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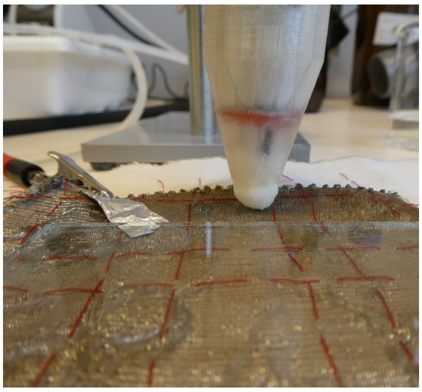
Electrolytic Cleaning of Silver Threads

-Effects of Electrolytes on the Condition of Silk



Karin Hindborg

Uppsats för avläggande av filosofie kandidatexamen i
Kulturvård, Konservatorprogrammet
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Handledare: Stavroula Golfomitsou

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UNIVERSITY OF GOTHENBURG
Department of Conservation
P.O. Box 130
SE-405 30 Goteborg, Sweden

www.conservation.gu.se
Ph +46 31 786 4700

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By: Karin Hindborg
Mentor: Stavroula Golfomitsou

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ABSTRACT

This thesis investigates localised electrolytic reduction as a method to clean tarnish on silver threads on silk. The tool used is an electrolytic pen called the Pleco that was developed for local treatment of metals on composite objects. Silver embroidery on silk fabric is typically left uncleaned because mechanical and chemical corrosion removal methods can be harmful to the silk. There is currently no widely accepted method to clean silver on silk. The main focus of the study was the assessment of the condition of silk after treatment using different electrolytes and accelerated ageing. Further aims were to investigate if it was possible to clean silver threads using the Pleco and methods to control the spread of the electrolytes. Experiments with the Pleco were performed on a silver thread ribbon, dated 1716, attached to contemporary silk and were executed with two different types of electrolyte, one alkaline and one acidic. The materials in the silver thread ribbon were identified by X-ray fluorescence spectroscopy (XRF) and polarized light microscopy. Light microscopy was carried out to compare the visual differences between areas of the silver thread ribbon that were cleaned by the Pleco and areas that were not cleaned. Scanning electron microscopy (SEM) was used to examine the silver threads, the morphology of the silk and to search for degradation symptoms. Energy dispersive X-ray spectroscopy (EDS) and attenuated total reflection- Fourier-transform infrared spectroscopy (ATR-FTIR) were used to investigate sodium salt residues in the contemporary silk, the silk in the warp of the silver ribbon and in the core of the silver threads. The physical effects of the treatments with the selected electrolytes before and after accelerated ageing were assessed by tensile strength testing and colour measurements. This study has shown positive results indicating that local electrolytic cleaning of silver threads on silk with the Pleco containing a suitable electrolyte could be a viable option.

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Preface

White silk with silver, violet silk with gold, floral gold and silver fabric, light brown cloth lined with yellow-brown satin embroidered with silver threads. This is part of a list of fabrics that can be found in the Danish Rosenborg collections from 1625 to 1695.

I have always had an interest in things of the past, especially textiles. A year ago me and my fellow conservator students were taught how to use the Pleco to reduce silver tarnish back to silver. This made me start to ponder about if it would be possible to clean silver embroideries with the same technique, which led to the writing of this thesis.

In the process I have been assisted by some wonderfully helpful people to whom I would like to send some thanks.

My mentor Stavroula Golfomitsou: Voula, thank you for all the time and effort you have devoted to supervising me in the experiments and the writing process.

The Swedish National Heritage Board: Thank you for welcoming me as a guest colleague at your laboratory. Special thanks to Marei Hacke and Elyse Canosa for assisting and guiding me in the lab, and Marei, thank you for encouraging me to send an abstract to ICOM-CC.

Studio Västsvensk Konservering: Thank you for letting me use the silver thread ribbon in my investigations and for support and encouragement in the preparatory work of the thesis.

Christian Degrigny: Thank you for advice regarding what electrolytes to use in the experiments.

Austin Nevin: Thank you for assisting me when using the XRF.

Finally Marcus, my husband and my love: Thank you for making our lives bearable while I have been focusing on experiments and writing. Thank you for feeding me and the kids, for driving them to school, for washing cloths and tidying up. And for never complaining about me being absent while present.

Karin Hindborg

Lerum, 21 May 2019

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1. Introduction

The day Gustav III came of age he wore a suit consisting of coat, vest and trousers. The coat was made of silver brocade on a silk rib weave with a pattern made of silver strips. It was decorated with tied silver lace. On each shoulder a double silver string was placed, used to keep the cordons in order. The seams of the arms were covered by silver lace (figure 1) (Kringla, Riksantikvarieämbetet 2010).

In museums, churches and other historic collections, many textiles decorated with metal threads can be found. This thesis investigates the possibility of using local electrolysis to clean silver threads on silk fabric, as a way to preserve parts of our cultural heritage.

1.1 Background

Silver embroidery on silk fabric is not usually cleaned. The reason for this is that the threads are delicate and thin and can be damaged by mechanical cleaning. Chemical methods for removing corrosion on silver can be harmful to the silk. There is currently no widely accepted method to clean silver threads on silk (Tímár-Balázsy & Eastop 2011, pp. 242-247).

Fig. 1.1. The clothes worn by Gustav III on the day he was coming of age, made from silk with silver thread decorations.

Electrolysis is a controlled way of reducing silver tarnish (silver sulphide) back to pure silver. Traditionally, to perform electrolysis, the object is placed in an electrolyte bath (Brown & Ford 2014, p. 443). This is not a widely used method in textile conservation as the immersion in an electrolyte might be harmful to the textile. The Pleco is an electrolytic pen developed to remove the need of immersing composite objects in electrolyte. It is designed like a pencil and performs local electrolysis through constant supply and extraction of the electrolyte through a microporous sponge.

1.2 Previous Research

Many methods to clean silver threads on textiles have been tried. In 2011 Jimenez-Cosme and Contreras-Vargas examined the problem of corrosion and cleaning gilded silver threads. Toth has written a paper that shares the experience gained in cleaning, conserving and restoring metal thread embroideries from Hungary (2013). The use of laser as a cleaning method for metal threads has been examined (Degrigny, Tanguy, Le Gall, Zafiropulos & Marakis 2003). In 2003 the possibility to clean metal threads by UV/Ozone treatment was investigated (Hacke & Carr). Létrange, Hourdet, Guerrier and Pons have tried using electrochemical treatment with three hydrogels to clean tarnished silver (2017).

To be able to use electrolysis to reduce the metal in composite objects, the Pleco has been developed by Degrigny, Jeanneret, Witschard, Baudin, Bussy and Carrel (2016). It has been used to clean a reliquary bust from Switzerland, comprising gilded and non-gilded silver plates and painted areas (Jeanneret, Degrigny, Fontaine, Witschard & Tarchini 2016). It has also been used to clean a reliquary head comprising partly gilded silver plates nailed on a wooden core (Degrigny, Jeanneret & Witschard 2015). Experiments have been made to clean a gilded silver fringe using the Pleco (Ovide, Luvidi, Prestileo, Ferro, Degrigny & Brunetto (2017).

1.3 Problem Formulation and Issues

Silver embroidery on silk fabric is typically left uncleaned. Silver threads are sensitive and can be damaged by mechanical cleaning and chemical methods for removing silver tarnish can be harmful to the silk. However, part of the appeal of the use of silver threads was based on its shiny, reflective qualities. Tarnishing leads to visual changes, from silver shining to black, altering significantly the aesthetic qualities and original appearance of the object.

The purpose of this project is to investigate whether local electrolytic cleaning can be used safely in a manner that does not cause serious degradation of silk.

The following issues will be investigated:

- Is it possible to clean silver threads using the Pleco?
- How does the electrolyte used affect the silk fibres?
- Are there methods to control the spread of electrolyte in silk?

1.4 Objective and Purpose

The objective of this thesis is to, through literature studies, experiments and analyses, reach an understanding of whether it is possible to use the method of local electrolysis to clean silver threads on silk without any long term side-effects on the silk.

The purpose is to enable conservators to clean metal threads on textiles and to explore the possibility of using the Pleco as an easy way to do so.

1.5 Methods

This thesis will use three comprehensive methods. A literary review will be used to get a deeper understanding of materials used, problems that can be found in conservation of metal threads and how electrolysis works.

Experiments will be performed to investigate the possibility of using the Pleco on silver threads on silk. Will the silver sulphide be reduced back to metallic silver? Are the silver threads too intricate to clean with local electrolysis? Will the silk be affected by the electrolyte? Will the electrolyte spread beyond the application point in the silk? Will I be able to find methods to control the spread?

Analyses of the treated silver and silk will be performed. They will help answering the questions in section 1.2.

Experiments and some of the analysis were performed at the Department of Conservation at University of Gothenburg. Other analytical methods were performed at the Swedish National Heritage Board in Visby, where I visited for a week as a guest colleague as part of this thesis.

It is important to note that 'clean' is used although the process carried out is electrolytical reduction. However, as in conservation these processes are widely referred to as 'cleaning', it has been decided to use it here too.

1.6 Limitations

Metal threads have been used in textiles for a very long time. There are examples in Exodus of how they used gold threads to work into fine linen around 1300 BC (The Holy Bible 1991, Exodus 39:3). Metal threads have been used mainly in embroideries and in the weft of textiles. The materials used and how they are combined have varied a great deal over the years (Tímár-Balázsy & Eastop 2011, p. 128). This study only investigated silver threads with a silk core, woven into a ribbon with a warp of silk.

Many different materials have been used as a base for metal thread embroidery. Silk has been used in combination with silver threads (Nilsson 2015, pp. 201-211), examples can be found of military coats that combine wool, linen, silk and cotton with silver threads (Tímár-Balázsy & Eastop 2011, p. 144). This study will be limited to examining contemporary silk fabric as a base for the silver thread ribbon. Silk is the most common fabric used as a base for silver threads (Landi 21992, p. 40). Both the silk and the silver ads lustre to the textile. It shows the wealth and power of the owner. Contemporary silk was chosen to limit the variation in relation to the types of silk that can be found in real conditions, to increase the reproducibility of the results and to increase the likelihood of equivalent results in the analyses.

Electrolytic cleaning can be performed with many different kinds of electrolyte. This study will be limited to two electrolytes of different pH, one alkaline and one acidic. After discussions with Source 1, one of the developers of the Pleco, it was decided to use sodium sesquicarbonate, pH 10 and sodium nitrate buffered to pH 5.

An additional method of controlling the spread of electrolyte in silk was tested using a vacuum table. The main reason to perform experiments on a vacuum table was to understand whether it might be a functional technique to control the spread of electrolyte in silk. Due to time restrictions the samples treated on the vacuum table were analysed only qualitatively using visual observation.

1.7 Theoretical Approach and Ethical Issues

This thesis will be an empirical study with quantitative and qualitative evaluation. The work is based on a literary review, experiments and analyses of samples used during the experiments. The Burra Carter determines that:

> ***Article 4.2***
>
> *Traditional techniques and materials are preferred for the conservation of significant fabric. In some circumstances modern techniques and materials which offer substantial conservation benefits may be appropriate.*
>
> ***Explanatory Notes***
>
> *The use of modern materials and techniques must be supported by firm scientific evidence or by a body of experience.*

(The Burra Charter 2013)

The problem with cleaning metal threads on textiles is that there is no widely accepted technique to perform it. There is a need to find new methods that are safe for both the silk and the metal alloy of a thread. Source 2 informed me that at one of the latest meetings at Svenska föreningen för textilkonservering (SFT, Swedish association for textile conservation) they were discussing the need of new cleaning methods. As stated in section 1.3 the purpose of this thesis is to explore the possibility of using local electrolysis with the Pleco as an easy way to clean metal threads. The experiments and analyses are attempts to provide some first “scientific evidence” as asked for in The Burra Charter (2013, § 4.2).

Ethical issues to consider are whether cleaning is indeed necessary. It is important to stress that each case should be considered individually and decisions regarding cleaning should be made based on the condition of both the silk and metal threads, the type of dirt to be removed, the aesthetic value of the object and the purpose of the treatment (e.g. display, use). However, one might decide not to clean because of the information trapped in the historical layers of the dirt/corrosion products. It is important to always consider the reason for cleaning and decide what values are of most importance for the specific object (Muñoz Viñas 2005, p. 37).

There are also ethical issues of a more personal professional note that will be embraced in this study. The Code of Ethics of the Canadian Association for Conservation of Cultural Property and of the Canadian Association of Professional Conservators determines that:

> ***VI.***
>
> *The conservation professional shall continue to develop knowledge and skills with the aim of improving the quality of his/her professional work.*
>
> ***VII.***
>
> *The conservation professional shall contribute to the evolution and growth of the profession by sharing experience and information with colleagues.*

(Code of Ethics 2000)

The work on this thesis will help me as a professional to develop knowledge and skills that will improve the quality of my professional work. The study is also a way to contribute to the evolution and growth of the profession, as it will be shared in the form of a thesis and also hopefully be presented at the coming ICOM-CC (International Counsel of Museums -Committee for Conservation) conference.

1.8 Guest Colleague at the Swedish National Heritage Board

The Swedish National Heritage Board has a program where any one working with cultural heritage associated with public institutions in Sweden can apply to become a guest colleague. As a guest colleague, you have the opportunity to come to the Cultural Heritage Laboratory at the National Heritage Board in Visby and receive support with an issue concerning a specific project on cultural heritage.

Being a guest gave me the opportunity to perform tests and analyses with the laboratory’s analysis and documentation equipment, that I otherwise would not have been able to perform. I also got to meet very knowledgeable people of different expertise in the field of cultural heritage science. It was a valuable experience to cooperate around the analytical methods I wanted to perform.

The experiments with the Pleco were carried out at the Department of Conservation at the University of Gothenburg, while accelerated ageing, SEM-EDS, FTIR, tensile strength testing and spectrophotometry were carried out in Visby. I worked together with Marei Hacke and Elyse Canosa to prepare samples and perform tests. I presented my work to two groups visiting the Board and was interviewed for an article in *k-blogg,* the blog of the Swedish National Heritage Board (Riksantikvarieämbetet 2019). I very much enjoyed this opportunity and I really recommend others to seek a place as a guest colleague at the Swedish National Heritage Board.

2. Literature Review

Literature was used to get a better understanding of the materials under study and their deterioration processes. In addition, issues related to conservation of metal threads and electrolytic reduction of silver were investigated.

2.1 Materials

2.1.1 METAL THREADS

The earliest metal threads were most often made from strips of so-called noble metals, which later on could be combined with organic materials such as fibres, gut or paper. There are four main types of metal threads:

- A strip, either solid or metal-coated organic material (figure 2.1)
- A solid metal strip wound around a core of fibres (figure 2.2)
- A wire (figure 2.3)
- A wire wound around a core of fibres (figure 2.4)

Predominantly gold, silver and copper alloys have been used in the making of metal threads. Contemporary metal threads are often made of aluminium. Metal threads can have coatings and finishes, examples are gilding or silvering of a solid metal strip. The core can be made from protein-based or cellulose-based fibres. If the metal thread is from the twentieth century, man-made fibres can also be found (Landi 1992, p. 12; Tímár-Balázsy & Eastop 2011, pp. 128-130). The solid metal strip was often cut from a sheet (foil/leaf) or hammered from a wire. The width of the strips was 0,2 - 0,3 mm and the thickness varied between 0,006 and 0,030 mm. Wires were often drawn through a drawing plate with successively smaller holes. The winding of a strip or wire were probably done with the help of a spindle, rolled manually on the thigh. If the metal strip was fed from the left the thread got a ‘z’-twist and from the right a ‘S’-twist (figure 2.2 and 4.16) (Tímár-Balázsy & Eastop 2011, pp. 128-130).

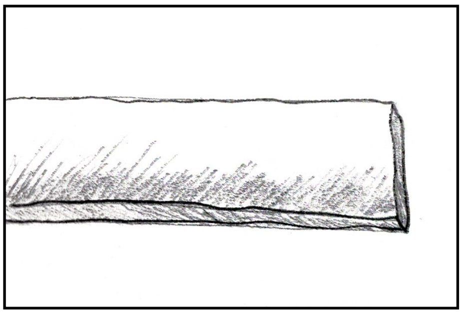


Fig.2.1. Metal strip.

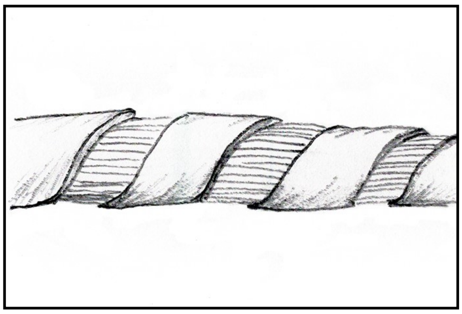


Fig.2.2. Metal strip wound around a core of fibres with a ’S’-twist.

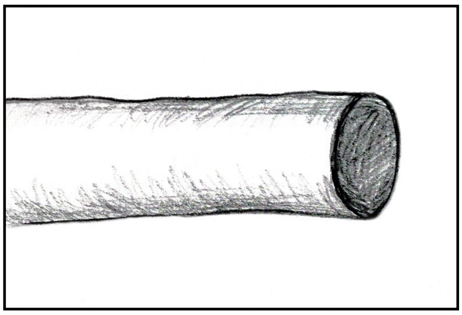


Fig.2.3. Solid wire.

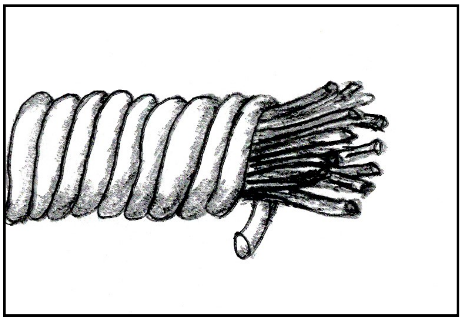


Fig.2.4. Wire wound around a core of fibres.

2.1.2 SILK

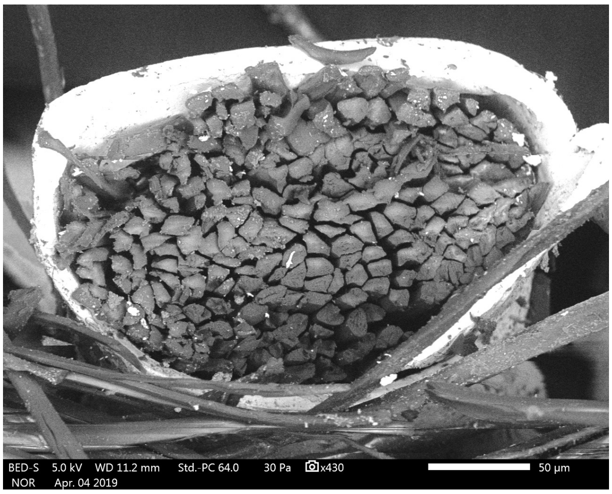


Fig. 2.5. SEM cross section showing the triangular shape of silk filaments in the core of a silver thread.

Silk is a protein fibre made by the silkworm when preparing a cocoon (Tímár-Balázsy & Eastop 2011, p. 43). The liquid protein hardens to two fibroin filaments with a triangular shape (figure 2.5). The two filaments are held together by a second protein called sericin. The fibroin is mainly composed of the three amino acids: glycine (45%), alanine (29%) and serine (12%). The fibroin is built of crystalline regions and amorphous regions with a ratio of 3:2 (May & Jones 2006, p. 74).

The natural colour of silk can range from grey to green or yellow depending on the colouring matter in the consumed leaves (King 1985, p. 43). The characteristic properties of silk are: an ability to bind water up till 30% of its dry weight, a high tensile strength, sensitivity to light and heat, a high resistance to alkali and a good resistance to diluted acid (Wiklund 1984, p. 86). The resistance to alkali and acid will be looked at more thoroughly in section 2.2.2. Silk has lustrous fibres and gives a shiny appearance. Tries have been made to produce silk in Sweden, but it has never become a big industry, so silk has had to be imported. Silk has always been exclusive and expensive. It has been used in garments, shoes, banners, textiles in the church, interior design, etc. (Wiklund 1984, pp. 86, 89-90).

2.2 Deterioration

2.2.1 CORROSION OF SILVER THREADS

Most metals have been extracted from their ores to elemental metal by the input of energy. In general, with the exception of noble metals such as gold, metals are unstable and have a tendency to return to their most stable form, which is that of their mineral. This process is called corrosion. Corrosion can act protectively and for this reason can be desirable for its colour, beauty or stability. However, in the majority of cases it is unstable, leading to the destruction of metals. It is considered undesirable as it is masking the object´s intended surface and can be dangerous for the physical surface of the object (Selwyn 2004, p. 19). Silver is a noble metal; it does not corrode as easily and as fast as many other metals. However, under certain circumstances, it will corrode. Of specific interest here is tarnishing, a relative stable corrosion form, which however, is altering significantly the appearance of silver. The most common corrosion products of silver are:

- Silver sulphide, Ag_2S, makes the silver grey to black and is a non-protective corrosion layer.
- Silver chloride, $AgCl$, a greyish, non-protective corrosion layer.
- Silver oxide, Ag_2O, a very thin, invisible and protective corrosion layer.

Silver sulphide, or acanthite, is the corrosion product that tarnish silver. It is the one corrosion product that can be found in abundance. It is formed when silver is exposed to sulphur-containing environments, is insoluble in water and needs the presence of oxygen and water to occur. The corrosion layer is usually not uniform, but can be (Gouda & Vassiliou 2013, pp. 218-222; Hacke 2006, p. 214; Jimenez-Cosme & Contreras-Vargas 2011, p. 28; Tímár-Balázsy & Eastop 2011, p. 135).

2.2.2 DETERIORATION OF SILK

Liquid water causes swelling of silk fibres, 16,5-18,7% in the transverse direction and 1,3% in the axial direction. Silk is sensitive to dry conditions. It might desiccate if the relative humidity (RH) is below 40% or if the temperature is too high. If the temperature is over 140°C the mechanical properties of silk changes considerably. Silk is the one natural fibre who is the most sensitive to electromagnetic radiation. If the wavelength is between 220-370 nm it causes yellowing and photodeterioration. Visible radiation causes fading (Tímár-Balázsy & Eastop 2011, p. 45). Due to its crystalline nature, silk is rather resistant to chemical attack. Higher concentrations of acids can attack the amorphous regions of the silk and cause hydrolysis. Hydrolysis means that the peptide bonds are cut, which leads to brittleness and loss of mechanical strength. Alkalis can also hydrolyse silk, but as the reaction is more rapid at the end of the amino chains, the process is slower than with strong acids (May& Jones 2006, p. 81). The swelling of the silk fibres in the core of a metal thread can cause problems as it will add tension to the metal (Ovide et al. 2017). Embrittled metal in the threads will probably be more sensitive to the swelling of silk fibres (Landi 1992, p. 20). If the silk in the thread that is used to stich silver threads to fabric is hydrolysed it will more easily be cut by the thin metal edge of the silver threads (Landi 1992, p. 95).

2.3 Issues Related to Conservation of Metal Threads

It has always been a challenge to conserve metal threads on textiles (Jimenez-Cosme & Contreras-Vargas 2011, p. 28). The fibres and the metal have a very close relationship which makes it impossible to clean one and not affect the other. The main reason to clean metal threads in composite with textile fibres is aesthetic. The balance of a design often gets ruined by dull black instead of shiny silver. The value of the design must be weighed against how degraded the materials are and how degraded they might become because of the treatment. Before attempting to remove corrosion from the metal threads the surface needs to be thoroughly cleaned from loose dust and greasy dirt. When cleaning the surface, extra care need to be focused on not damaging the vulnerable threads holding the metal threads in place (Landi 1992, pp. 39, 95). According to Tímár-Balázsy & Eastop (2011 p. 242) the main cleaning methods of metal threads can be divided in three groups:

- Mechanical cleaning methods.
- Mechanical and chemical cleaning methods in combination.
- Chemical cleaning methods.

Mechanical cleaning is considered a good treatment on metal objects, but silver threads are often delicate and sensitive, and both the metal, the fibrous core and the surrounding textiles can be damaged by the treatment. Examples of mechanical treatment methods are to use abrasives, a glass-bristle brush or ultrasonic treatment. Because of the damaging effects of those methods they are rarely recommended (Tímár-Balázsy & Eastop 2011, p. 242; Toth 2012, p. 308). Examples of combined mechanical and chemical methods are to use sodium bicarbonate powder, electrochemical treatments and electrolytic treatments. Silver and copper corrosion products cannot be removed with sodium bicarbonate. It is very alkaline and can harm degraded fibres as well as some dyes. Electrochemical and electrolytic treatment might cause prolonged wet cleaning which can cause harm to the metal threads, especially when they are metal coated organic strips. The prolonged wet cleaning might cause damage to the materials in the core of metal threads and to deteriorated textiles. Examples of chemical cleaning methods are the use of solvents, of sequestering/chelating agents and of ion exchangers. Solvents can remove oils, fats and loosely attached corrosion products, but not the firmly attached ones. Different sequestering agents act in different ways, for example the acid in thiourea in acidic solution can damage degraded fibres and in some dyes that are sensitive to acids, the colour can change. Ion exchange-based treatments often lead to a prolonged immersion of the textile in an aqueous solution which might harm organic materials (Tímár-Balázsy & Eastop 2011, pp. 242-247). The choice of cleaning agent must be influenced by its pH. Protein fibres, which is the most common in combination with metal threads, both in the core and in the textile base of the metal thread, can tolerate some acidity, but cellulose fibres can not. Apart from these technical problems there are also the ethical issue of cleaning and removing corrosion products to consider, as cleaning is one of the most irreversible of all conservation processes (Landi 1992, pp. 40, 79).

2.4 Electrolytic Cleaning

Electrolysis is the process where electric current is used to start and drive a non-spontaneous chemical process. The current can be used to reduce corroded metal to elemental metal. The reaction in an electrolytic cell is oxidation–reduction, where oxidation always occurs at the anode and reduction at the cathode (Brown & Ford 2014, p. 425; Hein & Arena 2013, pp. 403-404). An external electrical source drives the non-spontaneous redox reaction. Electrolyte is a conductive solution necessary for the reduction to take place. The electrolyte is an ionic liquid. A reduction means that the metal gain electrons and reduce from being an ionic metal (M^+) to an elemental metal (M). This happens at the negative electrode, the cathode. An oxidation means that anions (A^-) loose electrons and oxidise (A). This happens at the positive electrode, the anode (Brown & Ford 2014, ch. 9). Electrolytic 'cleaning' consists of an anodic mode or a cathodic mode in conduct with an electrolyte. When the object is the anode, oxidation is taking place. During this process bubbling of hydrogen might occur, which does mechanical cleaning. This is a common way to do electrolytic cleaning on ferrous materials. This method is not commonly used in conservation, as it leads to complete stripping of corrosion products. In the cathodic mode the object is connected to the cathode and reduction is taking place (Peterson 2016, p. 56). The process of electrolytic reduction is controllable. Very little of the material being cleaned is lost. When cleaning silver, the metal is connected as the cathode. The intention is to reduce it from tarnished to elemental metal. To clean the tarnish, a negative cathodic potential is needed. The treatment is carried out by immersing the object in an appropriate electrolyte. A constant potential is applied by monitoring the reduction current (Degrigny et al. 2016, p. 163). The name of the potential of a metal in contact with electrolyte is the corrosion potential (E_{corr}). It is measured against a reference electrode with a multimeter. If the metal is connected to a power supply, the potential of the metal will be changed, either become more negative (cathodic polarization) or positive (anodic polarization). The values of the potentials can be defined by a potentiostat and can later be used when cleaning with electrolysis (Pleco, Fablab-neuch, Hes.so 201x). Stemann-Petersen and Taarnskov (2006) states that the stress that is caused by the electrolytic treatment of historical silk with metal threads with an appropriate electrolyte is similar to that of careful aqueous cleaning.

2.4.1 LOCAL ELECTROLYSIS

Many objects are composites, i.e. the object consists of different kinds of materials (Degrigny et al. 2016, p.162). Some of those materials might be harmed if immersed in electrolyte. Recently two methods have been suggested to localize electrolytic treatment. One is to make a gel from the electrolyte and the other is an electrolytic pencil, the Pleco (Létrange, Hourdet, Geurrier, & Pons 2017).

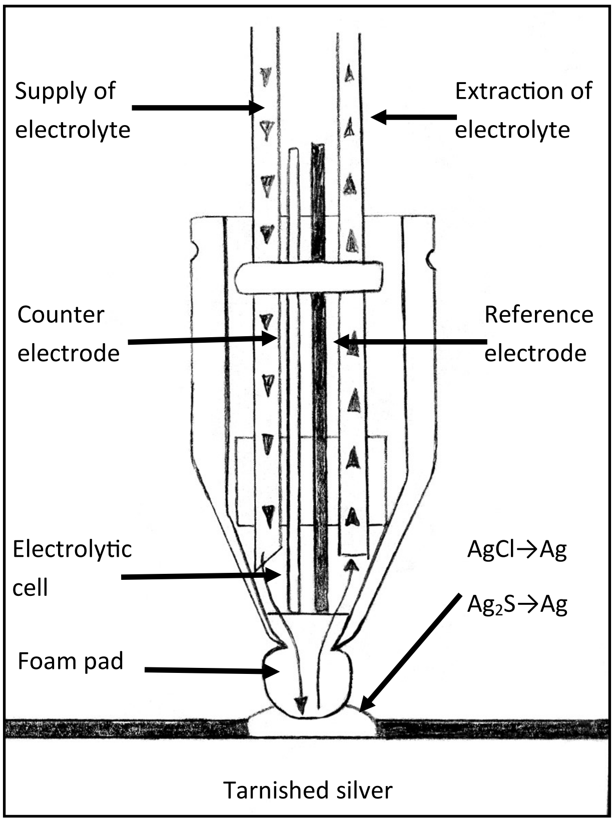


Fig. 2.6. Drawing showing a cross section of the Pleco.

2.4.2 THE PLECO

The Pleco is an electrolytic pencil originally designed to clean tarnished silver locally, as an alternative to immersion. It can also be used for consolidative reduction (Pleco, Fablab-neuch, Hes.so 201x). The tip of the pencil is a micro-porous foam pad which encloses an electrolytic cell. The pad is impregnated with electrolyte which is constantly renewed by pumps (Degrigny, Jeanneret & Witschard 2015, p. 20). In the core of the pencil, a reference electrode and a counter electrode can be found. There are also two tubes, one for supply and one for extraction of the electrolyte. The micro-porous foam pad makes contact with the object being treated (figure 2.6). The object is connected to a power supply and becomes the working electrode. The Pleco is connected to two diaphragm dosing pumps, to a power supply and to a multimeter. The power supply is connected to the object and the object is connected to the multimeter (figure 2.7) (Jeanneret, Degrigny, Fontaine, Witschard & Tarchini 2016, pp. 229).

2.5 Critical Review of Source Material

The literature used in this thesis comes from a variety of sources. Some of the books are found in lists of references from the Department of Conservation at the University of Gothenburg. They are considered as reliable sources. Other books used have been written by persons with a special competence in a certain area and are also considered as reliable sources. Two PhD thesis from the Faculty of Engineering and Physical Sciences at the University of Manchester and one from the Faculty of

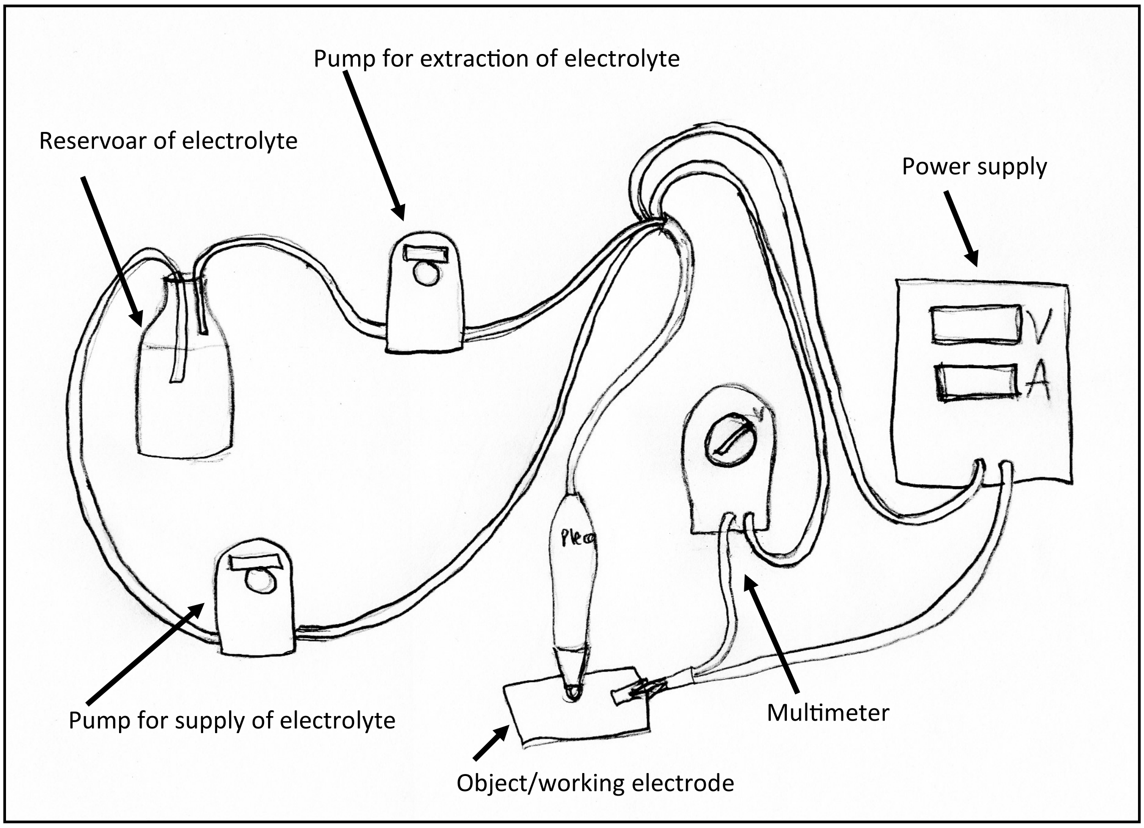


Figure 2.7. A schematic view of the different parts used with the Pleco.

Science at the University of Gothenburg have also been very useful. I have read and gained understanding from papers regarding cleaning of metal threads. These are peer reviewed journals and conference papers. I have used some web pages from companies which might be considered unreliable sources. The information has been considered with a critical eye so as not to use the parts that are sales pitches. The information used from those pages are about the function of the instrument, for example the function of the *golden gate* used with FTIR, so they are quite reliable.

2.6 Conclusions Drawn from the Literature Review

The silver strips in the silver threads are very thin. In combination with corrosion this can lead to delicacy and sensitivity, as corrosion weakens the metal. Silk is amorphous and can bind up to 30% of its dry weight in water, which causes swelling, predominantly in the transverse direction. A combination of swelling of silk in the core of a corroded metal thread can lead to deterioration of the metal thread. Silk is quite resistant to chemical attack. However, it might hydrolyse in the presence of acids and alkalis. Hydrolysis means that the protein chains are cut of, which leads to embrittlement and loss in mechanical strength.

There are no widely accepted ways to clean metal threads in combination with textiles, as the known methods causes deterioration of some sort. The use of reduction by local electrolysis using the Pleco might be an option for cleaning. Electrolysis does not mechanically damage the metal threads, and there are electrolytes whose pH is compatible with silk. The stress that is caused by the electrolytic treatment of historical silk with metal threads with an appropriate electrolyte is similar to that of careful aqueous cleaning.

3. Materials and Methods of Experiments and Analyses

To answer the research questions of whether it is possible to clean silver threads using the Pleco, how the electrolytes affect silk fibres and how to control the spread of electrolyte in silk, experiments were performed. The experiments consist of local treatment of silver thread ribbons on contemporary silk with electrolytic reduction, using two different electrolytes. The tool used is called the Pleco. The expectations are to determine whether it is possible to clean silver threads with local electrolysis using the Pleco, to gain an understanding of how electrolytes with different pH affect silk, to find out how the electrolyte interacts with the silk and to find ways to control that interaction. To execute the experiments, it was important to identify the materials of the metal thread, the warp of the ribbon and the core of the metal thread. X-ray fluorescens spectroscopy and polarized light microscopy were used to identify the materials.

The evaluation of the treatment was carried out using different analytical methods in the aim of answering the research questions. To do that, the treated samples were compared to the untreated reference samples. Part of this evaluation was carried out at the Swedish National Heritage Board where I was a guest colleague. To confirm that the silver was reduced by the electrolytic treatment, imaging with light microscopy, photography and scanning electron microscopy were done. To understand how silk was affected by the electrolytes, Fourier-transform infrared spectroscopy and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy were used in search for electrolyte residues (i.e. sodium). Other ways to increase understanding of how the electrolytes affect silk were to do tensile testing and spectrophotometry, where measurements of the physical effect of the treatments were made. Two ways were tested to control the spread of electrolyte in silk, normal treatment with the Pleco and treatment on a vacuum table.

3.1 Experimental Design

To plan the experiments and to be clear about what was to be obtained from them, an experimental design was set up (Morgan 1991, chapter 2). The first matter looked into was what factors were of importance to execute the experiments (table 3.1). One factor, thought significant to examine and which could potentially affect the experimental outcomes, was the condition of the silk and whether it was unaged or aged. The differences in age, and with that in deterioration of the silk fibres, would presumably be showing as differences when analysing the results of the experiments. Another factor thought to make a difference was what kind of electrolyte was being used, whether it was alkaline or

Table 3.1 FACTORS AND LEVELS

FACTORS/VARIABLES	**Level 1**	**Level 2**
Silk condition	Unaged	Aged
Type of electrolyte	Sodiumsesquicarbonate, pH 10	Sodiumnitrate, pH 5
Use of Pleco for cleaning	Vacuum table	No Vacuum table
After treatment, Rinsing	Yes	No

acidic as silk interacts slightly differently with alkali or acid (section 2.2.2). Two electrolytes were chosen, the alkaline sodium sesquicarbonate with pH 10, and the acidic sodium nitrate buffered to pH 5. The third (out of four) factor of importance was the circumstances when using the Pleco for cleaning. Two approaches were chosen; to execute the treatment without a vacuum table or to use a vacuum table. These two ways were hopefully going to help answering the issue of finding methods to control the spread of electrolyte in silk. The final factor thought to make a difference in the effects of electrolyte on silk was the after treatment, whether or not the silk would be rinsed to remove as much as possible of the elctrolyte.

A standardised set-up of the experiments was organised to make sure they were performed consistently (table 3.2). The fibres used in the experiments would be silk in the core of the silver thread, in the warp of the ribbon and in the contemporary fabric. Silver can be a little tarnished or very much so. In this project the focus was not on a complete removal of tarnish, but to investigate if it was possible to reduce silver sulphide back to elemental silver, using the Pleco, and to understand how electrolytes of different pH affect silk. This is the reason for choosing to treat all silver as if it had the same amount of tarnishing. The levels of tarnishing were not considered a factor to be investigated and the contact time for each treatment was set to one minute. Degrigny et al. (2015, p. 24) showed that the cathodic potential suitable for cleaning silver varies between –0,9 and –1,9, so those were the potential values chosen for the experiments. As seen in table 3.1 some of the experiments would consist of an after treatment with rinsing. The rinsing was done in deionized water, three times, each for two minutes. When using the Pleco it might be hard to hold it in the same position for one minute. To keep the Pleco stable and the contact between pad and silver similar between each experiment, the tool was placed on a stand. The extraction of electrolyte was set to 80-85 mL/min and the supply to 15 mL/min. Three replicates were made of each sample.

The final step of the experimental design was to evaluate the outcome of the experiments. In this part all the analytical methods used are accounted for and a schedule was set up (appendix 1) to be specific about which samples would be analysed with which analytical methods.

Table 3.2 STANDARDISED SET-UP OF THE EXPERIMENTS

Type of fibre, core of metal thread	Silk
Type of fibre, warp of ribbon	Silk
Type of fibre, contemporary fabric	Silk
Levels of tarnishing	One
Time of electrolysis	1 min
Cathodic Potential	between -0,9 and -1,9
Rinsing	3×2 min
Treatment using the Pleco	Using a stand to minimize variation in contact between pad and silver
Extraction of electrolyte	80 -85 mL/min
Supply of electrolyte	15 mL/min
Replicates	3/sample

3.2 Test samples

The experiments with the Pleco were performed on samples created from an old silver thread ribbon attached to a contemporary silk bought purposely for the project at Gårda textil. The old ribbon, which dates back to 1716, was attached to the new silk using a red polyester thread which is stable and does not shed colour. The attachment created rectangles in which the experiments with the Pleco were performed (figure 3.1). The size of the rectangles is 2 × 2,9 cm. Each experiment was repeated three times to render the results reliability. The contemporary silk was marked to know how it had been treated. V for vacuum table, N for sodium nitrate, R for rinsed and S for sodium sesquicarbonate (figure 3.1).

Test samples were also prepared for the tensile testing. The samples were made from the same contemporary silk. They were cut in the warp direction with 1cm width comprising 34 warp threads and a length of 10 cm. To help prepare the samples a light table (figure 3.7) and a light microscope were used (section 3.6.3).

3.2.1 SILVER THREAD RIBBON

The silver thread ribbon comes from a chasuble made in 1716. The chasuble has been discarded and the silver thread ribbon was saved and will now be of use in research purposes. A note was left explaining that the silver thread ribbon came from a chasuble made from black velvet which has been burned along with the lining. The year 1716 is also mentioned (figure 3.2). It was offered to the project by Studio Västsvensk Konservering

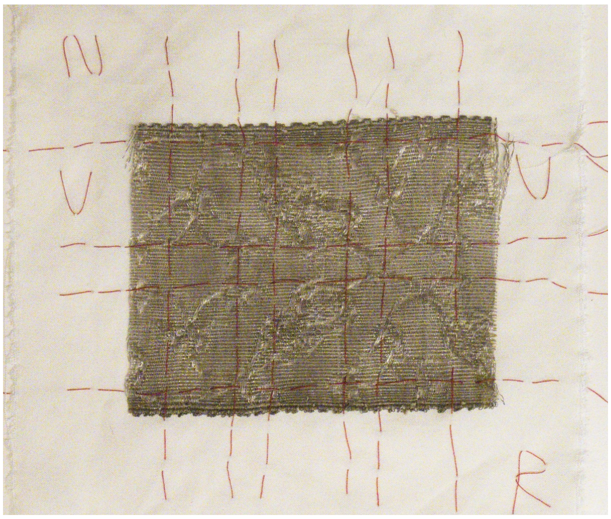
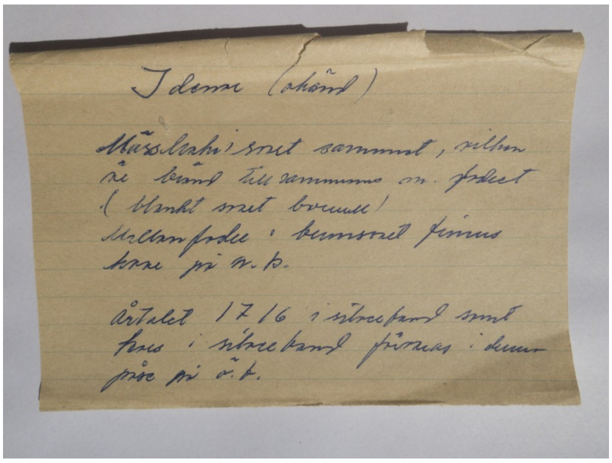


Fig. 3.1. Silver thread ribbon sewn onto contemporary silk. 6 rectangles marks where the electrolysis will take place, three of them on the vacuum table (V) and three without. The electrolyte is sodium nitrate (N) and the sample will be rinsed (R).



I denna (okänd)

Mässhake i svart sammet, vilken
är bränd tillsammans m. fodret
(blankt svart bomull)
Mellanfoder i [illegible] finns
kvar på w.k.

Årtalet 1716 i silverband samt
frans i silverband förvaras i denna
påse på ö.b.

Fig. 3.2. Text: ”Mässhake i svart sammet, vilken är bränd tillsammans m. fodret. (blankt svart bomull) Mellanfoder i *b...stail* finns kvar på w.k(?). Årtalet 1716 i silverband samt frans(?) i silverband förvaras i denna påse på ö.b.”.

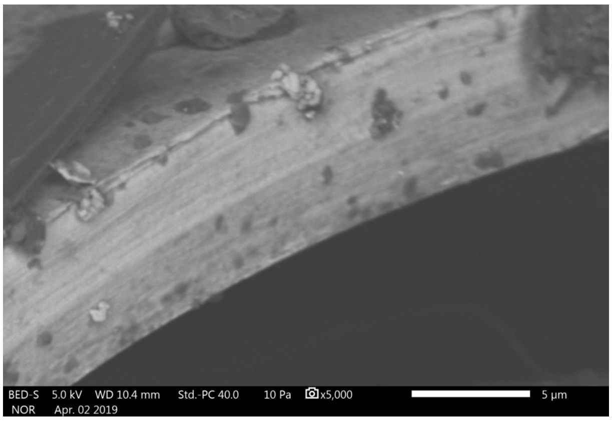


Fig. 3.3. SEM image showing the edge of a solid metal strip. ×5000

(SVK), and the remains will be returned to them upon completion of the project.

The ribbon has a warp made of silk filaments (section 4.1.2) and a weft made of metal threads with a diameter of 0,175 mm. The morphology of the metal thread is a solid metal strip (figure 3.3) wound around a silk core with a S twist (figure 4.16). The metal is silver with small amounts of copper, iron, lead and molybdenum according to tests with X-ray fluorescence (XRF) (section 4.1.1).

The weave has a recurring pattern with leaves, flowers and tendrils (figure 3.4). As can be seen in figure 3.5 the edge of the ribbon has a pattern with alternately 6 weft threads close to the warp and 6 weft threads with a larger end loop.

Fig. 3.4. The silver thread ribbon used for the experiments.

Fig. 3.5. The decorated edge of the silver thread ribbon.

3.2.2 CONTEMPORARY SILK

The contemporary silk is undyed with a plain weave. The fineness of the silk is 31,07 tex (measurements in g/km thread) (Tímár-Balázsy & Eastop 2011). 10 cm warp contains 360 warp threads and 10 cm weft contains 307 weft threads.

Before using the silk in experiments it was washed with Grumme detergent that has a pH of 7-9, after which it was rinsed three times in tap water.

The silk was used both as fabric underneath the silver thread ribbon and as samples for the tensile testing and spectrophotometry, see section 3.5.

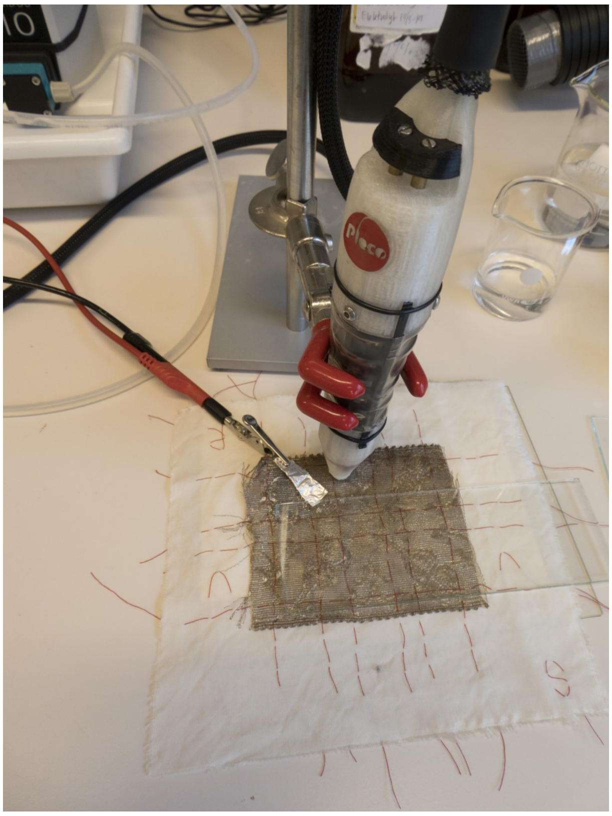


Fig 3.6. The Pleco, attached to a stand for stability while cleaning a test sample.

3.3 The Pleco

In section 2.4.2 a more thorough information of the construction and function of the Pleco can be found. The tip of the pads was trimmed into a profile with a slight curve. It was suggested by

Source 1 that, when using the Pleco on metal threads, the pad might need to be trimmed to a sharp tip instead of the normal curved profile. The reason for doing this was to be able to clean the threads one by one. The threads in the ribbon had a diameter of 0,175 mm and because they were so thin a decision was made to clean several threads at the same time. This is the reason the pads where given a different profile than suggested.

To make the Pleco stable and prevent differences of pressure between pad and metal, the Pleco was attached with a utility clamp to a ring stand while performing the electrolysis (figure 3.6). The electrolyte and the pumps were placed in a container to minimize the risk of spillage onto the fabric. When the Pleco was removed from the ribbon, a beaker was placed underneath to catch any leakage.

Two pumps (SIMDOS® 10 diaphragm dosing pump) were used, one that supplied the pad with electrolyte and one that drained the electrolyte from the pad. The supplying pump was set to 15mL/min and the draining to 80-85 mL/min. This made the pad moist enough both to perform electrolysis and minimize the risk of electrolyte leakage.

3.4 Electrolysis and Rinsing

Two electrolytes were selected because of their pH, sodium sesquicarbonate, $Na_3H(CO_3)_2$ with pH 10 and sodium nitrate, $NaNO_3$ buffered to pH 5 (table 3.3).

Table 3.3 THE FORMULAS FOR THE TWO ELECTROLYTES

Sodium Sesquicarbonate	Sodium Nitrate
4,4 g $NaHCO_3$ 5,6 g Na_2CO_3 in 1 L of Deionised Water	10 g $NaNO_3$ in 1L of Deionized Water ad 0,0136 g of Tri-hydrate Sodium Acetate 0,1 mL of 1M Acetic Acid

Table 3.4 TREATMENTS OF THE TEST SAMPLES

Electrolyte	Rinsed	Vacuum table
$Na_3H(CO_3)_2$		
$Na_3H(CO_3)_2$	V	
$Na_3H(CO_3)_2$		V
$Na_3H(CO_3)_2$	V	V
$NaNO_3$		
$NaNO_3$	V	
$NaNO_3$		V
$NaNO_3$	V	V

The test samples were treated in four different ways with each electrolyte. They were rinsed, treated on a vacuum table and rinsed, not rinsed, treated on a vacuum table and not rinsed (table 3.4). Each test was repeated 3 times. The effect of the treatment depends largely on how well the surface preparation with degreasing is done, if an appropriate cathodic potential is used and if the pad is clean (Jeanneret et al. 2016). Before starting treatment with the Pleco the silver thread ribbon was degreased by padding it with an ethanol infused piece of cotton wool and left in a fume cupboard until completely dry.

The pad at the tip of the Pleco fit 12 times in each rectangle. A decision was made to clean every spot the same amount of time and the time chosen was 1 minute (section 2.1).

Degrigny et al. (2015, p. 24) showed that the cathodic potential suitable for cleaning silver varies between –0,9 and –1,9 so those were the potentials used in the experiments. The total cleaning time per rectangle, including moving the Pleco and restarting the cleaning process, was approximately 17 minutes. Before the cleaning of a new rectangle, the pad was changed to a clean one.

A vacuum table (Mitka Ergonomic suctiontable 2008) was used with the intention of finding a way to prevent the electrolyte spreading in the contemporary silk. When using the Pleco without the suction table a blotting paper was used to soak up any residues from the electrolyte.

After cleaning a rectangle, the silver threads where wiped with a chemical sponge infused with deionised water (Ovide et al. 2017).

As seen in table 3.4 some of the samples were rinsed after treatment. The samples were rinsed three times in deionized water for 2 minutes each time. They were left to dry on the vacuum table.

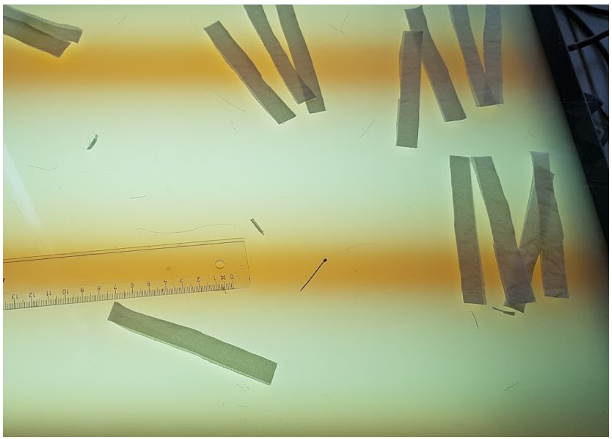


Fig. 3.7. Silk samples being prepared on a light table for tensile testing.

3.5 Accelerated Ageing

Apparatus: KBF climatic chamber from WBT Binder

Conditions: 80°C, 50% RH for 7 days +one additional day for samples Bb, G and H

Acclimation: 20°C, 50% RH for 24 h

As aforementioned, new silk was being used in the experiments. To be able to understand how silk and electrolytes interact under different circumstances the silk needed to be aged. Ageing would also make it more similar to silk found in cultural-historical objects.

Samples from the contemporary silk were prepared for accelerated ageing (section 3.2) (figure 3.7). The samples were treated in 11 different ways with 3-4 specimens per treatment. Each sample was given a code name in order to simplify handling and control (table 3.5).

Table 3.5 CODE NAMES FOR SILK SAMPLES

A silk untreated unaged

B silk aged 7 days

Bb silk aged 7 days plus 1 day

C silk dipped in electrolyte $Na_3H(CO_3)_2$ rinsed and aged 7 days

D silk dipped in electrolyte $NaNO_3$ rinsed and aged 7 days

E silk aged 7 days and then dipped in electrolyte $Na_3H(CO_3)_2$ rinsed

F silk aged 7 days to be aged and then dipped in electrolyte $NaNO_3$ rinsed

G silk aged 7 days and then dipped in electrolyte $Na_3H(CO_3)$ rinsed then aged again 1 day

H silk aged 7 days and then dipped in electrolyte $NaNO_3$ rinsed then aged again 1 day

I silk dipped in electrolyte $Na_3H(CO_3)$ not rinsed and aged 7 days

J silk dipped in electrolyte $NaNO_3$ not rinsed and aged 7 days

3.6 Analytical Methods

3.6.1 X-ray Fluorescence Spectroscopy

Equipment:	XG Elio Device: 1253
Characteristics:	Portable, non-contact, mounted on a tripod

X-ray fluorescence spectroscopy (XRF) is a non-destructive method used to identify the elements present in a small sample area (Wilson 2012, p. 28). XRF has the advantage that it is a non-contact technique that does not require any preparation of the object prior to analysis. The apparatus can be moved and placed in the position needed for the area to be analysed. XRF was used to identify the composition of the silver thread ribbon. To render reliability three spots were tested. Even though XRF is not as specific as SEM-EDS, the accuracy from SEM-EDS is not needed in this project, we just needed to know that the metal is predominantly silver. XRF analysis requires considerately less time than a SEM-EDS investigation would.

3.6.2 POLARIZED LIGHT MICROSCOPY

Equipment:	Nikon SE, ×10-40 mm microscope Nikon DS-Fi1 camera.

Transmitted light was used to observe the samples and identify the different textile fibres. Fibres from the contemporary silk, from the warp of the silver thread ribbon and from the core of the silver threads were placed on different slides in glycose and covered with coverslips (Greaves &Saville 1995, p. 7). There are different ways to identify textile fibres, for example looking at burning characteristics or do a solubility analysis (King 1985). Microscopy is often the first step used in fibre identification and was used in this investigation. If fibres cannot be identified via microscopy one of the other methods can be used.

3.6.3 LIGHT MICROSCOPY

Equipment:	Leica Stereozoom S9i microscope with an inbuilt digital camera Leica LED3000 RL light source and diffuser Struers LaboPol-5 polisher
Embedding Resin:	Technovit® 2000LC

Light microscopy was carried out to observe visual differences between areas of the metal thread ribbon that were cleaned using the Pleco, and areas that were not cleaned. It was used to compare contemporary silk that had been treated with electrolytes and rinsed, to samples that had not been rinsed. It was also used to observe potential stains on unrinsed samples. Small samples of ca 3 x 3 mm of the silver thread ribbon sections, treated with electrolytes and not rinsed, were mounted for analysis in cross section. The embedding resin was cured in blue light and polished using silicon carbide discs grades 320, 500, 1200, 2400 and 4000 and silicon carbide micromesh grades 6000, 8000 and 12000 under a flow of deionized water. Light microscopy was also used to document samples mounted for further analysis by SEM-EDS.

3.6.4 SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Equipment: Jeol JSM-IT500LA with a tungsten filament

Settings: Low vacuum mode

Scanning electron microscope (SEM) is a powerful microscope which uses an electron beam that scans the sample surface. The interaction releases secondary electrons, backscattered primary electrons which a secondary electron detector detects. The detector then transmits an amplified signal to the display unit. With its high magnification SEM allows the surface of the specimen to be meticulously examined and imaged. The interaction between the electron beam and the surface also releases X-rays which an energy dispersive X-ray spectrometer (EDS) detects. It converts X-rays into an electric current which makes it possible to measure and identify elements present in the sample (Wilson 2012, pp. 30-31).

SEM-EDS was used to examine the silver threads, observe and image visual differences between untreated and treated threads. It was used to observe the morphology of the silk and to assess whether there were visual or elemental evidence of sodium salt deposits on the textiles after treatment with electrolytes and rinsing. The samples (table 3.6) were mounted with adhesive carbon tape on aluminium stubs. Samples A, C, D, I, J (table 3.5), and S(fabric), S(salt) and N(fabric) (table 3.6) were coated with 6 nm gold.

The imaging where made in four different magnifications, x50, x100, x500 and x3000. EDS was made both on areas and on specific spots. The magnifications were selected as they showed 5 threads, three threads, one thread, a close up of one thread and also for standardisation purposes.

Table 3.6 SAMPLES WITH CODES USED IN SEM-EDS

Sample code	Sample description
Clean	Silver thread ribbon untreated clean (protected area originally tucked in seam)
Corroded	Silver thread ribbon untreated corroded
S	Silver thread ribbon cleaned with Pleco pen using $Na_3H(CO_3)_2$
SR	Silver thread ribbon cleaned with Pleco pen using $Na_3H(CO_3)_2$ and rinsed
N	Silver thread ribbon cleaned with Pleco pen using $NaNO_3$
NR	Silver thread ribbon cleaned with Pleco pen using $NaNO_3$ and rinsed
S(cross)	Cross section of silver thread ribbon cleaned with Pleco pen using $Na_3H(CO_3)_2$
N(cross)	Cross section of silver thread ribbon cleaned with Pleco pen using $NaNO_3$
S(fabric)	Silk fabric treated with $Na_3H(CO_3)_2$, not rinsed, sampled from beneath silver thread ribbon
SR(fabric	Silk fabric treated with $Na_3H(CO_3)_2$ and rinsed
S(salt)	Silk fabric treated with $Na_3H(CO_3)_2$, not rinsed, sampled from visible salt line on textile
N(fabric)	Silk fabric treated with $NaNO_3$, not rinsed, sampled from beneath silver thread ribbon
NR(fabric)	Silk fabric treated with $NaNO_3$ and rinsed
UT	Silk fabric untreated

3.6.5 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Equipment: Frontier FTIR spectrometer, Perkin Elmer
Golden Gate diamond ATR.

Fourier-transform infrared spectroscopy (FTIR) is a technique used to identify both organic and inorganic materials. The infrared light interacts with the outer shell electrons of a molecule and can identify different types of bonding between atoms. FTIR provides spectra from the infrared absorption region. It can be divided into the group frequency region (4000 to 1400cm^{-1}) and the fingerprint region (approximately 400-1400 cm^{-1}). In the fingerprint region the spectrum is characteristic for each molecule and can be used as an explicit identification by comparison to a standard (May & Jones 2006, pp. 18-19). Attenuated total reflectance (ATR) is a technique where FTIR can be used without a lot of sample preparation. The infrared beam gets in contact with the sample through an optically dense crystal that creates an evanescent wave which extends into the sample in contact with the crystal (PerkinElmer 2005). ATR-FTIR was carried out in order to assess whether any sodium salt deposits could be identified on the textile after treatment with electrolytes and after rinsing. Five textile samples, A, I, J and two samples with a salt line from sodium sesquicarbonate (table 3.5) of the contemporary silk were tested. They were placed in a *golden gate*, a pressure device that provides excellent optical contact between the sample and the instrument.

3.6.6 TENSILE TESTING

Equipment:	SHIMADZU Autograph AGS-X Trapezium Lite X software
Characteristics:	10 kN load cell Flat grips with rubber pads
Environmental conditions:	20°C, 50% RH

To determine a sample's breaking load and elongation at break, a tensile test can be performed. The test consists of application of tension to a sample. During the test, measurements of breaking point and elongation will be taken. From these measurements stress, strain, breaking load and extension at break can be calculated (Wilson 2012, p. 52).

The purpose of tensile testing in this study, were to assess and compare the influence of treatments with electrolyte and ageing on the silk and whether it affects its physical properties. Accelerated ageing was completed before testing. 11 different kind of samples (table 3.5) with three to four specimens each were tested. The samples were clamped centrally and straight in the grips of the apparatus without using pre-tension.

3.6.7 COLOUR MEASUREMENTS

Equipment:	Konica Minolta Spectrophotometer CM 2600d
Settings:	UV 0%, Observer angle 10° Geometry 8 di, 8 de

Calibration: White and black

Measurement diameter: 3 mm
Specular component: Excluded
Daylight illuminant: D65
Environmental conditions: 20°C, 50% RH

The literal meaning of spectrophotometry is to “measure the spectrum with photons” (Orna 2013). A spectrophotometer is an optical instrument that measure how materials reflect or transmit light. It consists of three parts: a light source, a photodetector and a monochromator where the individual wavelengths can be selected (Johnston-Feller 2001, pp. 5-6). The chromaticity system used was the CIA L*a*b* where L* shows lightness with 0 = Black and 100 = visible white, a* shows the green-red field where − is green and + is red and b* shows the blue-yellow field where − is blue and + is yellow (Mokrzycki & Tatol 2011, p.15). ΔE^*_{ab} shows the colour differences. The CIA L*a*b* was introduced in 1976 as a uniform colour space. ΔE* can be calculated with a quite simple equation (figure 3.8). It turned out that the colour space is a bit more complicated and in the year 2000 an improved ΔE equation, ΔE_{00}, was released which includes lightness (L*), chroma (C*) and hue (h°) (Wilson 2012, pp. 33-34). 1-2,5 ΔE is the minimal detectable difference (ViewSonic).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

Fig. 3.8. Formula used to calculate ΔE_{76}.

A spectrophotometer was used to measure colour differences before and after treatment with electrolytes and accelerated ageing. The measurements were used to assess how the treatments influenced the silk. The human eyes have different abilities to register colour differences and therefore measurements were done to find out if there were any differences, and how big they were. Untreated, unaged samples E, F, G and H acted as control samples to the unaged, untreated silk A. Measurements were done on the samples shown in table 3.5. Each sample was measured on 3 to 5 areas with 3 repeats each and a standard deviation of < 0.6 for L*, a* and b*.

4. Results

The results from experiments and analytical methods will mostly be presented as commented photos, charts and tables. Further photos and charts of some interest can be found in Appendix 2.

4.1 Identification of materials

4.1.1 METAL

The metal thread ribbon used in the experiments was analysed using XRF to identify the composition of the alloy (figure 4.01). The results from the three different points revealed a high percentage of silver and small amounts of copper, iron, lead and molybdenum (table 4.1). The molybdenum shown might be an element inside the equipment. The first sample showed, apart from the metals, some chlorides and sulphur and the third showed calcium. Most of the elements, apart from silver, showed a high percentage of error, often higher than the percentage of concentration, which leads to the conclusion that those concentrations were not very reliable. Therefore, these results are treated as indicative and not as absolute values.

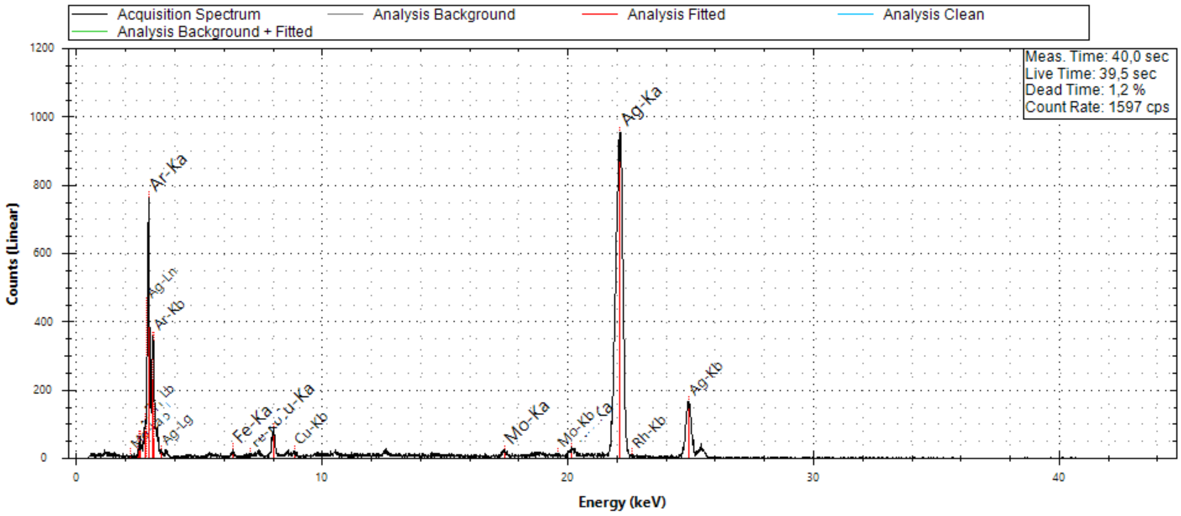


Fig. 4.01. XRF spectrum showing test number 2. Ar is an element inside the equipment and is to be ignored.

Table 4.1 ELEMENTS FOUND USING XRF, the metal elements are marked with a colour in the table.

Element	1. Concentration	Error	2. Concentration	Error	3. Concentration	Error
Ag	80,61%	±0,57%	98,72%	±0,59%	93,06%	±0,75%
Cl	15,91%	±5,37%				
S	2,36%	±20,77%				
Cu	0,68%	±3,33%	0,88%	±3,22%	0,91%	±3,96%
Fe	0,23%	±7,56%	0,29%	±7,29%	0,84%	±5,4%
Pb	0,22%	±4,42%				
Mo			0,11%	±6,09%	0,15%	±6,55%
Ca					5,04%	±8,32%

4.1.2 SILK

The contemporary silk, the weft of the silver thread ribbon and the core of the silver threads were examined with polarized light microscopy. When following a fibre identification flow chart from Microscopy of Textile Fibres (Greaves & Saville 1995, p. 9) all three were identified as textile man made (synthetics) or silk fibres. We know that the contemporary fabric is made of silk and the warp and the core are made before 1716, therefore cannot be synthetic. The conclusion is that all three samples are silk fibres (figure 4.02 and 4.03).

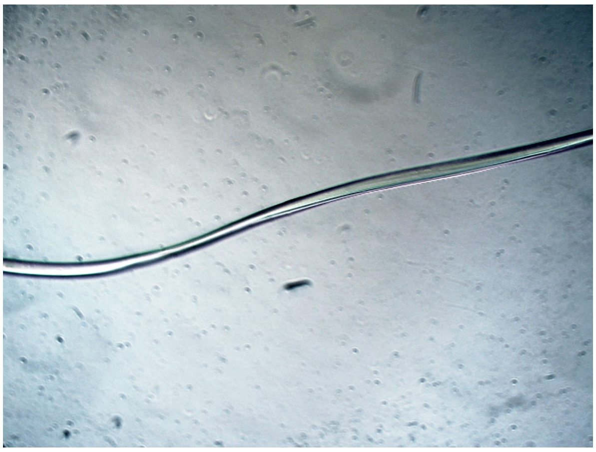


Fig. 4.02. Fibre from the warp of the silver thread ribbon. ×20.

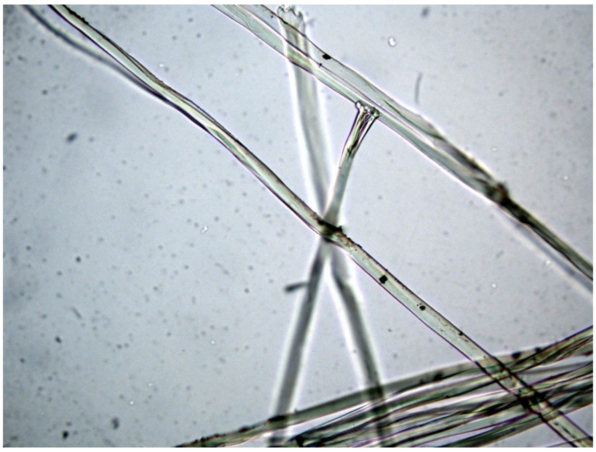


Fig. 4.03. Fibre from the core of the silver thread. ×20.

4.2 Using the Pleco and Controlling the Spread of the Electrolyte

To begin with it was challenging to handle and control the Pleco. There were some trial and error in how much contact and pressure should be applied between the pad of the Pleco and the ribbon. This led to leakage of electrolyte into the contemporary silk and various degrees of success in reducing all the silver in the rectangles of the test samples. If the pad of the Pleco is pressed to hard onto the silver thread, more electrolyte than necessary will leave the nozzle, which leads to spreading in the contemporary silk outside of the treated area. To reduce the spreading of electrolyte, blotting paper were placed underneath the samples not being treated on the vacuum table to absorb part of the electrolyte. This reduced the spreading some, but it did still spread. To minimize spreading of electrolyte at the vacuum table, Melinex$^{®}$ were placed under the contemporary silk as close to the area being treated as possible. This method in combination with placing the Pleco at an appropriate height, it should just touch the silver thread, minimized the spreading of the electrolyte. With some practice the amount of spreading was reduced, especially when working on a vacuum table (figure 4.04).

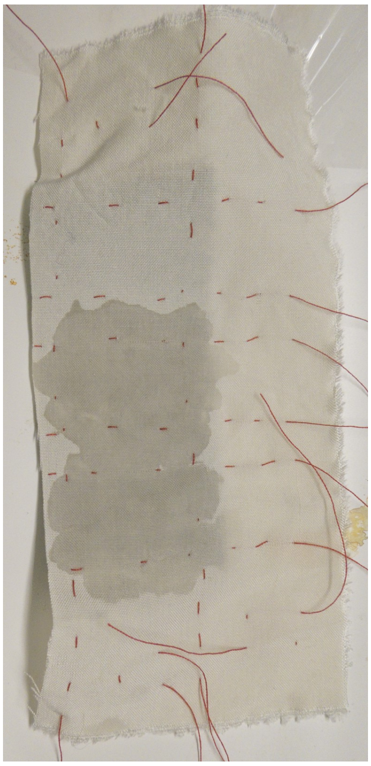


Fig. 4.04. While using the vacuum table the electrolyte has only spread in the treated area.

4.3 Comparison of Visual Differences

4.3.1 SILVER THREADS AND SILK USING LIGHT MICROSCOPY

Almost all of the silver thread ribbon was corroded, but one of the edges had been inside a seem and were still untarnished even though the ribbon is 300 years old. The difference between the corroded and the clean area can be observed in figure 4.05.

Figure 4.06 shows an area with the gap in between two rectangles, the red polyester thread and part of a rectangle that was treated with sodium sesquicarbonate. There is a clear difference between the untreated and the treated area. The silk warp has a beige/yellow tone which still gives the ribbon a yellowish appearance.

Figure 4.07 shows an area treated with sodium nitrate. In part of the area the contact between the electrolyte infused pad and the metal has not been enough to clean the silver.

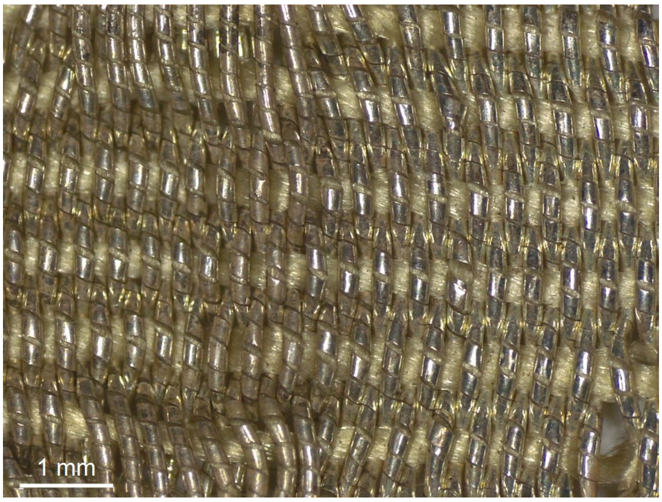


Fig. 4.05. Untreated piece of ribbon. Corroded to the left and clean to the right.

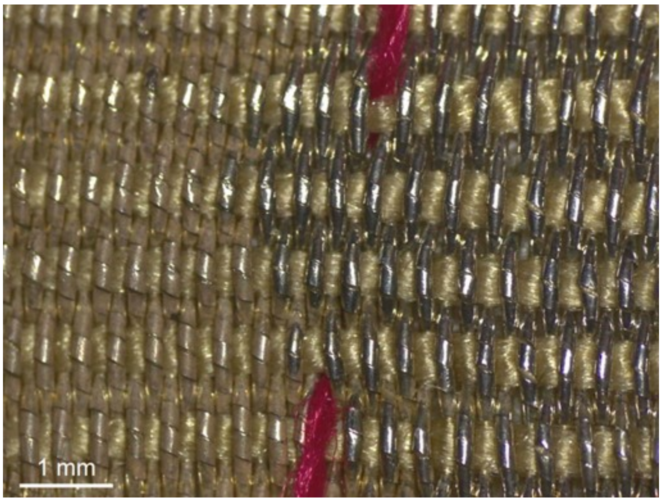


Fig. 4.06. Untreated to the left, treated with $Na_3H(CO_3)_2$ to the right.

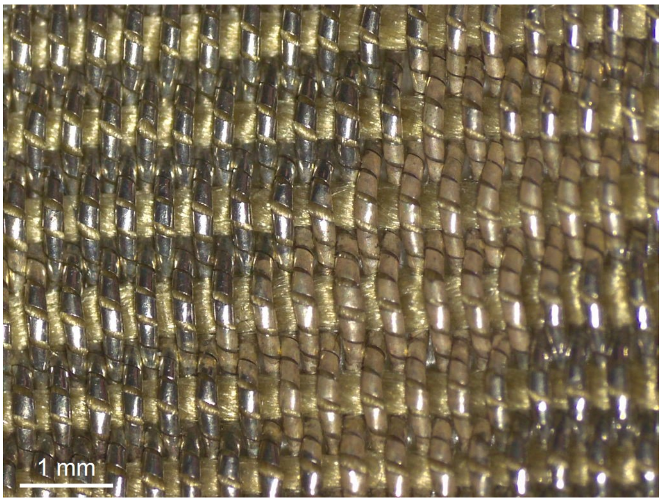


Fig. 4.07. Treated with $NaNO_3$. To the right a paler, not cleaned streak can be seen.

Figures 4.08- 4.10 shows the differences between the untreated and the treated silver threads at a higher magnification than in figures 4.05 - 4.07. There is a significant difference between the untreated and the treated. It is harder to detect if there are any differences between the two areas treated with different electrolytes (figures 4.09 and 4.10).

The contemporary silk in figures 4.11 and 4.12 were exposed to an excess of electrolyte, after which there was no rinsing. This led to a salt line being formed on the fabric, seen to the left in the photo.

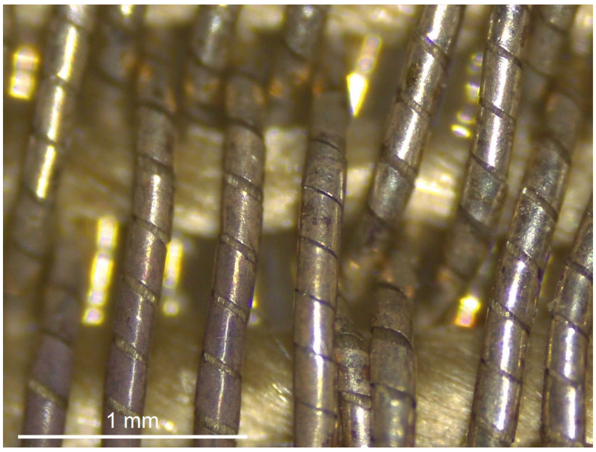


Fig. 4.08. Untreated silver threads.

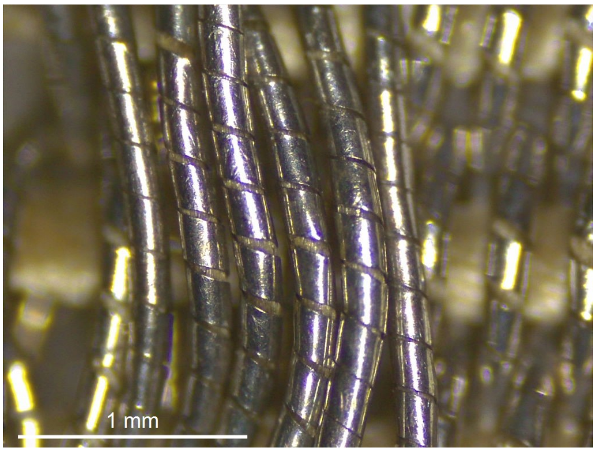


Fig. 4.09. Treated with $Na_3H(CO_3)_2$.

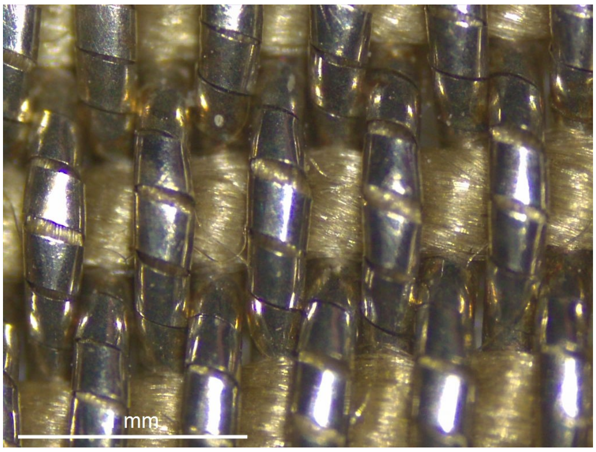


Fig. 4.10. Treated with $NaNO_3$.

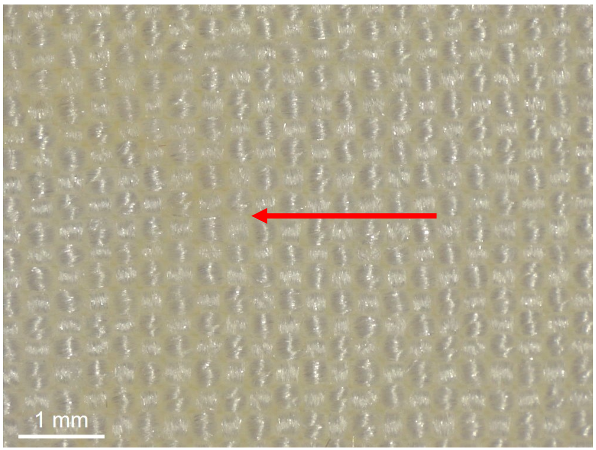
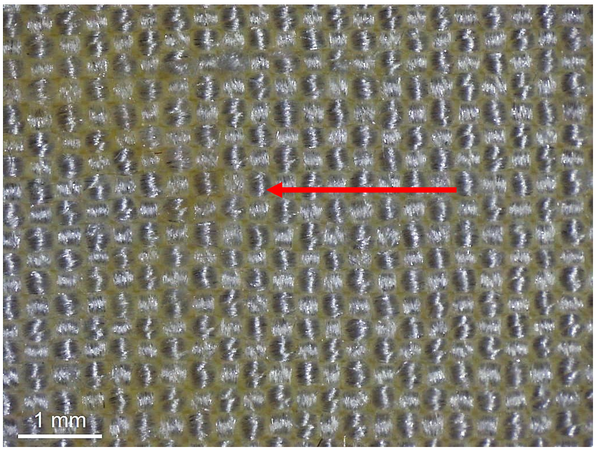


Fig. 4.11. Contemporary silk treated with $Na_3H(CO_3)_2$. The arrow shows where a salt line can be found.



4.12. Same photo with altered contrast to make the salt line more visible.

4.3.2 SILVER THREADS USING SCANNING ELECTRON MICROSCOPY

SEM was used to do imaging of the silver threads. Figure 4.13-4.18 shows corroded and treated silver threads in different magnifications. There are no major changes in the surface structure between the corroded and the cleaned silver threads. The images show the S-twist of the metal strips (figure 4.16).

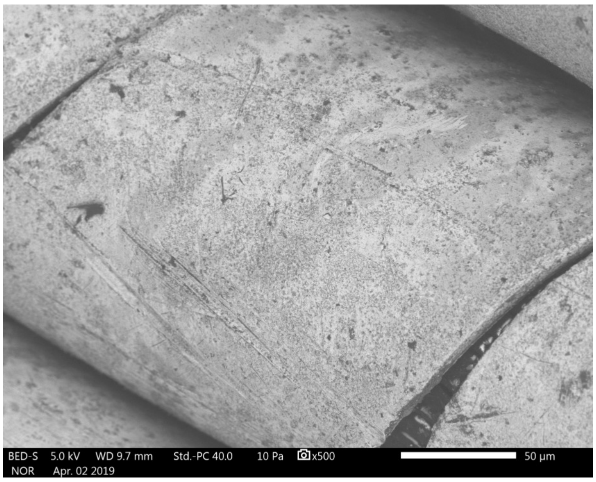


Fig. 4.13. Corroded. ×500

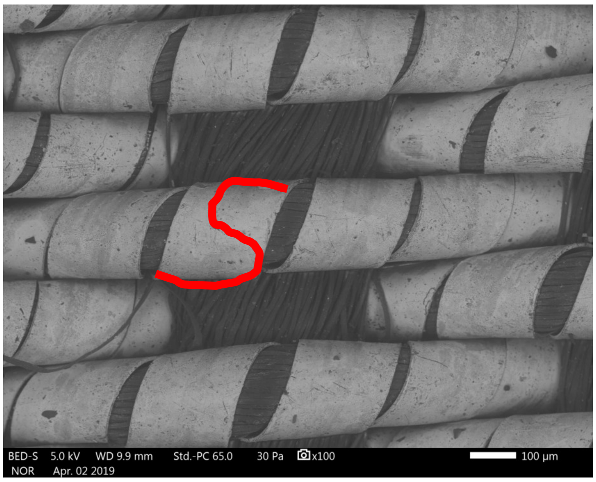


Fig. 4.16. Corroded. ×100 Shows the S-twist.

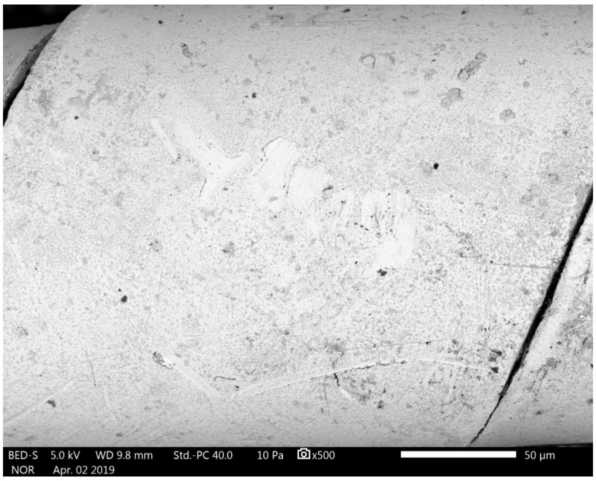


Fig. 4.14. Treated with $Na_3H(CO_3)_2$ and rinsed. ×500

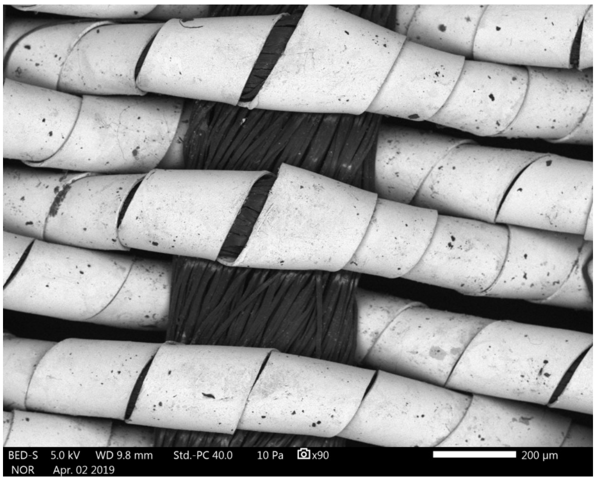


Fig. 4.17. Treated with $Na_3H(CO_3)_2$ and rinsed. ×90

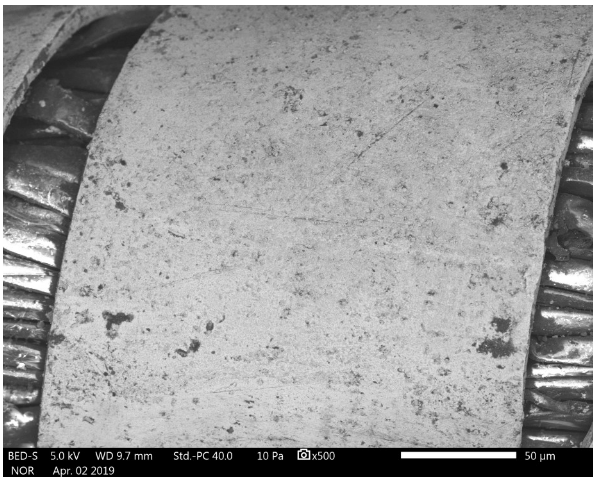


Fig. 4.15. Treated with $NaNO_3$ and rinsed.×500

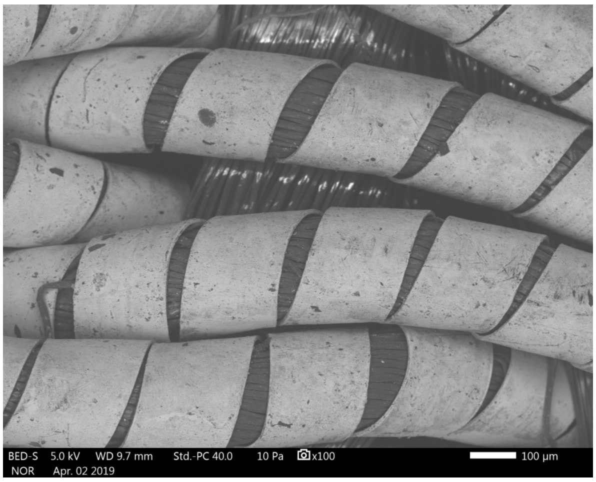


Fig. 4.18. Treated with $NaNO_3$ and rinsed. ×100

4.3.3 MORPHOLOGY OF THE SILK FABRIC USING SCANNING ELECTRON MICROSCOPY

In SEM imaging, the morphology of silk appeared unaltered by the electrolytic treatment, but salt deposits were present on several samples. Figures 4.19-4.24 shows untreated and treated, gold coated contemporary silk. The untreated silk shows specks of something that at first sight might be thought of as salt deposits (figure 4.22), but as it is untreated that would not be the case. In figures 4.23-4.24 specks that might be salt deposits can be seen (section 4.4).

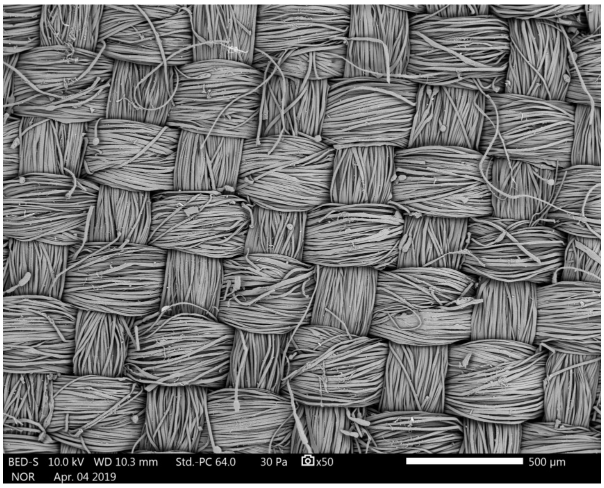


Fig. 4.19. Untreated silk. ×50

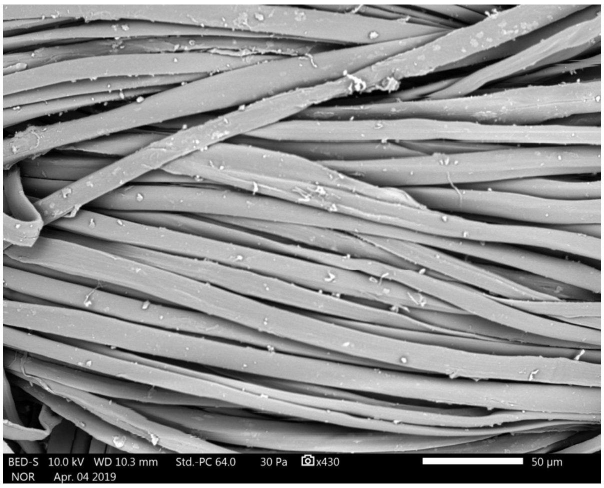


Fig. 4.22. Untreated silk. ×500

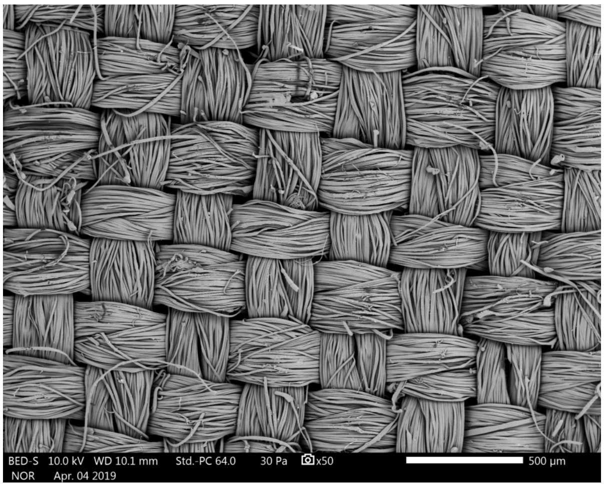


Fig. 4.20. Silk dipped in $Na_3H(CO_3)_2$, rinsed. ×50

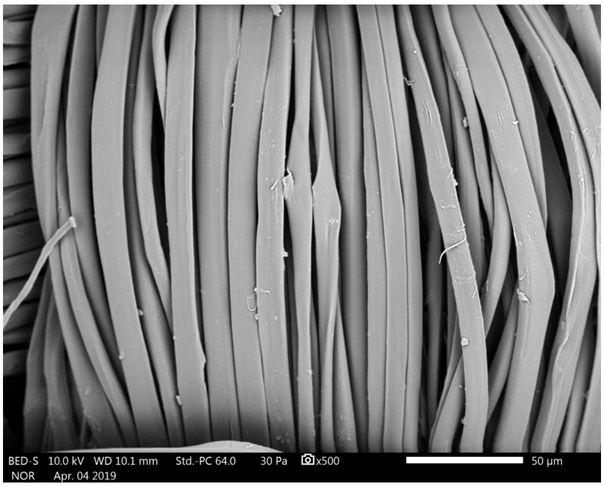


Fig. 4.23. Silk dipped in $Na_3H(CO_3)_2$, rinsed. ×500

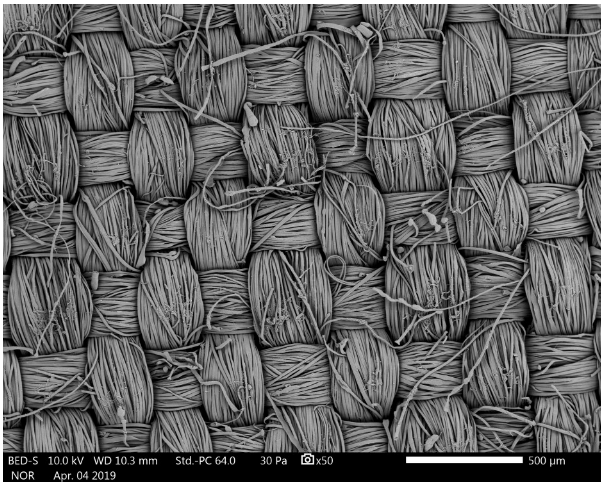


Fig. 4.21. Silk dipped in $NaNO_3$, rinsed. ×50

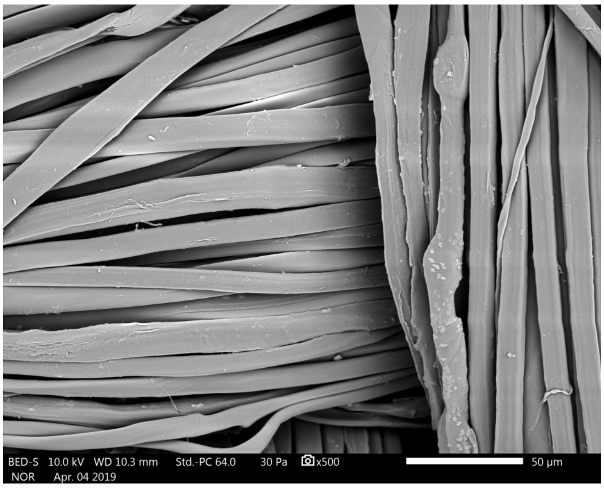


Fig. 4.24. Silk dipped in $NaNO_3$, rinsed. ×500

4.4 Sodium Salt Residues in Silk

FTIR and SEM-EDS were used to look for sodium salt residues in the contemporary silk, the warp of the ribbon and the core of the silver threads. Sodium is one of the key ingredients of the electrolytes used; therefore, its presence represents residues of the electrolytes.

4.4.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Samples A, I, J (table 3.5) and two samples with salt lines were analysed using ATR-FTIR. Initially the intention was to analyse the rinsed samples C and D as well, but as we did not get any distinct results (figure 4.25) from the unrinsed samples there was no point in testing the rinsed ones. Figure 4.26 displays the “fingerprint” spectral area. The peak in the sodium sesquicarbonate spectra, marked at 876 cm^{-1}, may indicate the presence of a carbonate. The main carbonate peak around 1420-1440 cm^{-1} may be masked by the protein peaks from the silk in that area.

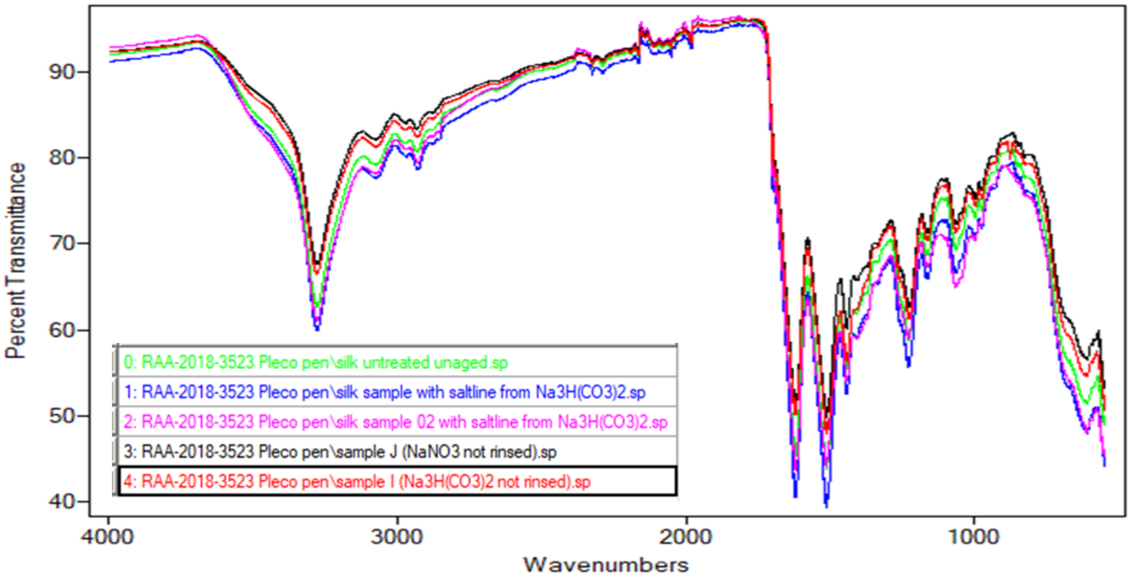


Fig. 4.25. Overview of entire spectral area for all samples.

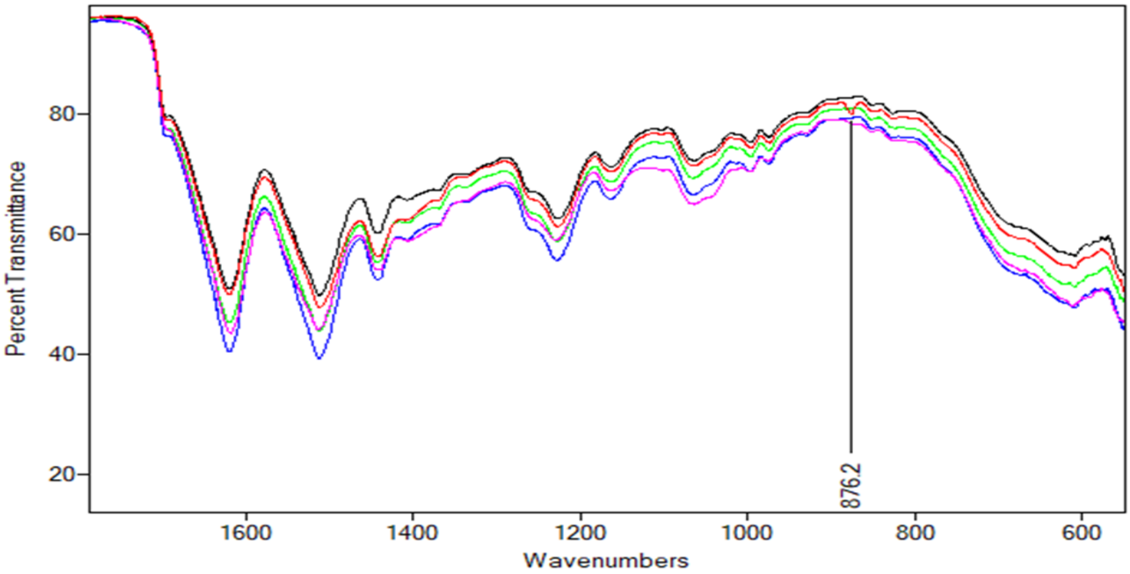


Fig. 4.26. Detail of the “fingerprint” spectral area with a peak that may indicate the presence of carbonate.

4.4.2 SCANNING ELECTRON MICROSCOLY WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY

SEM-EDS showed the presence of sodium in most samples, unlike FTIR. It does not give the amount of sodium present. Figures 4.27-4.28 looks at the presence of sodium in the warp of the ribbon. Figures 4.29-4.30 looks at the presence of sodium in the core of the silver thread. Figures 4.28 and 4.30, treated with sodium nitrate, does not show any presence of sodium. This is not a guarantee that there is no sodium present. The Al in the spectrum is probably the mounting of the ribbon or from the preparations of the cross section. The rectangles in the imaging shows the analysed area.

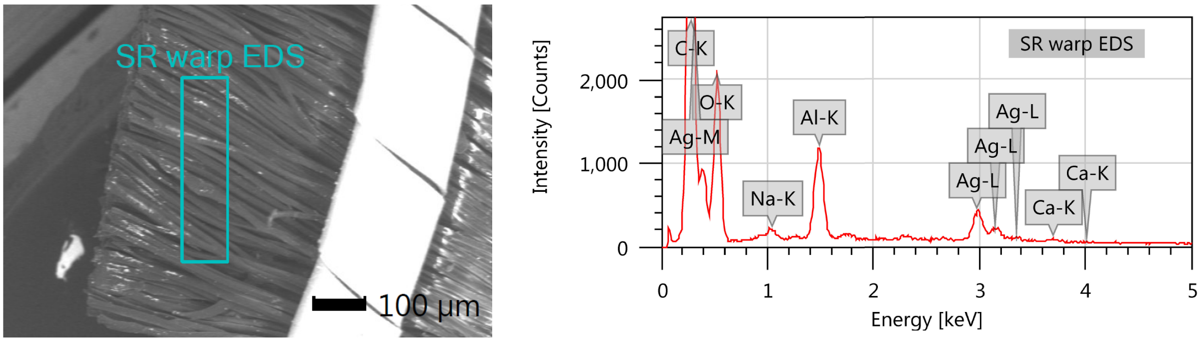


Fig. 4.27. Warp treated with Na$_3$H(CO$_3$)$_2$, rinsed. The EDS spectra shows that there is Na present. ×140

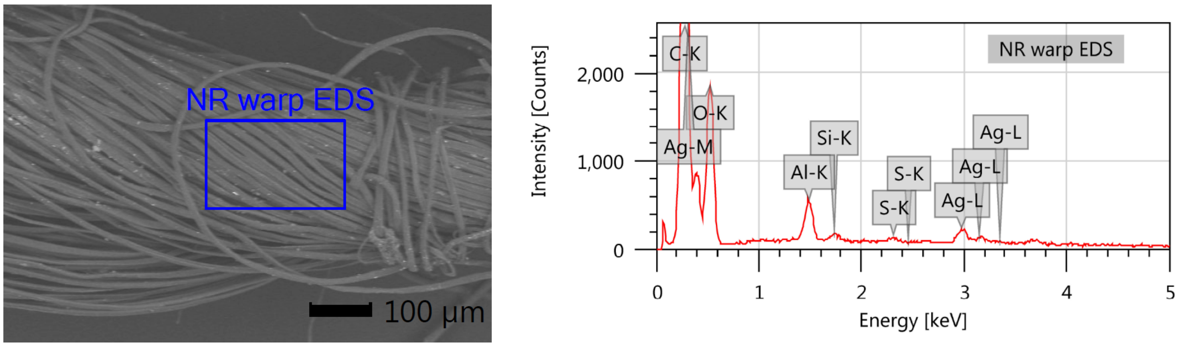


Fig. 4.28. Warp treated with NaNO$_3$, rinsed. The EDS spectra does not show any presence of Na. × 160

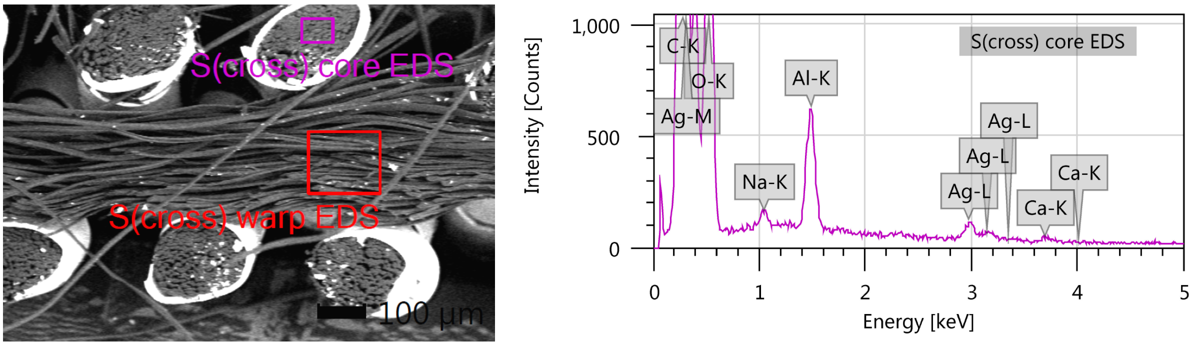


Fig. 4.29. Core treated with Na$_3$H(CO$_3$)$_2$, not rinsed. The EDS spectra shows that there is Na present. × 120

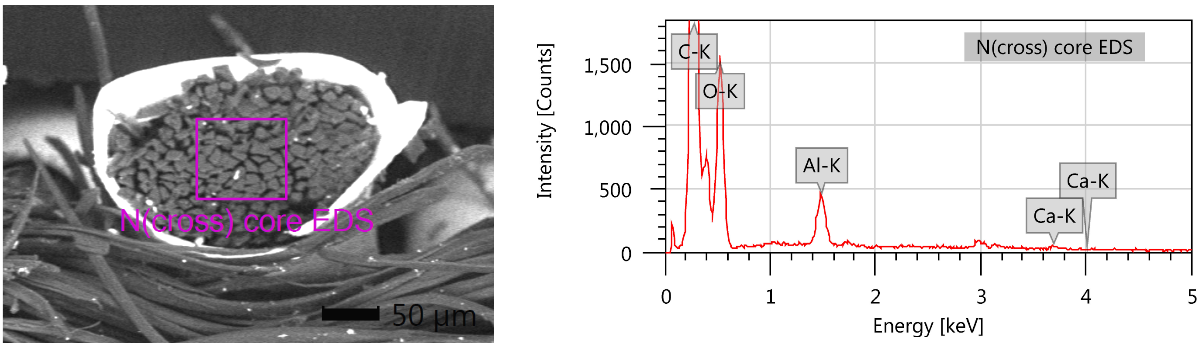


Fig. 4.30. Core treated with NaNO$_3$, not rinsed. The EDS spectra does not show any presence of Na. × 300

Figure 4.31 shows the image and different spectra from contemporary silk treated with sodium sesquicarbonate and rinsed. The whole area, an area with visible deposits and an area with no visible deposits has been measured with EDS. Sodium is present in all three areas. Figure 4.32 shows the image and different spectra from contemporary silk treated with sodium nitrate and rinsed. Sodium is present in all three areas. The EDS spectrum shown is calculated with different intensity, therefore the height of the peaks has different meanings. No sodium was detected in the untreated, unaged silk.

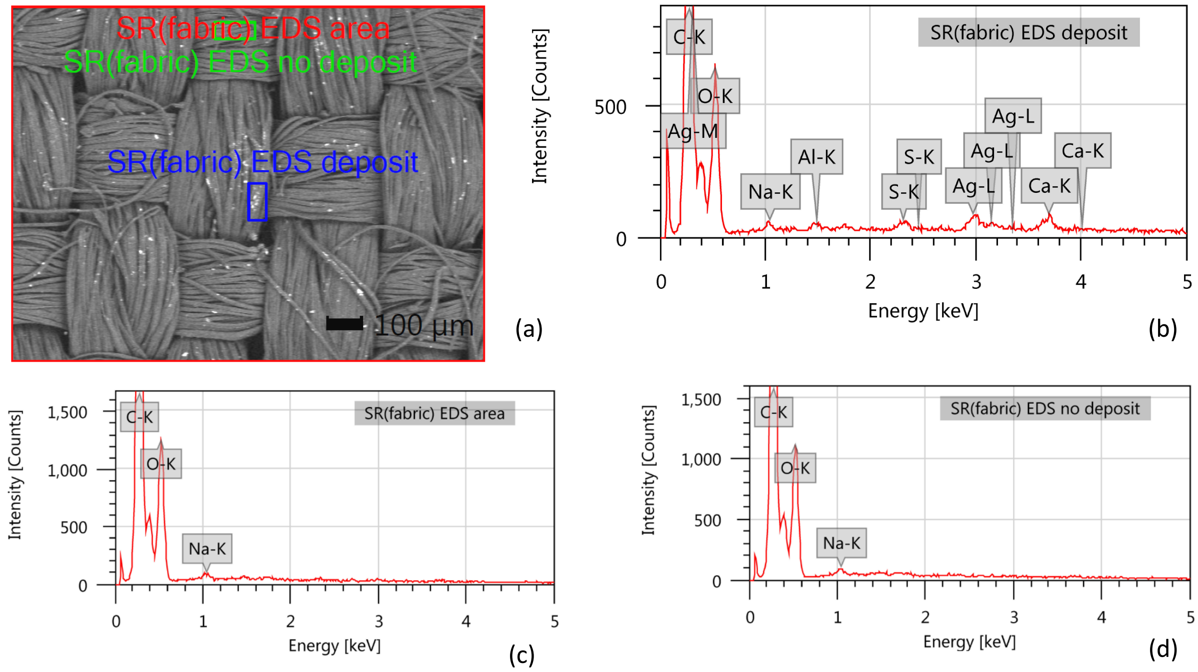


Fig. 4.31. Contemporary silk treated with $Na_3H(CO_3)_2$ and rinsed. (a) SEM image × 100 (b) EDS spectra from the area with deposit. (c) EDS spectra from the whole area. (d) EDS spectra from the area with no deposit .

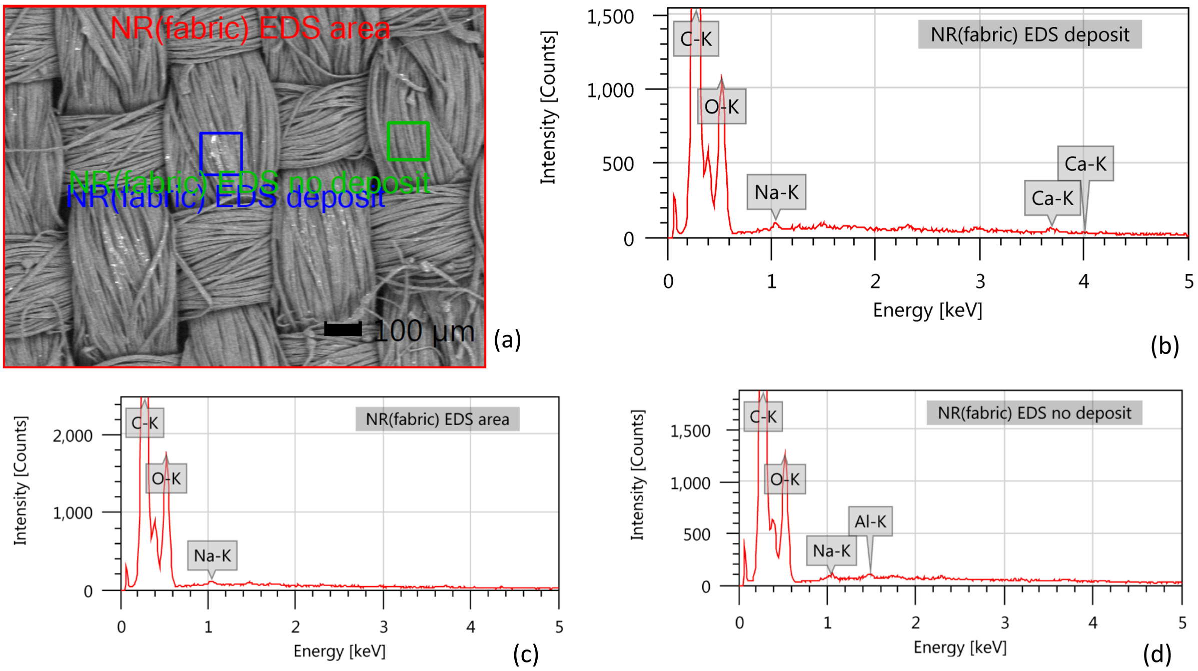


Fig. 4.32. Contemporary silk treated with $NaNO_3$ and rinsed. (a) SEM image × 100 (b) EDS spectra from area with deposit. (c) EDS spectra from the whole area. d) EDS spectra from the area with no deposit.

4.4.3 LIGHT MICROSCOPY

Two cross sections (figures 4.33 - 4.34) were made (section 3.6.3). The intention was to search for sodium residues in the core and warp of the silver thread ribbon. During the preparation they were polished under a flow of water. As sodium is an ion, it was washed away when the samples were prepared. These cross sections cannot be used as originally intended, but they can be used to get an understanding of the construction of the ribbon. Another set of simplified cross sections were made and used in SEM-EDS (figures 4.29 - 4.30).

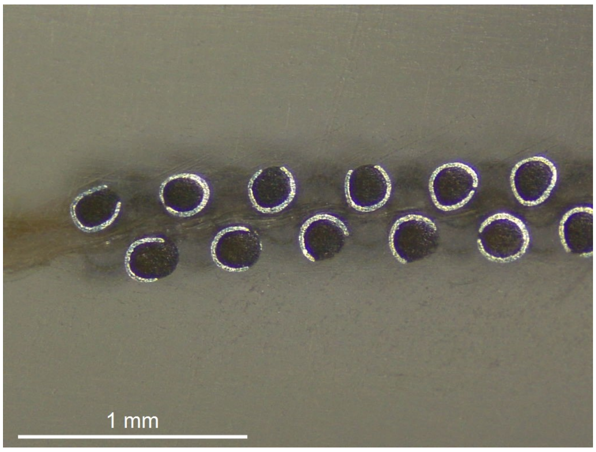


Fig. 4.33. Cross section of a silver thread ribbon treated with $Na_3H(CO_3)_2$. The cross section exposes the warp, the silver and the silk core.

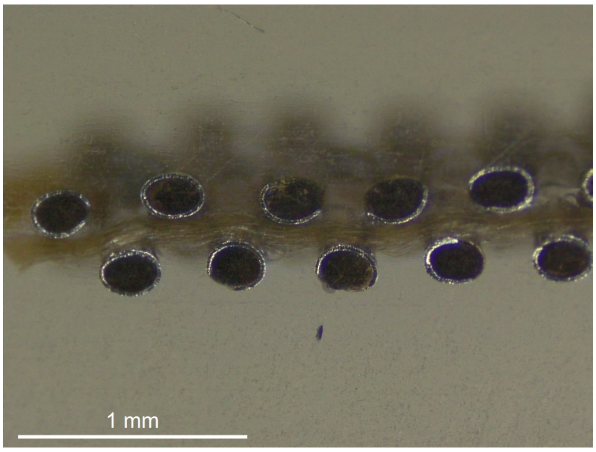


Fig. 4.34. . Cross section of a silver thread ribbon treated with $NaNO_3$.

4.5 Physical Effects of Treatment

Tensile testing and spectrophotometry were used to search for and analyse the physical effects of treatment on contemporary silk.

4.5.1 TENSILE TESTING

Table 4.2 shows the tensile test results giving the total averages for elastic modulus, breaking force, strain, maximum displacement and the respective standard deviations. Table 3.5 explains what the different letters in the test results symbolizes. Figure 4.35 explains what the different parts of a tensile test graph indicates. a) The specimen slacks. b) The warp yarns are stretched straight and tight; the stretch is still reversible and the deformation is called elastic deformation. c) The force is being taken by the fibres and the elastic modulus (N/mm^2) indicates how stiff the fibres are. Plastic deformations occur, the fibre does not regain its original form if the load would be removed. The steeper c) is the more brittle the fibres are. d) Shows the breaking point. From this point the breaking load (N), extension at break (%), strength and the extensibility can be settled. The notch in the line shows where one of the threads has broken (Source 3; Wilson 2012, p. 52).

Table 4.2 TENSILE TEST RESULTS

Sample	Number of specimens	Elastic [N/mm^2]	StDev	Break_Force [N]	StDev	Break_Stroke (Strain) [%]	StDev	Max_Disp. [mm]	StDev
A	4	274,6	1,8	131,4	3,6	29,7	0,8	14,8	0,4
B	4	289,0	9,1	131,7	8,4	27,9	1,1	14,0	0,5
Bb	3	281,7	5,3	133,5	2,5	28,6	0,6	14,3	0,3
C	4	272,4	11,9	131,6	5,2	29,0	1,3	14,5	0,6
D	4	265,6	13,0	119,0	6,0	28,5	1,7	14,2	0,8
E	4	239,7	2,3	121,9	6,1	31,4	0,8	15,7	0,4
F	4	281,3	3,9	139,3	3,3	29,3	0,5	14,7	0,2
G	2	240,1	3,4	137,4	0,6	33,1	0,1	16,1	0,0
H	3	260,3	6,6	131,2	3,8	29,6	1,4	14,8	0,7
I	4	265,9	2,9	121,1	4,6	28,9	1,0	14,5	0,5
J	4	273,6	7,0	131,7	9,6	29,1	0,4	14,6	0,2

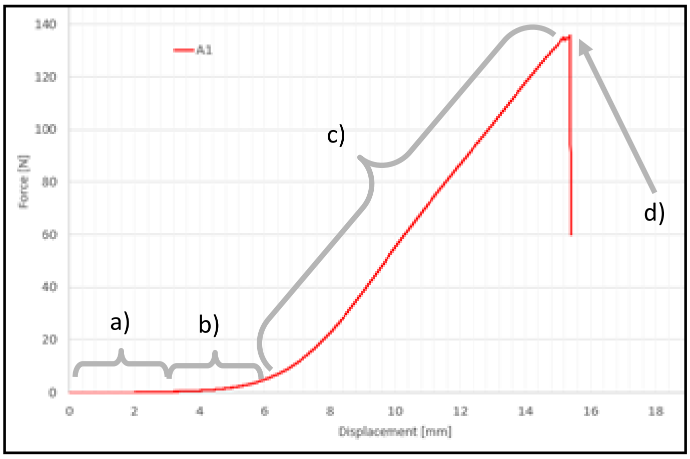


Fig. 4.35. Tensile test graph with different parts.

Figure 4.36 shows the total averages for breaking force versus breaking strain. The grey lines show standard deviations for breaking force. Standard deviations for breaking strain can be found in table 4.2. Only E and G have a higher breaking strain than reference sample A. They have both been treated with sodium sesquicarbonate after ageing. Figure 4.37compares samples A, B and Bb. A is unaged, B aged for 7 days and Bb aged for 7+1 days. None of them have been treated with electrolyte. The breaking force standard deviation of B and J are quite large, which shows that the samples behaved differently while tested.

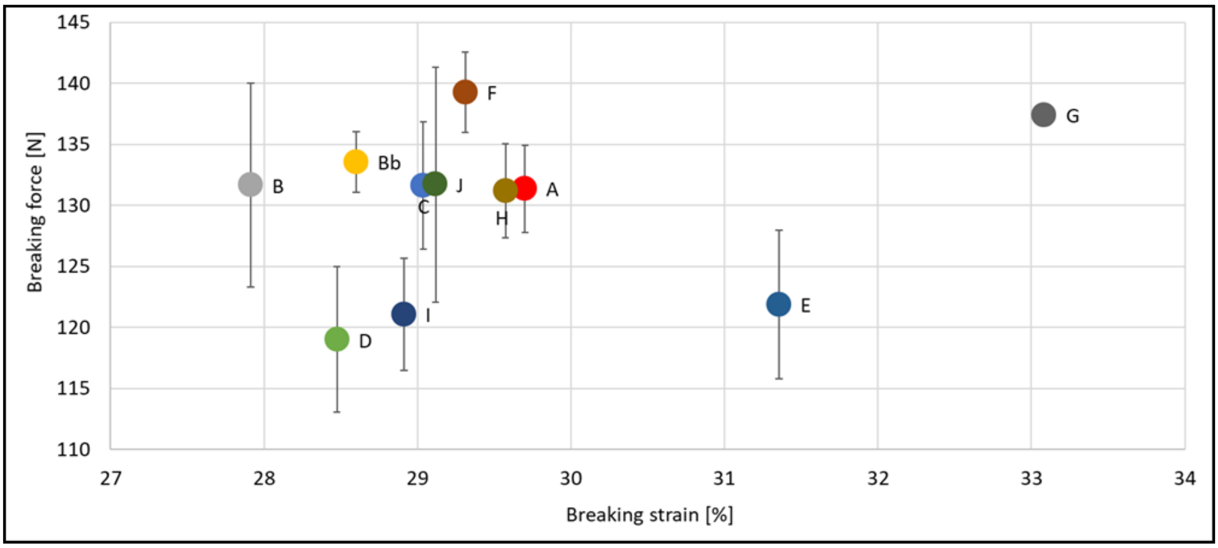


Fig. 4.36. Total averages for breaking force (with standard deviation) versus breaking strain.

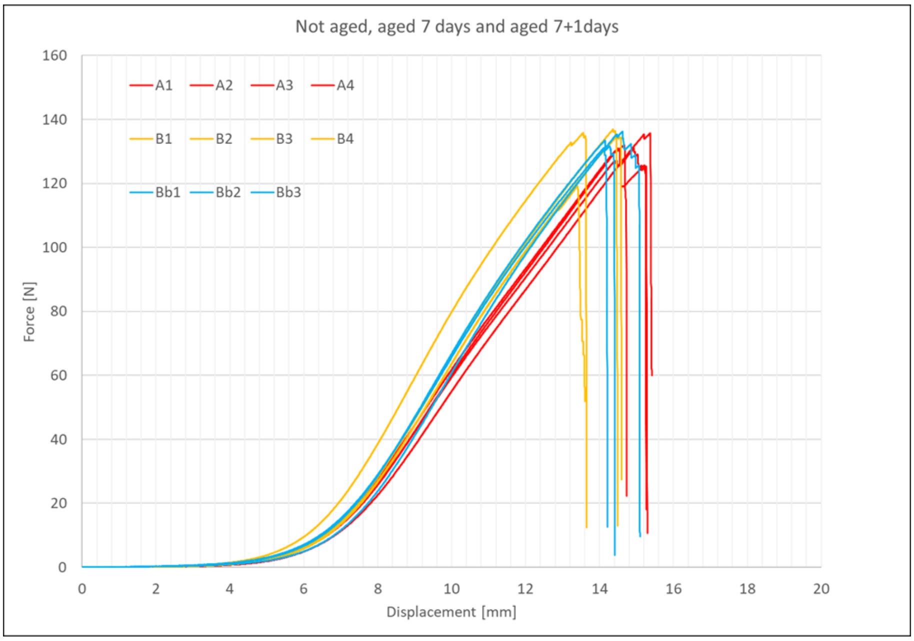


Fig. 4.37.Graph that compares A, untreated, unaged silk with B, untreated, aged for 7 days and Bb, untreated, aged for 7+1 days.

Figure 4.38 compare rinsed samples treated with sodium sesquicarbonate with reference sample A. E and G, treated after ageing, have a less steep gradient and a longer displacement than the reference samples. One of the G samples had to be discarded because there was a fold in the fabric where the fibres were broken. Table 4.2 shows that E and G has a lower elasticity and a higher break stroke and maximum displacement than the others. Figure 4.39 compares rinsed samples treated with sodium nitrate with reference sample A. All graphs are gathered quite close to A. Two of the four F samples have a slightly steeper gradient. Table 4.2 shows that it has the highest break force of all the samples.

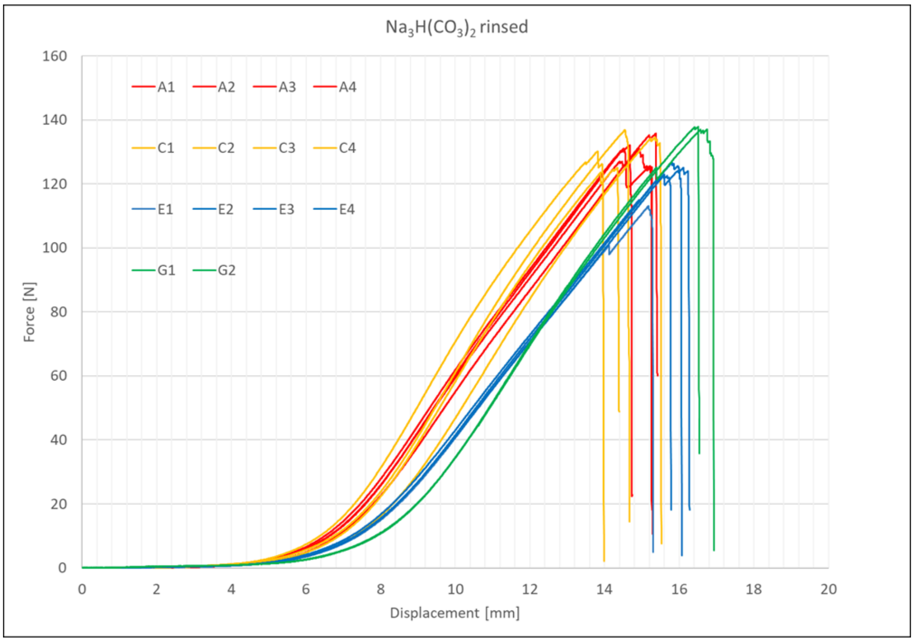


Fig. 4.38. The graph compares samples treated with sodium sesquicarbonate and rinsed to reference sample A.

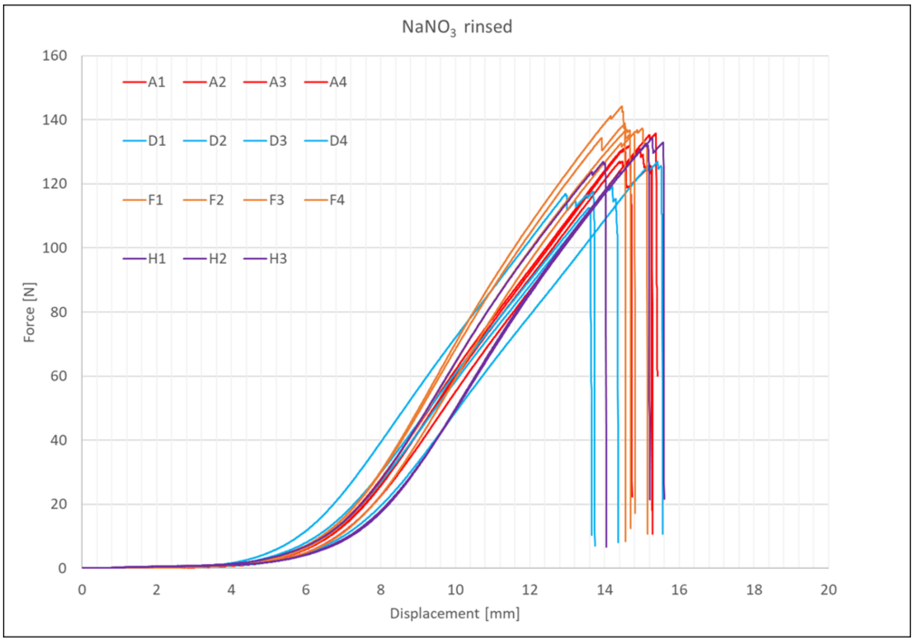


Fig. 4.39. The graph compares samples treated with sodium nitrate and rinsed to reference sample A.

The graph in figure 4.40 compares samples dipped in the two electrolytes, rinsed and aged 7 days to one another and to the reference samples. All of them have a similar gradient and most have a slightly shorter displacement than the reference samples. The graph in figure 4.41 compares samples aged 7 days, dipped in the two electrolytes and rinsed to one another and to the reference samples. The samples treated in sodium sesquicarbonate with pH 10 is showing a different gradient than the other two. The silk has a different behaviour than the reference samples. The gradients are less steep, which tells that the fibres are less brittle. The breaking points lie around 16 while they lie around 15 at the reference samples and the samples treated with sodium nitrate. They have a larger displacement than the others.

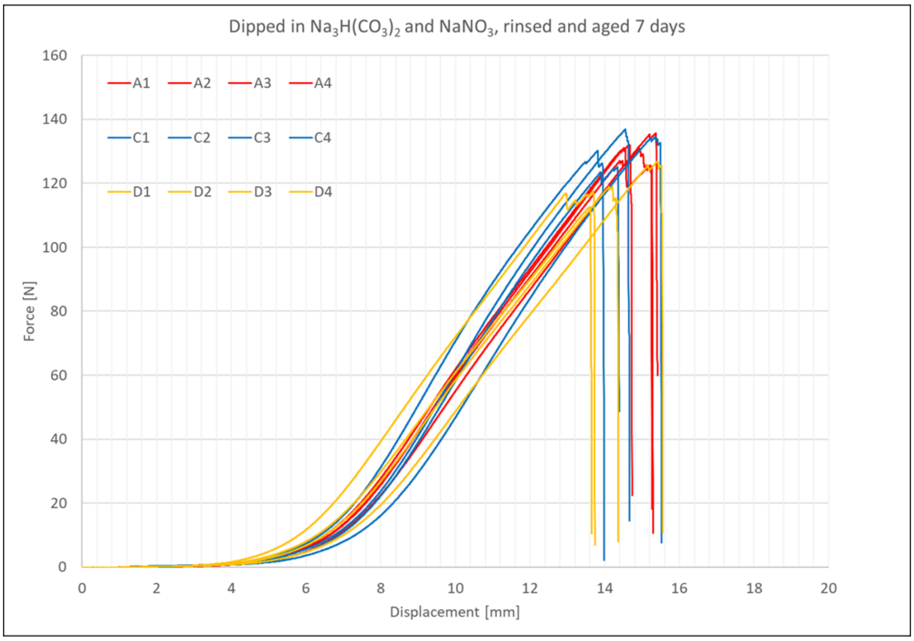


Fig. 4.40. The graph compares samples dipped in the two electrolytes, rinsed and aged 7 days to one another and to the reference samples. .

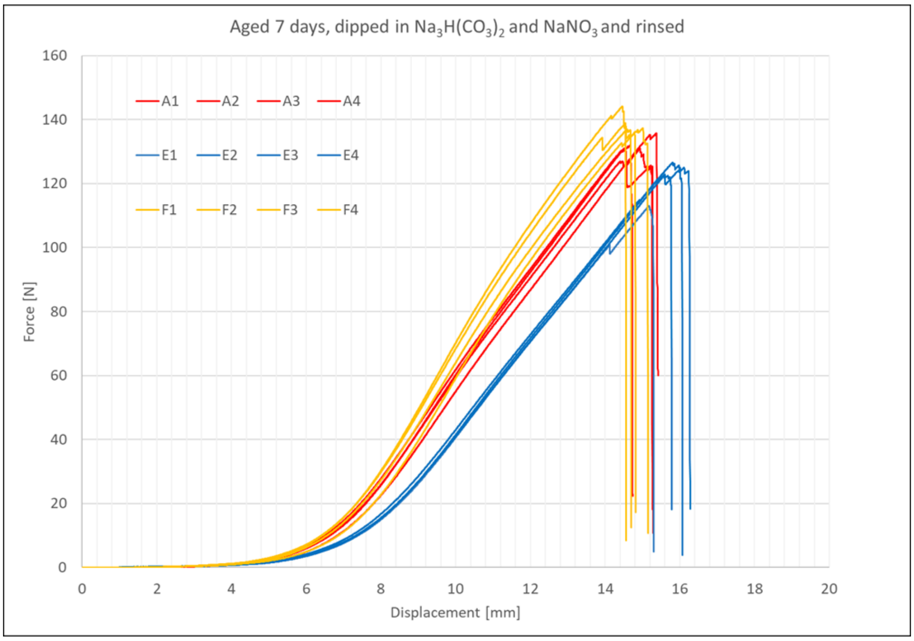


Fig. 4.41. The graph compares samples aged 7 days, dipped in the two electrolytes and rinsed to one another and to the reference samples.

4.2.2 SPECTROPHOTOMETRY

Table 4.3 shows CIELAB colour space values and colour differences of the samples. Table 3.5 on page 27 explains what the different letters of the samples symbolizes. The colours of the samples were measured unaged and after accelerated ageing with or without treatment. Untreated unaged samples E_1, F_1, G_1 and H_1 act as control samples to the unaged untreated silk A. They show ΔE_{00} values from 0,23 to 0,46 representing the inherent inhomogeneity of the silk fabric. L*, a* and b* are the measured values and the rest is calculated from those values.

Table 4.3. COLOUR MEASUREMENTS

Sample	ΔE00	dE* (1976)	L*	a*	b*	dL*	da*	db*
A untreated unaged	------	------	90,25	0,23	10,21	------	------	------
E_1 unaged untreated	0,46	1,54	89,6	0,26	10,52	-0,65	0,01	0,32
F_1 unaged untreated	0,42	0,94	90,07	0,19	10,8	-0,27	0,01	0,59
G_1 unaged untreated	0,38	0,73	90,04	0,2	10,73	-0,23	-0,04	0,5
H_1 unaged untreated	0,23	0,65	89,92	0,29	10,3	-0,32	0,03	0,08
C unaged	1,04	0,55	89,07	0,36	11,26	-1,15	0,09	1,02
D unaged	0,69	0,33	89,36	0,44	10,66	-0,83	0,13	0,44
I unaged	2,04	3,03	88,68	0,51	12,88	-1,53	0,23	2,61
J unaged	0,85	1,25	88,96	0,38	10,36	-1,24	0,08	0,15
B aged	1,49	2,17	89,9	0,04	12,4	-0,33	-0,22	2,13
C aged	2,46	3,78	88,74	0,22	13,69	-1,56	0,01	3,44
D aged	1,94	2,96	88,92	0,56	12,8	-1,31	0,26	2,64
E aged	2,2	3,31	89,03	0,32	13,36	-1,15	-0,01	3,1
F aged	1,7	2,57	89,46	0,09	12,65	-0,86	-0,1	2,42
I aged	3,69	5,69	87,79	0,69	15,43	-2,47	0,45	5,1
J aged	2,42	3,7	88,79	0,2	13,65	-1,42	-0,11	3,41
Bb aged twice	1,79	2,7	89,28	0,18	12,76	-0,96	-0,1	2,52
G aged twice	2,73	4,21	88,11	0,22	13,87	-2,12	-0,06	3,64
H aged twice	1,96	2,99	89,11	0,2	12,98	-1,11	-0,09	2,77

ΔE_{00} was calculated for all samples using the untreated unaged silk sample A as a reference.

Figure 4.42 shows a reflectance spectrum of all samples. The unaged untreated sample A is showed in green, all other unaged untreated samples in blue and all aged samples in red. The coloured scale underneath shows the colours seen in the different wavelengths.

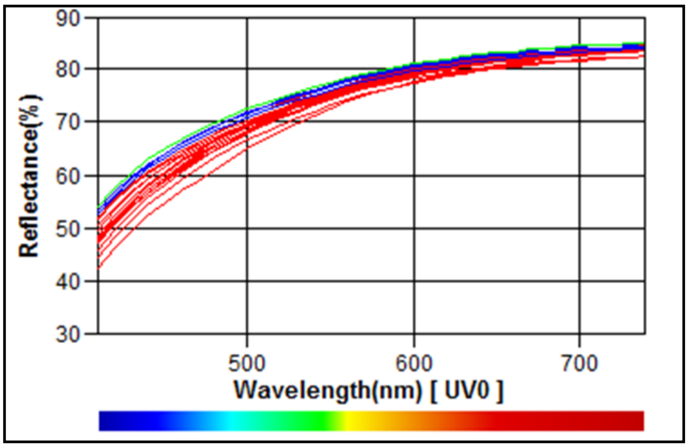


Fig. 4.42. Reflectance spectrum of all samples.

Figure 4.43 shows the colour differences between reference sample A with value 0 and ΔE_{00}, ΔL^*, Δb^* and Δa^*. The colour differences shown by ΔE^*_{00} are larger when the silk has been treated with the alkaline sodium sesquicarbonate. All measurements, apart from I, silk dipped in sodium sesquicarbonate, not rinsed and aged 7 days and G, silk aged 7 days, dipped in sodium sesquicarbonate and aged for 1 extra day, are within the minimal detectable difference field (section 3.6.7). ΔL^* and Δb^* shows the same tendencies, that the tests treated with sodium sesquicarbonate has bigger alterations than the tests treated with sodium nitrate. The ΔL^*, lightness, have all become a bit darker and the Δb^*, the blue-yellow field, have all become a bit more yellow. There have not been a lot of change in Δa^*, the green - red field. The aged, not treated sample B has very little changes in ΔL^* compared to the other aged and treated samples. The sample that stands out the most is sample I treated with sodium sesquicarbonate, not rinsed and aged.

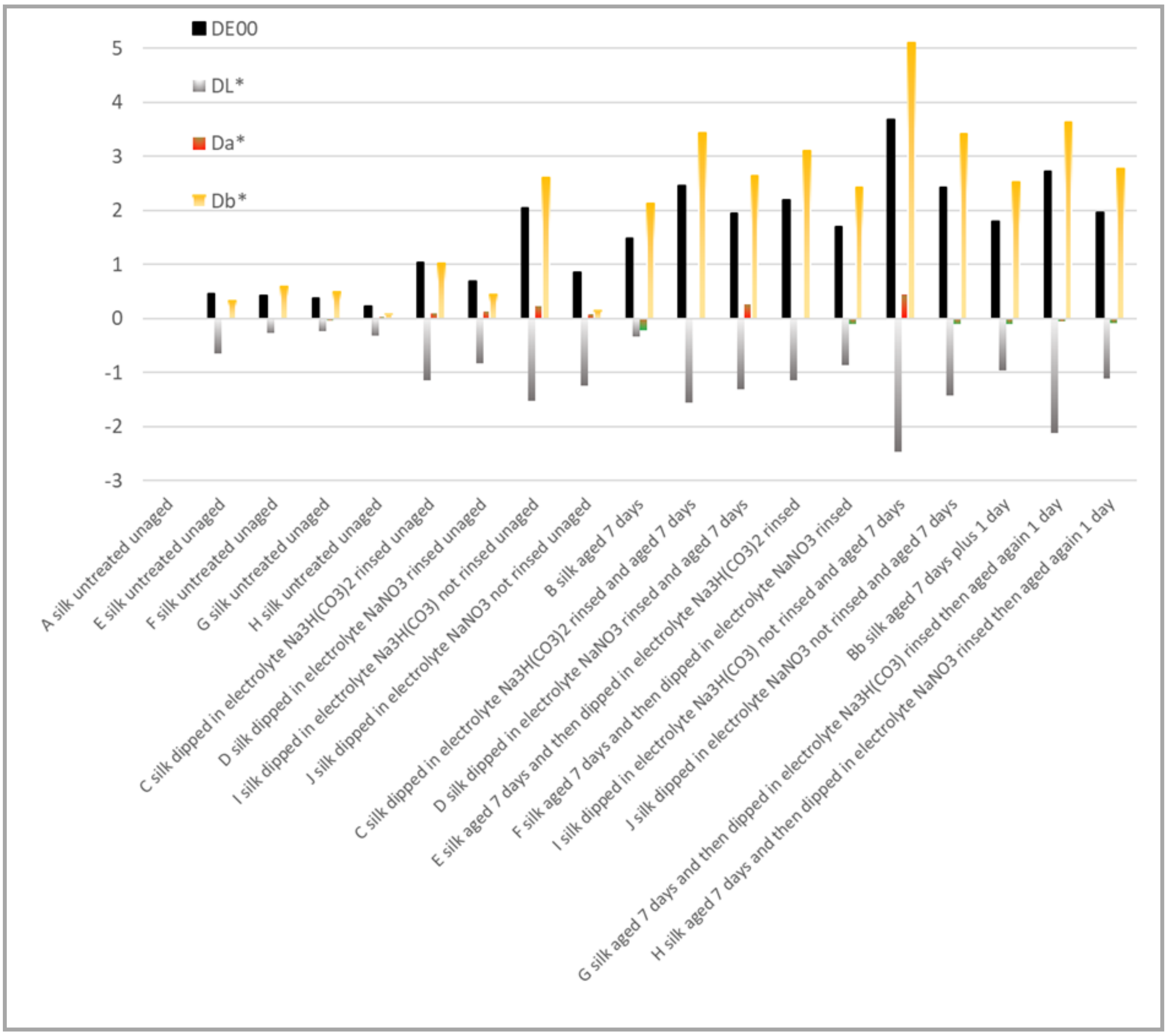


Fig. 4.43. Colour differences found when using spectrophotometry.

Figure 4.44 shows the colour difference values, ΔL* to the left and Δb* versus Δa* to the right. The unaged untreated sample A is showed in green, all other unaged untreated samples in blue and all aged samples in red. In ΔL* it can be seen that the treated samples have become slightly darker and in Δb* that the colour of the fabric has a more yellow hue. There is very little change in Δa*.

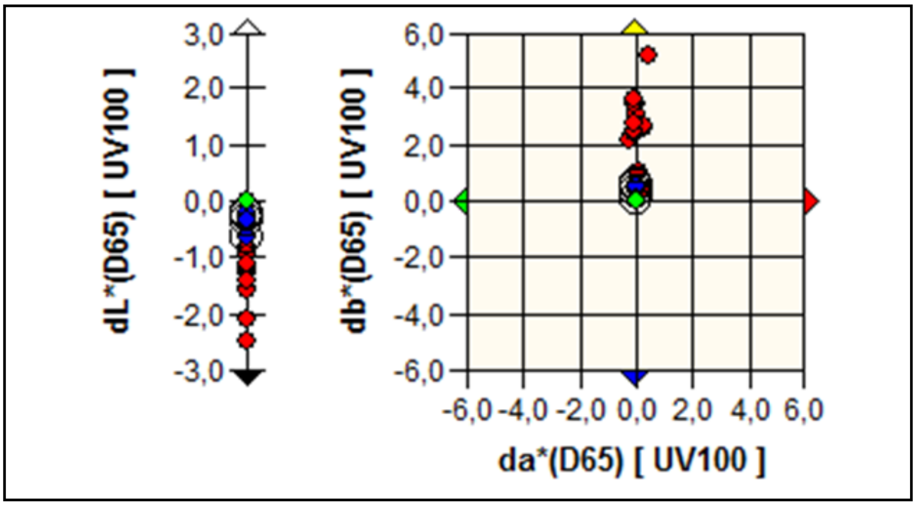


Fig. 4.44. Colour difference values ΔL* (left) and Δb* versus Δa* (right) .

5. Discussion and Conclusions

5.1 Discussion

5.1.1 IS IT POSSIBLE TO CLEAN SILVER THREADS USING THE PLECO?

The metal threads were made of silver alloys and therefore it was possible to reduce silver tarnish back to silver using the Pleco following the instructions given by Degrigny et al. (2015).

As seen in figure 4.06, it is possible to clean silver threads using the Pleco. There are some issues to be considered though. Before starting to clean an object with the Pleco, some training in using the tool is required. I noticed a big difference between my first attempts with the Pleco and the latter ones. There is a need to get an understanding of the relation between supply and extraction of the electrolyte and the object. You also need to understand how much pressure there ought to be between the pad of the Pleco and the object.
On the photos taken using light microscopy, areas which have not been successfully cleaned can be seen (figure 4.07). The reason for this is that the contact between the electrolyte infused pad and the metal was not sufficient to clean the silver. If a real object is treated with the Pleco, it is important to regularly observe the treated areas and, when needed, adjust the Pleco so that an adequate contact is being made.

The silver threads treated were cleaned where the contact between silver and electrolyte infused pad were adequate. Areas without contact were not cleaned. Even if all silver on the outside of the silver threads are cleaned, most likely it is still impossible to reduce the silver tarnish that might be found on the inside of the silver sheets. There is always a risk of re-tarnishing due to the presence of sulfides and the vulnerability of the recently cleaned silver surface (Tímár-Balázsy & Eastop 2011, p. 247). The outer layer of the metal is more active after cleaning which, in the wrong circumstances, can lead to re-tarnishing. The treated silver ought to be placed in a suitable environment to prevent re -tarnishing (e.g. in a Sulphur free environment or in the presence of active carbon). The use of lacquer cannot be recommended as a way to protect cleaned silver threads, as the layer needs to be completely homogenous and at the same time not make the textile stiff and brittle (Landi 1992, p. 40). In some cases, an intercept bag could be used. There are also corrosion inhibitors that might be helpful to prevent re-tarnishing (Moore, Liu & Tang 2009, p. 1). Silver cleaning should only happen when the object is going on display or are to be used. There is no reason to clean it if no one is going to see it.

The difference between the untreated and the treated silver threads was apparent. There were no obvious difference between the threads reduced by sodium sesquicarbonate and the ones reduced by sodium nitrate. This is something that could be examined in further research, using SEM-EDS.

It was diffiicult to interpret the images of the silver thread taken in SEM. The surfaces look very much the same on the corroded as well as the cleaned silver. This is actually something positive. The surface has not been ruined and there has not been a visible loss of material during cleaning. According to Source 3, a mechanical cleaning would have been very obvious in SEM.

5.1.2 HOW DOES THE ELECTROLYTE USED AFFECT THE SILK FIBRES?

In the analyses done, the electrolytes did not seem to affect silk very much. As seen in figure 4.4, the electrolyte spread in the silk in all experiments, even if it was only underneath the treated area. As silk has the ability to bind water up to 30% of its dry weight (Tímár-Balázsy & Eastop 2011, p. 45) and the electrolytes used were aqueous, this resulted in the presence of a salt line on all treated, unrinsed silk. The salt lines caused by sodium sesquicarbonate were more obvious for the naked eye, than the ones caused by sodium nitrate. The presence of salt lines can cause mechanical harm to the silk fibres. This leads to the conclusion that a recommendation can only be given to use this treatment on silk that can be rinsed. I find the idea of local electrolysis with the electrolyte in gel form interesting. It might provide a possibility to clean silver threads on silk that cannot be rinsed.

When using SEM on the treated silk (figures 4.23-4.24), specks that might be salt residues were found. SEM-EDS was also used to look for sodium residues in silk. All EDS spectra from silk treated with sodium sesquicarbonate (figures 4.27, 4.29 and 4.31) showed Na peaks. In the samples treated with sodium nitrate the EDS spectra of the contemporary silk (figure 4.32) showed Na peaks but the warp and the silk in the core of the silver threads did not (figures 4.28 and 4.30). This does not guarantee that there is no sodium present, but so far it seems more likely that residues from sodium sesquicarbonate can be found in the silk than residues from sodium nitrate.

ATR-FTIR was used as a way to look for the presence of Na in silk. The samples tested did not give a clear signal showing the presence of Na, even though parts with an obvious salt line were tested. There is no definite explanation of why we did not get a clear signal for Na-salts. Source 3 tells me that if the material investigated does not have strong IR absorptions, other absorptions might dominate so much that the material known to be present cannot be seen. In this case it would be the silk protein absorption that overshadows the sodium salt absorption.

The cross sections (section 4.4.2) showed presences of Na in the core of the silver thread in the unrinsed sample treated with sodium sesquicarbonate. It would be interesting to do a cross section on rinsed silver thread ribbon, to see if Na still could be found in the core of the silver thread.

Four groups of silk treated with sodium sesquicarbonate were tested for tensile strength. Two of them (C and I) (table 3.5) had an average breaking strain slightly lower than the reference samples but higher than the aged reference sample. The other two (E and G), the ones that were aged first and then treated with sodium sesquicarbonate, had a higher breaking strain than the reference samples, but the values were in no way extreme (figure 4.34). This can also be observed in the force/ displacement spectrum. The lines are a bit spread out, but they still have quite a similar profile (figure 4.36). When looking at the values of sodium sesquicarbonate from the spectrophotometer (table 4.3) we can see that all the ΔE values of the aged samples (C, E and H), apart from the one treated, not rinsed and aged (I), are around 2-2,7 which is almost in the minimal detectable difference zone (section 3.6.7). The sample that differed had a ΔE value of 3,7. All the aged samples had yellowed and darkened, but there were only differences in the red—green values on the sample that was unrinsed. Aged silk normally does yellow and darken so this was expected (Source 3). There is a difference of around 1 ΔE between the untreated aged silk and the rinsed samples. The control samples E, F, G and H differed around 0,5 ΔE from the reference sample A.They show ΔE_{00} values of 0,23 to 0,46 representing the inherent inhomogeneity of the silk fabric. This information clarifies that the differences of 1 ΔE is acceptable.

Four groups of silk treated with sodium nitrate were tested for tensile strength. All of them had an average breaking strain slightly lower than the reference samples but higher than the aged reference sample (figure 4.34). In the force/displacement spectra we can see that the lines have quite a similar profile (figure 4.37). When looking at the values of sodium nitrate from the spectrophotometer (table 4.3) we can see that all the ΔE values of the aged samples (D, F and H), apart from the one treated, not rinsed and aged (J), are around 1,5-2 which is in the minimal detectable difference zone (section 3.6.7). The sample that differed had a ΔE value of 2,5, also in that zone. All the aged samples had yellowed and darkened, but not as much as with sodium sesquicarbonate. There were small differences in the red—green values going either towards red or green. There is a difference of around 0,5 ΔE between the untreated aged silk and the rinsed samples.

It is interesting to learn that silk is quite resistant to chemical attack but can hydrolyse in both acidic and alkaline environments. According to May and Jones (2006, p. 81) alkalis hydrolyses silk slower then acids, as the reaction is happening mainly at the end of the amino-chains as opposed to acids that hydrolyse in the middle of a chain. The results found in this study indicates that silk was somewhat more affected by the alkaline sodium sesquicarbonate than by the acidic sodium nitrate. Further investigations with longer ageing processes might clarify these issues.

If silk were to be hydrolysed, there is a risk that the fabric used as a ground would be harmed by the thin metal edges of the silver threads, just like the silk in the thread used to stich silver threads to fabric described by Landi (1992, p. 95). The tensile tests show that the silk does not react too badly to the electrolytes, i.e. the silk does not seem to hydrolyse very much during treatment with neither sodium sesquicarbonate nor sodium nitrate.

Sample I was the one with the most extreme values from spectrophotometry (table 4.3). It was treated with sodium sesquicarbonate, not rinsed and aged for 7 days. It is interesting to notice that it did not have any extreme values in the tensile testing (table 4.2). It had one of the lowest values in break force, but the standard deviation was quite high. In appendix 2 (4.5, b) the graph shows that the gradients are quite similar to reference samples A.

When testing the samples for tensile strength, there were two tests that stood out slightly from the others (E and G). They were treated with sodium sesquicarbonate after ageing and rinsed. It seems that when silk is degraded by ageing, it is more sensitive to the influence of sodium sesquicarbonate then when it is aged after treatment. It also seems like silk degraded by ageing is less sensitive to the influence of sodium nitrate than that of sodium sesquicarbonate. When treating real objects with local electrolysis using the Pleco, the silk is already aged. Therefore, it seems more appropriate to use sodium nitrate as electrolyte in the reduction of silver tarnish. This is confirmed by the fact that sodium sesquicarbonate affects the lightness and colour tone of the silk more than sodium nitrate does, and that there seems to be a higher risk of residues in silk from sodium sesquicarbonate than from sodium nitrate.

5.1.3 ARE THERE METHODS TO CONTROL THE SPREAD OF ELECTROLYTE IN SILK?

With experience of using the Pleco it is possible to reduce the spread of electrolyte. When using a vacuum table, the spread of electrolyte is more easily controlled, and can be limited to the area underneath the part being treated. Another method considered as a way to control the spread of the electrolyte is to use cyclododecane around the areas being treated. It can be used to seal of areas and will automatically turn from solid to gas at room temperature. It is totally reversible and does not leave any residues on the material (Rowe & Rozeik 2014, p. 17). With the access of a vacuum table that can handle a lot of moisture, it would be possible to clean the silver threads surrounded by cyclododecane and then rinse only the treated parts on the table. This would be a viable option for textiles not well enough preserved to be immersed in water.

5.2 Conclusions

The thesis was built around three issues:

- Is it possible to clean silver threads using the Pleco?
- How does the electrolyte used affect the silk fibres?
- Are there methods to control the spread of electrolyte in silk?

The answer to the first issue, if it is possible to clean silver threads using the Pleco, is a clear yes. In the photographs (section 4.3.1) from light microscopy, it is clear that the silver of the silver threads treated with the Pleco have been cleaned/reduced.

Issue two investigates how the electrolytes used affects the silk fibres. Two electrolytes were used, the alkaline sodium sesquicarbonate and the acidic sodium nitrate. There are some differences between how they affect silk. The silk treated with sodium nitrate, pH 5, is slightly less affected than the silk treated with sodium sesquicarbonate pH 10. The results from analysing the test samples gives an indication that the effects of the electrolytes on silk are acceptable. To confirm the indication, more tests needs to be performed.

Issue three is asking whether there are methods to control the spread of electrolyte in silk. An experienced handling of the Pleco helped reduce the spread. The use of a vacuum table with sealed of treatment areas facilitated the control of the electrolyte even more (section 4.2). Thus, there are ways to control the spread of electrolyte in silk, however, the electrolyte will always spread in the fabric underneath the treated area. This means that the silk will always be affected by the electrolyte when metal threads are being treated with the Pleco. The conclusion is that a recommendation can only be given to use this treatment on silk that can be rinsed.

This project has shown positive results indicating that local electrolytic cleaning of silver threads on silk, using the Pleco, containing a suitable electrolyte, appears to be a viable option.

5.3 Further Research

When I was at the Swedish National Heritage Board as a guest colleague, it was suggested that we should try to publish the results from this study. To have a solid base, further tests are currently being performed. New silk samples have been cut for tensile testing and measurements with spectrophotometry. They are treated the same way as the samples in table 3.5. They will have a longer ageing period in the climate chamber. This will help in investigating how the electrolytes affects the silk. Silk will also be treated with the electrolytes and rinsed more vigorously, after which they will be analysed using SEM-EDS, looking for sodium residues from the electrolytes. An abstract has been sent to ICOM-CC to see if they are interested in a presentation at the world conference in Beijing 2020. The preparations are being performed together with the Swedish National Heritage Board and Dr Stavroula Golfomitsou.

As not everyone has access to a vacuum table, I suggest that further research should be done on how to control the spread of electrolyte in fabric. The method I have considered is to try cyclododecane to seal of the area being treated. There may also be other methods that should be considered.

Another suggestion for further research is to try to use the Pleco on metal threads on other materials than silk, such as wool, cotton and linen. It would also be interesting to investigate the differences between silver threads treated with sodium sesquicarbonate and sodium nitrate using SEM-EDS, which could show if there are any sulphur residues from the silver sulphide.

I would also like to see research where a comparison between the results of cleaning metal threads on fabric using local electrolysis with the Pleco and electrolyte infused gel were made.

6. Summary

In museums, churches and other cultural heritage collections, many textiles decorated with metal threads can be found. Silver embroidery on silk fabric is currently not usually cleaned, as there are no widely accepted cleaning methods. This thesis investigates the possibility of using local electrolysis to clean silver threads on silk fabric. The issue is not only whether local electrolysis, performed with a tool called the Pleco, can clean silver threads, rather, the main issue is how the electrolyte used in the cleaning process affects silk. Another issue investigated is if there are any methods to control the spread of electrolyte in silk.

To find answers to the issues presented, literature was reviewed and experiments were set up and analysed with different analytical methods. The experiments and some of the analysis were performed at the Department of Conservation at the University of Gothenburg. Other analytical methods were used at the Swedish National Heritage Board in Visby where I visited for a week as a guest colleague as part of this thesis.

The material used for the experiments and analyses were a silver thread ribbon, dated 1716, attached to a contemporary silk. The same contemporary silk was treated in different ways and analysed on its own as well.

The literature review gave answers to how the materials are structured, how they can be assembled and what can cause deterioration. The main corrosion product of silver is silver sulphide. Silk is quite resistant to chemical attack but can hydrolyse in both acidic and alkaline environments. In the literature I found examples of other cleaning methods for metal threads and the reasons why these are not widely used. I also learned about electrolytic cleaning. Tarnished silver can be reduced to elemental metal using electrolysis. The process requires an electrolyte and an external electrical source that drives the non-spontaneous redox reaction. It is a controllable process, where very little of the material being cleaned is lost. Local electrolysis can be performed using the Pleco or electrolyte infused gel. The Pleco is an electrolytic pen with a constant supply and extraction of electrolyte. The tip of the pen is made of a micro-porous foam which encloses an electrolytic cell. It is connected to a power supply, a multimeter and the object. It can be used both for cleaning and for consolidative reduction.

The experimental part of the thesis was executed with two different electrolytes, the acidic sodium sesquicarbonate, $NaH(CO_3)_2$ with pH 10 and the alkaline sodium nitrate, $NaNO_3$ buffered to pH 5. Before treatment the test samples were degreased with ethanol infused cotton wool. The treatment was performed either on blotting paper or on a vacuum table as ways of trying to limit the spread of the electrolyte in silk. After treatment the silver was wiped of with a deionized water infused sponge. Half of the tests were rinsed in deionized water 3×2 minutes, the other half were not rinsed. They were all dried on the vacuum table.

To execute the experiments, it was important to identify the silver alloy of the metal thread, the warp of the ribbon and the core of the metal thread. X-ray fluorescens spectroscopy and polarized light microscopy were used to identify the materials. The evaluation of the treatment was carried out using different analytical methods in the aim of answering the research questions. To do this the treated samples were compared to untreated reference samples. To confirm that the silver were reduced by the electrolytic treatment, imaging with light microscopy, photography and scanning electron microscopy were performed. To understand how silk were affected by the electrolytes, Fourier-transform infrared spectroscopy and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy were used in search for sodium residues from the electrolyte. Other ways to increase understanding of how the electrolytes affect silk were to do spectrophotometry and tensile testing, where measurements of the physical effect of the treatments were made.

The silver threads had a high percentage of silver and the fibres in the warp and the core were silk. This meant that the instructions of treating silver with the Pleco could be followed and that all three fibres that would be examined were made of silk. The imaging of the silver threads confirmed that the silver tarnish of the threads had been reduced .They also showed that there were little changes of the surface structure. If it would have been mechanically cleaned the surface structure would have been altered considerately. Fourier-transform infrared spectroscopy did not give a clear signal showing the presence of Na. As one of the samples were tested at a salt line, we know there were Na present. The reason why it did not show might be that the sodium compounds did not have as strong IR absorption as the protein from the silk. The protein absorption might dominate so much that the sodium compounds cannot be seen. Scanning electron microscopy coupled with energy dispersive x-ray spectroscopy did on the other hand show sodium residues in most silk samples. However, a few of the samples treated with sodium nitrate did not show any residues. Spectrophotometry showed a slight yellowing and darkening of the aged and treated silk. The changes were slightly greater in the silk treated with sodium sesquicarbonate than in the silk treated with sodium nitrate. The results from the tensile testing showed remarkably small differences when comparing the treated samples to the reference samples. Two of the samples treated with sodium sesquicarbonate after ageing had a somewhat lower elasticity, a slightly higher break stroke and maximum displacement than the reference and the rest of the samples. Before tensile testing, the samples were aged for one week and some of them were aged for an extra day after treatment. Some were treated before ageing and some were treated after.

The conclusions were that it is possible to clean silver threads using the Pleco, that sodium sesquicarbonate affects the silk a little more than sodium nitrate does, but that the indications are that the effects of the electrolyte on silk are acceptable. There are methods that can control the spread of the electrolyte in silk but the electrolyte will always spread in the fabric underneath the treated area, which means that the silk will always be affected by the electrolyte.

As I am writing this, further research is being performed. In the hope of publishing the result from this study, new silk samples are given an accelerated ageing. They were treated with the same electrolytes, in the same manner as previous samples, after which they will be measured with a spectrophotometer and tensile tested.

For further research it is suggested to test cyclododecane as a way to prevent the spreading of electrolyte. Another suggestion is to try to use the Pleco on metal threads on other materials than silk. I would also like to see research where a comparison between the results of cleaning metal threads on fabric using local electrolysis with the Pleco and electrolyte infused gel were made.

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7.1 List of Sources

Source 1	Dr Christian Degrigny, Professor HES, Senior Conservation Scientist. E-mail. March 2019
Source 2	Ann-Marie Ryding, Textile Conservator at Studio Västsvensk Konservering. Conversation: 11 May 2019
Source 3	Dr Marei Hacke, consevation scientist at Swedish National Heritage Board. Email: May 2019

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Schedual, outcome of the experiments. Table: Karin Hindborg

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c) *Silverribbon 3.* Spectrum: Austin Nevin. Instruments: XRF

4.1.2 Silk

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b) *Silk fibre from core of metal thread*. Photo: Karin Hindborg.
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4.2 Using the Pleco and Controlling the Spread of the Electrolyte

a) *Test sample where electrolyte has spread.* Photo: Karin Hindborg.

b) *Wiping the treated area with deionized water.* Photo: Karin Hindborg

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a) *Cross section silver thread ribbon.* Photo: Elyse Canosa. Instrument: SEM

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c) *Corroded.* Photo: Elyse Canosa. Instrument: SEM

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f) *Corroded.* Photo: Elyse Canosa. Instrument: SEM

g) *Sodium sesquicarbonate, rinsed.* Photo: Elyse Canosa. Instrument: SEM

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4.4 Sodium Salt Residues

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4.5 Physical Effects of Treatment

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b) *Dipped in sodium sesquicarbonate and sodium nitrate, not rinsed, aged for 7 days*. Graph: Karin Hindborg

Appendix 1. Schedual, outcome of the experiments.

EVALUATION/ OUTCOME		Abbrevi-ation			Tensile strength test	Optical microscopy	SEM imaging	SEM-EDS	ATR-FTIR	Spectrophotometry
Silk	Untreated	A/UT			■		■	■	■	■
Silk	Aged	B			■					■
Silk	Aged + aged again	Bb			■					■
Silk	Treated before ageing	C	Na3H(CO3)2	Rinsed	■		■		■	■
Silk	Treated before ageing	I	Na3H(CO3)2	Not rinsed	■		■		■	■
Silk	Treated after ageing	E	Na3H(CO3)2	Rinsed	■					■
Silk	Treated before ageing	D	NaNO3	Rinsed	■		■		■	■
Silk	Treated before ageing	J	NaNO3	Not rinsed	■		■		■	■
Silk	Treated after ageing	F	NaNO3	Rinsed	■					■
Silk	Treated	SR(fabric)	Na3H(CO3)2	Rinsed		■	■	■		
Silk	Treated	S(fabric)	Na3H(CO3)2	Not rinsed		■	■	■		
Silk	Treated	NR(fabric)	NaNO3	Rinsed		■	■	■		
Silk	Treated	N(fabric)	NaNO3	Not rinsed		■	■	■		
Silk	Treated, visible saltline on textile	S(salt)	Na3H(CO3)2	Not rinsed			■	■		
Ribbon	Untreated, clean	Clean				■	■			
Ribbon	Untreated, corroded	Corr				■	■	■		
Ribbon	After cleaning	S	Na3H(CO3)2	Not rinsed		■	■	■		
Ribbon	After cleaning	SR	Na3H(CO3)2	Rinsed		■	■	■		
Ribbon	After cleaning	N	NaNO3	Not rinsed		■	■	■		
Ribbon	After cleaning	NR	NaNO3	Rinsed		■	■	■		
Cross section	After cleaning	S(cross)	Na3H(CO3)2	Not rinsed		■	■	■		
Cross section	After cleaning	N(cross)	NaNO3	Not rinsed		■	■	■		
Silk	Aged, treated and aged	G	Na3H(CO3)2	Rinsed	■					■
Silk	Aged, treated and aged	H	NaNO3	Rinsed	■					■

Appendix 2

4.1.1 Metal

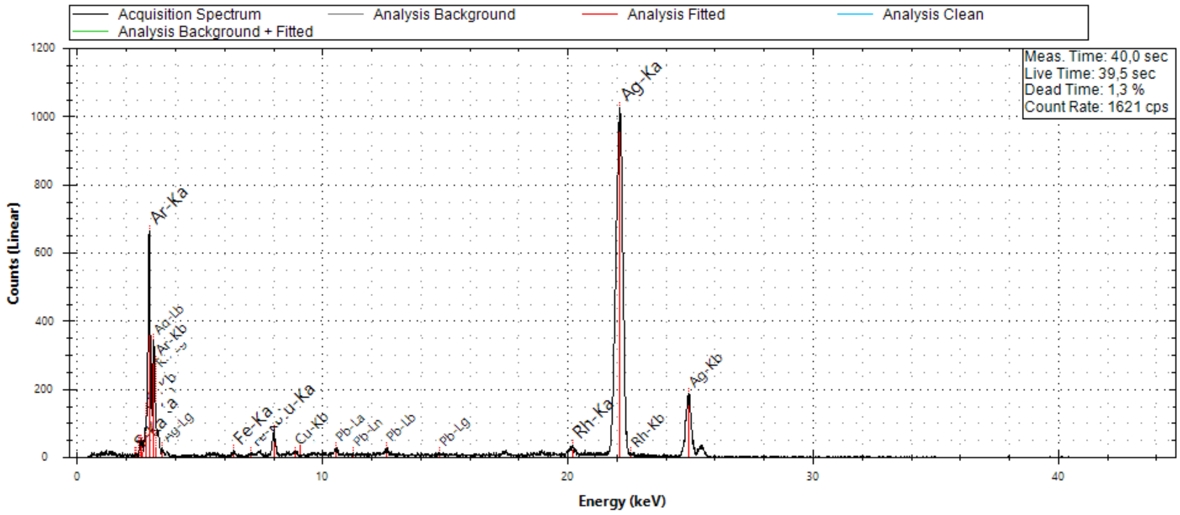
Measurement Time: 40,0 s
Tube Voltage: 40 kV
Tube Current: 20 µA
Tube Target Material: Rh
Elio Device: SN1253

Device Mode: Head
Acquisition Mode: Manual
Acquisition Channels: 4096
Sample to Detector Material: Air

a) The settings of the XRF during measurements.

b) Silverribbon 1

17/04/2019 13:56:43



Analysis Results:

Element Concentration Error

Ag 80,61% ±0,57%

Cl 15,91% ±5,37%

S 2,36% ±20,77%

Cu 0,68% ±3,33%

Fe 0,23% ±7,56%

Pb 0,22% ±4,42%

Included Elements for Fitting Analysis:

Ar, Cl, S, Pb, Ag, Cu, Rh, Fe

Analysis Date and Time: 17/04/2019 13:58:34

Analysis Type: Advanced

Spectrum Left Cut: 1 keV

Spectrum Right Cut: 50 keV

Spectrum Upper Limit: 50 keV

Use M Line: True

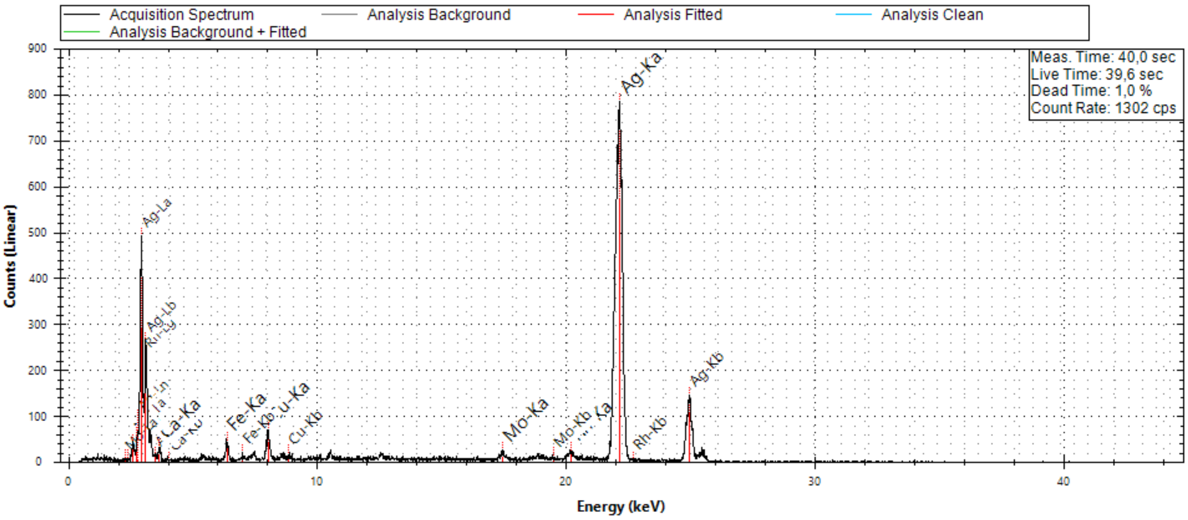
Super Impose Peak Areas: True

Selected Elements for Analysis:

Cl, S, Pb (K,L lines), Ag (K,M lines), Cu, Fe

c) Silverribbon 3

17/04/2019 14:05:08



Analysis Results:

Element	Concentration	Error
Ag	93,06%	±0,75%
Ca	5,04%	±8,32%
Cu	0,91%	±3,96%
Fe	0,84%	±5,4%
Mo	0,15%	±6,55%

Analysis Date and Time: 17/04/2019 14:04:37

Analysis Type: Automatic

Spectrum Left Cut: 1 keV

Spectrum Right Cut: 50 keV

Spectrum Upper Limit: 50 keV

Use M Line: True

Super Impose Peak Areas: True

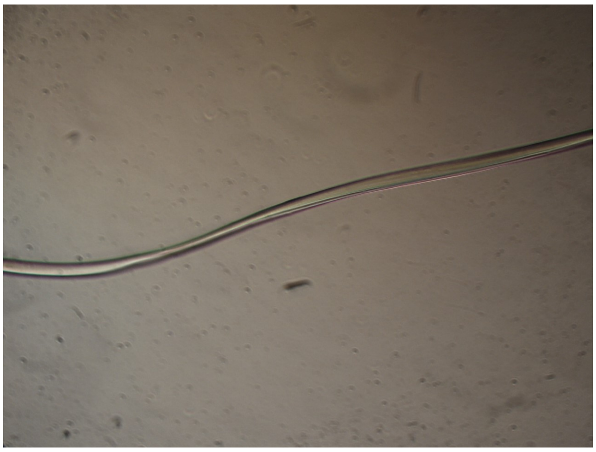
Excluded Elements for Fitting Analysis:

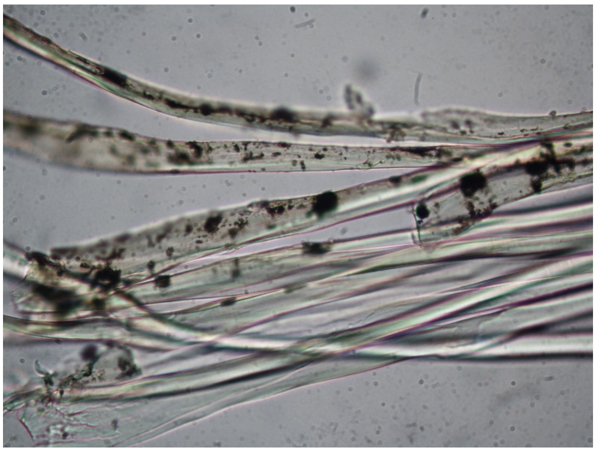
H, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Kr, Xe, Rn, At, Po, Fr, Ra, Ac, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, Pd, Ru

Excluded Elements for FP Analysis:

Rh, Ar, Ag:L, Tc:L, Nb:L, Mo:L, Cd:L, In:L, Sn:L, Sb:L, Pb:M, Bi:M, Tl:M, Hg:M, Au:M, Pt:M, Ir:M, Os:M, Re:M, W:M, Ta:M, Hf:M, La:M

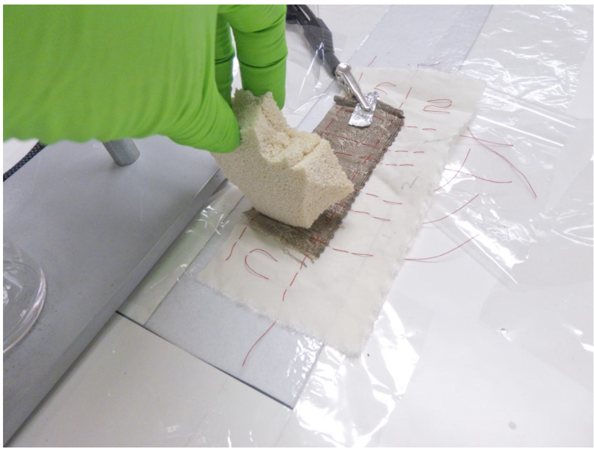
4.1.2 Silk


a) Silk fibre from contemporary silk. ×20

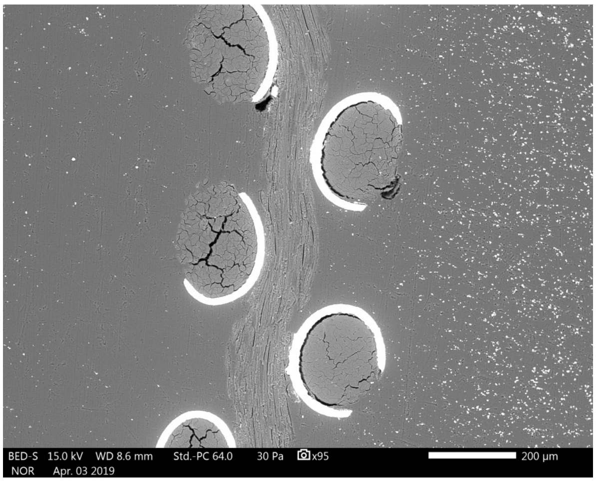

b) Silk fibre from core of a metal thread with some kind of stain.

4.2 Using the Pleco and controlling the spread of the electrolyte

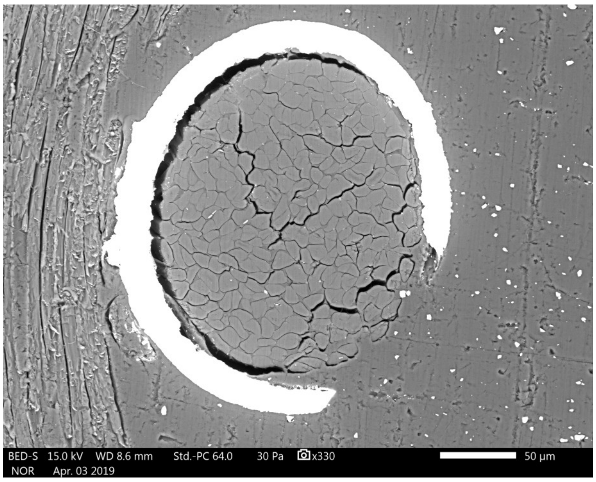

a) One of the first samples tested with the Pleco. The electrolyte has spread in the silk fabric.


b) Wiping the treated area with deionized water.

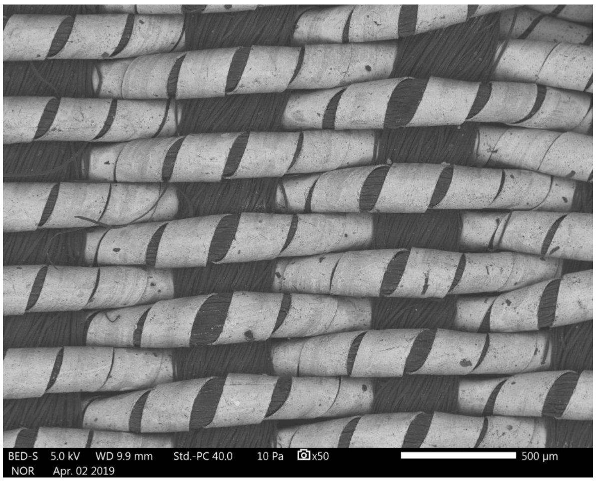
4.3.2 Scanning Electron Microscopy



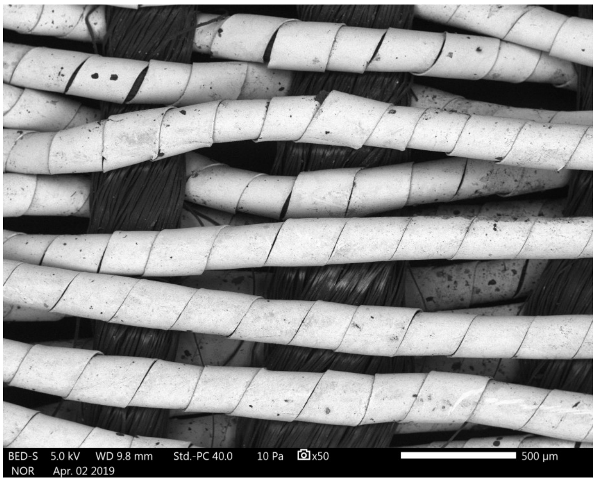
a) Cross section silver thread ribbon.



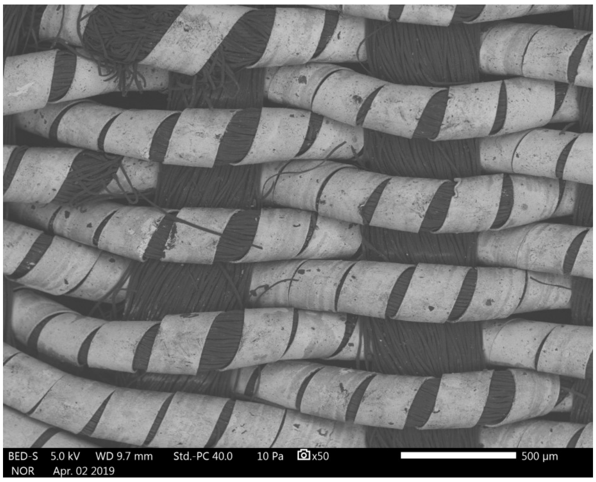
b) Cross section core of silver thread.



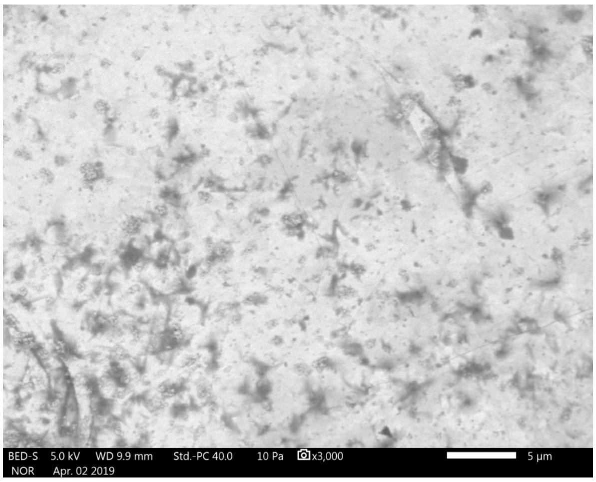
c) Corroded. ×50



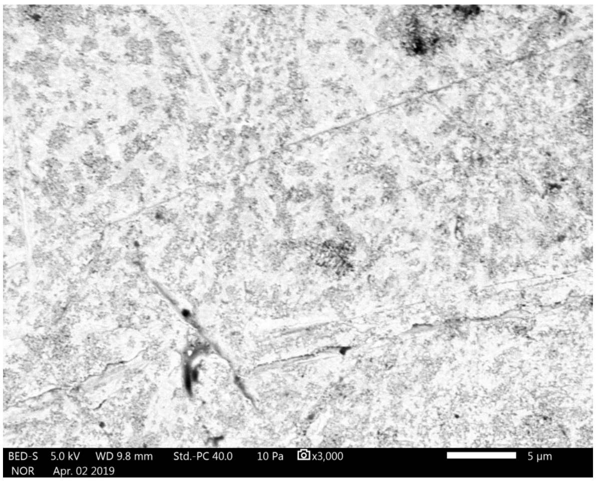
d) Sodium Sesquicarbonate, rinsed. ×50



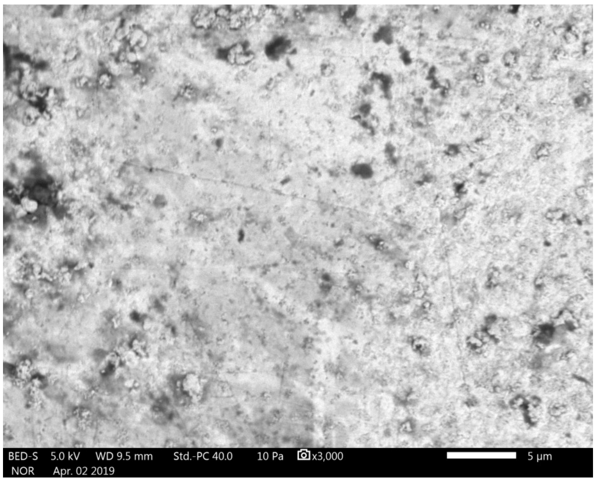
e)Sodium nitrate, rinsed. ×50



f) Corroded ×3000

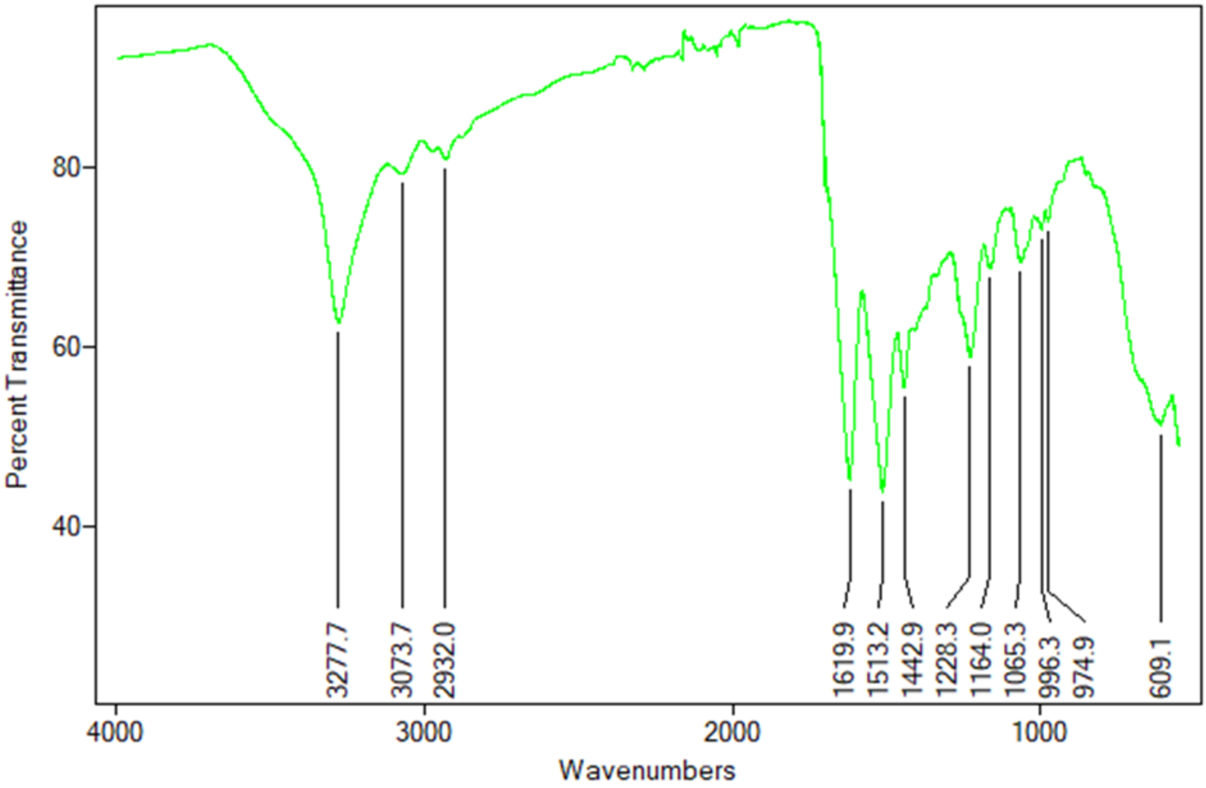


g) Sodium Sesquicarbonate, rinsed. ×3000



h) Sodium nitrate, rinsed. ×3000

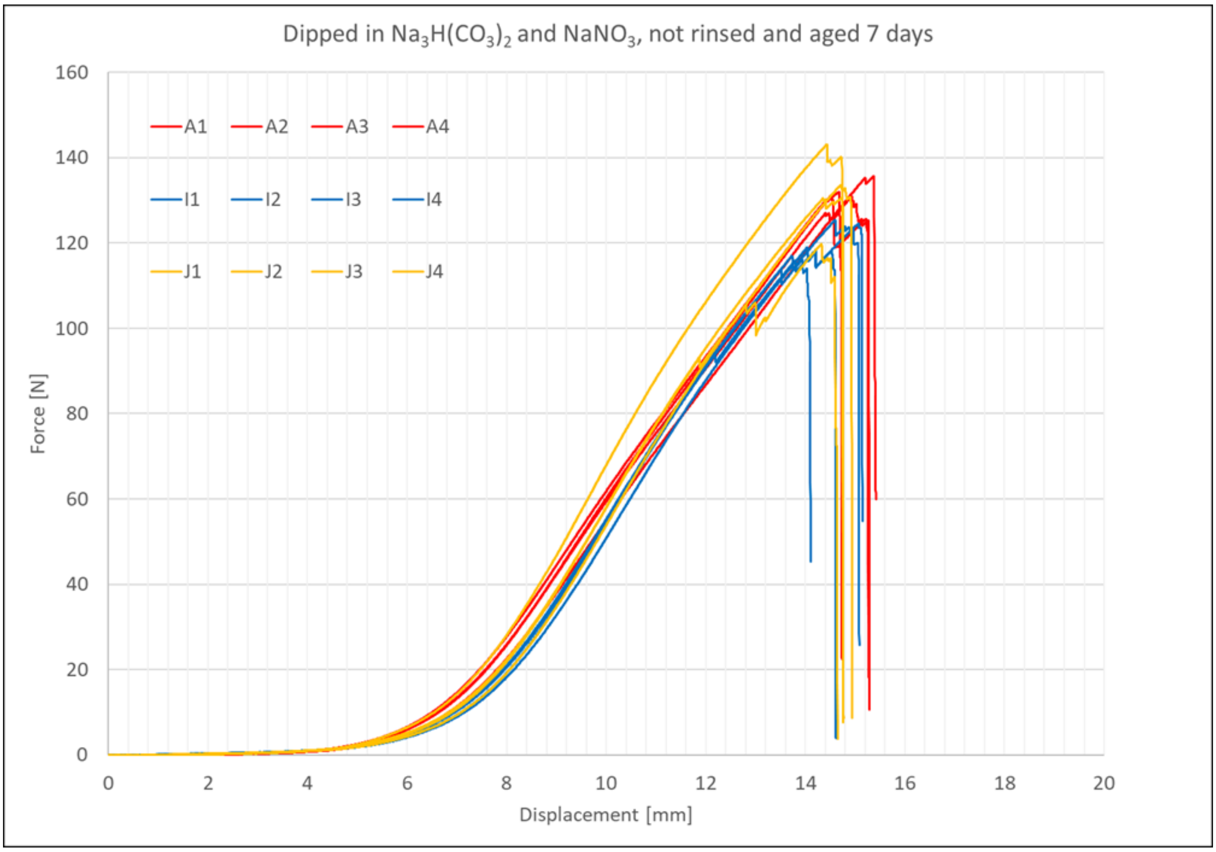
4.4 Sodium Salt Residues on Silk



a) The ATR-FTIR spectrum for the untreated unaged silk shows a typical fingerprint spectrum for protein with amide A and N-H stretching at 3278 cm^{-1}, amide I (primarily C=O stretching of polypeptide chains) at 1620 cm^{-1}, amid II (N-H bending and C-N stretching) at 1513 cm^{-1}, CH_2 vibrations (scissoring) at 1442 cm^{-1} and amid III (NH, CN and CC vibrationer) around 1228 cm^{-1}, as well as peptide C-C stretching at 1065 cm^{-1}.

4.5 Physical Effects of Treatment

a) Samples arranged on pure cellulose filter paper and placed in the climatic chamber.



b) Dipped in Sodium sesquicarbonate and sodium nitrate, not rinsed and aged 7 days + reference samples.