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Effect of Aqueous Treatments on Nineteenth-Century Iron-Gall-Ink Documents: Assessment Using Hyperspectral Imaging

ABSTRACT

Five original, nineteenth-century, iron-gall-ink documents were subjected to eighteen separate aqueous stabilization treatments. The effectiveness of eight of these treatments was evaluated after extended exposure to heat and humidity, high-intensity light, and elevated humidity at room temperature. Heat aging results confirmed the effectiveness of phytate-bicarbonate treatments. High humidity did not cause mold growth on phytate-treated samples. Continuous exposure to fluorescent lights (with UV) caused fading of the papers and some fading of the inks. Visible hyperspectral imaging was carried out using a NuanceTM Imaging system with a liquid crystal tunable filter (LCTF). The usefulness of hyperspectral imaging to evaluate the effect of aqueous treatments on one set of sample is discussed.

INTRODUCTION

The efficacy of iron-gall ink treatments is often tested on model papers and prepared inks in order to control the variables during experimentation. Evaluating these treatments on originals helps identify unforeseen problems and confirms their effectiveness (Neevel 2000; Reissland 2000; Kolar and Malešič 2005). The calcium phytate (Ca-phy) calcium bicarbonate ($Ca(HCO_3)_2$) treatment was consistently found to be effective in protecting model papers and inks during artificial aging. This study uses original documents (circa 1841–1875) donated by a Québec archive, and compares the effect of the phytate-bicarbonate and modified phytate treatments to other aqueous treatments. Phytate treatments are sometimes modified to eliminate crystal formations after treatment and/or the possibility of mold growth (Homolka 2001).

A total eighteen treatments were carried out on nine original documents (Orlandini 2006; Orlandini 2009). The effectiveness of eight of treatments on five documents was further tested by exposure to heat and humidity, high- intensity light, and elevated humidity at room temperature. Changes were evaluated against unaged or untreated controls. Methods of evaluation include hyperspectral imaging, color measurement, pH, iron (II) testing using bathophenthroline test strips (Neevel and Reissland 2005), and microfade testing. Some of these results have been previously reported (Tse et al. 2006).

Hyperspectral imaging combines spectroscopic information with the spatial information of the sample. In hyperspectral imaging spectral information is collected in narrow bands (10 nm) that are contiguous. In this sense spatial information about an object is obtained in two dimensions (x, y) and spectral information is obtained in a third dimension (z), which allows the storage of information in a three-dimensional data cube.

The important advantage of using hyperspectral imaging is that an accurate digital record can be acquired of an historical object (Kubik 2007). This makes it a very powerful technique for identifying and mapping pigments in paintings (Berns 2002; Baronti 1998). For written documents hyperspectral imaging has been used for enhancing the legibility of faint text (Goltz 2007), as well as revealing text that was over-written with another ink (Attas 2004).

This paper highlights the usefulness of hyperspectral imaging and image analysis techniques to evaluate the effect of aqueous treatments on iron-gall ink.

EXPERIMENTAL

Samples

The nine documents were previously donated for testing by an archive in the province of Québec, Canada, and subjected to eighteen different aqueous treatments. Details of the treatments have been described by Orlandini (2006; 2009). Five of the documents and eight of the treatments were subjected to further accelerated aging. A description of these samples can be found in table 1. Results from bathophenanthroline test strips were recorded using a calibrated color chart developed at the Canadian Conservation Institute (CCI),

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Sample #	Sample description	Ink condition				
		ICN Condition Rating	Bathophenthroline Test strips		FTIR-ATR	μXRF
			Fe^{2+}	Fe^{3+}		
1	1856 cream ledger, wove cotton rag paper with thin blue lines; ink dark brown	1	50+	50+	gelatin	Fe, K
2	1849 greyish cream ledger; wove cotton rag paper with thin blue lines; ink light brown	1	~10	50++	No gelatin	Fe, K
3	1864 blue ledger; laid cotton rag paper with visible chain and laid lines; ink light brown with dark strokes	1	~25	~25	gelatin	Fe, Ca, S
6	1846 cream ledger; wove cotton rag paper with no lines; ink thin dark brown strokes	1	50	50+++	gelatin	Fe, K
9	1846 green ledger; wove cotton rag paper with no lines; ink light brown	1	~10	~10	No gelatin	Fe, Cu, Mn, Ca, Cl, K

Table 1. Description of treated inked documents

where 1 = detectable; 10 = weakly positive; 25 = positive; and 50+ = strongly positive (fig. 1) (Vuori and Tse 2005).

Treatments

An untreated portion of each original document was kept as a control, and the treatments are described in table 2.

Methods of aging

One set of untreated and treated samples was kept for unaged controls. Heat aging was carried out in a Despatch Environmental Chamber LEA-69 at 80° C and 65% RH for eight weeks. Light aging was done with a bank of fourteen fluorescent lights (40-watt, 4-foot 1157 Vita-lite), vertically mounted, 15–20°C, 40±5% RH for ten weeks, without UV filters. Averaged accumulated irradiance was 5564 kJ/cm^2. The total light exposure was 3.71Mlux-hr. Humidity exposure was carried out in a desiccator maintained at 85% RH with a saturated KNO_3 solution, at 22°C, for twenty-two weeks. All the samples were mounted separately during aging. The samples after treatment and after aging are shown in figure 2.

Methods of evaluation

Visual evaluation was conducted by eleven paper conservators. Color measurements before and after aging were done using a Minolta 2022 spectrophotometer. The presence and recurrence of the ferrous (Fe (II)) and ferric ions (Fe (III)) in all aged samples were tested using bathophenanthroline indicator strips, with and without ascorbic acid, and compared to a calibrated color chart developed at CCI. Attenuated Total Reflection (ATR) IR spectra of selected ink and paper were obtained using the Travel IR ATR spectrometer (SensIR Technologies, Smiths Detection). Micro-extracted pHs of selected papers and inks were measured using a IQ-240 ISFET pH meter with microprobe. Calibrated Scan Mate F8 flatbed scanners, conventional, UV-fluorescence, and IR photography were used to document the appearance of the samples.

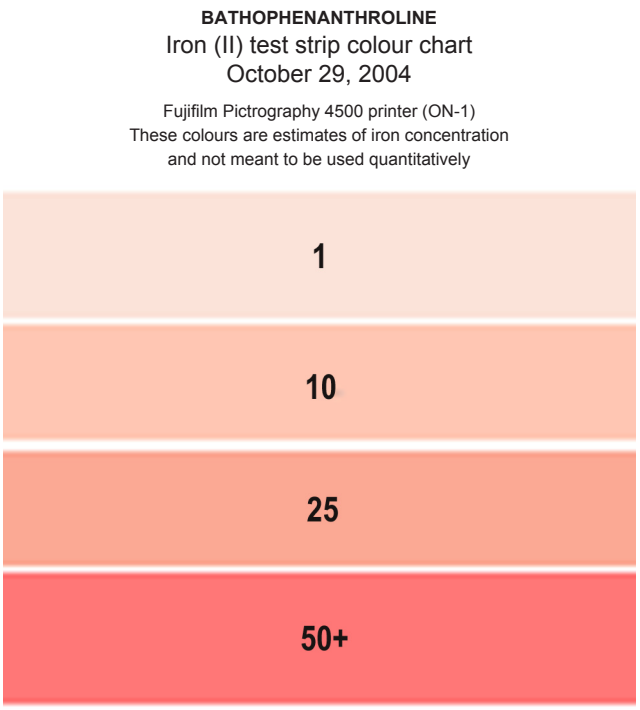


Fig. 1. Color chart developed by CCI for documenting bathophenanthroline Fe (II) test strip results

In 2008, visible hyperspectral imaging of the aged samples and controls was carried out at the University of Winnipeg, using a Nuance MSI (420–720 nm) multispectral imaging system

	Treatment Sequences & Duration
1	Untreated control
2	Alkaline wash: pH 8.5 $Ca(OH)_2$; 20min
3	RO water + 0.011M $Ca(HCO_3)_2$; 20min each
4	Reverse osmosis (RO) water + 0.086M $Mg(HCO_3)_2$; 20min each
5	Ethanol (EtOH) immersion + alkaline water simmer: pH 8.3 $Ca(OH)_2$; 90°C; 15min
6	Pre-wet with EtOH spray; Ca-phy + 0.011M $Ca(HCO_3)_2$; 20min each
7	Ca-phy + 0.011M $Ca(HCO_3)_2$; 20min each
8	Ca-phy diluted 1:1:1 with water and ethanol + $Ca(HCO_3)_2$; 20min each
9	Pre-wet with EtOH spray; Ca-phy (20min)+water rinse (3x10min)+$Ca(HCO_3)_2$ (20min)

Table 2. Treatments applied to original documents

(Channel Systems and CRI) equipped with a liquid crystal tunable filter, optics, and a charge-coupled-device (CCD) detector. The image sensor pixel count of the CCD is 1.3 megapixels and images were 1248 x 960 pixels. Images were acquired from 420 nm to 720 nm at intervals of 10 nm.

For visible imaging, Solux bulbs (3500K, 35W) (Tailored Lighting Inc.) were placed at approximately 0.5 m from the documents, at 45 degrees relative to the imaging camera. For visible imaging with an ultraviolet light source, a low-pressure fluorescent light source was used. This was a broad-band light source with a maximum intensity of 365 nm. The imaging camera was mounted in a face-down position at a distance of approximately 50–100 cm from the samples. An AF Micro Nikkor 105 mm f2D lens, mounted to the imaging camera with a C-mount, was used. An f-stop of 5.6 was used for visible imaging with the visible light sources and a fully open f-aperture (f/2) was used with the UV light source.

The white-reference standard used for this work was a 20 x 20 cm halon panel (98% reflectance at 550 nm). The data cube of the document was flat-fielded by dividing the pixel intensity of the document by the corresponding pixel intensity from the white cube reference image. The flat-fielded images were then processed with units of optical density (absorbance):

$$\text{optical density} = -\log (I_{image} \div I_{white})$$

All of the spectra are presented in units of optical density except where indicated (i.e., fluorescence imaging). Data from imaging experiments that were saved as cube files could also be treated statistically using algorithms in an imaging software package known as ENVI (Environmental Visual Imaging, version 4.2).

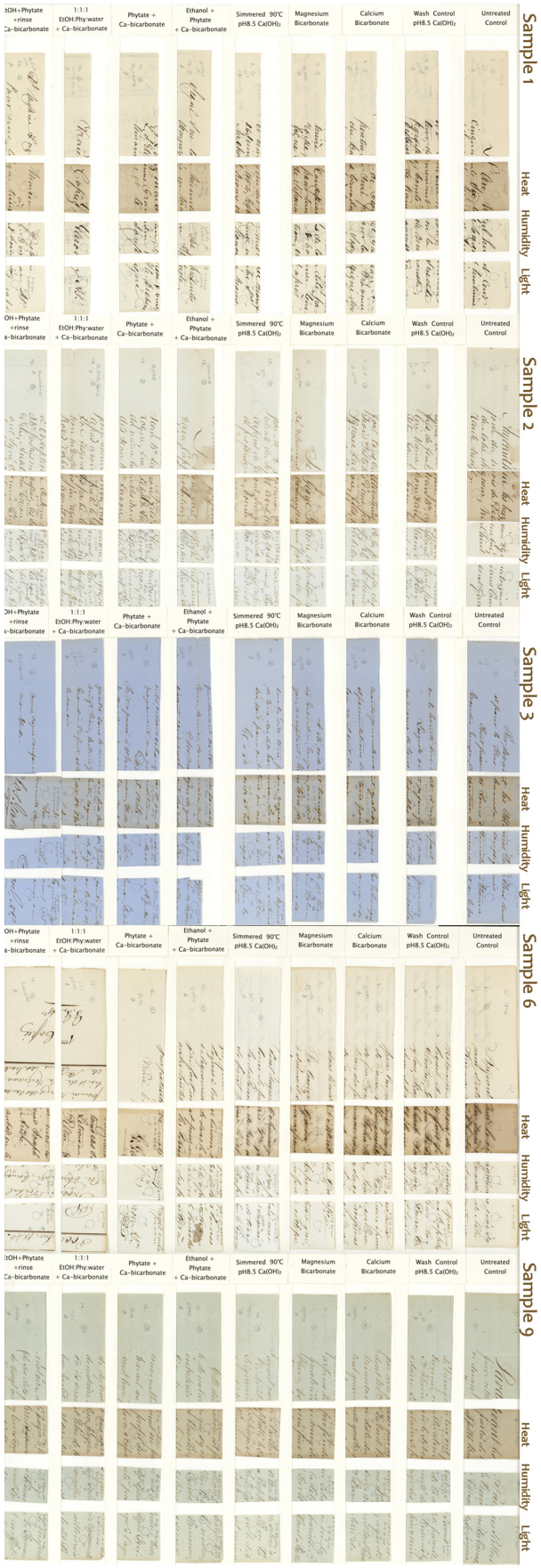
3 RESULTS

Extended exposure to heat and humidity

Artificial heat and humidity aging was used to evaluate the effectiveness of treatments to protect the inked samples. Visual evaluation, color measurements, and Fe (II) tests of heat-aged samples showed that the calcium phytate-bicarbonate combination—with or without ethanol spray, even with rinsing—gave the most effective protection. Dilution of Ca-phy with ethanol and water (1:1:1), without repeating treatment, reduced the effectiveness. Simmering, a controversial treatment for iron-gall ink (Tse et al. 2005), was found to be effective immediately after treatment. The color of the paper and some inks became lighter after treatment. After heat aging, simmered papers remained the brightest, but there was some haloing around some ink lines, and recurrence of soluble Fe (II) ions. Alkaline water wash and deacidification alone were the least effective, as there was significant yellowing and recurrence of soluble iron ions.

Extended exposure to high-intensity light

Exposure to high-intensity, unfiltered, fluorescent light was used to study the fading of the inks. Color measurements using the Minolta hand-held spectrophotometer (with a 8mm sample port) showed that the paper was bleached after light exposure. Evaluation of the change of ink color was not satisfactory because of the relatively large port compared to the thin ink lines. The Oriel Microfade tester will be used to determine the light-sensitivity of the inks and measure the average color change with and without light exposure. FTIR-ATR results showed that simmering removes some sizing and binder from the ink. Other aqueous treatments do not result in a detectable change in the compositions of ink or paper.



Extended exposure to high humidity

A high-humidity environment is not suitable for iron-gall ink documents, not only because of an increased rate of acid-catalyzed hydrolysis, but also because of the likelihood of ink migration—both laterally and also through the thickness of the paper resulting in "strikethrough" (Eusman and Mensch 2000; Reissland 2000). (Assessment of ink migration is discussed further in section 3.5.)

A secondary concern with high humidity is the possibility of mold growth for phytate-treated documents (Homolka 2001). In this study, the phytate treatment is modified by dilution with ethanol and water, as well as inclusion of a rinsing step, and their effectiveness is evaluated. Exposure to 85% RH for twenty-two weeks did not result in mold growth in any of the samples, including all the phytate-treated ones. This suggests that in a clean environment, not infested with active mold or spores, calcium-phytate treated samples do not become more susceptible to mold growth. For conservators who are still concerned that phytate treatment may be a problem, these results suggest that rinsing the artifact after phytate treatment, to remove excess phytate, would not diminish its effectiveness.

Feasibility of visible HSI for monitoring ink changes after treatment and after exposure to heat, humidity, and light

The most important advantage of using hyperspectral imaging (HSI) is the quantity of spectral data that can be collected in a relatively short time. One image cube contains more than 10^6 pixels, and each pixel represents a visible spectrum (420–720 nm) for a given spatial location. For ink studies this is especially important. Most conventional color measurement instruments have sample ports that are much too large (typically 3–8 mm in diameter) for the width of the ink line (typically less than 1 mm). Therefore it is not possible to obtain spectra of ink alone without the surrounding paper, making it impossible to follow changes in the ink as a result of treatment or aging.

With these samples, single wavelength images were collected from 420 to 720 nm at 10 nm intervals using both ultraviolet (365nm) and visible light sources. The highest contrast between paper and faint portions of ink was achieved at short visible wavelengths. Therefore images under UV illumination were collected at 430 nm with various exposures and are shown in figure 3.

Using visible HSI, we are able to measure spectral changes (fading, darkening, and changes in hue and chroma) in the ink as a result of treatment and accelerated aging. It is,

Fig. 2. Five sets of aged and treated iron-gall ink documents. Each column represents a different aging method: 1) unaged controls; 2) heat; 3) humidity; 4) light. Each row of samples represents a different treatment described in table 2

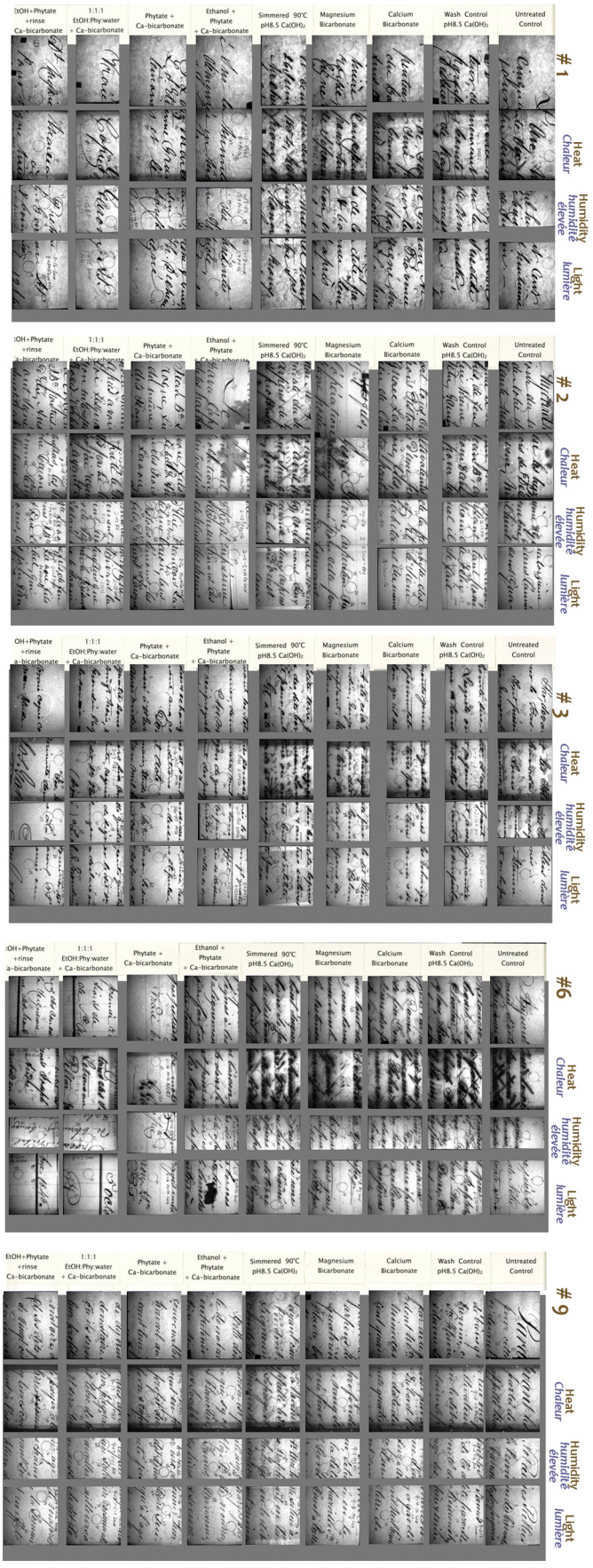


Fig. 3. Five sets of aged and treated iron-gall ink documents under UV illumination, examination at 430nm. Columns: 1) unaged controls; 2) heat; 3) humidity; and 4) light. Each row of samples represents a different treatment described in table 2

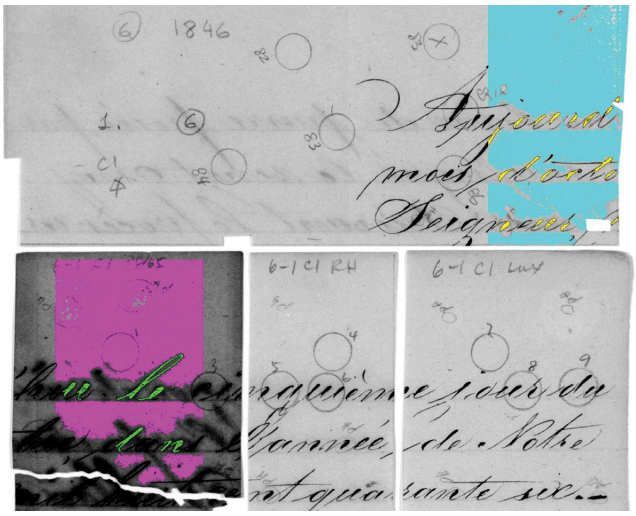


Fig. 4. Four regions of interest (ROI; 1000 pixels) for sample 6

however, limited by the variation (non-uniform nature) of the ink lines, typical of any original ink documents. So it can be difficult to determine whether differences in the ink are a result of treatment, aging, or simply sample variation. The criteria for selecting pixels becomes critical.

Figure 4 shows four regions of interest (ROIs) that were selected for sample 6. In this figure, the blue (control) and purple (artifical aging) ROIs represent pixels selected for paper, and the yellow (control) and green (artificial aging) pixels represent ink pixels. This figure illustrates the specific ROIs of the document that were selected for generating spatially accurate visible spectra of paper and ink shown in figure 4. Apart from examining visible spectra, measuring change in the visible spectra before and after treatment is also a useful tool. Determining differences in the visible spectra can be achieved by subtracting the average pixel optical density of inks that have undergone aqueous treatments from the control ink. The results are summarized in figure 5.

Spectral change occurred in most of the iron-gall inks after accelerated aging. By selecting a large number of ink pixels for each paper, the differences in ink thickness can be minimized. The ink and paper that were exposed to UV and humidity showed less change in optical density than those after heat aging. All of the heat-aged inks became darker, with an increase in optical density of 0.1 to 0.2.

Even when the largest number of pixels was selected (>1000), incorrect conclusions are possible, especially when treatment comparisons are made between different inks on

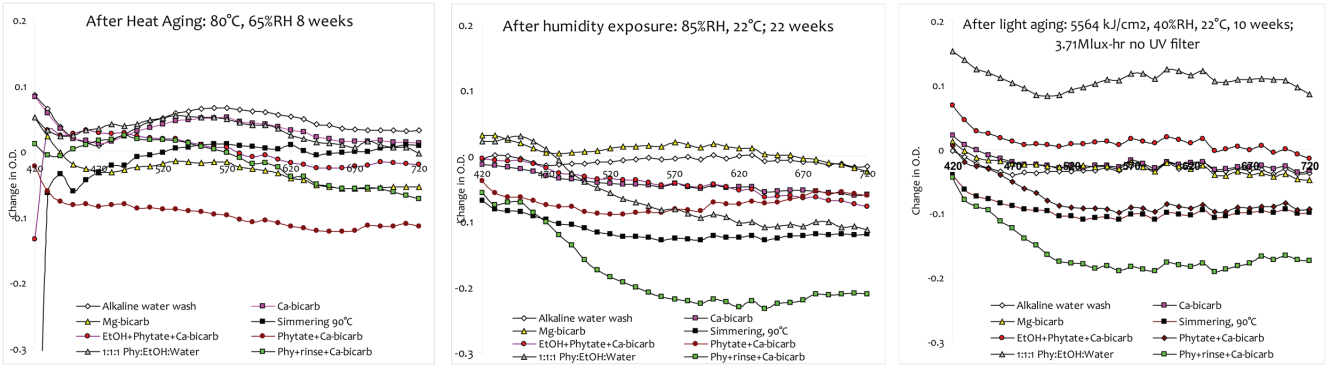


Fig. 5. Spectral differences between untreated control and treated samples after heat, humidity, and light aging for sample 6

different papers. The most reliable approach is to measure optical density of the same ink before and after a treatment.

Feasibility of visible HSI for documenting migration of ink components

The negative effects of high-humidity environments on iron-gall inks are well recognized. UV illumination has been used to visualize ink migration (Reissland 2000). In this study, visible HSI with UV illumination (365nm) was used to document and compare the impact of treatments on different inks after exposure to high relative humidity. The visible images in this report are collected at 430 nm.

Migration of ink components was clearly visible, especially with inks that have a lot of available ferrous ions (bathophenanthroline test results [Fe^{2+}]>50+). Of the five documents that were imaged, sample 6 has the highest [Fe^{2+}][1], therefore any migration would be most visible with this set of samples. Under UV illumination, migrated components appear as shadows or halos around ink lines after water washing, deacidification, and simmering. Exposure to very high humidity (85% RH) also resulted in lateral migration of some components of this ink, presumably Fe (II) ions. An example of darkening away from a primary ink line is shown in figure 6. For the purpose of obtaining visible spectra, three regions of interest (ROI) are shown in this image. The visible spectra of each of these ROIs (paper, ink, and migrated ink) are shown in figure 7. The visible spectra obtained from the UV source show a very prominent peak λmax = 520–540 nm. This peak arises from the excitation of π bonds of the paper. Because of the high fluorescence of the paper, the spectra of the ink halos contain some of the spectral features of the paper. Compared to the minimal fluorescence in the primary ink lines, this contrast means that the UV light source provides a very sensitive method for assessing the extent of haloing of the ink. Comparing illumination using 430 and 520 nm wavelengths, 430 nm showed a higher contrast between paper and ink and is more sensitive for assessing the extent of haloing of the ink. The decreasing signal at longer wavelengths is indicative of greater transparency of the migrated ink components above 600 nm.

Initially there were some puzzling results from bathophenanthroline test for Fe^{2+} and Fe^{3+} among the untreated inks after exposure to high humidity. All the inks tested negative for both types of iron ions. Initially this was believed to be caused by iron ions being converted to a water-insoluble form such as iron oxy-hydroxide, but UV examination showed that ink components, presumably Fe (II) ions, have migrated to the surrounding areas on the paper as a result of high humidity. The most migration occurs with untreated inks that have a very high initial Fe (II) content.

All phytate treatments, with or without modification, show no migration after treatment or when exposed to high humidity. This showed that phytate is effective in complexing the Fe (II) during treatment, preventing these ions from migration. Ink with less available Fe^{2+} also showed less migration after non-phytate treatments or humidity exposure.

CONCLUSIONS

The most important advantage of using digital imaging is that spatially accurate information can be acquired. In this sense it is possible to acquire visible spectra of a thin ink line without significant contribution by the surrounding paper. In these experiments, HSI was introduced after treatment and aging; the variation naturally existing in these original samples reduced the sensitivity of the technique to quantify change, making it difficult to distinguish, for example, between strikethrough (inks from the verso) and light-color inks. Even with this limitation, HSI was shown to be useful for assessing spectral changes of inks due to treatment or aging.

For the assessment of the migration of ink or ink components, the ultraviolet light source at 365 nm worked very well, especially when compared to images acquired with a visible light source. For visible imaging with the UV source, shorter (430 nm) single-band images were more useful than longer (600 nm) single-band images. Surprisingly, statistical approaches such as Principle Component Analysis (PCA) did

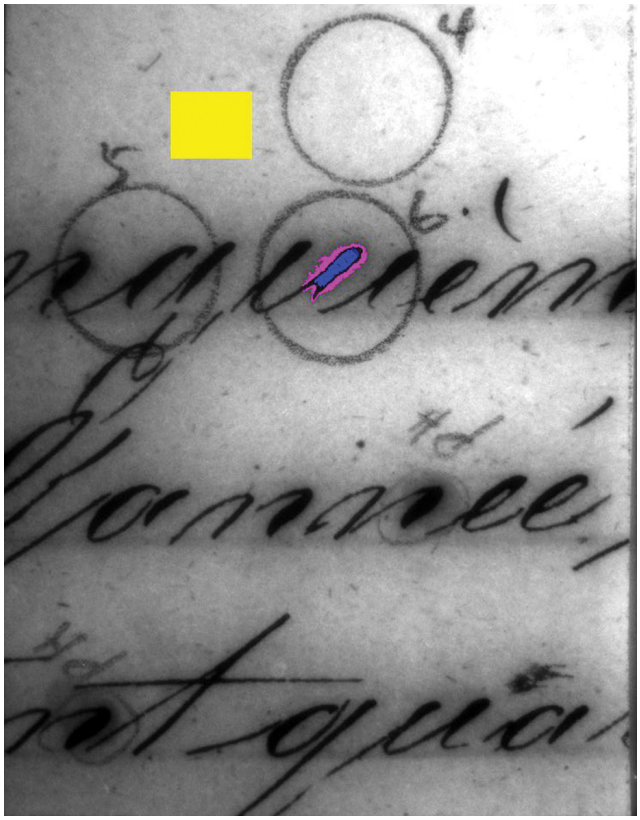


Fig. 6. An example of ink migration from a primary ink line as a result of high humidity exposure. Sample 6 untreated after humidity exposure (85% RH, 23° C; twenty-two weeks), three ROIs: yellow = paper; blue = ink; purple = migrated ink component

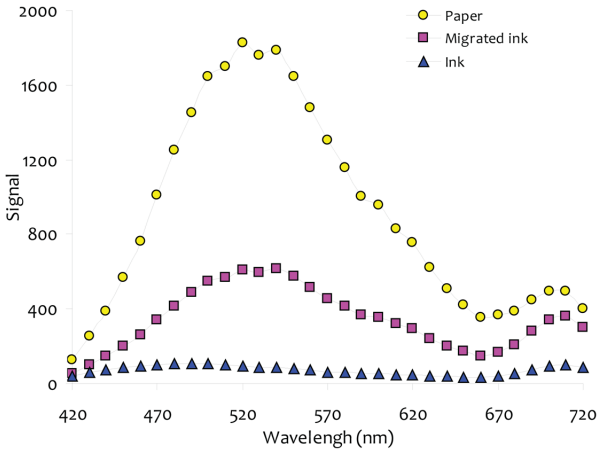


Fig. 7. Visible spectra of paper, ink, and ink migration components with UV Illumination. Sample 6 untreated after humidity exposure, three regions of interest (ROIs) corresponding to fig. 6 : yellow = paper; blue = ink; purple = migrated ink

not improve the visiblity of the migrated ink components and therefore were not used for assessing ink migration.

From a treatment evaluation viewpoint, UV examination showed that inks that have a lot of available Fe (II) ions (tested using bathophenanthroline strips) are most at risk of migration of ink components when subjected to aqueous treatments without phytate or when exposed to high-relative-humidity conditions. All ink samples treated with phytate showed much less or no ink migration compared to other non-phytate treatments. This showed that phytate is effective in complexing the Fe (II) ions, keeping the ions in the ink areas, and preventing lateral migration or "running ink." The immediate benefit of phytate treatments in preventing ink migration is less obvious with inks that do not have have high concentration of Fe (II) ions.

NOTE

1. High concentration of available Fe (II) ions can be a result of excess iron ions in the ink as well as the presence of gelatin size on the paper keeping the ink on the surface of the paper instead of penetrating into the matrix.

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