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XANES analysis of Fe oxidation state in artificially aged Byzantine iron gall inks-A preliminary study

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Iron gall inks have been widely employed in West Europe since the Middle Ages thanks to the simplicity of the recipes and the difficulties to be removed, it was so widespread that many different recipes can be found. Instead, very little is known about Eastern iron gall ink recipes and especially about Greek Byzantine recipes. The ingredients composing these inks are plant extracts containing tannins, iron sulfate, and a binder, usually gum Arabic. The presence of metal ions can cause precipitation with tannins. The main issue with these organometallic solutions is that they get easily oxidized and can interact in many ways with the substrate (usually paper or parchment) [1]; oxidation causes fading, and the impossibility to read the documents [2]. Moreover, a byproduct of the formation of iron gall ink is sulfuric ions, which cause an acidic pH in the documents written with these inks [3, 4]. The chemical complexity of these compounds contributes to color variation, whereas the environmental conditions influence the formation of degradation products and their interaction with the substrate.

In this work, we will present the preliminary XANES analyses performed on different iron gall ink mock-ups, prepared following two historic Byzantine recipes, dating to the first decades of the 15th century. A unique prescription, mentioned in Codex Vaticanus graecus 914, ff.2r describes the preparation process, of a black and a blond iron gall ink. Each mock-up was prepared on handmade hemp paper and it was thermally artificially aged to simulate the changes that can occur in old writings.

The iron gall inks have been previously analyzed by means of Raman spectroscopy and SEM-EDS [5] to characterize the corrosive products and elucidate the degradation process. The present XANES investigation aims to evaluate the changes in the oxidation state of Fe ions through the comparison of unaged, naturally, and artificially aged iron gall inks. The XANES measurements have been carried out in fluorescence mode at the XRF beamline of the Elettra synchrotron. The K-edge line of iron has been scanned with a Si 111 monochromator; the spectra have been collected on the XANES region from 9600 to 7300eV. The study of the pre-peaks and of the edge position has allowed us to evaluate the changes in oxidation with the aging process. This work is the first step of a more comprehensive project that will probe an in-depth insight into the changes occurring in these organometallic inks.

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