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Non-destructive condition assessment of painting canvases using NIR spectrometry

Marta Oriola Folch

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UNIVERSITAT DE BARCELONA

Faculty of Fine Arts
Painting Department
Conservation Section

PhD program: *Painting in the digital times: Afinity and specificity*
Years 2003-2005

Non-destructive condition assessment of painting canvases using NIR spectrometry

A thesis submitted by **Marta Oriola i Folch**
for the degree of PhD with a European mention

Thesis director: Dr. Gema Campo Francés

Barcelona, December 2011

To my family
and to all the good friends and colleagues
I am lucky to count with.

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Abreviations used

CRBMC	Centre de Restauració de Béns Mobles de Catalunya
DA	DiscriminantAnalysis
DP	Degree of Polymerisation
ISFET	Ion-Selective Field Transistor
MMC	Methoxymagnesiummethyl carbonate
MNAC	Museu Nacional d'Art de Catalunya
NIR	Near Infrared
PCA	Principal Component Analysis
PLS	Partial LeastSquares
RH	Relative Humidity
RMSECV	Root Mean Square Error of Cross Validation
RMSEP	Root Mean Square Error of Prediction
RMSEV	Root Mean Square Error of Validation
RSD	Relative Standard Deviation
SD	Standard Deviation
SEP	Standard Error of Prediction
T	Temperature
UCL	University College London
UB	Universitat de Barcelona
VOCs	Volatile Organic Compounds

Notes:

- Numbers in brackets indicate references used, the full citation of which is found at the end of the thesis ordered according to the different chapters under the References section.

- In many instances the exact pages in the cited references where ideas are found have been noted down since doing this was found to be very helpful in other's work and so it is hoped this will be useful for future cross-checking of information.

- Numbers in bold type indicate the samples and paintings used in this thesis, the full reference of which can be found in Annex I: Reference Sample Collection and Annex IV: Case studies catalogue.

Introduction

Ever since the first civilizations, humankind has cared for the conservation of its past and present cultural heritage. Artistic objects, such as paintings, are physical remains of previous human cultures and therefore they provide us with a tangible connection with our past. Moreover, they are also evidences of human artistic development throughout the centuries. Thus, cultural heritage helps us to build up our identity by telling us where we come from, and by preserving it for future generations to enjoy it, it also projects us into the future.

However, all matter has the natural tendency to change, and thus, regardless of how hard we try, with time, all objects will degrade. Nonetheless, we have the moral duty to try to slow down this degradation rate so that we pass our cultural heritage to the next generations in the best possible conditions (1). In order to be able to take the appropriate conservation actions, though, one first needs to assess and understand what the actual condition of the objects to be preserved is.

This PhD focusses on easel paintings, and more precisely on the study of the degradation of the canvas support. This is one of the most important layers in a painting, since if the canvas disappears there is no support to hold the paint layer which carries the aesthetic message.

Easel paintings have traditionally been painted on woven textiles of a vegetable origin (the fibres most often used have been linen, hemp, cotton and jute). All these textiles have cellulose as the main constituent, the most abundant natural polymer on Earth. Since cellulose is an organic polymer, it is easily affected by degrading agents such as heat, humidity, light, biological agents and pollution.

One of the most important effects of canvas degradation is its loss of mechanical strength. With degradation, canvas becomes more brittle than it was originally and can then be easily torn. If degradation proceeds further, the textile can become even powdery.

This natural degradation of the canvas has traditionally been overcome by adhering a new textile support to the reverse of the painting (lining). Nowadays, however, lining is considered a very intrusive treatment (2) that can have adverse effects (flattening of the paint layer, complete impregnation of the original support with adhesive etc.) and it is against the current conservation criteria of maintaining as much as possible the original integrity of the object (lining hides completely the original canvas and it implies the addition of lots of new foreign materials) (3 p. 15). Therefore, nowadays lining is only done in the cases where it is considered to be strictly necessary, that is to say when the original canvas is very much degraded.

Due to all this, now more than ever, being able **assess the present condition of the canvas support of paintings** is of paramount importance, so that informed conservation decisions can be taken.

There are different chemical and physical analysis that can be done to assess the condition of a canvas. The strength of a textile can be assessed with mechanical tests that measure, for instance, the stress/strain curves of the material or the maximum load before failure. These tests, though, need quite a large amount of sample and many repetitions to be done. Since the mechanical strength of a textile has been found to be related to the degree of polymerisation (DP) of the cellulose chains that form a textile (4), measuring the DP is another way of knowing the degradation state of a canvas, with the advantage that it requires a much smaller sample.

The main chemical degradation path of cellulosic materials is acid-catalysed hydrolysis. This means that if acidity is present in a cellulosic material (paper, canvas etc.),degradation proceeds at a faster rate. One of the results of acid-catalysed hydrolysis is the breaking up of the cellulose chains, lowering the DP of the material and therefore its mechanical strength.

Therefore, knowing the DP of cellulose and the acidity (pH) of a canvas, gives very relevant information on the condition of the canvas of easel paintings. However, both these analysis require a physical sample to be removed from the object in order to be measured.

Sampling works of art has always been a controversial issue, since, even if minimal, it requires the removal of original material from precious unique objects. This is why the development of non-destructive ways to analyse works of art has been favoured in the last decades and new additional techniques are very much welcomed.

Near Infrared (NIR) spectroscopy with multivariate data analysis represents a non-destructive method that has increasingly been applied with success in many different industrial fields in the last years (5). Once the method for a particular type of material and a specific analytical parameter has been developed, the technique does not require a physical sample to be extracted in other to determine the unknown parameter. Only a NIR spectrum needs to be measured, which is non-damaging, fastand can be done by inexperienced operators. This makes the new tool very valuable for conducting rapid collection surveys.

In the field of cultural heritage NIR spectroscopy and multivariate data analysis (or chemometrics) have been recently applied to the study of paper, parchment, silk and plastic objects (6)(7)(8)(9), but it had never been attempted on easel paintings yet.

Therefore the main aim of this thesis was to assess whether non-destructive NIR spectroscopy and chemometrics could be applied to the measurement of the pH and the DP of the canvas support of easel paintings as a way to identify its condition.

Although once built the technique is non-destructive, in order to build it, one first needs to do some destructive analysis. A large number of samples from real easel paintings needs to be gathered and the parameters of interest destructively analysed. The parameters chosen to assess the condition of the support of paintings were the DP and pH of the textile.

DP is usually measured through viscometry, a method by which the textile sample is dissolved in a solvent and the viscosity of the solution measured. Since the viscosity of the solution changes according to the length of the cellulose polymer chains, the DP can be therefore determined.

Acidity of a solid sample, which is what canvas support samples are, can be measured by the method of cold pH extraction in which the sample is placed in distilled water and the pH (alkalinity or acidity) of the solution is measured after some hours with a pH meter.

A very common analysis to be done on paintings by conservators is determination of the fibre type of paintings. Apart from helping in the identification of the painting materials, knowing the type of fibre of the canvas can help in choosing the appropriate conservation treatment.

Fibre type determination also requires a physical sample to be removed and identification can sometimes be tricky even for the expert. For these two reasons, this parameter was of interest so that non-destructive NIR spectrometry was also modelled to do fibre type identification.

The DP and pH of the canvas of paintings, had until now seldom been measured. Analysing the DP, pH and fibre type of the large body of real painting samples needed to develop the non-destructive NIR spectrometry method would therefore enable us to cover **the second aim of this PhD research: to learn about the typical pH and DP values found in real paintings as well as the fibre type used, and the relationships between these parameters.**

Once the DP, pH and fibre type had been destructively analysed, NIR spectra were collected from the very same samples and using chemometric tools, the spectrometer was calibrated by putting the analysed parameters and the spectra of the samples in relation. Three separate models weretherefore developed, one for each parameter.

The successful development of the non-destructive NIR spectrometric method to determine the DP, pH and fibre type of the canvas implies that now these parameters can be analysed very easily from a large amount of new paintings without needing to remove a physical sample and the results can be obtained immediately.

Acidity is measured in a pH scale from 0 to 14, pH 7-8 representing the ideal pH for a cellulosic object to have (10 p. 38). Less is known regarding the implications of particular DP values for paintings. It was therefore identified as important to learn what the different DP values mean when it comes to paintings in order to establish both the “critical DP” value for paintings under which a painting is considered to be “very fragile”, as well as the “safe DP” value for paintings, above which conservators can be confident about the “good condition[1]” of the canvas.

The third main aim of this thesis was,therefore, to establish the meaning of DP values when it comes to easel paintings, so that together with pH, a “Condition Assessment Classification” could be designed and applied to groups of paintings of which these two parameters are known.

To convert the possible DP values into meaningful information a “Condition Assessment Panel” was done where a range of new and old textiles thermally degraded for different periods of time (and thus with different known DP values), were sent to paintings conservators. They were asked to test the samples as if they were part of a larger painting and to class them into four different condition categories.

With the newknowledge about the meaning of DP values gained through the Condition Assessment Panel and taking pH also into account, a “Condition Assessment Classification” was designed. This classification grades paintings of which DP and pH are known according to their canvas condition, prioritizing them in terms of efforts to be taken and pointing towards possible conservation actions for each group of paintings (deacidification, lining, loose lining, denying a loan request etc.).

The last main aim of the thesis was to apply the non-destructive NIR spectrometry method developed to know the pH, DP and fibre type of real valuable paintings from the MuseuNacionald’Art de Catalunya (MNAC) on the one hand, and to produce a prioritised course of action to be taken on these paintings by applying the previously designed “Condition Assessment Classification” on the other.

This thesis is divided into five chapters.

The First Chapter offers an overview of the use of canvas as a support for easel paintings and the different types of plant fibres most often used in the history of painting. It also examines cellulose, the main component of plant fibres, the structure of the polymer and its characteristics. The chemical and physical paths along which cellulose, and therefore textiles, degrade is also discussed and the effectsthat the different external agents (heat, moisture, light, biological attack and pollution) have on it areexplained. Finally, special attention is given to the issue of acidity, due to the important role that this factor plays on cellulose degradation, and potential sources of acidity in paintings are explored.

The Second Chapter talks about the nature of the“Reference Sample Collection” used in this thesis, collected from real paintings, and all the analytical measurements done on them. All this data was needed in order to develop the chemometric models later on, so that NIR spectrometry could then be used to predict the chosen parameters (fibre type, pH and DP) for the canvas of easel paintings non-destructively.

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[1] The term “condition” has been used throught the thesis referring to the “object’s state of preservation at a moment in time” (11 p. 53).

This chapter is composed of an introduction into the Reference Sample Collection and three sub-chapters for each one of the three analysed parameters (fibre type, pH and DP). The introduction describes, thus, the Reference Sample Collection: where were the samples collected from, how many and what type of samples are they, of what age and from what painting materials. The Access database created in order to manage the large amount of data generated by the research is also shown.

The First Sub-chapter of the Second Chapter deals with the fibre type identification done of the Reference Sample Collection through optical microscopy. First an overview of the morphological characteristics of the most typical plant fibre types encountered is given, as well as the methodology followed to prepare and identify the fibre type of the samples. Then the results of the different types of fibres and combinations found as well as the percentages of each fibre type present in the Reference Sample Collection is explained. The different types of fibres are also put in relation with the date of the samples they come from and this is contrasted with information available in the literature on the use of certain fibres through history.

The Second Sub-chapter talks about pH. The first part of the sub-chapter explains what is pH, why is acidity important to know and how it can be measured. Acidity has long been measured in paper objects whereas it is a parameter that has not that often been checked on the canvas of easel paintings, even though the main component, cellulose, is the same. A brief outline is given on the measurement of the pH of paper objects and on what is the sample size typically used in these studies. After this, a review of the few cases found in the literature where the pH of the canvas of paintings has been measured is done. Then the particular method developed for measuring the pH of the canvas of paintings is explained. A new type of probe (ISFET type) was compared to the more traditional glass microprobe often used in paper pH studies, and since results were comparable, this former type of probe was used to do all the pH measurements. The new procedure was first tested on a set of test samples, then on a few of the samples from the sample collection, and once the new method had been validated, the rest of the collection was analysed. The last part of the sub-chapter analyses the results obtained for about 200 samples. The typical pH values obtained are examined and these are put in relation to the different dates of the samples and the fibre type. The pH of four samples deacidified with two different procedures more than a year ago is also analysed and commented. Conclusions are drawn regarding the typical pH values obtained for paintings and regarding the relationship between pH and date and between pH and fibre type.

The Third Sub-chapter of Chapter 2 is about DP. The first part of the chapter explains the concept of DP, how it is measured and the relationship between DP and mechanical strength and between DP and pH found in the literature. A literature review regarding DP determination of painting canvases is also included. Then the method developed for DP measurement through viscometry of the Reference Sample Collection is explained. The first important aspect that had to be determined was the required size of the sample in the particular case of easel paintings. Then different cleaning and pre-processing ways of treating the samples were tested as well as the application of the developed viscometry method to the measurement of the DP of real painting samples. Once the DP of the Reference Sample Collection had been measured, the values obtained are analysed. The relationship between DP and age, DP and pH and DP and fibre type found in our samples are explored both in the aforementioned pairs of parameters and alltogether using the chemometric tool of Principal Component Analysis (PCA). Interestingly, PCA offers an improved way to analyse the relationship between the four parameters (fibre type, pH, DP and date) and it shows that by taking other parameters into account (date and fibre type) a clearer correlation between pH and DP is found. A first approach as to whether visually more degraded samples have indeed lower pH and lower DP values is attempted, as well.

The Third Chapter focuses on the central technique used in this PhD: NIR spectroscopy and chemometrics. The chapter begins with an explanation of the basics underlying the NIR spectroscopy and chemometrics as well as giving an overview of the different types of cultural objects onto which it has already been applied successfully (paper, plastics, textiles and parchment). Then the particular method followed in this research for modelling the three calibrations is explained: pH and DP were done through the Partial Least Squares (PLS) method, while fibre type identification was done using Discriminant Analysis (DA). Two different models are reported in the case of DP to show how small differences in the calibration procedure can give significantly different end results. The outcome of the three modelling exercises is reported as well as the obtained errors of prediction for each case.

The Fourth Chapter explains the creation of a Condition Assessment Classification that helps in translating the different DP and pH values into meaningful information when doing a collection survey, so that actions to be taken can be prioritised accordingly. First, the literature where DP had been reported for the canvas of paintings is reviewed, critically examining what the different DP values obtained imply in terms of the condition of the paintings according to the authors and the conservation treatments that were subsequently chosen in each case. Then the materials and methods used for the “Condition Assessment Panel” done are explained. The main aim of this survey was to find the “Critical DP” value under which paintings are at serious risk of being damaged if handled and the “Safe DP” for paintings, above which a conservator can be confident of the good condition of the canvas. This was achieved and by combining the new information obtained for DP with the knowledge learned from pH in previous chapters, the Condition Assessment Classification was designed.

Finally, the Fifth Chapter reports on the application of the NIR spectrometry and chemometrics method developed to do a collection survey to determine the pH, DP and fibre type of real masterpieces from the Museu Nacional d’Art de Catalunya (MNAC). pH, DP and fibre type results obtained for 33 paintings from the end of the 19th C / beginning of the 20th C are analysed and put in relation one to the other. Troubles with DP prediction are reported as well as the differences found in pH and DP between regular canvas areas and darker areas of the same painting. Two small experiments on the application of the method to real cases are explained: one to determine the influence of the background when collecting the NIR spectra from paintings, the other to determine whether averaging of the three NIR spectra repeatedly taken in each location is better done before or after predictions. Finally the Condition Assessment Classification developed in Chapter 4 is applied to the paintings under study and prioritization in terms of action to be taken is done.

Finally the concluding section collects the findings of different chapters and explains how the different aims of the research have been covered. Interesting future avenues for research that have been identified during the research process are also noted down.

1. The canvas support in paintings

In order to be able to determine the condition of the canvas support in paintings we need to first understand the nature of the material; which types of canvas have been used for paintings and how its main component, cellulose, degrades due to the different environmental agents and the effects that this degradation has on the stability of paintings. This First Chapter examines these concepts and sets the ground for better understanding the subsequent the analytical results (pH, DP and fibre type) obtained from the Reference Sample Collection gathered to be able to calibrate the NIR spectrometer.

1.1 - Textiles used as a painting support

1.1.1 - The first textiles

Basket and textile weaving is one of the oldest technical processes carried out by man (1 p. 370). Sewing needles (to sew furs) have been already found from Palaeolithic times (20,000 BCE). Although no textiles have been found from the Stone Age (Palaeolithic, Mesolithic and Neolithic)[1], "negative" witnesses such as textile imprints on other objects or buttons have been found. It is thought that towards the end of the Stone Age (Neolithic times), man might have already been using a very rudimentary loom made with the horizontal branch of a tree and attaching the warp threads to it and adding weighting stones at the other end. In the Neolithic settlement of Tell-Halula (Syria), imprints of textiles dating from around 7,500 BCE have been found (2 p. 1).

Ancient textile fragments have been found and conserved from the Bronze age onwards, often linen and esparto grass (1), although due to their organic nature their number is much lower than ceramic and metal remains. In China and Egypt, the weaving art reached great perfection already in ancient times (2 p. 1).

Linen has been one of the first and most important fibres in the textile industry since prehistoric times (3). It is known to have been cultivated and used in the textile industry since the Neolithic times in Egypt, where it reached a high degree of perfection (4 p. 17). Its oriental or North-African origin is still questioned, but it is thought to have entered Europe through the Mediterranean area. In the Iberian peninsula it was already being cultivated in Neolithic times for textile use, among others (3). Pliny the Elder[2] talks about linen from Italy and about linen from foreign countries such as Spain, Gaul, the Low Countries and Egypt. In the medieval times the cultivation of linen fibre spread out to all Europe, even if the Egyptian linen kept its supremacy until the 13th C (4 p. 17). During the 17th C, linen manufacture became established as a domestic industry in many countries in Western Europe. Then, improvements in cotton manufacture, forced the linen industry a little bit into the background. In 1810 Napoleon I, in an effort to make flax industry advance, offered an economic reward to the person who could devise a machine for spinning flax. All these efforts certainly helped the flax manufacture industry, but compared with that of cotton, it progressed more slowly. Today, the flax plant is grown for its fibre mainly in Europe (5 pp. 5-6).

Wool was the other textile fibre often used in the Mediterranean area together with linen (2 p. 1) and the oldest surviving fragments conserved are from the Bronze Age. By the Greco-Roman times, almost all the

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[1] Prehistory is composed of the Stone age, the Bronze Age and the Iron Age (55).

[2] Pliny: (23-79), Roman statesman and scholar; Latin name *Gaius Plinius Secundus*; known as Pliny the Elder. His *Natural History* (77) is a vast encyclopedia of the natural and human worlds. He died while observing the eruption of Vesuvius (55).

countries of the world were already wool producers (4 p. 10) and from then on this type of fibre has been more or less produced (5 p. 80). However, the use of this type of fibre as a support for paintings can be said to be negligible (6 p. 270).

The silk industry started around 2,700 BCE in China, where for many years the secrets of its production were jealously kept. The Romans, for instance, knew the final woven product which they imported from China, but did not know how to produce it (they actually thought it was of plant origin). Apparently it was not until the 6th C, that the silk production worms reached Bizantium and from there the silk industry spread to Greece, the Arabic countries, and gradually to the rest of Europe (4 p. 13).

The oldest cotton fragments come from India and are from 3,000 BCE. There are also fragments from 2,000 BCE from Peru. Indian cotton is mentioned by Herodotus[3], Theophrastus[4] and Pliny, so it was known to the Greeks and Romans. Teophrastus also talks about cotton from Arabia and Pliny talks about cotton from Egypt (4 p. 16). There is even some evidence that cotton might have been used in Egypt in 12,000 BCE, before the use of flax was known (5 p. 35).

The Greeks first knew about cotton in 327 BCE through the Alexander the Great expedition to India. The Romans did not cultivate it, but they imported cotton products. From the 9th C, through the Arabs, growing and manufacturing of cotton was introduced into Sicily and Spain, but until the 18th C, cotton was imported into Europe from India, Cyprus and Syria (4 p. 16). Since its manufacture was labour-intensive it was considered a luxury product. From the 19th C on, however, large quantities of cotton were (and still are) imported from North America. The introduction of mechanical spinning techniques produced an explosion in cotton Western textiles, especially for household use (7 p. 5). Its industrial production in Europe started in England around 1840 (8 p. 322). Nowadays, most of the cotton still comes from the United States, but large quantities are also imported from Russia and China. Egypt still produces cotton that is famous for its long fibre (7 p. 5).

Hemp is thought to be originally from India, where it can be found to grow wildly and from where, from ancient times, it was introduced first into China and then into Russia and Europe. In Europe the first one to talk about it is Herodotus, and according to him, Thracians[5] already produced garments from it, Etruscans[6] also knew it and Romans used it for the sailing industry. In Europe its cultivation, and its manufacture, started to decline in the 19th C., when hemp products started to be replaced by cotton and the recently introduced artificial textile fibres (4 p. 20). Hemp is nowadays cultivated in almost every European country and in many parts of Asia (5 p. 17).

Ramie fibres have their origin in Asian countries, where it was known and manufactured into textile products since the ancient times. China has been since then the major producer of ramie, followed by India, Japan, and Indochina. It is not exactly known when ramie textiles were introduced into occidental countries, but these where already used in pre-dynastic Egypt (5,000-3,000 BCE) as linen substitutes for bandages of mummies. The plant was introduced into Europe and America in the 18th-19th C. The first industrial tests with the fibre took place in 1815 in England, and ramie products where presented that same year at the London Exhibition. From this year on, many different centres in Europe started to experiment with the fibre. However, the fibre was expensive to buy in the originating countries and the fibre extraction process from the plant proved difficult. This is why it was not until 1900 that a more active ramie industry could be developed (4 p. 24).

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[3] Herodotus: (5th C. BCE), Greek historian. He was the first historian to collect his materials systematically, test their accuracy to a certain extend, and arrange them in a well-constructed and vivid narrative (55).

[4] Theophrastus: (c. 370-c.287 BCE), Greek philosopher and scientist, the pupil and successor of Aritstotle. The most influential of his works was *Characters*, a collection of sketches of psychological types (55)..

[5] Thrace: An ancient country lying west of the Black Sea and north of the Aegean. It is now divided between Turkey, Bulgaria and Greece (55).

[6] Etruscan: Of or relating to ancient Etruria, its people, or their language. The Etruscan civilization was at its height ca. 500 BCE and was an important influence on the Romans, who had subdued the Etruscans by the end of the 3rd century BCE (55).

Jute was known and used for making cords and coarse textiles in India since ancient times, where the plant grew naturally. Its introduction to western countries, instead, is quite recent, being introduced into Europe and America only in the 18th C. The jute industry grew in England as a result of commercial relationships being forbidden to European countries with England by Napoleon in 1806. Since the English could not get linen and hemp from Russia, they started the development of new textiles using new fibres such as jute. In 1832, the first jute woven textiles were being produced in Dundee (Scotland). The scarcity of cotton coming from America due to the American Civil War, helped also to the growth of the jute industry. From here on, jute textiles where preferred over linen and hemp, when price was a major issue, since jute textiles, although being of a lower quality, where cheaper. It was used a lot for bags and for packaging. After the second half of the 19th C., jute manufacturers spread from England into France, Germany, Italy and later on into Belgium, Austria, Poland and Czechoslovakia (4 p. 22).

1.1.2 - Painting on canvas

The use of woven textiles as supports for paintings goes as far back as the Ancient Egypt times. However, since canvas is an organic material which degrades easily, surviving examples of very old textiles are not that common. In Europe, few examples of paintings on canvas remain prior to the 15th C., although there is evidence that there were quite many paintings on canvas before that too. Early paintings on canvas include religious and civil banners, paintings as substitutes for wall tapestries as well as the more traditional type of easel paintings. According to C. Villers (9), perhaps the earliest surviving example of a painting on canvas is "*Virgin and child with angels*" by Malouel (Museum Dahlem, Berlin-Dahlem) painted 1405-10. In this early period, paintings on canvas were often done with aqueous mediums (gums), such as Brueghel and Dürer are known to have done, which may account for the fact that few have survived since water mediums would not offer the same protection to the canvas as the preparation and oil paint layers would offer (9).

However, even if also common before that, it is true that the use of canvas as a painting support flourished in Venice around the 15thC (4 p. 62) (together with the explosion of the "new" oil painting technique), and from here it expanded to other European artistic centres. During the 16th C, Western art saw canvas being increasingly used (10 p. 137) and by the 17th C., this support was already more predominant for paintings than wood (9).

Oil painting on canvas was quickly adopted in Venice because its salty atmosphere was very unsuitable for wooden altarpieces and frescoes (11 p. 34). Also, the use of a canvas support made it possible to execute much larger scale paintings than was possible to do with wooden supports (12 p. 205). Vasari[7] already noted this development in Venice and suggested entirely practical reasons for it: "*unlike wood, canvas did not split and was light and easy to transport*" (9 p. 3). This was also written down by the Spaniard Francisco Pacheco[8] in 1649: "*The invention of painting with oil paint on a canvas was very useful due to the risk that panels have of splitting and because the lightness of a painting on canvas and the easiness with which one can transport paintings; and very big paintings are kept away from the risks of humidity by being kept taut and nailed onto thick wooden panels, where they can be kept for many years*[9]" (13 pp. 1649, Libro III, Capítulo V);(8 p. 79);(14 p. 207) ; (15 p. 110)

It is clear that painting on a canvas support produced lighter works of art that could travel more easily since canvas can even be rolled if desired. There was also an economic reason to it: these paintings were cheaper to produce (15 p. 110), and also cheaper to transport, thus facilitating art commerce. Also, the support preparation for receiving the paint layers was easier and faster to do on canvas than on wood (16 p. 377).

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[7] Vasari: Giorgio Vasari (1511-74), Italian painter, architect, and biographer. His *Lives of the Most Excellent Painters, Sculptors and Architects* (1550-1568) laid the basis for later study of art history in the West (55).

[8] The Spanish Francisco Pacheco wrote towards 1638, *El arte de la pintura* (40 p. 223).

[9] The original Spanish text is: "*La invención de pintar a olio sobre lienzo fue muy útil por el riesgo que tienen de abrirse las tablas y por la ligereza y comodidad de poderse llevar la pintura a diversas provincias; y muy grandes lienzos se aseguran de la humedad estirados y clavados sobre tablas gruesas, donde se conservan muchos años*" (13 pp. 1649, Libro III, Capítulo V).

Regarding artistic needs or possibilities, canvas also offered a more textured surface that artists could exploit to give their paintings a more vibrant effect (10 p. 137) (Figure 1) and this certainly favoured the choice of this type of support. Titian, for instance, used a wide variety of canvas weights and weaves during his long painting career and there was a general shift in his preference from a fine to a coarser weave (11 p. 34).

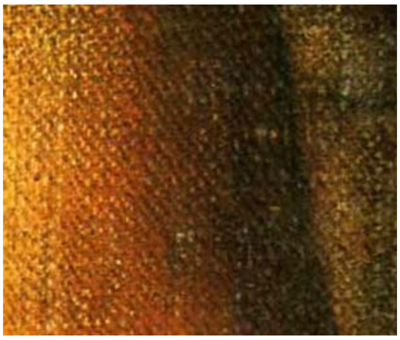

Figure 1. Detail of the vibrant texture of the canvas weave from *The Death of Acteon,* Titian, 1560s. From JANUSZCZAK, W.(ed.), *Techniques of the world's great painters.* New Jersey: Chartwell Books, 1980, pp. 34 (11).

Initially the canvases used by painters would come from the household canvases market. It is said, for instance, that the Spanish painter Murillo once painted on a stretched large napkin and this is why the painting is now known as the *Virgin of the napkin*, ca. 1666 (Museo de Bellas Artes from Seville) (8 p. 89). In other instances, it is known that the use of “old bed linens” was called for when making a commission to an artist, such as the one done by Hieronymus Bosch in 1493. It makes sense to think that old bed linens where demanded so that having gone through several washing cycles, the canvas would be of a whiter colour (17 p. 30). There is significant evidence in support of bleached linen being used in the past, especially when it comes to Northern-European *tüchlein* paintings, where no ground was applied and the colour of the support would certainly have an impact on the general view of the painting (18). From surviving documents, it is known, for instance, that several different types of linen were imported to London in the 16th C, amongst them both “brown” and “white” linen (this last one would have been bleached linen) (16).

With the oil painting technique being used on canvas its original colour less important. In fact, in many 17th C Dutch paintings the use of a raw brown canvas support by artists is depicted in paintings themselves (18 p. 615). Venice had a growing textile industry to supply the region with the needed sail cloths, and it seems that artists used unbleached linen “to avoid its fragility” (8 p. 89).

With regard to modern technologies entering the textile production, industrially woven cotton had been mechanised by 1780 (19 p. 50), whereas industrially produced linen textiles can be found from 1840 onwards (8 p. 95).

However, technical innovation during these centuries was not so much about the use of canvas as a support, but the use of oil as a painting medium on fabric (9).

Painting with oil

Painting with oil was done first in Italy and then in Northern Europe (9). For a long time, due to Vasari’s writings, it was said that Van Eyck (1395-1441) invented oil painting, but nowadays it is known that oil paint was already used in Europe before that, as old treatises such as the Eraclius[10] (10th C) and the Theophilus[11]

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[10] Nothing exact is known about Eraclius, although his manuscript, *De coloribus et artibus romanorum*, is thought to be from the 10th C and it is believed that he might have been Italian (104 pp. 169-170).

[11] The Theophilus manuscript, *De diversis artibus*, consists of three books in Latin, one on painting, one on glass and one on metalwork. Neither the date, nor place, nor the author are known with certainty. “Theophilus” is thought to

one (12th C) already describe how to extract the oil from the seeds and how to boil it with white lead (20 p. 36).

It is true, however, that it was the Flemish painters who started to systematically use linseed oil with hard resins as a medium from the mid 15thC on. The Dutch painters started to use this technique on wood (the most cited early oil painting on wood being *The Arnolfini Portrait,* Jan Van Eyck, 1434 (National Gallery)), as did the first Italian painters that used it (Antonello and Leonardo) (21 p. 269). In this early period, therefore, paintings on panel were executed in oil and those on fabric were mainly executed in watercolour (although banners were sometimes painted in oil) (9).

During the 14th and 15th centuries, thus, both tempera and oil painting coexisted. During the 15thC, new technological processes of oil purification and solvents distillation were developed and this certainly helped in the expansion of the oil paint technique (22 p. 53). Initially, oil was only used to do the glazes on a painting over the traditional egg tempera layers, but as the 15th C progressed, oil was used more and more in paintings to end up replacing the egg tempera technique completely (23 p. 67).

Due to its slow drying rate, oil paint had to be worked in a completely new manner but this also enabled very different results, such as transparent glazes and subtle colour transitions, which the previous techniques did not offer at all (22 p. 53).

Already Vasari talks about the new features of the oil technique that saturated colours more and that allowed blending the colours more easily than other mediums, softening the paint and making it more delicate, helping in a better representation of tridimensionality and new effects such as the famous "*sfumato*" by Leonardo (21 p. 270).

It is thus clear that the explosion of the use of the "new" oil paint technique was a result of the combination of both, new technical facilities (better solvent and oil production procedures) together with the new artistic need of a medium that enabled the production of even more realistic paintings. Once the oil technique started to be more widespread, it is easy to understand that it only took one step further for it to be extensively used on canvas, a lighter and more economic support.

On top of this, oil paint layers are also more flexible than egg tempera ones, and this made it a very suitable medium to be used on canvas, especially if this was to be rolled for travelling. This also explains why soon after, ground layers started to incorporate oil too, since this would make these layers more flexible too.

According to C. Villers, when artists continued to paint both on wood and on canvas (such as Rubens and Rembrandt did), they tended to have a freer style when painting on canvas (9). This could either be explained by the more textured surface of canvas, which induces a freer style in artists, or because painting with oil on canvas was already a departure of the traditional painting of the time and this probably translated already in the conception a painting.

The 20th C will see the birth of all sorts of synthetic mediums, the four most common groups in use by artists being: nitro-cellulose, alkyds, polyvinyl acetate (PVA), and acrylic resins. Of these, acrylic paintgs hold supremacy, and by the 1960s they were already the most often used paint medium, together with oil (24 pp. 2-33).

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be a pseudonym for the Benedictine monk and metalworker Roger of Helmarshausen (Germany). The original manuscript is not conserved, the two earliest ones being copies (may be third generation). It is thought the original was written in the early 12th C (123 p. XV).

Regarding the use of linseed oil, the Theophilus manuscript talks about using it to mix with all the pigments and use it on wood. I also talks about using it to make a varnish for paintings, boiling it with a resin (123 p. 28&32).

The introduction of oil paint into Catalonia and Spain

In Catalonia, oil paint has been found to have been used in wall painting already in the 14th C. There is a surviving contract from 1346 between the artist and the commissary to paint the Sant Miquel chapel of the Monestir de Pedralbes in Barcelona by the local artist Ferrer Bassa. The contract already states that the paint to be used must specifically be oil paint. This part of the contract reads: "*It is agreed by the Pedralbes abbess and Ferrer Bassa that the said Ferrer will paint with good oil colours the Sant Miquel chapel*[12]". Extensive research has been done on this marvellous set of paintings in the last years and indeed, it has been found that the background of the chapel was first painted with the traditional wall painting technique *al fresco*, but that the paintings were largely finished *al secco* with oil paint (25). Using oil as a medium enabled the use of certain rich pigments that could not withstand the traditional *al fresco* technique and this probably also indicates the high expectations that were put on these paintings, where very rich materials had to be used. The use of oil paint on wall paint, has also been found in France as early as the 1248 in the Saint-Chapelle from Paris and also at the Angers Cathedral (13th C) (26 p. 85). In Italy too, where the *al fresco* technique had a very strong tradition, around this centuries it was common to finish the *al fresco* painting with *al seco* paints with organic binders (25). In the case of the aforementioned thorough technological and condition research done on the paintings of the Sant Miquel chapel, this actually point towards the fact that Ferrer Bassa was well acquainted with the Italian techniques, either by having had Italian apprentices working with him or by having been to Italy he himself (25) since the technique he used is more similar to the Italian way of building the painting (25).

Regarding moveable works of art, one of the first known uses of oil paint in the time of the Crown of Aragon, is the "*Mare de Déu dels Consellers*" by the painter Lluís Dalmau, painted in 1443 (oil on wood) (even though the medium to be used is not specified in the contract done for the painting (23 p. 288)). Dalmau is known to have done a stage in the Netherlands, where he is supposed to have learnt the "new" technique and indeed, recent studies on the altarpiece have revealed that the medium used is mainly linseed oil (27 p. 53).

Just a month before the contract for the aforementioned "*Mare de Déu dels Consellers*" was done, in 1443, another altarpiece contract was done with the artist Pasqual Ortoneda where it was specified that the doors would be painted in "grisaille" that is to say "with the new type of paint and everything with the colours of linseed oil[13]" (28 p. 137).

However, prominent Catalan artists such as Jaume Huguet, twenty years after the "*Mare de Déu dels Consellers*" by Dalmau (1443) was painted, were still using mainly egg tempera as a painting medium, although he would use oil for specific colours such as copper green (22 p. 50).

It is not clear yet which is the oldest surviving oil on canvas painting from Catalonia, but the series of portraits of the kings of the Crown of Aragon painted by Filippo Ariosto in 1587-1588 must be at least one of the largest oldest remaining set of oil paintings (there are 54 of them). Apparently Filippo Ariosto painted this series of paintings first for the Aragonese part of the kingdom. After the success achieved there, the Catalan government of the time ("la Generalitat"), commissioned the artist to paint the same paintings again for the Catalan counterpart (from the time of the Queen Petronila (1162) onwards, the two then united parts of the Crown of Aragon (Aragon and Catalonia), shared the same rulers). The Aragonese paintings apparently have not survived, whereas most of their Catalan counterparts have done and are currently being restored at the CRBMC (29).

Regarding the rest of the actual Spain, it is known that by the 1480s and 1490s it had become common in contracts throughout the Crown of Aragon (though only rarely in Catalonia) to specify that colour be worked in oil (22 p. 53). However, even if until recently it was usually said that the oil paint technique started to be used in Spain from the 1450s onwards with the expansion of the Hispano-Flemish style, there are evidences

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[12] The original Catalan text says: "És convigut entre la senyora abadessa de Pedralbes i en Ferrer Bassa que el dit Ferrer pinti de bons colors amb oli la capella de Sant Miquel" (23).

[13] The original Catalan text says: "de pintura molt de nova ordonança e tot ab colors de oli de linós" (28 p. 137).

that indicate that oil paint was being used in Spain for other uses much earlier than that (as we have seen was the case in Catalonia too). Some Spanish documents from the 13th C and the 14th C talk about pigments being ground in linseed oil, suggesting that the technique was already in common use by this time and references are found for oil-painted shields, architectonic structures, wall paintings and so on. With respect to altarpieces, the Altarpiece of the Epiphany of Saint Paul's Convent in Toledo (c. 1430), has been analysed and linseed oil has been found to be the medium used for many of the pigments. The earliest contract found specifying the use of oil in Castile is from 1443, for the wings of a triptych. Once it was common practice to state the medium to be used in contracts, it was most often oil. This fact, together with the high technical skills of many of the Hispano-Flemish painters, are probably the reasons why some authors had thought, until recently, that oil paint was not used in Spain until this period (30).

All things considered, it can be concluded, however, that between the 15th and 16th C the oil painting technique was diffused in the Mediterranean area (22 p. 53) and its use flourished, as everywhere in Europe, in the following centuries.

Ground layers

Traditionally preparation layers were mainly done by mixing an animal glue with some sort of inert filler (31 p. 520). With the expansion of oil paint, however, grounds started to incorporate the more flexible drying oils too (32 p. 8). Already Vasari in the 16th C talks about the last priming layer applied on top of the animal glue ground layers being a coloured oil layer. And by the times of Rubens (the 17th C), it was common to still apply a first simple size layer on the canvas (this has remained throughout the times (31 p. 520).) but the ground layers could already be only bound in a drying oil (32 p. 9).

Initially artists would apply the ground layers themselves, but by the mid-17th C, pre-primed canvas was already being sold in London (33 p. 23) and in 1749, the first specific artists supplier was born in England. The texts by De Mayerne (17th C) and D. Dossie (18th C) already talk also about the selling of commercially prepared canvases (8 p. 89). Of course, even if primed canvases were already available, many painters would continue to prepare their own canvases, especially in the early times (33 p. 26). The 19th C will see the growth of industrial commercial companies that often marked their canvases with a stamp as a way to make their business known. With the advent of the painting competitions by Academies throughout Europe, the paintings measurements started to be standardized (8 p. 89) and still are nowadays.

From the 19th C on, most of the canvases had fatty preparations which included drying oils and in the 20th C, synthetic mediums (acrylic and alkydic) started to be used both in the priming layer and as a painting medium (14 p. 301).

1.1.3 - Types of fibres used for paintings

All textiles are made of threads, which in turn are made of fibres. According to their origin, fibres can be divided into natural and synthetic fibres (7). Natural fibres, which can be subdivided into plant, animal and mineral fibres, have been used since the origins of spinning and weaving thousands of years ago. From the 19th C on, synthetic fibres started to be introduced into textiles (34 p. 8).

Throughout the history of painting, the most often used type of fibres have been the natural plant fibres linen, hemp and cotton. Sparingly one can find other plant fibres such as jute, coconut or ramie. In the 19th C. mixtures of linen and cotton can be found, with synthetic fibres getting into the picture in the 20th C (8 p. 89).

Most of the plant fibres used in textiles derive from the stem of the plant (flax, hemp, jute and ramie), although others are obtained from leafs (sisal), from hairs or filaments from seeds (cotton) or from fruits of plants (coconut) (7). For easel paintings, those coming from the stem of the plant were initially used (linen and hemp), to be followed by those coming from the seeds (cotton).

In the case of bast fibres, in order to be able to separate the fibres from the stem of the plant, a process called “retting” has to be applied to it. In the past, the process was done by leaving the cut plants spread out on the fields for several weeks where moisture from rain and dew facilitated the growth of certain fungi and bacteria that dissolved the pectin holding the fibres together. Another way of doing it is leaving the stems for about three or four days in large tanks with water at around 30 ºC. Nowadays this process is done artificially by adding chemicals to the water that help to dissolve the pectin and reduce the needed time to about four to six hours. After this process, the stems have to be dried and mechanically combed to end up with a material that can be spun to form the threads to weave textiles (7 p. 5).

Cotton fibres are much easier to process, and thus making it a cheaper process than that of bast fibres, needing first to beat the cotton “fluff” to physically separate the cotton filaments from other parts of the plant and then the fibres have to be “combed”, similarly to how it is done with wool fibres (4 p. 17).

Although they are not frequently found as a painting support in Western art, some animal fibres such as wool and silk, can also be used. Wool is actually mentioned as a possible support in *The bolognese manuscript*, Italy, 15th (8 p. 90) and silk, apart from its extensive use in Oriental painting, has also been sparingly used by a few Western artists (10).

Even if the fibres most commonly used for painting supports are the ones we have mentioned here, it has to born in mind that any of the other fibres that have been ever been used to produce textiles could occasionally be found on paintings, such as sunn, kenaf, nettle[14], sisal, abaca, coconut[15] and so many others (5).

Linen

In English, the term “linen” is used when referring to fibres that are already woven into a textile, whereas the term “flax” is used to refer to the originating plant (*Linum usitatissimum*) (35 p. 2). Flax is cultivated both to obtain fibres for the textile industry and to obtain oil from its seeds. If the plant is left to mature in order to obtain the seeds, its fibres are more lignified and are not so useful for the textile industry, although the paper industry still can use them since they can be bleached (36).

Flax is a bast fibre, as hemp, ramie and jute are, which means that the fibres are extracted from the stem of the plant. These fibres have therefore a more structural function than cotton fibres, which are seed fibres, and this is why their cellulose have higher lignin contents and higher crystallinity.

Different types of textile supports have been used in the history, but linen has been, and still is, the fabric of choice, both for painting and for lining supports (9). Until the 19th century the raw materials generally used in painting supports were flax and hemp (10 p. 137). And even if nowadays, cotton accounts for half of all the vegetable fibre production worldwide, and synthetics for almost the other half (37 p. 3), linen still has the supremacy when it comes to good quality artist canvas.

Hemp

Hemp is a bast fibre that comes from the *Cannabis sativa* (and of which the drugs marihuana and hashish are also produced).

It has usually been thought that until the 19th century the raw materials generally used in fabric supports were flax and hemp (10 p. 137). Hemp has been traditionally used to produce coarser textiles, cords, threads and the fibres have been used to cover wood joints in panels. Apparently French treatises recommend the use of hemp for paintings because it is stronger (8 p. 93) and a study carried out in 1981 indeed concluded that in France hemp was more used than linen until the beginning of the 19th C, when linen took over.

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[14] Nettle is known to have been cultivated in Scandinavian countries for centuries for weaving sails (5 p. 25), which would indicate a strong canvas that could be probably be used for painting satisfyingly.

[15] Gauguin is said to have used “coconut fibre” textiles, for instance (10 p. 137).

Apparently this fact coincides exactly with the decline of hemp production in France which began ca. 1820 (38). Other authors state that the use of hemp as a painting support was at its peak in the 17th C in Italy (39 p. 16) and in France (19). Artists such as Caravaggio have been suggested to have used coarse hemp canvases quite frequently (33 p. 25). However, since linen and hemp can be very similar both when looking at the fibre under the microscope and when looking at the woven textile, it is believed that there is still a lot to be discovered regarding the exact use of these two fibres.

Cotton

Cotton is a seed fibre from the species *Gossypium*, the fibre probably serving to accumulate moisture for the germination of the seed (5 p. 35). This fact probably accounts for the high hygroscopicity of cotton.

As said, cotton was already known in India around 3,000 BCE. Although its growing and manufacture was introduced in Europe through the moors around the 9th C, until the 18th C, cotton in Europe was mainly imported from India (4 p. 16). Its industrial production in Europe started in England around 1840 (8 p. 322).

Regarding its use as a painting support, paintings on cotton can be found from the end of the 18th C onwards (40 p. 21), but it was not widely used as a support for paintings until the 19th C (10 p. 137). Mixtures of hemp and cotton have been found occasionally, such as the painting "*San Marcos liberando al esclavo*" by Tintoretto (S. XVI) (8 p. 89). Having been considered a luxury product for centuries (7 p. 6), it is not surprising that it only started to be used widely on paintings from the time it started to be industrially produced in Europe.

Commercial companies such as Winsor&Newton, introduced it in their catalogues in 1900 and from there on, cotton supports started to appear as cheap materials to be used by students or for sketching. With the advent of the two World Wars, though, due to the scarcity of the times, many artists chose to paint on cotton canvases (8 p. 323). Cotton was also extensively used by many artists after the 1950s, specially by many Americans that chose it due to its low cost and its big dimensions availability (39 p. 16). It has often also been chosen due to its natural off-white colour which can be left unpainted so that the support also takes part in the composition by artists such as Morris Louis and Helena Frankenthaler (Figure 2).

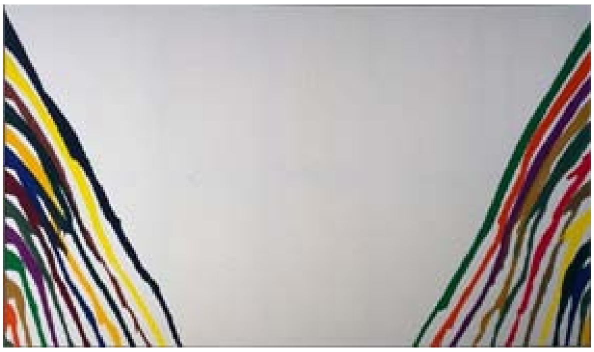

Figure 2. Painting on bare cotton canvas by Morris Louis, *Delta Lambda*, 1961, 2.60 x 4.50 m (The Cleveland Museum of Art). Modern paintings that leave the bare textile unpainted, pose new challenges regarding its protection from external degrading agents (especially light and pollution). From the CMA web page: http://www.clevelandart.org/collections [accessed 10/08/2011] (41).

Jute

The jute fibre is obtained from the bast of two plants: *Corchorus capsularis* and *Corchorus olitorius*. The main commercial supply for the world market is Bangladesh, although India produces an equivalent quantity but for internal use (42 p. 16).

Towards the end of the 18th C some paintings done on jute textiles can already be found, although sparingly (8 p. 89). It can be found more often towards the end of the 19th C and the beginning of the 20th C (39 p. 16). Van Gogh used jute for some of his paintings, such as the “Chair with pipe”, 1889 (Figure 3) (11 p. 118), Gauguin did so too (8 p. 322), and the German Expressionists artists, such as Kirchner, Müller and others (43 p. 111), chose it deliberately because it was a coarse material of inferior quality (10 p. 138).

Figure 3. Van Gogh, *Chair with pipe*, 1888 (National Gallery of London) painted on an unprimed jute canvas, leaving some of the dark brown-orange of the bare canvas to show through in different places. From JANUSZCZAK, W. (ed.), *Techniques of the world's great painters.* New Jersey: Chartwell Books, 1980, pp. 119 (11).

A very emblematic painting known to have been painted on a mixture of jute and linen canvas is the *Guernica*, by Picasso, painted in 1937 (Museo Reina Sofia, Madrid, DE00050). In this case the threads running along the horizontal direction have been identified as linen and the ones running in the vertical sense as jute. The canvas is a commercially primed one. The painting is very large (3.50 x 7.76 m) and has many cracks in both directions (44 pp. 51-53). It is very possible that the vertical cracks have been caused by the painting’s long history of rolling and unrolling and the horizontal cracks might have to do with the weakness of the jute threads. The painting was in fact wax-lined many years ago due to problems in the support, apparently due to the weakness of jute fibres (8 p. 323).

Mayer’s artists manual (first edited in 1940), already completely discourages the use of jute as a painting support since it becomes “brittle and lifeless on short ageing” (45 p. 289). (It also discourages the use of canvases with two different types of threads (linen and cotton), since their difference in moisture absorption will cause uneven tensions on the painting).

The firm Rowney & Co. introduced a jute canvas in 1913, for painting sketches (8 p. 322). And the company Winsor&Newton, who had introduced this fibre in their catalogue in 1920, discontinued its commercialization in 1948 because it was “not good for permanent works” (14 p. 115). The rapid deterioration of the fibre is the main reason why many of the paintings done on jute have already been lined during the 20th C (8 p. 322), such as the Chair with pipe by Van Gogh (Figure 3) (46 p. 33)

In the group of paintings from MNAC that will be analysed in Chapter 5, we actually have a painting by Casas done on a commercially primed jute canvas from 1904 (Figure 4).

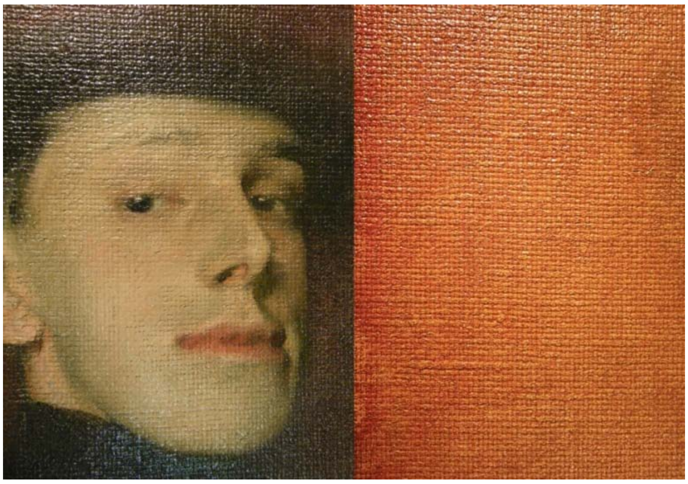

Figure 4. Two details from *Estudi del natural per al retrat del rei Alfons XIII*, by Ramon Casas, 1904, (MNAC 011382). Oil painting on a commercially prepared jute painting. The beautiful coarse surface of the textile is perfectly noticeable through the paint layer.

Ramie

Ramie is a bast fibre obtained from the stems of *Boehmeria nivea*. It has been grown in China for centuries (42 p. 18), was used in some of the Egyptian mummies instead of linen due to its high resistance and was manufactured in Europe in England in the 19th C (8 p. 94). Apparently, ramie was proposed as a painting support for the first time in 1928 by a commission from the Royal Academy of Arts of London since it is an almost pure cellulose fibre that has greater tenacity, less elasticity and is not as readily attacked by microorganisms as cotton is. But its use as an artistic support did not spread since it was not widely manufactured due to fibre extraction and manipulation complexity, which resulted in an expensive textile (8 p. 322).

However, so far we have not found any reference on a particular painting being executed on a ramie textile.

Silk

Silk is an animal fibre extruded through the head of the silkworm *Bombix mori*. Animal fibres are mainly made of protein and can be divided into hair/wool and silk. Proteins are made up of polypeptides which in turn are made of amino acids. Fibroin is the main protein of silk, whereas keratin is the main protein of wool (from sheep) (34 p. 9). Other animals of which their hair fibres have been used to make textiles are camel, alpaca (domesticated llama), vicuña (wild llama), mohair (Angora goat), angora (Angora rabbit) etc. (7).

Silk, which has been the main support in Asiatic painting, has not been much used in Europe (39 p. 16). However, silk is mentioned on several occasions in early sources (Cennini[16], Palomino[17], Mayerne) and it has been established, that it was used by, among others, Guido Reni (10 p. 137) for instance, in the painting "*Assumption of Mary*" from the Alte Pinakothek, 1642 (43 p. 111).Titian and Caravaggio also are known to have used silk occasionally (8 p. 89).

Synthetic fibres

Synthetic fibres started to be produced in 1846, when nitrocellulose proved to be suitable for making fibres. The term includes both semi-synthetic and synthetic fibres (47 p. 55).

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[16] Cennino d'Andrea Cennini, a painter and student of Agnolo Gaddi, wrote *Il libro dell'arte* (or *Trattato della Pittura*) towards 1390. He initially lived in Florence (40 p. 223).

[17] The Spanish Palomino wrote the book *El museo pictórico y Escala óptica* in the 18th C (8).

Semi-synthetic fibres are those produced by the modification of natural polymers (such as cellulose, or casein), whereas synthetic fibres are polymers produced from petrochemicals (47 p. 55).

Different semi-synthetic fibres were developed from the end of the 19th C and are still produced today from cellulose. Wood or the short fibres of cotton (called linters) are treated chemically so that the cellulose dissolves into a viscous liquid, called viscose. The viscous liquid is extruded and fine filaments are formed, the end product being once again pure cellulose. Depending on the chemical treatment applied, the way the filament is extruded, and its hardening, different types of products are obtained such as rayon, modal, lyocell and acetate (7 p. 10). Some protein-based fibres have also been developed, such as those based on casein, but although important in the development of synthetic fibres, they have not been commercially important (34 p. 9).

The most common synthetic fibre types are polyamide, polyester, acrylic and polyurethane (elastane) (48 p. 1). One of the first synthetic fibres to be produced is nylon, a polyamide that was first produced in 1938 in the United States by the DuPont Company. Polyester another very important synthetic fibre, was first produced in England in 1940 and acrylic fibres were produced from 1950 onwards (7 p. 12).

When the polymer is molten or dissolved, its chains are randomly (amorphously) arranged. When the filaments are extruded, these are stretched and by doing this, the polymer chains align themselves in the direction of the filament, forming bonds between the chains and thus increasing in crystallinity. These produces filaments with higher tensile strength, and by playing with the extend of stretching applied, it is possible to tailor the tensile properties of the fibre (47 p. 56).

Synthetic fibres generally have a higher tensile strength than natural fibres, and have less moisture absorption due also to their greater chain alignment too (47 p. 56) and suffer less microbiological attack (8 p. 324). As a drawback, they develop static electricity, attracting dust because of their low moisture content (47 p. 57).

Even though synthetic textiles have some superior qualities to natural fibres, natural fibres are still the main choice for painting supports, linen still being sold as the best quality canvas (19 p. 50). However, more and more commercially prepared canvases are mixtures of linen, cotton and various synthetic fibres (the true composition of which not always corresponds to the label). The inclusion of synthetic fibres in the painting support seems however, to be a choice more linked to their availability and lower cost than anything else (8 p. 325).

1.2 - Cellulose: The main component of plant fibres

Cellulose, the main constituent of all the existing higher plants on Earth, is the most abundant natural polymer (49 p. 33; 50 p. 263) and the most abundant organic compound (51 p. 73). Plants and trees are able to produce cellulose ($(C_6H_{10}O_5)_n$) by absorbing water (H_2O) from the earth through the roots, and carbon dioxide (CO_2) from the atmosphere and light energy from the sun through their leafs. This process is called photosynthesis and is mediated by the green plant pigment, chlorophyll (51 p. 69).

Cellulose is the basic constituent of the cell wall in plants and trees (47 p. 19) and since it has a structural function, we find it in the fibrous and woody tissue of leaves, trunks and roots (52 p. 255). It is never found pure in nature, but is usually associated with other substances such as lignin, hemicelluloses and pectin. The cotton fibre is probably the purest natural source of cellulose, with only about a 5% of other substances; whereas wood can contain between 40-55% cellulose, 15 to 35% lignin and 25-40 % hemicelluloses depending on the species (53 p. 15).

In cultural heritage objects, cellulose is found in wood, paper and textile objects (51 p. 73).

Cellulose is a linear polymer built up from many glucose units, although the repeating unit is considered to be the dimer[18], cellobiose (1,4-*β*-D-glucopyranosyl-D-glucose) (54 p. 61). Each cellobiose unit is therefore made-up of two glucose units.

The chemical formula of the cellulose polymer is $(C_6H_{10}O_5)_n$ (52 p. 255) and the sequence is: glucose (a monosaccharide[19]) → cellobiose (a disaccharide (two monosaccharides))→ cellulose (a polysaccharide (many monosaccharides)).

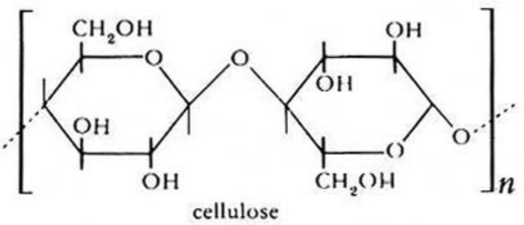

Figure 5. Cellulose structure. From MILLS, J.S.; WHITE, R. *The organic chemistry of museum objects.* London: Butterworth-Heinemann, 1987, pp. 73 (51).

1.2.1- Glucose

The term “glucose” comes from the Greek words “glukus” (sweet) and “gleukos” (sweet wine) (55).

Glucose is a simple sugar or monosaccharide with six carbon atoms. Monosaccharides can be grouped according to the number of carbon atoms they have: trioses (three), tetroses (four), pentoses (five), hexoses (six) and so on. Since glucose has six carbon atoms, it is a hexose, with the chemical formula $C_6H_{12}O_6$. Hexoses that have an aldehyde group (-CHO) at position one, which is the case of glucose, are named aldohexoses. Aldohexoses have all five hydroxyl groups (-OH) attached to the remaining five carbon atoms (50 p. 261). Depending on how these hydroxyl groups are positioned in the space, there are eight possible types of aldohexoses with the names: allose and altrose, glucose and mannose, gluose and idose, galactose and talose (51 p. 70).

Saccharides are carbohydrates. Carbohydrates are a large group of organic compounds found in food and living tissues which include sugars, starch and cellulose among others. They contain hydrogen and oxygen in the same ratio as water (2:1) and generally can be broken down to release energy in the animal body (55). Originally the term “carbohydrate” was applied to compounds with the formula $C_x(H_2O)_y$, since they were seen as “hydrates of carbon”. In practice we can take the term carbohydrate as referring to the sugars (monosaccharides) and their polymers (polysaccharides) (51 p. 69).

Other monosaccharides, apart from glucose, are fructose, galactose…The disaccharide sucrose (made up of glucose and fructose units) is the common white sugar we use to sweeten our coffee. Regarding natural polymers, another very important one appart from cellulose (based on *β*-D-glucopyranose) is starch (based on *α*-D-glucopyranose) (7 p. 3).

Glucose can have an open linear structure, although this form is not very stable and therefore is not very common in nature. In this linear shape, two stereoisomers[20] exist: D-glucose and L-glucose (Figure 6) (50 p. 261).

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[18] A dimer is a molecule consisting of two identical molecules linked together (55).

[19] Monosaccharide: Any of the class of sugars (e.g. glucose) that cannot be hydrolysed to give a simpler sugar (55).

[20] Stereoisomers are compounds that only differ in the spatial arrangement of their atoms (55).

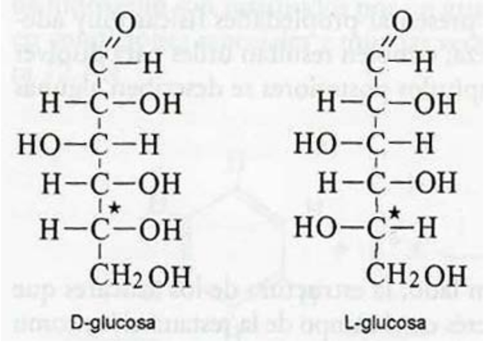

Figure 6. D-glucose and L-glucose. From SAN ANDRÉS MOYA, M.; DE LA VÍÑA FERRER, SÓNSOLES. *Fundamentos de química y física para la conservación y restauración.* Editorial Síntesis, 2004, pp. 262 (50).

D-glucose usually occurs in nature in a cyclic form in two forms: *α*-D-glucopyranose and *β*-D-glucopyranose. (56 p. 131). The term "glucopyranose" indicates that the molecule is cyclic and that it has the pyranoid structure. The pyranose ring is formed by the reaction of the hydroxyl group on carbon 5 of a sugar with the aldehyde at carbon 1 (Figure 7)(50 p. 261).

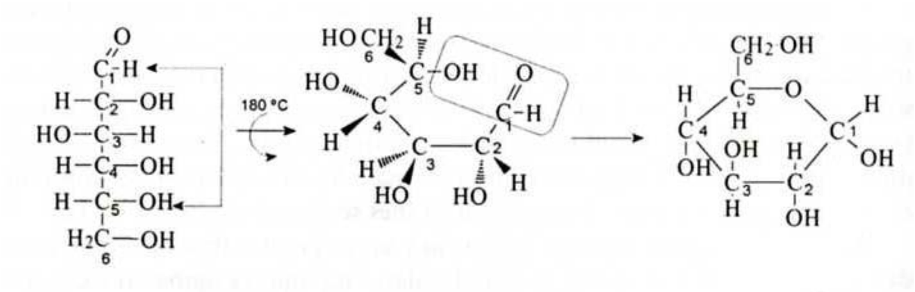

Figure 7. Formation of the glucopyranose ring. From SAN ANDRÉS MOYA, M.; DE LA VÍÑA FERRER, SÓNSOLES. *Fundamentos de química y física para la conservación y restauración.* Editorial Síntesis, 2004, pp. 262 (50).

The difference between *α*-D-glucopyranose and *β*-D-glucopyranose is in the position of the hydroxyl group attached to the first carbon (Figure 8) (7 p. 3). (For short, the terms *α*-glucose and *β*-glucose are often used instead.)

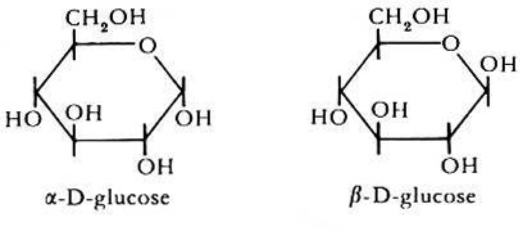

Figure 8. *α*-D-glucose and *β*-D-glucose. From MILLS, J.S.; WHITE, R. *The organic chemistry of museum objects.* London: Butterworth-Heinemann, 1987, pp. 72 (51).

1.2.2- Glycosidic bond

Cellulose is made up only from *β*-D-glucopyranose units forming a linear chain (51 p. 73). The glucose units are linked through a "glycosidic bond". To form the bond, the OH group from the C1 in the first molecule reacts with the OH group in the C4 in the second molecule and a water molecule is produced (which is why this is a condensation reaction). The polymer is thus called *β*-1,4- D-glucopyranose (see Figure 5)(50 p. 263).

This glycosidic bond is responsible for the rigidity of cellulose because the link cannot rotate and this gives the polymer its linear design, allowing for multiple hydrogen bonds between the OH groups of the chains. This produces a very rigid structure of parallel chains, used by nature to provide structural strength to plants and trees (50 p. 263; 435).

The chemical formula of cellulose is therefore $(C_6H_{10}O_5)_n$, where *n* represents the degree of polymerisation (DP), that is to say the number of times the elemental unit that makes up the molecule is repeated (57 p. 98). When DP is reduced due to degradation, this is most often due to the glycosidic bond being broken, fragmenting the cellulose chains into smaller pieces (50 p. 436).

1.2.3- The polymer

Due to the linear structure of the cellulose polymer chains, and the many hydroxyl groups it has, chains can be arranged in a parallel position and many strong hydrogen bonds are formed between the different parts of the long molecule and between different molecules (see Figure 9) (54 p. 61).

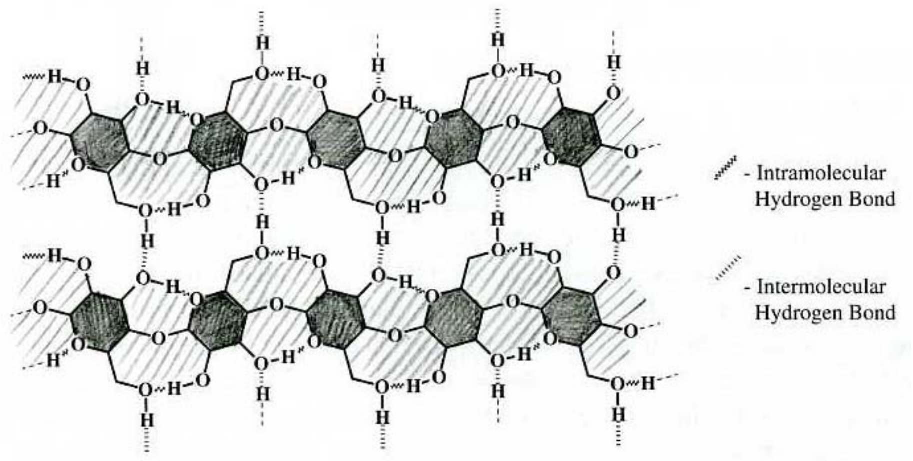

Figure 9. Intra- and inter-molecular bonding between cellulose chains. From MAY, E.; JONES, M. *Conservation science: Heritage materials.* Cambridge: RSC Pub., 2006. pp. 61 (58).

This intra- and inter-molecular bonding within and between cellulose chains gives rise to crystalline regions, which provide rigidity and stiffness to plants and trees (50 p. 263). There are other areas of the polymer where the chain takes a random coil shape: these are called the amorphous regions (Figure 10). These regions provide the material with flexibility and elasticity. Therefore, mechanical strength and stiffness of fibres is very much dependent on the amount of crystalline and amorphous regions (47 p. 11).

Amorphous regions, too, are more open to the penetration of water and to polluting agents, and therefore will swell more and degrade first (57 p. 98). Because of this, fibres with a higher proportion of amorphous areas, such as cotton, will degrade faster than, for instance, linen (47 p. 11).

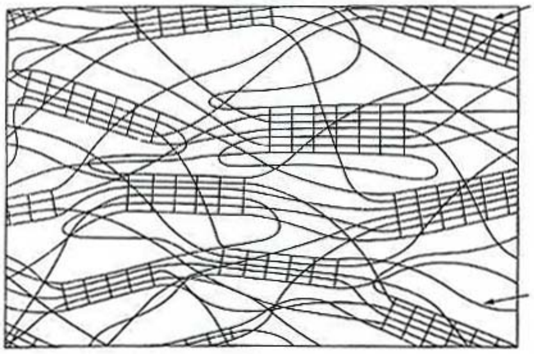

Figure 10. A long-chain polymer with crystalline and amorphous regions. From TÍMÁR-BALÁZSY, Á.; EASTOP, D. *Chemical principles of textile conservation.* Oxford: Butterworth-Heinemann, 1998, pp. 11 (47).

Cellulose has many hydrophilic side groups that are able to bond with water and that is why cellulose absorbs and holds moisture very easily. This moisture is held either in the amorphous regions or at the surface of the crystalline regions. However, these hydrogen bonds with water are not as strong as the hydrogen bonds between its own molecules and this is why cellulose is, although having a high affinity with it, not soluble in water (51 p. 73).

1.2.4- From cellulose to fibre

In cellulose, about 100 or so polymer chains arranged more or less parallel to each other make up a *micelle* (or elementary fibril), with a diameter of 5-6 nm. About 15 of these micelles form a *microfibril*, with a diameter of 75 to 90 nm. *Microfibrils*, which can be seen under an electron microscope, are further organised into *macrofibrils*, or just *fibrils* (≥100 nm of diameter) (54 p. 63) (Figure 11). Fibrils are laid down in the primary and secondary walls of the vegetable fibre cells (or "ultimate cells"). In the primary cell wall, fibrils are rather disordered, whereas in the secondary cell wall fibrils are more ordered, usually spiralling around the longitudinal axis of the cell (47 p. 23). The direction of this spiral goes in one sense in linen and ramie and in the opposite in hemp and jute. This difference is the one that makes the "twist test[21]" work for differentiating these two groups when doing fibre identification (59 p. 13).

In the case of cotton, one single cell constitutes the fibre, whereas in bast fibres, a number of fibre cells are stuck together in a bundle, forming the fibres we see under the optical microscope (47 p. 23).

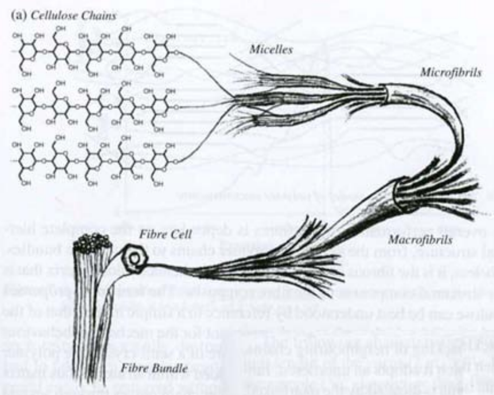

Figure 11. From the cellulose chains to the fibre. From MAY, E.; JONES, M. *Conservation science: Heritage materials.* Cambridge: RSC Pub., 2006. pp. 63 (58).

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[21] The "twist test" consists of wetting a fibre to be identified with water and seeing which way the fibre twists on drying over a hot plate (42 p. 225).

The sequence therefore is: Cellulose chains: Micelles: Microfibrils: Macrofibrils: Fibre cell: Fibre (54 p. 63). The spaces between micelles, microfibrils and macrofibrils are filled with non-crystalline components such as amorphous cellulose, hemicellulose, pectin and lignin (54 p. 62).

1.2.5- Other components of plant fibres

Hemicellulose

Contrary to what one might think, hemicelluloses are not forms of cellulose at all, and so the name is misleading. They are polysaccharides that differ from cellulose in three important aspects. Unlike cellulose, hemicelluloses are composed by several different sugars (primarily xylose and manose), are much shorter in chain length and are extensively branched polymers (54 p. 62). Also, unlike cellulose, the constitution of hemicelluloses differ from plant to plant (53 p. 16).

Lignin

Lignin is a natural polymer that gives strength to the plant and trees cells (51 p. 80), and this is why its percentage is much higher in wood. It is a small heterogeneous acidic phenylpropanoid polymer, with a complex amorphous structure. It is rather hydrophobic and highly sensitive to light, particularly to UV radiation, discolouring to a yellow-brown colour. It also becomes more acidic with degradation (54 p. 63) and is a cause for mechanical embrittlement when the fibres containing it are exposed to light containing UV (60).

Lignin has long been thought to be an undesirable compound for paper and textiles because of this increase in acidity on ageing (51 p. 80). However, the precise influence of lignin on the stability of cellulose is still not well understood (61). Recently it has been found that it could also have a limited antioxidant effect on cellulose (62)(63), although it is still thought that its rapid oxidation may lead to accumulation of acids in the cellulosic material, causing a destabilizing effect (61 p. 414).

Pectin

Pectins are jelly-like, acidic polymers composed of 1,4-β-(D-galacturonic acid) units, together with some galactose and arabinose (54 p. 62).

1.2.6- Differences between different types of fibres

Crystalline/ amorphous ratio

The mechanical strength and elasticity of fibres is very much dependent on the length and proportion of the crystalline regions. Crystalline regions are rigid and stiff and provide a strong structure whereas the amorphous regions provide flexibility and elasticity. These amorphous regions are more accessible to both water and pollutants, and therefore are the ones that will degrade first (47 p. 11).

The crystalline / amorphous ratio is characteristic of fibre type and this will have an impact on the strength, elongation, water absorption and degradation of the different fibres. Non-degraded cotton has about 70% crystallinity, whereas that of linen can be as high as 90% (47 p. 11). This difference in the crystalline / amorphous ratio explains why cotton absorbs more water, degrades faster under the same circumstances and has lower tensile strength but more elongation than linen.

The fact that cotton degrades faster than linen has long been noticed in real paintings, such as is the case of those by the Catalan artist Francesc Gimeno at the beginning of the 20th C, which are in a worse condition than its contemporary paintings on linen (64). Research has also proven that under the same circumstances, cotton has a higher degradation rate than linen (65 p. 313).

Strength and elongation

There are different mechanical properties of materials that can be measured, among which we can find the "tensile strength" and the "elongation at break". The "tensile strength" is the breaking strength of a fibre, which is expressed as the force needed to break the fibre per unit of cross-sectional area (i.e. kg/cm^2). The "elongation" tells us about the stretching properties of the fibre when subjected to a force, and the "elongation at break" tells us about the elongation reached when the fibre breaks. This is given as a percentage of the original length (47 p. 12).

	Tensile strength (Mpa)	**Elongation at break %**	**References**
Cotton	287-597	7.0 - 8.0	(66); (67)
Linen	351	2.5	(68)
Hemp	820	3.5	(68)
Jute	579	1.5	(68)
Aramid (Kevlar 49)	2900	2.5	(69)

Figure 12. Mechanical properties of fibres. From WANG, S.; LEE, S.H.; CHENG, Q., *Mechanical properties of cellulosic materials at micro- and nonoscale levels. In* LEJEUNE, A.; DEPREZ, T. (eds.), *Cellulose: Structure and properties, derivatives and industrial uses.* Nova Science Publishers Inc., 2010. pp.459-500, pp. 462 (70).

Natural fibres ordered according to tensile strength would be: hemp, jute, linen and cotton (70 p. 462) (Figure 12). The synthetic fibre Kevlar 49 has been added for comparison with the natural ones, since it has been recently started to be used in conservation to create networks to reinforce fragile canvas supports (71). Note that the tensile strength of Kevlar 49 is 2900 Mpa, about ten times more than that of linen.

In terms of elongation, cotton is the one that elongates the most. Natural fibres ordered from more to less elongation, would be: cotton, hemp, linen and jute (70 p. 462) (Figure 12).

Lignin content

Of the plant fibres used in paintings, jute is the one that has higher lignin content (Figure 13). Bast fibres ordered from more to less lignin content are: jute, hemp, flax and ramie (72 p. 33). Cotton has no lignin at all (47). The role of lignin in the degradation of cellulose, is still not clear however, since although it is known that its ageing will cause an increase in acidity on paper (61 p. 414), some studies have shown it to have too a limited antioxidant effect on cellulose (62)(63). In textiles, according to research results, it is thought that the higher lignin content of jute is responsible for its more extensive loss of mechanical properties during UV ageing, which also leads to formation of yellow-coloured products. Since cotton does not have lignin at all, UV radiation was found not to be so damaging to it as it was found to be for jute and linen textiles (60).

However, it also has to be taken into account that the lignin content in a fibre will vary depending on the age of the plant at the moment of harvest. If flax is left to mature so that linen seeds can be collected, the fibres will have a higher amount of lignin. For paper, this is not a particular problem since the bleaching process can remove lignin without too much trouble (36 p. 93).

	Cellulose %	Hemicellulose (%)	Pectin (%)	Lignin (%)
Jute	64.4	12.0	0.2	11.8
Hemp	67.0	16.1	0.8	3.3
Flax (retted)	64.1	16.7	1.8	2.0
Cotton	82.7	5.7		0.0

Figure 13. Cellulose, hemicellulose, pectin and lignin content of some plant fibres, ordered according to lignin content. From BATRA, S. K. *Other long vegetable fibres* in *Fibre chemistry*, edited by M.Lewin, and E. Pearce, Marcel Dekker (1985) (73). Cited in TÍMÁR-BALÁZSY, Á.; EASTOP, D. *Chemical principles of textile conservation.* Oxford: Butterworth-Heinemann, 1998, pp. 31 (47).

1.3 - The degradation of textiles / cellulose

Like all other organic materials, all textiles will, with time, turn to dust (7 p. 21).

Textiles are among the most sensitive objects in museum collections due to their organic nature (74 p. 1). In easel paintings, though, the preparation and paint layers have been seen to offer some protection, as noted by Berger when he removed the worm-eaten wood panel of a 15th C icon to find a layer of canvas between the wood and the paint layer in a perfect condition (75 p. 81). Easel paintings are protected from air/pollution at least on one of the sides due to the priming and paint layers. The priming also offers mechanical interlocking of the movement of the yarns, which diminishes the material's resistance to lacerations drastically (65 p. 314).

Changes during deterioration processes can be chemical or physical. Physical change means a rearrangement of the molecules of a material without any change in the chemical structure of the individual molecules. Chemical changes, instead, involve chemical reactions that imply the rearrangement of atoms in molecules, giving new molecular structures (76 p. 38). After a chemical change, since new substances will have been created, the material will have new physical properties (77 p. 49). This is often the case and the reason why in general chemical degradation leads to physical degradation too (78).

Chemical reactions are accelerated in the presence of moisture, light, air pollution and heat (7 p. 21). The presence of the canvas own degradation products will also be the source of further chemical reactions and by-products, increasing the degradation rate (79 p. 70).

1.3.1- Chemical degradation

Cellulose degradation can follow complex degradation paths and what happens exactly in all situations is not yet fully understood (80). The sensitivity of the glycosidic bond and the presence of three hydroxyl groups on each repeating unit govern the chemical reactivity of cellulose (81 p. 17).

There is a range of degradation processes happening at the same time that affect cellulosic materials. The most predominant degradation processes are hydrolysis and oxidation, which lead to both chain scission and cross-linking of the polymer. The result of all these degradation processes is a polymer with a lower degree of polymerisation (shorter chains), a higher crystallinity due to the aggregation of some of the smaller chains and the development of a network character. All this produces a weakening and embrittlement of the material (54 p. 67).

It is well known that in an acidic environment, the dominant degradation mechanism of cellulose is acid-catalysed hydrolysis, and in an alkaline environment, two reaction pathways, oxidation and alkaline degradation are predominant (53).

The different degradation processes can be accelerated or delayed by particular environmental factors (82 p. 250), such as heat, light, moisture or pollutants (7). However, degradation processes feed each other in many cases, as has been recently shown for oxidation and hydrolysis (83).

Hydrolysis

Hydrolysis is the chemical breakdown of a compound during reaction with water (55). Cellulose can suffer both acid-catalysed hydrolysis and alkaline hydrolysis. Both acid and alkaline hydrolysis break the cellulose chains and therefore cause depolymerisation. Acid hydrolysis however, is more dangerous since this type of hydrolysis happens even at low temperatures, whereas alkalis in general have noticeable effects only at higher temperatures (84 p. 10).

Acid-catalysed hydrolysis of cellulose

Acid-catalysed hydrolysis is probably the most important degradation pathway of cellulose materials to be counteracted. Its main reaction products are macromolecules with a lower degree of polymerisation and side products such as simple organic acids, aldehydes etc (49 p. 34). The breakdown of the cellulose chain happens at random points and results in depolymerisation that increases the brittleness of the material (77 p. 49). Depolymerisation will go on until reaching a very low value of ca. 250, which is often called levelling-off DP or LODP (85 p. 400). Glucose is also produced, which is why the presence of glucose molecules can be used to judge the condition of cellulosic materials too (51 p. 74) (86).

The glycosidic bond is particularly sensitive to acid-catalysed hydrolysis. The extent of the degradation depends on the acid strength, concentration, as well as on the temperature and duration of the reaction (81 p. 17). In acidic conditions, therefore, cellulose will degrade quickly. The rate, however, will depend on the concentration of acidity, that is to say, the lower the pH of the material, the higher the degradation rate will be (49 p. 33).

The chemical mechanism is simple, with the acid being consumed in the first step and released again during the last one, which is why it is defined as a catalyst, because it speeds up the reaction rate without being consumed (Figure 14). This mechanism explains why the more acid is present, the more bond scission will happen and thus the degradation rate will be higher (49 p. 33).

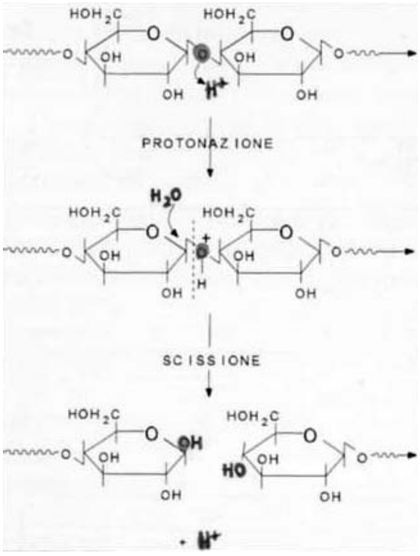

Figure 14. Acid catalysed hydrolysis of cellulose. The acid is used in the first step and produced again in the last one. From BANIK, G. *Nuove metodologie nel restauro del materiale cartaceo.* Padova: Il Prato, 2003, pp. 10 (84).

Alkaline hydrolysis of cellulose

Alkaline hydrolysis of cellulose also attacks the glycosidic bond. However, in this case, this happens only at the end of the chains and proceeds one unit at a time (Figure 15). Therefore this depolymerisation (peeling-off) does not cause so much degradation of the physical properties as acid hydrolysis does (54 p. 69). The reaction happens via ring opening and the reorganization of the molecule through the creation of a fructose ring that in an alkaline environment will separate from the cellulose molecule (50 p. 436). If there is pre-existing damage in the cellulose, such as hydrocelluloses and oxycellyloses (the products of hydrolysis and photo-oxidation respectively), then the material will degrade more rapidly under alkaline conditions (54 p. 69).

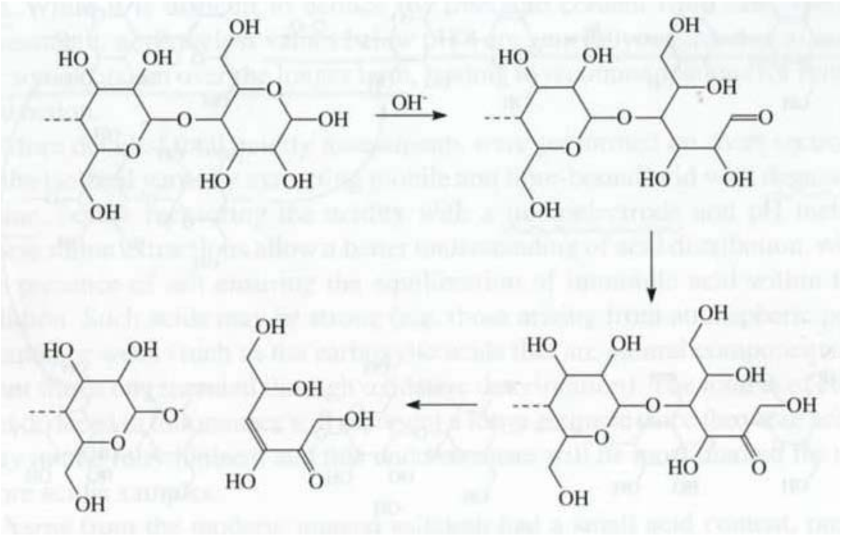

Figure 15. Alkaline hydrolysis provoking chain breakage. From MAY, E.; JONES, M. *Conservation science: Heritage materials.* Cambridge: RSC Pub., 2006. pp. 69 (58).

Oxidation

Oxidation is the process by which a molecule becomes chemically combines with oxygen (55). Atmospheric oxidation of organic materials is usually referred to as autoxidation (49 p. 34) Cellulose is relatively stable to autoxidation at ordinary temperatures although this will still happen progressively, especially under the influence of light (51 p. 73) (in which case it will be called photo-oxidation (55)).

If acid-catalysed hydrolysis was the main degradation path in an acidic environment, in neutral to moderately alkaline conditions, oxidation is the predominant degradation reaction, varying depending on the amount of oxygen in the surrounding atmosphere (49 p. 33).

In cellulose, oxidation reactions mean that the hydroxyl groups are converted into carbonyl and carboxyl group (81 p. 17).

Oxidation results in both cross-linking and chain scission (and therefore embrittlement of the material) and discolouration (54 p. 68).

Photo-oxidation can happen simultaneously by two main routes: oxidation of the cellulose hydroxyl side groups and rupture of the glycosidic bond. Oxidation of the hydroxyl side groups can happen in the primary hydroxyl group on carbon-6, resulting in an aldehyde group and on further oxidation in a carboxyl group and in the secondary hydroxyl groups on carbon-2 and carbon-3, producing, initially, ketone groups and on further oxidation, aldheyde groups and eventually carboxyl groups (47 p. 25).

Carbonyl groups (aldehyde and ketone groups) are well-known chromophores, which as part of conjugated systems cause the yellow colour of oxidized cellulose. On further oxidation, these carbonyl groups turn into carboxyl groups, which are acidic and can thus cause acid-catalysed hydrolysis of the cellulose chain in other areas (47 p. 26).

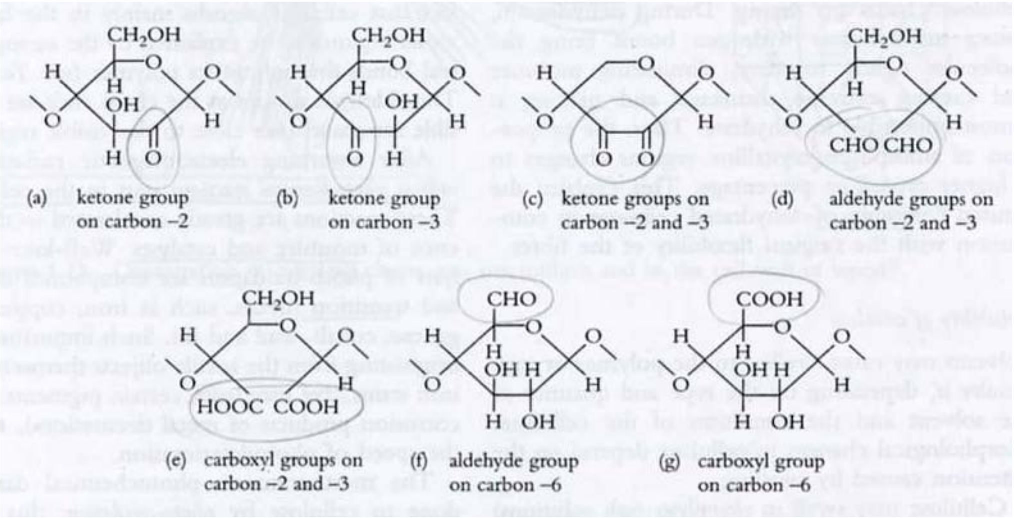

Figure 16. Oxidation products of the hydroxyl side groups of cellulose. From TÍMÁR-BALÁZSY, Á.; EASTOP, D. *Chemical principles of textile conservation.* Oxford: Butterworth-Heinemann, 1998, pp. 26 (47).

On absorption of ultraviolet radiation, a free radical chain process starts in cellulose producing chain scission of the polymer. The complex series of reactions taking place are generally simplified into three phases taking place: initiation (production of free radicals from non-radical species), chain propagation and termination (production of non-radical species from free radicals) (49 p. 35) (Figure 17).

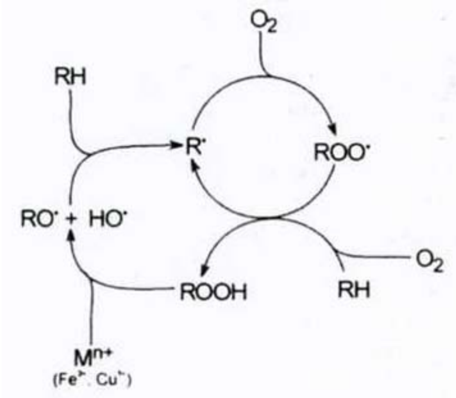

Figure 17. Schematic representation of the autoxidation reaction scheme of cellulose. From STRLIC, M.; KOLAR, J., *Degradation and stabilisation of cellulosic materials. In* JANAWAY, R.; WYETH, P. (eds.), *Scientific analysis of ancient and historic textiles: informing preservation, display and interpretation: postprints.* London: Archetype Publications Ltd., 2005, pp. 34 (49).

The final step of the chain reaction in photo-oxidation is the rupture of the glycosidic bond, and therefore decrease in DP, which is manifested in the weakening of cellulose. Photo-oxidation of cellulose by chain scission also produces small deterioration products that are yellow and acidic (47 p. 27).

In easel paintings, the canvas can also be further oxidized due to its contact with oxydizing substances such as drying oils (that form peroxides) and through the contact with oxides from the rusting of the iron tacks (4 p. 113).

1.3.2- Mechanical degradation

Textiles can also degrade due to physical-mechanical forces (damage caused by tension, stretching…etc.) (7 p. 21). In fact, it is known that textiles under tension degrade faaster than the ones that are not under tension. This is seen, for instance, in tapestries that are hung for long periods of time, were their top areas are more degraded than the rest because they hold the weight of the whole textile. The stress that these areas suffer, on top of provoking physical damage, favour chemical degradation too (87 p. 33).

In paintings it is also known that the constant weight of the canvas plus preparation and paint layers over a long period of time cause permanent deformation of the textile support. The area that suffers the highest tension is again, the folding line along the top stretcher bar (4 p. 113). Of course, this gravity effect will be worst for oversized objects (74 p. 3), such as *El gran dia de Girona* by Ramon Martí Alsina (MNAC), 5 x 11 m, weighing about 70 kg (88)! This is why large textiles are often displayed stitched onto a vertical support at a slight angle, so that the top part does not suffer so much stress (89 p. 65). An idea that maybe should also be used for large easel paintings… Other specific areas of a painting where stress is higher and this causes deterioration of the support are folding lines other than the top one, the corners (90) and along paint cracks (79 p. 70). Since tension in a painting is much higher at the corners than at the centre (8 p. 82), there will be different degradation of the canvas too (on top of a different degradation of the paint layer, which will usually be more cracked at the corners (91 p. 185)).

In a painting, the different layers react differently to changes in relative humidity (RH) and temperature (T). The canvas and the glue layer, for instance, are more absorbent than the paint layer and therefore will swell or contract more with changes in RH and will respond to it faster. In contrast the hydrophobic paint layer is more sensitive to changes in temperature, becoming more plastic at higher values and more brittle at lower levels. This difference in reaction to the environment of the complex system a painting is, causes that, after many cycles of changes in RH and T, different materials, being kept taut, end up breaking at certain points to release the tension (39 pp. 33-39).

This breaking up to release tension often happens at the paint layer level, this being usually less flexible than the canvas. However, it can also happen at the canvas level, as was the case of the big painting, *L'Industria* from the Galleria Vittorio Emanuele from Milan. This painting has big areas painted with tempera and others gilded. Along the line were the tempera ended and the gilding started, the canvas was seen to be broken at different points, indicating that the two areas had had different movements to respond to the changing environment, causing a failure of the canvas along the precise line of change of material (92).

1.3.3- Effect of the different degrading agents

The above explained chemical degradation processes can be accelerated by different external or internal agents. Heat, moisture, light, pollutants and microorganisms can all contribute to cellulose degradation (93 p. 15).

Heat

With heat, atoms and molecules move at higher speed and thus the risk of collision between them and of reacting chemically are higher. This is why, with an increase of the temperature, the chemical degradation proceeds faster for all materials, and so as well for cellulose (76 p. 39).

Moisture

Under moderate RH conditions (45-65 %), water is absorbed by cellulose in the amorphous regions of the polymer, acting as a plasticizer. Extreme levels, either high or low, however, cause problems (54 p. 67).

At higher relative humidity levels, it has been shown that cellulose degradation proceeds at a faster rate (94) whereas drier conditions (RH<30%) will lead to increased desiccation and this will give brittleness to the material (54 p. 67).

As said, a small amount of water contributes to material flexibility and this is why often a degraded old paper which is rigid and brittle because it is dehydrated can be regenerated just by putting it in a water bath, of course under controlled conditions (84 p. 8).

Higher moisture levels will also contribute to fungal growth. It is known that RH higher than 65% and temperature of 15 ºC or higher, is enough to facilitate the growth of fungi (57 p. 69). When paintings are hung, a favourable environment for the growth of microorganisms can be created between the wall and the verso of the painting (57 p. 108). The type of materials present will also play an important role in facilitating these fungi growth, flour and animal glue being particularly sensitive (40 p. 86).

Large RH fluctuations within a short period, can damage textiles too, especially when it comes to older textiles. When RH goes up, fibres absorb moisture and swell, when the RH decreases, they shrink. Older embrittled fibres might not be able to follow the fluctuations as easily as new ones and therefore mechanical damage can happen. Temperature fluctuations are also damaging since they make RH fluctuate too (74 p. 4).

Light

Light, especially that containing the UV part of the spectrum, is known to cause cellulose oxidation. This produces yellowing and embrittlement of the polymer (47).

Very interesting recent research to understand better the effect of light on textiles (60 p. 23) showed that neither cotton, nor linen or jute showed mechanical weakening when exposed to UV-filtered light. Jute showed considerable mechanical weakening when exposed to UV radiation and linen too, although to a lesser extend. Cotton did not weaken even when exposed to light with a UV component. It is pointed out that the weakening effect on jute is caused by its high lignin content. The weakening of linen is attributed to the possible presence of “photo-sensitizers”. All samples, whether exposed to UV radiation or UV-filtered light, discoloured after exposure; although those exposed to light with UV, discoloured more. This discolouration is also attributed to the presence of lignin. Jute turned darker in colour, whereas cotton and linen turned whiter, due to the destruction of chromophores. The authors also add the fact that the weakening effect of UV filtered light falling on textile objects reported by conservators might be due to a post-irradiation effect, meaning that the weakening might be not so much caused by the recent UV filtered light but by the previous non UV filtered light that might have already affected the objects in the previous decades, where light was not yet usually filtered for UV (60 p. 27).

However, further research is needed since other previous studies have shown instead that both pure cellulose filter paper and linen and jute textiles are affected by light without the UV component (95 p. 10).

Since UV radiation is thought to make lignin cross-link and this imparts an embrittlement of the cellulosic material (60), this effect will be higher on high lignin content fibres, such as jute.

Although photo-oxidation is said to cause acid products (47 p. 26), studies on the ageing of linen have shown that the increase in acidity was not that significant (96).

Luckily, the canvas in easel paintings is usually hidden in the reverse and receives little light. Things are different for contemporary paintings, were more and more artists are choosing to leave the bare canvas exposed to light (Figure 2). These areas, will probably degrade faster than areas covered by paint and could cause differences in stability throughout the canvas support.

Biological attack

Cellulose is a highly hygroscopic organic material. Therefore, in a environment (high RH levels, warm temperatures (≥15 ºC) and low air circulation), it is very susceptible to biological attack by bacteria and fungi. These contain cellulase (an enzyme) that help them break down the cellulose chains and use it for their nutrition (51 p. 74). On top of eating part of the cellulose away, the products of their metabolism are often acidic and coloured. Therefore, on top of the physical-mechanical damage caused, they cause optical damage and further chemical reactions (84 p. 12).

Pollutants and air circulation

Air is a gaseous mixture, the main components of which are nitrogen (78%) and oxygen (20.9%). Other gases in much smaller quantities are: argon (0.93%), carbon dioxide (0.03%), water vapour in variable quantities (0-7%), ozone and nitrogen oxides. On top of these gaseous components, air contains solid dust particles and microorganisms in suspension (50 p. 410).

Some of these gaseous components and solid particles act as catalysts in chemical reactions. Air pollutants such as nitrogen oxides (NOx) and sulfur oxides (SOx) form strong acids in the presence of moisture and thereby accelerate the hydrolysis of cellulose. Traces of metals such as iron, copper and manganese can act as catalysts in oxidation (7 p. 23).

Harmful gases result from the industry and vehicle or from products used in the museum such as wood, coatings and the collections themselves (74 p. 3). In the past SO_2 levels were high, and this would have been absorbed by cellulosic materials and lead to H_2SO_4 formation. A study done in 1984 on linen samples naturally aged for 24 years, showed that samples exposed to air had higher sulfur levels than those that had aged in an enclosed environment. Those samples aged in an enclosure also showed less mechanical damage. This experiment showed, thus, the benefits of creating enclosures for paintings (79 p. 11).

Enclosures are good because they limit access of external pollutants up to a point, and also because they reduce air circulation, which has been found to have an effect on the degradation rate (the higher the air circulation rate, the more degradation) (97 pp. 108-109). In a very interesting research, the pH values of different areas of several pages from an acidic book where measured. As could be expected, the central part of the book had higher pH values and the outer areas where air had been able to penetrate more, pH values where lower. Specially higher were the values at the top edge, indicating that probably the book had been kept upright in a shelf with both the bottom and vertical edges covered by the shelf and the wall (also very high were the values near the spine of the book which must have had some sort of acidic material in it) (98 p. 20).

That loose linings and backing boards are good at protecting against natural ageing in paintings has long been perceived by conservators (79 p. 73). Enclosures for paintings have been seen to be good for paintings in the sense that by physically obstructing air circulation, access to pollutants is limited (97 p. 109). However, cellulose degradation products have also been seen to be acidic too and therefore absorbing materials would be advisable to be included in enclosures (80).

Acidity

As already emphasised, acidity is the most important cause of degradation of cellulose materials to be counteracted, since it easily causes the glycosidic bond breakage reducing the DP and therefore mechanical properties (49 p. 34). For textiles, it has been corroborated that acid attack is more damaging than UV radiation or moisture damage (99).

After acidity, though, light can also be very damaging for textiles. However, since usually the canvas is not that much exposed to light, acidity should become a greater concern for modern paintings conservation. This is why the incipient deacidification studies on the canvas of paintings that where initiated in the 1980s-1990s (75)(100)(101) should be further developed, so that if needed it starts to be done more often. Strangely enough, this is still a seldom applied treatment in the field of paintings conservation. Recently, new nanotechnologies too are starting to be explored for deacidifying the canvas of paintings (102).

Acidity can come from polluted air (sulfur dioxide or nitrogen dioxide) , but also from the cellulose own degradation products (carboxylic acids produced by oxidation, for instance) (79 p. 72). In fact, studies of accelerated degradation of cellulose have shown that acidity increases (lower pH values are obtained) with thermal degradation (103). In particular, acetic acid has been characterised as a major degradation product of newsprint paper among other low molecular weight carboxylic acids such as formic, lactic, malonic, malic, succinic and *α*-ketoglutaric acid (81 p. 16). Degradation of pure cellulose in closed vessels has also proven that during degradation of pure volatile acidic products are also produced. Therefore, ventilation (or acidity absorbing materials) is thought to be a very good preservation action for cellulosic materials (80).

Other sources of acidity that could affect the canvas in paintings can also be the materials associated in the production of the painting itself.

The presence of animal glue in paintings is considered to be a degrading agent for the canvas by some authors (9). In older paintings, animal glue could be present at very high concentrations, since old manuscripts such as the Eraclius manuscript (written around the 10th C), calls for fully dipping the canvas in the animal glue before stretching it (104 p. 230). Mixtures of animal glue and flour have been found in paintings by Cranach the Elder, and many more cases are to be expected, if we take into account that these recipes for preparing canvases are found in old manuscripts such as Cenino Cennini's (14th C) (105 p. 435).

Studies on the effect of gelatine on paper have shown however, that its presence can be beneficial for the paper (there is less degradation of cellulose), although it is true that it induced some discolouration and a decrease in pH. Regarding acidity, gelatine sized papers were found to be more acidic than unsized papers (81 p. 113). Therefore the general belief that animal glues become acidic with time is found to be true. However, this acidity does not seem to induce degradation as has been found to happen to acidic paper (106 p. 205).

The oil paint itself can be a source of acidity in the painting system. To start with, drying oils used for painting contain fatty acids. The drying power of a particular oil is related to the concentration of polyunsaturated fatty acids in the oil, because their C=C double bonds enable polymerisation and oxidation reactions which promote the formation of a film. For an oil to be regarded as a drying oil this concentration should reach at least 65%. The presence of linolenic acid is essential for rapid drying (20 p. 36)

On drying, oils go through oxidation and polymerisation reactions that produce acidic compounds such as: propionic acid, azelaic acid etc. Thus with time, its acidity increases and this could be dangerous for the canvas. They also contain saturated fatty acids to start with, that are so stable that their concentration hardly changes on ageing (20 p. 38). Therefore, the presence of the oil paint layer, the acidity of which increases with ageing, will eventually degrade the canvas too (39 p. 30) (12 p. 212).

This has been known since the earliest of times of oil painting, and this is why traditionally a glue layer has been is applied to the canvas before painting (9 p. 5) (104 p. 728). The glue layer, on top of reducing the absorbance of the canvas, acts as a protection for the migration of the paint acidic compounds into the canvas (12 p. 212).

Recent research comparing the different effects of an oil-paint layer versus a tempera paint layer on a cellulosic canvas, indeed proved that an oil-paint layer caused more depolymerisation of the cellulose (107 p. 321). Certain pigments, can also be damaging for the canvas, as well as the well known iron tacks that rust the nearby textile (79 p. 70). It is well-known for instance, that verdigris, in common with other copper pigments, will degrade cellulosic materials (108 p. 137).

Preparation layers too can contain substances that degrade the canvas (4 p. 113). If initially the binding agent used was animal glue, from the 17th C on this could be substituted by drying oils. This was so because painting on a canvas support, instead of painting on wood, required more flexible layers that could follow the movement of the canvas (40 p. 179).

Different pigments need different amounts of oil and bond chemically to it differently (45 p. 181). In many instances conservators observe the migration of oils from the paint layer into the canvas. This can be seen as stains on the verso of the painting. Often this tendency of oils to migrate to the canvas happens more with darker colours (earth and black pigments) and thus the image in the recto is replicated on the verso of the painting (Figure 18). This observation correlates with the fact that brown and black pigments tend to require more oil than other pigments (109 p. 272).

Figure 18. Painting by Claudi Lorenzale (1814-1889), MNAC 038895. Recto and verso. Oil stains from the darker colours can be seen on the reverse.

The wooden stretcher can also be a source of acidity for the canvas in a painting, especially in a microclimate frame, since it is known that wood emits acidic VOCs (77 p. 49). Although the type of wood used in stretchers has been most commonly the softwood pine, nowadays we also find hardwood stretchers being made (110 p. 11). Hardwoods (such as oak) are known to emit more acetic acid than softwoods, although softwoods such as larch and red pine also emit a considerable amount of acetic acid. The higher the temperature and the higher the RH, the higher the amount of acid generated (111). While it is true that most woods release most of its polluting products at the beginning of their curing period, in the case of oak and cedar, even if they release progressively less polluting products after the curing period, they have been found to still have significant emission rates after 50 years of natural ageing (they will still have a noticeable smell of vinegar) (112 p. 39).

Conservation treatments, past and present, can also add materials that could potentially lead to an increase of acidity (Figure 19). Glue-paste linings are thought to introduce acidic components and to become acidic with time, since some have traditionally contained acidic substances such as vinegar, Venice turpentine[22] and alum[23] (4 p. 113) (113 p. 233 i 237).

Having read that the glue paste is acidic (114 p. 386), but not having found more precise information than this, a quick pH measurement was taken the last time that the Conservation Section students at the

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[22] Venice turpentine is a a thick viscous exudation from the Austrian larch tree, *Larix decidua*. It contains 63% resinous acids, 20% terpenes and 14% resins (123).

[23] "Alum" is a general name used for different aluminium sulfate salts. Most commonly the term is used to refer to aluminium potassium sulfate (this is the one used by papermakers, although they have also used the mixture of aluminium sulfates obtained by treating pulverized bauxite with sulfuric acid). Other aluminium sulfate salts that have also been referred to as "alum" are: aluminium ammonium sulfate (used in cooking), ferric ammonium sulfate, chromium sodium sulfate and chromium ammonium sulfate (123). It is clear, thus, that the term "alum" is a too general one and that we should know which type are we using in each case…

University of Barcelona prepared the adhesive while learning about glue-paste lining[24] (May 2011). The pH was found to be about 5 on the same day of preparing the adhesive and the same just before it was going to be used the next day (the recipe recommends letting the paste rest for a day before using it). Although it is not extremely acidic, it is already not neutral. Further research on the acidity increase of traditional glue paste linings would be very interesting, since this might prompt alterations to be done to the traditional recipes which are still being used when a lining has to be done (although this treatment is seldom done nowadays).

Consolidation of the reverse of the canvas by just brushing some sort of glue is a procedure done nowadays when a canvas is very degraded but it can still escape lining if some sort of consolidating treatment is carried out to reinforce a bit the degraded fibres. This is a procedure often done in Italy, and not so much done in Spain (115). Some of the adhesives that one could used for this are: rabbit skin glue, Beva 371, Plexisol P550 and Akeogard AT35 (116 p. 13). Even newer adhesives such as Aquazol 500 have been suggested (117). Some times this impregnation has also been done before doing a glue paste lining if the canvas was feared to shrink with the presence of water from the glue paste adhesive. In the earlier days, natural materials such as mastic varnish and wax could be used, more recently synthetic resins such as Plexisol P550 (50% in White Spirit) and Paraloid B72 have been used (118 p. 53). In the past, if the painting was not water sensitive, the Italian tradition for glue paste lining also called for an impregnation of the canvas with animal glue or diluted "colletta" before doing the lining, so as to consolidate the paint layers by introducing the adhesive from the reverse (118 p. 59). This is because in the past, the lining treatment was seen as a way to consolidate both the support and the paint layers.

Figure 19. *The Virgin of the rosary*, Conservation Section UB, 602_08. In the centre, the reverse of the painting before treatment where stains of oil migration are seen to correspond to the darker oil colours in the recto. On the right, the reverse after the animal glue consolidation treatment of the paint layer from the front. Here the glue has gone through the cracks and has been deposited on the canvas.

Other types of lining, such as the wax-resin mixture are also believed to induce some degradation. Its effects on linen naturally aged for 24 years were studied by Hackney et al. Although the mixture was seen to offer some protection when the textile was exposed to air and light, it was found that when aged inside an enclosure, the wax-resin mixture had a detrimental effect. The authors suspected that the presence of dammar resin and bleached wax in the lining adhesive could be the cause of this degradation (96 p. 9), since these substances would have given off acidic vapours.

Old conservation past treatments, such as the Italian "beverone", a mixture of drying oils, natural resins, vinegar and sometimes egg, described by De Mayerne in the 17th C (40 p. 40) as a very good remedy for canvases that lacked flexibility and that needed some paint consolidation (119 p. 67), would, of course introduce direct acidity to the canvas since it was directly applied to it from the reverse (118 p. 48). Luckily, it was soon seen that the remedy was worse than the illness, and the treatment was eventually discontinued.

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[24] The recipe used was the one traditionally used in Catalonia (which is different from the traditionial Spanish "gacha": 540 g of flour, 1.800 L of water, 200 g of "Italian colletta",30 g of alum (added as a plastifier) and a few drops of Neodesogén (added as a fungicide). The "Italian colletta" recipe contained: 200 g of animal hide glue, 200 g of water, 60 g of molasses (to give plasticity) and a few drops of ox gall (as a tensioactive).

Paintings impregnated with shellac have also been found to become glass-like, breaking really easily when trying to reattach them onto their stretcher. Although this does not seem to have been a common past treatment, this was found to be the case of a group of paintings belonging to the Biblioteca de Catalunya, Barcelona (88).

To sum up, cellulosic textiles are seen to be easily attacked by several different external and internal agents. It is curious to see that although it was already pointed out in the 1980s that synthetic textiles offered superior chemical and physical properties than cellulosic ones (9), painters and conservators are still using natural textiles much more.

In the artist’s materials market, linen canvases are still the ones being sold as the best quality range materials. The canvases containing partially synthetic fibres that are being currently sold are considered the lower quality range. In conservation, attempts from companies such as Lascaux to produce a cellulosic looking textile made of synthetic fibres (Polyester Fabric P110, (120)) has not been that widely adopted, at least in Spain, most probably due to its high cost. And although in the last years, the use of polyester sailcloth has gradually been adopted as a loose lining material (8 p. 229), linings are still usually being done with the traditional linen canvas.

Current research is actually trying to figure out synthetic textiles that could replace linen both in the artists’ materials and in the conservation fields (121). However, these types of research (very interesting ones) are looking into future better materials to be used. If we want to preserve all the paintings that have been done in the past so that we can pass our heritage to the future generations in the best possible conditions, we will have to keep learning about cellulose degradation, its analysis and its preservation.

2- The Reference Sample Collection

Once we have learned about the canvas material used as a support for paintings and about its degradation, we are ready to start the experimental part of our research by collecting a large amount of samples and analytically measuring its fibre type, pH and DP. This large amount of data, apart from being the ground onto which build our non-destructive NIR spectroscopy method later on (Chapter 3), will enable us to learn more about the degradation of easel painting supports: the typical pH and DP values obtained for paintings, their fibre type and the relationship between these parameters. This is what this second chapter deals with, starting by explaining the nature of the Reference Sample Collection.

2.1- The samples

In order to both know what are the typical pH, DP values and fibre types of paintings canvases and to be able to build a chemometric model through NIR spectrometry, a “large” amount of samples from real paintings was needed. The more variability there would be in the Reference Sample Collection, the better since we would both obtain more information valid for a larger spectrum of possibilities and be able to develop a more reliable NIR spectrometric method.

The amount of sample needed to do pH analysis is really small, between 250-350 µg. For microscopy fibre identification, a piece of a thread from each direction in the painting is needed, since they can be of different nature. However, pieces of threads[1] 1 cm long are more than enough for this, as only a few fibres are needed (actually the fewer the better, since if there are too many it makes visual identification more difficult). The parameter that needs a larger amount of material to do the measurement is viscometric DP analysis, where at least 30 mg of fibres from the canvas are needed.

2.1.1 - Where from

Canvas samples from original real paintings were collected from three Catalan institutions: Museu Nacional d’Art de Catalunya (MNAC), Faculty of Fine Arts Collection and Conservation Section (University of Barcelona (UB)) and the Conservation Centre (Centre de Restauració de Béns Mobles de Catalunya (CRBMC)). Along the project, some samples from individuals (Erminio Signorini, Anna Nualart, Marianne Odlyha, Stephen Hackney, Mª Dolors Folch, Marta Oriola, Núria Flos, Margarita Alcobé and Joan Rosàs) were also added to the collection.

The MNAC is the largest museum in Catalonia, with a collection of about 250,000 objects spanning from the 11th to the first half of the 20st century. The collection focuses on Catalan art, the main assets being its Romanesque and Gothic art collection as well as the *Modernisme* (Catalan Art Noveau), *Noucentisme* and Avant-garde objects from the end of the 19th C, beginning of the 20th C, two eras of the greatest splendour times of Catalan history. The samples that MNAC granted us to collect came mainly from the 19th and 20th C second-class paintings relegated to their storage rooms. Samples were always taken from the edges of the tacking margins and were about 1 cm^2 in size. A piece of a vertical thread and a piece of a horizontal thread were also taken from each painting from two of its sides in order to do fibre identification. The remains of these textile samples used for pH, DP and NIR analysis are each being kept inside a labelled plastic bag with an inner paper envelope, in the fridge to slow down any further degradation after analysis so that their

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[1] All textiles are made of threads, which in turn are made of fibres that are extracted from plants, in the case of “plant fibres” (5 p. 12).

condition is kept as constant as possible, in case further studies want to be done in the future and the already measured data are needed.

The Faculty of Fine Arts Collection has about 1.500 objects which technically belong to the UB but that are being housed and cared by the Faculty of Fine Arts. Its works are all from the 20th C. and 21st C, the majority of them being from the last thirty years. Since 1982, the faculty started to systematically collect/buy a few works each year from the most talented emerging students through the “Patrim” contest. Therefore the samples coming from the Faculty of Fine Arts are mainly from the last part of the 20th C and some from the beginning of this 21st C. As for MNAC, samples collected from this collection come from the edges of the paintings and are about 1 cm^2.

The Conservation Centre (CRBMC) belongs to the Catalan Government, Generalitat de Catalunya, and treats public works of art in its facilities through their small staff and the many free-lance conservators that work there. Paintings from all periods are treated in the Centre, although they have often access to older untreated paintings that come from local churches. Four samples were taken from older paintings that were being treated at that moment to increase the time span of the Reference Sample Collection.

Another important set of the Reference Sample Collection, came from the Conservation Section of the Faculty of Fine Arts (UB). Of these, 15 samples come from old glue paste linings that have been removed from paintings that underwent conservation treatment at the faculty over the years.

2.1.2- How many

The Reference Sample Collection is comprised of a total of 206 samples. Of these, there are 186 textile samples (a small piece of woven canvas) and 20 are tiny pieces of “threads for pH” analysis only. According to the source where these samples come from, the majority of them come from MNAC, followed in number by the Conservation Section (UB), the Fine Arts Collection (UB), donations by several different private owners and the Conservation Centre (CRBMC).

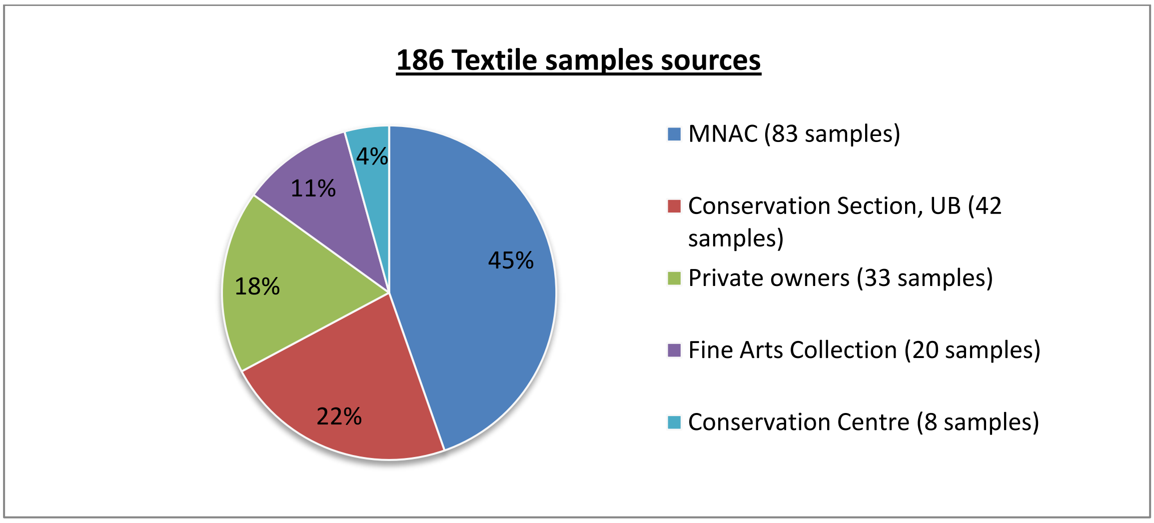


Figure 1. Sources of the 186 textiles of the Reference Sample Collection.

Since often a couple or even three samples were taken from the same painting, the collection of 186 grew to 206. This was done when one area of the painting was seen to be much more degraded than the rest, such as was the case of some of the paintings at MNAC, where the bottom area of the painting was seen to have suffered water damage and thus the canvas was much more fragile. The aim was to see if there were significant pH and DP differences where visually they looked in a different condition.

Thus the number of paintings/objects that the samples came from, are, ordered decreasingly: MNAC (63); Conservation Section-UB (35), private owners (24), Fine Arts Collection (19), Conservation Centre (6). The total number of objects studied was 147 (of which 108 were paintings). It has to be said that in the *Access* database (see this same chapter, later on), the number of "Paintings" increases to 156, because there are paintings of which we also had samples from the lining and thus a new entry had to be created in order to enter the different dates, materials and fibre type information. Thus in terms of the amount of textiles studied, the total number is 156.

On top of the 206 samples, a "vertical" and a "horizontal" piece of a thread ("vertical" and "horizontal" in relation to the painting) were taken from each painting to do fibre analysis. This means that an extra number of 312 thread samples were gathered.

2.1.3- What type

The main focus when gathering the samples, was to collect textiles from real paintings since this was our main center of interest. The aim was to cover broadly all types of paintings, with as many materials and dates as possible. Other types of textile samples were collected too, to add variability to the collection and to cover gaps in the collection regarding fibre type or high pH values. To fill in these gaps, known hemp and ramie textile samples and samples from a few deacidified paintings were added.

Each sample was classed as one of the following types:

More specific types of samples	**Number of samples**	**Broader types of samples**	**Number of samples**
P: Painting	124	Paintings	124
L(P): Glue paste Lining from known Painting	13	Glue paste linings from paintings	31
GL: Glue paste Lining (from unknown painting)	18		
LL: Loose Lining from known paintings (no glue)	4	Loose linings (primed and not primed); no glue	8
PLL: Primed Loose Lining from known paintings (no glue)	4		
HT: Bare old Household Textile	3	Non-historic samples (New and old textiles and primed new canvas)	23
BNT: Bare New Textile	16		
PNC: Primed New Canvas for painting	4		

Figure 2. Classification of paintings/objects into different types.

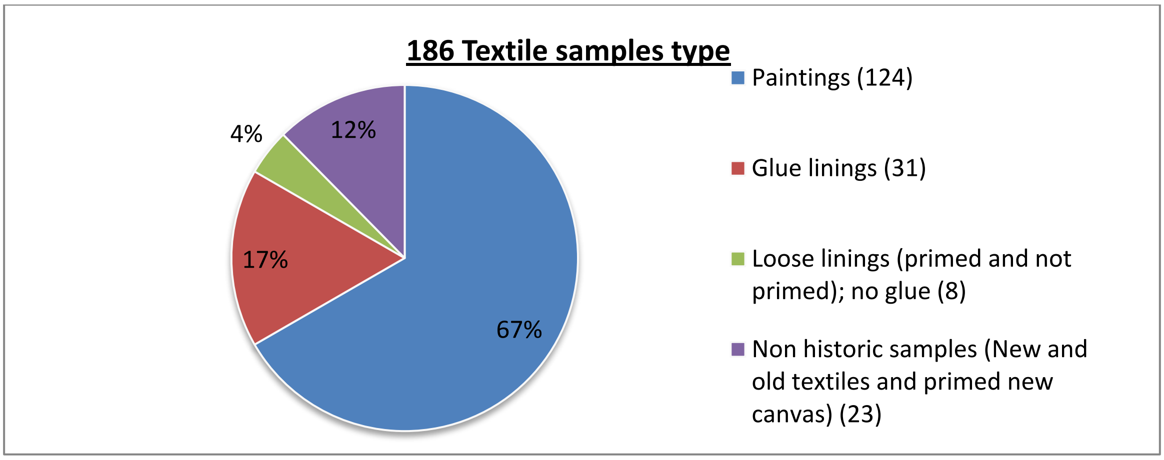


Figure 3. Textile samples according to type (Paintings, glue paste linings, loose linings and non-historic samples)

If we add all the samples from real paintings (samples from the paintings or from their linings (glue linings and loose linings), we have a total of 163 historic samples. Non-historic samples amount to 23.

2.1.4- What dates

Planning the gathering of such a large number of samples and especially when working in other people's institutions where you need help and attendance to move around the place and to access information is not easy. Although a whole week had been spent at MNAC in August 2009, before the sampling collection campaign took place in October 2009, to plan the list of works of which samples could be taken, something as simple as not knowing yet how much the needed 30 mg for DP meant when it came to paintings, meant the plan had to be changed when the time to collect the samples arrived. There were different constraints as to which paintings could be sampled: first paintings had to be in the storage rooms, there had to be a small surplus of canvas at the reverse of the painting where the textile sample would be taken, it needed to be possible to remove both one vertical and one horizontal piece of a thread and access to the NIR spectrometer probe had to be possible (at that point the plan was to later on analyse the centre of the paintings where no physical sample could be taken and compare it with the data from the sample taken from the margin and this is why an NIR spectrum was taken from the centre of the paintings that were being sampled). The other biggest constraint was time, since the NIR spectrometer was in Barcelona for only a few days. All this meant that the production dates of the paintings were not taken into account at that point, which would be something to consider if doing a similar study in the future. We were lucky enough that most of the sampled paintings had a known date of production, and those that were not dated could be assigned to broader period categories, more or less precisely, through the museum's documentation.

After having collected the samples, full information from the final list of paintings used was gathered. For some of the paintings, a precise date (year) was known, but for others date attribution was more vague, especially with older paintings (i.e. "17th C" or "19th C/20th C"). Since for treating data it was necessary to have a specific date as a number, each painting was assigned a "year" that, for the purpose of our analysis had the following meaning:

Paintings from:	The following year was assigned:
16th C	1550
17th C	1650
18th C	1750
from 1800 to 1849	1825
from 1850 to 1899	1875
from 1900 to 1949	1925
from 1950 to 1999	1975
from 2000 to 2010	2000

Figure 4. Date assigned to paintings with a precise date or century of production.

If the date available on the object was not so precise, then the following numbers were assigned:

Paintings from:	The following year was assigned:
“17th C- 18th C”	1700
“18th C- 19th C”	1800
“19th C”	1850
“19th - 20th C”	1900
“20th C”	1950

Figure 5. Dates assigned to paintings where imprecise data regarding their production dates was available. These samples could be removed if more accurate work regarding the relationship between the date of paintings and a particular parameter of interest is wanted.

The following table shows the particular number of samples each date category had:

More specific date categories	Number of samples	Broader date categories	Number of samples	%
1550	3	1500 (16th C)	3	2%
1650	6	1600 (17th C)	6	3%
1700	2	1700 (18th C)	12	6%
1750	10			
1800	2	1800 (19th C)	56	30%
1825	7			
1850	8			
1875	39			
1900	25	1900 (20th C)	93	50%
1925	37			
1950	11			
1975	20			
2000	16	2000 (21st C)	16	9%
Total	**186**		**186**	

Figure 6. Number of samples according to more specific and broader date categories.

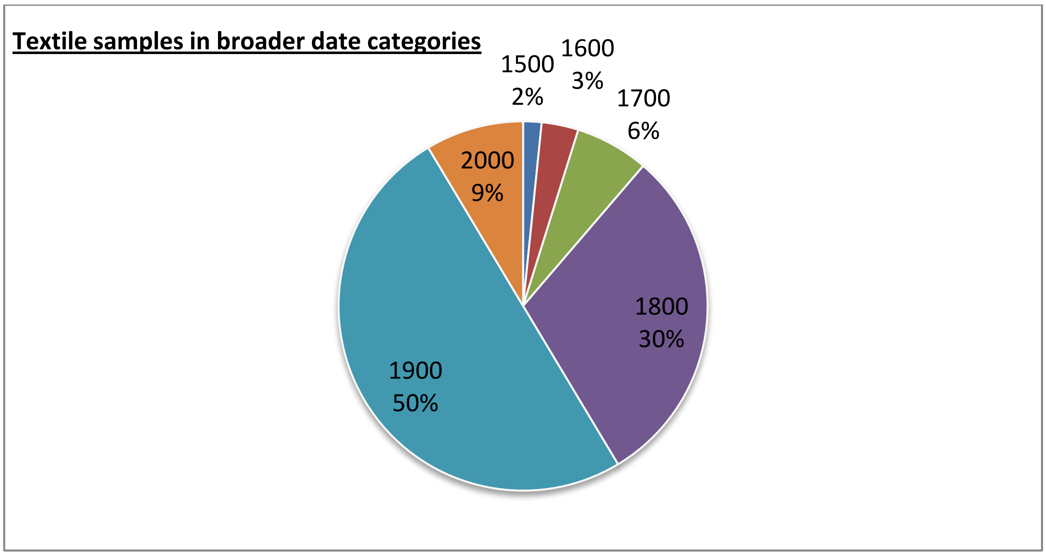


Figure 7. Proportion of textile samples in broader date categories.

The oldest sample in the Reference Collection is from the 16th C and the newest one is from 2006. Half of the samples (50%) are from the 20th C and 30% are from the 19th C. Therefore, our Reference Sample

Collection is mainly from the 19th-20th C (80%). The other 20% are either from the 21st C. (8.6%) or from before the 19th C, i.e. from the 16th to the 18th C (11.2%).

The scarce number of samples before the 19th C is due to the fact that there are less older paintings (16th - 18th C) that have survived until today (1). On top of that, the older paintings that have indeed survived, have many chances of having already been lined, just because they have a longer history. Also, the fact that there are few older paintings makes them more “precious” in comparison with the more modern and available paintings, and as valuable objects, they have often received more attention and thus conservation treatments such as lining.

Thus it has to be taken into account that our NIR spectrometry calibration for fibre type, pH and DP, if achieved, will only be useful for samples from the 19th-21st C, and more precisely from 1875 onwards, since most of the 19th C samples are from the end of the century (39 samples, out of the 56 samples from the 19th C, have a “1875” assigned date).

2.1.5- What painting materials

Samples from the 19th and 20th C, which are the majority in our collection, are mostly commercially primed canvases. From the 19th C on, most of the canvases had preparations based on drying oils. In the 20th C synthetic primings (acrylic and alkydic) were also introduced. What has remained constant, though, is the application of a first layer of animal glue (2 p. 301).

The 21 samples from between the 16th and 18th C would presumably have mostly artisan animal glue-based preparation layers. From the 17th C onwards, though, paintings could have a first glue sizing layer and a more flexible oil-based preparation layer. This was so to give more flexibility to the canvas support (3 p. 179). It is known that by the mid 17th C, pre-primed canvas was already being produced in parts of Europe (4 p. 23), so some of the samples in this early group could have already been commercially prepared. When a preparation layer has been manually applied by the artist himself, most often the tacking margins are left unprimed.

In some instances the samples also have a paint layer on them, but they mainly have either the priming or are bare canvas (having lost its original priming), since samples were taken from the edges of paintings.

Of the studied paintings, only three were known to be acrylic painted (numbers **61**, **63** and **64**) and one tempera (**79**). The rest of paintings, almost all of them, were done in oil paint. Obviously the acrylic painted paintings are from the end of the 20th C, while the tempera one is from the end of the 19th C.

Regarding the textiles used, it is obvious that older canvases have thicker and more irregular threads as well as more irregular weaves. With the advance of industry, both the threads and the woven textile became more regular.

Most of the samples have a plain-weave canvas structure, although a few twill examples were found. Most of the twill paintings found are from the end of the 19th C- beginning of the 20th C (**13**, **17**, **19**, **27**, **81**) but one from the 16th C was also found (**94**). Selvedges (the end of the piece of woven textile) along one of the painting’s edge were also found in some instances and documented. In one case, a painting from around 1875 (painting **24**) was found to have two selvedges: one on each side of the painting, revealing the original length of the woven textile, which was about 114 cm in this case.

2.2- The *Access* Database

To be able to manage such a large amount of very detailed information on all the samples and paintings gathered along the several months of research an *Access* Database was built. Since there are some paintings of which more than one sample was extracted, two different tables had to be created: one for the paintings and one for the samples. These two tables had to have the “from one to infinite” type of relationship, so that there could be one register line for each painting in the paintings table linked to one register line for each sample or more in the samples table.

One successive number was given to each painting, starting with number 1 and finishing with number 156. Samples were named by putting first the number of the painting they came from, a dash and then successive numbers for each specific sample. Like this, sample "10_3" means it comes from painting 10, and that there are 3 textile samples available. If a sample of a lining was taken, this was indicated in the sample name by adding an "L" after the number (i.e. "73_L"). An O from "original", was added in the sample name from the original canvas for clarity when a sample from the lining had also been taken (i.e. "73_O"). When a small piece of a thread for pH analysis only was taken, it was indicated by adding a "Th" (from "thread") after the painting number (i.e. "65_Th"). If there were more than two threads, this was indicated by a consecutive number (i.e. "5_Th2").

The paintings table included information related to the whole painting, that is to say: author, title, date of the painting, fibre type… Since this information was different for linings (they can be of a different type of fibre, a different date etc.), an internal "ordering number" had to be created for the paintings table, so that each painting and each lining could have its own register line.

Although every attempt was done to foresee and plan the naming of paintings and samples so that it could be as user-friendly as possible, it is clear that with so many particularities (different types of samples etc.) there is no one only way to do things. One of the drawbacks of the adopted method of naming samples was that including dashes and letters in the sample names implies that lists of samples are not easily ordered in *Excel*: when you order according to sample name, you get first the samples with only numbers in their name and then the ones with dashes and letters. This was overcome very often by adding an "ordering column", just with numbers that one had to remember to copy and paste when working with *Excel*. Although we found a way to work with it, it is certainly advised to just give correlative numbers to samples to avoid this pitfall in the future.

Further to the "Paintings" and "Samples" tables, two further tables were included with the information on the NIR spectra taken for each painting (centre of the paintings) and for each sample: name of the NIR file, how was NIR taken etc (Figure 8). These two tables also had the "from one to infinite" relationship with the Paintings and Samples tables, since there was more than one spectrum taken for both each painting and each sample.

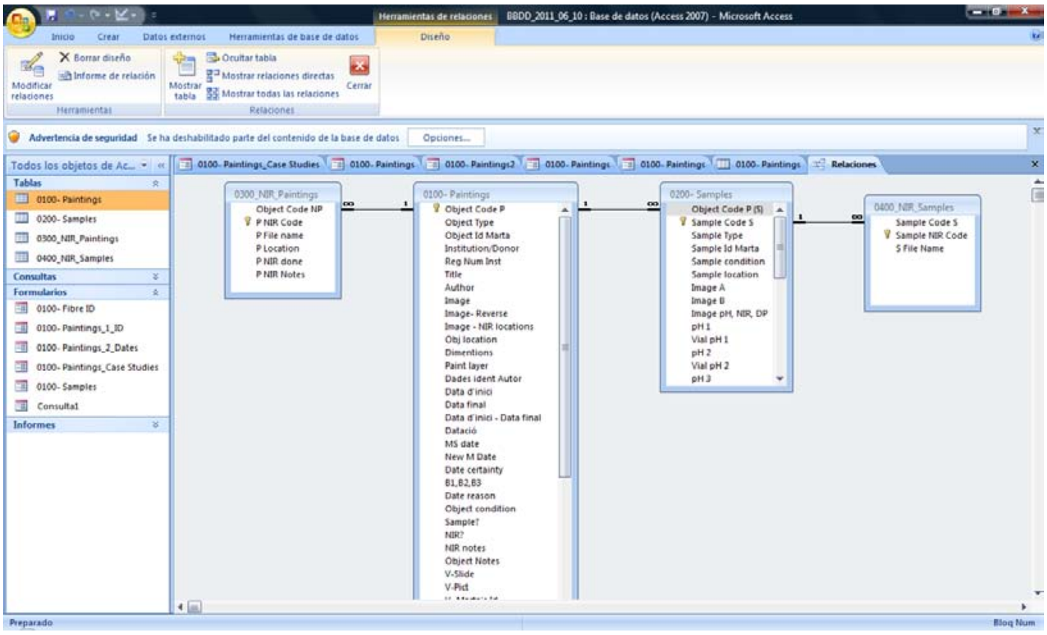
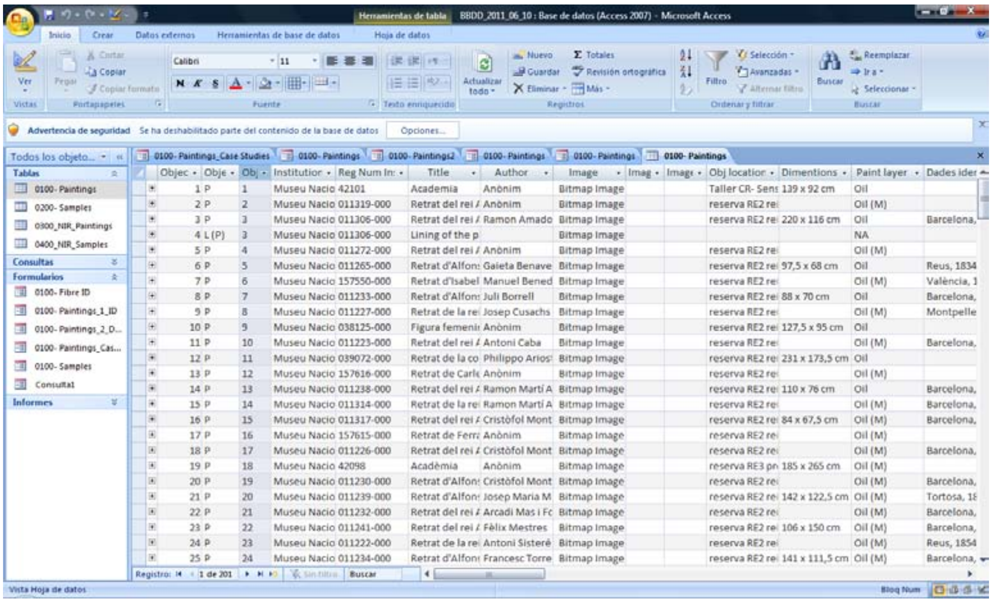


Figure 8. The four tables with their fields and how are they linked to each other.

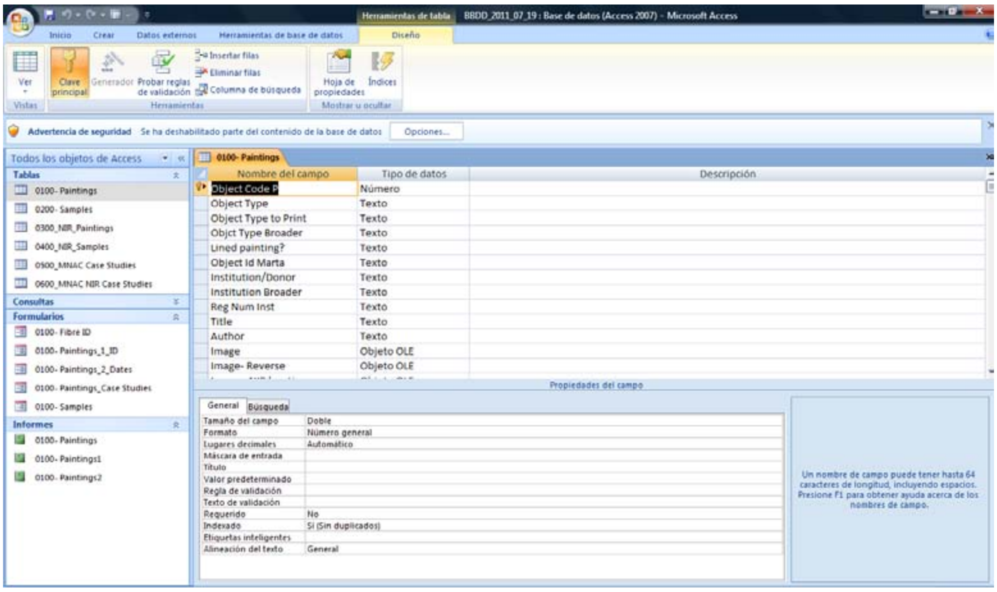
An *Access* database is very useful when managing so much information because each table has an unlimited number of possible registers (paintings, samples or spectra) and also an unlimited number of fields (pieces of information related to each painting, sample or spectra). This means that all the information can be stored in the database, but then you can chose which specific fields to see by creating different “forms”. Like this you can gather all sorts of bits of information on a painting, as detailed as you want, but just choose to see a few particular ones in every different form.

Having a database ensures that there is only one place where to update all the relevant information and guarantees that you are always working with the most up to date information. However, as with the sample naming, a lot of planning is needed in advance, since there are things like the type of field (text, numeric etc.) that cannot be changed once they contain information.



Objec	Obje	Obj	Institutior	Reg Num In:	Title	Author	Image	Imag	Image	Obj location	Dimentions	Paint layer	Dades ider
1	P	1	Museu Nacio	42101	Academia	Anònim	Bitmap Image			Taller CR- Sens	139 x 92 cm	Oil	
2	P	2	Museu Nacio	011319-000	Retrat del rei /	Anònim	Bitmap Image			reserva RE2 re		Oil (M)	
3	P	3	Museu Nacio	011306-000	Retrat del rei /	Ramon Amado	Bitmap Image			reserva RE2 re	220 x 116 cm	Oil	Barcelona,
4	L (P)	3	Museu Nacio	011306-000	Lining of the p		Bitmap Image					NA	
5	P	4	Museu Nacio	011272-000	Retrat del rei /	Anònim	Bitmap Image			reserva RE2 re		Oil (M)	
6	P	5	Museu Nacio	011265-000	Retrat d'Alfon:	Gaieta Benave	Bitmap Image			reserva RE2 re	97,5 x 68 cm	Oil	Reus, 1834
7	P	6	Museu Nacio	157550-000	Retrat d'Isabel	Manuel Bened	Bitmap Image			reserva RE2 re		Oil (M)	València, 1
8	P	7	Museu Nacio	011233-000	Retrat d'Alfon:	Juli Borrell	Bitmap Image			reserva RE2 re	88 x 70 cm	Oil	Barcelona,
9	P	8	Museu Nacio	011227-000	Retrat de la re	Josep Cusachs	Bitmap Image			reserva RE2 re		Oil (M)	Montpelle
10	P	9	Museu Nacio	038125-000	Figura femeni	Anònim	Bitmap Image			reserva RE2 re	127,5 x 95 cm	Oil	
11	P	10	Museu Nacio	011223-000	Retrat del rei /	Antoni Caba	Bitmap Image			reserva RE2 re		Oil (M)	Barcelona,
12	P	11	Museu Nacio	039072-000	Retrat de la co	Philippo Arios	Bitmap Image			reserva RE2 re	231 x 173,5 cm	Oil	
13	P	12	Museu Nacio	157616-000	Retrat de Carl	Anònim	Bitmap Image			reserva RE2 re		Oil (M)	
14	P	13	Museu Nacio	011238-000	Retrat del rei /	Ramon Martí A	Bitmap Image			reserva RE2 re	110 x 76 cm	Oil	Barcelona,
15	P	14	Museu Nacio	011314-000	Retrat de la re	Ramon Martí A	Bitmap Image			reserva RE2 re		Oil (M)	Barcelona,
16	P	15	Museu Nacio	011317-000	Retrat del rei /	Cristòfol Mont	Bitmap Image			reserva RE2 re	84 x 67,5 cm	Oil (M)	Barcelona,
17	P	16	Museu Nacio	157615-000	Retrat de Ferr	Anònim	Bitmap Image			reserva RE2 re		Oil (M)	
18	P	17	Museu Nacio	011226-000	Retrat del rei /	Cristòfol Mont	Bitmap Image			reserva RE2 re		Oil (M)	Barcelona,
19	P	18	Museu Nacio	42098	Acadèmia	Anònim	Bitmap Image			reserva RE3 pr	185 x 265 cm	Oil (M)	
20	P	19	Museu Nacio	011230-000	Retrat d'Alfon:	Cristòfol Mont	Bitmap Image			reserva RE2 re		Oil (M)	Barcelona,
21	P	20	Museu Nacio	011239-000	Retrat d'Alfon:	Josep Maria M	Bitmap Image			reserva RE2 re	142 x 122,5 cm	Oil (M)	Tortosa, 18
22	P	21	Museu Nacio	011232-000	Retrat del rei /	Arcadi Mas i Fo	Bitmap Image			reserva RE2 re		Oil (M)	Barcelona,
23	P	22	Museu Nacio	011241-000	Retrat del rei /	Fèlix Mestres	Bitmap Image			reserva RE2 re	106 x 150 cm	Oil (M)	Barcelona,
24	P	23	Museu Nacio	011222-000	Retrat de la re	Antoni Sisteré	Bitmap Image			reserva RE2 re		Oil (M)	Reus, 1854
25	P	24	Museu Nacio	011234-000	Retrat d'Alfon:	Francesc Torre	Bitmap Image			reserva RE2 re	141 x 111,5 cm	Oil (M)	Barcelona,

Figure 9. The table of Paintings, with all the information. This is the table with all the fields for each painting. There are so many fields that they do not fit on a screen.



Nombre del campo	Tipo de datos	Descripción
Object Code P	Número	
Object Type	Texto	
Object Type to Print	Texto	
Objct Type Broader	Texto	
Lined painting?	Texto	
Object Id Marta	Texto	
Institution/Donor	Texto	
Institution Broader	Texto	
Reg Num Inst	Texto	
Title	Texto	
Author	Texto	
Image	Objeto OLE	
Image- Reverse	Objeto OLE	

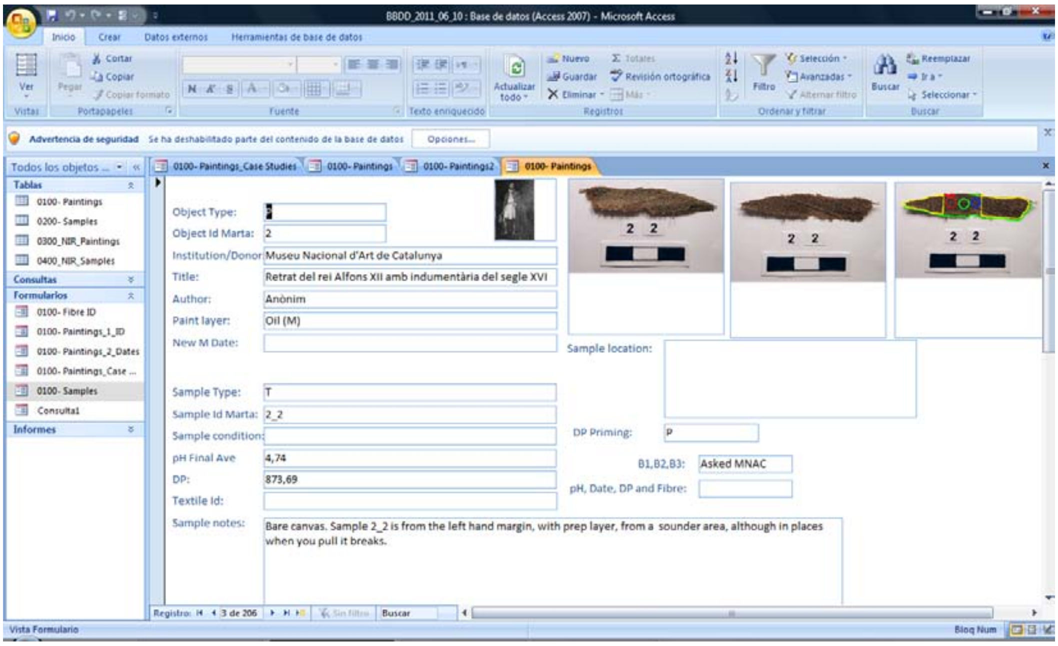
Tamaño del campo	Doble
Formato	Número general
Lugares decimales	Automático
Máscara de entrada	
Título	
Valor predeterminado	
Regla de validación	
Texto de validación	
Requerido	No
Indexado	Sí (Sin duplicados)
Etiquetas inteligentes	
Alineación del texto	General

Un nombre de campo puede tener hasta 64 caracteres de longitud, incluyendo espacios. Presione F1 para obtener ayuda acerca de los nombres de campo.

Figure 10. The “design mode view” of the same previous “Paintings” table.

In *Access*, each table needs to have one “key” field with a content that is specific for each register. This field is usually filled with numbers. If images are to be inserted, the specific image field type needs to be chosen (“Objeto OLE” in the Spanish *Access*). Numeric fields will only allow numbers in them. With numbers, one has to be careful when working with decimals and importing information from an *Excel* document. In Spain, the comma is used for the decimals, whereas in English one uses the point. This can create a conflict or import the wrong data if one of the programs is English and the other Spanish.

The key, the type of relationship between the tables and the type of each field are the first things to decide when designing the database.



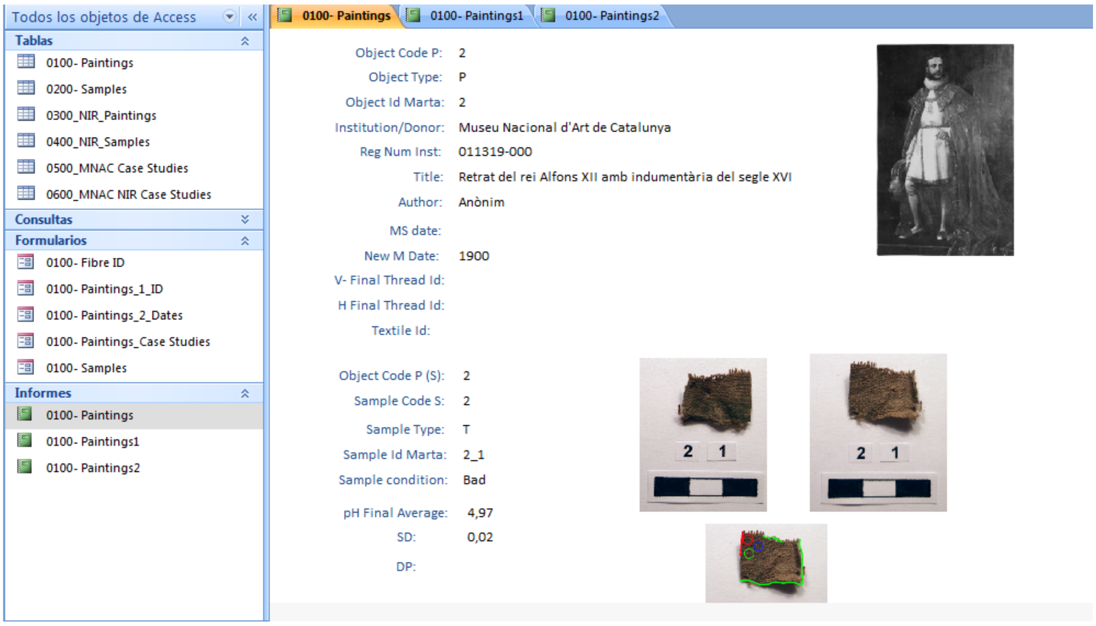
Object Type:
Object Id Marta: 2
Institution/Donor: Museu Nacional d'Art de Catalunya
Title: Retrat del rei Alfons XII amb indumentària del segle XVI
Author: Anònim
Paint layer: Oil (M)
New M Date:
Sample location:
Sample Type: T
Sample Id Marta: 2_2
Sample condition:
DP Priming: P
pH Final Ave: 4,74
B1,B2,B3: Asked MNAC
DP: 873,69
pH, Date, DP and Fibre:
Textile Id:
Sample notes: Bare canvas. Sample 2_2 is from the left hand margin, with prep layer, from a sounder area, although in places when you pull it breaks.

Figure 11. Specific form to view certain fields of a sample. This makes data introduction and visualization of information much more user-friendly.

Having the possibility of adding pictures in *Access* is very useful, since it is very much easier to relate certain information to a specific painting or sample by visually seeing which painting or sample the information is from. In *Access 2007*, so that images can be seen in the forms, they need to be first converted into the “.bmp” format.

Queries can also be created to search the content of a specific field and to get the relevant registers that agree with the search. This can be useful to answer all sorts of questions such as which paintings are lined, which samples are in a “bad” condition etc. One has to have thought, though, which type of queries one will want to make. To be able to get a list with the paintings that have “stamps”, we need a field that has been filled with the information of whether or not the painting has stamps. The good news about this is that even when the database has been created and it already has information, new fields can be added.

Finally, reports to be printed can also be extracted. However, with *Access 2007*, when a Word document is created, there is no way so that the images are also included. May be more useful than Word reports are *Excel* spreadsheets with all or part of the data that can also be exported too and then analysed properly.



Object Code P: 2
Object Type: P
Object Id Marta: 2
Institution/Donor: Museu Nacional d'Art de Catalunya
Reg Num Inst: 011319-000
Title: Retrat del rei Alfons XII amb indumentària del segle XVI
Author: Anònim
MS date:
New M Date: 1900
V- Final Thread Id:
H Final Thread Id:
Textile Id:

Object Code P (S): 2
Sample Code S: 2
Sample Type: T
Sample Id Marta: 2_1
Sample condition: Bad
pH Final Average: 4,97
SD: 0,02
DP:

Figure 12. Example of a report with both information on the painting and its samples.

Once all the information available on paintings and samples was organized in the *Access* Database, three physical parameters where determined: fibre type, pH and DP. The results of all these analysis were added to the database.

To know more about the specific samples used in this project, its particular analysed results, as well as the basic information on the paintings they come from, the reader is referred to Annex I (Reference Sample Collection Catalogue).

2.1- Fibre type

This Sub-chapter of Chapter 2 explains how the fibre types of the Reference Sample Collection were analysed, the type of fibres encountered, and the relationship between the fibre type and the date of the paintings.

2.1.1 - Introduction

Conservators are currently used to routinely checking the fibre type of the paintings they treat. Some of the textiles, are easy to properly identify visually, such as jute. However, it is good practice to check anyway under the microscope since degradation can make textiles look very different from their original state. One of the analysed samples for instance, sample **29_L**, was visually thought to be 100% jute (Figure 1), only to discover through microscope analysis that one of the threads was cotton. Because of the large amount of glue paste lining and the dark colour of both threads, this textile would have been misidentified if fibres had not been looked under the microscope. On top of these potential visual misidentifications of “easy-to-spot textiles”, such as jute, mixtures of other fibres are not easily spotted by the naked eye and so all samples are always better checked under the microscope.

Figure 1. Mixed sample: the threads running vertically are jute, the ones running horizontally are cotton.

The most important thing for conservators to know regarding fibre identification when it comes to the conservation treatment to choose, is whether a canvas is cotton or not. Cotton textiles shrink more than bast fibre ones when they come in contact with water because cotton is more hygroscopic (1 p. 92) and this is why aqueous treatments on cotton paintings, such as glue paste linings, have to be done with extra caution (2 p. 21). Paintings on cotton textiles also tend to shrink much more than linen ones because cotton can be more tightly spun and woven, and this is one of the characteristics of the so-called “shrinker” paintings (3 p. 114).

However, knowing the precise type of fibre used in the canvas is important for precise documentation and for gaining a better understanding of the historical uses of the different sorts of fibres. It has been traditionally thought that linen has been the most often used type of textile for paintings in the past, but doubts about the certainty of this argument arise when articles stating the importance of hemp fibres in paintings in certain periods are published (4). It is then understood that not that much is yet known about the type of fibres that have traditionally been used (probably aggravated by the fact that linen and hemp look very much alike under the microscope).

Fibre identification is an analysis that requires the removal of a physical sample and thus it would be very interesting if an NIR spectrometric method could be developed that could tell the type of fibre without the need to remove a physical sample.

Burn tests are usually able to offer a very good first distinction between cellulosic fibres (cotton, linen, hemp, jute etc.), proteinaceous ones (silk, wool etc.) or synthetic ones. When burnt, cellulosic fibres smell like burnt paper; proteinaceous ones smell like burnt hair and synthetic ones will smell like burnt plastic (5 p. 50). However, quite a bit of sample is needed and the sample is consumed in the analysis (6 p. 1). Since most of our samples are suspected to be cellulosic in nature (maybe with the addition of some synthetics mixed in some modern paintings), this test was seen not to be that helpful in our specific case and therefore it was not performed.

Another physical test that can be done to distinguish between some of the bast fibres is the “twist test”. This test is done by picking one fibre if possible with some fine tweezers and bending it and wetting it. Then, the fibre is placed over a hot plate while holding it, with the “bent” part of the fibre facing towards the viewer. On drying, due to the different disposition of the microfibrils on the cell walls, the fibre turns towards one side or the other (7 p. 13). Linen, ramie and nettle fibres twist clockwise whereas hemp, jute, sisal and many others turn counterclockwise (8 p. 124). With old degraded samples as is our case, though, this test can be misleading (9 p. 206). We actually did a small test to see if it could be helpful in our case and we tested it on three known new linen samples (**122**, **126** and **130**) and three known new hemp samples (**133**, **140** and **142**). The test worked in all these cases and the fibres twisted according to the expected (clockwise for linen, counterclockwise for hemp). It was then tested on an old household sample (**129**) that had been visually identified as ramie when checking under the microscope, but the two times the test was performed, the fibre twisted counterclockwise, which would indicate that the sample is neither linen, nor ramie. On top of the difficulty of getting reliable results from old more degraded samples, the test should be performed on a number of fibres for each textile in order to detect, for instance, mixtures between linen and hemp and therefore it was not done for the rest of the samples.

An interesting test to be done with a polarizing microscope and the “red plate” was found in the literature. This was to distinguish between flax and hemp (10 p. 36), based also on the different angle disposition of the fibrils of the inner secondary wall(9 p. 205). Even if no success was achieved with it, the basics of the method are described here in case success can be achieved later on in future attempts or by somebody else. However, the lack of general use in practice of this test, seems to point to the fact that it is either too complicated (9 p. 206) or that it does not work at all, although a reference from 2003 says it is a reliable and fast test (11 p. 63). From what is understood from the mentioned article (10), the sample is placed under the microscope, the analyser and the polarizer are crossed (crossed polars = black field) and a fibre that is found to “nearly extinguish” (that is to almost disappear because it turns black) when in the vertical position is selected. Then the “red plate” is put in. If the sample is flax, the selected fibre will be seen as yellow (the sample is at a right angle with the polarizer at this point), and when the stage is rotated until the sample is parallel to the polarizer, the sample will turn blue. If the sample was hemp, it would be blue when at a right angle with the polarizer and yellow when parallel (so the key fact is that they exhibit the opposite behaviour). If we don’t know which is the direction of the analyser and the polarizer (as was our case since they were not marked), then we need to find this out every time we start working, with a known sample. Although once deciphered how the method should work it seemed easy to do, contradictory results were obtained when testing “known” linen and hemp samples, as though the textiles were mixtures of the two. Therefore, this promising test was aborted too after quite some trials.

Staining tests are often used for paper fibre identification, since these can also point towards the treatment the pulp has undergone (12). However, when it comes to fibre identification applied to easel paintings, the most useful staining test would be one that helps distinguishing between linen and hemp. One such test is the one done by applying a drop of cuprammonium hydroxide solution (Schweitzer’s reagent) and observing the swelling of the fibre. Apparently linen fibres swell rapidly leaving only a fine twisted thread behind, whereas hemp fibres swell more slowly and contract in the process (13 p. 34). However, in both cases the reactions happen quite quickly and experience is needed to identify which of the two processes is going on (14). For this reason, together with the fact that the test is destructive, it was not applied to our samples.

The best way of properly identifying fibres is by looking at the morphological characteristics of the fibres under the microscope, although this technique also has its difficulties, such as differentiation between bast fibres, which is not easy even for the expert (13 p. 33). On top of its intrinsic difficulty, one has to add the fact that cultural heritage samples tend to be degraded and this can make identification even more difficult (15 p. 269) (Figure 2).

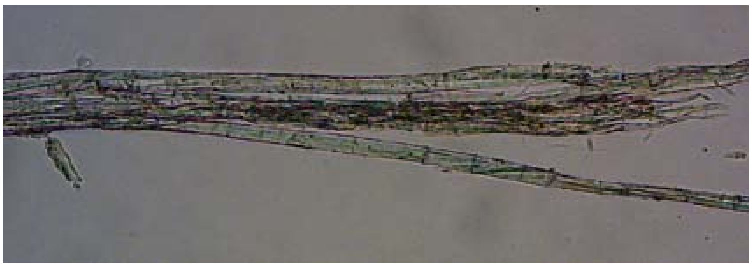


Figure 2. Fibres from sample 7_v. The textile is so degraded that identification on the basis of morphological features is difficult. Original magnification was 200x (All the images in this chapter were taken with a DinoEye® AM423X, a very handy new small camera that fits into the microscope in the place of the original eyepieces. Original magnification was thus 10x from the objective and 20x from the camera).

The optical microscope can be used to both look at the fibres along its length, as well as transversal sections of them. Sample preparation to observe cross-sections is much more complicated since the fibres have to be embedded in a medium and then transversally cut very thinly so that light can pass through (16). If well prepared, cross-section analysis to distinguish between linen and hemp can prove to be very helpful (13 p. 34). However, it is very difficult not to get the fibres shape distorted when cutting them and this might skew identification, since it is precisely this shape that is characteristic (17).

2.1.1.2 - Morphological characteristics of plant fibres

When looking at fibres under a microscope, there are different morphological characteristics that can help in identification of the fibre type. Fibres often have a central canal called lumen, which is sometimes visible. The width of the lumen with respect to the cell walls and the shape of it (regular or irregular) can be observed. Therefore, both the lumen and the cell walls can be helpful when looking at fibres longitudinally, especially when looking at the transversal section of fibres (13 p. 4). The nodes, dislocations and cross markings along the fibres are another important feature to pay attention to. Their presence or absence as well as their shape (like a V, X or I) can be very indicative of the fibre type (18 p. 1). Finally the shape of the fibre cell ends is often also explained in manuals, although they are not always present in the mounted samples (since fibres have been often cut from the thread) and even if we had some, this feature is not that useful since the same species can have a wide variety of tip shapes (18 p. 2).

Cotton and jute are relatively easy to identify. When it comes to distinguishing between linen and hemp, though, much more experience is needed (13 p. 34), especially since contradictory information can be found in the literature. It also has to be taken into account that not all the fibres will contain all the characteristic features and this might make it difficult to be certain about whether there is a mixture of similar fibres or just a single type.

Cotton

Luckily, cotton is one of the easiest fibres to distinguish under the microscope. It has very characteristic convolutions which results in ribbon-like fibres (19 p. 1). In cross-sections the lumen is large (typically more than half the full width of the fibre) and flat (on drying the cell walls collapse flattening the lumen). This collapse of the cell walls is what makes the fibre look like a flat ribbon (6 p. 3). Cotton does not have cross markings and this is another of its characteristic features. A polarizing microscope with a dark field makes these fibres even more easy to spot (Figure 3). One has to remember, though, that "mercerized cotton" has less convolutions due to the process of "mercerization" that improves the thread and textile lustre, dye affinity and strength by making the fibre swell and become more cylindrical in shape. This process was discovered in the 1850s, but this type of textiles have not been usually used for paintings (6 p. 3).

Figure 3. Sample 95_v, cotton observed with a dark field, convolutions are more easily seen. Original magnification was 100x.

Linen

Linen has very characteristic and marked cross-markings in the V, X or I shape along the fibre (Figure 4). The width of the fibre is irregular and the interior lumen is quite narrow, typically less than half the full width of the fibre (6 p. 3), the walls of the fibre being quite thick (9 p. 205). In transverse sections, the fibre cells are pentagonal or hexagonal (18 p. 16), with straighter edges than hemp, though (13 p. 36).

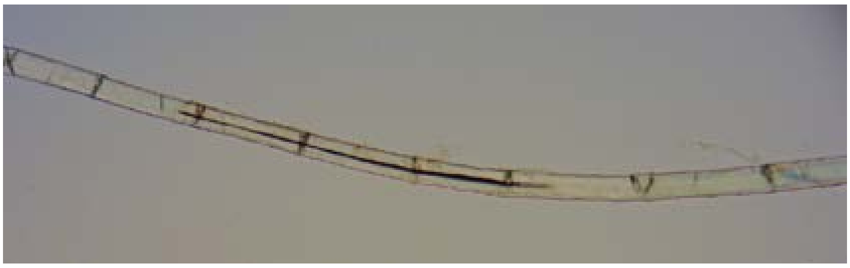


Figure 4. Sample 13_v, linen. A thin lumen, “thread-like”, and sharp V and I cross-marks can be seen. Original magnification was 200x.

Linen and hemp look very much alike when observing them under the microscope. One of the main differences between them is the width of the lumen, which in general is much narrower in linen than in hemp. Linen has a thread-like lumen and since the thickness of the walls is not regular, the lumen is seen to go from one side to the other. The other main difference between linen and hemp are the V or X cross-marks, which tend to be thinner and sharper in linen (17).

Hemp

Hemp also presents frequent dislocations and cross-markings in the X, V and I shape along the fibre. There is a wide range of wall thicknesses and lumen widths, but often, the lumen is quite wide, reaching one third or one half of the fibre width. The thickness of the walls is usually regular and therefore the lumen is quite parallel to the exterior of the fibre (18 p. 22). The cross-section of fibres has a polygonal shape similar to that of linen, but a bit more rounded in the case of hemp (13 p. 36).

Comparing hemp with linen, hemp's lumen tends to be much wider than that of linen and this can help in its identification. Regarding cross-marks, although as said, hemp has angled cross-marks in the V an X shape like linen, these tend to be more perpendicular to the fibre in hemp. Also, there seems to be less cross-marks in hemp and these tend to be "thicker" or "buckled", as if the fibre had been compressed. As a result, hemp fibres look a bit like bamboo (9 p. 205).

Hemp fibres tend to be broader than linen fibres, although this also depends on the maturity of the plant, the part of the plant where the fibre comes from and the conditions where the plant grew. In a study of 1000 fibres of hemp and linen, it can be seen that indeed hemp fibres in general tend to be wider, but that there is also a lot of overlap (9 p. 206).

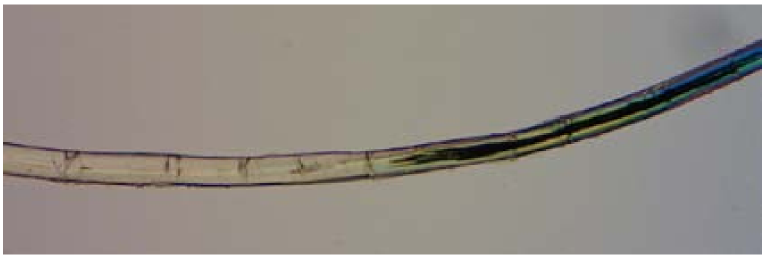


Figure 5. Hemp fibre from sample 24_v. The lumen is the same width as the fibre walls. Cross-marks tend to be more vertical. Original magnification was 200x.

Ramie

One of the features of ramie is that its lumen can go from being quite broad to being thinner. The inner walls are not so well defined and they are not linear but rough. Therefore, the width of the lumen is irregular, as well as the width of the fibre which is also irregular. Also, there can be debris or "dirt" inside the lumen (17).

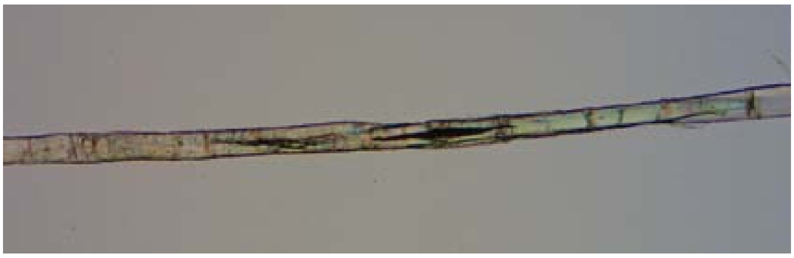


Figure 6. Ramie fibre from sample 18_v. The lumen varies in width along the fibre. Original magnification was 200x.

Jute

Although in this work we have at times separated fibres into: "cotton, jute or bast" (see Method development for fibre type identification in Chapter 3), it has to be remembered that jute is also a bast fibre. When this separation has been done in this PhD thesis, it was just for analysis purposes since jute is very different from the other bast fibres treated here (linen, hemp and ramie) and it was much more easily identified.

Jute fibres are often difficult to separate. Its main characteristic is its lumen, which can be seen to be "broken" or as though there were bubbles inside the fibre. These dislocations are not as common as in other bast fibres (18 p. 40). Luckily too, jute textiles and threads are often visually pre-identified because of its characteristic brown colour and thick threads. When teasing the fibre apart for microscope preparation, this fibre often is felt as very hard and brittle and bits and pieces separate easily.

Figure 7. Jute fibres from sample 68_v. Fibres are all stuck together and the broken lumen can be clearly seen. Original magnification was 200x.

Synthetics

Synthetic fibres are easily spotted under the polarized microscope because, unlike natural fibres, they are very homogeneous and that makes them present a very uniform fibre without the different polarizing colours typical of natural fibres. They do not have a lumen, have straight edges due to the cutting of the filament, and have a uniform diameter. Their surface is also very homogeneous, with colouring substances often being seen as dots(Figure 8) (7 p. 7). Depending on their composition, they appear dark under crossed polars, or glow with light. It is not possible, however, to identify synthetics just by examination under the optical microscope and it was not within the scope of this thesis to determine the specific type of the few synthetic fibres encountered. Synthetic fibres mostly found in the canvas of paintings are cellulose acetate and polyester fibres (7 p. 6).

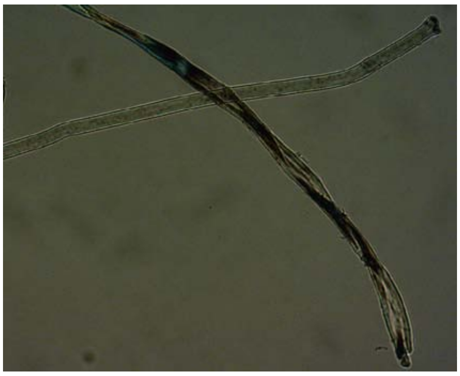


Figure 8. Mixture of cotton and synthetics from sample 67_v. The horizontal synthetic fibre can be seen to be from a very homogeneous material and with a dotted surface (maybe the pigments added to give colour). Original magnification was 200x.

2.1.2 - Materials and methods

Fibre type analysis is very time consuming. Since it was foreseen that there would not be enough time to prepare and analyse all the samples available, those with DP measured were prioritised (pH was available for all the Reference Sample Collection) (see Chapters 2.2 and 2.3). For this project, there were a total of 93 textiles identified, with two threads for each textile, one running horizontal to the painting, one running vertically. In the end a total of 186 threads were separately mounted, photographed and identified, to be able to give a final textile identification. This activity took about 2 months of one person full time work.

During the sampling campaign in October 2009, one thread running in each of the two directions from each painting had been collected. These threads came from a different area than the textile samples collected from the same paintings but since the fibre type is the same for all the painting, this was not a problem.

Samples were labelled with the number of the painting it came from and a “v” for vertical thread and “h” for horizontal thread according to the sense of the painting (i.e. “93_v” and “93_h”).

Several cleaning procedures with chemical solutions have been reported in the literature that can be applied to fibres before mounting them (20 p. 213). Cleaning would seem a very advisable step to be done one cultural heritage specimens from paintings since they might often be full of dirt, glue and other materials. However, the cleaning procedures proposed could be too harsh and damaging for already degraded cultural heritage samples (21 p. 56). On top of that, the sample would need to be completely dry so that a permanent mounting medium could be applied since the medium used was non-aqueous, and this could increase the chances of contamination of the samples since more than one sample would probably be hadled at the same time to use time more efficiently. Having also so many samples to be prepared, a more straightforward procedure was preferred which was preparation without previous cleaning.

Figure 9. Unclean sample 10_v. Some of the samples had a lot of dirt and glue that covered the fibres making visual identification difficult. In such extreme cases, fibres were prepared again by previously washing the samples with distilled water. Original magnification was 200x.

Not cleaning the samples worked fine for the majority of them. In a few cases, however, where too much glue was present and identification was impossible because of this (Figure 9), the sample was prepared again by washing the thread in hot water, teasing it apart and soaking up the excess of water with a tissue paper. A drop of alcohol was added to speed up the drying time. Placing the glass slide on a hot surface also sped up the drying process.

The fibres were prepared by taking a thread and teasing its end on a microscope slide with a long needle. It is better to have fewer fibres on the microscope than too many, otherwise it is difficult to see the single fibres when looking at the sample under the microscope (22 p. 7). There are several different adhesives that one can use to make a permanent slide, in our case “Entellan® new” from Merck was the one used. This resin has, at 20ºC, a refractive index of between 1.490 and 1.500. Its composition is reported to be “polymer of mixed acrylates in 60% (w/w) xylene” (23). When a few of the fibres are on the microscope slide, two drops of the resin are dropped on them. Again, the quantity of adhesive needs to be right: if there is too little the ends of the cover slip might be without support and will easily break away, if there is too much there will be a surplus of the adhesive all around the cover slip that will later on easily stick to other things, even if dry, through prolonged contact.

After placing the resin, one puts the glass cover slip standing on one of its sides and gently lets it fall on the sample with a long needle (22 p. 7). This way, air bubbles in the sample are avoided (Figure 10). Once it is lying flat on the microscope slide, the handle of the long needle can be used to press the cover slip and to thin down the resin layer. The thinner the resin layer is, the easier it will be to focus and take pictures of the different fibres observed, since they will all be within a similar focussing distance. Any air bubbles present in the sample can also be pushed towards the edges while the resin is yet not dry with a pressing tool (handle of a long needle).

Initially, the vertical and horizontal sample for each thread were mounted on the same microscope slide. This was thought to be a good idea in order to reduce the weight and amount of the prepared glass slides, and to increase its portability (initially the aim was to prepare about 400 samples). However, it was soon discovered, that with some microscopes, such as the Olympus PX-51, which is the one in use at the Conservation Section of the Faculty of Fine Arts, the prepared sample needs to be in the centre of the microscope slide, otherwise one cannot observe it! Therefore, samples were prepared one per slide from then on.

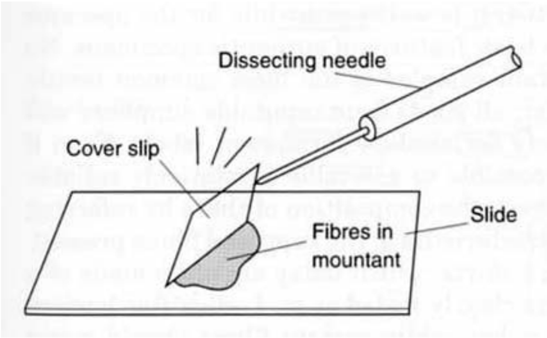


Figure 10. Lowering of the cover slip to complete the slide. From: GREAVES, P.H.; SAVILLE, B.P. *Microscopy of textile fibres.* Oxford: BIOS Scientific in association with the Royal Microscopical Society, 1995, pp.7.

Fibre sample preparation has to be done in a clean environment paying lots of attention not to get the samples contaminated. When preparing so many samples it is advised to get a good working routine, working with one sample at a time, writing the sample number on the slide with a permanent pen as soon as we start with a new one. It was found very useful to place the microscope slide on a large black piece of cardboard that made it easier to see the fibres. Since the resin used is dissolved in xylene, it is better to prepare the samples using a breathing mask, since working in a fume hood could blow our samples around. Slides were left to completely dry for some days before observation.

Samples were examined under a Leica polarising light microscope. This type of microscope was found to be very useful because polarised light makes natural fibres much more evident and clear due to their anisotropic nature. By rotating the stage, the dark or light background field which best suits a particular fibre can be chosen. Synthetic fibres are also more easily seen, since they are very homogeneous and they tend to show just one single homogeneous colour.

Looking at fibres under the microscope is a very tiring activity and thus it is advised not to do too many per day. If the number of samples to identify is large, such as was the case in this research, it is better to look only a few each day and combine this task with other activities, otherwise one risks to end up not seeing the proper features any more.

All samples were prepared and identified, comparing them to known reference specimens available from McCrone Microscopes and Accessories. Many pictures for each sample were taken so that identifications could be rechecked. This was done with a Dino-lite® AM423X eye-piece camera, which can be fit inside most microscopes eye-piece, and which is connected to the laptop through a USB port. Then, confirmation of the identification was given for all samples by the expert Dr. Paul Garside (The British Library), so that misidentifications could be corrected. It has to be said that most of the identifications done in the first instance were found to be satisfactory and that even the expert was not able to identify with a 100% certainty a few of the samples because the exhibited features were not clear. This fact reassured us in the sense that fibre identification of cultural heritage samples by morphological means is not easy.

Before starting fibre identification, we had thought about the fibre types that we expected to encounter such as linen, hemp, cotton, jute, cotton with synthetics, and textiles where one thread could be one material and the other a different one. However, while doing the analysis, it was found that new "categories" had to be added such as: "mostly linen, a few hemp"; "mostly hemp, a few linen" etc. As could be seen, more often than assumed, threads were mixtures of different fibres, especially between linen and hemp. It is difficult to know whether these mixtures were intentionally produced as such or whether they are just contamination due to thread producers working with different types of materials in the same place. Also, the fact that not all the fibres will show all the characteristic features of, e.g. linen or hemp, cast a shadow on these mixed identifications, since one wonders whether all the fibres might be hemp (although only a few are clearly identified as such) or are there more hemp fibres than just "a few" and the sample is a half and half mixture…

Finally, the textile identification types were defined as:

Fibre type category	**Meaning**
Linen	The two threads were identified as linen
Linen & Hemp	One of the threads was identified as linen, the other one as hemp
Linen?	The two threads were identified as linen, but it is not 100% certain.
Mostly linen, with a few hemp	Both threads were identified as "mostly linen, with a few hemp", or one of them as linen and the other one "linen with hemp".
Linen & Cotton	One of the threads was identified as linen, the other one as cotton
Hemp	The two threads were identified as hemp
Ramie	The two threads were identified as ramie
Ramie?	The two threads were identified as ramie, but it is not 100% sure.
Jute	The two threads were identified as jute
Jute & Cotton	One of the threads was identified as jute, the other one as cotton
Jute & Linen	One of the threads was identified as jute, the other one as cotton
Cotton	The two threads were identified as cotton
Mostly cotton, with a few other natural fibre	Both threads were identified with cotton, with a few other natural fibre
Mostly cotton (with a few synthetics)	The two threads were identified as mainly cotton, with a few synthetic fibres
Cotton with synthetics	The two threads were identified as cotton with synthetics, half and half.

For subsequent analysis of the fibre types found and for "Discriminant Analysis" done in Chapters 3 and 5, these categories were sometimes merged into new broader ones.

2.1.3 - Results and discussion

2.1.3.1- Fibre type of the paintings studied

Of the 93 samples of which fibre type was analysed, 84 of them were real historic paintings. The other 9 samples were newer textiles that had been added to increase the number of hemp and ramie specimens so that chemometric models could be developed for these types of fibres too (see later on Chapters 3 and 5). Here we will only take into account the 84 samples from paintings, in order to see what they tell us about our Reference Sample Collection.

Fibre category	Samples	Number of samples	%
Linen	1; 4; 8; 9; 10; 11; 13; 19; 24; 27; 32; 35; 36; 37; 44; 46; 47; 49; 65; 85; 89; 91; 93; 96; 104; 105; 106; 109; 110; 112; 115; 116; 117; 141; 107_1; 73_L	36	43%
Linen?	5; 30; 54; 120; 100_1; 73_O	6	7%
Mostly linen (with a few hemp)	77; 103; 113; 114	4	5%
Linen & Hemp	3; 28; 94	3	4%
Linen & Cotton	41; 145	2	2%
Hemp	7	1	1%
Ramie	18	1	1%
Ramie?	15; 22	2	2%
Jute	21; 48; 60; 38_L	4	5%
Jute & Cotton	68; 29_L	2	2%
Jute & Linen	51	1	1%
Cotton	43; 45; 52; 53; 55; 56; 57;58; 59; 61; 63; 76; 79; 90; 92; 95; 111; 118; 107_2	19	23%
Mostly cotton (with a few synthetics)	67	1	1%
Mostly cotton (with a few other natural fibre)	62	1	1%
Cotton with synthetics	64	1	1%
Total		**84**	

Figure 11. Table of the different fibre type classifications used

As can be seen, the most abundant fibre type encountered is linen. About 50% are found to have 100% linen canvases, and a total of 65% of the paintings have some linen in it (either on its own or mixed with other fibres) (Figure 12).

Cotton was the second type of fibre most often found, present in about 26% of samples, mostly on its own but also found combined with synthetics in two cases (**64** and **67**). Jute (**21**, **48**, **60** and **38_L**) and jute combinations with cotton (**68** and **29_L**) and linen (**51**), only accounted for 8% of the samples. Only one painting was found to have been done on a 100% hemp textile (**7**), representing about 1% of the studied paintings. Hemp was found mixed with linen, in different proportioins, in about 8% of the cases. Ramie was only positively identified in one case (**18**), with 2 other possible but dubious ramie attributions (**15** and **22**). These three ramie paintings would represent about a 3% of the samples collection.

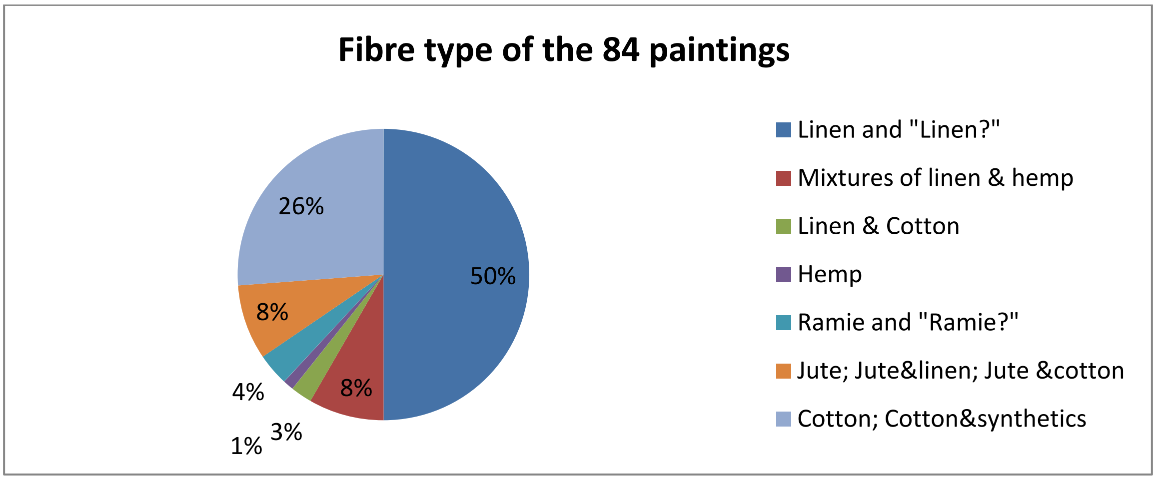


Figure 12. Fibre type of the 84 analysed paintings in percentage.

The fibre types found in the Reference Sample Collection fulfils expectations in the sense that linen is the most often found type of fibre. A high presence of cotton, was also expected given that the samples were mainly from the 19th C and 20th C, as well as a few jute paintings. Interestingly, although not in high proportion, a few textiles with combinations of two different threads were also found (linen/hemp; linen/cotton; linen/jute; jute/cotton). These “two different threads textiles” accounted for 9% of the total, maybe a higher proportion than anticipated, which certainly reinforces the idea that both threads need to be sampled when doing fibre type identification of a textile.

Hemp was found in a lower proportion than expected, although it also makes sense considering that our samples are mainly from the last two centuries and that we are missing older samples where this fibre type might be more common.

Ramie was an unexpected fibre to find, since, so far, we have not come across any documented Catalan or Spanish painting having been done on it. Of course, this does not mean that ramie has not been used, since it could just be that this type of fibre has often not been thought of as a possible fibre to have in a painting when doing fibre analysis.

Synthetic fibres were only found in two paintings and in both cases, these fibres were mixed with cotton fibres.

2.1.3.2 - Fibre type and date

Linen

Linen is found in paintings all along the available periods from the 16th C to today.

Linen and hemp, when they are present about half and half, are found in one painting from the 16th C (**94**) and in two from the end of the 19th C (**3** and **28**). (In the case of **28**, one thread is linen, the other hemp; whereas in **3** and **94** both threads contain linen and hemp half and half). When paintings were classed as “mostly linen, with a few hemp”, these were found to be either from the 18th C or from the end of the 19th C. In the 20th C, linen was found on its own in all cases, except for two (**41** and **145**) where one thread was linen, the other cotton. It is interesting to find that the mixtures of linen and hemp are found mostly in older canvases, when quality control procedures for textiles to be used in paintings might not have been so strict.

One painting from 1925 was found to have one thread from jute, the other cotton (**51**). This painting has suffered several small vertical tears, where the cotton threads running horizontally are seen to give way. (See later on in this same section under "jute" (Figure 14)).

Hemp

The only 100% hemp identified painting is from the beginning of the 20th C (**7**). As just explained, hemp is found mixed with linen in seven paintings with dates that go from 1550 to 1875. We have not found any hemp in our collection in paintings from the 20th C. This coincides with the information found in the literature in the sense that hemp was mostly used until the 19th C. However, in our samples we have found very low levels of hemp being used, and linen is much more predominant. Therefore it would seem that hemp was much less used in Spain than it has been said to have been used in France (4).

Ramie

Ramie is not a common fibre type used for paintings, or at least no specific example is known to us. The one ramie positively identified painting is from the beginning of the 20th C (**18**). The other two possible ramie paintings are also from this period (**15** and **22**). In the three cases, the paintings are commercially primed, and in the case of painting **22** the priming is not white but red. Therefore, if our identifications are correct, we have found that ramie was sometimes used commercially to prepare canvas for painting at the beginning of the 20th C. This fact coincides with the information found in the literature that the manufacture of this type of textiles spread out in Europe during this period, although its production decreased later on because it was a difficult textile to produce (1 p. 322).

Cotton

All the cotton samples found are from the 19th and 20th C. The oldest one is sample 95 from an original lining from a watercolour from the end of the 18th C / beginning of the 19th C. The earliest case of cotton being used in an easel painting is from a painting with an assigned date of "1850" (**45**), which actually means sometime in the 19th C (Figure 13). The fact that the canvas used is cotton, makes us think that this painting might be more from towards the end of the 19th C. This painting actually presents a very weak fine canvas that has torn along both vertical edges. This can probably be explained by the fact that cotton degrades faster than other fibres.

Figure 13. The oldest easel painting done on a cotton textile from our collection, *Retrat masculí*, anonymous, assigned date 1850 (19th C) (MNAC 121752). The painting is torn all along the vertical margins and this is why cotton straps are temporarily securing the canvas to the stretcher.

The first painting done on cotton, with a precise date, though, is from 1896 (**43**).

As expected, most of the cotton paintings are from the 20th C (18 of them), with only 4 paintings being from before the 1900. Of these four, three of them are from the end of the 19th C. Samples from the 20th C date mainly from the 1930s onwards, and there are a couple from the beginning of the 21st C.

Cotton and linen are found mixed in a painting from the 1945 (**41**), and in a strip lining probably from the 20th C (**145**).

Jute

All jute samples found are from the 20th C. Of these, a few are commercially prepared and are from already the turn of the 20th century. Like this, samples **51**, **68** and **21** are white primed commercially prepared canvases on a: 100% jute textile (**21**, from 1908), a mixture of one thread jute, the other cotton (**68,** from around 1925) and one thread jute, the other linen (**51**, from 1913). When a mixture of two threads was found, when teasing apart the textile it was found that clearly the jute thread was much weaker than the cotton or linen one. Painting **51** has indeed many tears running vertically and it was assumed that this was due to the fact that the jute threads that were running horizontally were giving way. However, it was checked and the cotton threads are the ones running horizontally in this case. The average pH for this sample was found to be 4.18 for the jute threads and 4.78 for the cotton ones. It is quite possible that the acidity in the cotton threads comes from the jute threads (which having a higher lignin concentration tend to have lower pH values), and since cotton degrades faster, this is why it is giving way. This **51** painting has also a commercial stamp of the company "Paul Foinet et Fils" (Toiles fines / Paul Foinet Fils/ 21, Rue BRÉA / Paris).

Figure 14. Reverse of painting 51 (*Dues figures femenines nues* by Joaquim Sunyer, 1913 (MNAC 039149)), a jute/linen canvas with many repaired tears running along the direction of the jute fibre thread.

Two modern paintings in which jute was found to have been used (**60** and **48**), were artisan-prepared. In the case of painting **48**, big tears were already present in the centre of the painting in 2009 (Figure 15). This painting is from around 1925, whereas painting number **60** is from around 1950s and is in a better condition (no tears are present).

Figure 15. Painting 48 (*Camp d'Astúries,* by Florentino Soria, ca. 1925 (MNAC 024158)), artisan preparation on jute. The painting has many tears due to the brittle jute canvas.

Jute is often also found as a lining canvas in old conservation treatments from the beginning of the 21st C when economic constraints meant very cheap materials had to be used in conservation treatments, something that fortunately has been surpassed. Sample **38_L** is a 100% jute lining and sample **29_L** is a one thread jute, the other cotton, lining. Both samples are full of glue and very brittle. From handling the samples for microscopy analysis it could be seen that jute is a more rigid textile to start with and that with ageing, it rapidly becomes even more brittle.

Synthetics

Synthetic fibres were only found in two paintings from 1998 and 2006 (**67** and **64**), so quite a lot towards the end of the 20th C beginning of the 21st. In both cases, they were mixed with cotton fibres.

2.1.4 - Conclusions

Contrary to expectations, even after analysing almost 200 different threads, the task of doing fibre type identification remains a difficult one in some instances. Some of the fibre types are easy to spot and identify without doubts (cotton and synthetics, for instance), whereas 100% certainty in the distinction of other fibres such as between linen and hemp still remains a task to be left to the experts. (In our case the expert Dr. Paul Garside from the British Library cross-checked all our identifications).

Threads and textiles were found to be composed mostly of the foreseen types of plant fibres, but a larger number of combinations of fibres than anticipated were found (linen/hemp; linen/jute; linen/cotton; jute/cotton…). Both, threads composed of more than one fibre type, and textiles composed of two different types of threads were found in many cases, even though the most typical case was to find textiles of a single 100% fibre type. Therefore, new “fibre type” categories had to be created along the way of analysis, as new cases arose.

As expected, the most common type of fibre found in our Reference Sample Collection is linen (62 % of all the samples contain some linen). And most often (in 50% of all the samples) the linen canvases found are 100% linen. In a few instances (12% of all the samples), linen can be found mixed with other fibres, often with hemp to produce mixed linen and hemp threads or with other types of threads, where one thread is linen and the other is either hemp, jute or cotton (3%). Linen is found both in older and newer paintings.

In contrast, hemp was found in a much lower proportion than expected. Only one painting was found to be 100% hemp and in a few instances it was found mixed in with linen (see above). This mixing of hemp and linen fibres was seen more in older than in newer paintings. From our results, it seems therefore, that hemp is not that present in Spanish paintings. However, it is true that the majority of our samples are from the 19th & 20th c, when hemp use seems to have already declined.

Ramie, which was for sure found in one painting, was a surprising fibre to find, since its use as a painting support is not that common. Although the literature says ramie has been used sparingly as a painting support (1 p. 95), we have not come across any specific example in the consulted references.

Cotton, as expected, is often found in more modern paintings (end of the 19th and 20th C). The presence of this type of fibre was found in 26 % of the Reference Sample Collection. The earliest cotton sample we have come across is from an original lining from a watercolour from the end of the 18th C / beginning of the 19th C, and the earliest dated painting done in cotton is from 1896.

Jute is sparingly found, also as expected, at the turn of the 20th C, and often already commercially primed. Sometimes it is found on its own (100% jute textile), sometimes one thread jute, the other linen or cotton. Later on, along the 20th C, if used by artists, they seem to have prepared it themselves. This is probably due to the fact that companies soon realised the poor quality of jute canvases and they discontinued their commercial priming and marketing (in 1948 in the case of Winsor&Newton) (24 p. 115). Jute is also found in crude old glue paste linings done in Barcelona at the beginning of the 20th C when poor economic conditions justified the use of this low quality textile for conservation treatments. The quick degradation of jute is exemplified by two not particularly old paintings in our collection that already have many tears.

Surprisingly, synthetic fibres were not that often found in newer paintings as we anticipated. Even if semi-synthetic fibres started to be produced in the mid 19th C (25 p. 55) and synthetic fibres developed a lot from the mid-20th C on (26 p. 11), the only two paintings that were encountered to contain some synthetic fibres were very new paintings that were less than 15 years old (so from the very end of the 20th C-beginning of the 21st C). In both cases, synthetic fibres were mixed in with a high proportion of cotton. It can be seen, thus, that the type of fibre to be used in artist canvases has very much adhered to the tradition of using plant fibres.

As previously mentioned, the microscopic distinction between the bast fibres linen, hemp and ramie, still remains a difficult task, even for the expert (13 p. 33). Therefore, all fibre identification analysis results regarding this type of fibres have to be taken with caution, both our own work done here as well as others', since often images of the identified samples are not published toghether with the text.

Since there is still a lot to be learnt about the fibre types used for easel painting throughout history and identification can be sometimes tricky, it would be advisable that conservators and researchers stored and documented permanent slides so that these could be shared if desired (perhaps even through the web nowadays) and knowledge in this field expanded through joint efforts.

Precisely because of the inherent difficulty of fibre type identification by visual means, a non-destructive, fast and reliable NIR spectrometric method would be very valuable. However, in our case, it can already be foreseen that precise distinction between some of the bast fibres (linen, hemp and ramie) might be difficult because we have too few examples of some of them, and because identification is not 100% certain in some of the instances to start with.

2.2- pH

The next parameter to be measured on the Reference Sample Collection was pH. In this chapter the importance of acidity (pH) is explained, as well as how it can be measured, the specific method developed and used for measuring the pH of the Reference Sample Collection. The results obtained in terms of the pH values of painting canvases and the relationship between the pH and the date and the fibre type of paintings is presented.

2.2.1- What is pH

pH is a measure of acidity or alkalinity. More precisely, it is a measure of the concentration (or, rather, activity) of hydrogen ions (H^+) present in an aqueous solution (moles per litre) and is defined by the following formula:

$$pH = -\log_{10} [H^+]$$

pH is commonly expressed with a value from 0 to 14, pH “0” meaning there are 10^0mol/L of H^+ present (that is 1 mol of H^+ per litre of the given aqueous solution) and pH “14” meaning there is a concentration of 10^{-14}mol/L of H^+ ions (that is 0.00000000000001 mol of H^+ per litre of solution).

This 0 to 14 scale is derived from the ionic product of water. Pure water has equal amounts of H^+ ions and OH^- hydroxide ions, both being present in the concentration of 10^{-7}mol/L. This corresponds to pH 7 and since pure water is neutral, therefore pH 7 is neutral (1 p. 1).

Acidic solutions have a higher concentration of H^+ (all acids have indeed two things in common: they are all solutions in water and they all contain hydrogen ions, which are relevant (2 p. 87)), and thus pH is less than 7. On the contrary, alkaline solutions have more OH^- ions, and therefore less H^+ ions, and so pH is higher than 7 (1 p. 1).

It is interesting to note that each subsequent pH value means that there are 10 times more H^+ ions, so for instance, pH 5 means there is 0.00001 mol H^+ ions per litre, whereas with pH 4 there is 0.0001 mol H^+ per litre. So, in a practical case with an object measured twice over a period of time we might find that although the difference is “only” 1 pH unit, let’s say 5 and 4, the concentration of H^+ is different by a factor of 10, and therefore its acidity considerably different.

Although the concept of pH only has meaning for aqueous solutions we often find pH values for solid materials such as paper, wood or canvas. This is so because these materials contain adsorbed water and therefore H^+ are partly present in solution. More importantly these materials contain water-soluble substances that can be diluted in an aqueous solution, of which pH can be measured (3 p. 4);(1 p. 1). For this to be made possible however, either some water has to be applied to the object and pH measured with a flat-surface pH probe, or a sample needs to be extracted and put in water to subsequently determine its pH.

2.2.1.1 - Why is acidity important to know

Acidity is an important factor to determine for cellulosic materials since it leads directly to a reduction of the degree of polymerisation and as a consequence, to a decrease of some of the mechanical properties of the material, such as tensile strength (4 p. 31).

The future stability of cellulosic material (such as paper and textiles) is largely determined by pH, since acid-catalysed hydrolysis in known to be promoted in an acidic environment, whereas the slower oxidation processes are dominant if the environment is alkaline (5 p. 159).

Indeed, it has long been known that cellulose degradation rate constant increases with decreasing pH, whereas in moderately alkaline conditions, the degradation rate is lower. In fact by shifting the pH from 4 to 8, the degradation rate of pure cellulose can be decreased by a factor of 3 (6 p. 409). This is why introducing moderately alkaline substances to paper such as $CaCO_3$ and $MgCO_3$ has been long studied and done in paper studies (7), because cellulose fibres are more stable in a slightly alkaline environment (pH 7-8.5) (8 p. 38).

For all this, pH determination is the most important analytical procedure used in the conservation of paper and the one performed more often and more widely (9 p. 33). Since the canvas of paintings is also of a cellulosic nature, it goes without saying that pH will also be a determining factor to control if canvas degradation is to be monitored (4). In fact, given the attention that the measurement and control of acidity has received in the paper conservation field, it is actually quite surprising that painting conservators have not taken this parameter much into consideration until recently.

2.2.1.2 – How to measure pH

There are different ways to measure pH, all of which include the extraction of the acidic compounds in water, and there are also different measuring devices available on the market (1). The two methods most often used in heritage research have been the “surface pH”, or the “extraction” techniques, either with hot or cold water (10).

Surface pH

The surface pH technique basically consists of applying a certain amount of water on a horizontal area of the object and placing a flat-surface pH probe against it to measure the pH of the water extract (1).

There are different standards produced by international bodies such as TAPPI (Technical Association of the Pulp and Paper Industry), ASTM (American Society for Testing Materials) and ISO (International Organization for Standardization) that can be followed regarding technical analytical processes. In Spain, the organism AENOR used to be the one in charge of adapting the International (ISO) and European norms (CEN) into Spanish Norms (UNE). Currently, though, any CEN standard is automatically a Spanish standard.

For surface pH measurement of paper the technical norm “T 529 om-09: Surface pH measurement of paper, 2009” can be followed. Tse, in her very didactic book (1), describes the method to be specifically used on cultural objects. For paper, a Mylar polyester film should be placed under the object, a 50 to 100 µL drop of distilled water should be added and left for 2 to 10 min so that soluble substances are extracted. If the paper is very absorbent, this can be reduced to 30 s. Then the flat-surface probe is placed on the surface, trying to avoid direct contact with the object (see Figure 1) (1 p. 9).

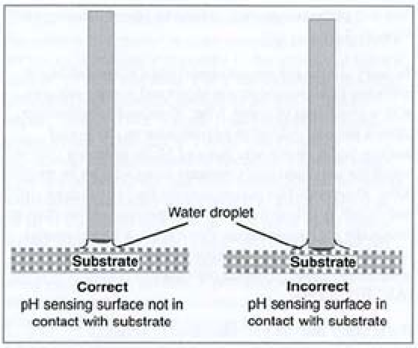


Figure 1.The proper way to place a flat-surface pH probe during measurement. From TSE, S. *Guidelines for pH measurement in conservation.*Ottawa; Ontario; Canada: Canadian Conservation Institute. Department of Canadian Heritage, 2007, pp. 9.

Studies done with paper samples comparing different ways of measuring pH (10 pp. 629-630), have shown though that pH determined this way can vary greatly depending on the amount of water added and the wettability of the object. Therefore, it is concluded that surface pH can give acceptable results as long as it is measured in controlled conditions (using the same sample size and amount of water: a volume of 40 µL of water is recommended). They found that compared to extraction techniques, pH values obtained with the surface electrode are always lower than the values obtained using cold extraction (due to the fact that little dilution occurs in the former) and the uncertainty of surface pH is also higher. These findings were corroborated in another study by Strlič et al. (11).

Since the time to obtain a stable reading depends on the wettability of the surface, this will also vary from object to object (10 p. 630). This might make reproducibility of the measurements difficult to achieve, since in the case of canvas, significant differences in wettability can be found and some canvases will soak water immediately whereas others will even repel it. Also, placing the probe at the right distance, not directly touching the object and with a layer of the water solution to be analysed in between, can be difficult to achieve if the object is highly absorbent (which is often the case of very degraded canvases).

All this makes this way of pH measurement not so attractive for painting canvases, although one would have thought so initially because of the apparent non-destructivity of the approach. On top of it, tidelines are inevitably left when applying a drop of water to a dirty canvas. It has been demonstrated that, in paper, degradation proceeds faster along the tideline, because degrading products have been brought there by the migrating water and are present in a higher concentration in the tideline (12). With paintings, another major concern when applying a drop of water on the reverse of a painting is the effect this might have on the paint layer due to the possible sudden localized shrinkage of the wetted area or to excessive moistening of the ground layer.

Due to all these drawbacks, other extraction techniques are preferred (10 p. 630).

Cold extraction pH

Extraction techniques for measuring pH consist of taking a measured amount of sample and placing it for a certain time in a specific volume of distilled water. This way, the acidic products solubilize and the pH of the solution is measured afterwards. These extraction techniques can either be carried out by using hot or cold water, the cold method being more common in heritage research.

Since pH has long been measured in the paper industry, there are several norms that one could follow. Regarding the cold extraction technique there is a TAPPI norm (T 509 om-06: *Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method)*, 2006) and an ISO norm (ISO 6588-1:2005: *Paper, board and pulps. Determination of pH of aqueous extracts. Part 1: Cold extraction*, 2005. There used to be an

ASTM norm (ASTM D 778-97 (2007): *Standard Test Methods for Hydrogen Ion Concentration (pH) of Paper Extracts (Hot-Extraction and Cold-Extraction Procedures)*, 2007) that was withdrawn in 2010 by ASTM because there was already an equivalent, the mentioned TAPPI T 509 om-06 (13). One of the differences between the ASTM (and therefore the TAPPI) and the ISO nom is that the former requires flushing the cold extract with nitrogen until pH is measured whereas the ISO norm does not (10 p. 631).

In the case of textiles, there is a standard from the Canadian General Standards Board (CAN/CGSB) 4.2 No. 74-M91/ISO 3071:1980, *Textiles- Determination of pH of the aqueous extract*, or its equivalent. ISO 3071:2005: *Textiles. Determination of pH of aqueous extract, 2005* (which updates ISO 3071:1980). (For a complete list of all pH standards available for different types of materials (leather, adhesive, textile and paper) see (1 p. 12).)

Standards for the industry call for a large amount of sample (2 g of sample per 100 mL of water in the case of ISO 6588 (1981), and 1 g per 50 mL in the case of ISO3071:1980) (10 p. 628)(1 p. 12)), since in their case physical sampling is not a problem. However, this amount cannot be extracted from cultural objects, and this is why studies of possible miniaturization in terms of sample size have been done (10);(11).

2.2.1.3- pH studies in paper research

Paper was initially produced from linen and hemp rags, which produced high quality strong long-fibred sheets of paper. In the 19th C paper started to be produced from wood, which has a high lignin content. With time, the lignin present in paper turns acidic and this deteriorates the cellulose fibres (14 p. 1). Wood-derived paper, thus, often degraded quickly turning yellow and brittle.

On top of the type of fibres used to produce papers, before ca.1850 they were sized in the traditional manner (often using starch or animal glue (15)), which produced papers with approximately neutral pH. However, papers from 1850 to 1990 frequently have pH less than 6 due to the use of alum-rosin size. (From 1990 on, paper production changed its sizing to an alkaline one due to environmental reasons, and thus contemporary papers are again more stable) (16 p. 6321).

The acidity of paper from 1850 to 1990 contributes to a decreased lifetime expectancy of this paper from several thousand years to only several hundred years. It has been estimated that 70-80% of Western library collections are degrading rapidly due to the low pH of its paper (5).

From early on, the fast degradation of this “modern” paper has been associated with its low pH and deacidification processes started to be developed. One of the first documented deacidification treatments for paper was described by O. J. Schierholtz (1936) in his patent for the conservation of wallpaper, using aqueous solutions of calcium bicarbonate (17 p. 5). And in 1943 W.J. Barrow developed a technique for lamination of paper with cellulose acetate, combined with deacidification of paper with aqueous solutions of calcium or magnesium carbonate (18).

Throughout the 20th C, lots of research into deacidification of paper was done, both for deacidification of single paper objects and for mass deacidification of books in libraries (for a complete and updated list on deacidification references check reference: (19 p. 8)). Washing paper objects is known to remove acidic products and checking the pH of the waterbath is nowadays a regular procedure in paper conservation treatments (20 p. 47).

Measuring paper samples - The sample size issue

The ratio of sample-to-water affects the concentration of the extracted materials and therefore has an impact on pH readings. To be able to compare results, this ratio needs to be constant. It is important to note that the final weight of a sample or the volume of water are not as important as the relative amounts (1 p. 3). This is why the proportional reduction of both sample and water amounts have resulted in successful translation of the standards of pH determination into the field of cultural heritage (10); (11).

Cold extraction pH norm ISO 6588 (1981) calls for a 2-g-sample/100-mL water ratio, whereas TAPPI 509om-02 calls for 1-g sample/70-mL. Saverwyns et al. studied with success a proportional reduction of ISO 6588 (1981) ratio down to 40 µg of sample, and thus 2 µL of water (10). Further reduction of the needed sample size has been successfully achieved by Strlič et al. and the following can be used: 30-50 µg sample / 2 µL water (11 p. 38); 20-50 µg sample / 1-2 µL water (5 p. 160) and 20-50 µg / 5 µL (21 p. 413).

In the end, the minimum extraction volume (and thus the minimum amount of sample needed) will also depend on the type of electrode available. For the smaller volumes of 1-2 µL (a small drop of water), the micro-glass combination microelectrodes will be needed. With other more robust probes such as the ISFET ones (see later on in this same chapter), one will be need to measure larger volumes, at least of 50 µL (half a small Eppendorf vial) (1 p. 10).

Figure 2. MI-4152 Micro-Combination Microelectrodes from Microelectrodes, Inc. The measuring tip is the really tiny ball at the end of the probe.

Real heritage samples are very heterogeneous (10 p. 632). This is why when measuring the pH of these types of objects with a micro-sampling technique one should take several samples until an acceptable standard deviation is obtained (11 p. 44).

Therefore, although the sample-to-water ratio is important, it has to be remembered that for micro-pH measurement methods, sample inhomogeneity will be the biggest source of measurement variability (11 p. 44).

2.2.1.4 - pH studies on textiles / paintings

As previously mentioned, there are numerous studies about pH of paper and this is a parameter routinely checked during paper conservation treatments. In contrast, the pH of the canvas support of paintings has been, comparatively, under studied even if the support is also cellulosic.

Therefore, little is known about the usual pH of painting canvases, although it can be suspected, that with ageing canvas becomes acidic.

According to G.A. Berger (22 p. 82), one of the main degrading factors for canvas in a painting is air pollution, particularly the acidic pollutants causing chemical degradation. In the picture from 1846 seen in Figure 3, he points the reader to the fact that areas where there was more air circulation (those areas not protected by the stretcher) have become dirtier, “more acidic” and more fragile. The upper left margin of the painting that was detached from the stretcher, also allowed more air circulation and therefore more degradation. Although he says that the centre of the painting has become more acidic than the stretcher-protected areas, he doesn’t say whether pH was measured and if so what were the values.

Figure 3. The stretcher bars have protected the reverse of a painting from dirt and acids. From BERGER, G.A.; RUSSELL, W.H. *Conservation of paintings: research and innovations.* London; United Kingdom: Archetype Publications Ltd., 2000, pp. 82.

Only two written references were found where pH of the textile supports had been measured. In one of them, pH of one painting and two linings had been measured and reported (23). In this article, two paintings were studied extensively in order to devise the best consolidation procedure of their canvas support. One of the parameters studied was pH. Surface pH was measured on 21 different points of the reverse of one of the paintings studied: "*Crocifissione*" by Giovanni Caliari, from the first half of the 19th C, oil on a manually prepared canvas. pH values ranged from 4.3 to 5.1. The authors realised that pH was slightly less acidic in the areas that had been protected by the stretcher and in the areas that had not suffered biological attack.

In this same study, the pH of two linings removed from two paintings (one from a watercolour from the 18th-19th C and the other being from an old flour-paste lining) was measured. The watercolour lining (most probably an original lining), had pH values from 3.9 to 5.2[1], the second lining had values from 4.2 to 4.6 (23 pp. 103-104). Therefore in all the three cases, acidic values were found. The darker colour of the canvas was also found to correspond with lower pH values, whereas lighter canvas areas had higher pH values. Tensile tests were also done and it was found that darker and more acidic areas of the same canvas were weaker than lighter and less acidic samples, that were stronger (23 p. 95).

The other reference found where pH values of canvas had been measured and reported is a project by C. Young where the physical properties of 19th C canvas linings were compared to acid-aged new canvas. Six loose linings and four glue linings from paintings from the 19th C (1820- 1900) were analysed. All of them except one, were found to have some glue present, the glue linings samples having a larger amount of glue paste lining on them than the loose lining samples. pH values were all between 3.6 and 5.0, that is to say quite low values! They checked the "number of folds to failure" a thread could withstand for each lining and it seems that canvas with lower pH values was able to withstand less folds (1 or 2 folds only for the five samples with pH lower or around 4). Therefore two conclusions can be drawn from this research: that linings were found to have low pH and that pH seemed to correlate with the fold resistance of the threads (24 p. 354).

An interesting study of ageing of linen was carried out in 1981 by S. Hackney and G. Hedley on samples that had been naturally aged for 24 years (25). Some of these linen samples had been impregnated with wax-resin and some not. Some had been protected from air circulation in an enclosure and some had been exposed to air circulation. Of these, some had been exposed to light and some had been protected from it. Among others, in 1981 they measured the tensile strength, pH and sulfur content of the different samples.

The most important finding was that indeed protection from air circulation provided considerable protection against degradation. Also that non-impregnated samples exposed to air, had lower pH values, higher sulfur

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[1] Sample **95** of our Reference Sample Collection which is from this very same piece of old lining, gave us a pH value of 4.89, which is in accordance with the pH values obtained by the authors of the mentioned study.

content and lower tensile strength of the yarns. However, light had a larger weakening effect on the yarns, and therefore pH alone cannot tell us the condition of an object (25). This research showed that the weakening of the canvas can follow different pathways, depending on whether it is light or air pollution induced. They found that if the mechanism is more air pollution induced, the pH will be lower.

Regarding sample size, some studies have also been done in the field of textile conservation in order to see if a sample reduction would give comparable results (26)(27). Following the standard ISO 3071:1980 that called for 1g of sample per 50 mL of water, this was successfully reduced to 1mg of sample (this is 0.001 g) per 50 µL of water.

Deacidification of the canvas in easel paintings has been a treatment known for a long time now, but that to our understanding, has received too little attention. Apparently, the first deacidification treatments on paintings were carried out by Gustav A. Berger who introduced the subject into conservation in 1974, at the famous Comparative lining techniques symposium that took place in Greenwich (22 p. 84).

Early deacidification experiments done with canvas by S. Hackney at the Tate Gallery (London) (28),(29),(30), showed that by reducing the pH through deacidification, the degradation rate is decreased. This proved again that pH has a decisive influence on the degradation rate and that the lower the pH, the faster degradation occurs. However, deacidification practice has not yet been widely adopted by paintings conservators. Probably more studies are needed to ensure conservators, that the treatment has more benefits for the canvas layer than risks for the paint layer. Conservators might rightfully worry about migration of the newly introduced substances to the surface of the paint layer and also about the chemical reaction with it, so this possibilities should be fully studied and understood.

Nowadays, nanotechnology has also entered into the field of deacidification of cultural heritage, with some experiments having been done on easel paintings too (31).

2.2.2- Method development for measuring pH of paintings

As previously mentioned, cold extraction methods are preferred over surface measurements since, although initially it might not look like it, surface measurements are also invasive (32 p. 81). Furthermore, in cold extraction methods the sample size can been hugely reduced, making it very feasible and much less risky than the surface method.

Most of the adaptations of the standards to reduce the amount of sample size in the field of cultural heritage, though, were found to be in the field of paper conservation (10)(11), although a few have also been done in the field of textile conservation (27). These had to be then translated into the field of easel paintings, where pH measurements are not yet a routine procedure in conservation workshops.

In order to use a small sample such as 20-50 µg (working therefore with a volume of about 2 µL of cold extraction water solution), the measurement needs to be done with a fine glass combination microelectrode (see Figure 2).This type of traditional pH electrode determines the concentration of H^+ of a given solution by measuring the potential difference between the solution of study and the internal reference solution through a sensitive glass membrane (1 p. 4). Being made of glass, they are fragile and require suitable maintenance by keeping the pH-sensing membrane always hydrated. The microelectrode probes are also very expensive (about 300 €) and are difficult to get since they are only produced in the USA at the moment, with the aggravating fact that they break very easily and so a couple of them are needed at least for every large project. The extracare needed when working with them also increment the time needed to make the measurements by almost four times.

Since there were lots of measurements to be done and paintings tend to be much larger than paper objects, we could afford to design a protocol using larger samples (it is usually not that difficult to be able to subtract a small thread from the edge of a painting). “Ion-Selective Field Effect Transistor” (ISFET) pH probes have recently been introduced in the market (1 p. 4). These types of pH probes have stainless steel metallic bodies with a small silicon sensor at the end. The probes come with different types of housing and different points, allowing the measurement of water volumes as small as 50-100 µL and are very robust and easy to use. Maintenance is also very easy since they have to be stored dry. The probe costs about 350 € too, but will last much longer than the glass microelectrodes.

Since this was the first time we were working with the ISFET probe, a preliminary experiment was done before starting to measure the pH of the Reference Sample Collection. The aim was to compare the pH results obtained with the glass combination microelectrode and the ISFET probe and to see if an ISFET-electrode based method could be developed to measure the pH of easel paintings.

<u>2.2.2.1- Glass combination microelectrode versus ISFET probe</u>

The same IQ160 pH meter from IQ Scientific instruments (USA)[2] was used for both types of probes, since both can be attached through different connectors. The glass combination microelectrode was a MI-4152 Micro-combination microelectrode from Microelectrodes, Inc.(USA) and the ISFET probe was the pHW17-SS from IQ Scientific instruments (USA).

Figure 4. ISFET stainless steel micro probe model pHW17-SS

Figure 5.The ISFET pH sensor at the end of the probe.

To see the specific working procedures and of each type of probe followed when measuring pH for this project, the reader is referred to Annex 2 - Measuring pH.

<u>Sample preparation</u>

The method followed is based on the miniaturization of the TAPPI 509 om-02 pH standard found in the literature (16 p. 413). For paper, a 10-20 µg sample can be used and this can be collected with a surgical hollow needle of about 0.5 mm in diameter in the inside, so that all samples are of the same size. When this needle is used, there is no need to weigh the samples since they will all be about the same weight (11 p. 44).

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[2] At the time the IQ160 pH meter and the ISFET probe were bought (July 2009), the company producing them was IQ Scientific instruments (marketed in Spain through BC Aplicaciones Analíticas, s.l.). By April 2010, though, the company IQ Scientific instruments had been absorbed by the Hatch company (USA), and now its them that produce these pH meters.

In order to be able to use the new ISFET probe, though, we needed a larger volume of solution to cover the pH sensor, and thus a slightly larger sample, but still really small for easel paintings. The minimum amount of water to use so that the sensor was covered with the probe we had (pHW17-SS) was found to be 100 µL in a 1.5 mL vial. A smaller amount (75µL) might have also just covered, but it was preferred to be on the safe side and have a bit of extra solution.

The samples size therefore was chosen to be between 250 and 350 µg. These were weighted with a Sartorious balance, with a precision of +/- 0.001 mg. Depending on the type of canvas this meant a shorter or longer piece of a thread, but typically consisted of 2 to 4 mm of a thread, much less for very thick threads, and even double for very fine threads.

Immediately after weighing, the sample was placed in a vial, closed and labelled. Samples were handled with tweezers and cut with scissors. Three sub-samples were taken from each sample to be measured. The area of the sample of which the sub-sample had been taken was directly documented on the digital image. All this process was quite time consuming, one being able to prepare about 30-40 samples per day.

Figure 6. Setting for weighing the samples and documenting the location directly on the digital image.

At the end of the day, between 5 and 7 pm, 100 µL of deionized water purified by a Mill-Q system (Millipore, Molsheim, France) with a resistivity value of 18 MΩcm (at 25ºC) were added using a micro-pipette to each vial. After adding the water one would check each vial to make sure that the lid was well closed and that the fibre was entirely submerged. Finally looking at the bottom of the grid ensured that all the vials had the same amount of water (in one case for instance, a mistake was detected at this stage just by doing this simple check and it could thus be corrected). Finally, each vial would be tapped against the table a few times (4 or 5) to shake its contents.

It is known that for acidic samples it would be ok to have extraction times from 1h to 24 h, whereas for alkaline samples at least 16 h of soaking are needed (11). Although we knew that most of our samples would be acidic, for time management issues, the easiest way to do it was to add water at the end of the working day and to measure them first thing in the morning, thus leaving the samples in water for about 15 h.

Next morning, usually between 9 and 11, the pH of the vials would be measured. First each vial would be tapped on the table 4 or 5 times again to make the solution homogeneous. Then the pH meter would be calibrated and all the samples measured. Before measuring each vial, this would be tapped again on the table to remove its contents. To make the actual reading, the electrode was placed inside the vial and moved around it a bit. Care was taken to make sure that the fibres were not touching the sensor when the reading was being taken or that there were no air bubbles on it. The ISFET probe proved to be very user-friendly since it could be left in a vial while waiting for the pH meter to come to a stable reading (Figure 10). The pH meter beeps when it reaches a stable value, although sometimes it will beep and immediately start changing the result again. In these cases one would wait until it reached another stable measure. When a measurement was stable for 10 s (or more) this was considered the final reading.

Working with the ISFET probe is indeed very recommended. Being very sturdy it allowed for work to be done much faster than when working with the glass microelectrode where every movement has to be carefully controlled to avoid damaging its tip. It only took about an hour or so to measure about 30 vials, which would have taken much longer with the glass probe.

Results

Fifteen samples were prepared as previously described and the same solutions were analysed with the IQ160 pH meter but using the two probes: the glass microelectrode one and the ISFET probe.

Twelve of the samples were old linings from the Reference Sample Collection (**112**, **110**, **109**, **108**, **107** (7b), **104** (centre), **104** (margin), **103**, **102**, **111**_1, **111**_2 and **111**_3) plus three new textile samples of linen, cotton and jute.

The glass microelectrode solutions were measured by placing a drop of the solution on a Melinex film and placing the electrode on top of it, whereas the ISFET solutions were measured by inserting the probe in the plastic vial with the solution (see Annex II- Measuring pH, for further details on the procedures).

Comparison of pH results between the two probes gave a very good correlation, producing an almost perfect match (Figure 7). Therefore, the ISFET probe was considered to be completely appropriate to be used for the 250-350 µg size samples.

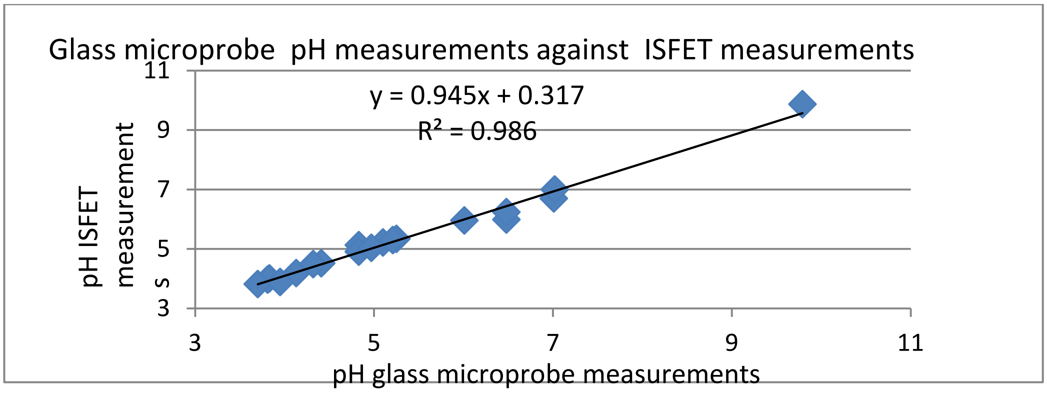

Figure 7.Glass microprobe pH results versus the IFSET probe pH results on the same samples. The correlation is almost perfect.

2.2.2.2- pH measurement of 10 test samples

Once the sample size and the new ISFET probe have been validated against the standard technique, an experiment was done to assess the measurement uncertainty, expressed as standard deviation. This was done by repeatedly measuring sub-samples from a set of ten test samples from the Reference Sample Collection (**111**_1 darker, **111**_1 lighter, **103**, **114**, **110**, **102** and **107**) plus new linen, cotton and jute samples.

Following the same procedure, three sub-samples were taken from each test sample. The three samples were cut from the same thread and thus they came from one next to each other. The standard deviation (SD) was calculated and the method was found to have a high reproducibility: SD was 0.0 - 0.3 pH units (see the next section for an explanation of the concept of “Standard deviation”).

Repeatability in the standard methods (TAPPI T 509 om-02 and ASTM D778-97(2002) is from 0.1 pH units for acidic papers to 0.3 pH units for alkaline papers (11 p. 36). Therefore such a low SD (0.3) in our samples that are heterogeneous is very good.

The concepts of “Standard deviation” and “Relative standard deviation”

The statistical concept of “Standard deviation (SD)” tells us about how spread a set of data is (33 p. 236). Two different sets of data can have the same “mean value” or average (all the values added together divided by the number of samples) of 100, for instance, but two different “Standard deviation” values (Figure 8). Data typically has a “Gaussian distribution” or “bell shaped” distribution. The standard deviation value tells us how broad or narrow this bell shape is, and therefore how far away from the mean can the data be scattered. In Figure 8, the red data population has a smaller standard deviation of 10, whereas the blue data population has a standard deviation of 50. When doing analytical measurements, the smaller the SD, the smaller the spread of data, and therefore the more consistent and precise our method is. That the red population has an SD of 10, in this case implies that 95% of the samples are within two standard deviations from the mean (100 in this case), i.e. 100±20 (34). Therefore it means that 95% of the samples are between 80 and 120. For the blue population, since the SD is larger (50), it means that 95% of the samples are within 0 and 200 (two standard deviations from the mean). 95% is generally taken by scientists as a good confidence percentage. If we don’t need such a high certainty, both the percentage and the times SD can be reduced (for instance, in this red population case, 68% of the samples (about two thirds) would fall within one standard deviation from the mean, meaning that 68% of the samples would be between 90 and 110 in our case). All this, of course, assuming a normal distribution of our samples, which is usually the case of random errors. If SD was “0”, then it means that all our values are exactly 100 (35). In conclusion, for most measurement methods, the smaller the SD, the better.

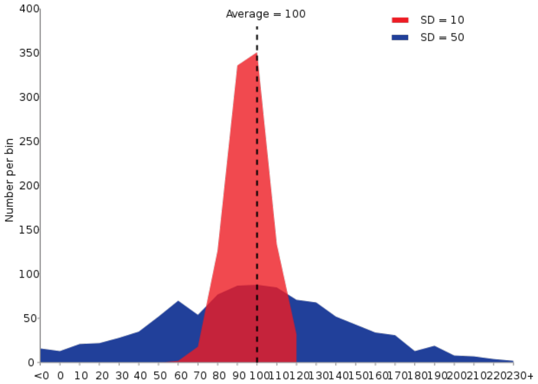

Figure 8.Example of two sample populations with the same mean and different standard deviations. From the English Wikipedia (http://en.wikipedia.org/wiki/Standard_deviation), accessed 25/09/2011 (35).

The Relative Standard Deviation (RSD) (also called the “coefficient of variation”), is another way of measuring the variability within a population. It is a ratio of the standard deviation to the mean (SD/Average). It we multiply the value by 100, it is then expressed as a percentage (35).

Both the SD and the RSD talk about the variability of our data. The SD is a measure of the absolute variability in a data set and it is expressed in the same units as the scores themselves. The RSD, instead, as the name says, is a measure of the relative variability. It produces an abstract number independent of the units of measurements, which is then often expressed as a percentage so that it is easier to understand.

RSD can therefore be useful for comparison between data sets with different units or very different mean values, since the mean is taken into account to produce it. SD will tell us about the specific variability value, whereas RSD will tell us about what it represents in relation to the different situations we might have.

2.2.2.3- pH measurement of 6 real samples

The next last test before measuring the pH of the canvas support of paintings on all the Reference Sample Collection, was to test the method developed on a set of six real samples (**94**, **95**, **96**, **54**, **61** and **22**), this time taking several sub-samples (from 6 to 9) from areas far apart, but within the same sample. The aim was to assess whether historic samples were very inhomogeneous or not and if the method was good for historic samples.

SD values obtained in this case were again very small, from 0.1 to 0.3. This proved that the method developed was very successful too for real painting samples and that they were not very inhomogeneous. It was therefore decided to go ahead and measure the pH of all the samples from the Reference Collection with the developed and successfully tested method.

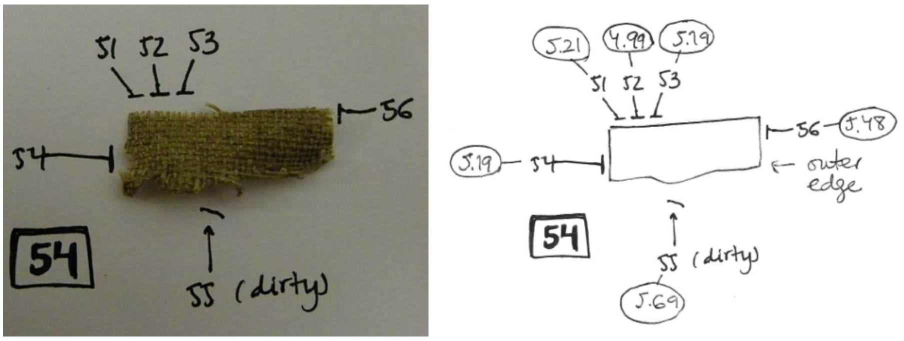

Figure 9. Sub-sample locations and pH values of sample 54, the one with the largest SD (0.2) of this test.

2.2.2.4- pH measurement of the Reference Sample Collection

Once it was established that the SD of the developed method was so good, we proceeded as follows: two 250-350 µg sub-samples were taken from each sample. Samples were only weighed once, since we do not need to know the accurate weight, but we just need to know that their weight is within the required range. (If we needed to know the accurate weight, the right way to do it would be to weigh three times the empty crucible, weigh three times the crucible with the sample, do the averages and then do the subtraction). Then the pH was measured and if the difference between the two pH readings was 0.3 (the SD of our developed method) or less, the average of the two pH values was calculated. If the difference was more than 0.3, a third sub-sample and measurement were taken.

Once we had measured all our samples, it could be seen that indeed measurement variability for all the analysis samples was mostly below 0.3 SD (a 92% of the samples), with only a small 8% of the samples presenting pH measurements with SDs between 0.3 and 0.7. The average SD for all the samples was 0.1. If we look at these values from the RSD point of view, the average RSD of all the samples was 2.3**%**, with 91% of the measurements exhibiting an RSD below 5%, and only 9% having RSDs between 5 and 11.3%.

pH sub-samples were not taken from entirely adjacent areas, but near the area that was to be used afterwards to take the three NIR spectra. Where possible, they were not taken from known outer edges of the sample, but from the inner edges, where pH would be more similar to the rest of the painting than the outer edge (presumably more degraded). Where possible, sub-samples were taken from different nearby edges. If samples were elongated in shape, then two sub-samples where often taken along the same edge of the sample. In this last case, a “vertical” and a “horizontal” thread from the same edge were picked by making a cut in the sample. Location of sub-samples were documented digitally on the photograph of each sample (see Annex I).

Figure 10.Set-up for pH measurement of the prepared samples. Note that the ISFET electrode can be left inside the plastic vial during pH measurement as it stands on its own.

2.2.3- Results and discussion

2.2.3.1- pH of the samples studied

The pH of a total of 179 textile samples was analysed, taking 2 or 3 sub-samples from each. There were also 20 pH "pieces of threads" of canvas for pH analysis only. All together it meant that a final number of 461 pH measurements were done. This work took about amonth of one person's full-time work.

If the average pH of all the measurements is calculated, we get the value of 5.5 (SD 0.8; RSD 14%). If we place every obtained pH value into a range (4.00 to 4.49; 4.50 - 4.99; 5.00 to 5.49 and so on), the range were we find most of the samples (32%) is the one from 5.00 to 5.49, followed by 20% in the range 5.50-5.99 and 18% in the 4.50 - 4.99. Therefore, 75% of all our samples have a pH<5.99; and 55% have pH<5.00.

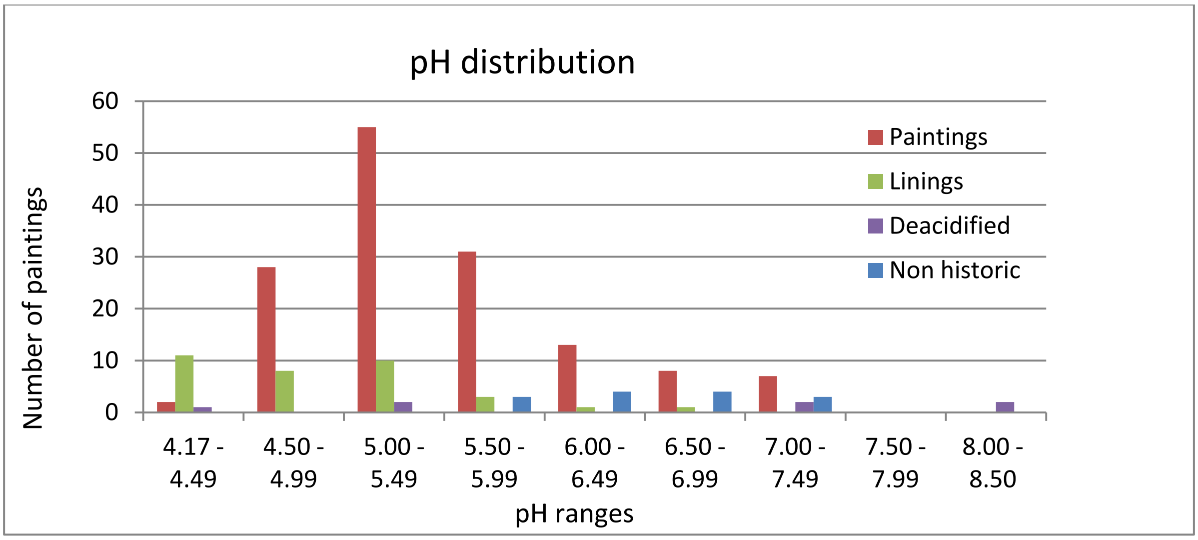

Figure 11. pH distribution of all the samples: Paintings, Linings, Deacidified samples and Non-historic ones.

The lowest pH value of all is 4.2 (**29_L**, a glue paste lining) and the maximum is 8.7 (**135**, a deacidified sample).

If we separate the samples into groups (Figure 12), we see that linings have a tendency to have lower pH values. The average pH for paintings is 5.5 (SD 0.7). The variability within the deacidified samples group (with a higher pH average, of course) is quite high (SD 1.5) (see later on in this same chapter for more information on these type of samples), and non-historic samples have an average pH closer to neutral, which makes sense since this samples are newer and cleaner.

Type of samples	Average pH	SD	RSD
All the samples	5.5	0.8	14.5%
Paintings	**5.5**	**0.7**	**12.0%**
Linings	5.0	0.6	12.1%
Deacidified	6.7	1.5	22.4%
Non-historic	6.6	0.5	8.2%

Figure 12. Average pH according to the different types of samples and the SD and RSD for each group.

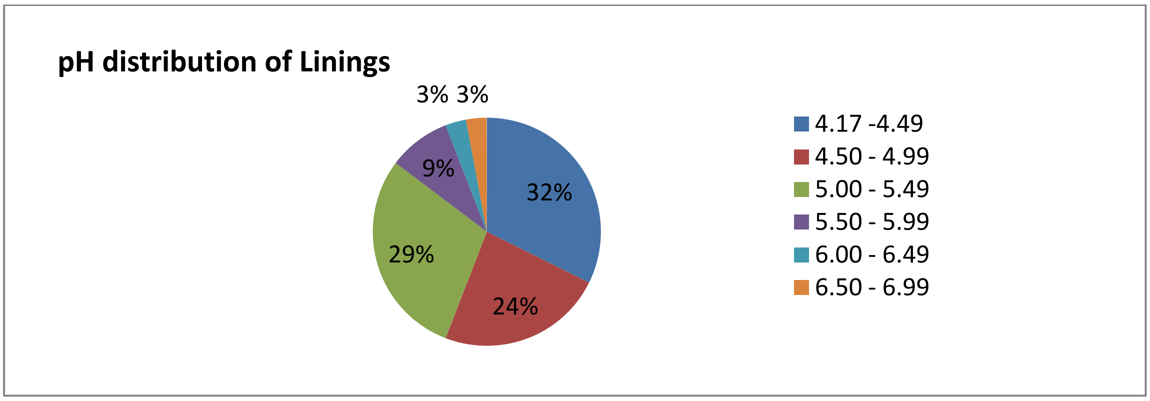

Figure 13. pH distribution of Linings.

When looking at the pH results of all the samples, it is interesting to note that the lowest eight pH values are all from old glue paste linings (**29_L; 105; 117_1; 116_1; 116_2; 104; 38_L; 117_2**). If we analyse the pH of linings (Figure 13), we see that 56% (19 out of 34) have pH below 4.9. The remaining 15 linings (44%) are more or less spread along all the ranges of pH, although it can be seen in Figure 11 and in Figure 13 that most of the linings are indeed in the lower ranges. Therefore, it is significant that so many of them have very low pH values, indicating that the glue paste lining is somehow a source for quite a lot of acidity.

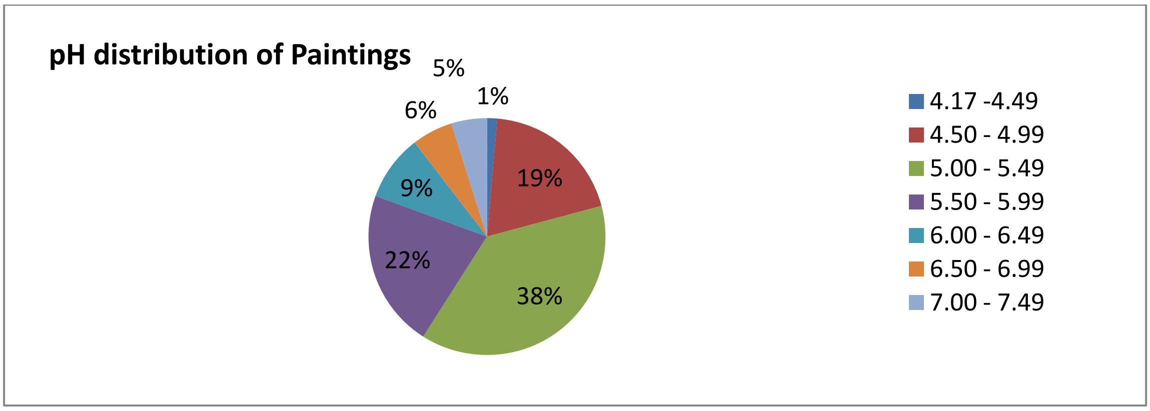

Figure 14. pH distribution of Paintings

Regarding paintings it can be seen the vast majority of them have acidic pH (Figure 14). 58% of the paintings analysed have pH<5.5 and 20% pH<5.0. Only 1% was found to have pH<4.5. On the other side, an 11% was found to have pH values between 6.5 and 7.5, which are around the neutral pH values thought to be ideal.

The lowest pH value obtained from a real painting is 4.5 (**51**) and the maximum 7.5 (**79**, a tempera painting on cotton from the end of the 19th C); followed by 7.4 (**94**, a painting from the 16th C in excellent condition), neither are exactly young examples.

Only seven paintings were found to have pH above 7 (5%). Surprisingly we found both old and new paintings in this group. There were samples from the 16th C (**94**), from the 18th C (**78**), from the 19th C (**79**) and from the 20th C (**62**, **120** and **138**). This means that 40% of the paintings in this "good" pH group were from before the 18th C. If we take the group of paintings with pH between 6.5 and 7.5 (a larger interval), we see that three paintings (27% of them) are paintings from between the 16th and 18th C.

2.2.3.2- pH and date

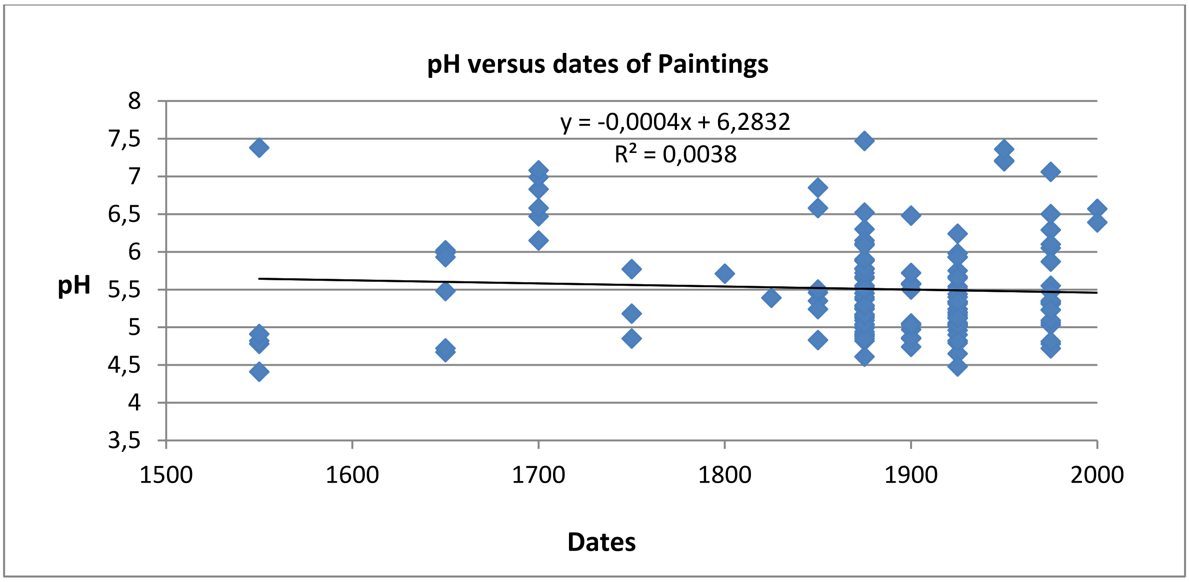

Figure 15.pH values against dates for all the painting samples

It is interesting to see that pH and dates of paintings do not seem to be correlated at all, since we have both low and high values across all periods of time (deacidified samples, non-historic samples and linings have been removed, so Figure 15 represents only paintings). The situation when looking at all the samples together or the linings alone, is very similar.

If we look in detail at the paintings that have pH between 6.5 and 7.5, we find that indeed from the eleven found, there are four which are very new paintings, from 1975 onwards, (**61**, **62**, **63** and **120**). Then there are four from the 19th C (8, 30, 77 and 79), and surprisingly we find in this group three really old paintings (**94**, **80** and **78**). These three paintings are, from the 16th C (the first), and from the 17th-18th C (the other two). Indeed by visually inspecting them, the samples already give the impression being in a very good condition, and if available DP measurements confirm this (1687 DP for sample **80** and 1512 DP for sample **94**). One thing these three paintings have in common is the fact that they are church paintings. It has been suggested (36), and it might well be the case, that lime traditionally applied to wall churches over the years both to paint and to clean them, might have offered a helpful alkaline environment for the reverse of these paintings (a sort of a "natural deacidification treatment" through the creation of a suitable microclimate in the reverse of the painting). This could explain their good condition. Another explanation could be the lower acidity of the original materials in older artisan paintings.

Newer paintings are also found to have low pH values as can be seen (Figure 15).

All this means that pH is not so much governed by the age of the samples but that there must be other factors that are more important such as the materials present in the painting and the environment in which the painting is placed.

2.2.3.3- pH and fibre type

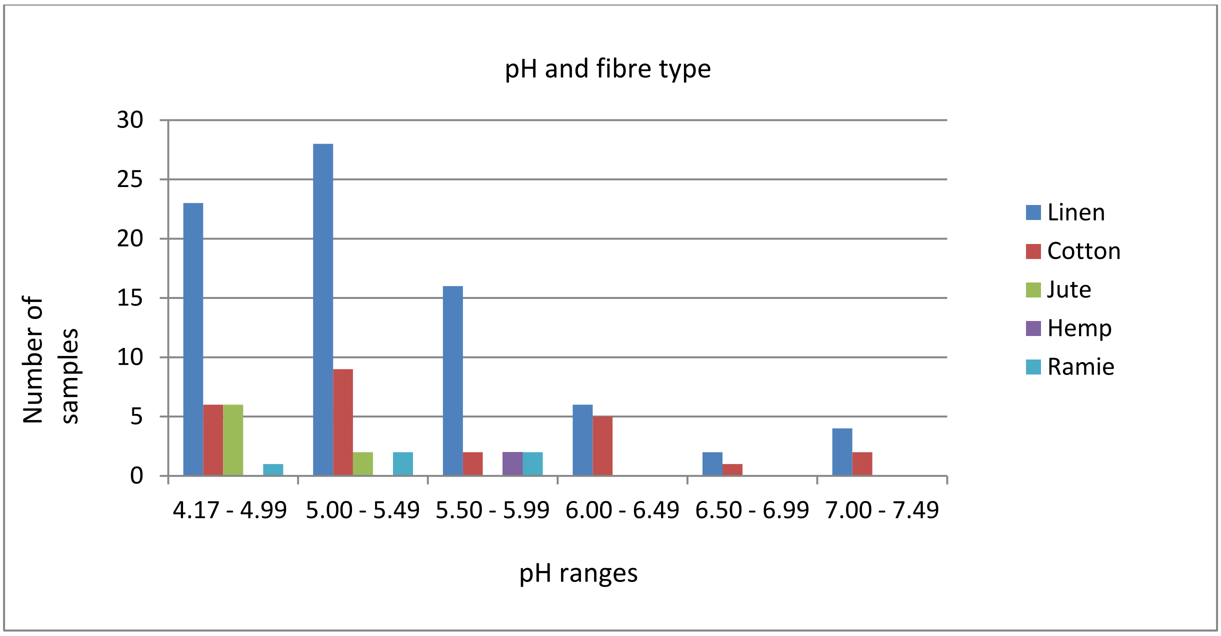

Figure 16. pH of paintings and linings according to fibre type

Deacidified samples, household new textiles and bare new textiles have been removed from this analysis, so Figure 16 shows only pH of paintings and linings. It can be seen that jute fibres tend to have lower pH (average is 4.7) and that cotton samples tend to have higher pH than linen ones (cotton average is 5.6, against a linen average of 5.4). However, the small substraction between linen and cotton (0.2) is actually similar to the SD of our method developed (0.3), so it should really not be taken as a significant difference. For hemp the average value is 5.8 and for ramie 5.4. Since we had very few hemp and ramie samples, though, these values should also be interpreted with caution.

If we look back at the specific values obtained with the glass microprobe against the ISFET probe, where the pH of new linen, jute and cotton textiles were measured, it can be seen that with new textiles we seem to obtain a similar trend. pH values obtained with the glass microprobe were: jute 4.3; linen 6.5 and cotton 7.0. However, these are too few measurements to draw conclusions and it would thus be good to do a larger study on this issue.

2.2.3.4 – A look at the deacidified samples in our Reference Sample Collection

The curious case of sample 113

Sample 113 is an old glue paste lining from the Conservation section. There are four samples of this canvas belonging to the Reference Sample Collection (**113**_1; **113**_2; **113**_3 and **113**_4) that received different treatments in January 2009 (a year before pH was measured).

		Treatment received	**pH**
113_1		Nothing	4.9
113_2		Washing in distilled water for an hour	5
113_3		Dipped twice in a calcium hydroxide solution in January 2009. Calcium hydroxide solution was prepared by mixing 15 g of $Ca(OH)_2$ with 1 L distilled water, the day before using it, having let it rest	8.0
113_4		Old lining brushed with Bookkeeper in January 2009	5.7

It is interesting to see that indeed, just by washing the sample in water, the pH increases a little bit, although not as much as expected (from 4.9 to 5.0). The feel of the washed sample was so much better, the textile felt more flexible, that a higher difference in pH was expected. This expectation was probably due to the fact, that although pH is not directly related with flexibility, it is usually linked to degradation, and degradation is usually felt through rigidity (of all materials, the canvas, the glue etc.). As it has been found to be the case for paper, washing introduces some moisture into the very dehydrated textile (37 p. 8) and this could be in part why it became more flexible. In this case, however, the glue present was probably also was washed away and this might be the main reason why it felt more flexible. The textile becoming more flexible (and thus feeling in a better condition), in any case, had nothing to do with pH, which was not that different from before washing.

The calcium hydroxide treated piece had a very high pH (it had gone from 4.9 to 8.0). Contrary to expectations, in the case of the Bookkeeper treated piece, the pH was a bit higher than the untreated one, but not that much (from 4.9 to 5.7). Bookkeeper is said to take 28 days for the complete conversion to magnesium hydroxide to place (38) and this textile had been treated a year before the pH measurement took place, so it is thought that all the conversion into magnesium hydroxide has already taken place. This low pH value obtained after the application of the Bookkeeper solution is a bit strange, since it is seen to be a very successful deacidification agent (increasing pH from a range of 4.3- 7.5 to a range of 7.6 - 9.0) (39 p. 158). Maybe not enough solution was applied to the thick canvas, because pH would have been expected to be higher.

The rest of the deacidified samples in our collection

We were lucky to count with 6 more deacidified samples generously provided by Dr. Marianne Odlyha, from the Birkbeck College (University of London). Dr. Odlyha had previously done research on deacidification of the canvas of paintings together with Stephen Hackney from the Tate Gallery of London. Some of the samples they used in their past research (40), treated mostly around the year 1997, are still kept at Birkbeck and this is why some of those could be added to our collection (Figure 17).

Number		Type of canvas		Deacidifying treatment		pH
131	🟨	Historic primed loose lining, (Hylda, Almina and Conway, Children of Asher Wertheimer" by Sargent, 1905)	🟥	Battelle treated in 1997	🟥	4.5
132	🟨	Historic primed loose lining, (Christ in the House of his Parents by Millais, 1849-1850)		Untreated	🟥	5.8
137	🟨	Historic primed loose lining, (Christ in the House of his Parents by Millais, 1849-1850)	🟪	Methoxy magnesium methyl carbonate (MMC) treated (brushed) in 1997	🟥	5.6
138	🟩	New primed Russell&Chappel superfine linen, from 1997		Untreated	🟦	7.3
134	🟩	New primed Russell&Chappel superfine linen, from 1997	🟪	MMC treated (brushed) in 1997	🟦	7.3
135	🟩	New primed Russell&Chappel superfine linen, from 1997	🟥	Battelle treated in 1997	🟦	8.7
139	🟩	New linen canvas treated with $MgHCO_3$. Then sized. Then chalk/glue priming. Then Cremnitz white Winsor & Newton oil paint. Aged 4 weeks in lightbox at 20,0000 Lux, with UV filter. (done in 1997)	🟥	$MgHCO_3$ applied on the canvas before adding the preparation and paint layers. Done in 1997	🟦	7.3

Figure 17. Six of the deacidified samples that were included in the Reference Sample Collection. In yellow historic samples, in green non-historic samples. In red pH values below 7 and in blue pH values above 7.

It is interesting to see the pH values we obtained on these samples 20 years after different deacidifying treatments were applied in 1997. The three different deacidification treatments used in 1997 were: the "Battelle" method, Methoxy magnesium methyl carbonate (MMC) and $MgHCO_3$. It is not in the scope of this thesis to explain the different types of deacidification treatments and thus the reader is referred to the specialized literature for more information on those.

The most important thing to note is that historic samples continue to have acidic pH values, and there is no difference between the treated and untreated pairs from the same painting (**132** and **137**), the treated sample actually having a lower pH (even if the difference is not very significant). Therefore it seems that in all cases, the deacidifying treatments were not able to counteract acidity, at least after 20 years.

The new samples all show pH above neutral, but so does the control sample that was not deacidified (138). We can see that the Battelle treatment of sample **135**, gives a higher pH value than the MMC treatment.

It is clear that more research is needed regarding the effectiveness of the different deacidifying treatments on the canvas of paintings as well as the amount of material that needs to be applied and the long term effects of the treatment.

2.2.4- Conclusions

The adaptation of the micro-pH measurement traditionally applied for paper artefacts for canvas supports proved to be very successful. Using 250-350 µg of sample with 100 µL of water and the ISFET microprobe it was possible to develop and validate a method of pH analysis for easel painting canvases. For textiles, 250-350 µg of material corresponds to a few millimetres of a thread, from 2 to 8 mm (typically from 2 to 4 mm) depending on the thickness of the textile. The new type of metallic probe ISFET gave also very good results compared with the traditional glass microprobes usually used for paper with the advantage that they are much more user-friendly.

Despite the great sample inhomogeneity envisaged, using two or three sub-samples for each textile sample was found to be ok, since the standard deviation found when testing the method (0.3 pH units) was in accordance with the SD allowed by industrial standards. Afterwards, once all the measurements had been done it was found that for most of the samples (92%), the SD was below 0.3 and that for 8% of the samples SD was from 0.3 to 0.7. The average SD of all the samples measured was 0.1, which is highly acceptable. This means that sample inhomogeneity (sub-samples were typically taken 1 or 2 cm away from each other, see Annex I) allowed for NIR measurements to be taken away from the actual pH measurement.

Regarding the specific pH values obtained from the Reference Sample Collection, it was found that the average pH for all the analysed samples (paintings, linings, deacidified samples and non-historic samples) was acidic: 5.5 (SD 0.8 and RSD 14%).

Regarding the pH data from paintings, their average pH was 5.5 (SD 0.6; RSD 12%). The most typical pH value for a painting to have was found to be in the range of between 5.0 and 5.5 58% of the paintings had pH<5.5, with a 20% of them having a pH<5.0. Surprisingly, only 1% of the paintings were found to have pH<4.5 (more paintings with lower pH values had been anticipated). The good news is that not all paintings were acidic, since a small group of them (11%) were found to have around neutral pH (between 6.5 and 7.5). However, looking at it the other way around, this means that 89% of the paintings were found to have pH<6.5.

Interestingly, a few old samples were found to be in the group of paintings with pH 6.5-7.5. Three of the eleven paintings in this group (27%) were older than the 18th C (16th C – 18th C). Some of these were church paintings and it is thought that the traditional wall materials might have provided a “passive deacidification” treatment for these paintings. It could also well be that older painting materials were already originally not so acidic.

The pH of glue paste linings was found to be markedly more acidic (56% of them having a pH<5.0). We did not find, though, so low values as others have reported to have found for 19th C linings with pH values as low as 3.7 (24 p. 354). The lowest pH value we found in a lining was 4.2. Acidity in the case of linings could come from different materials used in the glue paste mixture that the literature already point as possible acidifying agents: vinegar, Venice turpentine, alum… etc. We actually measured the pH of the freshly prepared glue paste adhesive (done using the “Catalan recipe”) and this was found to be around pH 5 (see Chapter 1). In the light of our findings, a very interesting future avenue of research would be the study of the pH values of different types of glue paste recipes (there are many) and pH change on ageing.

When pH was analysed in relation to the date of the paintings, it was found that indeed these two parameters are not correlated. As already suspected when analysing the pH of paintings, it was found that a few very old samples had remarkably good pH values (around neutral) and also that there were also some newer modern samples with lower pH values. This fact indicates that there must be other factors that influence pH more than date, such as painting materials or the environment the painting has been kept in.

Therefore it is crucial to do more research on these two issues so that sources of acidity in paintings are better identified so that they can be better counteracted.

A slight correlation between pH and the different fibre types was found, jute tending to have lower pH (average value 4.7), cotton having a tendency towards higher pH (average value 5.6) and linen having middle pH values in general (5.4 average pH). The difference between linen and cotton, though is so small that it should barely be taken into consideration. We had too few ramie and hemp samples to draw any conclusions between these fibre types and pH. In conclusion, the higher expected acidty of jute (thought to be linked to the higher lignin content of the fibre than the rest) is confirmed as well as the less acidic pH of cotton (which has no lignin at all).

A small incursion into the effects of deacidification was done through the analysis of some canvas samples that had been deacidified in 1997, of which pH was measured. Without entering into the analysis of the particular deacidifying treatments used, it was found that 20 years after they were applied, the historic canvases were acidic (similar to the untreated control samples) and that the new linen samples did have pH above 7 (although the untreated sample did so too). It was found that more research needs to be done to establish which is the best deacidification method to use, how much material one should apply to paintings, how often etc.

To conclude this pH chapter, it has to be said that it is clear that since the canvas of paintings has been found to be mostly acidic, more research on its deacidification is urgently needed. Acidity is one of the main causes of canvas degradation, and if this is not removed, DP will get lower and lower, the canvas eventually losing all mechanical stability. If lining is to be avoided, clearly deacidification treatments have to start to be generally applied as a preventive conservation treatment on paintings. But more research needs to be done first.

2.3-DP

Once we have identified the fibre type and measured the pH of all the Reference Sample Collection we can proceed to develop a specific method for DP determination applied to the canvas support of easel paintings. DP is an important parameter to measure since it is directly related to the mechanical strength of the canvas. Measuring the DP of our samples will give us an indication of the typical values encountered and the relationship between DP and pH, DP and fibre type and DP and date. Samples of visibly different condition will also be examined and their DP taken into account in data interpretation.

2.3.1- What is DP

The Degree of Polymerisation (DP), is the average number of monomer units in a polymer (1 p. 15). The higher the DP value, the longer are the chains of the polymer, and the lower the DP, the shorter its chains.

The same polymer with higher or lower DP will have the same chemical properties but different physical properties (2 p. 143). This is very clear in the case of synthetic polymers, such as PVAc for instance, that can be bought with different DPs from 150 to 1900, which gives them different physical properties (3 p. 91).

The DP of many synthetic polymers can be a few thousands or even millions (4 p. 16). For native cellulose, the DP might be as high as 14,000, but purification procedures usually reduce it to the order of 2,500 (5 p. 22) .

Since DP expresses the number of monomeric units[1], in the case of cellulose this value refers to the number of glucose units (6). Some, however, think it would be more correct to consider the dimer cellobiose (made up of two glucose units) as the real monomer in the cellulose polymer, since cellobiose is the repeating unit (7 p. 7). Like this, some researchers refer to cellobiose units when talking about DP (8), halving the values (i.e. 5,500 DP for cotton instead of 11,000) (9 p. 20), which is actually wrong.

The term “depolymerisation” is used to indicate the breaking down of a polymer into monomers (10). In the case of cellulose this happens through degradation of glycosidic bonds, especially during acid-catalysed hydrolysis actually leading to depolymerisation (6 p. 25).

Cellulose is a high molecular weight polymer and it has to be taken into account that even a small extent of degradation (oxidation or hydrolysis) which results in chain breaking, will have a disproportionate effect on physical properties, since only one such break per chain already halves the average DP (11 p. 73).

Also, since damage occurs first in the amorphous regions of cellulose, the polymer becomes more crystalline because the proportion between amorphous and crystalline regions is altered, and this produces a stiffer material (9 p. 27).

2.3.1.1 - Relationship between DP and molecular weight

A simple molecule is composed of different atoms. The molecular weight (M_r) of such a molecule is calculated by adding up the atomic weight of the different atoms multiplied by the number of such atoms

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[1] The “repeating unit” and the “monomer” in a polymer can be different in the sense that the “repeating unit” can be, for instance, “ABAA”, and the “monomer” (the smaller units), be “A” and “B”. According to this, in the case of cellulose, the monomer would be the glucose ring, the repeating unit the cellobiose.

present in the molecule. For instance, the molecular weight of glucose ($C_6H_{12}O_6$) is: (12 (atomic weight of carbon) x 6) + (1 (atomic weight of hydrogen)) x (12 + 16 (atomic weight of oxygen) x 6) = 180 amu (atomic mass unit) (4 p. 15).

For a polymer, one should do the same, calculate first the molecular weight of the repeating unit, and then multiply it by the number of how many of these repeating units (*n*) are linked to form a particular chain. For instance, in the case of a polymer chain of amylose (a linear polymer made up of D-glucose units that is found in starch), with a DP of 1000, its molecular weight would be 168[2] x 1000 = 168,000 amu (3 p. 14).

However, not all chains in polymers have the same length. They are always mixtures of polymer chains of different length. (Amylose for instance, can have molecular weights between 170,000 and 200,000 amu)(3 p. 15). Therefore the average molecular weight can be calculated. Different molecular weights can be calculated for the same sample, depending on where is the emphasis placed. Two types that are often used are M_n and M_w. M_n gives emphasis to the number of molecules that make up our mixture (M_n = polymer weight / number of macromolecules) whereas M_w gives emphasises the weight of molecules with the average molecular weight in the mixture. This last one is the one most often used (3 p. 15)(4 p. 16).

Therefore, DP and Mw are related and knowing one, the other can be calculated.

2.3.1.2 – How to measure DP

The DP of fibres can be measured by different methods: by osmotic pressure, by fluidity (viscosity), by ultracentrifuge, by scattering of light (physical methods) or by determining the quantity of end groups (chemical method) (9 p. 11). Of this, the most commonly used in labs is viscometry (12 p. 817) due to the ease of measurement and inexpensive equipment. However, since molecular weight is a distributed property, more complex techniques that measure this parameter such as gel permeation chromatography (GPC) (13 p. 978), size exclusion chromatography (SEC) (14)(15)(16)(17) and matrix-assisted laser desorption/ionisation (MALDI) (18)(19) can also be used. These techniques, although they might require less sample, require much more complex and expensive equipment and sample preparation times are highly increased, which would be a big inconvenience in our case, where many samples had to be measured. Also, in our case it was enough just to obtain the average DP, not needing to actually know the distribution of DP.

Viscometry and the viscometer

As mentioned, the DP of polymers can be determined by a relatively simple viscosity measurement. Polymers increase the viscosity of a solution because its large molecules create a resistance to flow (4 p. 17). Therefore, by comparing the time a solution with a sample dissolved in it takes to pass through a glass capillary with that of a solution without it, the ratio of viscosity of the two solutions can be calculated, and from this, DP can be determined.

A viscometer (or viscosimeter) is the apparatus used for measuring the viscosity of liquids and it basically consists of a glass capillary, inside a thermostated water bath set at 25ºC. The water bath is needed because viscosity is temperature dependent and thus all measurements need to be taken at the same temperature to get comparable results (20 p. 30).

To make a measurement, the sample solution is pulled up with a pump and left to run down through the internal capillary. The technician doing the measurement starts the chronometer when the solution passes a specific mark at the top of the viscometer and stops it when it passes the second mark, at which point exactly 1.0 mL of the solution has passed through the capillary. The time the solution has taken to pass through the viscometer (efflux time) is noted down.

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[2] The value 168 is taken as atomic mass unit of amylose instead of 180 here, since when two monomer units link, a molecule of water is released (180-12 = 168).

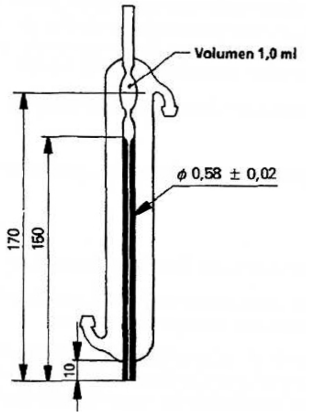

Figure 1.The standard viscometer. From AENOR.*UNE 57-039-92: Pastas: Determinación del índice de viscosidad límite de celulosa en disoluciones diluidas.Parte 1: Método de la cuprietilendiamina (CED) (Equivalente a ISO 5351/1: 1981)*, 1992 (21).

2.3.1.3 - DP standards and DP calculation

There are different standards regulating the measurement of DP produced by different bodies such as ISO and ASTM. The standard followed was ISO 5351/1-1981: *Cellulose in dilute solutions - Determination of limiting viscosity number - Part 1: Method in cupri-ethylene-diamine (CED) solution.* It was chosen because this standard has been extensively used for heritage samples (22).

It has to be noted that the ISO 5351 standard is useful to get the limiting viscosity number (or intrinsic viscosity), from which DP or molecular weight can then be obtained.

On doing the measurements, the efflux time of the solution that contains the sample is noted down. And from the ratio:

$$\frac{\eta}{\eta_0} = \frac{t}{t_0}$$

Where t is the efflux time of a cellulose sample solution and t_0 the efflux time of the solvent without any sample, the viscosity ratio (viscosity of the cellulose solution (η)/ viscosity of the solvent (η_0)) is calculated (20 p. 30).

The more viscous a liquid is (like honey) the more time it will take for it to pass through the viscometer. The less viscous it is (like water) the faster it will go through. In the case of textile analysis, the “blank” solution (that is to say the CED solution with no sample), will always go through faster than when the solution contains a sample. Also the better the condition of the sample (higher DP), the higher the viscosity of the solution.

Once we have the viscosity ratio, the amount of sample used is taken into account and the intrinsic viscosity is obtained using the Wetzel-Elliot-Martin’s equation (20 p. 30).

Once you have the intrinsic viscosity, you can get the DP of the particular cellulose sample by applying the Evans and Wallis equation (20 pp. 30-31):

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

From which the following is derived: $DP = (1.1\cdot[\eta])^{1/0.85}$

If desired, with the intrinsic viscosity one can also get the viscometric average molecular weight by applying the Mark-Houwink-Sakurada equation (20 p. 30).

2.3.1.4 - Relationship between DP and mechanical properties

Mechanical properties should be the principal focus of all stability studies regarding cultural heritage, since these will allow for more or less handling of the objects (20 p. 27).

As early as the concept of understanding cellulose as a large molecule appeared at the beginning of the 20th C, investigations were initiated to demonstrate the relationship between the fluidity of cellulose solutions and the mechanical properties of the fibres from which the solutions were made (23 p. 399). Already in 1937, H. G. Staudinger showed that the breaking strength of a series of hydrocelluloses[3] was directly related to the number of links broken in the cellulose chains (23 p. 400;404).

For pure cotton papers it has been determined that the loss of the paper strength is due to the fibre loss of strength, which is caused by degradation (caused by acid-catalysed hydrolysis)(24 p. 401). This research proves that acidity causes degradation and that this causes loss of strength.

Regarding textiles, it has been proven that tensile strength is a macroscopic property that can be used to monitor degradation in cotton cloth. In fact, although changes in other properties such as yellowness, oxygen uptake and percent weight loss were also found to give an indication of degradation, they were found not to be as good indicators as tensile strength (25 p. 65).

Research on the relationship between DP and tensile strength of canvas supports has been done by G. Scicolone et al. (26), (27). In their research, they artificially degraded (heat, light and acids) cotton and linen textiles and then measured DP and tensile properties. They proved that indeed there is a linear correlation between DP and yarn tensile strength and tenacity (27 p. 313), and thus between DP and tensile strength and tenacity of the woven textile (1 p. 16;19)(28). In these studies it is thus clearly shown that lower DP values mean lower mechanical strength (29 p. 13).

The drawback of doing mechanical tests on cultural heritage materials, though, is that a large sample is needed (25 warp yarns and 25 weft yarns of 2.5 cm each for yarn tensile strength), and this is not acceptable for museum objects (25 p. 65). But since DP and tensile strength are correlated, this means that DP can be used to infer mechanical properties of paintings, which is very good, since the sample needed for DP is smaller.

2.3.1.5- Relationship between DP and pH

Since an acidic pH is known to accelerate degradation of cellulose (30 p. 409), it makes sense to assume that lower pH samples will have lower DPs. Indeed, it has been found to be like this for paper (13 p. 205). In the case of paintings' canvas, where these two measurements have been done on historic samples (not that often so far), this has been indeed the case. In a study done by Bajocchi et al. (31 p. 96), two historic samples were measured for pH and DP: the one with the lower pH (3.0), also had a lower DP (175), whereas the one with the higher pH (5.2) it also had a higher DP (625).

In research studies on the degradation of cellulose, it has been seen that on ageing, pH and DP do correlate (32 p. 206). Therefore it has been suggested that further studying of this, could lead to an easier way of measuring the condition of a sample just by measuring the pH, since pH requires less amount of sample and it is easier to perform than DP analysis (32 p. 206). However, it has to be remembered that pH will tell us about the degradation rate (the more acidic the pH, the faster the degradation of cellulose will proceed), whereas DP tells us about the present condition of the material. Determining the object condition based only

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[3] Hydrocellulose is a substance obtained by partial hydrolysis of cellulose.

on pH could be misleading in real case scenarios: a low DP material could have been deacidified (on purpose or “by accident”, through contact with an alkaline material) and a high pH reading could lead us into thinking that the material is in a good condition, when in reality it is not. Or a material could have become suddenly more acidic than before for a very specific reason (contact with a very acidic material etc.), but chemical degradation would still not fully take place.

Therefore both pH and DP are of interest to know since they provide us with different information.

2.3.1.6- DP & paper

The DP of paper and its implications for its physical stability has long been studied, also in the cultural heritage field (20). Since its relationship with the mechanical strength of paper has been clearly identified (33 p. 415), many condition assessment studies of paper in the industry measure the DP to assess the mechanical stability (34), since determination of DP consumes a smaller sample than mechanical analysis (35 p. 80). For cultural heritage paper objects, though, this analysis is not routinely performed precisely due to the large sample needed, and this is why non-destructive techniques have been sought (36).

In a recent study done on forty linen papers from between the 15th and 18th C that had naturally aged until today, DP values were found to be from ~600 to 4,000 (13). The initial DP of rag papers can often be found to be around a DP value of 1,800, whereas that of paper produced from wood can be found to be around 2,500. Even if rag paper was produced from linen and hemp textiles, the initial DP of the formed sheet of paper is much lower than that of a paper produced from wood because the rags underwent a lot of beating and biodegradation in order to defiber the old textiles used to produce the paper. On ageing, however, papers produced from wood fibres, due to their lower pH, will see this DP value decrease at a faster rate than the rag papers, which sometimes will keep quite a high DP value until today (37).

2.3.1.7- DP & textiles / paintings

Since sample size is not a problem in the textile industry, the DP of textiles is often measured as a way to check the textile degradation stage and this is why standards on the technique exist.

The typical DP values of cellulose vary depending on its source (different plants produce cellulose with a different starting DP), the maturity of the plant, the processing method and the degradation of the fibres (9 p. 20). This is probably why one can find that the reported DP values for new non degraded cellulosic materials vary greatly depending on the bibliographic source consulted.

As already mentioned, according to T. P. Nevell, “native cellulose”, in general, can have a DP as high as 14,000 (5 p. 22). When native cellulose is processed and purified, however, these values can decrease to as much as 2,500 (5 p. 22).

According to the literature, the different fibres processed to be used in textiles have different typical DP values when new, but the ones used for canvases (cotton, linen, jute, hemp and ramie) usually have DP values between 2,100-3,000 (38 p. 258) (27 p. 312). Bleaching processes in linen can decrease it to as low as 1,200-1,300 (6 p. 30).

However, if we look at our own results for new textiles, we have found much higher values than the above ones reported in the literature: a new linen textile sample was found to have a DP value of 6,610 and a new cotton textile sample a DP value of 8,320 (see Chapter 4).

DP of the canvas support of easel paintings

Measuring the DP of the canvas support of easel paintings is an analysis very rarely performed and reported in the literature. This has to do mainly with the fact that the sample size needed, even if much smaller than that needed for mechanical tests, it is still too large for cultural heritage objects (30 mg of fibres). This is precisely one of the strengths of the present research, where about a hundred samples from different real paintings have had their DP measured through viscometry. This enabled us to see the typical values found in paintings, as well as the relationship between DP and other parameters such as pH, date and fibre type (see later on in this same Chapter).

G. Bajocchi et al. (31) reported two different DP values for two samples coming from two different areas of the same historic canvas, an old lining from a watercolour from the 18th C (pH measurements were also done on this sample, and this has already been discussed in Chapter 2.2). As already mentioned in this same chapter, one of the samples with a lower pH (3.9) had a DP of 175 (a very, very low value according to our experience), and the other sample with a higher pH (5.2), had a DP of 625 (31 p. 96). The authors also mention that the sample with the lower pH and DP had a darker colour, and that the sample with a higher pH and DP had a lighter colour. However, one should be careful to associate colour with DP since this can be misleading (37).

In a study by G. Scicolone et al. (39), where DP of textiles from paintings from the 16th, 17th and 18th C. was measured through viscometry, DP values obtained were respectively: 205, 590 and 1625 (39 p. 114). In this case we can see that the older the painting, the higher the DP value; although we don't know anything at all about the history of the paintings (if they were lined, which environment they had been kept in or not etc.). In another article appeared a year later and by authors from the same research group (1), it is stated that "some paintings from the 17th and 18th C show DP values of 750 and 500 and even lower". It is quite possible that this generalisation comes from the previously reported three measured values on real paintings in the first article mentioned at the begining of this paragraph (39).

Another painting of which its DP value has been measured and reported is a very interesting conservation project of a very large painting, *L'Industria* from the Galleria Vittorio Emanuele from Milan, (3.50 x 3.80 m) (40 p. 122). Only one DP measurement was done, probably due to the large amount of sample needed, although more would have been useful for such a big painting. The painting had several tears and the canvas was felt to be somewhat weak. The DP value was 239. (More information on the conservation decisions taken for this painting is given in Chapter 4 (Critical DP values for paintings in the literature)).

A large painting, "*La Crossifissione di Dro*" from the end of the 16th C (4.63 x 3 m), was found to have a DP value of 255, when this parameter was analysed (41). It has to be noted however, that the sample came from the centre of the linen canvas that was torn and where the paint layer had flaked off, so it was not protecting the canvas anymore. The authors comment that this particular area of the canvas had a darker colour and that it was clearly less sound mechanically than the rest of the painting. So it could be presumed that DP values were a bit higher in other areas of the painting (41 p. 17).

A more recent study on a 17th C painted cardboard stuck onto canvas, where the DP of the hemp canvas was measured, gave a higher value: 955 (42 p. 3). In contrast, the same group of researchers found that a newer painting (a cotton canvas from 1950) had a lower DP value of 580 (43 p. 6).

Studies exploring the degradation rates of linen and cotton textiles through the measurement of DP by viscometry and accelerated degradation have found that there is a first stage of degradation where this proceeds faster, and then a second stage were degradation happens at a slower rate. The DP point were the degradation rate decreases a lot was found to be around 350 (1). This means that a canvas with an already very low DP value, will maintain a similar DP for a very long period of time (27), whereas canvases with a higher DP can see it decrease more rapidly depending on the environment, and thus according to G. Scicolone, these should be the ones to take care of first since they would be the ones benefiting the most.

Of course, DP measurements are very localized and will tell us the condition of the canvas in a particular spot, which could be different from another area of the canvas, especially if the painting has suffered specific damage (water damage, for instance). It has been reported that DP differences between similarly looking areas of a painting can be of ±5% (44 p. 272)[4].

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[4] In this reference (44), the reader is directed to this other article for an explanation of this fact (±5% difference in DP in the same painting): (39), but there we could not find it explained.

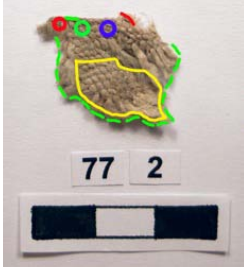
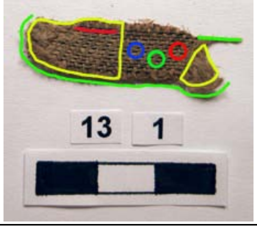
2.3.2- Method development for DP determination of painting canvases

2.3.2.1- Needed amount of sample

In accordance with the followed standard (45), about 30 mg of sample is needed for each measurement. If we were not dealing with cultural heritage material and more sample was available, we would take three sub-samples of the same sample so that three DP values were obtained to then an average would be done (that is we would take 90 mg of sample or more). In our case, since sampling of real paintings has to be limited to the minimum amount possible, only one DP value was obtained for each of the measured samples from the Reference Collection. However, each DP value obtained is the average of four to six efflux time measurements, which is how many measurements the 20 mL volume of solution usually allows for. Moreover, in our case it was not so much accuracy of the individual determinations that was looked for, but rather obtaining a broad survey on the DP of painting canvases.

Still, though, the first question we had to answer ourselves was “So, how large the sample coming from the canvas of an easel painting needs to be to end up with 30 mg of fibres?”. This is a difficult question because, as we realised with this research, it largely depends on the thickness of the threads, the tightness of the woven canvas and the presence or not of a priming layer more or less attached to the fibres that needs to be removed to avoid the clogging of the viscometer.

In the table below, the samples of which we ended up with 20-29 mg of fibres to do DP after cleaning and removing the priming layer have been selected. The sub-sample taken for DP measurement is marked in yellow, against a cm scale. They are ordered according to the “Reduction” coefficient, which is the result of the initial weight of the piece cut to do DP (“Piece for DP”) by the final weight of the fibres available to do DP (“Final DP fibres”). The larger this number, the larger the difference between the initial weight of the cut piece and the final weight of fibres. Of course, this difference tends to be smaller for bare canvases and larger when the sample has a thick preparation layer.

Sample name	Type of sample[5]	Image with the cut piece for DP in yellow	All sample (g)	Piece for DP (g)	Final DP fibres(g)	Reduction coefficient (Piece for DP/Final DP fibres)
77_2	Bare canvas		0.0648	0.0339	0.0264	1.2
13_1	Bare canvas		0.0714	0.0428	0.0296	1.4

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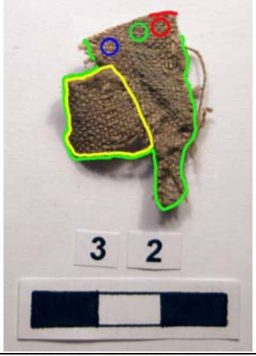
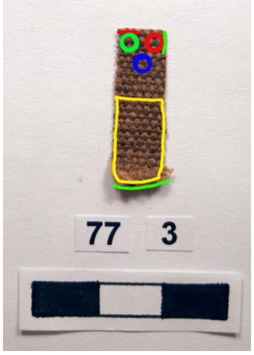
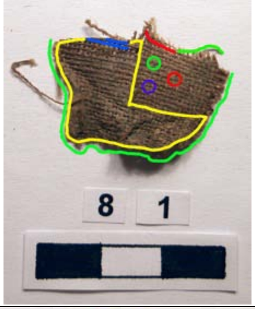
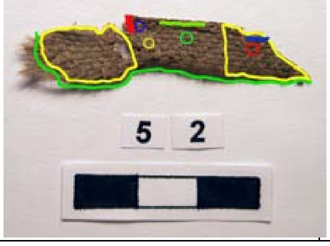
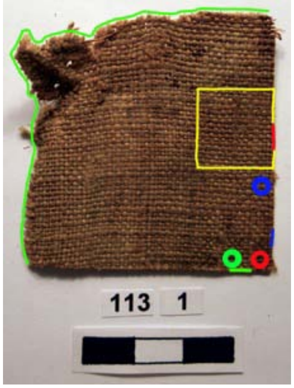
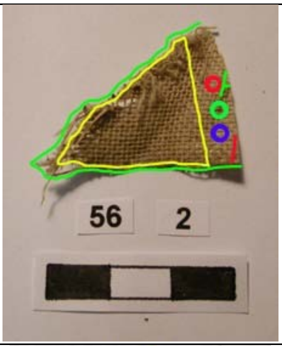
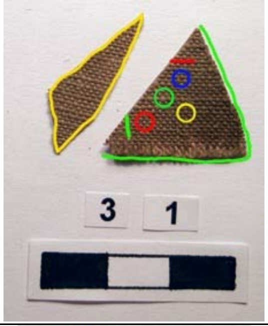
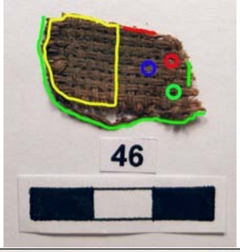
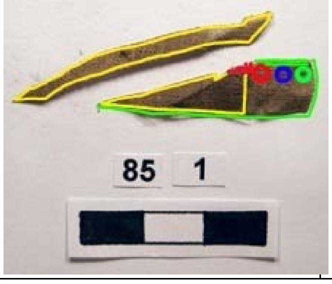
[5] Colours given to the different types of samples correspond to the following: yellow (bare canvas sample); orange (consolidated bare canvas); light blue (thin preparation layer); purple (thick preparation layer).

22_2	Bare canvas		0.1190	0.0340	0.0214	1.5
3_2	Bare canvas		0.1420	0.0480	0.0296	1.6
77_3	Thin preparation layer		0.0960	0.0423	0.0259	1.6
8_1	Bare canvas		0.0681	0.0495	0.0282	1.7
5_2	Bare canvas		0.0773	0.0438	0.0240	1.8

113_1	Consolidated bare canvas		0.9410	0.0610	0.0290	2.1
56_2	Thin preparation layer		0.0900	0.0635	0.0284	2.2
3_1	Thick preparation layer		0.1740	0.0580	0.0259	2.2
46	Thick preparation layer		0.1419	0.0641	0.0285	2.2
85_1	Thin preparation layer		0.0741	0.0581	0.0250	2.3

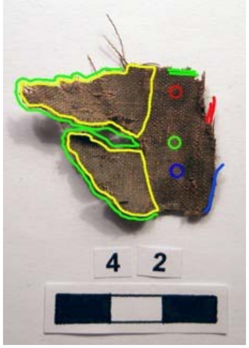
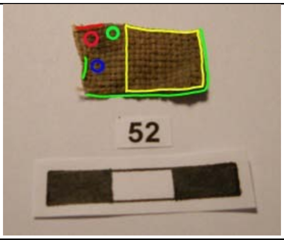
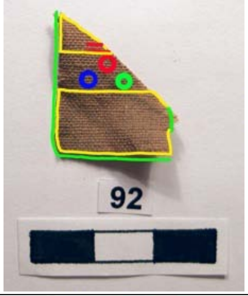
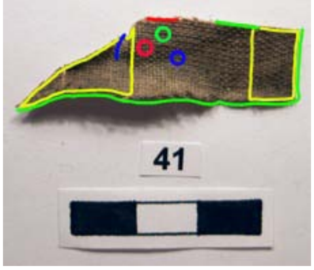
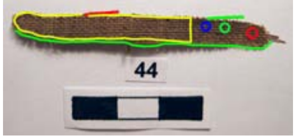
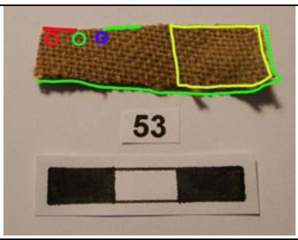
4_2	Bare canvas		0.1000	0.0506	0.0205	2.4
52	Thick preparation layer		0.1040	0.0670	0.0265	2.5
92	Thin preparation layer		0.0911	0.0608	0.0238	2.5
41	Thick preparation layer		0.2110	0.0872	0.0280	3.1
44	Thin preparation layer		0.0928	0.0699	0.0223	3.1
53	Thick preparation layer		0.2219	0.0894	0.0274	3.2

Figure 2. List of samples where the final amount of fibres available for DP analysis weighed between 20 and 29 mg. The images point out to the amount of original textile needed in different samples to end up with this amount of sample.

Looking at the surface area of the above samples (Figure 2), it can be said that ideally the minimum amount of sample from a painting to do viscometry measurements would have a surface of about 1 x 1.5 cm, so 1.5 cm^2. This was, for instance, the case of sample **53**, which is a tightly woven canvas with a thick preparation layer. The initial weight of the sample was 89 mg, and after removal of the preparation layer and cleaning, the final available sample for DP was 27 mg. If the sample had a more open weave or thinner threads, however, such as was the case of sample **8_1**, a slightly larger sample would be needed. For sample **8_1** the surface area used for DP has been estimated to be approximately about 2 cm^2. The initial weight of this piece was 68 mg and the final available amount offibres after cleaning was 28 mg.

Another important issue to take into account when taking a sample for DP, however, is the good or bad condition of the sample. If we look at the measurements taken with our viscometer we can indeed see that the good or bad condition of the sample has a very strong influence on the time the solution takes to pass through the viscometer (this is in fact the basis of the technique). The viscometer we were using had a blank time of 34.23 s (the average time 20 mL of the blank solution (solvent without any sample) would take to pass through). When 30 mg of sample were used, the effluent time for samples with lower DPs (300 to 1000) would be from 40-49 s. For samples with mid DPs (1000 to 3000), with 30 mg of sample, times would be 53-73 s. And for samples with higher DPs (3000 to 7000), again with 30 mg of sample, it could take up to 194 s for each measurement. This was clearly seen to give a very, very slow measurement, which took much longer, but more importantly decreased the measurement precision, since it if the solution goes down very slowly it is harder to press the clock button at the right time (imprecision is larger). Therefore, for very good condition samples, it is advised to reduce the sample weight, so that the effluent time is about 1 min (which is the ideal situation). It was concluded that for degraded textiles (300-1000 DP), the minimum amount needed was about 20 mg, better if we had 30 mg (measurements of bad condition samples have been done with as low as 10 mg, but then again, the solution goes through very fast and the precision of the measurement is lower (37)). However, if samples were in a better condition (1000-3000 DP), then about 15-20 mg were ok and if they were in a really good condition (DP>3000), just using about 10 mg is much better. Of course, we don't know the DP of a sample before measuring it, but with the experience gained after measuring the DP of several textiles, one can roughly class them into the broad categories proposed above.

As a conclusion, the surface area of a sample from a painting to be able to do DP viscometry would be between 1.5 and 2 cm^2. This would yield about 30 mg of fibres to run one DP measurement. For very good condition textiles (new modern ones), the size could be reduced to half or even less of this. Of course if sampling was not a problem (mock-up paintings etc.), then three times this size would be the ideal situation so that three replicate measurements can be done for each sample and the results averaged.

2.3.2.2- Cleaning the samples

The standard for industrial samples (45) calls for a regular washing treatment with petroleum ether and distilled water of the samples. For bast fibres it specifically calls for boiling the samples in a 1.5 mol/L sodium hydroxide solution for an hour, followed by neutralization with 0.1 mol/L acetic acid for 10 min and then rinsing it with distilled water until the sample has been neutralised. The newer version of this ISO norm, however, does not seem to call for this specific pre-treatment of bast fibres (46).

In the case of cultural heritage fibres, though, it has been reported that this sort of cleaning treatment, also advised for microscope sample preparation (47 p. 15), could be too damaging for already too weak samples and therefore discouraged (48 p. 56).

Since we had very particular samples (old textiles with preparation layer, glue paste lining remains, dirt etc, on it) we had to develop our own cleaning method. Several things were tested in order to be able to choose the best cleaning method for the Reference Sample Collection.

Sonication (S) vs. Double boiler (DB)

Sonication is a procedure by which samples are placed in an ultrasonic bath or sonicator where ultrasound is applied to the sample (10), which is placed in a vial with water inside a water bath. The aim was to test whether this procedure was better at cleaning the samples than just washing them in hot water in a double boiler for 10 min, which was thought could be a good way to solubilize any animal glue present in the samples.

Two different samples of which we had a larger amount, were selected to do the test. Sample **112** is a glue paste lining with "lots" of glue paste adhesive. Sample **110** is a sample with lots of preparation or oil paint layer attached to it. These two samples were chosen because they were seen to represent the different types of samples present in the Reference Collection: some with glue paste lining adhesive present, some with preparation layer. Sample **110** could also be seen to have more degraded fibres, while **112** presented a stronger condition, while still being an old canvas sample. Two 0.5 x 2 cm sub-samples from each ("a" and "b") were placed in 10 mL of hot water and left in it overnight.

The next day, "a" samples were sonicated in an ultrasonic bath for 10 min and "b" samples were put in a double boiler, with water outside of the sample boiling at 100 ºC, for 10 min.

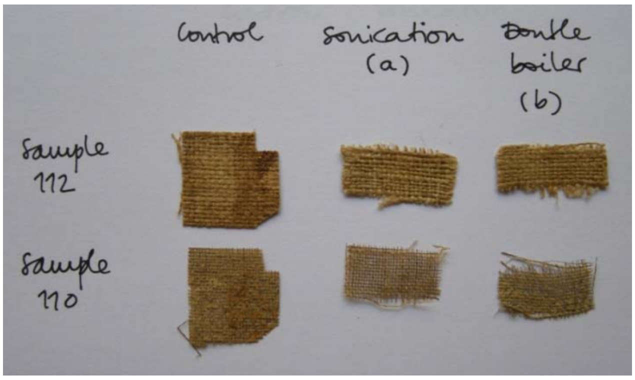


Figure 3. Visual evaluation of sonication versus double boiler for sample **112** and sample **110**.

In the case of sample **110**, sonication clearly worked much better: all the paint/preparation layer was removed. In the case of sample **112** (the glue paste lining), the result was similar with both methods, the one being treated with the double boiler seemed less stiff (indicating thus that more glue paste had been removed).

Combinations of Double boiler (DB) and Sonication (S)

Since the sonicated sample in the case of lining **110** was much cleaner (most of the preparation/paint layer present had gone) (see previous test), more tests were done combining the two procedures in different orders to see if this improved the cleaning results. 1 x 1 cm samples were cut, put in 10 mL of hot water in a glass vial and left in it overnight.

Sonication (S): samples were sonicated in a water bath for 10 min. (In the same water and vial they had been left overnight).

Double boiler (DB): samples were placed in a double boiler and were heated for 10 min. (In the same water and vial they had been left overnight).

S + DB and DB+S: the two procedures were done one after the other and with the sample in the same water.

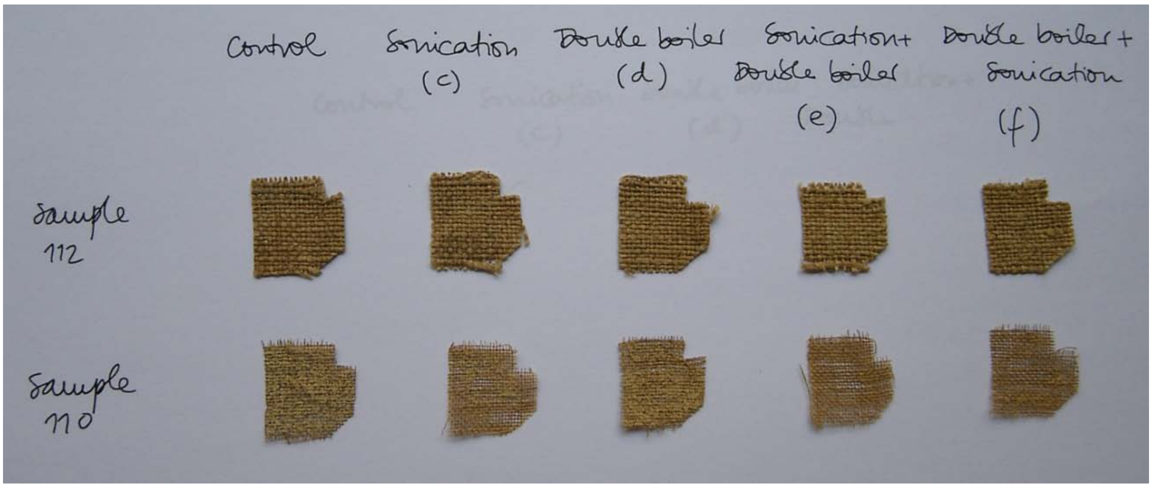


Figure 4. Visual evaluation of cleaning treatments: combination of Sonication and Double Boiler, on its own and one after the other.

Unexpectedly, no significant improvement of the technique was observed by doing the two procedures, Sonication (S) and Double Boiler (DB) one after the other, regardless of the order. Sonication, which was previously seen to be very effective for sample **110**, was not so effective this time. For this sample, just the Double Boiler produced very good results this time. For sample **112** the Double Boiler seemed again to be the one that worked the best.

In water overnight vs. not in water overnight

The previous test was repeated doing the same, just without leaving the samples in water overnight to see if this step was really necessary or if it could be avoided.

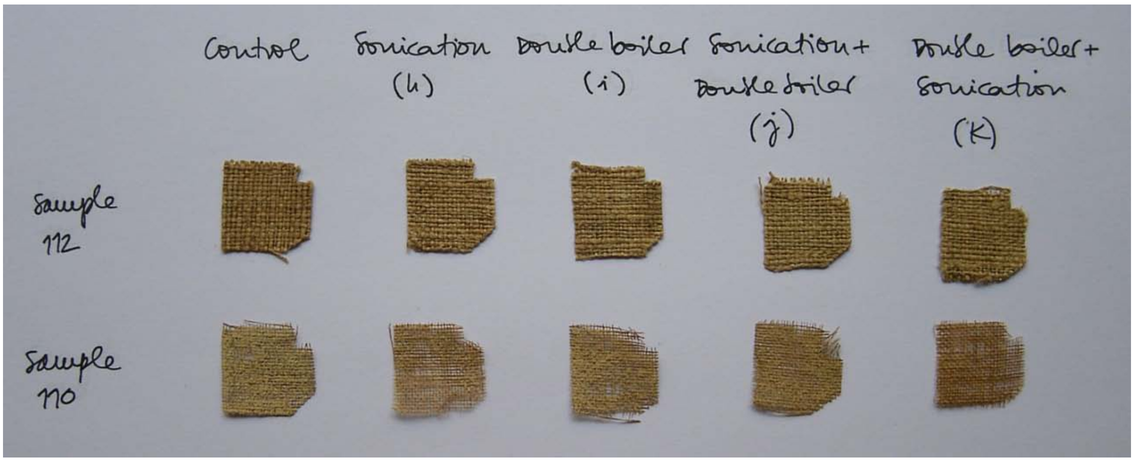


Figure 5. Visual evaluation of cleaning treatments: combination of Sonication and Double Boiler, on its own and one after the other, without having left the samples in water overnight.

Placing the samples in hot water and leaving them overnight (previous test), produced visually better results in all the cases than not doing so. It makes sense, indeed, that old animal glues present will be better removed if they have had more time to swell by being left in water overnight.

Sodium hydroxide solution

Another cleaning test called for in the literature (47 p. 15) for the washing of fibres to be looked under the microscope was tested to see if it was good for our samples.

Samples were placed in a glass vial with 10 mL of a 1% sodium hydroxide solution and then in a double boiler. They were heated for 10 min and then placed in distilled water and heated in a double boiler for 10 min.

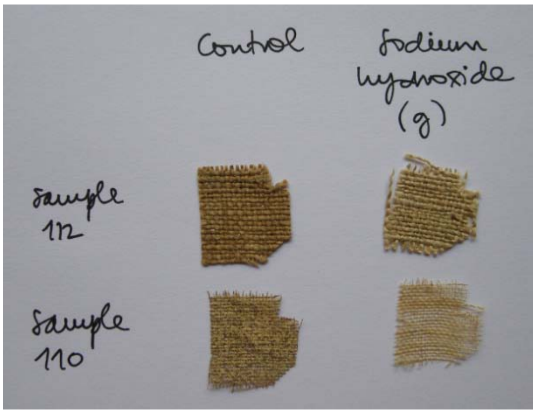


Figure 6. Visual evaluation of cleaning treatments: sodium hydroxide treatment for cleaning the samples.

These samples can clearly been seen to be the cleanest ones obtained of all, may be too much, since it can be seen that sample **110**, for instance, seems to have lost some of the fibres in the process (Figure 6). A significant colour change (lighter colour) can be seen both in sample **112** and sample **110** and the textiles seem more fragile.

Acetic acid (Vinegar)

Since some of the samples of which DP had to be measured had a preparation layer on it, a test with acetic acid (household vinegar, which typically contains 4-18% acetic acid by mass) was done to see if immersion in it would be helpful to remove the priming layer. There was the worry that preparation layer particles could be left in the mass of fibres and these could clog the viscometer. It was thought that an acetic acid treatment could dissolve the chalk present in the preparation layer and help in the cleaning procedure.

Five samples that contained different types of preparation layer were chosen and placed in household vinegar. The samples were visually evaluated after 1 h and after 24 h.

Samples	**1 h**	**24 h**
41	Did not dissolve	Not dissolved
54	Did not dissolve	Not dissolved
56_1	Dissolved	Dissolved
59	Did not dissolve	Not dissolved
96	Dissolved (bubbles)	Dissolved (glue layer left)

Figure 7. Table with the list of results of the priming layer dissolution test.

Figure 8. Vinegar test for sample **54**. This modern priming layer from the beginning of the 20th C is clearly not dissolved by the acetic acid: primer particles can be seen inside the glass vial.

Some of the preparation layers were dissolved by acetic acid (2 out of 5; samples **56_1** and **96**), but not all. Since it was not useful for all the types of preparation layers, and acetic acid could also be a potential source of further degradation of the canvas through acid-catalysed hydrolysis, it was decided to try to remove the solid particles manually and to run the first batch of about 30 DP measurements. It was seen that there were no problems with clogging the viscometer (solutions were run in all cases at least three times and efflux times were very similar in the three runs). Therefore it was decided to continue to remove the preparation layer just by manually cleaning the samples, which is also the safest way to do it when it comes to possible DP decrease during cleaning.

Cleaning method chosen

Sonication did not seem to improve the cleanliness of samples significantly (although in one case it produced good results). No improvement was achieved with 10 min sonication first and 10 min heating in the double boiler or the other way around. Cleaning with a 1% sodium hydroxide solution seemed to be too harsh for degraded canvas samples (the same appeared to have been discoloured and to have lost some of the fibre material). Leaving the samples in water overnight was seen to give good results as was placing them in the double boiler for 10 min. Therefore, of all the cleaning methods tested, the one finally chosen was to place the samples in 10 mL of hot water in a glass vial and leave it overnight to cool down. The next day, the vial was placed in a double boiler and when the water of the double boiler started boiling, 10 min were timed. Then the sample was removed and it could either be left to dry on a filter paper with a paper towel underneath or the fibres could be defibered with long needles in the wet state. The latter was felt to be easier to do than the former.

Nonetheless, DP was measured for pieces of sample **112** cleaned in these various ways to determine if the method chosen on what visually seemed to be the best option, was corroborated by DP measurements. (See later on in this same chapter, the section Evaluation of sample cleaning procedures)

2.3.2.3- Sample defibering

Once the samples were clean but still wet, they were placed on a concave hourglass dish with some drops of distilled water. With two long needles with handles, they were defibered completely, as the ISO standard requires (no cutting sharp object such as scissors should be used in this process) (46 p. 6). Any solid particles were removed with fine tweezers. This was a labour-intensive process that took more or less time depending on the condition of the sample, the thickness of the threads and the presence of extraneous materials or not (sometimes it took up to 2 h).

Then the samples were placed on top of a filter paper and left to dry out completely, to subsequently put them in a labeled plastic bag until measurement took place.

2.3.2.4- Viscometry

Viscometry measurements are quite time consuming (especially the process of dissolution). As an average, each day it was possible to measure only nine samples. The regular procedure followed each day was as follows.

The bags of samples to be measured had been left open in the lab the previous day, so that they reached an equilibrium with the environment and they all had the equilibrium moisture content, usually about 5% for cellulosic materials. They were then weighted with a precision scale. As mentioned earlier, depending on the condition of the sample, more or less of it was taken: between 10 and 30 mg.

Since the weight of each sample is taken into account in its DP calculation it does not matter if sample masses are different, they just need to be noted down, but 5 figures precision are needed (e.g. 0.02944 g or 29.44 mg).

The weighted samples were placed in completely dry bottles (so that no added drops of water which are not accounted for are present) and a few copper wire pieces of about 2 mm thick were put in the bottle to help defibre the samples through shaking (Figure 9). 10 mL of distilled water were poured into each bottle and the caps were secured. The number of the sample was written with a permanent pen both on the cap and the body of the bottle.

Figure 9. Glass bottles with samples already in and small pieces of copper wire to defibre the samples. Water is added and the solutions shaken for as long as needed to achieve this.

Then samples were shaken until completely defibred meaning that not a single knot of fibres could be seen. This is checked by looking at the solution against a light source, and can take just a few minutes for very degraded samples, and up to 2 h for good condition textiles!

Once the six samples that could go into the water bath were completely defibred (the water bath has six spots), 10 mL of 1 mol/L cupriethylenediamine solution (or copper(II) ethylenediamine, CED) was added to each bottle. CED is easily precipitated by CO_2, and therefore this had to be replaced with nitrogen both in the solvent original bottle and in our sample solution bottles by purging nitrogen gas for a while and then quickly securing the cap again. Then the samples were shaken until no solid fibre particles could be seen on the wall of the bottle.

It has been reported in the literature that in the case of measuring canvas samples from paintings, there is usually some “hard solid remains” that will not dissolve with the CED solution (6 p. 28). However, we did not encounter this problem for any of the measured samples.

Once CED had been added, samples had to be measured relatively soon afterwards (1 or 2 h maximum) because if too much time was left to go by, this could start degrading the sample and give wrong results.

Since viscometry is temperature dependent, solutions had to be pre-conditioned to 25ºC before running the measurement. Once the water bath had a temperature of 25.0ºC +/- 0.1ºC, the six bottles were placed in it and left for at least 15 min.

Each day, before starting viscometry measurements, a blank solution was run several times (five or more). The blank solution should give similar results as the efflux time given by the manufacturer of the particular viscometer (34.23 s in our case), but each day conditions can vary a little and give slightly different blank times, which will be taken into account in the DP calculation. In our case, on different days, we got values that went from 33.36 to 34.38 s. Doing this was also a way to make sure that everything was working properly.

To actually do the measurement, once the sample solution was ready, the sample solution was pulled through the viscometer with a pump (Figure 10). To do this, a glass piece that fits both the lower part of the viscometer and the top part of the glass bottles where the solution is, is needed. Then the solution was left to run paying attention to the moment the top of the solution passed the first mark in the viscometer, the moment at which the chronometer was started. The solution was observed until it reached the second mark and the chronometer was stopped. The time in seconds with two decimals was noted down. The used solution was discarded and a new run from the same 20 mL solution was done. Usually at least four runs could be done with 20 mL.

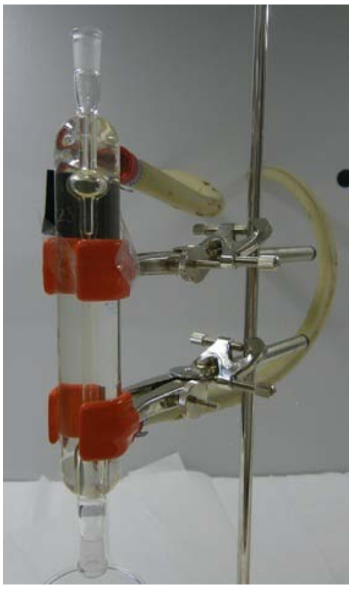
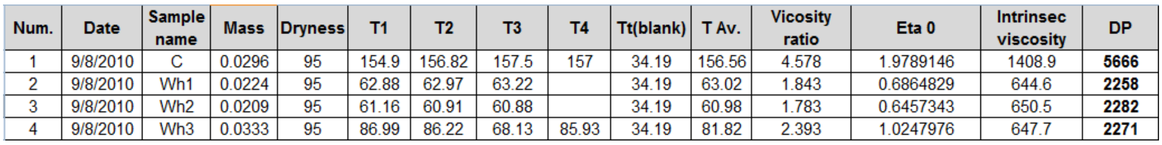


Figure 10. Glass viscometer used. Water kept at 25ºC coming from the nearby water-bath is constantly circulating around the capillary tube where the measured is pulled up, so that its temperature is constant.

If the procedure had to be stopped at some point, clean distilled water was used to clean the viscometer. At the end of the day, a solution of 1% HCl was used for cleaning, and the viscometer was rinsed with distilled water after it.

Obtaining the DP value

As explained in the introduction of this chapter, viscometry measurements give us the intrinsic viscosity of the solution measured. DP has to be then calculated. In order to calculate these two values, an *Excel* macro spreadsheet was used (Figure 11), so that just by entering the different parameters, DP would automatically be calculated.



Num.	Date	Sample name	Mass	Dryness	T1	T2	T3	T4	Tt(blank)	T Av.	Vicosity ratio	Eta 0	Intrinsec viscosity	DP
1	9/8/2010	C	0.0296	95	154.9	156.82	157.5	157	34.19	156.56	4.578	1.9789146	1408.9	**5666**
2	9/8/2010	Wh1	0.0224	95	62.88	62.97	63.22		34.19	63.02	1.843	0.6864829	644.6	**2258**
3	9/8/2010	Wh2	0.0209	95	61.16	60.91	60.88		34.19	60.98	1.783	0.6457343	650.5	**2282**
4	9/8/2010	Wh3	0.0333	95	86.99	86.22	68.13	85.93	34.19	81.82	2.393	1.0247976	647.7	**2271**

Figure 11.*Excel* spreadsheet DP calculations for the first four measured samples

The parameters that needed to be entered into the *Excel* for each measurement were: the weight of the sample (mass in g), the average efflux time of the four or more times the sample solution was run (T1, T2, T3 and T4, in s), the dryness of the sample (Dryness, in %) and the average efflux time of the blank solution run at the beginning of each measuring day (T($_{\text{blank}}$)).

When entering all this data, the average efflux time of all the sample measurements (T Av.), the viscosity ratio (T Av./T(blank); the Intrinsic viscosity (calculated by applying the Wetzel-Elliot-Martin's equation (20 p. 30)) and the DP value (through the Evans and Wallis equation (20 p. 31)) were calculated.

Dryness issue

According to the ISO standard (45) the dryness of the sample should be calculated for each sample by exposing it for 3 h to 105 ºC and measuring the mass again. However, for cultural material samples we do not have enough sample available to make this measurement. Therefore, a 5% of water is assumed to be in the sample and therefore a 95% is entered for all the samples. They had all been preconditioned to a 50% RH environment and therefore this assumption is thought to be true since it is known that at the usual ambient conditions (40-60% RH) the cellulose fibre will have an average water content of usually 3-5% (49 p. 33).

2.3.2.5- Evaluation of the method using Whatman paper

Whatman filter paper was measured six times in order to know what was the uncertainty of results. The results obtained aresummarised in the following table:

Measurement number[6]	Sample name	DP[7]	Average DP	SD	RSD[8]
2	Wh1	2258			
3	Wh2	2282			
4	Wh3	2271			
5	Wh1	2415[9]			
6	Wh2	2290			
7	Wh3	2281	2276	12	0.54%

Figure 12. Evaluation of viscometric measurements of Whatman paper.

One of the measurements (number 5) was not taken into account because the DP value was too far away from the others, and so we assumed that something went wrong with this measurement (wrong mass, something clogged the viscometer, there was a bubble of air etc.). The relative standard deviation (RSD) for the five remaining measurements is 0.54% which is very good since this proves that the technique is consistent and working properly.

2.3.2.6- Evaluation of the method using historical samples

Whatman paper is very homogeneous and a small RSD is expected. Historical samples can be very heterogeneous and thus the method developed had to be tested on this type of samples to see which was the RSD obtained to establish if the method was a solid one and worked for our aged easel paintings support samples too.

Three sub-samples were taken from different areas (MD1; MD2; MD3) of the same old glue paste lining (**112**) (Figure 22). They were prepared in the regular way (cleaning with 10 min in the double boiler etc.) and three different solutions were prepared from each one. DP was measured and averages, SD and RSD calculated.

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[6] Each measurement done was given a number and a name ("Sample name"). This has been added here only so that future checks can be done, if needed, with the original handwritten notes and *Excel.* Measurements start with number 2, since number 1 was just a measurement done to learn the technique and it is not reported here.

[7] All DP decimals have been removed everywhere to make work less cumbersome and because so much precision is not possible.

[8] The Relative Standard Deviation is the SD/Average (in %). With the SD you get the variability of your method in the measured units, whereas with the Relative Standard Deviation, you get the variability in %. RSD is better to be used when one wants to compare variability between different unit scales or when the mean of the experiments to compare is very different among them. Since this (comparing values with very different means) is easier to happen with large values, such as the ones encountered when measuring DP, RSD is often used to check the variability found in DP tests. As with the SD, the smaller the number, the more precise the method (see the section "The concepts of Standard deviation and Relative standard deviation" in Chapter 2.2).

[9] This measurement was not taken into account in the calculations because it was considered to be an outlier.

Measurement number	Sample name	DP	Average DP	SD	RSD
8	MD1-1	605			
11	MD1-2	726[10]			
12	MD1-3	608	607	2	0.3%
9	MD2-1	689			
13	MD2-2	755			
14	MD2-3	731	725	33	4.6%
10	MD3-1	696			
15	MD3-2	742			
16	MD3-3	702	713	25	3.5%

Figure 13. DP average results and SD and RSD for three sub-samples from different areas from the same old glue paste lining (**112**).

The RSD of the three measurements for each sub-sample goes from 0.3% to 4.6% (Figure 13). As expected, this value is higher than the Whatman paper tests done (RSD 0.54%), but still are very acceptable. With this test, it is concluded that our method can be successfully applied to historic canvas samples.

2.3.2.7- Evaluation of sample cleaning procedures

Cleaning the samples to be prepared for DP measurements by leaving them in water overnight and then putting them in the double boiler for 10 min had been the chosen method based on the cleaning tests previously done. However, we wanted to measure the DP of the same sample (old glue paste lining **112**) cleaned in three different ways to see if a significant difference in DP could be seen. To this end, one sample (MD1) was cleaned in the regular way (10 min in the double boiler after overnight soaking in water), the other one (MD4) was not cleaned at all and the third one (MD5) was cleaned with sodium hydroxide washing procedure to see if there was a significant decrease in DP or not. The three sub-samples came from a nearby area (Figure 14).

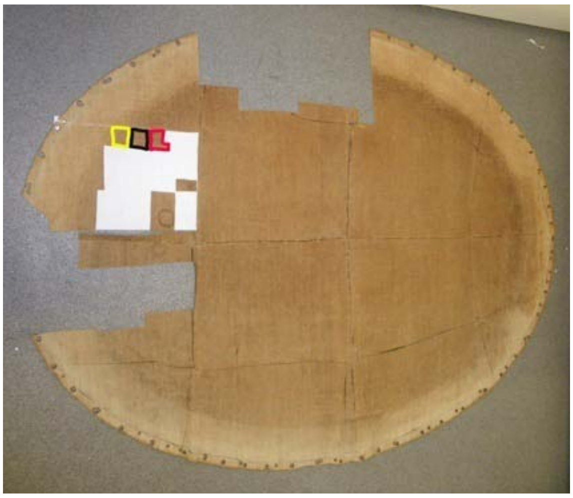

Figure 14. Locations where the sub-samples used for evaluation of sample cleaning procedures come from the old glue lining **112**: MD-1 (red); MD-4 (black); MD-5 (yellow).

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[10] This second measurement was not taken into account, as it was considered to be an outlier.

Measurement number	Sample name	Cleaning procedure	DP	Average DP	SD	RSD
99	MD4	Not washed at all (all glue present)	619			
8, 11, 12	MD1-1, MD1-2, MD1-3	Left in water overnight and 10 min in the double boiler.	607[11]	613	9	1.4%

Figure 15. Comparison between DP for the sample not washed at all and the sample washed with the double boiler.

Measurement number	Sample name	Cleaning procedure	DP	Average DP	SD	RSD
8, 11, 12	MD1-1, MD1-2, MD1-3	Left in water overnight and 10 min in the double boiler.	607[12]			
101	MD5	Left in water overnight and then boiling 10 min in sodium hydroxide and then 10 min in distilled water.	728	667	86	13 %

Figure 16. Comparison between the DP of the sample not washed at all and the sample washed with sodium hydroxide.

Regarding the washing of samples or not washing them at all (Figure 15), it can be seen that the difference between the two results is very small (smaller than the RSD), so in this case washing had no impact on the final DP, which is interesting because this sample had quite a lot of glue.

Regarding cleaning with sodium hydroxide 1% solution for 10 min (Figure 16), the sample treated this way, has a higher DP than the regularly washed sample. The difference between the regular washing procedure and the sodium hydroxide procedure is in this case much higher, however, it is still within one SD. Therefore, treating the samples with sodium hydroxide seems to have an effect, although it was expected that it would in the other direction: that DP would be lower because the sodium hydroxide treatment might have already broken some cellulose links. The sodium hydroxide treatment is actually recommended in the standard for bast fibres so that lignin is dissolved (45), and this maybe could explain the difference in DP in the sense that may be the regularly washed sample has some lignin present that skews our DP values a bit. Another explanation could be that low molecular weight material is washed away by the sodium hydroxide treatment, since samples treated in this way were seen to be lighter (Figure 6).

However, it has to be taken into account that many more measurements should be done to be able to draw more statistically significant conclusions on the effect of the cleaning method and the DP obtained. Seeing the results, it was decided to go on cleaning the samples for DP measurement by leaving the samples in water overnight and then 10 min in the double boiler.

2.3.2.8- Evaluation of defibering by hand and using a mortar

Unravelling the woven textile into fibres manually with the long needles is very time consuming when it comes to textile fibres: it takes about 2 h for each sample. Also if the textile is in good condition, the

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[11] Average DP of two measurements. The third one (MD1-2) was considered to be an outlier.
[12] Average DP of two measurements. The third one (MD1-2) was considered to be an outlier.

defibering process before measuring DP inside a glass flask with water and copper wires, can take an extremely long time of shaking (half an hour for the average original canvas sample, up to 2.5 h for very new textiles). This happened for instance for sample A1 from the Condition Assessment Panel (see Chapter 4 later on). At the end of this long shaking process of sample A1, copper particles could be seen at the bottom of the bottle (Figure 17). Although this should not be a problem, because only the top part of the solution is pulled up and used, shaking for so long for just one sample is too time consuming and if it has to be done for several samples there is a serious risk of suffering wrist injuries. This is why another method of sample preparation was tested, to improve the method for future projects.

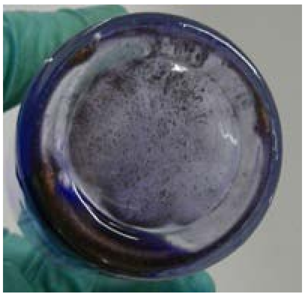

Figure 17. Copper particles left at the bottom of a measuring flask accumulated due to the long period of shaking of sample A1 (about 2 h), a sample in very good condition.

To do this test, the sample was placed in a small mortar with some drops of water and it was crushed with the pestle (Figure 18). When the mass was seen to be homogeneous and the threads were entirely defibred, the sample was ready to be left to dry. The crushing took very little time (a few minutes) and so sample time preparation was drastically reduced.

Figure 18. Mortar and pestle used and some of the samples tested.

To test this new procedure, a sample (D23-1) from a good condition old household textile (**129**) was taken and prepared the regular way (manual defibering). Three other samples of this textile were taken and prepared with the pestle and mortar (D23-2; D23-3; D23-4). On top of taking much less time than manual defibering, samples prepared this way took drastically less time too to prepare with the subsequent defibration in a measurement flask with copper wires.

Measurement number	Sample	DP	Average DP Mortar
102	D23-1 (Regular)	1378	
112	D-23-2 (Mortar)	1380	
113	D-23-3 (Mortar)	1802[13]	
114	D-23-4 (Mortar)	1443	1412

Figure 19. Testing the method of defibering samples with a mortar against the regular manual method with needles on sample D-23

The difference was found to be 33 DP units (~2.4%), which is less than the typical measurement uncertainty for DP determination of canvases (Fig. 13). It can be concluded that sample preparation with a mortar does not lead to any significant degradation. Sample preparation using the mortar is seen as a very good option since results are similar to those obtained with the regular procedure and the time used is drastically reduced. (It has to be taken into account that sample preparation by hand defibering is the most time consuming part of the process of measuring DP).

In order to test this new procedure with a different sample, it was also tested on the sample A1 from the Condition Assessment Panel (see Chapter 4). This sample had already been measured after preparation with the regular defibering procedure and it was now prepared with the new mortar tool.

Measurement number	Sample	DP	Average DP Mortar
71	A1-1	6614	
88	A1-2 (Mortar)	7279	
105	A1-3 (Mortar)	7183	7231

Figure 20. Testing the mortar new method of defibering samples against the regular manual method with needles on sample A-1

It has to be said that the extremely lengthy times needed for measurement number 71 (it took more than 3 min for the solution to go through the viscometer since 30 mg were taken and the sample was in very good condition), make the accuracy of this particular measurement doubtful. In any case, it can again be seen that the mortar-prepared samples, contrary to the expectations, led to a higher DP value and therefore the sample seems not to be further degraded by the mortar new preparation method. The difference is 617 DP units, which is 9.3% in this case, so higher than the typical measurement uncertainty.

To conclude, although more comparative measurements would need to be done, especially with samples of a different condition (good and bad), mortar sample preparation could be a very interesting future avenue of research in order to drastically reduce textile sample preparation time for DP measurement.

In this thesis, however, most of the samples were prepared by manual defibering, since this mortar test was done towards the end of the experimental phase and since the traditional method was seen as reliable. The samples that were prepared using a mortar are A1, A2, H2 and D23, all from the Condition Assessment Panel (see Chapter 4), which were also the ones in the best condition and thus suspected to need long sample preparation times.

2.3.2.9- Heterogeneity of a new canvas

To test the possible heterogeneity of new canvas, samples from three distant locations ("1", "2aZ" and "3aZ") were taken from a brand new linen textile (non-aged) named "A1" used for the Condition Assessment Panel (see Chapter 4). From the first location ("1"), two samples were prepared (A1-2 and A1-3). All the samples were prepared using the new mortar sample preparation procedure in this case, since these were

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[13] This measurement was not taken into account, because it was suspected to be an outlier.

very good condition samples and only about 10 mg of each was used for measurements for the same reason.

Measurement number	Sample	DP	verage DP for A1	Average DP	SD	RSD
88	A1-2 (M)	7279				
105	A1-3 (M)	7183	7231			
116	A1-2aZ (M)	7319				
117	A1-3aZ (M)	6937		7162	200	2.8 %

Figure 21. Testing the heterogeneity of new canvas on sample A1

From these measurements it can be seen that variability for new textiles, as expected, is not high, with 2.8% RSD for samples from different locations.

2.3.2.10- Heterogeneity of historical samples

The possible heterogeneity of historical samples was tested using again the old glue paste lining **112**. To do this, three samples (MD1; MD2; MD3) were taken from very distant locations, all from the darker area of the canvas, though (the exposed centre of the painting). Samples were, visually, in a similar condition.

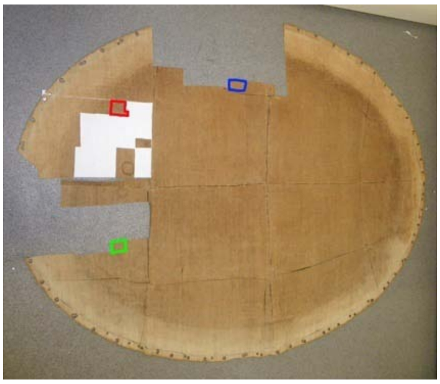

Figure 22.Sampling locations for the three sub-samples of the old glue paste lining **112**: MD-1 (red); MD-2 (blue) and MD-3 (green).

Measurement number	Sample name	DP	Average per location	Average	SD	RSD
8	MD1-1	605				
11	MD1-2	726				
12	MD1-3	608	646			
9	MD2-1	689				
13	MD2-2	755				
14	MD2-3	731	725			
10	MD3-1	696				
15	MD3-2	742				
16	MD3-3	702	713	694	54	7.8%

Figure 23. Results for three distant samples from the old glue paste lining **112**.

In this case the RSD for all three sets of measurements was 7.8% (SD being 54). As expected, it was higher than the RSD for Whatman paper (0.54%) and much higher too than that for new linen (2.8%). This value has to be taken into account went working with the DP values obtained for our Reference Sample Collection, which come from only one area of the painting. In this test case, the samples came from distant areas but they looked similar in condition to the human eye. These values mean that if for instance, a painting has a DP value of 600 in one area, in other areas, if they look similar, in two thirds of the cases (68%), these areas could have DP values that could be between 545 and 665 (± 1SD). In paintings, we can also find areas of apparently very different condition, especially if the painting has suffered localized damage, such as water damage or similar. In these cases the differences would be expected to be even higher (see this particular case in the section “Two samples from the same painting with visually different conditions” later on in this same chapter).

As already mentioned, according to G. Scicolone, DP differences between similar areas can be of ±5% (44 p. 272). Not being explicitly mentioned, we understand it is meant that variability is within this range for similarly looking areas.

2.3.3- Results and discussion

2.3.3.1- DP of the Reference Sample Collection

Viscometric DP measurements take much longer to do than cold extraction pH measurements. Both sample preparation and the measurement itself are quite time consuming. On top of this, the required equipment is also more difficult to have access to. Therefore, the number of samples of the Reference Collection that had their DP analysed was smaller. A total of 95 samples had DP analysed, against a total of 186 that had pH analysed. To analyse these 95 samples through viscometry took the time of one person working full time for about two months to do the laborious sample preparation, and about one month to do all the viscometric measurements.

The average DP value we got, if we take into account all the samples is 1167 (SD 962, RSD 82%). We see therefore that we have quite a big spread of values. However, if we only look at the samples that are from paintings (leaving out linings and non-historic samples), this value decreases to 1082 (SD 566, RSD 52%). If we only take the linings it is 818 (SD 402, RSD 49%). Therefore it can be said that in general we found that linings have lower DP than paintings.

The minimum DP value obtained for a real historic painting was 414 (**29_O**, a painting from the 17th C. with a glue paste lining) and the maximum was 4151 (**120**, a 20th C. painting). For linings, the minimum value obtained was 485 (**117_1**, a loose lining (no glue paste present) and the maximum 2136 (**103**, an old glue paste lining)). In the case of the minimum DP value obtained for linings, it is interesting to note that actually the two lowest values obtained are from two loose linings (**117_1** and **116_2**) that do not have glue paste lining on them but that come from two paintings from the Tate Gallery in London (see the section “Darker and lighter areas of the same canvas” later on in this same chapter). They could therefore be showing the degradation effects due to air pollution, which is known to have been a problem in London (50).

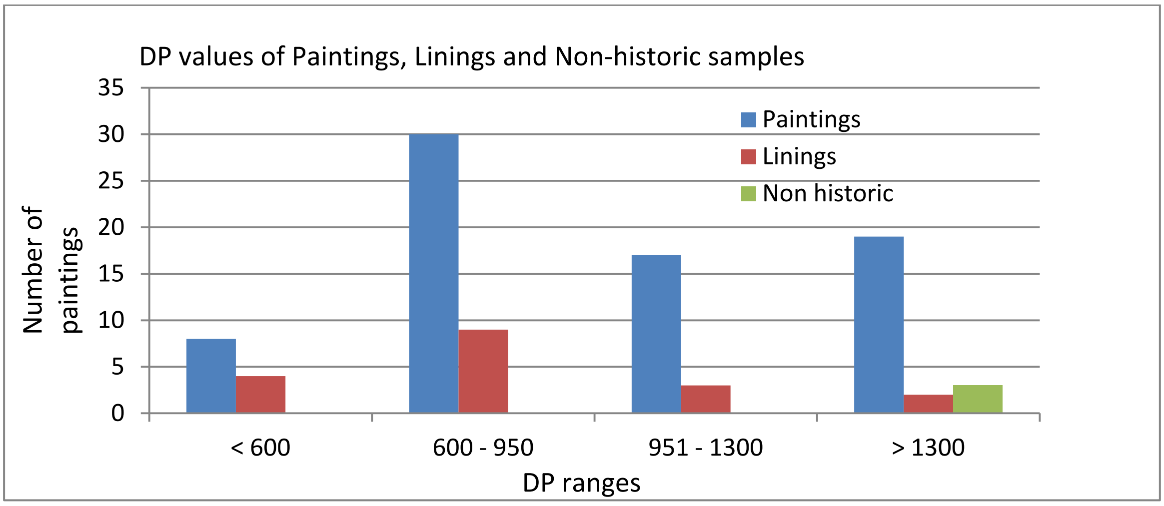

Figure 24. Graph showing the DP values obtained according to four DP ranges, for paintings, linings and non-historic samples.

In Figure 24 it can be visually seen that linings are mainly in the DP ranges <600 and 600-950, so again, on top of having lower pH values, linings also have lower DP values. Most of the paintings are seen to have DP values between 600-950 (40%), and the number that have DP values below 600 is the smallest one (11%), which indicates that most of our samples are not yet in the most degraded state. Nonetheless, we have 63% of paintings that have DP values between 600 and 1300, so they are indeed degraded to some extent compared with the values that they could have had originally ("native cellulose" can have a DP of as high as 14,000 that can already go down to 2,500 when processed and purified (5 p. 22). New linen measured for this thesis was found to have a DP of 6,614 and new cotton 8,310. See Chapter 4) . Non-historic samples, some of them being newer textiles, are all in the better condition range >1300.

2.3.3.2- DP and date

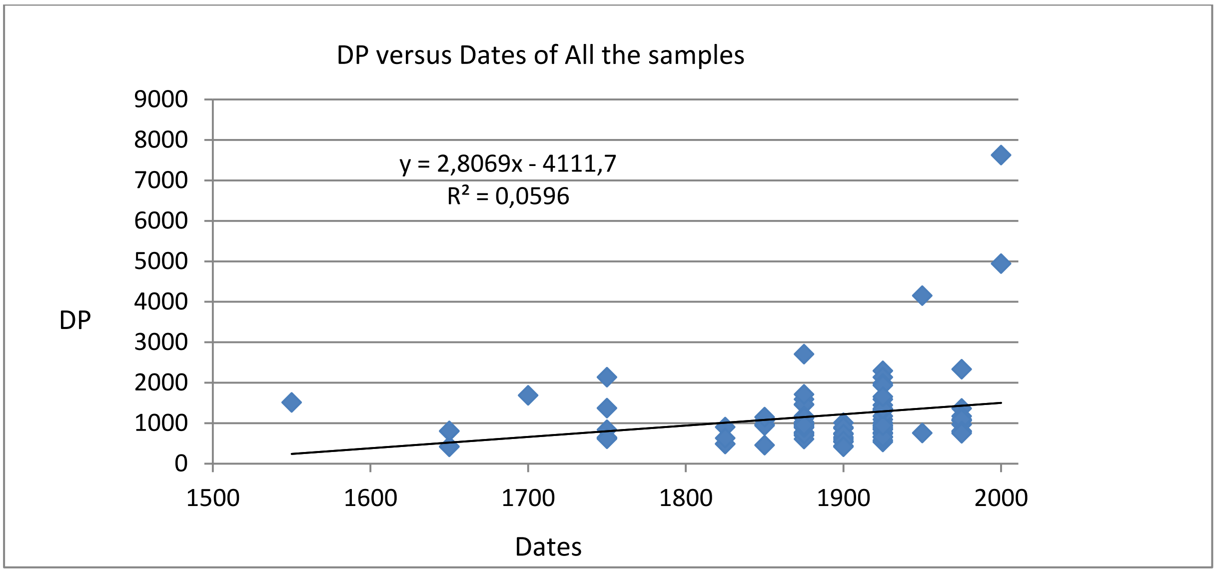

Figure 25.DP vs.date for all the samples. There is a very slight correlation between the two parameters.

As was the case for pH, no correlation was found between DP and the age of the samples: there are low DP samples of any age. Of the few older samples available, some had really high values, despite the many centuries these samples have survived. Of the three old samples that had very good pH values (between 6.5 and 7.5), two of them had their DP analysed and the values obtained were very good too: 1512 (**94**) and 1687 (**80**). These samples also felt in a better condition when handling them.

As it was found in the literature, DP and date are not necessarily correlated and thus DP could not be a way of dating paintings, since DP has a lot to do with the environment in which a painting has been, and as we have also seen, much older samples can have higher DP values if they have been conserved in a good environment (44 p. 265).

2.3.3.3- DP and fibre type

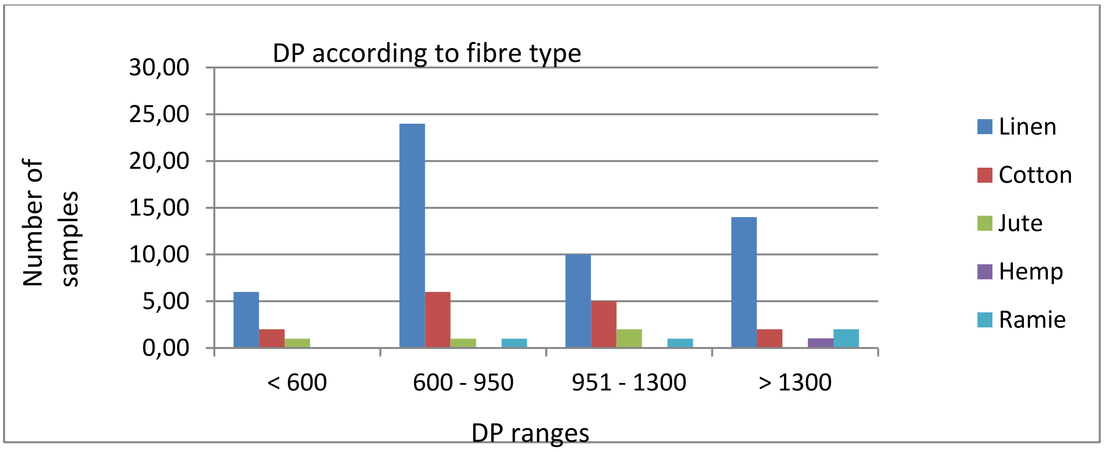

Figure 26. DP of paintings according to fibre type

Deacidified samples and non-historic samples have been removed, so Figure 26 shows DP of paintings and linings according to fibre type.The average DP for linen fibres is 1094 (SD 631; RSD 31%), whereas the average DP for cotton paintings is 899 (SD 266, RSD 30%). It is interesting to note that while cotton samples had, in average, a higher pH, when it comes to DP, this is lower. This could maybe be accounted for the fact that cotton is more sensitive to degradation than linen is (27 p. 313). Surprisingly, the average DP for jute (869, SD 273, RSD 31%) was not as low as expected, although it is indeed the fibre with the lowest average. Ramie had an average DP of 1408 and hemp of 1321. But again, like in the case of pH, there were too few hemp, ramie and jute samples to draw reliable conclusions. In any case, DP seems not to be as directly correlated with fibre type as pH seemed to be (jute having lower pH values, cotton having higher ones).

The curious case of sample 68 (a cotton and jute canvas)

Sample **68** came from a canvas that had threads in one sense made of cotton and threads in the other direction of jute (Figure 27). Since there was a large sample available in this case, the canvas was carefully unwoven separating the two types of threads and DP was measured for each type of thread. When preparing the two samples for DP measurement, the jute sample felt more brittle and broke much more easily, so a lower DP was expected. Surprisingly both DP values were very similar: the brown jute thread being 521, and the cotton thread being 547. An explanation to this could be the fact that cotton, being more easily degraded (9 p. 11), suffered from being next to a more acidic fibre (due to the higher lignin content (51 p. 33)). In fact, the average pH of the cotton thread was found to be 5.2 and the average pH of the jute thread was found to be 4.6, so indeed jute threads were more acidic and this could have both degraded the jute threads and the neighbouring cotton threads.

This situation is actually not that different from the other cotton/jute canvas encountered in our Reference Sample Collection (sample 51), where the painting had suffered tears, contrary to expectations, corresponded to the cotton threads breaking up (and not the jute ones) (this has already been explained in

Chapter 2.1). In this case, probably the more sensitive cotton thread is currently more degraded than the jute one and this is why these are the threads breaking apart.

The brittleness of the jute fibre encountered when unweaving sample 68 could be related to the higher rigidity characteristic of this fibre (due to a higher lignin content).

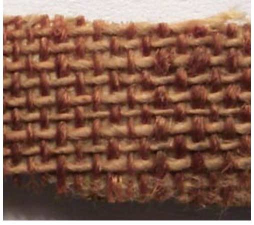

Figure 27. Sample 68: jute threads can be seen to run vertically, cotton threads run horizontally.

2.3.3.4- DP and pH

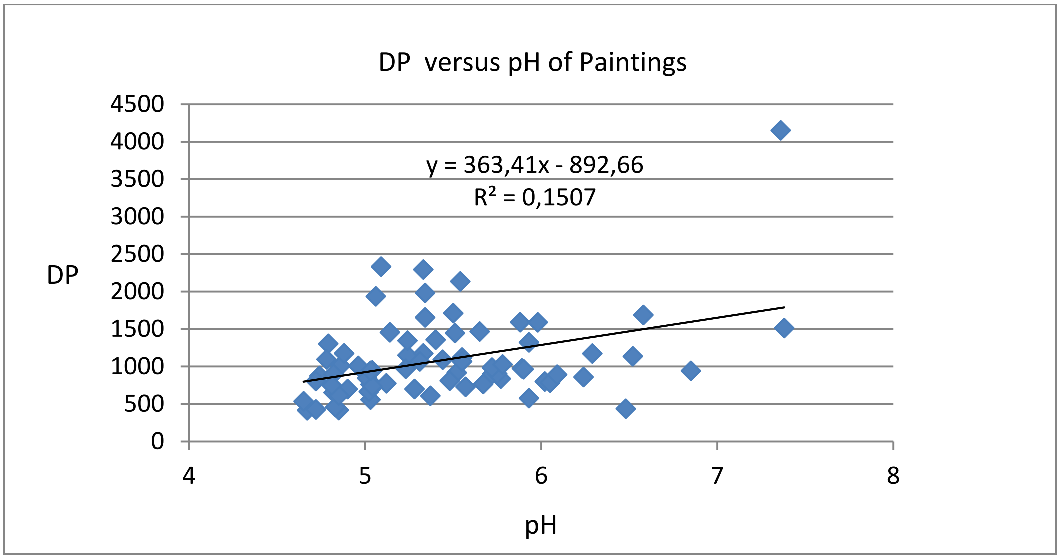

Figure 28.DP versus pH of the samples from paintings.

A slight correlation can be observed between pH and DP (Figure 28), which makes sense since lower pH values, in the long run, will mean lower DP values because acidity causes acid hydrolysis which depolymerizes cellulose (49 p. 34).

In the particular case of linings, it can be seen that as mentioned, they were found to have, in general, lower DP values than paintings. This finding is in accordance with the fact that linings were also found, in general, to have lower pH values, and thus it makes sense that they are more degraded. Indeed if we only take the data for the linings, the correlation between pH and DP improves a bit (Figure 28).

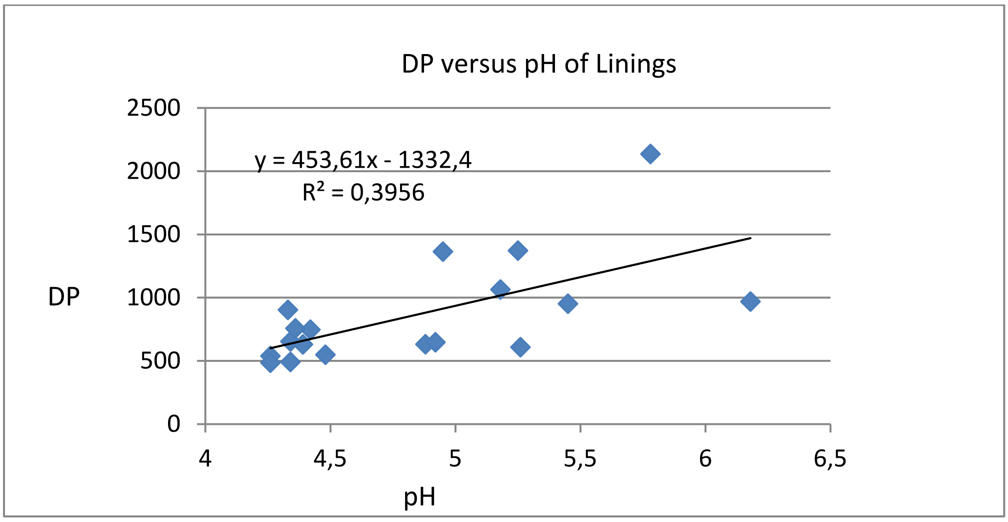

Figure 29.DP versus pH of the samples from the linings.

If we look at the particular case of the four 100% jute samples present in the collection, also in this case, lower DP values are more correlated with lower pH values than not with their production dates (Figure 30).

Sample	DP	pH	Date
38_L (glue paste lining)	756	4.4	1950
48	535	4.6	1925
60	1094	4.8	1950
21	1090	5.4	1908

Figure 30. Values obtained for the four 100% jute samples in increasing order of pH. Lower pH values are more correlated with DP than age of the sample.

2.3.3.5- Comparison between protected and unprotected areas of the canvas

An interesting set of four samples was available in the Reference Collection. These four samples came from two 19th C commercial loose linings that had been removed from two paintings from the Tate Gallery (London), one from W. Turner, the other from H. Landseer (**116** and **117**). Two samples from each loose lining were gathered to take part in the Reference Collection for this thesis. In the two cases, the loose lining had a central much darker area where the canvas had been exposed to air circulation and a lighter area that had been protected by the wooden stretcher (Figure 31)(Figure 32). The interest in taking these four samples was to see if differences could be seen regarding pH and DP values depending of where the sample came: from a more or less polluted area by the environment (darker or lighter colour) (Figure 32).

Figure 31.Two samples taken from a loose lining from a Turner painting from 1843 from the Tate Gallery in London. The sample on the left (**116**_1) comes from the area of the canvas that had been protected by the wooden stretcher, the sample on the right (**116**_2), comes from the darker area of the centre of the painting.

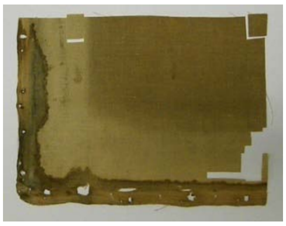

Figure 32.Two samples taken from a loose lining from a Landseer painting from 1843 from the Tate Gallery in London. The sample on the left (**117**_2) comes from the area of the canvas that had been protected by the wooden stretcher, the sample on the right (**117**_1), comes from the darker area of the centre of the painting.

Sample name	Painting	DP	pH	Fibre type
116_1	Turner (old loose lining), **lighter area**	903	4.3	Linen
116_2	Turner (old loose lining), **darker area**	491	4.3	Linen
117_2	Landseer (old loose lining), **lighter area**	630	4.4	Linen
117_1	Landseer (old loose lining), **darker area**	485	4.3	Linen

Figure 33.DP and pH results for four samples from two loose linings, coming from different areas of the canvas.

It is very interesting to see that whereas pH values are all more or less in the same range (quite low), DP values are indeed lower for the darker samples that come from the centre of the paintings, areas that had been much more exposed to air circulation. In this case, therefore, it is seen that air circulation and pollution indeed had a major degradation impact which was added to the degradation caused by acidity itself. On top of that, air must have brought more degrading agents to the canvas than the VOCs (Volatile Organic Compounds) emitted by the wooden stretcher. Wood is known to emit acidic compounds (52) and therefore in a non-polluted environment, the canvas under the wood could be the more degraded one. When the environment is more polluted, though, acids emitted from the stretcher seem to have a smaller impact in comparison (53). It should also be taken into account that, being from an industrialized place such as London, these two paintings must have been exposed to high levels of sulfur dioxide in the past (50).

2.3.3.6- Two samples from the same painting with visually different conditions

There are 11 paintings of which we had two (or three) samples of each and of which pH and DP had been measured (Figure 34). Often the condition of the two samples from the same painting was perceived to be very different, and they were taken with precisely the aim of studyingthe relationship between pH and DP, the differences in pH and DP that could happen in the same painting and to see if the perceived visual differences between the samples coincided with a difference in the measured values. (There were an additional number of 13 paintings of which we had two samples of each too, but we did not have all the DP values needed to do this small piece of research done here).

Sample	Image	pH	DP	Perceived visual condition	pH & DP	DP & Perceived visual condition
3_1		5.1	770		Lower pH means lower DP	Worse perceived condition does not mean lower DP
3_2		5.5	920	Worse condition		
4_1		5.0	560		Lower pH means lower DP	Worse perceived condition means lower DP
4_2		4.8	420	Worse condition		
10_1		5.9	1590		Lower pH means lower DP	Worse perceived condition means lower DP
10_2		5.1	1450			
10_3		5.6	1470	Worse condition		
13_1		5.9	970		Lower pH means lower DP	Worse perceived condition means lower DP
13_2		4.9	700	Worse condition (darker, yellower, more rigid)		

15_1		5.0	740		Lower pH does not mean lower DP	Worse perceived condition means lower DP
15_2		5.0	1010	Worse condition (yellower, more rigid)		
22_1		5.3	2290		Lower pH does not mean lower DP	Worse perceived condition means lower DP
22_2		6.0	1590	Worse condition		
36_2		5.7	900	Worse condition	Lower pH means lower DP	Worse perceived condition does not mean lower DP
36_3		5.6	730			
56_1		5.5	1070	Similar condition	Lower pH means lower DP	
56_2		5.2	970	Similar condition		
70_1		4.7	420	Worse condition (more rigid)	Lower pH means lower DP	Worse perceived condition means lower

70_2		**5.5**	**810**			**DP**
77_2		**6.5**	**1130**		**Lower pH means lower DP**	**Worse perceived condition means lower DP**
77_3		**5.0**	**740**	**Worse condition (darker, more rigid)**		
116_1		**4.3**	**900**		**Lower pH does not mean lower DP**	**Worse perceived condition means lower DP**
116_2		**4.3**	**490**	**Darker**		
117_1		**4.3**	**480**	**Darker**	**Lower pH means lower DP**	**Worse perceived condition means lower DP**
117_2		**4.4**	**630**			

Figure 34.List of double samples from the same painting, with their pH and DP values.In red lower values, worst conditions and unforeseen situations. pH and DP values have been rounded up in the table.

For 8 out of the 11 paintings, we see that the pH and DP correlation is maintained: the lower the pH, the lower the DP (Figure 34). This is the other way around only in three cases: **15**, **22** and **116**. In case **15**, the pH difference between the two samples is very small (0.1), which being lower than the measurement uncertainty, would be considered statistically insignificant. However, the difference in DP for sample **15** is quite large (740 and 1010). Painting **22** is a 1925 painting. The sample with a higher pH, visually seems to be more degraded and indeed the DP is lower (1590 against 2290). May be the more degraded sample suffered from water damage, which caused both a washing away of some of the acidity, and also more degradation linked with the water damage (microorganisms etc.) and this is why even if pH is higher, DP is lower in this case. In case 116, the difference in pH is also statistically insignificant (0.01) but then the difference in DP is much higher (900 against 490!). In this case, the big difference seems to be explained because one sample comes from an area of the canvas exposed to air circulation and pollution (lower DP) and the other comes from an area protected by the stretcher bar (this particular case has just been further explained in a previous section of this same chapter). Therefore, pH being almost the same, the big DP difference must have been caused by pollution (although most pollutants will lead to acidification of the material, this could not be the case if most of the pollution was ozone (37)).

Regarding pH, the minimum difference between the two samples is 0.01, the maximum difference is 1.5 (in painting **77** (*El gran dia de Girona)*). The average difference between samples from the same painting is 0.5, which is bigger than the measurement uncertainty.

Regarding DP, if we measure the difference between samples from the same painting, we see that we obtain differences that go from 90 DP units to 700! This last one is for painting 22, a painting from 1925 with a red priming and a good condition canvas (DPs 1590 and 2290). The average difference between the two different condition samples is 270, which is more than the measurement uncertainty (Fig. 12) and more than the typical difference between distant sub-samples of the same canvas (Fig. 13).

The variability found in DP of an old lining was found to be of 8% (see previous section in this same Chapter “Heterogeneity of historical samples”). In that case, samples were taken from different areas that looked similar. In the cases here, samples are taken from areas that are perceived to be in a different condition to start with, which is why we get even higher differences. We see that DP can be therefore very different in two different areas of a painting, especially if these areas already look very different. We see also that DP differences between two different areas are higher than pH differences, which are smaller (average RSD for DP 22%, average RSD for pH 10%).

Samples coming from the same painting were visually compared and their condition was assessed (usually one of the two was assessed to be in worse condition than the other). This was done according to what was visually perceived: yellowness, darker colour, stiffness, weaker threads when pulling etc. In all cases, except two (**3** and **36**), the sample perceived to be in worst condition also had a lower DP. With this small and quick test, it could be already envisaged that the future Condition Assessment Panel to be discussed later(see Chapter 4), would give valid results, since the perceived condition already seemed to correlate with DP.

For painting **3** (one of the two exceptions from the positive correlation between visual perceived condition and DP), the sample with lower DP (**3_1**), also had lower pH and although sample **3_2** looked to be in worst condition, it is clear that the lower pH had caused sample **3_1** to decrease to a lower DP value. This case might exemplify another situation in which water damage to the bottom edge of the painting (the priming and paint layer had been been washed away along this edge), where sample **3_2** came from, might have caused some of the acids to run away. In this case, this would have implied that the more acidic areas (the other sample taken more towards the centre of the painting) might have been more degraded over time. In the case of painting **36**, again, although the perceived worse condition did not match a lower DP value, a lower pH did indeed match with a lower DP.

2.3.3.7- Fibre type, pH, DP and date (PCA Analysis)

In order to be able to correlate more than two variables at the same time, other tools than the regular scatter graphs are needed. Principal Component Analysis (PCA) is one of the most often used chemometric tools. PCA is a mathematical method that reorganises data in order to see if multiple variables are statistically correlated (54 p. 1). For two variables (univariate analysis), linear regression is a good analytical tool (e.g. Figs. 25, 28), however, it is evident that in very complex sets of data, such as is the case here, multiple variables depend on each other. To visualise such data, PCA is very useful.

Surprisingly, PCA, has not been that often used in heritage science research, although recently it has been used more and more. The first time this tool was used for paper conservation studies was only ten years ago (55).

For PCA to work one needs to enter into the software program used (in our case Xlstat (Addinsoft, USA)), for each sample, information for the different variables that are taken into account. In our case we wanted to see which was the relationship between fibre type, pH, DP and date. Therefore only the samples of which we had these four types of information could enter into the PCA calculations. There were 61 samples from paintings for which we had all this information.

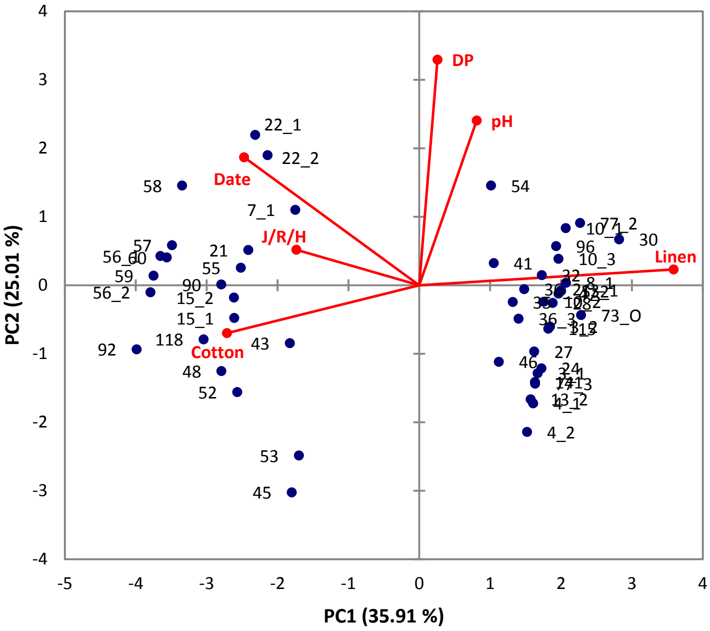

Figure 35.PCA of the relationship between pH, DP, date and fibre type of 61 samples from paintings.

PCA is a very helpful data visualisation technique to analyse large amounts of data, where the first principal component explains for most of the variability in the data set and each consecutive one progressively less (56). In our case 60.91% of variability in the data set is explained by the first two principal components (PC1 (35.91%) and PC2 (25.01%)). This is a significant number, allowing us to make valid conclusions on the observed correlation.

The individual samples can be seen in the graph in blue, this is the “scatter plot”. The “loading plot” (lines in red) shows us the different variables being analysed and the relationship between them. The length and position of these “loads” is what carries information. The longer a line is, the stronger the loading, the more significant this variable is. Regarding the position of the loadings, the closer two factors (or variables) are, the more correlated they are. If they are positioned at 90º, then they are not correlated at all. If they are positioned in two opposite directions, they are anti-correlated (the larger the first one is, the smaller the other one and so on).

Regarding fibre type, jute, ramie and hemp fibres were grouped together since there were too few of them and PCA is not good at dealing with little groups of samples. The three different fibre types (cotton, linen and the jute-ramie-hemp group (J/R/H)) were seen not to be correlated with pH or DP, since they are all at about 90º to these two variables. PCA also shows that linen is mainly associated with older canvases, while cotton and J/R/H are associated with newer ones.

In our case, it can be seen that pH and DP are strongly correlated, since they are quite close to each other. Since they are positively correlated (and not anticorrelated), this means that the higher the DP, the higher the pH, and so the lower the DP, the lower the pH. This makes a lot of sense, since lower pH is known to lead to cellulose degradation. It is important to note, that with this type of analysis, PCA, we see much better that pH and DP are correlated than when just plotting one parameter against the other, where the correlation was not that clear (see previously in this same chapter “DP and pH”). This means that fibre type and date also have an influence in this correlation, and this is why the correlation seems not to be so strong when taking into account only pH and DP data. PCA therefore is seen to be a very useful tool to get more reliable information.

It can also be seen that pH and DP are not correlated with date, although of the two, DP is a bit more correlated with it. This is interesting as it points out to the fact that pH has not so much to do with the age of a sample/painting, but with the materials used and the environment that the painting has been in. Since DP, though, is a bit closer to the date load, this indicates that younger canvases (with “higher” dates) tend to have higher DP values.

2.3.4- Conclusions

The ISO standard for viscometry (45) has been successfully adapted to DP determination of textile samples from easel paintings, with good repeatability obtained for different viscometric measurements done on the same historical samples (0.3% to 4.6% RSD).

The typical sample size needed to do the viscometric measurement was found to be between 10 to 30 mg of fibres: 10 mg for the very good condition samples and 30 mg for the more degraded ones. It has been determined that to end up with 30 mg of fibres from the canvas of a painting, one needs to take an initial sample that is between 1.5 and 2 cm^2 in size.

The best cleaning procedure for painting canvas samples from among the different ones tested, was found to be to place the samples in hot water, cool down and leave in water overnight and then put them in a hot water bath for 10 min. The samples were then manually teased apart with two long needles.

A very interesting future avenue of research identified here would be to further studying the defibering of the sample fibres through the use of a mortar and pestle instead of doing it manually. Preliminary tests done to this end, seem very promising in the sense that the sample time preparation is drastically reduced. It is very important that the sample seems not to be further degraded by the procedure as it was feared.

Variability between distant areas of the same textile was found to be much higher in historical samples (RSD 7.8%) than in new textiles (RSD 2.8%) or that in Whatman paper (0.5%). This higher variability for historical samples was expected, although the value found (RSD 7.8%) was higher than the variability found for paintings in the literature, where areas of the same canvas were said to have typical DP difference of ±5% (44 p. 272).

Regarding the DP values obtained with the Reference Sample Collection, the average DP for paintings is 1082 (SD 566, RSD 52%). However, most of the paintings fall in the DP range between 600 and 950 (40%). Old glue paste linings tend to have lower DP values with an average DP of 811 (SD 402, RSD 49%).

Using univariate analysis, DP was not found to be directly correlated with date (as was also the case for pH and date), whereas a slight correlation was found between DP and pH. Fibre type was not found to be that much correlated with DP (whereas a slight correlation had been found between pH and fibre type).

PCA analysis, a chemometric multivariate analysis tool, was used to analyse the relationships between pH, DP, fibre type and date. This confirmed a strong positive correlation between DP and pH, which means that the higher the pH, the higher the DP and viceversa. No correlation was found between pH and DP and between pH and fibre type. However, we have to take into account that for this analysis, the fibre types of jute, ramie and hemp were grouped together since we had few samples of each, and this might be masking the jute tendency previously detected towards a lower pH. Date was again found not to be correlated neither with pH, nor with DP, although of the two, DP was found to be a bit more correlated with it than pH. This indicates that pH is not so much dependant on the age of a painting, but that there are other factors of influence (such as could be the materials and the environment). Also, the fact that DP is a bit more correlated with age indicates that newer paintings will tend to have higher DP values.

Apart from the specific information obtained, it is important to note the value of PCA analysis, in the sense that with the traditional one-to-one analysis (scatter graph) of the relationship between DP and pH, these two factors were found to be only slightly correlated. Instead, this correlation was seen to be stronger when looking at it via PCA analysis, where four factors were being analysed together (pH, DP, fibre type and date). This means that fibre type and date influence the correlation of DP and pH and this is why the correlation is not seen to be so strong when only the two parameters are taken into account. Therefore, PCA analysis is seen to be amore powerful tool to use when having several different parameters to analyse.

The analysis of the pH, DP and perceived visual condition of samples from a set of 11 paintings, of which two or three samples were available for each painting, gave interesting results. The samples had been taken from areas of the paintings that looked very different in condition. It was found that lower pH generally correlated with lower DP and that the visually perceived worst condition of a sample also generally correlated with a lower DP. This latter finding gave us a good ground to plan the Condition Assessment Panel to be developed in Chapter 4.

Variability in pH and DP between the two different condition samples was found to be in average of 10.31% RSD for pH and of 22% RSD for DP. This last value is higher than the variability found in a test done with an historic old glue lining between areas perceived to be similar, which, as has already been said, had been found to be of 7.8% RSD. Therefore it is confirmed that when the condition of the canvas is visually already perceived to be very different between different areas of a painting, its difference in DP indeed will tend to be larger.

Air circulation and pollution are assumed to have a major influence on the degradation of four samples from two loose linings from the 19th C. Whereas pH values were very similar for all these four samples, areas that had not been protected by the stretcher of the painting, and that had therefore been more exposed to air pollution, had significant lower DP values. In the light of these findings, the introduction of loose linings, backing boards and pollution absorbing materials should be routine procedures to be incorporated by museums in their preventive conservation tasks.

3- NIR spectrometry/chemometrics for easel paintings

Having done all the experimental analysis on our historic samples' collection (fibre type, pH and DP), we are now ready to start the development of our non-destructive NIR spectrometry and chemometrics method.

3.1- NIR spectrometry and chemometrics

3.1.1- Electromagnetic radiation

Electromagnetic radiation is the propagation of a form of energy. This type of energy exhibits wave-like behaviour with both electric and magnetic field components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation (1 p. 202) (Figure 1).

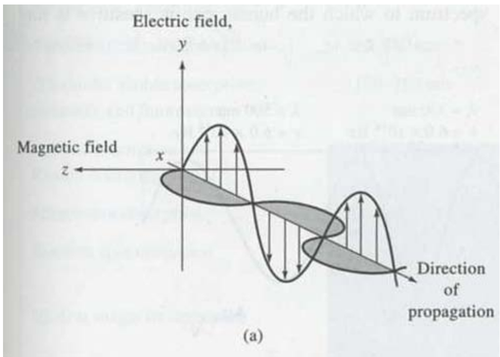

Figure 1. Representation of a beam of radiation, with the electrical and magnetic fields at right angles to one another and direction of propagation. From SKOOG, D.A.; LEARY, J.J. Principles of instrumental analysis. Fort Worth Tex. etc.: Saunders College, 1998, pp. 117.

All types of radiation can therefore be considered as waves that move at the same speed, the speed of light (300,000 km/s in vacuum). The difference between them is the amplitude and the frequency (wavelength) of the waves (Figure 2). The amplitude is the height of the wave, thus the intensity or volume of the signal. The frequency (v) is the number of oscillations per unit time, that is to say waves per second. The wavelength, λ, is the distance between two maxima or two minima peaks, that is the length of one wave (2 p. 5).

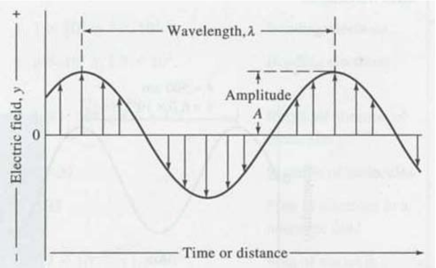

Figure 2. Two-dimensional representation of the electric vector of radiation. From SKOOG, D.A.; LEARY, J.J. Principles of instrumental analysis. Fort Worth Tex. etc.: Saunders College, 1998, pp. 117.

The wavelength of the radiation is inversely proportional to frequency. This means that high-frequency radiation such as X-rays, has short wavelengths and low-frequency radiation such as radio waves, has long wavelengths (2 p. 5). According to Planck’s law, energy is directly proportional to frequency. Since frequency is inversely proportional to wavelength, it follows that energy is also inversely proportional to wavelength. Thus shorter wavelengths, such as X-rays, for instance, have higher energythan radio waves (2 p. 5).

Different names are given to different parts of the electromagnetic spectrum, according to wavelengths (Figure 3). The divisions are based on the methods that are required to generate and detect the different types of radiations (3 p. 118) and this equates to the kinds of chemical and physical effects they produce when they interact with matter (2 p. 4).

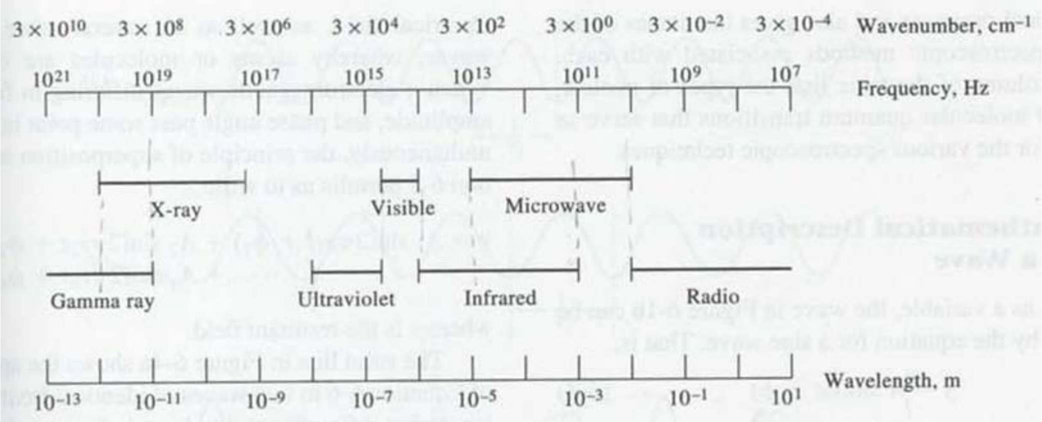

Figure 3. Regions of the electromagnetic spectrum. From SKOOG, D.A.; LEARY, J.J. Principles of instrumental analysis. Fort Worth Tex. etc.: Saunders College, 1998, pp. 119.

Apart from the wave model, the particle model is needed to account for phenomena associated with the absorption and emission of radiant energy. In this particle model, electromagnetic radiation is seen as a stream of energy packets called photons, where energy is proportional to the frequency of the radiation. The double view of radiation as both particles and waves are not mutually exclusive but rather complementary (3 p. 128).

Most of the electromagnetic spectrum is used in scientific analysis (4 p. 9). High-energy X-rays can cause electron transitions between inner electron levels, while visible and UV radiations alter the electron energies of loosely held outer electrons of atoms and molecules. IR absorption causes changes in the vibrational energy of molecules. As all compounds absorb radiation in multiple regions of the spectrum, information obtained from the different regions complements each other and helps to characterize materials (2 p. 4).

3.1.2- Infrared radiation

Infrared radiation was discovered in 1800 by William Herschel and is radiation associated with heat transfer. Fire, for instance, emits both visible light (visible radiation) and infrared (IR) radiation. This IR radiation is absorbed by our skin, which results in a rise in temperature, which is detected by our nerves and felt as heat. Herschel found that the heat maximum was beyond the red end of the spectrum and this is why this radiation was named “infrared” (4 p. 9).

Infrared radiation can be divided into three main regions: the near-infrared (780 – 2,500 nm or 13,000 – 4,000 cm^{-1}), the mid-infrared (2,500 –50,000 nm or 4,000 – 200 cm^{-1}) and the far-infrared (>50,000 nm or (<200 cm^{-1}) (4 p. 9).

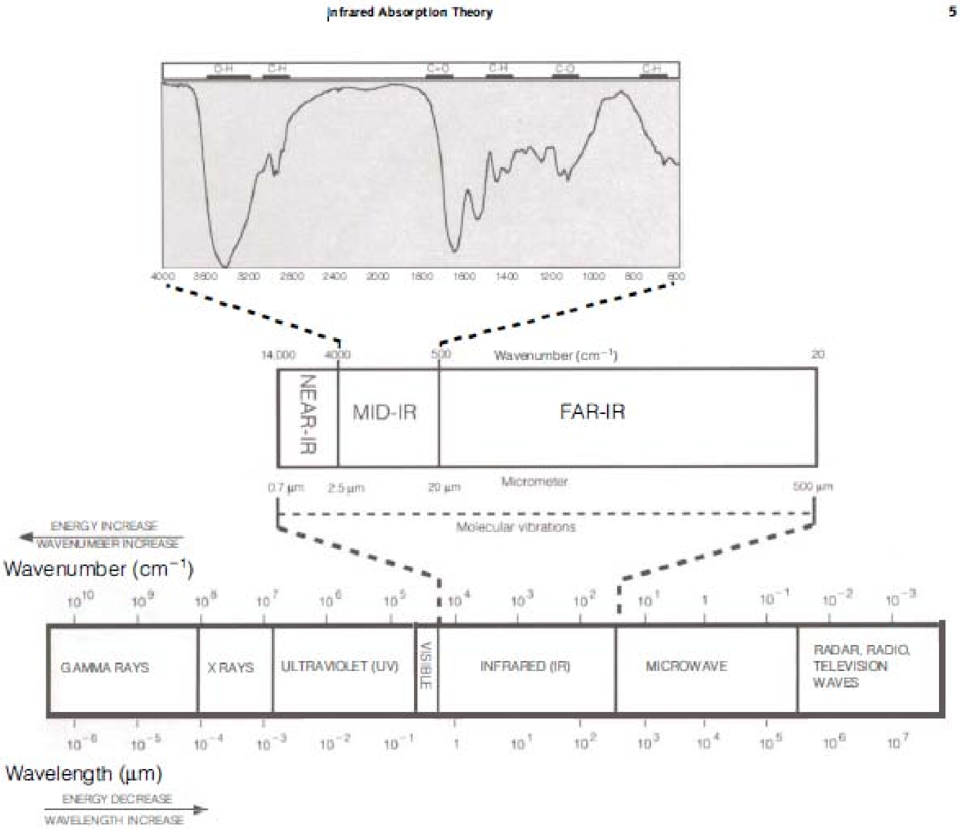

Figure 4 “Spectral regions of electromagnetic radiation, with expansion of IR region.“ From DERRICK, M.R.; STULIK, D.; LANDRY, J.M. *Infrared Spectroscopy in conservation science.* Los Angeles: The Getty Conservation Institute, 1999.

3.1.3 - NIR spectroscopy

Spectroscopy is the science that studies the interactions of radiation with matter (3 p. 116). More specifically, it is the analysis of the radiation absorbed, emitted or scattered by molecules or atoms of the material under study (5 p. 109). Different parts of the electromagnetic spectrum can be used to do various types of spectroscopy that will each yield particular type of information (5 p. 109).

There are two main types of spectroscopy: atomic spectroscopy, which looks at the atom level and molecular spectroscopy, which looks at the molecular level. Infrared spectroscopy is a type of molecular spectroscopy, that uses IR radiation to cause the excitation of vibrations of bonds in molecules (changing the bond length (stretching) or the bond angle (bending) (5 p. 109).

The instrument used, a spectrometer, generates energy in a particular region of the spectrum. The absorption of energy by the test samples is compared to a reference beam and thus a specific value is obtained for each wavelength by comparison. The results are generally plotted as a graph of absorption against wavelength (4 p. 9).

NIR spectroscopy uses NIR radiation (780 – 2,500 nm)to hit the sample and it is mainly used on organic samples, since the bonds it detects are mainly organic ones (O-H, C-H and N-H).

3.1.4 - NIR spectra

Absorptions in the NIR region (780 – 2,500 nm) consist of “overtones” and “combinations bands” generated by the fundamental vibrations that occur in the mid-IR region (5 p. 118).

Absorptions in the mid-IR (2,500 nm – 50,000 nm) are the result of fundamental vibrations of particular groups of atoms. Chemical bonds between atoms can be regarded as springs that naturally vibrate. When a particular packet of energy is added to the system, they will vibrate more energetically. Bonds can stretch or bend. Stretching vibrations require more energy than bending vibrations. Different chemical bonds (like O-H, C-H, N-H and S-H) will absorb different wavelength energies. In a visual analysis of a spectrum we can deduce which vibrations are taking place, and thus the chemical groups of atoms present in the material being analysed (4 p. 9). The region from 8,500 to 12,500 nm is very characteristic and this is why it is called the “fingerprint” region, because it is used to identify unknown substances (4 p. 9). This mid-IR region has been used extensively in research and identification of constituent materials (organic and inorganic) of easel paintings, from the support to the outer layers of varnish (6).

In the NIR region, overtones can be thought of as harmonics, so every fundamental vibration in the mid-IR region will produce a series of overtones in the NIR region (first, second, third overtones…) (4 p. 10). Combination bands are caused by the interaction of two or more vibrational modes and appear between 1,900 nm and 2,500 nm (7 p. 241). While the number of possible overtones from a group of fundamental absorptions in a molecule is limited to a few, a very large number of combinations will be observed. The overlapping of all these overtones and combination bands produce NIR spectra that do not tell much to the human eye since they consist of only broad peaks (4 p. 10), but that are very information-rich (8 p. 413). On top of these overlaps, NIR absorption bands are typically 10-100 times weaker than their corresponding mid-IR absorption bands (9 p. 5). This is why NIR wasinitially considered not to be useful to characterize samples, since its spectra were thought to be too complex to give clear information, unlike the mid-IR region that can be used in this sense (4 p. 9). In order to extract useful information from the NIR spectra, chemometric techniques are required instead of the traditional band assignation (7).

3.1.5- Chemometrics

Chemometrics could be defined as “the use of statistical and mathematical techniques to analyse chemical data”. Once all the chemical information has been collected (ie.measurements in a table), chemometric tools can be used to transform the data into useful information (10 pp. 1-2).

Chemometrics is used to develop reliable “models” when we have complex data and no known model.It is very important, though, to always validate the model produced. “Modelling” is done using “chemometric tools” or “methods of analysis” and there is no one only way to do it: once a model is produced it has to be seen whether it can be refined and whether it is reliable, which is called validation (10 p. 1).

Chemometrics makes it possible to analyse data where there are many variables such as in the case of NIR spectra, where each particular wavelength in a spectrum is considered to be one variable. The type of analysis done then is called “multivariate analysis” (multiple variables) and there are several chemometric tools that can be used to do it, of which Principal Component Analysis (PCA) and Partial Least Squares regression (PLS) are most often used (11 p. 18).

The quality of the correlations depends on different factors, amongst which two of the most important ones are the quality of NIR spectra and the quality of the chemical analytical data (12). Equally important is to do a good validation, since with a poor choice of training samples and insufficient emphasis on validation, it is possible to obtain a calibration that looks good at first sight but that proves not to be reliable when tested with unknown samples (11 p. 17).

3.1.6- NIR spectrometry and Chemometrics

NIR spectrometers have recently become smaller and smaller, with portable instruments nowadays enabling the instrument to go where the sample is and not the other way around. Huge advances in computers power and data storage capacity have also led to a spectacular increase in the application of NIR spectrometry and chemometrics (13).

Nowadays NIR is used in a vast array of industrial fields. The fastness and reliability once a method has been developed makes it a very useful technique. It is used very often to measure different parameters in the food industry, such as caffeine content of coffee, protein and moisture content of different cereals, milk composition, sugar content and pH of grapes etc. It is very much used too in the petroleum and plastics industry and in the pharmaceutical world, particularly in quality control. Recently, there has been a lot of research activity in the medical field too, where non-invasive testing is a very attractive characteristic of the technique (14).

One of the main attractions of the technique is the fact that the analysis, once developed, is reliable and non-destructive. For the industry, this means that predictions are lab-analysis free, so it makes it very fast and easy to check many products quickly, reducing quality control prices a lot.

NIR spectrometry and chemometrics can be used for chemical and physical parameters, since the spectra reflect chemical aspects of the sample which in turn are related to physical aspects. With ageing, materials also change in chemical composition (in paper for instance, there is a build-up of degradation products, a decrease of DP and pH, an increase in crystallinity…) and thus it is also possible to attempt to date materials based on NIR spectrometry and chemometrics: because the spectra reflect the associated chemical change (15 p. 6322).

NIR spectrometry and chemometric studies in the field of cultural heritage

In the last ten years, NIR spectrometry and chemometrics have also entered the world of cultural heritage. The fact that the technique is non-destructive, makes it very promising and for sure its growth in the future is guaranteed. Ideally, scattered efforts done throughout different European research projects will come together at some point to produce more and more reliable calibrated spectrometers to be used on masterpieces. It is very likely that in the future, physically sampling works of art will be seen as a thing of the past, to be done only on rare very specific occasions.

In the field of cultural heritage, NIR spectrometry and chemometrics has been tested for several different parameters on organic objects such as paper, textiles, plastics and parchment. However, up to now, no attempt had yet been done to apply thisnon-destructive technique to easel paintings. This is why this thesis is ground-breaking research in the field of easel paintings.

Paper

Studies done for the paper industry field, already had proved that chemometric models applied to NIR spectra of paper can provide a good correlation of spectra with sample age. In this case, the aim was to see if the technique could be used to assess the condition of paper used for insulation in electrical transformers (or foresee if they were already too degraded), and indeed it was found that the technique could successfully be used to characterise the ageing of cellulosic paper (16).

Regarding the application of NIR spectroscopy and chemometrics to the field of cultural heritage, without any doubt, the largest project has been applied to paper objects under the 6th Framework Programme European Project, SurveNIR (17), conducted from 2005 to 2008, and led by Dr. Matija Strlič (12)(18). In this project, nine European institutions analysed thirteen different chemical parametersof about 1.400 samples and correlated them with the NIR spectra of the papers. The parameters analysed were: degree of polymerisation, molecular weight, lignin content, gelatine content (9), pH, aluminium content, ash content, fibre composition, presence of optical brightener, rosin content, reducing group content, tensile strength and tensile strength after folding.All of these parameters were very successfully correlated with NIR spectra, except for aluminum content, for which a less satisfactory correlation was obtained (15),(19).

Concerning pH and DP of paper, the Standard Error of Prediction (SEP) achieved for historic paper was ±0.3 for pH and ±172 DP units. Dating was also attempted, since ageing leads to chemical changes that will be reflected in the NIR spectra. Therefore, dating of unknown samples was also achieved, more successfully for post-1850 samples, since the number of available specimens to do the calibration was larger (15 p. 6323). pH and DP have also been determined using NIR spectrometry and chemometrics for papers with iron gall ink applications, with similar results. This is proven to be very useful since iron gall ink turns acidic with time and this is known to corrode paper. Knowing the pH and DP of inked areas of paper, thus, allows for the classification of objects according to their fragility and risk of becoming critically fragile (8).

As a result of the project, a commercial instrument named “Survenir” is today marketed by the company “Lichtblau e.K.” (20).The commercial instrument can be used on four types of paper: rag, bleached pulp, coated and ground wood papers. For each type of paper, it is able to measure the following chemical and physical parameters:acidity (pH), degree of polymerisation, molecular weight, tensile strength and tensile strength after folding, lignin content, protein, and rosin as well as the presence of optical brighteners.

All this work done in the field of paper cultural objects suggested promising results in the field of paintings too, since the base material, cellulose, is the same in both cases. However, it may be that the required correlations between spectral information and the desired parameters are so weak that the approach does not work, and this is why it needs to be tested. There could be various reasons for this, e.g. in canvases, the desired signal for cellulose could be completely masked by glue, primer, dust and dirt and thus extraction of desired information very difficult and inaccurate.

Textiles

NIR spectrometry and chemometrics have been lately successfully applied to the textile industry to determine different parameters such as textile fibre identification, moisture content (21) andmixtures determinations: linen and cotton (22), and wool and polyester (23), among others.

In the field of cultural heritage, research has also started. Moisture content of silk is known to be related to its condition. Therefore, if NIR spectroscopy could predict it, this would be very valuable. In this case, univariate analysis of the NIR spectra alone (not using multivariate chemometric techniques) was seen to be enough, since both structural and bound water can be identified in specific NIR bandsof the NIR spectra and correlated directly with moisture content (24). In this study, on top of proving that NIR spectroscopy is useful for moisture determination of silk, they did a small experiment to prove the true non-destructive effect of NIR measurements. They subjected a piece of silk to an NIR spectrometer and took a measurement that took eight times longer than the regular one. They then thermally degraded the NIR-sampled and non-affected pieces of silk at 125 ºC for 120 days and compared their NIR spectra, they found that there were no differences in the spectra both before and after degradation, and thus concluded that taking an NIR spectrum from a silk textile is not damaging (24 p. 219).

In other instances, NIR spectrometry and chemometrics have indeed been successfully used for determining the physical properties of cultural heritage silk objects (25) and therefore their condition (26) or for determining the type of synthetic material of modern textiles without the need of physical sampling (27).

Plastics

Application of NIR to the degradation of plastic objects, such as polyurethane foams has recently been developed (28). Currently there is also another major European project that includes NIR spectroscopy and chemometrics to be used on cultural heritage plastic objects, under the 7th European Framework

Programme. The Popart project (Preservation of plastic artefacts in museum collections) focusses this time on plastic objects, a type of objects increasingly present in the collections of modern museums (29). This project has been running since 2008 and will last until 2012. There are eleven European partners taking part in it and NIR spectroscopy and chemometrics is being used to non-destructively identify plastics (30).

Parchment

Regarding parchment cultural objects, recent research has been able to determine the shrinkage temperature (and indicator of its degradation) with a RMSEV (Root Mean Square Error of Validation, a measure of the precision of the method) of 7ºC and to date these type of objects with an RMSEV of 72 years using NIR spectroscopy and chemometrics. This is very interesting, since this constitutes the only non-destructive dating method currently available for parchment (31).

Wood

In the wood industry, NIR and chemometrics have also found use in predicting the level of furfurylation[1] (32). For cultural heritage NIR spectroscopy has been applied to measure parameters in archaeological wood such as moisture content (33).

Paintings

The use of NIR spectra applied to the study paintings is still very limited. One such study has used the mathematical treatment of NIR spectra in order to enhance the features that make it possible to identify the organic compounds present in paintings (34). This way, they were able to non-destructively identify lipids, proteins and resins. But this study used a different technique than ours: working directly with the NIR spectra of the samples and trying to correlate it to a known spectral database, a method often used for the mid-infrared spectra region.

To our knowledge there is no previous work done on easel paintings where NIR spectroscopy and chemometrics have been used to develop a non-destructive way to assess the condition of the canvas support.

How is an NIR spectroscopy/chemometrics method developed

The main idea behind the development of the NIR spectroscopy and chemometrics technique, is that NIR spectra are collected from a large set of samples and the parameter of interest is also chemically or physically measured (usually destructively) from the very same samples. Then, using chemometrics (mathematical tools that enable to work with many variables (each wavelength of the spectrum)), a model or equation is created. If it is possible to do this calibration of the spectrometer, it means that there is some sort of pattern or relationship between the features of the many different analysed NIR spectra and the particular values that have been identified. This is what makes it then possible to predict this same parameter for similar samples just from the non-destructively taken NIR spectra, without needing to destructively do the measurement again (18).

NIR spectrometry and chemometrics is proving to be useful in more and more situations everyday, but it does not work for everything (14). According to T. Fearn (11 p. 18), “most NIR calibration problems will fall into one of two classes: NIR will work and any one of a dozen calibration methods will give good results, or it will not and no amount of chemometric sophistication will rescue it”. It is most important, however, to choose a good set of training samples and to validate the method properly (11 p. 18).

The steps in the multivariate model-construction process are (7 p. 244):

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[1] Furfurylation is a way of modifying wood by impregnating it with furfuryl alcohol.

- Choosing a set of representative calibration samples
- Determining the chosen parameter of the samples through a chemical or physical analysis
- Recording NIR spectra of the samples
- Subjecting spectra to appropriate pre-treatments using appropriate chemometrics computer software
- Constructing the model (calibration) using the appropriate chemometrics computer software
- Validating the model with samples that did not take part in the calibration using the computer software
- Predicting unknown samples by taking the NIR spectra and using the computer software

The samples

To develop a calibration model we need quite a large number of samples. The question that always arises is “How many samples are needed?” and the answer one usually gets is always the same: “The more, the better”. According to A.M.C. Davis (35 p. 24), however, a hundred would be the minimum he would advise, although one might be able to do a useful trial calibration with as few as thirty. Whereas commercial calibrations are based on several thousand samples, around 70 seems to be an appropriate number for cultural heritage samples, of which its availability is always very limited. Basically it should be taken into account that in the case of cultural heritage the number of samples has to be a compromise between availability, resources and accuracy.

It is important to understand that the method will only be useful to predict properties of samples similar to those that were used in the calibration. This is why the calibration set and the validation set should have a good spread of values of the parameter under study and be representative of the future samples to be analysed (12 p. 82). If our Reference Sample Collection does not contain older canvases, for instance, then our calibration will not be useful for these types of paintings.

If the “training set” (the samples used to do the calibration), are not well chosen, then it is possible to obtain a calibration that looks good at first sight, but that afterwards is seen not to be reliable. The ideal training set should be a randomly chosen set that represents the main sources of variability, such as, for industrial purposes, particle size and moisture content, for instance. This means that in the industry, for example, the training set should contain samples from all batches. According to T. Fearn, the number of samples is not so important as the fact that they cover the different sources of variability there can be between them (11 p. 17;18).

In a recent research project, for instance, where the technique has been applied to determination of the condition of silk textiles, it was found that since the calibration was done using new artificially aged samples, predictions on historic real silk objects gave large prediction errors. The authors therefore conclude, that in order to build a more robust method that could give better results on historic samples, these types of samples would need to be included when building the calibration (36 p. 7).

Of course it is obvious that in general the more accurate are the chemical measurements of our samples, the more accurate will be our predictions. However, it can also happen that NIR spectroscopic calibration equations produce predictions that are more accurate than the laboratory measurements used in the calibration set (37 p. 26). In any case, obviously, the more precise our physically analysed results are, the better.

Calibration

From all the samples of which we have measured the parameter of interest, we need to divide them into a calibration set and a validation set. The calibration set (or training set) should be larger than the validation set, about two thirds of all the samples. This set will be used to develop the model.

The collected spectra will contain, on top of the related information regarding the parameter we are studying, unrelated information (caused often by physical effects, such as particle size) and noise from the instrument and the environment. To reduce all these, several pre-treatment methods can be applied to the spectra before using them for the calibration. Some of the pre-treatments most often used are: derivatives, multiplicative scatter correction (MSC), standard normal variate (SNV), optimised scaling (OS) and orthogonal signal correction (OSC) (38 pp. 16-17). Such pre-treatment of the spectra is done using appropriate computer software.

Then spectra are checked to see whether we have samples that are "outliers"; that is to say samples that for some reason their spectra is very different from the rest. Outliers are seen to lie far apart from the rest of the samples when we do a first calibration attempt and plot predicted against measured values. These samples are then removed from the calibration and not used. Conventional measures for identification of outliers are applied, such as PCA, and various distance calculation methods.

Another parameter that can be varied is the particular part of the spectrum used to do the calibration. Towards the end of the spectrum usually there is a lot of "noise" and sometimes it helps to reduce the wavelengths taken. As a first trial one uses the whole spectrum, but in the end the most often used regions tend to be between 1300 and 2200 nm. Sometimes it is also useful to remove the water peak area, around 1950 nm.

Then the chemometric model (calibration and validation being two separate steps) is produced using computer software (such as *Grams*, or *Unscrambler*®) where all the spectra have been introduced with the corresponding value for the measured parameter of interest. This can be done using different chemometric tools, the ones most often used being Principal Component Regression (PCR) and Partial Least Squares (PLS) (11). When we plot the values for the calibration spectra set predicted with the model created, against the real measured values from the samples of which the NIR spectra was taken, we obtain a linear regression plot (Figure 20) with an R value, which is the "regression coefficient", a diagnostic parameter describing the quality of the model. R describes how distant from the regression line the scores are, that is to say how well prediction and reality match. In a perfect match all the scores would fall on the line and R would be 1, so the closer the R is to 1, the better the model is (and the closer the scores will be to the regression line). We also get the RMSECV value (Root Mean Square Error of Cross Validation). This value is the cross validation error we have in the predicted values of our calibration, so the lower it is, the smaller the error of our calibration is and therefore the better.

It is usually the case that one has to try different combinations of settings (spectra pre-treatment, number of factors, wavelengths chosen) to end up choosing the calibration with the best result of all trials.

Validation

To do the validation, we take the calibration created and apply it to the validation set of spectra to predict the values under study. This is the final check of how good the developed method is, since predictions are done on a set of samples that were not used for the calibration, and thus that are new to the model. The validation set of spectra need to be taken under the same conditions as the calibration set (7 p. 244). Since we also have real measured values for these samples, we can then plot predicted against real values to get another linear regression plot (Figure 20). This time we get the RMSEP (Root Mean square Standard Error of Prediction) that tells us how accurate our predictions are. This value is the uncertainty that we can expect when we will predict new unknown samples. So, again, the lower the RMSEP value, the better (10 p. 4).

3.2 - Materials and methods

3.2.1- Labspec 5000

In order to develop a method for pH, DP and fibre type prediction, NIR spectra of the Reference Sample Collection had to be taken. Spectra were taken using a portable Labspec 5000 spectrometer (Analytical Spectral Devices, USA) in the range of 350-2500 nm (UV-vis-NIR), by averaging 200 scans. Three spectra were taken of each sample on the canvas side near areas sampled for pH and DP. The samples were placed on the white reference calibration pad when taking the spectra, so as to always have the same reference background. The optical light probe that transmits the NIR radiation and collects it back had a purpose-made attachment at the end, so as to make sure that the beam would always be at the same angle with the surface (45º) (Figure **6**). The spot diameter of the beam was about 2 mm and it took, at 200 scans, about 20 s to collect a spectrum. The three spectra were taken in the same area, slightly moving the position of the probe a couple of millimetres each time. This was done so that a larger area of the sample was sampled and so that the effect of sample inhomogeneity was reduced by averaging the three spectra from the three locations.

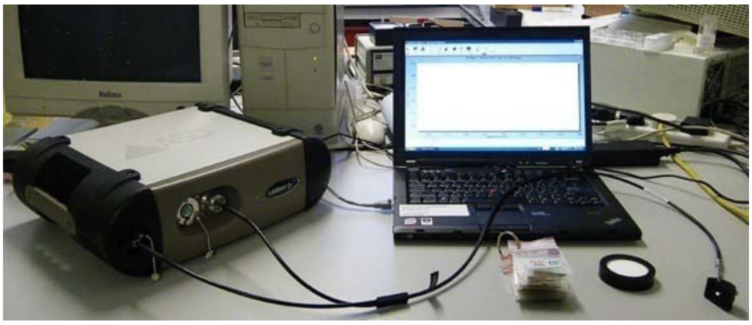


Figure 5. Labspec 5000 (Analytical Spectral Devices, USA). The instrument, the fibre optics probe, the computer and the white reference calibration pad.

Figure 6. The purpose-made attachment to the probe to have the beam always at a 45º angle. The beam diameter is about 2 mm.

The NIR spectrometer Labspec 5000 is a portable instrument since it only measures 13x36x30 cm and thus it can be transported in an airplane, for instance, as hand luggage. It comes with a portable computer and the whole set weighs about 13 kg. The computer comes with specific software to use the instrument, Indico Pro. Before taking an NIR spectrum, in Indico Pro you create a new project, select the number of scans you want to do and take a reference spectrum (baseline) of the white calibration pad. The white reference calibration pad used was a Spectralon 99% reflective standard (Labsphere, North Sutton, USA) (Figure 7). The baseline is plotted as a straight line of 100% and the spectra collected from real samples will be plotted in accordance with this baseline, understood as the maximum possible reflectance. For each sample, a graphic absorbance/reflectance spectrum will be plotted (Figure 8). This is plotted as a graph since it is visually easier to understand, but in fact it is a two columns table: all the different wavelengths in one side,the particular absorbance/reflectance value for each wavelength in the other.

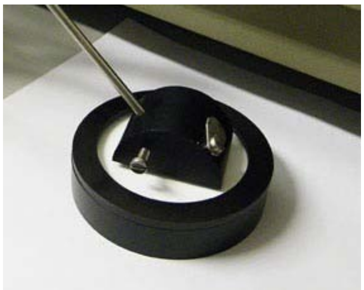
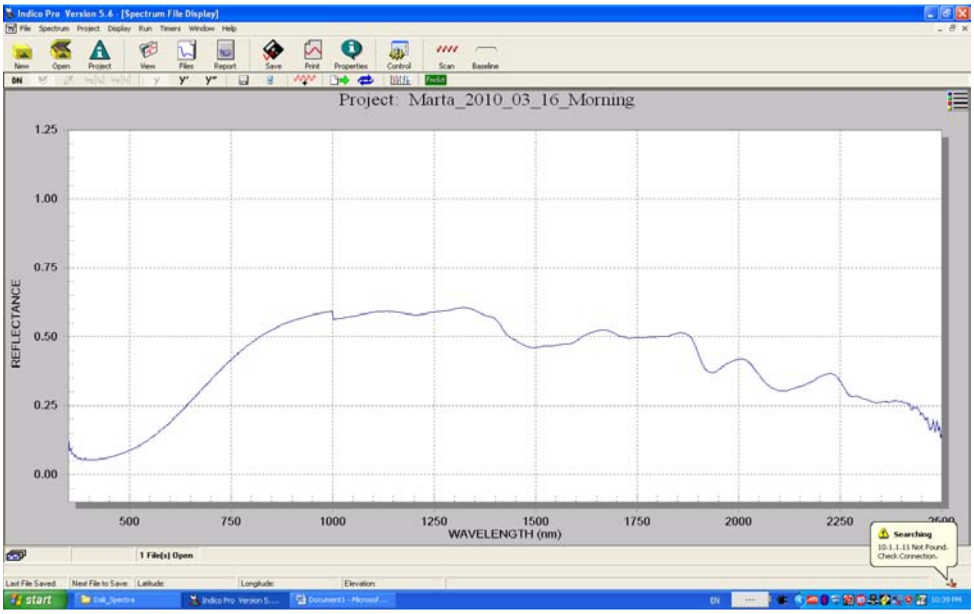


Figure 7. Optical light probe with the purpose made attachment on the white reference calibration pad where samples were measured.



Searching
10.1.1.11 Not Found.
Check Connection.

Figure 8. A spectrum of one of the samples, collected with Labspec 5000. Most of the spectra of canvases are visually very similar.

The Reference Sample Collection is currently being stored in a fridge (each sample is in a paper envelope in a plastic bag), in case future studies are of interest. The locations where NIR spectra were taken, as well as areas where pH and DP subsamples had been taken, were recorded graphically (see Annex I) (Figure 9).

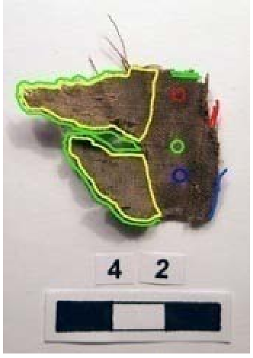
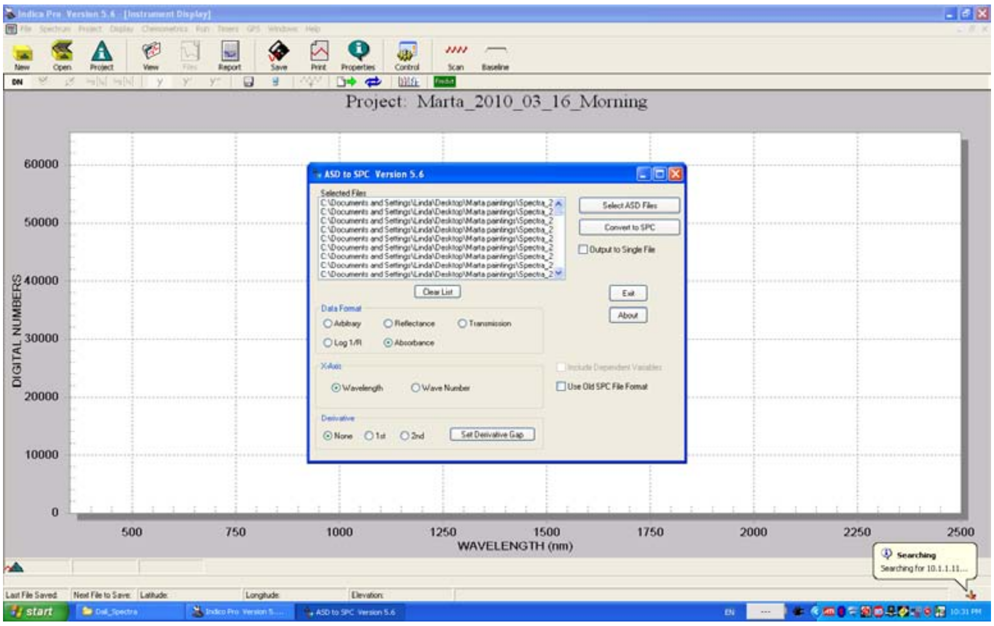


Figure 9. Example of graphic documentation of NIR spectra locations (coloured circles), pH subsampling (coloured lines), and subsampled area for DP measurements (yellowed area).

<u>3.2.2- *Grams AI spectroscopy* software</u>

There are several software programs on the market to do multivariate chemometric analysis (Unscrambler®, *Grams*, *Xlstat* etc.). For doing the DP and pH calibrations we used "*Grams AI spectroscopy software*" by ThermoScientific, with the chemometric add-ons"*Grams IQ*" and "*IQ Predict*". *Grams AIspectroscopy* was used for averaging the spectra and for converting them to *Excel* files, *Grams IQ* was used to the quantitative calibration for pH and DP and IQ Predict was used to do the validation of the two calibrations (pH and DP).

The software from Labspec 5000, Indico Pro produces files with the extension ".asd". These files need to be converted to other formats in order to be able to read them with other programs. In our case, files had to be converted into the ".spc" extension, so that *GramsAI* could read them. An important thing to remember was to convert from "asd" to "spc" format, in the "<u>absorbance</u>" mode so that the calibration can later on be done with *Grams IQ* (Figure 10).



Selected Files
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2
C:\Documents and Settings\Linda\Desktop\Marta paintings\Spectra_2

☐ Output to Single File

Data Format
○ Arbitrary ○ Reflectance ○ Transmission
○ Log 1/R ● Absorbance

X-Axis
● Wavelength ○ Wave Number

☐ Include Dependent Variables
☐ Use Old SPC File Format

Derivative
● None ○ 1st ○ 2nd

Figure 10. Indico Pro screen to convert original format spectra ".asd" into ".spc", so that *Grams AI* can read them.

Then, using also *Grams AI*, the three spectra taken from each sample were averaged to produce one single spectrumto be used in the calibration (Figure 11).

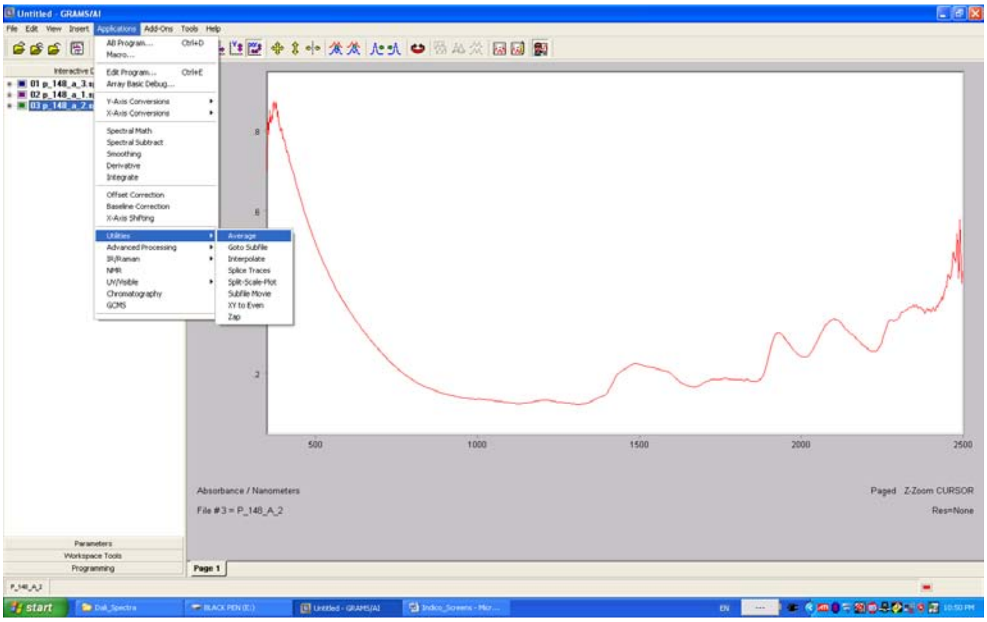
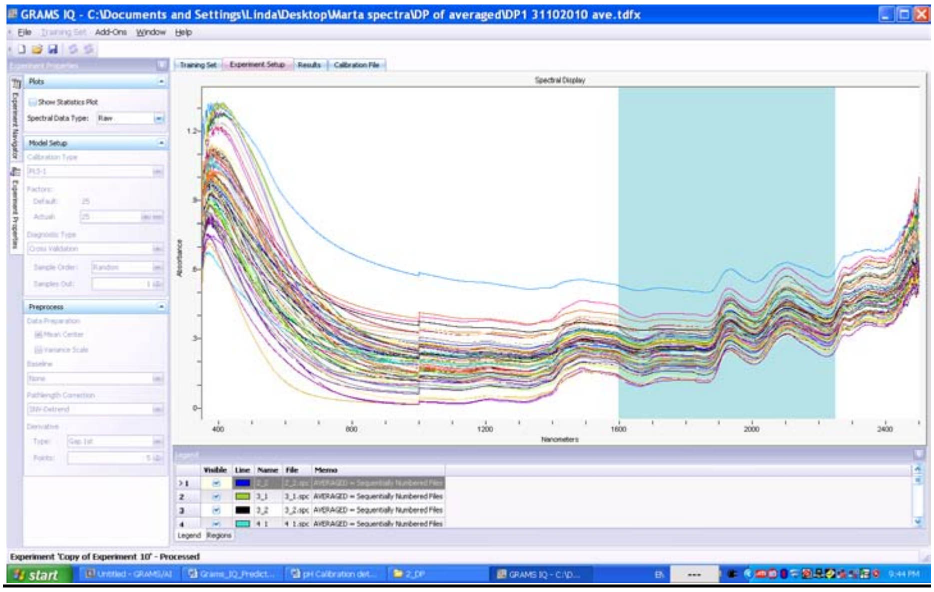


Figure 11. Averaging the three .spc spectra from each sample with *Grams AI*

3.2.3- Calibration (*Grams IQ*)

To create the calibration and validation sets, the spectra were sorted in the order of increasing value of the chosen parameter (pH or DP). Then every third sample was removed and put in the validation set. Doing it like this, samples were randomly selected to create the two sets, but at the same time a good spread of values in each set was still guaranteed (39 p. 29). Values that lie very far apart from the rest, either in the lower or higher end should also be removed.

We used the add-on *Grams IQ* from *Grams* to do the calibration. To do it, first of all a “New training set” is created, and the spectra are selected and imported. They appear graphically on the screen as well as in a table (Figure 12). Then we do “add constituent” (which in our case was either pH or DP) and for each spectrum we manually introduced the particular value of the chemical parameter. We developed first a calibration for pH, then a separate one for DP. Calibration was done by changing different parameters and choosing the calibration with the highest R (19 p. 193). (See the particular details for each calibration later on in this same chapter).

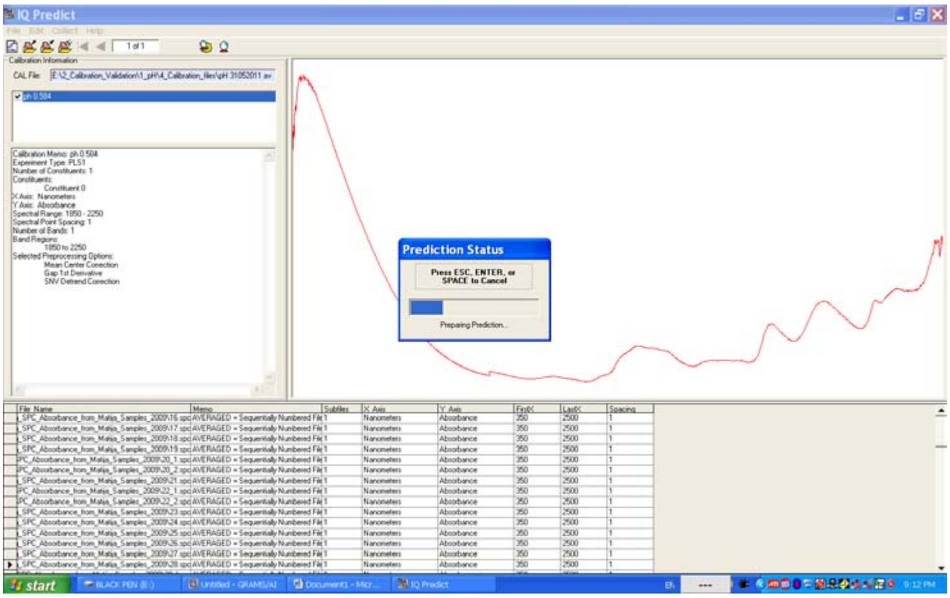


Spectral Data Type: Raw

Figure 12. Screen of *Grams IQ*, during the calibration process. The blue area is the part of the spectrum used for this particular calibration with all the imported spectra.

3.2.4- Validation (*IQ Predict*)

Once a calibration with a good enough RMSEP value (Root Mean Square Error of Prediction) is produced, we run the predictions of the validation set that did not take part in the calibration to further test our calibration. We did this with the program *IQ Predict* also from ThermoScientific, by choosing the calibration file created with *Grams IQ* and selecting the appropriate spectra. We select where we will want to save the prediction report and click on the "magic ball" icon, which is the one that effectively runs the prediction. This process is done very quickly, taking less than one minute (Figure 13).



CAL File: E:\2_Calibration_Validation\1_pH\4_Calibration_files\pH 31052011 av

ph 0.584

```
Calibration Memo: ph 0.584
Experiment Type: PLS1
Number of Constituents: 1
Constituents:
        Constituent 0
X Axis: Nanometers
Y Axis: Absorbance
Spectral Range: 1850 - 2250
Spectral Point Spacing: 1
Number of Bands: 1
Band Regions:
        1850 to 2250
Selected Preprocessing Options:
        Mean Center Correction
        Gap 1st Derivative
        SNV Detrend Correction
```

Press ESC, ENTER, or SPACE to Cancel

Preparing Prediction...

Figure 13. IQ Predict screen, while running the predictions with the created calibration on the validation set of spectra. The resulting predictions will be compared to the real chemical values and the Standard Error of Prediction calculated.

We then plot the predicted values against the measured values and calculate the RMSEP (the Root Mean Square Error of Prediction) (Figure 20). If the result is good, we can use the RMSEP to evaluate the uncertainty of predictions for unknown new samples (11).

If the results obtained indicate that the method developed is good (the error of prediction is small), we would then be ready to make predictions on the basis of any other NIR spectrum taken from paintings of which we have no physical sample. The way to run the predictions would be by using again this same program (IQ Predict), selecting the desired spectrum and using the PLS calibration to predict values, an operation that would only take a few seconds.

3.2.5- Method development for pH

Calibration set

The pH calibration set consisted of 127 spectra with its corresponding pH value, going from 4.2 up to 8.0. The types of samples included were: paintings, linings, deacidified samples (historic linings and loose linings and primed new canvas) and primed new canvases (Figure 14).

Sample Name	Sample Type[2]	pH Average[3]
29_L	Lining	4.17
105	Lining	4.26
116_1	Lining	4.33
116_2	Lining	4.34
38_L	Lining	4.36
117_2	Lining	4.39
106	Lining	4.42
111_1	Lining	4.44
131	Deacidified	4.47
51	Painting	4.48
100_3	Lining	4.51
107_1	Lining	4.56
5_1	Painting	4.61
48	Painting	4.65
98	Lining	4.69
75	Painting	4.72
2_2	Painting	4.74
60	Painting	4.78
118	Painting	4.79
92	Painting	4.81
46	Painting	4.82
86	Painting	4.82
45	Painting	4.83
4_2	Painting	4.85
25	Painting	4.86
112	Lining	4.88
95	Lining	4.89
13_2	Painting	4.90
11_2	Painting	4.91
113_1	Lining	4.92
73_L	Lining	4.95
15_2	Painting	4.96
113_2	Lining	5.00
42	Painting	5.00
53	Painting	5.02
4_1	Painting	5.03
89	Painting	5.03
141	Painting	5.03
19	Painting	5.04
1	Painting	5.05
15_1	Painting	5.05
31	Painting	5.09
65	Painting	5.09
87	Painting	5.12
3_1	Painting	5.12
40	Painting	5.13
10_2	Painting	5.14
14_2	Painting	5.17
16	Painting	5.18
111_2	Lining	5.21
56_2	Painting	5.23
83	Painting	5.24

---

[2] The different sample types have been given different colours so that they can be more easily spotted according to the following code: paintings (green), linings (blue), deacidified samples (orange), primed new canvas (cream), bare new textiles (pink) and household textiles (purple).

[3] pH values have been coloured so that the spread and weight of each pH range can be easily spotted: 4.17 -4.49 (red); 4.50- 4.99 (orange), 5.00 – 5.49 (yellow), 5.50 – 5.99 (green), 6.00 – 6.49 (blue), 6.50 – 6.99 (light purple), 7.00- 8.02 (dark purple)

33	Painting	5.24
50	Painting	5.24
26	Painting	5.25
110	Lining	5.26
24	Painting	5.28
39	Painting	5.31
59	Painting	5.31
44	Painting	5.33
22_1	Painting	5.33
54	Painting	5.34
12	Painting	5.35
67	Painting	5.35
3_L	Lining	5.36
73_O	Painting	5.37
100_4	Lining	5.39
90	Painting	5.40
8_2	Painting	5.40
115	Painting	5.45
23	Painting	5.45
70_2	Painting	5.48
36_1	Painting	5.50
96	Painting	5.50
6	Painting	5.51
3_2	Painting	5.52
34	Painting	5.55
28	Painting	5.55
56_1	Painting	5.55
36_3	Painting	5.57
18	Painting	5.58
100_2	Lining	5.60
7_2	Painting	5.65
49	Painting	5.67
20_1	Painting	5.67
9	Painting	5.71
43	Painting	5.72
113_4	Deacidified (lining)	5.75
41	Painting	5.75
119	Painting	5.77
103	Lining	5.78
108	Lining	5.79
132	Deacidified	5.87
10_1	Painting	5.88
13_1	Painting	5.89
123	Primed new canvas	5.90
7_1	Painting	5.93
69	Painting	5.93
99	Painting	5.93
122	Primed new canvas	5.97
22_2	Painting	5.98
74	Painting	5.99
100_1	Painting	6.02
57	Painting	6.05
66	Painting	6.10
77_1	Painting	6.11
55	Painting	6.24
58	Painting	6.29
101	Lining	6.37
64	Painting	6.39
32	Painting	6.48
61	Painting	6.50
77_2	Painting	6.52
124	Primed new canvas	6.53
81	Painting	6.58
80	Painting	6.58
136	Lining	6.74
30	Painting	6.85
62	Painting	7.06
120_2	Painting	7.20
120_1	Painting	7.21
139	Deacidified	7.33
134	Deacidified	7.34
94	Painting	7.38
79	Painting	7.47
113_3	Deacidified (lining)	8.02

Figure 14. Samples used for the pH calibration set, ordered according to pH value (coloured according to pH range). The pH values are not rounded.

There were nine samples of which both spectra and pH were available but that were not used either for calibration, or for validation because they were from modern textiles, and were thought to be too different from painting canvases (
Figure **15**).

Sample Name	Sample Type	pH Average
125	Bare new textile	6.16
126	Bare new textile	6.36

130	Bare new textile	6.42
133	Bare new textile	6.55
121	Bare new textile	6.84
129	Household textile	6.89
127	Household textile	7.16
128	Household textile	7.59

Figure 15. Bare new textile and household textiles not used for pH calibration

The calibration was done with *Grams IQ*, using the Partial Least Squares (PLS) chemometric method. The diagnostic method used was the "leave-one-out cross validation". What this method does is to routinely leave each sample out when doing the calibration and so it calculates the impact that that sample has on the calibration, by comparing the results of the calibration with and without it. Based on this, the calibration is optimised.

Outliers were found by two procedures. One of the methods was to calculate "spectral residuals". What this does is to compare the sample spectrum with the average of spectra and detect possible outliers, that is spectra that for some reason are very different to the rest. The other procedure was to check the Mahalanobis distance, which gives us a precise value of the distance of the chosen spectrum from the average of the rest. If this number is very high (typically, the value of 3 is taken as a threshold), the sample can be suspected to be an outlier. These two same procedures can be used for spectra of which we want to do a prediction to confirm that they are ok. The following samples turned out to be outliers when doing the calibration: 3_L; 14_2; 32; 45;58; 64; 66; 67; 113_3; 134.

After several trials, the final spectral region used was 1850-2250 nm. It is interesting to note that sometimes only by selecting just one or two more wavelengths on one of the ends or not, the calibration result can be seen to improve. In this particular calibration, for instance, it was found that slightly changing the spectral region selected, from 1598-2249 to 1600-2250, made the R^2 go from 0.584 to 0.600. It is entirely usual, however, to get a different R^2 every time a new calibration is started from scratch.

For pH, the best calibration was obtained by pre-processing the spectra by mean-centring; no baseline correction; 1st derivation (Gap, using 9 points); standard normal variate detrending. In the calibration, 9 factors were used. These are all different chemometric parameters (among others) that can be applied to the spectra before creating the model. The pre-treatments that produce the model with the lowest error of prediction are the ones finally chosen.

It has to be said that we also tried doing a calibration, excluding all the lining samples. Since the result obtained was the same (R^2=0.58), it was decided to leave these samples in so that we would have more variability in the spectra and the method would be able to be used on linings too.

Validation set used

The validation set consisted of 43 samples, covering also a good spread of pH values and sample types (Figure 16).

Sample Name	Sample Type	pH Average
117_1	Lining	4.26
104	Lining	4.34
107_2	Lining	4.48
29_O	Painting	4.67
70_1	Painting	4.72
11_1	Painting	4.78
17	Painting	4.82
97_2	Lining	4.83
71	Painting	4.85
27	Painting	4.88
68	Painting	4.90
2_1	Painting	4.97
14_1	Painting	4.94
52	Painting	5.01

77_3	Painting	5.04
85_1	Painting	5.06
97_1	Lining	5.10
93	Painting	5.12
85_2	Painting	5.16
102	Lining	5.18
88	Painting	5.23
35	Painting	5.24
109	Lining	5.25
82	Painting	5.29
91	Painting	5.34
84	Painting	5.39
21	Painting	5.44
72	Painting	5.50
37	Painting	5.54
137	Deacidified	5.58
10_3	Painting	5.65
97_3	Lining	5.70
36_2	Painting	5.72
20_2	Painting	5.77
47	Painting	5.78
5_2	Painting	5.90
8_1	Painting	6.09
114	Lining	6.18
14_3	Painting	6.30
63	Painting	6.57
78	Painting	7.08
138	Primed new canvas	7.33
120_3	Painting	7.36
135	Deacidified	8.71

Figure 16. Validation set of samples and pH values used.

A prediction was done using *IQ Predict* from *Grams*. Then these values were plotted against the real measured values and a linear regression plot obtained (see the Results and discussion section) (Figure 20).

3.2.6- Method development for DP

Calibration set

When looking at the range of DPs available to do the calibration, a lack of high DP samples was identified, which produced not very good calibrations with a low R^2. Because of this, five higher DP samples were selected (37; 54; 65, 80 and 85) and of these, two out of the three replicate spectra were used in the calibration to increase the number of DP values at the higher end. The averaged spectra (of the three replicates) of four of these samples (37; 54; 65 and 85) were used in the validation too, to increase a bit also higher DP values in this set. There were two samples of which the averaged spectra were used both in the calibration and in the validation (91 and 96). This is not best practice, however, in the absence of further such samples, was seen as the most reasonable option. Since using the very same spectra for both the calibration and the validation was only done in two cases, the results were thought to be valid for seeing whether DP calibration of canvases can be achieved by NIR/chemometrics.

The DP calibration set consisted of 70 spectra, from 65 paintings, containing a spread of DP values, going from 425 to 2332. Both linings and paintings were included (Figure 17).

Sample Name	Sample Type[4]	DP[5]
70_1	Painting	425
32	Painting	435
48	Painting	535
105	Lining	538
4_1	Painting	556
69	Painting	577
110	Lining	608
73_O	Painting	608
71	Painting	614

---

[4] The different sample types have been given different colours so that they can be more easily spotted according to the following code: paintings (green), linings (blue), bare new textiles (pink) and household textiles (purple).

[5] DP values have been coloured so that the spread and weight of each DP range can be easily spotted: <549 (red); 550- 949 (orange), 950- 1399 (green), >1400 (blue)

117_2	Lining	630
112	Lining	631
17	Painting	651
53	Painting	662
13_2	Painting	698
36_3	Painting	727
77_3	Painting	736
15_1	Painting	740
106	Lining	746
92	Painting	748
38_L	Lining	756
3_1	Painting	774
57	Painting	784
100_1	Painting	798
75	Painting	805
70_2	Painting	809
119	Painting	837
52	Painting	845
55	Painting	859
46	Painting	898
116_1	Lining	903
3_2	Painting	917
30	Painting	941
89	Painting	941
115	Painting	951
5_2	Painting	962
114	Lining	968
13_1	Painting	974
43	Painting	984
25	Painting	1010
47	Painting	1026
102	Lining	1064
56_1	Painting	1067
59	Painting	1067
21	Painting	1090
28	Painting	1119
35	Painting	1149
58	Painting	1172
44	Painting	1174
7_1	Painting	1321
83	Painting	1345
73_L	Lining	1363
109	Lining	1371
6	Painting	1446
10_2	Painting	1455
10_3	Painting	1466
22_2	Painting	1588
10_1	Painting	1590
91	Painting	1654
80	Painting	1687
80	Painting	1687
96	Painting	1711
85_1	Painting	1935
85_1	Painting	1935
54	Painting	1981
54	Painting	1981
37	Painting	2135
37	Painting	2135
22_1	Painting	2293
65	Painting	2332
65	Painting	2332

Figure 17. Calibration set of samples used for DP, ordered according to DP. The DP values are not rounded.

There were three samples of which DP was available, but that were not used because they were not from real paintings, but from bare textiles (Figure 18).

Sample Name	Sample Type	DP
126	Bare new textile	7625
129	Household textile	2705
133	Bare new textile	4942

Figure 18. Samples used neither for calibration, nor validation.

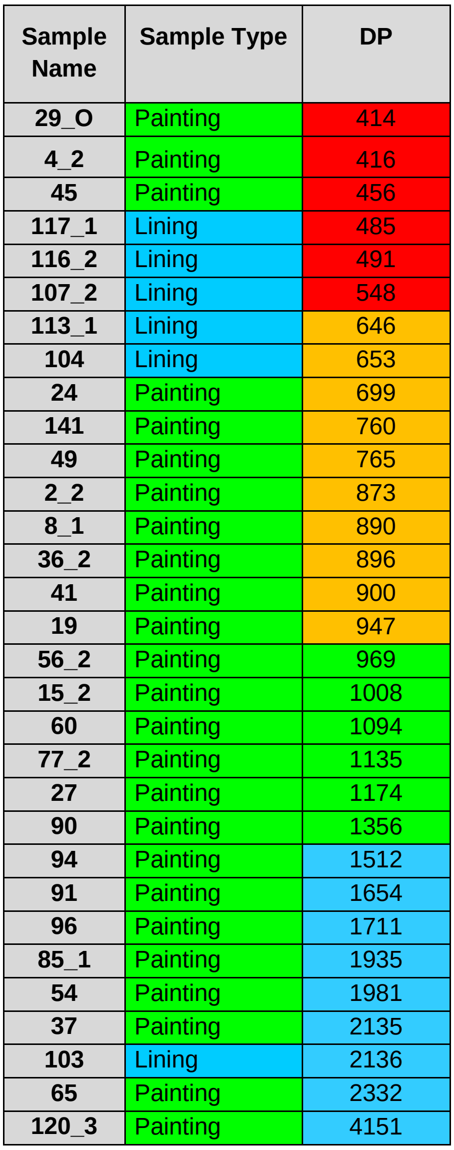
DP calibration was carried out very similarly to the previous pH calibration. It was done with *Grams IQ*, using PLS and leave-one-out cross validation. The outliers were found by checking spectral residuals and the Mahalanobis distance. For DP, samples found to be outliers were: 5_2; 22_1; 32; 38_L; 48; 58; 70_1; 110; 119.

There were three samples in the validation set (45, 120_3 and 141), that could not be predicted due to too large Mahalanobis distance.

Two different calibrations were done, by just changing the spectral range chosen, obtaining different results. Calibration "A"[6], as it was named, used the spectral range of 1200-1870 and 2000-2250 nm, thus avoiding the region 1870-2000 nm, which contains the water peak. The pre-treatments used were: mean centring;1st derivative (Gap, 11 points); standard normal variate detrending. In the calibration, 14 factors were used. The other calibration done was named "B" and here the spectral range used was from 1200 to 2250 nm. In this case, the pre-treatments were mean centring, 1st derivative (Gap, 17 points), standard normal variate detrending, and 12 factors were used in the calibration.

Validation set

The validation set consisted of 32 samples, with DPs ranging from 414 up to 4151 (Figure 19).



Sample Name	Sample Type	DP
29_O	Painting	414
4_2	Painting	416
45	Painting	456
117_1	Lining	485
116_2	Lining	491
107_2	Lining	548
113_1	Lining	646
104	Lining	653
24	Painting	699
141	Painting	760
49	Painting	765
2_2	Painting	873
8_1	Painting	890
36_2	Painting	896
41	Painting	900
19	Painting	947
56_2	Painting	969
15_2	Painting	1008
60	Painting	1094
77_2	Painting	1135
27	Painting	1174
90	Painting	1356
94	Painting	1512
91	Painting	1654
96	Painting	1711
85_1	Painting	1935
54	Painting	1981
37	Painting	2135
103	Lining	2136
65	Painting	2332
120_3	Painting	4151

Figure 19. Validation set for DP calibration. The DP values are not rounded

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[6] Calibration A, was originally named "m8" and calibration B, was originally named "m9" (and it has been kept like this in the original *Excel* files).

3.2.7- Method development for fibre type identification

Fibre type identification was done using a different chemometric tool, Discriminant Analysis (DA). This could also have been done with the same software used for pH and DP method development, *Grams IQ*, but in this case, because of easiness of use, it was done using the computer software *Xlstat* (Addinsoft, USA). Fibre identification is a qualitative method of determination (the spectrum has to be linked to a particular class of fibre) and not a quantitative one (such as pH and DP would be, where the spectra are linked to a numeric value). To do DA, the spectra and the identified fibre group are entered into the program in the form of an *Excel* table (wavelengths and values of absorbance). Both the known samples and the unknown new samples are entered and the calibration and prediction is done all at once. Identification of unknown samples is given with % of reliability.

Normally one would use the averaged spectrum for each sample (from the three spectra available for each sample). However, since it had been checked with the pH predictions (see Chapter 5), in our case there seemed not to be a big difference between taking the averaged spectra and predicting the pH values or predicting the values for the three spectra and then averaging them. This meant that in our case it is as reliable to work with the average of the three spectra or with one of the three replicates. Therefore, in order to simplify the work for fibre DA, just the first spectrum for each sample was taken (averaging about 300 spectra takes quite some time). Therefore an *Excel* table with both all the spectra with known fibre identification from the Reference Sample Collection and the set of new spectra from MNAC paintings (of which we did take the multiple spectra to do the predictions) was prepared (the details of this unknown new spectra are given in Chapter 5). Then modelling and prediction of the unknowns was done at the same time. We report here the results of the method development part whereas the prediction of the unknowns for the case study paintings is reported in Chapter 5.

The *Excel* file to do DA had to have different values and wavelengths of each spectrum arranged horizontally. The part of the spectrum used was from 1100 to 2250 nm. Since we originally had the spectral data in the vertical format, a special copy and paste had to be done: first one would copy the whole column of vertical values of the desired spectra, then would go to the new *Excel* for DA and do a “special paste” and chose the option “transpose”. This option copies the values in a horizontal arrangement. Also the *Excel* needs to be very wide for all the wavelengths to fit (the spectra had values from 350 nm to 2500 nm… so about 2150 columns) and, inexplicably, if a new *Excel* document is created with *Excel 2007*, it will not be able to accommodate all the available values. Therefore, one needs to obtain an *Excel* document previously used for this purpose which is sufficiently long, delete all the data and copy the new data in there. Then all the values will fit.

Looking at the fibre types available in the Reference Sample Collection it was seen that there were three situations. On the one side, there were paintings were both threads were identified as the same type of fibre, and thus the canvas was 100% one type of fibre. Of these we had: cotton, jute, linen, hemp and ramie. There was another case were the two threads were found to be mainly one type of fibre with a little bit of another type (“mostly linen with a few hemp”, “mostly cotton with a few synthetics”, “mostly cotton with a few other natural fibre”). In these cases, for fibre DA analysis, they were classified as “linen”, “cotton” and “cotton”, respectively, since they were mostly composed of this type of fibre. The last case was where one of the threads had been identified as one type of fibre, the other as a different one. The types of combinations we had examples of, were the following: cotton/linen; jute/linen; jute/cotton and linen/hemp.

Different DA attempts were done and it was found that the best way to do it was to do a first DA analysis that would classify samples into: cotton, jute, “bast” and “combination”. In this first DA,“bast” included: linen, hemp, ramie and linen/hemp combinations; whereas “combination” meant cotton/linen, jute/cotton or jute/linen combinations.

Then, only the samples classified as “bast” fibres in the first DA were analysed with a second DA analysis to separate them into linen, hemp, ramie or a combination of linen and hemp.

To do the DA analysis, a total of 174 samples of which the fibre type was known were used (see Chapter 2.1). 107 of these spectra came from the Reference Sample Collection, and they were from 81 different paintings (there were paintings with two or three samples). 67 spectra of the same group of paintings, but collected from the centre of the canvas in October 2009 when the NIR Labspec 5000 had come to Barcelona for the first time, were added to do DA too. We had no physical sample from these areas, but since fibre type is the same throughout the canvas, this was not necessary because the spectra were from the same paintings of which we had a sample from the margins and had been analysed. Since the NIR spectra collected from different areas, would be different, this was seen as a good way to increase the quality of the developed method.

3.3- Results and discussion

3.3.1- pH

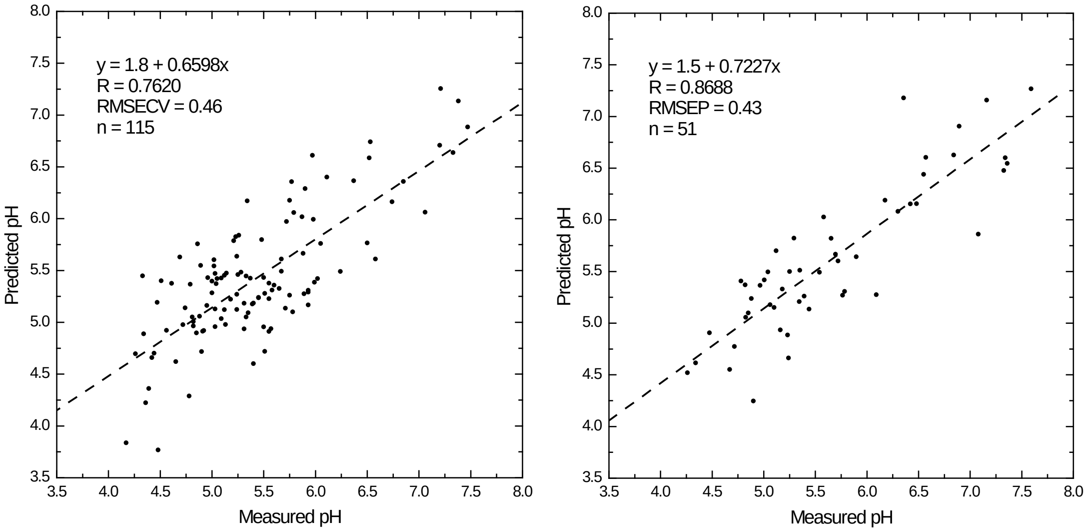

Figure 20. pH calibration plot (on the left) and validation plot (right) for pH

The RMSEP we got for pH validation was 0.43, which is smaller than the RMSECV for pH calibration (0.46). This result means that by using the proposed calibration, our predictions will have an error of ±0.43 pH units, which in the context of paintings conservation is very good, especially if we take into account that our lab measurements have also an SD of 0.3 (see Chapter 2.2). Paper pH error of prediction obtained through NIR/chemometrics has been as good as ±0.3 (15 p. 6323).

Therefore, NIR calibration for the pH of canvas from easel paintings was found to work very well. This makes sense, since pH depends on the content of organic acids and other degradation products which should give rise to particular absorption in NIR spectra (8 p. 414). Nonetheless, it could also have been that for various reasons, a method could not be built, particularly if the signals for cellulose or glue were overshadowed by signals for dirt, dust and other components of the canvases.

3.3.2- DP

Since we had few high DP values, the first calibration attempts were not that good, although they already indicated that calibration was possible. To surpass this and to see if DP predictions could be improved if we had more high DP samples, a few (five) non-averaged spectra of high DP samples were used both in the calibration and validation. However, the spectra from these high DP samples used in the two sets were not the same spectra, but the different replicates were used in different sets.

Doing it like this, it was seen that a PLS calibration for the DP of the canvas support paintings is possible, but the recommendation would be to obtain a larger set of calibration samples in general, and especially in the higher DP range.

Of the many calibrations attempted, the two below have been selected to show how a small difference in the parameters chosen can produce significant different results. The only difference between the two calibrations is the selected part of the spectrum, having used 1200 - 1870 and 2000 - 2250 nm for calibration A (Figure 21), and 1200 to 2250 nm for calibration B (Figure 22).

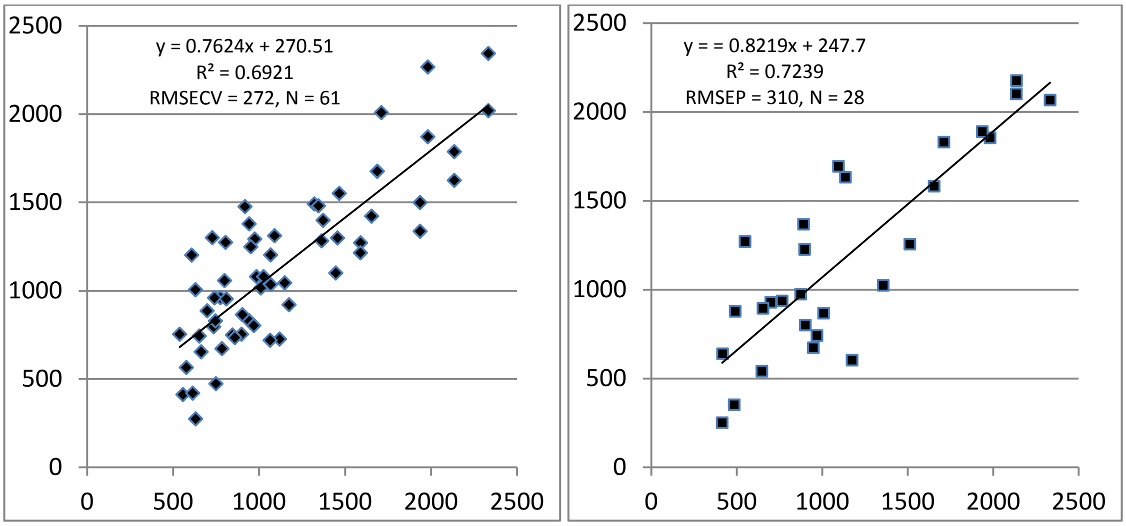

Figure 21. DP calibration plot (left) and validation plot (right) for Calibration A (initially named m8)

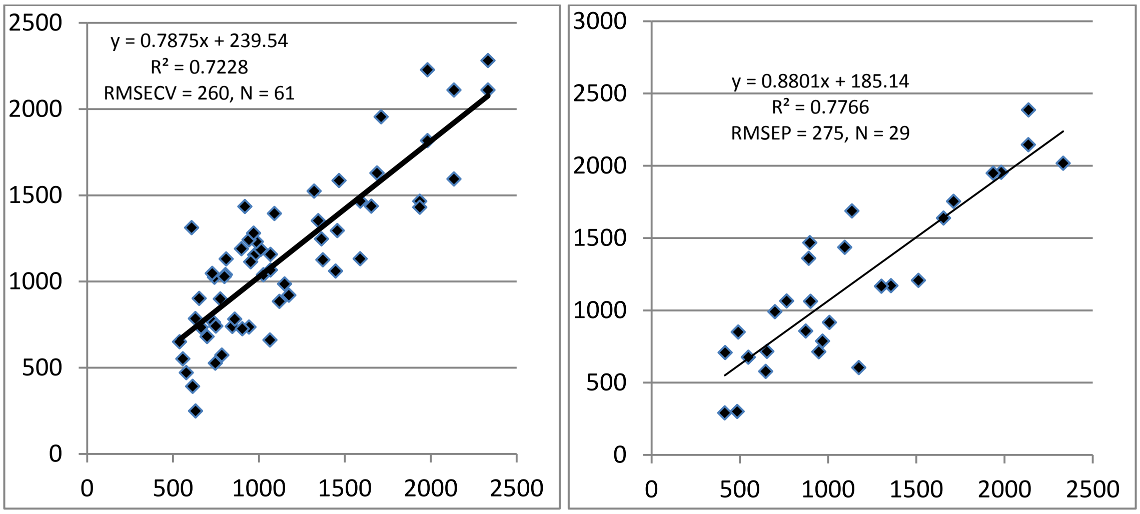

Figure 22. DP calibration plot (left) and validation plot (right) for Calibration B (initially named m9)

Both in terms of calibration and in terms of validation, prediction B is better because it gives a lower error of prediction (RMSEP = ±275 for calibration B, against a ±310 for calibration A). Also, the slope of the regression line is closer to 1 in calibration B, which is another quality parameter. Therefore, this will be the one used for unknown samples. It was also seen, though, that for unknown new samples, this calibration gave more blank results, that is to say it had more trouble in giving predictions for the case study paintings (see Chapter 5); whereas calibration A had a bit fewer blank results. However, it might be preferableto get less results, but with more precision than the other way around.

Regarding other studies done in the field of cultural heritage trying to develop a method for DP prediction of paper using NIR spectrometry and chemometrics, the lowest SEP achieved so far for paper has been ±175 (15). This is much better than the value obtained here, probably due to the higher amount of samples available (more than a thousand samples were used in the Survenir project (17)), but most probably due to the higher homogeneity of paper samples compared to canvas. Canvases can contain a significant amount of extraneous materials, and have a very irregular surface, so the quality of the calibration is actually surprising. In any case, it is a very important achievement having found that DP from the canvas of easel paintings can be effectively predicted using the non-destructive method NIR spectroscopy and chemometrics.

3.3.3- Fibre type

A two-step DA was developed because it was seen to work better this way. The first DA that distinguishes between cotton, jute, bast (linen, hemp, ramie and linen/hemp combinations) and combinations of cotton/linen, jute/cotton or jute/linen, was seen to be very good. The second DA identification within the bast category (linen, hemp, ramie or a combination of linen and hemp) was not so reliable, mainly because there were fewer samples available in the Reference Sample Collection that were classed as hemp (only 8) and ramie (only11), whereas there were 37 linen ones, for instance. On top of the smaller number of hemp and ramie samples, it has to be added the fact, that bast fibres are indeed difficult to distinguish under the microscope, and thus it was known that some of the identifications might not be 100% certain to start with. From the eight ramie samples, for instance, five of them had a question mark.

The results of the DA can be output in different ways. A very visual one is a scatter plot resembling the one obtained with PCA (Figure 23).

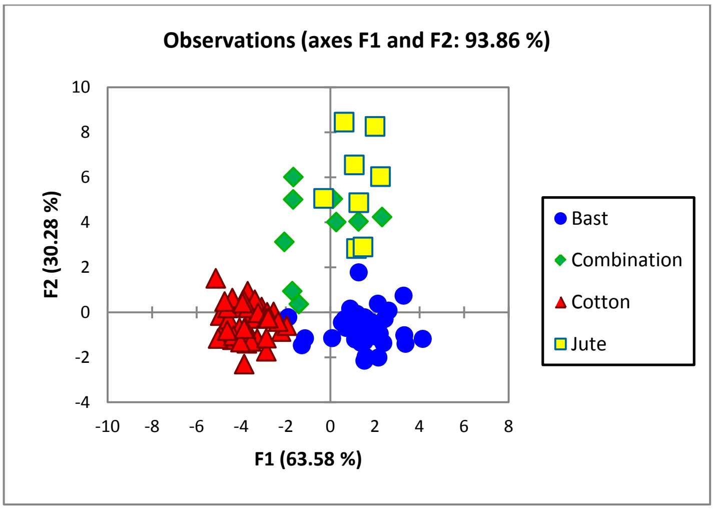

Figure 23. First DA scatter plot showing sample classification

The scatter plot helps us to visually evaluate how similar types of samples group together. We can also use it to plot the several spectra taken of an unknown sample or painting and visually assess how they classify (see later on Chapter 5).

Confusion matrix for the estimation sample:						
from \ to	Bast	Combination	Cotton	Jute	Total	% correct
Bast	110	0	1	0	111	99.10%
Combination	0	6	2	1	9	66.67%
Cotton	0	0	45	0	45	100.00%
Jute	1	1	0	6	8	75.00%
Total	111	7	48	7	173	96.53%

Figure 24. “Confusion matrix” for the first DA done. It is able to predict cotton with a 100% correctness, bast with a 99%, jute with a 75% and “combination” with a 66%.

Another output of the DA analysis is the “confusion matrix” (Figure 24). This tells us how good DA is for predicting the different types of fibre. The way to read it is, for instance for cotton: from a total of 45 cotton samples, it classes all 45 as cotton and this is a 100% reliability because all the ones that were cotton were indeed properly predicted. For jute, from the total of 8 jute samples, it classes 6 as jute, 1 as bast and 1 as combination. Since we know they were all jute, the developed method can be seen to have a reliability of 75% and so on.

In our case, the confusion matrix (Figure 24) tells us that the method is reliable at predicting cotton (100%). Then, it is very good, almost perfect (99%), at predicting that a fibre is from bast[7] (linen, hemp, ramie or a mixture of linen and hemp). Next, it can predict jute with 75% correctness. It is possible that this percentage is lower due to the smaller number of jute samples. Jute has a distinctly higher amount of lignin than the other types of fibres, and this should be reflected in the NIR spectra (In fact in Chapter 5 it will be seen that indeed, jute paintings are clearly identified). Finally the type that is not as good at predicting is the “combination” type (mixtures of cotton/linen, jute/cotton or jute/linen), with a 75%. Again, we had very few of these type of samples (6) and it is very likely that with a higher number of these samples, combinations would be better predicted. On the other hand, this is a very artificial class of samples and does not reflect natural grouping.

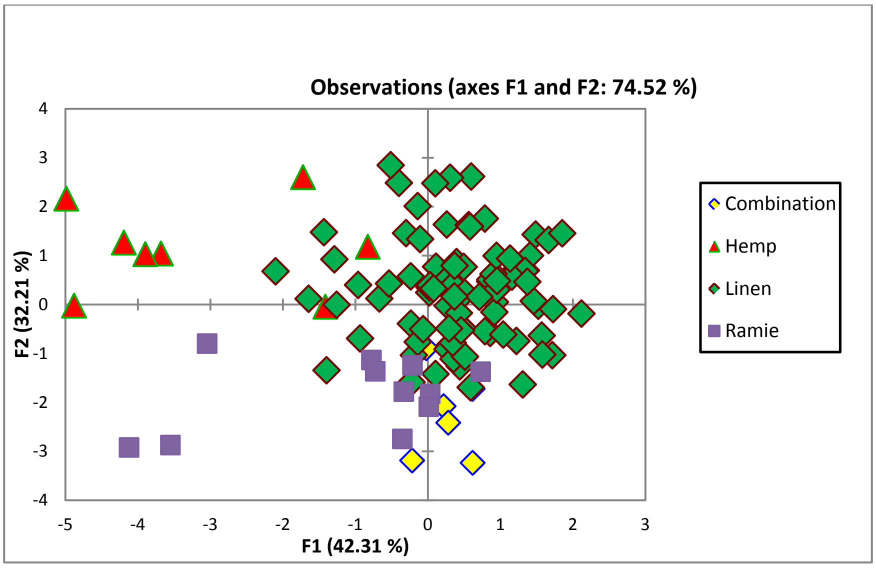

Figure 25. Second DA classification of samples done with PCA

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[7] As mentioned already, jute is also a bast fibre, but for the purpose of our DA analysis, we mean only linen, hemp and ramie when we talk about the “bast” category.

Confusion matrix for the estimation sample:						
from \ to	Combination	Hemp	Linen	Ramie	Total	% correct
Combination	6	0	0	0	6	100.00%
Hemp	0	6	2	0	8	75.00%
Linen	0	1	82	3	86	95.35%
Ramie	0	1	2	8	11	72.73%
Total	6	8	86	11	111	91.89%

Figure 26. The confusion matrix for the second DA done tells us that the method is able to predict the linen/hemp combination with a 100%, linen with a 95 % correctness, hemp with a 75% and ramie with a 72%.

The second DA is very good at classifying linen/hemp combinations (100%) and linen (95%). The precision is lower for predicting hemp (75%) and ramie (72%). In this case, though, we have to take into account again the lower number of samples available for ramie (11), hemp (8) and linen/hemp combination (6), some of which were already questionably identified using microscopy. Therefore, linen prediction is thought to be very good, due to the higher number of samples available, whereas other predictions will have a lower reliability.

Nonetheless, samples still group clearly together according to fibre type in the second DA analysis (Figure 25).

The success of fibre type prediction is due to the fact that different types of fibres lead to systematically and significantly different NIR spectra. In fact, fibre identification of cultural heritage objects using infrared radiation, attenuated total reflectance FTIR spectroscopy (ATR-FTIR), had already been proven to be successful (40)(41). In the case of FTIR, though, the part of the spectrum used to identify the samples was the mid-infrared region, and identification was done by determining the characteristic sense and angle of wind of the fibres from the IR spectrum. The advantage of our NIR spectroscopy method developed over the ATR-FTIR method mentioned is that for this last one, a fibre of about 1-2 cm in length needs to be extracted and placed on the instrument, whereas with the NIR spectrometre probe, the spectra can be directly taken from the reverse of a painting without needing to extract any physical sample.

3.4- Conclusions

NIR spectrometry and chemometrics is a very time consuming technique to develop, since it initially requires the availability of real samples, followed by analytical determination of the desired parameters for a high enough number of them (usually in a destructive manner). Once developed, though, if the technique works for the desired parameter, it becomes the most user-friendly technique of all since an NIR spectrum can easily be taken on site, by an inexperienced operator. The measurement is fast to do and the results of it can be immediately known. On top of all this, the technique is non-destructive and reagent-free, and one spectrum can tell us about as many parameters as there are methods available.

Therefore, the most important conclusion of this chapter, and in a way of this PhD thesis, is that indeed, the non-destructive NIR technique has been successfully modelled for each of the three attempted parameters to predict the pH, DP and fibre type of the canvas of easel paintings.

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). 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*".The Discriminant Analysis qualitative calibration for fibre type was done using the software *Xlstat* (Addinsoft, USA).

In the case of pH, on top of being possible to develop a method using PLS, the error of prediction obtained (±0.43) is very good, given that our destructive analytical technique (pH cold-extraction) already had a standard deviation of 0.3 pH units (see Chapter 2.2). NIR calibrations produced in the case of paper studies by others for this same pH parameter have been able to obtain a slightly smaller error of prediction of ±0.3 (15), most probably due to the use of a larger set of samples.

It was also possible to develop a PLS method for prediction of DP of the canvas of easel paintings. In this case, the lowest error of prediction obtained from the different calibrations that were done, has been of ±275 DP units. In paper studies done by others with a larger amount of samples, a lower error of prediction of ±175 has been achieved, but for the much more homogeneous material (15). We were also lacking a larger number of samples on the higher DP end, and this is why some adaptations had to be done when producing the calibration. It would actually be possible to re-do a new calibration in the future in a relatively easy way if more samples were available of which their DP was known, since the data and the spectra used for this first attempt are all safely kept and could be re-used.

Discriminant analysis (DA) was found to give very good results for fibre type identification. A two-step method was developed, where in the first step the distinction is done between cotton, jute, and "bast" (in our case this mean: linen, hemp, ramie and linen/hemp combinations) and combinations of cotton/linen, jute/cotton or jute/linen. The reliability of the method was very good, the confidence ranging from 75% to 99% for the different types of fibres. In the second step, the distinction was done between the bast fibres. In this case, the method was very good at predicting linen, since a large amount of this type of samples was available. For the other types of fibres (hemp, ramie and combination of these), although the reliability was also quite good (from 72% to 100%), it has to be taken into account that too few samples of hemp and ramie were available, and thus identifications for these samples might not be as reliable.This could also be improved in the future if more positively identified hemp, ramie and combination samples were available and a new calibration was carried out.

The successful results on this first attempt to predict chemical parameters of the canvas support of easel paintings through NIR spectroscopy are encouraging to improve the method both by adding more samples to the methods developed and thus making them more precise and by adding new parameters. A method that could be developed in the future relatively easily (since it would not require further chemical analysis to be done) would be the dating of paintings using NIR spectroscopy. The only requirement for this to be done, however, would be to have very precise known dates for paintings, which we are lacking in some instances.

In conclusion, that the NIR spectrometry and chemometrics technique works for pH, DP and fibre type is very good news since these parameters, especially pH and DP, are very important in defining the condition of the canvas support. As already explained, pH will tell us about the degradation rate of the object (the more acidic is the object, the faster its degradation is) and DP will tell us about the present condition of the object (the lower the DP, the worst is the condition of its cellulose chains).

One important thing to be taken into account, though, is that the developed method will only be successful for paintings similar to those included in the Reference Sample Collection, that is to say mainly 19th and 20th C oil paintings on linen, hemp, ramie, cotton and jute.

Therefore, conservators now have a very useful tool to make relatively fast condition surveys to predict the pH, DP and fibre type of the canvas of paintings from the 19th and 20th C. Before doing this, though, further research is needed in order to learn more about the meaning of the different pH and DP values that one could obtain with this new technique when it comes to paintings. This avenue of research is explored next in the Chapter 4.

4 – Condition Assessment Classification

This Chapter explains the research done in order to gain a better understanding of what particular pH and DP values obtained, either analytically or non-destructively with the newly developed NIR technique, mean. This knowledge could then be used to classify and prioritise conservation treatments to be done on paintings of which pH and DP are known, regarding the canvas support.

4.1- Introduction

Once we have developed a non-destructive method to predict the pH, DP and fibre type of the canvas support of a painting, the next step is to use this information to do a condition survey of a collection (always regarding the condition of the canvas only, of course). That is to say, to transform the predicted values into meaningful information that allows one to classify paintings according to some previously established condition categories, grading objects in terms of current mechanical stability. Like this, informed conservation decisions can be carried out, taking into account the different needs of the collection.

A very acidic painting might be a good candidate for a deacidification treatment, whereas a painting with a canvas with a very low DP (under the “critical DP value”) might be in need of a lining or some sort of consolidation treatment. We know that pH tells us about the degradation rate: the lower the pH, the faster the canvas will degrade (1 p. 409). Therefore, the ideal pH for a painting to have would be a pH around the neutral value. DP is related to the mechanical strength of the canvas (2 p. 31), and therefore it tells us about its actual state. If the pH is appropriate, the canvas might retain that DP value for a long time; if the pH is acidic, then the canvas is at a higher risk of quick degradation in the future (2 p. 31).

Knowing the pH and DP should therefore allow us to grade paintings according to the condition of the canvas support and recommend certain conservation actions to be taken for each grade, for instance: “very degraded” (no travel allowed); “acidic” (might benefit from a deacidification treatment) etc. But where do we establish the limits? Which is the “critical DP value” for paintings? Which is the “safe DP value” for paintings? This is something that still had not been established (3 p. 24) and one of the aims of this strand of research.

A “Condition Assessment Panel” experiment to understand the meaning of the various DP values was done. To do it, different textile samples of known DP were sent to experienced paintings’ conservators, and they were asked to test and judge the samples according to their conservation experience. The first aim was to determine which is the “critical DP value” for paintings; that is to say the DP value below which paintings are very fragile. This means that they would better not travel at all because they could risk suffering damage in the support or that if they were removed from their stretcher, they would need lining, strip lining or some sort of reinforcement to be done on them, since they are too fragile to be handled. The second aim was to determine the “safe DP value”, the value above which the canvas of the painting could be said to be in a very good condition. The third aim was to establish four different DP categories related to four different grades according to the condition of the canvas into which paintings could be classified. All this could be achieved, given that the subjective conservators’assessment of samples with regards to their mechanical strength was found to correlate with theirDP in the first place, of course.

Mechanical tests could have been carried out for the different samples instead of doing the Condition Assessment Panel, but this again would have left us with several numbers, the meaning of which when it comes to paintings we would still not know. We therefore needed the subjective conservators’ experience to tell us which was the condition of the different samples according to them: what paintings with similar conditions to the samples they were sent could or could not withstand according to their experience. Of course, conservators were asked to handle the samples and to think how would they grade a painting with that same sample condition, a test that was not 100% realistic because the samples were very small in relation to a painting, but still it was thought that conservators were used at handling the margins of paintings and that they could extrapolate their assessment when manipulating the edges of a painting to the manipulation of the test samples. It also has to be taken into account that the size of the painting will also have an effect on the conservators' judgement regarding what can or cannot be done with a painting, since large paintings have to hold their own heavier weight, as well as whether it is thickly or thinly painted etc., as was noted by some of the panellists (4).

Therefore, with the information gathered from the Condition Assessment Panel, and the analytical measurements done on the Reference Sample Collection (Chapter 2), the final aim of this chapter was to design a "Condition Assessment Classification" that would take into account both DP and pH values to grade paintings according to their canvas condition. In a way, combining the obtained information on DP and pH is a way of integrating information on the present condition (DP) with information on the potential for deterioration (pH), which has already been advised to be good practice (5 p. 127). Investing time in grading objects into different conditions categories, certainly helps in more efficient management and planning of budgets, time and actions to be taken regarding the objects, which is always of interest for institutions (6 p. 39)(7).

Attempts to create classifications for objects based on the condition of their support have previously been done in other cultural heritage fields, such as for paper collections (8 p. 416). In this research, the authors determined the critical DP for paper and then, they calculated the time (in years) that each object would take to reach the critical DP level. According to the "life expectancy" obtained for the studied objects (from 200 to 6500 years), they were classed into three condition categories (less than 340 years to reach the critical DP; between 340 and 680 years to reach the critical DPand more than 680 years) (8 p. 417).

4.1.1 - Critical DP for paper

In the industry, the end of the useful life of paper has been set to be at around DP 250, which is the value at which paper tears too readily making it impossible to perform a tensile test on it (9).This is a very extreme low level, and it can be suspected that damage might be inflicted on paper objects if handled much before this very low value.

When it comes to cultural heritage objects, the value of 400 DP has been the one taken as the critical DP value for paper where "the risk of damage during handling was considered to be high". This value was taken based on observations of the studied paper objects and their DP values. Objects with DP values around 400 were degraded, some already having cracks along the edges (8 p. 416).

4.1.2 - Critical DP values for paintings in the literature

It is interesting to know that in the textile sector industry, for natural fibres, an 800 DP is the limit below which the textile is considered to be degraded (3). Of course the demands of the textile industry in terms of wear and tear of a piece of fabric are much higher than in our case, where paintings are handled as little as possible, the canvas is not folded and unfolded several times and it is just kept taut on the stretcher.

Back in 1993, it was already pointed out that a link between a particular DP value of a painting canvas and conservation action to be taken had not yet been established (3 p. 24). This was probably due, in part, to the lack of DP measurements done on paintings, and therefore of what DP values meant when it came to paintings.

One of the persons that has done more analysis regarding the DP of canvas from easel paintings (as far as we know) is the Italian paintings' conservator Giovanna Scicolone. She uses viscometry to measure DP and follows the Italian standard UNI 8282[1]. In her earlier papers, at the beginning of the 1990s, values of DP below 500 are said to be considered alarming, since “it is thought that the mechanical strength of the material decreases below acceptable levels” (10 p. 30). In later studies, when talking (implicitly) about the critical DP of paintings, she says that a painting with a DP of 300 could either need a lining or simply consolidation, depending on the painting (11 p. 310). Since below 350 DP, the degradation rate proceeds more slowly (11), the author states that a painting with a “critical DP value” of 280, could in some cases only be consolidated since “to go down to an hypothetical value of 250, under normal conservation conditions, it could take about 70-80 years” (12 p. 265). Of course, whether to line or just consolidate paintings with such low DP values, would depend on other factors on top of DP such as: dimensions of the painting, type of weave, density, thread thickness, type of fibre, condition of the canvas along the tacking margins...etc (12 p. 265)(13 p. 107).

A canvas of a 17th C painting done on (cardboard stuck on canvas) with a DP value of 955, was judged by the authors, F. Boggero et al.(14), as to be in good condition and in accordance with the high DP value obtained (14 p. 3). In contrast, the value of DP 580 in a painting from 1950 was found to be low and although the authors (E. Isella et al.) thought it did not need lining, they thought the canvas needed consolidation which was done with Beva 371, and some perimetric reinforcement through a strip lining (15 p. 6).

The very large painting, *L’Industria* from the Galleria Vittorio Emanuele from Milan, (3.50 x 3.80 m) (already mentioned in Chapter 2.3), was found to have a DP value of 239 by M. Fratelli et al. (16). This was in correspondence with the fact that the painting had several tears and the canvas felt somewhat weak.Therefore, the big question there was to decide whether to line it or not. pH measurements of some unpainted areas were also done from the front of the painting giving values that went from 4.2 to 5.8. The authors state that the DP value obtained (239) is around the turning point at which a painting should be lined. They also did two mechanical tests on two samples from the painting, one in the sense of the warp, the other in the sense of the weft, and they say that despite the low DP, the canvas still had “good resistance to fracture”. It is interesting to note that the authors say that the twill structure of the canvas (1:4) gives it additional strength it would otherwise not have if it was a plain tabby weave[2], and also that the whole painting is a system in which the paint layer helps to hold the canvas. Taking into account the good mechanical strength of the canvas despite the low DP value, it was decided not to line the painting because this would be too intrusive and would add a lot of weight to the painting. A Kevlar thread net was attached to the back of the painting at regular intervals with the adhesive Lascaux 498 20x (16 p. 122). What the article does not say is where the analysed sample came from, although it can be inferred that it probably came from one of the margins.

In the case of the painting, “*La Crossifissione di Dro*” from the end of the 16th C. (4,63 x 3 m), with a DP value of 255, the authors (B.E.A. Tomasoni et al. (17)), state that it is in bad condition, but also take into account the fact the the sample comes from a very damaged area, where there was no paint layer and the canvas was more exposed to the air. They point out the fact that the paint layer, on top of protecting the canvas from degradation, also gave the painting some structural strength. Therefore, in this case they decided to just consolidate the canvas with a synthetic resin (Plexisol P550, 5-7% in ligroin) and not to line it at all, maintaining more, the integrity of the object. They also note that the painting had never been restored before and therefore had escaped from the introduction of foreign materials that are acidic to start with (proteinaceous adhesives, alum, natural resin varnishes...). These materials traditionally applied to the reverse of paintings, would therefore introduce acidity and rigidity to the canvas, causing faster degradation (17 p. 18).

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[1] *UNI 8282 (1994): Cellulosa in soluzioni diluite. Determinazione dell'indice della viscosità limite. Metodo che usa una soluzione di cuprietilendiammina (CED)*, 1994. (066_1994_847). This norm “partially agrees” with ISO 5351/1-1981.

[2] Actually, a study of the types of weaves used by Anthony Van Dyck, has found that indeed there is a correlation between the types of weaves used by the artist and the size of his paints. Van Dyck is found to have chosen the twill type for larger format paintings (47 p. 382).

These two last reported cases are from people working around the Cesmar7, a Conservators' Association created in Italy about ten years ago. Cesmar7 is advocating minimum intervention to be done on paintings and this is why no lining was carried out in these two cases eventhough the DP values were extremely low.

4.2- Materials and methods

4.2.1 - Samples

In order to be able to do the Condition Assessment Panel experiment, samples with different known DP values were needed. To obtain these textiles with different DP values (and thus different degrees of degradation), a set of samples was gathered and then they were thermally degraded for different periods of time (see later on in this same chapter under "Accelerated degradation" for the specific conditions used). There were two types of plain woven textiles used: the first group was composed of old textiles (mostly old glue paste linings that had been removed during conservation treatments) and the second group was composed of new bare textiles with different treatments applied to them to obtain different degrees of degradation. Each type of sample was cut into several pieces so that different periods of degradation could be applied to the different pieces (1 and 2 weeks were used for degrading even further the historic samples, and from 6 to 10 weeks were used for the new ones).

These two types of samples were selected so that older canvas representing heterogeneous historic paintings was present and also so that newer more homogeneous textiles, with nothing else interfering, were present too. Of course, ideally one would have wanted to use real old paintings with different DP values so that there was no need to artificially degrade the samples, but these were not available on this occasion. We did however make use of one oil painting from the around 1925 without any value that was included in the degradation and testing.

Old historic textile samples

	Degradation period →	**A (0 weeks = non-degraded)**	**B (1 week)**	**C (2 weeks)**
	Physical identification on the sample →	**All corners intact**	**One corner cut**	**Two corners cut**
Sample number ↓	**Sample type ↓**			
10	Tate Gallery 19th C. loose lining, **116** (pH 4.33 & 4.34)	A10	B10	C10
11	Tate Gallery 19th C. loose lining, **117** (Landseer) (pH 4.3 & 4.3)	A11	B11	C11
12	Tate Gallery 19th C. primed loose lining, **115** (Landseer) (pH 5.4)	A12	B12	C12
13	Glue paste lining Barcelona, **102** (pH 5.2)	A13	B13	C13
14	Glue paste lining Barcelona, **103** (pH 5,8)	A14	B14	C14
15	Glue paste lining Barcelona, **106** (pH 4.4)	A15	B15	C15
16	Glue paste lining Barcelona, **107** a (pH 4.6 & 4.5)	A16	B16	C16
17	Glue paste lining Barcelona, **109** (pH 5.2)	A17	B17	C17
18	Glue paste lining Barcelona, **111** (pH 4.4 & 5.2)	A18	B18	C18
19	Glue paste lining Barcelona, **112** (pH 4,9)	A19	B19	C19
20	Glue paste lining Barcelona, **113** (pH 4.9)	A20	B20	C20
21	Glue paste lining Barcelona, **114**. (pH 6.2)	A21	B21	C21
22	1925 oil painting, **76**	A22	B22	C22
23	Bleached household linen, **129** (pH 6.9)	A23	B23	C23
24	Glue paste lining Barcelona, **104** (pH, 4.3)	A24 (104)		
25	Glue paste lining Barcelona, **105** (pH 4.3)	A25 (105)		
26	Glue paste lining Barcelona, **110** (pH 5.3)	A26 (110)		

Figure 1. List of all the historic samples aged. In grey those that were finally used for the Condition Assessment Panel

Textile samples were sewn onto blotting paper that could be hung in the climate chamber. Old glue paste lining samples were sewn so that the glue paste side was placed inwards, and the "atmospheric dirt" layer outwards, as would be the situation in lined paintings.

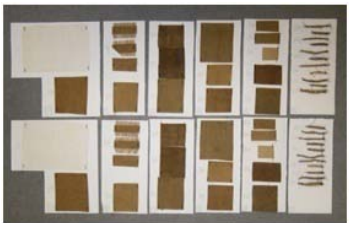

Figure 2. Sets B and C with all the historic samples before degradation. Note that some are already quite degraded (dark colour).

A total of 14 different types of old textiles were aged (1 week (B) and 2 weeks (C) plus the non degraded set (A). Therefore we had a pool of 42 different historic samples to choose from (+ 3 non degraded samples: 104, 105, 110).

New baretextile sample names

	Degradation period →	**A** **(0 weeks = non-degraded)**	**D** **(6 weeks)**	**E** **(7 weeks)**	**F** **(8 weeks)**	**G** **(9 weeks)**	**H** **(10 weeks)**
	Physical degradation identification on the sample →	**All corners intact**	**Square cut on the top left corner**	**Square cut on the top left corner & bottom right corner**	**Angle cut on the two top corners**	**Angle cut on three corners**	**Angle cut on all the corners**
Sample number ↓	**Sample type ↓**						
1	New linen	A1	D1	E1	F1	G1	H1
2	Cotton duck	A2	D2	E2	F2	G2	H2
3	New linen, sulfuric acid & ammonium hydroxide treated (one corner cut)	A3	D3	E3	F3	G3	H3
4	New linen, aluminium sulfate treated	A4	D4	E4	F4	G4	H4
5	New linen + animal glue	A5	D5	E5	F5	G5	H5
6	New linen + animal glue + chalk prep.	A6	D6	E6	F6	G6	H6
7	New linen + animal glue + chalk & oil prep.	A7	D7	E7	F7	G7	H7
8	New commercially acrylic primed linen (one corner cut)	A8	D8	E8	F8	G8	H8
9	New commercially oil primed linen	A9	D9	E9	F9	G9	H9
23	Bleached household ramie (100 years old)	A23	D23	E23	F23	G23	H23

Figure 3. List of all the historic samples that were degraded. In grey those that were finally used for the Condition Assessment Panel

A total of 10 different bare textiles were artificially degraded (Figure 4). Samples with “new linen” (1, 3, 4, 5, 6 and 7) were samples from the very same roll of linen, only with different treatments done to it. Samples 8 and 9 were commercially primed canvas bought at Cornelissen &Son. Samples 23 were from an old bare textile.

Of the linen samples finally used for the Condition Assessment Panel (1, 3 and 4), 1 was bare linen with nothing done to it.

Samples 3 had been dipped in a 10% solution of sulfuric acid into distilled water by volume (10 mL of concentrated sulfuric acid by 90 mL of distilled water) and left there for a week.Then they were neutralised with 1.4% ammonium hydroxide and washed several times in distilled water baths (18 p. 355). The pH of the last water bath of these samples (sulfuric acid treated) was pH 6.7. After drying, the pH of the samples was 6.5.

Samples 4 were placed into a 1% aluminium sulfate solution (1 g of aluminium sulfate per 100 mL of distilled water). The linen textiles were left to soak for 1 h, after which each piece was placed between blotting papers and weights added on to them, to absorb the excess solution. After a couple of hours, the canvases were transferred onto a new piece of blotting paper and left to dry horizontally in the air. The 1% aluminium sulfate solution had a pH of 3.4. After drying the samples had a pH of 4.7.

Since there were six sets of aged samples for each type (one non-degraded and five from 6 to 10 weeks of degradation), there was a total of 60 different “new samples” available. Not all of them were used for this experiment and in fact, many of them had been prepared already thinking that they could be used in future research studies (samples 5,6,7,8 and 9). Each new sample measures about 15 x 20 cm.

The number of available samples to chose from between new and old textiles and with the different periods of degradation was 102. Of these, 35 were selected for DP to be measured and those were the ones finally used for the Condition Assessment Panel.

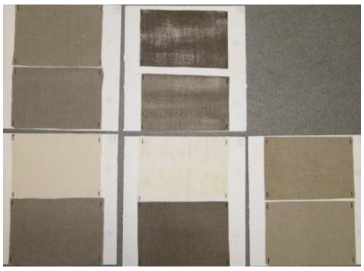

Figure 4. One of the six sets (set H) of new textiles before degradation, with the ten types of textiles.

Accelerated degradation

Accelerated (or artificial) degradation[3] of materials will never exactly mimic natural ageing, because natural degradation happens due to a number of different agents that influence each other (temperature, moisture, light, pollutants, air circulation etc.) and happen over a long period of time.

Even if artificial degradation will never be the same as natural ageing, it is used because it does indicate how future degradation of original objects or conservation materials might proceed, and because by singling out the different degradation agents, their particular effects on the tested object can be better understood (19 p. 248).

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[3] Henk Porck, in a report about the state-of-the-art on artificial ageing applied to paper (20), proposes the use of the term “artificially induced degradation tests” instead of “artificial” or “accelerated ageing”. The use of this new term suggests better what these laboratory tests produce: samples with a particular type of degradation depending on the degradation regime used.

In the conservation field there is yet no agreement on the artificial degradation procedures that best correspond to natural ageing and there is disagreement with respect to the conditions under which artificial degradation should be carried out (about forty different artificial degradation regimes used for paper have been collected in H. Porck's report *Rate of paper degradation* (20 pp. 9,16)). The industry has developed different international standards (ISO, TAPPI, ASTM…), and adaptations of these have been usually used in the conservation field (19 p. 249).

Artificial degradation normally includes elevation of temperature, because at higher temperatures, chemical reactions happen at a faster rate. It is also good if relative humidity is controlled, since if only temperature is increased, relative humidity can decrease to values that can be considered very unrealistic. The closer all the parameters are to natural conditions, the better, since extreme conditions will favour reactions which might never take place in real life. Therefore, it would be advisable to have a constant relative humidity of about 50-60%, similar to that in which the object would be under natural ageing conditions. Regarding temperatures, all ranges from 22 to 160ºC have been used (20 p. 21).

In our case, thermal degradation of our samples was done so that we would obtain different textiles with a good spread of DP values, especially in the lower ranges. No attempt was made either to predict what the degradation would mean in terms of natural ageing, or in order to understand degradation processes. A similar approach has been used for instance by Bonfatti et al. in a project that aimed at researching the effects of different consolidation treatments using consolidants on differently degraded linen textiles (21 p. 12). In their case the degradation regime they used to obtain textiles with different DP values was to dip the samples in a 1M hydrochloric acid solution at 50ºC for increasingly periods of time (they do not say how long these periods were). Samples were then washed until the pH of the washing solution was neutral. Then they were treated with adhesives they were researching and subsequent analysis of the samples before and after the adhesive treatment were done to inform the project.

Our samples were sewn onto blotting paper and these were sent to Slovenia, where they were hung inside a climate chamber (Vötsch VC 0020 climatic chamber) (Figure **5**). This was done by Alenka Možir at the Faculty of Chemistry and Chemical Technology, University of Ljubljana (Ljubljana, Slovenia). The temperature was set at 90 ºC and relative humidity at 65%, since it was known reasonably well how such degradation regime would affect our samples based on previous experiments with cellulosic samples (19 p. 268). The degradation started on the 17th May 2010 and samples were gradually removed from the oven over a 10-week period according to a timetable.

Figure 5. The samples inside the climate chamber running at 90ºC and 65% RH

The old historic samples were degraded for a shorter period of time (only two weeks) than the new textiles because they were seen to be already quite degraded and this period seemed to be enough (Figure 6). New textiles were degraded from 1 to 10 weeks (Figure 7).

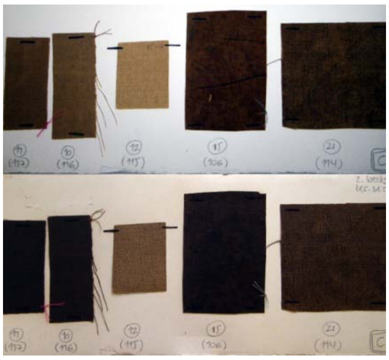

Figure 6. Some of the historic samples (part of set C), before and after two weeks of degradation.

Figure 7. Set H of new textiles before and after degradation.

Available DP values

Viscometric measurements of DP were done following the developed methodology (see Chapter 2.3). Of the pool of 102 textiles in different conditions, 35 were selected and DP measured. The selection of textiles of which to measure DP was done so that a broad range of DP was available, especially in the lower ranges since it was envisaged that very good condition textiles would be easy to agree on, but that with degraded canvases, disagreement could be higher. Besides, proper classification of the more degraded canvases might be more useful in decision making strategies.

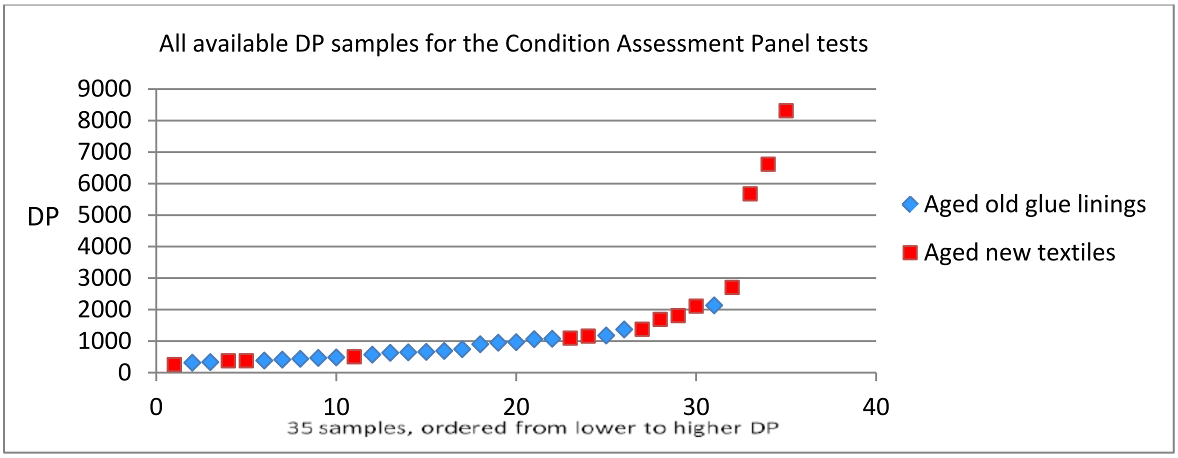

Figure 8. The available DP values of the 35 samples for the Condition Assessment Panel

The final range of DP values used for the Condition Assessment Panel was from 258 the lowest, to 8310, the highest value (Figure 8). This included both degraded and non-degraded samples, and both new and historic samples. In general, new textiles were used for higher DP values, historic ones for lower ones.

Old historic samples

Before degradation, historic old glue paste linings had DP values that spanned the interval of 485 to 2700. After degradation, the lower value limit decreased to 317 and more DP values in the lower range were obtained (Figure 9).

	Period of degradation→	**A** **(0 weeks = non-degraded)**	**DP**	**B** **(1 week)**	**DP**	**C** **(2 weeks)**	**DP**
Sample number ↓	**Sample type ↓**						
10	Tate Gallery 19th C. loose lining, **116** (pH 4.3 & 4.4)	**A10**	**903**	**B10**		**C10**	
11	Tate Gallery 19th C. loose lining, **117** (Landseer) (pH 4.0 & 4.7)	**A11**	**485**	**B11**		**C11**	
12	Tate Gallery 19th C. primed loose lining, **115** (Landseer) (pH 5.4)	**A12**	**952**	**B12**		**C12**	
13	Glue paste lining Barcelona, **102** (pH 5.2)	**A13**	**1064**	**B13**	**386**	**C13**	**317**
14	Glue paste lining Barcelona, **103** (pH 5.8)	**A14**	**2136**	**B14**	**1181**	**C14**	**1077**
15	Glue paste lining Barcelona, **106** (pH 4.4)	**A15**	**746**	**B15**		**C15**	
16	Glue paste lining Barcelona, **107** a (pH 4.6 & 4.5	**A16**		**B16**		**C16**	
17	Glue paste lining Barcelona, **109** (pH 5.2)	**A17**	**1372**	**B17**	**440**	**C17**	**337**
18	Glue paste lining Barcelona, **111** (pH 4.44 & 5.2)	**A18**		**B18**		**C18**	
19	Glue paste lining Barcelona, **112** (pH 4.9)	**A19**	**631**	**B19**	**469**	**C19**	**415**
20	Glue paste lining Barcelona, **113** (pH 4.9)	**A20**	**647**	**B20**		**C20**	
21	Glue paste lining Barcelona, **114**. (pH 6.2)	**A21**	**969**	**B21**	**691**	**C21**	**573**
22	1925 oil painting, **76**	**A22**	**661**	**B22**		**C22**	
23	Bleached household linen, **129** (pH 6. 9)	**A23**	**2706**	**B23**		**C23**	
24	Glue paste lining Barcelona, **104** (pH, 4.3)	**A24 (104)**	**654**				
25	Glue paste lining Barcelona, **105** (pH 4.3)	**A25 (105)**	**538**				
26	Glue paste lining Barcelona, **110** (pH 5.3)	**A26 (110)**	**608**				

Figure 9. Table with all the historic glue paste linings samples available and the DP values, where this parameter was analysed.

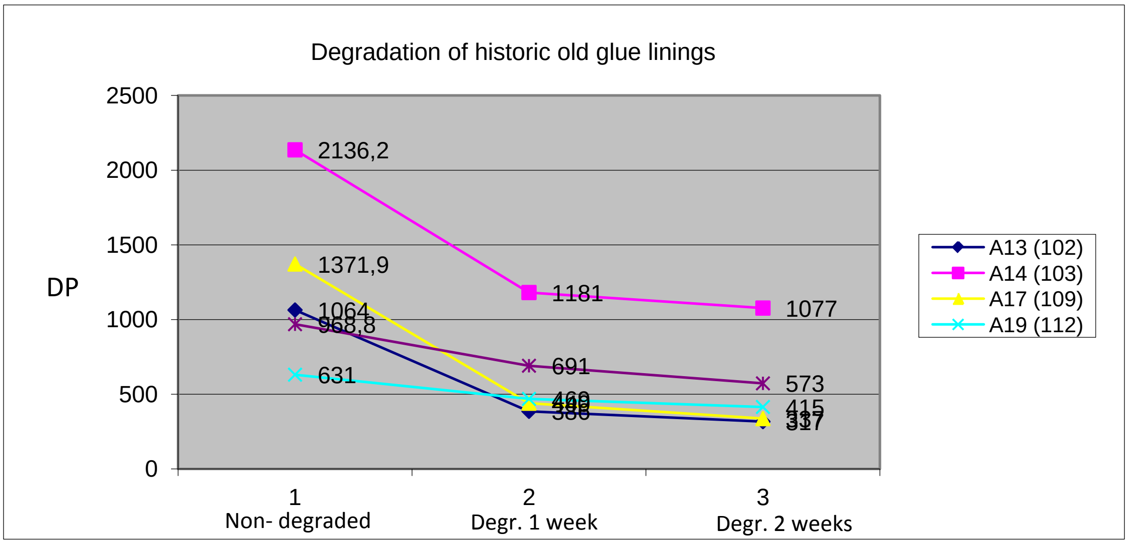

Figure 10. DP decrease on degradation for five of the historic samples.

For those historic glue paste linings where DP was measured of the non-degraded sample and of the samples degraded 1 and 2 weeks (Figure 10), it was noticed that there was a strong decrease on the DP value after the first week of degradation, but a lower decrease after the second week. Therefore it was the right decision not to age these samples for longer than two weeks, since many of them degraded to very low DP values already within two weeks.

<u>New samples</u>

Before degradation, the DP values of the new textiles ranged from 1812 to 8310 (the sulfuric acid treated linen having the lowest value and the new cotton duck having the highest). After degradation, this range shifted to 258-1691 (the aluminium sulfate having the lower DP value and the bare linen the highest)(Figure 11).

It is interesting to note that before degradation the textile with the lowest DP is the one that had been treated with sulfuric acid, whereas after degradation, the sample with the lowest DP (258) is the one that had been aluminium-sulfate treated.

Once again, this proves how much pH influences degradation. As mentioned earlier, before thermal degradation, sample 3 (sulfuric acid treated) had pH 6.6, since after the treatment the sample had been neutralised with ammonium hydroxide and rinsed in many water baths until the pH of the water was almost neutral. The pH of sample 4 (aluminium sulfate-treated) had a significantly lower pH of 4.7 since the sample had been immersed in the aluminium sulfate solution, rinsed off and left to dry. Therefore, degradation proceeded much faster in sample 4 (see Figure 12).

Non-degraded cotton had the highest DP (8310) and after degradation its DP decreased to a value lower than that of linen (1097 for degraded cotton and 1691 for degraded linen), when originally the DP of linen was 6614 (Figure 11). These results support the fact that under the same circumstances, cotton degrades faster than linen. This is due to the higher proportion of amorphous regions of cellulose in cotton, making it more susceptible to degradation (11).

	Period of degradation →	**A** **(0 weeks = non-degraded)**		**D** **(6 weeks)**		**H** **(10 weeks)**	
Sample number ↓	**Sample type ↓**						
1	New linen	**A1**	**6614**	**D1**	**2111**	**H1**	**1691**
2	Cotton duck	**A2**	**8310**	**D2**		**H2**	**1097**
3	New linen, sulfuric acid & ammonium hydroxide treated (one corner cut)	**A3**	**1812**	**D3**	**506**	**H3**	**379**
4	New linen, aluminium sulfate treated	**A4**	**5674**	**D4**	**378**	**H4**	**258**
23	Bleached household ramie (100 years old)	**A23**	**2706**	**D23**	**1379**	**H23**	**1161**

Figure 11. All the DP values available from the new textile samples.

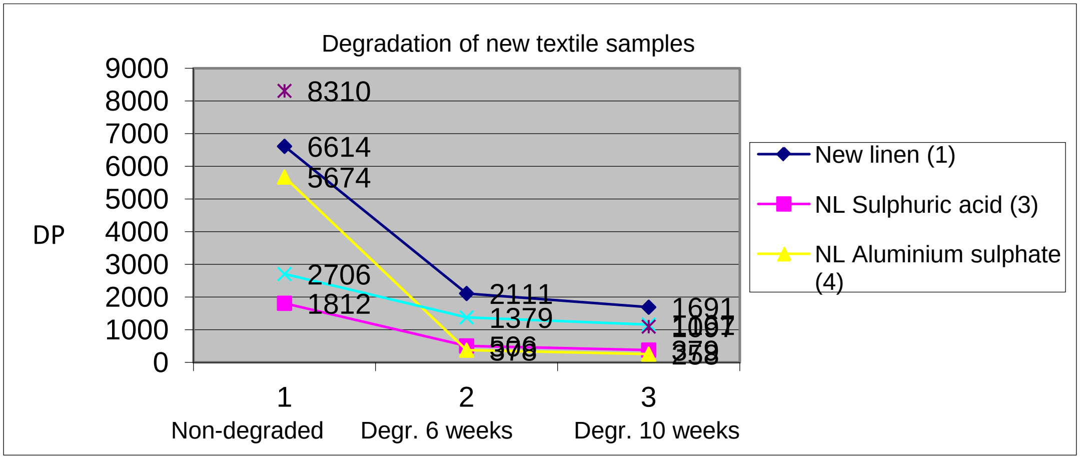

Figure 12. Degradation of new textile samples used for the Condition Assessment Panel after 6 and 10 weeks.

As was the case of old lining samples, DP decreased more in the first stage of degradation than in the following one. In this case, however, it has to be noticed, that the first stage is after 6 weeks of degradation, and the second one after 10 (which actually means only 4 weeks more).

As expected, old glue paste linings being already quite degraded and full of acidic products (from the glue paste linings, from the cellulose degradation products, from dirt etc.), degraded quite significantly with just one or two weeks of thermal degradation. With further 6 or 10 weeks of degradation of these samples they would have degraded to a state unsuitable for the survey. On the contrary, for new samples, with just one or two weeks of degradation, we would not have seen such a significant DP drop and thus the degradation regime used was found to be appropriate. Note that it took 10 weeks of thermal degradation at 90 ºC for linen samples without any treatment degrade from DP 6614 to DP 1691. If lower DP values need to be obtained for bare linen textiles, longer thermal periods of degradation are needed.

4.2.2 – Condition Assessment Panel

The Condition Assessment Panel test was designed in order to understand the meaning of DP values, that is to say, to establish both the “critical” DP and the “safe” DP for paintings and to establish four different condition categories.

The test relied on the conservators’experience when it comes to handling paintings and thus, the first “pre-aim” to check was if their perception correlated with the measured DP of the samples.

Each “panellist” received about six 1.5 x 6 cm textile samples and a set of instructions on how to manipulate them. They were asked to pull, bend and stretch the sample, assuming it was part of a painting and to class them into one of four categories, according to what they thought they could do with a painting with a canvas in such a condition. The worst category was category 1, “Very fragile canvas”. A painting classed in such a condition would be a painting the canvas of which would be at serious risk of being easily accidentally torn, unfit for travel without some previous sort of action taken (cushioned backing board etc.) or that one would not be able to reattach to its stretcher if the painting was removed from it without lining it.

The best condition category, “Canvas in good condition”, would be for those paintings that a conservator would say are in good condition, such as new paintings.

The difference between the two middle categories (“Fragile canvas” and “Somewhat fragile canvas”) are not so clear, and therefore lower agreement on these two categories was expected. However, they were introduced, so that there was a larger gradation than just three categories (“very bad”, “very good” and “intermediate”). Also, having four categories instead of three made it easier that those samples that were in VERY bad shape and those that were in VERY good shape, were easily separated from the rest and were classed as such. In fact, three categories have been identified as too few when trying to design condition grades to be used in surveys, and five as too many since then the majority of the objects are assigned to the middle, indeterminate grade, which is not very useful. This is why many institutions have gone for four categories for condition rating of objects (22 p. 9). Nonetheless, other researchers doing condition analysis of heritage materials, have recently gone for five categories when trying to class objects (very poor condition, poor, fair, good, very good) (23 p. 7).

Of course, conservators’ subjectivity and the natural inhomogeneity of samples playing an important role, precise limits within categories were not expected but more general broad categories that could be used as a guide.

Figure 13. Samples as received by panellists, together with the testing instructions and the results grid to be filled in.

Instructions sent to panellists

The following are the instructions that were sent to panellists together with the samples:

You should do the following test with each of the textile samples you have received and record the category number you would give to each sample:

1- Handle the piece of canvas with your fingers as though it was part of a painting:
  - by pulling the canvas with your fingers
  - by bending it at 90º over the edge of a table and pulling down (as though you were tacking the painting back to the stretcher)

You can pull and handle it as much as you need to get a feel of its condition: you can even try tearing it into small pieces.

2- After handling the canvas put it in one of the following categories:

☐1- Very fragile canvas, it cannot be re-stretched without reinforcing it.

☐2- Fragile canvas, re-stretching might lead to tearing.

☐3- Somewhat fragile canvas, re-stretching can be done carefully.

☐4- Canvas in good condition, it can be handled.

4.2.3 - Participants

A total of 17 different participants took part in the Condition Assessment Panel. They were mainly paintings' conservators and a few scientists from seven different countries (Spain, UK, France, Italy, Denmark, USA and South Korea). They were all professionals with long-standing careers in the field of conservation from well-established leading institutions (Figure 14).

Acronym	Name	Profession	Institution	Country
NP	Núria Pedragosa	Paintings' conservator	MNAC	Spain
MT	Maite Toneu Pau Claramonte (fellow) Nadir López (fellow)	Paintings' conservator Paintings' conservator Paintings' conservator	CRBMC	Spain
P	Maite Jover Lucía Martínez	Biologist Paintings' conservator	Museo del Prado	Spain
IC	Irene Civil	Paintings' conservator	Fundació Gala- Salvador Dalí	Spain
MO	Marta Oriola	Paintings' conservator	UB	Spain
GC	Gema Campo	Paintings' conservator	UB	Spain
SH	Stephen Hackney	Paintings' conservator	Tate Gallery	UK
CY	Christina Young	Paintings' conservator	Courtauld Institute of Art	UK
AB	Anne Bacon	Paintings' conservator	Northumbria University	UK
JD	Jim Devenport	Paintings' conservator	Haughton Studios	UK
MS	Matija Strlic	Chemist and paper conservator	Centre for Sustainable Heritage (UCL)	UK
JFH	Jean François Hulot	Paintings' conservator	Conservation Consultant, France	France
Er	Erminio Signorini	Paintings' conservator	Cesmar7	Italy
CKA	Cecil Kraup Andersen	Paintings' conservator	School of Conservation	Denmark

ES	Eileen Sullivan	Paintings’ conservator	Cleveland Museum of Art	USA
KB	Kenneth Bé	Paintings’ conservator	Gerald Ford Conservation Center	USA
EK	Eun-Jin Kim	Paintings’ conservator	National Museum of Contemporary Art	South Korea

Figure 14. List of professionals who performed the Condition Assessment Panel, grouped according to their country of origin.

Each participant received a set of about six samples and the instructions to follow. Each sample was placed inside a paper envelope and send out by regular mail in hard plastic boxes to avoid the fragile textiles being crushed and damaged. Sample envelopes were not ordered according to DP values but mixed on purpose to encourage more unbiased results (see Annex III). It is believed that most of the conservators did the tests following the order they received the samples in. Doing this six samples test took about 30-45 min and all the conservators who had agreed to do the tests did so in a very timely manner.

35 different DP textiles were tested a total of 187 times. This means that on average, every sample was tested by 5 different panellists. In reality, however, all the samples were tested at least by 2-3 panellists, some of them by 11. Higher DP values, where agreement was assumed to be much higher, were given to fewer people, so that samples with DP values lower than 1000 (where less agreement was expected) could be tested by more people (See Annex III for all the Condition Assessment Panel results).

4.3- Results and discussion

4.3.1 – Condition Assessment Panel results

Once all the Condition Assessment Panel results were received, categories that had been assigned a sample were averaged. If the average category was 1, it meant all panellists agreed that the category of that sample was 1. Similarly if the average result was 4, it meant that everybody agreed in that that sample was in very good condition. For numbers between 1 and 4, there was a certain level of disagreement for all samples, which was actually not a surprise, the test being a subjective one. In Figure 15 it can be seen that most of the samples were classified between two categories (orange), some were placed in three different categories (red) and two were placed four different categories by different panellists (black). The final average category number, though, usually indicates which was the predominantly assigned category for each sample. In all the cases where samples had been assigned to two or three different categories, these had always been assigned to subsequent categories.

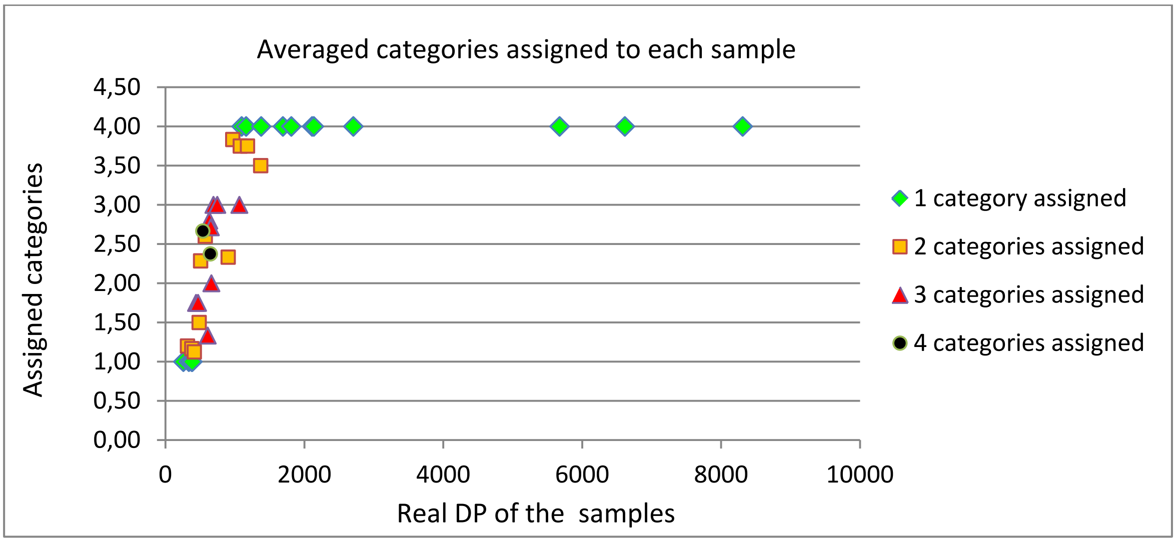

Figure 15. All the samples placed according to the averaged category given by conservators and its DP, with indication of the level of agreement between panellists.

The first thing to note, however, is that there is high level of correlation between the conservators' feel of the canvas condition and it's DP (Figure 15), since higher DP values samples are classed as better condition ones and the other way around.

It is clear that agreement is much higher at the two ends: with very degraded samples and with those in very good condition. As expected, more disagreement is found in the middle range samples, were the distinction between what one considers to be a "fragile canvas" or a "somewhat fragile canvas" is more subjective.

It is interesting to know that similar research where the condition of silk was first visually assessed by a conservator and then established using NIR spectrometry and chemometric methods developed for determining the tensile strength of silk, a matching trend between the two was also found (23).

To see things more clearly, the same graph is plotted but only with samples with DPs lower than 1400, which is where we have our lower three categories (Figure 16).

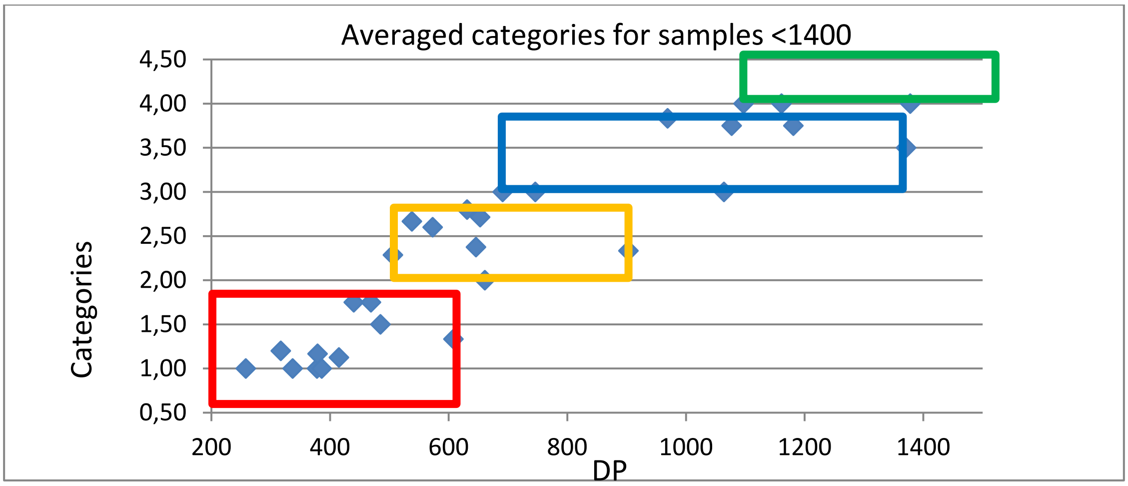

Figure 16. Samples with DP<1400 placed according to the averaged category given by conservators and DP. The rectangles delimit the DP values of the samples present in each category.

In Figure 16 we see that in Category 1 (very fragile) we find samples with DP values that go from 258 to 608. (Here we understand that all samples that have an average category of less than 2, are Category 1, since this means that at least somebody thought they were Category 1, and this makes the number to be less than 2. We are therefore taking a more conservative approach, by thinking that if somebody thought the sample was Category 1, we already put it in there).

Following with the same logic, in Category 2 we have samples with DP values that go from 506 to 903. Category 3 contains samples with DPs ranging from 691 to 1371 and Category 4 from 1097 to 8310. It is clear then that if we only look at the samples tested and the averaged categories, the limits between categories overlap a lot. However, it has to be taken into account that we are working with averages, subjective testing, subjective understanding of instructions and with inhomogeneous samples. Therefore if we add the regression line, assume no overlap of categories and extrapolate information to the missing DP values we did not test, we can work out category divisions that enable us to work with particular and defined DP ranges (Figure 17). Nonetheless, it will always have to be remembered that with paintings, the limits between one category and the other will never be that sharp (Figure 16), and that the divisions are done so that they offer us general guidelines to work with.

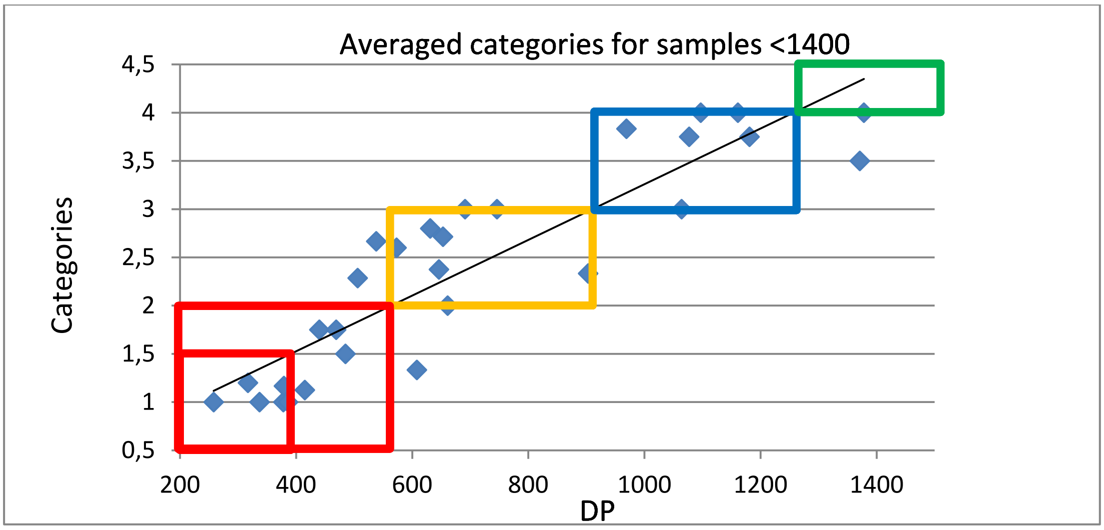

Figure 17. Averaged categories for samples with DP<1400, with the 4 defined categories broadly represented.

Category 1, “Very fragile canvas”, could be established therefore at around DP<550. Category 4, “Good condition canvas” would go from DP 1300 onwards.

Regarding the “Critical DP” of paintings, if we want to be more restrictive and identify those paintings that are really very fragile, this limit could be established at DP<400, since at this value there is an agreement of above 50% within all the panellists that these samples were “Very degraded”. Between 400 and 550 DP, above 50% of the panellists thought these samples were in Category 2, so although they are placed in Category 1 because their average is below 2, some experts did not assess them as that degraded. Below 400, however, there was much better agreement that these samples were Category 1. Therefore, according to our results, a painting with a DP below 550 has many numbers of being at risk, and below 400 it is judged to be clearly at risk if it is removed from its stretcher or if it is allowed to travel, for instance. The critical DP value for paintings, as defined here, would therefore be below 400.

As we have already explained (see the section “Critical DP values for paintings in the literature” in this same chapter), some researchers state that paintings with much lower DP values (as low as 239, (16 p. 122)) can still remain without lining, although consolidation with adhesive was carried out. Others found that at 580 DP, a painting did not need full lining, but they carried out strip lining (15). We are not saying at all that paintings below 400 should be lined, since if a painting is left alone, it can be ok even with much lower DP values. However, it is true that the very low DP values found in the literature on two large paintings (DP 239 (16 p. 122) and DP 255 (17 p. 18)) puzzle us a little bit since, according to the experience gained through our research, these are really low values. This low values make us wonder how such large paintings in this condition are able to hold their own weight and not be falling apart. An explanation could be that the two examined samples came from very degraded areas (in fact, for one of the paintings this is actually the case and it is clearly explained in the article itself (17 p. 18)). If this was the case for both paintings, this would explain how such large paintings could get away only with canvas consolidation: because other areas of the canvas had slightly higher DP values. (We have actually seen in Chapter 2.3 that DP variability between different areas of the same painting could actually be large (average RSD 22%) in cases where a sample is taken from a visibly more degraded area.

Regarding the “Safe DP for paintings”, it can be seen that from 1300 onwards, the samples are classed as the best condition category (Category 4). The agreement between experts is 100% for samples with DP >1400 and therefore, if we are a bit conservative again, it could be said that the safe DP for paintings could be established at >1400 DP. Therefore a painting with a DP higher than 1400 means that even if the canvas has suffered some degradation, the canvas is still in very good shape (new canvas can have much higher DP values than 1400, as it is exemplified by the two best condition samples that were used in the Condition Assessment Panel: raw new linen (DP 6614), and raw new cotton (DP 8310)).

The two intermediate categories, Category 2, “Fragile canvas”, spanned DP 550 – 950, and Category 3, “Somewhat fragile canvas”, DP 950 - 1300. These findings are consistent with published DP values for a painting which, with a DP value of 955, was perceived not to be in a very bad condition (14).

The four categories according to the DP value, would therefore be established as:

Category	Meaning	DP range
Category 1	Very fragile canvas	<550
Category 2	Fragile canvas	550 – 950
Category 3	Somewhat fragile canvas	950 – 1300
Category 4	Canvas in good condition	> 1300

Figure 18. The four DP categories resulting from the Condition Assessment Panel.

Coming back to the conservators’ agreement, it is interesting to note that there was much more variability in category assignation regarding old linings whereas agreement was much higher for the new aged textiles. In the case of old linings, it was common to find that 2 or 3 different categories had been assigned to the same sample and even the four different categories had been assigned in two cases **113** (A20) with a DP of 646 and sample 105 with a DP of 538). In these two cases, although the samples had been assigned to category 2 by most of the panellists, at least one other expert had chosen one of the remaining three categories.

For new aged textiles, this variability was much smaller, everybody agreeing to category 4 for samples in good condition, and two categories being used at the maximum for degraded samples.

This could be a consequence of the higher inhomogeneity of old historic samples, as could be anticipated, which is possibly why there was a higher disagreement between panellists.

The specific case of sample 110

Sample **110**, with a DP of 608, offers a very interesting case to reflect on. This sample consists of a very open weave, with very thin threads that seem to be impregnated with some sort of adhesive. This impregnation makes the threads quite rigid. The sample was perceived to be very fragile, since just by folding it, it would break without any effort. When pulling it from both ends in the opposite directions, it did not seem so fragile, but it did not resist much force either. This is why, finding out it had a DP of 608 was puzzling. Comparing it with sample **112** (A19), that had a similar DP of 631 and sample **113** (A20) that had a DP of 646, the weakness of sample **110** was found to be out of the norm. Comparing the mechanical resistance of the three textiles, it was seen that **110** was clearly much weaker, susceptible above all to folding: as said, **110** would break after just one fold, whereas sample **113** needed about 4-5 folds and some pulling force and sample **112** more than 7 folds and again some pulling force.

Figure 19. Detail of samples **110**, **112** and **113** (from left to right)

The explanation for this can be a combination of the two differences found between sample **110** and samples **112** and **113**: on the one side the thinness of the threads and of the textile (open weave) and on the other side the impregnation of the threads with some sort of material that makes them much more rigid. The thinness of the textile seems to make the textile less strong to mechanical strength when pulling the textile from both ends, the rigidity of the material clearly makes it more sensitive to folding forces, transforming it a bit more like a glass-like material. Both things will have to be taken into account and kept in mind since it is clear that together with the size of the painting, the thickness of the threads, the tightness of the woven textile and its impregnation with other materials, all these factors will play an important role regarding the canvas mechanical stability on top of its particular DP value.

In fact, it is known that for very degraded canvas, a less intrusive conservation treatment than lining is consolidating the canvas by adding glue to its reverse. This technique is specially practised in Italy and it has been proven by A. M. Bonfatti et al. to make degraded canvas more mechanically resistant (21 p. 13). However, another very interesting finding of the aforementioned research, is that consolidation can make the canvas more rigid and block the movement between yarns, lowering the resistance to tear propagation (this means therefore that consolidated canvas is more prone to tear propagation if accidentally hit, for instance). Between the four adhesives studied in the mentioned article, animal glue seems to be the one that produces this effect the most (against Beva 371, Plexisol P550 and Akeogard AT35). Interestingly, the application of the glue and preparation layers to the linen canvas when preparing it for painting is also seen to produce this same effect (21 pp. 14-15)(18 p. 356).

This “rigidifying effect” of the glue, preparation and paint layers is well known to conservators. If a piece of canvas was to be cut out of a painting, this could be most often kept upright without the canvas falling down and it is clear that it is the paint and preparation layers that would be holding the whole system upright since there is no stretcher here (Figure 20).

Figure 20. Piece of a painting (**76**), with a cotton canvas and DP 660. It is clear that in this case the paint layer is holding the canvas and not the other way around, since the untacked textile would not stay up right on its own.

This fact of the paint and preparation layers "holding" the canvas can already be seen when we just have a glue layer applied to the canvas (Figure 21).

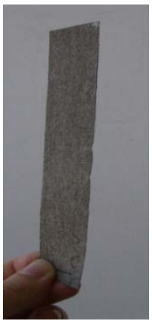

Figure 21. Animal glue applied to bare canvas. The glue makes the canvas already rigid enough to be kept upright.

Therefore the fact that the preparation and paint layers also give some sort of mechanical "support" to degraded canvases has to be kept in mind. In fact, according to M. Mecklenburg who has studied the forces between different painting layers, once the painting canvas is stretched and dry, the tautness of the canvas comes from the dried glue and not the canvas. At this stage, according to him, the primary support of the paint layers is the glue, and not the canvas (24 p. 175). However, paint layers become brittle with ageing (25 p. 69) and it is clear that a degraded canvas will be less able to support an impact if accidentally hit, whereas a canvass in a better condition might be able to "absorb" the impact without breaking.

4.3.2 - Condition Assessment Classification

Once we have established four categories according to the DP value of paintings, it is time to take pH values also into account. pH will be an important parameter to pay attention to, especially for those canvases which still are in the two intermediate categories. Paintings in these ranges that have a neutral pH, will probably keep their DP values for a long time (we have seen that samples several centuries old with neutral pH have been kept in extremely good condition with high DPs until today (i.e.samples **80** and **94**)). However, the more acidic the pH is, the faster this canvas degrades. Acidic paintings would be paintings where some conservation action still could be taken, and deacidification or the addition of acid absorbing materials, could be good preservation actions (8 p. 417).

Of course, both very degraded and very good condition canvases that were acidic, would benefit too from deacidification treatments, but if there were economic and time constraints, the middle range paintings would be the ones to prioritise since in the case of very degraded canvases, much of the damage already has been produced and there, the higher risk is that of mechanical damage. Therefore they would probably benefit more from support consolidation (8 p. 417)(21). In the case of very good condition canvases that are acidic, there is still some time left until they reach a critical condition level (although, again, they would of course also benefit from deacidification treatments).

When it comes to what is too low a pH, it has to be remembered that the higher the pH the better, since the lower it is, the faster the degradation rate of cellulose is (26 p. 205) and since cellulose fibres are considered to be stable in a slightly alkaline environment (pH 7- 8.5) (27 p. 38).

Moreover, it is good to remember when trying to figure out what pH values mean that pH works on a logarithmic scale, therefore a drop in 1 unit, means there are 10 times more H^+ ions, which means that the difference between 7 and 6, is that in pH 6 there are 10 times more H^+ ions, in pH 5 there are 100 times more H^+ ions than pH 7, in pH 4 there are 1000 times more H^+ ions than pH 7 and so on… (28 p. 1)

Even if all of the acidic paintings (pH <7) would benefit from a deacidification treatment, we would like to identify among the acidic ones (which are the vast majority of paintings as seen in this research (see Chapter 2.2)), those that should be treated first. Of course, the lower the pH, the higher the priority. But in order to separate them into two categories, we should decide on a threshold pH value to distinguish between those that should be treated first because they are “very acidic”, and those that could be treated second, because they are “not so acidic”.

In order to establish this threshold pH value, we turn our eyes to the paper conservation domain, since there, pH determination and deacidification has been in use for over half a century.

There are large volumes of literature on mass deacidification of books, talking mainly about the different deacidification processes, comparing them, explaining the methods chosen by particular institutions etc., but in these articles, we have not been able to find none that specifies under which pH value, deacidification is advised. At the most, they specify what the expected pH after deacidification should be (between 7 and 8 (29 p. 40); between 8 and 9 (30); and between 6.8 and 10.4 (31) (even if pH>9.5 is not advisable since alkaline degradation and oxidation could be accelerated (32 p. 81)). Therefore, the assumption is that for libraries, every book that is acidic (below pH 7) is considered a candidate for being deacidified (33). On consulting the experts, however, some think pH 5.5 is the decision point when it comes to books (34).

When it comes to paper art works, then a more individualized approach seems to be taken based on each particular object (35 p. 2). Research on paper and cellulose degradation has shown that below pH 5.5, cellulosic materials degrade and become brittle too fast, and textiles with a pH between 5.5 and 8.5 have been accepted to be used in contact with objects in permanent exhibitions (36 p. 26), which means that these pH values have been considered to be ok. Therefore pH 5.5 could be taken as the threshold we are looking for, under which the acidity of the canvas would start to be considered worrying.

However, from all the pH measurements done in our research (see Chapter 2.2), we have seen that most of the paintings have a pH that falls in the 5.0 and 5.5 range. If we choose the limit to be 5.5, we would therefore get most of the paintings prioritised for deacidification. If we choose the limit to be 5.0 we would instead get a smaller number of paintings and they would be the ones that are more acidic than the rest (since we know that the majority of the paintings are acidic anyway). So, if we prefer to be more restrictive and focus first on those really acidic paintings, pH 5.0 seems to be a better threshold.

The limit of 5.0 as the pH value “of concern”, makes sense if we look at the DP results from the Reference Sample Collection: samples with DP below 500 all have pH values between 4 and 4.9, with only one exception out of the seven samples in this group. On the other side, samples with DP values above 1400, have pH values that span the interval 5.0 to 7.5. So it makes sense to establish 5. 0 as the limiting value.

The following classification has thus been designed by taking into account all the gathered information regarding the meaning of the different DP and pH values of the canvas of paintings:

Class	**Mechanical strength (DP)**	**Acidity (pH)**	**High risk**	**Recommended course of action**
A	Low (< 400)	--	High mechanical risk	- Consolidation, lining or strip lining will be needed if the painting is removed from the stretcher (the canvas cannot be “handled” because the canvas is fragile: it breaks easily when pulling or bending). - The painting is unfit for travel (there is risk of tears with shocks and vibrations)
B.1	Medium / low (400- 950)	Strongly acidic (<5.0)	High risk of degradation	- Deacidification? Acid absorbing materials included in the microframe? - Loose lining or backing recommended
B.2	Medium / low (400- 950)	Mildly acidic (>5.0) or neutral/alkaline		- Nothing? Deacidification? - Loose lining or backing recommended

		(>7)		
C.1	Medium / high (950 - 1400)	Strongly acidic (<5.0)	High risk of degradation	- Deacidification? Acid absorbing materials included in the microframe?
C.2	Medium / high (950 - 1400)	Mildly acidic (>5.0) or neutral/alkaline (>7)		- Nothing? Deacidification?
D	High > 1400	--	--	- Nothing

Figure 22. Condition Assessment Classification of surveyed paintings according to the DP and pH of the canvas, with the recommended course of action to be taken. Suggested order of prioritization is red, orange, yellow, green, blue.

In the devised classification, both DP and pH values of the canvas have been taken into account. Therefore, there are four DP categories (A: <400; B: 400-950; C: 950-1400; D: >1400[4]) and the two middle categories (B and C) have been further split up into two subcategories each, depending on whether the pH is below or above 5.0 (B.1 and C.1: more acidic paintings; B.2 and C2 not so acidic). Based on this, the order of prioritization to treat paintings would be: B.1 (red); C.1 (orange); A (yellow); B.2 (green); C.2 (green) and D (blue) (Figure 22).

The rationale behind the order of prioritization suggested is as follows. Class A paintings (DP<400), are at higher risk of suffering mechanical damage, and would certainly need some sort of treatment (consolidation, lining, strip lining, tear mending etc.) if they had to travel, or the stretcher needed to be removed. So one could think that they should be treated first. However, most of the damage has already been done, and if they can be left untouched in a safe storage or gallery area, they could still “live” without problems for a long time (it is well known that if you want to limit degradation, limiting handling is one of the best approaches (37 p. 3)). Classes B.1 and C.1 paintings, instead, would be the ones to deal with first because there is a greater future benefit to be gained by removing the acidity of their canvas before their DP value turns to be class A. After dealing with the acidity of the classes B1 and C1, then it would be the turn to treat class A that could benefit from some sort of prevention of mechanical damage. After this, if there were still resources available, paintings from categories B.2 and C.2 could also be treated to reduce their acidity. Finally, category D paintings, would be the last ones to worry about regarding the condition of their canvas.

This classification will allow us therefore to do a collection survey that will both inform us of the condition state of the collection and will help us in planning and prioritizing the treatments to be done (7 p. 228).

We have to remember, though, that the pH and DP values we will be able to obtain, with the NIR spectrometer, specially the DP one, will have a large error of prediction. Therefore the values will not be so much important on their own, but they will help us in grading paintings among them and therefore in prioritizing treatments. In a similar study to ours, where NIR was used to predict the tensile strength values of silk, the method did not give exact values of condition either, but it enabled a comparative ranking of the objects condition, which helped in prioritizing future conservation treatment (38 p. 7).

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[4] Note that for the classification, the lower DP and the higher DP values correspond to the “critical DP” and the “safe DP” values determined for paintings and not to the Condition Assessment Panel DP categories (Figure 18), so that more extreme higher and lower thresholds are used when dealing with real paintings. This was done so that extreme conditions can be better singled out.

A note on the deacidification of canvas

Regarding the deacidification of the canvas of paintings, this is a treatment that we consider should be more often done on paintings, specially having confirmed that most of the paintings are acidic. On top of that, paintings cannot be washed as paper objects can, acids and pollution staying on the cellulose for all the paintings' life, with the aggravating fact that the canvas is constantly exposed to the air (whereas works of art are most often protected at least by a backing board or folder).

Paintings deacidification started to be researched already about thirty years ago (2)(39)(39), but although there are experts that use it occasionally nowadays (40)(41), the practice is still not widespread enough. Probably conservators worry about applying foreign materials, of which they don't know the effects on the paint layer. Therefore, more research should be done on the possible deacidifying agents, how to apply them and on the possible effects on the paint and varnish layers.

More recently, some more research has been done again on the deacidification of canvas (42), and ground breaking research is being done on the use of nanotechnologies too (30). The promising combination of deacidifying agents plus antioxidants to prevent canvas degradation has also been recently pointed at (43). The topic of canvas deacidification will also be discussed in the next *Colore e conservazione* congress by Cesmar7 (Italy), to take place in 2012, which is encouraging, since it means more attention will be given to this important topic.

Regarding books deacidification, it is interesting to know that just interleaving acidic books pages with alkaline sheets containing calcium carbonate, has been found to deacidify them in the long run (29 p. 36), so similar solutions could be approached regarding paintings. Dusting book pages directly with calcium carbonate (so that their thickness is not increased by an interleaving paper) can also be done (44 p. 2). Actually, when it comes to paintings, dusting the reverse of the canvas with a deacidifying agent in the dust form has been suggested and used by G.A. Berger as a safer method for water sensitive canvas (he used calcium hydroxide or barium hydroxide) (45 p. 83). Although it is difficult to know whether enough material or if more than necessary is being applied, it seems to be a more superficial and less intrusive treatment for paintings, since the particles will tend to remain on the surface, at least at the beginning and therefore this is a treatment that could be initially more easily adopted by conservators.

The same way that archival quality materials can be used to act as a "molecular sieve" by trapping acids coming from the outside when putting papers in boxes (27 p. 38), similar materials could be used inside of microframes on the reverse of paintings. In this regard, the "MicroChamber®" board could be a good material to use since the outer layer is paper with an alkaline reserve, the middle layer has activated charcoal and molecular sieves (zeolite) and the inner layer has pure pH-neutral alpha cellulose (46 p. 52).

Indeed, there is a large and important avenue of research here to find ways to remove the acidity found on the canvas of paintings, now more than ever if we are trying as much as possible to preserve the original integrity of the work of art and the original canvas for as long as possible. On top of this, deacidification could be a very inexpensive treatment and a strategy with a high cost/benefit gain.

4.4- Conclusions

Paintings are complex systems composed of different layers. Although the DP of the canvas is not the only factor in determining the stability of a painting in terms of its support, it is a very important factor that has been proven to be linked with the mechanical strength of the canvas (21).

Artificial degradation of samples used in a Condition Assessment Panel test corroborated some existing evidence of canvas degradation. On the one hand, degradation (checked here through DP) was seen to proceed much faster in the earlier stages of accelerated degradation and then not as much in the subsequent stage, both in new and older samples. This is normal and can be explained in terms of chemical kinetics. On the other hand, old glue paste linings, already quite degraded and full of acidic products, degraded quite significantly in just one week, whereas much longer was needed for new samples: it took 10 weeks of artificial degradation at 90ºC and 65% RH for a new linen sample to degrade from DP 6614 to DP 1691. Finally, the same new linen sample that had been immersed in aluminium sulfate and left to dry, and thus with a very acidic pH of 4.7, degraded from DP 5674 to the very low value of DP 258, illustrating the high influence of acidity on the degradation of canvas.

The "Condition Assessment Panel" done with these artificially degraded samples, showed that the conservators' subjective testing and assessment of textile samples is indeed correlated with the various DP values of the samples. Samples with lower DP values were generally classed as worse condition ones and samples with higher DP values were generally classed as better condition ones.

As a result of the Condition Assessment Panel, the "Critical DP" value for paintings has been established to be 400. At around 550 DP a painting was seen to be starting to be "at risk" and when it reached 400, it was already very degraded. This "Critical DP" concept was defined as meaning that if the canvas had to be handled on its own (the stretcher being removed) it would need some sort of reinforcement (strip lining etc.). This is in line with others' findings (15 p. 6). In the literature, paintings with lower values than this, have also sometimes gotten away without lining, although in these cases the paintings were not removed from their stretchers and the canvas support was consolidated by impregnating it with an adhesive (17 p. 18).

Comparing the critical DP for paintings obtained here and the one determined for papercultural heritage objects by others (8 p. 416), we find that the value is the same: 400. This is so because the term has been defined in both cases in terms of handling. This also explains why paintings with lower DP values can still be left unlined, as long as they are left alone and not manipulated. Since this is the case for most paintings, it can be concluded that paintings with DP values lower than 400 can still be ok for a long time, as long as they are not moved around, their stretcher does not need to be removed and they are not accidentally hit.

At the other end, the "Safe DP" value for paintings was determined to be at >1400. At this point the canvas will already have suffered some degradation (new linen was found to have a DP of 6614), but the canvas still retains good mechanical properties that make one reassured about a painting regarding its support.

Looking back at the notes taken when collecting the Reference Sample Collection, it is indeed found that those samples with DP values around 400 were often already felt to be "very degraded" and samples that were seen to be "in very good shape" were later on found to have much higher DP values (above 1000 DP). However, it has to be remembered that there might be exceptions to the norm such as is the case of sample **110**. This sample looked much more degraded than later on was found to be (DP 608). In this case factors other than DP were found to also have a large influence on the sample's condition perception, namely: the presence of a "rigidifying" material (possibly an adhesive), the open weave of the canvas and the thinness of the threads. Obviously, all these factors and others (dimensions of the painting, type of weave, type of fibre) play also a role on the mechanics of a painting, on top of DP (12 p. 265) (13 p. 107).

Middle range DP categories were determined to span the range of 550 to 950 and from 950 to 1300. In these two categories pH plays and important role: paintings that are more acidic should be prioritised for deacidification since there could be a greater future benefit of treating these paintings before their DP decreases too much. When the DP is already very low (<400), most of the damage has already been done and this damage is irreversible. Of course acidic paintings with very low DP would also benefit from deacidification, but if priorities have to be established and collections are large, it might be better to focus first on those paintings with a DP range 550-1300 and lower pH.

Regarding pH, most of the paintings from our Reference Sample Collection (89%), were found to have pH below 6.50, that is to say, the majority of paintings were found to be acidic (see Chapter 2.2). Since the most common pH for a painting was found to be between 5.0 and 5.5, pH 5.0 was chosen as the threshold below which paintings were considered to be in greater need of deacidification, since these would be the most acidic paintings.

Taking into account the information obtained on the meaning of the various DP and pH values of the canvas support when it comes to easel paintings, a “Condition Assessment Classification” system was designed to help prioritise which paintings to treat first in a collection of which these two parameters are known (through a canvas condition survey done with the new non-destructive NIR spectrometry method just developed, for instance).

According to this classification, the paintings to treat first would be those with a DP between 400 and 950 that are more acidic (pH<5.0), followed by those that have a DP between 950 and 1400 and are also more acidic (pH<5.0). These paintings would greatly benefit from a deacidification treatment, and to a lesser extend from the inclusion of acidic absorbent materials in their microframe, for instance. Then paintings with the lowest DP (<400), might be treated structurally if they need so or their support might be padded if they need to travel or other. Then the next group of paintings to treat would be the two middle groups in terms of DP (400-950 and 950-1400) but that are not that acidic (pH>5.0). These paintings might benefit from loose linings or backing boards that protect the canvas, and even deacidification if resources are available (since we have found that the majority of paintings are somewhat acidic, they will all probably have a pH below 7). Finally there is the group of paintings in the best condition, with a DP above 1400. Again, acidic paintings here would also benefit from deacidification, but the time margin left here is larger, so nothing or canvas protection could be enough of a treatment for the moment.

Knowing the negative effects of acidity on the canvas of paintings, its deacidification of some sort (“active” through the impregnation of the canvas with deacidifying agents or “passive” through the use of acid-absorbing materials), is seen to be a treatment that clearly needs to be encouraged. Unlike paper, canvas cannot be washed and thus dirt and acids build up and stay on it for all the paintings’ life. It has been confirmed that the canvas of paintings is in most of the cases acidic (see Chapter 2.2), and acidity is known to promote degradation of cellulose (43 p. 34). If paintings are to be left unlined for as long as possible, actions need to be taken to neutralise the acidity present in the canvas.

It is clear that the adoption of deacidification treatments by conservators needs to go hand in hand with far more research in this field, so that the best methods are found and all its positive and negative effects are singled out. In this regard, here we have a very much needed clear future avenue of research. However, having said that, while new results are awaited, we conservators, should also assess if letting time go by without starting to deacidify the canvas of paintings can be more dangerous than its unknown potential negative effects. The least intrusive treatments, such as adding acid absorbing materials inside microframes, or slightly alkaline loose linings or backing boards, should certainly, to our understanding and in the light of the research results of this PhD, be quickly taken as routine procedures by museums.

5 –Collection survey: NIR spectrometry applied to MNAC masterpieces

Now that we have learned about the typical pH and DP values found in paintings, have developed a non-destructive method to determine them and have devised a classification to prioritise what to treat, we are ready to test our method on a painting collection and do a real collection survey.

5.1– Introduction

After having successfully developed a chemometric method for non-destructively predicting the pH, DP and fibre type of the canvas support in paintings, conducting a condition survey of part of the MNAC collection was seen as the perfect way of testing the applicability and robustness of the developed method (or not). On the other side, it also allowed us to do a condition survey on real MNAC paintings from between the end of the 19th C / beginning of the 20th C. Since, as already said, not much was known until now about the pH and DP of real paintings, the study would give us an idea of what is the condition of the canvas of paintings that are already 100 years old. The information gathered would be used too to apply the Condition Assessment Classification developed in Chapter 4, and to give the museum action priorities regarding this group of paintings.

MNAC is the institution that contributed the most to the Reference Sample Collection and therefore it made sense to apply the developed method to their paintings since the variability in their paintings would have already been taken into account in terms of materials, dates and environmental conditions. Also, it was a chance to give something in return to the museum for all the facilities that we had been given by them to carry out the previous part of this research.

To obtain interesting information at the same time that the developed technique was being tested, it was decided to focus on Catalan paintings produced around the 1900.This chosen period allowed us to include paintings by some of the most important Catalan artists of the well-known turn of the century movements: *Realism* (Joaquim Vayreda), *Modernism* (Ramon Casas, Santiago Rusiñol, Isidre Nonell, Joan Llimona), *Noucentism* (Joaquim Sunyer), *impressionism* (Joaquim Mir) and *post-impressionism* (Francesc Gimeno, Marià Pidelaserra) (1 p. 261). A couple of jute paintings by Juli González and Mela Mutermilch were also included so that this particular type of canvas support could also be studied. All the paintings selected from these artists, were done between 1888 and 1912. Finally a painting by Pablo Ruiz Picasso, *Dona amb barret i coll de pell (Marie-Thérèse Walter)*[1], a so-called "Picasso style" painting (2), was also analysed eventhough it was painted in 1937. This one was chosen just because of Picasso's importance. A total of thirty-three paintings by twelve different artists were thus included in the survey.

In Europe, the 19th C was a century of industrialisation and growth of the bourgeoisie, which will commission art for their own satisfaction (3 p. 250). In Catalonia, the economic growth of this period, especially due in part to the lifting of the ban in 1778 by the Spanish government to trade with the American colonies, helped the flourishing of the middle and upper class through the growing textile industry (4), and this enabled an explosion of local art and artists. The *Renaixença*, born in 1833, was a nationalist movement that looked back into Catalonia's "glorious past" of the medieval ages, initially with political and literary roots but that spread onto all aspects of culture. *Modernism* was to be born between the 1880s and the 1890s as a reaction to the *Renaixença* movement, as a "breath of fresh air", with a tendency to embrace new ideas and

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[1] Titles of the paintings have been left in the original museum's way (in Catalan) throughout the chapter, so that future on site work at MNAC is made easier, facilitating both communication with their employees and searching in their database.

modern things. Modernist artists such as Casas and Rusiñol or the young Picasso, then living in Barcelona and spending time with the *Modernists* at the artists' café Quatre Gats, all went to Paris at some point, then the capital of modern art. After the golden age of Catalonia in the medieval times, this period towards the end of the 19th C and beginning of the 20th C was certainly one of the most thrilling ones in the history of Catalan art. Barcelona was one of the most rapidly growing cities in Europe and the economic growth favoured progress and full engagement with the international avantgarde. This produced other artistic movements that followed *Modernisme*, such as *Noucentisme* just at the turn of the century and the new avantgardes (surrealism, rationalism etc.) just at the beginning of the 20th C. All this progression came to a halt with the advent of the Spanish civil war in 1936, to be followed by the "long night" of Franco dictatorship that lasted until 1975 (5).

Materials used by artists often depend on their economic means. Like this, Casas and Rusiñol, for instance, are artists that came from families with good economic means and therefore their paintings are usually done with good quality materials (6 p. 112). Two of the Rusiñol paintings under study here and one by Casas have a "Pignel-Dupont" stamp on the textile, which reveals the shop in Paris, where they got their supplies from during this years (around 1900). Unlike them, Martí Alsina and Gimeno, for instance, are known for the contrary: they had economic troubles at some points and thus their paintings are found to be of lower quality materials (7)(8). It will be interesting to see if differences in the condition of the canvas are found between the paintings of these artists. On the choice of materials, for instance, Joan Llimona is known to have often used Planella's commercially prepared canvases (Figure 1), although he has also been found to use canvases from the companies Bertrand and Teixidor, other Catalan companies from Barcelona too (6 p. 100). The two paintings from Llimona that are part of this study have this Planella stamp on their reverse.

Figure 1. Planella stamp from the painting *Pasturant*, by Joan Llimona, (MNAC004006) (**181**).

Picasso is known for using all sorts of materials not intended for artist's use, such as the recently well studied use of household Ripolin paints (9). As usual, so far, much more research has been done on the paint layer than on the type of supports he used. Regarding the support, it is known that he also used supplies from the Planella company when he lived in Barcelona, since this stamp is found in the painting *La primera comunió*, 1896 (Museu Picasso de Barcelona 110.001) (6 p. 50). As already reported, the famous large scale *Guernica* painting, 1937 (Museo Reina Sofia, Madrid, DE00050), was done on a commercially primed canvas where the threads running vertically are jute and the threads running horizontally are linen (10 p. 51).

5.2- Materials and methods

The same NIR spectrometer Labspec 5000 (Analytical Spectral Devices, USA) used for collecting the Reference Sample Collection spectra and belonging to the Centre for Sustainable Heritage (UCL), was brought to Barcelona in May 2011, in order to take spectra of the selected MNAC masterpieces.

Spectra from 33 MNAC paintings were collected throughout five full-work days by two people with the help of the museum's employees. Most of the paintings were examined in the storage room RE3 where they were being kept at that time. On Monday the 23rd of May 2011, taking advantage of the closure of the museum to the public, five masterpieces that are usually hanging in the galleries were analysed. In those five days, a total of 670 spectra were collected, taking three or four repetitions at each different location. An average of six different spots were analysed for each painting, although this number was higher in some instances, such as the Picasso painting where up to 15 different locations were analysed, and sometimes it was lower, such as the case of very small paintings by Pidelaserra with a very regular canvas where only 3 different spots were measured.

Paintings were unframed and backing boards removed when present. Since the beginning of this 21st C, it has been a regular practice of the museum to add a transparent polycarbonate backing board every time a painting is asked for loan and once the painting returns, the backing is left on the painting. This is done to safeguard the canvas (and thus the whole painting) by minimizing humidity fluctuations as well as air and dust circulation (7). More recently, a thin black foam is usually added along the edges to increase the tightness of the system, although the aim is not to make it fully hermetic. For larger paintings, where the canvas could flap against the stretcher during travelling or movement, one or two pieces of white foam are attached to the backing board in central areas (Figure 2).

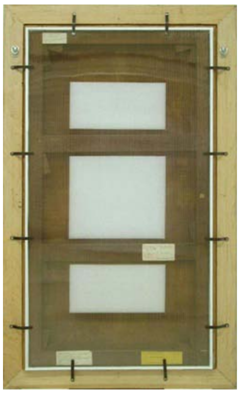
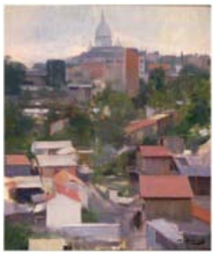


Figure 2. Backing board and white foam on the reverse of painting 179, *Dona rentant-se*by Juli González (MNAC 113503).

To take the NIR spectra, paintings were laid face down flat on a table on top of four raised pads that left room for the calibration pad to be placed underneath the painting, against the paint layer. Like this, the NIR probe could rest onthe canvas that was laid against the calibration pad flat surface, avoiding any damage to the paint layer (Figure 3). All NIR spectra were taken using the same substrate: the calibration pad Spectralon 99% reflective standard (Labsphere, North Sutton, USA) and under constant temperature and relative humidity conditions, so that all measurements would be comparable. Spectra were taken at 200 scans, as had been done for the spectra of the samples used to calibrate the instrument. During the days the spectra were taken, temperature at MNAC storage room RE3 was 19.3 – 21.0 ºC, with an average of 19.6 ºC. Humidity went from 59 to 65%, with an average of 62%. All paintings of this study were analysed in storage room RE3, except for the following ones, which were analysed in the museum galleries: **176**, *Lassitud* by Nonell*;* **177**, *Dona amb barret i coll de pell (Marie-Thérèse Walter)* by Picasso*;* **178**, *"La Butte"* by Rusiñol*;* **179**, *Dona rentant-se* by González and **187**, *Plen air* by Casas*.* Temperature conditions in the galleries on the 23rd of May 2011, the day the measurements of these five last paintings were taken, went from 21.4 ºC to 21.8 ºC, with an average of 21.6 ºC and relative humidity went from 57.8% to 59.8%, with an average of 58.0%.

Figure 3. Taking NIR spectra in the MNAC galleries on a Monday, while the museum was closed to the public. Paintings were unframed and laid on four raised pads to leave room for the calibration pad to be placed underneath while taking the measurement.

The list of paintings that were analysed is the following (ordered according to the author's surname):

Id	Image	Author, *Title*, date, MNAC number	Observations
155		Ramon **Casas**, *Estudi*, circa 1899, (MNAC 004038)	
156		Ramon **Casas**, *Le Sacré Coeur, Montmartre*, 1891, (MNAC 004040)	
157		Ramon **Casas**, *Pati de l'antiga presó de Barcelona*, 1894, (MNAC 004033)	

159		Ramon **Casas**, *Dona en un interior*, 1890, (MNAC 069042)	
183		Ramon **Casas**, *Noia de París*, 1888-1890, (MNAC 004039)	Lined painting
186		Ramon **Casas**, *Estudi del natural per al retrat del rei Alfons XIII*, 1904, (MNAC 011382)	Jute painting
187		Ramon **Casas**, *Plen air*, 1890-1891, (MNAC 10901)	 Pignel Dupont stamp[2]
170		Francesc **Gimeno**, *Llegint el diari*, 1886, (MNAC 069023)	

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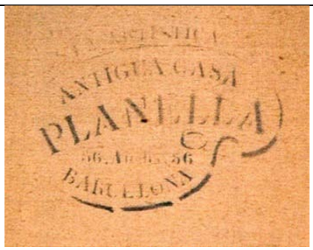
[2] The French commercial stamp "Pignel Dupont" is found in paintings at MNAC by the artists Casas, Rusiñol and Nonell (6 p. 60).

179		Juli **González**, *Dona rentant-se*, 1912-1913, (MNAC 113503)	Jute painting
180		Joan **Llimona**, *La novícia*, 1898, (MNAC 004005)	 Planella stamp[3]

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[3] Joan Llimona is known for having used very often primed canvas from the local Barcelona Planella company (15 p. 27). Other paintings by Joan Llimona known to contain the Planella stamp, apart from the two that we have analysed here (*La novícia*, 1898 (MNAC 004005) and *Pasturant*, 1901(MNAC 004006)) are: *Tornant del tros* (MNAC 10818) (15 p. 27); *St. Rafael*, 1896 (Monestir de Pedralbes 147.256) and *Avemaria*, 1903 (6 p. 102).

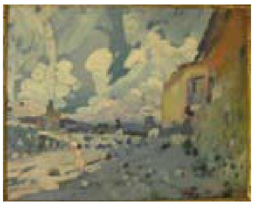
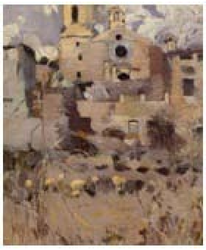
Other artists where the Planella stamp has been found so far are: Rigalt, *Ruïnes*, 1865 (MNAC 10559) (label) and *Paisatge*, 1866 (MNAC 10555) (label); Armet, *Un país. Record dels Pirineus*, 1866 (MNAC 44403); Caba, *Retrat de Lluïsa Dulce i Tresserra, marquesa de Castellflorite*, 1880 (MNAC 42373); Nonell, *Acadèmia Artística Lliure de Barcelona*, 1894; Picasso, *La primera comunió*, 1896 (Museu Picasso) (22); Canals, *Nen malalt*, 1903 (MNAC 3806) (6).

As usual, commercial stamps on industrially prepared canvases of the same company change over the years according to the different business relocations and change of style. It would be therefore very helpful to start tracing the history and typologies used by companies, so that undated paintings could be dated due to their stamps on the canvas if present, as has been done in England for the company Winsor&Newton (22). This work has been started in Catalonia by Dr. Pedragosa and it would be very useful to create, starting from her work, a growing database where museums could contribute with the stamps present in their collection so that knowledge in this field is organised. From the work done by Dr. Pedragosa, we can already establish which were the contents of the Planella stamp at different dates (of course, dates could be earlier than the ones noted here, since a painter could have had the canvas in his studio for a while before painting it):

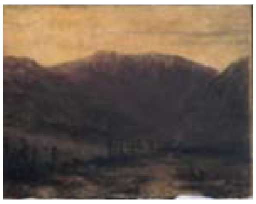
- 1866: Label on the stretcher: “*Bellas Artes / Alejandro Planella /Escudillers nº 80/ Litografia, Dorar / Arquitectura”* from the painting by Rigalt, *Paisatge*, 1866 (MNAC 10555)
- 1865: Label on the stretcher: “*Bellas Artes / Alejandro Planella /Calle Escudillers nº 80 / especialidad / en / objetos para dibujo /pintura / matemáticas” (*from the painting by Rigalt, *Ruïnes*, 1865 (MNAC 10559))
- 1880: Stamp on the canvas: “*Planella / Calle ancha 62 /.dibujo”* from the painting by Caba, *Retrat de Lluïsa Dulce i Tresserra, marquesa de Castellflorite*, 1880 (MNAC 42373)
- 1896: Stamp on the canvas: *“Planella / Barcelona” (*from the painting by Llimona *Tornant del tros*, 1896 (MNAC 10818))
- 1896: “*Antigua casa Planella / ------ 36 / Barcelona”* (from the painting by Llimona St. *Rafael*, (Monestir de Pedralbes 147.256) (22)).This last stamp seems to be the type we have in the two Llimona paintings analysed here (**180** and **181**).

The Planella business was apparently opened in 1833 at the Ample street in Barcelona (6 p. 50) and as it can be seen above changed address several times.

Knowing more about the products that the different companies produced, would also give more information on the quality of the materials of a certain painting. Planella paintings, for instance, visually seem to be good quality ones.

			
181		Joan **Llimona**, *Pasturant*, 1901, (MNAC 004006)	 Planella stamp
167		Joaquim **Mir**, *Paisatge (Maspujols. Camp de Tarragona)*, 1907-1910, (MNAC 004630)	
168		Joaquim **Mir**, *Paisatge*, 1907-1910, (MNAC 004631)	
169		Joaquim **Mir**, *Hort amb casa de pagès*, (MNAC 042090)	
185		Mela **Mutermilch**, *Retrat de J. Dalmau*, 1911, (MNAC 65291)	Jute painting

163		Isidre **Nonell**, *Gitana jove*, 1903, (MNAC 010921)	
164		Isidre **Nonell**, *Gracieta*, 1907, (MNAC 065620)	
165		Isidre **Nonell**, *La Pilar*, 1907, (MNAC 010926	
166		Isidre **Nonell**, *Júlia*, 1908, (MNAC 004660)	
176		Isidre **Nonell**, *Lassitud*, 1910, (MNAC 065623)	
177		Pablo Ruiz **Picasso**, *Dona amb barret i coll de pell (Marie-Thérèse Walter)*, 1937, (MNAC 214090)	

182		Marià **Pidelaserra**, *Un dia d'hivern en el jardí del Luxemburg*, 1900, (MNAC 004093)	 E. Lafontaine stamp
184		Marià **Pidelaserra**, *Vall de Querol*, 1897, (MNAC 043719)	
158		Santigo **Rusiñol**, *La riallera*, 1894, (MNAC 004003)	
160		Santigo **Rusiñol**, *Jardí de Montmartre*, 1890-1891, (MNAC 040095)	
161		Santigo **Rusiñol**, *Entrada al parc del Moulin de la Galette*, 1891, (MNAC 045267)	Pignel Dupont stamp
162		Santigo **Rusiñol**, *Retrat de nen*, 1893-1895, (MNAC 063980)	

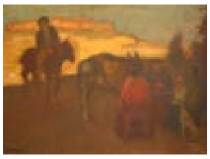
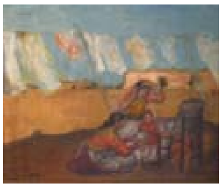
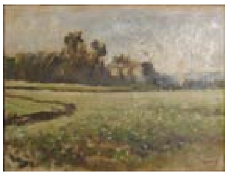
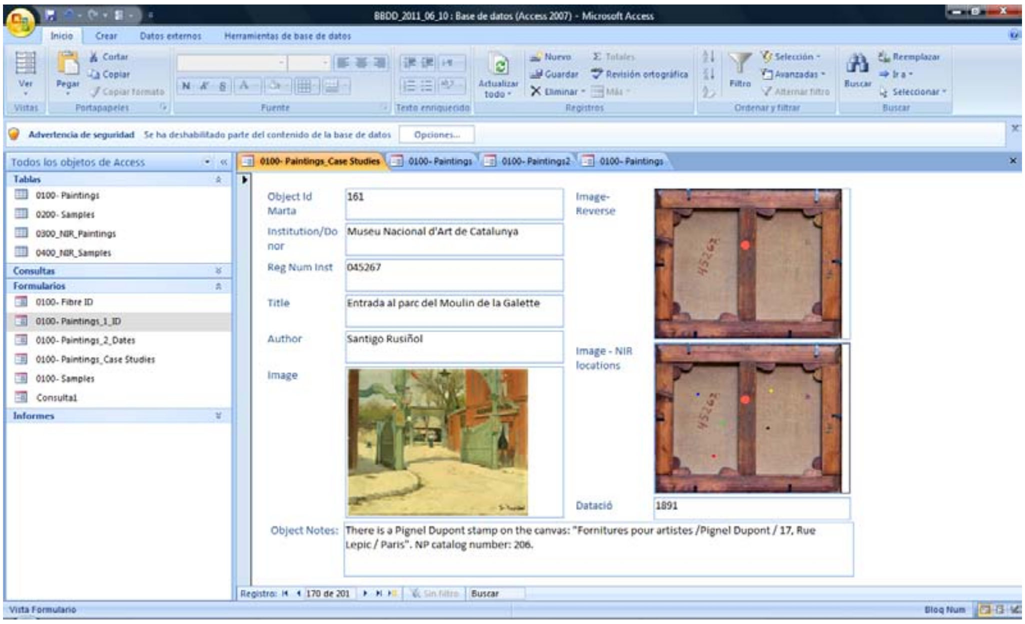
178		Santigo **Rusiñol**, *"La Butte"*, 1892, (MNAC 004048)	Pignel Dupont stamp
171		Joaquim **Sunyer**, *Gitanes*, 1906, (MNAC 039143)	
172		Joaquim **Sunyer**, *Gitanes*, 1907, (MNAC 039144)	
173		Joaquim **Vayreda**, *Nens jugant (estudi)*, 1889, (MNAC 010588)	
174		Joaquim **Vayreda**, *Camp de fajol (apunt)*, 1892, (MNAC 010593)	
175		Joaquim **Vayreda**, *La roureda*, 1892, (MNAC 010589)	

Figure 4. List of MNAC paintings of which NIR spectra was collected from the reverse, ordered according to the author's surname.

All the information available on each painting, location where NIR spectra had been collected, predicted results for each location, averages, standard deviations etc. was again gathered in a single *Access* database (Figure 5), so that information was all together and from here, the desired fields could be exported onto *Excel* or other types of files to treat and analyse data.



Object Id Marta: 161

Institution/Donor: Museu Nacional d'Art de Catalunya

Reg Num Inst: 045267

Title: Entrada al parc del Moulin de la Galette

Author: Santiago Rusiñol

Image

Image-Reverse

Image - NIR locations

Datació: 1891

Object Notes: There is a Pignel Dupont stamp on the canvas: "Fornitures pour artistes /Pignel Dupont / 17, Rue Lepic / Paris". NP catalog number: 206.

Figure 5. A view of the basic information on one of the paintings (161), with images from the recto and verso as well as NIR analysed areas.

Each painting was given a number, starting at 155 and ending at 187 for our internal records. This is the order they appear in Annex IV- Case studies catalogue, which recollects the identification information, the locations on the reverse that were analysed using NIR, and the different results (pH, DP and fibre type) for each painting.

The models developed for pH, DP and fibre type and explained in Chapter 3 where the ones used to predict the values for these parameters from the NIR spectra collected from MNAC paintings.

5.2.1- Influence of the background when taking NIR spectra

For paper, it has been determined that NIR radiation will not penetrate more than four layers of Whatman filter paper no.1 (11 p. 6320). To determine this, they compared the NIR spectra obtained by measuring one, two, three, four and five layers of the same paper. They saw that from four layers on, the spectra was exactly the same. As a result, several layers of Whatman filter paper no.1 can be put under paper objects when taking NIR spectra (12 p. 414).

For cultural heritage silk measurements, in the literature found, NIR spectra were reported to be taken by placing the sample on the white calibration pad (13), the same way we did. The authors state that information was obtained from the depth of up to 1 mm (13), although the penetration of NIR radiation could be deeper than that.

In order to know the influence that different backgrounds had in the case of easel paintings so that the proper method could be established, a small experiment was done. NIR spectra of the canvas were taken from exactly the same place from a set of four paintings, using different backgrounds. These paintings where all Salvador Dalí paintings owned by the Fundació Gala-Salvador Dalí, where some measurements were taken on some of their paintings due to the existence of collaborative research projects between the two institutions. The full results of the studied Dalí paintings, though, will be published elsewhere.

The studied backgrounds were: the white table, two layers of thick blotting paper and the calibration pad. Four different locations for each painting were measured, so that a total of sixteen different locations could be analysed. The locations were always near the corners, so that by placing the probe against the stretcher bars and recording its direction, the exact same spot could be measured using the three different backgrounds. pH values were predicted for all the NIR spectra and the results compared (see Annex V - Background studies results).

The conclusion to this test was that all the different backgrounds tested were suitable in the case of oil easel paintings: differences between the predicted results were really small (SD between 0.0 and 0.2 for pH), so no influence from the different backgrounds was detected. Although all the NIR spectra gathered for the present MNAC survey were taken using the white calibration pad as the background, it is good news to know that blotting paper, for instance, is ok to be employed in future paintings projects, since this might be easier to use and even safer for the paintings (with blotting paper there is less risk to scratching the paint layer).

5.2.2- Averaging the three spectra versus averaging the three pH values

As explained in Chapter 3, before doing the predictions, usually the three repeated spectra taken from the very same location (only moving slightly the probe 1-2 mm) are averaged using the program *Grams AI* and some prediction is obtained per location. This is quite a tedious operation to do since averaging the spectra has to be done individually for every three spectra (selecting them, asking the software to average the spectra and then naming it and saving it accordingly). As we had collected over 600 spectra for this project, this operation took about 3 h.

Since once we had done this, we had both the averaged spectra and the "starting non-averaged spectra", we decided to run predictions on both sets in order to see whether the final predicted values we obtained were different: if we obtained them from the three original spectra and then average the pH predictions, or if we averaged the three spectra first and then got just one predicted pH.

We did so and we found that results were very similar, almost identical (R^2=0.99[4]) (Figure 6), and therefore it was concluded that averaging of the predicted values could be done after predictions, which was much faster to do in *Excel*.

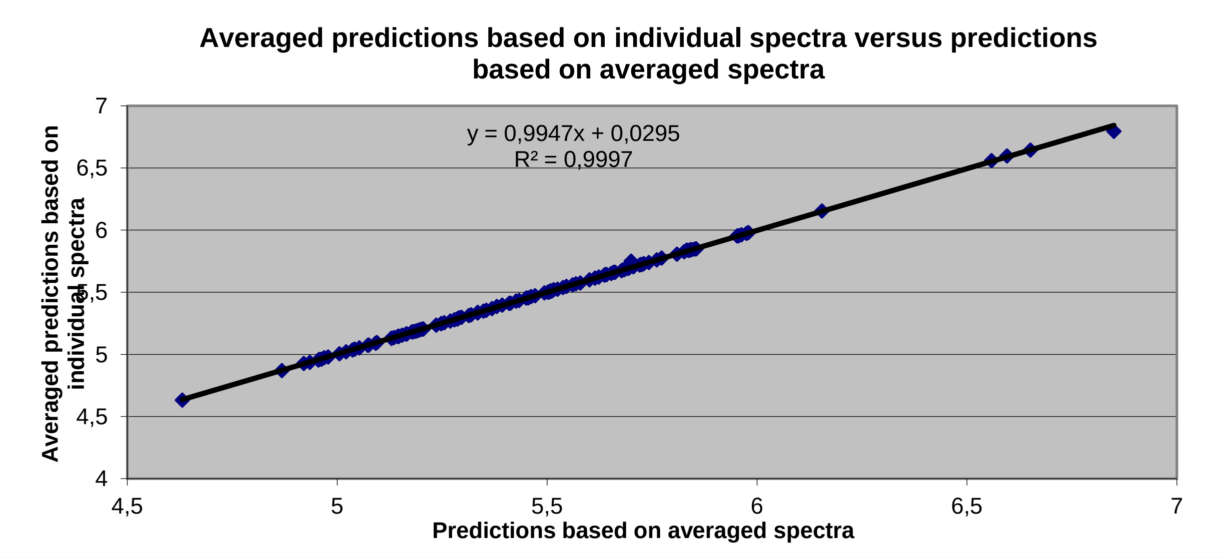


Figure 6. Averaged predictions based on individual spectra versus predictions based on averaged spectra. The correlation between them is almost perfect.

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[4] R is the "regression coefficient". The closer this number is to 1, and the closer the slope is to 1 and the intercept to 0, the better is the correlation between the two analysed set of data.

5.3- Results and discussion

5.3.1- pH

As just discussed, the pH predictions were carried out using all the 670 individual (non-averaged) NIR spectra (three repetitions per location) using the chemometric model developed in Chapter 3, and then averages were calculated for each location.

Looking at the obtained values from all the spectra before averaging, though, (Figure 7), we see that all the predicted values for MNAC paintings around 1900, go from 3.7, the lowest obtained value, to 6.2, the highest value. The average of all the 670 predicted values obtained is 5.1, with an SD of 0.4 and an RSD of 8%.

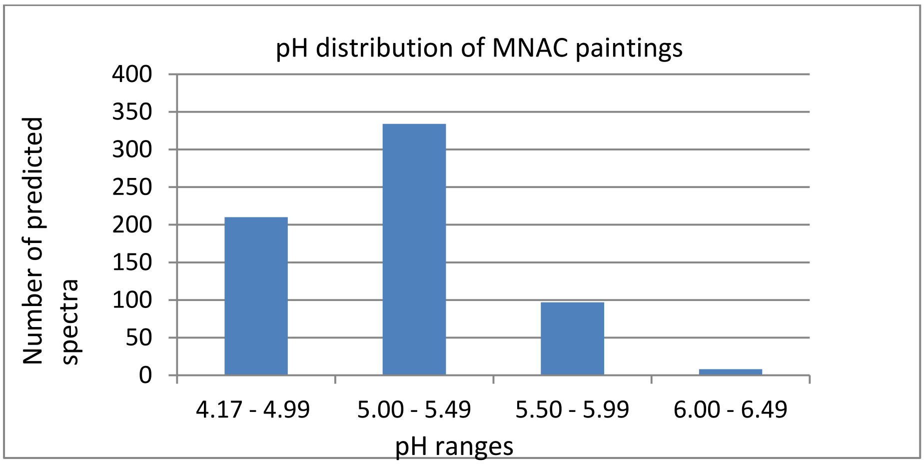

Figure 7. All pH predictions for MNAC 670 spectra taken (different locations per painting, three repetitions), ordered according to pH value.

Each painting was analysed at different locations. In many instances, we deliberately chose some areas where the canvas appeared to be in a better condition or with no visible degradation (we called those “regular canvas” locations) and some areas that were seen to be darker due to varnish, oil migration or other (we called these “darker areas”). The idea behind was to see whether there were noticeable differences between these areas regarding canvas condition (pH and DP) and if the effect of varnish going through the cracks, or oil migration could be determined.

Three or more spectra were taken from each different location in a painting. An average of the predicted pH was calculated for each different location. These averaged pH values for the different locations range from 3.9 to 6.0.

If we only look at the “regular canvas” locations, and we do one “regular canvas” average and one “darker areas” average per painting, we find that averages for the regular areas go from 4.0 to 5.7, and averages for the “darker areas” range from 4.4 to 5.5, so no significant conclusion can be drawn from this since regular canvas is seen to have a broader range of values and thus include “darker areas” values.

If we remove the jute (**179**, **185**, **186**) and cotton paintings (**164**, **166**, **179**, **177**), that tend to have lower and higher pH values respectively, and only look at the bast fibres, we can see that the average for all the regular areas of paintings is 5.2 (SD 0.2; RSD 4.6%), and the average for darker areas of all the paintings is 5.1 (SD 0.2; RSD 3.3%). So in general, there does not seem to be a marked difference between regular and darker areas of paintings, although there is a small tendency for darker areas to have a slightly lower average pH. Regular canvas areas also seem to have slightly more variability in pH values. This strand of research is further explored later on in this same chapter in the section “Difference between darker and lighter areas”.

From the pH obtained for each location in a painting, an average was calculated per painting, so that these could be compared (Figure 8). Of course, one has to keep in mind, that the pH changes across the canvas and that the average is just this, an average of the different analysed locations. How much pH variability is encountered inside each painting is analysed later on in Figure 10.

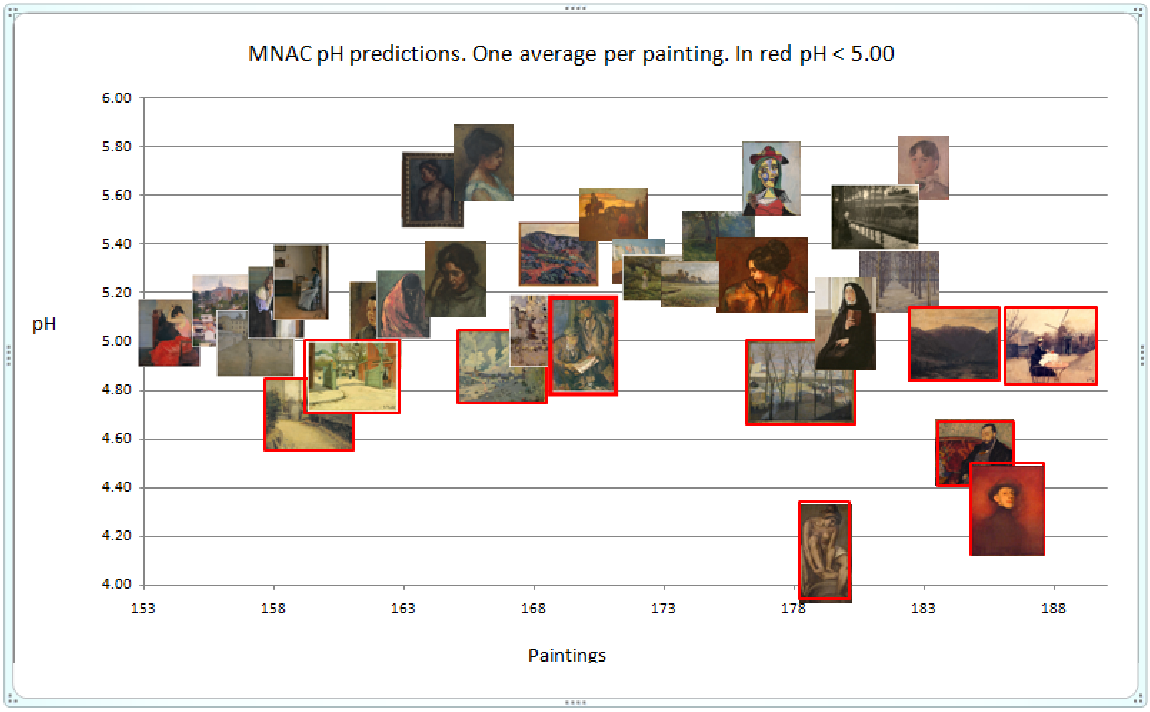

Figure 8. Predicted average pH for MNAC paintings. The image of each painting has been superimposed to the place where the average value would fall for each painting to facilitate the analysis. In red, those paintings with a predicted average <5.0 (**160**, **161**, **167**, **178**, **179**, **184**, **185**, **186**, **187**).

If we look at the final pH averages for the whole painting (Figure 8), we see that we get values that range from 4.1 to 5.7, so all the paintings are acidic. The average pH for MNAC paintings is 5.1, with an SD of 0.4 and RSD of 7.1%, so there is not a lot of variability within paintings.

30% of the paintings have pH below 5.0 (10 paintings out of 33), of which, the three with the lower pH are the jute paintings (**179**, **185** and **186**). And 81% of the paintings (27 paintings out of 33), have a pH below 5.5.

Two paintings out of the 33 (6% of the total) were found to have pH below 4.5, whereas in our Reference Sample Collection we had only found a 2% of the samples from paintings to have such low pH. We are therefore finding a bit higher pH values in the MNAC survey than in our Reference Sample Collection. This could be explained by the fact that the MNAC paintings, being masterpieces, have suffered many more intrusive conservation treatments than the physically sampled paintings, that were lower quality ones and this has led to lower pH values. Another thing to take into account would be the fact that MNAC-surveyed paintings are all from around the 1900, whereas the Reference Sample Collection has broader dates, going from the 16th C to the 21st C, although it is mainly centred around the 19th and 20th C.

In our Reference Sample Collection we had found many low pH values for glue paste linings. One lined MNAC painting (**183**) was analysed precisely for this reason: to see if its pH was also quite low. However, this painting had an average pH of 5.7 (this is for the lining canvas, of course, since we did not have access to the original canvas). In this case, the pH was not that low and this could be because the lining is quite a new one: although there is no documentation in the MNAC record files of when this lining was done, it looks very new (the canvas is not dark at all) and it is a very clean textile with no excess paste showing through.

All this points towards a very possible Beva lining (Figure 9) and this could explain the not so acidic pH value. However, we should be cautious here, since we do not know how the presence of Beva might be affecting the spectra and therefore the predictions, since this material was not included in the calibrations.

Figure 9. Detail of the clean reverse of the lined painting 183: *Noia de París*, Ramon Casas, 1888-1890 (MNAC 004039)

Next, pH variability found between the different locations within each painting was explored (Figure 10).

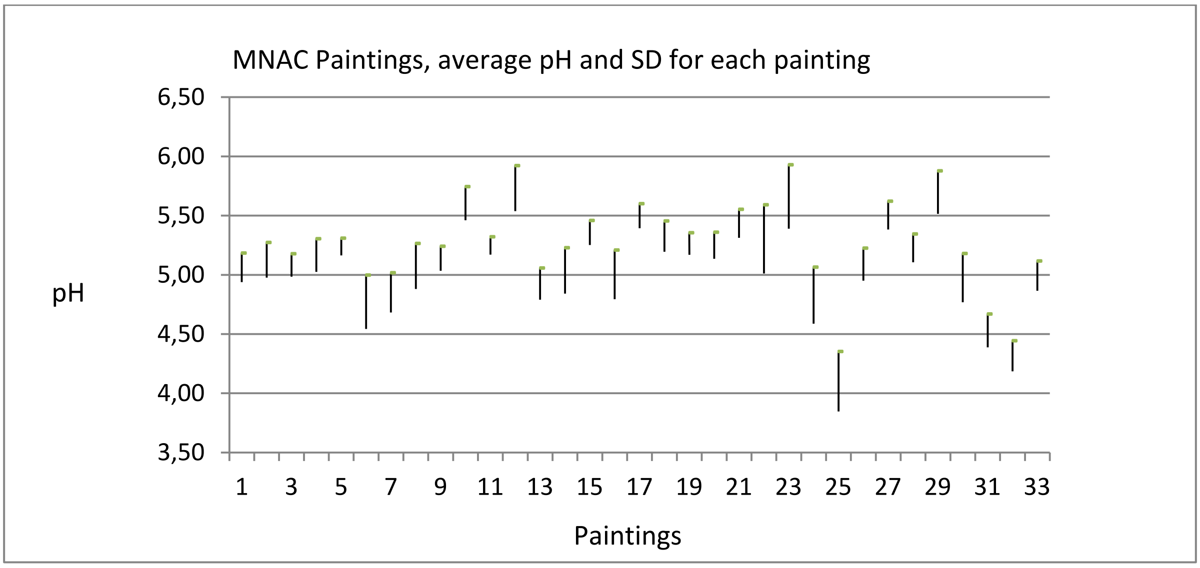

Figure 10. pH of MNAC paintings around 1900, showing the variability of pH values obtained: average pH for the whole painting from the different locations is in the middle of the bar, the extremes of which represent ±2SD.

Variability of pH (expressed as SD) within the different locations in each painting can be seen to range from 0.1 to 0.3 pH units (Figure 10), on average being 0.15. In terms of RSD, variability within a painting, ranges from 1.4% to 6.2%, the average being 3.0%. This means that variability of pH values within one painting is not significant (3.0 % RSD on average). Also, on average, variability within regular canvas areas within each painting, and within darker areas within each painting are very similar too, average RSD for regular canvas being 2.6%, average RSD for darker canvas being 2.7%.

An average SD of 0.15 pH units for the different locations in one painting means that if the average for a particular painting is, for instance, 4.0; 68% of the pH values across the surface of the canvas will be between 3.9 and 4.2 (one standard deviation). (The reader is referred back to Chapter 2.2 for an explanation of the SD and RSD concepts).

The variability within a painting found here (average RSD 3.0%) is smaller to that found within two very different condition analysed samples coming from the same painting, where the average RSD was found to be 10.3% (see Chapter 2.3 “Two samples from the same painting with visually different conditions”). This makes a lot of sense because when two samples were taken from the same painting to take part in the Reference Sample Collection, they were taken precisely because two markedly different condition areas were observed in that particular painting. Measurements taken from the MNAC collection survey, do not present such big differences between them, even if "regular canvas" areas and "darker" areas were sampled.

Next the pH values obtained are analysed in relation to the fibre type (also determined through NIR spectroscopy and explained later on in this same chapter) (Figure 11).

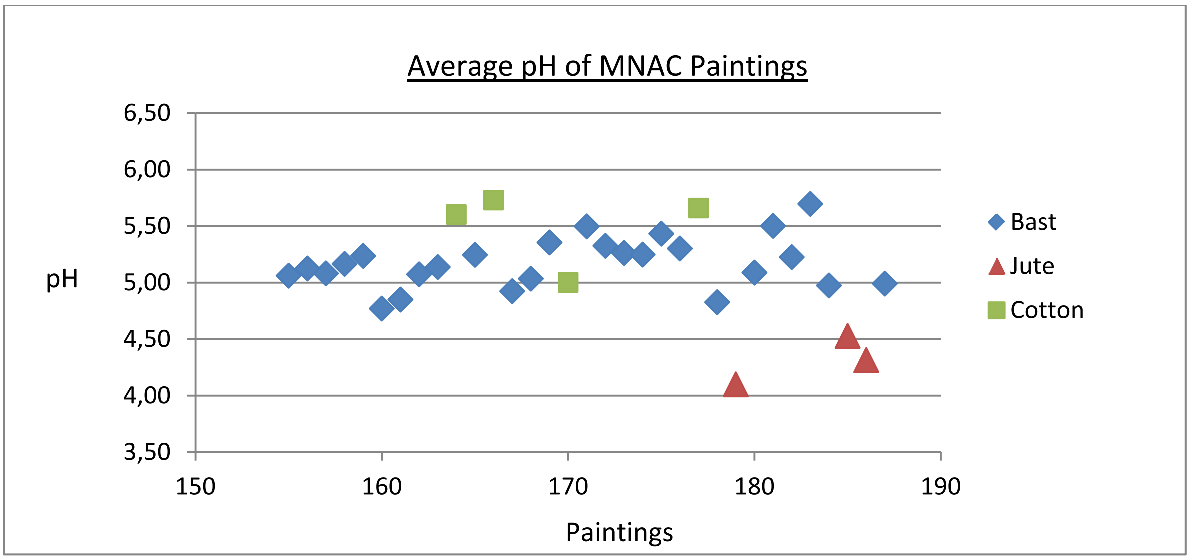

Figure 11. pH of MNAC paintings taking the average pH per painting and showing jute, cotton and bast fibre paintings specifically.

In this graph it is again clear that most of the analysed paintings have a pH between 5 and 5.5, which as discussed, is in accordance with the findings using our Reference Sample Collection (Chapter 2.2). It can also be clearly seen that jute paintings have a systematically lower pH, than linen and cotton.

5.3.2 - DP

DP predictions were not has good as pH predictions in the sense that quite a lot of spectra were considered as outliers and could therefore not be used for predictions. This means that in many cases, the developed method could not give us a reliable prediction for quite some NIR spectra, and therefore the prediction was left as a blank. One of the ways the method has to check whether the new unknown spectra are similar to the spectra used in the calibration is by checking the "Mahalanobis distance[5]" between them. If the Mahalanobis distance is too high (>3.00), then we a prediction would be so uncertain that it is not calculated.

In the case of DP, 43% of the NIR spectra could not be predicted (289 out of 670 spectra had a Mahalanobis distance >3.00). Of the total number of spectra, 37% had a Mahalanobis distance between 2.00 and 3.00 and only in a 19% of the spectra we got a Mahalanobis distance of <2.00 (Figure 12).

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[5] The Mahalanobis distance, as seen in Chapter 3, is a numeric value that gives us the distance between the chosen spectrum from the average of the rest.

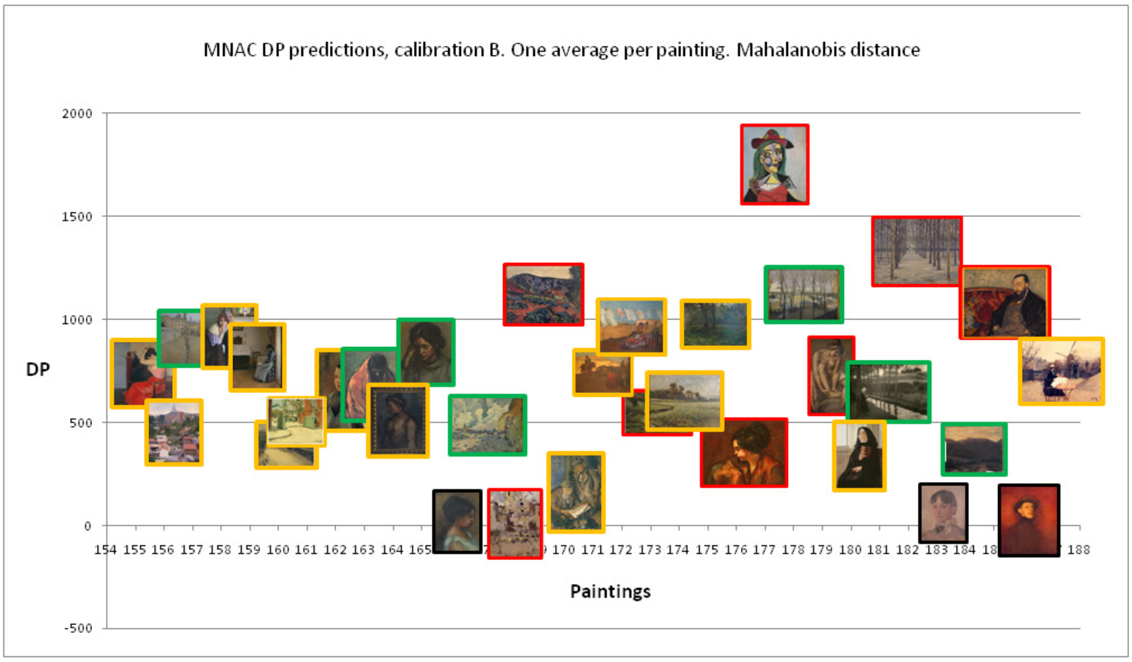

Figure 12. Paintings plotted according to the average DP obtained. In red, the ones where more than 50% of the spectra did not get a prediction value and in black the three paintings of which none of the spectra could be predicted. In orange, the paintings where most of the spectra had a high Mahalanobis distance (1.99-2.99) and in green the paintings where spectra had generally a lower Mahalanobis distance (<1.99).

If we compare these results with the pH predictions, we see that for pH, 86% of the predictions had a Mahalanobis distance of <2.00; a 10% of between 2-3, and only in the 3% of cases, a blank prediction was given because the Mahalanobis distance was higher than 3. Therefore it can be seen that there is some sort of trouble with DP predictions. Our intuition is that given the high variability and inhomogeneity of painting canvas samples, a larger calibration and validation sample set is needed to improve the DP predictions. It has to be remembered that we used 170 pH samples and only 102 DP samples for developing the two different methods. Even if a group of 30 is said to be ok for regular samples (14 p. 24), in the case of cultural heritage and specifically in the case of so diverse samples as is the case of easel paintings, a larger set of around 200 might be better.

If we look at the paintings where spectra were not of the required quality for predictions, we see that they are not randomly scattered through the NIR spectra analysed, but that they do tend to be concentrated more on certain paintings. This means that it is the particular materials and condition present in some paintings, that the method cannot handle. This fact reinforces the idea that it might be due to certain type of sample materials not present in the calibration and validation sets.

There are four paintings of which for all the spectra we got no DP prediction. These paintings are numbers **166**, **168**, **183** and **186** (see Figure 12, paintings marked in black). Interestingly, in two other cases, **164** (Nonell, *Gracieta*) and **169** (Mir, *Hort amb casa de pagès*), we only got values from the "darker" areas of the paintings and none from the "regular" areas of the canvas.

In the case of the Picasso painting (**177**), one of the paintings of which we collected more spectra, 45, aiming at doing a sort of "pH and DP mapping" of the canvas, unfortunately only 4 NIR spectra gave us DP predictions. The Picasso canvas has some particular darker spots (Figure 13) and in an attempt to find out if these areas were more degraded than the rest, 27 spectra were taken from the "regular canvas" areas and 18 where taken from these spots (or at least that was the aim: the spots being very small sometimes, we cannot be 100% sure that they were targeted all the times). Again, interestingly enough, the four predictions we got were all from these"darker spots" areas.

Figure 13. Reverse of the painting *Dona amb barret i coll de pell (Marie-Thérèse Walter)* by Picasso (**177**). The canvas has some darker yellow spots, which are the areas from where we did get a DP prediction.

In any case, the values that we obtained are to be considered reliable values, since otherwise they could not be calculated. The only pity is that we get a less clear picture since we have fewer results.

Of the two calibrations developed (see Chapter 3), MNAC predictions were done using Calibration B (initially named "m9") because it had a lower RMSEP of ±275, than Calibration A. Calibration B gave us also more blank predictions than Calibration A, and thus less information. However, it was preferred to select a calibration that would give us more precise values or no values at all if the spectra were not of a good quality.

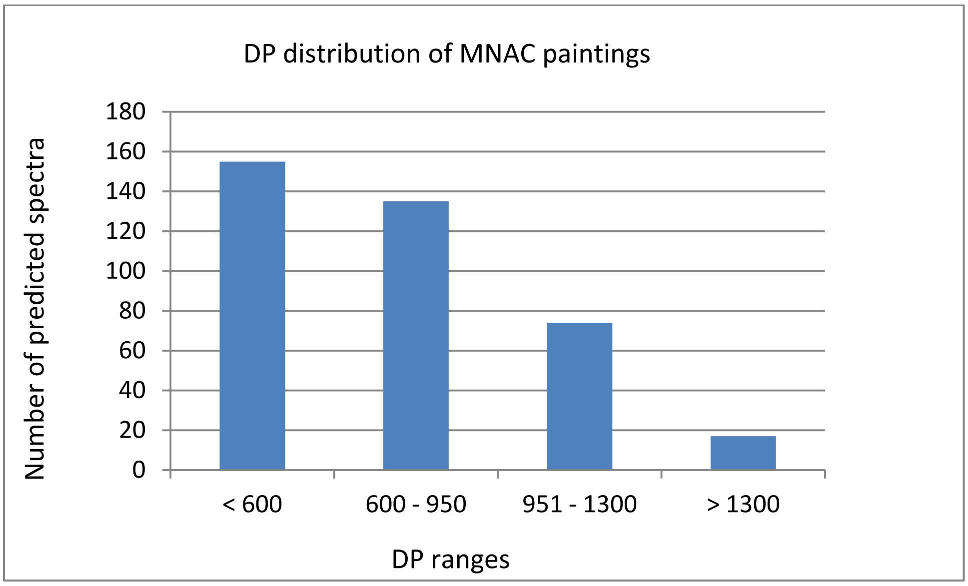

Figure 14. All the DP values obtained for MNAC paintings from the 382 spectra for which predictions were obtained.

Of all the 382 spectra of which we got predictions, we got values that go from <400 to 2140, the average being 690 DP (SD 360, RSD 52%). From this we see that, for the same paintings, there is a much higher variability within DP values (RSD 52%) than there is for pH values (RSD 8%).

If we look at the different averages for each painting, we get values that go from <400 to 1734, the average being 706 with SD being 362 and the RSD being 52%, so there is quite a lot of variability between the DP of paintings. There is a 32% of paintings with a DP<550; a 41% with a DP between 550-950, a 19% with a DP between 950-1300, and only a 3% with a DP>1300. Therefore the majority of paintings fall in the range 550-950 (Figure 15).

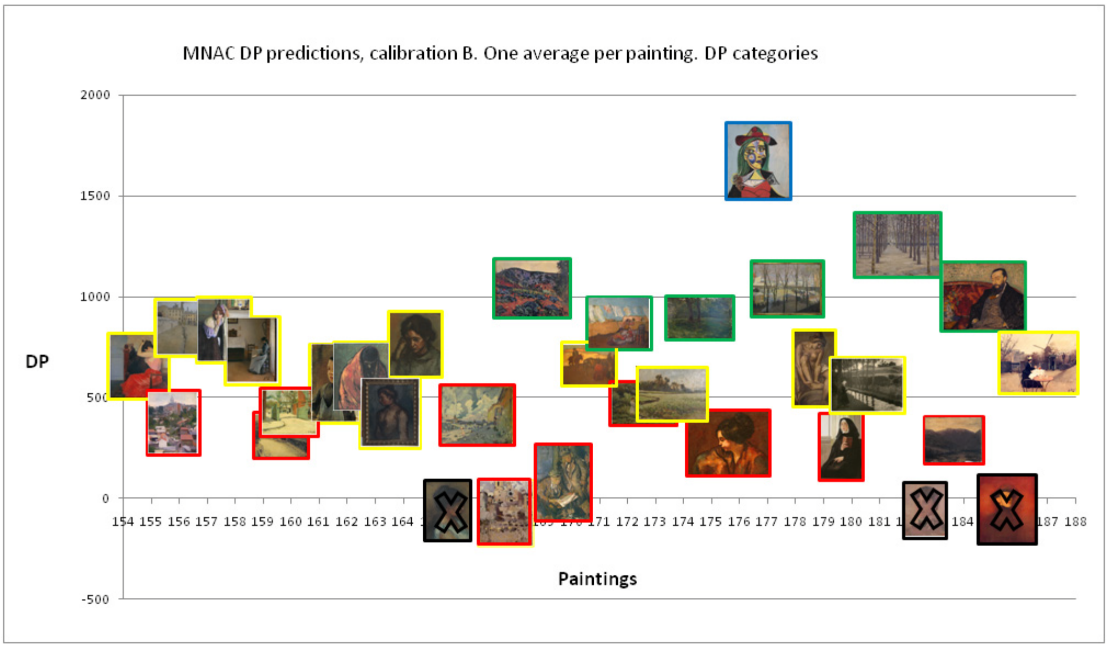

Figure 15. Averaged predicted DP for MNAC paintings. In red, those that would fall in DP category 1 (<550), in yellow those in DP category 2 (550 - 950); in green DP category 3 (950 - 1300) and in blue category 4 (>1300). In black and with a cross those where spectra could not be predicted.

We obtained a few negative values, and this fact has to be understood in the sense that we are working with a numeric scale. However, predictions that are outside the calibrated range of DPs are additionally unreliable and should be reported as <min DP used for calibration, which in our case was 425. We are looking at specific numbers, so that we have some way of analysing the data, but we have to remember that we have a large error of prediction for DP (275 units) and therefore, such negative values are a result of this error of prediction being applied. Similarly with the other positive values, we have to bear in mind that this error of prediction applies, and therefore, numbers are just to be taken as an indication and as a way to grade the different studied paintings among them.

The average for all the darker areas of the paintings is 741 (SD 360, RSD 47%) and the average for the regular areas is 673 (SD 320, RSD 48%). So in this case, the average DP is lower for regular areas for about 100 units and variability within regular and darker areas is similar.

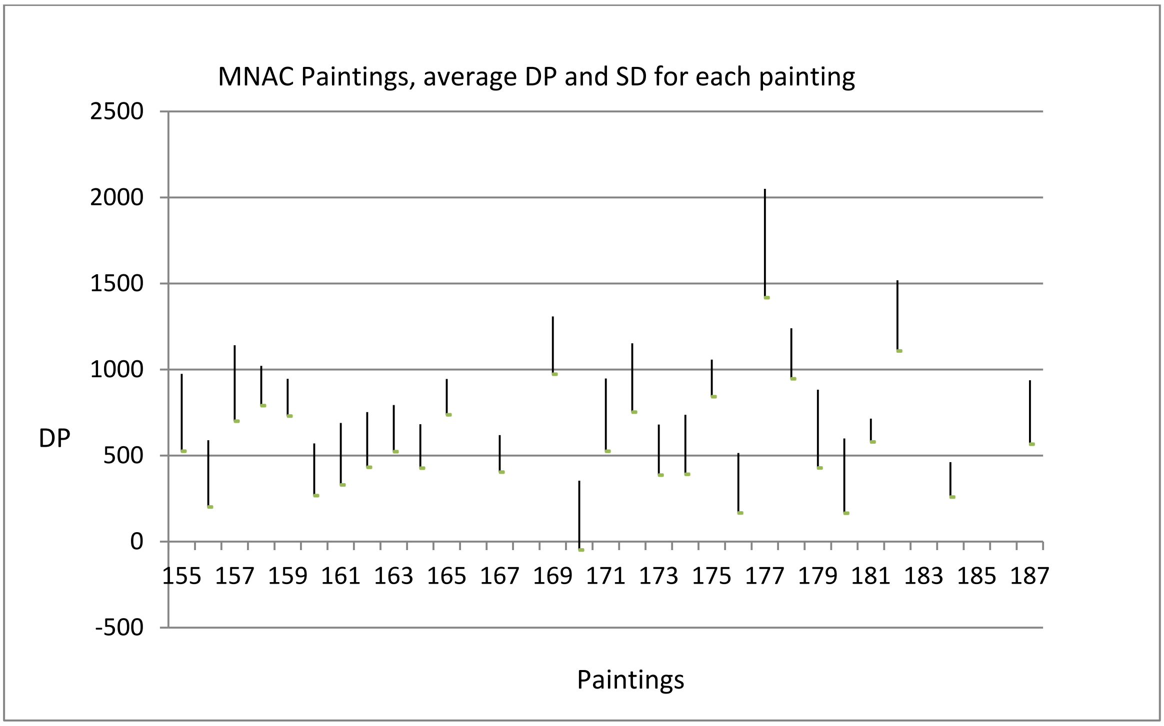

Figure 16. Average DP for each painting with its own SD (±SD), indicating the variability of DP results from the different locations measured in a painting.

Variability of DP values we get within each painting goes from 106 to 317 SD, the average SD being 167 DP units, and the RSD 29% (Figure 16). This means that if for instance we get the value of 1000 DP in a particular spot, from our analysis we see that 68% of other areas could be within one SD and therefore could have a DP that could typically go from about 833 to 1167. In our Reference Sample Collection (see Chapter 2.3), we got similar variability values within paintings(average RSD 22%) of which we had two samples in a visually different condition.

If we look at the average DP we obtain for the paintings depending on their fibre type we obtain the following graph:

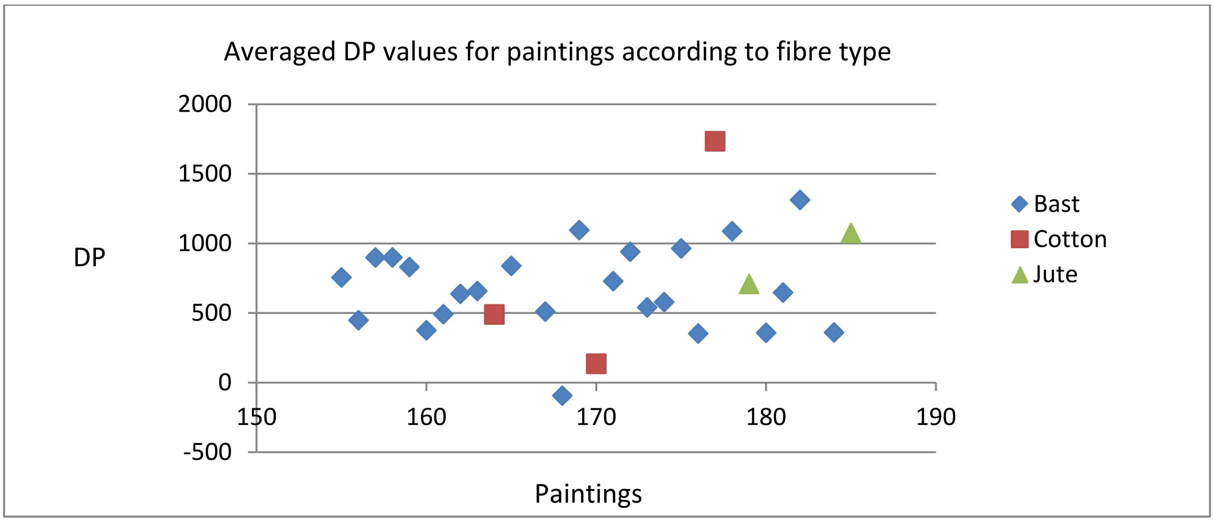

Figure 17. Averaged DP values for paintings according to fibre type.

If we look at DP and fibre type, in these case we see no big conclusions (and this situation is similar to what we found for our Reference Sample Collection), having cotton paintings both low and high DP. However, we should take into account that the high DP cotton painting is the Picasso one which is almost four decades younger than the rest of the paintings. Seen in this way, the two other cotton paintings are in the lower DP range, which could be accounted for the fact that cotton is more easily degraded than linen and bast fibres textiles. The only two jute paintings (**179** and **185**) of which we got DP predictions are in a middle positions among the other paintings and not in the lowest end as it was expected. Painting **179** has a low pH (4.1) and seems to be painted directly on the jute textile without any priming layer, for which a very low DP was expected. Painting **185** also has a low pH of 4.5 and in contrast, the DP is still quite high (1080).

5.3.3 - Fibre Identification

Fibre type identification was done using Discriminant Analysis, and as explained in Chapter 3, and the calibration and prediction were done at the same time. Identification was done in two steps: the first DA classified samples into: cotton, jute, "bast fibre[6]" and "combination" and the second DA further classified those samples that had been classed as "bast fibres" in the first DA, classing them now into: linen, hemp, ramie or a combination of linen and hemp.

In the first DA, "bast fibre" included: linen, hemp, ramie and linen/hemp combinations. "Combination" included: cotton/linen, jute/cotton or jute/linen. Jute is also a bast fibre, but it has been separated here since it is such a distinct fibre that the calibration is able to pick it up easily)

The prediction results are given with a percentage indication on how reliable the prediction is.

First DA

The results of the first DA are as follows:

Num.	Image	Bast	Cotton	Jute	Combination	Likely ID
166		0%	**93%**	0%	7%	**Cotton (93%)**
164		9%	**91%**	0%	0%	**Cotton (91%)**
177		16%	**84%**	0%	0%	**Cotton (84%)**

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[6] As already mentioned before, jute is also a bast fibre, but for the purpose of our method here it has been separated from the rest of the other bast fibres, as it could be clearly identified in the first DA step.

						
170		20%	**76%**	0%	4%	Cotton (76%)
186		0%	0%	**100%**	0%	**Jute (100%)**
179		0%	0%	**99%**	1%	**Jute (99%)**
185		0%	0%	**97%**	3%	**Jute (97%)**
156		**100%**	0%	0%	0%	**Bast (100%)**
158		**100%**	0%	0%	0%	**Bast (100%)**
159		**100%**	0%	0%	0%	**Bast (100%)**
162		**100%**	0%	0%	0%	**Bast (100%)**
163		**100%**	0%	0%	0%	**Bast (100%)**
172		**100%**	0%	0%	0%	**Bast (100%)**
173		**100%**	0%	0%	0%	**Bast (100%)**
174		**100%**	0%	0%	0%	**Bast (100%)**
175		**100%**	0%	0%	0%	**Bast (100%)**
178		**100%**	0%	0%	0%	**Bast (100%)**
181		**100%**	0%	0%	0%	**Bast (100%)**
182		**100%**	0%	0%	0%	**Bast (100%)**
171		**98%**	0%	0%	2%	**Bast (98%)**
187		**96%**	0%	0%	4%	**Bast (96%)**

184		**95%**	0%	0%	5%	**Bast (95%)**
155		**94%**	2%	0%	4%	**Bast (94%)**
183		**93%**	5%	0%	1%	**Bast (93%)**
176		**89%**	4%	6%	1%	**Bast (89%)**
167		**87%**	0%	0%	13%	**Bast (87%)**
165		**86%**	14%	0%	0%	**Bast (86%)**
161		**83%**	0%	0%	17%	**Bast (83%)**
169		**82%**	0%	16%	2%	**Bast (82%)**
157		**74%**	17%	0%	9%	Bast (74%)
180		**75%**	0%	0%	**25%**	Bast (75%) possible combination of bast with cotton or jute.
168		**72%**	0%	0%	**28%**	Bast (72%) possible combination of bast with cotton or jute.
160		**57%**	0%	0%	**43%**	Bast (57%), possible combination of bast with cotton or jute.

Figure 18. First-step DA predictions. Cotton, jute and other bast fibres canvas paintings are identified. In green, the predictions with a certainty above 80%. Images of the cotton and jute paintings have been included.

If we look at the percentage of precision in the fibre type prediction (Figure 15), we see that cotton paintings were predicted with certainties that go from 76% to 93%, jute with certainties that go from 97% to 100% and bast fibres with certainties that go from 57% to 100%. The vast majority of the paintings (28 out of 33, representing a 84%) had fibre type identified with certainties of 80% or above in the first-step DA.

In our survey we found four cotton paintings,representing 12% (the Picasso one being from a later period, 1937; one painting by Gimeno and two by Nonell), three jute paintings, representing a 9% (by Casas, Mutermilch and Gónzalez) and the rest, the majority, are of bast fibres (27 out of 33). Of the bast fibre ones, there are three that could also be combinations of bast with jute or bast with cotton (**180**, **168** and **160**), since their highest percentage is the bast type, but they also have significant percentages of "combinations" (between 25% and 43%).

Francesc Gimeno is known to have used cheap quality cotton supports in many occasions due to the artist's economic problems (8 p. 61) If we check Núria Pedragosa's PhD thesis (6), we find that among the seven Gimeno's paintings she looked at, six of them were cotton and one was a bast fibre. Regarding Isidre Nonell, from the eleven paintings Núria Pedragosa looked at, one of them was found to be cotton, the rest bast. In our research here we have found that from the five paintings analysed by Nonell, two of them are cotton, so we have found a higher proportion of cotton canvases in Nonell, although the total number of analysed paintings is smaller. Other artists of which we have studied paintings and of which Núria Pedragosa found cotton to be used in some cases were: Casas (she found 3 mixtures of cotton and bast out of 15 paintings); Mir (2 cotton, 1 mixture of cotton and bast out of 9 paintings) and Pidelaserra (1 cotton out of 7 paintings). For these artists we did not find cotton paintings. Other artists that we have also studied and that were only found to use bast fibre canvases by Núria Pedragosa (and by ourselves) were: Llimona (3); Martí Alsina (8); Rusiñol (12); Sunyer (11); Vayreda (8).

The fact that we find already some cotton and some jute canvases around the year 1900 but that the majority are bast fibres (linen, hemp etc.) corresponds to the information found both in the literature and in our samples' collection (see Chapter 1 and Chapter 2.1).

Eleven of the case study paintings analysed here had fibre identification analysis done on them through optical microscopy by Núria Pedragosa too for her PhD in 2005 (6). All of her identifications coincide with the results of this First DA analysis. One of the paintings was identified as cotton (**170**), three of them as jute (**179**, **185**, **186**) and six of them as bast fibres (**156**, **157**, **161**, **163**, **176**, **178**, **187**).

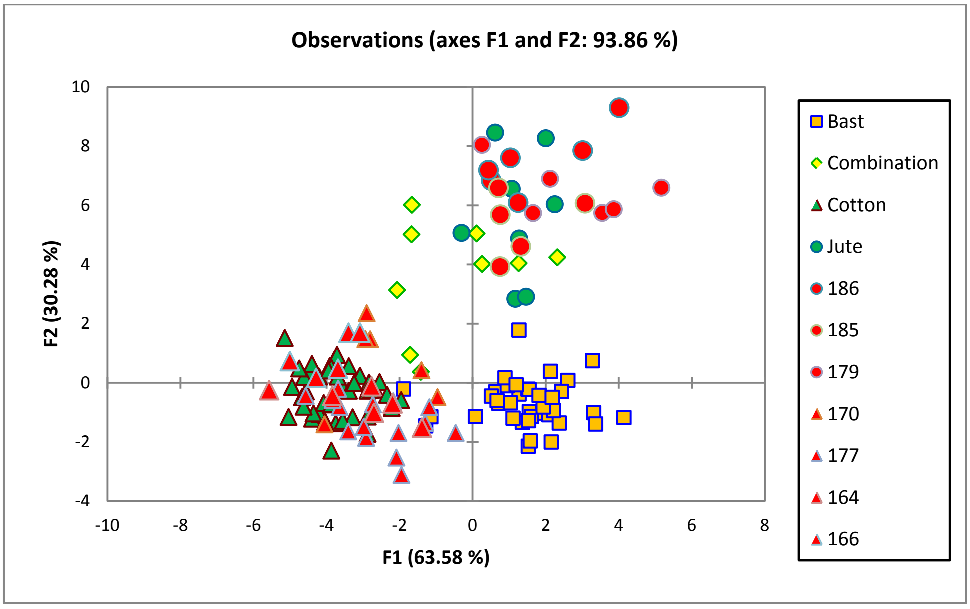


Figure 19. DA scatter plot for the newly identified MNAC jute (**186**, **185**, **179**) and cotton paintings (**170**, **177**, **164**, **166**) together with bast, cotton, jute and combinations (cotton/linen; jute/cotton; jute/linen) samples from the Reference Sample Collection used to build the model.

As explained in Chapter 3, when doing DA, both the NIR spectra of known fibre identified samples and the NIR spectra of the unknown samples (MNAC paintings in our case) are entered into the software at the same time. The chemometric model and the prediction of the unknowns are done at the same time. Both the known and unknown samples can be plotted in the same scatter graph (Figure 19).

Figure 19 shows how, indeed, all MNAC paintings identified as jute (**186**, **185** and **179**) fall near the known jute samples and all MNAC paintings identified as cotton (**170**, **177**, **164** and **166**) fall in the same area as the known cotton samples.

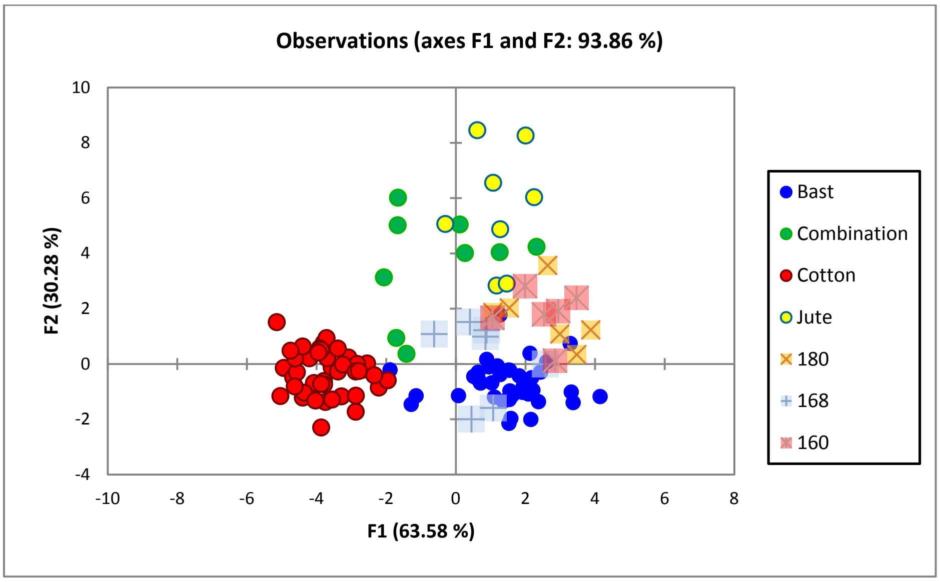


Figure 20. DA scatter plot for the three possible “combination paintings: **160**, **168** and **180** together with bast, cotton, jute and combinations (cotton/linen; jute/cotton; jute/linen) samples.

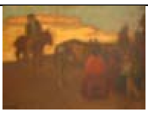
The DA scatter plot of the samples according to fibre type shows how observations are usually classified (Figure **20**). If we take the three last paintings of the list (168 (Joaquim Mir, *Paisatge*), 160 (Santigo Rusiñol, *Jardí de Montmartre*) and 180 (Joan Llimona, *La novícia*)) that could either be bast or “combination” (cotton/linen; jute/cotton, jute/linen) we can plot them together with the known samples and see where they are placed (Figure 20). In this case, according to the graph, they could all be bast fibres since they all fall near this cluster of samples.

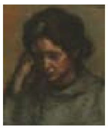
Second-step DA

The second-step DA analysis was only run on those samples that had been classed as “bast fibres” in the first-step DA and the aim was to further distinguish between different bast fibres. The second DA classed paintings according to: linen, hemp, ramie or a “combination”, which in this case meant a mixture of “linen and hemp”.

The results obtained were the following:

Num.	Image	Linen	Hemp	Ramie	Combination	Likely ID
174		**100%**	0%	0%	0%	**Linen (100%)**
162		**99%**	0%	0%	0%	**Linen (99%)**
171		**99%**	0%	1%	0%	**Linen (99%)**

						
187		**98%**	0%	2%	0%	**Linen (98%)**
175		**97%**	0%	3%	0%	**Linen (97%)**
163		**93%**	0%	6%	2%	**Linen (93%)**
172		**87%**	0%	12%	0%	**Linen (87%)**
155		**85%**	0%	15%	0%	**Linen (85%)**
161		**85%**	0%	0%	15%	**Linen (85%)**
169		**84%**	0%	15%	0%	**Linen (84%)**
156		**80%**	0%	19%	0%	**Linen (80%)**
173		**76%**	0%	24%	0%	Linen (76%)

						
165		**74%**	0%	26%	0%	Linen (74%)
184		**72%**	0%	27%	0%	Linen (72%)
167		**69%**	0%	7%	24%	Linen (69%)
182		**69%**	0%	28%	3%	Linen (69%)
157		**65%**	0%	32%	3%	Linen (65%)
159		**65%**	0%	35%	0%	Linen (65%)
176		**65%**	0%	23%	12%	Linen (65%)
158		**60%**	0%	39%	0%	Linen (60%)
178		**58%**	0%	**42%**	0%	Linen, possibly ramie

						
181		**59%**	0%	**41%**	0%	Linen, possibly ramie
180		**39%**	0%	**48%**	13%	Ramie, may be linen
160		**75%**	6%	15%	4%	Linen, possibly combination with jute or cotton[7]
168		**41%**	0%	29%	30%	Linen, possibly combination with hemp.
183		32%	0%	19%	**49%**	Combination of linen and hemp, possibly only linen.

Figure 21. Second-step DA analysis on the samples classified as "bast" fibres to distinguish between linen, hemp, ramie or combination of linen/hemp, ordered according to prediction certainty. In green, predictions with a certainty above 80%.

This second-step DA, as could be anticipated, offers a lower degree of certainty, with only 33% of the paintings obtaining predictions with an 80% certainty or above. This is so because we had few known hemp, ramie and linen and hemp samples.

Regarding the predictions, as expected, most of the paintings are found to be linen. We find that there are 20 out of the 33 paintings (a 60%) that are found to be "linen 100%", with certainties going from 60% to 100%. We got three paintings that could be ramie (**178**, **180** and **181**), although in two cases, certainty percentages point more towards linen (**178**, **181**). Interestingly, two of these three paintings are by Llimona and have a "Planella" stamp. Another painting by Llimona at MNAC and that has a Planella stamp (*Tornant del tros*, MNAC 10818) has been found in the literature identified by optical microscopy as a "bast fibre, possibly hemp" (15 p. 31). May be these "Planella canvases" are not 100% linen and this is why its identification is

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[7] Even though the high probability obtained for linen (75%) in the second-step DA for this painting, the final likely identification is "linen, possibly combination with jute or cotton", due to the high percentage of possibly being a combination (45%) obtained in the first-step DA.

not straightforward. Curiously enough one of the two Planella stamp paintings studied here (**180**) did not appear that degraded visually (it did not have a brown colour typical of degraded canvases) but then was found to have quite a low predicted DP (358).

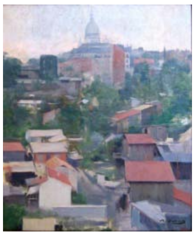
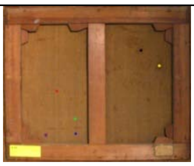
We also found two paintings (**168** and **183**) that could be mixtures of linen and hemp. Finally painting **160** is possibly linen, but it might be combined either with cotton or jute since we got a high percentage (43%) of this in the first-step DA analysis.

5.3.4 – Specific case studies

Difference between darker and lighter areas

There were 19 paintings of which we had analysed “regular canvas” spots (usually around 3 different locations per painting) and “darker areas” (usually around 3 different locations per painting too), and of which we had predictions both for pH and DP (Figure 22). Darker areas were seen to be the result of oil migration from the paint layer, varnish migration through the paint layer cracks or other unknown reasons. Values from the different locations have been averaged so that we have one “regular canvas” average per painting and one “darker area” average per painting and these are the ones compared (Figure 23 and Figure 24).

Object Id	Recto	Verso	pH Regular canvas	pH Darker canvas	DP Regular canvas	DP Darker canvas
155			**5.1**	**5.1**	**740**	**770**
158			**5.1**	**5.2**	**860**	**960**
160			**4.7**	**4.8**	**<400**	**480**
161			**4.8**	**5.0**	**470**	**700**
165			**5.2**	**5.3**	**800**	**880**

173			5.2	5.3	530	540
176			5.3	5.3	<400	460
162			5.0	5.1	660	520
156			5.1	5.2	430	<400
163			5.1	5.2	730	580
172			5.3	5.3	890	1020
178			4.8	4.8	1060	1120
157			5.1	5.1	1100	740

167			**5.0**	**4.9**	**560**	**480**
170			**5.1**	**4.9**	**<400**	**<400**
174			**5.3**	**5.2**	**670**	**460**
175			**5.5**	**5.4**	**1020**	**880**
182			**5.3**	**5.1**	**1350**	**1200**
187			**5.0**	**5.0**	**820**	**680**

Figure 22. pH and DP averages for the paintings of which we had analysed "darker" and "regular canvas" areas. In red those values that are lower, shaded rows correspond to "darker" areas.

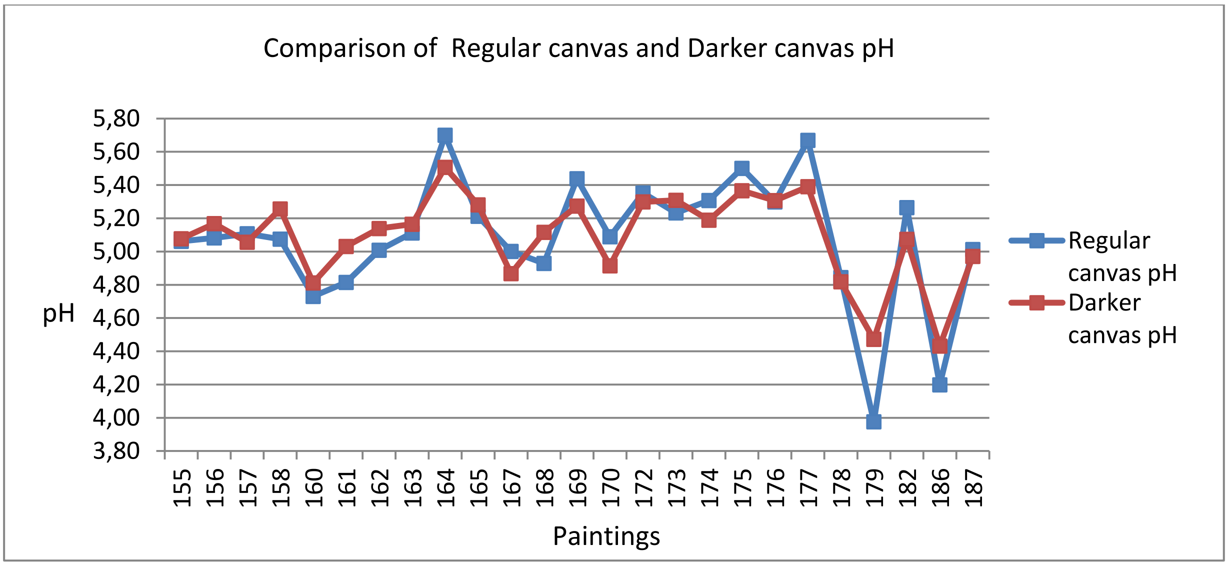


Figure 23. pH values averages for each “regular canvas” area (blue) and each “darker canvas” area (red) for each painting. It can be seen that half the times, the regular canvas has a slightly higher pH, but the other half it is the darker canvas that has a slightly higher pH. In all cases, though, differences are very small.

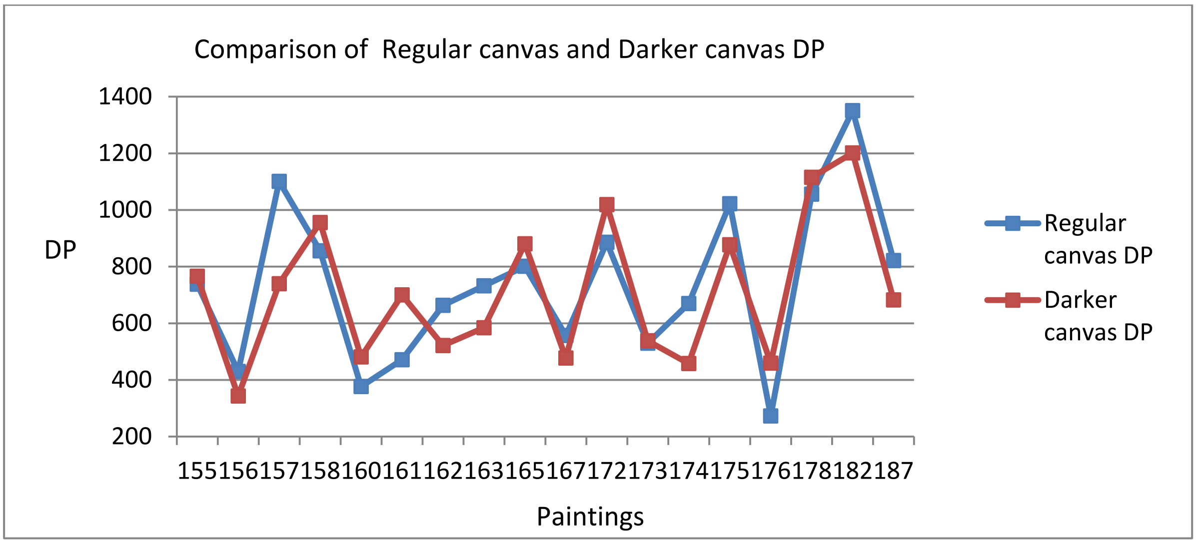


Figure 24. DP value averages for each “regular canvas” area (blue) and each “darker canvas” area (red) for each painting. It can be seen that half the times, the regular canvas has a slightly higher DP, but the other half it is the darker canvas that has a slightly higher DP. Again, differences are not significant.

The conclusion to this particular strand of research was that no significant differences were found between darker and lighter areas of the canvas support of paintings. Sometimes darker areas tended to have slightly better pH and DP values (higher), and sometimes it was the other way around. What was corroborated againg, though, was the positive correlation between pH and DP values.

Lassitud, by Isidre Nonell (**176**)

The painting *Lassitud*, by Isidre Nonell (**176**) offered a very interesting verso with a large and intense water stain, lots of dirt accumulated at the tideline of the stain, plus varnish impregnation of the canvas that had diffused through the paint layer cracks in several points (Figure 25). Since it was seen to be a very interesting case study, 18 different locations where analysed: 5 spots of “regular canvas”; 5 spots of “washed canvas” (areas in the centre of the big water stain, where dirt was supposed to have been washed away by the running water); 5 areas along the “tideline” (dark end of the water stain where dirt and degradation products were supposed to have accumulated) and 3 areas of “varnish” (where the varnish applied in the front of the painting can be seen to have gone through the cracks on the paint layer) (Figure 25).

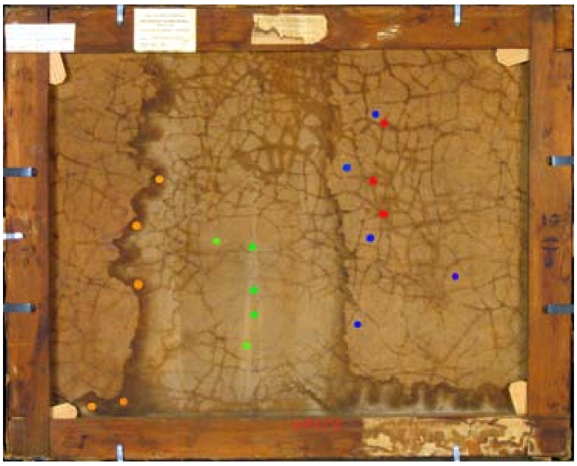


Figure 25. Verso of the painting *Lassitud*, by Isidre Nonell (**176**). In blue, analysed “regular canvas” areas; in green, “washed areas”; in orange, “tidelines” and in red, “varnish areas”.

Regarding pH, it is indeed interesting to see that the average for the washed area is higher than the average for the “regular canvas” area (washed canvas 5.5; regular canvas 5.1) (Figure 26). This would indicate, that canvases do accumulate dirt and acidic degradation products that would be better washed away, as is often done with paper objects. Of course, removing the dirt from painting canvases is a big challenge, and this could be a very interesting future avenue of research. On top of this, the organic canvas support in paintings is usually kept taut all the time, exposed to the air circulation and pollution this might bring in, which is added to its own degradation products.

It is interesting to note too that in this case, the varnish area is the area with the lowest pH of all (5.0). This would imply that these areas will suffer faster degradation than other areas. This fact linked to the fact that the paint layer is cracked at these very same points (the varnish went through because there was a crack), will make these areas of the canvas more susceptible to future degradation and tears since presumably there will be more air circulation in these areas. In this case, the varnish seemed to indeed be found to be acidic.

Contrary to expectations, the tideline area appears to have a higher pH average (5.5) of all (Figure 26). This result puzzles us a bit and makes us wonder if our method might have some problem in predicting this sort of samples, since we did not have samples with so much dirt accumulated on them in our Reference Collection.

	pH	DP
Varnish	**5.0**	460
Regular canvas	5.1	<400
Washed canvas	5.5	**<400 ***
Tideline	5.5	470*

Figure 26. DP and pH results for the different analysed areas of the painting *Lassitud*, by Isidre Nonell (176). In red the lowest pH and the lowest DP value obtained. * few DP predictions were obtained from these areas

Regarding the situation with DP, unfortunately for this painting, many of the analysed areas could not be predicted. Only a 40% of the NIR spectra returned with a DP prediction (24 out of 61). The method did not seem to have that much trouble predicting the regular canvas areas (10 out of 15 spectra got a prediction) and the varnish areas (11 out of 12). However, it did have trouble with the washed canvas area (only 2 spectra out of 15 got a prediction) and with the tideline area (only 1 out of 19).

If we look at the two areas where we got many predictions, we get an average of <400 DP for the regular canvas area and a slightly higher DP of 460 for the darker varnish area. In this case, even if the pH of this varnish area is lower, the DP is not the lowest one in relation to the other analysed areas. The washed areas give a much lower DP of <400, that could either mean that even if water washed away some of the acids (this area has the higher pH), it degraded the canvas more. However, we got very few predictions from this area, so this makes us wonder if the <400 value is a proper one. The tideline area also makes us wonder if we are getting the proper DP valuehere (470), especially since we did not have so dark and dirty samples in the calibration and validation, and this might account for the low number of predictions we got from this area.

The two areas with the higher DP are the varnish and the tideline areas, although differences are very small. If results from these areas were valid, one could think that these two “materials” (the tideline might contain dirt particles and part of the sizing layer of the canvas) have somewhat “protected” the canvas from degrading effects of air circulation and pollution, which we know have a clear degrading effect.

All in all, though, the DP values obtained for this painting are in the lower range and therefore indicate that the canvas is quite degraded. MNAC has another painting (*Nen malalt*, by Canals, 1903 (MNAC 003806)) which presents a similar verso as *Lassitud* by Nonell with a pronounced water stain. It would therefore be very interesting to eventually analyse it too and see if there are similarities with the information found on the Nonell painting (Figure 27).

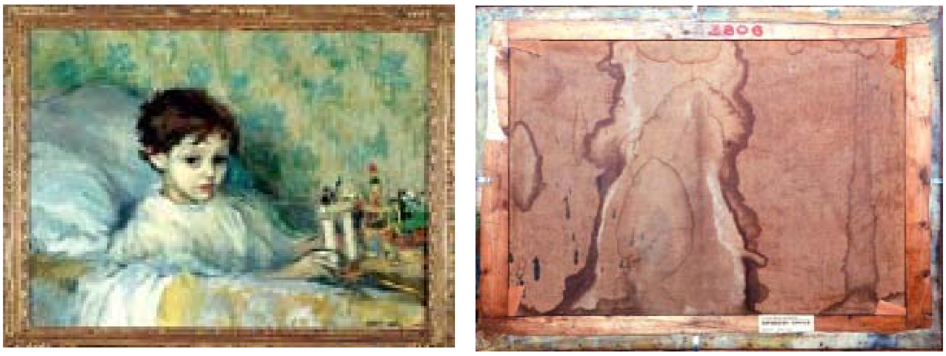


Figure 27. Painting with a similar case of pronounced water damage, *Nen malalt*, by Canals, 1903 (MNAC 3806)

El Gran dia de Girona by Martí Alsina

El gran dia de Girona by Martí Alsina, 1863-64, is a very large painting of which many NIR measurements were taken in November 2009, the first time that the Labspec 5000 instrument was brought to Barcelona. This painting measures 5x11m and at the time the measurements were taken, it was being restored at the Centre de Restauració de Béns Mobles de Catalunya (CRBMC) (Figure 28), in a collaborative big project with MNAC, who is the actual owner of the panting. Since the canvas was being repaired, the painting was laying down flat on the floor and so access to its reverse was easy. With the idea in mind to study thoroughly what differences in pH and DP could exist within one same painting, many measurements were taken in sixteen different locations grouped in three areas of the canvas (the bottom at the centre of the painting (spectra 1 to 18); the left bottom angle (spectra19 to 37) and the top at the centre of the painting (spectra 38 to 61)). Measurements were taken placing eight layers of Whatman paper underneath the canvas in all cases, except for the last six spectra taken (56 to 61), where it was not possible to do so (Figure 28).

Figure 28. Taking NIR spectra from the reverse of the large painting *El gran dia de Girona* by Martí Alsina (MNAC 12084).

Out of the total of 61 spectra collected, we only got pH predictions for 39. The average pH value of the predictions obtained is 6.0 and the SD 0.3. For DP, we did not get a single prediction when using Calibration B (m9), the one we chose to use for the other MNAC masterpieces. If we used Calibration A (m8), then we got 10 predictions out of 61 spectra, with an average of 1280, SD 160. Again, blanks seem to be more concentrated on certain areas of the painting: we took measurements basically from three very distant areas (a: bottom area at the centre of the painting; b: the left bottom angle and c: top area at the centre of the painting) and we got: 1 prediction from area a, none for b, and 9 from c. There were three physical samples also taken from this painting that are part of our Reference Sample Collection, 77_1 (which comes from area c), 77_2 (which comes from area b) and 77_3 (which comes from an area that was not measured using NIR, the far right side of the painting). Sample 77_3 took part in the DP calibration, and sample 77_2 took part in the DP validation. All samples took part in the pH calibration (77_1 and 77_2) and validation (77_3).

	Average predicted pH	**Average predicted DP**	**Physical sample**	**Measured pH**	**Measured DP**
Area a (Bottom at the centre of the painting (spectra 1 to 18))	6.2	1240	**No physical sample taken**		
Area b (Left bottom angle (spectra19 to 37))	6.1	---	**77_2**	6.5	1140
Area c (Top at the centre of the painting (spectra 38 to 61))	5.9	1290	**77_1**	6.1	---
Right side of the painting			**77_3**	5.0	740

Figure 29. DP and pH predicted and measured values for the big painting *El gran dia de Girona*, by Martí Alsina (MNAC 12084).

Interestingly we see that the for the DP predictions we got, we have quite a high value (1280), and the SD being relatively small (160), means that all the predicted values are quite close to this figure. The lower DP value we obtained when we measured sample 77_3, might be thus a more localized effect, may be of a particular acidic material. Actually, this sample came from the right side edge of the painting (while being face down) and the canvas was visibly darker than other areas. (This sample was taken right next to the place where a larger sample to do some mechanical tests on the canvas had been taken by CRBMC). In the past, the torn canvas of this painting had been consolidated with generous amounts of Beva 371 (16 p. 6), and this might have been a notable source of acidity.

In conclusion, however, it can be said that the average pH of the canvas (6.0) is quite good in comparison with that obtained for the analysed MNAC masterpieces. This painting is from an earlier period than the other MNAC paintings (1863) and this makes us wonder if the difference in pH has to do with different industrial materials and techniques having changed along the 19th C. Another very plausible reason for such a better pH could be the fact that this painting had been kept rolled over itself from the year 1939 until today: during the Spanish Civil bombardments, the painting suffered large horizontal tears (one of them over six meters long) and since it was not possible to restore it properly, the painting was rolled up and stored away. Obviously, the good pH value has also made the canvas retain a very favourable DP in general (average predicted being 1280).

A general comparison between the condition of MNAC masterpieces and Dalí paintings

During the May 2010 campaign when the Labspec 5000 was brought to Barcelona to analyse the 33 MNAC masterpieces, the opportunity was taken to also analyse 12 paintings by Salvador Dalí from the Fundació Gala-Salvador Dalí. The particular results obtained for Dalí paintings are still being analysed and will be reported and published elsewhere, but the general trend of the results can already be anticipated here and compared to the results obtained for the MNAC paintings.

If we produce one average of all the results obtained, we obtain a general pH average of 5.5 (SD 0.4; RSD 7%) and a general DP average of 950 (SD 330; RSD 35%) for the Dalí paintings, where for MNAC paintings we obtain an average pH of 5.1 (SD 0.4; RSD 8%) and an average DP of 690 (SD 360; RSD 52%). Therefore we get, in general, lower pH and lower DP values for MNAC paintings.

The correlation between lower pH and lower DP is maintained here too, and in this case, the older MNAC paintings are in a slightly worse condition. The differences between the two sets of paintings are, on the one hand, the age: the analysed MNAC paintings are all from around the year 1900, whereas Dalí paintings span from the early 1920s to the late 1960s and in the location where they are being kept: in Barcelona the MNAC masterpieces and in Figueres (Girona), the Dalí paintings. All of them are commercially primed canvases, but of course from different periods. It is clear it would be very interesting to know more about the particular materials used by the industry during the different periods and its degradation and about the effects of a particular more or less polluted environment (such as the one in Barcelona) on the degradation of the canvas.

5.3.5 - Condition assessment survey

Once we have gathered and analysed all the pH and DP values for the different MNAC paintings, we can make use of the Condition Assessment Classification designed in Chapter 4, so that meaningful information can be obtained and treatment priorities established.

We know that those paintings that are acidic will suffer DP decrease over time. If they already have lower DP, then they are already more sensitive (Figure 30).

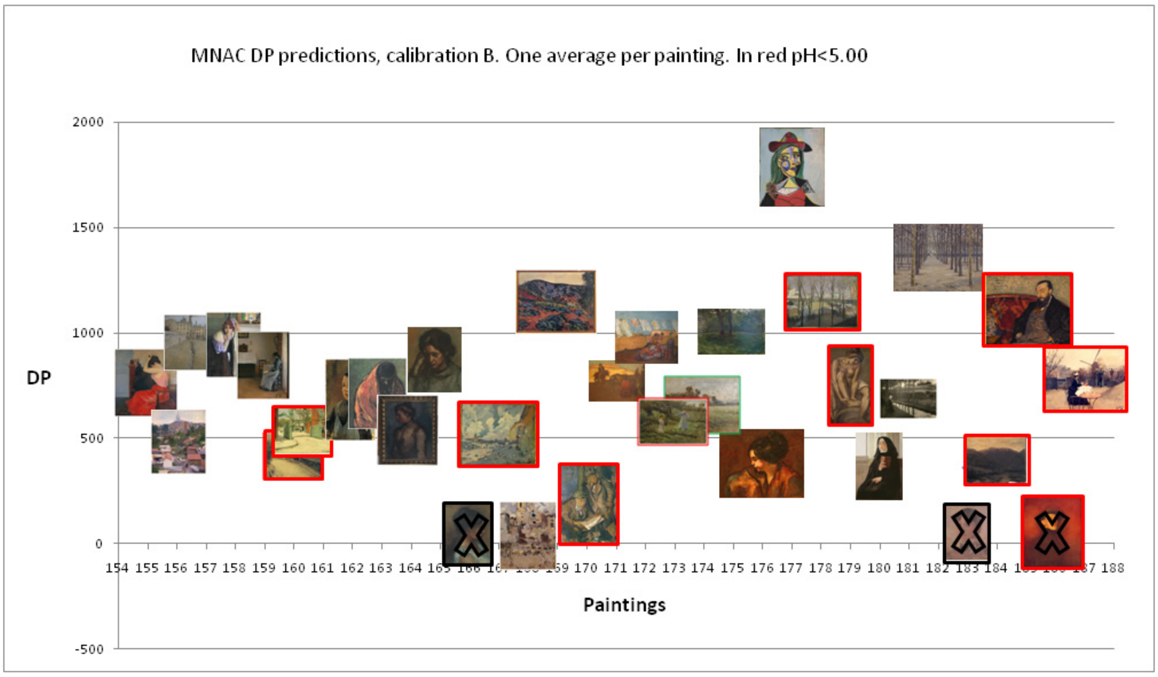
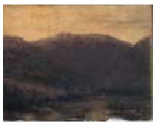
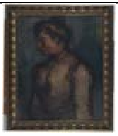
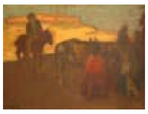
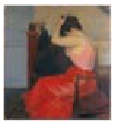


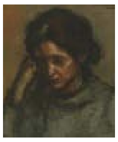
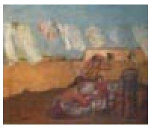
Figure 30. Paintings arranged according to average predicted DP. In red those paintings at higher risk of degradation in the future due to their lower pH (pH < 5.0).

If we put the average pH and DP per painting in a list, we get the following table, ordered from smaller to larger DP values (Figure 31). Depending on the particular DP and pH values we can class each painting into one of the six designed classes (see Chapter 4). We have to remember, though, that especially for DP, we have a large error of prediction (±275) and that we use the predicted DP values because we need numbers to be able to somehow grade paintings condition among them. Values should not be taken as final but as a mere indication as to whether paintings are towards the lower or higher range regarding DP.

Number	Image	DP	pH	Condition assessment class
168		**<400**	**5.0**	**A**
170		**<400**	**5.0**	**A**
176		**<400**	**5.3**	**A**

180		**<400**	**5.1**	**A**
184		**<400**	**5.0**	**A**
156		**<400**	**5.1**	**A**
160		**420**	**4.8**	**B1**
161		**510**	**4.8**	**B1**
167		**510**	**4.9**	**B1**
179		**650**	**4.1**	**B1**
187		**750**	**5.0**	**B1**
164		**550**	**5.6**	**B2**

				
173		**530**	**5.3**	**B2**
174		**560**	**5.2**	**B2**
162		**590**	**5.1**	**B2**
181		**650**	**5.5**	**B2**
163		**660**	**5.1**	**B2**
171		**740**	**5.5**	**B2**
155		**750**	**5.1**	**B2**
159		**840**	**5.2**	**B2**

165		**840**	**5.2**	**B2**
157		**920**	**5.2**	**B2**
158		**910**	**5.2**	**B2**
185		**1080**	**4.5**	**C1**
178		**1090**	**4.8**	**C1**
175		**950**	**5.4**	**C2**
172		**950**	**5.3**	**C2**
169		**1140**	**5.4**	**C2**
182		**1310**	**5.2**	**C2**
177		**1730**	**5.7**	**D**

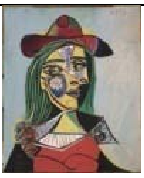
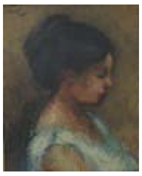
				🟦
186		**---**	**4.3**	
183		**---**	**5.7**	
166		**---**	**5.7**	

Figure 31. Paintings arranged according to increasing DP value. According to the classification designed in Chapter 4, priority paintings to treat would be: red (B1: pH<5.0 and DP between 400-950); orange (C1: pH <5.0 and DP between 950-1400); yellow (A: DP<400). In green categories B2 and C2, with pH >5.0. In blue class D. pH in red indicates those that are <5.0. pH and DP values have been rounded.

If we follow the priority order established in Chapter 4, we find that 16% of the studied MNAC paintings from around the year 1900 are in the B1 class (<5.0 pH and 400-950 DP) and these would greatly benefit from some urgent deacidification treatment, so that DP does not proceed to decrease. From this point of view, this would be the first group of paintings to deal with if some sort of action was to be taken. Secondly, a smaller 6% of the studied paintings are in class C1, where although they have a higher DP (950 – 1400) they would also greatly benefit too from some sort of deacidification treatment, since they have a pH < 5.0. Then there is a 20% of the paintings with very low DP values (<400) that are at high mechanical risk (class A). If these paintings are not to be moved, it would be ok not to do anything with them, but if they had to be sent on loan or other, their fragile condition would certainly need to be taken into account. This means that 42% of the studied paintings are either slightly acidic (<5.0) or have very low DP values (<400).

The rest of the analysed paintings (56%), exhibit better pH values and so they could be left as they are for the time being. Of this 56%, most of the paintings are class B2, 40%, with pH>5.0 and DP between 400 and 950 (DP values that are of concern) and another 13% are class C2 (DP 950-1400). There is one painting, the Picasso one (3%), which is in class D (pH < 5.0 and DP > 1400). To visually identify the paintings that are in the different priority classes, the reader is referred to Figure 32.

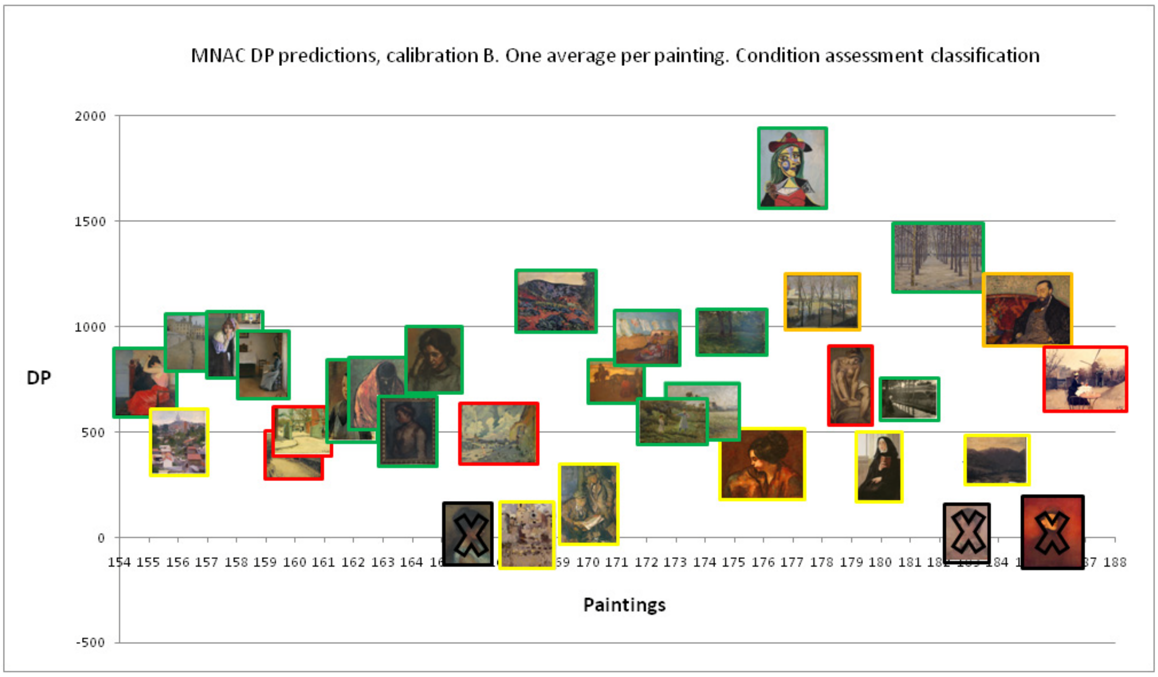


Figure 32. Condition survey categories. Red (B1: pH<5.0 and DP between 400-950); orange (C1: pH <5.0 and DP between 950-1400); yellow (A: DP<400). In green categories B2, and C2 (with pH>5.0) and category D.

Even if “only” 30% of the paintings have pH >5.0, we have to take into account that they are still all acidic. Therefore, if means were available, all the paintings would benefit from some sort of deacidification treatments, direct or indirect.

Among the five paintings we have in category B1, the ones that would benefit most from some sort of deacidification, we find painting **187** (*Plen air* by Casas), which is an emblematic painting for the museum. This painting represents quite a dark canvas and being a jewel of the collection, must have been restored several times. Documentation conserved at the museum points towards the fact that the painting had its varnish removed and was re-varnished in 1983[8] (17). One of the other paintings in this category is painting **179** (*Dona rentant-se* by González), a painting done on jute, where the oil paint is directly applied to the canvas without any priming layer. It is not surprising, therefore, that being a jute painting, it pH is in the lower range (4.1). The DP (660) was not as low as expected, which is good news. The canvas is also seen in several areas of the painting from the front since the oil paint does not cover it completely (for example at the top right corner). These areas are therefore more prone to suffering more degradation due to the effect of light and pollution. (There is another painting by González in the same technique on jute and that is also currently on permanent display at MNAC (*Noia adormida a la platja*, 1914, MNAC 113504). Our advice would be that these two paintings, being on jute and the canvas being exposed in different points, where not always on display, but had some period of rest in the store rooms. The other three paintings in category B1 are one by Mir (*Paisatge (Maspujols. Camp de Tarragona*, **167**) and two by Rusiñol (*Entrada al parc del Moulin de la Galette*, **161**) and (*Jardí de Montmartre*, **160**). There is a painting, of which we did not get a DP prediction, but that is painted on jute and has a low pH, which is the *Estudi del natural per al retrat del rei Alfons XIII*, by Casas (**186**). Casas is known to have used good quality materials, and the use of this jute painting must have been an occasional experiment to exploit the vibrant surface offered by this type of canvas (see the detail of the surface of this panting in Chapter 1) (6 p. 112).

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[8] The short conservation report from 1983 says: "Limpieza de contaminación; Disolución de barniz; Varias reintegraciones pictóricas; Barnizado general", which could be translated as: “Pollution cleaning. Varnish removal. Several inpaintings. General revarnishing”.

The two canvases that are in category C1, with a pH < 5.0 are *Retrat de J. Dalmau* by Mela Mutermilch (**185**, pH 4.5) and "*La Butte*" by Rusiñol (**178**, pH 4.8). The painting by Mela Mutermilch is not surpring that has a more acidic pH, being painted on jute. The painting by Rusiñol has a clear migration of some of the oil from the paint towards the reverse showing the composition in the front on the reverse of the painting. Although it is obvious that this work has suffered several conservation treatments (four patches can be seen on its reverse), only the 2006 treatment record is kept in the museum archives, when the painting was cleaned using distilled water[9]. These two paintings have a reasonable DP for the moment, but could degrade in the future years if their acidity is not neutralised.

In the group of paintings classed as A, paintings that are at higher mechanical risk, we find a Gimeno painting, *Llegint el diari* (**170**), on a cotton support. The low DP found on this painting corroborates the idea that Gimeno's use of low quality painting materials, often translates into a worst condition of his supports (8 p. 61). The other painting we find in this group is *Lassitud*, by Nonell (**176**), the specific case of which has previously been examined in this same chapter. Moisture damage might have been an important factor in lowering the DP of this painting. Other paintings in this group are: *Vall de Querol* by Pidelaserra (**184**); *Paisatge* by Mir (**168**) and *Le Sacré coeur* by Casas (**156**) and *La novicia by* Llimona (**180**). From this last group, a curious result is the low DP value obtained by this last painting by Llimona (**180**) with a DP of 388, since according to the visual inspection of the canvas we did not expect such a low value (it looked in quite a good condition).

Of the rest of the paintings which are in a better condition it is worth noting the excellent condition of the Picasso painting, which having a slightly higher pH (5.6) is foreseen to retain its higher DP (1730) for quite some time.

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[9] 2006: Conservation treatment: "Paint layer is cleaned with distilled water."

5.4- Conclusions

The possibility of applying the non-destructive NIR spectroscopy method developed for predicting pH, DP and fibre type arose and thus thirty-three masterpieces from the MNAC collection from around the year 1900 (±10 years) were surveyed using the novel technique. NIR spectra from the reverse of the paintings were collected from several different locations for each painting, gathering 670 spectra in total, coming from 208 different locations from 33 paintings. The instrument used to take the NIR spectra was the same one used for producing the calibrations, a Labspec 5000 spectrometer (Analytical Spectral Devices, USA). Once the spectra had been averaged, the predicted results for the three parameters of interest were obtained almost instantly, using the "*Grams AI spectroscopy software*" from ThermoScientific, with the add-on "*IQ Predict*" for pH and DP and the software *Xlstat* (Addinsoft, USA) for fibre identification.

Regarding pH, the technique proved to work very well. All the spectra could be predicted, except for a 3% of them, and 86% of them had a Mahalanobis distance of <2.00, which means that reliable predictions were obtained. The error of prediction of the developed method was also very small, ±0.43, and this gave quite accurate results.

For DP, reliable results were obtained, with a proportionally larger error of prediction (±275). In this case, though, predictions were obtained for 65% of the spectra, with quite a large amount of them (45%) being left unpredicted. The reason for this could be the fact that the calibration set of samples for DP was smaller than for pH (102 samples for DP against 170 samples for pH). We also found that blanks were not randomly scattered throughout the spectra, but that they tended to concentrate more on certain paintings, maybe indicating that certain materials spectra were not present in the calibration and this is why the method had trouble in predicting these. If the number of samples available was to be increased in the future, the error of prediction would also probably be lowered and results could be obtained for the present blank results.

Regarding fibre type identification, the method is proven to work with very high certainty for distinguishing between cotton, jute and bast fibres. 84% of the paintings got fibre type predictions of the first DA analysis with certainties of 80% or above, so therefore the first DA is a complete success. This has probably been achieved by the fact that cotton and jute are very different fibres from the rest and this is translated into their NIR spectra which is picked up by the calibration.

The second-step DA gave also good results, and allowed more precision among the "bast" fibres group, although since few hemp and ramie samples were present in the calibration, the precision of prediction was lower than in the first-step DA (here only a 33% of the paintings were predicted with a certainty of 80% or above).

If more precisely identified hemp and ramie samples were available in the future (maybe through the use of ATR-FTIR, a destructive analytical technique that has proven useful to this end (18)(19)), the method could certainly be improved, which, given the identification difficulties bast fibres pose to the every day conservator, would result in a very useful tool. This would certainly help to increase the knowledge on the fibres used along history and in different geographical areas for paintings, where there is still a lot to be learned.

A small test was done to see if there was a difference in results by using different backgrounds (white table, two layers of thick blotting paper or calibration pad) when taking the NIR spectra of easel paintings. The conclusion to this test was that in the case of easel paintings all these different backgrounds can be used since they do not influence the result. For the safety of the paintings, therefore, the advised method would be (if there is no raised impasto or flaking paint present) to place the painting face down directly on two layers of blotting paper. If there are raised impasto areas, then putting the painting face down on four raised pads at each corner and placing the calibration pad under the area to be analysed is the advised method. Of course, impasto areas and flaking areas are to be avoided.

Three repeated NIR spectra are usually taken from each analysed location so that an average spectra can be obtained and from this, one prediction per location is obtained. We ran predictions of our spectra this way but we also ran the predictions without spectral averaging, obtaining, thus, one prediction for each original spectrum and then did the average of these predictions. It was found that the final results were almost identical and thus it was discovered that in our case, final predictions can be obtained in the way that is less time consuming (no averaging).

In conclusion, the developed technique, although with some limitations regarding DP predictions, has been proven to work and has therefore given us very valuable information on the condition of the MNAC paintings studied without having removed a single physical sample from them.

Regarding the actual results obtained, it was found that all of the MNAC paintings under study are acidic. A "final" average was calculated for each painting from the values obtained for each different location analysed, so that paintings could be graded in terms of canvas acidity. Average pH values obtained for paintings went from 4.1 to 5.7, so all the paintings are acidic. Doing the average of all the paintings, we got a pH average of 5.1 (SD 0.4 and RSD 7.1%). Looking at the particular pH averages obtained for paintings, we see that 81% of them had an average pH<5.5 and that 30% of the paintings had an averageof pH<5.0. Only 6% had an average pH<4.5.

All this is in accordance with the acidic pH found on most of the samples of the Reference Sample Collection, where we got an average of 5.5 (SD 0.8, RSD 14%) and most of the paintings were in the pH range 5.0 – 5.5 (see Chapter 2.2). MNAC paintings, however, are seen to be slightly more acidic, since there is a larger percentage of paintings with a pH<4.5 (6%), whereas only a 2% of the paintings in the Reference Sample Collection had such low values.

The main difference between the MNAC studied paintings and our Reference Sample Collection is that MNAC paintings are all (except for one) from around the year 1900, whereas our Reference Collection covered a broader period: mainly 19th to the 21st C, including also a few older paintings. Since both groups of paintings come mostly from the same institution (MNAC), and therefore with the same storage and environmental conditions, one wonders if the slightly higher acidity present in the MNAC masterpieces, might be a result of specific commercial manufacturing materials and procedures being used around the year 1900. Another cause could be a difference in the artistic and historic value between the two groups of paintings, which might have been translated into a difference in care and attention throughout their history (and thus conservation treatments).

Variability of pH within each examined painting was found to be small, the average SD for the different examined locations in a painting being 0.2, average RSD 3%, even if areas that looked quite different ("regular canvas" and "darker areas") had been sampled in many occasions.

Regarding the correlation between pH and fibre type, it was corroborated what we had found regarding our Reference Sample Collection (see Chapter 2.2) in that jute canvases tend to have a markedly lower pH than the rest.

If we look into the DP results, we find that the average DP for paintings is 710, but we also get quite a high variability (SD 360, RSD 52%), so we have quite a high spread of values: we have paintings with a very low DP and paintings with a very high DP (from <400 to 1730).

DP variability within each painting was found to be quite high (in average SD 170 and RSD 29%) and similar to the variability found in the Reference Sample Collection between samples visually in different condition (average SD 190; average RSD 22%).

A large mount of the analysed paintings from MNAC, a 41%,fall in the DP category 2 (DP 550-950), with a significant 32% of them in DP category 1 (<550) and a 19% in category 3 (950-1300). There is only one painting classed in the best condition category (>1300) and this is the Picasso painting, which is not from the years around 1900 but from a later date (1936) and represents a 3%.

Our fibre identification results confirm that some cotton (12%) and jute canvases (9%) are already found around 1900 and also the fact that the majority of the analysed paintings are 100% linen (60%). We also found three paintings that could be ramie (9%), although, as said we had few of these samples in the calibration and therefore this is only a tentative classification. The fact that two of these paintings have a Planella stamp could point, if ramie was confirmed as the fibre type used, towards a possible preference for these textiles by this specific company.

During the period of collection of NIR spectra, many of the analysed paintings were found to have non homogeneous versos with darker areas due to varnish migration through the cracks, oil migration from the paint layer or other substances. This is why attention was put to sample “darker” and “regular canvas” areas in those paintings were a visible difference was detected to see if any trends could be detected. Interestingly no significant differences were found between the pH and DP of “darker” and “regular canvas” areas, although the positive correlation between pH and DP was generally corroborated.

Once we had all the pH and DP values for the MNAC analysed paintings we were ready to apply the designed Condition Assessment Classification (see Chapter 4) and therefore grade paintings according to the pH and DP of their canvas and thus advice on a prioritised course of action to be taken.

The majority of the MNAC studied paintings (56%), are in the better classes (40% of the total are in class B2, 13% in class C2 and 3% in class D). Paintings in these three classes, although they have different DP levels, have all a pH > 5.0. This means their acidity is not on the lowest side, so there are other paintings to be deacidified before them. However, all MNAC paintings have acidic pH values, (pH is below the neutral pH 7) and therefore they would all benefit from some sort of deacidifying treatment. (These findings, however, are in accordance with the general pH values of paintings found on Chapter 2.2, so it is neither too surprising, nor too worrying).

There are about 16% of studied paintings that are in the B1 class (< 5.0 pH and 400- 950 DP) and 6% in class C1 (< 5.0 pH and DP 950 – 1400). Both the paintings in these two groups would greatly benefit from some sort of deacidifying treatment and if this was to be done, these should be the first paintings to treat of the 33 studied here. (Paintings in class B1 are paintings: **160**, **161**, **167**, **179**, **187** and paintings in class C1 are paintings **178** and **185**.)

Regarding mechanical instability, 20% of paintings have been found to be at higher risk than the others since their DP values are <400. As found in the literature (see Chapters 2.3 and Chapter 4), paintings with these low values can still be restored without lining them, but often some sort of reinforcement treatment will be needed if the painting is to be removed from the stretcher (either strip lining, open net applied on the reverse or consolidation of the canvas). If the paintings are not moved from where they are hanging, they can be left without any further treatment. (Paintings in class A were found to be **156**, **168**, **170**, **176**, **180**, **184** and **180**.)

One of the 33 analysed MNAC paintings, *Lassitud*, by Nonell (**176**), presented a very interesting reverse due to a pronounced water stain. Results obtained from this painting showed that indeed areas of the canvas were water had been running along, had lower pH values (so acidic products had been washed away). However, these areas also seemed to have much lower DP values (although only 2 spectra out of 15 got a prediction from these areas). Here water damage would seem to have been a very degrading agent. The varnish impregnated areas, instead, were seen to be the more acidic, but then had higher DP values. It is inferred that even though the acidity present in these regions, some sort of physical protection is given by the varnish and this protects the canvas somehow.

A side experiment was done on an extra MNAC painting by Martí Alsina, *El gran dia de Girona*, 1864 (5 x 11 m). Several locations were analysed, and this painting showed a relatively high pH (average 6.0) and high DP (1280) when compared with the other analysed MNAC paintings. It is interesting to note that this painting is a few decades older than the others and it seems to be in a much better condition. This is thought to either be due to different materials and procedures being used earlier on in the 19^{th} C or due to the fact that since 1937 the painting has been kept rolled on itself and therefore there has been very little air circulation around the canvas.

A quick preliminary analysis of the results obtained for a set of 12 paintings by Dalí from the Fundació Gala-Salvador Dalí of which NIR spectra had also been collected (the full results of which will be reported somewhere else), showed how the MNAC masterpieces tend to have, in general, lower pH and DP values than these Dalí paintings. The two sets of paintings are done on commercially primed canvas and they differ mainly in their age (around the year 1900 for MNAC paintings and along the 20th C for Dalí paintings) and in the location where they have been kept for the last years (Barcelona, for MNAC paintings and Figueres for the Dalí ones). Again, the difference in materials and in the environment could be, among others, the source of their different canvas condition.

Regarding the canvasses used for the MNAC masterpieces, as already mentioned, they were all done on commercially prepared canvases. Along the 19th C some of the commercial companies are known to have started stamping their name on the reverse of their products (20) and thus it is not surprising to find that five out of the thirty three paintings we analysed contained a commercial stamp. In our case we found stamps from the local Catalan commercial company Planella (**180** and **181**), and two French companies: Pignel Dupont (**161** and **178**) and E. Lafontaine (**182**). Too little is known yet about which materials were used by each company, the quality of their canvases and the precise dates associated with each subsequent stamp design. It is firmly believed that it would therefore be very interesting that a collaborative project was started soon among different institutions that own paintings from these periods so that knowledge is expanded in this regard.

As a final conclusion for this chapter, it can thus be said that the developed non-destructive NIR method proved to work in a real case scenario, to obtain information on the condition state of the canvas of MNAC paintings, giving us information to which our designed Condition Assessment Classification could be applied. This enabled us to return to the museum a prioritised possible conservation course of action to be taken for the collection surveyed.

Conclusions

This final section of the PhD thesis explains how the different aims set at the beginning of the project were covered, which are the main findings of the research done and where do they lead us, to finally end with future interesting avenues of research that have been identified in the course of it.

The main aim of this thesis was to assess whether non-destructive Near Infrared (NIR) spectroscopy and chemometrics could be applied to the measurement of the pH and the DP of the canvas support of easel paintings as a way to identify its condition.

Knowing the condition of the canvas support in an easel painting is important since this layer is the one holding the paint, which carries the aesthetic message. The current minimal conservation intervention trend calls for paintings not to be lined unless it is unavoidable. If paintings are to be left unlined for as long as possible, it is therefore of paramount importance to evaluate its condition so that proper actions can be taken in time.

Traditionally, paintings have been done on textiles of plant origin (mostly linen, hemp, cotton and jute), the main component of which is, in all cases, cellulose. Cellulose is a natural polymer the degradation of which is complex and still not completely understood. One of its main degradation paths is acid hydrolysis, which implies that in an acidic environment (low pH), the polymer degrades at a faster rate. Acidity can come from different sources, such as the painting's own materials, the cellulose own degradation by-products or from the environment. This is why knowing the pH of the canvas is important, since if the canvas is very acidic, a deacidification treatment of some sort can help in reducing its degradation rate.

One of the consequences of cellulose degradation through acid-catalysed hydrolysis is the breaking up of the polymer chains. This, in its turn, translates into a weakening of the plant fibres and as a consequence of the textile. The average length of the polymer is measured by Degree of Polymerisation (DP), which can be measured, among others through viscometry. Native cellulose can have DP as high as 14,000, which can already be decreased to 2,500 for a newly processed textile. This DP number decreases as the canvas degrades until the textile, in extreme circumstances, will eventually disintegrate.

Taking physical samples of cultural heritage objects is more and more controversial, since nowadays it is increasingly understood that objects are finite and that we have the moral duty of passing them into future generations for them to enjoy in the best and more complete possible condition. This is why research on non-destructive analytical techniques applied to cultural heritage has seen an outstanding development in the last decades.

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, plastic, silk and parchment objects, but it had never been applied to easel paintings and this is why this research was ground breaking in this sense.

Infrared spectra of organic materials at the near infrared (NIR) region (780 - 2500 nm) are composed mainly of "overtones" and "combination bands" that are related to the stretching and bending of the bonds between the atoms present in the material. This region is very information rich but since absorption bands overlap a lot, patterns are not clearly visible to the naked eye, as can be the case of spectra from the mid-infrared region. This is why multivariate data analysis tools (chemometric tools) are needed, so that the large amount of variables (one for each of the absorption bands of each spectra) 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 from just an NIR spectra of new objects. However, since there are many factors that can influence the spectra, this is not always possible and so a calibration needs to be attempted and developed for each new situation to determine if the technique can be used in that particular case.

Ergo, to develop the technique, first a large set of real samples from paintings had the parameters of interest analytically measured (pH, DP and fibre type) and their NIR spectra taken with an NIR spectrometer. To this end, a Reference Sample Collection, the brief details of which are explained later on in this same section, was gathered. Then, using chemometric tools (mathematical and statistical tools that enable “multivariate analysis”), a “model” or “calibration” was created.

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). 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*”. The Discriminant Analysis qualitative calibration for fibre type was done using the software *Xlstat* (Addinsoft, USA).

Regarding this main first aim thus, it can be concluded that a calibration for non-destructive predictions of pH, DP and fibre type 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 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.

Since fibre type identification is a qualitative parameter, a different chemometric tool had to be used. Satisfactory classification was obtained by using the Discriminant Analysis (DA) tool in a two-step process. The first DA step is able to distinguish between cotton, jute, a group of bast fibres (linen, hemp, ramie and linen/hemp combinations) and combinations of cotton/linen, jute/cotton or jute/linen with confidence ranging between 75% to 99%. The second DA step is able to further classify bast fibres among them and differentiate between: linen, hemp, ramie and linen/hemp combinations with also quite good confidence percentages, from 72% to 100%, although here it has to be taken into account that there were fewhemp, ramie and linen/hemp samples taking part in the calibration, so identifications for these samples might be not as reliable. If more positively identified samples were available in the future, these could be added and a new calibration attempted.

Therefore,the successful calibration of the NIR spectrometer for predicting pH, DP and fibre type gives us a very powerful instrument for non-destructively and very quickly determining the present condition of the canvas support of easel paintings. 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.

The second aim of this PhD research was to learn about the typical pH and DP values found in real paintings as well as the fibre type used, and the relationships between these parameters together with the date of paintings.

The pH, DP and fibre type analysis of a “Reference Sample Collection” was needed in order to develop the non-destructive NIR spectrometry and chemometrics method previously explained. At the same time, there are not that many paintings of which the pH and DP of their canvas support has been measured and the results have been reported in the literature. This is why both measuring these two important parameters of a large group of real paintings and learning about the relationship between pH, DP, fibre type and date, was foreseen to be very enlightening.

A large set of real samples of about 1-2 cm^2 was gathered from the edges of around 100 second-class paintings. Since more than one sample was taken from some of the paintings and other types of samples were added to the collection, such as old glue linings removed during the course of conservation, primed new canvases for painting and household textiles, a final amount of about 200 samples was gathered.

Most of the samples from the Reference Sample Collection were 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.

Fibre type was visually identified by looking at the mounted fibres under the polarized optical microscope. Two threads were analysed for each sample, one running horizontally to the painting and the other running vertically. This parameter was checked for about 100 paintings, producing a total of almost 200 slides.

Regarding fibre type, it was found that paintings had mostly the foreseen types of plant fibres expected: linen, hemp, ramie, cotton, jute and synthetics. Usually, the canvas was made using only one type of fibre, but more often than anticipated, a combination of fibres was also found: linen/hemp, linen/jute, linen/cotton, jute/cotton, cotton/synthetics.

Linen is the most frequently type of fibre encountered, mostly on its own. It is found across all periods, often together with hemp in older canvases. Hemp, on its own, was only found in one painting. Cotton was found in paintings from the end of the 19thC and 20thC and jute was sparingly found in commercially primed canvases at the turn of the 20thC and, later on along the century, in artist's prepared canvases. Ramie, quite unexpectedly, was positively identified in one of the analysed paintings. Synthetic fibres were found sparingly in paintings less than two decades old and always mixed with cotton.

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) and thus a very small amount of sample (250-350µg) and 100µL of water were used for each measurement. The use of the new type of ISFET metallic microprobe proved to be extremely user-friendly, not time-consuming, cheaper and therefore intensely recommended.

All the Reference Sample Collection had this parameter measured and the pH of the canvas of paintings 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.

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 mg) to do the analysis.

Sample preparation was determined to be best done by leaving the samples in water overnight and then putting them in the double boiler for 10 min. Then the fibres were defibered manually with two long needles through a laborious process that could take up to two hours per sample. An interesting study to be carried in the future apropos of sample preparation for viscometry, was identified to be the effect of crushing the sample with a mortar and pestle instead of doing it by meticulous hand defibering. A preliminary test done in this regard indicated that the mortar and pestle was not a source of further degradation of the sample, as was initially feared, and that sample preparation time was reduced quite notably.

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, pointing to the fact that subjective perception of canvas condition might be correlated with DP. Old glue paste linings, were again found to have lower DP values than paintings, which already manifests a relationship between acidity and DP.

Once these three parameters had been analysed, the correlation between the obtained results for pH, DP, fibre type and the age of the paintings was explored. This was done both by plotting one parameter against another in a traditional correlation plot and also through the more suitable multivariate analysis tool, Principal Component Analysis (PCA).

Date and pH were discovered not to be correlated, modern paintings having sometimes lower pH values and older paintings having some times higher pH values. A few of the old samples available (16th C- 18th C) were found to have the highest of pH values (6.5-7.5) and it is thought that this might be due to a good slightly alkaline environment provided by the wall of the churches these paintings came from. The lower pH of some of the modern materials could be, presumably, explained either by the use of more acidic materials to start with or by the effects of a particular more acidic environment.

Concerning date and DP, although it could not be said they were found to be strongly correlated either, these two parameters were seen to be, nonetheless, a bit more correlated than date and pH. This means that newer canvases generally tend to have higher DP values.

The different amount of lignin different fibres have was seen to be slightly correlated with pH, since jute fibres, which have higher amounts of it, presented lower pH values than the rest of the fibres. The average pH for cotton (which does not have any lignin at all) was slightly lower than that of linen fibres, although the difference was smaller than the SD of the method developed and thus it should not be considered significant. With reference to DP, jute canvases tended to have lower DP values than linen, but not that different to cotton. This would make evident the fact that cotton even if being under similar or even slightly better circumstances (higher pH) than the rest, can degrade faster than other types of fibres probably due to the higher amount of amorphous regions its cellulose has, which offers an easier access to pollutants (and makes it also more moisture absorbent and elastic).

The relationship between pH and DP was seen to be slightly correlated when plotting one parameter against the other, and strongly correlated when analysing this relationship via PCA, indicating that the lower the pH, the lower the DP and vice versa. Acidity is therefore confirmed to have an influence on the DP value of canvases. Since DP is correlated with the strength of the textile, acidity becomes, therefore, a very important factor to monitor with respect to the support stability.

The fact that the correlation between pH and DP is not that clear when analysing the two parameters on their own but that it stands out very clearly when the analysis is done using PCA (combining it together with fibre type and date), demonstrates that the two parameters are definitely correlated but not directly. This means that if we were to measure for instance only pH, DP could not be predicted just from this since there are other factors, such as fibre type and date that are seen to have an influence on the relationship. These results also highlight the power of PCA analysis, where the correlation between more than two parameters can be studied.

Hence 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 strongly 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.

The third main aim of this thesis was to establish the meaning of the various DP values when it comes to easel paintings, so that together with pH, a "Condition Assessment Classification" could be designed and applied to paintings of which these two parameters are known.

Once a technique has been developed for determining the pH and the DP of the canvas support of easel paintings in a non-destructive and fast way, very fruitful condition collection surveys can be conducted with relative little effort. However, one needs to know what the particular values obtained will convey regarding easel paintings, so that the numbers obtained become meaningful. This is why it was important to determine what these values meant, so that by taking into account both parameters, a classification system that would prioritise paintings according to their canvas conservation needs could be designed.

A "Condition Assessment Panel" was done, where artificially aged new and historic canvas samples of which DP was known, were sent out to an international team of conservators. They were asked to test and grade the samples in terms of canvas condition, according to their subjective feeling. The most important conclusion of this test was that conservator's subjective testing of textile samples generally does correlate with the sample's DP: lower DP samples were perceived to be in worst condition than higher DP samples. This finding endorses thus, the subsequent results of this experiment.

Conservators were asked to rank the samples into four different condition categories ("very fragile canvas", "fragile canvas", "somewhat fragile canvas" and "canvas in good condition"). Although the divisions between categories were found not to be sharp at all (mainly due to the test's subjectivity and the inhomogeneity of the samples), specific DP limits were established so that some sort of grading between paintings was possible. DP values for each category were established as: 1-"Very fragile":<550; 2-"Fragile": 550-950; 3-"Somewhat fragile": 950-1400 and 4- "Good condition": >1400.

On the other hand, the "Critical DP" for paintings, understood as the DP value below which if a painting is removed from its stretcher it will need some sort of reinforcement (lining, strip lining or other) because the canvas is too fragile, was found to be <400. Also, the "Safe DP" for paintings, the value above which one could consider that the canvas, even if it might have suffered some degradation still retains good mechanical properties, was determined to be above 1400 DP.

With respect to pH, since most of the Reference Sample Collection were found to be in the pH range between 5.0 and 5.5, pH <5.0 was established as the threshold value below which paintings would be considered to be "strongly acidic", since these would be the most acidic paintings.

By taking into account the implications identified regarding the DP and pH values on the canvas of easel paintings, a "Condition Assessment Classification" was designed. Thereby which, paintings the pH and DP values of which are known could be prioritised in terms of conservation actions to be taken according to the canvas condition.

Since acidity has been seen to be of supreme importance, more acidic paintings would be the ones to treat first by doing some sort of deacidification treatment of the support, either active or passive. However, in acidic paintings with very low DP values (<400), much of the damage has already been done in this regard and they might actually benefit more from some sort of mechanical treatment that reinforces the support Also, since degradation proceeds much faster in the earlier stages, very low DP canvases are likely to retain the same values for a longer period. Very high DP canvases that are also strongly acidic would benefit too from deacidification treatments, but if time and resources are limited, the treatment of these paintings could be postponed for a while, since there is still some time margin left. Thus, paintings with middle range DP values, but more acidic, would be the ones benefiting the most from deacidification treatments and this is the idea that guided the rationale followed when designing the Condition Assessment Classification.

Consequently, once we have the DP and pH values for the canvas of paintings, these can be prioritised with respect to the treatment of their support in the following order: paintings with DP 400-950 and with pH<5.0 (Class "B1") first, and then paintings with DP 950-1300 and pH also<5.0 (Class "C1"), would be the ones to treat initially in terms of their acidity. Then paintings in Class "A" (DP<400), which are at higher mechanical risk, could then be dealt with if they need any reinforcement operation. Next, paintings in Class "B2" and Class "C2" (those with middle range DP but with pH>5.0) could then be deacidified if resources are still available, since they would most probably, in the light of the previous findings, be acidic too. Finally in Class "D", we would have the paintings in the best condition, with DP >1400, the more acidic of which could still be left as they are for a while, if means are limited, since their stability is not as strongly compromised as that of paintings with lower DP values.

The "Condition Assessment Classification" is seen to be, therefore, a very useful tool since it establishes a prioritised sequence of conservation intervention for the canvas support by taking into account both DP and pH. Of course, if time and resources are not a problem, then all acidic paintings would benefit from some sort of treatment in this line and the designed classification would not need to be applied.

The last main aim of the thesis was to apply the non-destructive NIR spectrometry method developed to know the pH, DP and fibre type of real valuable paintings from the Museu Nacional d'Art de Catalunya (MNAC) on the one side, and to produce a prioritised course of action to be taken on these paintings by applying the "Condition Assessment Classification" previously designed on the other.

After developing the non-destructive NIR spectrometry technique for determining the pH, DP and fibre type in the lab, the final step was to apply it to real paintings to test the robustness of the various calibrations produced. Besides, conducting a canvas condition survey on a group of MNAC paintings would give us valuable information on the condition of a set of relevant paintings from around the year 1900.

Thirty-three MNAC masterpieces, mainly by Catalan artists, had the NIR spectra taken in different locations of their verso. Twelve Dalí paintings from the Fundació Gala-Salvador Dalí that span from the 1920's to the 1960's (all Dalí's life) were also analysed, although these results will mainly be reported somewhere else.

On applying the non-destructive NIR spectrometry calibrations to MNAC masterpieces, results were successfully obtained for the three parameters developed: pH, DP and fibre type. The DP calibration, however, returned with a 45% of blank results that were not randomly scattered along the different NIR spectra taken, but that tended to concentrate more on some paintings than others meaning that may be some types of materials had not been included in this calibration. The fact that for DP a smaller calibration set of samples was used (102 against the 170 used for pH), leads us to think that the applicability of the method could be improved if the number of samples to be used in the calibration was raised.

As anticipated, concerning fibre type identification, the first-step DA, distinguishing between jute, cotton and a group of bast fibres, gave higher precision identifications than the second-step DA distinguishing between different bast fibres (mainly linen, hemp and ramie). This could be due to the fact that bast fibres, being of a similar originating nature, might produce more similar NIR spectra also, whereas the differences between this group of fibres and cotton and jute might be more pronounced in the NIR spectra too. However, it is thought that the main reason for the lower error of prediction of the second DA is the fact that the number of other bast fibres apart from linen (hemp, ramie etc.) was very small. If these were available in the future, a better model could be built.

A small test on how the NIR spectra from paintings would be better collected, indicated that one can use indistinctly the three types of backgrounds studied: two layers of thick blotting paper, a white reference calibration pad and the white table. These results are helpful since this offers a broad range of options to be used when applying the technique.

Given the success of the NIR spectroscopy technique for the studied parameters of the canvas of easel paintings, attempting to build more models for other parameters in the future looks promising. In this regard, a parameter that could be quite easily developed since it requires no further analytical measurements, would be the dating of paintings. However, to develop this parameter, it would be better if the specific production dates were known for all the paintings, a degree of precision that we are lacking in some of the cases.

Concerning the actual results on the three parameters analysed, the main conclusion is that all MNAC paintings were found to be acidic. pH values were found to range from 4.1 to 5.7, with a significant 81%, a vast majorityof them, having pH<5.5. About a third of all the paintings were found to be below pH 5.0 and a small but important 6% were found to be below pH 4.5.

With reference to DP, the canvas of MNAC paintings from around the year 1900 was found to have values that go from <400 to 1310, so quite a lot of variation between the different paintings was detected. Negative values obtained have to be understood in the sense that, DP being a quantitative type of measurement, what predictions do is actually grade paintings according to this parameter in a metric scale. Since the average error of prediction we got for the DP calibration is quite a large number (±275), this explains the negative values.

Most of the studied paintings, 41%, are classified in the DP category 2 (DP 550-950), so they are not in the worst condition category yet, but they are starting to be significantly degraded. A remarkable 32% of them are in DP category 1, with quite low DP values (<550) and a smaller 19% in category 3 (950-1300). Only 3% of them (as a matter of fact, only the Picasso painting which is actually from 1937), are in the best condition category (>1300).

The application of the developed Condition Assessment Classification (and thus taking both pH and DP into account) manifests that 56% of the studied MNAC paintings are found in the three better condition classes: B2; C2 and D. Therefore, part of the collection studied can be said to be in a moderate state of condition regarding its canvas, although degradation has certainly occurred to a certain extent (DP has decreased from what it would have originally been).

However, an outstanding 20% of the paintings were found to be in Class A (DP<400), which implies too that a significant part of the collection examined is quite degraded in terms of its canvases. The paintings in this group should thus be treated accordingly and for instance some sort of padding would be advisable if they need to travel. Nevertheless, they might be perfectly ok if they are left hanging in the galleries or the storage rooms.

Finally, about a quarter of the surveyed collection was found to be in the group of paintings that would greatly benefit most from actions to counteract acidity before their DP values gets too low since they are more acidic than the rest: a 16% of them were found to be in the Class B1 (400- 950 DP and <5.0 pH), and 6% of them were put in Class C1 (DP 950 – 1400 and <5.0 pH).

With reference to the fibre types found, the most common one is linen (60%), with some cotton paintings (12%) and a few jute ones(9%). Another 9% was also identified as possibly ramie. This last finding is in accordance with one painting in the Reference Sample Collection having been also identified as ramie and suggests that this type of fibre has been used more often than known until now. An improvement of the method by adding more confidently identified ramie as well as hemp and linen/hemp samples could give a clearer picture of the situation regarding the use of ramie as a painting support.

A very interesting strand of research was done aiming at determining whether darker areas of canvases (due to varnish, oils or others), tended to be in a worst condition than the “regular canvas” areas. Contrary to expectations, no significant differences were found between the pH and DP values of these areas (although the positive correlation between pH and DP was again corroborated).

The degrading effect of pollution had actually been already clearly seen in a set of samples from the Reference Sample Collection where areas of the canvas that had been protected by the stretcher were compared to areas from the centre of the painting. Interestingly, it was seen that while pH was very similar for all the samples, DP was significantly lower in those areas that had been exposed to air pollutants. Wood is known to emit acidic products but probably where air is significantly polluted, the effects of the latter outweigh the effects of the former.

Another degrading agent for canvas was found to be direct water damage. It was observed, in the case one painting with a broad water stain on its reverse, that the central areas of the stain had lower pH values (acidic products having probably been washed away), but lower DP values too. Further research on the effects of water damage on the canvas of paintings could give new interesting insights in this regard, especially since quite a few paintings were found to have suffered this type of damage in the past (either from water leaks or from floods) when examining the MNAC collection.

Variability within different areas of the same painting was found to be small in terms of pH (RSD 3%), but much higher in terms of DP (RSD 29% and SD 167).These numbers mean that for instance, if we obtain a DP value of 800 in one area of a painting, other areas could have values between 633 and 967.

A preliminary study of the results obtained on the canvas condition from the analysed paintings by Salvador Dalí (Fundació Gala-Salvador Dalí), indicates that the paintings by Dalí in general have higher pH and higher DP values than the MNAC ones. This better condition could maybe either be explained by the difference in date between the two groups of paintings, and thus a difference in materials, (around 1900 for the MNAC paintings and along the 20th C for the Dalí ones) or maybe by the difference in the environment where the two sets of paintings have been kept (Barcelona for the MNAC paintings and Figueres for the Dalí ones).

Hence, the study of a group of MNAC and Dalí paintings has again revealed that indeed the canvas of paintings is mostly acidic. This fact strengthens the most important conclusion this PhD comes to: if lining is to be avoided for as long as possible, active or passive deacidification treatments should start to be more routinely done. Otherwise, the acidity present in the canvas is bound, as has been proven here, to promote degradation of the canvas.

Some research has already been done on the deacidification of the canvas of easel paintings, in England about twenty years ago, and more recently in Italy by applying nanotechnologies. Counteracting acidity can be done either by actively applying a deacidifying agent to the canvas, or passively by adding acid absorbing materials inside microframes or near the canvas of paintings.

Thus, during the course of this PhD, a couple of major interesting future avenues of research have been identified. On the one hand, the study of acidity sources in the case of paintings would be very helpful since this would make it easier to counteract acidity at the origin. Acidity can either come from the painting’s own materials (or those added during conservation and from the degradation of both) or from the environment surrounding the painting. Regarding the possible acidity of conservation products, in this research it has been seen that glue paste linings present a markedly lower pH, and this could be a very interesting starting point of a new strand of research to end up, may be, adjusting the traditional glue paste recipes used to this end.

On the other side, since acidity has been confirmed to play an important role in the degradation of canvases and if paintings, considering the current more cautious conservation practices, are to be left unlined for longer, further research on the deacidification, both active and passive, applied to the canvas of paintings would be very valuable.

To sum up, the main conclusions that this PhD research comes to are:

- **The development of an NIR spectroscopy and chemometrics technique to determine pH, DP and fibre type of the canvas of paintings non-destructively has been successfully achieved.**

- **The pH of the canvas of paintings has been found to be mostly acidic, and that of glue paste linings even more. The age of paintings was not seen to influence pH, a few older paintings having near neutral pH values and a few modern paintings having lower pH values. Jute canvases were found to be slightly more acidic than the rest.**

- **pH and DP were found to be strongly correlated, confirming the idea that canvases with a lower pH will degrade at a faster rate. Since DP and mechanical stability are known to be correlated, the key role of acidity has in the degradation of the canvases of paintings is highlighted even more.**

- **Subjective conservators' assessment regarding canvases is generally in agreement with the DP of a textile: lower DP samples were perceived as weaker, higher DP samples stronger.**

- **The "critical DP" value under which paintings should be classed as "very fragile" by conservators, has been established to be around 400. The DP value above which the canvas of paintings could be classed as in "good condition" is above 1400 DP.**

- **When doing a collection survey of canvas condition, both DP and pH are very important parameters to take into account. The paintings with a lower pH, but with DP values that are not yet significantly low, would be the ones benefiting the most from a deacidification treatment (active or passive).**

- **All the canvases of the MNAC masterpieces studied from around the year 1900 were found to be acidic. DP values ranged from "very fragile" (<400) to "somewhat fragile" (<1400) condition. Both these findings are in line with the results obtained when analysing the Reference Sample Collection that was used for building the NIR calibration.**

- **Dalí paintings from along the 20th C were found to have slightly higher pH and DP values than the MNAC paintings from the 1900s.**

- **Having confirmed the importance of acidity in the degradation of the canvas support in easel paintings, more research should be strongly encouraged into how to counteract it (actively or passively), as well as into studies of the possible sources of this acidity.**

References

References used in each chapter are listed here in order of appearance and with the corresponding number used in the text. Some references have been used in more than one chapter and thus they will appear cited more than once, but it was judged to be more convinient for the reader to have references grouped according to topic than having a never ending list with all the references mixed. It was also easier to work with separate Word documents, one per chapter, and this is why the numbering starts from scratch for each chapter.

The numbers in brackets at the end of each reference are my personal archival numbers that help me in finding the papers physically and digitally. They have been left to make future consultation of the work easier.

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Annex I - Reference Sample Collection catalogue

This annex is the output of part of the information gathered in the Access database for each sample of the Reference Sample Collection. Each page corresponds to one painting and all the samples extracted from it. Each sample has the pH, DP final values and the final fibre identification. This annex is therefore related to Chapter 2.

The pH is the average of usually two or three (sometimes more) measurements. The DP values are the average of several measurements run from the same sub-sample. The final fibre identification ("Textile Id" field) is based on the separate identification of the vertical and horizontal threads (vertical and horizontal, according to the way the painting is hung). When the information is left blank, it means that particular analysis was not performed for that sample.

On each sample, sub-samples extracted for pH and DP are marked, as well as where the NIR spectra were taken. pH colours correspond to the order of measurements and numbering seen in Figure 1, so that values can be checked back if desired. NIR spectra were taken from areas as close as possible to those sampled for pH and DP and marked with the coloured circles (Figure 2). The sample used for DP analysis is marked with the **yellow** perimeter. The **green** line present in some of the samples represents the end of the painting, since this side would be expected to be more degraded than the other edges. pH sub-samples were generally taken from " inner" edges that were thought to better the represent the condition of the rest of the canvas. If a selvedge was detected, this was marked with a **purple** line.

	Colours used
pH 1	Red
pH 2	Green
pH 3	Blue
pH 4	Yellow
pH 5	Black
pH 6	Purple
pH7	Brown

Figure 1. Colours to indicate the different pH measurements done in each sample.

	Colours used
NIR 1	Red
NIR 2	Green
NIR 3	Blue
NIR 4	Yellow
NIR 5	Black
NIR 6	Purple

Figure 2. Colours to indicate the different spectra taken from each sample.

All these samples are currently being kept in a fridge (each one in a plastic bag between paper sheets), so that their degradation is slowed down as much as possible and their condition is kept as close as possible to the one they had when the NIR spectra were taken. In the future, other parameters could be measured and linked to the same NIR spectra taken for this research or new ones could be taken if desired.

There are two types of samples that were taken: textile samples and “threads for measuring pH”. From the first ones, a picture was taken and pH measured for all of them. Half of them had DP measured and fibre type identified. The “threads for measuring pH”, had only pH measured and no pictures were taken of this threads. (Whether one sample is one type or the other, it can be seen in the field “Sample type” and because there is a picture or not).

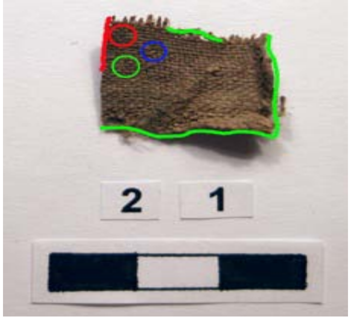
Object Id: 1
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 42101
Title: Academia
Author: Anònim
Assigned period: 1900

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen

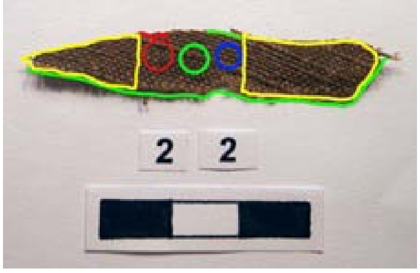
Sample Type: Textile
Sample Id: 1_1
Sample condition: Regular
pH Final Average: 5,05
DP:

Object Id: 2
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011319-000
Title: Retrat del rei Alfons XII amb indumentaria del segle XVI
Author: Anònim
Assigned period: 1900

Vertical thread Id:
Horizontal thread Id:
Textile Id:



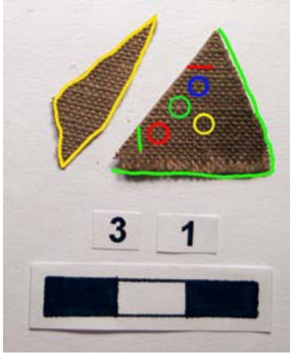
Sample Type: Textile
Sample Id: 2_1
Sample condition: Bad
pH Final Average: 4,97
DP:



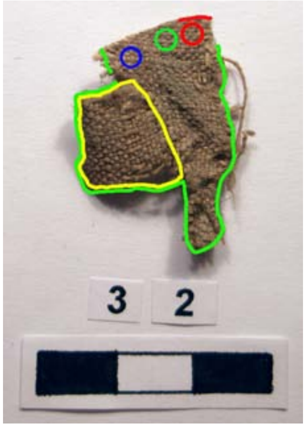
Sample Type: Textile
Sample Id: 2_2
Sample condition: Regular
pH Final Average: 4,74
DP: 873

Object Id: 3
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011306-000
Title: Retrat del rei Amadeu de Savoia
Author: Ramon Amado
Assigned period: 1875

Vertical thread Id: Linen & Hemp
Horizontal thread Id: Linen & Hemp
Textile Id: Linen & Hemp



Sample Type: Textile
Sample Id: 3_1
Sample condition: Regular
pH Final Average: 5,12
DP: 774

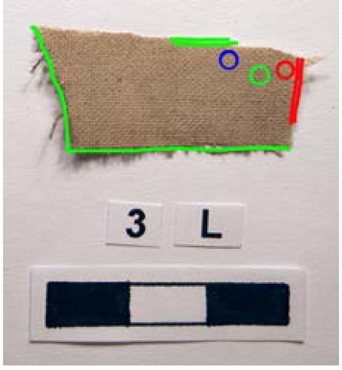


Sample Type: Textile
Sample Id: 3_2
Sample condition: Bad
pH Final Average: 5,52
DP: 917

Sample Type: Thread
Sample Id: 3_Th
Sample condition:
pH Final Average: 5,45
DP:

Object Id: 3
Object Type: Lining
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011306-000
Title: Lining of the painting : Retrat del rei Amadeu de Savoia
Author:
Assigned period: 1950

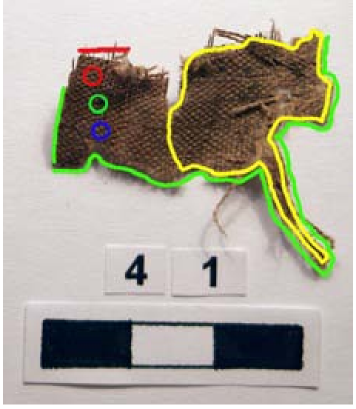
Vertical thread Id:
Horizontal thread Id:
Textile Id:



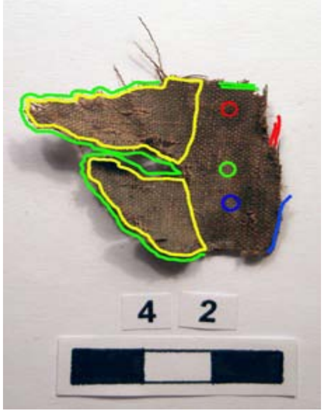
Sample Type: Textile
Sample Id: 3_L
Sample condition:
pH Final Average: 5,36
DP:

Object Id: 4
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011272-000
Title: Retrat del rei Alfons XII
Author: Anònim
Assigned period: 1900

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



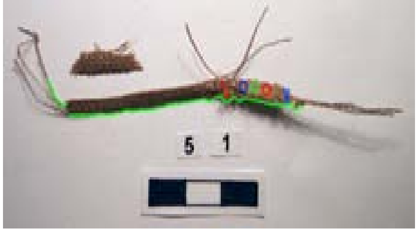
Sample Type: Textile
Sample Id: 4_1
Sample condition: Bad
pH Final Average: 5,03
DP: 556



Sample Type: Textile
Sample Id: 4_2
Sample condition: Bad
pH Final Average: 4,85
DP: 416

Object Id: 5
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011265-000
Title: Retrat d'Alfons XII dempeus i de front
Author: Gaieta Benavent
Assigned period: 1875

Vertical thread Id: Linen?
Horizontal thread Id: Linen
Textile Id: Linen?
Sample Type: Thread



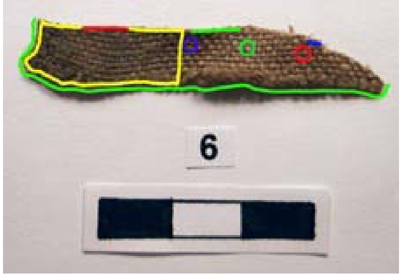
Sample Type: Textile
Sample Id: 5_1
Sample condition: Regular
pH Final Average: 4,61
DP:

Sample Type: Textile
Sample Id: 5_2
Sample condition: Bad
pH Final Average: 5,9
DP: 962

Sample Type: Thread
Sample Id: 5_Th1
Sample condition:
pH Final Average: 4,99
DP:

Sample Type: Thread
Sample Id: 5_Th2
Sample condition:
pH Final Average: 4,91
DP:

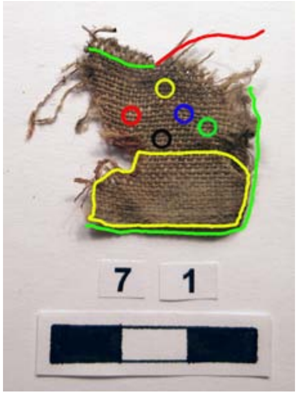
Object Id:	6
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	157550-000
Title:	Retrat d'Isabel de Borbón
Author:	Manuel Benedito
Assigned period:	1925
Vertical thread Id:	0
Horizontal thread Id:	-
Textile Id:	-



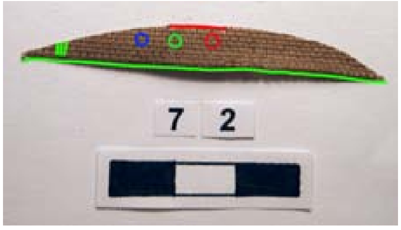
Sample Type:	Textile
Sample Id:	6
Sample condition:	Good
pH Final Average:	5,51
DP:	1446

Object Id: 7
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011233-000
Title: Retrat d'Alfons XIII
Author: Juli Borrell
Assigned period: 1925

Vertical thread Id: Hemp
Horizontal thread Id: Hemp
Textile Id: Hemp



Sample Type: Textile
Sample Id: 7_1
Sample condition: Bad
pH Final Average: 5,93
DP: 1321

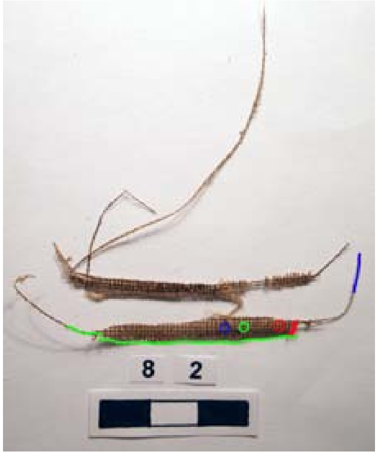


Sample Type: Textile
Sample Id: 7_2
Sample condition: Regular
pH Final Average: 5,65
DP:

Object Id:	8
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011227-000
Title:	Retrat de la reina Maria Cristina d'Habsburg i el seu fill
Author:	Josep Cusachs
Assigned period:	1875

Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

Sample Type:	Textile
Sample Id:	8_1
Sample condition:	Regular
pH Final Average:	6,09
DP:	890



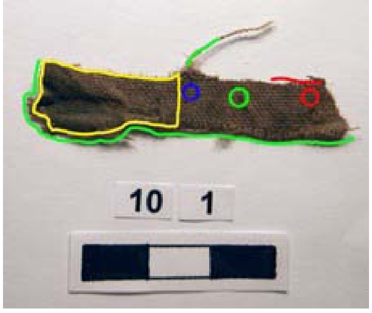
Sample Type:	Textile
Sample Id:	8_2
Sample condition:	
pH Final Average:	5,4
DP:	

Object Id:	9
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	038125-000
Title:	Figura femenina
Author:	Anònim
Assigned period:	1800
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

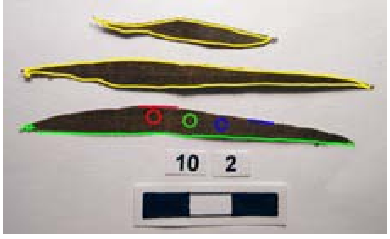
Sample Type:	Textile
Sample Id:	9
Sample condition:	
pH Final Average:	5,71
DP:	

Object Id: 10
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011223-000
Title: Retrat del rei Alfons XII
Author: Antoni Caba
Assigned period: 1875

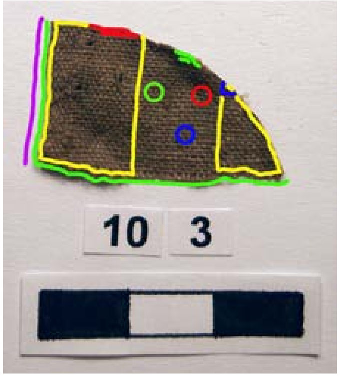
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 10_1
Sample condition:
pH Final Average: 5,88
DP: 1590



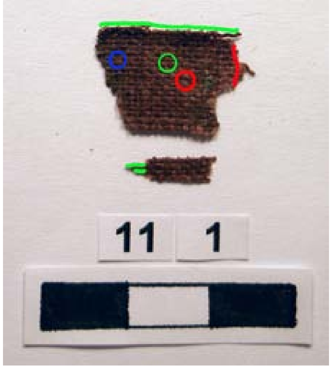
Sample Type: Textile
Sample Id: 10_2
Sample condition:
pH Final Average: 5,14
DP: 1455



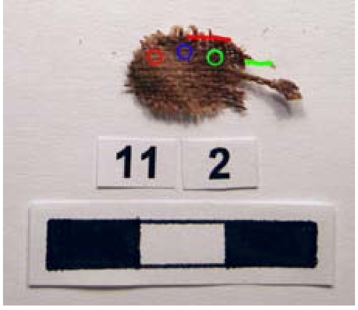
Sample Type: Textile
Sample Id: 10_3
Sample condition:
pH Final Average: 5,65
DP: 1466

Object Id: 11
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 039072-000
Title: Retrat de la comtessa Petronil·la
Author: Philippo Ariosto
Assigned period: 1550

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 11_1
Sample condition: Bad (brittle textile)
pH Final Average: 4,78
DP:



Sample Type: Textile
Sample Id: 11_2
Sample condition: Bad (brittle textile)
pH Final Average: 4,91
DP:

Sample Type: Thread
Sample Id: 11_Th1
Sample condition:
pH Final Average: 4,82
DP:

Sample Type: Thread
Sample Id: 11_Th2
Sample condition:
pH Final Average: 4,41
DP

Object Id: 12
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 157616-000
Title: Retrat de Carles IV
Author: Anònim
Assigned period: 1850

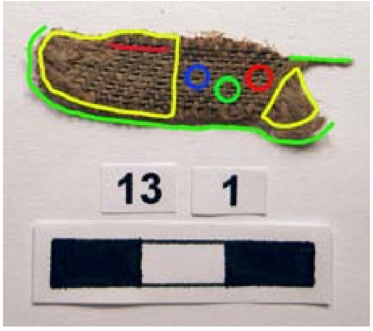
Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 12
Sample condition:
pH Final Average: 5,35
DP:

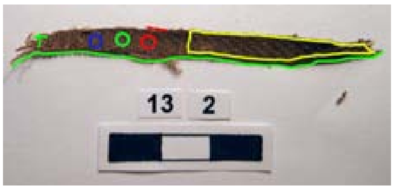
Sample Type: Thread
Sample Id: 12_Th
Sample condition:
pH Final Average: 5,46
DP:

Object Id: 13
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011238-000
Title: Retrat del rei Alfons XII
Author: Ramon Martí Alsina
Assigned period: 1875

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



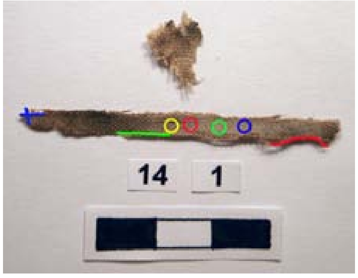
Sample Type: Textile
Sample Id: 13_1
Sample condition:
pH Final Average: 5,89
DP: 974



Sample Type: Textile
Sample Id: 13_2
Sample condition:
pH Final Average: 4,9
DP: 698

Object Id: 14
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011314-000
Title: Retrat de la reina Mercedes
Author: Ramon Martí Alsina
Assigned period: 1875

Vertical thread Id:
Horizontal thread Id:
Textile Id:



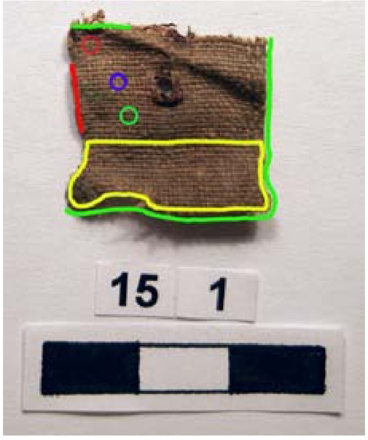
Sample Type: Textile
Sample Id: 14_1
Sample condition:
pH Final Average: 4,94
DP:

Sample Type: Textile
Sample Id: 14_2
Sample condition:
pH Final Average: 5,17
DP:

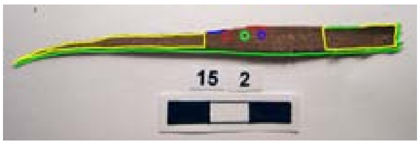
Sample Type: Textile
Sample Id: 14_3
Sample condition:
pH Final Average: 6,3
DP:

Object Id:	15
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011317-000
Title:	Retrat del rei Alfons XIII
Author:	Cristòfol Montserrat
Assigned period:	1925

Vertical thread Id:	Ramie?
Horizontal thread Id:	Ramie?
Textile Id:	Ramie?



Sample Type:	Textile
Sample Id:	15_1
Sample condition:	
pH Final Average:	5,05
DP:	740



Sample Type:	Textile
Sample Id:	15_2
Sample condition:	
pH Final Average:	4,96
DP:	1008

Object Id:	16
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	157615-000
Title:	Retrat de Ferran VI
Author:	Anònim
Assigned period:	1750
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	16
Sample condition:	
pH Final Average:	5,18
DP:	

Object Id: 17
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011226-000
Title: Retrat del rei Alfons XIII
Author: Cristòfol Montserrat
Assigned period: 1925

Vertical thread Id: Linen? Hemp?
Horizontal thread Id: Linen? Hemp?
Textile Id: -

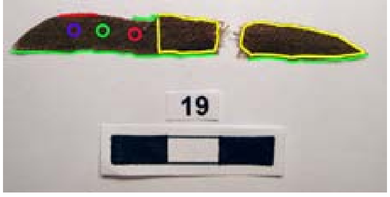
Sample Type: Textile
Sample Id: 17
Sample condition:
pH Final Average: 4,82
DP: 651

Object Id:	18
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	42098
Title:	Acadèmia
Author:	Anònim
Assigned period:	1900
Vertical thread Id:	Ramie
Horizontal thread Id:	Ramie
Textile Id:	Ramie

Sample Type:	Textile
Sample Id:	18
Sample condition:	
pH Final Average:	5,58
DP:	

Object Id: 19
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011230-000
Title: Retrat d'Alfons XIII
Author: Cristòfol Montserrat
Assigned period: 1925

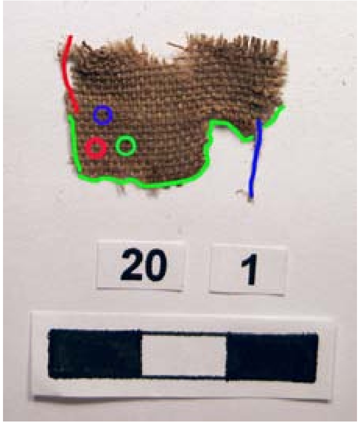
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



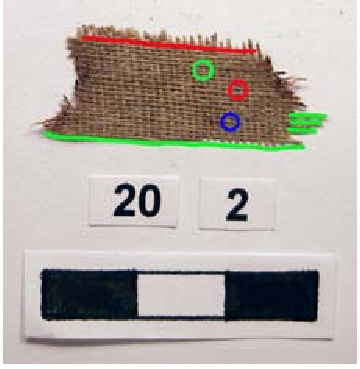
Sample Type: Textile
Sample Id: 19
Sample condition:
pH Final Average: 5,04
DP: 947

Object Id: 20
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011239-000
Title: Retrat d'Alfons XIII dempeus i amb l'uniforme de cadet
Author: Josep Maria Marquès
Assigned period: 1875

Vertical thread Id:
Horizontal thread Id:
Textile Id:

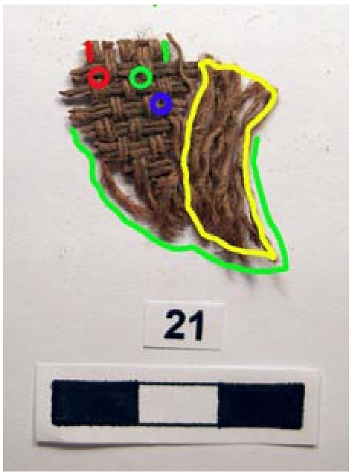


Sample Type: Textile
Sample Id: 20_1
Sample condition: Bad
pH Final Average: 5,67
DP:



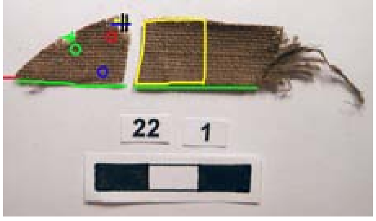
Sample Type: Textile
Sample Id: 20_2
Sample condition: Regular
pH Final Average: 5,77
DP:

Object Id:	21
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011232-000
Title:	Retrat del rei Alfons XIII
Author:	Arcadi Mas i Fondevila
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	Jute



Sample Type:	Textile
Sample Id:	21
Sample condition:	
pH Final Average:	5,44
DP:	1090

Object Id:	22
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011241-000
Title:	Retrat del rei Alfons XIII
Author:	Fèlix Mestres
Assigned period:	1925
Vertical thread Id:	Ramie?
Horizontal thread Id:	Ramie?
Textile Id:	Ramie?

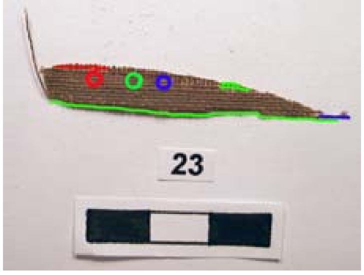


Sample Type:	Textile
Sample Id:	22_1
Sample condition:	Good
pH Final Average:	5,33
DP:	2293

Sample Type:	Textile
Sample Id:	22_2
Sample condition:	Bad
pH Final Average:	5,98
DP:	1588

Object Id: 23
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011222-000
Title: Retrat de la reina Maria Cristina d'Habsburg
Author: Antoni Sisteré
Assigned period: 1875

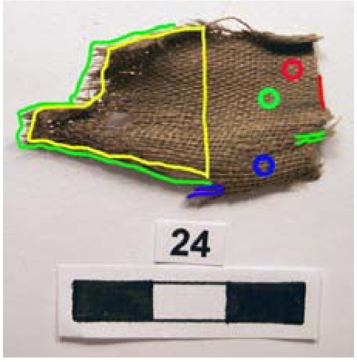
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 23
Sample condition: Regular-good
pH Final Average: 5,45
DP:

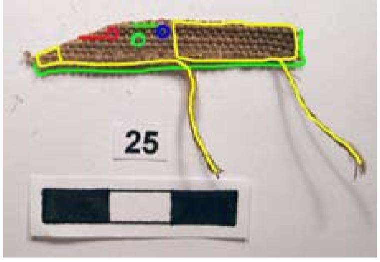
Object Id:	24
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011234-000
Title:	Retrat d'Alfons XII
Author:	Francesc Torrescassana
Assigned period:	1875

Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



Sample Type:	Textile
Sample Id:	24
Sample condition:	Regular
pH Final Average:	5,28
DP:	699

Object Id:	25
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011224-000
Title:	Retrat del rei Alfons XII
Author:	Anònim
Assigned period:	1900
Vertical thread Id:	?
Horizontal thread Id:	Linen? Ramie?
Textile Id:	0

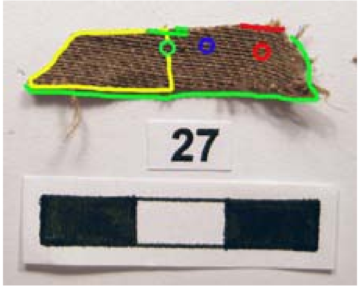


Sample Type:	Textile
Sample Id:	25
Sample condition:	Good
pH Final Average:	4,86
DP:	1010

Object Id:	26
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011240-000
Title:	Retrat del marquès de Castelltort
Author:	Manuel Ferran Bayona
Assigned period:	1875
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

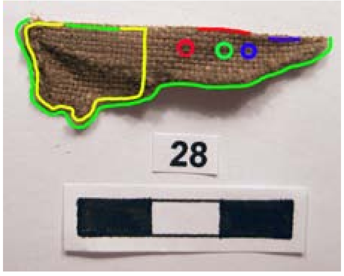
Sample Type:	Textile
Sample Id:	26
Sample condition:	
pH Final Average:	5,25
DP:	

Object Id:	27
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011256-000
Title:	Retrat d'Isabel López de Güell, marquesa de Castellvell
Author:	Manuel Ferran Bayona
Assigned period:	1875
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



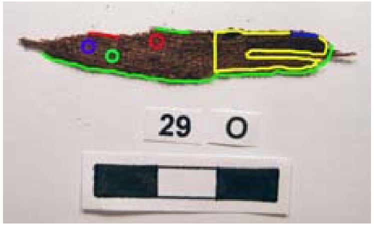
Sample Type:	Textile
Sample Id:	27
Sample condition:	Good
pH Final Average:	4,88
DP:	1174

Object Id:	28
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	010121-000
Title:	Retrat eqüestre de Dolors Ribé Andreu, comtessa de Figuerola
Author:	Ramon Martí Alsina
Assigned period:	1875
Vertical thread Id:	Mostly hemp (with a few linen)
Horizontal thread Id:	Linen
Textile Id:	Linen & hemp



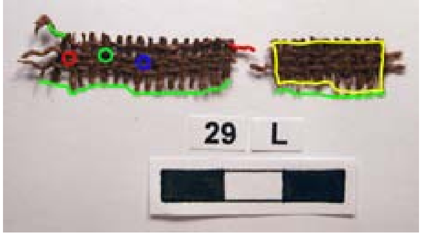
Sample Type:	Textile
Sample Id:	28
Sample condition:	Good
pH Final Average:	5,55
DP:	1119

Object Id:	29
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	213463-000
Title:	Adoració dels mags
Author:	Francesco de Ponte
Assigned period:	1650
Vertical thread Id:	0
Horizontal thread Id:	-
Textile Id:	-



Sample Type:	Textile
Sample Id:	29_O
Sample condition:	Bad
pH Final Average:	4,67
DP:	414

Object Id:	29
Object Type:	Lining
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	213463-000
Title:	Lining of the painting : Adoració dels mags
Author:	
Assigned period:	1950
Vertical thread Id:	Cotton
Horizontal thread Id:	Jute
Textile Id:	Jute & Cotton



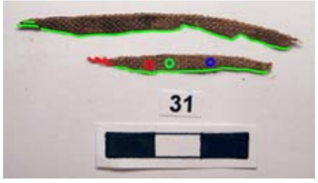
Sample Type:	Textile
Sample Id:	29_L
Sample condition:	Bad (brittle textile)
pH Final Average:	4,17
DP:	

Object Id:	30
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	043887-000
Title:	Natura morta
Author:	Anònim
Assigned period:	1850
Vertical thread Id:	Linen?
Horizontal thread Id:	Linen?
Textile Id:	Linen?

Sample Type:	Textile
Sample Id:	30
Sample condition:	Good
pH Final Average:	6,85
DP:	941

Object Id: 31
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011308-000
Title: Còpia d'un retrat del rei Jaume I
Author: E. Castro
Assigned period: 1875

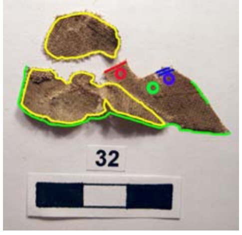
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 31
Sample condition:
pH Final Average: 5,09
DP:

Object Id:	32
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	068807-000
Title:	Al·legoria de la música
Author:	Anònim
Assigned period:	1900

Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



Sample Type:	Textile
Sample Id:	32
Sample condition:	Bad
pH Final Average:	6,48
DP:	435

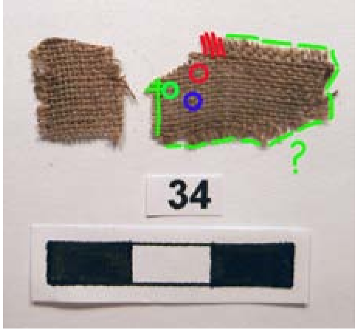
Object Id: 33
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011257-000
Title: Retrat del polític Antoni Maura Montaner (1853-1925)
Author: Lluís Graner
Assigned period: 1925

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 33
Sample condition:
pH Final Average: 5,24
DP:

Object Id: 34
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 121749-000
Title: Acadèmia
Author: Anònim
Assigned period: 1875

Vertical thread Id:
Horizontal thread Id:
Textile Id:



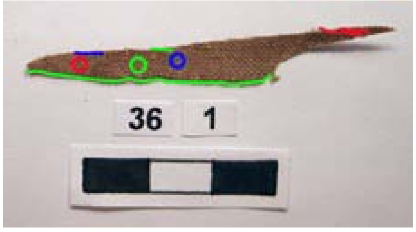
Sample Type: Textile
Sample Id: 34
Sample condition:
pH Final Average: 5,55
DP:

Object Id:	35
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	121751-000
Title:	Retrat masculí
Author:	Anònim
Assigned period:	1850
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

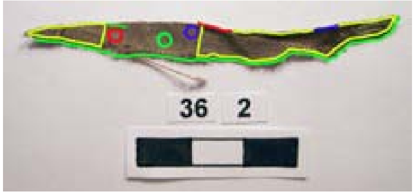
Sample Type:	Textile
Sample Id:	35
Sample condition:	
pH Final Average:	5,24
DP:	1149

Object Id: 36
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011254-000
Title: Retrat d'un general
Author: Anònim
Assigned period: 1900

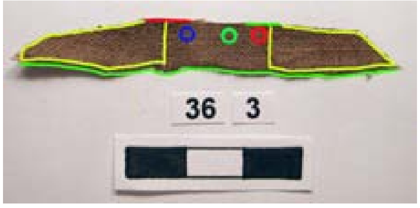
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 36_1
Sample condition:
pH Final Average: 5,5
DP:

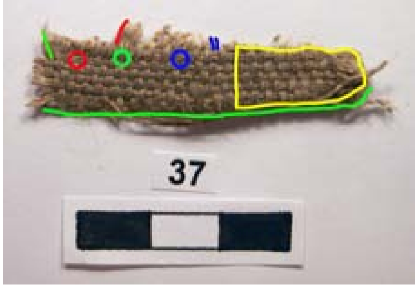


Sample Type: Textile
Sample Id: 36_2
Sample condition:
pH Final Average: 5,72
DP: 896



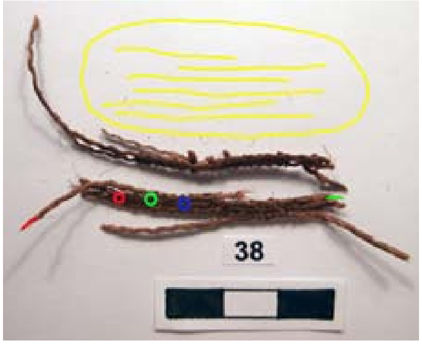
Sample Type: Textile
Sample Id: 36_3
Sample condition:
pH Final Average: 5,57
DP: 727

Object Id:	37
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	008639-000
Title:	Retrat del Rei Don Alfons XIII
Author:	Ricard Canals
Assigned period:	1925
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



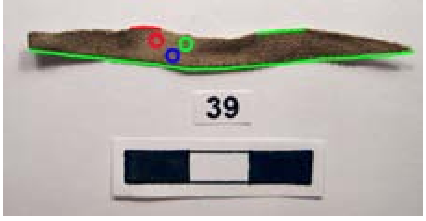
Sample Type:	Textile
Sample Id:	37
Sample condition:	Good
pH Final Average:	5,54
DP:	2135

Object Id:	38
Object Type:	Lining
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	
Title:	
Author:	
Assigned period:	1950
Vertical thread Id:	Jute
Horizontal thread Id:	Jute
Textile Id:	Jute



Sample Type:	Textile
Sample Id:	38_L
Sample condition:	Bad
pH Final Average:	4,36
DP:	756

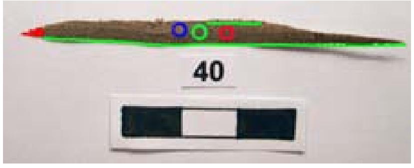
Object Id:	39
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011461-000
Title:	Retrat de Lola
Author:	Joaquim Sunyer
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	39
Sample condition:	
pH Final Average:	5,31
DP:	

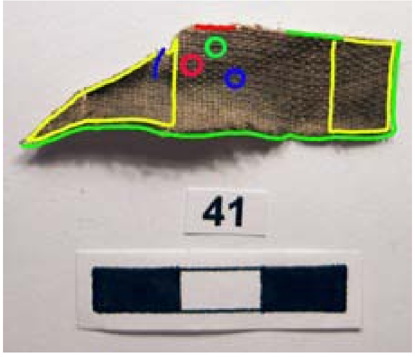
Object Id: 40
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 003838-000
Title: La meva filla Victòria
Author: Joaquim Sunyer
Assigned period: 1925

Vertical thread Id:
Horizontal thread Id:
Textile Id:



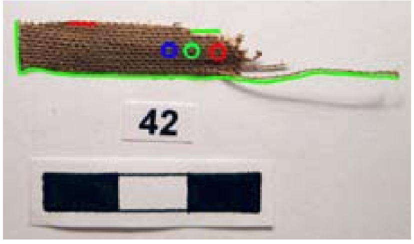
Sample Type: Textile
Sample Id: 40
Sample condition:
pH Final Average: 5,13
DP:

Object Id:	41
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	065299-000
Title:	La colla
Author:	Olga Sacharoff
Assigned period:	1925
Vertical thread Id:	Cotton
Horizontal thread Id:	Linen
Textile Id:	Linen & Cotton



Sample Type:	Textile
Sample Id:	41
Sample condition:	
pH Final Average:	5,75
DP:	900

Object Id:	42
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011451-000
Title:	Harmonies del bosc
Author:	Josep Maria Tamburini
Assigned period:	1875
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



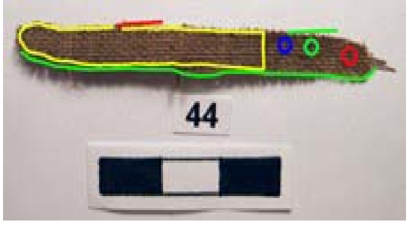
Sample Type:	Textile
Sample Id:	42
Sample condition:	
pH Final Average:	5
DP:	

Object Id:	43
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011069-000
Title:	La benedicció del dinar
Author:	Carles Vázquez Ubeda
Assigned period:	1875
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton

Sample Type:	Textile
Sample Id:	43
Sample condition:	
pH Final Average:	5,72
DP:	984

Object Id: 44
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 050433-000
Title: Retrat de la dona del pintor
Author: Carles Vázquez Ubeda
Assigned period: 1925

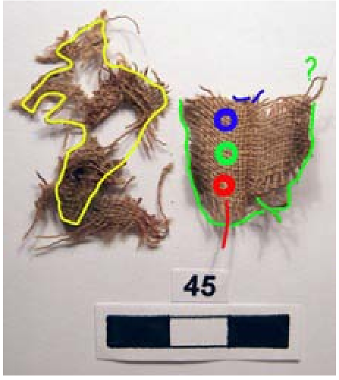
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 44
Sample condition:
pH Final Average: 5,33
DP: 1174

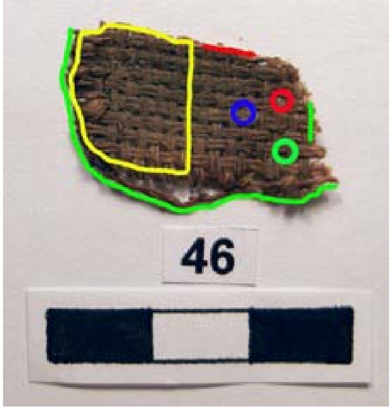
Object Id:	45
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	121752-000
Title:	Retrat masculí
Author:	Anònim
Assigned period:	1850

Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	45
Sample condition:	
pH Final Average:	4,83
DP:	456

Object Id:	46
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011455-000
Title:	Riera de Barata
Author:	Joaquim Vancells
Assigned period:	1875
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

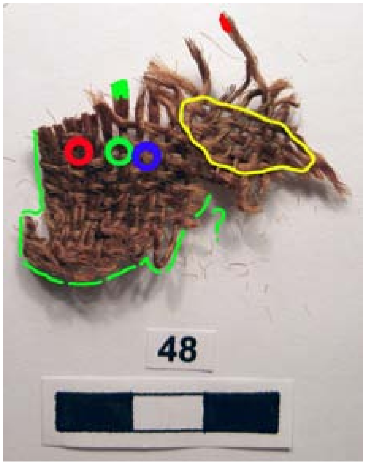


Sample Type:	Textile
Sample Id:	46
Sample condition:	
pH Final Average:	4,82
DP:	898

Object Id:	47
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	024675-000
Title:	Paisatge (Alcala de Guadaira)
Author:	Emilio Sánchez Perrier
Assigned period:	1875
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

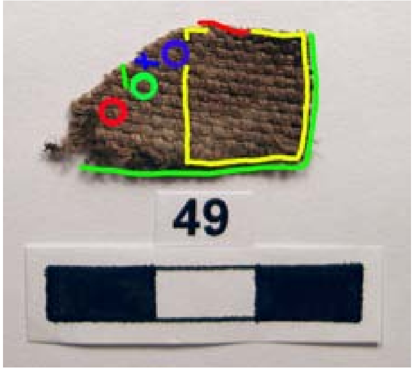
Sample Type:	Textile
Sample Id:	47
Sample condition:	
pH Final Average:	5,78
DP:	1026

Object Id:	48
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	024158-000
Title:	Camp d'Astúries
Author:	Florentino Soria
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	Jute



Sample Type:	Textile
Sample Id:	48
Sample condition:	
pH Final Average:	4,65
DP:	535

Object Id:	49
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	038282-000
Title:	Largo
Author:	Paul Rieth
Assigned period:	1925
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



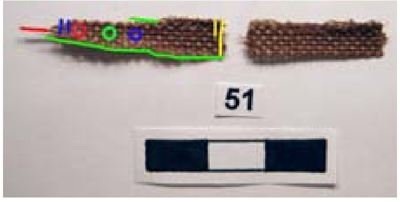
Sample Type:	Textile
Sample Id:	49
Sample condition:	
pH Final Average:	5,67
DP:	765

Object Id:	50
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011255-000
Title:	Retrat d'infant
Author:	Émile Roumens
Assigned period:	1875
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	50
Sample condition:	
pH Final Average:	5,24
DP:	

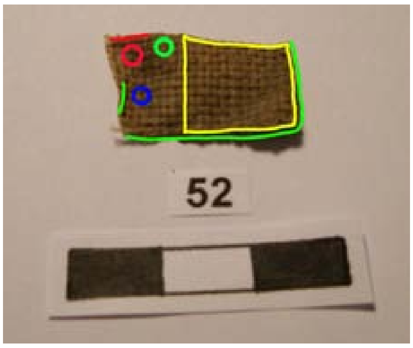
Object Id: 51
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 039149-000
Title: Dues figures femenines nues
Author: Joaquim Sunyer
Assigned period: 1925

Vertical thread Id: Jute
Horizontal thread Id: Linen
Textile Id: Jute & Linen



Sample Type: Textile
Sample Id: 51
Sample condition: Bad (brittle textile)
pH Final Average: 4,48
DP:

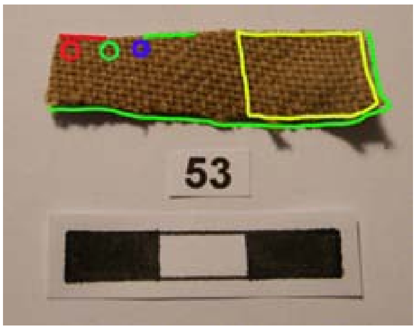
Object Id:	52
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	771
Title:	S/T
Author:	Anònim
Assigned period:	1925
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	52
Sample condition:	
pH Final Average:	5,01
DP:	845

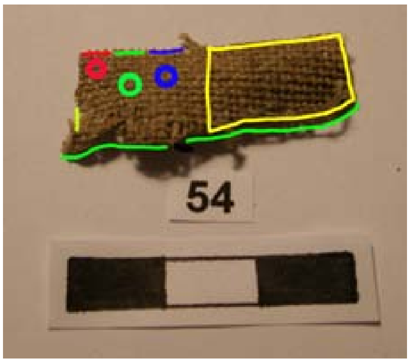
Object Id: 53
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 3
Title: S/T
Author: Lluís Muntané Muns
Assigned period: 1925

Vertical thread Id: Cotton
Horizontal thread Id: Cotton
Textile Id: Cotton



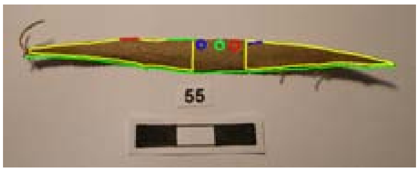
Sample Type: Textile
Sample Id: 53
Sample condition:
pH Final Average: 5,02
DP: 662

Object Id:	54
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	1024
Title:	S/T
Author:	Leonardo Platón
Assigned period:	1925
Vertical thread Id:	Linen?
Horizontal thread Id:	Linen?
Textile Id:	Linen?



Sample Type:	Textile
Sample Id:	54
Sample condition:	
pH Final Average:	5,34
DP:	1981

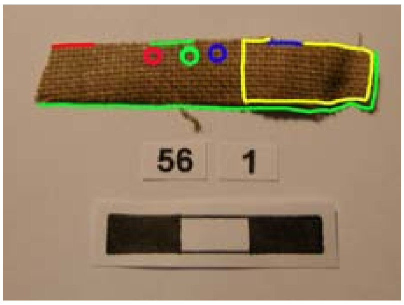
Object Id:	55
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	858
Title:	S/T
Author:	Jorge Fornas
Assigned period:	1925
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



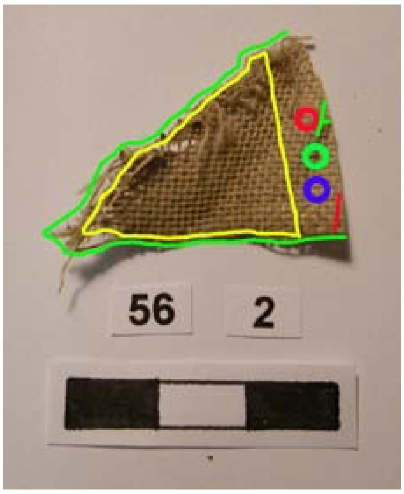
Sample Type:	Textile
Sample Id:	55
Sample condition:	
pH Final Average:	6,24
DP:	859

Object Id: 56
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 1
Title: S/T
Author: M. Camps
Assigned period: 1975

Vertical thread Id: Cotton
Horizontal thread Id: Cotton
Textile Id: Cotton

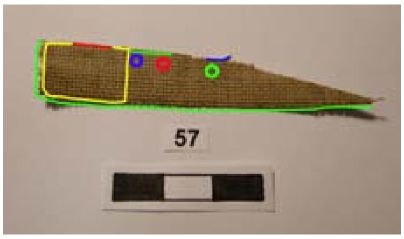


Sample Type: Textile
Sample Id: 56_1
Sample condition:
pH Final Average: 5,55
DP: 1067

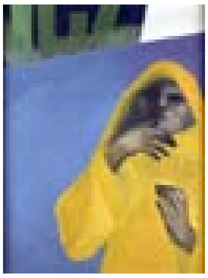


Sample Type: Textile
Sample Id: 56_2
Sample condition:
pH Final Average: 5,23
DP: 968

Object Id:	57
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	45
Title:	S/T
Author:	Mº Teresa Jou Paulet
Assigned period:	1975
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton

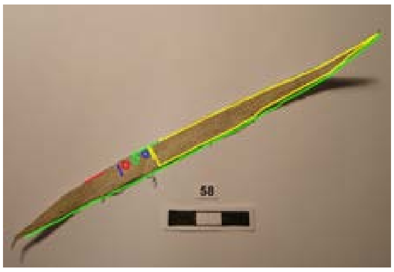


Sample Type:	Textile
Sample Id:	57
Sample condition:	
pH Final Average:	6,05
DP:	784



Object Id:	58
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	885
Title:	S/T
Author:	Andrés Terrades Moragues
Assigned period:	1975

Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	58
Sample condition:	
pH Final Average:	6,29
DP:	1172

Sample Type:	Thread
Sample Id:	58_Th
Sample condition:	
pH Final Average:	5,47
DP:	

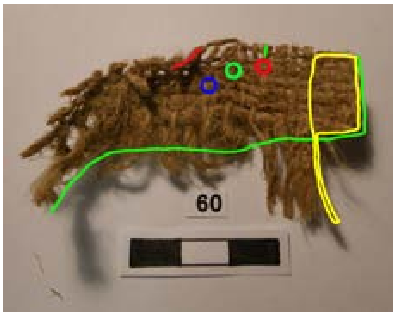
Object Id:	59
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	138
Title:	S/T
Author:	Ramon Canet Font
Assigned period:	1975
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton

Sample Type:	Textile
Sample Id:	59
Sample condition:	
pH Final Average:	5,31
DP:	1067

Sample Type:	Thread
Sample Id:	59_Th
Sample condition:	
pH Final Average:	5,33
DP:	

Object Id: 60
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 48
Title: S/T
Author: Joan Lleo
Assigned period: 1975

Vertical thread Id: Jute
Horizontal thread Id: Jute
Textile Id: Jute

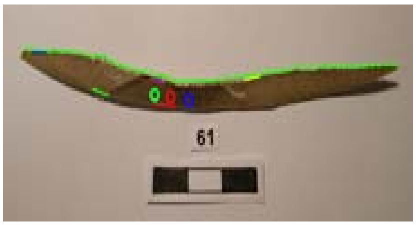


Sample Type: Textile
Sample Id: 60
Sample condition:
pH Final Average: 4,78
DP: 1094

Sample Type: Thread
Sample Id: 60_Th
Sample condition:
pH Final Average: 5,06
DP:

Object Id: 61
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 148
Title: S/T
Author: Xavier Grau
Assigned period: 1975

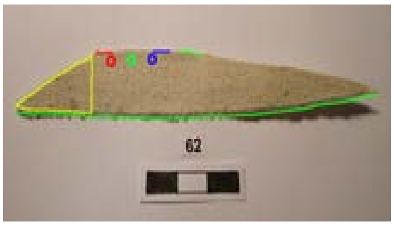
Vertical thread Id: Cotton
Horizontal thread Id: Cotton
Textile Id: Cotton



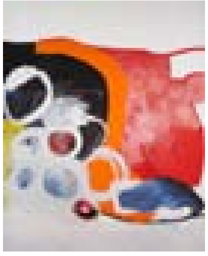
Sample Type: Textile
Sample Id: 61
Sample condition:
pH Final Average: 6,5
DP:

Object Id: 62
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 615
Title: S/T
Author: Carles Joaquim Gacez Alcolea
Assigned period: 1975

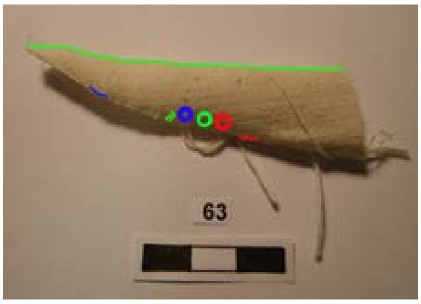
Vertical thread Id: Cotton
Horizontal thread Id: Cotton
Textile Id: Mostly cotton (with a few other natural fibre)



Sample Type: Textile
Sample Id: 62
Sample condition: Good
pH Final Average: 7,06
DP:



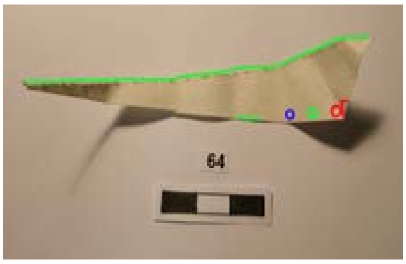
Object Id:	63
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	1038
Title:	El Viaje
Author:	María Enfedache Sancho
Assigned period:	2000
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	63
Sample condition:	Good
pH Final Average:	6,57
DP:	

Object Id: 64
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 1339
Title: La flor de Ana
Author: Alan Sastre
Assigned period: 2000

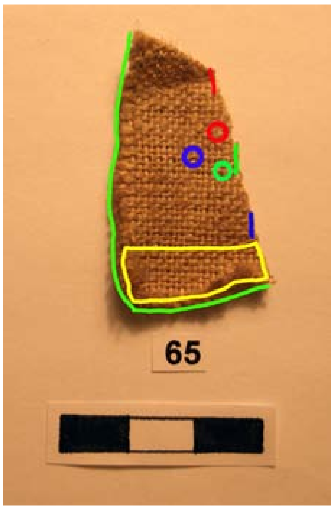
Vertical thread Id: Cotton & Synthetics
Horizontal thread Id: Cotton & Synthetics
Textile Id: Cotton & Synthetics



Sample Type: Textile
Sample Id: 64
Sample condition: Good
pH Final Average: 6,39
DP:

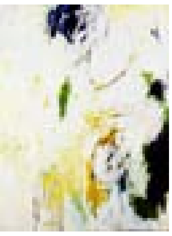
Object Id: 65
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 82
Title: S/T
Author: Joaquim Cancho Cabré
Assigned period: 1975

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



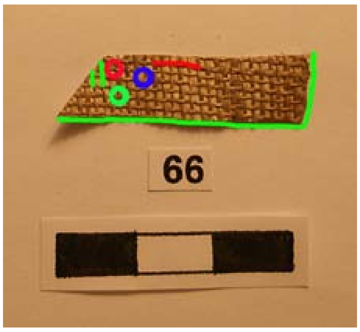
Sample Type: Textile
Sample Id: 65
Sample condition: Good
pH Final Average: 5,09
DP: 2332

Sample Type: Thread
Sample Id: 65_Th
Sample condition:
pH Final Average: 5,03
DP:



Object Id: 66
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 178
Title: S/T
Author: Xavier Grau Massip
Assigned period: 1975

Vertical thread Id:
Horizontal thread Id:
Textile Id:

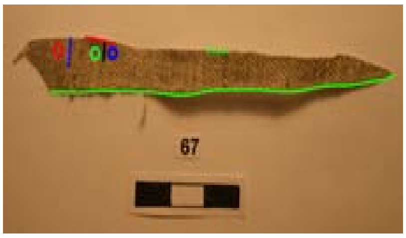


Sample Type: Textile
Sample Id: 66
Sample condition:
pH Final Average: 6,1
DP:

Sample Type: Thread
Sample Id: 66_Th
Sample condition:
pH Final Average: 5,87
DP:

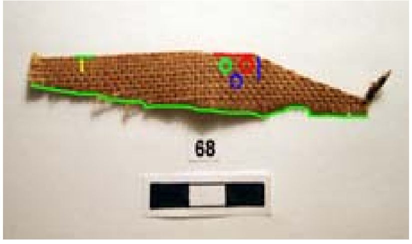
Object Id: 67
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 521
Title: Premonició n. 13
Author: Pau Casanovas
Assigned period: 1975

Vertical thread Id:
Horizontal thread Id:
Textile Id: Mostly cotton (with a few synthetics)



Sample Type: Textile
Sample Id: 67
Sample condition:
pH Final Average: 5,35
DP:

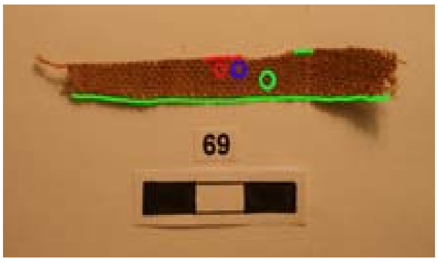
Object Id:	68
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	863
Title:	S/T
Author:	Joan Lahosa
Assigned period:	1925
Vertical thread Id:	Jute
Horizontal thread Id:	Cotton
Textile Id:	Jute & Cotton



Sample Type:	Textile
Sample Id:	68
Sample condition:	Bad (brittle textile)
pH Final Average:	4,9
DP:	

Object Id: 69
Object Type: Painting
Institution / Donor: Col.lecció de la Facultat de Belles Arts (UB)
Number Institution: 772
Title: S/T
Author: Anònim
Assigned period: 1925

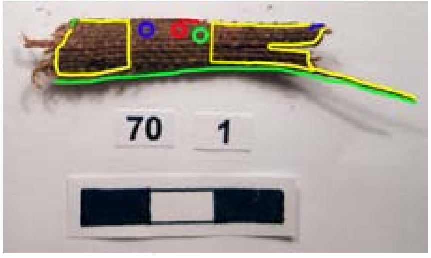
Vertical thread Id:
Horizontal thread Id:
Textile Id: -



Sample Type: Textile
Sample Id: 69
Sample condition:
pH Final Average: 5,93
DP: 577

Object Id: 70
Object Type: Painting
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution: 602
Title: La Verge del Rosari
Author: Atribuït a Juan de Ucena Castroverde, 1623
Assigned period: 1650

Vertical thread Id: Linen
Horizontal thread Id: -
Textile Id: -

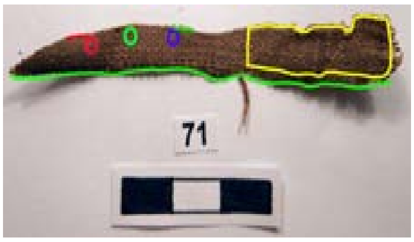


Sample Type: Textile
Sample Id: 70_1
Sample condition:
pH Final Average: 4,72
DP: 425

Sample Type: Textile
Sample Id: 70_2
Sample condition:
pH Final Average: 5,48
DP: 809

Object Id: 71
Object Type: Painting
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution: 610
Title:
Author:
Assigned period: 1750

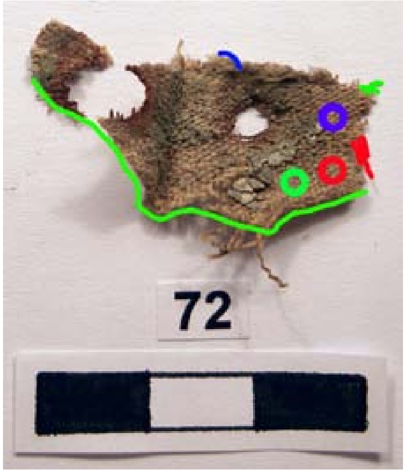
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 71
Sample condition:
pH Final Average: 4,85
DP: 614

Object Id: 72
Object Type: Painting
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution: 655
Title:
Author:
Assigned period: 1850

Vertical thread Id:
Horizontal thread Id:
Textile Id:

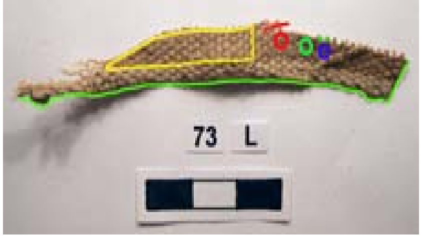


Sample Type: Textile
Sample Id: 72
Sample condition:
pH Final Average: 5,5
DP:

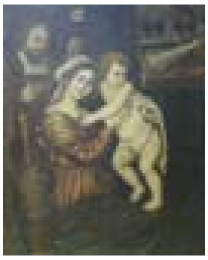
Object Id:	73
Object Type:	Painting
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	634_09
Title:	Figura femenina costumista
Author:	Josep Juliana i Albert
Assigned period:	1875
Vertical thread Id:	Linen?
Horizontal thread Id:	Linen
Textile Id:	Linen?

Sample Type:	Textile
Sample Id:	73_O
Sample condition:	
pH Final Average:	5,37
DP:	608

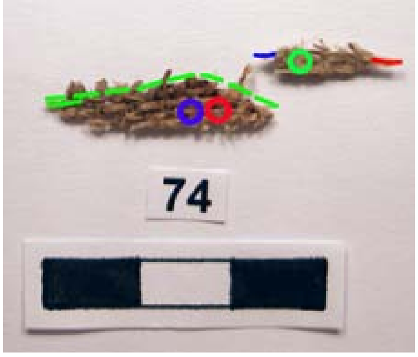
Object Id:	73
Object Type:	Lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	634_09
Title:	Lining of the painting : « 73 »
Author:	
Assigned period:	1975
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



Sample Type:	Textile
Sample Id:	73_L
Sample condition:	Good
pH Final Average:	4,95
DP:	1363



Object Id:	74
Object Type:	Painting
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	522_06
Title:	Sagrada família
Author:	
Assigned period:	1650
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	74
Sample condition:	
pH Final Average:	5,99
DP:	

Object Id:	75
Object Type:	Painting
Institution / Donor:	Col.lecció de la Facultat de Belles Arts (UB)
Number Institution:	49
Title:	S/T
Author:	Oriol Muntané
Assigned period:	1975
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	75
Sample condition:	
pH Final Average:	4,72
DP:	805

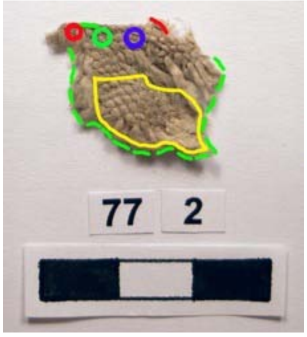
Object Id:	76
Object Type:	Painting
Institution / Donor:	Private owner
Number Institution:	1
Title:	Paisatge
Author:	Francesc Folch Margarit
Assigned period:	1925
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton

Sample Type:	Textile
Sample Id:	76
Sample condition:	
pH Final Average:	
DP:	660

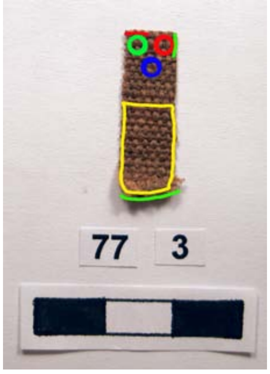
Object Id: 77
Object Type: Painting
Institution / Donor: Centre de Restauració de Béns Mobles de Catalunya
Number Institution: 11017 (MNAC: 12084)
Title: El gran dia de Girona
Author: Ramon Martí Alsina
Assigned period: 1875

Vertical thread Id: Linen
Horizontal thread Id: Mostly linen (a few hemp)
Textile Id: Mostly linen (with a few hemp)

Sample Type: Textile
Sample Id: 77_1
Sample condition:
pH Final Average: 6,11
DP:



Sample Type: Textile
Sample Id: 77_2
Sample condition:
pH Final Average: 6,52
DP: 1135



Sample Type: Textile
Sample Id: 77_3
Sample condition:
pH Final Average: 5,04
DP: 736

Sample Type: Thread
Sample Id: 77_Th1
Sample condition:
pH Final Average: 6,15
DP:

Sample Type: Thread
Sample Id: 77_Th2
Sample condition:
pH Final Average: 5,16
DP:

Sample Type: Thread
Sample Id: 77_Th3
Sample condition:
pH Final Average: 4,85
DP:

Object Id: 78
Object Type: Painting
Institution / Donor: Centre de Restauració de Béns Mobles de Catalunya
Number Institution: 10765
Title: Sant i el Nen Jesús, de la capella de Santa Margarida o del Roser de la catedral de Girona.
Author:
Assigned period: 1700

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 78
Sample condition:
pH Final Average: 7,08
DP:

Sample Type: Thread
Sample Id: 78_Th1
Sample condition:
pH Final Average: 6,47
DP:

Sample Type: Thread
Sample Id: 78_Th2
Sample condition:
pH Final Average: 6,83
DP:

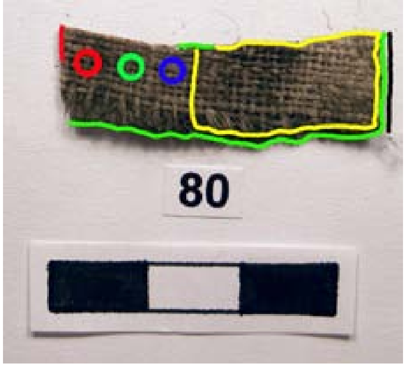
Sample Type: Thread
Sample Id: 78_Th3
Sample condition:
pH Final Average: 6,99
DP:

Object Id:	79
Object Type:	Painting
Institution / Donor:	Centre de Restauració de Béns Mobles de Catalunya
Number Institution:	10480-A
Title:	Maria als peus de la creu amb Crist crucificat
Author:	J. Oromí
Assigned period:	1875
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton

Sample Type:	Textile
Sample Id:	79
Sample condition:	
pH Final Average:	7,47
DP:	

Object Id: 80
Object Type: Painting
Institution / Donor: Centre de Restauració de Béns Mobles de Catalunya
Number Institution: 10764
Title: Sant Joan Baptista assenyalant l'Anyell de Déu, de la capella de Sant Esteve, de la catedral de Girona
Author:
Assigned period: 1700

Vertical thread Id: 0
Horizontal thread Id: -
Textile Id: -



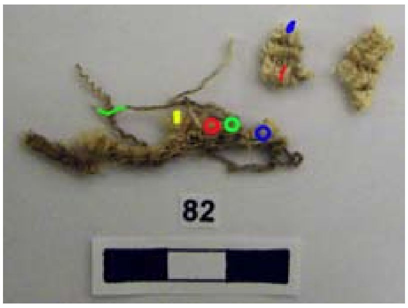
Sample Type: Textile
Sample Id: 80
Sample condition:
pH Final Average: 6,58
DP: 1687

Sample Type: Thread
Sample Id: 80_Th
Sample condition:
pH Final Average: 6,15
DP:

Object Id:	81
Object Type:	Painting
Institution / Donor:	Centre de Restauració de Béns Mobles de Catalunya
Number Institution:	
Title:	Tela pràctiques
Author:	
Assigned period:	1850
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

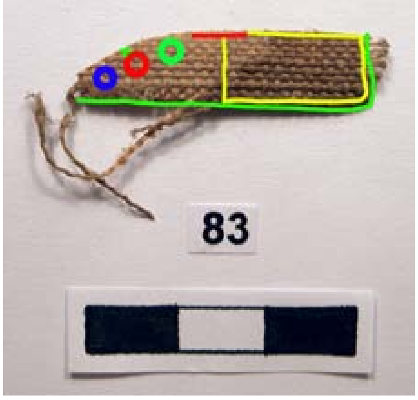
Sample Type:	Textile
Sample Id:	81
Sample condition:	
pH Final Average:	6,58
DP:	

Object Id:	82
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	029517-000
Title:	Figura femenina alada
Author:	Alexandre de Riquer
Assigned period:	1875
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



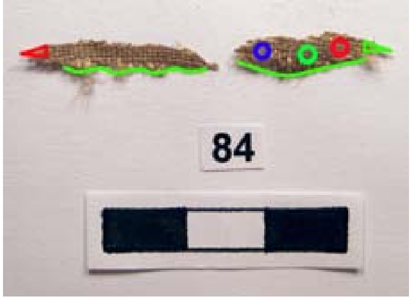
Sample Type:	Textile
Sample Id:	82
Sample condition:	
pH Final Average:	5,29
DP:	

Object Id:	83
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	022850-000
Title:	Les molineres
Author:	Carlos Reis
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



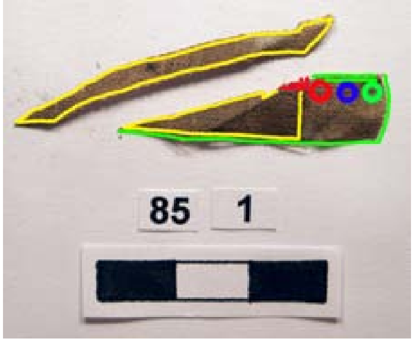
Sample Type:	Textile
Sample Id:	83
Sample condition:	
pH Final Average:	5,24
DP:	1345

Object Id:	84
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011621-000
Title:	Interior gòtic (projecte)
Author:	Pau Rigalt
Assigned period:	1825
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

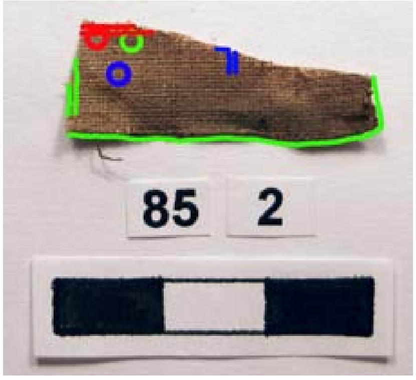


Sample Type:	Textile
Sample Id:	84
Sample condition:	
pH Final Average:	5,39
DP:	

Object Id:	85
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	004337-000
Title:	La noia del mocador blanc
Author:	Pere Pruna
Assigned period:	1925
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

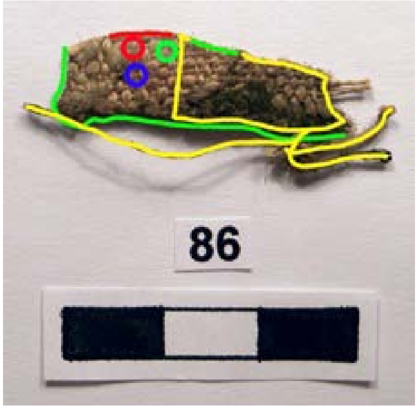


Sample Type:	Textile
Sample Id:	85_1
Sample condition:	
pH Final Average:	5,06
DP:	1935



Sample Type:	Textile
Sample Id:	85_2
Sample condition:	
pH Final Average:	5,16
DP:	

Object Id:	86
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	004603-000
Title:	Roureda. Tardor (Olot), Vilanova i la Geltrú, 1883 – Riudarenes, 1949
Author:	Iu Pascual
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	86
Sample condition:	
pH Final Average:	4,82
DP:	

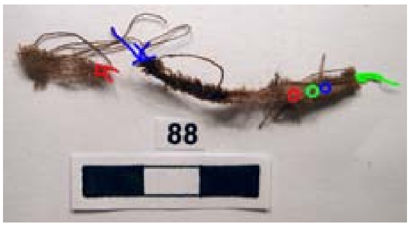
Sample Type:	Thread
Sample Id:	86_Th
Sample condition:	
pH Final Average:	5,2
DP:	

Object Id: 87
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 011466-000
Title: Mirant la plaça
Author: Francesc d'Assis Planas
Assigned period: 1925

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 87
Sample condition:
pH Final Average: 5,12
DP:

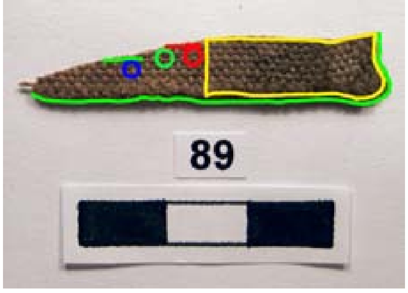
Object Id:	88
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	065410-000
Title:	Retrat d'un home amb uniforme de falangista
Author:	Llucia Oslé
Assigned period:	1975
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	88
Sample condition:	
pH Final Average:	5,23
DP:	

Object Id: 89
Object Type: Painting
Institution / Donor: Museu Nacional d'Art de Catalunya
Number Institution: 200713-000
Title: Gitanes assegudes
Author: Isidre Nonell
Assigned period: 1925

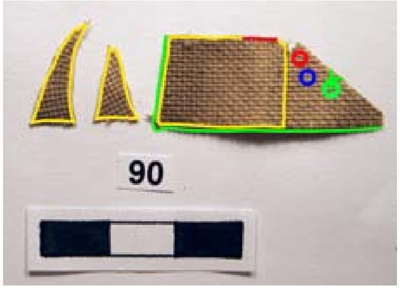
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 89
Sample condition:
pH Final Average: 5,03
DP: 941

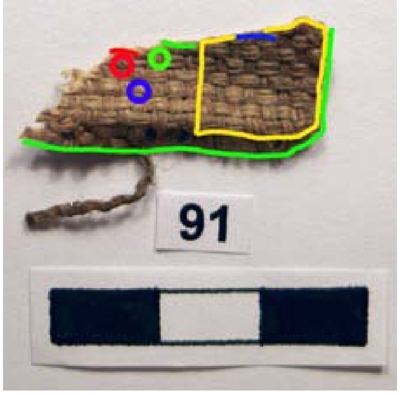
Sample Type: Thread
Sample Id: 89_Th
Sample condition:
pH Final Average: 5,19
DP:

Object Id:	90
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	010788-000
Title:	Retrat
Author:	Lluís Muntané
Assigned period:	1925
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



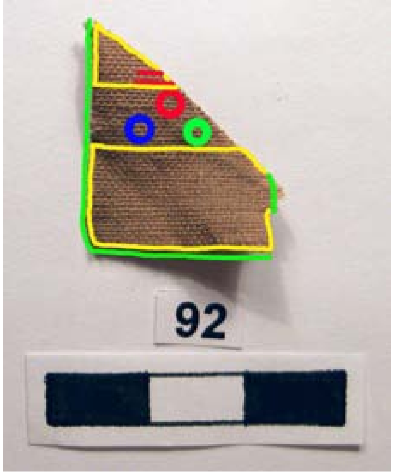
Sample Type:	Textile
Sample Id:	90
Sample condition:	
pH Final Average:	5,4
DP:	1356

Object Id:	91
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	011032-000
Title:	Retrat de noia amb rosa a la ma
Author:	Lluís Martí Gras
Assigned period:	1925
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



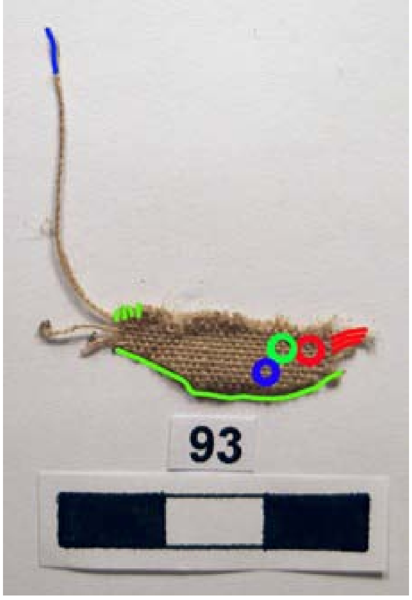
Sample Type:	Textile
Sample Id:	91
Sample condition:	
pH Final Average:	5,34
DP:	1654

Object Id:	92
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	121774-000
Title:	El planter
Author:	Armand Miravalls
Assigned period:	1975
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	92
Sample condition:	
pH Final Average:	4,81
DP:	748

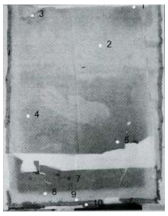
Object Id:	93
Object Type:	Painting
Institution / Donor:	Museu Nacional d'Art de Catalunya
Number Institution:	042090-000
Title:	Hort amb casa de pagès
Author:	Joaquim Mir
Assigned period:	1925
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



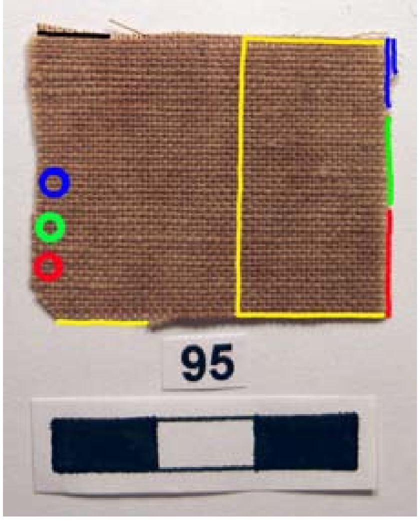
Sample Type:	Textile
Sample Id:	93
Sample condition:	
pH Final Average:	5,12
DP:	

Object Id:	94
Object Type:	Painting
Institution / Donor:	Private owner
Number Institution:	1
Title:	
Author:	
Assigned period:	1550
Vertical thread Id:	Linen and hemp
Horizontal thread Id:	Mostly linen (a few hemp)
Textile Id:	Linen & hemp

Sample Type:	Textile
Sample Id:	94
Sample condition:	
pH Final Average:	7,38
DP:	1512

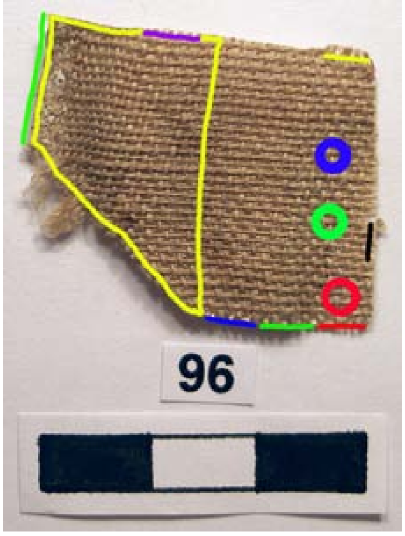


Object Id:	95
Object Type:	Lining
Institution / Donor:	Private owner
Number Institution:	2
Title:	
Author:	
Assigned period:	1800
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	95
Sample condition:	
pH Final Average:	4,89
DP:	

Object Id:	96
Object Type:	Painting
Institution / Donor:	Private owner
Number Institution:	3
Title:	
Author:	
Assigned period:	1875
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



Sample Type:	Textile
Sample Id:	96
Sample condition:	
pH Final Average:	5,5
DP:	1711

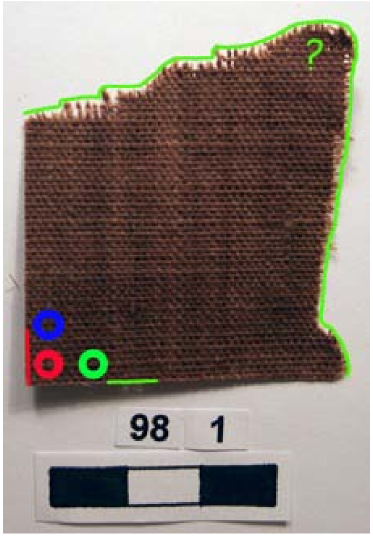
Object Id:	97
Object Type:	Lining
Institution / Donor:	Painting belonging to the Museo del Prado, deposited at the Gremi de Fabricants de Sabadell
Number Institution:	1
Title:	La huida de Egipto
Author:	
Assigned period:	1900
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	97_1
Sample condition:	
pH Final Average:	5,1
DP:	

Sample Type:	Textile
Sample Id:	97_2
Sample condition:	
pH Final Average:	4,83
DP:	

Sample Type: Textile
Sample Id: 97_3
Sample condition:
pH Final Average: 5,7
DP:

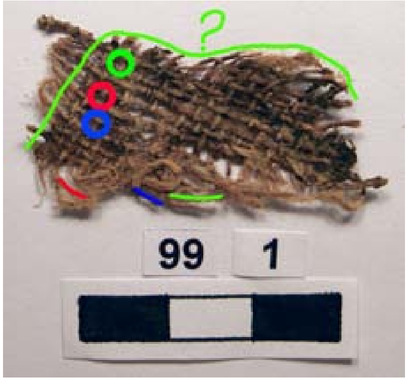
Object Id:	98
Object Type:	Lining
Institution / Donor:	Painting belonging to the Museo del Prado, deposited at the Gremi de Fabricants de Sabadell
Number Institution:	2
Title:	Lining of the painting “San Pedro de Alcántara”
Author:	
Assigned period:	1900
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	98
Sample condition:	
pH Final Average:	4,69
DP:	

Object Id: 99
Object Type: Painting
Institution / Donor: Painting belonging to the Museo del Prado, deposited at the Gremi de Fabricants de Sabadell
Number Institution: 3
Title: Jesucristo y el Centurión
Author: Alonso Cano?
Assigned period: 1650

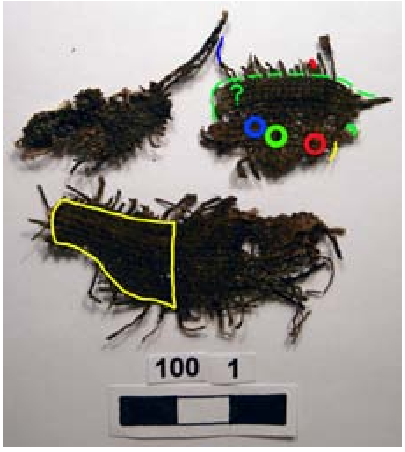
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 99
Sample condition:
pH Final Average: 5,93
DP:

Object Id: 100
Object Type: Painting
Institution / Donor: Painting belonging to the Museo del Prado, deposited at the Gremi de Fabricants de Sabadell
Number Institution: 4
Title: San Felipe en extasis
Author: José García Hidalgo
Assigned period: 1650

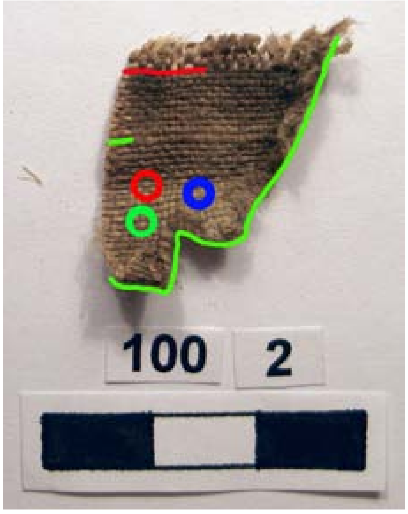
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen?



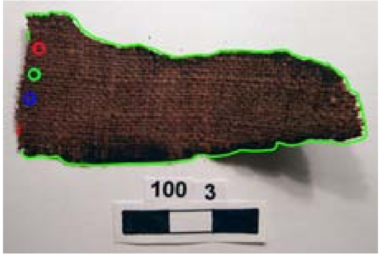
Sample Type: Textile
Sample Id: 100_1
Sample condition:
pH Final Average: 6,02
DP: 798

Object Id: 100
Object Type: Lining
Institution / Donor: Painting belonging to the Museo del Prado, deposited at the Gremi de Fabricants de Sabadell
Number Institution:
Title: Lining of a painting
Author:
Assigned period: 1900

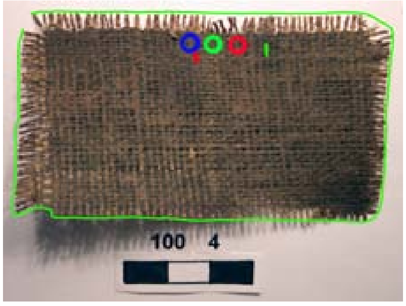
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 100_2
Sample condition:
pH Final Average: 5,6
DP:

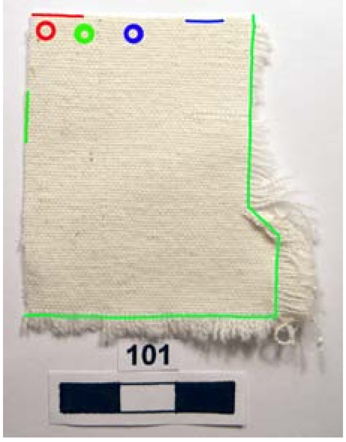


Sample Type: Textile
Sample Id: 100_3
Sample condition:
pH Final Average: 4,51
DP:

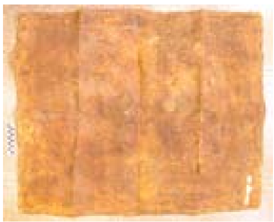


Sample Type: Textile
Sample Id: 100_4
Sample condition:
pH Final Average: 5,39
DP:

Object Id:	101
Object Type:	Bare new textile
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	1
Title:	Lining 101
Author:	
Assigned period:	1950
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Textile
Sample Id:	101
Sample condition:	Good
pH Final Average:	6,37
DP:	



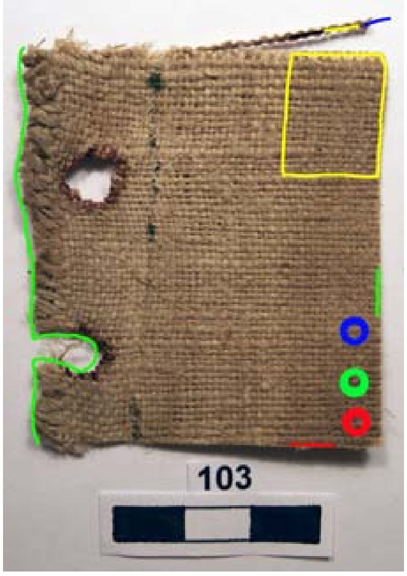
Object Id: 102
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 2
Title: Lining 102
Author:
Assigned period: 1850

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 102
Sample condition:
pH Final Average: 5,18
DP: 1064

Object Id: 103
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 3
Title: Lining 103
Author:
Assigned period: 1750

Vertical thread Id:
Horizontal thread Id:
Textile Id: Mostly linen (with a few hemp)



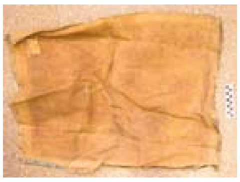
Sample Type: Textile
Sample Id: 103
Sample condition:
pH Final Average: 5,78
DP: 2136

Object Id:	104
Object Type:	Glue lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	4
Title:	Lining 104
Author:	
Assigned period:	1900
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

Sample Type:	Textile
Sample Id:	104
Sample condition:	
pH Final Average:	4,34
DP:	653

Object Id:	105
Object Type:	Glue lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	5
Title:	Lining 105
Author:	
Assigned period:	1900
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

Sample Type:	Textile
Sample Id:	105
Sample condition:	
pH Final Average:	4,26
DP:	538



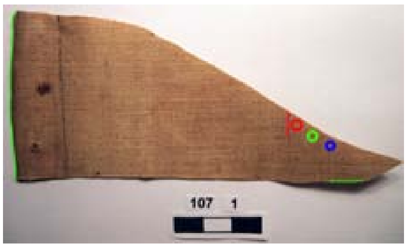
Object Id: 106
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 6
Title: Lining 106
Author:
Assigned period: 1900

Vertical thread Id: Mostly linen
Horizontal thread Id: Mostly linen
Textile Id: Linen

Sample Type: Textile
Sample Id: 106
Sample condition:
pH Final Average: 4,42
DP: 746

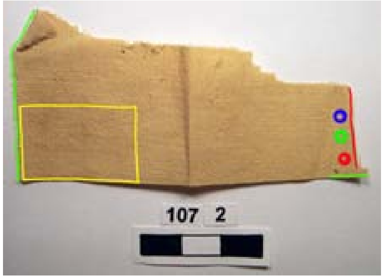
Object Id: 107_1
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 7
Title: Lining 107
Author:
Assigned period: 1900

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



Sample Type: Textile
Sample Id: 107_1
Sample condition:
pH Final Average: 4,56
DP:

Object Id:	107_2
Object Type:	Glue lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	
Title:	Lining 107
Author:	
Assigned period:	1900
Vertical thread Id:	Cotton
Horizontal thread Id:	Cotton
Textile Id:	Cotton



Sample Type:	Textile
Sample Id:	107_2
Sample condition:	
pH Final Average:	4,48
DP:	548

Object Id:	108
Object Type:	Bare new textile
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	8
Title:	Lining 108
Author:	
Assigned period:	1950
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

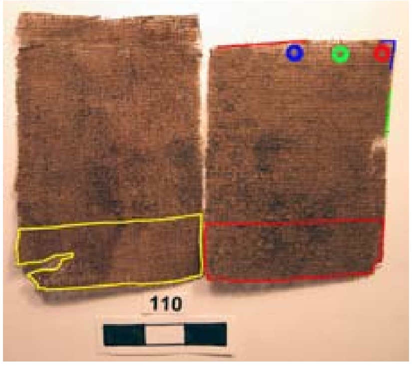
Sample Type:	Textile
Sample Id:	108
Sample condition:	
pH Final Average:	5,79
DP:	

Object Id:	109
Object Type:	Glue lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	9
Title:	Lining 109
Author:	
Assigned period:	1750
Vertical thread Id:	Linen
Horizontal thread Id:	Mostly linen
Textile Id:	Linen

Sample Type:	Textile
Sample Id:	109
Sample condition:	
pH Final Average:	5,25
DP:	1371

Object Id: 110
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 10
Title: Lining 110
Author:
Assigned period: 1900

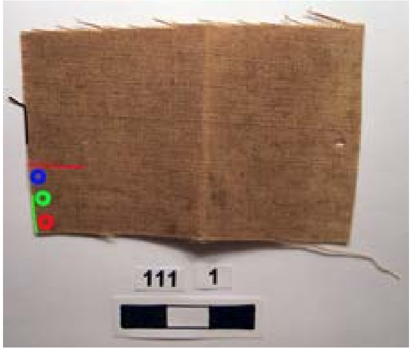
Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen



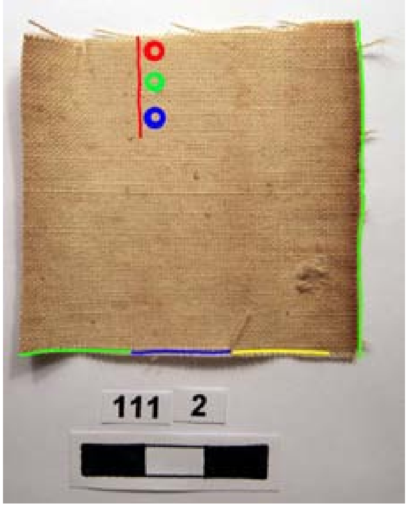
Sample Type: Textile
Sample Id: 110
Sample condition: Bad (brittle textile)
pH Final Average: 5,26
DP: 608

Object Id: 111
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 11
Title: Lining 111
Author:
Assigned period: 1950

Vertical thread Id: Cotton
Horizontal thread Id: Cotton
Textile Id: Cotton

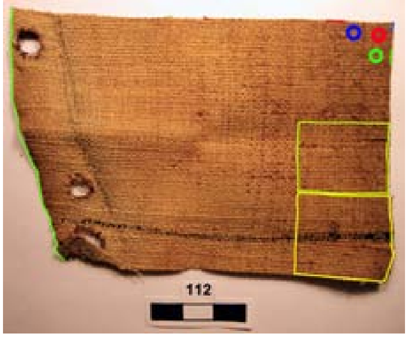


Sample Type: Textile
Sample Id: 111_1
Sample condition:
pH Final Average: 4,44
DP:



Sample Type: Textile
Sample Id: 111_2
Sample condition:
pH Final Average: 5,21
DP:

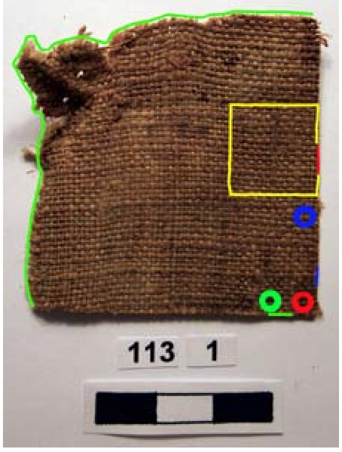
Object Id:	112
Object Type:	Glue lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution:	12
Title:	Lining 112, Ovalat
Author:	
Assigned period:	1750
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



Sample Type:	Textile
Sample Id:	112
Sample condition:	
pH Final Average:	4,88
DP:	631

Object Id: 113
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 13
Title: Lining 113, Small lining
Author:
Assigned period: 1750

Vertical thread Id: Mostly linen (a few hemp)
Horizontal thread Id: Linen
Textile Id: Mostly linen (with a few hemp)



Sample Type: Textile
Sample Id: 113_1
Sample condition: Bad (brittle textile)
pH Final Average: 4,92
DP: 646

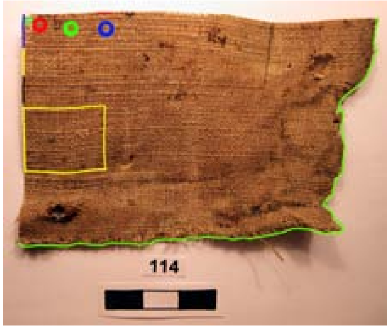
Sample Type: Textile
Sample Id: 113_2
Sample condition:
pH Final Average: 5
DP:

Sample Type: Deacidified textile
Sample Id: 113_3
Sample condition:
pH Final Average: 8,02
DP:

Sample Type: Deacidified textile
Sample Id: 113_4
Sample condition:
pH Final Average: 5,75
DP:

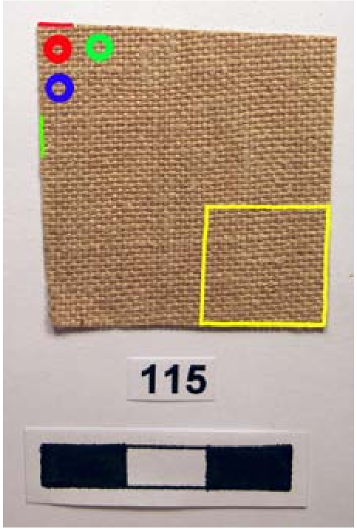
Object Id: 114
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Old linings
Number Institution: 14
Title: Lining 114, gran
Author:
Assigned period: 1850

Vertical thread Id: Mostly linen, a few hemp
Horizontal thread Id: Mostly linen, a few hemp
Textile Id: Mostly linen (with a few hemp)



Sample Type: Textile
Sample Id: 114
Sample condition:
pH Final Average: 6,18
DP: 968

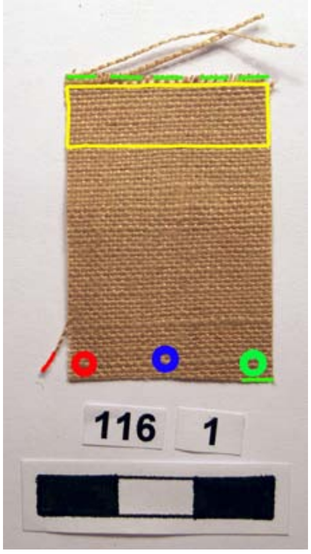
Object Id:	115
Object Type:	Primed lose lining
Institution / Donor:	Private owner
Number Institution:	1350
Title:	Study of a Lion
Author:	Henry Landseer
Assigned period:	1875
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



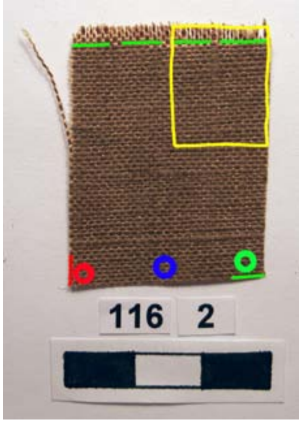
Sample Type:	Textile
Sample Id:	115
Sample condition:	
pH Final Average:	5,45
DP:	951

Object Id: 116
Object Type: Lose lining
Institution / Donor: Private owner
Number Institution: 535
Title: The Sun of Venice
Author: Joseph Mallor William Turner
Assigned period: 1825

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen

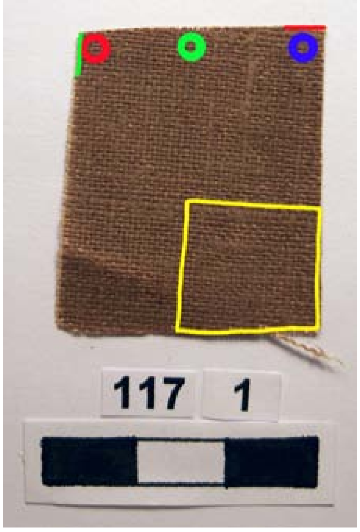


Sample Type: Textile
Sample Id: 116_1
Sample condition:
pH Final Average: 4,33
DP: 903

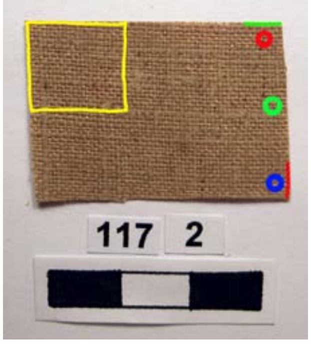


Sample Type: Textile
Sample Id: 116_2
Sample condition:
pH Final Average: 4,34
DP: 491

Object Id:	117
Object Type:	Lose lining
Institution / Donor:	Private owner
Number Institution:	Tate N00605
Title:	The Defeat of Comus
Author:	Henry Landseer
Assigned period:	1825
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen



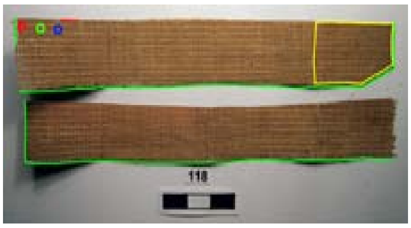
Sample Type:	Textile
Sample Id:	117_1
Sample condition:	
pH Final Average:	4,26
DP:	485



Sample Type:	Textile
Sample Id:	117_2
Sample condition:	
pH Final Average:	4,39
DP:	630

Object Id: 118
Object Type: Painting
Institution / Donor: Private owner
Number Institution:
Title: El rebesavi al llit de mort.
Author: Francesc Folch Margarit
Assigned period: 1925

Vertical thread Id:
Horizontal thread Id:
Textile Id: Cotton



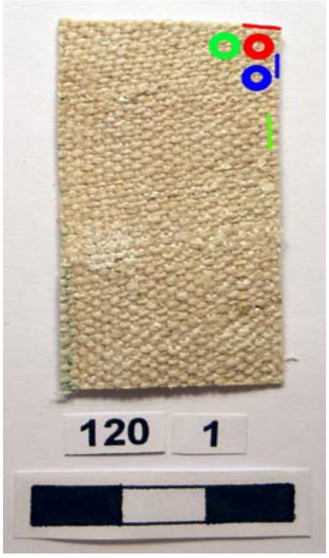
Sample Type: Textile
Sample Id: 118
Sample condition:
pH Final Average: 4,79
DP: 1302

Object Id: 119
Object Type: Painting
Institution / Donor: Private owner
Number Institution:
Title: “Hemp” from a painting from Palazzo Spinelly. Glued?
Author:
Assigned period: 1750

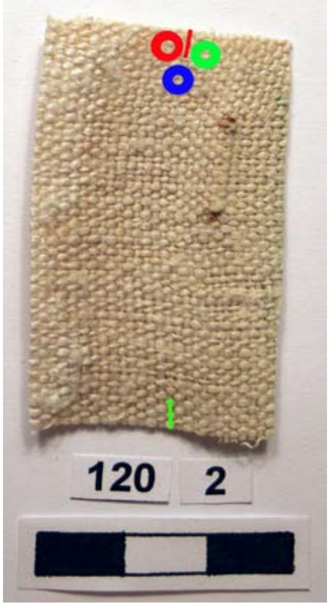
Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 119
Sample condition:
pH Final Average: 5,77
DP: 837

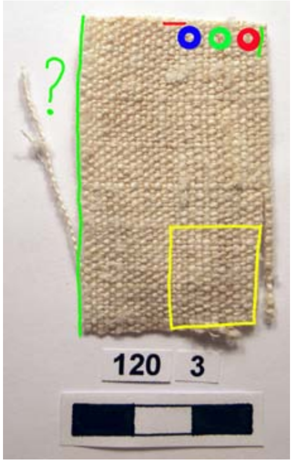
Object Id:	120
Object Type:	Painting
Institution / Donor:	Private owner
Number Institution:	
Title:	Retrat pare. Modern painting on bleached linen
Author:	Marta Oriola Folch
Assigned period:	1950
Vertical thread Id:	Linen
Horizontal thread Id:	Linen?
Textile Id:	Linen?



Sample Type:	Textile
Sample Id:	120_1
Sample condition:	Good
pH Final Average:	7,21
DP:	



Sample Type:	Textile
Sample Id:	120_2
Sample condition:	Good
pH Final Average:	7,2
DP:	



Sample Type:	Textile
Sample Id:	120_3
Sample condition:	Good
pH Final Average:	7,36
DP:	4151

Object Id: 121
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Lienzos Levante
Number Institution:
Title: New textile, linen. Linezos levante. Ref. 30
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 121
Sample condition: Good
pH Final Average: 6,84
DP:

Object Id: 122
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Lienzos Levante
Number Institution:
Title: New textile, linen + animal glue. Lienzos levante. Ref. 30
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 122
Sample condition: Good
pH Final Average: 5,97
DP:

Object Id: 123
Object Type: Primed new canvas
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Lienzos Levante
Number Institution:
Title: New textile, linen + alquidic priming. Lienzos levante. Ref. 30
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 123
Sample condition: Good
pH Final Average: 5,9
DP:

Object Id:	124
Object Type:	Primed new canvas
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Lienzos Levante
Number Institution:	
Title:	New textile, linen + acrylic priming. Lienzos levante. Ref. 30
Author:	
Assigned period:	2000
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	124
Sample condition:	Good
pH Final Average:	6,53
DP:	

Object Id: 125
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB) - Lienzos Levante
Number Institution:
Title: New textile, linen & cotton mixed in the threads (62% cotton, 38 % linen). Lienzos levante. Ref. 45.
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id:

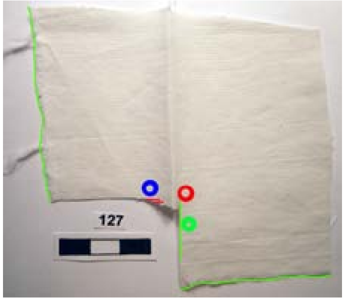
Sample Type: Textile
Sample Id: 125
Sample condition: Good
pH Final Average: 6,16
DP:

Object Id:	126
Object Type:	Bare new textile
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	
Title:	New textile, linen. Aged for 30 days at 90ºC and 60% RH (Leitat)
Author:	
Assigned period:	2000
Vertical thread Id:	Linen
Horizontal thread Id:	Linen
Textile Id:	Linen

Sample Type:	Textile
Sample Id:	126
Sample condition:	Good
pH Final Average:	6,36
DP:	7625

Object Id: 127
Object Type: Bare old household textile
Institution / Donor: Private owner
Number Institution:
Title: Houselhod textile, cotton? From the 1950's. (N. Flos)
Author:
Assigned period: 1975

Vertical thread Id:
Horizontal thread Id:
Textile Id:

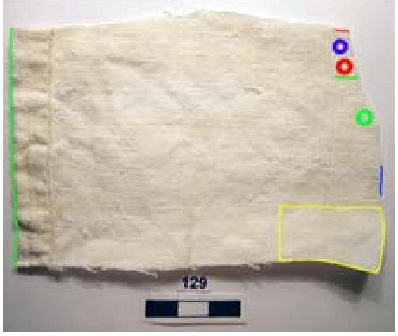


Sample Type: Textile
Sample Id: 127
Sample condition:
pH Final Average: 7,16
DP:

Object Id:	128
Object Type:	Bare old household textile
Institution / Donor:	Private owner
Number Institution:	
Title:	Houselhod textile, linen. From the 19th C. (J. Rosas)
Author:	
Assigned period:	1875
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Textile
Sample Id:	128
Sample condition:	
pH Final Average:	7,59
DP:	

Object Id:	129
Object Type:	Bare old household textile
Institution / Donor:	Private owner
Number Institution:	
Title:	Houselhod textile, linen. From the 19th C. (Marga)
Author:	
Assigned period:	1875
Vertical thread Id:	Ramie
Horizontal thread Id:	Ramie???
Textile Id:	Ramie?



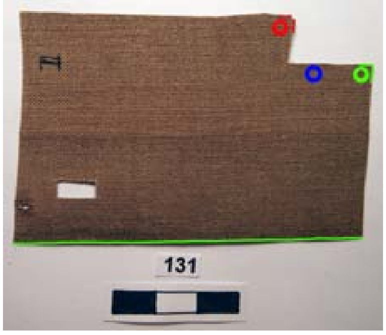
Sample Type:	Textile
Sample Id:	129
Sample condition:	Good
pH Final Average:	6,89
DP:	2705

Object Id: 130
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: New linen (Lino "Uka natur", n. 8 carpeta verda)
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id:

Sample Type: Textile
Sample Id: 130
Sample condition: Good
pH Final Average: 6,42
DP:

Object Id:	131
Object Type:	Primed lose lining
Institution / Donor:	Private owner
Number Institution:	N03712 (Tate Gallery)
Title:	Primed loose lining, (Hylda, Almina and Conway, Children of Asher Wertheimer", Sargent, 1905),
Author:	Sargent
Assigned period:	1925
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

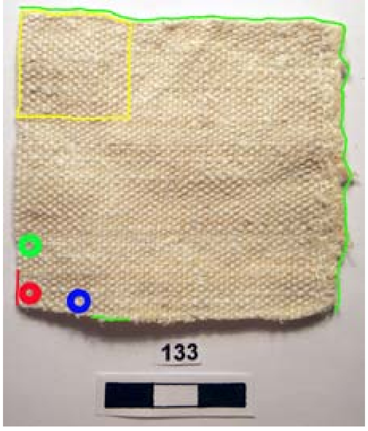


Sample Type:	Deacidified textile
Sample Id:	131
Sample condition:	
pH Final Average:	4,47
DP:	

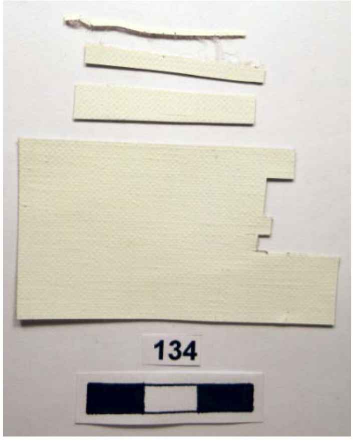
Object Id:	132
Object Type:	Primed lose lining
Institution / Donor:	Private owner
Number Institution:	3584
Title:	Christ in the House of his Parents
Author:	Millais
Assigned period:	1825
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Deacidified textile
Sample Id:	132
Sample condition:	
pH Final Average:	5,87
DP:	

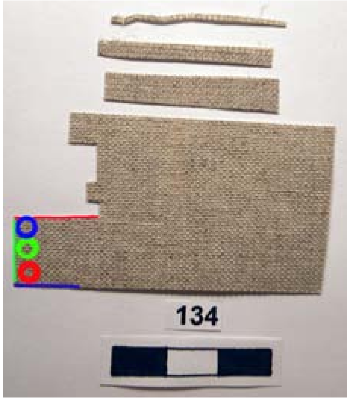
Object Id:	133
Object Type:	Bare new textile
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	
Title:	New hemp (Canem 1, Taller textil de Triste)
Author:	
Assigned period:	2000
Vertical thread Id:	Hemp
Horizontal thread Id:	Hemp
Textile Id:	Hemp



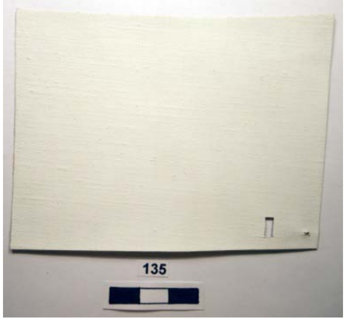
Sample Type:	Textile
Sample Id:	133
Sample condition:	Good
pH Final Average:	6,55
DP:	4942



Object Id:	134
Object Type:	Primed new canvas
Institution / Donor:	Private owner
Number Institution:	
Title:	Primed Russell&Chappel superfine linen, MMC treated (brushed) in 1997.
Author:	
Assigned period:	1975
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	



Sample Type:	Deacidified textile
Sample Id:	134
Sample condition:	Good
pH Final Average:	7,34
DP:	

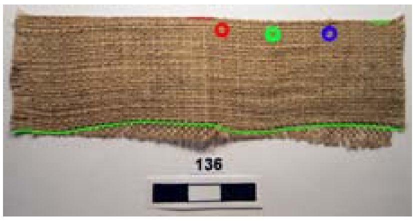


Object Id:	135
Object Type:	Primed new canvas
Institution / Donor:	Private owner
Number Institution:	
Title:	Primed Russell&Chappel superfine linen, Battelle treated in 1997.
Author:	
Assigned period:	1975
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Deacidified textile
Sample Id:	135
Sample condition:	Good
pH Final Average:	8,71
DP:	

Object Id: 136
Object Type: Glue lining
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Old lining clean (linen or hemp), (Mostrari CR, n.4)
Author:
Assigned period: 1900

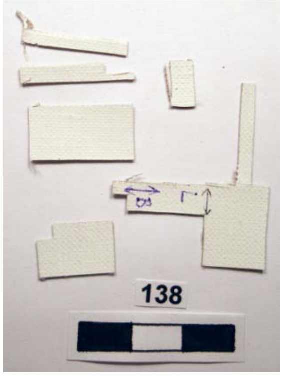
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 136
Sample condition:
pH Final Average: 6,74
DP:

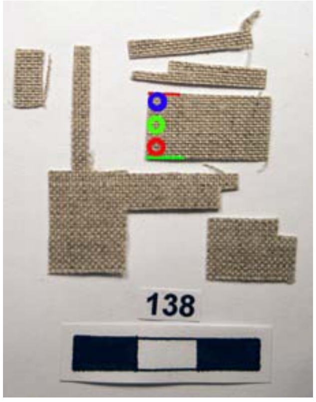
Object Id:	137
Object Type:	Primed lose lining
Institution / Donor:	Private owner
Number Institution:	
Title:	Primed loose lining, (Millais, 1849-1850), MMC treated (brushed) in 1997.
Author:	Millais
Assigned period:	1825
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	

Sample Type:	Deacidified textile
Sample Id:	137
Sample condition:	
pH Final Average:	5,58
DP:	



Object Id: 138
Object Type: Primed new canvas
Institution / Donor: Private owner
Number Institution:
Title: Primed Russell&Chappel superfine linen, untreated. From 1997.
Author:
Assigned period: 1975

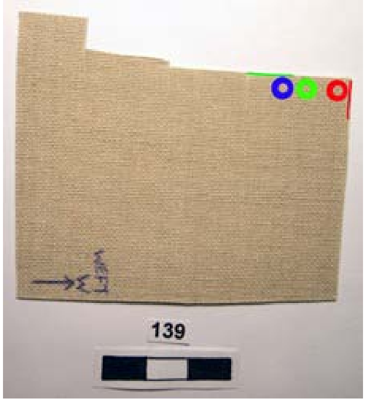
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Textile
Sample Id: 138
Sample condition:
pH Final Average: 7,33
DP:

Object Id: 139
Object Type: Primed new canvas
Institution / Donor: Private owner
Number Institution:
Title: Linen canvas treated with MgHCO3. Then sized. Then chalk/glue priming. Then Cremnitz white
Author:
Assigned period: 1975

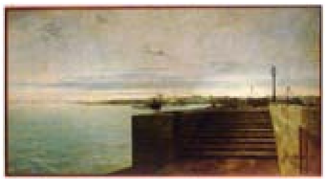
Vertical thread Id:
Horizontal thread Id:
Textile Id:



Sample Type: Deacidified textile
Sample Id: 139
Sample condition:
pH Final Average: 7,33
DP:

Object Id:	140
Object Type:	Bare new textile
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	
Title:	Hemp Núria Pedragosa
Author:	
Assigned period:	2000
Vertical thread Id:	
Horizontal thread Id:	
Textile Id:	Hemp

Sample Type:	Textile
Sample Id:	140
Sample condition:	
pH Final Average:	
DP:	



Object Id: 141
Object Type: Painting
Institution / Donor: Museu Marítim de Barcelona (Autoritat Portuaria de Barcelona)
Number Institution:
Title: El port de Barcelona
Author: Eliseu Meifren
Assigned period: 1875

Vertical thread Id: Linen
Horizontal thread Id: Linen
Textile Id: Linen

Sample Type: Textile
Sample Id: 141
Sample condition:
pH Final Average: 5,03
DP: 760

Object Id: 142
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Hemp 2 Triste
Author:
Assigned period: 2000

Vertical thread Id: Hemp
Horizontal thread Id: Hemp
Textile Id: Hemp

Sample Type: Textile
Sample Id: 142
Sample condition:
pH Final Average:
DP:

Object Id: 143
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Canem 1 Adela web
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id: Hemp

Sample Type: Textile
Sample Id: 143
Sample condition:
pH Final Average:
DP:

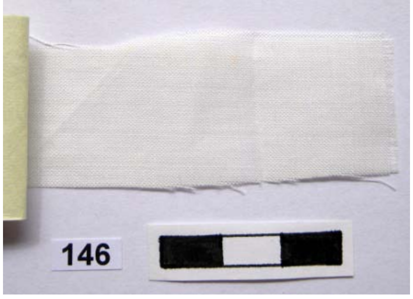
Object Id: 144
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Canem 2 Adela web
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id: Hemp

Sample Type: Textile
Sample Id: 144
Sample condition:
pH Final Average:
DP:

Object Id:	145
Object Type:	Lining
Institution / Donor:	Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:	
Title:	Strip lining from Bodegó Projectes
Author:	
Assigned period:	1950
Vertical thread Id:	Cotton
Horizontal thread Id:	Linen
Textile Id:	Linen & Cotton

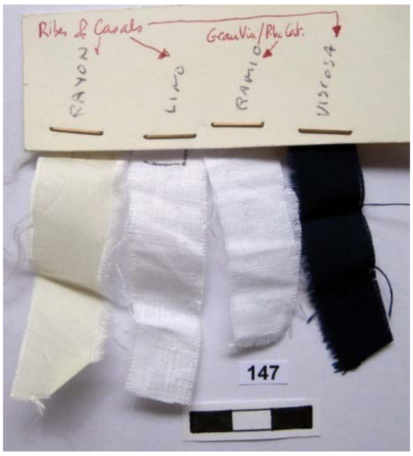
Sample Type:	Textile
Sample Id:	145
Sample condition:	
pH Final Average:	5,33
DP:	



Object Id: 146
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Ramie- JB
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id: Ramie

Sample Type: Textile
Sample Id: 146
Sample condition:
pH Final Average:
DP:



Object Id: 147
Object Type: Bare new textile
Institution / Donor: Secció de Conservació-Restauració, Facultat de Belles Arts (UB)
Number Institution:
Title: Ramie-Adela (Ribes i Casals)
Author:
Assigned period: 2000

Vertical thread Id:
Horizontal thread Id:
Textile Id: Ramie

Sample Type: Textile
Sample Id: 147
Sample condition:
pH Final Average:
DP:

Annex II - Measuring pH

This annex contains both the working procedure for the glass combination microelectrode probe and the ISFET probe used for all the pH measurements done in Chapter 2.2. They are recollected here as a guide for future work to be done.

1- Working procedure for the glass combination microelectrode

The following instructions are to be followed when working with the glass combination microelectrode.

Setting the stage

- Place a clean Melinex on top of a paper towel. Tape everything on the table or onto a flat tile so it doesn't move around. The paper towel will give some cushion on which to rest the electrode and make it easier for its tip to be covered by the small drop of solution.

- Get a stand with a clamp where to place the electrode while doing the measurement of the drop of water. The probe doesn't need to be clamped to it, it can just be leaning against it. It doesn't matter if the probe is not exactly perpendicular to the table when taking the measurement, it can be slightly tilted. The important thing is that the tip of the electrode, the round ball that measures the pH, is all covered by the solution.

Measuring the pH

- The hole in the electrode should be covered by the transparent rubber band during storage and uncovered when using the electrode.

- Calibrate the ph meter every time you switch it on. Check also with one of the buffering solutions that it is working alright every hour or so. If you were to change probes, do so everytime you change the probe too. If you are calibrating with the solution of pH 4 and you get a value between 3.8 and 4.2, you should consider it ok.

- Calibration with the two solutions should be done in the same way that we will measure pH, that is: taking 4 μL of the buffered solution with a new pipette tip, placing it on the Melinex, placing the electrode on top of it… etc.

- Take 4 μL of the solution to be measured with a pipette an place it on the Melinex. Place the electrode so that the measuring bulb is completely surrounded by the water. Wait until the reading is stable.

- Once finished, rinse the electrode with distilled water by putting it in a beaker with water. When using it again, wipe the excess of water with a paper towel so that this water is not diluting the drop you want to measure.

- Wipe the measured drop out of the Melinex with a paper towel. Take a new tip for the pipette and place your next drop to be measured.

- We just leave the pH meter on while we are taking our readings. If we need to switch it off at some point, we have to calibrate it again when we switch it on again.

- With the glass electrode, we have to remember to manually add the ambient temperature on the meter. (This probe doesn't have a temperature sensor like the ISFET one does).

Storage of the electrode

- Glass electrodes have a short life. One should be bought for each large project such as this one (about 500 measurements).

- The blue sponge in the tube should always have some of the liquid that it comes with. If it gets dry, add some of the solution provided by the manufacturer to it.

- Glass electrodes are very easy to break. What usually breaks is not so much the probe along its length as one would think, but the measuring small bulb in the end.

- If possible take three measurements of each sample.

2- Working procedure for the ISFET probe

The following instructions are to be followed when working with the ISFET probe and the IQ160 pH meter.

Calibration

The pH meter is usually set to a 2 point calibration (pH 7 & pH 4 by default). It is always better to use a two point calibration, than a three point calibration. When measuring acidic samples we should calibrate with pH 7 and pH 4. When measuring alkaline samples we should calibrate with pH 7 and pH 10.

How to calibrate the IQ160 pH meter

- Switch on the pH-metre

- Press CAL. The CAL sign (right bottom corner) will start flashing. Place the probe inside buffer 7.

- Then press Enter to tell the pH meter that it can calibrate for buffer 7. The pH 7 in the centre of the screen will start flashing until it is ready for the next buffer. Then the CAL sign will start flashing again and it will ask for pH 4.

- Clean the probe (rinsing it with distilled water and drying it) and place it inside the buffer 4. Press Enter to tell the pH meter that it can calibrate against the buffer pH 4. It will beep once it finishes and will be ready to measure pH.

- After calibration one can re-check the values for buffers pH 7 and pH 4 as if they were unknown samples. If one gets 3.90 to 4.09 for pH 4 and 6.90 and 7.09 for pH 7, this can be considered ok. If one gets a larger difference (it can happen occasionally), then calibrate again.

- After having measured 20 or 30 samples it is good practice to re-check buffers pH 4 and 7. It is usually found that pH 7 is more off than pH 4. If one gets values of 7.13 or more it is better to calibrate again.

- It would be good to calibrate the pH meter every one or two hours if it has been continuously functioning.

Storage of the ISFET electrode

- Unlike the glass pH meters, ISFET probes should be kept dry as much as possible (in between readings and overnight), since if left in water its life is shortened. In between readings, rinse the probe with distilled water and dry it with a clean piece of paper towel (it is a good idea to cut strips of paper towel and use a new one each time, so that cross contamination is avoided).

Annex 3 – Condition Assessment Panel results

This annex contains the list of samples each panellist received to do the Condition Assessment Panel expalined in Chapter 4 and the particular results each one of them gave for each sample.

1- Which samples were tested by who and in which order

Together with the test reported in this PhD thesis with textiles, another test to be done with threads from the same samples was also sent out. In general, both a piece of canvas and a set of six threads were sent out. Were only the piece of canvas was sent out, this is indicated by a "C". Were only the set of threads was sent out, this is indicated by "T" (Figure 1).

No threads were available for samples H4 and A22. H4 because it was so degraded, it was not possible to extract threads after artificial degradation. Sample A22 belonged to my grandfather's painting and the threads broke if pulled away.

The numbers indicate the order in which the samples were given to conservators and presumably this is the order in which they carried out the test. The samples were not ordered by DP but mixed according to it on purpose.

The acronyms for each panellist are:

NP: Núria Pedragosa
MT: Maite Toneu, Pau Claramonte (fellow) and Nadir López (fellow)
P: Maite Jover and Lucía Martínez
IC: Irene Civil
MO: Marta Oriola
GC: Gema Campo
SH: Stephen Hackney
CY: Christina Young
AB: Anne Bacon
JD: Jim Devenport
MS: Matija Strlic
JFH: Jean François Hulot
Er: Erminio Signorini
CKA: Cecil Kraup Andersen
ES: Eileen Sullivan
KB: Kenneth Bé
EK: Eun-Jin Kim

Sample	DP value	SH	CY	ES	EK	P	NP	MT	MS	Er	IC	AB	KB	JFH	CKA	JD	MO	GC
H4	258	7, C				8, C	8, C										32	36
C13 (102)	317	1										1		1			1	1
C17 (109)	337		1				4										2	2
D4	378			1				4			1						5	5
H3	379				1				4, T	1			1				11	11
B13 (102)	386	4				1					3		6				3	3
C19 (112)	415		4		6		1					4		4	1	1	12	12
B17 (109)	440			4				1									25	13
B19 (112)	469	2			4	5			1, T	4			4			3	4	4
A11	485										7, T			7, T			28	14
D3	506		2			6	5							5			6	6
105	538	8, C		7, C				7	2, T	2	2		5		4		17	34
C21 (114)	573	6		2				5									16	15
110	608		8, C		7, C		7		8, C	6		2		6	6	5	32	35
A19 (112)	631			6	2	4			5				2	2	5	6	7	7
A20 (113)	646	5	6			2			9, C		5					4	14	16
104	653		7, C	8, C					7, T	5		5			2		15	33
A22	661				8, C	7, C	7, C	7, C										
B21 (114)	691		5		5		2										22	17
A15 (106)	746			5				2			6		3			2	24	18
A10	903											7, T	7, T				8	8
A21 (114)	969	3					6			3		6					30	19
A13 (102)	1064		3					6									26	20
C14 (103)	1077			3					6, T			3					27	21
H2	109				3												9	9

	7																	
H23	**1161**					3											29	22
B14 (103)	**1181**						3								3		10	10
A17(109)	**1371**							3						3			13	23
D23	**1378**																31	24
H1	**1691**																18	25
A3	**1812**																19	26
D1	**2111**																23	27
A14 (103)	**2136**								3, T		4						20	28
A23	**2705**																35	29
A4	**5674**																34	30
A1	**6614**																33	31
A2	**8310**																21	32

Figure 1. Table indicating which samples (ordered by DP value) were tested by who. Fewer high DP values were send out since the interest was in the lower DP range.

2- Specific results that each panellist gave for the Condition Assessment Panel test

Sample	DP	Category number	Conservator
H4	258	1	GC
H4	258	1	MO
H4	258	1	SH
H4	258	1	NP
H4	258	1	P
C13 (102)	317	1	GC
C13 (102)	317	1	MO
C13 (102)	317	1	AB
C13 (102)	317	1	JFH
C13 (102)	317	2	SH
C17 (109)	337	1	GC
C17 (109)	337	1	MO
C17 (109)	337	1	NP
C17 (109)	337	1	CY
D4	378	1	GC
D4	378	1	MO
D4	378	1	ES
D4	378	1	MT
D4	378	1	IC
H3	379	1	GC
H3	379	1	MO
H3	379		MS
H3	379	1	EK
H3	379	1	P
H3	379	1	KB
H3	379	2	Er
B13 (102)	386	1	GC
B13 (102)	386	1	MO
B13 (102)	386	1	SH
B13 (102)	386	1	IC
B13 (102)	386	1	KB
C19 (112)	415	1	GC
C19 (112)	415	1	MO
C19 (112)	415	1	EK
C19 (112)	415	1	CKA
C19 (112)	415	1	NP
C19 (112)	415	1	JFH
C19 (112)	415	1	CY
C19 (112)	415	1	JD
C19 (112)	415	2	AB
B17 (109)	440	1	GC
B17 (109)	440	1	ES
B17 (109)	440	2	MO
B17 (109)	440	3	MT
B19 (112)	469	1	GC
B19 (112)	469	1	P
B19 (112)	469	1	Er
B19 (112)	469	1	KB
B19 (112)	469	2	MO
B19 (112)	469	2	EK
B19 (112)	469	3	SH
B19 (112)	469	3	JD
A11	485	1	MO
A11	485	2	GC
D3	506	2	MO
D3	506	2	CKA
D3	506	2	NP
D3	506	2	JFH
D3	506	2	CY
D3	506	3	P
D3	506	3	GC
105	538	1	ES
105	538	2	CKA
105	538	2	GC

105	538	2	MO
105	538	3	IC
105	538	4	Er
105	538	4	KB
105	538	4	SH
C21 (114)	573	2	GC
C21 (114)	573	2	ES
C21 (114)	573	3	MO
C21 (114)	573	3	SH
C21 (114)	573	3	MT
110	608	1	GC
110	608	1	MO
110	608	1	CKA
110	608	1	AB
110	608	1	JFH
110	608	1	MS
110	608	1	EK
110	608	1	CY
110	608	2	NP
110	608	3	Er
110	608	3	JD
A19 (112)	631	2	P
A19 (112)	631	2	JFH
A19 (112)	631	2	MS
A19 (112)	631	3	GC
A19 (112)	631	3	MO
A19 (112)	631	3	EK
A19 (112)	631	2	ES
A19 (112)	631	3	CKA
A19 (112)	631	4	KB
A19 (112)	631	4	JD
A20 (113)	646	1	MS
A20 (113)	646	2	P
A20 (113)	646	2	CY
A20 (113)	646	2	GC
A20 (113)	646	2	MO
A20 (113)	646	3	SH
A20 (113)	646	3	IC

A20 (113)	646	4	JD
104	653	2	MO
104	653	2	CKA
104	653	2	CY
104	653	3	GC
104	653	3	AB
104	653	3	ES
104	653	4	Er
A22	661	1	MO
A22	661	1	MT
A22	661	2	GC
A22	661	2	EK
A22	661	3	NP
A22	661	3	P
B21 (114)	691	2	NP
B21 (114)	691	3	GC
B21 (114)	691	3	MO
B21 (114)	691	3	CY
B21 (114)	691	4	EK
A15 (106)	746	2	MO
A15 (106)	746	2	ES
A15 (106)	746	3	GC
A15 (106)	746	3	IC
A15 (106)	746	3	KB
A15 (106)	746	4	JD
A15 (106)	746	4	MT
A10	903	2	GC
A10	903	2	MO
A21 (114)	969	3	NP
A21 (114)	969	4	GC
A21 (114)	969	4	MO
A21 (114)	969	4	SH
A21 (114)	969	4	Er
A21 (114)	969	4	AB
A13 (102)	1064	2	CY

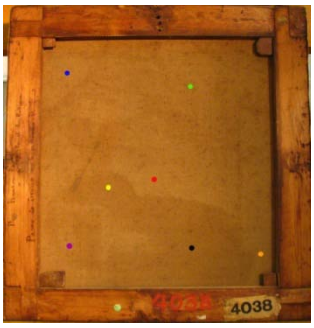
A13 (102)	1064	3	GC
A13 (102)	1064	3	MO
A13 (102)	1064	4	MT
C14 (103)	1077	3	MO
C14 (103)	1077	4	GC
C14 (103)	1077	4	ES
C14 (103)	1077	4	AB
H2	1097	4	GC
H2	1097	4	MO
H2	1097	4	EK
H23	1161	4	GC
H23	1161	4	MO
H23	1161	4	P
B14 (103)	1181	3	NP
B14 (103)	1181	4	GC
B14 (103)	1181	4	MO
B14 (103)	1181	4	CKA
A17(109)	1371	3	MO
A17(109)	1371	3	JFH
A17(109)	1371	4	GC
A17(109)	1371	4	MT
D23	1378	4	GC
D23	1378	4	MO
H1	1691	4	GC
H1	1691	4	MO
A3	1812	4	GC
A3	1812	4	MO
D1	2111	4	GC
D1	2111	4	MO
A14 (103)	2136	4	GC
A14 (103)	2136	4	MO
A14 (103)	2136	4	IC
A23	2705	4	GC
A23	2705	4	MO
A4	5674	4	GC
A4	5674	4	MO
A1	6614	4	GC
A1	6614	4	MO
A2	8310	4	GC
A2	8310	4	MO

Figure 2. List of categories each panellist assigned the different samples. In grey samples from new textiles, in white samples from old glue linings.

Annex IV - Case Studies Catalogue

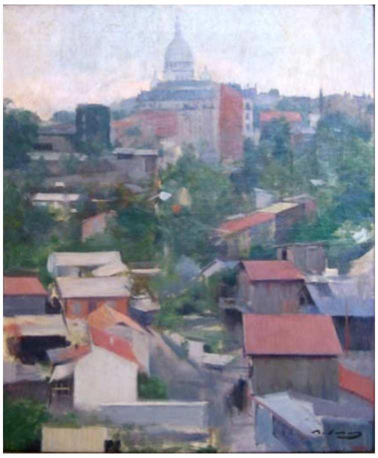
This annex collects all the predicted pH and DP values for the 33 MNAC masterpieces from Chapter 5 as well as the fibre type identification. All this information was obtained from the NIR spectra collected from the reverse in different areas that are marked on the verso pictures. The pH and DP averages of each spot are given for each painting in the first grid. The “Notes” field describes whether each particular location was considered to be a “regular canvas” area or a “darker” area. Below, the average pH and DP for “regular canvas” areas (in **green**) and for “darker” areas (in **red**) as well as the SD are given for each painting. In **black** the final average DP and pH for all the locations in that particular painting is given. Fibre identification with the certainty percentage in brakets is given at the end of each record.

Object Id:	155
Institution:	MNAC
Number Institution:	004038
Title:	Estudi
Author:	Ramon Casas
Date:	Circa 1899
Observations:	

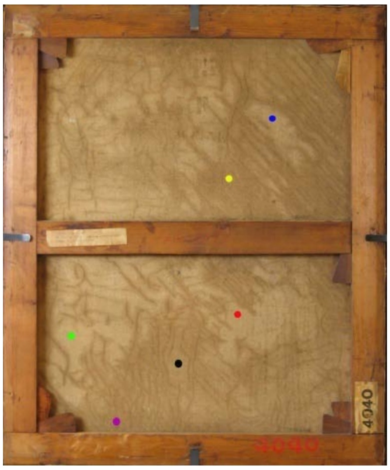


NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.18	990	Regular canvas
b (green)	4.94	377	Regular canvas
c (blue)	4.92	799	Regular canvas
d (yellow)	5.09	796	Darker (oil migration)
e (black)	4.95	527	Darker (oil migration)
f (purple)	5.19	975	Darker (oil migration)
g (orange)	5.16	785	Regular canvas

	Value	SD
Predicted pH average Regular canvas:	5.06	0.14
Predicted pH average Darker:	5.08	0.12
Predicted DP average Regular canvas:	738	258
Predicted DP average Darker:	766	226
Predicted pH average Painting:	5.06	0.12
Predicted DP average Painting:	750	225
Likely Fibre Id:	Linen (85%)	



Object Id:	156
Institution:	MNAC
Number Institution:	004040
Title:	Le Sacré Coeur, Montmartre
Author:	Ramon Casas
Date:	1891
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.22	138	Regular canvas
b (green)	5.20	641	Regular canvas
c (blue)	4.83	510	Regular canvas
d (yellow)	5.14		Darker (varnish)
e (black)	5.15	396	Darker (varnish)
f (purple)	5.21	290	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.08	0.22
Predicted pH average Darker:	5.17	0.03
Predicted DP average Regular canvas:	430	261
Predicted DP average Darker:	343	75
Predicted pH average Painting:	5.13	0.15
Predicted DP average Painting:	395	194
Likely Fibre Id:	Linen (80%)	

Object Id: 157
Institution: MNAC
Number Institution: 004033
Title: Pati de l'antiga presó de Barcelona (Pati dels "Corders")
Author: Ramon Casas
Date: Circa 1894
Observations:

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.25	1225	Regular canvas
b (green)	5.04	1104	Regular canvas
c (blue)	5.03	974	Regular canvas
d (yellow)	5.09	812	Darker
e (black)	5.12	766	Darker
f (purple)	4.96	641	Darker

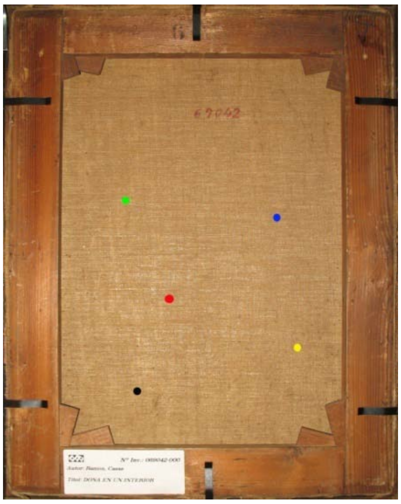
	Value	SD
Predicted pH average Regular canvas:	5.11	0.12
Predicted pH average Darker:	5.06	0.08
Predicted DP average Regular canvas:	1101	126
Predicted DP average Darker:	740	88
Predicted pH average Painting:	5.08	0.15
Predicted DP average Painting:	920	221
Likely Fibre Id:	Linen (65%)	

Object Id: 158
Institution: MNAC
Number Institution: 04003
Title: La riallera
Author: Santiago Rusiñol
Date: 1894
Observations:

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.19	1008	Regular canvas
b (green)	4.97	692	Regular canvas
c (blue)	5.07	868	Regular canvas
d (yellow)	5.20	955	Darker (oil migration)
e (black)	5.38	928	Darker (oil migration)
f (purple)	5.19	984	Darker (oil migration)

	Value	SD
Predicted pH average Regular canvas:	5.07	0.11
Predicted pH average Darker:	5.26	0.11
Predicted DP average Regular canvas:	856	159
Predicted DP average Darker:	956	28
Predicted pH average Painting:	5.17	0.14
Predicted DP average Painting:	906	116
Likely Fibre Id:	Linen (60%)	

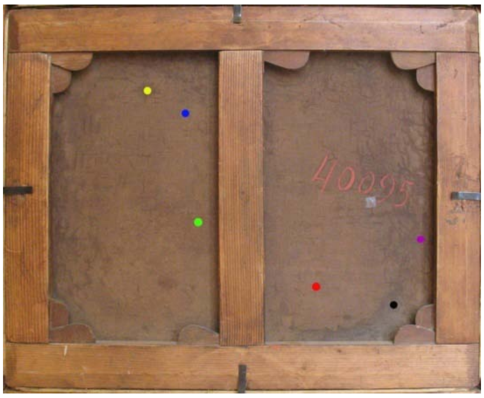
Object Id: 159
Institution: MNAC
Number Institution: 069042
Title: Dona en un interior
Author: Ramon Casas
Date: 1890
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.15	827	Regular canvas
b (green)	5.25	882	Regular canvas
c (blue)	5.19	663	Regular canvas
d (yellow)	5.34	862	Regular canvas
e (black)	5.25	953	Regular canvas

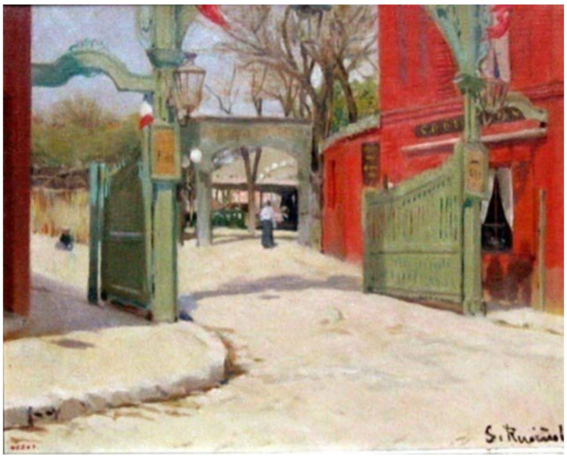
	Value	SD
Predicted pH average Regular canvas:	5.24	0.07
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	838	108
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.24	0.07
Predicted DP average Painting:	838	108
Likely Fibre Id:	Linen (65%)	

Object Id: 160
Institution: MNAC
Number Institution: 040095
Title: Jardí de Montmartre
Author: Santigo Rusiñol
Date: 1890-1891
Observations:

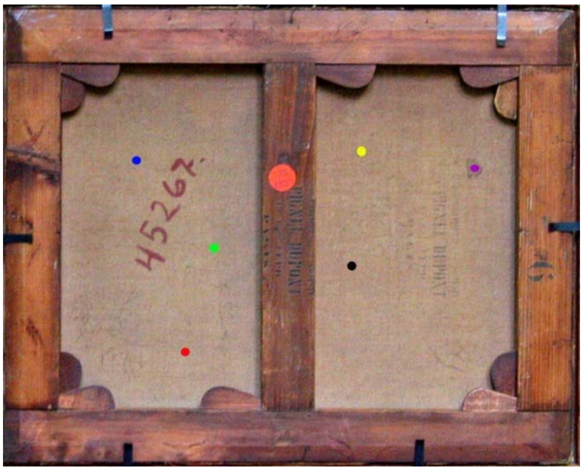


NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.83	504	Regular canvas
b (green)	4.81	222	Regular canvas
c (blue)	4.55	405	Regular canvas
d (yellow)	4.48		Darker
e (black)	5.11	619	Darker
f (purple)	4.85	344	Darker

	Value	SD
Predicted pH average Regular canvas:	4.73	0.16
Predicted pH average Darker:	4.81	0.32
Predicted DP average Regular canvas:	377	143
Predicted DP average Darker:	481	195
Predicted pH average Painting:	4.77	0.23
Predicted DP average Painting:	419	152
Likely Fibre Id:	Linen Possibly combination with jute?	



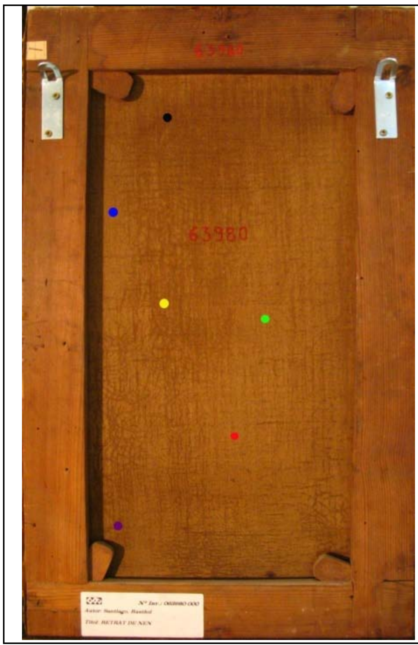
Object Id:	161
Institution:	MNAC
Number Institution:	045267º
Title:	Entrada al parc del Moulin de la Galette
Author:	Santigo Rusiñol
Date:	1891
Observations:	Pignel Dupont stamp



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.08	278	Regular canvas
b (green)	4.84	567	Regular canvas
c (blue)	4.68	560	Regular canvas
d (yellow)	4.73	655	Regular canvas
e (black)	4.75	296	Regular canvas
f (purple)	5.03	700	Darker (Stain)

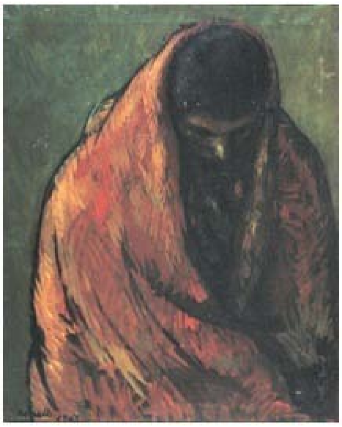
	Value	SD
Predicted pH average Regular canvas:	4.81	0.16
Predicted pH average Darker:	5.03	--
Predicted DP average Regular canvas:	471	172
Predicted DP average Darker:	700	--
Predicted pH average Painting:	4.85	0.17
Predicted DP average Painting:	509	180
Likely Fibre Id:	Linen (85%)	

Object Id: 162
Institution: MNAC
Number Institution: 063980
Title: Retrat de nen
Author: Santigo Rusiñol
Date: Circa 1893-1895
Observations:

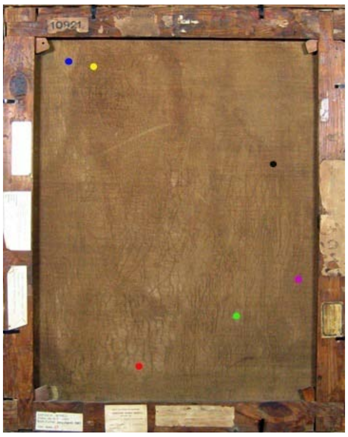


NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.04	634	Regular canvas
b (green)	5.09	594	Regular canvas
c (blue)	4.90	763	Regular canvas
d (yellow)	5.12	422	Darker (varnish)
e (black)	4.88	386	Darker (varnish)
f (purple)	5.42	756	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.01	0.10
Predicted pH average Darker:	5.14	0.27
Predicted DP average Regular canvas:	663	88
Predicted DP average Darker:	521	204
Predicted pH average Painting:	5.07	0.19
Predicted DP average Painting:	592	161
Likely Fibre Id:	Linen (99%)	



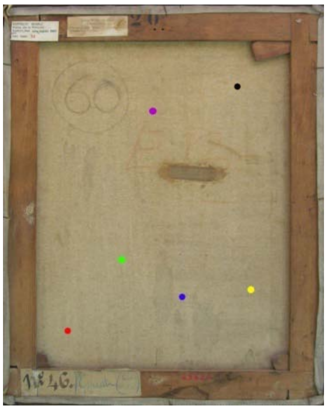
Object Id: 163
Institution: MNAC
Number Institution: 010921
Title: Gitana Jove
Author: Isidre Nonell
Date: 1903
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.21	732	Regular canvas
b (green)	5.07	803	Regular canvas
c (blue)	5.06	662	Regular canvas
d (yellow)	5.08	480	Darker (varnish)
e (black)	5.09	508	Darker (varnish)
f (purple)	5.32	765	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.11	0.08
Predicted pH average Darker:	5.16	0.13
Predicted DP average Regular canvas:	732	70
Predicted DP average Darker:	584	157
Predicted pH average Painting:	5.14	0.10
Predicted DP average Painting:	658	136
Likely Fibre Id:	Linen (93%)	

Object Id:	164
Institution:	MNAC
Number Institution:	065620
Title:	Gracieta
Author:	Isidre Nonell
Date:	1907
Observations:	



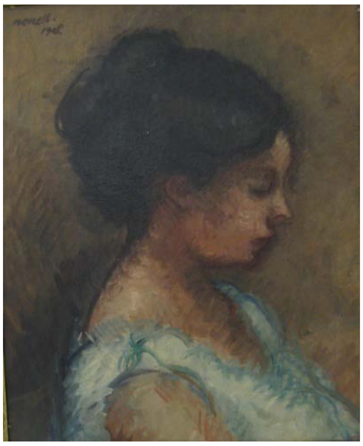
NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.55		Regular canvas
b (green)	5.78		Regular canvas
c (blue)	5.77		Regular canvas
d (yellow)	5.43	681	Darker
e (black)	5.49	426	Darker
f (purple)	5.60	556	Darker

	Value	SD
Predicted pH average Regular canvas:	5.70	0.13
Predicted pH average Darker:	5.51	0.08
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	554	127
Predicted pH average Painting:	5.06	0.14
Predicted DP average Painting:	554	127
Likely Fibre Id:	Cotton	

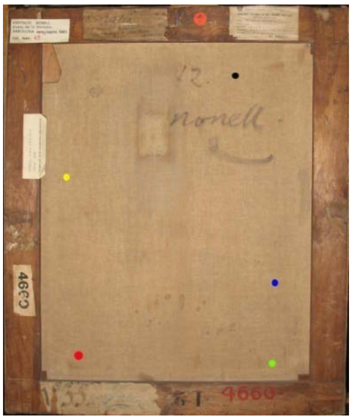
Object Id:	165
Institution:	MNAC
Number Institution:	010926
Title:	La Pilar
Author:	Isidre Nonell
Date:	1907
Observations:	

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.13	918	Regular canvas
b (green)	5.22	645	Regular canvas
c (blue)	5.29	841	Regular canvas
d (yellow)	5.26	899	Darker (varnish)
e (black)	5.23	920	Darker (varnish)
f (purple)	5.35	822	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.21	0.08
Predicted pH average Darker:	5.28	0.06
Predicted DP average Regular canvas:	801	140
Predicted DP average Darker:	881	52
Predicted pH average Painting:	5.25	0.08
Predicted DP average Painting:	841	104
Likely Fibre Id:	Linen (74%)	



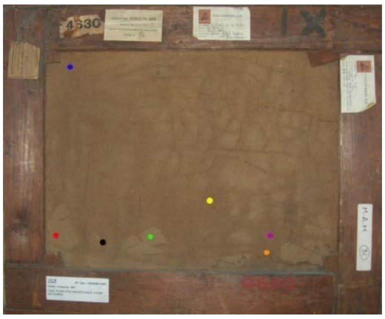
Object Id:	166
Institution:	MNAC
Number Institution:	004660
Title:	Júlia
Author:	Isidre Nonell
Date:	1908
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	6.02		Regular canvas
b (green)	5.75		Regular canvas
c (blue)	5.66		Regular canvas
d (yellow)	5.74		Regular canvas
e (black)	5.48		Regular canvas

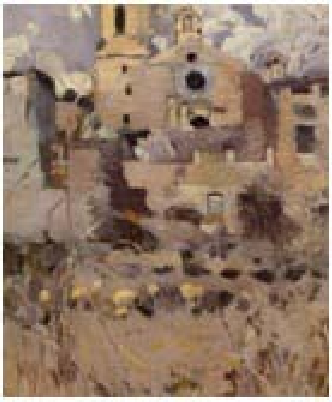
	Value	SD
Predicted pH average Regular canvas:	5.73	0.19
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.73	0.19
Predicted DP average Painting:	--	--
Likely Fibre Id:	Cotton	

Object Id:	167
Institution:	MNAC
Number Institution:	004630
Title:	Paisatge (Maspujols. Camp de Tarragona)
Author:	Joaquim Mir
Date:	1907-1910
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.07	599	Regular canvas
b (green)	5.13	657	Regular canvas
c (blue)	4.81	415	Regular canvas
d (yellow)	4.91	400	Darker (varnish)
e (black)	4.89	567	Darker (varnish)
f (purple)	4.92	391	Darker (varnish)
g (orange)	4.75	550	Darker (Tideline)

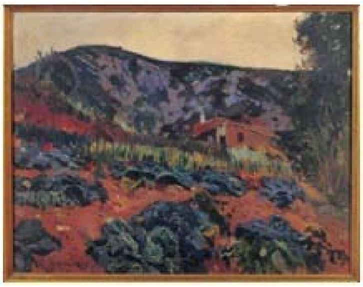
	Value	SD
Predicted pH average Regular canvas:	5.00	0.17
Predicted pH average Darker:	4.87	0.08
Predicted DP average Regular canvas:	557	126
Predicted DP average Darker:	477	94
Predicted pH average Painting:	4.92	0.13
Predicted DP average Painting:	511	108
Likely Fibre Id:	Linen (69%)	



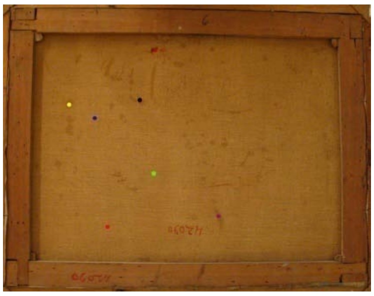
Object Id: 168
Institution: MNAC
Number Institution: 004631
Title: Paisatge
Author: Joaquim Mir
Date: 1907-1910
Observations:

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.77		Regular canvas
b (green)	4.96		Regular canvas
c (blue)	5.06	-94	Regular canvas
d (yellow)	5.18		Darker
e (black)	4.93		Darker
f (purple)	4.98		Darker
g (orange)	5.37		Darker (Stain)

	Value	SD
Predicted pH average Regular canvas:	4.93	0.15
Predicted pH average Darker:	5.12	0.20
Predicted DP average Regular canvas:	-94	--
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.04	0.19
Predicted DP average Painting:	-94	--
Likely Fibre Id:	Linen, possibly combination with hemp. Possible combination with cotton?	



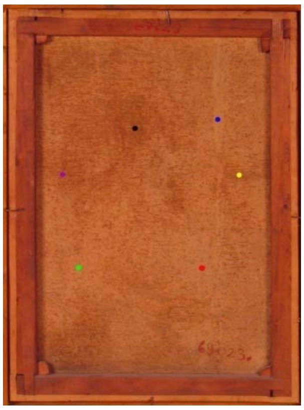
Object Id: 169
Institution: MNAC
Number Institution: 042090
Title: Hort amb casa de pagès
Author: Joaquim Mir
Date:
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.42		Regular canvas
b (green)	5.51		Regular canvas
c (blue)	5.38		Regular canvas
d (yellow)	5.30	1217	Daker (Stain (oil?))
e (black)	5.22	1256	Daker (Stain (oil?))
f (purple)	5.30	948	Daker (Stain (oil?))

	Value	SD
Predicted pH average Regular canvas:	5.44	0.07
Predicted pH average Darker:	5.27	0.05
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	1141	168
Predicted pH average Painting:	5.36	0.10
Predicted DP average Painting:	1141	168
Likely Fibre Id:	Linen (84%)	

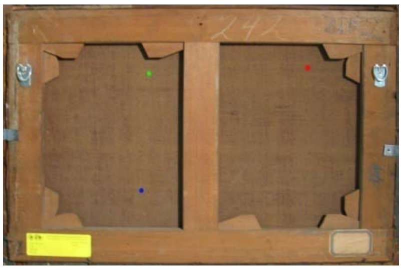
Object Id:	170
Institution:	MNAC
Number Institution:	069023
Title:	Llegint el diari
Author:	Francesc Gimeno
Date:	1886
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.95	-60	Regular canvas
b (green)	4.90	293	Regular canvas
c (blue)	5.41	439	Regular canvas
d (yellow)	4.95	235	Darker
e (black)	4.97	-43	Darker
f (purple)	4.82	51	Darker

	Value	SD
Predicted pH average Regular canvas:	5.09	0.10
Predicted pH average Darker:	4.91	--
Predicted DP average Regular canvas:	224	211
Predicted DP average Darker:	81	--
Predicted pH average Painting:	5.00	0.10
Predicted DP average Painting:	152	201
Likely Fibre Id:	Cotton	

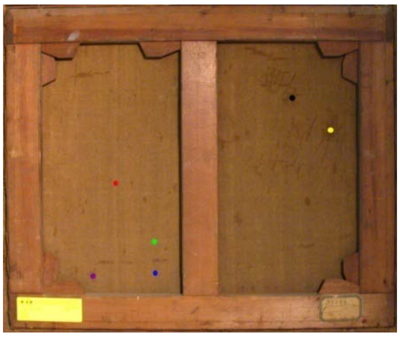
Object Id: 171
Institution: MNAC
Number Institution: 039143
Title: Gitanes
Author: Joaquim Sunyer
Date: 1906
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.48	685	Regular canvas
b (green)	5.40	968	Regular canvas
c (blue)	5.61	555	Regular canvas

	Value	SD
Predicted pH average Regular canvas:	5.50	0.10
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	736	211
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.50	0.10
Predicted DP average Painting:	736	211
Likely Fibre Id:	Linen (99%)	

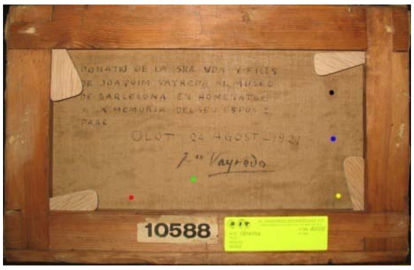
Object Id:	172
Institution:	MNAC
Number Institution:	039144
Title:	Gitanes
Author:	Joaquim Sunyer
Date:	1907
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.25	825	Regular canvas
b (green)	5.24	882	Regular canvas
c (blue)	5.56	951	Regular canvas
d (yellow)	5.32	898	Darker (varnish)
e (black)	5.21	876	Darker (varnish)
f (purple)	5.37	1283	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.35	0.18
Predicted pH average Darker:	5.30	0.08
Predicted DP average Regular canvas:	886	63
Predicted DP average Darker:	1019	229
Predicted pH average Painting:	5.33	0.13
Predicted DP average Painting:	952	167
Likely Fibre Id:	Linen (87%)	

Object Id: 173
Institution: MNAC
Number Institution: 010588
Title: Nens jugant (estudi)
Author: Joaquim Vayreda
Date: 1889
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.28	609	Regular canvas
b (green)	5.28	485	Regular canvas
c (blue)	5.14	495	Regular canvas
d (yellow)	5.39	343	Darker
e (black)	5.22	734	Darker

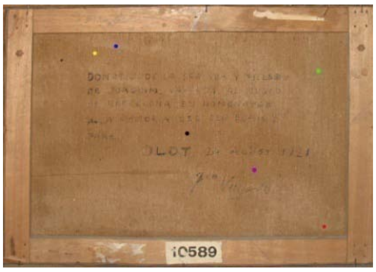
	Value	SD
Predicted pH average Regular canvas:	5.23	0.08
Predicted pH average Darker:	5.31	0.12
Predicted DP average Regular canvas:	530	69
Predicted DP average Darker:	538	277
Predicted pH average Painting:	5.26	0.09
Predicted DP average Painting:	533	147
Likely Fibre Id:	Linen (76%)	

Object Id:	174
Institution:	MNAC
Number Institution:	010593
Title:	Camp de fajol (apunt)
Author:	Joaquim Vayreda
Date:	1892
Observations:	

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.33	844	Regular canvas
b (green)	5.26	619	Regular canvas
c (blue)	5.33	546	Regular canvas
d (yellow)	5.34	508	Darker (varnish)
e (black)	5.06	310	Darker (varnish)
f (purple)	5.16	555	Darker (varnish)

	Value	SD
Predicted pH average Regular canvas:	5.31	0.04
Predicted pH average Darker:	5.19	0.14
Predicted DP average Regular canvas:	670	155
Predicted DP average Darker:	458	130
Predicted pH average Painting:	5.25	0.11
Predicted DP average Painting:	564	173
Likely Fibre Id:	Linen (100%)	

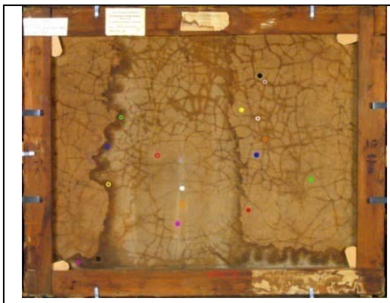
Object Id: 175
Institution: MNAC
Number Institution: 010589
Title: La roureda
Author: Joaquim Vayreda
Date: 1892
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.63	990	Regular canvas
b (green)	5.50	1106	Regular canvas
c (blue)	5.38	971	Regular canvas
d (yellow)	5.28	867	Darker
e (black)	5.37	794	Darker
f (purple)	5.45	971	Darker

	Value	SD
Predicted pH average Regular canvas:	5.50	0.13
Predicted pH average Darker:	5.37	0.08
Predicted DP average Regular canvas:	1022	73
Predicted DP average Darker:	877	89
Predicted pH average Painting:	5.43	0.12
Predicted DP average Painting:	950	108
Likely Fibre Id:	Linen (97%)	

Object Id:	176
Institution:	MNAC
Number Institution:	065623
Title:	Lassitud
Author:	Isidre Novell
Date:	1910
Observations:	



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.04	423	Regular canvas
b (green)	5.01	158	Regular canvas
c (blue)	5.15	169	Regular canvas
d (yellow)	5.34	469	Regular canvas
e (black)	5.06	491	Regular canvas
f (purple)	5.64		Regular canvas (Washed)
g (orange)	5.60	90	Regular canvas (Washed)
h (white)	5.29		Regular canvas (Washed)
i (grey)	5.42		Regular canvas (Washed)
j (red)	5.42	109	Regular canvas (Washed)
k (green)	5.36	468	Darker (Tideline)
l (blue)	5.18		Darker (Tideline)
m (yellow)	5.32		Darker (Tideline)
n (black)	5.70		Darker (Tideline)
o (purple)	5.98		Darker (Tideline)
p (orange)	4.92	334	Darker (Varnish)
q (white)	4.99	519	Darker (Varnish)
r (grey)	5.00	516	Darker (Varnish)

	Value	SD
Predicted pH average Regular canvas:	5.30	0.23
Predicted pH average Darker:	5.31	0.37
Predicted DP average Regular canvas:	273	179
Predicted DP average Darker:	459	87
Predicted pH average Painting:	5.30	0.29
Predicted DP average Painting:	341	174
Likely Fibre Id:	Linen (65%)	

Object Id: 177
Institution: MANAC
Number Institution: 214090
Title: Dona amb barret i coll de pell (Marie-Thérèse Walter)
Author: Pablo Ruiz Picasso
Date: 1937
Observations:

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.66		Regular canvas
b (green)	5.74		Regular canvas
c (blue)	5.88		Regular canvas
d (yellow)	5.66		Regular canvas
e (black)	5.86		Regular canvas
f (purple)	5.52		Regular canvas
g (orange)	5.51		Regular canvas
h (white)	5.83		Regular canvas
i (grey)	5.36		Regular canvas
j (red)	5.31	2140	Darker (Stain)
k (green)	5.26	1648	Darker (Stain)
l (blue)	5.51	1771	Darker (Stain)
m (yellow)	5.45		Darker (Stain)
n (black)	5.61		Darker (Stain)
o (purple)	5.20	1378	Darker (Stain)

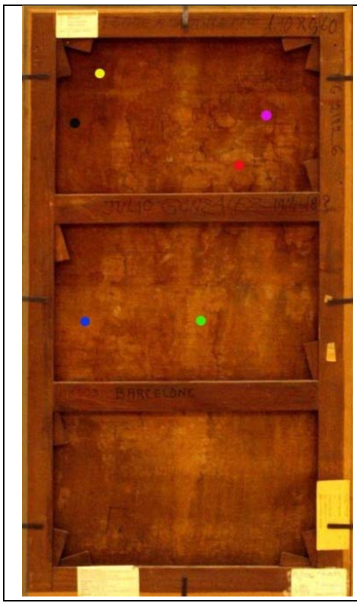
	Value	SD
Predicted pH average Regular canvas:	5.67	0.18
Predicted pH average Darker:	5.39	0.16
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	1734	317
Predicted pH average Painting:	5.56	0.22
Predicted DP average Painting:	1734	317
Likely Fibre Id:	Cotton	

Object Id:	178
Institution:	MNAC
Number Institution:	004048
Title:	“La Butte”
Author:	Santiago Rusiñol
Date:	1892
Observations:	Pignel Dupont stamp

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.92	1155	Regular canvas
b (green)	4.85	1121	Regular canvas
c (blue)	4.76	892	Regular canvas
d (yellow)	4.97	1300	Darker (oil migration)
e (black)	4.86	953	Darker (oil migration)
f (purple)	4.91	1084	Darker (oil migration)
g (orange)	4.25		Darker (Glue area)
h (white)	5.12	1265	Darker (Glue area)
i (grey)	4.80	975	Darker (Glue area)

	Value	SD
Predicted pH average Regular canvas:	4.84	0.08
Predicted pH average Darker:	4.82	0.30
Predicted DP average Regular canvas:	1056	143
Predicted DP average Darker:	1115	175
Predicted pH average Painting:	4.83	0.24
Predicted DP average Painting:	1093	147
Likely Fibre Id:	Linen, possibly ramie	

Object Id:	179
Institution:	MNAC
Number Institution:	113503
Title:	Dona rentant-se
Author:	Juli González
Date:	Circa 1912-1913
Observations:	Jute painting



NIR Location	**Predicted average pH**	**Predicted average DP**	**Notes**
a (red)	4.00	816	Regular canvas
b (green)	4.03		Regular canvas
c (blue)	3.90	494	Regular canvas
d (yellow)			Darker (oil migration?)
e (black)			Darker (oil migration?)
f (purple)	4.47		Darker (oil migration?)

	Value	**SD**
Predicted pH average Regular canvas:	3.98	0.06
Predicted pH average Darker:	4.47	--
Predicted DP average Regular canvas:	655	228
Predicted DP average Darker:	--	--
Predicted pH average Painting:	4.10	0.25
Predicted DP average Painting:	655	228
Likely Fibre Id:	Jute	

Object Id:	180
Institution:	MNAC
Number Institution:	004005
Title:	La novícia
Author:	Joan Llimona
Date:	1898
Observations:	Planella stamp

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.01	430	Regular canvas
b (green)	5.11	630	Regular canvas
c (blue)	5.30	443	Regular canvas
d (yellow)	4.93	373	Regular canvas (or Slightly darker??)
e (black)	5.18	34	Regular canvas (or Slightly darker??)
f (purple)	4.99		Regular canvas (or Slightly darker??)

	Value	SD
Predicted pH average Regular canvas:	5.09	0.14
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	382	217
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.09	0.14
Predicted DP average Painting:	382	217
Likely Fibre Id:	Ramie, possibly linen. Possible combination with jute?	

Object Id: 181
Institution: MNAC
Number Institution: 004006
Title: Pasturant
Author: Joan Llimona
Date: 1901
Observations: Planella stamp

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.57	581	Regular canvas
b (green)	5.36	716	Regular canvas
c (blue)	5.57	644	Regular canvas

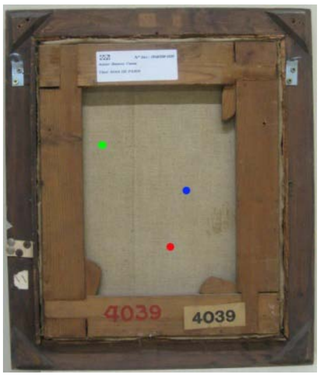
	Value	SD
Predicted pH average Regular canvas:	5.50	0.12
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	647	68
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.50	0.12
Predicted DP average Painting:	647	68
Likely Fibre Id:	Linen, possibly ramie	

Object Id: 182
Institution: MNAC
Number Institution: 004093
Title: Un dia d'hivern en el jardí del Luxemburg
Author: Marià Pidelaserra
Date: 1900
Observations: E. Lafontaine stamp

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.30	1309	Regular canvas
b (green)	5.35	1603	Regular canvas
c (blue)	5.29		Regular canvas
d (yellow)	5.12	1140	Regular canvas
e (black)	5.07	1201	Darker (Stain)

	Value	SD
Predicted pH average Regular canvas:	5.06	0.10
Predicted pH average Darker:	5.08	--
Predicted DP average Regular canvas:	738	234
Predicted DP average Darker:	766	--
Predicted pH average Painting:	5.06	0.12
Predicted DP average Painting:	1313	205
Likely Fibre Id:	Linen (85%)	

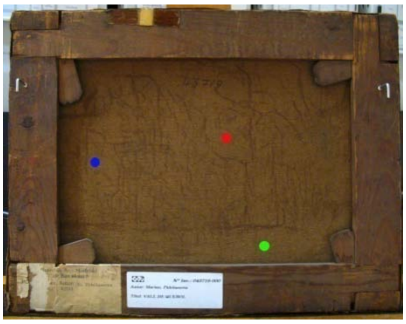
Object Id:	183
Institution:	MNAC
Number Institution:	004039
Title:	Noia de París
Author:	Ramon Casas
Date:	1888-1890
Observations:	Lined painting



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.52		Regular canvas
b (green)	5.68		Regular canvas
c (blue)	5.89		Regular canvas

	Value	SD
Predicted pH average Regular canvas:	5.70	0.18
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	--	--
Predicted pH average Painting:	5.70	0.18
Predicted DP average Painting:	--	--
Likely Fibre Id:	Combination of linen and hemp, possibly only linen.	

Object Id: 184
Institution: MNAC
Number Institution: 043719
Title: Vall de Querol
Author: Marià Pidelaserra
Date: 1897
Observations:



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.77	304	Regular canvas
b (green)	5.18	478	Regular canvas
c (blue)	4.98	299	Regular canvas

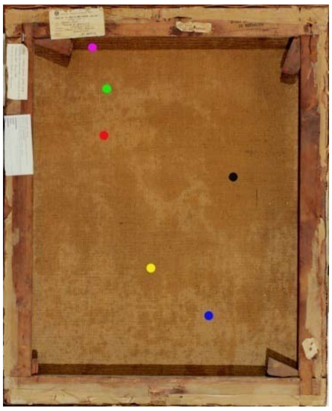
	Value	SD
Predicted pH average Regular canvas:	4.97	0.21
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	360	102
Predicted DP average Darker:	--	--
Predicted pH average Painting:	4.97	0.21
Predicted DP average Painting:	360	102
Likely Fibre Id:	Linen (72%)	

Object Id:	185
Institution:	MNAC
Number Institution:	65291
Title:	Retrat de J. Dalmau
Author:	Mela Mutermilch
Date:	1911
Observations:	Jute painting

NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.52		Regular canvas
b (green)	4.53		Regular canvas
c (blue)	4.59		Regular canvas
d (yellow)	4.69	1076	Regular canvas
e (black)	4.31		Regular canvas

	Value	SD
Predicted pH average Regular canvas:	4.53	0.14
Predicted pH average Darker:	--	--
Predicted DP average Regular canvas:	1076	--
Predicted DP average Darker:	--	--
Predicted pH average Painting:	4.53	0.14
Predicted DP average Painting:	1076	--
Likely Fibre Id:	Jute	

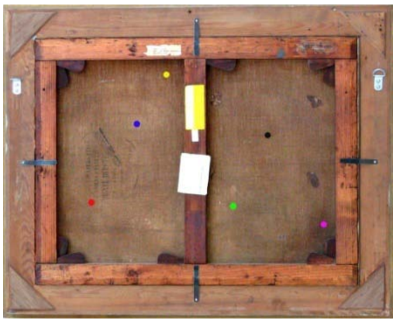
Object Id:	186
Institution:	MNAC
Number Institution:	011382
Title:	Estudi del natural per al retrat del rei Alfons XIII
Author:	Ramon Casas
Date:	1904
Observations:	Jute painting



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	4.19		Regular canvas
b (green)	4.19		Regular canvas
c (blue)	4.22		Regular canvas
d (yellow)	4.43		Darker
e (black)	4.46		Darker
f (purple)	4.40		Darker

	Value	SD
Predicted pH average Regular canvas:	4.20	0.02
Predicted pH average Darker:	4.43	0.03
Predicted DP average Regular canvas:	--	--
Predicted DP average Darker:	--	--
Predicted pH average Painting:	4.32	0.13
Predicted DP average Painting:	--	--
Likely Fibre Id:	Jute	

Object Id: 187
Institution: MNAC
Number Institution: 10901
Title: Plen air
Author: Ramon Casas
Date: Circa 1890-1891
Observations: Pignel Dupont stamp



NIR Location	Predicted average pH	Predicted average DP	Notes
a (red)	5.00	760	"Regular canvas"
b (green)	5.18	635	"Regular canvas"
c (blue)	4.86	1070	"Regular canvas"
d (yellow)	4.84	524	Darker
e (black)	5.01	707	Darker
f (purple)	5.06	816	Darker

	Value	SD
Predicted pH average Regular canvas:	5.01	0.16
Predicted pH average Darker:	4.97	0.12
Predicted DP average Regular canvas:	821	224
Predicted DP average Darker:	682	148
Predicted pH average Painting:	4.99	0.13
Predicted DP average Painting:	752	186
Likely Fibre Id:	Linen (98%)	

Annex V – Background study results

This annex recollects the predicted pH, DP and the standard deviations for each location analysed from four Dalí paintings from the Gala-Salvador Dalí Foundation. Three different types of backgrounds where used to take NIR spectra and the results compared in Chapter 5. The aim was to see which was the best background to use and if we had interferrence from them.

Object Code	NIR location	Background used	Predicted pH	SD pH	Predicted DP	SD DP
188	d	Blotting paper	5.4	0.0	925	149
188	d	Calibration pad	5.3		1223	
188	d	Table	5.3		1082	
188	e	Blotting paper	5.8	0.2	779	259
188	e	Calibration pad	5.9		1277	
188	e	Table	5.5		1148	
188	f	Blotting paper	5.5	0.1	1161	28
188	f	Calibration pad	5.6			
188	f	Table	5.7		1201	
188	g	Blotting paper	5.5	0.1	692	232
188	g	Calibration pad	5.7		1049	
188	g	Table	5.8		1126	
189	g	Blotting paper	5.2	0.1	680	26
189	g	Calibration pad	5.1		638	
189	g	Table	5.2		685	
189	h	Blotting paper	5.0	0.1	788	65
189	h	Calibration pad	5.2		749	
189	h	Table	5.2		876	
189	i	Blotting paper	5.3	0.1	863	124
189	i	Calibration pad	5.5		1038	
189	i	Table	5.5			
189	j	Blotting paper	5.3	0.1	691	107
189	j	Calibration pad	5.5		902	
189	j	Table	5.5		822	
190	d	Blotting paper	5.0	0.1		---
190	d	Calibration pad	5.1		1287	
190	d	Table	4.9			
190	e	Blotting paper	5.0	0.2		---
190	e	Calibration pad	4.9			
190	e	Table	4.6			
190	f	Blotting paper	5.3	0.0	1554	116
190	f	Calibration pad	5.4		1449	
190	f	Table	5.3		1323	
190	g	Blotting paper	5.5	0.2	1672	64
190	g	Calibration pad	5.3		1701	
190	g	Table	5.1		1579	
191	h	Blotting paper	5.1	0.0	504	332
191	h	Calibration pad	5.2		1131	
191	h	Table	5.1		629	
191	i	Blotting paper	5.1	0.0	789	67
191	i	Calibration pad	5.1		906	
191	i	Table	5.2		906	
191	j	Blotting paper	5.2	0.1	601	83
191	j	Calibration pad	5.2		738	
191	j	Table	5.0		752	
191	k	Blotting paper	5.2	0.1	866	177
191	k	Calibration pad	5.0		992	

191	k	Table	5.2		1215	

Abstract in English

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. 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, 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.

The main aim of this thesis was to assess whether the Near Infrared (NIR) spectroscometer Labspec 5000 could be calibrated to non-destructively assess the condition of the canvas support in easel paintings by measuring its pH and DP. This was indeed successfully achieved through the use of the chemometric tool PLS (Partial Least Squares), obtainting good error of predictions (±0.43 for pH and ±275 for DP). A successful fibre type identification modelling was also created through the Discriminant Analysis tool.

In order to build the non-destructive NIR method, though, a large set of real samples from paintings mostly from the 19th and 20th C, had to be first destructively analysed. The second aim of this PhD research was to learn about the typical pH and DP values and fibre type found in real paintings. In this regard, paintings were found to be mostly acidic (average pH for all the analysed paintings was 5.51, SD 0.66) and degraded to some extend (average DP values 1082, SD 566). Interstingly glue paste linings were found to be marketly more acidic and more degraded than paintings. Jute canvases were found to be more acidic than linen and cotton. The date of paintings was not seen to be correlated at all with pH, and only very slightly with DP. pH and DP were seen to be strongly correlated between them, although not in a direct manner, implying that other factors such date, fibre type or others have an influence on this relationship.

The third main aim of this thesis was to establish the meaning of the various DP values when it comes to easel paintings, so that together with pH, a “Condition Assessment Classification” could be designed and applied to paintings of which these two parameters are known to grade them in terms of condition and conservation actions to be taken. Conservator’s feelings regarding textiles was found to be generally correlated with DP and this allowed us to establish the “critical DP” value for paintings at <400 and the “safe DP” value at >1400. A “Condition Assessment Classification” was designed by taking all this new information into account and thus those more acidic paintings with yet not so low DP values were prioritized, since these were found to be the ones benefiting the most from some sort of deacidification treatment (active or passive).

The last main aim of the thesis was to both apply the non-destructive NIR spectrometry method developed and the “Condition Assessment Classification” to a set of real valuable paintings from around the year 1900 from the Museu Nacional d’Art de Catalunya (MNAC). A smaller set of Dalí paintings from the Fundació Gala-Salvador Dalí was also studied. The results corroborated on the one side the good applicability of the non-destructive developed method, and the acidity (and certain degradation) of the canvas support of all paintings on the other side.

Having both confirmed that the canvas of paintings in mostly acidic and the importance of acidity in its degradition rate it is thought to be of paramount importance to actively start taking measures to counteact acidity, specially if paintings are to be left unlined for as long as possible. Together with this, far more research on the potential positive and negative effects of the deacidification of paintings is needed, as well as the study of the specific origins of the acidity of paintings.

Resumen en español (Abstract in Spanish)

El soporte de tela de los cuadros, se compone mayoritariamente de celulosa. Una de las vias de degradación de la celulosa es la hidrólisis ácida, que implica que en un ambiente ácido (bajo pH), la degradación se produce a una velocidad mayor. La principal consecuencia de esta acidez es la ruptura de las cadenas del polímero de celulosa que se mide a través del grado de polimerización (DP). Una disminución del DP implica que las fibras y los tejidos tienen una resistencia mecánica menor, y consecuentemente este parámetro se puede utilizar para monitorizar el estado de conservación de estos materiales. Así pues, el conocimiento de estos dos parámetros, pH y DP puede ser muy útil para la mejor conservación del soporte textil de los cuadros.

El objetivo principal de esta tesis ha sido determinar si el espectrómetro de infrarrojo cercano (NIR) Labspec 5000, se podría calibrar para que, de manera totalmente no destructiva, pudiera determinar el estado de conservación del soporte de tela de los cuadros a través de medir el pH y el DP. Esto efectivamente se consiguió utilizando la herramienta de quimiometría PLS (Partial Least Squares). Se obtuvieron errores de predicción de ±0.43 para el pH y de ±275 para el DP. La calibración para la identificación del tipo de fibra también se pudo hacer utilizando el Discriminant Analysis, otra herramienta de la quimiometría.

Para poder construir el método NIR no destructivo, primero había que analizar de manera destructiva un número significativo de muestras que fueron tomadas de cuadros mayoritariamente de los siglos XIX y XX.
El segundo objetivo principal de esta tesis ha sido conocer cuáles son los valores típicos de pH y DP y el tipo de fibra de los cuadros. Por lo que a esto se refiere, los resultados han sido que la tela de los cuadros tiene, la mayoría de las veces, un carácter ácido (la media de los resultados de todos los cuadros fue de pH 5.51, con una desviación estándar de 0.66). El estudio del pH ha permitido constatar que la tela de los reentelados realizados con pasta de harina, en general, es claramente más ácida que la tela de los cuadros no reentelados. En relación al tipo de fibra, se ha detectado que las telas de yute són más ácidas que las de lino y algodón. No se ha encontrado una relación directa entre la fecha de los cuadros y su valor de pH, y sólo una ligera relación entre la fecha y el DP. Se detectó que pH y DP están fuertemente correlacionados, aunque no de manera directa, cosa que implica que hay otros factores como el tipo de fibra, la fecha del cuadro u otros, que influyen en la correlación entre estos dos parámetros.

El tercer objetivo principal de esta tesis ha sido establecer el significado de los varios valores de DP por lo que se refiere al estado de conservación de la pintura sobre tela. Esta información junto con el valor de pH, sirvió para diseñar una “Clasificación según el estado de conservación”, cosa que habría de permitir establecer una organización de los cuadros según las acciones de conservación-restauración a emprender. Se realizó un test con la participación de un grupo de conservadores-restauradores especializados en pintura sobre tela y procedentes de distintos países que permitió ver que la apreciación subjetiva del conservador-restaurador sobre el estado de conservación de las muestras de tela, en general se corresponde con el grado de polimeración de éstas. A través de los resultados de este estudio se pudo establecer que el valor de “DP crítico” para un cuadro está en <400 y el valor de “DP seguro” está en >1400. La “Clasificación según el estado de conservación” se diseñó teniendo en cuenta toda esta nueva información y por eso se priorizó el tratamiento de aquellos cuadros con una tela más ácida pero con valores de DP todavía no muy bajos, puesto que los resultados indicaban que estos cuadros serían los que más se beneficiarían de algún tipo de tratamiento de desacidificación (activo o pasivo).

El último objetivo de la tesis ha consistido en aplicar la técnica NIR no destructiva desarrollada, así como la “Clasificación según el estado de conservación” sobre un caso real de pinturas pertenecientes al Museu Nacional d’Art de Catalunya (MNAC), fechadas alrededor del año 1900. También se ha estudiado un grupo menor de cuadros de Salvador Dalí de la Fundació Gala-Salvador Dalí. Los resultados han corroborado por un lado la buena aplicabilidad del método no destructivo dessarrollado y, por otro, la acidez (y la presencia de cierta degradación) de la tela de todos los cuadros.

Habiendo confirmado, tanto que la tela de los cuadros es mayoritariamente ácida como la influencia que ésta tiene en la velocidad de su degradación, se considera que es de vital importancia empezar a tomar medidas para contrarrestar la acidez de las telas; especialmente si la intención es no aplicar operaciones tan intrusivas como el reentelado en los cuadros durante el máximo tiempo posible. Juntamente con esto, se detecta que es necesaria mucha más investigación sobre los efectos positivos y negativos de la desacidificación de la tela de los cuadros, así como también el estudio de los orígenes concretos de esta acidez (materiales originales, materiales de restauración, entorno de las obras, etc.).

Resum en català (Summary in Catalan)

Introducció

Ja des de les primeres civilitzacions, la humanitat s'ha preocupat per la conservació del seu patrimoni cultural passat i present. Els objectes artístics, com els quadres, són evidències físiques de cultures humanes prèvies i per tant ens proporcionen una connexió tangible amb el nostre passat. A més a més, també són mostres del desenvolupament artístic de l'home al llarg dels temps. Per tant, el patrimoni cultural ens ajuda a construir la nostra identitat a través de mostrar-nos d'on venim i, a través de la seva preservació per al gaudi de les properes generacions, ens projecta també cap al futur.

Malgrat tot, la matèria té la tendència natural a canviar, i per tant, amb el temps, tots els objectes es degradaran. De totes maneres, tenim el deure moral de mirar de retardar la velocitat d'aquesta degradació de manera que passem el nostre patrimoni cultural a les generacions futures en les millors condicions possibles. Per tal de poder prendre les accions de conservació-restauració adequades, però, primer cal analitzar i entendre quin és l'estat de conservació actual dels objectes a preservar.

Aquesta tesi doctoral se centra en la pintura sobre tela, i més concretament en l'estudi de la degradació del suport de tela. Aquesta és una de les capes més importants en un quadre, ja que si la tela desapareix, desapareix també el suport que aguanta la capa pictòrica, que és la que porta el missatge estètic.

Els quadres tradicionalment s'han pintat sobre teixits fets de fibres d'origen vegetal (les fibres més utilitzades han estat el lli, el cànem, el cotó i el jute). Tots aquests teixits tenen la cel·lulosa com a constituent majoritari, el polímer natural més abundant de la Terra. Com que la cel·lulosa és un polímer orgànic, és degradada fàcilment per agents externs com la temperatura, la humitat, la llum, l'atac biològic i la pol·lució.

Un dels efectes més importants de la degradació de la tela és la pèrdua de la seva força mecànica. Quan una tela es degrada esdevé més fràgil del que era inicialment i llavors es pot esquinçar més fàcilment. Si la degradació continua fins a l'extrem, el teixit pot tornar-se fins i tot pols.

Aquesta degradació natural de la tela dels quadres tradicionalment s'ha superat adherint un nou teixit al revers de la tela original (reentelat). Avui en dia, però, el reentelat es considera un tractament molt intrusiu que pot tenir efectes adversos (aixafament de la capa pictòrica, impregnació total del suport original de tela amb adhesiu, etc.) i va en contra dels criteris actuals de conservació-restauració de mantenir la integritat de l'objecte el màxim de temps possible (el reentelat amaga completament la tela original del quadre i implica l'afegit de gran quantitat de materials forans). Així doncs, avui en dia, el reentelat només es fa en els casos en què es considera que és estrictament necessari, és a dir quan el teixit original està tan degradat que ja no és capaç de suportar més el seu propi pes.

Per tot això, ara més que mai, és de vital importància poder **establir l'estat de conservació present del suport de tela dels quadres**, de manera que es puguin prendre accions de conservació-restauració a partir d'informació fidedigna.

Hi ha diferents tipus d'anàlisis químiques i físiques que es poden dur a terme per tal d'avaluar l'estat de conservació de la tela. La resistència d'un teixit es pot calcular a través de proves mecàniques que mesuren, per exemple, les corbes de força/elongació del material o el "punt de trencament mecànic". Aquestes proves, però, necessiten una quantitat de mostra bastant important i la repetició del mateix test diverses vegades. Com que la resistència mecànica dels teixits se sap que està relacionada amb el grau de polimerització (DP) de les cadenes de cel·lulosa que formen el teixit, mesurar el DP és una altra via per determinar l'estat de degradació d'una tela, amb l'avantatge que requereix una mostra molt més petita.

La via més important de la degradació dels materials cel·lulòsics és la hidròlisi per acidesa. Això vol dir que si hi ha acidesa en els materials cel·lulòsics (paper, tela, etc.) la velocitat de degradació és més alta. Un dels resultats de la hidròlisi àcida és el trencament de les cadenes de cel·lulosa, que fan baixar el grau de DP del material i conseqüentment la seva resistència mecànica.

Així doncs, saber el DP de la cel·lulosa i l'acidesa (pH) de la tela, ens dóna una informació molt rellevant sobre l'estat de conservació de la tela dels quadres. De totes maneres, ambdues anàlisis, requereixen extreure una mostra física de l'objecte per tal de poder-los determinar.

Treure mostres de les obres d'art ha estat sempre un tema controvertit, ja que tot i que puguin ser minúscules, impliquen retirar material original d'obres valuoses i úniques. És per això que el desenvolupament de tècniques no destructives que permetin analitzar les obres d'art ha crescut significativament en les últimes dècades i cada cop es valoren més aquest tipus de tècniques.

L'espectrometria d'infraroig proper (NIR) i la quimiometria, és una tècnica no destructiva que s'ha anat aplicant cada cop més en els últims anys i amb èxit en camps industrials molt variats. Un cop el mètode per a un determinat tipus de material i per a un paràmetre analític concret s'ha desenvolupat, la tècnica ja no requereix la presa d'una mostra física per tal de determinar el nou paràmetre. Només cal prendre un espectre NIR de l'objecte, cosa que és molt ràpida i fàcil de fer, fins i tot per la persona més inexperta. Això fa que aquesta nova eina sigui molt valuosa per tal de dur a terme estudis sobre l'estat de la col.lecció de manera relativament ràpida.

En el camp del patrimoni cultural, l'espectrometria NIR i la quimiometria s'han aplicat recentment en l'estudi del paper, el pergamí, la seda i els objectes de plàstic, però mai no s'ha provat encara en quadres de pintura sobre tela.

Així doncs, l'objectiu principal d'aquesta tesi era investigar si l'espectrometria NIR i la quimiometria servirien per determinar el pH i el DP de la tela de suport dels quadres de manera no destructiva, com una via per a establir-ne el seu estat de conservació.

Tot i que un cop desenvolupada, la tècnica és no destructiva, per tal de poder-la crear, primer cal fer una sèrie d'anàlisis destructives. Així doncs, en aquest cas cal recollir un grup significatiu de mostres de quadres reals sobre les quals es puguin mesurar els paràmetres desitjats de manera destructiva. Els paràmetres escollits per tal d'avaluar l'estat de conservació del suport dels quadres van ser el DP i el pH de les teles.

El DP sovint es calcula a través de la viscometria, un mètode en el qual la mostra de teixit es solubilitza en un dissolvent i la viscositat d'aquesta solució és el que es mesura. Com que la viscositat de la solució canvia en funció de la llargada de les cadenes de cel·lulosa, el DP es pot determinar a partir de la viscositat.

L'acidesa d'una mostra sòlida, com és la tela dels quadres, es pot mesurar a través del mètode del pH per extracte en fred, en el qual la mostra és posada en aigua destil·lada i el pH (alcalinitat o acidesa) de la solució es mesuren després d'algunes hores amb un pH-metre.

Actualment, una anàlisi molt típica de fer als quadres tractats pels pròpis conservadors-restauradors és la determinació del tipus de fibres del suport d'un quadre. A part d'ajudar en la caracterització adequada dels materials pictòrics usats, saber el tipus de fibra de la tela pot ajudar a l'hora de triar el tractament de conservació-restauració més adequat.

La determinació del tipus de fibra, també requereix l'extracció d'una mostra física i la identificació pot ser complicada de vegades, fins i tot per a l'expert. Per això, aquest paràmetre va ser afegit, per tal de fer-ne també la calibració amb l'espectrometria NIR i que aquesta també pogués determinar el tipus de fibra usat.

El DP i el pH de la tela dels quadres, fins ara, s'havia mesurat poques vegades. Analitzar el DP, el pH i el tipus de fibra d'un grup significatiu de mostres de quadres reals, necessaris per desenvolupar la tècnica no destructiva de l'espectrometria NIR, ens ajudaria, doncs, a cobrir **el segon objectiu principal d'aquesta tesi doctoral: aprendre sobre els valors típics de pH i DP dels quadres reals, així com el tipus de fibra més utilitzat i la relació entre aquests paràmetres (pH, DP, tipus de fibra i data).**

Un cop el DP, el pH i el tipus de fibra es van haver analitzat destructivament, es van obtenir els espectres NIR de les mateixes mostres, i utilitzant tècniques quimiomètriques, es va calibrar l'espectròmetre posant en relació els espectres NIR i els valors dels tres paràmetres analitzats. Així doncs, es van desenvolupar tres models, un per a cada paràmetre.

El desenvolupament exitós de la tècnica no destructiva de l'espectrometria NIR per a determinar el DP, pH i el tipus de fibra de la tela implica que ara aquests paràmetres es poden analitzar de manera ràpida, d'un grup gran de quadres sense la necessitat d'extreure'n cap mostra física i que els resultats es poden obtenir immediatament i molt fàcilment.

L'acidesa es mesura en una escala de pH que va del 0 al 14, on el pH 7 és el pH neutre i ideal per a un objecte cel.lulòsic. Se saben menys coses, però, sobre les implicacions que tenen els diferents valors de DP de les teles dels quadres. Així doncs, es va creure important d'esbrinar el significat dels diferents valors de DP pel que fa als quadres, de manera que es poguessin establir tant el "DP crític" per sota del qual un quadre es pot considerar molt fràgil, com el "DP segur", per sobre del qual els conservadors-restauradors poden estar tranquils sobre el bon estat de conservació de la tela.

El tercer objectiu principal d'aquesta tesi va ser, doncs, establir el significat dels diferents valors de DP pel que fa a la pintura sobre tela, de manera que conjuntament amb el pH, és pogués dissenyar una "Classificació segons l'estat de conservació" que és pogués aplicar als grups de quadres dels quals se sabessin aquests dos paràmetres.

Per tal de convertir els possibles valors de DP en informació amb significat, es va dur a terme una "Enquesta", on un seguit de teixits nous i històrics, envellits artificialment en un forn durant diferents períodes de temps (i per tant amb diferents nivells de DP) van ser enviats a un grup de conservadors-restauradors internacionals. Se'ls va demanar que manipulessin les mostres com si fossin fragments de quadres en tractament de conservació-restauració i que els classifiquessin en quatre categories segons l'estat de conservació.

Amb el nou coneixement adquirit sobre el significat dels diferents valors de DP a través de l'Enquesta als conservadors-restauradors i tenint en compte també el paràmetre del pH, es va dissenyar una "Classificació segons l'estat de conservació". Aquesta classificació organitza els quadres dels quals se sap el pH i el DP i els prioritza segons les accions de conservació-restauració a prendre (desacidificació, reentelat, "reentelat lliure", negació d'una petició de préstec, etc.).

L'últim objectiu principal d'aquesta tesi era aplicar, per una banda, el mètode no destructiu de l'espectrometria NIR per conèixer el pH, DP i el tipus de fibra d'un grup de quadres del Museu Nacional d'Art de Catalunya (MNAC) i aplicar la "Classificació segons l'estat de conservació" prèviament dissenyada, per l'altra.

Conclusions

Desenvolupat tot el treball, aquesta tesi doctoral arriba a les següents conclusions, ordenades segons els objectius establerts a l'inici.

L'objectiu principal d'aquesta tesi era investigar si l'espectrometria NIR i la quimiometria servirien per determinar el pH i el DP de la tela de suport dels quadres de manera no destructiva, com una via per establir-ne el seu estat de conservació.

Saber l'estat de conservació del suport de tela dels quadres és important ja que aquesta capa és la que rep la capa pictòrica, que és la que transporta el missatge estètic. El corrent actual de la mínima intervenció de conservació demana que els quadres no siguin reentelats, a no ser que sigui inevitable. Si es volen mantenir els quadres sense reentelar per tant de temps com sigui possible, és primordial avaluar el seu estat de conservació de manera que les accions correctes es puguin prendre a temps.

Tradicionalment, la pintura sobre tela s'ha fet sobre teixits d'origen vegetal (sobretot lli, cànem, cotó i jute), el component principial de les quals és, en tots els casos, la cel·lulosa. La cel·lulosa és un polímer natural, la degradació del qual està format per un conjunt de processos complexos, i encara no entesos del tot. Una de les principals vies de degradació és la hidròlisi per via àcida, cosa que implica que, en un ambient àcid (baix pH), el polímer es degrada a una velocitat més alta. L'acidesa pot venir de diferents fonts, tals com són els propis materials del quadre, els sub-productes de la pròpia degradació de la cel·lulosa o l'ambient. Per això és important saber el pH de la tela, ja que si la tela és molt àcida, un tractament de desacidificació podria ajudar a reduir-ne la degradació.

Una de les conseqüències de la degradació de la cel·lulosa a través de la hidròlisi àcida és el trencament de les cadenes del polímer. Això, al seu torn, es tradueix en un enfebliment de les fibres vegetals i com a conseqüència, del teixit. La llargada mitjana de les cadenes del polímer es mesuren a través del grau de polimerització (DP), que es pot mesurar, entre d'altres a través de la viscometria. La cel.lulosa sense processar pot tenir un DP de fins a 14.000 unitats, que pot baixar ja fins a 2.500 en un teixit processat. Aquest nombre de DP disminueix a mesura que el teixit es degrada, fins que en circumstàncies extremes, amb el temps es desintegrarà.

Prendre mostres físiques dels objectes de patrimoni és un tema cada vegada més controvertit, ja que avui en dia cada vegada s'entén més que els objectes són finits i que tenim el deure moral de passar-los a les generacions futures perquè en puguin gaudir en el millor i més complet estat possible. És per això que la recerca en tècniques analítiques no destructives aplicades al patrimoni cultural ha tingut un creixement significatiu en les últimes dècades.

L'espectrometria NIR i la quimiometria, és una tècnica que s'ha desenvolupat àmpliament en la indústria des de ja fa alguns anys per tal de determinar, d'una manera ràpida, moltes característiques de tot tipus de productes. En el camp del patrimoni cultural, recentment s'ha aplicat per determinar diferents paràmetres en objectes de paper, plàstic, seda i pergamí, però no s'havia aplicat mai encara en la pintura sobre tela i per això aquesta recerca és molt innovadora.

L'espectre infraroig dels materials orgànics a la zona de l'infraroig proper (780 - 2500 nm) es compon bàsicament de "matisos" i "bandes de combinació" que estan relacionats amb l'estirament i doblegament dels enllaços entre els àtoms presents al material. Aquesta regió de l'espectre conté molta informació, però com que les bandes d'absorció se sobreposen molt les unes a les altres, els patrons no són visibles a ull nu, com potser seria el cas dels espectres de la zona de l'infraroig mitjà. És per això que calen eines d'anàlisi de múltiples variables (eines quimiomètriques), de manera que es puguin analitzar de manera simultània gran quantitat de variables (una per a cada longitud d'ona de l'espectre). Això permet la creació d'una complexa equació (calibració) que explica les relacions repetitives i els patrons entre els espectres i els paràmetres d'interès corresponent. Si això s'aconsegueix, llavors les prediccions per als paràmetres calibrats es poden obtenir a partir d'un espectre NIR de nous objectes. De totes maneres, com que hi ha molts factors que poden incidir en l'espectre, no sempre és possible fer-ho i per això en cada nova situació cal provar i desenvolupar una nova calibració per determinar si la tècnica es pot usar en aquell cas particular.

Per tant, per desenvolupar aquesta tècnica, primer es van mesurar de manera analítica i destructiva els paràmetres d'interès (pH, DP i tipus de fibra) d'un grup gran de mostres de quadres reals, de les quals també es va prendre l'espectre amb un espectròmetre NIR. Per poder aconseguir això es va elaborar una

"Col·lecció de Mostres de Referència", els detalls de la qual s'expliquen una mica més endavant. Llavors, utilitzant eines quimiomètriques (eines matemàtiques i estadistíques que permeten l'anàlisi de moltes variables a la vegada), es va crear una "calibració" o "model".

L'instrument utilitzat per agafar els espectres NIR va ser un espectròmetre Labspec 5000 (Analytical Spectral Devices, USA) que treballa amb un interval de l'espectre dels 350 als 2500 nm (UV-vis-NIR). Els espectres de les mostres es van prendre sobre el patró de referència blanc que s'usa per calibrar l'aparell. Les calibracions fetes amb PLS per al pH i el DP es van fer utilitzant el programa informàtic Grams *AI spectroscopy* (ThermoScientific), amb els mòduls addicionals "*Grams IQ*" i "*IQ Predict*". La calibració per a la determinació del tipus de fibra utilitzant la tècnica del Discriminant Analysis es va fer utilitzant el software "*Xlstat"* (Adddinsoft, USA).

Pel que fa a aquest primer objectiu, doncs, es pot concloure que es va poder elaborar amb èxit una calibració per poder predir el pH, DP i el tipus de fibra de la tela dels quadres de manera no destructiva utilitzant un espectròmetre NIR. Les calibracions per al pH i el DP es van fer utilitzant l'eina de quimiometria Partial Least-Square (PLS) i els errors de predicció van ser respectivament: ± 0.43 per al pH i ± 275 per al DP. Aquest resultats cal considerar-los molt satisfactoris, sobretot pel que fa al pH, si els comparem amb resultats obtinguts per altres pel que fa a objectes culturals de paper, un material cel·lulòsic similar, que són de ± 0.3 pel pH i ± 175 pel DP.

Com que la identificació del tipus de fibra és una anàlisi qualitativa, va caldre utilitzar una eina quimiomètrica diferent. Es va obtenir una calibració satisfactòria utilitzant el Discriminant Analysis (DA) en un procés amb dos passos. El primer DA és capaç de discernir entre cotó, jute i un grup de fibres liberianes (lli, cànem, rami i combinacions de lli/cànem) i combinacions de cotó/jute, jute/cotó, o jute/lli, amb un grau de seguretat que va del 75% al 99%. El segon DA, és capaç de classificar les fibres liberianes entre elles i diferenciar entre: lli, cànem, rami i combinacions de lli/cànem amb un alt grau de seguretat, que va del 72% al 100%, tot i que cal tenir en compte que hi havia poques mostres de cànem, rami i lli/cànem en la calibració i per tant la identificació d'aquest tipus de mostres segurament no és tan fiable. Si en el futur hi hagués disponibilitat de més mostres identificades positivament amb aquest últims tipus de fibres, es podria provar de fer una nova calibració.

Així doncs, l'èxit de la calibració de l'espectròmetre NIR per predir el pH, DP i el tipus de fibra, ens dóna un instrument molt poderós per determinar de manera no destructiva i molt ràpidament, l'estat de conservació actual del suport de tela dels quadres. De totes formes, cal tenir en compte que el mètode desenvolupat, només serà útil per a mostres similars a aquelles que es van utilitzar en la calibració, cosa que en el nostre cas vol dir bàsicament quadres dels segles XIX i XX.

El segon objectiu principal d'aquesta tesi era aprendre sobre els valors típics de pH i DP dels quadres, així com el tipus de fibra més utilitzat i la relació entre aquests paràmetres (pH, DP, tipus de fibra i data).

L'anàlisi del pH, el DP i el tipus de fibra de la "Col·lecció de Mostres de Referència", era necessària per tal de poder desenvolupar el mètode no destructiu de l'espectrometria NIR prèviament exposat. De la mateixa manera, però, no hi ha gaires quadres dels quals s'hagi mesurat el pH i el DP del seu suport i que els resultats s'hagin publicat. Per això, mesurar aquests paràmetres d'un gran grup de quadres reals i aprendre sobre la relació entre els diferents paràmetres (pH, DP, tipus de fibra i data) s'entreveia que podia ser molt prometedor.

Es va crear una Col·lecció de Mostres de Referència a partir de treure mostres d'una mida aproximada d'1-2 cm^2 de tela dels marges d'uns 100 quadres de segona categoria. Com que de vegades es va agafar més d'una mostra del mateix quadre, i també es van afegir a la col·lecció altres tipus de mostres per incrementar-ne la variabilitat, com ara teles de reentelats retirats durant el procés de conservació-restauració, teles noves imprimades per a artistes i teixits comuns, al final es va reunir una Col·lecció de Referència d'unes 200 mostres.

La majoria de les mostres de la Col·lecció de Mostres de Referència eren del segle XIX i XX i tot i que també n'hi havia unes quantes (11%) de molt més antigues (16th – 18th C) i unes quantes (9%) més noves, del s XXI.

El tipus de fibra es va identificar visualment, observant les fibres muntades en un porta-objectes amb el microscopi de llum polaritzada. Es van analitzar dos fils per cada mostra, un d'horitzontal i un de vertical. Aquest paràmetre es va analitzar d'unes 100 mostres, produint un total d'unes 200 preparacions de fibres.

Pel que fa al tipus de fibra, es va trobar que els quadres tenien els tipus més típics de fibres vegetals: lli, cànem, cotó i jute. Normalment les teles estaven fetes a partir d'un sol tipus de fibra, però més sovint del que imaginàvem, es va trobar combinació de fibres; lli/cànem, lli/jute, lli/cotó, jute/cotó, cotó/sintètics.

El lli és el tipus de fibra que es va trobar més freqüentment, i el trobem majoritàriament sol, és a dir en teles de 100% lli. Es va trobar al llarg de tots els períodes i sovint barrejat amb cànem en teles més velles. El cànem, per si sol, només el trobem en un quadre. El cotó es va trobar en quadres de finals del segle XIX, i del XX i el jute es va trobar ocasionalment, preparat comercialment al tombant del segle XX i, al llarg d'aquest, també ocasionalment preparat pels mateixos artistes. Un quadre, de manera bastant inesperada, va ser identificat com a rami. Les fibres sintètiques es van trobar en poques ocasions en quadres de menys de dues dècades i sempre barrejades amb cotó.

El pH es va mesurar aplicant el mètode de micro-pH de l'extracció en fred que normalment es fa servir en els objectes culturals de paper (que és una adaptació de l'estándar internacional ISO 5351:2010) i per tant es va fer servir una mida molt petita de mostra (250-350µg) i 100µL d'aigua destil·lada. L'ús del nou tipus d'elèctrode metàl·lic ISFET va resultar ser molt convenient ja que aquest permet un treball molt més ràpid i eficaç ja que és un elèctrode que no es trenca tan fàcilment com els tradicionals de vidre i en conseqüència acaba essent també més econòmic.

Es va mesurar el pH de totes les mostres de la Col·lecció de Referència i el resultat va ser que el pH de la tela dels quadres en general és àcid. El valor més típic de pH per un quadre es va veure que estava entre 5.00 i 5.50. El pH de les teles de reentelat es va veure que generalment era més àcid que les teles originals dels quadres no reentelats. Això indica que hi podria haver alguns ingredients àcids dins la recepta de la pasta de farina (com el vinagre, l'alum de roca, la trementina de Venècia, etc.) que podrien ser els causants d'aquesta major acidesa trobada en aquestes mostres.

El DP es va mesurar en la meitat de les mostres de la Col·lecció de Referència a través de la viscometria, seguint l'estàndard internacional ISO standard ISO 5351/1-1981. La conclusió va ser que, en el cas dels quadres, per obtenir la quantitat necessària de fibres per dur a terme l'anàlisi (30 mg), calia, en general, una mostra del suport d'un quadre d'una mida entre 1.5 i 2 cm^2. També es va trobar que si la mostra a mesurar està en molt bon estat de conservació, és molt millor utilitzar una quantitat menor de fibres (10 mg) per fer-ne l'anàlisi.

Es van fer diferents proves pel que fa a la preparació de la mostra per tal de fer l'anàlisi de viscometria i es va determinar que el millor mètode era deixar les mostres en aigua durant la nit i posar-les al bany maria durant 10 minuts l'endemà. Llavors les fibres del teixit es separaven manualment amb dues agulles llargues a través d'un procés molt laboriós que podia arribar a durar dues hores per cada mostra. Es va fer un estudi preliminar pel que fa a obtenir una preparació més curta de les mostres a través de separar les fibres del teixit amb un morter. El resultat va ser molt positiu, ja que els primers resultats obtinguts indiquen que l'ús del morter no introdueix una major degradació de la mostra com es temia, i en canvi el temps de preparació de la mostra per a la posterior mesura viscometrica es redueix considerablement.

La majoria de les mostres dels quadres analitzats tenien un DP entre 600 i 950. Comparant mostres que venien de dues zones diferents d'un mateix quadre, es va veure que quan visualment es percebia que les zones tenien estats de conservació molt diferents (zones concretes amb degradacions evidents a causa d'humitats, etc.), això es traduia en valors de DP també molt diferenciats. Això indicava ja, que la percepció subjectiva de l'estat de conservació, sovint està correlacionada amb el valor de DP (teles en pitjor estat tindrien valors més baixos de DP). Les teles de reentelats vells, altre cop mostraven valors de DP més baixos, cosa que ja indicava una relació entre l'acidesa i el DP.

Un cop aquests tres paràmetres van ser analitzats, es va explorar la correlació entre els resultats obtinguts pel que fa al pH, al DP, al tipus de fibra i la data dels quadres. Això es va fer a través d'analitzar un paràmetre contra l'altre (de dos en dos) amb un gràfic de dispersió tradicional, i també amb l'eina quimiometrica d'anàlisi de múltiples variables, Principal Component Analysis (PCA).

La data dels quadres i el pH es va descobrir que no estaven correlacionats, ja que alguns quadres moderns presentaven, de vegades, valors baixos de pH i alguns quadres molt antics, presentaven, de vegades, valors més alts. Es va detectar que algunes mostres disponibles de quadres molt antics (s. XVI-XVIII), tenien els valors més alts de pH de tota la col·lecció analitzada (6.50-7.00) i es creu que això podria ser degut a un ambient lleugerament alcalí proporcionat per les parets de les esglésies d'on provenien aquests quadres. El pH més baix dels quadres moderns es podria explicar, bé per l'ús de materials més àcids en la producció comercial de les teles, bé pels efectes d'un ambient pol·lucionat i més aviat àcid.

Pel que fa a la data dels quadres i el DP, tot i que no es pot dir que estiguin relacionats de manera gaire directa, si que es veu que estan una mica més correlacionats que la data i el pH. Això vol dir que els quadres més recents, en general tendeixen a tenir valors de DP més alts.

Els diferents tipus de fibres vegetals tenen diferents quantitats de lignina, i això es va veure que estava relacionat amb el pH: les fibres de jute, que són les que més quantitat d'aquesta substància tenen, es va veure que eren més àcides que les de lli i cotó. Pel que fa al DP, les teles de jute es va trobar que tendien a tenir valors de DP més baixos que el lli, però no tan diferents del cotó. Això posa de relleu el fet que el cotó, tot i trobar-se en circumstàncies lleugerament millors que la resta de fibres (un pH més alt), es pot degradar més ràpidament que els altres tipus de fibres, probablement a causa del major percentatge de zones amorfes que té la seva cel·lulosa, ja que aquestes zones ofereixen una entrada més fàcil als agents de degradació de l'ambient.

Analitzant la relació entre el pH i el DP de manera directa (només tenint en compte aquests dos paràmetres), es va veure que els dos paràmetres estan relacionats en certa mesura. Quan l'anàlisi de la relació es va fer a través de la PCA, es va poder detectar que els dos paràmetres estan altament relacionats, indicant que un pH més baix implica un DP també més baix i viceversa. L'acidesa, doncs, es confirma que és un factor determinant pel que fa al DP dels quadres. Com que el DP està directament relacionat amb la resistència mecànica dels teixits, l'acidesa es converteix en un paràmetre molt important a controlar pel que fa a la monitorització de l'estabilitat del suport.

El fet que la correlació entre el pH i el DP no es detecti de manera tan clara quan s'analitza només un paràmetre contra l'altre i en canvi es vegi molt clarament quan es fa l'anàlisi a través del PCA (en el qual també s'analitzaven la influència del tipus de fibra i la data dels quadres), demostra que aquests dos paràmetres estan molt correlacionats però no unidireccionalment. Això vol dir, doncs, que si per exemple es mesurés el pH de la tela, no seria possible inferir el seu DP només a partir del pH, ja que queda clar que hi ha altres factors, com poden ser el tipus de fibra i la data dels quadres, que tenen a veure en la relació entre aquests dos paràmetres. Aquests resultats també posen de relleu el poder de l'anàlisi a través del PCA, on es pot estudiar la correlació entre més de dos paràmetres al mateix temps.

Conseqüentment, el fet que s'hagi trobat que la tela dels quadres és majoritàriament àcida, ens fa molt més conscients de la necessitat de trobar maneres de neutralitzar aquesta acidesa de la tela, especialment perquè també s'ha corroborat que el pH i el DP estan altament relacionats i per tant queda clar que les teles àcides veuran el seu DP disminuir a una velocitat més gran que les teles amb un pH neutre o lleugerament alcalí, i això afectarà clarament l'estabilitat mecànica del suport.

El tercer objectiu principal d'aquesta tesi era establir el significat dels diferents valors de DP pel que fa a la pintura sobre tela, de manera que conjuntament amb el pH, és pogués dissenyar una

"Classificació segons l'estat de conservació" que és pogués aplicar als grups de quadres dels quals se sabessin aquests dos paràmetres.

El desenvolupament d'una tècnica no destructiva per determinar el pH, DP i el tipus de fibra de la tela dels quadres permetia, doncs, l'anàlisi de l'estat de conservació d'una col·lecció de quadres de manera ràpida i amb relatiu poc esforç. De totes maneres, calia saber el significat dels diferents valors obtinguts amb l'espectròmetre pel que fa a la pintura sobre tela, de manera que les xifres concretes preguin significat. És per això que es va veure com a molt important determinar el significat d'aquests valors, de manera que tenint en compte tant el DP com el pH es pogués dissenyar un sistema de classificació que els tingués en compte a l'hora de prioritzar els tractaments de conservació-restauració dels quadres de la col·lecció analitzada.

Per tal d'aconseguir tot això, es va fer una "Enquesta" a un grup de conservadors-restauradors internacionals, als quals se'ls van enviar un seguit de mostres noves i històriques i envellides artificialment, de les quals se sabia el valor de DP. Es va demanar als conservadors-restauradors que ordenessin les mostres segons l'estat de conservació que ells creguessin adient, d'acord amb la seva experiència professional. La conclusió més important d'aquest experiment va ser que, en general, la percepció subjectiva dels conservadors-restauradors està correlacionada amb el DP de les teles: les mostres amb DP més baixos, generalment eren percebudes com a teles més fràgils que les teles amb valors de DP més alts. Aquest resultat, doncs, avala els altres resultats d'aquest experiment.

També es va demanar als conservadors-restauradors que classifiquessin les mostres rebudes en quatre categories (« tela molt fràgil », « tela fràgil », « tela fràgil però no excessivament", "tela en bon estat"). Tot i que es va veure que la divisió entre categories certament no era molt clara (a causa sobretot de la subjectivitat de la prova i a la heterogeneïtat de les mostres), es van establir uns limits concrets per tal de permetre una classificació de les teles en funció del seu estat de conservació. Els valors de DP de cada categoria es van establir com a: : 1-"Molt fràgil": <550; 2-"Fragil": 550-950; 3-"Fràgil però no excessivament": 950-1400 and 4- "Bon estat": >1400.

Per altra banda el "DP crític" per als quadres, entès com el valor de DP per sota del qual si un quadre és retirat del seu bastidor necessitarà algun tipus de reforç (reentelat, bandes o altre) ja que la tela és massa fràgil, es va determinar com a <400. A l'altre extrem, el "DP segur" per als quadres, per sobre del qual es pot considerar que la tela, tot i haver sofert una degradació, encara conserva bones propietats mecàniques, es va establir per sobre del DP 1400.

Pel que fa al pH, com que la majoria de les mostres de la Col·lecció de Referència es va trobar que queien entre un pH 5.00 i 5.50, es va establir el pH 5.00 com al llindar per sota del qual es consideraria els quadres com a "molt àcids", ja que aquests quadres serien els més àcids.

Tenint en compte les implicacions identificades pel que fa al DP i al pH de la tela dels quadres, es va dissenyar una "Classificació segons l'estat de conservació". Amb aquesta, els quadres dels quals se sabés el DP i el pH, es podrien prioritzar pel que fa als tractaments de conservació-restauració del suport de tela.

Com que l'acidesa s'ha vist que és un factor altament determinant pel que fa a l'estat de conservació, els quadres més àcids haurien de ser els primers a ser tractats amb algun tipus de desacidificació del suport (bé activa, bé passiva). De totes maneres, en els quadres amb un DP molt baix (<400), la major part del dany ja està fet en aquest sentit i de fet aquests quadres, si calgués, es veurien més aviat beneficiats per tractaments de reforç mecànic. A més a més, com que la degradació es dóna més ràpidament en els primers estadis, els quadres amb un DP molt baix, es provable que mantinguin un DP similar durant més temps. Els quadres amb un DP molt alt que també són molt àcids també es veurien beneficiats per tractaments de desacidificació, però si el temps i els recursos són limitats, el tractament d'aquests quadres es podria posposar per un temps, ja que encara hi hauria un cert marge abans que el DP no baixés a nivells perillosos. Per tant, els quadres amb nivells intermitjos de DP, però més àcids que la resta, serien els que més es beneficiarien de tractaments de desacidificació, i aquesta és la idea que es va seguir a l'hora de dissenyar la "Classificació segons l'estat de conservació".

Conseqüentment, un cop tenim els valors de DP i pH d'un grup de quadres, aquests es poden ordenar segons la prioritat del tractament del seu suport de la manera següent: els quadres amb un DP entre 400-950 i un pH<5.00 (Classe "B1") primer, seguits dels quadres amb un DP 950-1300 i un pH també de <5.00 (Classe "C1"), serien els primers que haurien de ser tractats pel que fa a l'acidesa. Després els quadres de la Classe A (DP<400), que tenen un risc mecànic major, serien tractats si necessitessin alguna operació de reforç del suport. Llavors, els quadres a la Classe "B2" i la "Classe C2" (aquells amb valors de DP intermedis i amb un pH no molt àcid >5.00) es podrien desacidificar si encara hi hagués recursos, ja que molt probablement també tindrien, pel que hem trobat en la nostra recerca, valors de pH àcids. Finalment, a la Classe "D", trobaríem els quadres en el millor estat de conservació, amb un DP>1400, els més àcids dels quals, si els recursos són limitats, es podrien deixar sense tractar per un temps, ja que l'estabilitat del seu suport encara no estaria tan fortament compromesa com la dels quadres amb valors de DP més baixos.

La Classificació segons l'estat de conservació, doncs, s'ha vist que és una eina molt útil ja que estableix una seqüència prioritzada pel que fa a les intervencions de conservació respecte al suport de tela, tenint en compte tant el DP com el pH. És clar que si el temps i els recursos no són un problema, tots els quadres amb una tela àcida, es veurien beneficiats per algun tipus de tractament en aquesta línia i que llavors no caldria aplicar-los la Classificació dissenyada.

L'últim objectiu principal d'aquesta tesi era aplicar, per una banda, el mètode no destructiu de l'espectrometria NIR per conèixer el pH, DP i el tipus de fibra d'un grup de quadres del Museu Nacional d'Art de Catalunya (MNAC) i aplicar la "Classificació segons l'estat de conservació" prèviament dissenyada, per l'altra.

Després d'haver desenvolupat la tècnica no destructiva de l'espectrometria NIR per a determinar el pH, el DP i el tipus de fibra al laboratori, el pas final era aplicar-la en un cas real de quadres valuosos per provar la solidesa de les diferents calibracions produïdes. A més a més, elaborar l'anàlisi de quadres del MNAC ens donaria una informació molt valuosa sobre l'estat de conservació d'un grup de quadres importants de l'entorn de l'any 1900.

Així doncs, es va prendre l'espectre NIR de trenta tres quadres del MNAC, majoritàriament d'artistes catalans, en diferents llocs del seu revers. També es va aprofitar per analitzar dotze quadres de Salvador Dalí pertanyents a la Fundació Gala-Salvador Dalí que anaven del 1920 al 1960 (al llarg de la vida de Dalí), tot i que els resultats complets d'aquestes anàlisis no s'han exposat en aquesta tesi.

L'aplicació de la tècnica NIR desenvolupada va permetre, efectivament, obtenir resultats pel que fa al pH, al DP i al tipus de fibra dels quadres del MNAC, posant de manifest la validesa del mètode. De totes maneres, cal dir que el model creat per al DP, va retornar amb un 45% de resultats en blanc que no es distribuïen aleatòriament per tots els espectres NIR recol·lectats sinó que tendien a concentrar-se més en certs quadres que en altres. Això ens indueix a pensar que potser hi havia alguns tipus de materials que no estaven presents en la calibració desenvolupada i que per això hi havia certa dificultat per fer una predicció en alguns casos. El fet que la calibració per al DP es va fer amb un nombre de mostres menors que la calibració feta per al pH (102 mostres per al DP i 170 mostres usades per al pH) ens fa pensar que si en el futur hi hagués més mostres disponibles de les quals se'n sabés el DP, la precisió de la calibració es podria millorar significativament.

Tal com anticipàvem, pel que fa a la identificació del tipus de fibra, el primer DA que distingeix bàsicament entre el jute, el cotó i un grup de fibres liberianes, va donar identificacions més precises que no pas el segon DA que distingeix entre algunes de les fibres liberianes (lli, cànem i rami). Això es podria explicar pel fet que provablement les fibres liberianes, com que tenen un origen similar, produeixen també espectres NIR més semblants, mentre que les diferències entre aquest grup de fibres i el cotó i el jute potser també són més pronunciades en els propis espectres NIR. De totes maneres, també es creu que una de les raons principals d'aquesta major incertesa en la segona DA és el fet que el nombre de mostres liberianes identificades positivament, a part del lli, era molt baix (cànem, rami, etc.). Si en el futur hi haguessin més mostres d'aquest tipus, es podria construir un model millor.

Es va fer una prova sobre quina seria la millor manera de prendre l'espectre NIR en el cas dels quadres i aquesta va revelar que els tres tipus de suport provats per posar a l'anvers del quadre serien adequats en el nostre cas: dues capes de paper assecant gruixut, la referència blanca de calibració de l'aparell i la taula mateixa de treball. Aquests resultats són útils ja que ens ofereixen una gamma d'opcions entre les quals triar quan s'apliqui la tècnica en pintura sobre tela en el futur.

Donat l'èxit de l'espectrometria NIR desenvolupada per als paràmetres analitzats de la tela dels quadres, la possibilitat de mirar de crear més models per a altres paràmetres en el futur sembla prometedora. En aquest sentit, un paràmetre que es podria potser modelar de manera relativament senzilla, ja que no es requereix de més anàlisis químiques, seria la datació dels quadres. De totes maneres, per poder fer això, aniria molt millor tenir les dates concretes de producció de totes les mostres amb un grau de precisió que nosaltres no tenim per a totes elles.

Pel que fa als resultats concrets dels tres paràmetres analitzats, la conclusió més important que es va trobar és que la tela de tots els quadres del MNAC és àcida. Els valors de pH es va trobar que anaven de 4.10 a 5.73, i que la gran majoria d'ells (un 81%) tenien un pH<5.50. A l'entorn dun terç dels quadres es va trobar que tenien un pH per sota de 5.00 i un petit però important 6% dels quadres es va trobar que tenien un pH per sota de 4.50.

Pel que fa al DP, es va trobar que la tela dels quadres del MNAC a l'entorn de l'any 1900 tenia valors de DP que anaven des de <400 fins a 1313, és a dir que es va detectar força variació pel que fa a aquest paràmetre. Els valors negatius obtinguts cal entendre'ls en el sentit que, com que el DP és una anàlisi de tipus quantitativa, el que les prediccions de fet fan és ordenar els quadres pel que fa a aquest paràmetre en una escala mètrica. Com que la mitjana de l'error de predicció obtingut per a la calibració del DP és un nombre força gran (± 275), això explica els valors negatius.

La majoria dels quadres estudiats, un 41% estaria a la categoria 2 de DP (DP 550-950), és a dir que encara no estarien a la categoria més baixa pel que fa a DP, però estarien començant a estar bastant degradats. Un significatiu 32% cauria en la categoria 1 de DP, amb valors bastant baixos (<550) i una menor proporció del 19% cauria en la categoria 3 (950-1300). Només un 3% (de fet només el quadre de Picasso també inclòs i que de fet és del 1937), estarien en la categoria amb més bon estat de conservació (>1300).

L'aplicació de la Classificació segons l'estat de conservació desenvolupada (i per tant tenint en compte tant el pH com el DP), posa de manifest que el 56% dels quadres del MNAC estudiats es troben entre les tres classes amb millor estat de conservació: B2, C2 i D. Així doncs, es pot dir que part de la col·lecció estudiada està en un estat moderat de conservació pel que fa a la tela, tot i que és evident que hi ha hagut una certa degradació (els valors de DP de les teles són més baixos del que originalment haurien estat).

De totes maneres, hi ha un 20% dels quadres que es troben en la Classe A (DP<400), cosa que implica també que una part significativa de la col.lecció examinada està bastant degradada pel que fa a la tela. Els quadres en aquest grup, doncs, haurien de ser tractats tenint això en compte i per exemple, seria aconsellable afegir algun tipus de suport de reompliment en el seu revers si haguessin de viatjar. De totes maneres, aquests quadres també podrien continuar perfectament bé si se'ls deixa penjats on ara estan (els magatzems o les sales) i no se'ls mou de lloc.

Finalment, hi ha a l'entorn d'una quarta part de la col·lecció analitzada que es veuria enormement beneficiada d'accions que contrarestessin l'acidesa present a les teles, abans que els seus valors de DP arribin a ser massa baixos ja que són clarament més àcids que la resta: un 16% d'elles es troben a la Classe B1 (DP 400-950 i pH<5.00) i un 6% a la Classe C1 (DP 950 – 1400 i pH 5.00)

Referent al tipus de fibres trobades, el tipus més comú és el lli (en un 60% dels casos), amb alguns quadres sobre tela de cotó (12%) i uns pocs sobre tela de jute (9%). Un altre 9% es va identificar també com a rami. Aquesta últim resultat va d'acord amb un quadre de la Col·lecció de Referència que es va identificar com a rami i suggereix que aquest tipus de tela s'ha utitlitzat més del que fins ara es creia. El perfeccionament del mètode pel que fa a la identificació del tipus de fibres podria donar una idea més clara de l'ús del rami com a suport de pintura al llarg de la història.

Una part molt interessant de la recerca es va fer per tal de determinar si les zones més fosques de la tela dels quadres (a causa de vernissos, olis o altres), tendeix a tenir un pitjor estat de conservació que les zones "regulars". Contràriament al que es creia, els resultats mostraren que no hi havia diferències significatives entre aquestes zones dels quadres (tot i que sí que es va corroborar altre cop la correlació positiva entre pH i DP).

L'efecte degradant de la pol.lució, de fet, es va poder comprovar molt clarament en un grup de mostres de la Col·lecció de Referència on les mostres de la zona que havia estat protegida pel bastidor es van comparar amb mostres de la part central del mateix quadre. Així doncs, es va poder veure que mentre que totes les mostres presentaven un pH més o menys semblant, el DP era marcadament més baix per a les mostres de les àrees que havien estat més exposades a la circulació de l'aire (part central del quadre). Se sap que la fusta emet vapors àcids però segurament, quan l'aire està més pol·lucionat, els efectes d'aquest últim són més importants que no pas els efectes del contacte amb la fusta del bastidor.

Un altre agent de degradació per a la tela es va trobar que era l'efecte del contacte directe amb l'aigua. En un quadre amb una gran taca d'humitat al revers, fruit d'una gotera, es va poder comprovar que les parts centrals de la taca tenien valors de pH més baixos (segurament els productes àcids havien estat retirats per la pròpia aigua), però també tenia valors de DP més baixos. Així doncs, s'entreveu que la recerca sobre els efectes del contacte directe de l'aigua amb la tela dels quadres podria donar resultats molt útils, especialment ja que aquest tipus de degradació es va trobar en uns quants dels quadres del MNAC i se sap que és un tipus de degradació que s'ha donat de tant en tant, sobretot en el passat.

La variabilitat entre les diferents àrees d'un mateix quadre es va trobar que era petita en termes de pH (RSD 3%), però molt més alta en termes de DP (RSD 29% i SD 167). Aquests valors volen dir que si per exemple obtenim un valor de DP de 800 en una zona del quadre, en d'altres àrees del quadre, el més provable és que tinguem valors de DP entre els 633 I els 967.

L'estudi preliminar dels resultats obtinguts pel que fa als quadres analitzats de Salvador Dalí (Fundació Gala- Salvador Dalí), indica que els quadres de Dalí en general tenen un pH i un DP més alt que no els quadres del MNAC. Aquest més bon estat de conservació es podria explicar per una banda per la diferència entre les dates de producció dels dos grups de quadres, i per tant en una diferència en els materials (entorn del 1900 per als quadres del MNAC i al llarg del segle XX per als quadres de Dalí) o potser també per la diferència entre l'ambient en els quals els dos grups de quadres s'han conservat (Barcelona per als quadres del MNAC (un ambient més pol.lucionat) i Figueres per als quadres de Dalí).

Conseqüentment, l'estudi dels quadres del MNAC i de Dalí altre cop ha revelat que, certament, la tela dels quadres és majoritàriament àcida. Aquest fet, reforça la conclusió més important a la qual arriba aquesta tesi doctoral : si la intenció és evitar el reentelat dels quadres el màxim de temps possible, els tractaments de desacidificació, actius o passius, s'haurien de començar a implementar més, de manera fins i tot rutinària en els tractaments de conservació-restauració. Si no es fa, l'acidesa present en la tela dels quadres està destinada, com s'ha demostrat en aquesta recerca, a accelerar-ne la despolimerització natural.

A Anglaterra ja es va iniciar fa uns vint anys la recerca en el camp de la desacidificació de la tela dels quadres i més recentment a Itàlia també s'han començat a aplicar les nanotecnologies. La neutralització de l'acidesa es pot fer: de manera activa, aplicant agents desacidificants o de manera passiva, afegint materials que absorbeixin l'acidesa dins dels marcs-vitrina o posant aquests materials a prop de la tela.

Així doncs, al llarg del treball d'aquesta tesi doctoral, s'han identificat dues futures vies de recerca possibles. Per una banda, seria molt interessant estudiar les possibles fonts d'origen d'aquesta acidesa pel que fa a la pintura sobre tela. Això seria molt útil ja que permetria contrarestar-la justament a l'origen. L'acidesa pot venir dels propis materials del quadre (o dels materials afegits posteriorment i de la degradació d'ambdós), o de l'ambient que l'envolta. Pel que fa a la possible acidesa dels materials de restauració, en aquesta recerca s’ha vist que la pasta de farina presenta un pH que és clarament més baix, i aquest podria ser un punt de partida d’una recerca molt interessant per potser acabar ajustant les receptes tradicionals per tal d’evitar aquest efecte.

Per altra banda, com que l’acidesa s’ha confirmat com un element determinant en la degradacó de la tela dels quadres, i com que actualment sota les normes més respectuoses de conservació-restauració s’intenta no reentelar els quadres a no ser que sigui estrictament necessari, s’ha detectat que cal molta més recerca en el camp de la desacidificació, tant activa com passiva, aplicada a la pintura sobre tela.

En resum, les principals conclusions a les quals arriba aquesta tesi doctoral són :

- **El desenvolupament de l'espectrometria NIR / quimiometria per determinar el pH, el DP i el tipus de fibra de la tela dels quadres de manera no destructiva s'ha aconseguit amb èxit.**

- **El pH de la tela dels quadres s'ha trobat que és majoritariament àcid, i encara més el de les teles de reentelat amb pasta de farina. La data dels quadres s'ha vist que no tenia a veure amb el pH, ja que de quadres molt antics tenien valors de pH neutres mentre que altres de més moderns tenien valors de pH àcids. Les teles de jute s'ha vist que tendien a ser més àcides que la resta.**

- **El pH i el DP s'ha vist que estan intensament correlacionats i això confirma la idea que les teles amb un pH més baix es degradaran a una velocitat més alta. Com que el DP i l'estabilitat mecànica del suport se sap que estan correlacionats, el paper clau que juga l'acidesa queda encara més evidenciat.**

- **La percepció subjectiva dels conservadors-restauradors pel que fa a l'estat de conservació de les teles, s'ha vist que en general va d'acord amb el DP dels teixits: mostres amb un DP més baix en general són percebudes com a més febles, mentre que mostres amb un DP més alt es perceben com a més fortes.**

- **El valor "crític de DP", per sota del qual la tela dels quadres majoritàriament és classificada com a "molt fràgil" pels conservadors-restauradors, s'ha establert al voltant de 400. El valor de DP per sobre del qual la tela dels quadres s'ha classificat com a "en bon estat", s'ha establert per sobre de 1400 DP.**

- **Quan es fa un examen de l'estat de conservació del suport de tela, el pH i el DP són paràmetres importants a tenir en compte. Aquells quadres amb un pH més baix, però amb valors de DP que encara no són gaire baixos, són els que es veuran més beneficiats pels tractaments de desacidificació del suport.**

- **S'ha detectat que totes les teles dels quadres del MNAC de l'entorn del 1900 estudiats tenen un pH àcid. Els valors de DP s'ha trobat que anaven des de l'estat de conservació « molt fràgil » (<400) fins al de « fràgil però no excessivament » (<1400). Aquests dos resultats s'ha vist que anaven d'acord amb els resultats obtinguts en analitzar la Col.lecció de Mostres de Referència que es va utilitzar per a construir la calibració de l'espectròmetre NIR.**

- **Els quadres de Dalí de la Fundació Gala-Salvador Dalí creats al llarg del segle XX, s'ha trobat que tenien valors de pH i DP lleugerament més alts que els quadres analitzats del MNAC de l'entorn del 1900.**

- **Havent corroborat la importància de l'acidesa en la degradació de la tela del suport dels quadres, es conclou que cal molta més recerca sobre mètodes de desacidificació per contrarestar-la (de manera activa o passiva), així com l'estudi dels possibles orígens d'aquesta acidesa.**

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Conservation research most often needs real samples, even if they are small and come from “second-range” objects. This is why the collaboration with cultural heritage institutions is so crucial in this type of projects. In this regard, I would specially like to thank the collaboration of Mireia Mestre and Dr. Núria Pedragosa, from the Museu Nacional d’Art de Catalunya (MNAC), who were from the very start really eager to collaborate in this research. They were always ready to put all their means so that a good outcome could be achieved and this is very much appreciated. Similarly, Dolo Pulido (Col.lecció de la Facultat de Belles Arts, Universitat de Barcelona) and Maite Toneu (Centre de Restauració de Béns Mobles de Catalunya) were also always helpful, collaborative and offered everything they could.

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Marta Oriola i Folch
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