Step by step: Modelling as a first key to introduce an indirect method of studying heritage inks

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Manuscripts written in inks which are a combination of soluble compounds of transition metals with plant tannins are a large part of collections in archives, libraries and museum throughout the world. It has been noticed that, despite a generally consistent concept of their production, the inks are characterized by a wide variety of chemical compositions, mostly as a result of randomness in the proportions and addition of unusual compounds, such as wine or honey. Lack of reproducibility and significant changeability of inks' compositions often results in their instability, leading to the degradation of paper or parchment substrate.

In 2005 Neevel proposed a use of colorimetric reaction of iron (II) ions with a 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) ligand for the evaluation of ink corrosion risk in manuscripts [1,2]. During the use of an indicator paper soaked with the ligand, ions present in the ink migrate to its surface. Presence of iron (II) ions is manifested by a strong colorimetric effect, while others can be detected with advanced measurements, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [3]. It seems that the study of indicator papers could enable indirect and non-invasive measurements of inks' elemental composition. However, it requires a knowledge of particular individuals' effectiveness in migrating into the indicator papers [4].

Figure 1. Model inks and gall nuts - a natural source of tannins (photo by B. Wagner)

The aim of the ALINA project is to engage machine learning methods in encoding the chemical information hidden in the indicator papers used by the conservators during the examination of the manuscripts. The baseline for the project requires creation of a database containing diverse model metal-tannin inks and corresponding indicator papers. Therefore, a large group of inks with compositions based on the literature and their variations was produced. The inks were manufactured by mixing a gall nut extract with gum arabic and salts of iron or other metals, e.g. copper, zinc, lead, tin or cobalt. 102 mock-ups of the paper inscribed with the obtained inks were aged in the conditions of increased temperature and alternating humidity. The actual composition of the obtained inks and migration of their compounds to the indicator papers will be studied with the use of the spectral methods, including LA-ICP-MS and X-Ray fluorescence (XRF).

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