Paper and Copper Pigment Degradation in European Early Printed Books

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Introduction

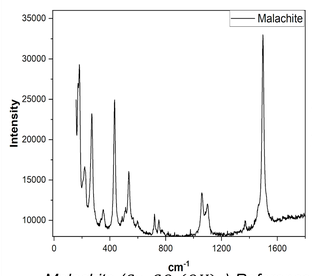
Early European printed books printed before 1500, referred to as Incunabula were painted with copper carbonate based green (Malachite) and blue (Azurite) pigments. As the Incunabula age, it seems that these pigments and the underlying paper have degraded at an accelerated rate.

In this project, the aging process of Incunabula was simulated and the effects of temperature, pH, binder solution, and pigments were studied using a factorial design approach. The products of the artificial aging process were characterized using Raman spectroscopy and Gel Permeation Chromatography to evaluate the degradation of the pigment and paper, respectively.

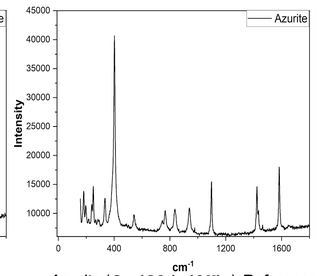
Recto: the front side of a page of an incunabula[1].

Verso: the reverse side of a page of an incunabula[1].

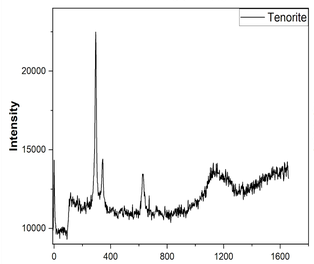
Reference Raman Spectra



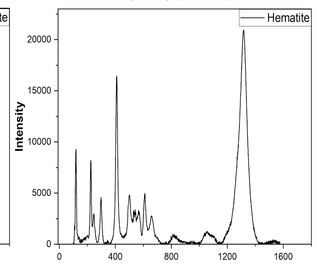
Malachite ($Cu_2CO_3(OH)_2$) Reference



Azurite ($Cu_3(CO_3)_2(OH)_2$) Reference



Tenorite (CuO) Reference



Hematite (Fe_2O_3) Reference

Methods

Sample Preparation:

The samples were prepared using a 2^4 Factorial Design approach. For each sample, one parameter per column was chosen.

Factorial Design Parameters

Input Parameter	A	B
Pigment	Malachite (M)	Azurite (Z)
Binder	Gum Arabic (A)	Gelatin (G)
Temperature	80˚C (W)	4˚C (C)
pH	10 (H)	5.5 – 6.5 (L)

The samples were subjected to two temperature treatments. The pH was controlled by adding a $Ca(OH)_2$ solution to the binder-pigment mixtures. After the aging process (10 days), the samples were analysed using Raman Spectroscopy.

Gel Permeation Chromatography (GPC):

GPC analysis, was used in order to determine how the above parameters impact the degradation of cellulose. The samples were processed using a five-phase preparation and dissolution procedure which allowed for the measurement of the cellulose structure degradation. Gel permeation chromatography testing was performed using an Agilent PL-220 Gel Permeation Chromatogram equipped with an autosampler, thermostatted column oven, and refractive index detector. Conclusions were drawn using the following Molecular Weight Moments (MWMs):

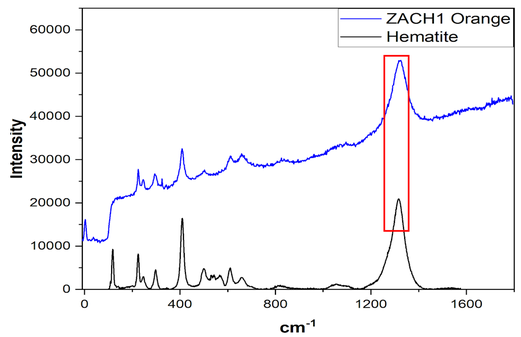
Number Average MWM: $M_n = \frac{\sum M_i N_i}{\sum N_i}$

Weight Average MWM: $M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$

M_p , the weight at apex of the distribution was also reported.

Results

Pigment Analysis:

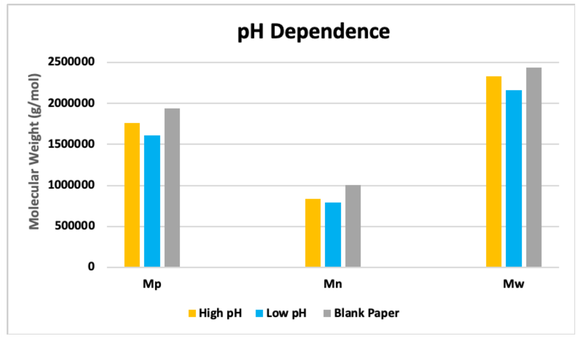


Orange area on an Azurite sample matches the representative peak of Hematite.

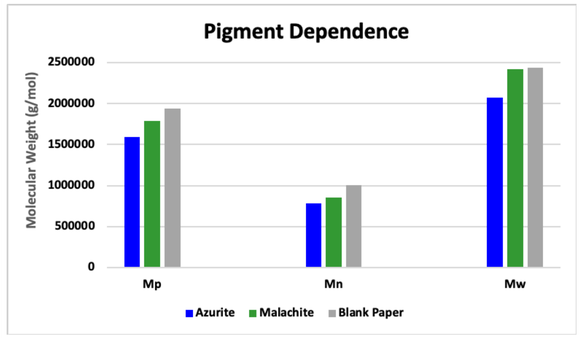
Malachite Representative Peaks:	Azurite Representative Peaks:
155	117.888
178	224.721
217	246.67
268	297.68
354	409.606
433	501.207
509	542.524
553	566.044
558	610.551
757	660.63
1051	820.443
1085	1058.108
1492	1316.187

Representative Peaks of both Malachite and Azurite; the peaks indicated in red are too close to the Representative Peaks of Tenorite to be differentiated.

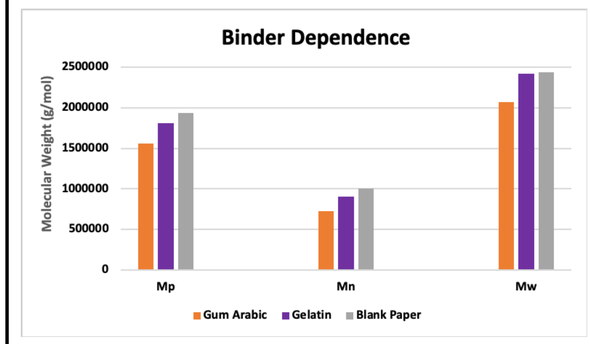
Paper Analysis:



Paper aged with low pH shows lower polymerization.



Paper painted with Azurite shows lower polymerization.



Paper treated with Gum Arabic shows lower polymerization

Conclusions

It is impossible to draw conclusive evidence, based on the current data, that Tenorite is the “dark” found on the aged samples. Hematite is, conclusively, the “orange”, the representative peak of 1200-1300 cm^{-1} can be seen clearly in all of the samples which have the “orange” impurity.

Lower Cellulose polymerization (indicative of paper degradation) occurs when the sample is treated with one, or more of the following conditions:

- Elevated temperature (80℃)
- Gum Arabic binder
- Acidic paint solution
- Azurite pigment

Note that when the samples were aged at High Temperature, the degradation is increased **regardless** of which parameter is used.

Acknowledgements/References

1. Hagadorn, Alexis. “An Investigation into the Use of Blue Copper Pigments in European Early Printed Books”. Version 1194. In: Book and Paper Group Annual 23 (2004), pp. 41–55.