



X-ray and ion irradiation effects on azurite, malachite and alizarin pictorial models

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ABSTRACT

The analysis by intense radiation sources of painting materials used in artworks gives valuable information about their composition and state of conservation, but it can also induce undesired modifications on the studied substrates. Here we use X-ray photoelectron spectroscopy (XPS) to follow the surface chemical changes that prolonged irradiation with soft X-rays (with maximum doses ranging from $\sim 1.2 \times 10^{17}$ to $\sim 3.4 \times 10^{17}$ photons cm^{-2}) produce on azurite, malachite and alizarin pigments and on two egg-yolk temperas containing azurite or alizarin. The effects following exposure to Argon ion irradiation have been also studied for malachite and azurite tempera. XPS spectra of the samples show that both types of radiation induce similar superficial alterations, although, at the selected experimental conditions, the modification rate is slower for exposure to soft X-rays. The highest radiation stability is shown for alizarin and, on the contrary, azurite and malachite experience a progressive chemical reduction of Cu^{2+} to Cu^+ . The reduction of copper takes also place in the azurite tempera, while the proteins and lipids of the egg-yolk binder of azurite and alizarin temperas are subjected to degradation by irradiation with photons and ions. By employing XPS, the cleavage of C–N, C–O(H) and C=O bonds has been identified in the egg-yolk temperas.

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1. Introduction

The observation of beam-induced changes during the characterization of cultural heritage materials by intense radiation sources (synchrotron radiation, ion and laser beams) has revealed the necessity of studying radiation damage mechanisms and has encouraged the development of mitigation strategies [1]. Both issues are relevant for the analysis of paintings, given the known sensitivity of pigments and painting materials to irradiation by proton induced X-ray emission (PIXE) [2 and references therein], by synchrotron X-rays [3] or by lasers [4–7]. The assessment of damage of Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$) and zinc white (ZnO) pigments following irradiation by synchrotron X-rays [3,8], and of lead white pigments by protons in PIXE [2,9], exemplify a recent approach oriented towards the analysis of radiation-induced side effects in pictorial pigments, their recording for future studies, as well as the minimization of their impact. In the case of lead white pigments ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), structural and chemical modifications induced by PIXE have been identified, and these include dehydration and, under high irradiation dose and current, the transformation of the original lead carbonate to lead oxide [2,9]. Apart from controlling the irradiation conditions, and considering the physical and chemical characteristics of the pigment, the full paint complexity seems to

determine the irradiation impact. The photoreduction of Prussian blue was shown to be dependent on the interactions with the surrounding materials. The photosensitivity was higher when Prussian blue was mixed with zinc white and diluted or constituted by particles of small size [3]. Furthermore, the degradation of the cellulosic fibre substrate, where the paint was applied [8], seems to produce ambient conditions that trigger the reduction of the pigment, suggesting that the mitigation strategies should be targeted on the substrate (especially if the latter is organic). On the other side, the possibility of early detection of irradiation-induced alterations of painting materials is advantageous for the development of mitigation strategies and a surface-sensitive technique can be suitable for this purpose. X-ray photoelectron spectroscopy (XPS) can provide the elemental composition, chemical state and electronic state of the elements present within the uppermost 1–10 nm of a substrate. This analytical technique has been employed occasionally to identify aging effects of pigments used in artworks, as well as to study the degradation induced by irradiation with X-rays, protons and laser photons [9–13]. The main objective of the present work is to apply the XPS technique to the analysis of a selection of traditional painting materials in order to determine experimental conditions that minimize the impact of exposure to radiation, and to evaluate the first indications of induced radiation damage which might be of practical interest for the analysts and researchers working in the field of cultural heritage. Supplementary characterization by selected analytical techniques (as proposed explicitly in the following sections) is considered

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very valuable but lies beyond the scope of the present study. The study has focussed on a representative selection of pigments, of inorganic nature as azurite, malachite, and organic as alizarin. These pigments with three different primary colours of blue, green and red respectively have been commonly employed in the traditional painting practice.

In this study, XPS is used to characterize pure malachite, azurite and alizarin pigments and their egg yolk temperas, as well as to follow as a function of the irradiation time, the induced chemical modifications by prolonged exposure to soft X-rays (with maximum doses ranging from $\sim 1.2 \times 10^{17}$ to $\sim 3.4 \times 10^{17}$ photons cm^{-2}) coming from the same source of the analytical equipment.

In addition, this technique is employed to detect the immediate chemical alterations in the copper based pigments and temperas produced by successive exposures to an Ar ion source. A comparison of the irradiation effects induced by photons and ions is also provided. The work is focused on the assessment of alterations at the early stages of damage following irradiation, before a surface modification is observed by visual inspection. This study has obtained further insight into the initial chemical processes of degradation, through the identification of specific chemical functional groups that are prone to alteration following irradiation of painting materials.

2. Material and methods

2.1. Samples

The irradiation study was performed on pure azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, Kremer), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, Aldrich) and alizarin (1,2-dihydroxyanthraquinone, $\text{C}_{14}\text{H}_8\text{O}_4$, Acros Organics) pigments and on azurite and alizarin tempera paint mock-ups, where the pigments were mixed with egg yolk and applied on primed panels. The selection of pigments is motivated by the fact that they are very often used in the traditional painting practice and because they constitute representative examples of pigments of inorganic and organic origin with three different primary colours of blue, green and red, while the tempera samples constitute a realistic reconstruction of traditional unvarnished paintings. The procedure of preparation of the tempera samples was described elsewhere [4]. The tempera mixtures were prepared by a qualified paint restorer following the traditional artist's recipes for tempera paints reported in [14]. The pigment was mixed with the fluid egg binder in proportions that produced a paintable paste and an adequate colour from the restorer's perspective. The tempera mock-ups were subjected to natural aging for fifteen years in the dark at ambient conditions (around 295 K and 50% R.H.) before the present study. Aged paint models have been used since it is commonly considered that, regarding the irradiation damage effects, they simulate better than a freshly prepared one the case of an historical painting.

Small rectangular samples of approximately $10 \times 10 \text{ mm}^2$ were cut from the panels. The pure pigments in powder form were pressed into pellets of 12 mm diameter at $8 \text{ ton} \cdot \text{cm}^{-2}$. All the samples, with a thickness of 1.5 mm (or less), were fixed to metallic sample holders for XPS measurements by double-sided adhesive graphite tape.

2.2. Analytical techniques

X-ray photoelectron spectra were acquired in two different spectrometers: a Leybold LHS-10 XPS with a CLAM2 analyser operated under a vacuum better than 2×10^{-8} mbar and a Specs XPS equipped with a hemispherical Phoibos 150 analyser operated under a base pressure of 8×10^{-10} mbar. All the spectra were recorded at a take-off angle of 90° using Mg $K\alpha$ radiation (1253.6 eV) at 135 W. The step energy was 1 eV for survey scans and 0.1 eV for high resolution ones. The constant analyser pass energy for high-resolution scans was 50 eV in the CLAM2 analyser and 20 eV in the Phoibos 150 analyser, and 200 and 100 eV respectively for wide scans. The binding energy (BE) values were charged-corrected to the adventitious C 1s signal, which was set

at 284.6 eV. High-resolution spectra were fitted with pseudo Voigt line profiles after combined Shirley-linear or Shirley background subtraction (depending on the analysed region) using the CasaXPS software (version 2.3.16). The Lorentzian/Gaussian mixing ratio and FWHM were fixed at the same value along the series of spectra. The quantification of Specs XPS data includes the transmission function correction, the escape depth compensation and the relative sensitivity factors (CasaXPS RSF library) according to the spectral evaluation procedure of the selected software. Quantification of Leybold XPS data uses the relative sensitivity factors from Wagner et al. [15].

The X-ray irradiation alterations in each sample were assessed by recording successive high-resolution spectra on the same spot. The continuous exposure to X-rays of each sample varies between 24 and 59 h. The X-ray beam irradiates an area of about 1.5 cm^2 , as measured by the beam spot size on a phosphor sample. The distance of the sample to the X-ray gun is approximately 4 cm in the Specs system (due to the sample holder block size) and 2.5 cm in the Leybold XPS system. The flux of Mg $K\alpha$ X-rays reaching the samples has been estimated by comparison with the work of Pepper and Wheeler [16] and having into account the attenuation by the $2 \mu\text{m}$ thick Al window. The obtained values are $\sim 1.2 \times 10^{12}$ photons $\text{cm}^{-2} \text{ s}^{-1}$ for the Specs equipment and $\sim 3.4 \times 10^{12}$ photons $\text{cm}^{-2} \text{ s}^{-1}$, for the Leybold XPS system. For the copper pigments, the X-ray irradiation studies were performed at the same power conditions (135 W), both in the Leybold set-up and at the Specs XPS chamber. Following X-ray exposure, the observed spectral changes were equivalent in both set-ups, allowing the generalization of the obtained results. In turn, alizarin pigment and tempera were analysed in the Leybold XPS system.

Additional Ar^+ bombardment experiments at 1 keV, followed by XPS characterization, were performed in the analysis chamber where the Specs XPS system is installed. The ion current was set to 10 mA for the malachite pigment and to 1 mA for the azurite tempera. The focused ion beam was raster scanned over the sample surface for a total bombardment time of 60 min for each sample, applied in short treatments of 5 or 10 min duration. After each short treatment interval, XPS spectra were immediately acquired to follow the induced modifications. The results presented in the next section concerning the copper-based pigments, azurite and malachite, display the spectra acquired in the same Specs XPS chamber, for better comparison of the effects induced on the studied samples following irradiation with both X-rays and Ar ions. The total acquisition time for each spectrum (see Table 1) was selected to avoid changes during and among accumulated scans, while trying to get the optimum signal-to-noise ratio.

3. Results and discussion

3.1. Azurite and malachite pigments

Fig. 1 shows the effects of X-ray irradiation on the Cu 2p core level XPS spectra of azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) at different exposure times up to nearly 56 h and a dose of 2.4×10^{17} photons cm^{-2} . For clarity, the spectra are presented vertically displaced. At short exposure times, the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks are located at 934.6 eV and 954.4 eV, respectively, and two intense shake-up satellites are observed at ~ 944 eV and ~ 962 eV. All these features are characteristic of Cu^{2+} [17]. By

Table 1
Total acquisition time (in minutes) for each selected core level XPS spectrum.

Irradiated samples	Cu 2p	C 1s	O 1s	N 1s
Azurite	25	10	6	–
Malachite	25	10	6	–
Alizarin	–	19	8	–
Alizarin tempera	–	10	15	45
Azurite tempera (X-rays)	70 ^a	7	11	30
Azurite tempera (Ar^+)	70	7	14	32

^a 12 min. for the first spectrum of the series.

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