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Investigating the deterioration and corrosion of ancient Iranian manuscripts using ion beam analysis techniques

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HIGHLIGHTS

- Micro-ion beam techniques, applied to identify the factors responsible for the deterioration of Iranian ancient manuscripts.
- The micro-PIXE analysis reveals that copper is the main element that forms the decoration of this manuscript.
- The results demonstrate that the black ink in this manuscript is carbon-based and does not contribute to the corrosion.
- The micro-RBS analysis indicates that the ink has fully permeated and diffused in the bulk of paper.

ABSTRACT

In this study, few number of pages from ancient manuscripts that have undergone significant damage, were analyzed using micro-Ion Beam Analysis (micro-IBA) including micro-PIXE, micro-RBS, and micro-STIM to identify the factors responsible for the deterioration of these manuscripts. The micro-PIXE results indicate that the yellow decoration ink that has suffered severe corrosion is composed of a combination of Cu and Zn pigments. Moreover, the micro-PIXE analysis reveals that Cu is the main element that forms the decoration of this manuscript. The studying the various Cu pigments, it was discovered that one of the Cu pigment types, which is made up of Cu mineral elements, is verdigris or copper acetate (II) with the chemical formula $\text{Cu}(\text{CH}_3\text{COO})_2$. This pigment is highly susceptible to environmental moisture. As a result, favorable environmental conditions such as optimal humidity and elemental composition like Cu can cause local oxidation of paper to destroys the paper substrate. Furthermore, the results demonstrate that the black ink used to write the text in these manuscripts are carbon-based and do not contribute to the corrosion of the paper. However, the micro-RBS analysis indicates that the ink has fully permeated and diffused in the bulk of paper and it increased the corrosion effect.

KEYWORDS

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Ink and paper
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Micro-RBS
Pigment

HISTORY

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1 Introduction

Throughout numerous years, paper has served as a prominent medium for documenting scientific and cultural accomplishments (Abdullatef et al., 2023; Idjouadiene et al., 2021). Consequently, the significance of these manuscripts is evident to all. Paper primarily consists of cellulose, with the addition of minor quantities of mineral and organic additives like starch. A significant and critical issue that poses a threat to ancient paper documents, books, and manuscripts stored in libraries and personal collections is the gradual deterioration and erosion of the paper material (Abdullatef et al., 2023; Faubel et al., 2007). Numerous factors contribute to the deterioration and loss of paper documents. Some of these factors are associated with the

composition of the paper itself or the chemicals applied to it, while others are influenced by environmental conditions like humidity and temperature (Titubante et al., 2020). Throughout history, soot or carbon black (Goltz, 2012; Christiansen et al., 2017) and iron-gall inks have been extensively employed for writing and documenting human ideas (Duh et al., 2018). The well-documented phenomenon of paper degradation and corrosion resulting from Fe content in iron-gall inks is widely recognized (Gore et al., 2017). Numerous studies have investigated this type of corrosion (Gore et al., 2017; Haddadi et al., 2023; Adami et al., 2016). Recently, another factor contributing to the deterioration and loss of paper substrates in certain documents has been attributed to the presence of transition elements, such as Fe and Cu, in the compounds used

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Figure 1: An optical image of a page from this manuscript that shows a significant deterioration (the manuscript containing verses from Dua Sabah).

(Adami et al., 2016; Pessanha et al., 2012; Kamngießer et al., 2004; Šelih et al., 2007; Fazio et al., 2020). An examination of handwritten documents in our country reveals that numerous paper manuscripts are corroded and face the risk of destruction. Given that the composition of paper and composite materials significantly influences corrosion, identifying the constituents of both is crucial for preventing this process (Adami et al., 2016). Our research focuses on investigating the factors contributing to the deterioration of an ancient manuscript. In the present study, ancient manuscripts from the Qajar dynasty (18th to 19th century AD) from Iran, written in Arabic, were analyzed by micro-IBA. The manuscripts containing verses from different prayers such as Dua Kumayl and Dua Sabah. Dua Sabah, is one of the prayers that Imam Ali (AS) used to recite after his morning prayers. This prayer is composed of eloquent and literary phrases, but it encompasses many mystical themes. We employ elemental analysis to determine the paper and composite components. By studying samples from damaged areas across different pages, using techniques like micro-PIXE, micro-RBS, and micro-STIM, we aim to uncover the relationship between corrosion causes and the chemical composition of the composite used in this manuscript.

2 Experimental

The Micro-Ion Beam analysis was performed with micro-probe system manufactured by Oxford Instruments using the 3 MV Van de Graaff accelerators at the Nuclear Science and Technology Research Institute in Atomic Energy Organization of Iran (Agha-Aligol et al., 2007; Oliyai et al., 2009; Watt, 1997). The samples were analyzed in a vacuum chamber using a beam of 2.2 MeV protons focused to a diameter less than 10 μm . The beam current was in the range of 30 to 50 pA. Micro-PIXE or “Particle Induced X-ray Emission in micron-scale” was performed to measure the elemental composition of papers and inks. During the interaction of the high-energy proton with the analyzed samples, the characteristic X-rays of the constituent elements are emitted from the samples. The energy of

X-rays of each element is specific, which can be used to detect the elements are presented in the sample. Also, the number of X-rays with specific energy determined the concentration of the elements within the sample (Johansson, 1989; Nastasi et al., 2014). Characteristic X-rays were detected using a Si(Li) detector with an active area of 60 mm^2 positioned at an angle of 135° relative to the incident beam direction and with an energy resolution of 150 eV for Fe- K_{α} . Moreover, the spectra were processed using the GUPIXWIN package to obtain the elemental composition of the glass objects (Russell et al., 2018). Scanning Transmission Ion Microscopy (micro-STIM) measurements were carried out using a surface barrier detector at angle of 20° to the incident beam direction. Moreover, the Rutherford Backscattering Spectrometry (micro-RBS) was used to determine the thickness and redistribution of the ink in the paper with a surface barrier detector placed at 160° scattering angle to the incident beam direction.

3 Results and Discussion

In this research, different samples from the ancient manuscript containing verses from Dua Kumayl and Dua Sabah, have been chosen for examination and analysis. The manuscripts originates from the Qajar dynasty period (18th to 19th century AD) and is written in Arabic. The optical image of one of the manuscript pages is presented in Fig. 1. As depicted in the figure, the manuscript features include dark yellow lines used for calligraphy and ornamentation across all pages. However, as clearly illustrated in the figure, the paper near these yellow lines has suffered from corrosion. In certain sections of the manuscript, this corrosion has advanced to the point of causing visible cracks, as evident in Fig. 1-b. The objective of this study is to explore the factors contributing to the deterioration and corrosion of the manuscript. Additionally, we aim to establish a connection between the causes of corrosion and the chemical composition of the pigments employed in the decoration lines within this manuscript.

The samples selected for this investigation were carefully chosen to minimize any potential harm to the pages.

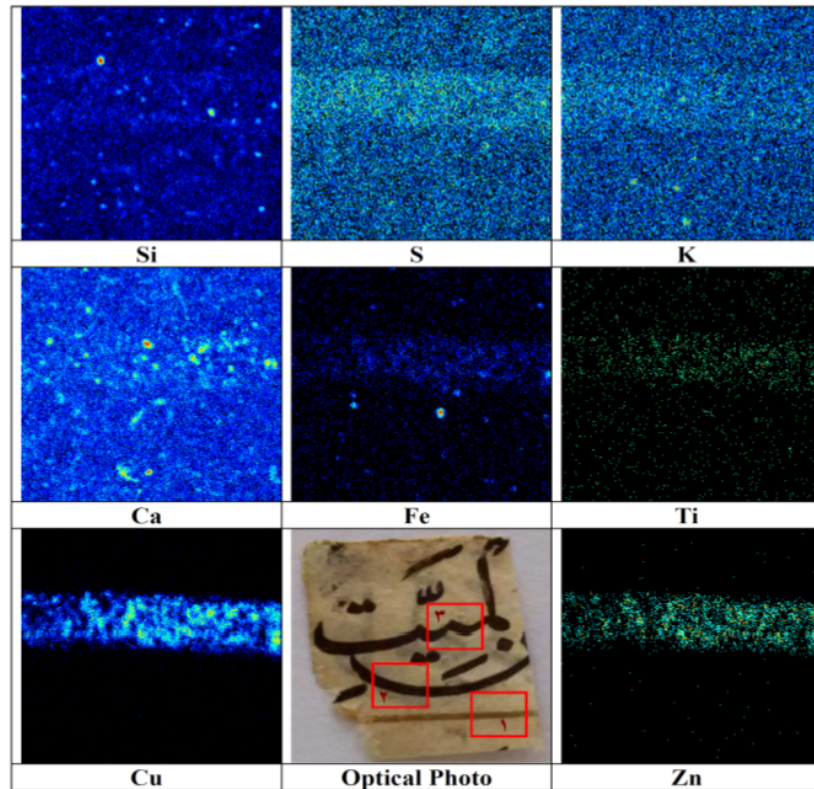


Figure 2: The distribution of micro-PIXE elemental maps for a sample in the analyzed manuscript in area with/without ink (area 1). The optical image of the sample and different analyzed regions is shown in the figure. The dimensions of the analyzed regions are $2.5 \times 2.5 \text{ mm}^2$.

Consequently, these samples were taken from approximately less than 1 cm^2 within the manuscript, and various areas of these samples were subjected to analysis. Fig. 2 illustrates the elemental distribution maps for paper and the decoration line in analyzed sample. The optical image of sample displays various analyzed regions, marked by red squares. In this sample, three distinct regions were examined. Focusing on region 1, the elemental distribution maps reveal that the decoration line mainly consist of Cu and Zn elements. A comparison between the optical image of region 1 and the micro-PIXE elemental maps, confirms that Cu and Zn are exclusively abundant within the area where the decoration lines are present, while they are absent outside these line. Furthermore, the elemental distribution maps depicted in Fig. 3 reveal the presence of trace amounts of S, Ti, and Fe within the decoration lines (Virro et al., 2008; Remazeilles et al., 2001). An additional significant finding arising from the elemental maps distribution of non-uniform elemental maps of Ca in the analyzed areas. The X-ray map of Ca gives interesting information about the surface of the paper and also the fabrication process (Agha-Aligol et al., 2007). Usually, Ca concentration in the paper is not uniform and X-ray maps show islands of high calcium content. This effect is probably due to a Ca compound such as bone powder, which would have been used for filling and treating the paper (Agha-Aligol et al., 2007). The composition of the black ink was investigated by examining additional regions within the analyzed sample, specifically regions 2

and 3. The analysis findings indicate that Fe is absent in the black ink. Instead, the black ink is likely composed of carbon soot (Agha-Aligol et al., 2007; Burgio, 2021).

The X-ray spectra corresponding to the dark yellow ink and paper, specifically for region 1 within the analyzed sample shown in Fig. 2, have been displayed in Fig. 3. Clearly, when examining the two spectra in Fig. 2, the elemental contrast between the decoration line and paper becomes fully evident that Cu and Zn constitute the primary elements in the decoration lines, while other elements detected in the sample such as Mg, Al, Si, S, Cl, K, Ca, Ti, and Fe, compose the paper substrate.

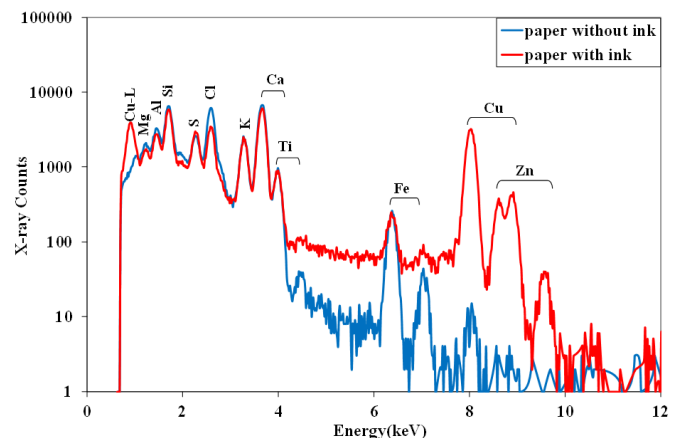


Figure 3: The micro-PIXE spectra obtained for region 1 within the analyzed sample shown in Fig. 2.

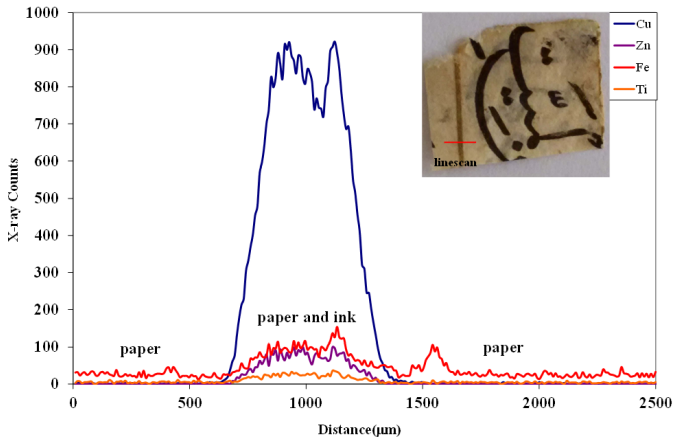


Figure 4: The elemental profile of line scan in the X direction, for the analyzed sample.

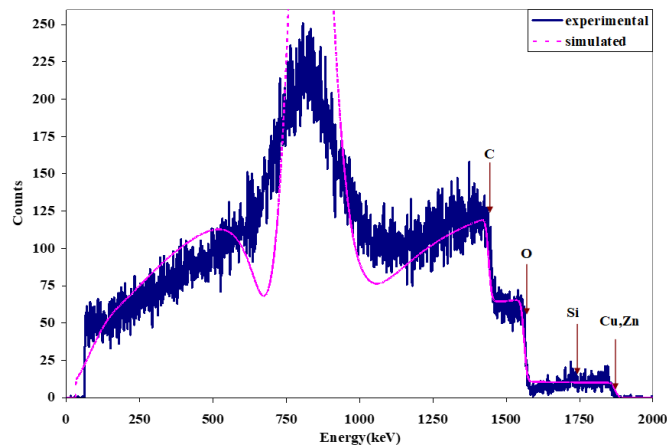


Figure 5: The RBS spectrum obtained from area 1 in the sample shown in Fig. 2 along with the simulated spectrum obtained using SIMNRA.

In Fig. 4, we observe the profile and distribution of Cu, Zn, Fe, and Ti within the sample under investigation. These distributions were obtained through linear scanning in the X direction. The figure is plotted based on the total number of characteristic X-rays recorded in the X direction, as depicted in the optical image of Fig. 4. Notably, this figure provides a clear differentiation between the elements present in the decoration lines and those constituting the paper substrate. Furthermore, it allows for a semi-quantitative analysis of the elemental composition of both the decoration lines and the paper substrate. Based on Fig. 4, the Cu concentration in the decoration lines is approximately ninefold higher than the Zn content. The Cu element profile in the scanning line exhibits non-uniformity and significant fluctuations due to ink diffusion within the paper. The findings from semi-quantitative analysis of ink and paper in ancient manuscript, as demonstrated earlier, indicate that these methods are adequate for assessing the elemental composition and identifying inorganic pigments used in different manuscripts. Micro-PIXE mapping and the semi-quantitative analysis of pigments indicate that Cu predominantly constitutes the applied pigment within

the decoration lines. Through analysis of various copper compounds, it becomes evident that one of the distinct types of copper pigments, composed of mineral elements, is verdigris or copper(II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$). This pigment exhibits high sensitivity to environmental moisture (Fazio et al., 2020). Hence, favorable environmental conditions, including humidity and an optimal Cu chemical composition, can lead to localized oxidation of paper or cellulose- the primary paper component- resulting in complete destruction of the paper substrate. The findings from our study align with previously published reports. These articles highlight Cu element as catalysts in the oxidation of cellulose and other related products. The observed corrosion, linked to Cu pigments, is understood as the detrimental impact on ancient papers when adorned with pigments containing transition elements.

In the recent study, Koochakzai et al. (2022) examined Qajar manuscripts from Iran (Koochakzai et al., 2022). Their results reveal that a golden pigment was used as a strip along the margins of the pages. However, some pages show damage to this pigment, suggesting the possibility of two different types of gold being used. Micro-XRF analysis indicates that the first type of golden pigment, which is not corroded, contains gold. In contrast, the micro-XRF spectrum of the second type of golden pigment shows peaks for Cu and Zn, indicating that imitation gold was used in some decorations of the Qajar manuscripts, which aligns perfectly with our findings. Additionally, research conducted by Mousavi et al. demonstrated that Cu alloy pigments were used as a substitute for gilding in illuminated manuscripts from the eighteenth to nineteenth centuries (Mousavi et al., 2015). A notable feature in these manuscripts was the transformation of metallic Cu pigments into greenish residues, and in some sections, the paper showed signs of degradation, appearing as brownish discoloration. Moreover, Aceto et al. conducted a study on the degradation of an alloy pigment found in an Italian manuscript from the early 19th century (Aceto et al., 2006). Using portable XRF and Raman instruments, they discovered that the green coloration is due to a significant degradation process that has changed the original composition of the pigment, which was an alloy of Cu, Pb, and Zn.

Furthermore, we employed the micro-RBS technique, to explore the penetration of the ink into the paper substrate and assess the depth of penetration, as well as to estimate the presence of light elements not measurable by micro-PIXE. Figure 5 displays the Rutherford Backscattering Spectrometry (RBS) spectrum (blue line) acquired from region 1 of the sample depicted in Fig. 2, as well as the simulated spectrum (pink dash line) generated using SIMNRA software. The figure clearly indicates that the main elements within the paper are light elements, specifically C, O and H. The atomic percentages obtained for these elements through fitting the experimental spectrum using SIMNRA.6 software are as follows: C \approx 29.3%, O \approx 23.2% and H \approx 46.3%. Remarkably, these values closely align with the atomic composition of cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$), and is consistent with it which constitutes the funda-

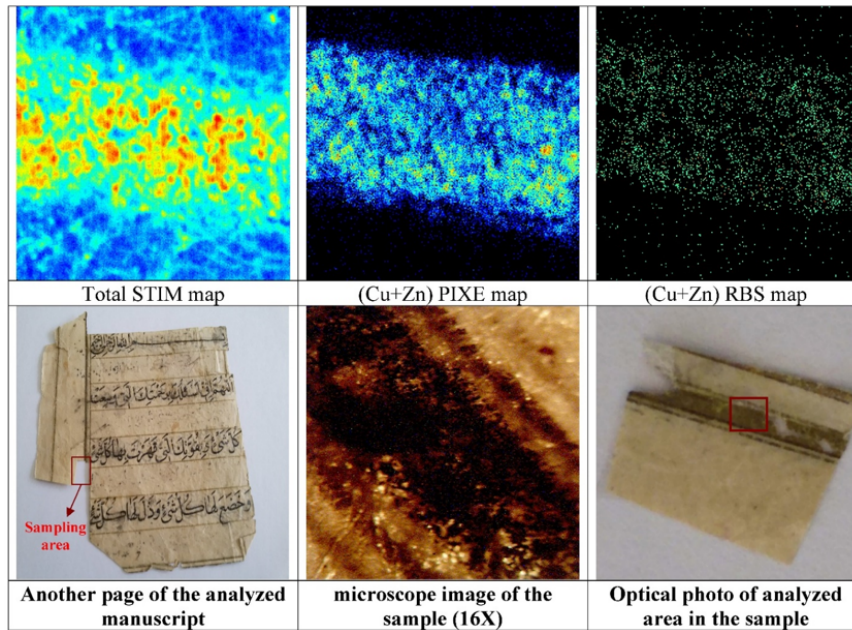


Figure 6: The micro-PIXE, micro-RBS, and micro-STIM maps for another analyzed sample in the manuscript. Also, the optical photo and microscope image with a magnification of 16X are shown in the figure (the manuscript containing verses from Dua Kumayl).

mental elements of paper (Mathayan et al., 2021). Moreover, Fig. 5 illustrates the presence of heavier elements—specifically Cu and Zn in the decoration lines. The atomic percentages for Cu and Zn are approximately 0.9% and 0.1%, respectively. Remarkably, these values consistent perfectly with the semi-quantitative findings from Fig. 4, where the ratio of Cu-to-Zn was approximately 9.

Furthermore, micro-RBS analysis reveals that the ink employed for decorating the manuscript has completely penetrated the paper substrate, seamlessly integrating with it. Had this not been the case, we would have anticipated observing a distinct peak corresponding to the ink layer, with a thickness proportional to the peaks width in the Fig. 5 spectrum. However, no such layer is evident.

By employing Micro-STIM technique, valuable insights into the mass density distribution at various depths within the thin sample like ancient manuscripts can be acquired. Figure 6 displays the result obtained from an additional sample of this particular manuscript. The sample analyzed using micro-PIXE, RBS, and STIM techniques, simultaneously. Furthermore, the figure displays both the optical image and the sampling location of analyzed from another page in the manuscript. Additionally, it includes an image of the analyzed area captured using a light microscope at a magnification of 16X. In this figure, it is apparent that the decoration line contains both Cu and Zn elements, as indicated by the elemental distribution obtained from the analyzed area. Additionally, the two-dimensional distribution image obtained from the micro-STIM reveals the heterogeneity of the analyzed region. However, in the STIM map, the fiber tissue forming the paper substrate is fully visible. Considering the well-defined dimensions of the analyzed area, one can estimate the dimensions of the fibers constituting the paper (Mathayan et al., 2021).

4 Conclusions

The current study demonstrates that elemental mapping using Micro-Ion Beam Analysis provides valuable insights into the composition and depth profiles of inks and papers utilized in ancient manuscripts. Based on the findings from micro-PIXE analysis, Cu is the predominant element constituting the decoration lines in this ancient manuscript. Under suitable conditions, such as humidity and with the presence of Cu in the inks, local oxidation of paper or cellulose can occur to complete destruction of the paper substrate. However, the findings also indicate that the black ink employed for writing this manuscript does not belong to the iron-gall ink category. Furthermore, by employing complementary techniques such as micro-RBS and micro-STIM, valuable insights regarding paper properties are ink profile inferred. Notably, it has been demonstrated that the paper exhibits non-uniform thickness.

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Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

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