# FE IONS IN IRON GALL INK DOCUMENTS AT THE NATIONAL ARCHIVES OF MALTA

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9<sup>th</sup> European Heads of Conservation Meeting 4-5<sup>th</sup> May 2017  The aim of this presentation is to share the information collected from a survey carried out in the holdings at the National Archives of Malta in order to identify the presence of Fe ions in documents written with iron gall ink  Published scientific research suggest that the strongest effects on the deterioration of manuscript documents has proved to be the radical mechanism catalyzed by iron(II) compounds, even under neutral conditions. The effect of iron(II) compounds was proved to be much stronger than the destructive action of acids.

- Hence knowing the extent of documents containing iron(II) compounds in our holdings gives us a clearer view on:
- The state of conservation of our collection,
- The number of documents which are at risk,
- The way forward for their preservation.

### The Risks of Iron Ions in Paper or Parchment

- The Presence of Fe ions in paper can be traced back to several sources during the production of the paper itself.
- Like most transition metal ions, Fe ions are harmful to paper and parchment. They can be present in two oxidation states: as Fe(II) or as Fe(III) ions. Fe(II) ions catalyse the decay of cellulose and collagen by promoting the decomposition of pre-formed peroxides to hydroxyl- and alkoxy radicals. Those species initiate the oxidation of the substrate, which results in discolouration and loss of mechanical strength.

- Fe(II) ions can be absorbed by the substrate and transported to reactive sites on cellulose or collagen through water
- Fe(III) ions tend to exist predominately as hydroxides, which have low water solubility. Unfortunately, Fe(III) ions can be 'recycled' to Fe(II) ions by reducing substances such as cellulose degradation products present in the paper, like low-molecular carbohydrates or tannic and gallic acid present in iron gall inks.

- This conversion is accelerated under acidic conditions, e.g. those prevailing in iron gall inks. The oxidation / reduction reactions will always continue in the presence of air and reducing substances.
- Fe(II) ions have to be considered as a direct threat to the permanence of the substrate, whereas Fe(III) hydroxides are a future hazard, especially when acidity increases.

 Raised humidity or local wetting of papers contaminated with Fe ions will cause migration of soluble Fe ions and leads to accumulation of iron salts in the evaporating area, e.g. in the area of tide lines.

#### **General Condition survey**

- As the first step for the preservation of the holdings of the NAM in March 2011 a General Condition Survey on the whole collection was initiated. This covered all the fonds housed at the Santo Spirito Archive in Rabat.
- Sampling of the fonds was done sporadically with 3.28% of the 23,534 units (a box, volume or bundle) being surveyed. The data collected was in relation to the following visible damage:- Wear & Tear; Surface Dirt; Water Stains/Mould; Acidic Ink Damage; light Damage; Pest Damage: Rust Damage; Covers Detached; Covers Missing; Binding Damage; Others.

- Acidic ink was found only in 2.72% of the sampled items. This means that in proportion around 652 units are affected with acidic ink.
- For the purpose of this survey the term 'acidic ink' is being used for ink which when visually inspected showed: severe yellowing, cracking or losses of the ink.

#### Survey for presence of Fe II ions

- The sampling for this survey was done on 10% of the sample used for the General conditions survey which resulted in having Acidic ink.
- Methodology : Description of the testing technique (Dutch method)
- Testing for Fe(II) was done using the Bathophenanthroline indicator paper for Fe(II) ions which was developed by the Conservation Research Department at the Netherlands Institute for Cultural Heritage (ICN), in the context of their extensive research into iron gall ink corrosion.

- This non-bleeding iron test paper was developed as a simple and quick method to detect Fe(II) ions in hydrophylic substrates. The test paper is non-bleeding, therefore it can be applied to the original documents.
- Fe(II) ions are water soluble and will migrate into a dampened test paper in contact with the ink. The indicator (bathophenanthroline) forms an intensely red-coloured complex with Fe(II) ions.

# Survey for presence of Fe(III) ions

- Since Fe(III) ions can be 'recycled' to Fe(II) ions by reducing substances such as cellulose degradation products present in the paper, it was decided to check for their presence.
- This procedure was done using a drop of 1% ascorbic acid solution in water on the test paper indicator following the test for Iron(II).



Images showing one of the documents during testing for Fe(II) ions



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Total amount of items surveyed 772

(3.28% of 23,534 items )

#### Acidic ink damage

Not present 751 (97.28% of 772)	present 21 (2.72% of 772)			
Extrapolation (22,882) (97.23%)	Extrapolat	Extrapolation (652) (2.77%)		
	Testing	g for Fe II ions		
	Positive 9(43%)	Negative 12 (57%)		
	Extrapolation (280)	Extrapolation (372) (1.58%) Testing for Fe III ions		
	(1.19%)			
		Positive	Negative	
		6 (50%)	6 (50%)	
		Extrapolation	Extrapolation	
		186 (0.79%)	186 (0.79%)	
	Extrapolatio			
466 (1.98%)				

# Results

- During the General condition survey carried out in 2011, 2.72% of the collection was considered to contain acidic ink.
- Following the tests for Fe ions 1.98% of the collection was found positive for Fe(II) or Fe(III) ions
- It also should be noted that in most cases out of a whole volume/box/bundle only a few folia are actually affected by deterioration attributed to iron ions

# **Post-Results**

- Given that the amount of documents effected by decay resulting from Fe(II) ions is so small the next step will be an evaluation of the importance of these sampled documents in order to prioritise conservation work.
- Calcium-phytate /calcium-bicarbonate treatment will be carried as required
- New documents being added to the collections will be monitored for signs of Iron Gall ink degradation.

# **Leaf-casted Documents**

Since the inauguration of the Conservation Lab in 2012, about 10,400 folia from the MCC fond where treated. In most cases leaf-casting was carried out due to severe insect damage. 10 folia from ten different gatherings where chosen randomly and tested for Fe ions. All resulted Negative for Fe(II) and only 2 resulted positive for Fe(III).

- Test before treatments suggested a presence of 14% of Fe(II) and 50% of Fe (III).
- These results indicate that during the leafcasting process Fe ions are being removed from the ink.

