MARTA ORIOLA*
Conservation Section
Faculty of Fine Arts, University of Barcelona
Barcelona, Spain
martaoriola@ub.edu
GEMA CAMPO
Conservation Section
Faculty of Fine Arts, University of Barcelona
Barcelona, Spain
gcampo@ub.edu
MATIJA STRLIČ
Centre for Sustainable Heritage
The Bartlett School of Graduate Studies,
University College London
London, UK
m.strlic@ucl.ac.uk
LINDA CSÉFALVAYOVÁ
Centre for Sustainable Heritage
The Bartlett School of Graduate Studies,
University College London
London, UK
l.csefalvayova@ucl.ac.uk
MARIANNE ODLYHA
School of Biological and Chemical Sciences
Birkbeck College, University of London
London, UK
m.odlyha@chemistry.bbk.ac.uk
ALENKA MOŽIR
Faculty of Chemistry and Chemical Technology
University of Ljubljana
Ljubljana, Slovenia
alenka.mozir@fkkt.uni-lj.si
*Author for correspondence

NON-DESTRUCTIVE CONDITION ASSESSMENT OF PAINTING CANVASES USING NEAR INFRARED SPECTROSCOPY

Keywords: painting canvas, condition assessment, cellulose degradation, non-destructive analysis, NIR spectroscopy, acidity, degree of polymerisation

ABSTRACT

Canvas is the crucial structural element of a painting. Often, most attention is given to the paint layer carrying the aesthetic message. However, degradation and weakening of the canvas can lead to damage caused by manipulation or transportation, and conservation interventions are very resource demanding. Despite this, there is a lack of scientific methods of condition assessment for painting canvases. In this work, we determined the material properties (acidity and degree of polymerisation of cellulose) of 199 canvas samples, the majority of which were historic. We designed two manual, but statistically sound methods of canvas condition assessment, validated by a number of international experts. These being destructive, we also developed a method based on near infrared spectroscopy, which now allows us to determine the condition of a painting canvas rapidly, without sample preparation and in an entirely non-destructive manner.

RÉSUMÉ

La toile est l'élément structurel essentiel d'un tableau. Souvent, l'attention porte essentiellement sur la couche picturale, qui véhicule le message esthétique. Pourtant, la dégradation et l'affaiblissement de la toile peuvent entraîner des dommages lors des manipulations ou des transports, et les interventions de conservation exigent de nombreuses ressources. Malgré cela, les méthodes scientifiques permettant d'évaluer l'état des toiles peintes font défaut. Dans cet article, nous avons déterminé les propriétés matérielles (acidité et degré de polymérisation de la cellulose) de 199 échantillons de toiles, anciennes pour la

INTRODUCTION

Easel paintings have traditionally been done on canvas made of natural fibres such as linen, hemp and cotton (Villers 1981). In all these materials, cellulose is the main component. With time, cellulose degrades through oxidation and hydrolysis, which results in a decrease in the degree of polymerisation (DP) (Strlič 2005). Low DP implies loss of fibre strength (Seves 2000), whereas low pH promotes the degradation rate.

A stretched canvas supports the paint layer and its deterioration can lead to tears and paint and ground losses. The corners and tacking edges are often the points where canvases are least structurally stable (Hackney 1990) and visual assessment of these elements is often the basis of condition assessment by conservators. An empirical test has been suggested, by which a loose thread is removed from the edge of a painting and gently pulled apart. If it "breaks easily or appears to powder or crumble, the canvas might not be strong enough for the painting to travel" (CCI 1993). Since minimal intervention is now the governing rule in conservation, especially when it comes to treating the support (Ackroyd 2003), knowing its condition is even more important for establishing conservation priorities, or to evaluate the fitness of an object for transportation or handling.

NIR spectroscopy, a non-destructive instrumental technique, has recently found increased use in heritage material characterisation, e.g. of paper, silk and plastics (CostD42 2008). The success of NIR methods crucially depends on the availability of a considerable number of well-characterised material samples and on their basis the spectrometer can then be calibrated using multivariate data analysis. NIR spectra are namely characterised by a relatively small number of absorption bands, representing overtones and combination vibrations of groups usually observed in the mid-IR spectrum. Because of this, the information of interest is scattered in the spectra and overlapped, and needs to be extracted using multivariate data analysis, with the quantitative method of particular interest being the partial least squares (PLS) method.

Once such a method is developed, the properties of an unknown canvas can be predicted by taking a NIR spectrum. Provided that a correlation between the DP and the condition assessment can be established, a canvas condition assessment can be performed quickly and non-destructively.

plupart. Nous avons mis au point deux méthodes d'évaluation manuelles mais statistiquement fiables de l'état de la toile, validées par plusieurs experts internationaux. Celles-ci étant destructives, nous avons également conçu une méthode basée sur la spectroscopie infrarouge, qui nous permet de déterminer l'état d'une toile peinte rapidement, sans préparation d'échantillon, et de manière absolument non destructive.

RESUMEN

El lienzo es el elemento estructural principal de una pintura. Normalmente se presta más atención a la capa pictórica que porta el mensaje estético. Sin embargo, la degradación y la debilitación del lienzo pueden provocar daños derivados de la manipulación o el transporte, y las intervenciones de conservación requieren muchos recursos. A pesar de esto, hay escasez de métodos científicos para el análisis del estado de conservación de los lienzos para pintura. En este trabajo determinamos las propiedades del material (acidez y grado de polimerización de la celulosa) de 199 muestras de lienzos, en su mayoría históricos. Para analizar las condiciones de los lienzos diseñamos dos métodos manuales, pero con una sólida base estadística y validados por varios expertos internacionales. Debido a que éstos eran métodos destructivos, también desarrollamos un método basado en espectroscopía de infrarrojo cercano, que ahora nos permite determinar el estado de un lienzo rápidamente, sin preparación de la muestra y de una forma completamente no destructiva.

MATERIALS AND METHODS

Study collection and sampling

A collection of samples was assembled in collaboration with three institutions: the Museu Nacional d'Art de Catalunya (MNAC), the Collection of the Faculty of Fine Arts (University of Barcelona), and the Centre de Restauració de Béns Mobles de Catalunya (CRBMC) and through donations. The paintings are all from the 19th and 20th century, except for ten or so which were produced between the 16th and 18th century. With permission and accompanied by extensive documentation, samples of ~1 cm^2 were taken from the edges of paintings of inferior value that are not displayed. Additional samples consisted of old linings removed from paintings during conservation procedures at UB, as well as modern textiles. In some cases, only threads were extracted and used for pH analysis. The total collection of samples thus consisted of 125 samples from painting canvases, 8 deacidified canvases, 34 linings, 3 historic textiles and nine new textiles, and 20 threads for pH determination only, numbering 199 in total. After analyses, a small area of each sample was retained and is now stored and documented for future studies.

A number of canvases and linings available in larger quantities were degraded in an accelerated manner at 90^{o}C, 65% RH (Vötsch VC 0020 climatic chamber) in order to have a wide selection of threads and canvas pieces for the condition assessment experiment.

Determination of pH

The acidity of the canvases was determined following a modified micro-pH determination procedure published previously (Strlič 2004). An IQ-160 ISFET pH-meter with the pHW47-SS probe (Loveland, CO) was used. Ca. 250-350 μg thread (visible remains of primer were removed) was soaked overnight in 100 μL distilled water in a 1.5-mL vial. After extraction, the sample was removed and the pH of the resulting extract was measured. The typical measurement uncertainty for historic samples using the ISFET electrode is ~0.3 pH units. For most samples, two repeated measurements were thus made, and if they differed by more than 0.5 units (for very inhomogeneous samples), another measurement was taken.

Determination of the DP

The standard viscometric method (ISO 5351:2010) was used to determine the DP of the cellulosic fraction of canvases. It was calculated from intrinsic viscosity using the following equation (Evans 1987):

$DP^{0.85} = 1.1 \cdot [\eta]$.

The sample preparation consisted of manual removal of the primer layer (if present), soaking and washing in warm tap water to remove gelatine, and drying. After the sample was dry, it was manually defibred in order to facilitate the dissolution process. The DP of 95 samples was determined this way.

TFT – Thread folding test

Individual threads (6 of 3 cm in length) were extracted from the canvas, and the primer removed. The following procedure was prescribed:

1. Fold the thread and press the fold between the fingertips, not using the nails. If the thread brakes, the result is "0".
2. Unfold and pull the thread apart gently, and reproducibly. If the thread breaks apart at the fold, the result is "1". If it breaks anywhere else, the result is invalid.
3. If the thread does not break, fold it again in the opposite direction and press between fingertips gently. Repeat instructions no. 2 and 3 as many times as necessary for the thread to break apart and note the number of folds needed.
4. If the thread does not break after 10 folds, note the result as "10" and finish the test (more precise evaluation of stable and strong threads is not necessary).

CPA – Canvas piece assessment

A piece (1.5 × 6 cm) of canvas was manipulated with the fingers as if it were part of a painting by pulling the canvas while bending it at 90° over the edge of a table as if it had to be tacked to a stretcher. The piece of canvas was then put into one of the following categories:

1. Very fragile canvas, it cannot be stretched without reinforcement. Excessive stress not advisable.
2. Fragile canvas, stretching might lead to tearing.
3. Somewhat fragile canvas, stretching can be done carefully.
4. Canvas in good condition.

Near infrared spectroscopy

Near-infrared reflectance spectra were measured using a LabSpec 5000 spectrometer (Analytical Spectral Devices, USA). The spectra were measured with a purpose-made accessory which allowed for collection of spectra in the 45^o/45^o geometry (spot diameter ca. 2 mm), using a 1-m fibre-optics jumper cable to interface with the instrument. The spectra were measured over the range 350–2500 nm, using 200 scans. A Spectralon 99% reflective standard (Labsphere, North Sutton, NH) was used for calibration. Each sample was analysed three times and the spectra were averaged.

Multivariate data analysis

PLS regression (Haaland 1988) was performed using Grams 8.0 software (ThermoScientific). Multiplicative scatter correction (MSC), standard normal variate (SNV) with or without detrending and smoothing using Savitzky-Golay algorithm, were used for spectral pre-treatment (Geladi 1985, Haaland 1988, Barnes 1989). The leave-one-out cross validation procedure was used along with the number of latent factors resulting in the lowest root mean squared error of cross validation (RMSECV).

RESULTS AND DISCUSSION

The degradation of painting canvases is a result of a number of processes, dependent on both the environment and on the nature of the material itself (ICOM 1960). However, very little is known about what agents of deterioration affect canvas stability most. It is in line with the current knowledge of cellulose degradation that acidic samples should be less stable, as a result of rapid degradation due to acid-catalysed hydrolysis (Strlič 2005). Acidification could be the result of many processes: accumulation of degradation products, absorption of acidic gases (particularly past SO_2 pollution), or the degradation byproducts of the painting itself (Rizzo 2003), particularly of the linseed-oil medium (Seves 2000).

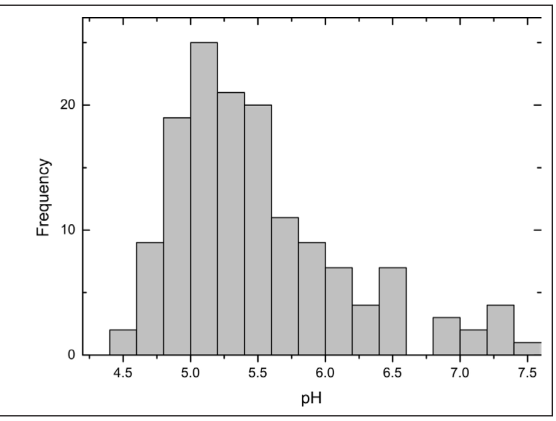
Material analyses

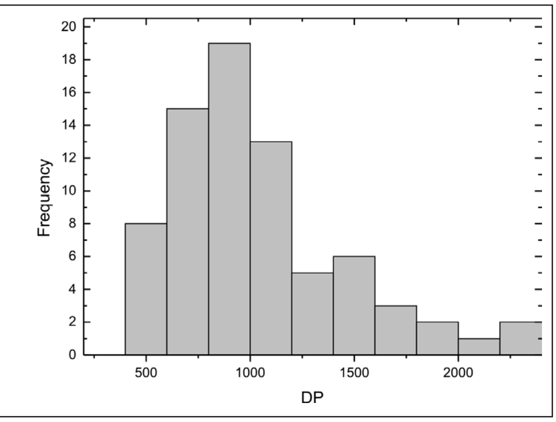
More than half of the analysed samples were acidic, pH 4.5 – 6.0, the most common range being 5.0 – 5.5 (~30%, Figure 1). Old linings were more acidic: 11 out of the 34 were in the range of 4.2 – 4.5, which indicates that glue-paste lining could be a major source of acidity. The DP values showed a normal distribution (Figure 2), with most samples having DP < 1000.

However, in order to evaluate the above measurements, a meaningful interpretation is needed based on a comparison between scientific measurements and object condition assessment.

Condition assessment of canvases and material properties

In everyday conservation practice, the methodology in use to assess the fitness of painting canvases to withstand stress during handling or transportation is very subjective and predominantly involves visual and manual examination. It was the purpose of this strand of research to devise a testing methodology which would be reproducible and relatively easy to carry out and which would enable us to interpret the data reported above. As with all destructive testing methods, it is unlikely that assessment methods as proposed here could be routinely performed on original objects; however, if a correlation could be found with microscopic properties of canvas, which are scientifically measurable, then the need for large samples would be removed. Two methods were designed, one of which corresponds to real situations better (CPA); however, it also requires a





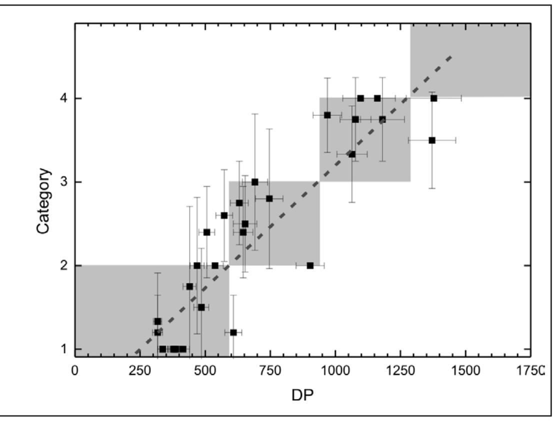


Figure 1
pH distribution of 145 historic painting canvases

Figure 2
DP distribution of 95 historic samples

Figure 3
Correlation between CPA category and degree of polymerisation of cellulose. The error bars represent standard deviations in the assessment of 2-6 assessors per individual canvas sample

larger sample. The TFT procedure only requires individual threads for analysis, so it might be more straightforward to perform.

In Figure 3, the correlation between canvas condition categories (CPA procedure) and DP of cellulose in canvas threads is explored. There is a good linear correlation between the two, indicating that categories broadly correspond to cellulose DP. Category 1, representing all canvases categorised in average <2 (i.e. at least one assessor thought the canvas was category 1), spans DP < 600, category 2: 600 < DP < 950, category 3: 950 < DP < 1300, category 4: DP > 1300. Due to the high standard deviation of category assessments, the borders between categories are certainly not well defined. The observed standard deviation is not only due to the level of (dis)agreement between different assessors, but also due to the inherent inhomogeneity of canvas samples, as a number of pieces of canvas had to be prepared for this test and their homogeneity was difficult to assure.

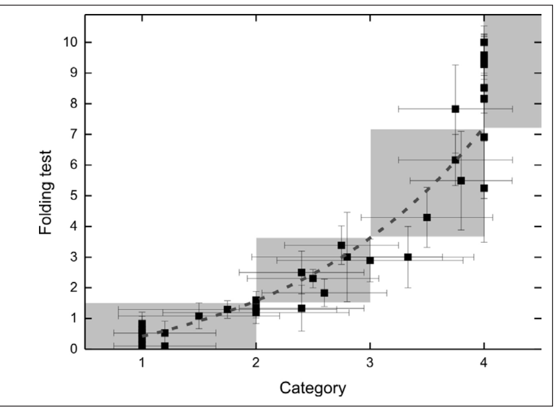


Figure 4
Correlation between the TFT (average number of folds for 6 threads) and the CPA test (categories)

It is of interest that the limiting DP defining category 1 is quite high, considering that for paper, the value 250–300 is usually taken as the value at which paper loses all mechanical properties (Shroff 1985), and recently, DP 400 was considered to be the value at which historic paper containing iron gall ink is considered at risk (Strlič 2010). In canvases, better mechanical properties are required to perform the pulling and stretching operations to tack a canvas onto the stretcher, so the value of DP 600 is not surprising. From among the painting canvas samples measured in this study, about 11 percent had a DP < 600.

In Figure 4, the correlation between the folding test and canvas condition categories is explored. TFT is not unlike the so-called Stanford test developed for historic paper (Buchanan 1987). It is of interest to compare the standard deviations of both methods: at very low values of folding, TFT uncertainty is much smaller than that of CPA. This means that in order to recognise a very degraded canvas, the TFT test will be more reliable. This is of particular importance, as recognising category 1 canvases helps to prevente major structural damage during handling or transportation.

The correlation between the two methods is exponential rather than linear, but still allows the average number of folds to be approximately classified as category 1: <1.5 average fold number; category 2: 1.5 – 4, category 3: 4 – 7, category 4: >7 average fold number. This demonstrates that the folding test could be used to categorise canvas condition, which is welcome, as it is easily performed. However, if the canvas condition needs to be performed non-destructively, then categorisation could be performed using NIR spectroscopy.

Near infrared spectroscopy and non-destructive condition assessment

Since near infrared spectra are typically strongly overlapped, the traditional analytical approach is rarely useful (Siesler 2002). However, because various functional groups lead to several absorption bands in the same spectrum, the spectra are particularly information rich, and this information needs to be extracted using multivariate analysis (Garthwaite 1994, Brereton 2003).

The partial least squares regression method allows for correlation between a set of analytically obtained data using a reference method with a set of spectral data. In the correlation, entire spectra are usually used. In the method presented in Figure 5, spectral data between 1600 and 2250 nm were used with SNV spectral pre-treatment to optimise the model. Leave-one-out cross-validation was used due to the small number of samples not allowing for validation using a separate validation set.

The PLS method allows for determination of DP based solely on an NIR spectrum. The procedure takes a reasonably short time, and can be performed by non-specialists in non-laboratory environments (Figure 6). It should also be taken into account that the method will only be reliable for canvas samples which are similar to those used for method development. For canvases made of materials other than cotton, linen, hemp, jute or ramie, and for canvases older than 18th century, the method has not been validated.

The DP error of cross validation of 320 is reasonable, given that canvases were in no way prepared or cleaned for analysis, as would be the case in laboratory situations. Despite the extreme heterogeneity of samples, the method still allows for reasonably good determinations of DP thus allowing for non-destructive condition assessment of painting canvases based on the correlation presented in Figure 3.

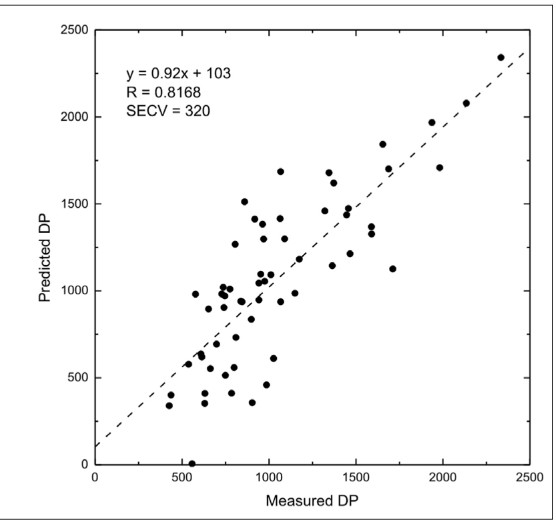


Figure 5
PLS method showing correlation between the DP predicted from NIR spectra and the DP as determined using the reference viscometric method

Figure 6
Measurement of NIR spectra on the verso of a painting

CONCLUSIONS

In this work, the possibilities for condition assessment of painting canvases based on their material properties were explored using two newly proposed procedures. A number of canvases were tested, and the results were compared with microscopic material properties: acidity (pH) and degree of polymerisation (DP). This led to the following conclusions:

- There is a good correlation between the two proposed condition assessment tests with a remarkable agreement between 15 assessors.
- Categories based on the CPA procedure correlate with DP very well, leading to the conclusion that categorisation of canvases could be done based on DP determination of canvas threads.
- A method of DP determination based on NIR and multivariate data analysis is proposed, which is entirely non-destructive, requires no sample preparation and is suitable for use in a non-laboratory environment. To increase the reliability of the method, it would be advisable to include further samples in the calibration.

The NIR method developed is extremely interesting for surveys of painting collections, but also in decision-making related to mechanical stability of paintings and their fitness for handling and transportation. However, for the purpose of the later, not only the condition of the canvas, but also that of the paint layer needs to be assessed.

ACKNOWLEDGEMENTS

Financial support by the COST Action D42 and by the University of Barcelona is gratefully acknowledged. This research would not have been possible without access to real works of art and sampling permission from the following people and institutions to whom the authors are truly grateful: MNAC (Mireia Mestre), Collection of the Faculty of Fine Arts, Univeristy of Barcelona (Dolo Pulido), and CRBMC (Maite Toneu). In addition to the authors of the paper, the following colleagues helped with the canvas tests and their assistance is gratefully acknowledged: Cecil Kraup Andersen (School of Conservation, Denmark), Anne Bacon (Northumbria University), Kenneth Bé (Gerald Ford Conservation Center), Irene Civil (Fundació Gala – Salvador Dalí), Jim Devenport (Haughton Studios), Stephen Hackney (Tate Gallery), Jean-François Hulot (Conservation consultant, France), Maite Jover and Lucía Martínez (Museo Nacional del Prado), Eun-Jin Kim (National Museum of Contemporary Art, South Korea), Núria Pedragosa (Museu Nacional d'Art de Catalunya), Erminio Signorini (Private conservator and Cesmar7, Italy), Eileen Sullivan (Cleveland Museum of Art), Maite Toneu, Pau Claramonte and Nadir López (Centre de Restauració de Béns Mobles de Catalunya), and Christina Young (Courtauld Institute of Art).

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