CHARACTERIZATION of FOXING STAINS in EIGHTEENTH CENTURY BOOKS

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ABSTRACT

Foxing is a form of chromatic alteration of paper which appears as spotty or diffuse yellowish, brownish, reddish or blackish areas. Although the nature of foxing stains is not fully understood, microorganisms and metallic impurities (iron, copper, etc.) in paper have been considered the main causes of foxing formation.

This paper deals with the application of scanning electron microscopy (SEM) and elemental analysis for the presence of metals and/or microorganisms in foxing spots, found in eighteenth century books. The selected spots are also examined in normal and UV light to determine the relationship between the visual appearance of the paper and its chemical composition.

The conservation methods suitable for the removing of foxing stains and prevention of their recurrence are discussed.

Keywords: *foxing, paper damage, UV fluorescence, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), book and paper conservation*

1. INTRODUCTION

The development of discoloured areas on the surface of paper, known as „foxing“, is undesired alteration of paper-based artefacts (manuscripts, books, prints, maps, drawings) which indicates that chemical changes have occurred. Over years of storage, foxing can penetrate into paper and even migrate through successive pages in books, often referred to as folios, and causes serious damage. The paper becomes weaker, brittle and more acidic than the unfoxed, uncoloured one. Fungal activity and metal-induced degradation, as well as a combination of both are the most frequently reported causes of foxing [1, 2, 3 and 4]. A main concern for conservators is both structural and aesthetic consequences of artefact destruction. Unfortunately, the slow-forming of foxing stains complicates the identification of their origin, and very little is known about the initiation process. Whatever the cause, it seems certain that their frequency is increased by poor environment (light, pollution, microclimatic conditions), and poor quality materials [5].

Discolouration can be seen on paper from the sixteenth century to recent times but seems to increase on paper from the eighteenth century on, coinciding with the changes in composition and manufacturing processes [6]. Foxing usually appears as stains various colours and sizes. The variety in colour ranges from yellow to reddish and brown to black with sharp or irregular edges, while their size may vary from just visible spots to large areas covering most of pages. Foxing should be distinguished from other stains which represent a different alteration [7]. The general agreement is that a better description is needed. Therefore, Cain and Miller proposed a classification method by shape, colour and UV light examination [8]. They divided various stains into two main groups: „bullesey“ with dark centre and concentric rings, and „snowflake“ with light brown to yellow areas having scalloped edges and/or irregular shapes. Florian has classified the different discoloured spots based on visual appearance

and cause: irregular fungal fox spot, circular fungal spot, corroded iron spot, metal particulate spot, calcium particulate spot and protein spot [9]. Strzelczyk and Pronobis-Bobowska proposed four main types of foxing spots: eyes, clouds, freckles and star, based on visual appearance [9].

This study investigates both the nature and the structure of the stains with the aim of getting insight into paper degradation by foxing prior making decisions about adequate conservation treatments. When dealing with artefacts of intrinsic value, the physical integrity of the investigated items should be respected. This means that valuable artefacts can only be investigated without any visible damage or loss.

2. MATERIALS AND METHODS

2.1. Foxed book paper

The investigation was focused on two books kept in the National and University Library in Zagreb: *Scriptores rerum Hungaricarum veteres ac genuini* (1746) and *Scriptores Rerum Hungaricum, Dalmaticarum, Croaticarum et Slavonicarum veteres ac genuini III* (1748). Cura et studio Ioannis Georgii Schwandtneri. [Vienna]: Impensis Ioannis Pauli Kraus, bibliopolae Vindobonensis, 1746-1748 (II-2.040, vol. 1, 3). The watermarks indicated that the papers in both books were produced in the same manufacture. 18th century papers were made by hand from recycled rags.

The text is written on paper leaves of about 310 × 180 mm. The leaves vary in thickness (10- 15μm). On the whole, the paper of both books is basically in good shape, only a slight mechanical damage around the edges was present, and the folds were broken in some places. But it presents complex physical degradation caused by natural aging and poor storage conditions. It showed foxing and tide stains, and local discolorations due to contact with excessive moisture.

It was assumed that the foxing occurrence was related to manufacture of paper and humid conditions. The examples of foxed pages in these items are presented in Figure 1.

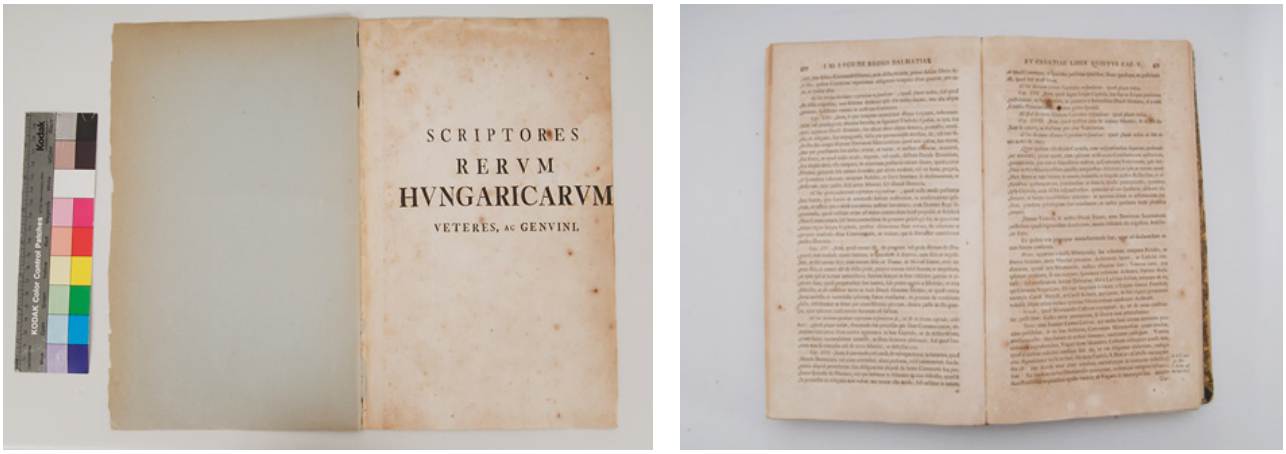


Figure 1. *The foxed pages in the investigated books: Scriptores rerum Hungaricarum veteres ac genuini (left) and Scriptores Rerum Hungaricum, Dalmaticarum, Croaticarum et Slavonicarum veteres ac genuini III (right).*

2.1.1. Samples

Samples for qualitative studies were taken from the different pages of the *Scriptores rerum Hungaricarum veteres ac genuini* and from *Scriptores Rerum Hungaricum, Dalmaticarum, Croaticarum et Slavonicarum veteres ac genuini* (Figure 2).

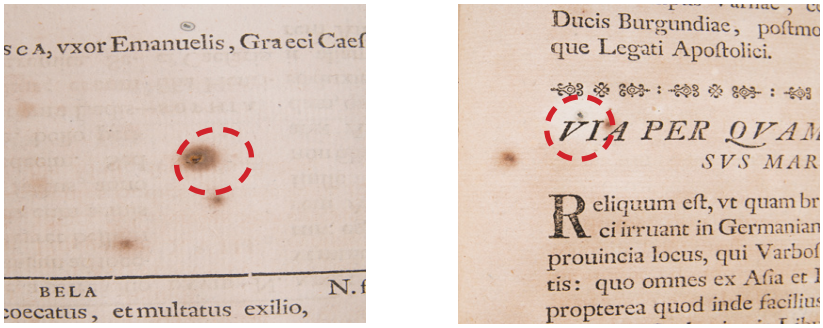


Figure 2. *The visible areas of foxing that were selected for taking samples*

Sampling was done under a stereo binocular microscope with a fine, sterile tweezers, and the samples (1- 2 mm2), each corresponding to a foxing stain, were collected using sterile needle. Areas without discolouration in the natural light and not change colour when they are exposed to the ultraviolet light were used as control samples. The samples were divided according to colour and degree of staining considering fluorescence intensity, and analysed by SEM/EDS described below.

2.2. Experimental methods

Knowledge about the characteristics of foxing stains will lead to a better understanding of how to preserve the books under consideration [9, 10, 11 and 12]. The books, due to their rarity or value, were analysed using non-destructive methods. Visual, macroscopic and microscopic examinations as well as SEM/EDS have been used to analyse foxing structure and chemical composition.

2.2.1. Visual examination in normal and ultraviolet light

The colour, shape, depth (within the sheet), and distribution of foxing stains were determined under visible light together with characteristics of surface conditions of the paper in textbook. Successive pages were checked for migration of stains and ultra-violet light used in determining their characteristics.

The stains were examined in darkness using a Camag UV Lamp dual wavelength (354/366 nm). Illumination with UV radiation can cause a material to fluoresce, emitting visible light. The changes in fluorescence and the discolouration of the papers were assessed visually. UV fluorescence photography was used to take a closer look at foxing stains. This is photography in the visible range, and it does not require special lenses and may be carried out with a UV-cut filter on the lens. The ultraviolet (UV) photographs of 8 details, 11 single folios and three openings (facing pages) were taken with the Nikon D5000 camera with a Sigma DC 18–50 mm, f/3.5–4.5 lens and Cokin P006 green filter with 6 watt longwave UV lamp as a light source. The exposure ranged between 20 and 25 seconds at f/22 and ISO 100/200.

Figure 3. UV photograph of folio 431r *Scriptores Rerum Hungaricum, Dalmaticarum,…*, indicating the new sampling area.

2.2.2. Stereo microscopic examination

The stereo microscope is the conservator's one of the primary investigative tools, enabling him to observe details of an artefact. The microscope reveals surface characteristics such as paper structure, stains, dirt, deposits and damage (recent or ancient). Higher magnifications are used to reveal more information, such as the differentiation of the paper fibres and the differences between types of inks and other materials. Discoloured areas were observed under a Nikon SMZ-10 stereo microscope.

2.2.3. SEM/EDS analysis

The investigated samples were mounted onto a small metal stub by means of double-sided carbon adhesive tape. This was found to hold the paper sufficiently firmly in the proper position for analysis. The samples were examined using a 10 kV electron beam. These conditions were chosen in order to obtain a high lateral resolution of the top fibre surface, although the depth resolution was sacrificed. In the cause of fungal infection, microscopy is the most reliable method of proof than culture, considering that fungal spores are ubiquitous and can grow on virtually any kind of paper.

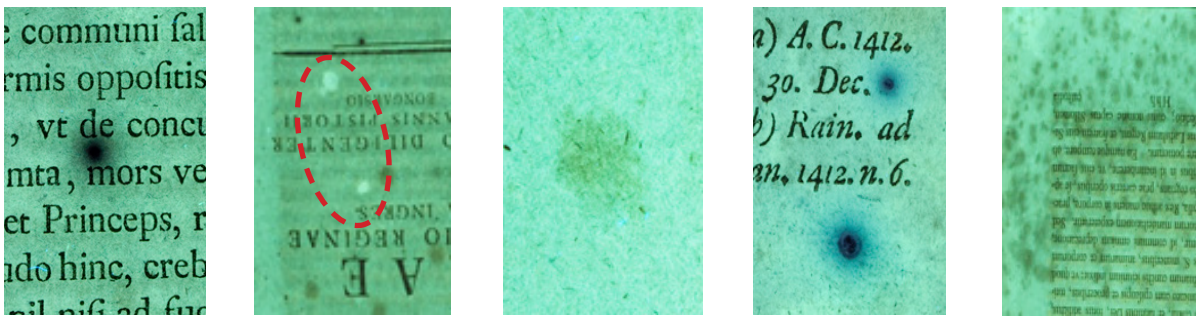
A combination of SEM with Energy Dispersive X-ray Spectral Analysis (EDS) enables detection of elements present in foxing spots, and this technique is mostly used to identify metals as the instrument is sensitive to elements with an atomic number higher than three.

Analysis was made by use of scanning electron microscope VEGA TESCAN TS5136LS in high vacuum with voltage of 10kV. Microanalysis of chemical composition was made with Oxford EDS detector, while the area of analysis of detector was 20keV.

3. RESULTS AND DISCUSSION

The results of the *in situ* macroscopic and microscopic observation of discoloured areas in the books, the analysis of the folios with UV-fluorescence, and the analysis of the samples with SEM/EDS are discussed by visual appearance. Some examples of examined areas/ folios are shown in Figures 2 and 3.

Five typical foxing stains are presented in Figure 4, showing different colour intensities, edges and shapes under UV light. Foxing vary in size from just visible spots to large areas covered most of the page.



a) b) c) d) e)

Figure 4. *Typical foxing stains under UV light (Nikon D5000)*

In UV light, the foxing stains that were not visible to (barely) visible in normal light fluorescence from white to yellow, while stains that have the deepest (dark brown or black) colour in normal light little or no fluorescence (Figure 5). The areas which fluoresce under UV but show no visible foxing also may indicate a previous bleaching treatment.

Figure 5. *Folios 762v-763r in Scriptores rerum Hungaricarum veteres ac genuini. Foxing stains in early stage: slightly brown coloured stains, and slightly visible (left), but clearly distinguishable under UV-light (right).*

Visual examination under stereo microscope showed that some stains with dark centre had irregular, bumpy surfaces, and others had nearly smooth surfaces. Figure 6 shows some results of microscopic examination. Attempts to remove dark brown stain (Figure 6, image on the right side) with a preparation needle showed that it penetrated through the paper. The visual evidence indicated that the stain in question was probably from the metal impurities in the paper, which can arise during the papermaking process.

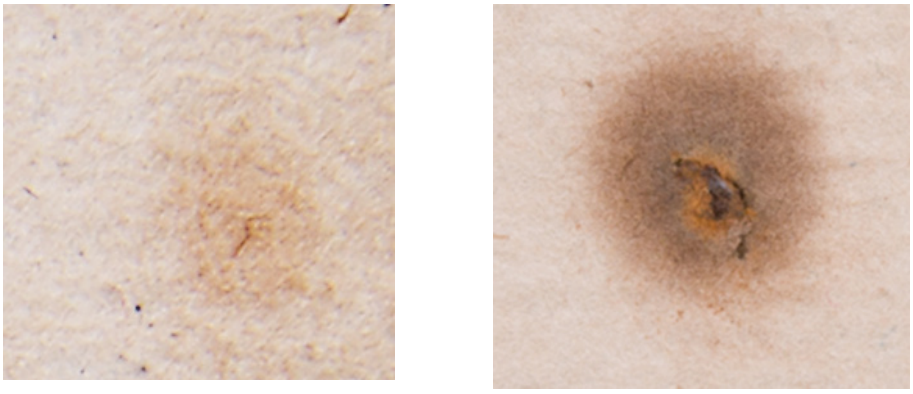
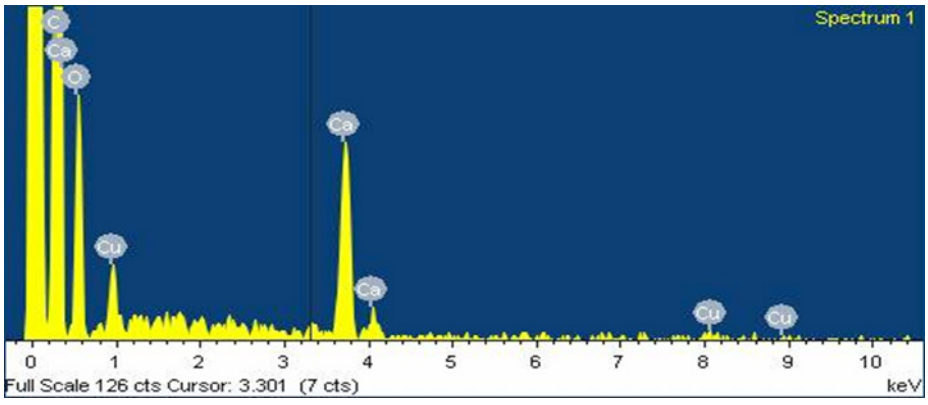
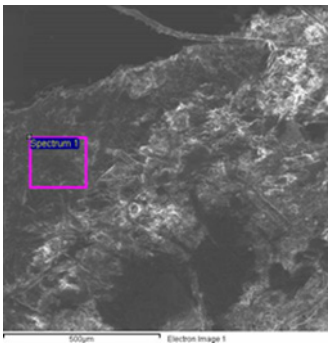


Figure 6. *Foxing in Scriptores rerum Hungaricarum veteres ac genuini: „Snowflake“ on folio 438 v (left) and „Bullesey“ on 871r (right) under stereo microscope at 10× magnification*

The positive results on the presence metals in the foxed areas compared to surrounding paper were obtained by SEM/EDS (Figures 7 and 8). No evidence can be proved that the foxing in the affected papers of both books was caused by fungal growth. Further investigations regarding the fungal activity are needed.





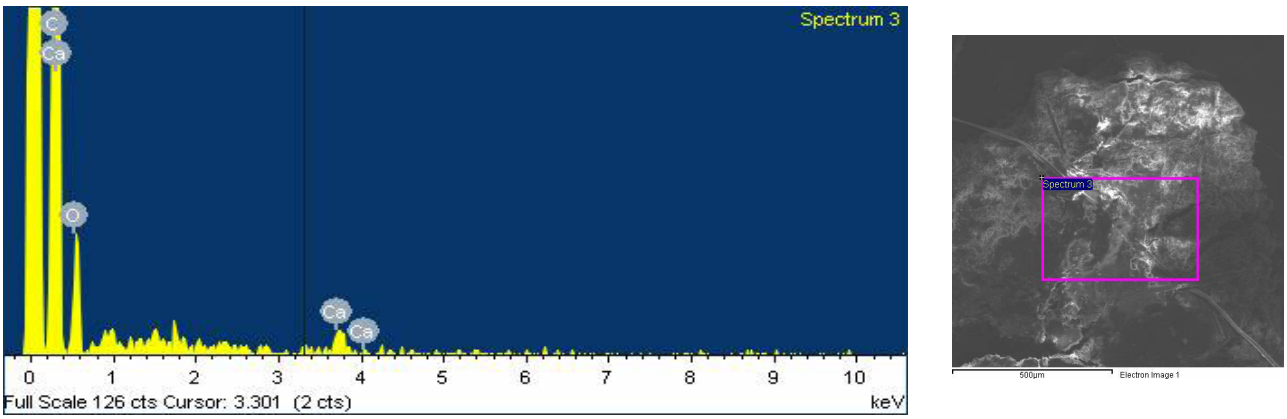


Figure 7. *The EDS spectra from the scanned areas of the paper in Figure 3 with (bottom page 38) and without foxing (above) are clearly distinguishable.*

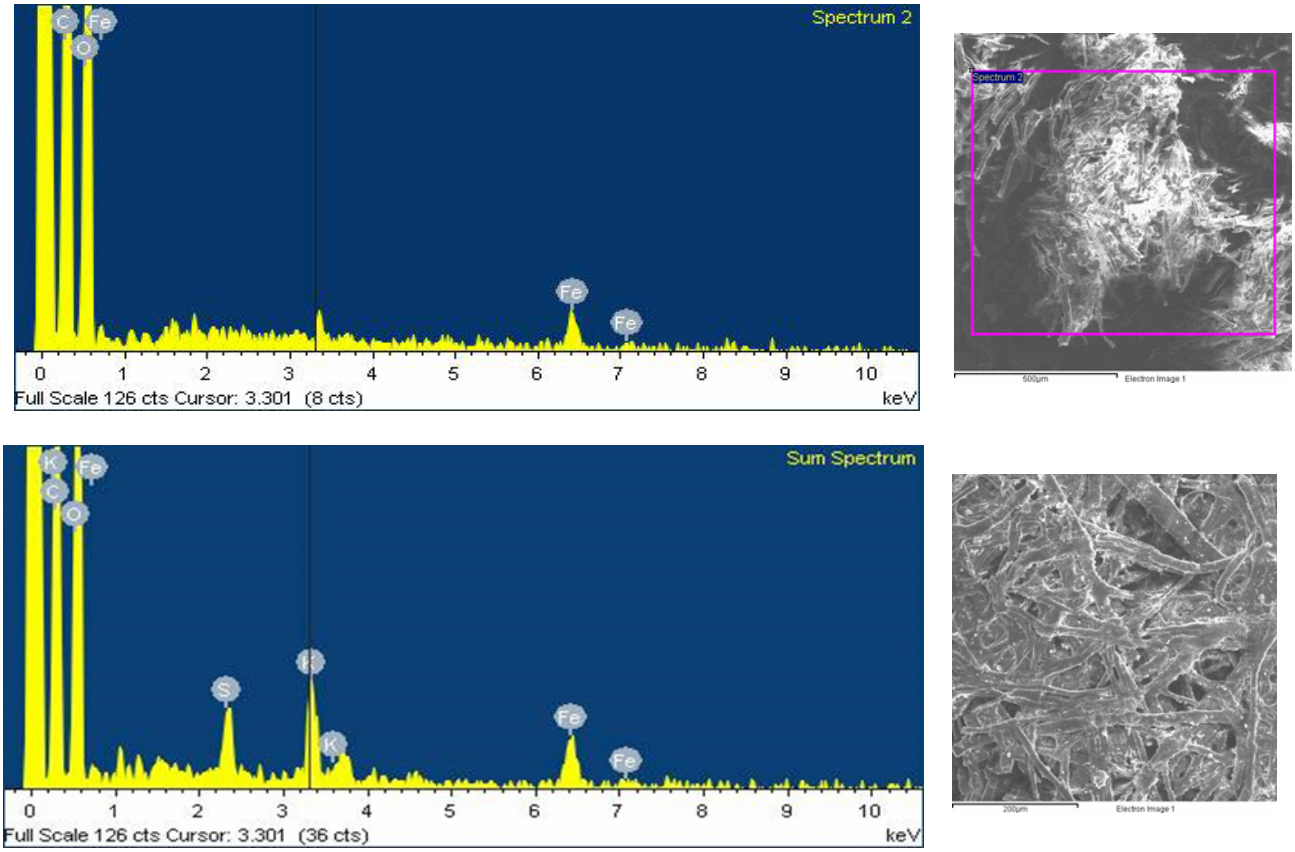


Figure 8. *The EDS spectra from the scanned areas of light brown stain (above) and dark brown stains (below) in the affected papers presented in Figure 6.*

Analysis by EDS revealed that the samples of foxed paper contain iron, copper, calcium, potassium, carbon, oxygen and sulphur, unlike the unfoxed area that contain calcium, carbon and oxygen. These elements in the paper are believed to result from papermaking process. First, it was assumed that potassium, oxygen and sulphur belong to alum, i.e. aluminium potassium sulphate, used in sizing of paper, and iron and copper as impurities originate from alum or metal equipment or contaminated water used in the process of paper production. Because the presence of aluminium is not confirmed, they can be attributed to alkalis (lime water and potash) together with carbon and calcium, used in preparatory operations for the removing dirt and colouring matter of old, dirty rags. Furthermore, water with high calcium content certainly had an impact on the content of calcium in the paper.

The presence of iron or copper was confirmed in all samples with foxing stains.

Though it is only discussed a few samples from both books, it is possible to conclude that the similar types of foxing in both books, respectively, metal-induced degradation processes in the paper have been present.

Prevention and conservation treatment of foxed books

Foxing stains in an early stage, when they are still invisible, can be diagnosed by examining of the suspected books under UV light. It is possible to inhibit foxing to develop further by controlled storage conditions and wrapping a book, and packing or mounting with acid-free paper. The use of antioxidants such as compounds forming complexes with transition metals seems to be useful, but this needs further investigation. Removing the stains should be done by skilled conservator who may treat the paper with chemicals (reducing or oxidizing agents). Chemical bleaching is a very risky treatment and may cause serious damage like breaking down the paper cellulose and bleeding the ink. Recently, laser-based techniques have been successfully used to remove foxing stains in the paper [13, 14 and 15].

4. CONCLUSION

Consequently, in order to determine the most appropriate method for removing the stains, it is highly important to differentiate foxing from other stains on paper, and find out, to the extent possible, the origin of foxing. The authors recommend visual and microscopic observations of foxing stains, and UV-light as a diagnostic tool that is simple and generally available. In other words, these techniques provide a means of differentiating various types of stains, while do not require expensive equipment and are non-destructive.

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