CONTRIBUTION OF VISIBLE AND FLUORESCENCE LIGHT MICROSCOPY TO A NON-INVASIVE AUTHENTICITY CONTROL OF PAPER SUBSTRATES OF 19TH CENTURY WATERCOLOUR PAINTINGS

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The present study has aimed at investigating non-invasively the authenticity of watercolour paintings based on their paper substrates by Visible Light Microscopy (VLM) and Fluorescent Light Microscopy (FLM) techniques. A set of samples, which imitate substrates of fake watercolour paintings, has been constructed according to art forgery recipes. This set and 19th century original watercolour paper substrates have been observed in different microscopy images. Image analysis has been performed to objectively evaluate and quantify the information provided by the microscopy images. Thus, an automate classification of the samples has been achieved. The results attained clearly indicate that stand-alone digital microscopy, although it is considered as a low-tech tool, has to be an inseparable part of an integrated protocol for authenticity control of watercolour paintings in storage, based on paper analysis.

Keywords: watercolour painting, artistic paper, Visible Light Microscopy, Fluorescence Light Microscopy, forgery

INTRODUCTION

Throughout history, the enforcement of cheaper production of paper, as well as the development of relevant technology, brought about a falloff in constitution and consequently in permanence of several paper types. Nevertheless, artistic papers, such as watercolour substrates, have always been of finer quality and purity, especially those dating back to the late 19th century.[1] At the same time, art forgers have used several methods to imitate the appearance and condition of old original artistic paper substrates. Colouring with a wide range of materials has been one of the most popular among them.[2]

The authenticity control of paintings on paper, such as watercolour paintings, is not covered as a separate subject by the fundamental or current relevant literature.[3-5] Furthermore, in museums, authenticity studies are usually based on painting stylistic criteria, as well as on visual methods of examination by art historians. If physicochemical analysis is carried out, the protocol is mainly defined by an investigation of pigment anachronisms.[5]

An integrated procedure for non-invasive authenticity control of watercolour paintings based on paper substrate analysis would give a totally new perspective to this topic. Relevant experimental research would first aim at adding analytical tools to the characterisation “toolbox” and ultimately at integrating all these inputs in a diagnostic expert protocol, which could be used as a decision-support tool of art historians and conservation scientists. For this purpose, several methods popular for the non-invasive analysis of paintings and usually accessible to museum laboratories, such as Visible Light Microscopy and Fluorescence Light Microscopy, have to be initially investigated.[6]

EXPERIMENTAL

Under normal conditions of storage, the aging processes of fine papers and, more specifically, watercolour papers are very slow, leading mainly to yellowing and loss of strength.[7] Thus, several original watercolour paper substrates belonging to the collection of the National Gallery of Greece, present yellowing as the main macroscopic aging effect. Hence, tinted paper samples are considered to satisfactorily approximate the appearance of original watercolour papers of the late 19th and early 20th centuries. Furthermore, the standard conservation procedure at the Paper Conservation Laboratory of the National Gallery of Greece does not include bleaching or deacidification of watercolor paintings. Thus, the influence of such treatments on the appearance of the original surfaces under investigation is excluded.

Two types of modern, commercially available watercolour papers of high quality, present on the market for several decades, even during the 19th century, were treated in different ways in order to imitate the paper substrate of fake paintings, according to an art forger's recipes.[2] More specifically, a mould made French watercolour paper (185 gsm, rough, 100% rag, gelatin tub-sized (ARCHES, France)) and a mould made British watercolour paper (300 gsm, cold pressed/not, internally and externally sized, acid free, wood free (COTMAN, UK)) were selected. Samples of these papers were tinted by the application of various water solutions, *i.e.* tea, instant coffee, chicory, liquorice, stout, watercolour and permanganate.[2] Other samples were smoked, ironed and treated with boiled water and sulfuric acid.[2]

Furthermore, samples from the two papers were subjected to artificial aging for various periods according to two different protocols: a) a set of samples was aged by dry heating at 105 °C, according to an art forger's recipe,[2] for 14, 27, 45 and 52 days; b) 1 × 7 cm strips of the two substrates were suspended on cotton threads in headspace vials (SU860101 Supelco, with stainless steel screw cap and PTFE/silicone septum, with a thickness of 1.3 mm, Sigma-Aldrich Ltd., Dorset, UK) above 5 mL of 15% sodium chloride solution for analysis (MERCK, KGaA, Germany), thus achieving a relative humidity of ~77%.[8] All samples were aged at 90 °C for 1, 4, 7, 14, 21 and 28 days in an ageing chamber. The latter ageing protocol has been used in recent published work for simulating natural ageing of artistic paper substrates.[9]

The Visible Light Microscopy (VLM) and Fluorescent Light Microscopy (FLM) images obtained from the above described reference samples were compared to those from: (a) a sample from an original watercolour book dated from 1880 belonging to the Greek painter Odysseas Fokas (1857-1946) (FOKAS), (b) the paper substrates of two watercolour paintings by the British painter James Burrell Smith dated from 1891 (ORb) and 1879 (ORc) respectively, and (c) the paper substrate of a watercolour painting by the Greek painter Aggelos Giallinas (1857-1939) (GIAL1).

A complete list of abbreviations for both reference samples and original substrates is presented in Table 1.

VLM and FLM were applied directly on the surface of the paper substrates by the use of a Leica DM/LM microscope equipped with a digital infrared camera DC 300 F and an inset high pressure mercury lamp (50W). For the application of FLM, filter cube A of Leica was used (excitation filter BP340-380, suppression filter LP425). Each sample was observed in four light conditions: (a) transmitted polarized light (TPL), (b) reflected cross analyzed-polarized light (RXP), (c) reflected dark field (RDF), (d) UV excitation (FLM). Images of different magnification (x50, x100 and x200) were preliminary captured.

RESULTS AND DISCUSSION

The microscopic images were initially qualitatively evaluated and compared to each other in different combinations. None of the microscopy images was corrected and were thus evaluated as provided directly by the microscope software, so as to avoid the danger of rendering distorted images, which would bear little resemblance to the original ones, and to ensure the same conditions of comparison.[10]

RDF x100 images have been proved to provide the most legible and helpful information about the morphology and porosity of a fibre network, thus enabling sample documentation and also the non-invasive estimation of the constitution of fibres, fillers and/or inclusions (Figs. 1, 2). Nevertheless, comparisons among RDF images, as well as among RXP images of all samples, do not reveal any clear difference between the naturally or artificially aged and the modern paper substrates before or after the tinting treatment.

On the contrary, TPL images and FLM images reveal very interesting information. Figure 3 presents a representative TPL x100 image of the untreated watercolour paper reference sample (AR0), while Figure 4 presents the TPL x100 image of the paper substrate of the same British watercolour painting dated from 1891 (ORb).

The grey colour and cool tone of the untreated sample (AR0) is distinguishable from the orange-brown colour and warm tone of the old original paper sample. A similar colour and tone is also observed in the other untreated watercolour paper reference samples of different composition and origin (COT0). Respectively, the TPL x100 images of the other three examined old original paper substrates FOKAS, ORc and GIAL1 present orange-brown colours and warm tones comparable to those of ORb.

Furthermore, all tinted AR and COT samples present colours and tones comparable to those of the relevant untreated papers. Actually, the most interesting observation is that all the tinted samples present TPL images of similar grey colour and cool tone range, irrespective of the type of the tint solution, while the same samples macroscopically present clearly different colours. Respectively, all the old original papers examined present TPL images of a similar orange-brown tone, irrespective of their composition, while the same substrates macroscopically present clearly different colours.

Table 1
Labelling of paper samples

ARCHES watercolour paper (AR)	Treatment
ARTEA	Tinted with tea
ARC	Tinted with instant coffee
ARLYK	Tinted with stout
ARL	Tinted with liquorice
ARCH	Tinted with chicory
ARM	Tinted with permanganate
ARW	Tinted with watercolour
ARF	Smoked
ARIR	Ironed
ARB	Treated with boiled water
ARS	Treated with sulfuric acid
AR0	Untreated
AR14	Aged for 14 days at 105 ^{o}C
AR52	Aged for 52 days at 105 ^{o}C
AR59	Aged for 59 days at 105 ^{o}C
AR4	Aged for 14 days at 90 ^{o}C, 77% RH
AR5	Aged for 21 days at 90 ^{o}C, 77% RH
AR6	Aged for 28 days at 90 ^{o}C, 77% RH
COTMAN watercolour paper (COT)	**Treatment**
COTTEA	Tinted with tea
COTC	Tinted with instant cofee
COTLYK	Tinted with stout
COTL	Tinted with liquorice
COTCH	Tinted with chicory
COTM	Tinted with permanganate
COTW	Tinted with watercolour
COTF	Smoked
COTIR	Ironed
COTB	Treated with boiled water
COTS	Treated with sulfuric acid
COT0	Untreated
COT14	Aged for 14 days at 105 ^{o}C
COT52	Aged for 52 days at 105 ^{o}C
COT59	Aged for 59 days at 105 ^{o}C
COT4	Aged for 14 days at 90 ^{o}C, 77% RH
COT5	Aged for 21 days at 90 ^{o}C, 77% RH
COT6	Aged for 28 days at 90 ^{o}C, 77% RH
Original watercolour painting substrates	**Description**
FOKAS	Sample from an original watercolour book by Odysseas Fokas dated from 1880
ORb	Watercolour painting by James Burrell Smith dated from 1891
ORc	Watercolour painting by James Burrell Smith dated from 1879
GIAL1	Watercolour painting by Aggelos Giallinas dated from 1890

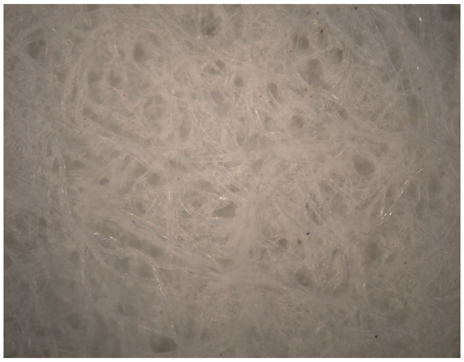

Figure 1: RDF x100 image of the untreated watercolour paper reference sample (AR0)

Figure 2: RDF x100 image of a British watercolour painting dated from 1891 (ORb)

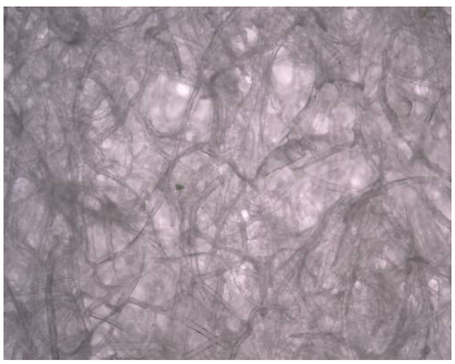

Figure 3: TPL x100 image of the untreated watercolour paper reference sample (AR0)

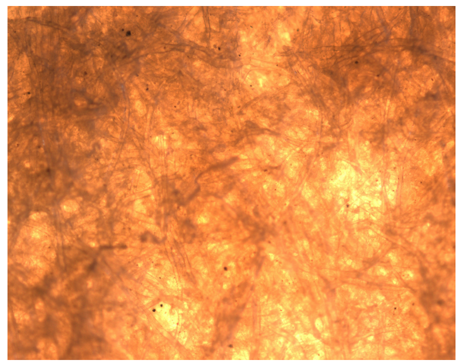

Figure 4: TPL x100 image of the British watercolour painting dated from 1891 (ORb)

In the next step, TPL images of the artificially aged reference samples, which were considered to approximate naturally aged watercolour papers in storage, were compared to each other, to untreated reference samples, to tinted reference samples and to old original papers. A comparison of the TPL x100 image of the samples AR0, AR5 and AR6 reveals a progressive change from a grey colour and cool tone to an orange-brown colour and warm tone.

The next step of the image analysis was an effort of "quantifying" the color information contained in the TPL images and objectively assessing the observed differences and similarities. By means of the public domain open source software *ImageJ*,[11] the parameters of the 2D histograms representing the RGB colour features of each TPL X100 image have been calculated (mean value, standard deviation, minimum, maximum, skewness, kurtosis). Different types of plotting and classification have been created based on these features. Hierarchical Clustering based on the Ward method, achieved by means of the free software environment for statistical computing and graphics *R-project*,[12] provides a clear classification of the substrates into two main categories (Fig. 5).

The first main cluster contains the untreated reference substrates, all reference samples that imitate fake watercolor painting substrates by treatments other than ageing, as well as substrates that have been artificially aged not long enough as to reach the level of the original 19^{th} century watercolor paintings. The second cluster contains all the examined original substrates and some of the extensively artificially aged reference substrates, whose TPL x100 microscopy images present similar RGB color features.

The above mentioned observations suggest that the chromophores produced during ageing of paper (both natural and artificial) are easily legible through optical differentiation recorded in TPL images. At the same time, tinted reference paper, although macroscopically of the same colour and tone with the aged samples, does not microscopically record the presence of these chromophores.

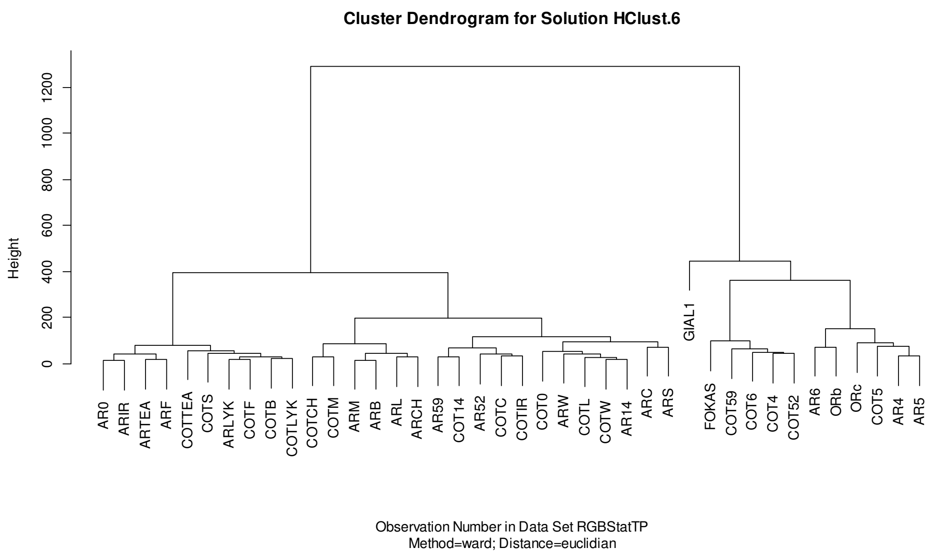

Figure 5: Cluster dendrogram of reference samples and original paper substrates

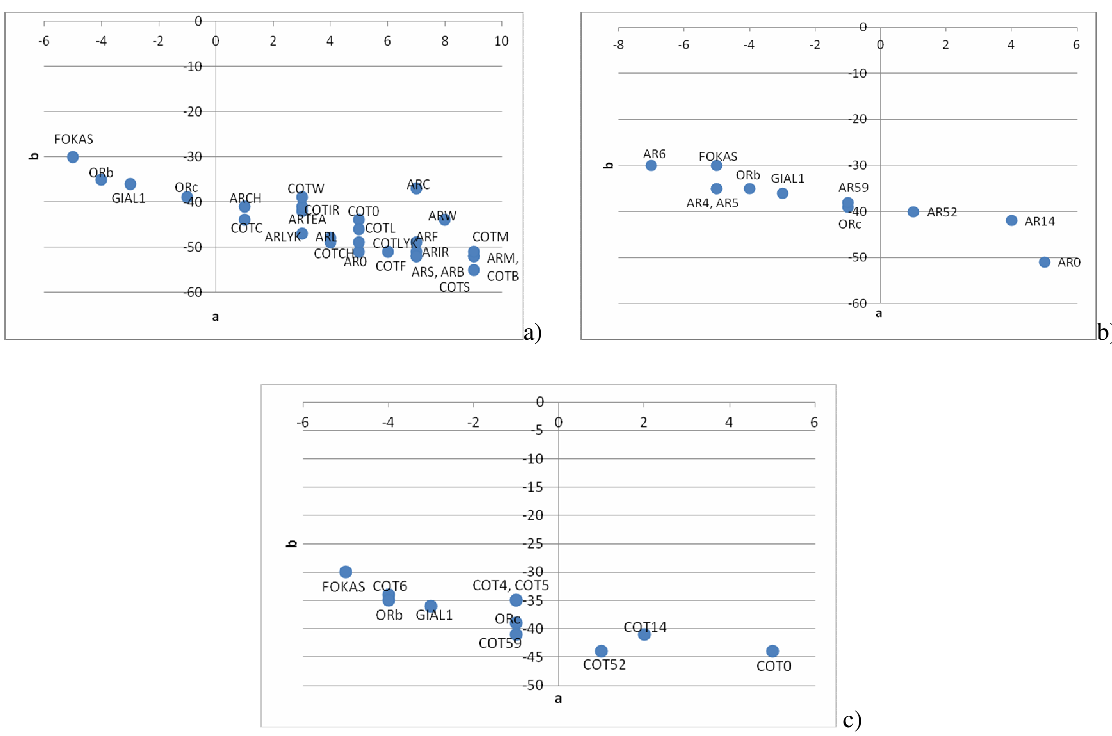

Figure 6: Dispersion based on "a" *vs* "b" values of processed FLMX100 microscopy images of (a) all reference samples that imitate fake watercolor painting substrates by treatments other than ageing, and original watercolour painting paper substrates; (b) all artificially aged AR and original watercolour painting paper substrates; (c) all artificially aged COT and original watercolour painting paper substrates

The production of such chromophores during ageing is well known by the relevant literature.[13-16] Nevertheless, there are no references providing their clear and easy depiction through TPL images of substrates of great weights like watercolour papers. At the same time, other authors report the yellow to brown fluorescence of such degradation products and consequently of yellowed papers.[17] Indeed, the Fluorescence Light Microscopy images of all the reference samples, as well as of the original paper substrates, confirmed this fact. More specifically, the blue colours and cool tones of the untreated samples are distinguishable from the blue-grey colours and warmer tones of the old original paper samples. Furthermore, all tinted AR and COT samples present colours and tones comparable to those of the relevant untreated papers, irrespectively of the type of the tint solution.

For "quantifying" the color information contained in the FLM images and objectively assessing the observed differences and similarities, the approach was quite different, since each color-space model provides a color representation scheme that seems to be tailored for a particular application.[10] By means of the commonly used Adobe Photoshop software, an average blur filter was applied to all images, and the average "Lab" values were measured. Even compared to more sophisticated approaches, the dispersion of "a" *vs* "b" values (Fig. 6a-c) proved to be adequate to visualize the differences and classify the samples into two main categories. The first group contains the untreated reference substrates, all reference samples that imitate fake watercolor painting substrates by treatments other than ageing, as well as the substrates that have been artificially aged not long enough as to reach the level of the original 19th century watercolor paintings. The second group contains all the examined original substrates and some of the extensively artificially aged reference substrates. The processed FLM images of all the components of this first group present positive "a" values, while the images of the components of the second group present negative "a" values.

CONCLUSION

Visible Light Microscopy (VLM) and Fluorescence Light Microscopy (FLM) proved to be very useful tools as part of an integrated protocol for non-invasive authenticity control of watercolour paintings based on paper substrate analysis.

More specifically, Reflected Dark Field x100 images have proved to provide helpful information for a watercolour paper substrate's documentation and for the non-invasive estimation of its composition. Such data can provide evidence with respect to the manufacturing process of the paper under examination, thus helping to verify if this is in accordance with the features one would expect of papers available in the specific time period and area to which the painting is attributed.

Furthermore, Transmitted Polarized Light (TPL) images of all magnifications and especially those of x100 demonstrated the ability to easily distinguish between original and tinted reference watercolour paper samples. Thus, TPL x100 could be used to distinguish between original watercolour paper substrates of the 19th century and substrates that are tinted to imitate them, according to art forgery recipes. Old original papers are expected to present TPL images of orange-brown colour and warm tone, while tinted modern substrates are expected to present grey colour and cool tone. This qualitative observation is subjectively depicted through the formation of two separate clusters by statistical processing based on hierarchical clustering of RGB color features of the TPL microscopy images.

Indeed, the Fluorescence Light Microscopy (FLM) x100 images proved to be able to record a similar differentiation. The dispersion of "a" *vs* "b" values of the images processed by an average blur filter leads to the formation of two separate groups. The first group contains components of positive "a" values, namely the untreated reference substrates, all reference samples that imitate fake watercolor painting substrates by treatments other than ageing, as well as substrates that have been artificially aged not long enough as to reach the level of the original 19th century watercolor paintings. The second group contains all the examined original substrates and some of the extensively artificially aged reference substrates. All these substrates present negative "a" values.

Nevertheless, VLM and FLM images do not seem to be able to distinguish between naturally and extended artificially aged paper substrates. The proof of this kind of deception may require the inspection by means of another non-invasive technique, such as ATIR Spectroscopy. The substantiation of the contribution of this technique to the integrated protocol is a subject for further research by the authors.

Simultaneously, further research has to focus on microscopic examination of more original watercolour painting of the 19th century, since every new result would play the further role of a reference sample. Finally, the investigation of a large number of painters' original artworks could contribute towards the creation of a database of the representative types of paper substrates they used, thus providing an additional tool towards the authenticity control of watercolour paintings.

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