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Original article

Unmixing-based cleaning methods evaluation for re-polychromated plasterwork

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ABSTRACT

The cleaning of re-polychromated plaster is a rather challenging task for Conservators. The optimal choice of solvents and its application instruments may depend on the original polychromy (binder and pigment) that aims to be revealed and the overlay polychromy (binder and pigment) as well. We present a new image-processing based method that uses hyperspectral imaging to obtain a non-invasive quantitative evaluation of cleaning procedures. It is based on the application of unmixing techniques for this problem. The method computes three quality indices: efficiency, destructivity, and alteration, that are based on the residual amounts of overlay pigment, the detection of excessive abrasion in the sample and the change in color that the cleaning produces. It produces as well pixel-by-pixel concentration maps and presence maps for plaster and overlay pigment, and it can self-evaluate by computing the error map comparing the modelled spectral reflectance with the measured spectral reflectance from the samples.

Introduction

The plasterwork is one of the most representative examples of patrimonial wealth which exists in Spain and nowadays it is referent for knowing and understanding its history and cultural development [1]. The use of gypsum in Spain is linked to the existence of wide deposits of this material in the provinces of Aragón, the East, and the South. This fact has favored its use since ancient times, and in the peninsula, it has acquired a high technical and material quality [2].

There was a great splendor in its use during The Middle Ages as a consequence of Arabs' arrival at Iberian Peninsula [3]. From the 8th century onwards, a new technique in the production of plasterwork began to develop, which extended until the 15th Century. Remarkable examples are La Madraza, the Cuarto Real de Santo Domingo and the Alhambra in Granada [4–6] or the Qars ibn Sa'd and Al-Dâr-al Sugrà palaces in Murcia [7]. The technique of execution consisted of sculpting at first, and the subsequent incorporation of the mold technique in the Nasrid period. In both techniques colors are applied in tempera. [8,9]. The chromatic palette is very rich and common binders are animal glue, gum Arabic or egg, mixed with a wide range of pigments (red earth, cinnabar, azurite, malachite, lampblack, or yellow ochre, among others) [10,11].

Plasterwork continued after the conquest in the new Christian kingdoms with Mudejar art. In this period, Arab craftsmen lived side by side with Christians and passed on their knowledge. Examples from this period are the plasterwork of the Alcazar and the Giralda in Seville [12,13], or the plasterwork of the Royal Chapel in the Mosque-Cathedral of Cordoba [14].

However, despite their great importance, these works have undergone a significant process of deterioration. In many cases this is due to the passage of time itself, with alterations such as dirt, stains or dust that cause a change in their original appearance [5]. The most important alterations are those caused by human action: the application of lime layers or re-polychromies based on tempera and oils [4]. In both cases these interventions are undertaken due to the deterioration of the work, restructuring or changes in the taste of the period to adapt it to the style of the time. This implies that the final image of the plaster works is very different from their original image [15,10].

In order to recover the original appearance of the medieval plasterwork, it would be essential to remove these later layers. This is not always possible given that these overlapped layers deteriorate the underneath layers. In many cases the re-polychromy is of a very similar composition to the initial layer, which increases the complexity of the outer layer removal. Because of its difficulty, this work focuses on the removal of a specific type of alteration, re-polychromy with oil painting. This type of alteration has been identified in several examples of great heritage significance, such as the plasterwork of the Palacio de La Madraza in Granada [4]. It

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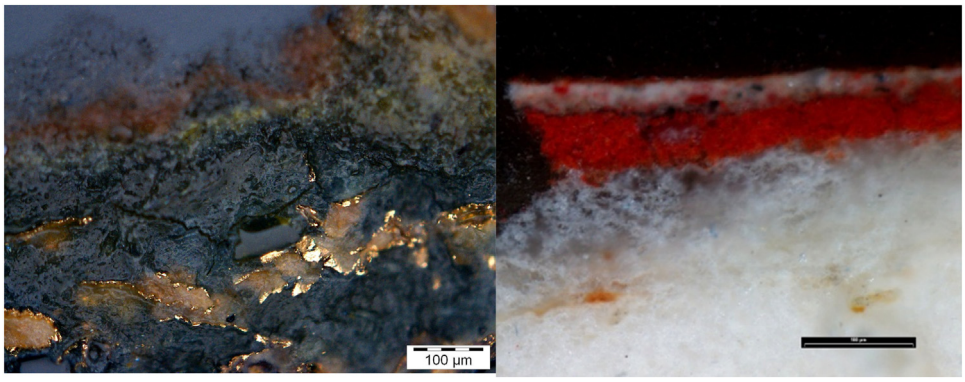

Fig. 1. Impregnation of oils and resins in a sample taken from the Patio de las Doncellas of the Real Alcazar of Seville. Right: Identification of the original red polychromy, over which a layer of lime and a new red polychrome with a different pigment was applied in the Madraza oratory in Granada.

has been also identified re-polychromies of gilding incorporated in the 19th century on oil and terpenic resin bases on the plasterwork of the Alcazar of Seville (see Fig. 1).

Until now, the removal of these layers has been mainly based on physical-mechanical (surgical scalpel or scalpel) or abrasive physico-chemical (application of solvents through cotton and cellulose poultice) cleaning methods. These methods are excessively abrasive and difficult to control in terms of performance and effects on the work, and this undertakes a risk that can lead to the loss of the original polychrome layer [15]. This study proposes the use of gentler physico-chemical cleaning methods based on the use of solvents, applied through gels and thickening agents. These mechanisms allow control of both the time of action and the degree of penetration of the solvent [16]. These factors are decisive in achieving effective removal of the alteration with minimum damage to the original work. Furthermore, its use reduces the toxicity to which the work and the restorer are exposed.

One of the current difficulties in choosing a cleaning method is the evaluation of its effectiveness in a more quantitative way. In a previous study [17] we addressed the problem of removing lime layers, and proposed some quantitative indices based on the volume of the color clouds in $L^*a^*b^*$ space, in the average alteration of the color of the samples after cleaning, and unsupervised classification methods (clustering) to detect areas of the sample with traces of lime or with excessive abrasion, without being able to differentiate between the two.

In this study it is addressed, on the one hand a different problem (re-polychromed with pigments), and on the other hand, an evaluation of the result of the cleaning process, which is significantly different. All the analytic techniques used are based on hyperspectral image processing and the application of unmixing methods as a preliminary step, which constitutes a novel approach in this field of study.

The remainder of the paper will be organized as follows: Section 2 explains the main research aim of this work. Section 3 will describe the methodology used for the fabrication of the probes, the nine solvent-based cleaning methods, and the quantitative evaluation of the results based on spectral image processing techniques. Section 4 will focus on the main results obtained and the determination of the set of best candidates for each of the three pigments tested. Finally, Section 5 will list the main conclusions reached and some research lines that could be pursued in the future.

Research aim

This work aims to propose a way for conservators and curators to optimally choose the materials and methods applied to clean wall paints on plaster that have been re-polychromed. For such task, a novel methodology for the evaluation of different cleaning techniques has been used on re-polychromated plaster probes. A new image processing method based on hyperspectral imaging is proposed, as well as three quality indices (efficiency, destructivity, and alteration) for the quantitative evaluation of nine different cleaning techniques. The proposed method yields pixelwise results and is able to self-evaluate. This means that conservators will have a non-invasive analysis tool for deciding the materials and techniques used for recovering the original appearance of wall paints re-painted on top.

Methods

Plaster probes

Three probes which reproduce medieval plasterwork (technique and materials) from different places and ages were prepared. Specifically, the analysis about Nasrid plasterwork of La Madraza dated from the 14th century [10], Nasrid plasterwork of the Alhambra [6], and Mudejar plasterwork of the Alcazar de Sevilla dated from the 15th century were consulted to achieve historically accurate approaches.

The literature proposes using coatings made by gypsum ($CaSO_4$ $2H_2O$), with a small addition of lime ($CaCO_3$) as an additive to delay setting [18,19]. Regarding polychromy, the analysis with Fourier Transform Infrared Microspectroscopy (FTIR) and Gas Chromatography (GC) allow to identify two different kind of binders: gum Arabic identified in the Cuarto Real de Santo Domingo [6,10], and the animal glue used in the plasterwork of Alcazar de Sevilla [12]. Regarding the pigments, the published results identify a wide range chromatic (natural azurite, cinnabar, lead red, iron red, malachite, verdigris, or ultramarine, among others). For this reason, the study has been delimited to three of most significant pigments in plasterwork decoration: natural azurite as blue pigment, and cinnabar and lead red as red pigments [20,11] (See Fig. 2). The materials used to make the probes, and the notation used in this study for identifying the different pigments is the following. The support for each probe is a ceramic brick of size 20.5 × 10×2.7 cm. The plaster is made with a mix of 95% calcium sulfate (AENOR®) and 5% calcium hydroxide (CALCINOR®). The binders used are animal glue (CTS®) for azurite (AZ) and cinnabar (CN), and gum Arabic (CTS®) for cinnabar + lead red (CN+LR). All pigments were purchased to the company Kremer Pigmente GmbH & Co.KG®. The commercial codes are: Natural Azurite (K.10200), Cinnabar (K.42000) and Lead Red (K.42500).

The plaster probes were naturally aged for six years before being re-polychromed. The dimensions of the probes are 10.25×10×2 cm. The initial pigmented layer was between 23 and 25 µm thick, and the re-polychromy between 49 and 51 µm thick

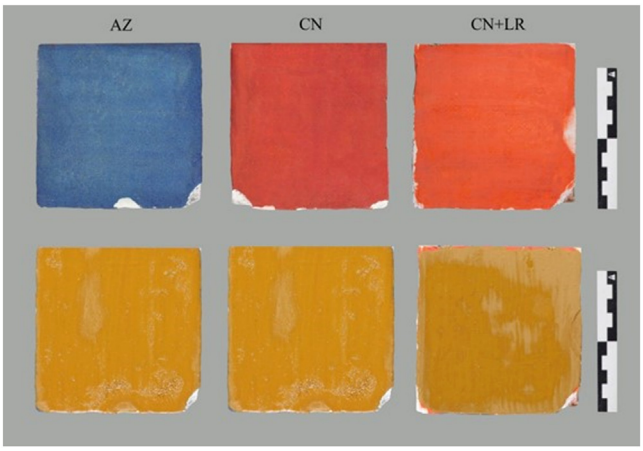

Fig. 2. Top row: probes prepared. AZ: animal glue binder and natural azurite pigment; CN: animal glue binder and cinnabar pigment CNĹR: gum Arabic binder and mixture of cinnabar and lead red pigments (50:50). Bottom row: same probes with oil re-polychromed layers made by linseed oil and ochre pigment.

(measurements taken using photogrammetry techniques). Thus, the initial layer was not perceivable through transparency after the re-polychromy was deposited.

Alteration of the probes by re-polychromy

Once the three probes have been made, the oil re-polychromed layer is applicated. This type of alteration has been identified in examples studied such as La Madraza [9]. The oil re-polychromed alteration is characterized using fatty binders such as oil. Regarding pigments, this alteration is characterized using traditional mineral pigments and the incorporation of pigments developed during the Industrial Revolution. The use of materials of a different nature with respect to original materials is important given that it supposes a different aging and degradation behavior which affects the original. This means that the oil re-polychromed works appearance is different from its original appearance. Specifically, the original tempera technique dries by water evaporation, while the oil dries slower via apolymerization process [4]. Moreover, the oil re-polychromed is less permeable and porous since to the oil prevents the transpiration of the rest of layers which make up the plasterworks. This generates problems of transpiration and condensation of the humidity, which causes a deterioration of original hygroscopic materials.

The re-polychromy alteration in this study was applied using Linseed oil Windsor and Newton® as binder, and natural ochre as pigment (K40070-Kremer Pigmente GmbH and Co.KG (see Fig. 2).

Cleaning methods and controlled conditions

Cleaning methods

The study and selection of treatments has been divided into two parts. On the one hand, a revision was undertakento select the solvents depending on the composition of the materials intended to be removed. In this case is studied the oil re-polychromed, so that the attention is focused on solvents which soften and remove oils, specifically organic solvents such as hydrocarbons, alcohols, and acetones [21]. For this purpose, the [22] and [23] studies of cleaning treatments to remove re-polychromies are considered. After reviewing the bibliography, the solvent mixtures White Spirit and Acetone (3:1 and 1:1), and the mixture of solvents: Water, Alcohol and Acetone (1:1:1) were selected. On the other, the way of application of this kind of solvent mixture is studied. For this purpose, different thickeners are selected: cellulose and cotton poultice [24], direct and flexible gels of methylcellulose (Culminac MC 2000®) and hydroxypropylcellulose (Klucel G®), physical and flexible gels of polyacrylic acids (Carbogel®), and physical and rigid gels of complex polysaccharides (Gellano Kelcogel® y Agarat®) [25].

These methods are complemented by the application of traditional physico-mechanical treatments such as surgical scalpel, or scalpel and glass fiber pencil [26].

The selection of these solvents and application methods is aimed at reducing the danger to the work and the restorer. To achieve this aim are used solvent mixtures of hydrocarbons with alcohols and acetones to obtain more volatility and less toxic solvents, and gels which allows a greatest control of penetrability of these solvent mixtures [21] See Table 1.

Control study areas selected

To be able to evaluate the effectiveness of these treatments is important to determine the areas in which the cleaning tests will be undertaken and its size. To this aim, an acetate template is established as a control system. This control system is a methodology developed by Nanorestart Project (2018) [27] which is focused on studying cleaning treatments in cultural heritage.

This template is designed to adapt the size of each probe and is divided into nine areas to be tested. The size of each area is 2 × 2 cm, according to UNE EN Standard (2021) [28] about the analytical evaluation of cleaning treatments on inorganic porous material in cultural heritage. The use of this acetate template has several advantages such as a thickness of 0,2 mm and semiflexible nature. These characteristics allow the adaptation of the cleaning area to each probe and its alteration. In addition, the transparent material makes it possible to observe the behavior of the surface during the cleaning process (see Fig. 3 and figure A on the supplementary material). The use of acetate template is standardized control protocol in the study of cleaning treatments and their effectiveness. Currently it is being used in different fields such as textile heritage [29] and contemporary paintings [30], among others.

Quantitative assessment based on spectral image processing

The rationale behind the design of our assessment method is the following: the cleaning method can fail in removing all of the ochre layer (lacking effectiveness), or else it can remove not only the ochre but the original pigment as well (being destructive). Our method is based on detecting the presence of either ochre or plaster in the cleaned surface. However, a partial success or a partial destruction of the sample is also possible. Hence, one can find in some of the areas a mixture of the three components: the original pigment, the ochre pigment and the plaster which is the foundation of the probes.

Our method aims to detect the possible presence of ochre and plaster in each pixel of a spectral image of the cleaned probe, using unmixing techniques that are common in the satellite imaging domain [31] and that have recently been applied to the detection of pigments in artworks [32]. We have used a subtractive mixing model for solving the unmixing problem, with three mixture components (endmembers): pure pigment (either AZ, or CN or the mixture of cinnabar and lead red, CN-LR), ochre and plaster. The reflectances of the endmembers have been obtained from an average of a 100×100 pixel area of the probes in top row of Fig. 2 (original pigments), from an average of eleven 160×160 pixel areas of the covered probes in bottom row of Fig. 2 (ochre) and from the average of two 1000×1000 pixel areas of uncovered plaster probes. The spectral capture device used to obtain the spectral images was a PikaL camera from Resonon Ltd coupled to a linear stage in which the probes were placed. The capture device

Table 1
Cleaning tests selected.

Probe	AZ	CN	CN+LR
Solvent	White Spirit and Acetone (3:1)	Water, alcohol, and acetone (1:1:1)	White Spirit and Acetone (1:1)
Cleaning Treatments	Method 1: Cotton poultice + surgical scalpel Method 2: Methylcellulose gel (Culminac MC 2000®) + surgical scalpel Method 3: Cellulose poultice + surgical scalpel Method 4: Polyacrylic acid gel (Carbogel®) + surgical scalpel Method 5: Polyacrylic acid gel (Gellano Kelcogel®) + surgical scalpel Method 6: Cotton swab+ surgical scalpel Method 7: Polyacrylic acid gel (Agarat®) + surgical scalpel Method 8: Hydroxypropylcellulose gel (Klucel G®) + surgical scalpel Method 9: Glass fiber pencil		

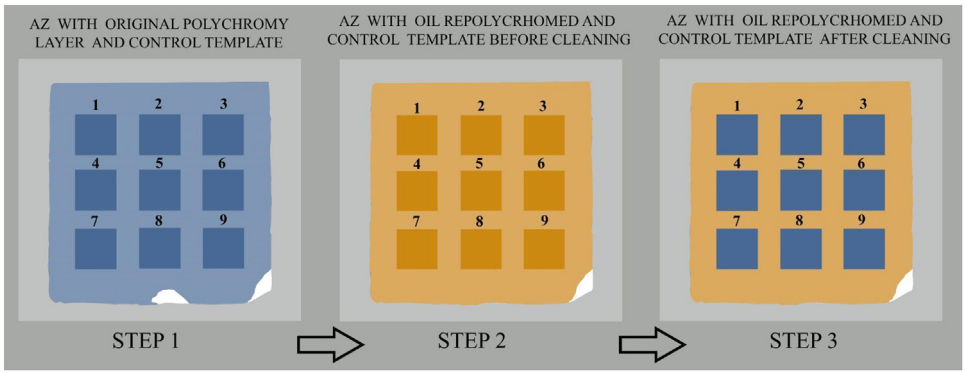

Fig. 3. Recreation of system control of cleaning treatments. Step 1: probe AZ with original polychromy and its acetate template control with the distribution of the nine areas for the cleaning tests. Step 2: probe AZ after applying oil re-polychromed layer with its acetate template control and with the distribution of the nine areas for the cleaning tests. Step 3: probe AZ with its acetate template control after applying cleaning treatments in their respective area for control and later evaluation.

covers the spectral range from 380 to 1080 nm and has a spatial resolution of 900 pixels per line, equivalent to 0.112 mm per pixel. The extremes of the range have been cropped, and we have considered spectral data from 400 to 1000 nm in this study. Figure B from the supplementary material shows the mean spectral reflectances of the plaster and the ochre areas. The spectral reflectances of the eleven ochre covered areas are quite similar, so we have averaged them to obtain the ochre endmember. The subtractive mixture model applied, as shown in Eq. (1) assumes that each pixel is a subtractive mixture of the three endmembers$E_{i\lambda}$:

$$R_\lambda(x,y) = E^{c1}_{1\lambda}(x,y) \cdot E^{c2}_{2\lambda}(x,y) \cdot E^{c3}_{3\lambda}(x,y) \quad (1)$$

The unmixing technique aims to obtain c_1, c_2 and c_3 (concentrations of the endmembers in the mixture) given the measured spectral reflectance of the mixture (R_λ) and the measured spectral reflectances of the set of endmembers ($E_{1\lambda}$, $E_{2\lambda}$ and $E_{3\lambda}$ in our case). x and y are the spatial coordinates of each pixel. The concentration vector has then three components, which will reflect the amount of pure pigment, ochre pigment, and plaster present in each pixel. The unmixing technique uses optimization methods to minimize the distance between R_λ and the spectral reflectance built from the endmembers mixed in different proportions using a given mixing model (subtractive mixture in our case, since additive mixture models obtained worse results in spectral reconstruction accuracy). The concentration vector that results in minimal distance from R_λ is the corresponding solution for that pixel. The unmixing method has been implemented in Matlab© using constrained nonlinear optimization with the interior-point algorithm [33] and the cGFC distance metric [34]. This is a metric that is sensitive mostly to shape changes in the spectrum, and it has proven to work more effectively than RMSE in preliminary trials of the method. It has also provided better reconstruction accuracy than the fully constrained Least squares (FCLS) solution with the additive model. The constraints for the concentration vectors are non-negativity and sum-to-one, as shown in Eq. (2).

$$c_i \geq 0, \;\; for\ i = 1..3 \;\; c_1 + c_2 + c_3 = 1 \quad (2)$$

Once we have the concentration vectors for each pixel of the cleaned sample, we can then compute a comprehensive set of quantitative indices for the evaluation of the cleaning method and show graphically the results of the different amounts of each endmember found for each pixel (concentration maps), as well as mark all the pixels that have a significant amount of ochre or plaster or both (presence maps, see Section 4).

We have defined three global indices for the cleaning assessment: efficiency, destructivity and alteration.

The Efficiency index is computed considering the number of pixels in the sample that contain less than 25% concentration of ochre pigment (c_2 <0.25). The index is defined as the proportion of pixels that comply with this condition, in percentage. For example, if c_2 <0.25 in 60% of the pixels, then the Efficiency index will be 60%.

The Destructivity index is obtained in a similar way but considering the pixels that contain more than 25% concentration of plaster (c_3 >0.25). These pixels are considered as partially destroyed by the cleaning procedure, so the proportion of destroyed pixels is defined as the Destructivity index.

Finally, the Alteration index is obtained by first isolating the pixels for which the cleaning has worked satisfactorily (i.e., c_2 <0.25 and c_3 <0.25). Then, the average spectral reflectance is obtained from these pixels, and the CIEDE00 color difference [35] under D65 is calculated with respect to the reference pigment spectral reflectance ($E_{1\lambda}$). In this way, it is possible to evaluate if the solvent or physical procedures involved in the cleaning method have produced a significant alteration of the color of the original pigment after the cleaning.

The definition of the three indices is based on a threshold to consider the amount of plaster or ochre as significant (in our case,

this threshold has been fixed as 25%). Nevertheless, this threshold can be varied freely if there is need to be more conservative or less stringent with the cleaning results.

One of the advantages of using unmixing as the base idea for the evaluation is that it can self-evaluate itself. The estimated reflectance for each pixel using the endmembers and the concentration weight can be obtained, as shown in Eq. (1). It can very well be that the optimization method is not able to find a concentration vector that produces a mixture which is similar enough to the reflectance of the pixel. By computing the distance in any metric of interest between the original measured reflectance at a pixel and its estimated reflectance, we can have an idea of how well the unmixing method worked for each pigment and each cleaning method. We can then build error images showing the distance found for each pixel, as shown in Section 4. In this way, we can obtain a confidence map and have an idea of how much we could trust the concentration vector estimations for each pixel.

Alternative assessment systems for the cleaning methods tested

We have validated the proposed method by visually comparing with the results of a photogrammetry analysis and (for some small regions) a microscopy-based analysis. The photogrammetry analysis consists in the development of photogrammetric models by AutoDesk Recap® software [36]. These models are obtained from the 3 probes before and after applying the cleaning treatments. These models are compared using the Cloudcompare® software [37], and it is obtained a color map indicating the degree of depth of the cleanings undertaken. In this way it is possible to determine the amount of material which has been removed in each cleaning treatment, and, besides, up to which layer has been reached in each treatment. This allows us to know whether the alteration has been removed, and whether the original polychromy or other deeper layers have been also removed. This type of analysis evaluates the effectiveness qualitatively and quantitatively in each treatment. Photogrammetry analysis is a methodology which has been tested in the evaluation process of cleaning treatments on wall painting. [38].

The second type of analysis consists in undertaking imaging by Stereo Microscopy. The microscope used is a NIKON SMZ 1000 with a parallel optical beam and integrated camera for taking microphotographs. The images are obtained from the polychrome layer before and after applying the alteration and cleaning treatments. In this way it is possible to evaluate visually and qualitatively the degree of cleanliness achieved with each treatment.

We have also used an alternative method for evaluation based on Fuzzy-C-Means clustering using the full spectra of each pixel, to validate the proposed unmixing-based method. Fuzzy-C-Means [39] is a method of unsupervised classification, and we have set the number of clusters or groups as three. The technique will give an estimation of the probability of each pixel to belong to each of the three clusters (original pigment, ochre, and plaster). The three groups are formed by randomly setting three spectra as members of each cluster, and then assigning the other spectra to the cluster that is most similar to it using a distance metric (RMSE in our case). Using this second method, each pixel has a probability vector with three components, and the Efficiency, Destructivity and Alteration indices have been calculated using the same 25% threshold as in the unmixing-based model (see Section 4). The Fuzzy-C-Means clustering used is the default version implemented in Matlab© with a maximum number of iterations of 1000 and minimum amount of variation in the distance function of 10^{-5} set as stopping criteria. In all cases, the algorithm converged before the maximum number of iterations was reached.

Results and discussion

In this subsection, we demonstrate the capabilities of the proposed method for evaluation of the cleaning procedures. We also show the Fuzzy-C-Means results and the sRGB images of each sample with histogram equalization applied to enhance the contrast, as a means of validation for the unmixing-based system.

Concentration map images

In Fig. 4 we show the concentration map images for Fuzzy-C-Means (FCM) and the unmixing-based method (UNMX), along with the sRGB images of the samples extracted from Fig. 2, for the AZ pigment. The concentration maps have been built using either the probability or the concentration vectors for each pixel. In the case of AZ, a pixel with 100% probability or concentration of ochre looks yellow; a pixel with 100% probability or concentration of plaster looks white, and a completely blue pixel corresponds to a probability or concentration of 100% of pigment. For CN and CN-LR (not shown in Fig. 4), the 100% concentration of pigment pixels look red, and for CN-LR they look orange. The pixels with mixed appearance (not purely yellow, white or blue/red/orange) indicate that several endmembers are present in the case of the unmixing-based method.

It is apparent from Fig. 4 that the concentration images obtained with the unmixing-based method are much more visually similar to the sRGB images (which reproduce the visual appearance of the sample with enhanced contrast) than the probability images obtained with the Fuzzy-C-Means clustering. For the AZ pigment, the visual evaluation of the concentration images allows to locate more precisely the areas that have left-over ochre pigment, or else that have been destroyed during the cleaning process. Upon visual assessment, the best methods would be 4 and 5, followed by 3. The worst methods would be possibly 7 and 9 for this pigment (mainly due to too much remaining ochre pigment). For the CN pigment, the best results are obtained by methods 5, 6 and 3, and the worst results by methods 2 and 9. Finally, for the CN-LR pigment, the best methods would be 1 and 8, and he worst 2, 3 and 6. The concentration images allow for a convenient visual evaluation, but do not offer any quantitative ranking of the methods.

Presence map images

Other interesting feature of both Fuzzy-C-Means and unmixing-based methods is the possibility of highlighting the pixels for which the concentration or probability of ochre or plaster is above the threshold (i.e., above 25% in our case). In this way, we can generate presence maps for ochre or plaster. In Fig. 5, the presence maps corresponding to the unmixing-based method are shown for the CN pigment, along with the sRGB images.

The presence maps allow to visualize the pixels that contain more than 25% of ochre and plaster in the mixtures. If a pixel contains for instance 27% of ochre, it would appear mostly red in the concentration image, while it would appear as yellow in the presence image. From Fig. 5, we can easily identify the most destructive methods as 9, 7 and 8, while clearly the method which has left more traces of ochre pigment (hence being less effective) is 2 for the CN. For the CN-LR pigment, methods 2 and 7 were the most destructive and 2,3 and 6 contained more pixels with ochre traces. For the AZ pigment, the most destructive were 9 and 2, while the traces of ochre were very much pervading in 1,2,6, 7, 8 and 9 methods. The presence maps will be used to compute the Efficiency and Destructivity indices, which are analyzed in the next subsections.

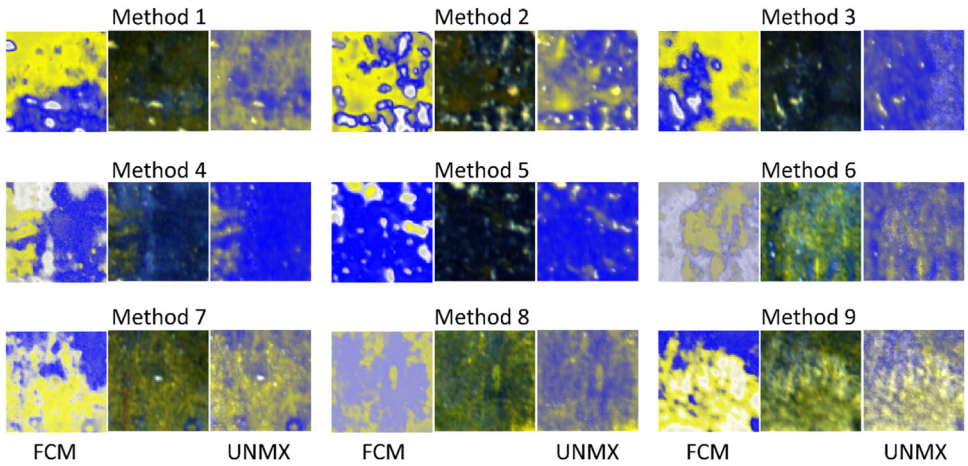

Fig. 4. AZ concentration/probability maps resulting from Fuzzy-C-Means (FCM on the left sub-figures) and Unmixing-based methods (UNMX on the right sub-figures) for the nine different cleaning procedures tested (see Table 1). The middle sub-figure corresponds to the sRGB image of the region used to evaluate the cleaning methods.

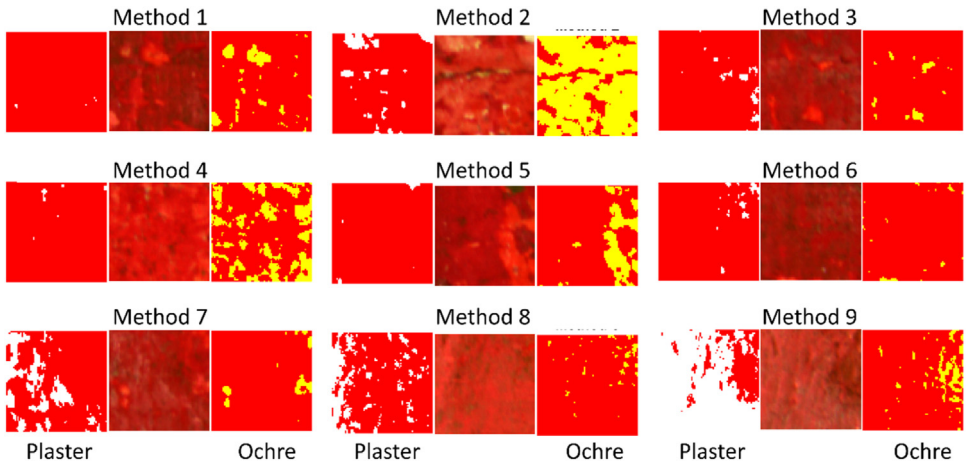

Fig. 5. Plaster (left sub-figures) and ochre (right sub-figures) presence maps for the unmixing -based evaluation method, with a threshold of 25%.

Efficiency index

All results from the proposed quality indices are shown together in Fig. 6 for the ease of comparison.

The efficiency index values computed from both Fuzzy-C-Means and unmixing presence maps for each method and each of the three pigments are shown in the top row of Fig. 6. Comparing first among pigments, in general the cleaning procedures have worked more efficiently for the red pigments than for the azurite. This is something that is also apparent by comparing either the concentration maps or the sRGB images captured after the cleaning. Fuzzy-C-Means tends to underestimate the ochre remnants in azurite for most methods (except for methods 3 and 4). For the red pigments, on the other hand, there is more ochre detected (i.e., less efficiency) according to Fuzzy-C-Means in comparison with the unmixing-based evaluation method, but the efficiency results are closer between the two evaluation methods in general.

Averaging the results for each cleaning method across all three pigments, both Fuzzy-C-Means and unmixing-based evaluations agree that the most efficient method is M5 (Kelcogel© + scalpel), followed by M4 (Carbogel© + scalpel). The least efficient method would be M2 (Culminac MC 2000® + scalpel) according to unmixing-based evaluation, and M8 (Klucel G® + scalpel) according to Fuzzy-C-Means evaluation. The average results across pigments for all three indices and the two evaluation methods tested are shown in Table 2.

There are also some differences regarding the method of choice across pigments, although M5 is well placed for all three of them. According to the unmixing-based evaluation, the maximum efficiency is reached for M5 for AZ, M6 for CN and M1 for CN-LR. Fuzzy-C-Means points out M5 again as the most efficient for AZ, but M3 is most efficient for CN and M9 for CN-LR. However, for the red pigments in general the efficiency values are closer among them in both evaluation methods.

Destructivity index

The efficiency index considers the ochre that has not been removed, but it is also important to consider if the solvent or the scalpel acted too strongly on the pigment and eliminated the pigment layer as well, leaving the plaster to be seen. The destructivity index evaluates this problem by computing the fraction of pigments that either have more than a 25% probability of being classified as plaster (for Fuzzy-C-Means based evaluation) or that have more than 25% concentration of plaster in the mixture (for unmixing-based evaluation). Then, worse results for the cleaning method correspond to higher destructivity index values.

Save for M9 (AZ and CN) and M2 (CN-LR), the destructivity indices for the Fuzzy-C-Means based evaluation are much higher than for the unmixing-based evaluation. When looking at the sRGB images of the cleaned samples, we realize that the Fuzzy-C-Means evaluation strongly tends to overestimate the presence of plaster in general for all pigments.

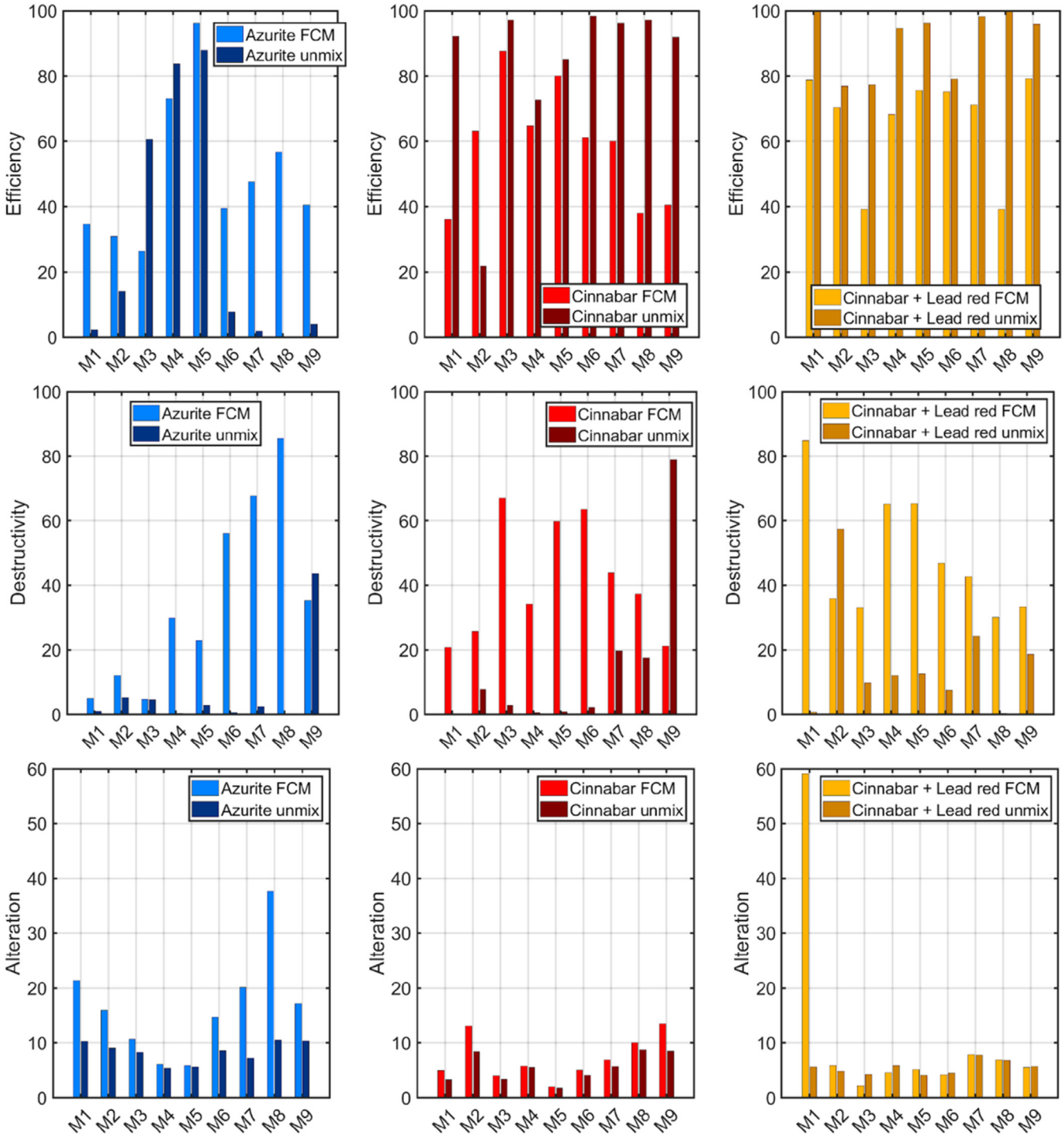

Fig. 6. Tops row: Efficiency index values for both evaluation methods and the three pigments studied. Each group of bars corresponds to one of the nine cleaning procedures tested (M1 to M9). Middle row: Destructivity index values. Bottom row: Alteration index values.

Comparing across pigments, the worst results in destructivity occur for CN-LR according to the Fuzzy-C-Means and the unmixing-based evaluation, for most cleaning methods. Averaging across pigments (see Table 2), the best results correspond to M1 (unmixing) and M2 (Fuzzy-C-Means), while the most destructive methods would be M9 (unmixing) and M6 (Fuzzy-C-Means). By examining in detail, the data in Fig. 6 (middle row), we can see that the least destructive methods are M8 for AZ, M4 for CN and M1 for CN-LR (unmixing-based evaluation). For Fuzzy-C-Means based evaluation, the methods of choice would be M3 for AZ, M1 closely followed by M9 for CN, and M8 for CN-LR.

The relatively high values of Destructivity observed for some methods do not mean that the plaster is necessarily visible in the cleaned sample (this happens relatively infrequently), but that the reflectance values of the cleaned sample tend to be higher, and so the unmixing tends to assign more concentration of plaster to those pixels. This partial desaturation can be a consequence of the action of the solvent on the pigment layer and influences

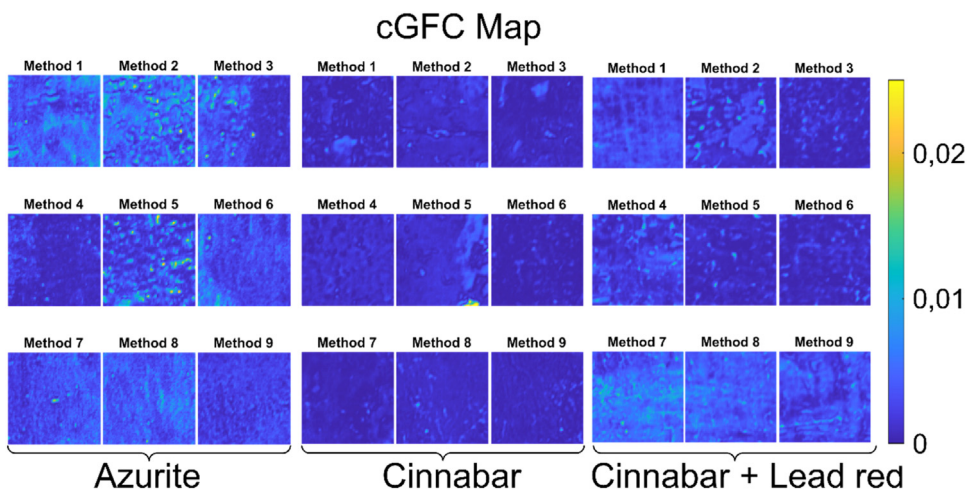

Fig. 7. Error maps for the cGFC metric. Left: AZ Middle: CN. Right: CN-LR pigments.

Table 2
Average evaluation indices across pigments.

Cleaning Method	D UNM	EFF UNM	ALT UNM	D FCM	EFF FCM	ALT FCM
1	**0,62**	64,82	6,39	36,82	49,86	28,46
2	23,45	37,60	7,40	**24,58**	54,84	11,66
3	5,75	78,32	5,29	34,91	51,12	5,63
4	4,32	83,67	5,63	43,05	68,66	5,49
5	5,38	**89,72**	**3,81**	49,28	**83,96**	**4,39**
6	3,41	61,71	5,71	55,46	58,61	7,93
7	15,42	65,43	6,92	51,39	59,67	11,62
8	6,05	65,69	8,73	50,95	44,63	18,20
9	47,10	63,92	8,20	29,94	53,46	12,09

Notes: (D=Destructivity, EFF=Efficiency, ALT=Alteration) for Unmixing-based and Fuzzy-C-Means-based methods. The best methods are highlighted in bold.

the results of the alteration index which are shown in the next section.

Alteration index

As explained in Section 3, the alteration index is the CIEDE00 color difference computed using the average spectral reflectance of the pixels that are not included in any of the presence maps as ochre or plaster, and the average spectral reflectance of the probes before the ochre layer is applied (reference samples). The higher the alteration index is, the more the cleaning process has varied the color of the sample. A good cleaning method would then have a low alteration index.

Comparing first across pigments, in general the higher alteration index values correspond to the AZ, showing that the cleaning methods have worked worst for this pigment (in agreement with the results of the Efficiency index). In average across pigments (see Table 2), both evaluation methods agree in considering M5 as the best method (again in agreement with the Efficiency index results), while the worst method would be M8 (unmixing) and M1 (Fuzzy-C-Means evaluation).

According to the average values (see Table 2) and the individual distributions of Alteration index for each pigment, all the methods would result in a visually perceptible alteration in color of the sample with respect to the reference before cleaning. We consider here the threshold for noticeable color differences as one CIEDE00 unit as an indicative value.

Self-evaluation of the method (error map images)

As explained in the methods section, the unmixing-based method that we propose has the additional advantage of being able to self-evaluate regarding the accuracy in the prediction of the mixed spectral reflectance using the concentration vectors and the endmembers spectral reflectances. By computing the cGFC difference metric pixel by pixel, we can then build the error distribution images using a common color scale for reference, for all pigments and methods tested. The error map images then show us an indication of how much can we trust the results of the concentration vector estimation, for each pixel. The results for all three pigments are shown in Fig. 7.

The results of the unmixing process are in general satisfactory (especially for the CN pigment), a bit les for the AZ in method 5. Nevertheless, in average across pixels all the error maps have a maximum value of 0.0055, which can be considered very accurate. These results show that we can trust the index computation and the presence and concentration maps derived with the unmixing method, confirming the robustness of the proposed methodology.

Wrap-up of the unmixing method: the CN-LR example

To show comprehensively the results of the proposed method, in Fig. 8 the best (M1) and worst (M2) cleaning methods images (according to the efficiency index) are displayed for the CN-LR pigment. We begin on the left by the sRGB images as visual reference. Then, on the next columns we show the concentration maps, followed by the ochre and plaster presence maps with the values of the Efficiency and destructivity indices obtained from them, and finally the error map images on the rightmost column. We can then be aware of the clear differences arising between methods for this pigment, and how the proposed evaluation procedure is clearly able to quantify and adequately reflect these differences.

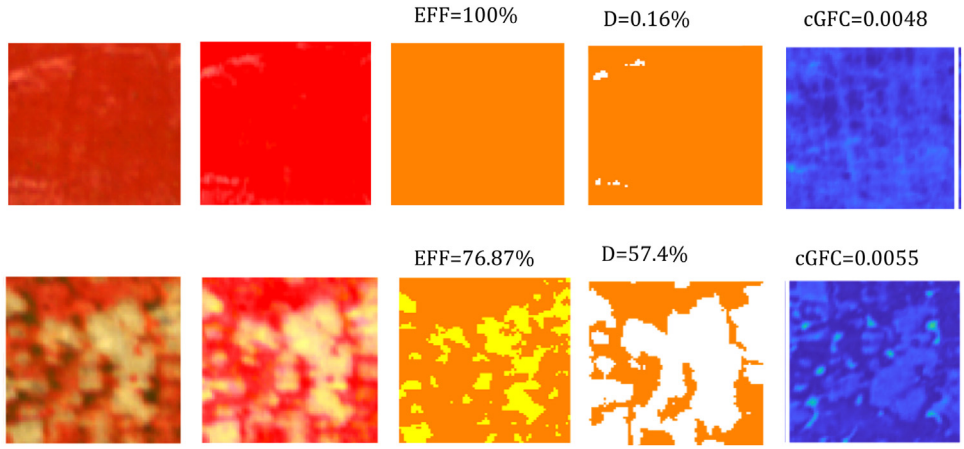

Fig. 8. Best (M1, upper row) and worst (M2, lower row) methods for the CN-LR pigment. First column: sRGB images. Second column: concentration map images. Third column: ochre presence maps. Fourth column: plaster presence maps. Fifth column: error images. The Efficiency and Destructivity indices, and the average cGFC values are also shown for both methods.

It is also remarkable in this example that the alteration indices are similar for both methods (5.54 for M1, actually a bit worse than 4.75 for M2). This suggests that the degradation of color has been similar across methods for this pigment, which is the case, because the alteration index varies between 4.06 and 7.78 for the CN-LR, with the worst alteration corresponding to method M7.

Finally, we have analyzed the samples using photogrammetry and optical microscopy images (results not shown, see Supplementary materials). Only one of these two methods (photogrammetry) offers a quantitative evaluation of the cleaning results. However, visual assessment of the results of these two techniques has allowed us to conclude that in most cases, the best and worst methods chosen according to these two standard techniques would be the same obtained by the proposed method.

However, photogrammetry and microscopy establish that test 7 (Agarart® complex polysaccharide gel) is also effective as a cleaning treatment. This result differs from that obtained by the methodology proposed here (see figure C from supplementary material).

Conclusions

The different techniques applied allow us to establish which treatments have been the most effective in the cleaning of oil repolychromes from the average values.

The methods 4 (Carbogel® polyacrylic acid gel) and 5 (Gellano Kelcogel® complex polysaccharide gel) have been the most effective for all three test probes, AZ (solvent White Spirit and Acetone 3:1), CN (mixture of solvents: Water, Alcohol and Acetone 1:1:1) y CN+LR (solvent White Spirit and Acetone 3:1). These two methods show the highest values on average of the EFF (Efficiency index) with both UNM (unmixing-based method) and FMC (Fuzzy-C-Means) systems (Table 2). Furthermore, these gels have been the application mechanisms in which the original color was least altered, with the lowest average values in ALT UNM= 5.63 and ALT FCM= 5.49 for method 4, and ALT UNM= 3.81 and ALT FCM= 4.39 for method 5. This demonstrates the effectiveness of chemical gels for the use of solvents, given that they allow to control the degree of penetration and wettability compared to other methods. In this way, the solvent used only acts on the layers to be removed (re-polychromed), without altering the layers underneath (original polychrome layer).

Regarding the solvent applied, the mixture of solvents Water, Alcohol and Acetone (1:1:1) used in NC has been the most effective. This probe shows the best results in terms of color alteration (Fig. 6- Alteration Index), loss of polychromy (Fig. 6- destructivity index), and cleaning efficiency (Fig. 6- Efficiency index).

On the other hand, it is important to evaluate the results obtained from the cleaning tests according to the binder present in the polychrome layer (glue animal and gum Arabic) as their behavior and aging is different due to their nature. This implies that animal glue, due to its protein nature, is more resistant to aging than the vegetable gum Arabic. This is because proteins have peptide bonds, together with salified amino and carboxyl groups which are very unreactive, what makes proteins chemically more stable substances [40].

In this sense, in the case of having to clean oil polychrome on a pictorial layer of gum Arabic, it is important to point out that the most effective treatment would be the method 1 of cotton poultice (White spirit and acetone 1:1). This cleaning method shows the best results in the different techniques used (*Comparison of photogrammetric models, Efficiency index and Destructivity index).*

The data obtained show the effectiveness of the use of gels and sustaining elements compared to traditional methods such as cleaning with a cotton swab, fiberglass, or scalpel.

The method presented here assumed a priori knowledge about the spectrum of the initial layer deposited on the plaster probe. In a real case scenario, this knowledge would not be available, so the initial layer pigment could be identified using analytical techniques like SEM/EDX *(Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy)*, among others.

The possibility of using just spectral information as the only source of data for a complete pre-restoration study including material identification in plaster samples is certainly interesting and will be considered as a matter of future work, along with the artificial accelerated aging of samples of a smaller size, and the inclusion of a higher number of pigments in the study.

One of the limitations of the proposed methodology is that it would not work well in the case when the initial layer and the repolychromy were done using exactly the same pigment. However, it is not common to find re-polychromies with the same pigment as the initial layer, mostly because re-polychromies were done at a much later time than the initial layer and with the explicit purpose of changing the appearance of the plaster to get in line with the tastes of the period. Besides, they were commonly done using less expensive and poorer quality materials. In Fig. 1 right, we have shown an instance of a case with Cinnabar original pigment re-polychromated with Red Earth. Both pigments are red, but the spectrum of the Red Earth is different enough from the Cinnabar to allow for the method to work. We have however cho-

sen an ochre pigment to showcase the method because of the convenience of using different colors in initial and re-polychromated layers, which allows for a direct visual evaluation of the cleaning results.

Other limitation is that we did not present any data obtained from real artworks in plaster, which could add strength to the results shown in the study by showcasing the method in a real-case scenario.

The proposed methodology has proven valid for determining the effectiveness of cleaning treatments on historic painted surfaces. Regarding traditional methods based on the observation of the restorer or photography, these applied methods allow progress in the evaluation of the results obtained in an objective, non-invasive, sustainable, and low-cost quantitative way, which is applicable to new tests in the future.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.10.019.

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