



# Investigation of the deterioration degree of parchment marked with iron gall inks

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## Introduction

**Parchment** is a collagen-based biomaterial which is prepared from animal hides, like cattle, calf, sheep and goats, after particular process.<sup>1</sup> Its use as archival material bears the testimony of recorded cultural history and this makes its preservation important.<sup>5</sup> So, it is significant to understand the degradation paths in order to control the changes induced to the material either by the environment or by writing media.<sup>4</sup> Among the writing media, **iron gall inks**, which are produced mainly of gallotannins, vitriol (iron(II) sulphate), Arabic gum and a fluid medium (usually water), are particularly known for their corrosive nature.<sup>3</sup> This study aims at determining the damage extend of parchment samples in the presence of iron gall inks under artificial ageing conditions.

## Materials and methods

The experimental design that followed the literature review was divided into four main parts :

### • Preparation of iron gall inks

Two different inks prepared based on simple traditional recipes.<sup>2</sup>

MK: Iron sulfate, Gallic acid & Gum Arabic in deionized aqueous solution.

MN: Iron sulfate & Gallic acid in deionized aqueous solution.

### • Preparation of samples

Parchment from goat was chosen for sampling. Parchment samples (sized 0,6 x 1,2 cm) from the backbone area, marked with above inks. For a reliable evaluation of results, reference samples of neighboring parchment regions were analyzed in parallel.

### • Accelerated ageing

The samples were subjected to accelerated ageing at 80°C in the presence of humidity (RH=80%); ageing parameters levels followed the IDAP protocol (2007).<sup>6</sup> Different parchment samples examined after 1, 2, 4, 8, 16 and 32 days of ageing.

### • Analytical Methods

**SEM-EDAX**: Scanning Electron Microscope JEOL JSM-5310 with Energy Dispersive X-Ray Analyzer OXFORD LINK ISIS L310 was used for the examination of the samples, which were subjected conducting with carbon coated samples.

**FTIR**: The equipment used for the research included two FTIR instruments: Perkin Elmer Spectrum GX and a Bruker Tensor 27 FT-IR spectrometer (both with DTGS detector). All samples were gently scraped by means of a scalpel, pressed in potassium bromide (KBr) pellets, and were subsequently subjected to analysis.

**MHT**: Thermal Analysis - Shrinkage temperature measurements were performed with a Mettler Toledo FP82HT Micro Hot Stage thermostatically controlled through a Mettler FP90 Central Processor. Shrinkage activity was recorded under a stereo microscope (×40 magnification).

## Results

▪ Macroscopic examination showed that there was ink discoloration after ageing: dark blue color tint of iron gall ink was changed into brown.(Fig. 1,2) After 32 days of ageing there were deformations, especially at samples marked with MK ink. (Fig.1)



Fig.1 : Parchment samples marked with MK ink , before & after accelerated ageing at 32 days (T=80 °C, RH=80 % ) respectively

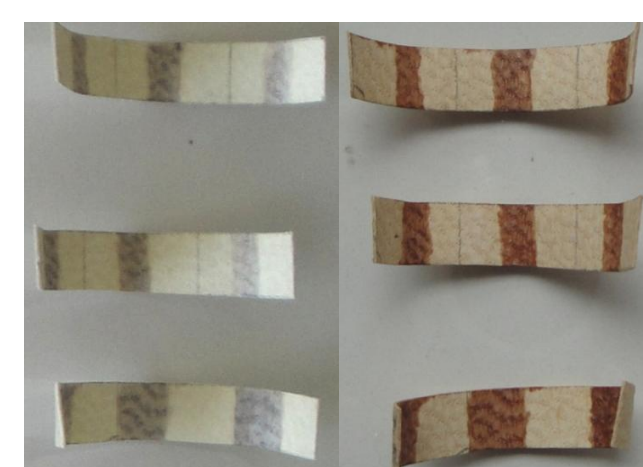


Fig.2 : Parchment samples marked with MN ink , before & after accelerated ageing at 32 days (T=80 °C, RH=80 % ) respectively

▪ Scanning electron microscopy revealed extensive formation of crystals on the surface of the aged samples. Furthermore, increased amounts of calcium (Ca), in combination with high levels of sulphur (S) lead to the formation of calcium sulphate (CaSO<sub>4</sub>). (Fig. 3,4) However, there are differences between these crystals: those inside ink regions, appear to be bigger and fewer, while those in non-inked parchment regions where smaller and of higher quantity. (Fig.5)

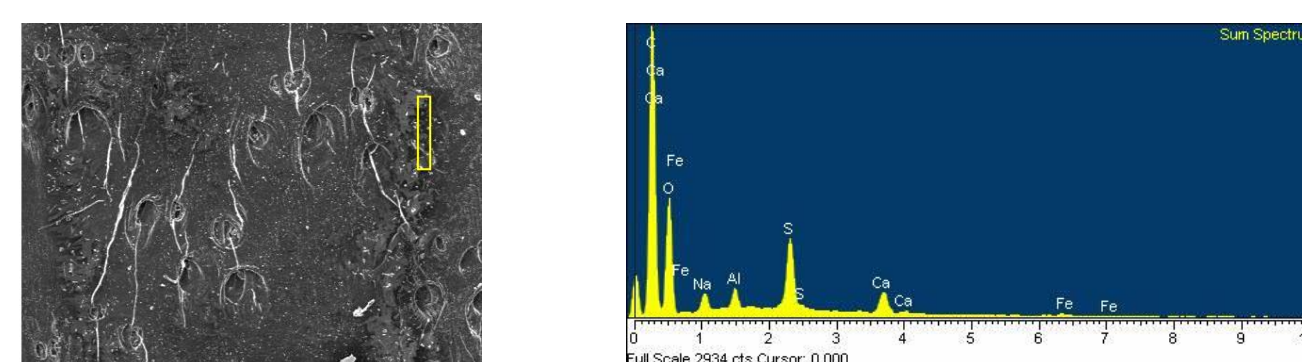


Fig.3 : Electron micrograph of parchment sample marked with MK ink after accelerated ageing at 32 days (T=80 °C, RH=80 % ) , ink region (x50)

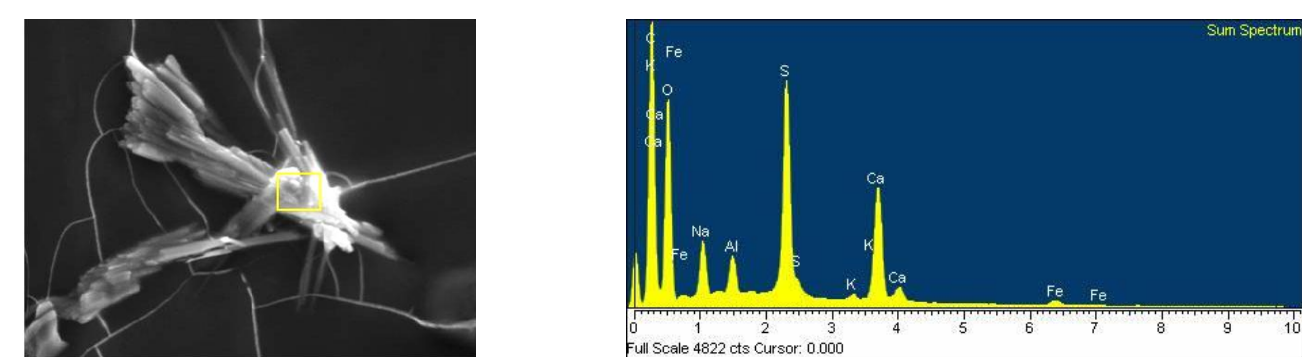


Fig.4 : Left: Electron micrograph of parchment sample marked with MK ink after accelerated ageing at 32 days (T=80 °C, RH=80 % ), ink region (x2000). Right: EDX spectrum of a crystal.

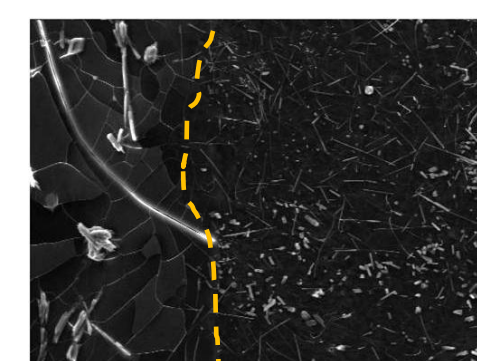


Fig.5: Parchment sample marked with MK ink after accelerated ageing at 32 days (T=80 °C, RH=80 %) Left: ink region, right: non-inked parchment region; at both regions CaSO<sub>4</sub> crystals are recognizable in different size and quantity (x500).

▪ Analysis with FTIR spectroscopy showed evidence for changes in the amide A, I and II bands of collagen after prolonged artificial ageing of ink-marked samples, reflecting changes in collagen molecular structure. Spectroscopic evidences of transposition of amide A (to 1660 cm<sup>-1</sup>) on an aged (32 days) sample marked with MK ink, are shown in Fig.6. Also, spectral subtraction showed evidence of ink oxidation and/or interaction of ink components with parchment material (peak at 1715 cm<sup>-1</sup>); this could be a possible source of deterioration of the parchment/ink system.

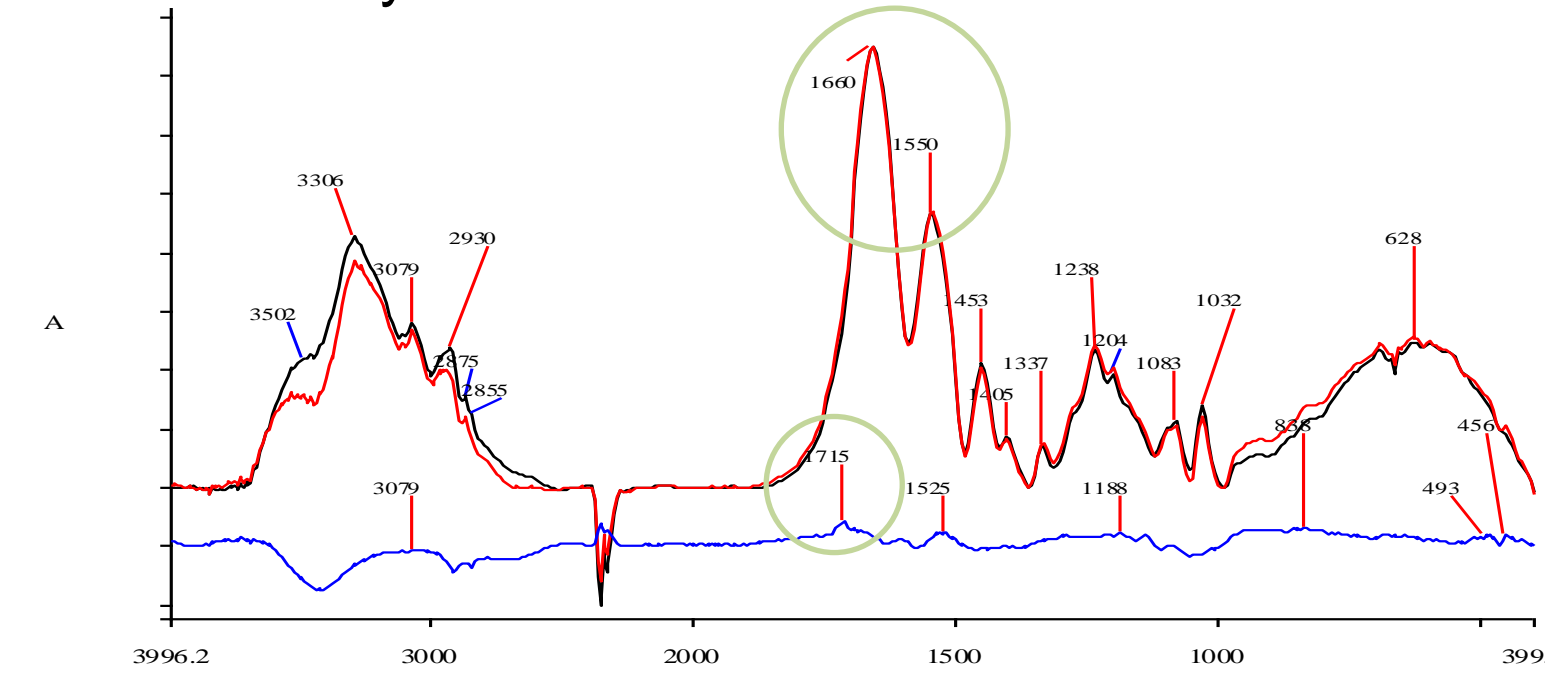


Fig.6 : FTIR spectra, showing changes in the structure of parchment and ink after 32 days of artificial ageing (sample marked with MK ink)

▪ Micro hot table measurements showed a gradual decrease of the shrinkage temperature (Ts) in parchment samples marked with ink containing Arabic gum, as accelerated ageing proceeded. Furthermore, collagen fibers from areas with ink marks presented lower shrinkage temperature than fibers from non-marked areas. (Fig.7)

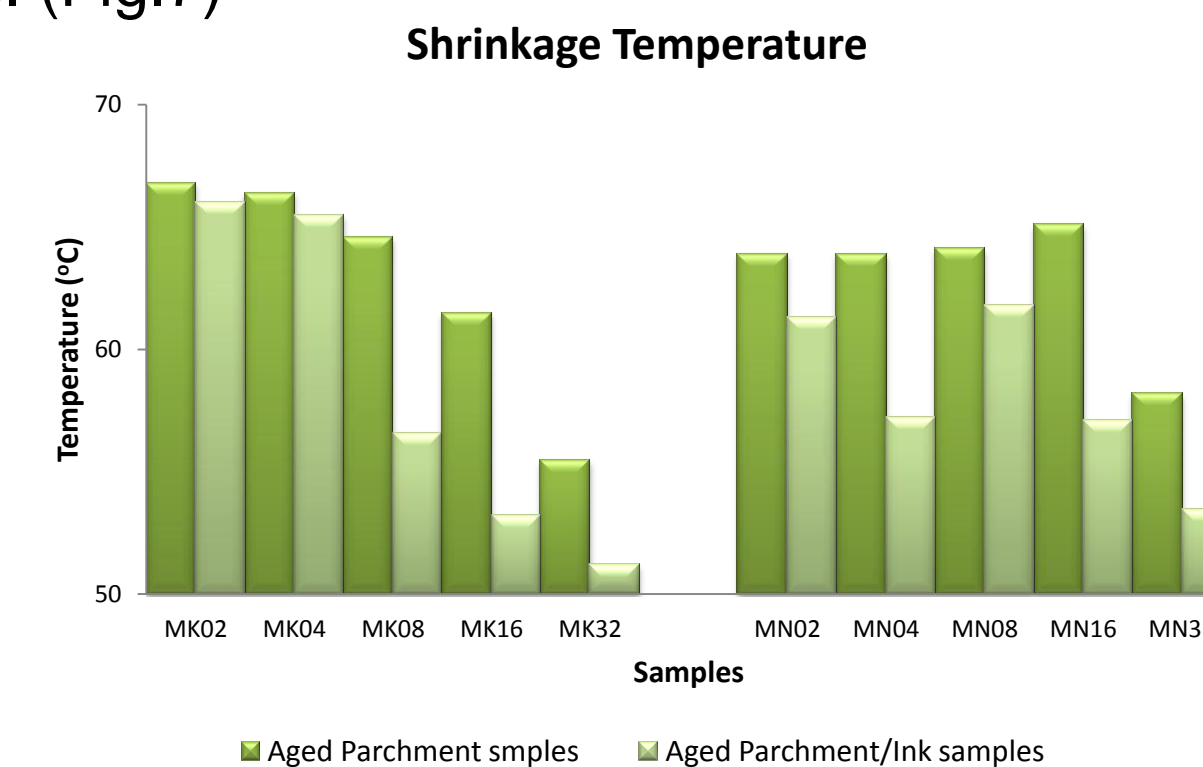


Fig.7 : Diagram shows the decrease of shrinkage temperature of parchment samples marked with MK and MN inks respectively, in 2,4,8,16,32 days of ageing.

## Conclusions

The experimental results can be summarized in the following points:

➤The discoloration of inks after ageing is due to the oxidation of ferrous in iron gall ink ; Fe(II) →Fe(III) , which colors the ink as it forms a coordination complex with Gallic acid.

➤Encrustations of salts on the surface of the samples can be detected at samples marked with MK ink as well as the ones marked with MN ink.

➤FTIR spectroscopy showed degradation on parchment structure separately and on parchment/ink system, as accelerated ageing proceeded.

➤Hydrothermal stability of parchment was examined by MHT. Samples after 8 days of accelerated ageing contain damaged dehydrated fibres. Additionally, samples marked with inks showed lower physical strength on the fibre structure in comparison to non-marked samples.

## Future research

Further work is under way involving increased sample numbers and statistic elaboration in order to establish a trend between the obtained results and the state of parchment preservation.

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\* This study presents the first results of a Thesis supervised by Ekaterini Malea, Lecturer (Lab. Conservation of Organic Materials) & Dr. Stamatis Boyatzis, Assistant Professor (Lab. Instrumental Chemical Analysis) of Dept. Conservation of Antiquities & Works of Art, Technological Educational Institute of Athens.