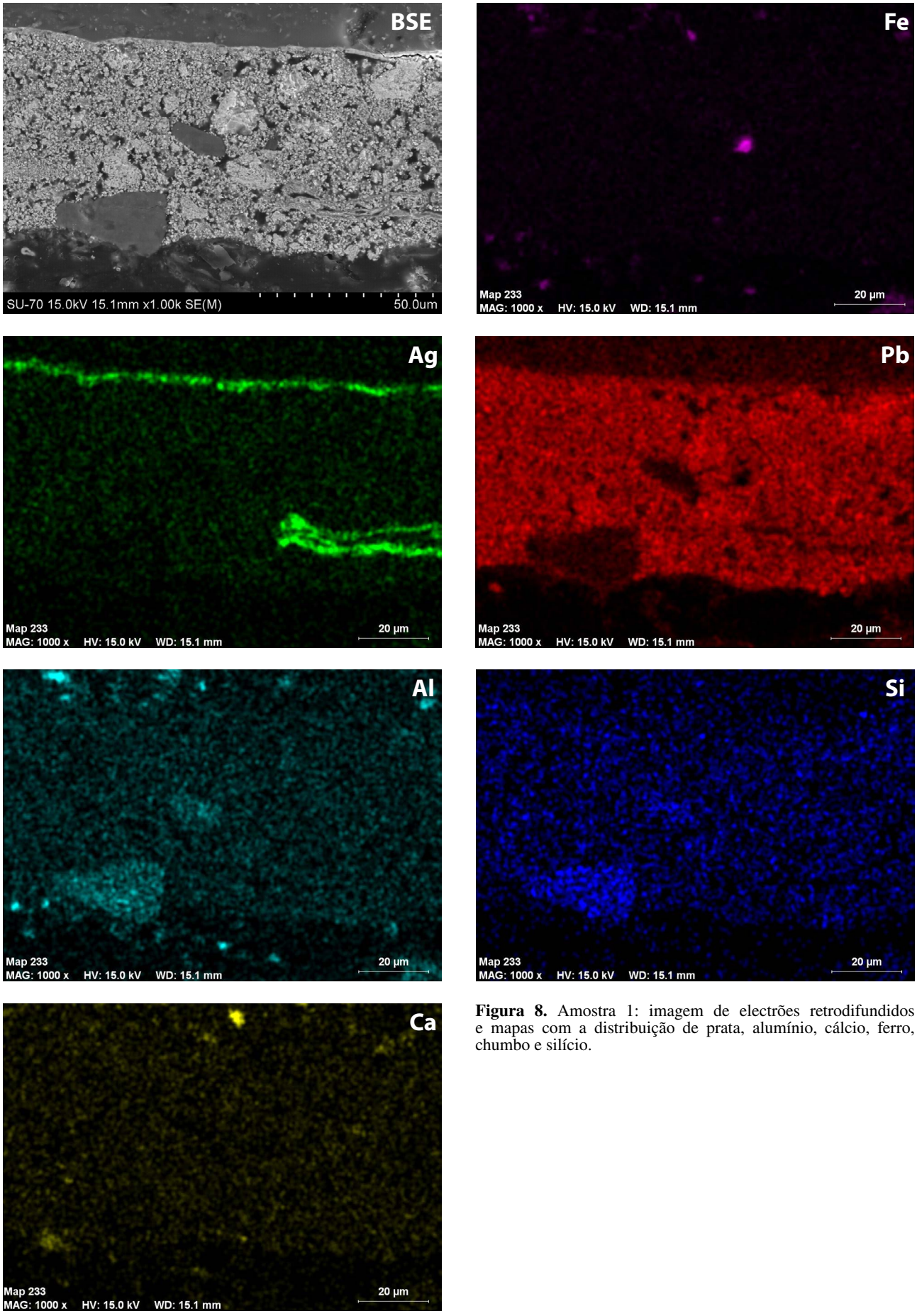

Figura 8. Amostra 1: imagem de electrões retrodifundidos e mapas com a distribuição de prata, alumínio, cálcio, ferro, chumbo e silício.

em algumas das amostras e identificada por microscopia óptica. Esta observação sugere que a diferença de cor observada poderá ter a sua origem na utilização de um adesivo orgânico, aplicado directamente sobre a camada de preparação, para colocação da folha metálica. Não foi identificada a presença de bolo ou de qualquer outra camada intermédia associada a um douramento ou prateamento tradicional [7-8]. A análise da folha metálica revelou a presença de prata, aplicada sob uma camada espessa de verniz colorido (Figura 8). Em certas zonas, a utilização de prata sob uma camada de verniz de cor amarela teve por objectivo mimetizar o efeito da folha de ouro — prata dourada —, enquanto noutras zonas a folha foi aplicada sob vernizes vermelhos ou azuis, conferindo riqueza decorativa e um efeito visual distinto às figuras principais. Historicamente a utilização de prata dourada teve como função inicial a substituição do ouro, reduzindo os custos associados à sua utilização, no entanto, adquiriu com o tempo um carácter próprio, assumindo-se como uma técnica de decoração autónoma. Esta técnica apresenta uma grande fragilidade devido à degradação da folha metálica e à reduzida estabilidade de muitos dos pigmentos, corantes e ligantes utilizados [7, 9]. A análise da folha de prata apenas permitiu detectar concentrações muito reduzidas do metal, estando os principais vestígios localizados em zonas onde o verniz terá sido aplicado numa camada mais espessa e onde assume actualmente um aspecto opaco (Figura 9).

A análise da cor branca do lençol do Menino, para além dos elementos comuns às restantes amostras, detectou ainda a presença de bário (apenas identificado nesta amostra) e zinco (Figura 10). O facto de esta amostra apresentar características físicas e químicas distintas das restantes, como a existência de apenas uma camada estratigráfica e a presença de branco de zinco, apontam para um repinte; apesar da utilização de branco de zinco estar referida desde a Antiguidade, apenas foi utilizado em larga escala a partir da segunda metade do século XIX [10]. As cores castanha, cinzenta e preta serão, muito provavelmente, compostas por pigmentos de carbono ou pigmentos orgânicos cujos elementos não são passiveis de detecção por SEM-EDS [11].

O facto das amostras analisadas apresentarem uma elevada semelhança elementar, com presença quase constantes de alumínio, cálcio, ferro, chumbo e silício, torna complexa a identificação dos pigmentos utilizados. Os mapeamentos efectuados revelam agregados de maiores dimensões compostos por cálcio, silício, alumínio ou ferro, envolvidos numa matriz de branco de chumbo, principal pigmento presente na preparação. As cores vermelhas e azuis são compostas pelos mesmos elementos, podendo no entanto apontar-se para uma possível presença de vermelho de chumbo na cor vermelha e branco de chumbo e vermelho de chumbo nas carnações. Ambos os pigmentos são utilizados desde a Antiguidade, sendo que o vermelho de chumbo foi utilizado até ao século XIX. No entanto, não deverá ser colocada de parte a possibilidade de se tratar de ocre vermelho, um pigmento

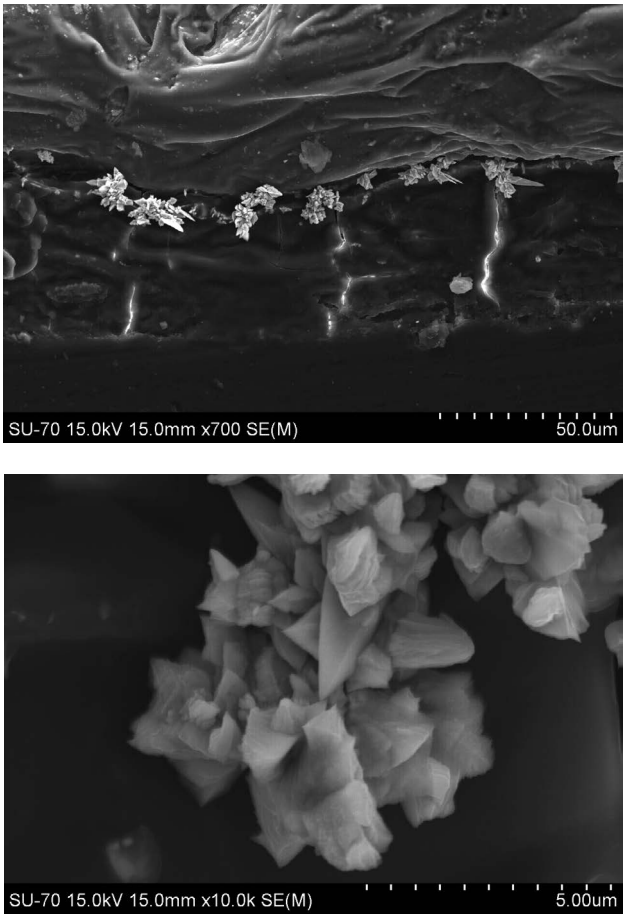

Figura 9. Imagem de electrões secundários de cristais de prata na amostra 3 (ampliação de 700× e 10.000×).

natural que contém minerais presentes nas argilas como alumino-silicatos e compostos de ferro. Também este pigmento é utilizado desde a Antiguidade. A identificação do pigmento azul torna-se igualmente complexa, podendo ser considerado como Azul da Prússia, utilizado desde o início do século XVIII [10].

Conclusões

Nenhum dos resultados obtidos a nível experimental permite delimitar de forma precisa o período de execução da obra, mas pode ser definido um intervalo mais amplo. Considerando a presença de azul da Prússia e de branco de zinco (repinte), torna-se possível limitar temporalmente a data de execução entre o início do século XVIII (1704) e o início do século XIX (1834). Um pormenor de carácter decorativo relevante é a utilização de prata dourada, com aplicação de vernizes de cores diferentes, sendo ainda perceptível a sua utilização em algumas zonas das esculturas. Invulgar é a não utilização de uma superfície adequada à aplicação da folha metálica, não tendo sido identificada a presença de bolo. Estes resultados, combinados com a análise estilística do presépio e dada a inexistência de qualquer referência documental relativa

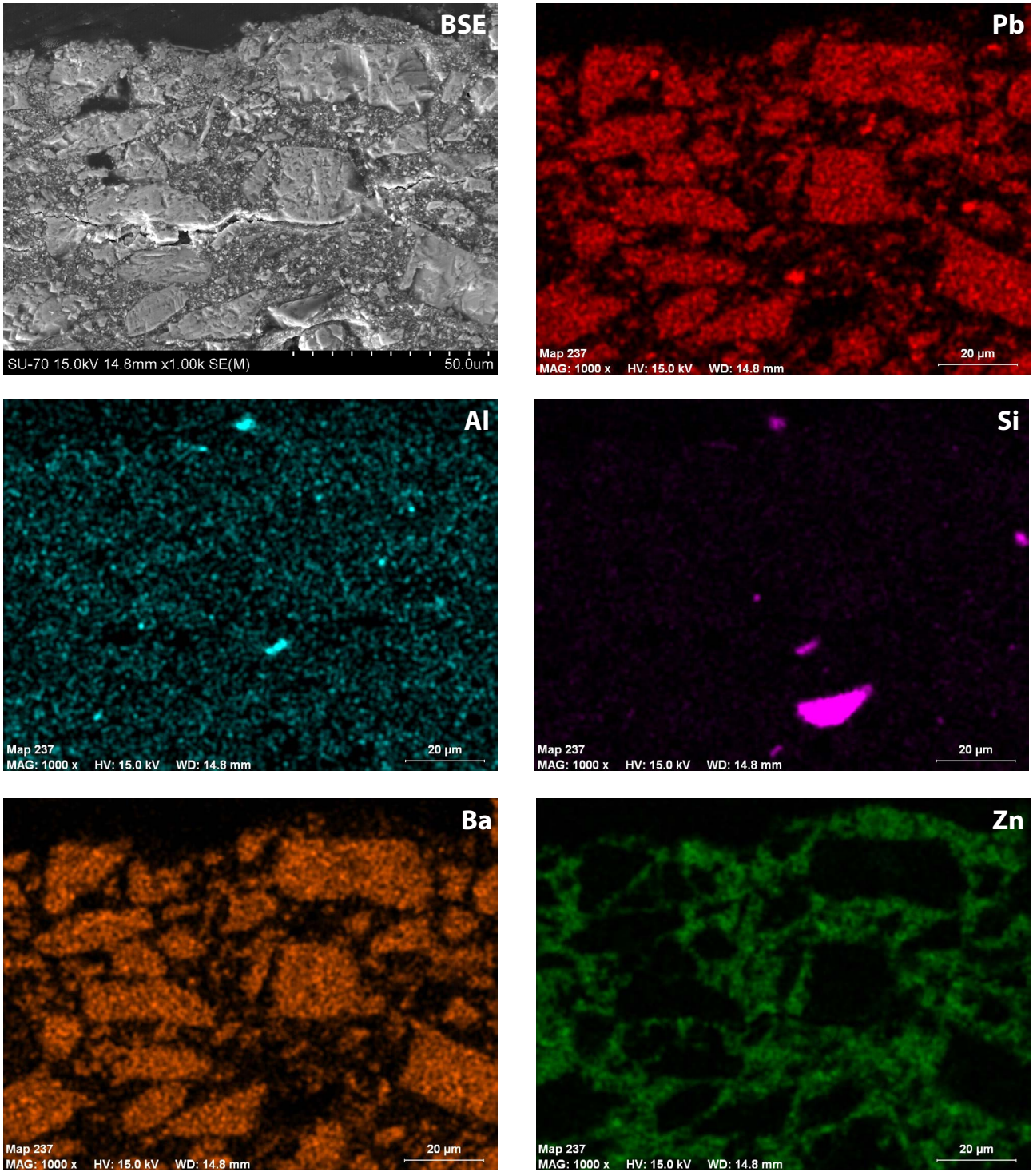

Figura 10. Amostra 4: imagem de electrões retrodifundidos e mapas com a distribuição de alumínio, bário, chumbo, silício e zinco.

à encomenda, compra ou forma de aquisição da obra, apontam como provável período de execução a segunda metade do século XVIII.

O estudo do presépio do Santuário de Nossa Senhora dos Remédios em Lamego, permitiu uma abordagem mais pormenorizada da tecnologia de produção do conjunto, apontando aspectos que lhe conferem unicidade e originalidade.

Agradecimentos

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Colorimetric measurements as control elements in wood conservation status

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Abstract
This paper is a methodological proposal for the study of altarpieces on wooden supports. The process was implemented to study the altarpiece of San Antonio de Padua in Garachico, Tenerife. For this, we conducted a review of key aspects appropriate to the discipline of wood identification carried out by macroscopic examination and for the characterization of the status of deterioration by colorimetric analysis. For the evaluation of the wood conservation status, the samples were subjected for the first time to colorimetric measurement. As a result we have created an online database to provide information for conservation professionals permitting them to design a proposal for preventive conservation and intervention individually for each object.

Keywords
Colour
Colorimetry
Wood
Preventive conservation
Geolocation
Restoration

Colorimetria como análise de controlo do estado da madeira

Resumo
Este trabalho é uma proposta metodológica para o estudo de retábulos em suportes de madeira. O processo foi implementado para estudar o retábulo de San Antonio de Pádua em Garachico, Tenerife. Para isso, foi realizada uma revisão dos aspectos-chave adequados para a disciplina de identificação de madeira realizada por meios macroscópicos e para a caracterização do grau de deterioração por análise colorimétrica. Para a avaliação do estado de conservação da madeira, as amostras foram submetidas pela primeira vez a análise colorimétrica. Como resultado, criámos um banco de dados on-line para fornecer informações para os profissionais de conservação que lhes permitam apresentar uma proposta de conservação preventiva e de intervenção de forma individual para cada objecto.

Palavras-chave
Cor
Colorimetria
Madeira
Conservação preventiva
Geolocalização
Restauro

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Introduction

Up to the present time studies and interventions that are carried out within the field of Heritage Conservation and Restoration in the Canary Islands make use of infrastructure and specialists who are outside the island territory. Due to the insular nature, budgets and waiting time increase significantly and in many cases causes the impossibility of a good and complete performance of the work, inasmuch as the analysis are the foundations for establishing further intervention.

This study aims to provide professional access to basic information collected in a digitized database of the type of wood to be analysed and extrapolated to other future studies. This catalogue also contains colorimetric analysis results, specially the patterns of variation in colour and brightness, which will be the control points for good preventive conservation.

The knowledge of the chromaticity coordinates of the wood will play a fundamental role not only in the conservation of the original colour after cleaning, reinstatement or any other intervention, but also in establishing a reference to perform periodic measurements, with the aim to follow the degree and chromatic deterioration rate and therefore, to investigate its causes.

To carry out this proposal, we began with macroscopic wood identification. Then, the samples were subjected for the first time to colorimetric measurement. As a result we have created an online database to provide information for conservation professionals about the geographical location of the cultural property studied.

Methodology

The CIE, or Commission Internationale de l'Eclairage (translated as the International Commission on Illumination), is the body responsible for international recommendations for photometry and colorimetry. In 1931 the CIE standardized colour order systems by specifying the light source (or illuminants), the observer and the methodology used to derive values for describing colour.

The colour space used here was the perceptual or uniform CIELAB, recommended by CIE (*Commission Internationale de l'Éclairage*) for studies of secondary sources, whose lightness (L^*) is related to Y from system CIEYxy, both going from 0 (black) to 100 (white), and whose colour coordinates a^* and b^* define the degree of pitch (from green to red, a^*, and from blue to yellow, b^*).

The key tool in colour measurement is the spectrophotometer, photometric device that measures spectral transmittance, spectral reflectance or relative spectral emittance. Its information regarding the spectral composition, is not only necessary to solve many problems related to the colour (the degree of metamerism — a phenomenon exhibited by a pair of colours that match under one or more sets of illuminants, be they real or calculated, but not under all illuminants —, the nature of

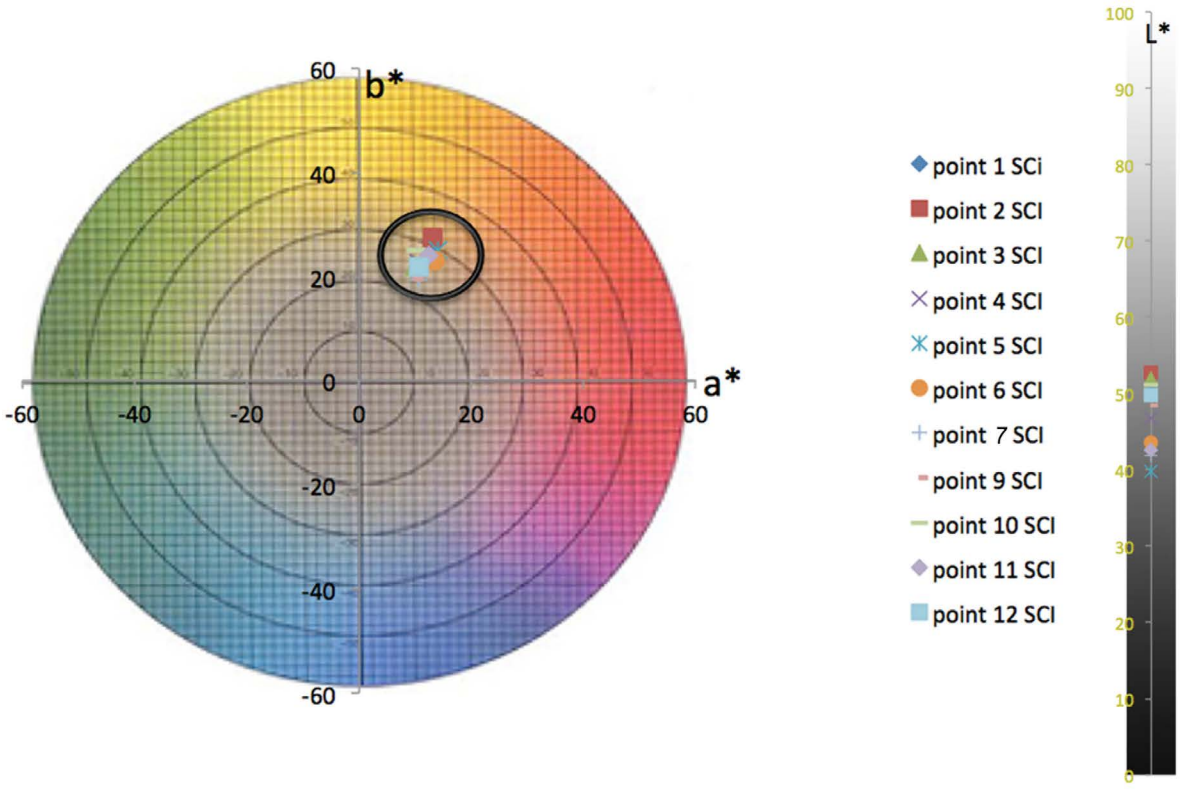

Figure 1. Representation of the CIELAB measurements in the chromaticity diagram.

Table 1
CIELAB data obtained.

Sample	Section	Name	*L** (SCI)	*L** (SCE)	*a** (SCI)	*a** (SCE)	*b** (SCI)	*b** (SCE)
Sample 4	Transversal	Point 1	50.0880	50.3202	12.5757	12.4786	24.4417	24.5935
	Tangential	Point 2	52.7751	52.6670	13.1310	13.0517	27.4193	27.5547
	Radial	Point 3	51.9541	52.0105	9.8061	9.7295	22.2097	22.3461
Sample 3	Transversal	Point 4	46.7352	46.8134	10.6720	10.6209	22.5444	22.7269
	Tangential	Point 5	39.8523	39.8650	14.0451	14.0394	24.9348	25.1736
	Radial	Point 6	43.6439	43.7945	13.5464	13.4589	23.0342	23.1039
Sample 2	Transversal	Point 7	41.9336	42.1134	10.5637	10.5154	19.4754	19.6479
	Radial	Point 9	48.4014	48.2435	9.7271	9.7099	19.6980	19.9186
Sample 1	Transversal	Point 10	51.1794	51.3031	10.1166	10.0364	24.9296	25.0750
	Tangential	Point 11	42.6305	42.7030	12.4997	12.4582	24.1448	24.3573
	Radial	Point 12	49.7986	49.8015	10.6653	10.6231	21.9345	22.2132

the pigment, the protection and conservation techniques, etc.), but also linking the results with the CIE standard specifications.

Minolta Spectrophotometer CM-2600D has been used for the colorimetric study in measurement conditions SCE/100 (specular reflectance excluded) and SCI/100 (specular reflectance included), D65 illuminant (the CIE standard illuminant that represents a colour temperature of 6504 K, which is the colour temperature most widely used in graphic arts industry), 10° observer and small measurement area.

Anatomical wood comparison

The anatomical structure of the wood is the same since its formation in the trunk and is retained until it is degraded. It can be approached with a ×10 lens or an optical microscope.

Identification of the woods by anatomical comparison is not free of problems. In fact, presents gender and generic subgroup limitations, as in the case of oak (*Quercus sp.*). In such cases it is very rarely to identify the species with only anatomical description, so that any information on its chorology, origin, common name, country or geographic region is also important for the determination.

Another limitation is that the species belonging to the same gender are often hardly distinguishable [1].

For this study, we delimited the search to a specific number of woods used in Cultural Heritage objects and discard hundreds of others that are present in nature. We obtained four samples to work with.

Wood colorimetry

There are many studies about the colour of the wood collected in various colour atlas, but all are based either on a single area of the sample (sapwood, heartwood...) or in a single tree species.

In recent years there has been progress in this field, analysing the colour changes due to artificial drying, assessing the visual appearance of species for solid uses or determining the optical properties more desirable for pulp and paper [2].

The optical properties of the wood can be modified according to the site, the clone, the tree and the position within the individual, so it is essential to know these patterns of variation.

The most complete and meaningful way to characterize the visual appearance of a material is to use three-dimensional colour data, but within these, the parameter *L* or Lightness (Figure 1), is the more simple and satisfactory way to specify the endpoint of an objective, therefore both the chromatic and non-chromatic values (Table 1) are necessary to characterize the colour changes [3].

Results

The parameter *L** or clarity was set as the most important criterion, especially when carrying out control over future photo-degradation (Figure 1). Similar studies (2) have measured the colour in 97 species to determine their suitability for use, establishing relationships between parameters of the system CIELAB and obtaining mean values of *L** that varied within a broader range than the data of the chromaticity coordinates *a** and *b**. According to this, future changes in this parameter will alert us about changes in climate conditions and obviously in wood conservation status.

In the same way, spectral reflectance curves indicate the features present at the time of measurement in terms

of brightness and hue of the wood. Based on these, future changes in the depth and shape of the reflectance spectrum could be interpreted as changes in the brightness and hue of the wood respectively.

With all the information obtained we have created an online database (Figure 2) to provide information for conservation professionals about the geographical location of the cultural property studied. We used the open web app *Google Maps* which allowed us to create our own paths and slides according to the results and the data we had collected and to upload them into an open database like *Google Earth*.

Finally, we can conclude this phase of the research affirming that when there is no data available to establish comparative studies, merely external data as hue and chroma are not enough for analysis. That means we need a period of time to enrol the professionals and request them to improve and complete the colorimetric database.

Conclusions

With the application of the proposed methodology, we will be able to manage relevant data about the amount and type of wood used in the Cultural Heritage objects on the island of Tenerife, in addition to information about their conservation status thanks to the new colorimetric control points.

The database will collect the information about the location, environmental conditions such as altitude, temperature, relative humidity and bioclimatic belt. Furthermore, the colorimetric analysis will be included for the first time with the "control points". This control points can serve as a standard for monitoring the successive processes of restoration with a georeferenced database (that is, geolocated) in geographical space and chronologically. Thereby, environmental changes in bioclimatic belt will affect colorimetric parameters of wood, allowing professionals to design a proposal for preventive conservation and intervention, individually for each object.

The database contributes to apply global trends of information and communications technology in the new information society and knowledge, which helps social, cultural and economic support for sustainable development.

Because the study is still in progress, we must wait a certain period of time to consider the effects of its application in the professional field as well as the process of training and technical information appropriate to monitor cultural property listed in the catalogue.

Furthermore, this work began with limited objectives that are expanding day by day. As a future project, is planned to include in the database environmental parameters of the area surrounding cultural goods, moisture content in the wood and everything that would show that the methodology presented here is well suited for application in the field of conservation and restoration of heritage.

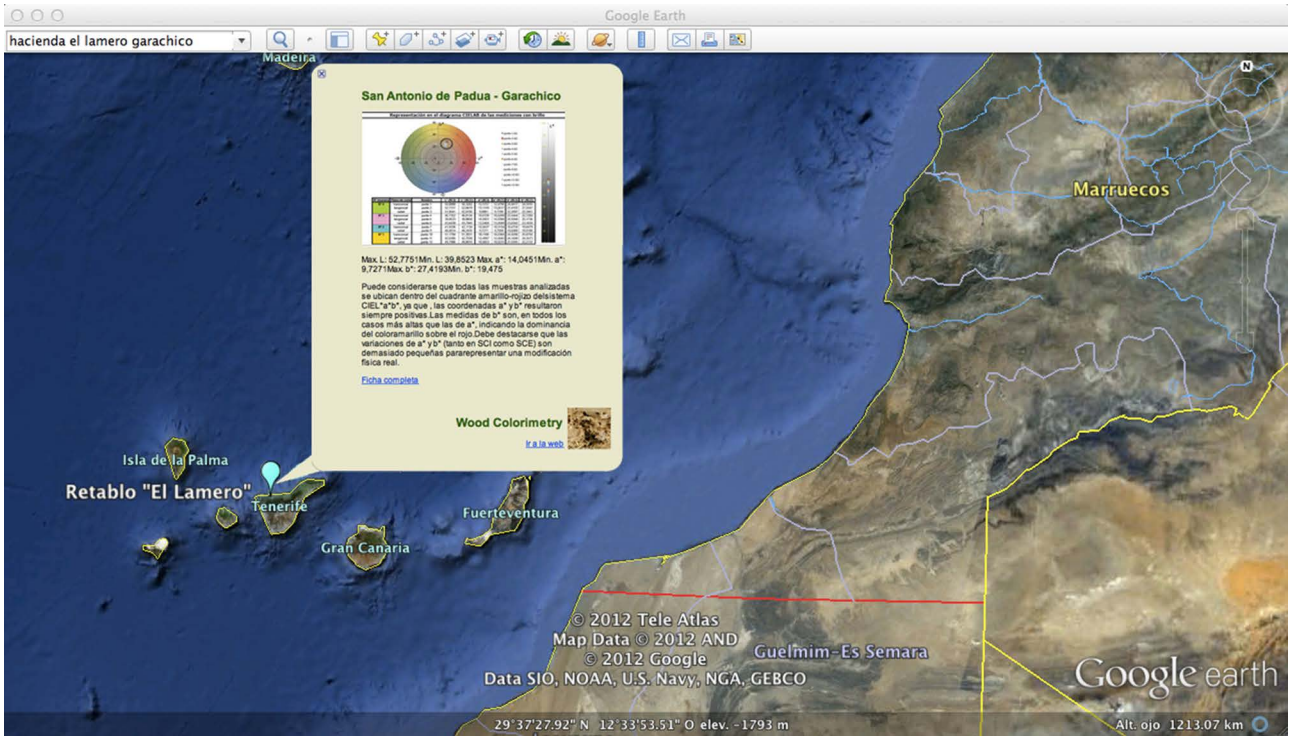

Figure 2. Georeferenced database screenshot.

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Normas de colaboração e instruções para os autores

Norms for collaboration and author guidelines

Âmbito da revista

A revista *Conservar Património* é uma revista científica que pretende publicar semestralmente estudos relacionados com a conservação e restauro, nas suas várias modalidades e perspectivas, e estudos sobre as múltiplas dimensões das obras que constituem o património cultural provenientes de disciplinas como a história da arte, a arqueologia, a museologia, a química, a física, a biologia ou outras.

A revista é publicada pela Associação Profissional de Conservadores-Restauradores de Portugal (ARP), mas os autores não têm que ter qualquer ligação a esta associação. A revista agradece todas as colaborações que espontaneamente lhe sejam enviadas desde que se enquadrem nos seus interesses e estejam de acordo com os padrões de qualidade que pretende manter. Embora estas colaborações não solicitadas constituam o essencial de cada número, a direcção da revista pode dirigir convites de colaboração a autores com excepcional currículo nas áreas de interesse da revista.

About the journal

Conservar Património is a scientific journal that aims to biannually publish research papers related to conservation-restoration in its various modalities and perspectives. It is also interested in papers from other fields of knowledge, such as history of art, archaeology, museum studies, chemistry, physics and biology or others, about the multiple dimensions of cultural heritage works.

The journal is published by the Associação Profissional de Conservadores-Restauradores de Portugal (ARP), although the authors are not obliged to a relationship with ARP. The journal is glad to receive any paper submissions that reflect its editing policy and quality standards. Although spontaneously submitted papers constitute the essence of each volume, the editors may invite collaborations from authors with relevant knowledge within the universe of interest of the journal.

Princípios éticos

As colaborações submetidas para publicação devem ser inéditas e, portanto, não devem ter sido previamente publicadas ou estar a aguardar publicação ou terem sido submetidas noutro local.

Considera-se que as colaborações submetidas para publicação são efectivamente da autoria dos autores indicados, dão conta dos trabalhos desenvolvidos por

Ethics

The papers submitted for publication must be original, i.e. they should not have been previously published, nor submitted or pending publication elsewhere.

It is assumed that the contributions submitted for publication were actually authored by the designated authors; that they constitute accounts of the authors' work and research; and that they do not pose any falsification

estes e não colocam qualquer problema de falsificação ou de plágio — algo que a revista considera inadmissível.

Nos casos em que isso seja relevante, os autores devem declarar de forma clara eventuais conflitos de interesse. As colaborações submetidas que, directa ou indirectamente, tiveram o suporte económico de terceiros, devem claramente declarar essas fontes de financiamento.

Tipos de colaboração

A revista tem diversas secções, conforme a natureza e o fôlego das contribuições, designadamente as seguintes:

— *Artigos*, para as contribuições mais importantes, que podem dar conta de tratamentos de conservação efectuados com recurso a estudos envolvendo outras disciplinas, apresentar estudos realizados sem qualquer relação com intervenções de conservação e restauro ou constituir artigos de revisão sobre os materiais, as técnicas, a história ou as intervenções de conservação;

— *Intervenções*, onde são apresentadas intervenções de conservação realizadas sem o recurso a estudos laboratoriais ou outros;

— *Notas*, secção dedicada à divulgação de textos de temática semelhante à dos artigos e das intervenções, mas com menor dimensão;

— *Opiniões*, onde são divulgadas opiniões pessoais, devidamente justificadas, sobre os diversos aspectos envolvidos na conservação, bem como notícias ou recensões sobre outras publicações ou acontecimentos relevantes. São incluídas aqui contribuições recebidas na forma de carta, bem como comentários a outras contribuições publicadas na revista.

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Todas as colaborações não convidadas submetidas para publicação são alvo de uma primeira avaliação de natureza geral por parte da Direcção com vista à determinação do seu interesse e da sua adequação à revista. Após parecer favorável, são sujeitas a avaliação anónima por pares (*peer reviewing*). Sempre que possível, nessa avaliação participarão membros do Conselho Editorial. As colaborações convidadas não estão sujeitas a este processo. As colaborações destinadas à secção de *Opiniões* podem passar apenas pela avaliação da Direcção.

Em qualquer caso, a opinião dos autores não traduz necessariamente a opinião da ARP ou da Direcção ou do Conselho Editorial da revista e são os autores os únicos responsáveis pelas opiniões manifestadas, mesmo nas situações em que são sugeridas modificações aos textos inicialmente submetidos.

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Embora a revista privilegie a utilização da língua portuguesa, poderão igualmente ser publicadas contribuições

or plagiarism problems – something the journal deems inadmissible.

Where applicable, authors should clearly declare any conflicts of interest. Submitted contributions that, directly or indirectly, had the economic support of third parties, should clearly state these sources of funding.

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The journal has different section headings according to the content nature of the submitted papers. The available sections are listed below:

— *Articles*, for the main contributions. The papers may present conservation treatments done with the support of other fields of knowledge, studies not directly connected to conservation-restoration interventions, or reviews about subjects related to materials, techniques, history and intervention methodologies;

— *Interventions*, for contributions reporting on conservation interventions without the support of laboratory studies or others;

— *Notes*, for contributions similar to those included in articles and interventions, but smaller in size;

— *Opinions*, for personal but relevant opinions on different conservation aspects and for reports on relevant occurrences or reviews of published materials. Letters and comments about published contributions are also included here.

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All the contributions submitted for publication are subject to a first general review from the Editors to ascertain whether they are within the journal scope and objectives. After passing this first stage, the papers are subjected to peer reviewing. The Editorial Board will participate as often as possible in this stage of review. Invited contributions are not subjected to this type of reviewing. Contributions to the *Opinions* section may be reviewed solely by the Editors.

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Although the Portuguese language is privileged, other languages may be accepted for publishing, namely

noutros idiomas, designadamente, inglês, francês, espanhol ou italiano. Ainda que a Direcção da revista use a variante do português europeu anterior ao acordo ortográfico de 1990, são igualmente aceites colaborações noutras variantes do português, como a variante do acordo ortográfico ou a variante brasileira. Nestes casos, como em qualquer outro idioma em que também existam variantes, de forma coerente deverá ser usada uma só variante em todo o texto.

Os textos destinados às secções de *Artigos*, *Intervenções* e *Notas* devem ter título e resumo em português e inglês e, se forem escritos noutro idioma, também devem ser acompanhados de título e resumo nesse mesmo idioma.

Organização dos textos

Excepto os textos destinados à secção de *Opiniões*, a organização de qualquer contribuição deve obedecer à seguinte estrutura geral: título no idioma do texto, em português e em inglês, nomes dos autores e instituição, organização ou empresa a que pertencem e respectivos contactos, resumo, palavras-chave, texto, agradecimentos, referências bibliográficas, tabelas e figuras. Os textos destinados à secção de *Opiniões*, além do título no idioma do texto, deverão ter o título em português e em inglês.

Cada resumo não deve ultrapassar as 150 palavras e deve funcionar como um pequeno texto autónomo sem remeter para o texto principal. Deve haver resumos em português, em inglês e no idioma original do texto, se o mesmo for diferente daqueles. As palavras-chave, até um máximo de seis, devem ser apresentadas da mesma forma, isto é, em português, em inglês e no idioma original do texto. As palavras-chave devem ajudar a enquadrar o texto no seu contexto geral e devem complementar as palavras usadas no título, portanto, sem as repetir.

Os textos, sobretudo os de maiores dimensões, devem estar divididos em secções e subsecções, de acordo com o seu conteúdo.

Os textos devem ser cuidadosamente revistos tendo em atenção a correcção ortográfica e gramatical. As notas de rodapé devem ser evitadas e as referências à bibliografia devem ser feitas através de números entre parêntesis rectos.

Podem ser utilizadas tabelas e figuras, devendo usar-se esta última designação e não as de imagem, foto, fotografia, ilustração, esquema ou outra. Todas as tabelas e figuras devem estar referenciadas no texto através dos respectivos números. Devem ser colocadas no final, cada uma numa folha diferente, e ser acompanhadas das respectivas legendas. Os autores devem obter as permissões necessárias para a utilização de figuras ou outros materiais sujeitos a *copyright*.

A bibliografia referenciada deve ser apresentada no final do texto através de lista numerada de acordo com o local de citação no texto e com o formato adiante apresentado.

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A lista final das referências bibliográficas citadas (e apenas estas) deve ser apresentada segundo a ordem de

English, French, Spanish or Italian. While the Editors will continue to use the European Portuguese spelling prior to the 1990 Orthographic Agreement, collaborations in other spellings will be accepted, such as the variant spelling of the Orthographic Agreement or the Brazilian variant. In such cases, however, there must be consistence throughout the texts; the same holds true for other languages with spelling variants.

The papers destined to the *Articles*, *Interventions* and *Notes* sections must contain a Portuguese and an English title and abstract and, if written in another language, must also incorporate the title and abstract in that language.

Text organization

All papers except those destined to the *Opinions* section must obey the following structure: Title written in the original language, as well as in Portuguese and English, authors' names and affiliation, respective contacts, abstract, keywords, text, acknowledgements, references, tables and figures. The texts destined to the *Opinions* section shall have the title written in the original language, as well as in Portuguese and English.

The abstracts must not surpass 150 words and must function as a separate text without referring to the main text. The abstracts should be written in Portuguese, English and in the original language if different from the former two. A maximum of six keywords should also be presented in Portuguese, English and the original language. The keywords should help to frame the text in its general context and should complement the words in the title without repetition.

The texts should be divided in sections and subsections in accordance with their content.

The orthographic and grammatical review should be done carefully. Footnotes should be avoided and reference marks should be numbered between straight brackets.

Tables and figures may be used, and should be thus designated — and not as images, photos, photographs, illustrations, schemes or other. All tables and figures must be referenced in the text by their respective numbers. They should be placed at the end of the text, each with its respective legend on a separate sheet. The authors must gain the necessary permission to use the figures or other copyright materials.

References should be listed at the end of the text, numbered in accordance with the text citations and the following styles.

References

The list of references (cited references only) at the end of the paper should follow the citation sequence of the text.

citação. Como modelo, sugere-se a consulta de artigos já publicados na revista.

No caso das referências bibliográficas que têm um Identificador de Objecto Digital (DOI), o mesmo deve ser indicado no final da referência.

Para as situações mais comuns, o formato das referências é o seguinte:

Livro

Formato:

Apelido, Iniciais dos nomes próprios; Apelido, Iniciais dos nomes próprios, *Título em Itálico e Maiúsculas*, vol. [se houver mais do que um volume], edição [se não for a 1.ª], Editora, Local (data), doi:doi ou url.

Exemplos:

Bomford, D.; Dunkerton, J.; Gordon, D.; Roy, A., *Art in the Making. Italian Painting Before 1400*, National Gallery, London (1989).

Douglas, J., *Building Surveys and Reports*, 4th ed., Wiley-Blackwell, Chichester (2011), doi:10.1002/9781444391091.

Berrie, B. H. (ed.), *Artists' Pigments. A Handbook of their History and Characteristics*, vol. 4, National Gallery of Art – Archetype Publications, Washington – London (2007).

Deneffe, D.; Fransen, B.; Henderiks, V.; Mund, H., *Early Netherlandish Painting. A Bibliography. 1999-2009*, Centre d'Étude des Primitifs Flamands (2011), http://xv.kikirpa.be/fr/publication.htm#Bijdragen.

Capítulo de livro ou comunicação em volume de actas

Formato:

Apelido, Iniciais dos nomes próprios, 'Título do capítulo ou da comunicação em minúsculas', in *Título do Livro em Itálico e Maiúsculas*, ed. Iniciais dos nomes próprios e apelido do autor ou organizador do livro, vol. [se houver mais do que um volume], edição [se não for a 1.ª], Editora, Local (data) 1.ª página-última página, doi:doi ou url.

Exemplos:

McManus, N. C.; Townsend, J. H., 'Watercolour methods, and materials use in context', in *William Blake. The Painter at Work*, ed. J. H. Townsend, Tate Publishing, London (2003) 61-79.

Chastang, Y., 'The conservation of two pietre dure and gilt-bronze-mounted cabinets made by Domenico Cucci for Louis XIV', in *The Decorative: Conservation and the Applied Arts*, ed. S. Cather, A. Nevin, J. H. Townsend, M. Spring, J. K. Atkinson e D. Eastop, IIC, London (2012) 73-79, doi:10.1179/2047058412Y.0000000016.

Artigo de revista

Formato:

Apelido, Iniciais dos nomes próprios, 'Título do artigo em minúsculas', *Revista em Itálico e Maiúsculas* **volume**

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Douglas, J., *Building Surveys and Reports*, 4.ª ed., Wiley-Blackwell, Chichester (2011), doi:10.1002/9781444391091.

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Deneffe, D.; Fransen, B.; Henderiks, V.; Mund, H., *Early Netherlandish Painting. A Bibliography. 1999-2009*, Centre d'Étude des Primitifs Flamands (2011), http://xv.kikirpa.be/fr/publication.htm#Bijdragen.

Chapter in a book or paper in conference proceedings

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Examples:

McManus, N. C.; Townsend, J. H., 'Watercolour methods, and materials use in context', in *William Blake. The Painter at Work*, ed. J. H. Townsend, Tate Publishing, London (2003) 61-79.

Chastang, Y., 'The conservation of two pietre dure and gilt-bronze-mounted cabinets made by Domenico Cucci for Louis XIV', in *The Decorative: Conservation and the Applied Arts*, ed. S. Cather, A. Nevin, J. H. Townsend, M. Spring, J. K. Atkinson e D. Eastop, IIC, London (2012) 73-79, doi:10.1179/2047058412Y.0000000016.

Paper in a journal

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Exemplos:

Carr, D. J.; Young, C. R. T.; Phenix, A.; Hibberd, R. D., 'Development of a physical model of a typical nineteenth-century English canvas painting', *Studies in Conservation* **48**(3) (2003) 145-154, doi:10.1179/sic.2003.48.3.145.

Cultrone, G.; Madkour, F., 'Evaluation of the effectiveness of treatment products in improving the quality of ceramics used in new and historical buildings', *Journal of Cultural Heritage* **14**(4) (2013) 304-310, doi:10.1016/j.culher.2012.08.001.

Le Gac, A.; Seruya, A. I.; Lefftz, M.; Alarcão, A., 'The main altarpiece of the Old Cathedral of Coimbra (Portugal): Characterization of gold alloys used for gilding from 1500 to 1900', *ArcheoSciences* **33** (2009) 423-432, http://archeosciences.revues.org/2562.

Internet (documentos com conteúdo que pode ser alterado)

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Apelido, Iniciais dos nomes próprios, 'Título do documento em minúsculas' (data do documento), in *Nome do Site em Itálico e Maiúsculas,* Instituição, url (data de acesso no formato dia-mês-ano).

Exemplos:

'Azurite', in *Cameo*, Museum of Fine Arts, Boston, http://cameo.mfa.org/wiki/Azurite (acesso em 16-7-2013).

Tracing Bosch and Bruegel: Four Paintings Magnified, http://www.bosch-bruegel.com/index.php (acesso em 16-7-2013).

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'Folhas da obra da Igreja e o mais que ficou arruinado por cauza do terramoto que houve em dia de todos-os-santos do ano de 1755', manuscrito, Arquivo Histórico da Misericórdia, Almada, Maço 6, n.º 15, L.º 25–A (1757).

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Holanda, F., 'Do tirar pelo natural', manuscript, Academia das Ciências de Lisboa, Lisboa, Ms. Azul 650 (1790).

'Folhas da obra da Igreja e o mais que ficou arruinado por cauza do terramoto que houve em dia de todos-os-santos do ano de 1755', manuscript, Arquivo Histórico da Misericórdia, Almada, Maço 6, n.º 15, L.º 25–A (1757).

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