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Non-destructive study of iron gall inks in manuscripts

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ABSTRACT

The aim of this research is to establish an effective procedure of iron gall ink characterization using complementary non-destructive methods. By this, it is possible to better understand correlation of chemical composition of the inks and the state of preservation of iron gall ink manuscripts, as well as the effects of conservation treatment performed upon them. This study was undertaken on a bound 16th century manuscript comprised of different types of paper and ink from the National and University Library in Zagreb. Analytical methods used included Particle Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF). Paper fibers were identified by optical microscopy and the degradation state, as well as ink differentiation, transit metal migrations and detection of stains, with ultraviolet (UV) and infrared (IR) photography. The techniques applied on original writing materials gave important information about paper and ink composition, its preservation state and efficiency of conservation treatment performed upon them.

1. Introduction

Iron gall inks were the most widespread writing ink in Europe from the early Middle Ages until the 20th century. Even though chemical composition of each ink type is different, all of them have three main components in common: Fe (II) sulphate, gull nuts (tannin) and gum Arabic. There are more than 250 known historic recipes for iron-gall inks on European soil alone which count numerous different additives to the primary ingredients [1]. Apart from that, chemical composition of the inks is influenced by the state of each ingredient's purity, as well as the environment in which the manuscripts were kept after being made.

Under certain conditions, iron-gall inks can cause a significant degradation of its paper support. Corrosion of iron gall inks is a long known process that threatens a vast part of the worlds written heritage since the degradation of manuscripts is fast and the damage irreversible. It comes about by two separate chemical mechanisms, one being the hydrolysis of cellulose in paper due to acidity of the ink, and the other being oxidation of cellulose which results in its depolymerization [2].

The most tested and widely accepted conservation treatment for damaged iron gall ink manuscripts is the calcium phytate/calcium bicarbonate treatment [3]. After an optional washing treatment, it consists of immersing the manuscript in a calcium phytate solution for chelating, followed by immersion in calcium bicarbonate solution for neutralization. Optional infills are then made by one of the standard restoration methods.

2. Experimental

2.1. Manuscript selection and sampling

A bound 16th century manuscript from the Manuscripts and Old Books Collection of the National and University Library in Zagreb, with additional letters inserted on the back of the book block was chosen for this study because of its several characteristics. These transcripts of letters from pontifical delegate Flamino Delfini sent to notables at the end of the 16th century reveal very interesting facts about Croatian history and political sovereignty. Their value in present day Croatia comes not only from their age and uniqueness, but also from their historical and political significance.

The manuscript is comprised of three different types of handmade paper varying in thickness, colour, surface roughness, papermaking mould matrix and watermark. Each type of paper was written upon with different type of ink. Since they were all dated in the same year and bound together, it can be assumed they have undergone similar environmental conditions trough time.

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The manuscript exhibits different stages of degradation regarding paper and ink types, its location in the book block and distance from the outer edges where damage and soiling are most prominent.

Microsamples for fiber analysis were taken in a way that the ink samples do not interfere with manuscript legibility and that the blank paper samples are representative (not contaminated with stains, migrated soluble compounds and dust particles). Different corrosion states of inks were also taken into account during sampling. All non-invasive techniques on each piece of paper were performed in approximately same spots.

2.2. Imaging diagnostics

UV and IR photography were used for ink differentiation, perception of migrations and the extent of paper degradation examination (Fig. 1). A high-resolution camera with digital sensor (Nikon D300) with Af Nikkor 50 mm f/1.4D lens was used to record UV and VIS images. Four longwave UV lamps (350 nm) served as the UV source pointed under 45° to the manuscripts. UV images were taken with Cokin P006 filter on the camera lens. NIR images were taken with FujiFilm IS Pro camera and the same Nikkor lens. For images taken under standard bulb light, Heliopan IR filters of different wavelengths (780 nm/810 nm/1000 nm) covered the camera lens. No filters were used for images made with no visible light and two sets of 950 nm wavelength LED-diodes pointed to the manuscript under 45°.

2.3. Elemental analysis

Inks and paper supports were analyzed using the non-invasive PIXE and XRF techniques. The external beam PIXE measurements were carried out at the Rudjer Boskovic Institute (RBI) Tandem accelerator facility in Zagreb. External beam PIXE using proton beams of 2 MeV initial energy was performed on the selected spots on the manuscript. The beam with the final energy of about 1.65 MeV on target was collimated to the beam spot of 1 mm in diameter. X-rays were detected with 60 mm^2 RONTEC Si(Li) detector collimated to 30 mm^2 having resolution of about 150 eV at 5.9 keV. Samples were aligned in front of the proton beam with the help of a laser pointer and camera using data acquisition and sample positioning home-made software SPECTOR [4]. The beam current on the samples was kept as low as possible to avoid any possibility for radiation damage. It is estimated that the ion beam current on the target was at all times below 0.1 nA, although ion beam current was not measured directly but the Ar Kα X-ray yield was used as a measure of the relative ion beam dose on the target. A set of thin targets of SiO_2, KCl, CaF_2, Ti, V, Cr, Fe, and Cu was used to evaluate the Minimum Detection Limits (MDL) for thin targets. Based on the related measured spectra we estimated respective MDLs to below 10 μg/cm^2. Thick standard Reference Materials (SRM) were also measured, like IAEA-Soil 7 and Montana Soil. MDLs estimated from these thick standards for low Z elements like Al and Si are at the level of below 1 w%, and for elements between K and Zn are at the levels between 20 and 40 ppm.

XRF measurements were conducted using a custom made portable XRF instrument, at the Department of Conservation-restoration at the Academy of Fine Arts in Zagreb. It consists of a 50-kV Rh transmission excitation tube (Moxtek, USA) and a Peltier cooled silicon drift detector (Amptek, USA) with energy resolution of 145 eV at the Mn Kα excitation line. Depending on the analytical needs, the device can provide either mili or micro X-ray beam for sample excitation, by employing a motorized collimator interchanger to switch between a pinhole collimator (spot size ca. 1.5 mm) and a polycapillary lens (IfG, Germany, spot size ca. 45 μm). The operating parameters for tube voltage and anode current during the measurements were set to 35 kV and 100 μA, respectively, and the acquisition real time was 100 s. The diameter of the beam was set to 1.5 mm. For easy and reproducible alignment of the sample in front of the X-ray source and the detector, a two laser beam system is used. The lasers are aligned in such a way that the point of their beam intersection coincides with the cross-point of the X-ray tube and detector axes (Fig. 2). The MDLs for XRF were not precisely determined, because this method was primarily used for on-site screening before choosing which manuscript parts will be further investigated with PIXE spectroscopy, and for basic relative comparisons between different ink types before and after the treatment.

Both PIXE and XRF have already shown to be efficient, precise and rapid multielemental analytical tools for cultural heritage examination [2,5–8]. When comparing the two methods, it becomes apparent that PIXE and XRF are quite complementary and there are many benefits regarding their analyzing capabilities

Fig. 1. Manuscript photographed in NIR (950 nm), UV and VIS respectively. Recorded ink migrations and document preservation state are comparatively shown. The UV photograph shows a thick halo of absorbed UV radiation around the original pen stroke (best seen in the NIR photograph) indicating the spread of ink component migrations. Strong radiation absorption, as well as some fluorescence in the location of the text verso, is also seen. No further stains, burn-troughs or cracks have been revealed under UV or NIR that has not already been detected under day light.

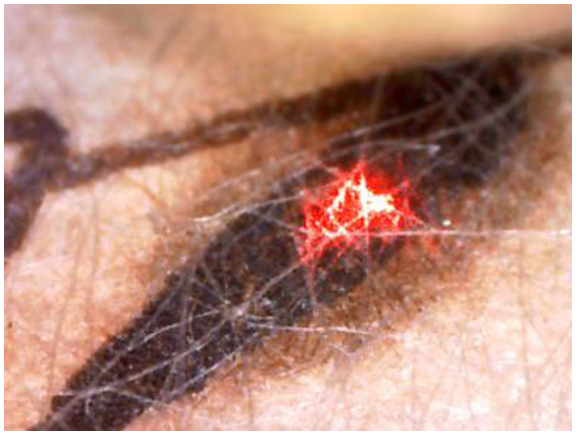

Fig. 2. Photo taken with a built-in microscope (94x magnification) during XRF measurements. Red laser dot marks the spot being irradiated with the primary X-ray beam. Ink degradation and line broadening is clearly visible.

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