An innovative multi-analytical approach for the characterization of Iron-gall inks

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Introduction

Iron-gall inks (IGI)were the most common writing material starting from the late Middle Age until the beginning of the 20th century. Their use ranges from everyday letters and indenture documents to some of the most important scripts and drawings in human history, including precious medieval illuminated manuscripts, the musical composition of J.S. Bach and Beethoven, and sketches by Rembrandt and Van Gogh (Lee et al., 2006). Such a ubiquitous use of IGI in the past has led to a great variety of recipes for their production, showing differences not only in the ingredients used but also in the production process.

Generally, all IGI have three basic ingredients (Díaz Hidalgo et al., 2018): galls, as natural polyphenol source, vitriol to create the colored metal-polyphenol complex, and Arabic gum as a binder to maintain the complex dispersed in the aqueous medium and to improve the writing properties of the ink by modifying its viscosity. The special attention given to the study of iron gall inks is due to their high acidity. By the reaction between polyphenols and iron sulphate, sulfuric acid is developed and with time, its concentration can increase yielding to a very low pH (c.a 1.5 -2) at the interface parchment/ink. The formation of this leads to the damaging of the parchment becoming fragile and brittle until holes were formed (Fig 1). Moreover, for reviving scriptures that tended to discolour, it was common to intervene by spreading a infuse of gallnuts, in order to reform the iron(III)complex. This procedure revealed to be very disruptive for the support.

Fig.1 Fragment of parchment discovered by the Merowe Dam Archaeological Salvage Campaign in 2007, on the island of Sur above the Fourth Nile Cataract in Northern Sudan showing the presence of strong degradation (holes).

The present work is a preliminary study dedicated to the development of an innovative multi-analytical procedure for the characterization of IGI with special focus on the study of the chemical structure of polyphenols-iron complexes in IGI, their properties, and degradative behaviour. The in-depth study of the chemical structure of the complexes present in IGI can have an important role in the understanding of the degradation patterns and therefore in the definition of new conservation strategies for manuscripts.

Sample Preparation and Experimental Procedure

The iron-polyphenolic complexes present in IGI are resulting from the interaction of iron(II) cations with a series of phenolic and especially polyphenolic substances present in the gallnuts water extracts. Gallotannins and their hydrolyzation products, such as gallic acid, are known to be abundant in gallnuts (Perron and Brumaghim, 2009). However, the actual range of possible organic compounds present in gall extracts includes also ellagitannins, proanthocyanidines, flavonoids, and cinnamic acids. As all these organic compounds are capable of forming iron-complexes with different structures and properties, oak galls with different characteristics in terms of provenance, botanical species and maturity were used (e.g. Italian vs Turkish gallnuts). For this reason, as to access this variability, the first part of the study involved the preparation and the characterization of aqueous alls extracts starting from different galls typologies.

The formation of the dark insoluble complexes follows a double step mechanism (Ponce et al., 2016). In the first step, the polyphenols present in the extract act as organic ligands binding the iron(II) cations. In the second step, Fe^{2+} is naturally oxidized by atmospheric oxygen into Fe^{3+} resulting in the final insoluble dark complex (Fig.1).

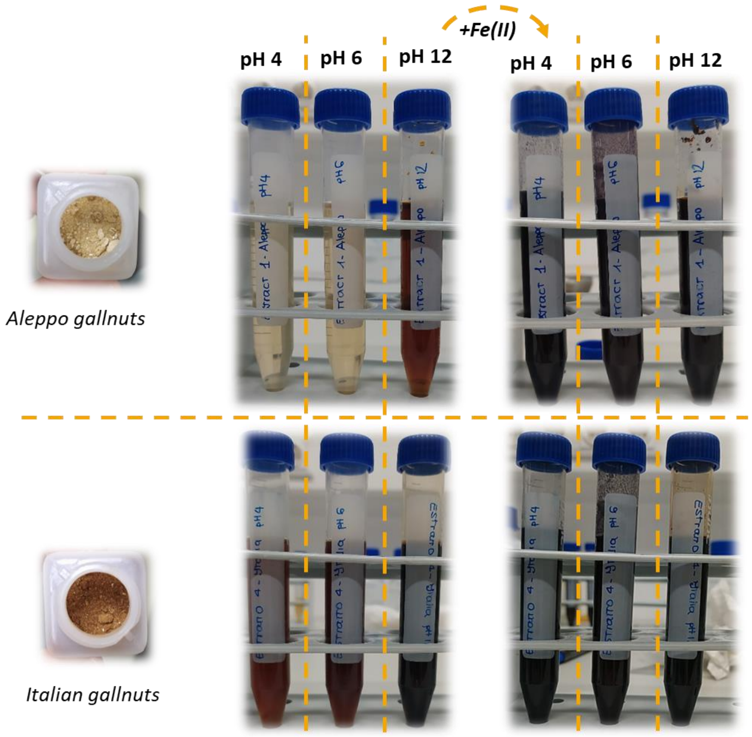

Fig.2: The formation of the Fe-Polyphenols complexes in pH-controlled conditions starting with the galls water extracts

The first step of this mechanism is strongly dependent on the pH (an index of the acidity or alkalinity of aqueous solutions) which drives the protonation/deprotonation equilibria of the polyphenols and therefore the final structure of the complexes. This aspect has never been properly addressed in studies upon IGI before. Therefore, in order to access these structural differences, iron-polyphenolic complexes have been synthetised in controlled pH conditions: both gallic acid and the previously mentioned freeze-dried gallnuts extracts have been dissolved in buffer solutions at pH 4, pH 6, and an alkaline solution at pH. Subsequently, a freshly prepared $FeSO_4{\cdot}7H_2O$ solution was rapidly added. The resulting complexes were kept in a dark place for 5 days, allowing the oxidation and thickening. Finally, the insoluble complexes were isolated from the solution in an optimized procedure including centrifugation and drying.

The analytical procedure is divided into two main steps:

- *Step 1 – The use of Nuclear Magnetic Resonance (NMR) techniques in the study of oak galls water extracts*

Once prepared, the oakgalls water-extracts have been freeze-dried (physical method for water removal performed to obtain dried powders suitable for the analyses) and the resulting powders were analysed with two NMR techniques: Heteronuclear single quantum coherence spectroscopy (HSQC) and ^{31}P NMR, an innovative methodology which, using a suitable phosphorous-containing reagent, enables to distinguish, characterize, and quantify the different types of phenolic groups present in the sample.

➢ *Step 2 - Potentialities of Electron Paramagnetic Resonance (EPR) in the study of iron-polyphenolic complexes*

The iron complexes were instead characterized via Continuous Wave (CW) – EPR experiments. Giving information about the coordination environment of Fe^{3+}, EPR spectroscopy enables to better explore the actual range of iron complexes present in IGI and, eventually, to detect organic radicals.

Preliminary Results

Both NMR and EPR are spectroscopic techniques (analytical methods based on the interaction between matter and radiations) that can provide useful information for the characterization of different chemical compounds. The characterization of the gall extracts via NMR techniques highlighted the complexity of organic compounds present: different kinds of polyphenolic compounds have been detected together with an important amount of sugars (both free sugars and esterified with galloyl units) and traces of aliphatic compounds, probably related to waxes.

Concerning the preliminary results obtained with CW-EPR spectroscopy, two important aspects should be highlighted:

1. EPR measurements clarified the Fe(III) coordinative environment for the complexes prepared at different pH condition and the results are coherent with the expectation based on literature (Zoleo et al., 2010) (Fig. 2).
2. No organic radicals were detected in the spectra acquired. This evidence suggests that the process of organic radicals formation is promoted after strong aging conditions (e.g. light, temperature, humidity, etc.). The formation of radicals is an extremely important point to study the degradation processes of IGI since they are reactive areas in which subsequent undesired chemical reactions could take place.

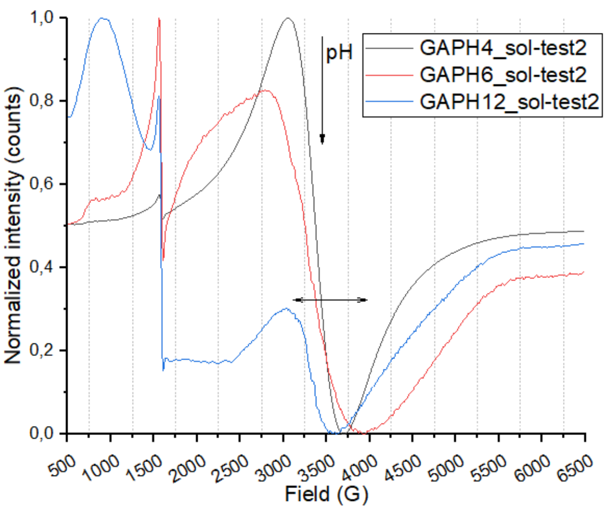

Fig.2 EPR spectra acquired at room temperature on solid iron-GA complexes prepared in different pH conditions.

Conclusions & Future developments

The multi-analytical approach presented in this work, allowed deepening the knowledge about the molecular composition and the paramagnetic species present in the ink solutions. The NMR investigation allowed us to detect and classify the actual range of organic substances present in the galls extracts. This piece of information is extremely important to understand the diversity of coordination compounds structures present and the general composition of iron-gall inks. The EPR data instead highlighted different coordination environments of iron within the complexes varying with the pH of the solution in which they were formed. The complementarity of the chosen analytical methods will help the understanding of the deterioration pathways of the inks, as well as the detection and localisation of possible reactive radicals responsible for aging reactions. The preliminary results of this work constitute the starting point of a more extensive project entitled “Synergetic Interactions of Writing Materials” (FWF Project n. P 35484-N).

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Conflict of Interests Disclosure

The authors declared not to have competing interests.

Author Contributions

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