Assessing the pH and DP of canvasses with NIR spectroscopy

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Introduction

The canvas support in easel paintings is composed mainly of cellulose. One of the main degradation paths of cellulose is acid-catalysed hydrolysis, which means that in an acidic environment (low pH), its degradation proceeds at a faster rate (Strlič et al., 2005).

The main effect of acid-catalysed hydrolysis is the breaking up of the polymer chains, measured by the "Degree of Polymerisation" (DP). The lowering of the DP value implies a lower mechanical strength of the textile (Scicolone, 1993), and thus this parameter can be used to monitor degradation. Knowing these two parameters can, therefore, be very informative regarding the condition of the canvas support.

Until now, though, physical samples needed to be taken to have these two parameters (pH and DP) analysed. The main aim of this investigation was, therefore, to assess whether a Near Infrared (NIR) spectrometer could be calibrated to non-destructively assess the condition of the canvas support in easel paintings.

NIR spectrometry and chemometrics is a technique that has been largely developed and used in the industry for many years now to determine, in a fast and non-destructive way, many different features of all sorts of products.

In the field of cultural heritage, it has recently been successfully applied to determine different parameters for paper (Trafela et al., 2007), plastic (Keneghan, 2011), silk (Richardson and Garside, 2009) and parchment objects (Možir et al., 2011), but it had never been applied to easel paintings and this is why this research was ground-breaking in this sense.

Methodology

Infrared spectra of organic materials at the near infrared (NIR) region (780 - 2500 nm) is very information rich but since absorption bands overlap a lot, patterns are not clearly visible to the naked eye. This is why multivariate data analysis tools (chemometric tools) are needed, so that the large amount of variables can be analysed all together to create a complex equation (calibration) that explains repetitive relationships and patterns between the spectra and the corresponding parameter of interest. If this is achieved, then predictions for the calibrated parameters can be obtained non-destructively from just one NIR spectra taken from new objects.

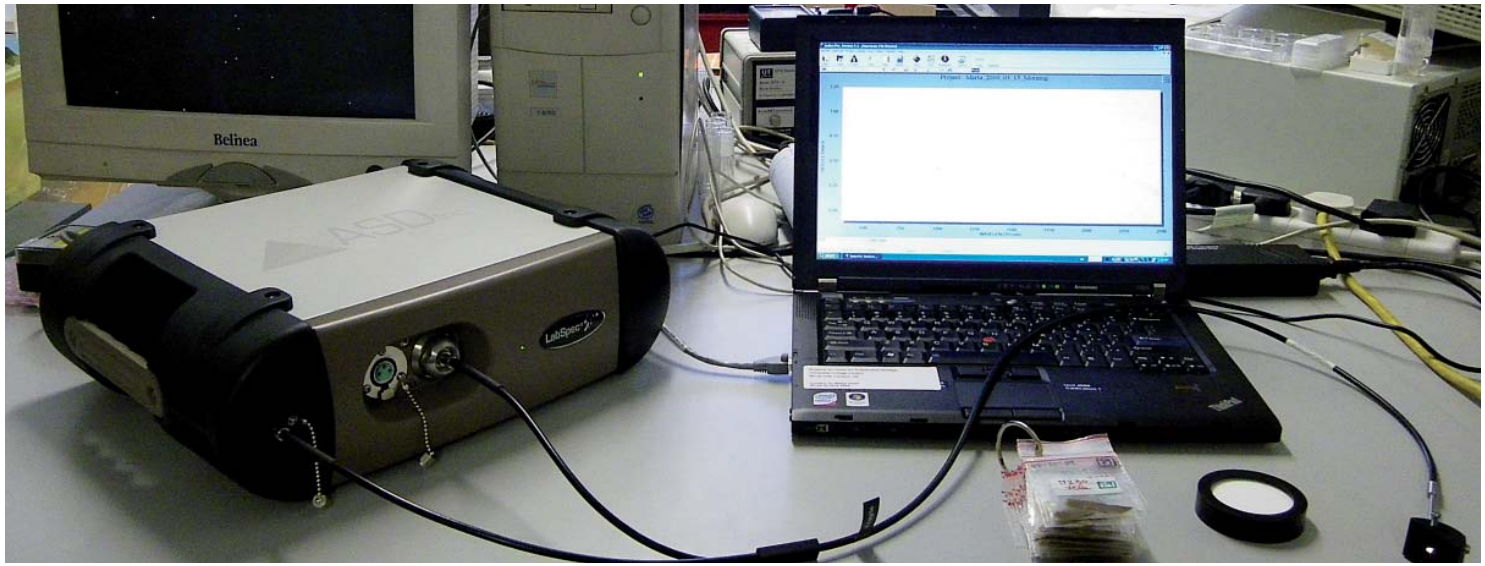

Figure 1. The NIR spectrometer Labspec 5000 (Analytical Spectral Devices, USA) used to take the NIR spectra —property of the Centre for Sustainable Heritage (UCL)—.

However, to develop the technique, first a large set of real samples from paintings need to have the parameters of interest analytically measured and their NIR spectra taken with the NIR spectrometer. To this end, a Reference Sample Collection of about 200 samples mainly from paintings, was gathered. Then, pH and DP were analysed and the results used to create a "model" (or "calibration") using chemometric tools (mathematical and statistical tools that enable "multivariate analysis").

The instrument used to take the NIR spectra was a Labspec 5000 spectrometer (Analytical Spectral Devices, USA) that works in the range of 350 - 2500 nm (UV-vis-NIR) (Figure 1). Spectra of the samples were taken on the white calibration pad, using 200 scans. PLS calibrations for pH and DP were performed using the "*Grams AI spectroscopy software*" from ThermoScientific, with the chemometric add-ons "*Grams IQ*" and "*IQ Predict*".

Most of the samples from the Reference Sample Collection were from paintings from the 19th and 20th C, although there was also a few (11%) much older ones (16th – 18th C) and a few (9%) very new ones, from the 21st C. As a result of this investigation, we also learned about the typical pH and DP values of paintings from these periods (Oriola, 2012).

pH was measured by applying the micro-pH cold extraction technique normally used for cultural heritage paper objects (an adaptation of the standard ISO 5351:2010 (Saverwyns et al., 2002 and Strlič et al., 2004) and thus a very small amount of sample (250-350µg) and 100µL of water were used for each measurement. The Ion-Selective Field Effect Transistor (ISFET) metallic microprobe used was found to be cheap, quick and extremely user-friendly and therefore this type of probe is strongly recommended.

About half of the Reference Sample Collection had their DP measured through viscometry by following the ISO standard ISO 5351/1-1981. It was concluded that, in the case of easel paintings, to obtain the needed amount of fibres to do the measurement (30 mg), a sample size of between 1.5 and 2 cm^2 of the canvas support is generally needed. It was also found that if the sample to be measured is in very good condition, it is much better to use a smaller amount of fibres (10 cm^2) to do the analysis.

Discussion and conclusions

A calibration for non-destructive predictions of pH and DP of the canvas of easel paintings using an NIR spectrometer has been successfully achieved. pH and DP calibrations were modelled by using the Partial Least Squares (PLS) chemometric tool and the error of predictions achieved were, respectively, ±0.4 for pH (Figure 2) and ±275 for DP. These results are to be considered quite successful, especially regarding pH, if we compare them with those that have been obtained for cultural heritage paper objects, a similar cellulose-based material, which are ±0.3 for pH and ±175 for DP (Trafela et al., 2007).

The successful calibration of the NIR spectrometer for predicting pH and DP gives us a very powerful instrument for non-destructively and very quickly determining the present condition of the canvas support of easel paintings, which has already been used in the case of twelve paintings by Salvador Dalí (Oriola, 2013). However, one has to take into account that the developed method will only be useful for similar samples to those that were used in the calibration, which in our case means mainly 19th and 20th C paintings.

All the Reference Sample Collection had pH measured and this was found to be mainly acidic. The most typical value for a painting to have was determined to fall between pH 5.0 and 5.5. Interestingly the pH of a large set of old glue paste linings was found to be markedly more acidic than that of paintings. This indicates that there could be some acidic ingredients in the glue paste lining recipe (such as vinegar, alum, Venice turpentine etc.) that induces this lower acidity discovered in these samples.

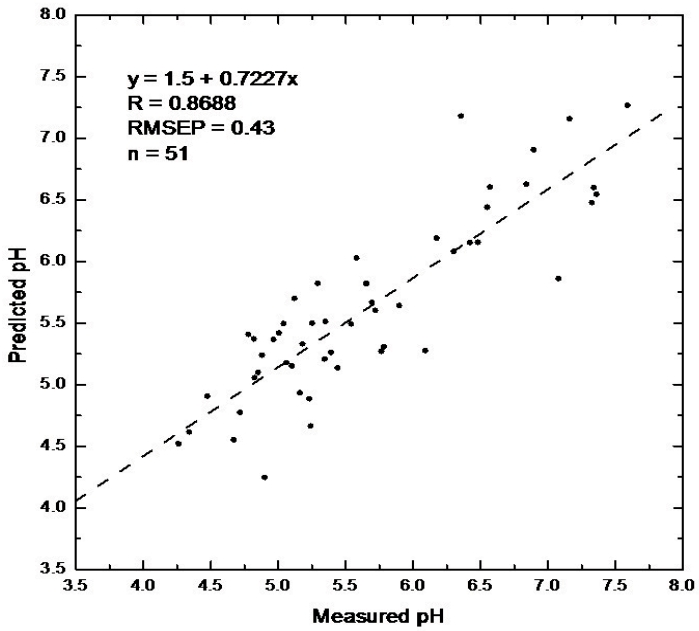

Figure 2. The validation plot for pH showing "Predicted pH" (pH predicted by our calibration) and "Measured pH" (that is to say pH analytically measured of the same samples). The closer the dots are to the line, the better our predictions are, since this means that the "Predicted pH" value and the "Measured pH" value are very similar.

Figure 3. Example of a very degraded sample with an acidic pH of 4.8 and a low DP of 410. The threads of this sample could be easily broken just by pulling them with the fingers.

It was found that most of the analysed samples had DP values between 600 and 950. Comparison between samples coming from the same painting that looked/felt visibly in a very different condition, were found to present indeed markedly different DP values. Old glue paste linings, were also found to have lower DP values than paintings. Paintings with lower pH values were generally found to have lower DP values too, indicating that acidity plays indeed a very important role in the degradation of canvas (Figure 3).

The fact that paintings have been clearly found to be mostly acidic makes us more aware about the need for actively finding ways for removing this acidity from the canvas of easel paintings, especially since it has been corroborated that pH and DP are correlated and thus it is clear that acidic canvases will see their DP lowered at a faster rate than neutral or slightly alkaline canvases, and this will clearly affect the support's mechanical properties.

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