Cleaning of Watercolour Drawings

A study of the use of Gellan gum gel on water sensitive media

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ABSTRACT
Gellan gum is a non-toxic and biodegradable polysaccharide widely used in pharmaceutical and food industries. 2003 the use of a rigid gel of Gellan gum was introduced in paper conservation for cleaning of works of art on paper. The method has been thoroughly evaluated and highlighted as an ideal method for treating sensitive and degraded papers. This study aims to evaluate the suitability of the method on watercolour drawings.

This study comprises a comparison between cleaning with Gellan gum gel and washing by immersion. An experiment has been conducted on paint-outs of six historic madder lake pigments and three historic Prussian blue pigments together with one modern synthetic pigment painted onto three different papers. Evaluation of eventual changes of the media during treatment has been made with respect to colour change, morphological changes i.e. loss of colour and redistribution of pigments, and migration of pigments into the paper matrix using colorimetry, UV-vis spectroscopy, absorption spectroscopy and microscopy.

The results indicate that there are a significant difference between gel cleaning and immersion wash. Regarding the risk for colour change due to pigment loss, gel cleaning is preferable, as long as no top layer is added to the cleaning sandwich. Regarding wash fastness, cleaning with Gellan gum gel has proved to increase morphological changes.

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1. INTRODUCTION

1.1. Background and Presentation of Context

Wet treatments are fundamental actions in the conservation of works of art on paper (Basoli et al. 2014, p. 205; V. D. Daniels & Shashoua 1993, p. 442): cleaning, delamination from old mounting supports, lamination with Japanese paper and removal of old mendings are examples of treatments, which often require complete water saturation of the object. Paper does, in most cases, respond well to water; rather it is the graphic medium, which may cause problems. Fatty media such as printing inks and grease pens are water fast and can thus be immersed in water without showing any changes in appearance or in the adhesion of the media to the support. Water based inks and watercolours on the other hand, can be soluble in water and wet treatments must therefore be carried out with much caution. In many cases, faced with the risk for fading, bleeding or loss of the media, conservators avoid aqueous treatments of watercolours, finding other solutions, or leaving the damages untreated (Lunning & Pavelka 2002).

During internship at *Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivisto e Librario, (ICRCPAL),* in 2013, I was introduced to the method of cleaning paper with the use of a rigid hydrogel of Gellan gum. The advantages of the method were reported to be the controlled and slow diffusion of water into the paper material, the almost non-existent effect of the treatment on the paper surface and how the treatment could easily be interrupted at any time. The method is used at the institute for treating graphic documents and art on paper with water fast media. The method, however, appears to be almost ideal for the treatment of water sensitive material, and this is my impetus to investigate the subject.

1.2. Current Studies in the Field

Several alternatives to washing by immersion have been proposed, all of which attempt to reduce the risk of damaging the medium during cleaning treatment. In paper conservation four main groups of methods for the washing of single-sheet paper objects are used: immersion washing, float washing, blotter washing and suction table washing (G Banik et al 2011, p. 314). A comparison between immersion washing, suction table washing and blotter washing has shown that, regarding the reduction of acid compounds in the paper; the two latter methods are less efficient than washing by immersion (Kijima et al. 2007). However, the blotter paper and suction table methods are considered safer and more controlled than washing by immersion, though the risk for bleeding or loss of pigment during these treatments still is present (G Banik et al 2011, p. 335)

Since 2003, Simonetta Iannuccelli and Silvia Sotgiu, paper conservators at *ICRCPAL* have investigated the use of the rigid hydrogel of Gellan gum in paper conservation (Iannuccelli & Sotgiu 2010b, p. 25). Several articles have been published describing the application of the gel, emphasizing the efficiency and suitability of the method for delicate and fragile objects (Basoli et al. 2014; Botti et al. 2011; Casoli et al. 2013; Iannuccelli & Sotgiu 2010a, 2010b, 2012). These articles are all, except for one (Casoli et al. 2013), written by, or in cooperation with the conservators at ICRCPAL. In *Evaluation of Cleaning and Chemical Stabilization of Paper Treated with a Rigid Hydrogel of Gellan gum by means of Chemical and Physical Analyses,* a comparison with other cleaning methods shows that the efficiency of the cleaning with Gellan gum versus that of immersion washing is equivalent, and regarding some factors, such as pH augmentation, the Gellan gum can be even more efficient (Botti et al. 2011).

To date, no studies have been published about the application of Gellan gum on water sensitive media such as watercolours. However, several paper conservators in Norway, and presumably elsewhere, do use the gel for treatment of watercolour drawings (Informant 1, 2).

General experiences seem to be positive, and the opinion among these conservators appears to be that Gellan gum is a 'safe' cleaning method. However, examples of non-successful treatments exist. A professional paper conservator, practising in Norway, has observed a violet paint on a relatively modern watercolour to bleed during gel treatment, creating large violet patches and causing irreversible damage to the object[1] (Informant 2).

Research on how the treatment with Gellan gum affect water sensible media such as watercolours, seems to be of great need.

1.3 Definition of Problem and Issues

Despite the fact that there has been no published research done on the suitability of applying Gellan gum on water sensitive material, paper are using the method to clean potentially water sensitive watercolour drawings.

This thesis will study the following question: **How does treatment with Gellan gum affect watercolours in comparison with washing by immersion, regarding fading and/or change of the colour by leaching and/or bleeding?**

In accordance to the *American Institute for Conservation, (AIC)*, Code of Ethics, §6, evaluation of conservation methods and their eventual negative effects are considered of need for the conservation profession (Works 1994). In this study the following assumptions are made:

- Cleaning can be considered positive for the conservation of an object.
- Changes of the medium such as fading, colour change, pigment loss or bleeding are considered negative and as unwanted side effects.

1.4 Purpose and aim

The purpose of this study is to investigate the suitability of the use of the rigid gel of Gellan gum for cleaning of water sensitive watercolours. The aim is that the results of this study may serve as a guide for conservators in their decision-making while handling watercolours, and contribute to safer treatments.

1.5 Methods and Materials

A literature study will serve to give information about Gellan gum gel; its chemical composition and the method used for cleaning single-sheet objects with the gel. The literature study will also generate general information about cleaning of paper and the issue of cleaning watercolour drawings, this to allow understanding of the actions taking place when water is introduced to paper with pigment containing media.

A comparative experiment will then be conducted. Cleaning with Gellan gum gel using two different methods will be compared with washing by immersion. The experiment will be executed using paint-outs of nine historic pigments and one modern pigment. Furthermore, a case study on two watercolour miniatures will be conducted.

1.6 Restrictions

The cleaning efficiency of Gellan gum has already been studied and research results published, therefore evaluation of the cleaning efficiency will not be included in this study (Basoli et al. 2014; Botti et al. 2011)

Iannuccelli and Sotgiu propose indirect application of the gel while treating sensible objects. A sheet of Japanese paper should then be placed between the gel and the verso of the object

[1] Fortunately, the treated object was owned by the conservator her-self and of little economic value.

(Iannuccelli & Sotgiu 2010b, p. 35). This application method will not be used in the experimental part of this study. The selection and inclusion of a Japanese paper would add another variable and multiply the number of samples needed for the study. Thus, the experiments will be executed with direct application of the gel.

Furthermore only a limited number of colorants and paper substrates will be studied. The influence of the particle size of the pigments will not be investigated.

2. GELLAN GUM

2.1 History and Applications

Certain microorganisms produce, during fermentation, extracellular polysaccharides, a sort of *extracellular polymeric substance (EPS)*. In 1978 experiments with *Sphingomonas elodea*, previously known as *Pseudomonas elodea,* part of the Sphingomonadaceae family, were begun in order to find a biofilm applicable in food and pharmaceutical industries (Placido 2012, p. 26).

Gellan gum is produced through inoculating a carbon-containing fermentation medium with the Spingomonas bacteria which can be extracted from the elodea plant (Kang et al. 1982, p. 1086). The fermentation takes place in sterile environment and under strict control. The viscous broth secreted by the bacteria is pasteurised with alcohol. This can be done either directly by precipitation to yield the substituted native *high acyl form (HA)*, Fig. 1, or directly after an alkali treatment of the broth which yields the unsubstituted, *low acyl form (LA*), Fig. 2. The obtained substances are called Gellan gums and are commercially available as white powder. In low concentrations with water and in the presence of promoting cations, the gum is able to form gels with different characteristics. The substituted HA forms soft elastic gels while the unsubstituted LA forms hard and brittle gels. Common for all Gellan gum gels are their transparency a feature which can nevertheless be increased by clarification (Bajaj et al. 2007, p. 348; Sworn 2009, pp. 204, 205).

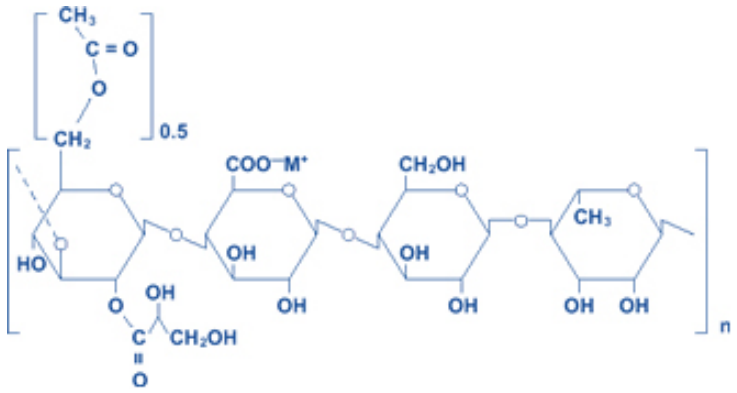


Fig. 1: High Acyl Gellan gum tetrasaccharide repeat unit (Zhejiang Tech-Way Biochemical Co 2014).

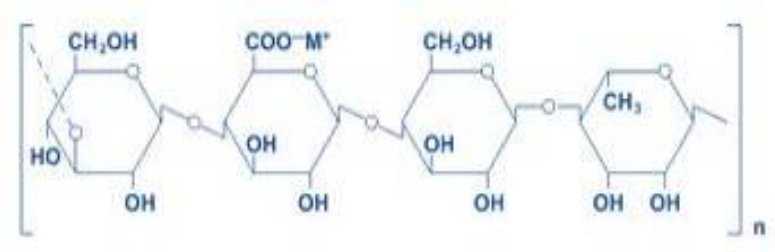


Fig. 2: Low Acyl Gellan gum tetrasaccharide repeat unit (Zhejiang Tech-Way Biochemical Co 2014)

Gellan gum is completely biodegradable and is non-toxic. The gum was approved for use in food production in the United States in 1992 and later also in Asia and Europe (Jani & Shah 2009, p. 48). Today Gellan gum is commercially used in the food, the biomedical and the pharmaceutical industries as well as in the biological and microbiological research field (Iannuccelli & Sotgiu 2010b, p. 31). The gel is produced by the Japanese Kelco Company and the European/American company Sigma-Aldrich. There are four different brands to be found: Kelcogel®, Gelrite®, Phytagel® and GelGro@ (Bajaj et al. 2007, p. 342; Placido 2012, p. 26).

2.2 Chemical Composition

Gellan gum is a water-soluble eteropolysaccharide composed by a linear tetrasaccharide repeating unit. The repeating unit consists of the following three monosaccharides: α-L-rhamnose, β-D-glucuronic acid and β-D-glucose in a molar ratio of 1:1:2 (Jani & Shah 2009, p. 48). The polymer has a linear structure, and in its native form two acetyl substituents are present; one L-glyceryl per tetrasaccharide repeating unit and one acetyl every two units. The substituents are present on carbons 2 and 6 respectively (Sworn 2009, p. 206). The LA form has found application in paper conservation, and the following text will be limited to concern this form only.

In Gellan gums' solid phase the polymers are structured in co-axial, three-folded double helices. The solid, powdery Gellan gum can be dispersed in cold water and hydrated upon heating > 90°C. It will then turn into a solution of non-ordered coils, single polymers, in water. When cooled to the transition temperature, around 35°C, in the presence of mono- or divalent cations at low concentration, the solution will undergo a disorder-order transition to form a hard and brittle gel. In the first step of the gelation process the double helices will form. In a second step the cations will promote formation of a three-dimensional network of the double helices, kept in order by week hydrogen bonds and Van der Waals forces (Bajaj et al. 2007, p. 348; Iannuccelli & Sotgiu 2010b, pp. 30, 31). The gel can be held at a temperature of 80°C for over an hour without loss of essential characteristics. The sol-transition process is thermo-reversible and the gel can, if heated, be turned into solution again for an unlimited number of times (Placido 2012, p. 28; Sworn 2009, p. 208)

2.3 Preparation of gel

The gel of Gellan gum is prepared by dispersing the Gellan gum powder in cold water. Tap water naturally contains enough cations to promote gelation of the gum. However, in conservation and in other application fields, the preparation of the gel in de-ionized water with a controlled amount of cations is recommended. Different cations can be used. The concentration of the cation-containing substance can be decreased when using elements forming divalent ions (Kang et al. 1982, p. 1088). In his PhD thesis from *Departemento di Scienze della terra* at Sapienza Università in Rome, Italy, Matteo Placido evaluates the use of five different cation forming compounds: $CaSO_4$, $CaCl_2$, $Ca(OH)_2$, $Ca(HCO_3)_2$ and $Ca(CH_3COO)_2$ Regarding pH of the obtained gel and the solubility of the compound in water, $Ca(CH_3COO)_2$, calcium acetate, is recommended in a concentration of 0.4 g/l water (Placido 2012, p. 54). This is also the recommendation given by Iannuccelli and Sotgiu and the concentration used in all other conservation literature found on the topic (Basoli et al. 2014; Botti et al. 2011; Casoli et al. 2013; Iannuccelli & Sotgiu 2010a, 2010b, 2012).

1-4 % Gellan gum concentration is proposed for use in conservation. The rate of water release by the gel is depending on the concentration. Gels of 2-4 % are recommended for absorbent papers while gels of 1-2 % are suitable for less absorbent papers. Drop angle test is proposed to get an indication on the papers wettability, and an angle above 45° indicates the need of a gel with a low concentration, together with prehumidification of the paper (Iannuccelli & Sotgiu 2010b, pp. 33-35).

After the Gellan gum has been dispersed in the water, the liquid is heated in a microwave oven at about 600–900 W power until it has turned into a transparent solution. The solution is poured onto a plate of glass or heat-supporting plastic to form a 1-3 cm thick layer. The plate is left to cool in the fridge or at room temperature. Once the gelation temperature is reached, the solution turns rapidly into a brittle, transparent gel (Iannuccelli & Sotgiu 2010b, p. 32).

2.4 Application in Paper Conservation

After preparation, the gel can be cut into the size of the object. Iannuccelli and Sotgiu propose different treatment methods for sensitive and non-sensitive material. However, before treating any material, they recommend the stability of the eventual media to be tested. The method is only considered suitable for treating waterfast media or safely consolidated water sensitive media (Iannuccelli & Sotgiu 2010b, p. 32; Informant 4).

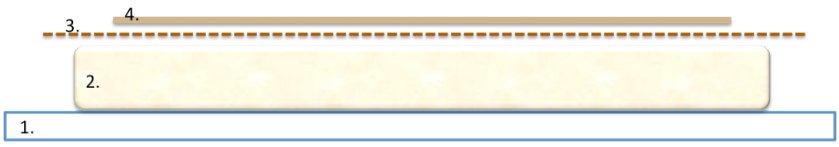
The following procedure is used for non-sensitive material such as graphic prints and blank paper. After prehumidification in a sandwich or in a humidity chamber, the object is placed on a sheet of plastic, such as Melinex. The gel is placed on top, directly on the objects recto enabling the image or text to be seen through the transparent gel. Over the gel another sheet of Melinex is placed. To assure complete and homogenous contact between the object and the gel, a glass or plexiglass plate is placed on top of the sandwich. When needed further weights can be added, see Fig. 3 (Iannuccelli & Sotgiu 2010b, pp. 32, 33).

1. Plexiglass 2. Melinex 3. Object 4. Gellan gum gel 5. Weight

Fig 3: Cleaning sandwich for regular gel cleaning

The interaction between the gel and the paper will start immediately. The time of treatment depends on the nature of the paper, its wettability, thickness and degradation state. Treatments from 30 min and more appear in the literature (Casoli et al. 2013; Placido 2012.). The treatment can be stopped at any time and the gel removed from the object. No rinsing is needed, as the gel does not leave any traces on the paper surface (Casoli et al. 2013). Due to the movement of degradation products and dirt from the paper into the gel, the gel will turn yellow during treatment, indicating its efficiency (Iannuccelli & Sotgiu 2010b, pp. 32, 33).

More sensitive materials such as drawings, fragments of objects and very thin or degraded papers are recommended to be treated from the verso. The gel is prepared in the same way, but placed directly on to the Melinex and the object placed on top of it, with the verso facing the gel. A Japanese paper can be introduced between the gel and the object to simplify the handle and act as an isolation, see fig. 4 (Iannuccelli & Sotgiu 2010b, p. 35).



1. Plexiglass 2. Gellan gum gel 3. Japanese paper 4. Object

Fig. 4: Cleaning sandwich for sensitive objects

For further information about the application of Gellan gum gel as a conservation tool in paper conservation, please see Appendix 1.

3. CLEANING OF PAPER

3.1 Introduction

The following chapter will give a brief overview of different mechanism occurring when paper is subjected to water. The first section will look at the interaction between the paper matrix and the water, whilst the second section will look closer at the influence of water on the media, in particular watercolours.

3.2 The Interaction between Paper and Water

Paper is an organic material. All organic materials have an equilibrium moisture content, EMC, changing with fluctuations in the surrounding relative humidity, RH. Depending on its constitution and state, paper can be more or less hygroscopic, and different papers will thus hold different EMC exposed to the same RH (G. Banik et al. 2011, p. 260). The more hygroscopic and the higher EMC, the more direct and faster will the process of soaking be when the paper is subjected to liquid water.

In order to explain the mechanism of wetting, an understanding of the paper structure is necessary. The paper and the surrounding space can be described as consisting of three principal, potential water reservoirs. The first reservoir is found inside the solid paper fibres where cavities occur between the cellulose fibrils. This reservoir is called the intrafibrillar space. Between the paper fibres the matrix contains voids or pores, the so-called interfibre spaces. The third region is the surrounding space, the washing bath, the gel or the humid air (Lienardy & Van Damme 1990, p. 23).

When paper is subjected to water transfer of water takes place between these three regions through four dominating actions: *Gas Diffusion, Surface Diffusion, Bulk-Solid Diffusion* and *Capillary Transport.* These actions can be described as follows:

Gas Diffusion: Gas diffusion takes place when water molecules in their gas face move through the paper pores. This action dominates at low RH, and the greater thermal energy present, the more rapid gas diffusion.

Surface Diffusion: Takes place when water molecules accumulate on the paper surface and move into the paper matrix. Surface diffusion coexists with gas diffusion and bulk-solid diffusion. The surface diffusion increases with increasing RH but ceases as soon as the paper pores becomes saturated with water.

Bulk-solid Diffusion: Designates the transport that occurs within the fibre cell wall, and causes fibre swelling. Increases with increasing RH and continues after the pores have been filled with water.

Capillary Transport: Capillary transport occurs when paper pores are saturated with water. The capillary transport can move degradation products from the interfibre pores to the paper surface, and is the dominating action during immersion washing.

(G. Banik et al. 2011, pp. 268, 269)

Based on the objects nature and preservation state, different washing methods are used. Depending on method, one or several of these actions will dominate the washing.

3.2.1 The Rate of Washing

Different factors influence the rate of washing, these have been thoroughly studied by Dr Vincent Daniels (G. Banik et al. 2011, pp. 290-318; V. Daniels & Kosek 2002). He describes how the extraction of discoloured products during immersion washing can be divided into three steps of transition. In the first step the solid degradation products are dissolved by the

water and move from the interior of the fibres to the fibre surfaces, that is movement in the intrafibrillar region. The degradation products will then be transported from the fibre surfaces, through the interfibre pores to the paper surface. In the succeeding step they will leave the paper surface and diffuse into the water bath (G. Banik et al. 2011, p. 296).

The transition of dissolved substances can take place in both directions; substances can be extracted from the paper as well as up taken by it, depending on the concentration gradient. When balance between the concentration of substances in the paper matrix and the washing bath is balanced, the gradient is zero and the diffusion ceases. By increasing the concentration gradient the speed of the washing can be increased. This can be made by ascertain a constant flow or change of water over/around the paper surface (G. Banik et al. 2011, pp. 298, 299; Lienardy & Van Damme 1990, p. 26). A range of other factors also plays an important role in the speed and efficiency of washing, such as temperature and addition of surfactants to the water. The choice of method is, however stated to be of little importance provided that the cleaning is carried out long enough. Research indicates that cleaning for 90 min, will give equivalent results regardless if the wash is carried out using immersion, float, blotter or suction table washing (V. Daniels and Kosek 2002, p. 50).

If the water has equal access to both sides of the paper it could seem logic that the wash will be more efficient than if the paper lies on the bottom of a tray, thus giving free access to only one of its surfaces. This presumption has been rejected, instead experiments have indicated that double-sided washing is faster than single-sided, but that the two treatments create the same extend of cleaning after washing periods of about 40 min and longer (V. Daniels & Kosek 2002, p. 48).

3.3 Cleaning of Watercolour Drawings

3.3.1 Pigment Transport during Washing

During washing, changes of the media can occur either within the plane of the surface of the object or out of plane, e.g. bleed through lateral movement in the horizontal plane of the surface or migrate vertically into the paper matrix respectively. These two movements can take place during both immersion washing and Gellan gum gel cleaning. In the case of immersion washing, a third dimension must be considered; media can lift off the sample surface and diffuse into the washing bath, generating loss of pigment (or in some cases reset on the verso of the object). In the case of gel cleaning there is no contact between the recto surface of the object and the cleaning substance and this three-dimensional movement is not possible, see Fig. 4. However, when contact between the gel and the object is enhanced through the use of a weight, as in Fig. 8, p. 25, there is a risk of loss and redistribution of pigment due to contact between the wetted medium and the interleaving medium, i.e. Melinex.

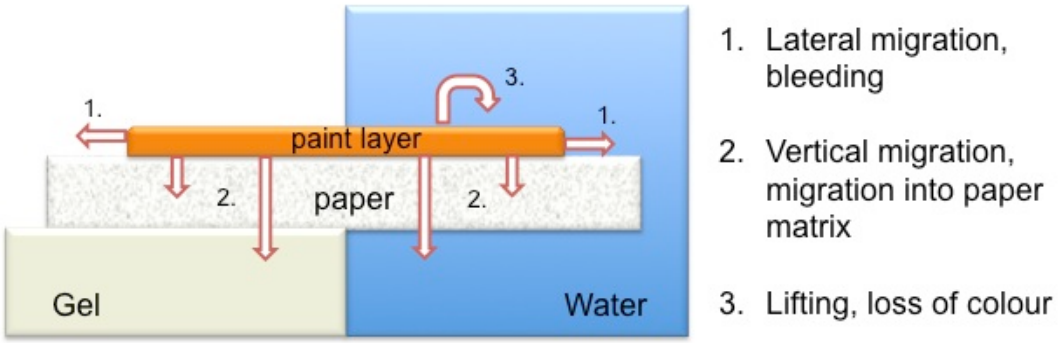


Fig. 5: Illustration of 2- and 3-dimensional migration

Fig. 6 and 7 are examples of how redistribution of colour and loss of colour can cause morphological changes.

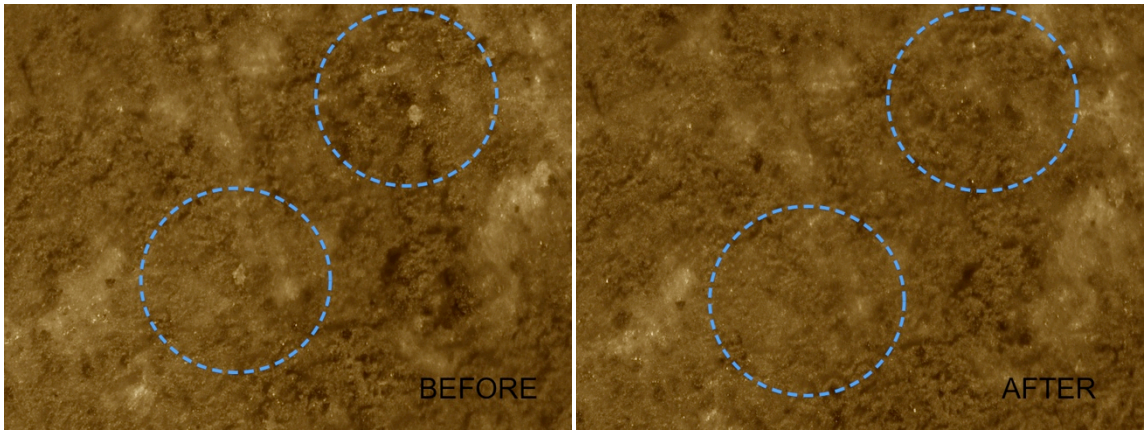


Fig. 6: Example of lateral migration, redistribution of pigments: white areas have disappeared during washing.

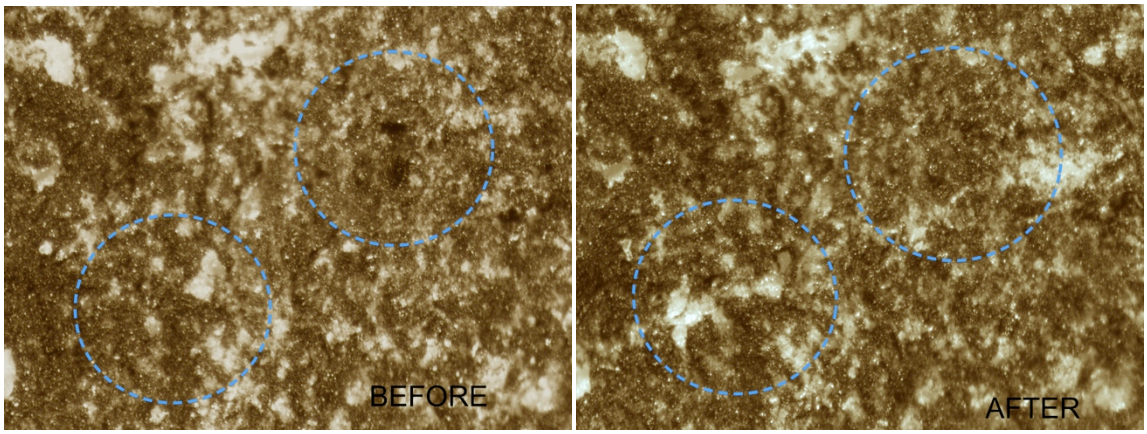


Fig. 7: Example of lifting, loss of colour: new white areas can be seen after treatment together with loss of dark areas.

3.3.2 Wash Fastness

Factors influencing the wash fastness of watercolours and the rate of movement between the substrate and the media during washing have been studied. Dr. Vincent Daniels is author of two publications on the subject.

Daniels (1995, p. 31) states that old (more than 60 years old) watercolour cakes, and by extension watercolour drawings, generally are less soluble than new ones. He concludes that the cross-linking of the gum Arabic, binding medium in the paint, is the main reason for the development of insolubility (V. D. Daniels & Shashoua 1993, p. 445). Cross-linking of the gum Arabic can be enhanced by the presence of transition metals such as manganese, cobalt, chromium and aluminium, metals that often occur in the substrate of lake pigment or in inorganic pigments. The presence of zinc oxide and barium sulphate, compounds that are often present as extenders in paints, can inhibit cross-linking of the gum media and thereby reduce wash-fastness of watercolour drawings (V. Daniels 1995, pp. 36-39).

The wash-fastness of a watercolour is influenced not only by internal factors such as the solubility of the binder, but also of a range of external factors. For example, the nature of the paper support and the thickness of the paint layer, have an important impact. The outcome of Daniels' research indicates that unsized low-density paper has a positive effect on the wash-fastness (V. Daniels 1995, pp. 33, 36).

The influence of the nature of the paper support has been further investigated by Aeli Clark. Clarke (1998 pp. 160, 163) proposes the theory that madder lake pigments would be among the pigments the most prone to migration on washing. A porous paper is supposed to be more accessible for the media to penetrate. Lake pigments, such as madder lakes, are prepared of dyes fixed on white pigment substrates. In the case of madder lakes, the dye is composed of a mixture of anthraquinone dyes. These pigments are known to fade on exposure to light. During fading of the anthraquinone dyes, inter alia, a redox reaction occur which sensitize the surrounding materials, e.g. the paper substrate to degradation. Degraded paper becomes more porous as the degree of polymerisation decreases, and thus the paper supporting anthraquinone containing pigments, will upon aging be more susceptible to pigment migration The chemical reactions and mechanisms occurring in paper in the presence of anthraquinone. containing dyes in combination with transition metals have been further investigated and described in *A Chemiluminescencec Study of Madder Lakes on Paper* (J. Thomas et al. 2010)

Following the same argument, low density and unsized paper can be postulated to be more accessible to media migration into the paper support. However, as stated previously, results indicate, that watercolour drawings painted on unsized paper, are more wash-fast than drawings on hard sized paper. This is interpreted by Daniel (1995, p. 36) to be due to the pigments being able to penetrated into the paper matrix during painting, and thus creating stronger bonds between the paint and the paper support. Taking both these theories under consideration, the conclusion could be drawn, that paper which has lost its sizing due to degradation, will provide ideal conditions for pigment migration, in contrast to originally unsized paper.

Clarke (1998, p. 164) highlights the importance of the particle size of the pigments. The outcome of his experiments shows that despite the degrading effect on the paper created by the anthraquinone dyes, the pigment being the most prone to migration among the nine tested pigments[2], was the carmine. In the case of low-density paper the media change occurs in the form of vertical migration into the paper matrix, while lateral movement occur in the cases with denser and less easily wetted paper. The migration of the carmine is interpreted by Clarke as being due to the very fine, dye-like nature of the paint. Supporting the anthraquinone dye theory, the rose madder was the pigment showing the second greatest migration, regardless of the rose madder being one of the paints having the coarsest pigments.

3.3.3 Three Main Factors to Consider

This very brief over-view of the published literature treating the question of wash-fastness make clear that it is a complex matter and that it seems very difficult to predict the reaction of watercolour paint when introduced to water. Three main factors though seem crucial: **The presence of extenders in the paint; The presence of transition metals in the paint; The presence of sizing in the paper.**

In order to evaluate the suitability of cleaning watercolour drawings with Gellan gum gel it seemed in consequence important to test the following hypothesis:

- How does the presence of extenders in the paint influence the wash-fastness of watercolours when subjected to cleaning with Gellan gum gel and immersion wash respectively?

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[2] Watercolours: Burnt umber, cadmium yellow, carbon black, carmine, gamboge, genuine rose madder, Indian red, vermilion and warm sepia. Papers: Arches acquarelle 185 g/m2 (100% cotton, gelatine tub-sized), BFK Rives Blanc 180 g/m2 (100% cotton, internal sized), Sugar paper 140 g/m2 (mixed fibres, containing ligning, starch sized) (Clarke 1998, p. 161)

- How does the presence of transition metals in the paint influence the wash-fastness of watercolours when subjected to cleaning with Gellan gum gel and immersion wash respectively?
- How does the presence of sizing in the paper influence the wash-fastness of watercolours when subjected to cleaning with Gellan gum gel and immersion wash respectively?

4. EXPERIMENTAL METHODS AND MATERIALS

4.1 Introduction

To evaluate the outcome of the two treatments, cleaning with **Gellan gum gel** and **washing by immersion**, a comparative experiment was conducted.

A mainly quantitative study consisting of a comparison between how the cleaning with Gellan gum gel respectively cleaning by immersion affect watercolour drawings regarding redistribution of pigments in the horizontal plane, vertical migration and loss of media. The experiment was conducted using small **circular samples** (8 mm in diameter) of watercolour paint-outs. The cleaning was conducted using microwell plates with 24 wells ca. 3 ml, 20 mm in diameter.

A more qualitative evaluation of the eventual bleeding of the colours during treatment (the movement of pigment in the horizontal plane) together with loss of pigments was conducted. In this second part washing by immersion was evaluated in comparison to two gel cleaning methods, which further were mutually compared. The sample set for this second part consists of **rectangular samples** (ca 25 x 25 mm), whereas each sample contains both coloured and uncoloured areas.

Aiming to simulate a more real conservation situation a **case study** was effectuated. Two discardable miniature watercolour drawings served as case study objects. The miniatures are depicting the same seascapes, made out of the same colorants and painted by the same artist. While very similar, the miniatures are, however, not identical. One of them was washed by immersion and the other one treated with Gellan gum gel.

4.2 Sample Materials

The sample material consists primarily of paint-outs produced for the *Anoxic Frames Project, (AFP),* at Tate, London, UK in 2007. The material has been produced as a result of *Art Technology Science Research, (ATSR),* aiming to reproducing arts material used by J.M.W Turner at the end of the 18th/first half of the 19th century (J. L. Thomas 2012, p. 38). In complement to these "historic" samples, one modern watercolour together with two modern papers were also used.

4.2.1 Pigments

To test the hypothesis presented in section 3.3.3, p. 21 three categories of pigments were chosen. One set of three historic Prussian blue pigments, two of them being identical pigments whereas one without and the other with extenders (P1, P3), and one, third, extender-free Prussian blue pigment with differing origin (P2). One set of six different historic madder lake pigments whereas five made out of the same madder dye laked onto different substrates, with different metal ratios, (M1, M2, M3, M5, M6) and one made out of a differing type of madder dye (M4). For the last set one modern violet pigment was chosen (Mo).

The historic pigments originate from J.M.W Turner's studio, part of the Turner Bequest at Tate. Two of the Prussian blue pigments, P1 and P3, do not belong to the Turner studio pigments collection, but are early to mid 20th century Cornelissen pigments from the Tate Conservation Archive (J. L. Thomas 2012, pp. 45, 46). The pigments were prepared by AFP as paints made out of pure Gum Arabic, hand ground pigment and deionised water. The painted paper samples were then exposed to accelerated photo- and thermal degradation in line with *American Society for Testing and Materials,* ASTM D6819-02. For detailed information, please see Thomas 2012 Ch. 3.

Table 1: Pigment information (J. L. Thomas 2012, pp. 45, 46, 87; Townsend 1993, pp. 234, 235)

Sample name	AFP name	Pigment	Substance	Chemical description	Additional information
P1	TCA1	Antwerp blue	Prussian blue	M+FeIII[FeII(CN6)] M+=Na+, K+, NH4+	ZnO and $BaSO_4$ present as extenders
P2	TTB6	Prussian blue	Prussian blue	M+FeIII[FeII(CN6)] M+=Na+, K+, NH4+	Synthetic precursors possibly from animal sources. Al present in the pigment lattice.
P3	TCA7	Chinese blue	Prussian blue	M+FeIII[FeII(CN6)] M+=Na+, K+, NH4+	Pure Prussian blue, only K and Fe present as metals
M1	TTB1	Madder lake *Scarlet madder*	Rubia tinctorum L	Purpurin, pseudopurpurin, alizarin, unidentified high hR[5] component	Al, Ca , Cu, Fe, (Mn) -containing substrate
M2	TTB5	Madder lake *Brown madder*	Rubia tinctorum L	Purpurin, pseudopurpurin, alizarin, unidentified high hR component	Ca, Cu, Fe, Mn-containing substrate
M3	TTB8	Madder lake *Red Madder*	Rubia tinctorum L	Purpurin, pseudopurpurin, alizarin, unidentified high hR component	Ca, Cu, Fe, Mn, Si-containing substrate Fine pigment grain
M4	TTB13	Madder lake *Yellow madder*	Rubia cordifolia L	Munjistin, rubiadin, alizarin, other unidentified high hR component	Ca, Cu, Fe, (Mn), Si-containing substrate
M5	TTB14	Madder lake *Rose shade of madder*	Rubia tinctorum L	Purpurin, pseudopurpurin, alizarin, unidentified high hR component	Al, Ca, (Cu), Fe, (Mn)-containing substrate
M6	TTB2	Madder lake *Rose madder*	Rubia tinctorum L	Purpurin, pseudopurpurin, alizarin, unidentified high hR component	Al, Ca, (Cu), Fe, (Mn)-containing substrate
Mo	Not part of AFP	Winsor Violet	Carbozole dioxazine		Modern watercolour paint.

Winsor and Newton *Artists' Water Colours Winsor Violet* was chosen as modern pigment. Information about the exact composition of the paint is unfortunately not available due to trade secrets, only the chromophore containing substance are known, see table 1. This modern watercolour was applied on three different papers for the circular sample set, and on four different papers for the rectangular sample set. The paint was dissolved in deionised water and

[5] Thin layer chromatography analysis, *TLC*, have shown this unidentified component to have high retention value, *h*R

painted with a 13.7 mm flat synthetic artist brush. The samples were dried in open air at room temperature. The paint was bought 20th February 2014 and the paint-outs produced the following day, 21 days before the experiments were begun.

Details about the pigments and their labelling can be found in table 1.

4.2.2 Paper Supports

Historic paper (Hi): The paper used in the AFP was produced as a reconstruction of an original paper used by J.M.W Turner. The paper was hand made at the Ruscombe Paper Mill from a pulp composed of 60 % flax and 40 % Cotton linters with $CaCO_3$ as alkaline reserve. The paper, ca 200 g/m^2 were tube sized with 3 % edible hide gelatine, with an addition of 5 % $KAl(SO_4)_2$ (J. L. Thomas 2012, p. 47). Three variants were produced with different surface roughness. All historic pigments are painted on the roughest paper, labelled GSH by AFP.

Gelatine sized paper (Ge): The smoothest form of the reconstruction paper, labelled GSG by AFP has been used for the modern pigment paint-outs.

Whatman n. 1 (Wh): Whatman paper n.1, 100 % cotton has been used for the modern pigment paint-outs, representing unsized paper.

Fabriano 200 g/m^2 (Fa): High quality modern watercolour drawing paper of 100% cotton has been used for the modern pigment paint-outs representing neutral synthetic sized paper.

4.2.3 Blank Reference Samples

A total of four different papers were used in the study. Circular samples of each paper type, 8 mm in diameter, taken from the same sheet/piece of paper as the coloured samples, were sampled to serve as blank references. These were labelled P:Hi, P:Ge, P:Fa, P:Wh

4.2.4 Replicates

Triplicates of samples were used, e.g. three equal samples originating from three different paint-out pieces of the same type. From the three samples, two circular, respectively three rectangular, samples were made, giving a sample set with three replicates of each type for each method. For an over-view of all samples please see table 2 and table 3.

Table 2. Circular samples set. 1x for cleaning with Gellan gum gel (Gel), 1 x for immersion wash (Water). 36 x 2 = 72 samples

PRUSSIAN BLUES *The influence of extenders*			MADDER LAKE PIGMENTS *The influence of transition metals*						DIOXAZINE VIOLET *The influence of the sizing*		
P1: $BaSO_4$ ZnO			M1: Al, **Ca**, Cu, **Fe**, Mn			M4: **Ca**, **Cu**, Fe, Mn, Si			Ge: Gelatine sized		
P2: No extenders			M2: **Ca**, Cu, **Fe**, Mn			M5: Al, **Ca**, Cu, **Fe**, Mn			Fa: Synthetic sized		
P3: No extenders			M3: **Ca**, **Cu**, Fe, Mn, Si			M6: Al, **Ca**, Cu, **Fe**, Mn			Wh: Unsized		
$P1_I$	$P2_I$	$P3_I$	$M1_I$	$M2_I$	$M3_I$	$M4_I$	$M5_I$	$M6_I$	Ge_I	Fa_I	Wh_I
$P1_{II}$	$P2_{II}$	$P3_{II}$	$M1_{II}$	$M2_{II}$	$M3_{II}$	$M4_{II}$	$M5_{II}$	$M6_{II}$	Ge_{II}	Fa_{II}	Wh_{II}
$P1_{III}$	$P2_{III}$	$P3_{III}$	$M1_{III}$	$M2_{III}$	$M3_{III}$	$M4_{III}$	$M5_{III}$	$M6_{III}$	Ge_{III}	Fa_{III}	Wh_{III}

Table 3. Rectangular sample set. 1x for cleaning with Gellan gum gel no top layer (Gel I), 1x for cleaning with Gellan gum gel with top layer (Gel II), 1x for immersion wash (Water). 12 x 3 = 36 samples

HISTORIC MADDER LAKE PIGMENT	MODERN DIOXAZINE PIGMENT		
M4:Hi_{I}	Mo:Ge_{I}	Mo:Fa_{I} (missing Gel I)	Mo:Hi_{I}
M4:Hi_{II}	Mo:Ge_{II}	Mo:Fa_{II} (missing Gel I)	Mo:Hi_{II}
M4:Hi_{III} (missing Gel II)	Mo:Ge_{III}	Mo:Fa_{III} (missing Gel I)	Mo:Hi_{III}

4.3 Case Study Material

The three sacrificial miniature watercolour drawings, 51 x 103 mm, for example, see Fig. 10, used as case study objects are painted by Tony Smibert, during AFP. The drawings were made on the smooth gelatine sized reconstruction paper, labelled GSG by AFP and Ge in this study, without being artificially aged. The motif contains six colorants: *Prussian blue* P2, *yellow madder* M4, *scarlet madder* M1, *brown madder* M2 and *gamboge*, the latter was not included in this study due to its toxicity (Informant 3).

4.4 Methods

4.4.1 Humidification and Preparation of Gel & Water

Before cleaning all samples were humidified in a sandwich for ca 15 min, with polyester felt as water barrier. Due to differing absorption properties of the different paper substrates, the choice of humidification time was a delicate question. 15 minutes was chosen based on water content during different stages of humidification (G. Banik et al. 2011, p. 278).

A 2 % gel was chosen to serve for the experiment. 2 % is a medium strong concentration, usable for the broadest range of papers. This is also the concentration used in all experiments found in the literature. The gel was prepared with a solution of 0.4 g/l calcium acetate in deionised water and heated for five minutes in a microwave oven at 800 W. The gel-containing beaker was kept in hot water during distribution of the gel. For the circular sample set 1.8 ml gel was put into each well of a microwell plate using a 5 ml syringe. To fill an entire plate required about 5 min. For the rectangular sample set and the case study, gel was poured into glass plates generating 7 mm thick layers, and cooled at room temperature. The gel was then sealed with parafilm and stored in the fridge before and after use.

To enable comparison between the gel and the water in the subsequent analyses, deionised water with an addition of 0,4 g/l calcium acetate was used. The addition of calcium acetate can be considered in line with common conservation practice (Lienary and van Damme 1990, p. 24). For the circular sample set the washing was conducted in microwell plates, and 1.8 ml of cleaning water used in each well. The water was measured using a 5 ml syringe. For the rectangular samples beakers with about 20 ml cleaning water were used and the case study object was washed using750 ml water in a rectangular plastic tray.

4.4.2 Cleaning with Gellan gum gel

After distribution of gel into a microwell plate, the plate was left for about 3 min in order to let the sol-gel transition start at the surface of each well. The circular samples were then gently placed with their verso onto the gel surface. The well plate was directly put between two freezer blocks for about 5 min, accelerating the gelation. The described procedure was developed because previous experimentations had shown that due to the surface tension of

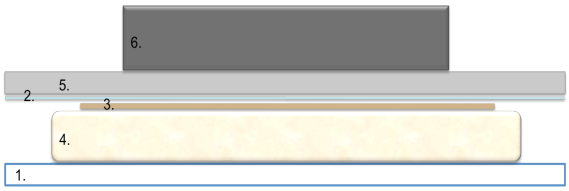
the gel, the gel surface gained a concave shape upon gelation, thus obstructing the contact between the gel and the sample to be established. The limited amount of time the samples were in contact with the not yet completely solid gel, using this method, was short enough to be considered insignificant (<6 % of the treatment period). To further ascertain complete contact, each sample was after another 5 min gently pushed against the gel with the use of a plastic stick with a convex end, about 6 mm in diameter.

Treating the rectangular samples, two different cleaning methods were used. For both methods the gel was cut into rectangular pieces, slightly bigger than the samples. The samples were then placed with their recto on the surface of the rectangles. Cleaning following the first gel cleaning method, Gel I, each sample was then covered with Bondina and pressed against the gel with a gentle stoke by the hand. The Bondina was then removed and the samples left without further interaction. See Fig: 8. Cleaning following the second gel cleaning method, Gel II, a methodology regularly used and described by Informant 1 was used. Each sample was in this case covered with a piece of Melinex and over the Melinex pieces of polyester felt. Ceramic plates (Informant 1 describes the use of plexiglass plates) were then laid over the felt, and a small weight placed on top, see Fig. 9.

Cleaning of the case study object was conducted following Gel I.

1.Plexiglass 2.Gellan gum 3.Object, verso facing the gel

Fig. 8: Cleaning sandwich for Gel I



1.Plexiglass 2.Melinex 3.Object 4.Gellan gum gel
5.Ceramic plate 6.Weight

Fig. 9: Cleaning sandwich for Gel II

4.4.3 Cleaning by immersion

The circular samples were put directly into the immersion bath without support. The plate was gently shaken every 15 min to obtain an agitation of the water. The rectangular sample set was also immersed in the water without support. The beakers were in this case swirled in the vertical plane every 15 min. The case study object was placed between to sheets of supporting rough Bondina before immersion. The water was agitated every 15 min, the object removed from the bath by lifting in the corners of the supporting sheets, and then subsequently replaced.

4.4.4 Drying

After 90 min (from the point when the samples had been put on to the gel/immersed in the water) the treatment were stopped and the samples placed between Bondina to slightly dry. When the samples started to curl at the edges grey cardboard was placed under and above, and the pack put under weight for about 24 h.

5. ANALYTICAL METHODS

5.1 Photographic Documentation

Qualitative evaluation of bleeding and changes of the surface morphology by lifting or lateral migration can be monitored comparing microscopic images of the painted paper surface before and after treatment. Vertical migration into the paper matrix can be monitored by microscopic documentation of the paper cross section before and after treatment. Microscopic investigation of the protective sheets of Melinex used for Gel II can give an indication of whether pigments have been lifted off the surface or not and examination of the gel surface after treatment can in the same way give an indication of eventual transfer of pigment from paper to gel through vertical migration alternatively bleeding.

5.1.1 Performed Documentation

All samples were photographed before and after treatment. The surface morphology of the circular and rectangular samples was documented using stereomicroscope (Nikon SMZ800, eyepieces: 10x, objective: Plan 1x) with a total magnification of 10 and 63 times magnification. Great emphasis was placed on finding exactly the same, corresponding, spot on the samples before and after treatment by the use of a paper template together with a small pencil mark on the edge of each sample. The author of the thesis then performed subjective comparison between the pictures from before and after treatment. The overall colour of the samples was not considered; instead only changes of the amount of blank spots and areas were noted.

The two objects used for the case study were documented with digital photography. Complementary, three points of the design were also documented using microscope, 10 and 63 times magnification. See fig. 10 for the positioning of the three spots. Subjective comparison before and after treatment was made by the author in terms of morphological changes regarding the microscopic images and in terms of colour change and overall changes in appearance regarding the regular, macro, photographs.

Fig 10: Approximate position of investigates spots on case study objects.

The cross sections of the circular samples were also documented with stereomicroscope, 63 times magnification, after performed cleaning. Untreated sample material, originating from the

same pieces of paint-outs as the circular samples, was likewise cross-sectioned to serve as references. One reference for each triplicate set was used. The cross sectioning was made using a sharp scalpel and the sample thereafter put into upright position using a incised eraser gum. Subjective comparison between the cross sections was performed by the author. The comparison was made using the untreated papers as reference.

Microscopic examination of the gel used for the cleaning of the circular samples was conducted. Notes were taken of findings in and on the surface of the gel. A selection of pictures was taken. Two of the pieces of Melinex used for Gel II; one used for cleaning of a sample with the modern dioxazine pigment and one used for cleaning of the historic madder lake samples.

5.2 Reflectance Spectroscopy

Colour is not a simple concept, because the colour we see is not objective or independent neither of the viewer, nor of internal and external factors. The main factors influencing colour are the nature of the coloured surface, the light that illuminates the surface and in particular the observer (Xin & Textile Institute 2006, p. 24).

During the 20th and 21st century, different attempts have been made to enable exact reproduction of a specific colour. The most important systems for colour description have been developed by *Commission Internationale de l'Éclairage (CIE)*. The first system was set up in 1931, and since two main revisions have been presented, the CIE1976 and CIE2000. In very simple terms, the basis for the systems can be described as follow: Using a very well defined standard observer, illuminant, illumination viewing geometrics and primaries, a colour is described by the amount of each of the three primaries needed to obtain exactly the same colour impression. The (Xin & Textile Institute 2006, pp. 25, 33-35) difference between two colours can be calculated using the CIE-systems in the form of ΔE.

5.2.1 Performed Colour Measurements

The reflectance of all circular samples was measured before and after treatment using UV-Vis reflectance spectroscopy (UV-Vis FORS). The derived colour values, expressed in CIE L*a*b* system, were used. Colour change was calculated and noted in the form of ΔE_{00}. ΔE_{00}, part of the CIE 2000 system, is a modified and improved form of the more commonly known ΔE_{76}. ΔE_{00} is considered a more reliable measurement for colour change than ΔE_{76} since it gives data better adapted to the human eye in the blue and near neutral regions (Xin & Textile Institute 2006, pp. 62-64). Because many researchers still use the ΔE_{76} (Informant 3), this form has also been derived from the measurement data, so serve as a reference for comparison with other studies. In addition the difference in L*, a* and b* value respectively were also noted and calculated to give an indication of the nature of the changes, in other words whether the changes occurred as lightning, darkening or other types of changes such as the colour turning less yellow, greener, more red or bluer.

The measurements were performed using a handheld Konica Minolta CM-700 spectrophotometer. This spectrophotometer measures diffuse reflectance using a 40 mm integrated sphere and a d/8° geometry. It has a pulsed xenon lamp (with UV cut filter) and different standard illuminants can be chosen. The spectral range goes from 400 to 700 nm with a resolution of 10 nm. The samples were placed on a pile of Whatman filter paper and the centre of each sample measured. To ascertain the correct position of the sample during measurement, double sided pressure sensitive tape was used and a circular template drawn with a pencil on the filter paper. The D^{65} standard illuminant was used together with a 10° observer and the measured area was chosen to 3 mm. The instrument was calibrated using a standard white plate. To compensate for the eventual difference between the measurements

before and after treatment regarding calibration and positioning of the instrument on the sample surfaces, the entire sample set was measured twice, recalibrating the instrument in between.

The circular samples on unsized paper (Wh_{I-III}) were measured after treatment using a Perkin Elmer Lambda900. The instrument was set with the same geometry, illuminant and observer as the Konica Minolta, and the same background, e.g. Whatman filter paper, and the same procedure of recalibration was used. The measurement spot was however rectangular and not circular. The exact area of the rectangle is not known, but could be considered roughly equal to a 3 mm circle.

All colour data were imported to excel for interpretation via the colour data software SpectraMagic^{TM}NX.

5.3 Absorption Spectroscopy

Absorptions spectroscopy has been one of the most useful tools for quantitative analysis of mostly organic but also some groups of inorganic compounds such as transition metals and ferro/ferricyanide complexes. Absorption spectres can also serve for qualitative analysis, for example in the identification of lake pigments. (Mills & White 1994, p. 23; Skoog & Leary 1992, pp. 156, 159, 161). Depending on the chemical structure of a compound or a mixture of compounds, matter adsorbs radiation of different energy to various extents. By measuring the transmitted or absorbed spectra of a compound or mixture of compound, indications of its constitutions and the concentration of the ingoing components can be measured. The spectra of the near ultraviolet and the visible region extend from 10 -700 nm, but since the optical components of the spectroscopic instruments are made of quartz, absorbing in the region between 10-200, the region measured in UV-Vis spectroscopy, range from 200 to 700 nm, or sometimes even up to 950 (Mills & White 1994, pp. 18, 22).

UV-Vis spectroscopy measures of the water and gel used for cleaning of the circular and rectangular were chosen as analytical methods to give a quantitative indication of the three-dimensional movement of colour during treatment. Proof of eventual lifting and/or leaking of colour were supposed to be present in the water in the form of inorganic matter[15] or organic dyestuffs[16]. Due to several internal and external factors the measurements did not succeed and/or did not prove useful. The obtained data has thus been excluded.

For further information, please see Appendix 2.

5.4 Elemental Analysis

Elemental analysis of the pigments was not executed due to time limitations. Information about metal content and chromophore content were found in Thomas et al 2010, Thomas 2012 and Townsend 1993; the XRF data from Thomas et al 2010 and Thomas 2012 has been used as it was performed on the same samples as used in this study (J. Thomas et al. 2010, p. 2345; J. L. Thomas 2012, pp. 45, 46; Townsend 1993, pp. 234, 235).

5.5 Exploration of Data

The collected data from the different analysis was in a first step explored manually by organisation in tables, visualisation in graphs and investigation of the reliability of the colour

[15] transition metals from the madder lake substrates and ferro/ferricyanine complexes together with $BaSO_4$ and ZnO from the Prussian blues

[16] from the madder lakes

measurements. The data from the circular samples was thereafter further explored using different chemometric methods.

Paired Student's T-test is a univariate statistical hypothesis-testing method, which can be used to evaluate whether the means of two data sets differ significantly from each other or not. In this case the two sets of data are the gel cleaned and the immersion washed samples respectively.

In a second step *K-means clustering* and *Agglomerative Hierarchical Clustering, AHC,* were used. These two methods identify clusters in a population based on similarity and dissimilarity (respectively) in all variables. Thus these chemometric methods are not dimensional reducing. AHC is an unsupervised method and groups the population into a non-controlled number of clusters and gives quantitative values (as Euclidian distances) of how much the detected clusters differ from one another. K-means clustering on the other hand, is a supervised method, and the analyst must him/her self specify the number of clusters and the samples are assigned to clusters based on similarities within all the variables and the clusters are grouped into a 2D matrix based on similarities between clusters of samples. K-means clustering can be used in a quasi-unsupervised manner by giving a range of possible numbers of clusters. The method then builds a series of models for each number of clusters.

In the last step of the data exploration *Principle Component Analysis*, *PCA,* was used. PCA is a variable reducing statistic method, which combines the imputed variables into a reduced set of factors, *Principle Components, PCs*. These PCs form an n-dimensional space where n is the number of variables inputted to form the model. Normally only 2 or 3 PCs are used to define a 2- or 3 dimensional system onto which the variables and the samples are plotted according to their loading factors on each PC. PCs are selected for defining the space based on the amount of variance they are capable of explaining. By viewing how different variables and samples load on to the PCs it is possible to discriminate clusters in samples and define how different variables correlate and anti-correlate with one another. For interpretation it is important to separate descriptive and dependent variables, while the correlation between descriptive values should not be mutually interpreted.

The chemometric data exploration was ordered from dr. Jacob Thomas, supervisor of this thesis, and the interpretation conducted in cooperation with the same dr. Jacob Thomas.

6. RESULTS

6.1 Manual Data Exploration

6.1.1 Morphological changes

Morphological changes were noted during comparison between the circular sample surfaces before and after treatment. A scale from 1 to 3 was used to grade the amount of visible changes. 1 was given to the samples showing no visible change. 2 were given to the samples where changes could be found at either 10 or 63 times magnification. 3 were given to the samples displaying changes both in 10 and 63 times magnification. See fig. 11-13 for examples of each category for the circular samples.

The total sum from all 36 gel treated circular samples is 96 while the immersion washed samples have a sum of only 76. The tendency of the gel treated sample set to have the same or a higher degree of morphological change than the immersion washed ones, is consequent for all sample types with only two exceptions: Ge and M6. Since the difference between gel and water treated samples in these two cases is minor, the significance of the exceptions is considered negligible. See table 2.

Table 4: Sum of values for each sample regarding morphological changes. Sample types differing from the general trend highlighted in blue.

MORPHOLOGICAL CHANGES CIRCULAR SAMPLES 3=Great Visible difference 2=Small noticeable difference 1=No visible difference									
	Gel_I	Gel_{II}	Gel_{III}	Sum	$Water_I$	$Water_{II}$	$Water_{III}$	Sum	G/W
P1	3	3	3	9	3	2	3	8	9/8
P2	3	2	3	8	1	1	2	4	8/4
P3	3	3	3	9	3	3	2	8	9/8
M1	3	3	3	9	3	3	2	8	9/8
M2	2	3	3	8	3	2	3	8	8/8
M3	3	3	3	9	3	3	2	8	9/8
M4	3	3	3	9	1	1	1	3	9/3
M5	3	2	3	8	2	1	1	4	8/4
M6	1	2	1	4	1	2	2	5	4/5
Wh	3	1	2	6	1	1	1	3	6/3
Ge	3	3	2	8	3	3	3	9	8/9
Fa	3	3	3	9	3	3	2	8	9/8

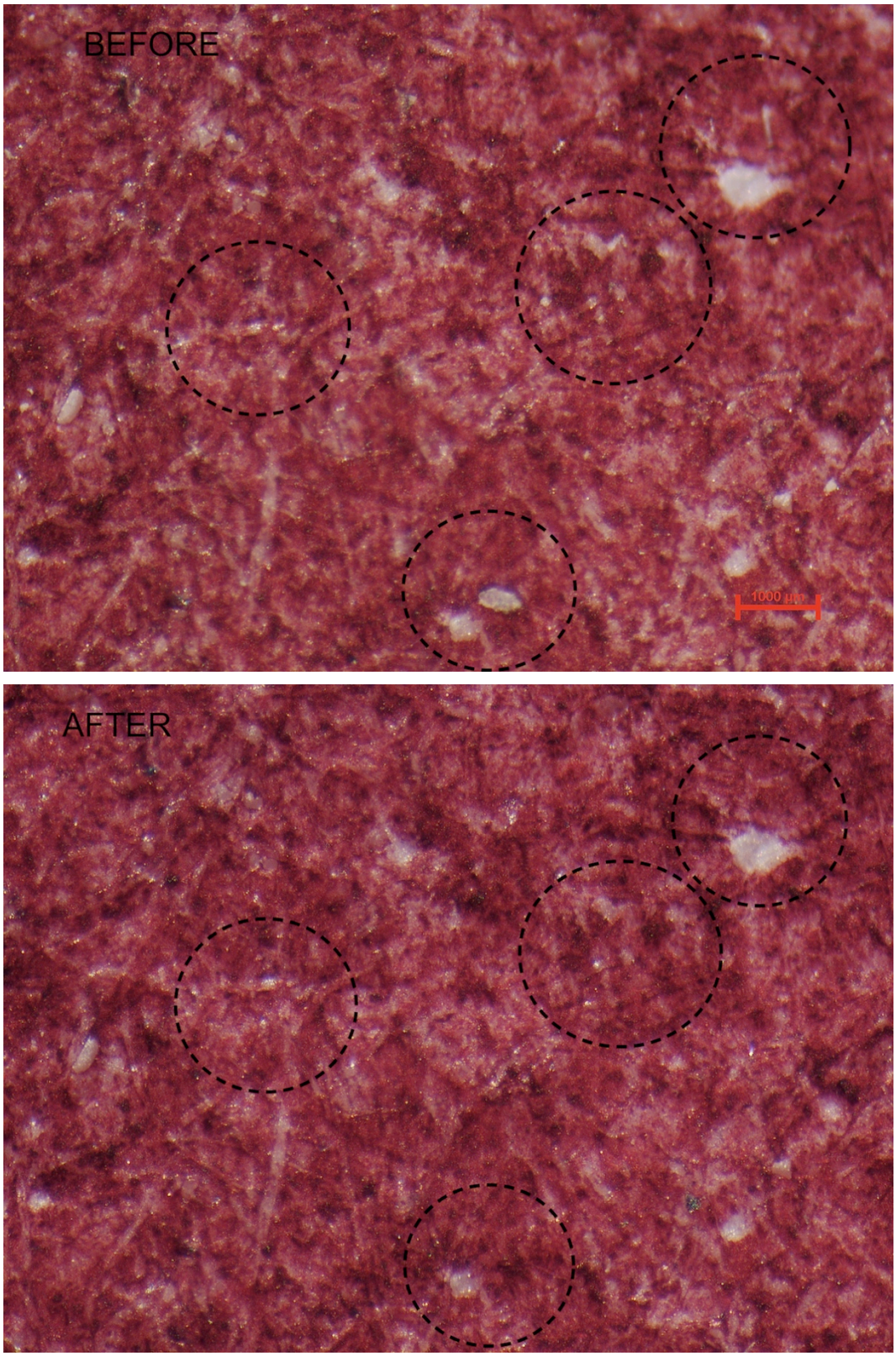


Fig. 11: Example of category 3: obvious differences present. $M3_{II}$ Before and after treatment with Gellan gum. 63 times magnification

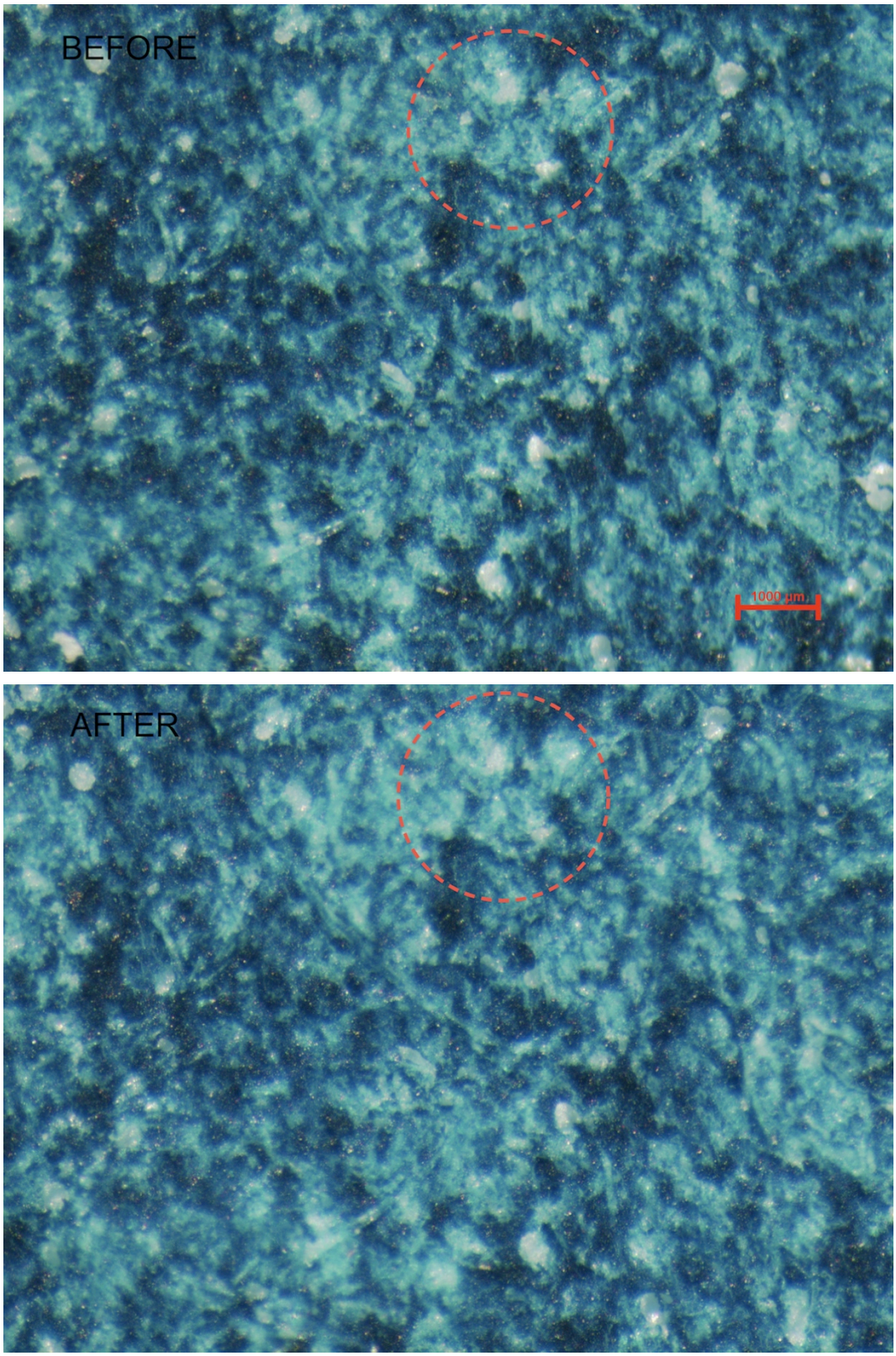


Fig. 12: Example of category 2:small noticeable difference. $P2_{II}$ Before and after treatment with Gellan gum. 63 times magnification

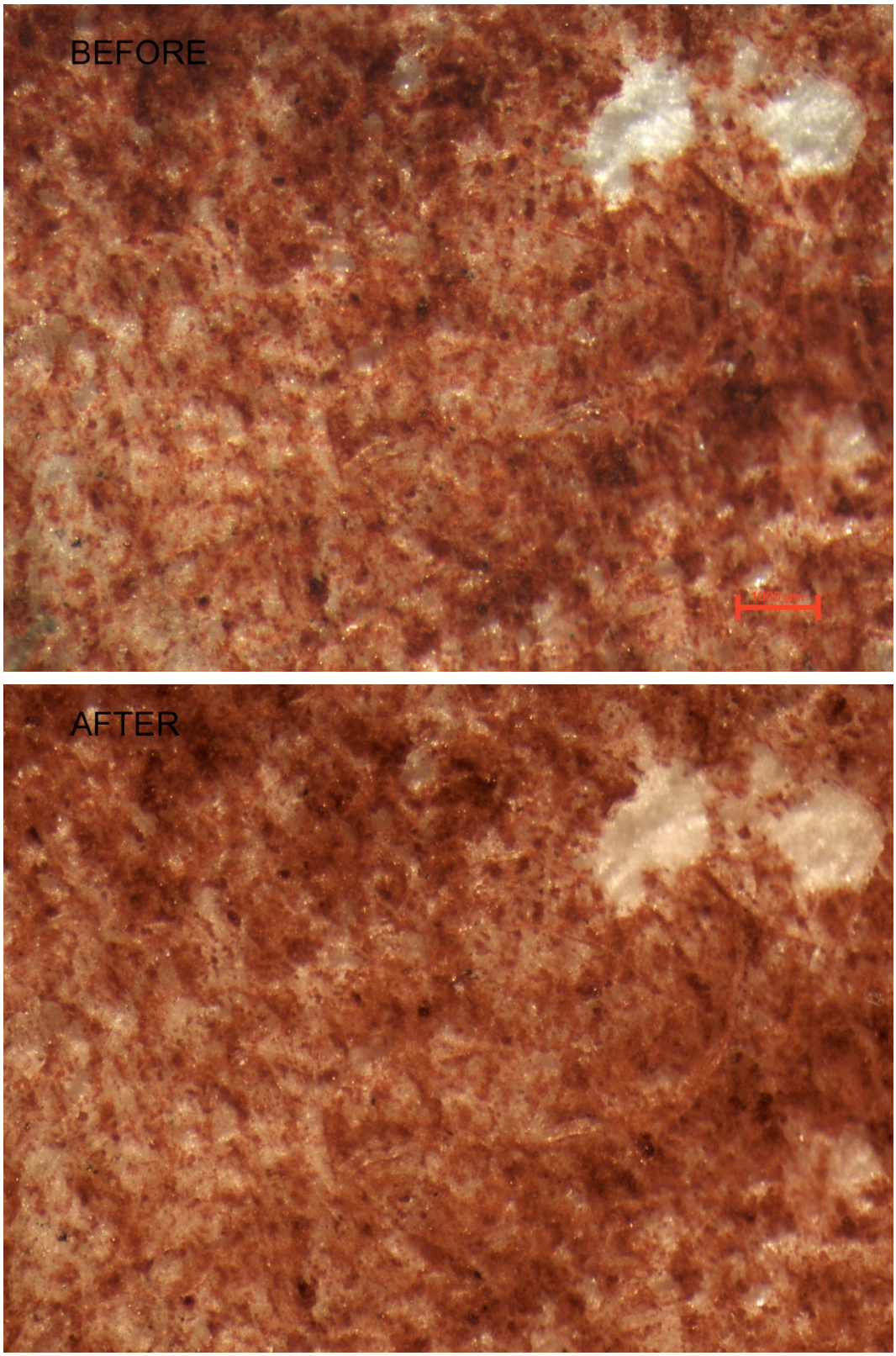


Fig.13: Example of category 1: No noticeable morphological difference. $M5_{II}$ before and after immersion wash. 63 times magnification.

6.1.2 Lateral migration

Comparison of the borders between painted and blank areas on the rectangular samples was performed and the samples divided into the following categories: 1=No visible change, 2=Minor change, 3=Obvious change. Examples of each category can be seen in fig. 14-16.

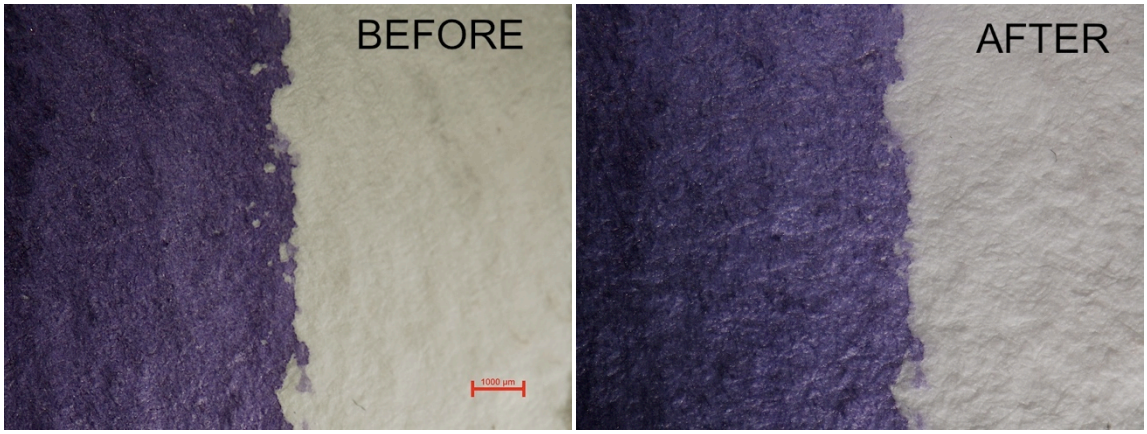


Fig.14: Example of category 3: Obvious lateral migration. Mo:Hi_{II} before and after Gel II treatment

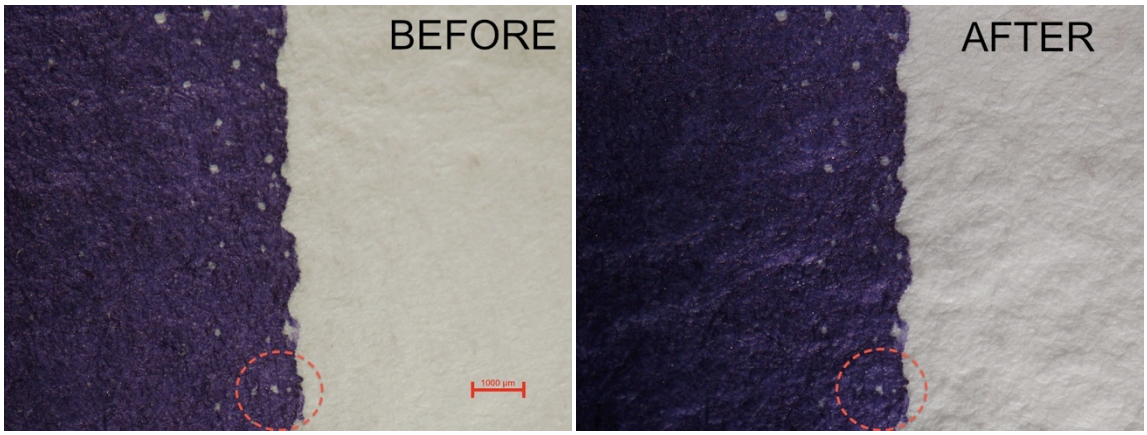


Fig.15: Example of category 2: Some lateral migration noticeable. $MoHi_{I}$ before and after Gel I treatment

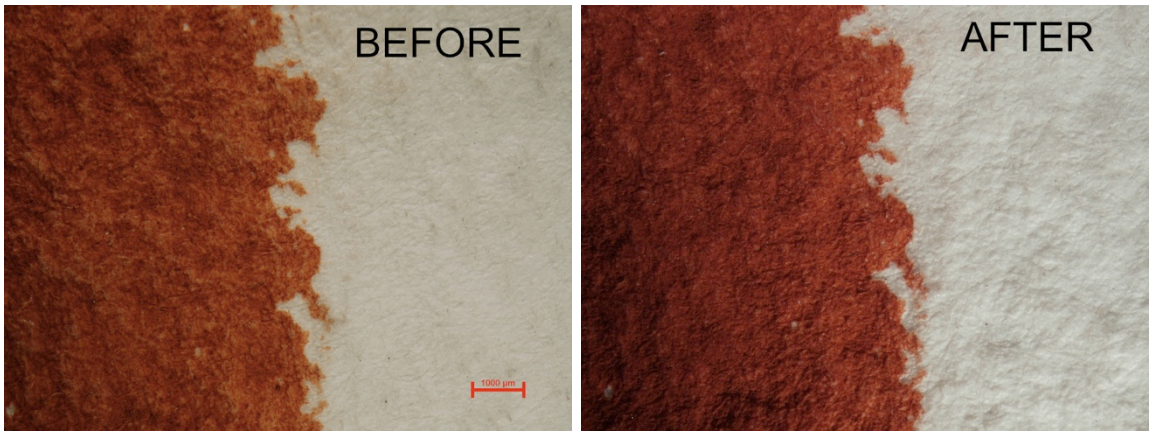


Fig.16: Example of category 1: No noticeable lateral migration. M4:Hi_{I} before and after immersion wash

It was found that the first gel treatment method, Gel I, see section 4.2.3, caused very little lateral migration. Only three samples exhibited any changes: one of the three Mo:Ge samples had undergone obvious lateral migration, and two of the three Mo:Hi samples were found to have undergone some minor changes.

Table 5. Gradation of lateral migration

LATERAL MIGRATION RECTANGULAR SAMPLES 3=Visible difference 2=Small difference visible 1=No visible difference									
	Gel I_I	Gel I_{II}	Gel I_{III}	Gel II_I	Gel II_{II}	Gel II_{III}	$Water_I$	$Water_{II}$	$Water_{III}$
M4:Hi	1	1	1	2	1	missing	1	3	3
Mo:Fa	missing	missing	missing	3	3	3	3	3	2
Mo:Ge	1	1	3	3	3	3	3	3	2
Mo:Hi	2	2	1	3	3	3	3	1	3

Gel II nonetheless turned out to have caused slightly more lateral migration than the immersion washed samples. Since the majority of both Gel II treated and immersion washed samples were put in category 3, see table 2, and thus could be considered to have undergone unacceptable changes, see fig. 14, grading them as one causing more damage than the other, was considered being of little importance.

6.1.3 Vertical Migration into paper matrix

Cross sections of the circular samples were examined and migration into the paper matrix noted using the same scale as for the morphological changes. For examples of each category see fig. 17-19.

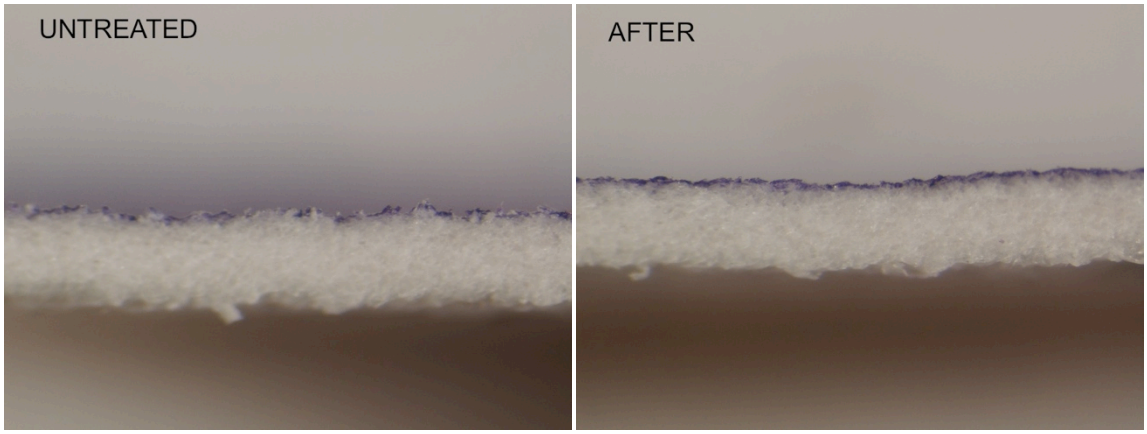


Fig. 17: Example of category 3: Noticeable vertical migration. Reference of Fa together with Fa_{III} after gel treatment

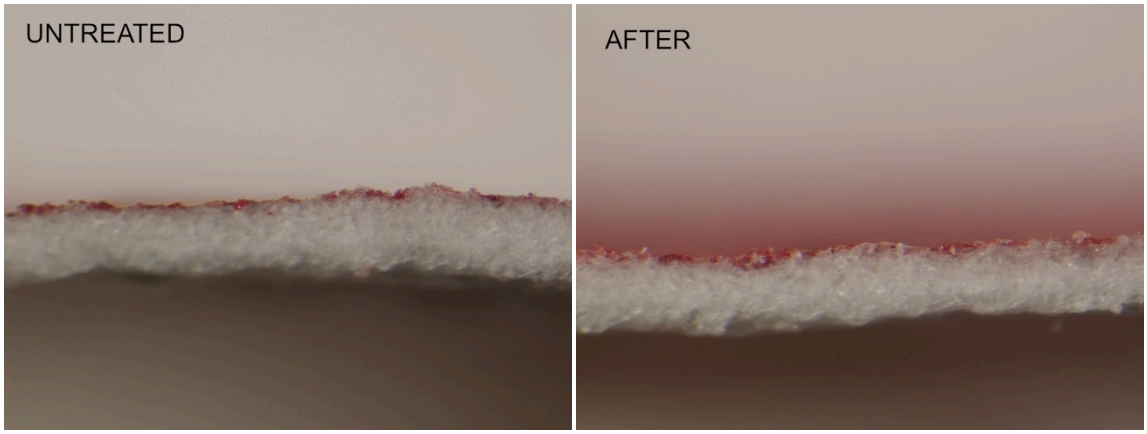


Fig. 18: Example of category 2: Eventually some vertical migration. Reference of M5 and $M5_{II}$ after immersion wash

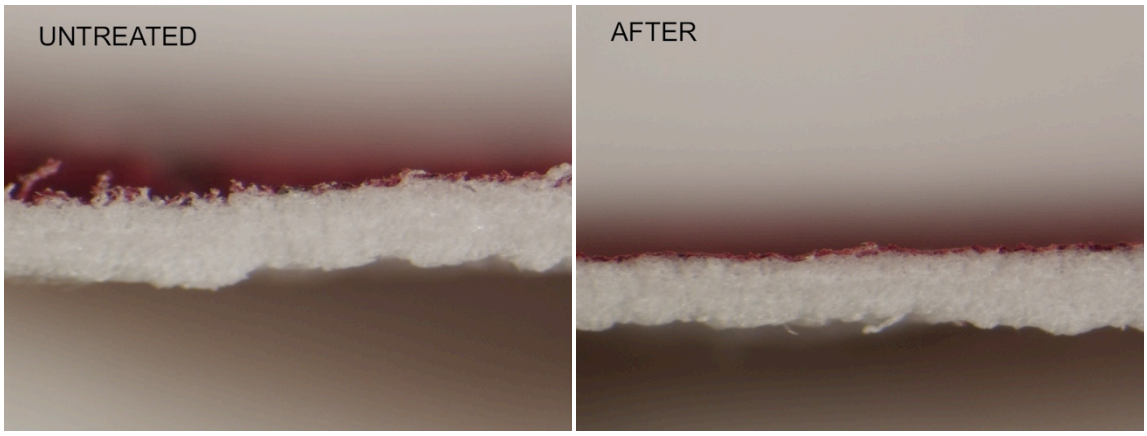


Fig. 19: Example of category 1: No vertical migration noticeable. Reference of M1 and M1:I after immersion wash

Only the gel treated modern dioxazine on historic gelatine sized smooth paper, Fa, demonstrated any clearly visible changes. Since the historic paper is well sized and the historic pigments are hand ground and thus presumably coarse-grained, the lack of migration can be considered expected. However, it should not be precluded that migration may occur during treatment with one or both of the treatments in cases with more finely grained pigment and more absorbent paper. For the full data set, please see Appendix 3 (I).

The cross sections of the Wh samples were not possible to evaluate inasmuch as the pigment already spread throughout the entire cross section of the paper before treatment. Migration could thus not be either proved or disapproved. Following the argument above, it is thought possible that a sample of the same type but with the colour being painted with less water containing paint and thus allowing the paint to stay on the paper surface might have caused visible migration.

6.1.4 Migration into gel/water

Since a quantitative measurement of the migration into the gel could not be performed, see Appendix 2, a qualitative evaluation was made, see section 5.1.1 Findings on the gel surface was noted using a scale ranging from 1 to 4: 1=No pigments found, 2=unidentified finding, 3=pigments found on edges of sample imprint, 4=pigments found on surface of sample imprint. The full data set can be found in Appendix 3 (I)

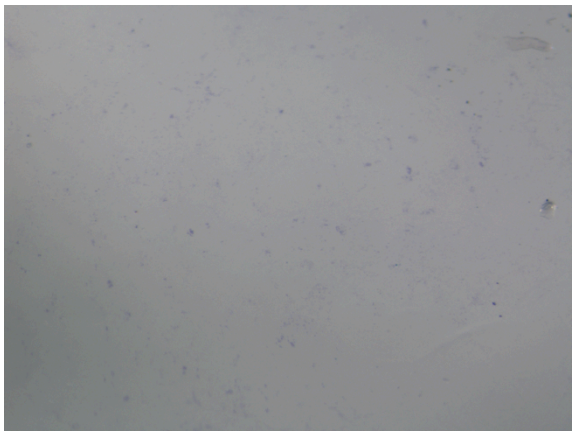
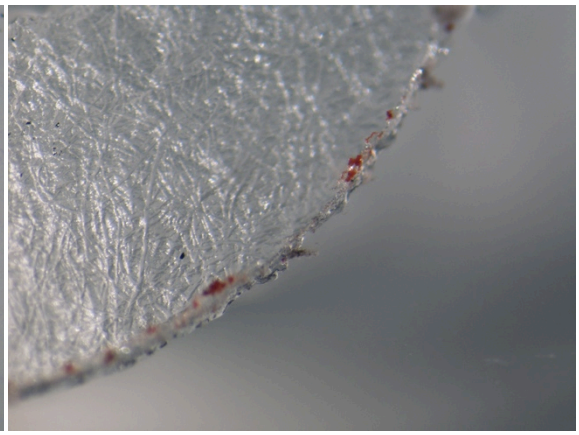


Fig. 20: Violet pigments on gel surface, Wh.



Fig, 21: Pigments on edges of sample imprint, M4.

Wh and Fa samples exhibited pigments on the surface of the sample imprint on the gel, see fig. 20. The occurrence of pigments on these samples corresponds with the results from the examination of cross sections, see section 6.1.3. Pigments were also found on the gel from one of the P1 samples. The reliability of this latter finding has not been proved by any other

analysis. On the edges of one or more of the sample imprints from M1, M3, M4 and M5 pigments were found, please see fig. 21 for illustrative example.

To evaluate the occurrence of pigment loss during Gel II (cleaning with addition of a top layer) the interleaving sheet, in this case Melinex was examined. The results demonstrate very clearly that pigment loss using this method could be critical. See Fig. 22 and 23.

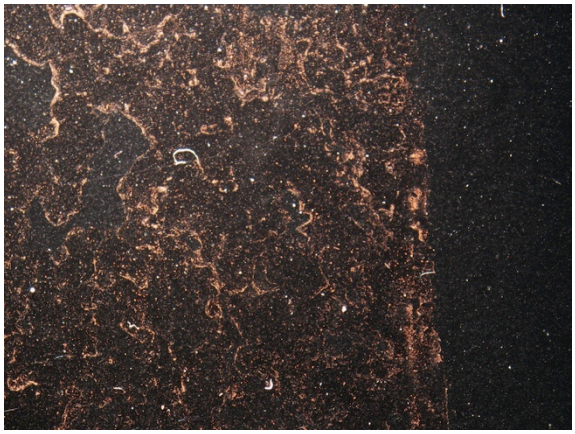


Fig 22. Melinex used for cleaning of H:Hi. 10x magn.

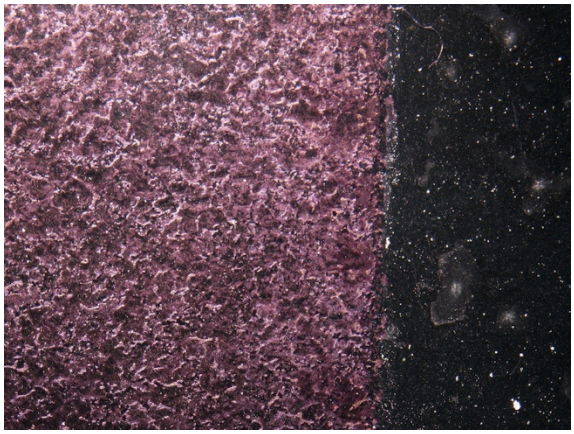


Fig. 23: Melinex used for cleaning of Mo sample

6.1.5 Colour change

For the full data set of colour measurements, please see Appendix 4. The average values from the first and second measurements of the colours before and after treatment respectively were calculated. Colour change in the form of ΔE_{00} was then derived from these values. Plotting the data from the gel treated vs. the immersion washed samples, a clear tendency of the water causing higher ΔE_{00} values, e.g. causing greater colour change, could be seen. See fig. 24.

To explain the presence of exceptions from this tendency, the repeatability of the colour measurements was examined. The ΔE between the first and second measurement of each sample was calculated, and measurements with $\Delta E \geq 1$ were considered unreliable. None of the three M2 samples was found to have acceptable values, probably due to their dark colour, and was thus excluded. See Appendix 5. Since all other sample types had at least measurements from one sample with acceptable repeatability, a new chart including only the reliable measurements could be plotted. Examining the second chart the same tendency could be seen with only one great exception, the Wh samples. See fig. 25. The M6 samples also exhibited greater colour change after gel treatment than after immersion wash. The changes in this case were however <2 and thus considered being of little interest.

The same procedure was done using ΔE_{76}. The same tendency appeared, but less clear. Please see Appendix 6.

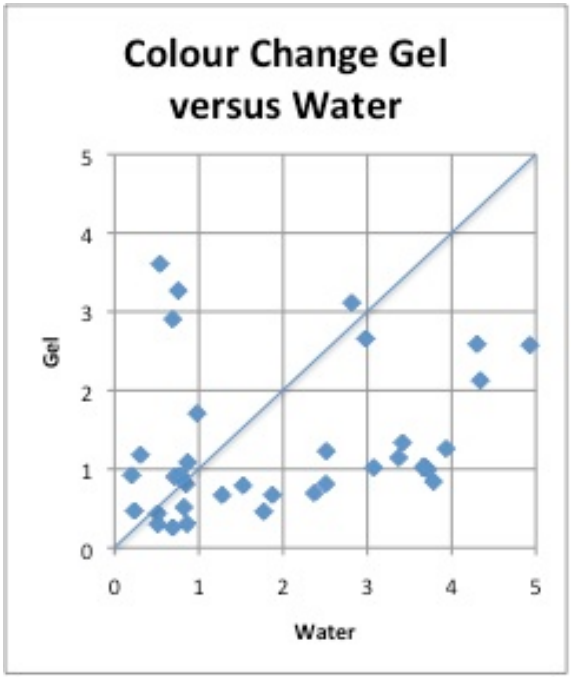


Fig. 24: Diagram of ΔE_{00}, Gel cleaning plotted against immersion wash. All samples.

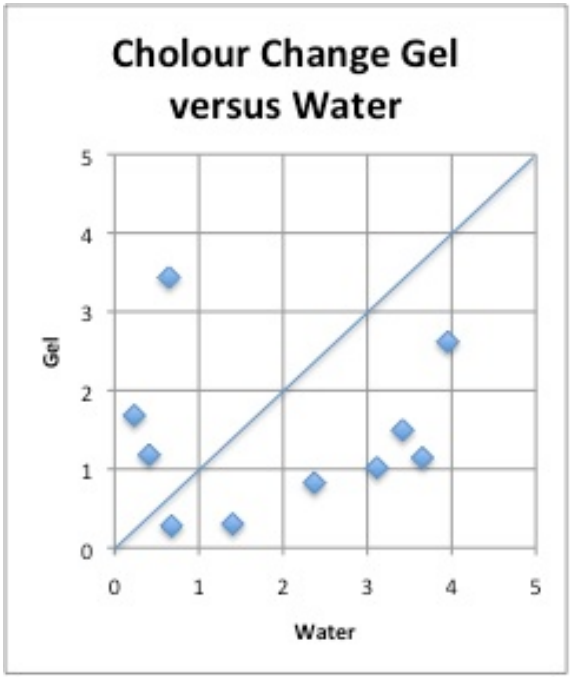


Fig. 25: Diagram of ΔE_{00}. Gel cleaning plotted against immersion wash. Only "reliable" measurements included

6.1.6 Case Study

Comparing the photos taken before and after treatment of the gel cleaned watercolour miniature, slight differences were found. The yellow wash, containing gamboge, appears to be less distinct. The leaking from the brown clouds, almost invisible before treatment appears more evident. Whether this is due to new leaking or due to enhanced contrast to the background because of the latter having lost colour, is difficult to determine. See fig. 26 & 27. Examining the microscopic pictures a clear pigment loss was found at point 1. No noticeable difference was found at point 2. Some overall colour loss was noted for point 3 (For positioning of the three spots, please see fig. 10 on page 28). For microscope pictures, please see Appendix. 7 (I)

Comparing the photos taken of the immersion washed miniature before and after treatment, some obvious change was noted. Clear loss of yellow pigments creating greater contrast between different areas in the design and loss of Prussian blue pigment in the sky were particularly distinct. Examination of the microscopic pictures did however not confirm the immersion washed sample to have undergone greater changes than the gel washed. Instead only eventual overall leaking was distinguishable; please see Appendix 7 (II).

None of the cleaned watercolour miniatures demonstrated any major difference after treatment. Nevertheless both treatments seem to have caused some visible changes.

Fig 26: Gel cleaned case study object before and after treatment.

Fig 27: Colour chart for Fig. 26 after treatment, including rectangular pieces of each colour from before treatment

Fig 28: Immersion washed case study object before and after treatment.

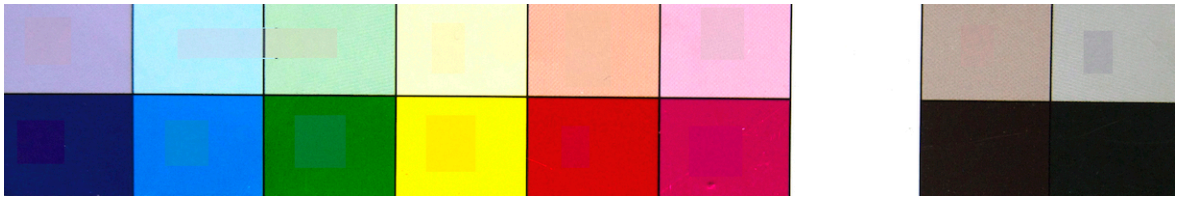


Fig 29: Colour chart for Fig. 28 after treatment, including rectangular pieces of each colour from before treatment

6.2 Chemometric Data Exploration

Aiming to investigate and answer the three hypothesis concerning the influence of extenders, the role of transition metals and the role of the sizing, chemometrics were used to explore the collected data from the circular sample set. The exploration was made separating the three, inherent sample groups; the Prussian blue sample set, the madder lake sample set and the modern dioxazine sample set.

Paired student T-tests were first run to understand whether the samples had reacted upon the two treatments in a significantly differing way or not, and in the case of the madder lake samples to understand if the six madder lake pigments had behaved in a mutually similar way and thus could be treated as one homogenous group.

Clustering analysis was conducted only in the case of the madder lake sample set since this group was the only set containing enough samples to give interpretable results.

Principle component analysis was run on the Prussian blues and the madder lakes. The analysis was run on the entire sample set as well as separately on the gel cleaned and the immersion washed respectively. In order to find underlying structures and clarify which factors being the most crucial, different variation was run in all three cases; including all variables and excluding one or more descriptive or dependent variables such us morphological changes or chromophore content. In the case of both the Prussian blues and the madder lakes, exploring the gel cleaned and the immersion washed samples separately appeared to be the most informative, and the results found investigating these runs will be described in the following sections.

6.2.1 The Role of Extenders

The influence of extenders on the wash fastness was tested using the circular Prussian blue samples, P1-P3.

Student's T-test: A paired (gel vs immersion washed) student's T-test was first run on the entire Prussian blue sample set including both morphological change, and colour change. For a list of all variables, please see table 4. The null hypothesis, e.g. there being no difference between the gel cleaned and the immersion washed samples**,** was stated not to be rejectable. Therefore, further T-tests of morphological changes and colour change separately were performed. The T-test of morphological changes indicated the same thing as the one including both variables, that the null hypothesis could not be rejected with confidence. Regarding colour change however, the T-test indicated that the null hypothesis could be rejected with a 95 % certitude and thus demonstrating the difference between the wash methods to be significant. For details, please see Appendix 8 (I).

Further decomposition comparing P1 to P3 for each wash type was considered impossible due to the low number of sample replicates. Therefore, it was decided that multivariate analyses would be of greater utility.

Table 6. Variables used for data exploration of Prussian blue pigment samples. *values individual for each sample

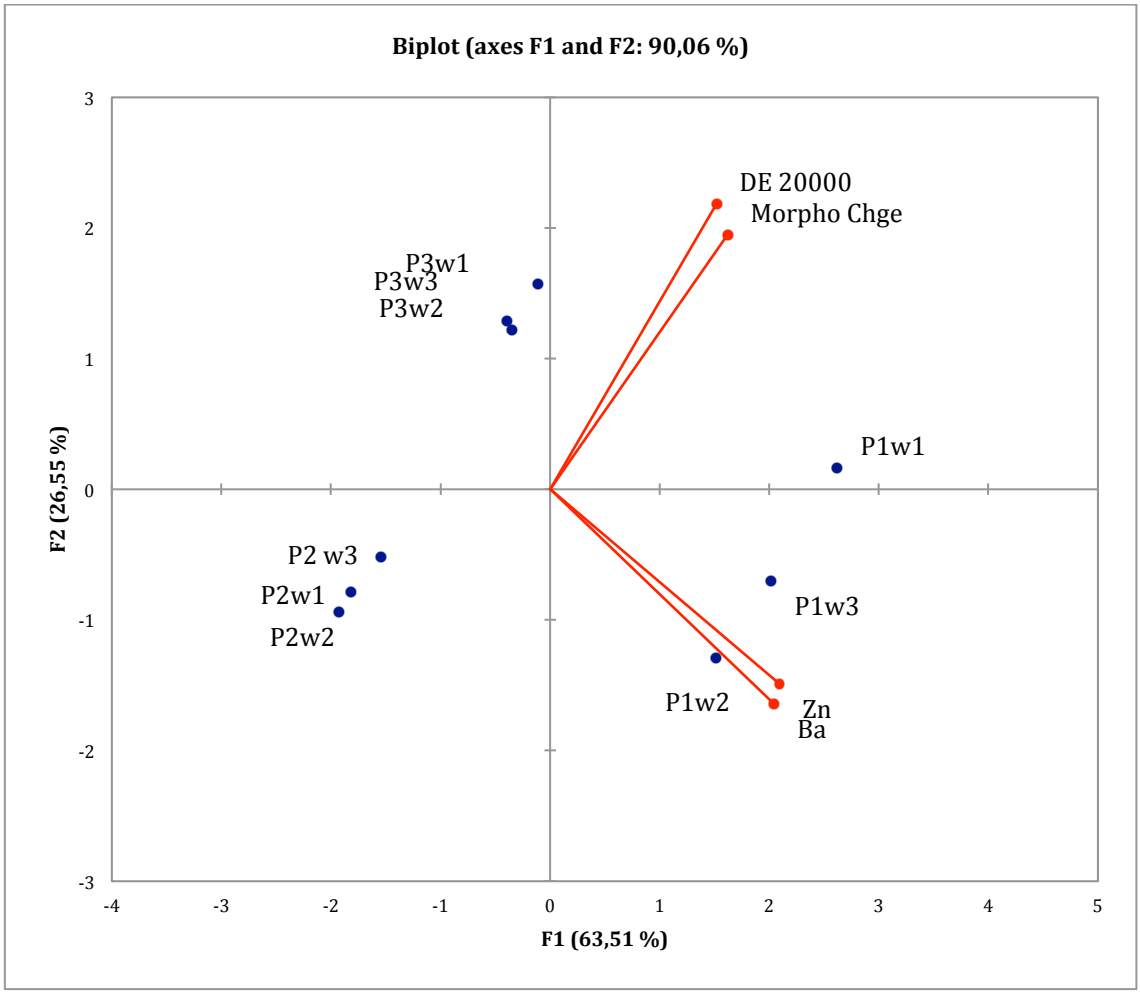
	DESCRIPTIVE VARIABLES										DEPENDENT VARIABLES	
Type	Ba	Ca	Co	Cr	Cu	Fe	Mn	Ni	Sn	Zn	ΔE	Morphological Change
P1	54	102	1	18	1	67	7	0	0	259	*	*
P2	6	131	6	2	1	312	13	1	0	4	*	*
P3	3	101	1	2	1	58	1	0	0	4	*	*

Principle Component Analysis: During exploration using PCA it was found that including P2 did not contribute to the fitness of the model, but rather rendered the tendencies less clear. Since P1 and P3 are paints composed of identical pigments, differing only by P1 containing extenders of $BaSO_4$ and ZnO, and P2 being an unrelated historic Prussian blue pigment with

complete different origin and physical and chemical properties, it was decided to exclude P2 from the PCA analysis.

Exploring the immersion washed sample set a significant correlation between both colour change and morphological changes and the presence of extenders was demonstrated: The more extenders present, the greater morphological change and the higher ΔE values. See Fig. 28 and table 5.

Exploration of the gel cleaned samples provided less clear results. No correlation between extenders and colour change was observed, and only a slight correlation between morphological changes and extenders could be distinguished. However, this correlation was not strong enough to be statistically significant.



Factor loadings:		
	F1	F2
Ba	0,887	-0,461
Zn	0,908	-0,418
DE 20000	0,660	0,613
Morph Chge	0,702	0,546

Above: Fig. 30: PCA chart of Prussian blue pigments. Only immersion washed samples included, P2 excluded. Left: Table 7. Factor loading of PC1 and PC2 in Fig. 30

6.2.2 The Role of Transition metals

Student's T-test: Student's T-test was first run on the entire sample set of madder lakes (M1-M6). The null hypothesis (there being no difference between the gel cleaned and the immersion washed samples), was stated not to be rejectable.

Since the manual exploration of the data had indicated morphological change and colour change not necessarily to correlate, the T-test was thereafter repeated twice. In the first repetition only colour change was included, and in the second repetition only morphological change. (Please see Table 6 for a list of all the included variables).

The T-test including colour change demonstrated the null hypothesis not to be rejectable whilst for the T-test performed on the morphological data, the null hypothesis could be rejected with a 95 % level of significance. (For detailed data from T-testing, please see Appendix 8(II)) This means that regarding morphological change, all six madder lake pigments acts as one population, behaving differently when subjected to gel treatment and immersion wash respectively. Regarding colour change, on the other hand, the difference in behaviour between the different pigment types is significant enough to overshadow the difference between the two treatments. Regarding colour change, each pigment should thus be considered a separate population.

Table 8. Variables used for data exploration of Madder lake pigment samples. *values individual for each sample

Colours added to highlight similarities and dissimilarities between samples.

	DESCRIPTIVE VARIABLES										DEPENDENT VARIABLES	
	Transition Metals				Chromophores							
Type	Ca	Cu	Fe	Mn	alizarin	Purpurin	pseudopurpur	rubiadin	munjinstin	unknown sub	ΔE	Morph Chge
M1	66	20	29	3	2	2	2	0	0	2	*	*
M2	103	8	64	8	2	2	2	0	0	2	*	*
M3	51	30	14	6	2	2	2	0	0	2	*	*
M4	54	62	23	4	1	0	0	1	2	2	*	*
M5	68	2	20	4	2	2	2	0	0	0	*	*
M6	66	1	16	5	2	2	2	0	0	0	*	*

Clustering Analysis: Running Both K-means clustering and AHC the metal content numbers were divided by 10 in order to bring all the variables into the same order of magnitude and reduce the weighting applied to the metal content during multivariate analysis.

To reduce the in-class variance and optimize the number of classes 12 models of K-means clustering with 1-12 classes respectively were run. The final cluster assignment for each model was optimised using 100 repetitions. Examining the 12 models it was found that from 5 classes and on it was possible to see differences in behaviour within the total group of madder lake pigments. From 6 classes and on, differences between gel treated and immersion washed samples with the same pigment. From 9 classes and on, the number of classes did not change the in-class variance, which became <1. Please see Appendix 10 (I-II)

Examining the 7 classes model (see table 7), it could be seen that M2 and M4 differ significantly from the rest of the samples. M2 and M4 have also the most differing pigment compositions from the other madder lakes: M4 while being the only pigment containing the chromophores munjistin and rubiadin, and M2 while containing significantly higher ratio of Ca and Fe than all other pigments (see table 6). It could also be seen that M5 and M6 have a

very similar behaviour and group together even when the number of classes became ≥ 9. M5 and M6 are the two pigments the most similar in composition to one another of all six madder lakes, they have the same chromophore ratio and very similar metal content, (see table 6). Looking at the measurements of colour change of M5 and M6 it becomes clear that they demonstrate very similar values, except for some outliners (see Appendix 4 & 9).

Table 9. K-means clustering 7 classes. Colours added to highlight M2, M4 and M5, M6

Class	1	2	3	4	5	6	7
Objects	8	6	5	7	7	1	2
Sum of weights	8	6	5	7	7	1	2
Within-class variance	1,936	0,282	0,568	5,633	0,595	0,000	0,510
Minimum distance to centroid	0,731	0,333	0,324	1,277	0,406	0,000	0,505
Average distance to centroid	1,162	0,462	0,610	1,931	0,668	0,000	0,505
Maximum distance to centroid	2,159	0,667	1,065	4,401	1,188	0,000	0,505
	M1gel1	M2gel1	M3gel1	M3gel3	M5gel2	M6water2	M6water3
	M1gel2	M2gel2	M3gel2	M4gel1	M6gel1		M6water1
	M1gel3	M2gel3	M3water1	M4gel2	M6gel2		
	M5gel1	M2water1	M3water2	M4gel3	M6gel3		
	M54el3	M2water2	M3water3	M4water1	M5water1		
	M1water1	M2water3		M4water2	M5water2		
	M1water2			M4water3	M5water3		
	M11water3						

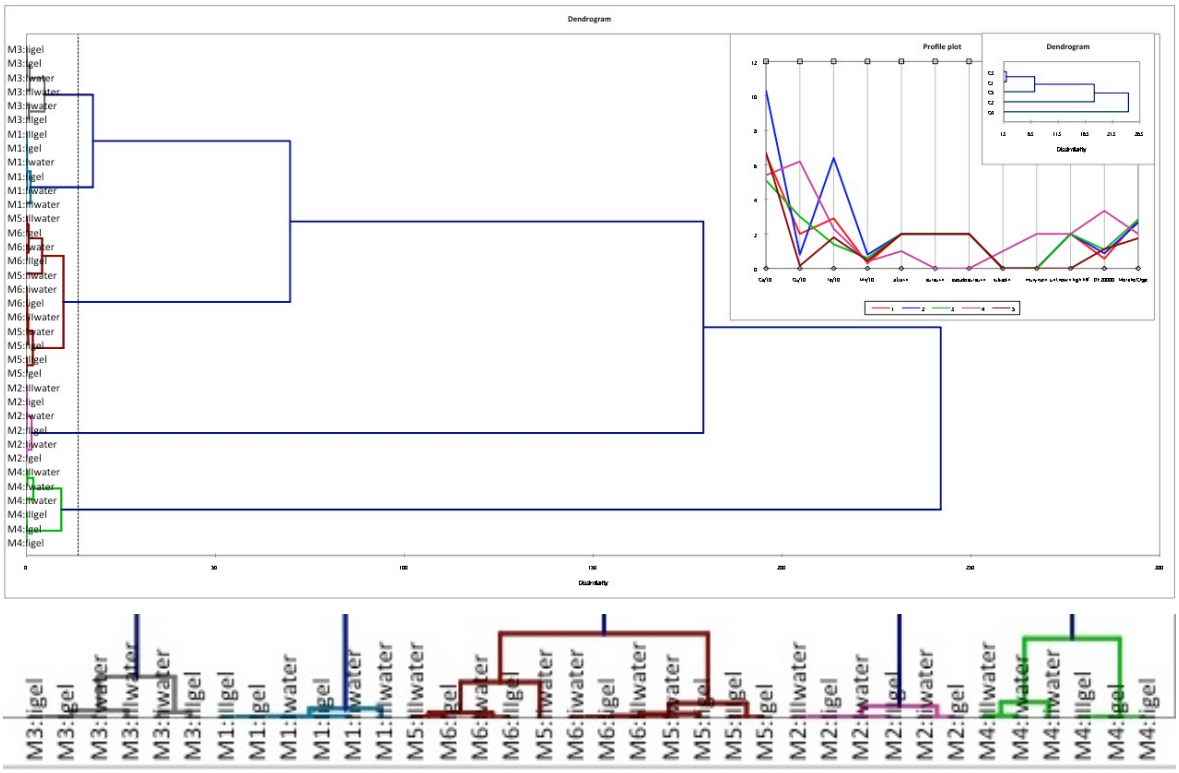


Fig 31: Dendrogram from AHC of the madder lake pigments, including all factors

AHC was performed several times first with all variables included and then repetitions with different variable combinations in order to explore how they contributed to cluster

assignment. In the AHC performed on all samples 5 significant clusters were identified, as well as further non-significant sub clusters, (see fig 31). The data set was thereafter decomposed to treat morphological change and colour change, separately. With regard to morphological change, AHC was performed twice, the first time all descriptive factors (both metal content and chromophore ratio) were included and the second time, only the metal content was included. Both models gave rise to five clusters but including also the chromophores, the class arrangement improved. This can be taken as clear indications of the interaction between ratio of chromophores and metal content in the pigment to influence the pigment behaviour when subjected to different cleaning methods(see Appendix 11(I-II) for further data).

Principle Component Analysis: PCA was run using the unrescaled metal content data, because trials demonstrated the scaling not to produce significant difference in the results.

Examining the PC1 and PC2 biplot including only gel cleaned samples, a significant positive correlation between Cu content and both morphological and colour change became clear. It became however also clear that there were no correlation, neither positive nor negative, between morphological change and colour change, please see Appendix 12 (I)

The PC1 and PC2 biplot including only immersion washed samples demonstrated a strong anti-correlation between morphological change and colour change: the higher ΔE the less morphological change. A strong positive correlation between morphological change and high Fe, Mn and Ca content could also be seen. The correlation between Cu content and morphological change was however found to be less distinct than for the gel-cleaned samples. Cu in combination with munjistin demonstrated nevertheless a strong colour change-promoting tendency.

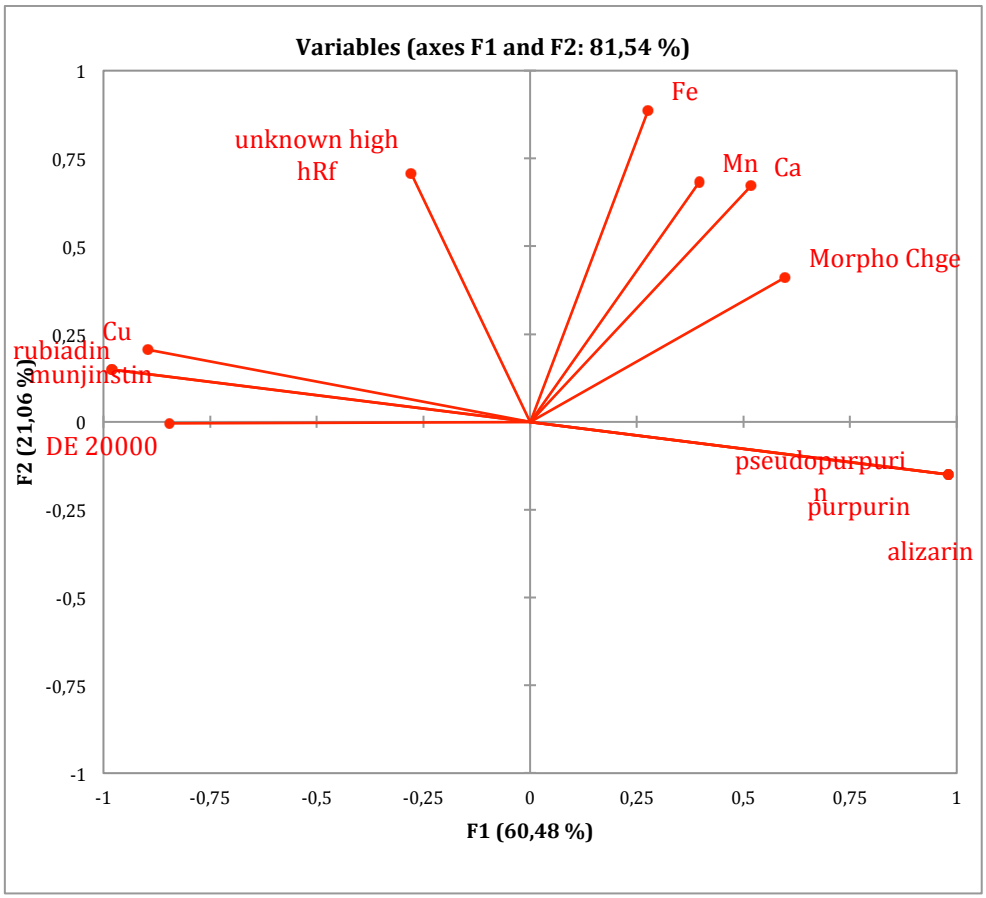


Fig. 32: Plot of the factor loadings of the variables onto PC1 and PC2 for the PCA of water cleaned samples of madder lake pigments. All factors included.

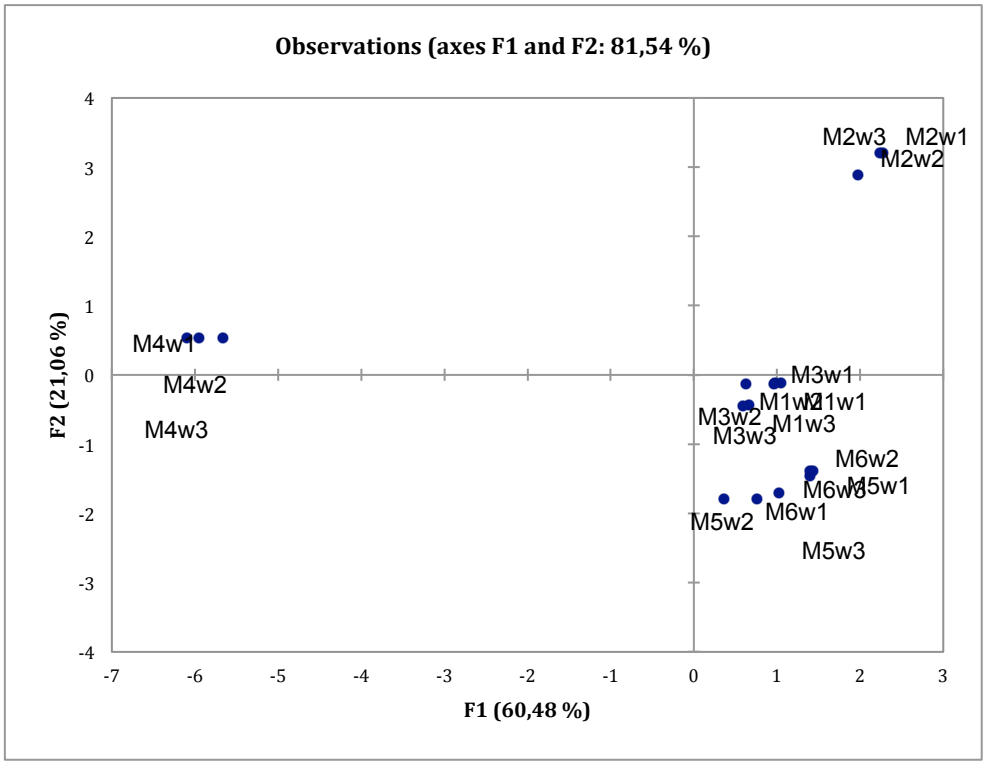


Fig. 33: Plot of the samples of the variables onto PC1 and PC2 for the PCA of water cleaned samples of madder lake pigments. All factors included.

Table 10: Factors loading of PC 1-7.

Factor loadings:							
	F1	F2	F3	F4	F5	F6	F7
Ca	0,518	0,672	-0,491	-0,189	-0,054	0,016	-0,006
Cu	-0,895	0,205	0,383	0,069	0,048	-0,058	0,027
Fe	0,277	0,887	-0,288	-0,230	0,003	-0,033	0,016
Mn	0,397	0,684	-0,176	0,585	0,039	0,015	-0,001
alizarin	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
purpurin	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
pseudopurp	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
rubiadin	-0,980	0,150	-0,066	0,008	-0,107	0,026	-0,004
munjinstin	-0,980	0,150	-0,066	0,008	-0,107	0,026	-0,004
unknown h	-0,279	0,706	0,599	-0,093	0,172	-0,164	-0,017
DE 20000	-0,845	-0,004	-0,263	-0,050	0,429	0,173	-0,001
Morpho Ch	0,598	0,411	0,615	-0,060	-0,102	0,285	0,000

The role of the sizing agent

Student's T-test: Student's T-test was run on the three sample types in the group of modern dioxazine pigment painted onto three different papers. The null hypothesis could not be rejected neither including only gel treated nor including only immersion washed samples. The three sample types in the group could thus not be treated as one population but two or three separate populations. Due to each population consisting of only six/twelve observations, the generalizability of eventual correlations was considered to be small. Further exploration of the data using multivariate chemometric methods was thus not conducted.

6.3 Sources of error

6.3.1 Sample population

Due to the limited amount of available sample material, the number of replicates was chosen to be three. To be able to evaluate the reliability of a group and discard measurements considered to be outliers, a number of at least five simples are needed. The statistical significance of the study must therefore be considered relatively low. However, clear tendencies have been observed, and exploring the data with successful use of chemometric analysis i.e. PCA, HCA and T-tests, have demonstrated that the results possess significance.

6.3.2 Sample materials and sampling methods

The provenance of the sample materials from the AFP is well known and recorded. Since the end of the project in 2012 the materials have nevertheless not been archived in a proper way. The paint-outs have been stored as a private property, kept together in a pile recto against verso, one pigment on top of the other. Transfer of pigments to the verso of the paint-outs could have occurred which in turn could have influenced the amount of pigments in the wash water and on the gel surface after completed treatments. In the case of the gel surface large pigment clusters were found during microscopic examinations. These were however interpreted to originate from transfer during storage and thus considered not to posses significance and therefore not included in the data.

The cross sections of the samples were made by cutting off one side from the circular samples using a scalpel. The trimmed samples were kept in upright position trough placing in an incised eraser gum. The procedure was rapid and efficient, but not perfect since contamination of the cuts could be noted.

6.3.3 Performance of cleaning

The size of the circular samples was chosen to allow a greater total of samples to be treated. The amount of available sample material was also limited and contributed to the selection of 8 mm diameter discs. During experimentation, problems arose due to the sample size and the size of the wells in which the cleaning was performed. It turned out to be difficult to establish complete contact between the gel surface and the sample surface. In order to overcome this issue, the method of placing the samples on the gel while still liquid was developed. Since the cleaning consequently was not performed using the method described in the literature, the results can be considered not fully reliable.

The results from examination of the rectangular samples indicate that the way the gel cleaning is performed has a great influence on the vertical migration and the loss of colour by lifting. This fact should also be taken into consideration while evaluating the results. During cleaning the circular samples were pushed down onto the gel with the use of a plastic stick so as to ascertain complete contact with the gel. This possibly exercised influence on the samples surface morphology, and thus the treatment could be considered similar to the Gel II method. Treating the case study however, the cleaning was conducted using the method purposed for sensitive objects, with no modification.

The pigments found on the gel surface at edges of the circular sample imprints are presumably consequences of the handling of the samples during application and removal on/from the gel. Since the cleaning method for the circular samples was modified to enable treatment of samples with such a small the interpretation of these findings should be made taking this into consideration together with the fact that no Japanese paper was used as an interleaving sheet between the gel and the sample.

The author's relatively pore of experience; both in performing cleaning with Gellan gum gel, as conservator and in conducting experiments, should also be taken into consideration.

6.3.4 Analysis

Colorimetric analysis: The colorimetric measurements were replicated only twice. Comparing the measurements from the first and second measurements of the same samples, great differences were in some cases observed. Various reasons for this could be found. Since the paint was not homogeneously applied to the sample paper, difference in the positioning of the instrument could have given rise to different colour coordinates. In addition Konica Minolta d700 is one of the most sensitive instruments on the market. Small differences in the handling of the instrument, such as difference in the force applied while placing the instrument on the sample, could also have influenced the measurements.

Regarding the fact that repetitions of the measurements of the Whatman paper samples were not made using the same instrument as the other measurements, the results from this group of samples should be accounted as being less reliable.

Furthermore, the samples used for this study were mainly painted with an abundance of pigments resulting in an over saturated paint. Loss of pigments would thus not necessarily give rise to change of colour, seeing that an oversaturated paint has the same colour as a one which is just at the point of saturation (V. Daniels 1995, p. 33).

Comparison of morphological changes and cross sections: Comparison of surface morphology before and after treatment, together with the comparison made of cross sections of treated and untreated sample material, were executed by the author of the thesis. The comparisons were based on examination of microscope images. An analysis of this kind always includes a certain amount of arbitrariness. Given the fact that during comparison the author was aware of which treatment the samples had been subjected to, bias could not be precluded.

Photographic documentation of case study objects: Great caution was made to obtain comparable images of before and after treatments. Even though the documentation was made using the same camera, the same illumination, the same background and the same camera settings, the pictures before and after treatment nevertheless differed significantly in their white balance. Attempts were made by informant 5 to compensate for the differences during photo editing. Unfortunately it turned out to be very difficult to make them identical, and thus the evaluation of changes due to cleaning became difficult. The results from the case study should therefore be interpreted bearing this in mind.

7. DISCUSSION

7.1 Interpretation of results

This study is a first try to evaluate the suitability of Gellan gum gel cleaning for watercolour drawings. The results should be seen as indications rather than taken for statements. Further research on the subject is needed, multiplying the number of replicates of both samples and measurements. It would also be necessary to repeat the experiment using larger samples in order to increase the similarity to regular conservation procedure.

7.1.1 Morphological changes and colour change

Comparison of the results from the analysis of morphological changes and colour changes indicates that colour change and morphological change does not correspond.

The manual data exploration showed that all gel cleaned circular samples, with the exception of $Wh_{I\text{-}III}$, prove higher rates of morphological changes but lower rates of colour colours change than immersion washed samples. This tendency is confirmed by the case study. The immersion washed watercolour miniature appears to be more different than the gel cleaned when the overall appearance of the two watercolour miniatures before and after treatment is compared. Looking on the watercolour drawings under microscope, on their surface morphology, the gel washed example turns out to have undergone more changes.

The chemometric analysis of the circular samples, treating them as three separate groups, also confirms colour change and morphological changes nor to correspond nor to always correlate. The fact that the T-test of the Prussian blues including both morphological change and colour change was not successful whilst the one including only immersion wash did succeed, indicates that morphological change and colour change do not correlate, and should thus not be interpreted to be consequences of the same chemical and/or physical action. With regard to the madder lakes, the tendency is confirmed in the same way; including both colour change and morphological changes the Student's T-test did not succeed but separating them, clearer patterns could be found.

The chemometric analysis together with the manual analysis of the data further confirms what can be concluded from fig. 4 on p. 18; that the lack of correspondence between morphological changes and colour change is due to them not being consequences of migration in the same dimensional plane. Fig. 4 on p. 18 predicts that gel cleaning should results in more morphological change when the wash-fastness of the objects' media is decreased. The colour should in this case not be affected, since no pigment loss would occur.

Daniels (1995, s. 39). proposed that the presence of extenders such as $BaSO_4$ and ZnO would decrease water fastness. Regarding immersion wash this thesis was confirmed. Regarding gel cleaning on the other hand, the correlation could not been confirmed. Since the correlation being completely absent concerning colour change it can be assumed that the colour change occurring during gel cleaning of the Prussian blues origin not only from pigment loss but from some chemical reaction. During manual analysis of the colour change data from the Prussian blues, it was noted that the difference in L* value for P3 was negative and not positive, indicating the colour to have become darker and not lighter upon treatment, see Appendix 9. Since pigment loss normally would promote fading, lightning of the colour; the darkening could be thought to be consequence of some chemical reaction. The idea that the Ca^{2+} content in the gel could have induced an ion exchange in the Prussian blue was proposed. Since Calcium acetate was added in the wash water as well as in the gel, the pigment loss must, in the case of immersion wash, have had greater impact on the colour change than this assumed ion exchange.

The tendencies and correlations found examining the PCA charts of the madder lake pigments confirm, that the relation between chromophore ratio and transition metals influences the rate of morphological change, in other words, the wash fastness of madder lake pigments. Regarding colour change, the picture is less clear. The theory that colour change does not necessarily originate only from pigment loss but being due to some kind of interaction, could be applicable also in the case of madder lakes. With Clarke's theory and Thomas's statements in mind about anthraquinone dyes promoting paper and media degradation upon fading, the following hypothesis arose (Clarke 1998, s. 160, J. Thomas et al. 2010, pp. 2347, 2348). An old layer of madder lake could be believed not having a homogenous colour since the top layer would have been exposed to air and its pigments undergone fading. Loss of the top layer of the same madder lake paint during immersion wash, would not render its colour lighter, because eliminating the top layer of pigments would expose underlying, still not faded pigments. Lightning from pigment loss and darkening from elimination of faded pigments could thus counter act and reduce the colour change.

Taking the findings presented in the previous section into consideration it could be stated that describing wash fastness by degree of colour change is insufficient. Wash fastness should instead be described in the terms of tendency to undergo morphological changes in the form of redistribution of pigments, because colour changes can be consequences of chemical reactions having little to do with wash fastness.

7.1.3 Extenders, Transition metals and Sizing Agent

During data exploration it became clear that the presence of extenders, transition metals and the type of sizing agent influences the two treatments differently. Regarding immersion wash the presence of extenders and transition metals, in particular copper, decrease the wash fastness significantly. Regarding gel cleaning, the correlation appears to be less clear. Considering only morphological change as indication of wash fastness the correlation remains, however including colour change, contradictory tendencies appear.

Student T-tests and clustering analysis of the madder lakes indicate that with regard to the gel cleaned samples all six madder lakes can be considered being one population, but with regard to the immersion washed samples, the differences between the pigments are greater than the difference between the treatments. As a consequence the before treatment risk analysis will be simplified, the identification of the exact type of madder lake pigment will be less important than the knowledge of it being a madder lake. It should nevertheless be noted that the chemometric exploration of the madder lake pigments made it clear that organic madder dyes from Rubia Cordifolia are very different from dyes originating from the Rubia Tinctorum plant; pigments from Rubia Cordifolia with a Cu content seem to be of a very water soluble type.

How the presence of sizing influences the two treatments was not fully explainable by the data. The amount of sizing, in contrast to the type of sizing, though appears to be of greater impact. Manual analysis of the ΔE and morphological changes revealed that the dioxazine on gelatine sized paper and synthetic sized paper have a very similar behaviour, whilst the samples on unsized filter paper demonstrate great dissimilarity. The results have also indicated that the combination of paper thickness and density together with the amount of sizing could be a crucial factor.

Manually examining the colour change of the qualitative study, it was seen that the unsized samples was the group demonstrating the only complete contrary tendency from the rest of the 12 sample types, see Appendix 4 and 6. The colour change of the gel treated samples was in this case clearly higher than it was for the immersion washed ones. The theory proposed by Daniels that pigment would adhere stronger to unsized paper while being able to penetrate

into the paper matrix could be applied to give an explanation (Daniels 1995, pp. 33, 36). In the case of the unsized samples, the pigment had been soaked into the paper during paining, rendering the verso surface of the samples not blank but coloured. During gel cleaning pigments were thus in direct contact with the gel, and transfer from the sample to the gel occurred, see section 6.1.3. Concerning vertical migration into the paper matrix, evaluation of the unsized samples could not be made since the paper matrix even before cleaning was coloured by pigment. Occurrence of migration could though be considered plausible. Pigment loss from the recto surface of the gel treated samples would in this case have taken place, not due to migration from the recto surface to the surrounding space as in the case of immersion wash, but due to migration into the paper matrix and eventually further out into the gel. A displacement of pigment of this kind would explain the presence of high ΔE values for the gel treated samples. Concerning immersion wash, the stronger bound between the pigment and the unsized paper fibre would load higher than the action of surface diffusion and capillary transport and thus promoting minor loss of pigments and further low ΔE values.

7.1.2 Cleaning with Gellan Gum Gel versus Washing by Immersion

Manual evaluation of the results from the different experiment parts, together with chemometric exploration of the data from the circular sample set both indicate that there is a significant difference between the two cleaning methods; cleaning with Gellan gum and washing by immersion. Cleaning with Gellan gum gel has proved the advantage of being able to promote only 2-dimensional migration of the paint in contrast to immersion wash, which enables three migration dimensions. Colorimetric measurements of gel treated and immersion washed samples have indicated that 3-dimensional migration yields greater colour change than migration in only two dimensions. Morphological changes (lateral migration in the form of redistribution of pigments), appears on the other hand to increase with decreasing migration dimensions. During experimentations it turned out to be difficult to establish complete contact between object and gel when treating thick, hard sized or high-density paper. Need for adding weight on top of the object/gel sandwich in this case became necessary. Comparison between the results from the rectangular samples cleaned using, Gel I (without top layer), and the corresponding samples cleaned using Gel II (with top layer), confirms that addition of a top layer is critical. The addition of a top layer gives access to the same third migration dimension as in the case of immersion wash; loss of pigment by transfer to the surrounding space (water and interleaving tissue between object and gel, respectively). The risk of loss of pigments by transfer from the object to the top layer seems difficult to avoid and it is plausible to believe suchlike treatment to yield colour change of the same magnitude as immersion wash.

Cleaning with Gellan gum gel also has the advantage of being easy to control and to interrupt at any time. It should however be noted that the use of the same top layer reduces the possibility of monitoring the object constantly during treatment.

7.2 Conclusion

The use of Gellan gum gel to treat water sensitive material such as watercolour drawings cannot be assumed to eliminate the risk to cause changes to the object. Addition of weight on top of the cleaning sandwich should be accompanied with a discussion about how much pigment loss could be considered acceptable.

Since the presence of extenders, transition metals and the amount of sizing have been shown to be critical; identification or estimations of the inherent pigments and paper of the object could help in choosing the appropriate cleaning method.

7.3 Further research

In further research it would be of great interest to experiment with gels of different concentrations, especially gels of 1 and 1,5 % could prove suitable. Lowering the Gellan gum concentration means increasing the speed of water release from the gel and thus rendering the humidification of the object more rapid, which is believed to perhaps be able to resolve the problem of establishing complete contact between object and gel (Informant 6).

It would also be of great interest to further investigate the correlation between morphological changes, colour change and wash fastness and establish the underlying actions and reactions causing colour changes.

9. SUMMARY

Wet treatments are fundamental actions in paper conservation. In 2003 Simonetta Iannuccelli and Silvia Sotgiu introduced a new gel cleaning method into the field: cleaning with Gellan gum gel. The method has been thoroughly evaluated regarding treatments of works on paper with water fast media. The cleaning method has however, also come to use for treatment of potentially water sensitive material such as watercolour drawings. No research aiming to evaluate the suitability of the method for water sensitive media has been found. The purpose of this study is thus to evaluate how cleaning with Gellan gum gel affects watercolour drawings in comparison to washing by immersion.

Gellan gum gel is a biodegradable, non-toxic polysaccharide able to form rigid hydrogels in the presence of cations in low concentration. The gel has been widely used in food, pharmaceutical industries and in biochemical research. In paper conservation the gel can be used for several purposes. Pure gel can be used for controlled, slow and efficient washing of single sheet objects. The gel can deliver reducing agents and buffer compounds such as tert butyl aminoborane and calciumproprionate respectively. Enzymatic solutions can be added to the prepared gel to serve for removal of protein and starch based adhesives. It has also been demonstrated that the gel can hold organic solvents.

During cleaning the gel is regularly placed directly onto the recto surface of the object and weights added on top. Treating more sensitive material the object can instead be placed on top of the gel with the verso side of the object in contact with the gel. To ascertain complete contact between the gel and the object, an interleaving material such as Melinex can be placed over the object and weight added on top.

This study is divided in three parts. In the first part small circular sample discs, 8 mm in diameter have been used whilst the second part consists of a set of larger rectangular samples, containing both painted and blank areas. The last part is a case study. The three parts aims to evaluate the effect of the two treatments on a micro, macro and object level respectively.

For the first part and for the case study, the cleaning method recommended for sensitive material (without addition of top layer) has been used. In the second part, a comparison between both gel cleaning with and without top layer and cleaning by immersion wash, has been conducted. A 2 % Kelcogel CM Gellan gum gel prepared of deionised water and 0.4 g/l calcium acetate has been used in all parts.

The main part of the sample materials and the case study objects originate from *the Anoxic Frame Project, AFP* at Tate, London UK. In 2008, under AFP, three Prussian blue pigments and six different madder lake pigments from the late 18th or early 19th century were hand ground and prepared with pure gum Arabic and painted on to artificially aged gelatine sized rag paper. Three watercolour miniatures painted by Tony Smilbert with the use of the same historic pigments but with addition of historic gamboge were also produced under AFP. In this study circular discs of the paint-outs have been used in the first part together with discs of recently prepared paint-outs of modern diaoxazine pigment on three different papers; a glazed variant of the above mentioned artificially aged paper, a synthetic sized modern Fabriano paper and a unsized Whatman filter paper respectively. For the second part rectangular samples of the same dioxazine paint-outs on different papers and rectangles of one of the madder lake pigment paint-outs have been used.

Colour measurements using *reflectance spectroscopy, colorimetry,* comparison of the *microscopic paper morphology* before and after treatment, comparison of the samples *cross sections,* examination of the *gel surface* after use, and measurements of the *absorption spectres of the washing water* before and after treatment, have served as analytical tools.

The collected data were in a first step compiled and visualized as tables and charts. Secondly the analytical data together with information about pigment composition were explored using chemometric methods, i.e. *Student's T-test*, *K-means clustering*, *Agglomerative Hierarchical Clustering, AHC*, and *Principle Component Analysis, PCA*.

Results indicate there is a significant difference between gel cleaning and immersion washing. The results also indicate there is a non-correlating and significant difference between wash fastness (absence of morphological change) and colour change. Regarding gel cleaning, this method could not eliminate morphological changes that arise during cleaning. Loss of colour did not occur during gel treatment without addition of a top layer and colour change was reduced. Indications of increasing risk for colour loss when top layer is added during gel cleaning were nevertheless apparent.

In addition to these results, the chemometric analysis of the data could confirms two of the hypothesis proposed by Vincent Daniels in *Factors Influencing the Wash fastness of watercolours*: The presence of extenders such as $BaSO_4$ and ZnO, and presence of transition metals, in particular copper, Cu, reduce wash fastness. No clear indications about exactly how the paper sizing influences the wash fastness could be found, however, close examination of the results hints that the amount of sizing, rather than the nature of the sizing agent, could be the critical factor. Paper density and thickness in combination with sizing is also believed to interact and have important impact upon wash fastness. These factors are proposed to become further explored in a more in depth study.

10. SAMMANFATTNING

Olika typer av våta behandlingar vilka kräver fullständig eller delvis blötläggning av objektet är fundamentala inom papperskonservering. 2003 införde Simonetta Iannuccelli och Silvia Sotgiu en ny rengöringsmetod för konst på papper; geltvätt med Gellan gum. Metoden har blivit noggrant utvärderad vad gäller behandling av material med vattenfast medium. Metoden har dock börjat användas även för konst med potentiellt vattenlösligt medium så som exempelvis akvareller. En genomsökning av de viktigaste konserveringsinriktade tidskrifterna visar att ingen studie kring applicering på vattenkänsligt material finns publicerad. Denna studie syftar till att utvärdera hur geltvätt med Gellan gum påverkar akvareller. Undersökningen har gjorts som en jämförelse mellan geltvätt med Gellan gum (i den vidare texten förkortat till geltvätt) och tvätt i vattenbad (förkortat till vattentvätt).

Gellan gum är en biologiskt nedbrytbar polysackarid som i kombination med positiva joner i låg koncentration har förmågan att bilda hård, transparent gel. Gellan gum gel används inom mat- och läkemedelsindustrin samt inom biokemisk forskning. Gelen kan användas på olika sätt inom papperskonservering. Den rena gelen kan användas för kontrollerad, långsam och effektiv tvätt av tvådimensionella pappersobjekt. Gelen kan också beredas med tillsats av buffrande och reducerande ämnen så som tertbutylaminboran och kalciumproprionat. Enzymatiska lösningar kan också tillsättas gelen för att underlätta vid borttagning av protein- och stärkelseadhesiv. Det finns också en studie som visar på att gelen av Gellan gum kan hålla organiska lösningsmedel.

Vid tvätt placeras gelen normalt sätt direkt på objektets recto, med plexiglas och vikter ovanpå. När mer känsligt material behandlas rekommenderar Iannuccelli och Sotgiu att objektet istället placeras ovanpå gelen, verso nedåt, med ett japanpapper emellan. För att säkerhetsställa fullständig kontakt mellan objektet och gelen, kan ett mellanlägg av exempelvis Melinex läggas på och plexiglass plus tyngder placeras ovanpå.

Denna studie är uppdelad i tre delar vilka syftar till att utvärdera de två tvättmetoderna på mikro- respektive makro- och föremålsnivå. I den första delen har små cirkulära prover, 8 mm i diameter, använts medan större rektangulära prover med både bemålade och obemålade ytor har använts i studiens andra del. Den tredje delen har bestått av en fallstudie.

Den största delen av provmaterialet kommer från *the Anoxic Frame Project, AFP* som pågick på Tate i London, Storbritannien. 2008 inom ramen för AFP, handrevs tre olika preussiska blå och sex olika *madder lake* pigment från sent 1700- och tidigt 1800-tal. Pigmenten blandades därefter till med dejoniserat vatten och ren gummi arabicum till en färg för att sedan målas på ett artificiellt åldrat, gelatinlimmat lumppapper. I samband med detta målade Tony Smibert ett flertal miniatyrer, ca 5 x 10 cm stora, med samma pigment (med tillägg av ett på samma sätt berett pigment av *gamboge*) på samma artificiellt åldrade papper. I denna studie har små rundlar av materialet från AFP använts tillsammans med likadana runda prover av ett modernt dioxazinepigment struket på tre olika typer av papper; en hårdpressad och därmed mindre grov variant av det artificiellt åldrade lumppappret, ett modernt syntetlimmat akvarellpapper från Fabriano samt ett olimmat filterpapper av 100 % ligninfri cellulosa. Prover. Till de rektangulära proverna har samma moderna pigment på olika papper använts i kombination med prover av ett av de historiska madder lake-pigmenten. Fallstudien har gjort på två av tony Smiberts miniatyrer.

I studiens första del, för de runda proverna och för fallstudien har geltvättmetoden för känsligt material (utan tillägg av topplager) använts. I studiens andra del har de två metoderna, med och utan topplager, jämförts sinsemellan samt resultaten även ställts mot vattentvätt

Färgmätning med hjälp av reflektans spektroskopi, kolorimetri, jämförelse av provernas mikroskopiska morfologi före och efter behandling, jämförelse av provernas tvärsnitt, undersökning av gelens yta efter att den använts för tvätt samt mätning av tvättvattnets absorptionsspektra före och efter rengöring har använts för analys av behandlingarna.

All insamlad data strukturerades först upp i tabeller och visualiserades i diagram. Detta kan beskrivas som en ”manuell” analys. I ett andra skede ställdes datan från studiens första del mot information om de olika pigmentens metallinnehåll och innehåll av olika färggivande ämnen genom applicering av olika statistiska modeller; Student's T-test, K-means clustering, Agglomerative Hierarchical Clustering, AHC, och Priciple Component Analysis, PCA.

Resultaten visar på att det finns en betydande skillnad mellan geltvätt och vattentvätt. Reslutaten indikerar också att det finns en signifikant skillnad mellan att ett pigment är vattenfast (dvs. att den bemålade ytan inte undergår morfologiska förändringar när det kommer i kontakt med vatten) och att det inte förändras i sin kulör när det tvättas. Vad gäller geltvätt så visar resultaten på att denna metod inte kan eliminera risken för morfologiska förändringar. Då det inte kan ske något pigmentbortfall under tvätt med gel utan topplager, så minimeras dock risken för kulörförändringen. Resultaten från studiens andra del påvisar dock att risken för pigmentbortfall under geltvätt med topplager är mycket stor. Detta skulle betyda att när ett topplager måste användas för att säkerhetsställa kontakt mellan objekt och gel, så är risken för både morfologiska förändringar och färgförändringar stor.

Utöver dessa resultat beträffande geltvättens tillämplighet vid behandling av material med vattenkänsligt media, har den statistiska analysen av datan från den kvantitativa studien kunnat bekräfta två hypoteser presenterade av Vincent Daniels i *Factors Influencing the Wash Fastness of Watercolours* (1995): Pigment som innehåller fyllnadsmedel av bariumsulfat och/eller zinkoxid samt pigment bestående av organiska färgämnen fixerade på substrat innehållande multivalenta metaller, särskilt koppar, är mer vattenlösliga än andra. Inget statistiskt belagt mönster beträffande hur papprets limning påverkar vattenlösligheten, kunde hittas. Utifrån de observationer som gjordes under den manuella analysen av datan från de runda proverna och de rektangulära proverna kan det förutsättas att mängden limning snarare än typen adhesiv är den avgörande faktorn. Det tycks också som att papprets tjocklek och densitet tillsammans med mängden limning samverkar och gemensamt utgör en betydande faktor för hur vattenfast ett färglager på papper är.

TABLE & FIGURES

Tables

Tables in Appendix

Figures

Photos taken by Lotta Möller. All illustrations made by Lotta Möller if nothing else indicated.

Figures in Appendix

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APPENDIX 1

Applications for Gellan gum in paper conservation

Reducing Bleaching and Buffering

Iannuccelli and Sotgiu introduced the use of Gellan gum gel in paper conservations during their work with the conservation of *La Chinea di Papa Clemente VIII* from 1598 at ICRCPAL in 2004: To treat the documents they used Gellan gum gel of the type Phytagel® (Iannuccelli et al. 2004). They continued to study the characteristics and potentials of different types of Gellan gum gels, in order to find an ideal substance, presenting a method as efficient as washing by immersion but suitable for more sensitive material. An important factor in the choice of gel was the capacity to deliver reducing agents and buffer compounds such as tert butyl aminoborane and calciumproprionate respectively. The research led them to introduce Gelzan CM and Kelcogel GC-LA (Iannuccelli & Sotgiu 2010b, pp. 31, 32).

Calcium proprionate can be solubilised in the water during preparation of the gel of Gellan gum. After regular cleaning procedure, objects can be subjected to a second treatment with the buffered gel, following the regular application methods described in 3.3.1. This second gel treatment will thus function in the same way as a second buffered immersion bath. Tert butyl aminoborane should be added to the gel directly after heating in the microwave oven when the dispersion has turned into a transparent solution. The aminoborane will dissolve immediately and will not affect the subsequent sol-gel transition. After reduction treatment, residues of the tert butyl aminoborane should be removed by cleaning with a pure Gellan gum gel.

Reduction with tert butyl aminoborane should only be used on paper with copper free media. The addition of the aminoborane compound must be done under a fume hood and personal safety equipment must be used during the operation. After treatment the used gel must be disposed of as hazardous waste (Iannuccelli & Sotgiu 2010b, pp. 37, 38).

Removing of Auxiliary Supports

To remove auxiliary supports that have been attached to the object with amylose or protein based adhesives, a rigid gel of Gellan gum can reduce the mechanical action required. The intervention is recommended to be conducted after the cleaning of the object has been completed. A second sheet of gel is used to humidify the object. The gel is in this case placed on top of the recto of the object with a sheet of Japanese paper in between. Using two plates of plexiglass the sandwich is turned over and the removal executed on the verso. The constant and homogenous release of water molecules from the gel into the paper will promote softening of the adhesive and enable the removal of the support and the adhesive using a minimum of mechanical action (Iannuccelli & Sotgiu 2010b, pp. 35, 36).

Enzymatic Treatments

Complete removal of undesired adhesive, cannot, in most cases, be made without the application of enzymes that will depolymerise the adhesive by hydrolysis. A concentrated solution of enzymes prepared in water with the same proportion of calcium acetate as the gel, can be applied to the gel after complete gelation. The enzymatic solution is distributed on the surface of the gel with the use of a micropipette. After a few minutes the enzymatic solution will be homogeneously spread throughout the gel, which can thereafter be applied directly to the glued surface (Iannuccelli & Sotgiu 2010b, pp. 36, 37).

Solvent gel

Jayme Vallieres, second year master student at *Art History &Art Conservation department*, Queen's University, Canada, has conducted a research project investigating the use of Gellan gum gel as a solvent gel. A poster describing the project can be found on the university home page. Methanol, ethanol and 2-propanol are added to the gel in two different ways, by addition to the gel before setting, e.g. same methodology as used for tert butyl aminoborane, or by addition after gelation, e.g. following the procedure for enzymes. In the experiments, solvent prepared gel is used for removal of degraded adhesive residues from pressure sensitive tape. Out of the two types of preparation methods, the first one is highlighted as the most appropriate. The effects of the solvent on the characteristics of the Gellan gum gel matrix are not investigated in the study. However, the study makes clear that insertion of solvents in the gel is possible (Vallieres 2013).

APPENDIX 2
Absorption Spectroscopy of Gel and Water

Performed Spectroscopy Measurements

UV/Vis spectroscopy was used to measure the absorption of the water used for immersion washing of circular and rectangular samples. The measurements were performed using a NanoPhotometer® Pearl from IMPLEN. The wavelength scan range of the instrument is 200-950 nm and the wavelength accuracy < ±0.2 nm. The path length was 1.00 mm and the sample quantity 3 µl. The sample liquid was quantified and transferred to the instrument with the use of a micropipette. Triplicates of each measurement were done, and the solution was stirred once before the first sampling of each solution.

In the case of the circular samples the absorption spectra of the water used to clean the blank reference samples were used as *blanks*, which means directly subtracted from the sample spectres. Spectres of the absorption of the blank reference samples were then measured subtracting the spectra of clean washing water. In the case of the rectangular samples, clean washing water was used as blanks, and the absorption of the coloured sample water measured in direct comparison to this clean blank.

Trials were made to measure the absorption of the gel used for cleaning, in order to make a quantitative comparison between the amount of leaking during immersion respectively gel cleaning. Unfortunately this turned out impossible with the available equipment. Using the NanoPhotometer® Pearl it was necessary to reliquefy the gel to permit transfer of the 3 µl of gel onto the instrument. According to the literature, reliquefying of the gel by heating is possible. Before starting the experiments, reheating of the gel in microwave oven was thus tested, with positive results. Problems though arose while trying to repeat the operation with the gel after treatment, and only a few times was the procedure successful. Different methods of reheating the gels were tested: heating in microwave oven at 800W and 300W; heating in water bath with boiling water, with and without addition of a small quantity of distilled water[1]; heating the entire wellplate as well as removing of the gel from each well and heating each portion separately in small beakers; heating of gel prepared two weeks earlier and only the day before. Some trials succeeded whilst others failed. The reason for this is not known. No clear correlation pattern was distinguished.

Trials were made using the micropipette to transfer a successfully reliquefied gel, however, it proved to be impossible to keep the 3 µl of gel above the gellification temperature during the transfer from the micro pipette to the UV-Vis instrument. The analysis was thus considered unperformable under the prevailing circumstances, and the analysis excluded. The use of a plate reader connected to the UV-VIS instrument could have been a more successful method. Though, reliquefying the gel would still be needed.

The absorption of the washing water was measured. Due to the high ratio of background noise and low concentration of eventual pigments in the water, the collected spectres were not usable for analysis. The signal to noise ratio could be improved by using a longer path length, such as with a 1 cm cuvette, however, this option was not considered due to the small sample volumes.

[1] Advised by informant 4

Absorption spectres of the water used for cleaning of the qualitative study were collected, however as noted above the signal to noise ratio was poor and thus the spectra were difficult to interpret. Regardless, peaks from the dioxazine chromophore structures were identified by Informant 3 in the water used for cleaning of samples MH:I-III, MGe:I-III and MFa:I-III while comparing with spectres from blank paper samples. For example, please see fig. 23.

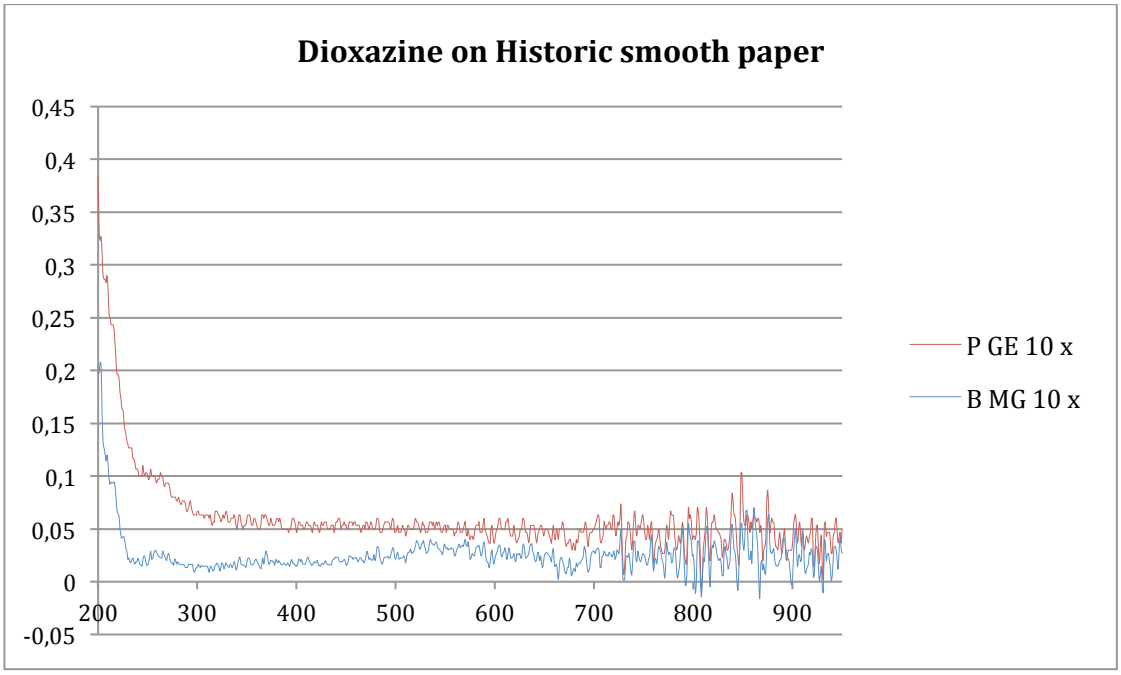


Fig. i: Absorption spectra from Mo:Ge.

A calibration curve could have been made in order to enable quantitative comparison between the samples. The calibration curve could have been constructed in three ways: based on the painted sample area, based on wash time or based on the concentration of pigment in solution. The third alternative would have been preferable since the nature of the media gives rise to uneven thickness of the paint on the paper surface, and homogeneous loss between samples and between different areas of the same sample, cannot be expected. Due to time limitation and the aim of this part of the study to be a qualitative evaluation, a calibration curve was not made and the spectres left without further exploration.

APPENDIX 3 (I) Microscopy of gel after treatment

Table i: Gradation of findings on the gel surface after use, quantitative study

MICROSCOPY of GEL AFTER TREATMENT				
3=pigments found on surface 2=pigments found on edges 1=possibly something 0=No pigments found				
	I	II	III	sum
Wh	3	3	3	9
Ge	0	0	0	0
Fa	3	3	0	6
P1	0	0	3	3
P2	1	0	0	1
P3	0	0	1	1
M1	2	0	2	4
M2	0	0	0	0
M3	2	0	0	2
M4	2	0	0	2
M5	2	0	0	2
M6	0	0	0	0

APPENDIX 3 (II) Microscopy of cross sections

Table ii: Gradation of differences in sample cross section before and after cleaning, quantitative study

MICROSCOPY CROSS SECTIONS CIRCULAR SAMPLES									
3=Visible transfer 2=Eventually some transfer 1=No visible transfer									
	Gel I	Gel II	Gel III	sum	Water I	Water II	Water III	sum	G/W
P1	1	1	1	3	1	1	1	3	3/3
P2	3	1	miss	4	1	1	1	3	4/3
P3	1	1	1	3	1	1	2	4	3/4
Wh	1	1	1	3	1	1	1	3	3/3
Ge	1	1	1	3	1	1	1	3	3/3
Fa	3	3	3	9	1	1	2	3	9/3
M1	1	1	2	4	1	1	2	4	4/4
M2	1	1	1	3	1	3	2	6	3/6
M3	1	1	2	4	1	1	1	3	4/3
M4	1	1	2	4	1	1	1	3	4/3
M5	1	1	2	4	1	1	1	3	4/3
M6	1	1	1	3	1	1	1	3	3/3

APPENDIX 4 Complete data set ΔE_{00} and ΔE_{76}

Table iii: Colour differences before and after treatments, quantitative study

	Water DE00	Gel DE00	Water DE76	Gel DE76
P1:1	3,785807361	0,842480817	4,437310559	0,943093315
P1:2	2,50777811	0,811221281	2,976453426	1,461831044
P1:3	2,371222416	0,694636029	2,746584242	1,700095586
P2:1	1,526197222	0,791008642	1,757768472	1,228881605
P2:2	1,277945082	0,669084116	1,486220038	1,004465032
P2:3	0,860109356	0,304477571	1,332497655	0,517204022
P3:1	3,075741896	1,018850385	3,389435794	1,412878268
P3:2	2,512827581	1,228202495	3,51663902	1,830143437
P3:3	3,715876135	0,993948066	5,491579918	1,349944443
Wh:1	0,538823457	3,606821469	1,352285103	4,194964243
Wh:2	0,782308898	0,923447996	1,158425656	2,264779239
Wh:3	0,755605576	3,267666795	1,354187949	5,07127203
Ge:1	3,660229547	1,022484639	4,832191532	1,782729649
Ge:2	4,340558249	2,126196148	5,935414897	3,283264382
Ge:3	3,418597383	1,336405389	4,743008012	2,361276138
Fa:1	3,372439974	1,144272759	5,511136453	1,974151717
Fa:2	3,934963948	1,259401022	6,295480522	2,372567175
Fa:3	2,814882614	3,113566983	5,027141335	3,9347681
M1:1	0,51389085	0,299939259	0,616015422	0,404320417
M1:2	0,824251503	0,514604271	1,096779376	1,002110273
M1:3	0,990032001	0,25817267	1,143022309	0,405154292
M2:1	0,71293792	0,902960105	0,804456338	1,065610154
M2:2	0,850134989	0,810612013	0,918926004	0,93820307
M2:3	0,866797714	1,085716	1,174744653	1,376490102
M3:1	0,234358738	0,46972535	0,322606572	0,698104577
M3:2	1,770722747	0,460311409	2,237057219	0,612066173
M3:3	0,690414579	2,905097517	1,150630262	3,737362038
M4:1	4,301920172	2,587409816	6,300212298	4,191103673
M4:2	2,979812649	2,6578387	4,737140488	4,256697664
M4:3	4,929846455	2,575614708	6,45073833	3,165852966
M5:1	0,202908013	0,922633439	0,254852899	1,531388259
M5:2	3,681217714	1,02982649	3,787403464	1,114540264
M5:3	1,873662019	0,671486858	2,37176622	1,209969008
M6:1	0,979385122	1,708252559	1,587773598	3,2496846
M6:2	0,513554359	0,437990966	1,036170835	0,9246621
M6:3	0,306938436	1,18017324	0,629066769	2,297901216

APPENDIX 5. Reliability of colour measurements, ΔE_{00} of repetition a and b.

Table iv: Colour difference between measurement a and b, before and after treatment, quantitative study. Red= ΔE >1. Samples highlighted in blue=reliable

	WATER	WATER	GEL	GEL
	Before	After	Before	After
P1:1	2,067247295	0,887120187	0,143250806	0,442130324
P1:2	1,110793229	0,338397978	0,044769097	0,177361236
P1:3	0,409921724	0,393761471	5,637656632	5,544895116
P2:1	0,295487697	0,689195618	3,197189937	1,949796562
P2:2	0,241675699	0,875554982	0,57169255	1,631990628
P2:3	4,291143002	4,852183319	0,517876928	0,115951104
P3:1	1,502043809	0,73902801	0,256956329	0,422996105
P3:2	0,242563366	0,591882645	0,710174402	3,673094286
P3:3	0,973535354	0,58951518	0,189141139	1,83397328
Wh:1	0,347911183	0,4106	0,18918507	0,464610961
Wh:2	1,462530691	1,0456	0,07333674	1,045632398
Wh:3	0,715896642	0,4646	0,692775557	0,410620354
Ge:1	0,019810796	1,169420045	0,081202664	0,194349187
Ge:2	0,116580869	2,14757223	0,22068795	0,032356478
Ge:3	0,917290425	0,337535933	0,195449749	0,021763168
Fa:1	0,59736595	0,376590705	0,402344529	0,329415297
Fa:2	0,233160689	0,618503874	1,687089704	0,264017758
Fa:3	1,38067306	1,954015935	0,128751504	1,661870302
M1:1	0,522140082	0,215431009	0,3859613	1,039941459
M1:2	0,328616547	0,361263955	0,373982857	1,425248052
M1:3		0,490032673	0,533847683	0,464310645
M2:1	0,321489122	0,220949875	1,27392064	0,406731029
M2:2	1,036759794	1,195190567	1,177872787	1,044599159
M2:3	1,023996364	0,290974706	0,358604096	3,401157305
M3:1	0,622125172	0,951286619	0,318291682	1,041212275
M3:2	2,219673203	1,209444392	0,089726604	0,506943243
M3:3	1,157598792	0,400236322	0,803516823	0,579349898
M4:1	1,301822006	0,096077715	3,248108195	2,86812173
M4:2	0,749275396	0,521742465	0,116385848	0,498524878
M4:3	0,484085821	0,939523274	0,208495242	0,456998661
M5:1	1,081841486	0,584661786	1,661943634	0,191137537
M5:2	1,564919922	0,56144086	0,929185971	3,476609747
M5:3	2,177895101	0,520018	0,578421575	0,454836547
M6:1	1,289419703	1,20996679	0,755088032	0,800495711
M6:2	0,670597995	0,38019635	0,588402001	1,001100909
M6:3	0,598902627	0,463319473	0,560676515	0,04436585

APPENDIX 6. Diagrams of ΔE_{00} and ΔE_{76}

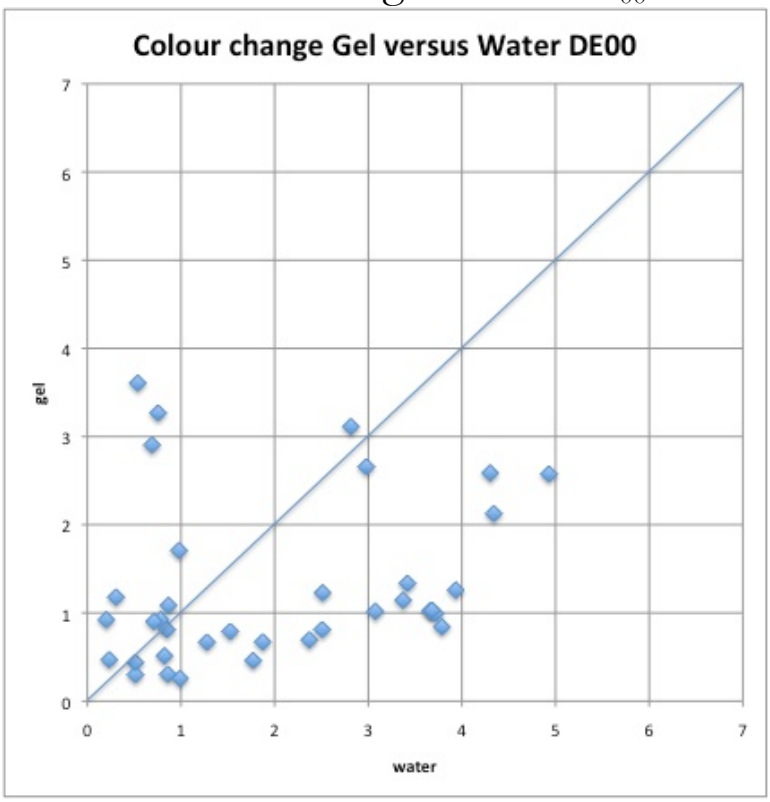


Figure ii: Diagram of colour change measured in ΔE_{00} before and after treatment, quantitative study. Gel cleaned samples plotted against immersion washed samples

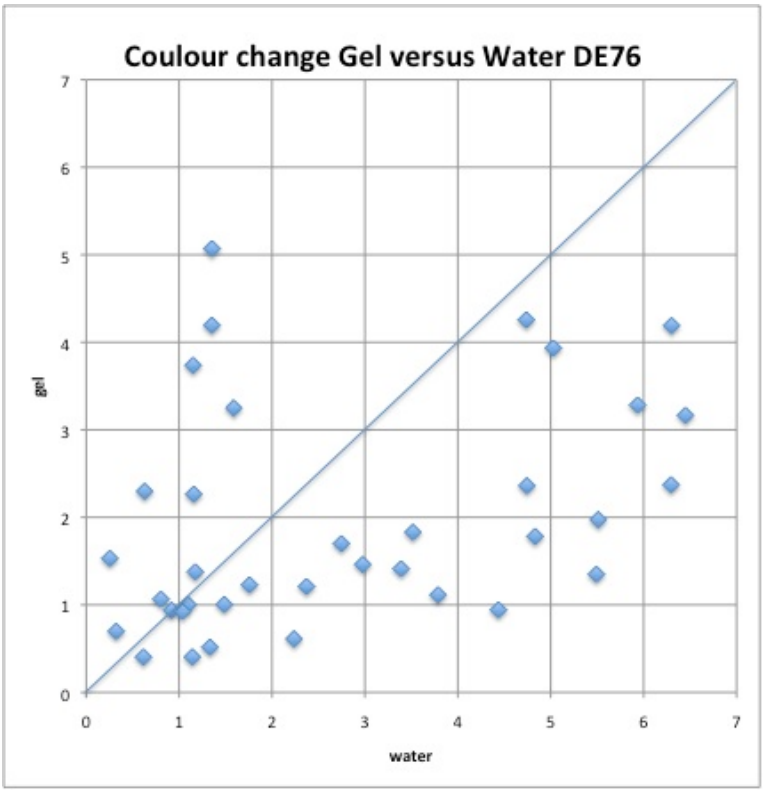


Figure iii: Diagram of colour change measured in ΔE_{76} before and after treatment, quantitative study. Gel cleaned samples plotted against immersion washed samples

APPENDIX 7 (I) Microscope pictures Case study object, before and after cleaning with Gellan gum gel

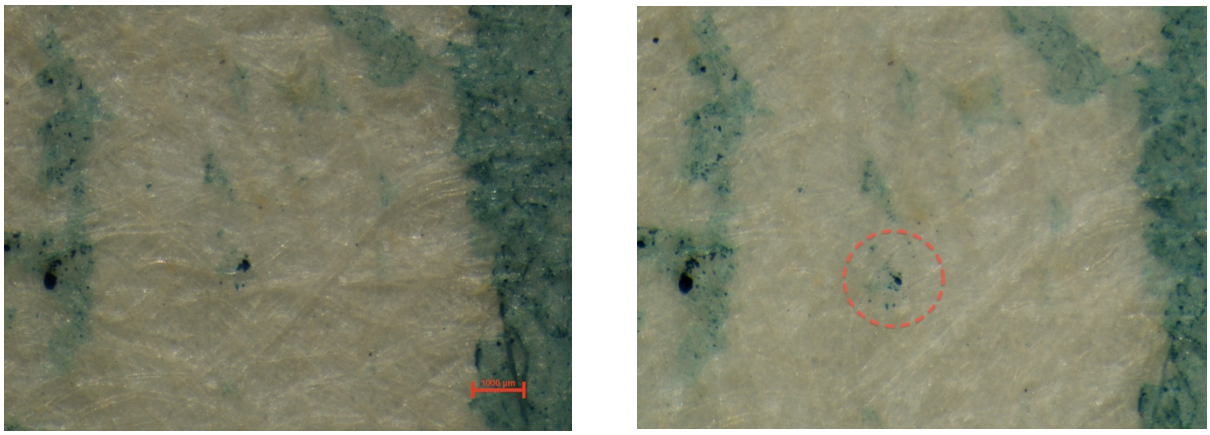


Figure iv: Spot 1: Before (left) and after (right) cleaning with Gellan gum. Note missing pigments

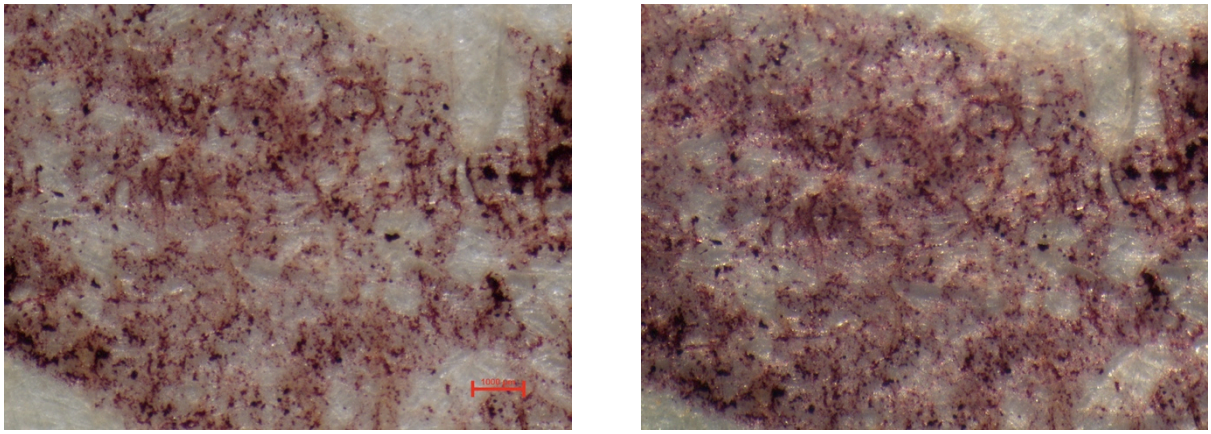


Figure iii: Spot 2 Before (left) and after (right) cleaning with Gellan gum. No noticeable difference

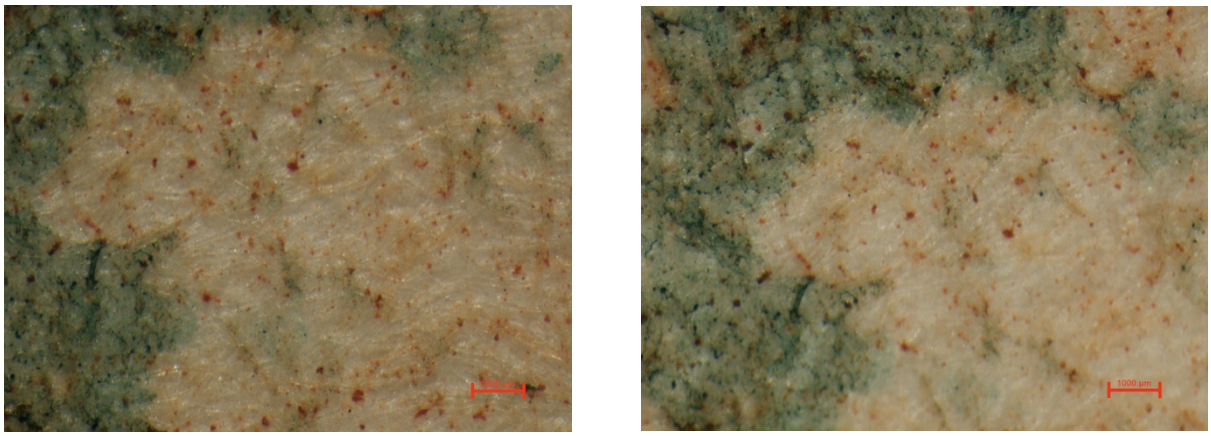


Figure ivi: **S**pot 3: Before (left) and after (right) cleaning with Gellan gum. No noticeable difference

APPENDIX 7 (II) Microscope pictures Case study object, before and after immersion wash

Figure vii: Spot 1: Before (left) and after (right) cleaning by immersion wash. No noticeable difference

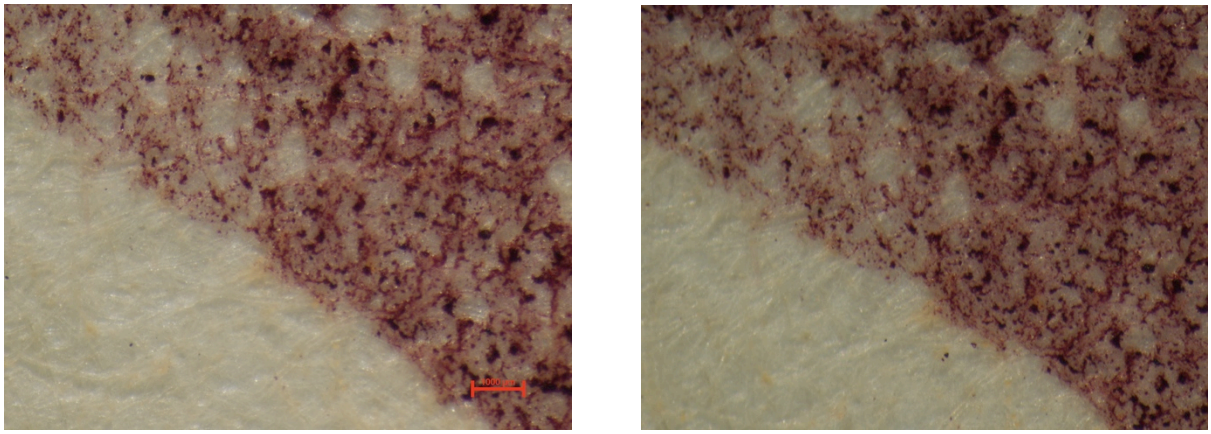


Figure vi: Spot 2: Before (left) and after (right) cleaning by immersion wash. No noticeable difference

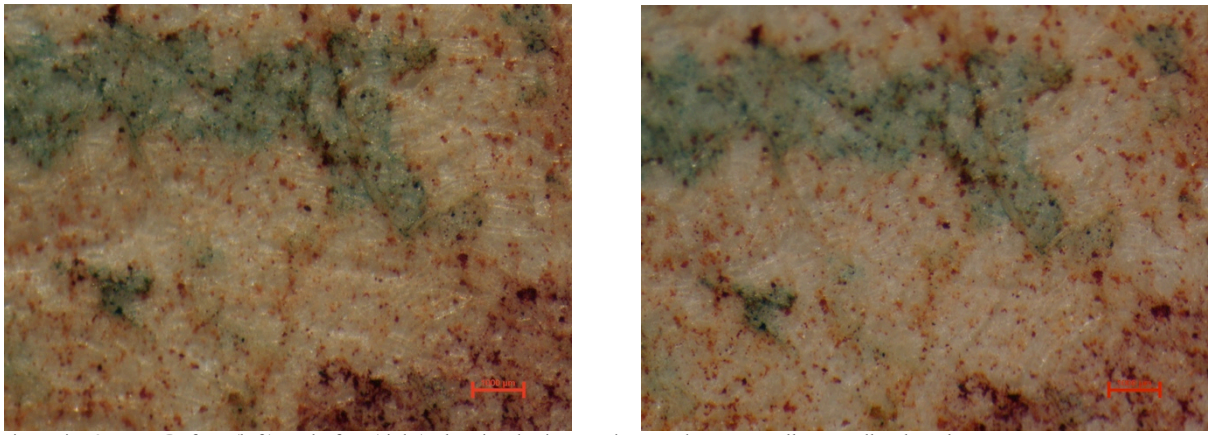


Figure ix: Spot 3: Before (left) and after (right) cleaning by immersion wash. Eventually overall colour loss

APPENDIX 8 (I). Student's T-test, Prussian blues

Table v: T-test of Prussian blue pigments. Morphological changes included, colour change excluded

Summary statistics:								
Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation	
Var1	8	0	8	1,000	3,000	1,250	0,707	
Var1	8	0	8	1,000	2,000	1,125	0,354	
t-test for two paired samples / Two-tailed test:								
95% confidence interval on the difference between the means:								
] -0,573 ;	0,823 [							
Difference		0,125						
t (Observed value)		0,424						
|t| (Critical value)		2,366						
DF		7						
p-value (Two-tailed)		0,685						
alpha		0,05						
Test interpretation:								
H0: The difference between the means is equal to 0.								
Ha: The difference between the means is different from 0.								
As the computed p-value is greater than the significance level alpha=0,05, one cannot reject the null hypothesis H0.								
The risk to reject the null hypothesis H0 while it is true is 68,45%.								

Table vi: T-test Prussian blue pigments. Colour change included, morphological change excluded

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation	
Var1	8	0	8	1,000	3,000	1,250	0,707	
Var1	8	0	8	1,000	2,000	1,125	0,354	
t-test for two paired samples / Two-tailed test:								
95% confidence interval on the difference between the means:								
] -0,573 ;	0,823 [							
Difference		0,125						
t (Observed value)		0,424						
|t| (Critical value)		2,366						
DF		7						
p-value (Two-tailed)		0,685						
alpha		0,05						
Test interpretation:								
H0: The difference between the means is equal to 0.								
Ha: The difference between the means is different from 0.								
As the computed p-value is greater than the significance level alpha=0,05, one cannot reject the null hypothesis H0.								
The risk to reject the null hypothesis H0 while it is true is 68,45%.								

APPENDIX 8 (II). Student's T-test, Madder lakes

Table vii: T-test of Madder lake pigments. Morphological change incllued, colour change excluded

Summary statistics:								
Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation	
Var1	18	0	18	1,000	3,000	2,611	0,698	
Var1	18	0	18	1,000	3,000	2,000	0,840	
t-test for two paired samples / Two-tailed test:								
95% confidence interval on the difference between the means:						]0,125;	1,098 [	
Difference	0,611							
t (Observed value)	2,650							
|t| (Critical value)	2,110							
DF	17							
p-value (Two-tailed)	0,017							
alpha	0,05							
Test interpretation:								
H0: The difference between the means is equal to 0.								
Ha: The difference between the means is different from 0.								
As the computed p-value is lower than the significance level alpha=0,05, one should reject the null hypothesis H0, and accept the alternative hypothesis Ha.								
The risk to reject the null hypothesis H0 while it is true is lower than 1,69%.								

Table viii: T-test of madder lake pigments Colour change included, morphological change excluded

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation	
Var1	18	0	18	0,258	2,905	1,193	0,894	
Var1	18	0	18	0,203	4,930	1,512	1,466	
t-test for two paired samples / Two-tailed test:								
95% confidence interval on the difference between the means:						] -0,916 ;	0,278 [	
Difference	-0,319							
t (Observed value)	-1,128							
|t| (Critical value)	2,110							
DF	17							
p-value (Two-tailed)	0,275							
alpha	0,05							
Test interpretation:								
H0: The difference between the means is equal to 0.								
Ha: The difference between the means is different from 0.								
As the computed p-value is greater than the significance level alpha=0,05, one cannot reject the null hypothesis H0.								
The risk to reject the null hypothesis H0 while it is true is 27,49%.								

APPENDIX 9. Differences in L*, a*, b* values before and after cleaning

Table ix: Difference in L*, a*, b* values before and after cleaning, all samples quantitative study. Red= Negative difference in L* values. Gel cleaned samples of P3 highlighted in blue since all three samples have negative difference in L*

WATER	Dif L	Dif a	Dif b	GEL	Dif L	Dif a	Dif b
P1 1	3,69	-2,435	-0,38	P1 1	0,82	0,1	-0,455
P1 2	2,295	-1,895	0,035	P1 2	0,665	-0,175	-1,29
P1 3	2,245	-1,46	0,61	P1 3	0,175	0,06	-1,69
P2 1	1,455	-0,95	-0,265	P2 1	-0,99	0,405	-0,605
P2 2	0,76	-0,975	-0,825	P2 2	0,81	-0,425	0,415
P2 3	0,295	-0,275	-1,27	P2 3	0,07	-0,15	-0,49
P3 1	1,535	-1,705	-2,495	P3 1	-0,815	0,18	-1,14
P3 2	0,47	-0,265	-3,475	P3 2	-0,56	0,16	-1,735
P3 3	1,075	-0,06	-5,385	P3 3	-1,07	-0,115	-0,815
Wh 1	-0,095	-0,67	0,41	Wh 1	3,955	-1,765	1,37
Wh 2	-1,945	-0,33	-0,045	Wh 2	-0,375	-1,26	1,06
Wh 3	0,725	-0,66	0,41	Wh 3	0,255	-2,445	1,905
Ge1	3,375	-0,985	3,315	Ge1	0,845	-0,71	1,4
Ge2	4,01	-1,645	4,055	Ge2	1,9	-1,265	2,36
Ge3	3,15	-1,395	3,26	Ge3	1,075	-0,98	1,86
Fa 1	3,14	-1,695	4,2	Fa 1	0,945	-0,745	1,565
Fa 2	3,865	-1,685	4,675	Fa 2	0,995	-1,005	1,905
Fa 3	2,345	-1,61	4,145	Fa 3	2,98	-1,36	2,18
M1:1	0,615	-0,035	0,005	M1:1	0,225	-0,085	0,325
M1:2	1,045	-0,25	-0,22	M1:2	0,04	0,545	0,84
M1:3	missing	missing	missing	M1:3	-0,125	-0,355	0,15
M2:1	0,57	0,485	0,295	M2:1	-0,87	0,48	0,385
M2:2	0,73	0,53	0,175	M2:2	-0,715	0,51	0,33
M2:3	-1,17	0,055	-0,09	M2:3	1,24	0,43	0,415
M3:1	0,305	-0,105	-0,005	M3:1	0,535	0,415	0,17
M3:2	2,17	0,45	0,305	M3:2	-0,49	0,17	0,325
M3:3	-0,445	0,895	0,57	M3:3	-3,405	1,275	0,865
M4:1	-3,265	0,885	-5,315	M4:1	-1,945	0,135	-3,71
M4:2	-1,74	1,48	-4,15	M4:2	-1,965	0,555	-3,735
M4:3	-3,77	2,47	-4,615	M4:3	-2,25	0,99	-1,995
M5:1	0,19	0,115	0,125	M5:1	-0,765	0,905	0,97
M5:2	3,76	0,115	0,44	M5:2	0,98	0,03	0,53
M5:3	2,075	-1,075	-0,405	M5:3	-0,56	0,72	0,795
M6:1	1,12	-1,095	-0,26	M6:1	1,64	-2,765	-0,475
M6:2	0,385	-0,945	-0,18	M6:2	0,34	-0,85	-0,13
M6:3	-0,115	-0,48	-0,39	M6:3	-0,825	1,85	1,085

APPENDIX 10 (I). K-mean clustering

Table x: K-mean clustering of madder lake pigments, five clusters.

Class	1	2	3	4	5
Objects	9	6	11	7	3
Sum of weights	9	6	11	7	3
Within-class variance	1,827	0,282	3,243	5,633	1,968
Minimum distance to centroid	0,832	0,333	0,760	1,277	0,342
Average distance to centroid	1,202	0,462	1,467	1,931	1,031
Maximum distance to centroid	1,931	0,667	3,267	4,401	1,511
	M1gel1	M2gel1	M3gel1	M3gel3	M5water2
	M1gel2	M2gel2	M3gel2	M4gel1	M5water3
	M1gel3	M2gel3	M5gel1	M4gel2	M5water1
	M1water1	M2water1	M5gel2	M4gel3	
	M1water2	M2water2	M5gel3	M4water1	
	M1water3	M2water3	M6gel1	M4water2	
	M3water1		M6gel2	M4water3	
	M3water2		M6gel3		
	M3water3		M5water1		
			M6water2		
			M6water3		

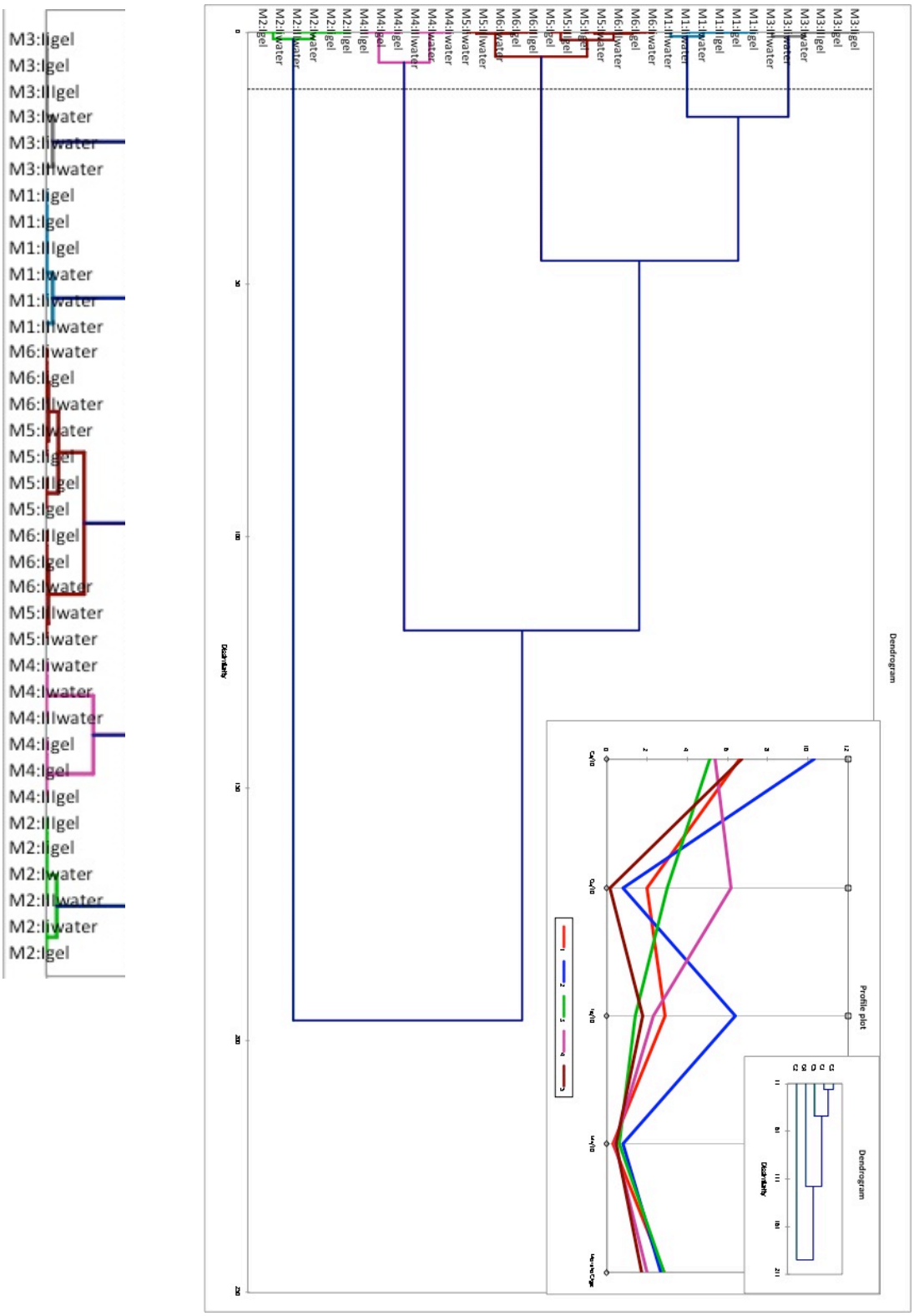
APPENDIX 10 (II). K-mean clustering

Table xi: K-mean clustering of madder lake pigments, nine clusters

Class	1	2	3	4	5	6	7	8	9
Objects	6	1	4	6	6	10	1	1	1
Sum of weights	6	1	4	6	6	10	1	1	1
Within-class variance	0,250	0,000	0,025	1,253	2,240	0,814	0,000	0,000	0,000
Minimum distance to centroid	0,175	0,000	0,002	0,641	1,062	0,353	0,000	0,000	0,000
Average distance to centroid	0,376	0,000	0,108	0,935	1,341	0,786	0,000	0,000	0,000
Maximum distance to centroid	0,935	0,000	0,217	1,824	1,879	1,296	0,000	0,000	0,000
	M1gel1	M2gel1	M2gel2	M3gel1	M4gel1	M5gel1	M2water2	M5water2	M5water3
	M1gel2		M2gel3	M3gel2	M4gel2	M5gel2			
	M1gel3		M2water1	M3gel3	M4gel3	M5gel3			
	M1water1		M2water3	M3water1	M4water1	M5gel1			
	M1water2			M3water2	M4water2	M5gel2			
	M1water3			M3water3	M4water3	M6gel3			
						M5water1			
						M6water1			
						M6water2			
						M6water3			

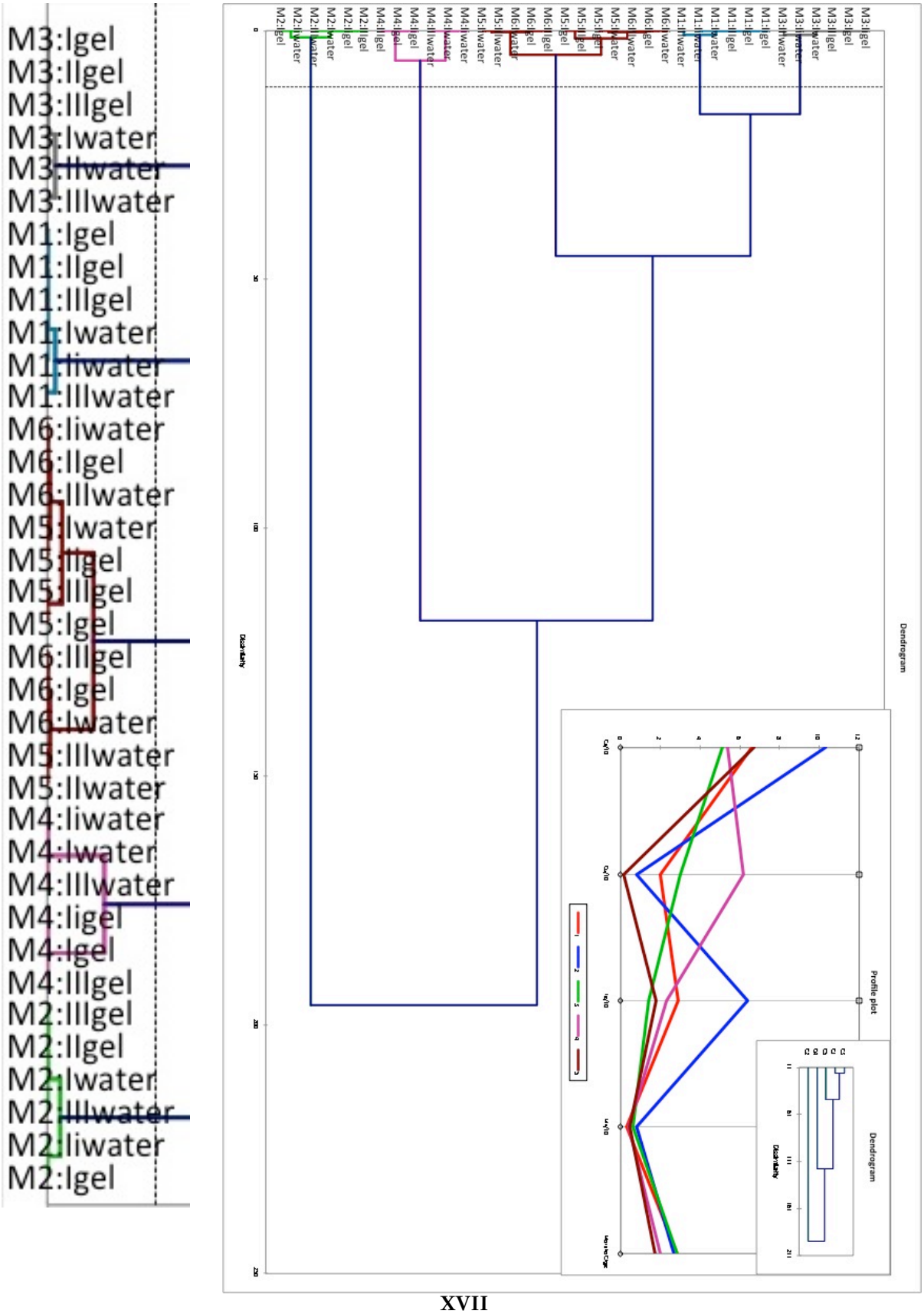
APPENDIX 11 (I). Dendrogram Madder Lakes, all samples, no colour change with chromophores

Figure vi: Dendrogram of madder lake pigments. All samples included. Chromophore ratio included, colour change excluded



APPENDIX 11 (II). Dendrogram, Madder Lakes, all samples, no colour change, no chromophores

Figure viii Dendrogram of madder lake pigments. All samples included. Chromophore ratio excluded, colour change excluded



APPENDIX 12 (I) PCA Madder lakes, all variables only gel cleaned samples only

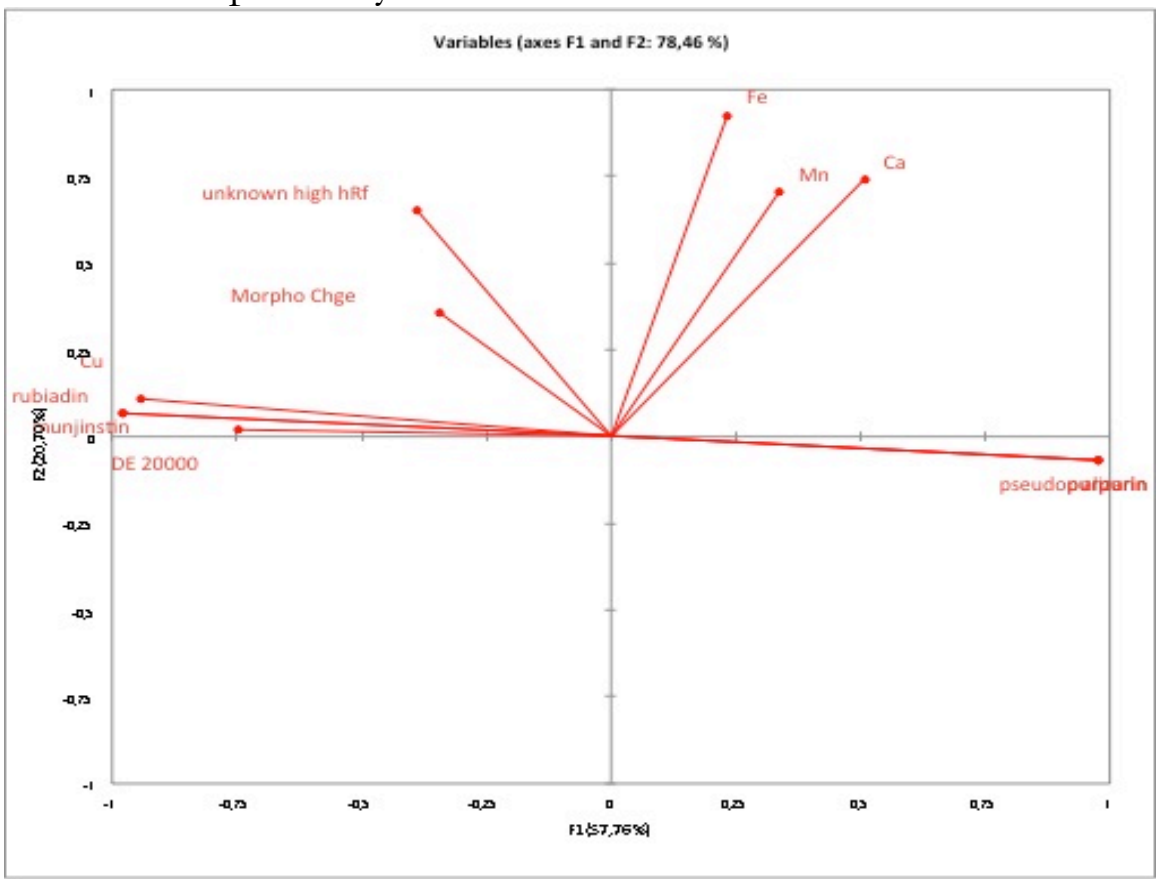


Figure viiii: Plot of variables: PCA of gel cleaned madder lake pigments. All variables included

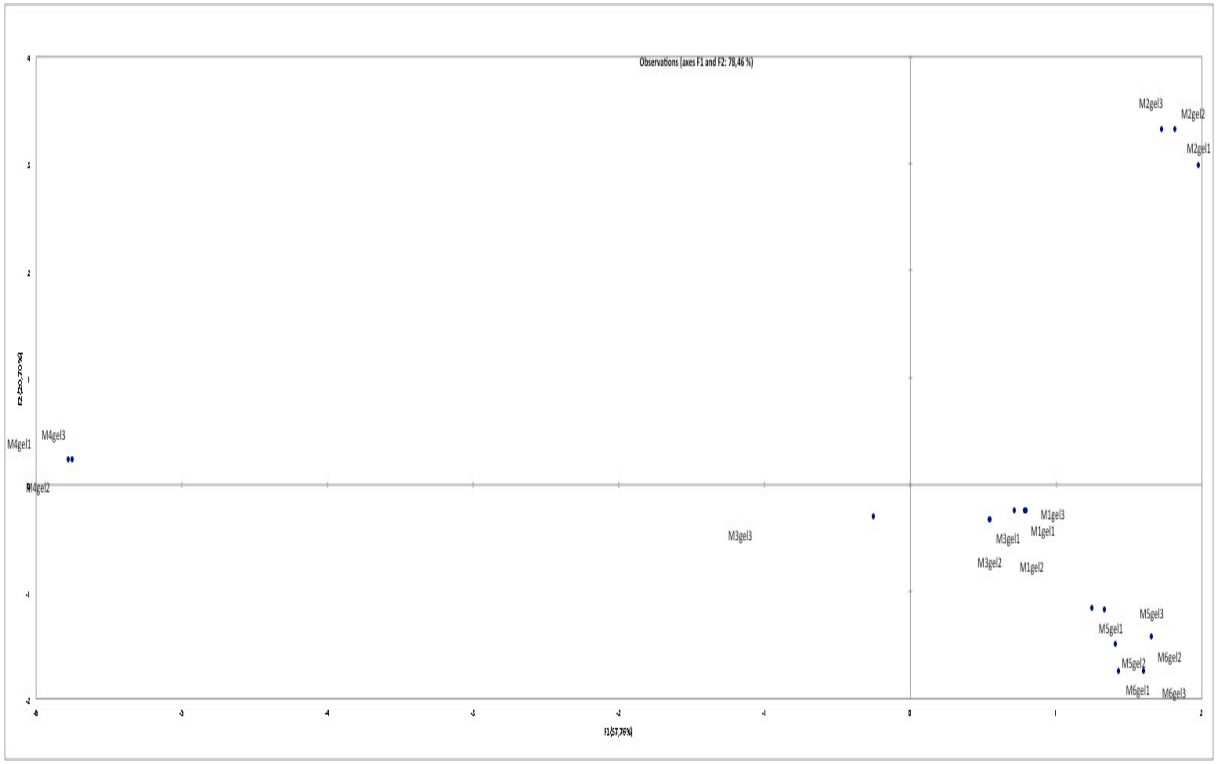


Figure ixi: Plot of samples for PCA of gel cleaned madder lake pigments. All variables included

Table xii: Factors loading for PCA of gel cleaned madder lake pigments. All variables included

Factor loadings:							
	F1	F2	F3	F4	F5	F6	F7
Ca	0,507	0,739	-0,332	-0,280	0,057	0,066	-0,005
Cu	-0,941	0,111	0,251	0,154	-0,122	-0,020	0,020
Fe	0,233	0,926	-0,150	-0,232	-0,020	0,107	0,012
Mn	0,337	0,702	-0,294	0,472	0,051	-0,286	-0,001
alizarin	0,979	-0,068	0,150	0,108	0,010	0,055	0,003
purpurin	0,979	-0,068	0,150	0,108	0,010	0,055	0,003
pseudopurpurin	0,979	-0,068	0,150	0,108	0,010	0,055	0,003
rubiadin	-0,979	0,068	-0,150	-0,108	-0,010	-0,055	-0,003
munjinstin	-0,979	0,068	-0,150	-0,108	-0,010	-0,055	-0,003
unknown high hRf	-0,388	0,650	0,531	0,213	-0,283	0,139	-0,012
DE 20000	-0,749	0,019	-0,366	0,399	0,247	0,290	0,000
Morpho Chge	-0,345	0,357	0,770	-0,099	0,382	-0,065	-0,001

APPENIX 12 (II) PCA madder lakes, all variables only immersion washed samples

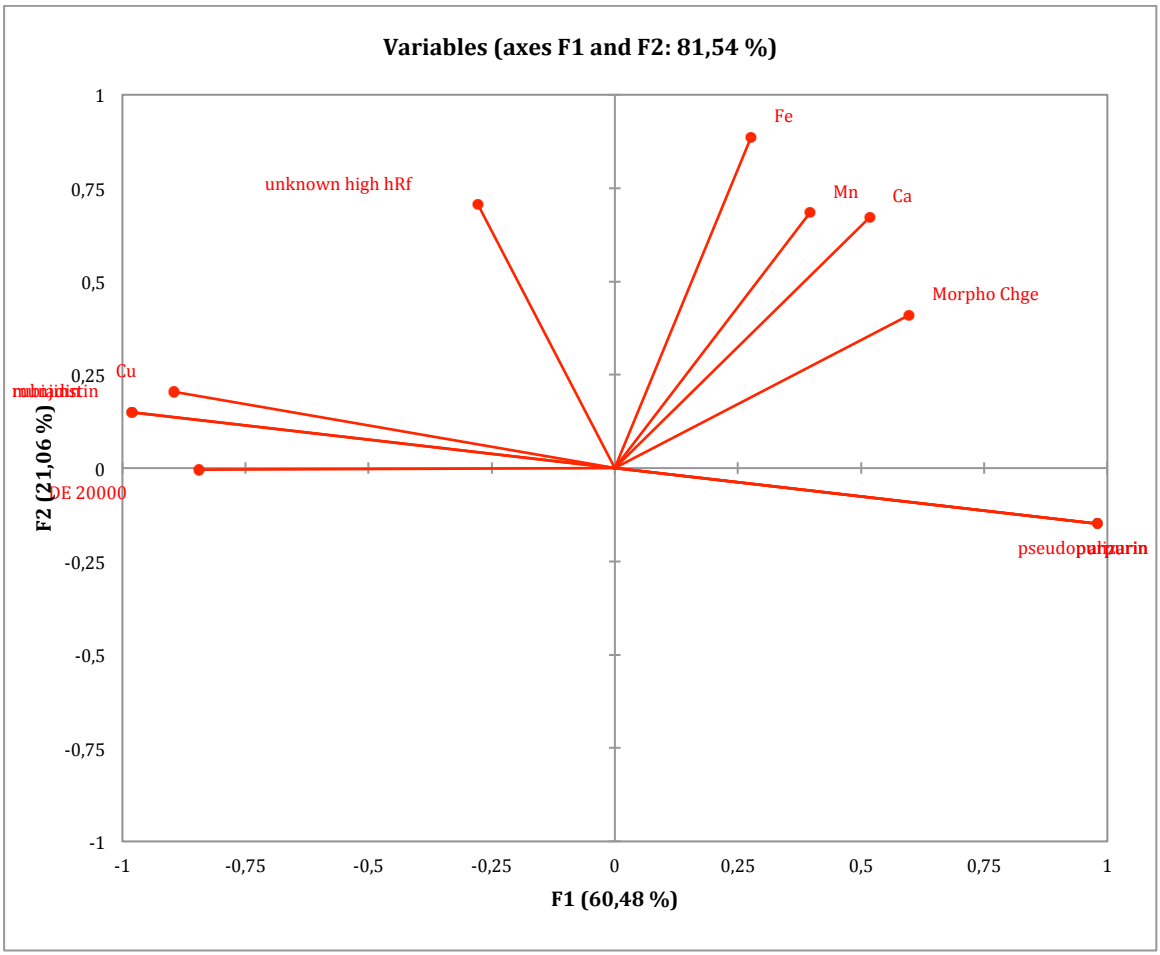


Figure xiv: Plot of variables: PCA of immersion washed madder lake pigments. All variables included.

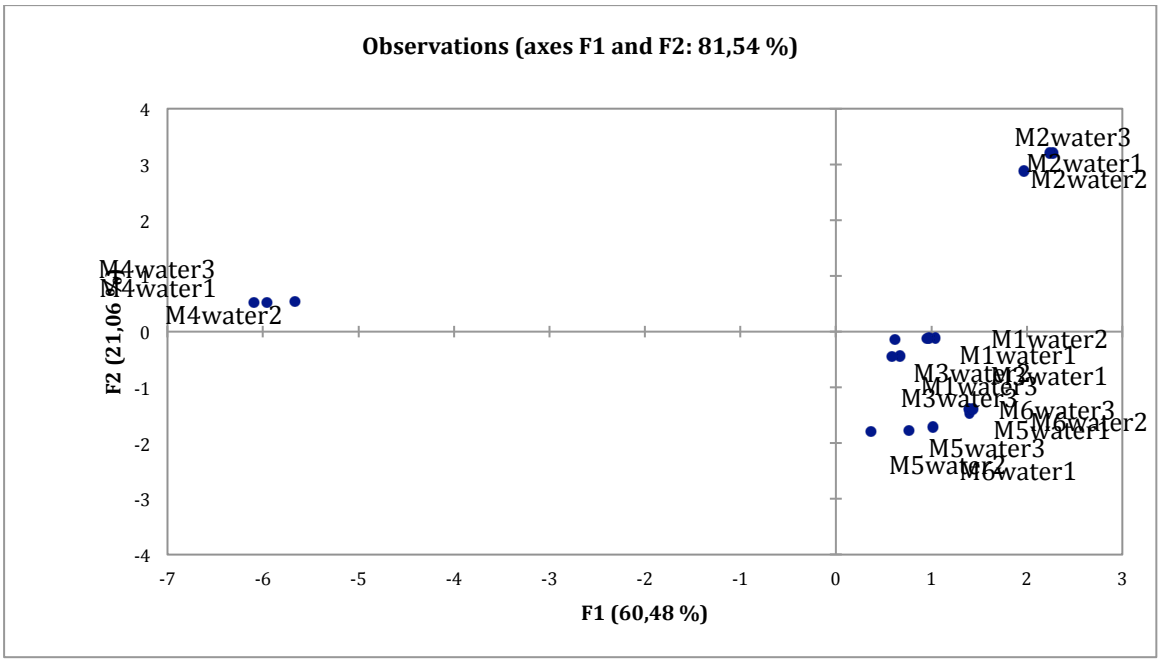


Figure xv: Plot of samples: PCA of immersion washed madder lake pigments. All variables included

Table xii: Factors loading for PCA of immersion washed madder lake pigments. All variables included

Factor loadings:							
	F1	F2	F3	F4	F5	F6	F7
Ca	0,518	0,672	-0,491	-0,189	-0,054	0,016	-0,006
Cu	-0,895	0,205	0,383	0,069	0,048	-0,058	0,027
Fe	0,277	0,887	-0,288	-0,230	0,003	-0,033	0,016
Mn	0,397	0,684	-0,176	0,585	0,039	0,015	-0,001
alizarin	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
purpurin	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
pseudopurpurin	0,980	-0,150	0,066	-0,008	0,107	-0,026	0,004
rubiadin	-0,980	0,150	-0,066	0,008	-0,107	0,026	-0,004
munjinstin	-0,980	0,150	-0,066	0,008	-0,107	0,026	-0,004
unknown high hRf	-0,279	0,706	0,599	-0,093	0,172	-0,164	-0,017
DE 20000	-0,845	-0,004	-0,263	-0,050	0,429	0,173	-0,001
Morpho Chge	0,598	0,411	0,615	-0,060	-0,102	0,285	0,000