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Hyperspectral Fluorescence for Organic Pigment Characterization in Contemporary Artwork

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ABSTRACT

Modern artworks are often made by using new and unconventional materials that have been introduced to decorate outer surfaces. These materials, such as the organic pigments, might be subject to quick degradation. The characterization of materials constituting pictorial layers, i.e. pigments, binders, consolidants and possibly the substrate, becomes therefore necessary in order to prevent phenomena of alteration and degradation of the painted surfaces. The Laser Induced Fluorescence (LIF) is a non- destructive technique used for the investigation, characterization and preservation of Cultural Heritage, thanks to its peculiar advantages of high sensitivity, non-invasiveness and prompt response. Its application to the characterization of painted surfaces in contemporary artwork is for the first time considered in this paper.

Phtalocyanines (Pcs) and AzoCompounds (ACs) were selected among organic pigments considered for the first tests and LIF technique was extensively applied for the spectrofluorimetric characterization of reference samples composed by pigment-binder mixtures prepared in different composition ratios. The samples were irradiated by a UV laser source operating at 266 nm; the spectrally resolved fluorescence emission was recorded remotely as hyperspectral images and analyzed.

As expected, a sample surface containing different compounds generated a remarkable problem in the assignment of the spectral signatures to different constituents, because of the broadband emission associated to fluorescence bands of most organic compounds which appear together and interfere in the spectrum. To resolve the individual contributions, multivariate approaches for data analysis were used: in particular the Principal Component Analysis (PCA) and the Multi Curve Resolution (MCR) were applied. After laboratory experiments aimed at the construction of a database of modern fluorescent materials, the remote LIF technique was applied on real surfaces of artworks housed at the Museum of Contemporary Art of Rome (MACRO). The considered Pcs and ACs were identified on the collected images, and their space distribution was obtained after the assignment, by applying the Spectral Angle Mapper (SAM) algorithm.

1. INTRODUCTION

The need to preserve large surfaces of historic and artistic monuments and the corresponding demand from the institutions authorized to carry out conservation and restoration, is one of the main reasons that lead to the development of non-destructive techniques suitable to remote characterization of painted surfaces. Before preserving a pictorial layer, it is necessary to know its main constituents, through a characterization of the material. The identification of organic compounds used in modern painting as pigments and binders, is more complex than in case of ancient pigments. The difficulty arises from the nature and variety of materials used, which often are present on surface in form of multi-component mixtures with unknown composition or components concentration [1]. Non-invasive and non-destructive diagnostic techniques, allowing for the immediate recognition and the correct characterization of these new materials, have still

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to be established and validated. Spectroscopic methods, based on laser sources, have significantly improved the possibility to investigate the chemical composition of work of arts [2]. Among the most advanced techniques, the Laser Induced Fluorescence (LIF) is used for surface characterization, because of its peculiar advantages of high sensitivity, non-invasiveness and prompt response coupled to imaging capabilities.

LIF is a molecular spectroscopic technique based on the detection of the UV-VIS radiation emitted by luminescent materials onto which a laser beam at a selected UV wavelength with sufficient energy to activate allowed electronic transitions impinges [3]. In particular, the LIF technique has already been recognized as a powerful technique in the remote sensing of several different kinds of CH surfaces, allowing the researchers to detect characteristics invisible to the naked eyes in the collected hyperspectral images. One of strong point of LIF technique is its non-destructivity and non-invasiveness, that makes it particularly suitable to the study of fragile and precious specimens. Additional technical advantages are the possibility of remote control in the positioning of the scanner by means of robotics/automation systems and the parallel development of semi-automatic methods data processing algorithms.

Hyperspectral remotely scanned LIF images of painted CH surfaces have already been collected by prototypes and successfully analyzed to study different problems related to the conservation and restoration of artworks. In particular, the LIF imaging, remotely applied on large areas, allowed for the identification of original and added surface materials on frescoes in the Baptistery of Padua (Padova 2010)[4] and in the Renaissance churches in Seville[5]; on small part of frescoes it already provided information on the presence of biological agents (Romania 2008)[6] and different additives (Hrastovljie 2009)[7].

The objective of this work is the spectral identification of Phthalocyanines (Pcs) and Azo Compounds (ACs) used as pigments in modern and contemporary paints, by means of the ENEA LIF-scanning system [4]. In order to reach this purpose a database of spectral components, together with their assignments to the reference materials, has been constructed. In order to resolve the individual contributions, multivariate approaches for data analysis were implemented; in particular the Principal Component Analysis (PCA) and the Multi Curve Resolution (MCR) were applied. After laboratory experiments, the remote LIF technique was applied on real surfaces of artworks hosted at the Museum of Contemporary Art of Rome (MACRO), a significant example is reported and discussed.

2. MATERIALS E METHODS

2.1 Phthalocyanine

The Phthalocyanines are heterocyclic compounds whose chemical structure is similar to that of natural porphyrins and closely related to that of porphyrazine. These molecules represent the most important chromophoric system of the twentieth century. The dispersion medium greatly affects the absorption coefficient and the fluorescence quantum yield of phthalocyanine; it has also been proven that in solution with aromatic solvents causes a significant red shift in the emission spectrum [8], due to the presence of the central metal.

In medical studies related to photodynamic therapy (PDT), Pcs show a characteristic fluorescence, which manifests itself with multiple emission bands peaked between 400 and 600 nm. The wavelength position of the fluorescence bands mostly depends on the type of the central metal. The presence of a dispersion medium has a remarkable effect on Pcs absorption bands intensity and on respective fluorescence emissions, that are remarkably weaker, but does not originate significant spectral shifts [9,10] . Due to the rigid packing of atoms in molecules, only a limited displacement was observed. Pcs indeed possess an extremely rigid structure, unlike, for example, ACs.

2.1 Azo Compounds

The Azo Compounds are synthetic compounds having the functional group RN = N-R', wherein R and R' can alternatively be an aryl or alkyl. The chemical bond between two nitrogen atoms, N = N, is named Azo group and is peculiar to their structure. ACs show characteristic absorption in the UV region, with a corresponding emission band located at 500-520 nm, their fluorescence emission is weaker than the Pcs one. When ACs are in mixtures with Pcs, the fluorescence spectra suggests the presence of both compounds, however usually do not allow identifying the specific Azo Compound while the Pc is easily recognized. The fluorescence intensity of ACs can be considerably improved by treatment with surfactants [11], as we tested also upon excitation at 266 nm.

2.2 Color Strips

In order to create a significant *database*, it is necessary to analyze modern organic pigments in a dispersion comparable to what has been found on contemporary artwork surfaces. To this aim, strips have been prepared with a slowly varying gradient of the pigment in the binder. Specimens consisted of a binder with a pigment density that gradually increases, as showed in Fig.1. At the ends of the substrate (black cardboard) it has two pure compounds: on one side the pure pigment (mainly dissolved in a minimum amount of binder that does not interfere in the measurements) and on the other the pure binder without any pigment.

Figure 1: Picture of the reference Color Strips. Pigment used: PB.15 (blue), PG.7 (green), PY.1 (yellow), PG.7/PG.8 (dark green) and PG.7/PY.1 (light green).

For the implementation and characterization of a LIF database as our standard reference, we selected three pigments belonging to the Pc family, (PB.15, PG.7 and PG.8), and one pigment belonging to Azo Compound class, the PY.1. As a binder we have chosen the acrylic PRIMAL B-60, widely utilized in contemporary paints and fully compatible with the selected pigments.

LIF images of the strip specimens were collected and the extraction of the spectral components was performed by principal components analysis (PCA) and by Multivariate Curve Resolution (MCR). By the latter, it was possible to discriminate the contribution of the binder from that one of each pigment, assigning single resolved bands to functional groups of constituents.

3. EXPERIMENTAL APPARATUS

The ENEA LIF scanning system is capable to collect hyperspectral fluorescence images scanning large areas in applications to CH surfaces (e.g. fresco's, decorated facades, etc.). A compact set up has been built and patented [12] achieving high performances in terms of space, time resolution, and data acquisition speed (Fig.2). Major achievements have been reached by a critical review of the optical design and consequently of the detector:

- A line focalization mode has been adopted by using a quartz cylindrical lens and an imaging spectrograph (Jobin-Yvone CP240);
- A square ICCD sensor (ANDOR iStar DH734, pixel size 13 μm), mounted behind a slit parallel to the laser line footprint during the scanning, has been utilized.

By means of this arrangement the spatial and spectral information are collected on two mutually orthogonal directions imaged on the detector, with submillimetric spatial resolution and a spectral resolution better than 2nm. Additionally it is possible to implement time resolved measurements on the nanosecond scale by controlling the electronic detector gate. The overall current system performances are horizontal resolution 640 pixel, 0.1 mrad angular resolution, minimum acquisition time per line 200 ms, FOV aperture 5.7° (corresponding to a scanned line of 2.5 m at 25m distance). With the latter optics, an image of 1.5 × 5 m is scanned in less than 2 minute at 25 m.

Analytical performances of the instrument are based on the spectral signature characteristic for each chemical compound laying on the examined surface. Due to the weak autofluorescence emission of most historical inorganic pigments, pigments analysis on fresco, although possible, has been seldom applied starting from LIF spectra alone [13]. In the following, we demonstrate that the situation is much more favorable to the use of LIF technique for organic pigments discrimination in contemporary artwork.

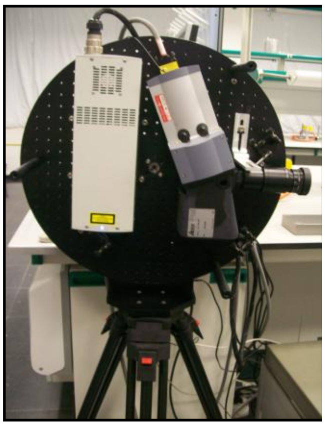

Figure 2: Picture of the compact LIF line scanner. The circular optical table is vertically mounted on a tripod: the vertical scanning is performed by rotating the optical table accurately thanks to a stepper motor mounted on the back. The optical transmission (laser, mirrors, lenses) and receive (lens, spectrograph, ICCD) are on the front.

4. DATA ANALYSIS

The data collected by LIF scan are acquired in the form of packets of monochromatic spectral images, each centered on a single wavelength. Usually the rendering of these images is in grayscale or false color RGB (Red, Green, and Blue) reconstruction, using a single wavelength or a combination of the most intense spectral components.

Multivariate analysis, as the name indicates, includes an ensemble of mathematical techniques dedicated to the analysis of data sets with more than one variable. Particularly, it can help reducing data set dimensions and extracting effective information based on variance analysis [14, 15, 16]. Methods of multivariate analysis used in the present work were: Principal Component Analys (PCA) and Multivariate Curves Resolution (MCR).

Additionally the Spectral Angle Mapper (SAM) projection algorithm was utilized to characterize the surface.

To speed up the processing of acquired images, the most relevant spectral features are first identified by Principal Component (PC) analysis. Although it is commonly accepted that the PCs loadings do not possess any direct physical meaning, they can nevertheless be described in terms of bands. In some cases, a given PC loading has well defined spectroscopic bands with associated peaks, while in other cases more complicated trends and shapes are observed: most frequent is the case of combination of positive and negative peaks. A few PCs are usually retained for subsequent analysis: typically 5 to 8 components are enough to describe the entire spectral data set. It is also worth noticing the possibility to build suitable linear combinations of the computed PCs to achieve a faithful representation of each pixel spectra, eventually used for the computation of standard CIE/lab colorimetric measurements.

The other multivariate method used in this work is the Multi Curve Resolution analysis (MCR) that aims at retrieving the real contributions belonging to the spectral components of the mixture through a mathematical resolution of the corresponding data. The objective of the MCR technique consists in finding and applying appropriate constraints to reduce and eliminate ambiguity, in order to obtain unique solutions. The MCR analysis is clearly more advantageous than the PCA, as the solutions obtained from the MCR have a direct physical meaning and describe the true nature of the contributions of the components, without the need of additional efforts for interpretation. They provide directly the analytical information requested, like in chromatographic separation methods [17, 18]: qualitative results are easily obtained and quantitative analysis becomes feasible. An additional advantage of using MCR in mixtures lies in the fact that the resolution comes from mathematical methods and then can be achieved in a short time, compared to analytical separation techniques.

A different method, used in the analysis of spectral images, concerns the identification of regions having a specific spectral content, i.e. the space distribution of a material onto the examined surface. Typical is the case of identification of a given component (pigment, binder) in an image. Such a task can be accomplished by using projection algorithms like SAM (Spectral Angle Mapper) or SCM (Spectral Correlation Mapper) in combination with an available data base containing its signature. In this work the calculation of the spectral mapping is performed by SAM whose projection algorithm, described in [19], calculates the spectral angle between a reference spectrum and the spectrum of each pixel in the image to be analyzed. SAM has already been successfully applied to the analysis of LIF images [13]. Although the mapper algorithms perform well with a low computational cost, their performances are generally lower with respect to a complete band analysis procedure based on spectral deconvolution, whenever the latter can be achieved.

5. RESULTS

5.1 Reference Measurements

All reference samples produced as strips were analyzed by PCA and MCR, in each case we noticed that the intensity of pure binder decreases gradually with the increase of the concentration of pigment within the binder; the spectral shapes of the binder, however, remain dominant even when we are in the area of the (almost) pure pigment. The Pc's spectral contribution appears a main shoulder at 630-650 nm and second one at 400-420 nm, while in the Azo's spectra show a weaker band at 520 nm.

To recognize dominant spectral features, the data acquired were processed using the statistical analysis PCA. However, we can notice that the deconvoluted curves are not always positive (Figs. 3-4-5).

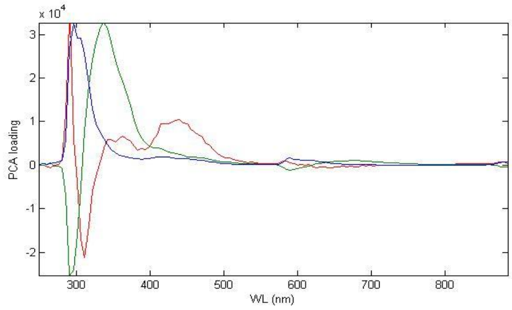

Figure 3: PCA of PB.15 and PRIMAL B-60

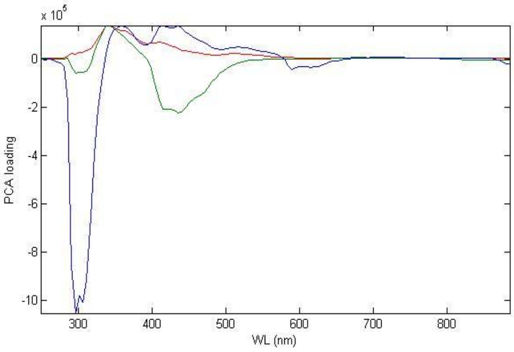

Figure 4: PCA of PY.1 and PRIMAL B-60

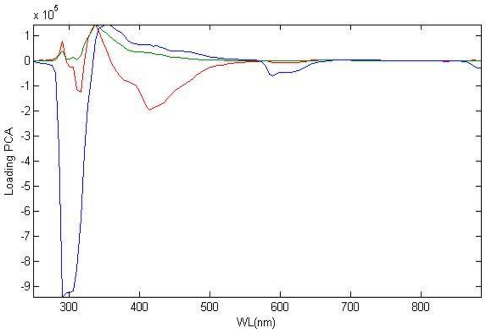

Figure 5: PCA of PG.7 and PRIMAL B-60

In order to assign single positive components with a physical meaning the MCR-ALS (Multivariate Curve Resolution - Alternate Least Square) was implemented and the analysis of data collected on our strips was performed. The constraints imposed in the decomposition MCR were: the number of pure components equal to 3, non-negativity of loading, non-negativity of the score, and convergence within 5000 iterations.

We came to the identification of the three components in the sample analyzed, binder, pigment, substrate, by the tool Singular Value Decomposition. Note that in general it is possible that the interaction mixture/binder gives rise to additional peaks, relevant to the mixture, and not to individual compounds, but this did not occur in the examined cases.

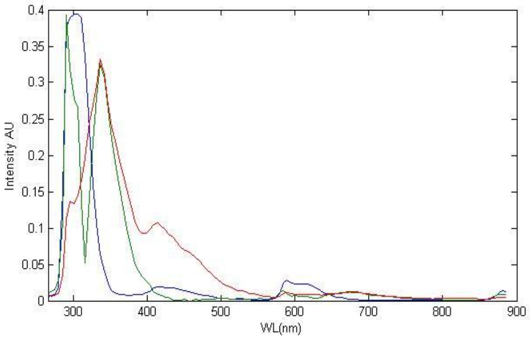

Figure 6: MCR-ALS of PG.7 and PRIMAL B-60

The MCR analysis reveals three spectral components, two sharing a prominent peak at 290nm, and a third component with peaks at 630/650nm and 400-420. From the comparison with the spectra of pure ligands, present on the right side of the specimen we have the confirmation that the emission at 290 nm is present and can be definitely attributed to the acrylic binder PRIMAL B-60. The band at 360 nm may be representative of titanium white powder used as an additive in PG.7, while the shoulders at 400 and 600 nm may be representative of the Pc pigment itself (Fig.6).

When the Phtalocyanine PG.7 is mixed with Azo Compound and PRIMAL B-60 we obtained a MCR spectra where is clearly identifiable the three components relates to PG.7 at 600-650 nm; PY.1 at 520 nm and PRIMAL B-60 at 300 nm (Fig.7).

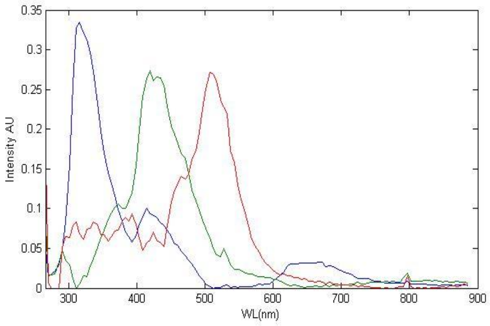

Figure 7: MCR-ALS of mixture Pc and Azo Compound.

5.2 Renato Mambor, Tappezzamento a Pezzi, (1993), painting housed at MACRO, Museum of Contemporary Art Of Rome.

After a preliminary analysis performed with a portable spectrofluorometer, we focused on the areas of surface where the fluorescence response was most intense (Fig. 8).

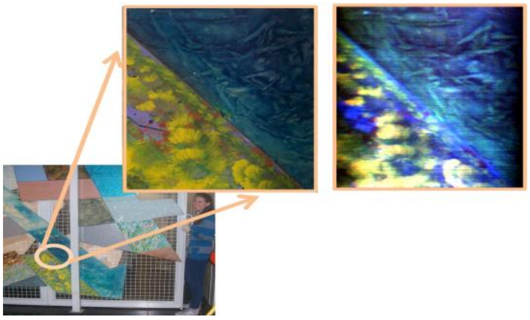

Figure 8: Details of the scan area of R.Mambor selected for the fluorescence analysis (left) and LIF false-color image with the emission intensity at 400, 500 and 600nm, (right).

The LIF scan lasted about 15minutes, after which the data were made available in the form of digitized spectra and we proceeded to process them.

Using spatial averages of homogeneous areas and contiguous from the scan of 512 x 300 pixels, 221 were extracted spectra representative of the entire scan (Fig.9).

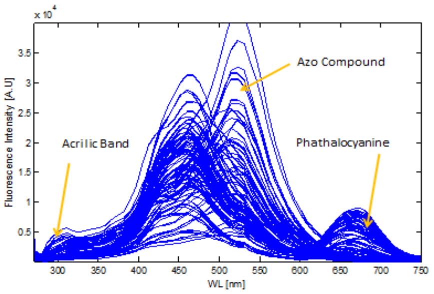

Figure 9: extraction of 221 representative spectra of the entire scan

Note the presence of a band at 290 nm due to acrylic binders, and additional bands centered at 420, 450, 520 and 650 nm. The initial association between spectral emissions and materials is made leveraging on the mere presence of spectral bands centered on the emission spectra of reference samples. For example, the band at 650 nm is representative of the class of pigments belonging to the family of Pcs, blue-green hues, while that at 520 nm is attributable to the family of ACs.

To show dominant spectral features, the data acquired were processed using the statistical analysis PCA, which gives also the number of independent components. PC's shown in figure 10 confirm the hypothesis based on the average spectra accounting for fluorescent emissions attributable to acrylic binders and pigments. However, these PC components cannot be directly related to single compound spectra, since all of them but PC1 have a bipolar performance. Furthermore, the latter corresponds to the average spectrum and then does not supply additional pieces of information.

In order to achieve a classification based on significant spectral features, MCR was applied. Lacking other information, we have decided to use as the starting components of the MCR a number of spectral bands of 6 and with Gaussian shape, centered respectively at 266, 290, 420, 500 and 660 nm. The position and width of the first band corresponds to the elastic scattering, which also appears in the reference spectra of pure substances. The choice of the others is instead partly arbitrary, corresponding to emissions with larger intensity and relative maxima on average spectra and in PCA. [Fig. 9 - 10]

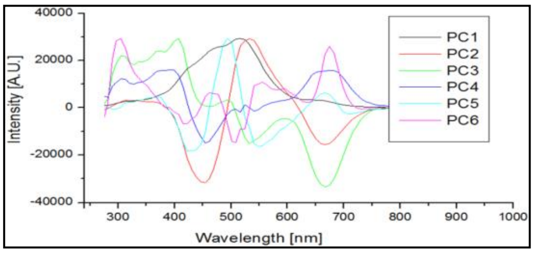

Figure 10: PCA loading; six components of the PCA

The constraints imposed on the MCR analysis, as in reference spectra, are: non-negativity of loading, non-negativity of the score and convergence in 5000 iterations. The analysis produces six MCR spectral components. From the comparison with the spectra of laboratory specimens, we note that the similarities between the components of the MCR and some spectra of individual substances are significant; the peak at 520 nm that appears in MCR5 can be attributed to the fluorescence spectrum of the pigment Hansa Yellow PY1. Interestingly, the emission at 650nm shown in MCR6 which is also representative of phthalocyanine blue, PB15. The emission at 290 present in MCR2 nm indicates the presence of acrylic binder on the surface of the work. [Fig. 11]

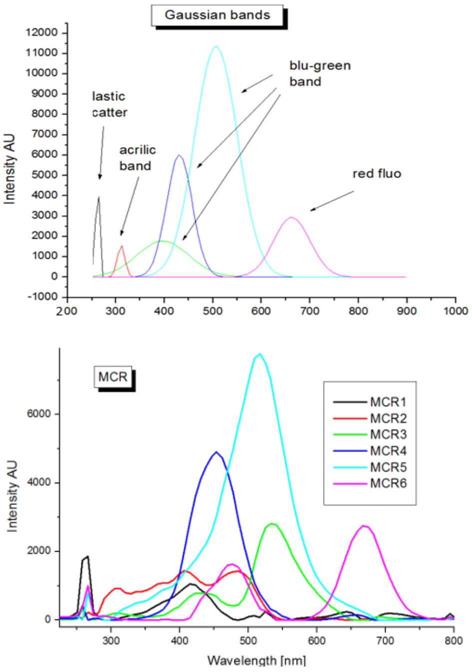

Figure 11: Selected reference bands (up) and MCR- ALS Decomposition (down)

After MCR processing, thanks to the assignments of majors features, the distribution of pigments was investigated. The calculation of the spectral mapping is performed using the Spectral Angle Mapper technique that calculated the spectral angle between the MCR5/6 reference spectra and the spectrum of each pixel in the analyzed image.

The SAM distribution of the pigment PB.15 assigned to MCR6 and PY.1 assigned to MCR 5 are shown in figure (Fig.12). The spectral similarity (black in the black and white representation adopted) shows that the band MCR6 is most represented in the upper right corner chromatically dominated by the color blue/cyan, typically of Phtalocyanine. On the contrary the band MCR 5 is most represented in the lower corner chromatically dominated by the yellow color, typically of Azo Compound. [Fig.12]

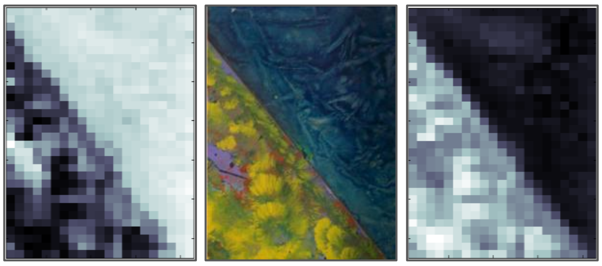

Figure 12: Mapping SAM grayscale with reference spectral band MCR 5 (left) and MCR 6 (right), photo of scanned area (center); in the black and white representation the black corresponds to a lower spectral angle (correlation next to one) and the white to a larger spectral angle (correlation near zero).

CONCLUSIONS

The current results have confirmed the interference of binders on the analytical determination of the pigments present on painted surfaces whenever contemporary materials are considered. Such a sample surface, containing different compounds, generated a remarkable problem in the assignment of the spectral signatures to different constituents, because of the broad band emissions associated to fluorescence bands of most organic compounds, which appear together and interfere in the spectrum.

The acrylic binder's spectra are clearly identifiable whereas the same cannot be said for all organic pigments. Significant results were obtained by PCA on Phthalocyanines showing characteristics fluorescence bands at 420 and 650 nm, Azo Compounds could be also recognized by the emission band at 520 nm.

We noticed that Pcs mixed with binders presented a red shift on the spectra. In order to be able to isolate the individual components, a good approach was to analyze mixtures of pigment/binder, building up the color strips. The PCA and MCR analysis have provided valuable computational support to isolate the individual components in order to obtained good diagnostic results. Once completed the assignment, the application of SAM was tested to obtain the organic pigments space distribution.

A real contemporary artwork produced by Renato Mambor (1995) has been examined to test the diagnostic capabilities of the LIF technique. To this aim, we have used the experimental results obtained on reference materials for the qualitative analysis of fluorescence spectra. In this case, it was possible to identify pure compounds thanks to effective performance of MCR, which permitted a statistically significant discrimination of the constituents of the examined painted layer.

The successful classification achieved resulted in complete agreement with the literature examined, and constitutes an excellent starting point towards the realization of a fluorescence database for contemporary materials. In conclusion, the LIF imaging technique, with its potentiality for remote and automatic application, resulted to be suitable to perform diagnostic on material used on painted surfaces in Contemporary Art.

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