Development of a multi-analytical approach to investigate the fading of eosin in painting matrices

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Development of a multi-analytical approach to investigate the fading of eosin in painting matrices

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Abstract. Eosin is a xanthenic synthetic organic dye/pigment synthesized by Caro in 1873. It was precipitated with lead and aluminum salts and commercialized as geranium lake and it was one of the most brilliant hues in the palette of the Impressionist painter Vincent van Gogh. Unfortunately, the high photosensitivity of eosin has caused the evident fading of the intense pink colorations of his canvas paintings into lighter ones.
This work aims at underlying the contribution of several complementary different analytical techniques in disclosing a very complex and still little-known topic such as the degradation process of eosin.

1. Introduction

Eosin, also called Pigment Red 90 or Acid Red 87, is a xanthenic synthetic organic dye/pigment synthesized by Caro in 1873 (Figure 1). Although widely commercialized after precipitation with lead and aluminum salts as geranium lake, its identification in historical artworks has been rarely achieved due to its high photo-instability [1,2,3]. Moreover, the description of the involved mechanisms in its loss of color is still missing. Characterizing eosin degradation products is rather challenging, not only due to eosin strong pH sensitivity and photosensitivity, but also to the presence of impurities in commercial products. When dealing with historical materials, the complexity of the heterogeneous painting matrix increases the number of variables involved in the rate and the mechanism of organic pigments ageing [4]. Thus, for shading light on the phenomena involved in the degradation of eosin, the application of a multi-analytical approach is fundamental. In this work, a multi-analytical approach was applied to study eosin both in solution, and in oil media. The potentialities and limitations of the different approaches are herein discussed. First, colorimetry was used for monitoring the fading. Then, artificially aged paint replicas where characterized using luminescence spectroscopy and an optimized HPLC-DAD method.
Infrared imaging techniques based on Synchrotron Radiation were also applied to establish the chemical distribution of eosin-based compounds within the micrometric layers of paint model systems.

2. Materials and Methods

2.1. Chemicals

Standard sodium eosin (EO-Na) was purchased from Sigma Aldrich (USA). Stock solutions were prepared in dimethyl sulfoxide (DMSO; J.T. Baker, Holland) and kept in the dark. All the solvents were HPLC grade and were used without any further purification. The eluents for the HPLC-DAD analyses were: bi-distilled water and acetonitrile both HPLC grade (Sigma-Aldrich, USA). All eluents were added with 0.1% v/v Trifluoracetic acid (TFA; 99% purity, Sigma Aldrich (USA)). PTFE filters (4 mm thickness and 0.45 μm pore diameter) were used for the purification prior to HPLC injection.

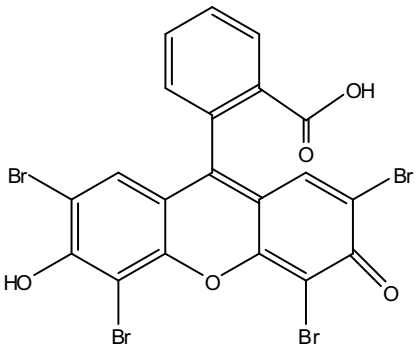

Figure 1: Eosin in its fully protonated form.

2.2. *Reference samples*

Paint replicas were prepared by admixing eosin with linseed oil, and eosin, linseed oil and lead white (Kremer Pigmente, Germany).

2.3. *Colorimetric measurements*

The colorimetric measurements were performed with a Konica-Minolta Mod. CM-700d, with a spot of 8 mm (diameter), with a wavelength range of 360-740 nm and D65/10° for the illuminant/observer, specular component excluded (SCE). The data were acquired in triplicates on two different spots of the sample. The standard deviation of the three replicates in terms of ΔE was below 0.1.

2.4. *Chromatographic analyses*

HPLC-DAD: a HPLC consisting of a PU-2089 Quaternary Pump with degasser, equipped with an autosampler AS-950 and coupled to a spectrophotometric diode array detector MD-2010 was used (Jasco International Co, Japan). The data were processed with ChromNav software. The working conditions were: DAD spectra acquisition in the 200-650 nm range every 0.8 sec with a resolution of 4 nm; liquid chromatographic separation at room temperature (30 °C) on an analytical reverse phase column TC-C18 (2) (4.6 x 150 mm, particle size 5 μm, Agilent) with a precolumn TC-C18 (2) (4.6 x 12.5 mm, particle size 5 μm, Agilent), flow rate 1 mL/min and injection volume of 50 μL. The two eluents were 0.1% (v/v) TFA in water (A) and 0.1% (v/v) TFA in ACN (B). The elution program was 85% A for 5 min, then to 50% A in 25 min, then 30% A in 10 min, then to 0% in 1 min and hold for 4 min, and re-equilibration took 7 min.

LC-ESI-Q-ToF: a HPLC 1200 Infinity, coupled with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector by a Jet Stream ESI interface (Agilent Technologies, (USA)), was used for confirmation of the chromatographic peak assignments [5].

The sample pre-treatment was the same for both the instrumentations. C.a. 0.1 mg of each paint model system was submitted to extraction with 700 μL of dimethylsolfoxide (DMSO). The solution was sonicated for 10 min at 30° C, filtrated using a PTFE filter and then injected in the chromatographic system.

2.5. *Micro-FTIR analyses*

Synchrotron radiation micro-Fourier Transform Infra-Red Analysis (micro-FTIR) was carried out at the IRIS beamline (BESSY II) at Helmholtz-Zentrum, Berlin (Germany) on a Thermo Nicolet Continuum™ microscope equipped with a mercury–cadmium–telluride (MCT) detector. The sample was mounted on a diamond cell on a motorized microscope stage and raster scanned through the synchrotron beam with a diameter of 15 μm collecting a grid-like pattern of IR spectra spaced in 10-μm increments. Measurements were performed in transmission mode at a magnification ×32 using confocal objectives. Infrared spectra were registered between 4000 and 650 cm−1 with a spectral resolution of 4 cm−1. An accumulation of 128 scans per point was used. The spectrum and mapping acquisition was performed by using the OMNIC Atlμs™ software. The sample preparation protocol consisted in the microtoming at 10 μm of the samples with an embedding-free approach as described in the literature [6].

2.6. *Luminescence measurements*

Luminescence measurements were performed at IPANEMA laboratory (Saint Aubin, France). A spectroradiometer SPECBOS 1211 UV (JETI Technische Instrumente GmbH, Jena) that allows collecting measurements in irradiance mode was used. The spectroradiometer was equipped with a focusing optics allowing a collection area of 0.5 mm diameter. A CoolLed model PE-4000 (Andover, UK) was used as excitation source. The detection range was 350-1100 nm and integration time was 626 ms.

3. Results and discussion

The study of the reference materials and aged specimens through the plethora of analytical techniques available allowed to evaluate the fading of eosin and to assess the presence of possible degradation products.

In particular, the application of colorimetry to the paint replica prepared with linseed oil allowed to quantify the color change after artificial ageing. Figure 2 reports the color changes observed in the course of accelerated ageing, including the shift in the values of lightness/darkness (L*), redness/greenness (a*), yellowness/blueness (b*) and total color (E*). It is important to highlight that in theory, only $\Delta E^* > 0.8$ are noticeable by the human eye [7, 8]. In this case, the lightness sharply increases after the first few hours of accelerated ageing, and the ΔE changes abruptly, as a* and b* slowly approach zero [4].

The paint replicas were analysed, after solubilisation in DMSO. The chromatographic profiles obtained before and at the end of the artificial ageing experiments for the paint replica containing eosin and linseed oil are reported in Figure 3. The presence of degradation products can be appreciated in the chromatogram of the aged paint replica (d1 and d2), whose DAD spectra features absorbance in the range of yellow compounds. Moreover, it is worth noticing that the chromatogram of standard eosin (Eo) presents a peak due to tribromofluorescein or dibrominated eosin (DBEo), possibly as a synthesis by-product. The nature of the synthesis by-product and of degradation products was confirmed by mass spectrometric detection and is the object of a forthcoming publication.

The decrease in the concentration of eosin in the chromatogram of the extract of the aged sample correlated with the increase observed for L*. Nonetheless, the loss of eosin was not as dramatic as expected from the evaluation of the ΔE change, suggesting that the analysis of the bulk sample by chromatographic analysis only yields partial information. Thus, experiments aimed at locating eosin in the paint cross section were performed.

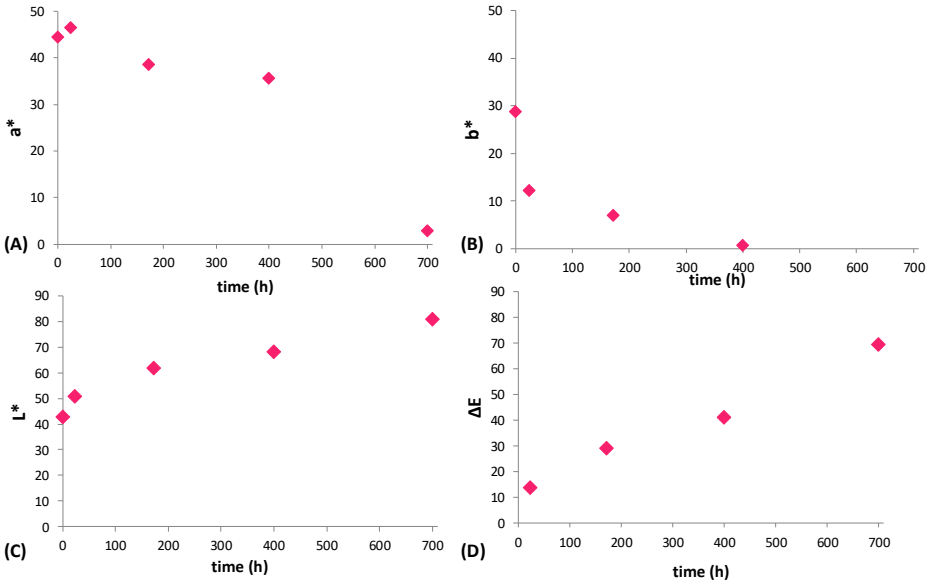

Figure 2: Results of the colorimetric analysis of the paint replica subjected to increasing doses of UV-Vis light (accelerated ageing) in CIELAB coordinates: values of a* (**A**); b* (**B**); L* (**C**) and ΔE (**D**) with ageing time.

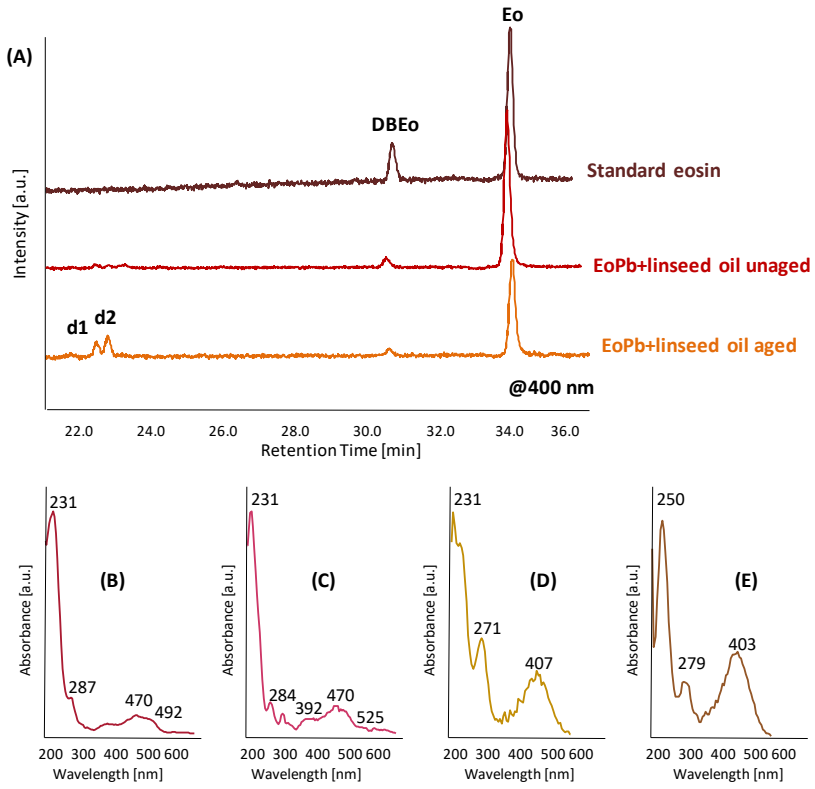

Figure 3: (**A**) Chromatographic profiles at 400 nm of the DMSO extracts of the reference paint replicas before and after artificial ageing, along with the profile obtained by the analysis of a DMSO solution of standard eosin; UV-Vis spectra of (**B**) eosin, Eo; (**C**) debrominated eosin, DBEo; (**D**) ageing product d1; (**E**) ageing product d2.

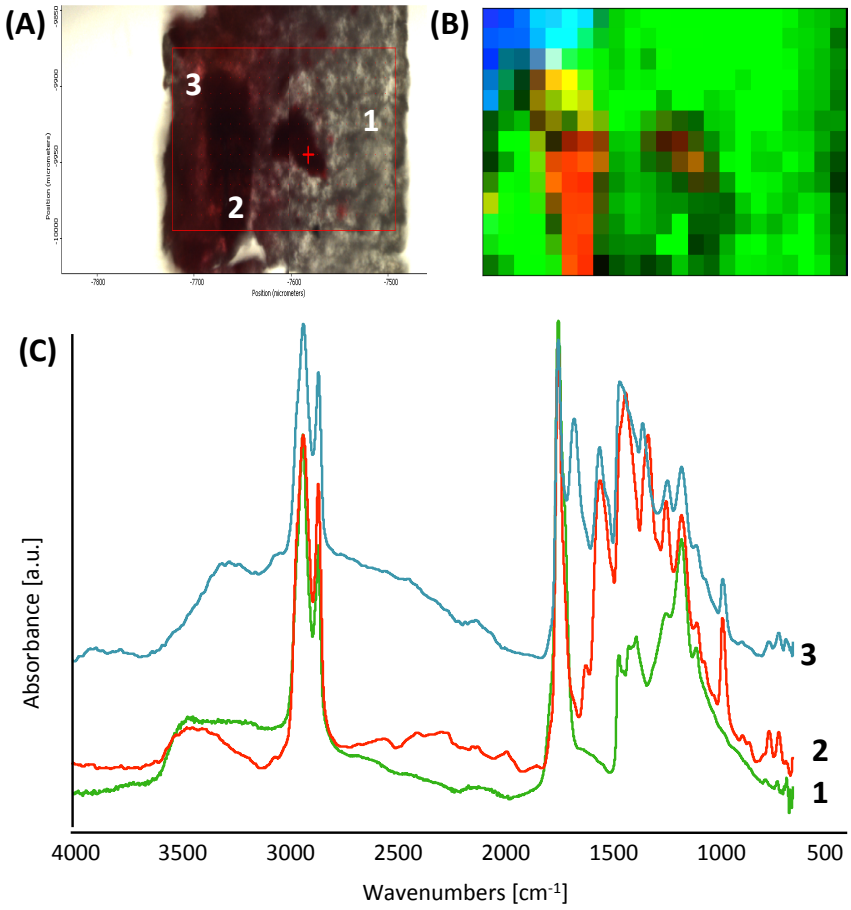

Figure 4: SR μ-FTIR study of aged PMS admixed with lead white: (**A**) microphotograph of the thin section analyzed. The area mapped (red square) shows the red paint layer with big red grain of eosin and the faded superficial layer; (**B**) chemical maps of a carbonyl group stretching at 1739 cm^{-1} corresponding to the oil as binder (green areas), eosin (1550 cm^{-1}, red areas), band at 1660 cm^{-1} from an unknown compound (blue area) (**C**) SR μ-FTIR spectrum of the three points labeled in (A).

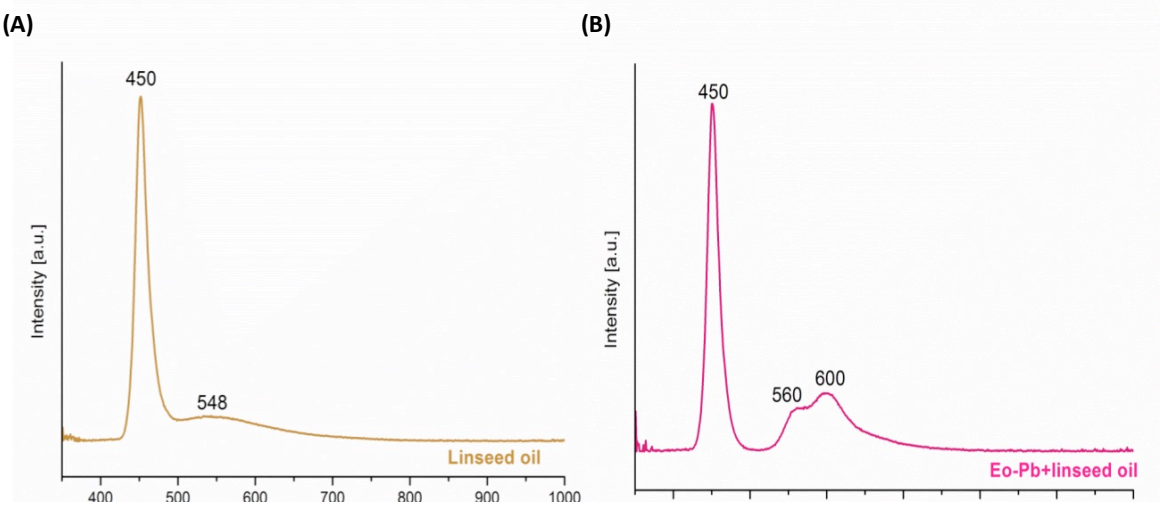

Figure 5: Luminescence spectra of the reference paint replicas: (**A**) linseed oil, used as blank; (**B**) eosin in linseed oil. (λ_{ecc}= 450 nm).

The application of synchrotron radiation-based techniques allowed us to identify different areas in the paint cross-section, namely a superficial layer where eosin was almost completely faded, and an inner layer where particles of the organic pigment were still visible. The results are depicted in Figure 4.
In order to increase our ability to detect eosin in very degraded samples, both by microdestructive (i.e. chromatographic) and non-destructive (i.e. spectrophotometric) techniques, the applicability of luminescence related methods was investigated (Figure 5).

4. Conclusions and perspectives

The application of a multi-analytical approach to the understanding of the behavior of eosin lakes in paintings highlighted the need for sensitive and selective methods. Most important, it was proved that the necessary following step will entail the use of mapping techniques to establish the chemical distribution of eosin-based compounds within the micrometric layers of paint model systems before and after ageing and to evaluate the influence and interaction of the whole paint matrix in eosin degradation process. Work in progress comprises the interpretation of the fading mechanism in eosin lakes through spectroscopic and spectrometric detection, in order to elucidate the nature of the degradation products. Moreover, the application of fluorescence and luminescence based analyses is ongoing.

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