



Knight, Elizabeth (2017) *An investigation of alternative reducing agents to sodium dithionite for solubilising rust stains on cotton.* [MPhil].

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An Investigation of Alternative Reducing Agents to Sodium Dithionite for
Solubilising Rust Stains on Cotton

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Submitted in partial fulfilment of the requirements for the Degree of
Master of Philosophy in Textile Conservation in the
School of Culture and Creative Arts, University of Glasgow, 18 August 2017

Word Count: 15,664

Abstract

Rust stains can be problematic for historical textiles, weakening stained areas and eventually leading to losses as iron ions catalyse polymer chain scission. The reducing agent sodium dithionite effectively removes rust stains from cotton textiles, but its rapid aqueous degradation and health and safety restrictions have limited its use in textile conservation. Sodium metabisulfite and ascorbic acid were identified as potential conservation appropriate reducing agents. Test treatments were carried out with each reducing agent in combination with the chelator tri-ammonium citrate to determine effective solution concentrations. An evaluation framework was devised to compare the working properties of each reagent. Stain removal was evaluated using spectrophotometry and bathophenanthroline test strips. Reagents' effects on the cotton fibres were evaluated by measuring treated stained and unstained samples' surface pH and using optical microscopy. A rust stained historical sampler was treated with the most successful concentration of each reducing agent. Sodium metabisulfite removed little staining throughout testing. Ascorbic acid removed lighter rust stains but the low pH of higher concentration solutions made it an inappropriate reducing agent for acid-sensitive cellulosic textiles. Sodium dithionite was the most successful reducing agent. Recommendations for its use were made based on the findings of this research.

Acknowledgements

My dearest thanks to my research supervisor Anita Quye for all her guidance during this research.

My heartfelt thanks go to the staff at the Centre for Textile Conservation for their support over the past two years. They have made my time in Scotland truly special. I am especially grateful for the CTC's support of purchasing supplies for this research. Special thanks to Sarah Foskett for contributing the historical nails and for checking in with me during the many weeks of testing in the laboratory. Thank you to Margaret Smith for the help with my graphs. To my mom and dad - thank you for your love, support, and editing at any hour. Finally, thank you to my friends and family for listening to me ramble about rust all summer.

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1. Introduction

1.1 Research Context

Stains caused by iron corrosion products, commonly called rust, can occur when textiles contact metal objects exposed to high humidity or water such as tacks or metal fastenings.¹ Rust stains can also occur after textiles have been washed in high iron content water, depositing iron ions onto the fibres that oxidise to rust.²

Rust stains can be problematic, weakening stained areas and eventually leading to losses as the iron ions catalyse polymer chain scission.³ Though stains are not often removed from textiles because of their historical and evidential nature, the inherent degradative nature of rust staining can justify removal from historical textiles. The losses caused by nails or tacks remain as evidence of original attachment methods.

Rust stains are composed of iron oxides - most commonly oxyhydroxides.⁴ Iron (Fe) ions in rust are typically iron (III) ions bonded ionically to oxygen (O^{2-}) or hydroxide (OH^-) ions in an octahedral (or less commonly tetrahedral) arrangement (Fig. 1).⁵ Different spatial arrangements of the octahedrals lead to the formation of different oxyhydroxides (Fig. 2).⁶

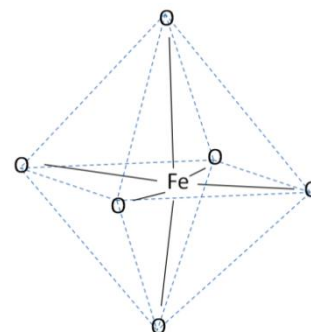


Fig. 1 Simplified representation of the octahedral base unit of iron oxides

¹ R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, 2nd ed. (Weinheim: VCH Publishers, 2003), 493.

² Antesar Elmagirbi, Hermin Sulistyarti, and Atikah, "Study of Ascorbic Acid as Iron(III) Reducing Agent for Spectrophotometric Iron Speciation," *Journal of Pure and Applied Chemistry Research* 1, no. 1 (2012): 11.

³ Johan Neevel, "The Development of a New Conservation Treatment for Ink Corrosion, Based on the Natural Anti-Oxidant Phytate," *8th IADA Congress* 5 (1995): 93.

⁴ Cornell and Schwertmann, *Iron Oxides*, 497–98.

⁵ *Ibid.*, 9–15.

⁶ *Ibid.*, 14–15.

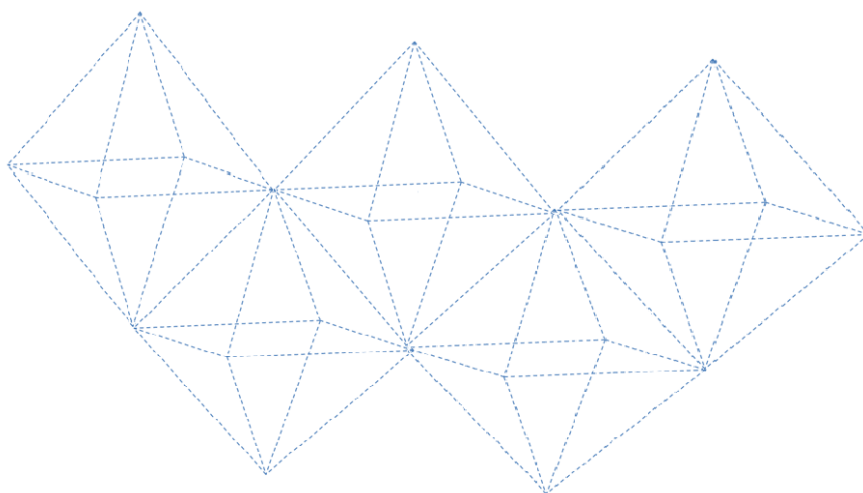


Fig. 2 Simplified representation of a single layer of lepidocrocite in which the base units link along edges

Iron (III) is a coloured ion responsible for the orange-brown colour of rust stains. Iron (III) ions have very low solubility in water so aqueous removal treatments are ineffective.⁷ Iron ions can also exist as the water soluble and colourless iron (II) ion. When rust is converted from iron (III) to iron (II), the stain can be removed using traditional textile conservation aqueous wet cleaning or spot cleaning treatments.

A common conservation treatment for rust staining has been using the reducing agent sodium dithionite to chemically convert iron (III) to iron (II), but it has practical limitations. SDT is highly reactive with oxygen and water causing it to quickly decompose during treatment.⁸ Multiple fresh solutions may be needed throughout a single treatment, increasing its cost. It is highly reactive in air, posing a risk of spontaneous heating and potential ignition. SDT also decomposes in the presence of acids, often present in textiles from rust-catalysed degradation, and can evolve toxic sulfur dioxide gases so fume extraction must be used - a logistical difficulty for large objects.⁹ The limitations of SDT make it a less than ideal choice for conservation treatments.

The evaluation of alternative reducing agents for suitable and effective rust removal from textiles would be valuable and is the primary aim of this research project. Staining on cotton will be discussed specifically because the mechanisms of rust-catalysed degradation differ between cellulosic and proteinaceous materials.¹⁰

⁷ Ibid., 201.

⁸ Lyndsie Selwyn and Season Tse, "The Chemistry of Sodium Dithionite and Its Use in Conservation," *Reviews in Conservation* 9 (2008): 68, doi:10.1179/sic.2008.53.Supplement-2.61.

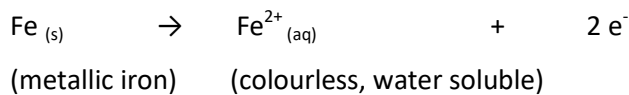
⁹ Ibid., 69–70.

¹⁰ Ibid., 66.

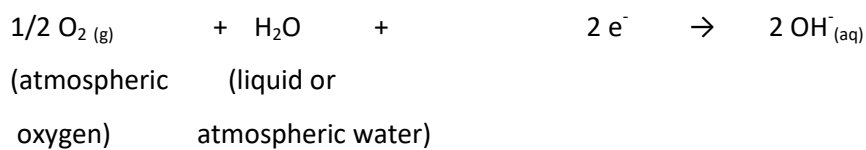
1.2 Rust Formation

Examining the mechanisms of rust formation, an electrochemical process, can help determine its effective removal. Rust forms in high relative humidity ranges (above 65%) or when iron has been wetted and oxygen is present.¹¹ The two half reactions are:

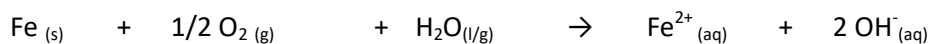
Anodic



Cathodic



Overall



Reaction 1 Metallic iron reaction with water¹²

The iron (II) ions proceed through multiple and sometimes competing pathways depending on the pH of the environment, oxygen content, and temperature. Oxidation is slow in acidic conditions; some iron (II) ions remain soluble while others are oxidised to iron (III) by dissolved or atmospheric oxygen.¹³ Various radicals are formed throughout the process - only the overall reaction is presented (Reaction 2).



Reaction 2 Oxidation of iron (II) ions¹⁴

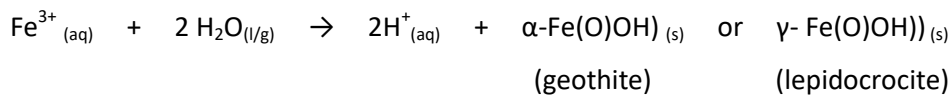
¹¹ Lyndsie Selwyn, *Metals and Corrosion A Handbook for the Conservation Professional* (Ottawa: Canadian Conservation Institute, 2004), 104.

¹² *Ibid.*, 101.

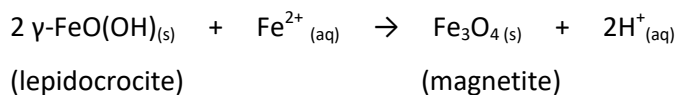
¹³ *Ibid.*, 102.

¹⁴ Werner Stumm and Fred G. Lee, "Oxygenation of Ferrous Iron," *Industrial and Engineering Chemistry* 53, no. 2 (1961): 143, doi:10.1021/ie50614a030.

Iron (III) ions and water react to form iron oxides typical of rust. Three oxides are usually formed, each with distinct characteristics and formed under different conditions.¹⁵ They are goethite (α -Fe(O)OH), lepidocrocite (γ -Fe(O)OH), and magnetite (Fe_3O_4).¹⁶ Goethite and lepidocrocite are iron oxyhydroxides, while magnetite is simply an oxide.¹⁷ Magnetite usually forms through the transformation of another iron oxide such as lepidocrocite in an excess of iron(II) ions and therefore also contains iron (II) ions.¹⁸ Generic mechanisms for goethite/lepidocrocite (Reaction 3) and magnetite (Reaction 4) formation at room temperature are provided.



Reaction 3 Formation of iron oxyhydroxides¹⁹



Reaction 4 Formation of magnetite from lepidocrocite²⁰

Rust is therefore a competing system of iron (II) ions, iron (III) ions, and iron oxides. Rust can contain some water soluble iron (II) ions, but is largely insoluble. An appropriate conservation treatment reducing agent must reduce multiple types of iron oxides without risk of re-oxidation and potential transformation to a different iron oxide.

1.3 Iron and Cellulose Interactions

In addition to forming rust, iron (II) ions catalyse the formation and regeneration of radical species on cellulose polymer chains ultimately leading to chain scission, fibre weakening, and material loss. Iron (II) ions form hydrogen peroxide and iron (III) ions (Reaction 5).²¹

¹⁵ Cornell and Schwertmann, *Iron Oxides*, 101–2.

¹⁶ *Ibid.*, 499.

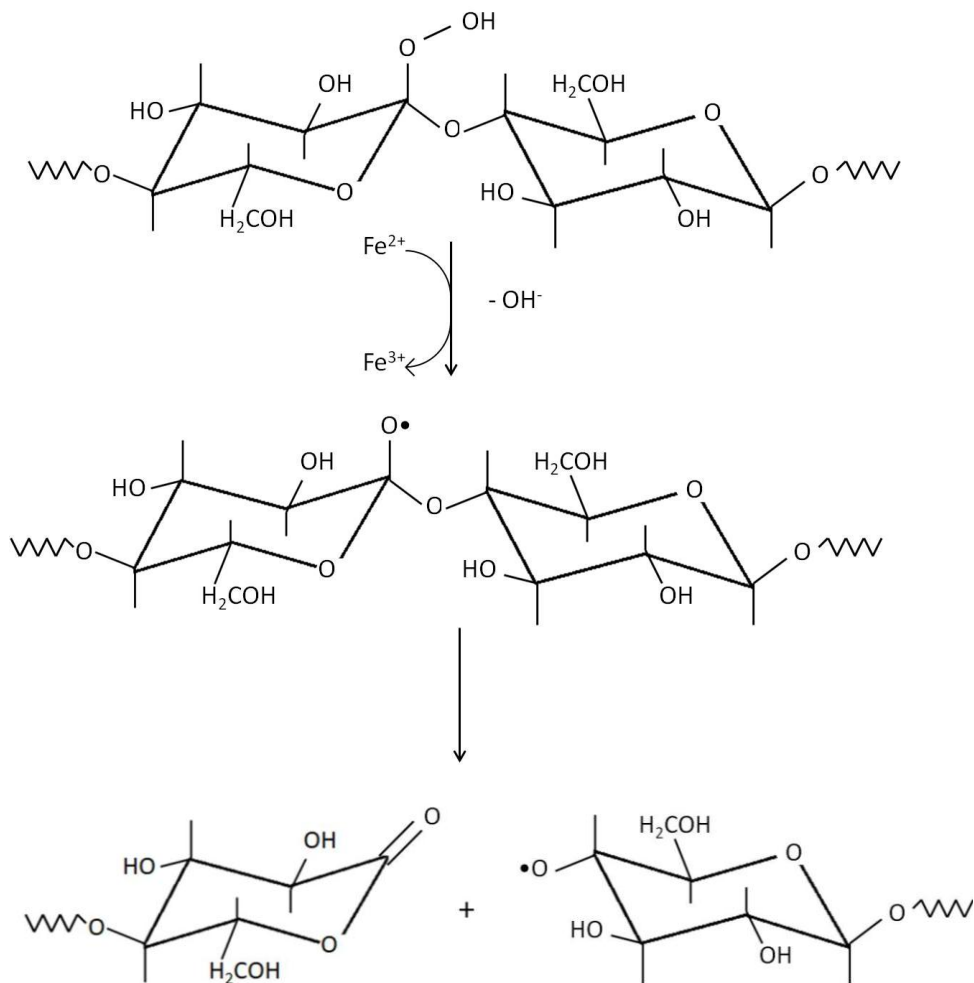
¹⁷ *Ibid.*, 15–19, 33.

¹⁸ *Ibid.*, 405.

¹⁹ Selwyn, *Metals*, 102.

²⁰ Cornell and Schwertmann, *Iron Oxides*, 405.

²¹ Neevel, "Development," 93.



Reaction 7 Mechanism of cellulose polymer glycosidic linkage scission catalysed by iron (II) ions

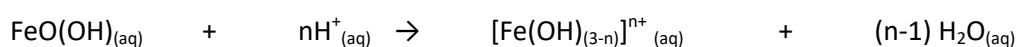
1.4 Removing Rust

Chemically converting iron oxides to their ionic components, called dissolution, is an effective and acceptable rust removal treatment for textile conservation. Iron oxide dissolution mechanisms have been widely researched in soil science and vary for the same oxide depending on dissolution system and the iron oxide properties.²⁵ Despite the range of possible parameters, generic mechanisms have been established for three common iron oxide dissolution methods.

²⁵ Cornell and Schwertmann, *Iron Oxides*, 298.

1.4.1 Protonation

Proton-rich environments (acidic solutions) can cause dissolution of iron oxides. Three protons per iron ion are adsorbed onto the surface of an iron oxide crystal hydroxyl group, imparting a positive charge that weakens the Fe-O bond. The polarised bond allows the iron ions to dissociate from the crystalline network.²⁶ Protonation can be a slow method of dissolution with a high activation energy that can be overcome with a very low solution pH (typically 1-2).²⁷ The generalised mechanism Reaction 8 shows sequential addition of protons where n = 1, 2, or 3 and their terminal product: free iron (III) ions.²⁸



For example, when n = 2, the reaction is:



Reaction 8 Dissolution by protonation

The necessary low pH is inappropriate for cellulosic materials which are sensitive to acid hydrolysis of the fibres.²⁹

1.4.2 Chelation

Chelators are organic molecules capable of sequestering metal ions, which can aid or cause dissolution. They have at least two side groups, called ligands, that are acid or basic. Ligands have electrons available to bond, or complex, with metal ions.³⁰ The side groups are called coordination sites. The pH of a solution affects the protonation or deprotonation of these ligands and consequentially the number of available coordination sites.³¹ Metal ions have a corresponding coordination number: sites that must be occupied to sequester the ion.³² Iron (II) and (III) ions

²⁶ Ibid., 299.

²⁷ Ibid., 300.

²⁸ Ibid., 299–300.

²⁹ Ágnes Tímár-Balázsy and Dinah Eastop, *Chemical Principles of Textile Conservation* (Oxford: Butterworth-Heinemann, 1998), 28–29.

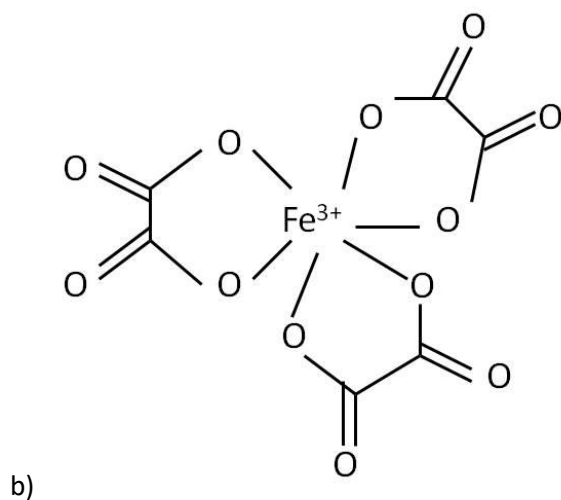
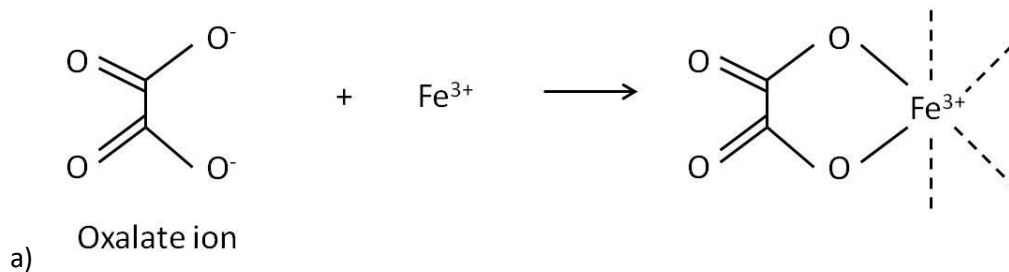
³⁰ F.P. Dwyer and D.P. Mellor, eds., *Chelating Agents and Metal Chelates* (London: Academic Press Inc., 1964), 17.

³¹ Helen Burgess, "The Use of Chelating Agents in Conservation Treatments," *The Paper Conservator* 15, no. 1 (1991): 36, doi:10.1080/03094227.1991.9638395.

³² Dwyer and Mellor, *Chelating Agents*, 15–16.

have a coordination number of 4 or 6. Multiple chelator molecules are necessary to sequester a single metal ion whose coordination number is higher than the chelator's available coordination sites. Conservation treatment chelators should be chosen based on their metal ion affinities and their concentrations should be in excess of the metal ion concentration to ensure full sequestration.³³

Chelation can occur through two pathways. In the first pathway, chelators sequester free iron ions and can prevent iron (II) ion re-oxidation to iron (III) during conservation treatments. The side groups complex the metal ions, forming cyclic structures with central metal ions, sequestering them from a solution (Reaction 9a).³⁴

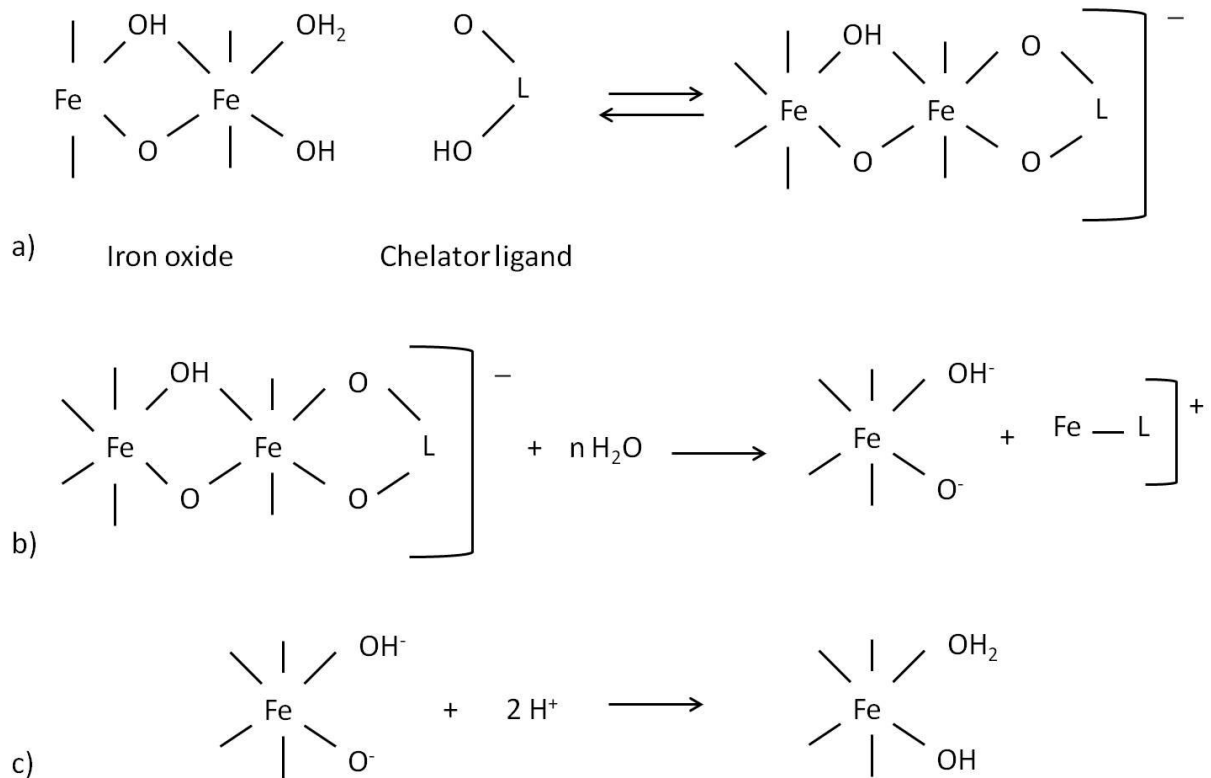


Reaction 9 a) Oxalic acid's two acidic coordination sites can bond with iron. b) Iron (III) can have a coordination number of 6, so two additional oxalate ions are needed to fully sequester it.

³³ Burgess, "Chelating Agents," 37.

³⁴ Dwyer and Mellor, *Chelating Agents*, 18.

In the second pathway, the chelator ligands adsorb onto the iron oxide, weakening the Fe-O bonds to detach the ligand-Fe complex and working in tandem with protonation (Reaction 10).³⁵ Many chelators are also acids which can donate protons to the dissolution system such as oxalic acid and ethylenediaminetetraacetic acid (EDTA).³⁶



Reaction 10 a) The chelator ligand adsorbs onto the iron oxide surface. b) The iron ion detaches with the chelator. c) The iron oxide surface is protonated.

Because chelation dissolution also requires protonation, pH environments of 4 or lower are needed that are often too low for conservation treatments.³⁷ Chelators for sequestration do not need to break bonds, so they have wider and less acidic pH ranges. Sequestering chelators can be paired with another dissolution method that is efficient at a safer pH for conservation treatments.

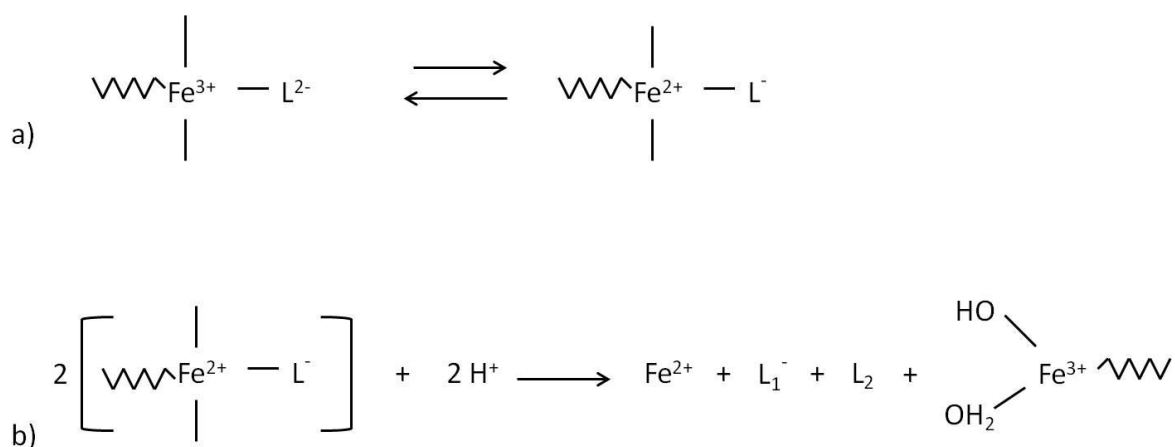
³⁵ Cornell and Schwertmann, *Iron Oxides*, 301–3.

³⁶ Burgess, "Chelating Agents," 36–37.

³⁷ Cornell and Schwertmann, *Iron Oxides*, 302.

1.4.3 Reduction

SDT causes iron oxide dissolution through reduction. Electrons are transferred to iron (III) ions in rust through the adsorption of a reducing agent onto the iron oxide surface, which donates electrons and forms soluble iron (II) ions. This polarised iron oxide network causes an electron density shift towards surface iron (III) ions, reducing iron (III) to iron (II).³⁸ Weak iron (II)-O bonds cause detachment from the oxide network, releasing soluble iron (II) ions.³⁹ Protonation aids iron (III) detachment, so acidic environments accelerate reduction if the reducing agent stable in low pH.⁴⁰ The exact step of iron (II) ions formation is still being experimentally determined and can vary between reducing agents.⁴¹ A generalised reaction is shown in Reaction 11.⁴²



Reaction 11 a) The reducing agent (L) adsorbs onto the iron oxide surface, donating electrons to reduce the iron (III) to iron (II). b) The weak Fe^{2+} -O bond allows for iron (II) detachment, sometimes also creating oxidised side products. The remaining iron oxide is protonated, continuing the reaction.

Reduction occurs at mildly acidic or near neutral conditions, so it is a safer dissolution method for cellulosic material conservation treatments. Reducing agents are highly reactive so their dissolution rate can be influenced by pH, temperature, iron oxide type, and other electron donors and receivers like oxygen and other cations.⁴³ Reducing agents for textile conservation treatments must be

³⁸ Ibid., 306.

³⁹ D. Parias et al., "Mechanisms of Dissolution of Iron Oxides in Aqueous Oxalic Acid Solutions," *Hydrometallurgy* 42, no. 2 (1996): 260, doi:10.1016/0304-386X(95)00104-O.

⁴⁰ Cornell and Schwertmann, *Iron Oxides*, 306–12.

⁴¹ Ibid., 306.

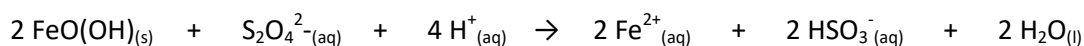
⁴² Parias et al., "Mechanisms," 260–61.

⁴³ Cornell and Schwertmann, *Iron Oxides*, 312–16.

compatible with acceptable conservation environments: near neutral conditions, room temperature, and oxygenated water.

1.5 Applications in Conservation

All three dissolution methods (protonation, chelation, and reduction) have been employed with varying degrees of success in the conservation field to reduce rust stains. Aqueous treatments using reducing agents in combination with chelators has been the most successful method in textile conservation.⁴⁴ The reducing agent SDT (also called sodium hydrosulfite) has been referenced in conservation literature since 1968.⁴⁵ It reduces rust via Reaction 12 at neutral or slightly acidic pH.⁴⁶



(Iron oxyhydroxides) (SDT)

(hydrogen sulfite)

Reaction 12 Sodium dithionite reduction of iron oxyhydroxides

Its efficiency at near neutral pH is advantageous for acid-sensitive historical textiles. However, as mentioned in the introduction, SDT's disadvantages include rapid decomposition in air, acids, and water along with its health and safety risks and cost leading to limited use of SDT in textile conservation despite its proven efficiency in rust removal. There is therefore a need to explore other safer rust removal treatment options.

1.6 Aims and Objectives

This research will explore one central research question: Is there an effective alternative reducing agent to sodium dithionite for rust stain removal from historical undyed cotton fabric? Linen and dyed fabrics are not considered here to limit the testing variables.

⁴⁴ Selwyn and Tse, "Sodium Dithionite," 62–65.

⁴⁵ *Ibid.*, 61.

⁴⁶ Cornell and Schwertmann, *Iron Oxides*, 312.

Investigation of reducing agents has been limited in conservation. Other fields including soil decontamination, photography development, and the medical field have extensively researched the reduction of iron (III) compounds to iron (II) compounds. Many options have been explored such as mild acids and derivatives of sodium dithionite that may be able to reduce iron stains sufficiently in less acidic environments and without the health and safety concerns of SDT.

To investigate potential alternatives to the reducing agent SDT, the following research aims were explored:

1. Which reducing agents could be potential alternatives to sodium dithionite based on practical criteria like pH, temperature restrictions, health and safety concerns, and cost?
2. Is their rust removal effective under acceptable conservation conditions?
3. If there is an effective alternative agent, what optimised conditions can be recommended?

The objectives used to meet these aims were:

- Undertaking a literature review of conservation and non-conservation literature to identify two alternative iron reducing agents, current conservation usage of SDT, and a chelator that efficiently sequesters iron ions
- Testing SDT and the alternative reducing agents on model rust stained cotton samples and unstained new cotton samples in immersive baths to evaluate their comparative rust stain removal efficiencies, working properties, and effects on new cotton fibres
- Evaluating if laboratory created rust stains are comparable test models for aged stains by treating rust stains on an historical cotton textile using the most efficient concentrations of the SDT and alternative reducing agents
- Making recommendations for optimised usage of each reagent based on testing outcomes

Both qualitative and quantitative methodologies were used to assess the effectiveness of the reducing agents and their effects on the cotton fibres. Qualitative methods involved visual analysis, bathophenanthroline indicator strips and low-power optical microscopy. Quantitative methods included spectrophotometry and pH measurements. Conclusions were made about SDT and the alternative reducing agents' rust stain removal efficiencies in a conservation treatment context.

2. Literature Review

2.1 Introduction

Rust stains on historical cotton textiles have been treated using all three types of dissolution (protonation, chelation, and reduction). This literature review focuses on reducing agents and aims to examine how sodium dithionite (SDT) has been used on cellulosic materials and its particular limitations in order to find a feasible alternative. It also aims to determine which chelator most effectively sequesters iron (II) ions. Literature from conservation and other fields such as soil science and historic laundering will be reviewed to inform alternative reducing agent options.

2.2 Sodium Dithionite

Conservation scientists Selwyn and Tse's comprehensive review of SDT's use and chemistry across conservation specialisms serves as a primer for rust stain chemistry and SDT treatments.⁴⁷ They highlight that despite SDT's broad usage, there is a gap in conservation publications about its chemistry.⁴⁸ The authors draw on soil science literature to fill this gap. The discussion of SDT's electric potentials is technical, but illustrates why SDT is most efficient at alkaline pH and less efficient at acid pH, which is useful when choosing treatment conditions.⁴⁹ They clearly explain the chemistry behind why aqueous SDT rapidly degrades by showing the reaction equation for SDT and dissolved oxygen in water. However, the accompanying graphs of SDT decomposition rates are for deaerated solutions and are not representative of conservation treatments.⁵⁰

An especially useful feature of Selwyn and Tse's article is a table comparing SDT usage up to the 2008 publication date.⁵¹ The textile conservation listings are fairly complete, including unpublished and less accessible sources such as Queen's University and the University of Rhode Island dissertations.⁵² However, it is missing research from the Textile Conservation Centre from Häkäri.⁵³ It

⁴⁷ Selwyn and Tse, "Sodium Dithionite."

⁴⁸ *Ibid.*, 61.

⁴⁹ *Ibid.*, 67–68.

⁵⁰ *Ibid.*, 68.

⁵¹ *Ibid.*, 63–65.

⁵² *Ibid.*, 64.

Note: Queen's University publications are inaccessible outside of Canada because of lending policies. This may also be why Häkäri's UK-based unpublished work was not included since the authors are from the Canadian Conservation Institute.

excludes generic recommendations for SDT usage often found in textile and paper conservation bleaching literature that could inform how SDT is used in treating cellulosic materials. Appendix C, inspired by Selwyn and Tse's table, includes generic literature and more recent publications, but excludes inaccessible sources such as Queen's University dissertations.

Throughout the literature, SDT is generally effective from 2-10% (w/v) and removes the most visible staining if it is used with a chelator (Appendix C). The variety of SDT concentrations and combinations of chelators does not allow for direct comparisons between sources, so concentrations are generally excluded from the following discussion unless they are noteworthy. Instead, different working parameters for SDT usage have been evaluated across the literature and are discussed below.

2.2.1 Application Method

SDT can be applied locally or in an aqueous immersion treatment. The majority of paper conservation publications discuss full immersion treatments, but almost all published textile conservation case studies discuss localised applications likely because rust stains are usually isolated on textiles.

Feniak's case study is the first published use of SDT on a textile (dyed and undyed cotton and silk).⁵⁴ The rust stains were "reduced to an acceptable level" by saturating the stains (application method unspecified), restricting wicking using blotting paper, and reapplying the solution and fresh blotter paper every few minutes.⁵⁵ The treatment details are vague, but she shows that SDT can be effectively applied locally.

⁵³ Anna Häkäri, "Removal of Rust Stains from Historic Cellulosic Textile Material" (MPhil diss., Courtauld Institute of Art, 1992).

⁵⁴ Christine J. Feniak, "Treatment of a Parasol Using a Reductive Bleach," *IIC-CG: Journal of the International Institute for Conservation, Canadian Group* 6, no. 1 (1981): 31–33.

⁵⁵ *Ibid.*, 31–33.

Bede's treatment of the Wright Flyer III's cotton wings 20 years later examined different localised SDT treatments. Dropping and swabbing the SDT solution insufficiently reduces the rust stains and the solution wicked onto the unstained fabric, bleaching it.⁵⁶

Both Potter and Bede report SDT degrading cellulose derivative gels for poultice treatments, but neither give specific SDT concentrations or explanations for gel structure failure. Bede notes that some unspecified methylcellulose would not form a gel and tested parameters including different types of methylcellulose, gel viscosity, treatment time, age of solution, and rinsing amount.⁵⁷ Potter states that SDT degraded the cell structure of Klucel G (hydroxypropylcellulose) gel.⁵⁸ For both authors, details about testing parameters and failed solutions are unpublished, but would have been useful as a starting point for other conservators. Bede ultimately formed a successful gel using Aqualon 7HC (carboxymethylcellulose).⁵⁹ Potter used Laponite (synthetic silicate) and Sepiolite (magnesium silicate).⁶⁰ Both report the formation of bleached halos after treatment using poultices.^{61,62} Potter used 7.5% SDT, which is higher than Bede's 2%.⁶³ Other research used 10% SDT bleaching.⁶⁴ The bleaching cause and SDT's incompatibility with some cellulose derivative gels are unclear and should be investigated.

All three authors applied their poultices multiple times (Feniak: unspecified, Bede: twice, Potter: three times) to fully remove the rust staining.⁶⁵ Poultices with SDT may require multiple applications, but treatment parameters (poultice material and additives like chelators) were inconsistent so direct comparisons cannot be made.

Textile conservation graduate research projects have shown that full immersion treatments do not always necessitate multiple applications of SDT. Margariti removed all visual staining using SDT with various pH adjustments and additives in a single bath and then successfully removed staining from a sampler tacking margin.⁶⁶ It is notable that case studies of immersive treatments are limited to paper conservation, likely because textiles often have components such as dyed materials that may

⁵⁶ Deboarah Bede, "Conservation of the Wright Flyer III: Serendipity and Substantiation," in *Strengthening the Bond: Science and Textiles. Preprints of the North American Textile Conservation Conference* (Philadelphia: North American Textile Conservators Conference, 2002), 22.

⁵⁷ Bede, "Wright Flyer," 22.

⁵⁸ Potter, "Rust Removal," 42.

⁵⁹ Bede, "Wright Flyer," 22.

⁶⁰ Potter, "Rust Removal," 42–43.

⁶¹ *Ibid.*, 50.

⁶² Bede, "Wright Flyer," 23.

⁶³ Potter, "Rust Removal," 50.

⁶⁴ Håkari, "Removal of Rust Stains."

⁶⁵ Feniak, "Parasol," 32; Bede, "Wright Flyer," 22; Potter, "Rust Removal," 48.

⁶⁶ Christina Margariti, "The Use of Chelating Agents in Textile Conservation: An Investigation of the Efficiency and Effects on the Use of Three Chelating Agents for the Removal of Copper and Iron Staining from Artificially Soiled Cotton Fabric" (MPhil diss., University of Southampton, 2002), 88.

be affected by SDT. Case studies about SDT use in textile conservation are few and none have been published in recent years, perhaps signalling a hesitation to use SDT in practice.

2.2.2 Treatment Time

Immersion treatments can increase the working time of SDT and decrease the treatment time needed. Häkäri demonstrated that 10% SDT with 0.1 M EDTA heated to 45-50°C can remove most staining from artificially stained cotton and barkcloth samples in an hour.⁶⁷ Fredette and Margariti showed the fastest treatment times of all the literature by removing historical and artificial rust stains in 10 to 15 minutes using different concentrations of SDT and different additives.⁶⁸ Treatment times have been extended in paper conservation, such as Gent and Rees's treatment of a photograph for 22 hours in 8% SDT with 0.1 M EDTA at pH 8.5.⁶⁹ Fully immersing objects during treatment helps to limit the amount of oxygen that can accelerate the degradation of SDT.

2.2.3 pH Adjustments

Selwyn and Tse illustrate rapid SDT's degradation with decreasing pH, though no rates are provided.⁷⁰ The pH requirements for SDT solutions and rust removal conflict: iron (III) ions cannot be reduced at alkaline pH, so neutral or acidic pH is necessary despite acid-catalysed degradation of SDT. They recommend near neutral pH when treating acid-sensitive materials (like cellulose).⁷¹ In practice, conservators have adjusted their solution pH from 3.5 to 9 (Appendix C). Alkaline conditions are used when EDTA is included as a chelator to prevent its degradation in acidic conditions.⁷² This illustrates the often conflicting solution conditions that must be balanced by conservators when making treatment decisions.

Conservators have come to the same conclusions as chemists about pH catalysed SDT degradation trends, but without providing detailed decomposition explanations. Feniak added 1% (v/v) ammonium hydroxide to extend the life of her SDT solution, though it was only active for about 5

⁶⁷ Häkäri, "Removal," 22, 30.

⁶⁸ Margariti, "Chelating Agents Investigation," 88; Tess Fredette, "The Identification and Removal of Iron Stains from Historic White Cotton" (MS thesis, University of Rhode Island, 1998), 78.

⁶⁹ Megan Gent and Jacqueline Rees, "A Conservation Treatment To Remove Residual Iron From Platinum Prints," *The Paper Conservator* 18, no. 1 (1994): 93, doi:10.1080/03094227.1994.9638592.

⁷⁰ Selwyn and Tse, "Sodium Dithionite," 68.

⁷¹ *Ibid.*, 69.

⁷² Gent and Rees, "Conservation Treatment," 93.

minutes at the elevated pH. She reflectively observes after the treatment that SDT without pH adjustments (no pH is reported) is stable for about one hour.⁷³ Selwyn et al. tested temperature, oxygen exclusion, different chelators, and pH adjustments of SDT treatments of paper test surrogates for a marine wood treatment.⁷⁴ The comprehensive article answers many questions that were raised in Selwyn and Tse's review of SDT literature. Specifically, Selwyn et al. showed that SDT treatments are faster and more effective at pH 5 (30 minutes) than an unadjusted pH (45 minutes).⁷⁵ Margariti also tested the effects of adjusting the pH to 6, 7, and 8 for SDT solutions on cotton and concluded that both with and without a chelating agent, SDT removed more staining and worked most quickly at pH 6.⁷⁶ Lower pH conditions (5 to 6) may therefore increase SDT's efficiency in practice.

2.2.4 Temperature

Many aqueous treatments are ideally undertaken near or at room temperature since heat can accelerate the degradation of fibres.⁷⁷ Selwyn and Tse show that heat has been proven to increase iron oxide dissolution rates and accelerate SDT decomposition in non-conservation publications.⁷⁸ This was proven by Feniak and Häkäri, who both heat their SDT solutions to 45°C.⁷⁹ Neither cite the temperature recommendations' origins. Selwyn et al. investigate the effects of temperature on SDT on paper: 22°C (room temperature) and 35-44°C are tested. Again, temperature choice was not explained, but the results demonstrated that heated SDT solutions became ineffective after a few hours. Solutions at room temperature could still be used to remove some iron staining the following day.⁸⁰ This research therefore supports the general practice seen in paper and textile conservation literature of using SDT at room temperature.

⁷³ Feniak, "Parasol," 33.

⁷⁴ Lyndsie Selwyn et al., "Iron Stain Removal from Archaeological Composite Artifacts Made of Wood and Iron," *Journal of the Canadian Association for Conservation* 38 (2013): 31–42.

⁷⁵ *Ibid.*, 37.

⁷⁶ Margariti, "Chelating Agents Investigation," 34–35.

⁷⁷ Tímár-Balázsy and Eastop, *Chemical Principles*, 35–36.

⁷⁸ Selwyn and Tse, "Sodium Dithionite," 70.

⁷⁹ Feniak, "Parasol," 32; Häkäri, "Removal," 22.

⁸⁰ Selwyn et al., "Iron Stain Removal," 35–36.

2.2.5 Effects on Fibres

Examination of changes to cotton fibres has been mainly carried out in graduate research projects and some of the results are conflicting. Suryawanshi found a decrease in the folding strength of paper treated with SDT, indicating some tensile strength loss.⁸¹ Contradictorily, Margariti found a slight increase in the tensile strength of cotton fabric after artificial ageing and SDT treatment.⁸² Hawley showed that tensile strength of paper treated with SDT was mostly unaffected.⁸³ Fredette used Harrison's Silver Test for aldehyde reducing groups and Turnball's Blue Test for carboxyl groups and detected chemical changes caused by SDT treatments, but did not carry out any further testing of the fabric properties to quantify any fibre damage.⁸⁴ All of these results indicate a need for further exploration of SDT's effects on cellulosic fibres to build on available research. More sophisticated analytical techniques like scanning electron microscopy (SEM) could help conservators gain better understandings of the microscopic changes that may be occurring during treatment.

Häkäri's monitors changes in fibres by measuring pH changes and examining treated cotton fibres using optical microscope as a conservator would in practice. She reported no visual changes to the fibres (though her examination criteria are undefined) and the pH of her samples remained fairly consistent.⁸⁵ Hawley also recorded consistent pH readings on paper.⁸⁶ Generally researchers conclude that because of SDT's neutral or near neutral pH, there will be no degradative effects to the fibres.⁸⁷ This conflicts with some of the above investigations. Selwyn and Tse's comprehensive literature review of SDT does not include any discussion of the effects of SDT on organic fibres, nor do subsequent publications. Even though SDT has been proven to efficiently remove iron staining, there is still a gap in the literature about its effects on cotton textile fibres.

⁸¹ D. G. Suryawanshi and S. K. Bisaria, "Removing Metallic Stains from Paper Objects Using Chelating Agent EDTA," *Restaurator* 26, no. 4 (2005): 282–83, doi:10.1515/REST.2005.276.

⁸² Margariti, "Chelating Agents Investigation," 65–66.

⁸³ Janet K. Hawley, Elizabeth A. Kawai, and Christopher Sergeant, "The Removal of Rust Stains from Arctic Tin Can Labels Using Sodium Hydrosulfite," *IIC-CG: Journal of the International Institute for Conservation, Canadian Group* 6 (1981): 19.

⁸⁴ Fredette, "Identification and Removal," 80–82.

⁸⁵ Häkäri, "Removal," 24–27.

⁸⁶ Hawley, Kawai, and Sergeant, "Removal," 19.

⁸⁷ Selwyn et al., "Iron Stain Removal," 40.

2.2.6 Chelators as Additives

Though SDT alone can remove rust stains, conservation literature generally shows that including a chelator aids in iron stain removal.⁸⁸ Chelators alone do not cause dissolution quickly and only the soluble iron (II) ions are sequestered, leaving the iron (III) ions behind.⁸⁹ Chelators are examined here as additives to SDT solutions rather than as a separate treatment method.

Chelators are included in the same solution as SDT in most case studies. Selwyn et al. found no appreciable difference between combining a chelator and SDT or treating samples in separate subsequent baths, but testing was carried out in stoppered beakers to exclude air that could re-oxidise the iron staining.⁹⁰ This testing method is ideal in minimising degradation caused by oxygen but does not represent a practical treatment like a large immersive bath where air cannot be fully excluded. Best practice is to include chelators in SDT solutions.

Many different chelators have been tested with SDT and at varying concentrations. Burgess's 1991 article has persevered as a primer of chelators and includes a section about iron stain removal on paper.⁹¹ She recommends using a 0.1 M solution of EDTA adjust to pH 7 to 8 and a 2% (w/v) SDT solution to remove iron staining because of EDTA's six coordination sites and strong affinity for iron (II) and (III) ions, though she contradicts herself by stating that EDTA will not chelate iron oxyhydroxides at alkaline pH.⁹² This specific recommendation has often been referenced in subsequent literature.⁹³ Gent and Rees treated a platinum print with 8% SDT and 0.1 M EDTA and found with ED-XRF (energy dispersive x-ray fluorescence) examination that all calcium and zinc fillers had been removed during treatment.⁹⁴ EDTA binds other non-ferrous cations and can possibly be too aggressive for some treatments. Lockwood examined the chelators sodium tripolyphosphate (STPP), diethylenetriaminepentaacetic acid (DTPA), and dihydroxyethylglycine (DHEG) in SDT solutions. STPP was the most effective chelator for paper, but has not been extensively reported in textile conservation.⁹⁵

⁸⁸ Selwyn and Tse, "Sodium Dithionite," 62.

⁸⁹ Christina Margariti, "The Use of Chelating Agents in Textile Conservation," in *Dust, Sweat and Tears: Recent Advances in Cleaning Techniques* (London: United Kingdom Institute for Conservation of Historic and Artistic Works, 2003), 33.

⁹⁰ Selwyn et al., "Iron Stain Removal," 38.

⁹¹ Burgess, "Chelating Agents."

⁹² *Ibid.*, 37–38.

⁹³ Bede, "Wright Flyer," 22.

⁹⁴ Gent and Rees, "Conservation Treatment," 93.

⁹⁵ Kenneth Lockwood, "The Effectiveness of Selected Chelate-Reducing Agent Systems in the Removal of Iron Stains from Paper," in *Art Conservation Training Programs Conference, Cambridge, Massachusetts, Center for Conservation and Technical Studies* (Cambridge: Harvard University Art Museums, 1984), 93.

Chelators with more specific affinities for iron ions have been explored. Oxalic acid is a chelator and acid.⁹⁶ Burgess suggests that though acids are effective at removing iron stains, a pH below 4 can damage cellulosic fibres, which is why acids at that point (1991) were not recommended for iron stain treatment.⁹⁷ Tímár-Balázsy and Matefy reported tensile strength loss on cotton treated with oxalic acid.⁹⁸ It has not been tested in combination with SDT, likely because its low pH would rapidly degrade the SDT solution.

A compelling case for citrates has been made by Phenix.⁹⁹ He provides a more detailed primer than Burgess's and explains how factors like pH affect the efficiency of different chelators. Though his focus is on painting conservation, the information is relevant to sequestering iron staining. Citrates and their various salts have the highest stability constants (and therefore best binding ability) with iron (III) ions up to pH 8 and will preferentially bind iron ions in solution.¹⁰⁰ They also act as mild buffers with each salt performing best within different pH ranges. Tri-sodium citrate (TSC) and tri-ammonium citrate (TAC) have been used in textile conservation. At 5%, TAC's pH range is 6.0-7.5 while TSC's is 7.5-9.0.¹⁰¹ The lower pH range of TAC is better suited to the neutral and mildly acidic pH ranges conducive to rust stain removal using SDT.

Comparative investigations of TAC and TSC in textile conservation have conflicting results. Adler and Eaton found that TAC is as effective as TSC, but TSC was preferable because of its lower cost.¹⁰² Margariti's publication of her dissertation research states that TAC removed more staining than TSC and EDTA.¹⁰³ TAC may be a good chelator for use in textile conservation treatments with SDT because of its better efficiency over EDTA and lower buffering pH range than TSC.

2.3 Alternative options

While SDT has been proven as an effective rust stain reducing agent, its limited and non-standardised use in conservation literature suggests a hesitation in the field to utilise it.

⁹⁶ Burgess, "Chelating Agents," 36.

⁹⁷ *Ibid.*, 39.

⁹⁸ Ágnes Tímár-Balázsy and Gyork Matefy, "Effects of Stains and Stain Removal on Historic Textiles," in *ICOM Committee for Conservation 10th Triennial Meeting Washington, DC, USA 22-27 August 1993* (Washington, D.C.: ICOM Committee for Conservation, 1993), 334.

⁹⁹ Alan Phenix and Aviva Burnstock, "The Removal of Surface Dirt on Paintings With Chelating Agents," *The Conservator* 16, no. 1 (1992): 29, doi:10.1080/01400096.1992.9635624.

¹⁰⁰ Phenix and Burnstock, "Removal," 29.

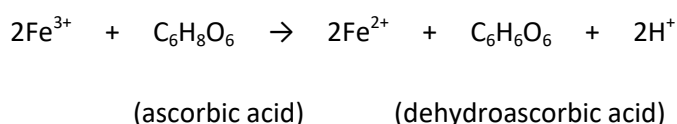
¹⁰¹ *Ibid.*

¹⁰² Susan Adler and Linda Eaton, "Chelating Agents in Wet Cleaning Systems," *AIC Textile Specialty Group Postprints* 5 (1995): 76.

¹⁰³ Margariti, "Use of Chelating Agents," 33.

Research into reducing agents has been limited in textile and paper conservation: most comparative studies of SDT examine other chelators and acids.¹⁰⁴ Literature from other fields dealing with these rust oxides can provide suggestions for reducing agents. Soil scientists and geochemists have extensively studied the reductive dissolution of goethite and lepidocrocite. A recurring theme is ascorbic acid. Houben examines various reducing agents and chelators to remove iron oxides in wells and is thoroughly referenced.¹⁰⁵ He examines goethite and ferrihydrite interactions and shows that, as in textile conservation, SDT and oxalic acid can fully dissolve goethite.¹⁰⁶ Ascorbic acid, the second most effective reducing agent, did not fully dissolve the goethite, but it may still be a viable option.¹⁰⁷

Dos Santos Afonso et al. also reduced iron oxides like hermatite and magnetite using ascorbic acid, but showed that chelators like EDTA and oxalate can slow treatment times.¹⁰⁸ The authors also show that ascorbic acid causes iron oxide dissolution most effectively at pH 3 to 4, but that dissolution still occurs regardless of ascorbic acid's protonation state.¹⁰⁹ Elmagirbi et al.'s research into alternative reducing agents for spectrophotometric measuring of iron (II) ions confirms this pH range (maximum efficiency at pH 3, but tested through pH 5) and provides a reaction equation for iron and ascorbic acid:¹¹⁰



Reaction 13 Ascorbic acid reduction of iron (II) ions

Ascorbic acid is mentioned in *Chemical Principles of Textile Conservation*, but without references.¹¹¹ No previous applications in textile conservation were found. It is also recommended as a reducing

¹⁰⁴ Håkari, "Removal of Rust Stains," 14–16.

¹⁰⁵ G. J. Houben, "Iron Oxide Incrustations in Wells. Part 2: Chemical Dissolution and Modeling," *Applied Geochemistry* 18, no. 6 (2003): 941–54, doi:10.1016/S0883-2927(02)00185-3.

¹⁰⁶ *Ibid.*, 953.

¹⁰⁷ *Ibid.*

¹⁰⁸ Maria Dos Santos Afonso et al., "The Reductive Dissolution of Iron Oxides by Ascorbate," *Journal of Colloid and Interface Science* 138, no. 1 (1990): 78–81, doi:10.1016/0021-9797(90)90181-M.

¹⁰⁹ *Ibid.*, 77.

¹¹⁰ Elmagirbi, Sulistyarti, and Atikah, "Ascorbic Acid," 13–15.

¹¹¹ Tímár-Balázs and Eastop, *Chemical Principles*, 239.

agent for testing with bathophenanthroline indicator test strips to specifically reduce iron (III) ions to iron (II).¹¹²

Ascorbic acid is also known as Vitamin C. Carter cites historical laundry suggestions such as lemon juice to remove rust staining.¹¹³ Restoration literature also recommends using lemon juice to remove rust stains from washable white fabrics.¹¹⁴ Ascorbic acid therefore may be a viable alternative reducing agent to SDT.

Paper conservation also deals with cellulosic materials and can provide suggestions. However, as with textile conservation, little research has been published about reducing agents. Instead the focus is primarily on chelators. One article stands out: Irwin, a paper conservator in Alaska, could not use SDT because its combustion risk prevented shipping via air carrier and the conservation lab was not equipped with fume extraction. Irwin instead tested sodium metabisulfite because it is chemically similar to SDT (Fig. 3).¹¹⁵

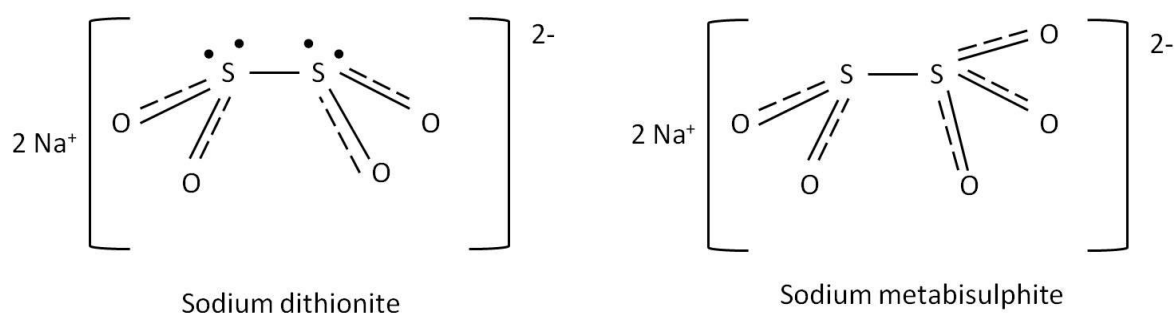


Fig. 3 SDT and SMB molecules

Using several immersive treatments over several days, Irwin successfully used 10% sodium metabisulfite (SMB) and 10% EDTA to reduce rust staining from paper.¹¹⁶ He proposes that SMB is a viable alternative because both SDT and SMB react with water to form sodium bisulfite and hydrogen atoms which allow for the reductive dissolution of iron oxides (Reaction 14).¹¹⁷

¹¹² Johan G. Neevel, "Application Issues of the Bathophenanthroline Test for Iron(II) Ions," *Restaurator* 30 (2009): 4.

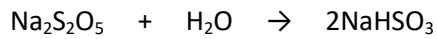
¹¹³ Carter, "Iron Stains," 84.9.11.

¹¹⁴ Lorraine Johnson, *How to Restore and Repair Practically Everything* (London: Michael Joseph Ltd, 1977), 122.

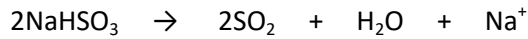
¹¹⁵ Seth Irwin, "A Comparison of the Use of Sodium Metabisulfite and Sodium Dithionite for Removing Rust Stains from Paper," *The Book and Paper Group Annual* 30 (2011): 37.

¹¹⁶ *Ibid.*, 39.

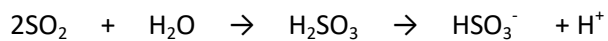
¹¹⁷ *Ibid.*, 40.



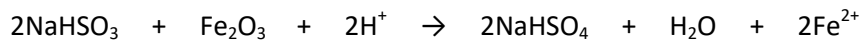
(SMB) (sodium bisulfite)



(sulfur dioxide)



(sulfurous acid)



(generic iron oxide)

(soluble iron (II) ions)

Reaction 14 SMB goes through a series of reactions to ultimately reduce iron (III) to iron (II)

Irwin tested SMB and SDT after the treatment with SMB presumably in a lab with extraction. 10% SDT with 10% EDTA visually removed rust staining in four hours with a single bath, while 10% SMB with 10% EDTA took three bath changes and 24 hours to remove the staining and higher concentrations precipitated in solution.¹¹⁸ The SMB samples remained near pH 6 throughout treatment.¹¹⁹ Irwin concluded that because SMB removed most staining in practice and in testing, SMB can be a viable alternative when SDT is too expensive or not feasible for health and safety reasons.¹²⁰ His research shows potential for SMB to be applied to other cellulosic materials like cotton textiles, though treatment times will likely not be faster than those with SDT.

¹¹⁸ Ibid., 42.

¹¹⁹ Ibid.

¹²⁰ Ibid., 44–45.

2.4 Conclusion

SDT treatments of rust staining have not been widely published in the field of textile conservation, especially in practical case studies. Despite its clear efficiency in removing iron staining, more evaluation of SDT's effects on cellulosic fibres is needed. Many chelators have been explored for use with SDT, but TAC appears to be the most efficient for cellulosic materials. Alternative reducing agents were found in other fields. SMB was moderately effective in paper conservation and may be translatable to textile conservation, while ascorbic acid is effective in soil science. No studies in conservation compare these reagents, so sodium metabisulfite and ascorbic acid will be tested alongside sodium dithionite to evaluate which is the most efficient reducing agent to remove rust stains on cotton fabrics. Their working properties will be established, the stain removal efficiencies will be evaluated, and their effects on the cotton fibres will be investigated.

3. Testing Procedures

3.1 Introduction

In order to compare sodium metabisulfite (SMB) and ascorbic acid (AA) to sodium dithionite (SDT), each reducing agent should be tested and evaluated on similar rust stains. Three questions were used to guide treatment and analytical testing choices:

1. Is this a reasonable and practical conservation treatment option?
2. How much of the stain is removed?
3. What are the effects on the fibres?

The rationale and specific procedures chosen to answer these questions are discussed in this chapter.

3.2 Rust Stained Model Sample Preparation

Rust Stained Fabric

Ideally the reagents would be tested on naturally aged rust stained cotton fabric, but finding enough comparably stained fabric samples was impractical. Commercially produced standardised test fabrics were considered, but they are made from rust particulate applied to the fabric surface rather than being ingrained stains, so they were not used.¹²¹ Instead, rust stained model samples were created.

Previous conservation researchers have created models either through contact staining or chemically creating iron oxides. Chemically produced staining is the purest form of rust staining because it excludes other metal ions in metal alloys from contact with wetted iron.

Recipes for chemically creating rust staining in conservation texts typically use ferrous sulfate and a base without explanation of the iron oxide product mechanism or why the chemicals were chosen. The base likely provides the hydroxide ions to form the rust. Chemists have created used these

¹²¹ Heather Woodruff, Science Services S/D, Inc., email message to author, 10 April 2017.

reagents to create iron oxides at temperatures below 35°C and confirmed the presence of lepidocrocite and goethite - the typical iron oxides of rust.¹²²

Initial recipe testing is in Appendix F. Morton's recipe was chosen because it was the most heavily stained.¹²³

A single 900 mm x 800 mm piece of cotton lawn fabric was used to create a bulk sample from which smaller samples would be cut. This ensured consistent conditions across all samples. The bulk sample was created using 5% w/v ferrous (II) sulfate solution (175 g in 3500 mL tap water) for 10 minutes, stirring the fabric constantly to ensure even deposition, air drying it overnight, then immersing it in 10% v/v ammonium hydroxide (350 mL of 35% concentrated solution in 3150 mL of tap water) for 20 minutes, stirring constantly. The fabric was rinsed in tap water to remove any excess solution and air dried.¹²⁴

The ferrous sulfate deposited less evenly on the fabric than in the smaller initial test samples, causing stripes that varied in colour from pale orange to dark brown (Fig. 4). In contrast to Morton's recipe, the fabric was not oven dried to remove thermal ageing as an additional testing variable. Iron oxides are transformed at temperatures exceeding 100 °C, so it is unlikely that the recipes were significantly altered by excluding this step.¹²⁵

The stained fabric was ironed at a cool setting to remove wrinkles that could interfere with later spectrophotometry measurements and cut into 80 x 120 mm samples to fit inside the bath trays. Because of the uneven staining of the fabric, samples were chosen that contained each shade of colour if possible - 55 samples were retained for testing. The upper right corner of each sample was cut off at an angle to help orient the samples throughout testing. Five replicates were retained and labelled for each solution to be tested. The samples for each set were chosen from different areas around the original large piece of fabric to ensure all types of staining were represented. Each set contained one heavily stained, one lightly stained, and one evenly stained sample (Fig. 5).

¹²² E. Yu. Karateena et al., "Effect of Synthesis Conditions on the Size and Aspect Ratio of Acicular Iron(III) α-Oxyhydroxide Particles Prepared in the FeSO₄-H₄O₂-H₂O System," *Inorganic Materials* 37, no. 1 (2001): 39, doi:10.1016/S0167-577X(03)00508-1.

¹²³ Jennifer Morton, "Calcium Phytate: A Treatment for Degraded Tacking Margins," 2012, <http://www.queensu.ca/art/sites/webpublish.queensu.ca.artwww/files/files/JenniferMortonposter.pdf>.

¹²⁴ NH₄OH is often sold as a diluted solution (ex. 28% or 35% concentrated from Fisher Scientific), but Morton does not detail any dilution equations. The recipes list the percentages as v/v so it was assumed that no compensation was made and the solutions used were 10% based on volume of the solution from the supplier. This could have resulted in a discrepancy between the recipes, but the staining product was satisfactory.

¹²⁵ Cornell and Schwertmann, *Iron Oxides*, 528-540.



Fig. 4 Full stained fabric before cutting samples



Fig. 5 Typical sample set of five replicates

3.3 Unstained Fabric

The staining can obscure changes to the fibres, so the reagents were also tested on unstained samples to evaluate their effects. Twenty-five 80 mm x 120 mm samples of original (unstained) cotton lawn fabric were cut from the same bolt of fabric. The highest concentrations that were deemed feasible for treatment for each reagent were tested using the same conditions as the stained samples to determine if any colour changes, dimensional changes, or breakage of the fibres occurred.

3.4 Sample Treatment Procedure

The literature review revealed SDT treatment practices are inconsistent. Neither SMB nor AA has previously been tested on cotton textiles. Preliminary test treatments were performed to find the most effective concentration of each reducing agent. The solutions were prepared with deionised (DI) water (model B114 Deioniser) to limit water contaminants. Triammonium citrate (TAC) was used as the chelator in each solution because it is most effective in the low pH to neutral pH range expected of the reagents being tested.¹²⁶ To limit the testing variables, the TAC concentration was kept constant. Per literature suggestions, 5% (w/v) TAC was used.¹²⁷ Five replicates of each reducing agent concentration were tested to gain statistically significant data sets. The 5% TAC solutions were

¹²⁶ Phenix and Burnstock, "Removal," 29.

¹²⁷ Potter, "Rust Removal," 44.

tested to evaluate how much of the staining reduction could be attributed to the chelator. Stained controls were immersed in DI water to evaluate the effects of water. SDT percentages vary from 2 to 10% (w/v), though multiple sources agree that 5% (w/v) is the maximum effective concentration.¹²⁸

For SMB, Irwin recommends 10% (w/v) and observed that concentrations exceeding 10% degrade quickly in solution forming a white precipitate over time.¹²⁹ A 15% SMB solution was preliminarily tested without rust stained fabric and turned yellow after about 20 minutes, possibly indicating rapid degradation of the solution. 10% was established as the upper limit and lower percentages were tested that mirrored SDT percentages to compare (though percentages do not equate to stoichiometric equivalents). Irwin's white precipitate may have been an interaction of the EDTA and SMB.

Initial tests for AA were carried out using solutions ranging from 5% to 20% on rust stained fabrics (procedure in Section 3.5). The pH of each solution was measured. Concentrations above 15% were below pH 4 and were expected to cause rapid acid hydrolysis of the cotton fibres, so the maximum concentration of AA used was 15%. The test solutions are outlined in Table 1.

Set Label	Reducing Agent	Reducing agent concentration (w/v)	Chelator concentration
SDT 1-5	Sodium dithionite	1%	5% (w/v) Tri-ammonium citrate used in each solution
SDT 6-10		2%	
SDT 11-15		5%	
SMB 1-5	Sodium metabisulfite	2%	
SMB 6-10		5%	
SMB 11-15		10%	
AA 1-5	Ascorbic acid	5%	
AA 6-10		10%	
AA 11-15		15%	
TAC 1-5	Tri-ammonium citrate	5%	No additional chelator added
C 1-5	None - tested only in DI water		

Table 1 Preliminary test treatment solutions

¹²⁸ Ibid., 52; Fredette, "Identification and Removal," 76–78.

¹²⁹ Irwin, "Comparison," 43.

Test treatments were performed in shallow plastic trays using 70 mL solutions to create a bath of about 5 mm depth, which is typical of wet cleaning treatments and allowed for economical use of reagents. Examples of the weight calculations for each reagent are below:

Equation: Percentage x total volume = mass used

$$1\% \quad 0.01 \times 70 \text{ mL} = 0.07 \text{ g}$$

$$2\% \quad 0.02 \times 70 \text{ mL solution} = 1.4 \text{ g}$$

$$5\%: \quad 0.05 \times 70 \text{ mL solution} = 3.5 \text{ g}$$

$$10\% \quad 0.10 \times 70 \text{ mL solution} = 7 \text{ g}$$

$$15\% \quad 0.15 \times 70 \text{ mL solution} = 10.5 \text{ g}$$

Test treatments were done in the fume hood to limit exposure to toxic sulfur dioxide gas evolved by the SDT and SMB.¹³⁰ The samples were agitated by tipping the trays back and forth and side to side every two minutes during treatment. A sponge was not used during this testing to minimise mechanical action on the fibres for a truer evaluation of the reagents' effects on the fibres and pure capability of removing the stains.

The samples were immersed in the solutions until two minutes after all staining appeared to be removed to ensure full reaction of the reducing agents or for one hour (the typical length of a wet cleaning treatment) - whichever occurred first. The samples were rinsed in DI water for two minutes (using approximately 2 litres of DI water) after treatment to remove any remaining reagent residues and solubilised rust staining.

3.5 Testing Methods and Procedures

Each method of testing was done on the same day if possible to ensure testing and the instruments were calibrated each day. A Melinex® (polyester film) template overlay was created for each sample

¹³⁰ Selwyn and Tse, "Sodium Dithionite," 70.

to help locate each test's measurement area. All tests were carried out before treatment (BT) and after treatment (AT).

3.5.1 Visual Analysis

All replicate sets were photographed as a visual record treatment effects.

3.5.2 Evaluation Framework

An evaluation framework for working properties was devised to determine if each reagent could be a reasonable and practical conservation treatment option. Factors like treatment method (immersion or spot treatment), treatment length, solution pH, treatment cost, and health and safety concerns can all be vital factors when deciding if and how to treat a stain.¹³¹ Spot treating rust stains near sensitive materials like dyes are often ideal. However, spot treatment is difficult to control for the purpose of testing and would add another variable affecting the fibres. Immersion was chosen as the treatment method.

The cost of each treatment was calculated and tabulated (Appendix I). Also, health and safety risks and requirements for each reagent were noted (Appendix E).

The pH of the solutions was measured using a Hanna Instruments HI 9024 pH meter with a flat-headed electrode because the reducing agents can interfere with pH test strip results.¹³² It was calibrated and stabilised for about one hour each day to produce consistent measurements. The solutions' pH before treatment was measured before immersing the textile to prevent any immediate reaction from affecting the measurement. The solutions' pH AT was measured while the textile was immersed to measure the final local environment.

3.5.3 Surface pH Testing

Rust stains are acidic, so the pH of the fabric AT should be slightly more alkaline after the removal of the rust staining. A pH below 4 will likely cause severe cellulose degradation - an important consideration for ascorbic acid treatments.¹³³ Ideally, fabric pH measurements are measured by

¹³¹ Tímár-Balázsy and Eastop, *Chemical Principles*, 237.

¹³² Burgess, "Chelating Agents," 40.

¹³³ Burgess, "Chelating Agents," 39.

taking samples and the pH is extracted using the cold extract method. This type of destructive sampling is often not possible for historical textiles. Instead, surface pH can be measured by dampening a pH electrode or paper strip and holding it in contact with the textile surface. This method is less accurate than pH extraction, but it is ideal for non-destructive testing.¹³⁴ An electric pH meter will be used throughout testing to ensure the consistency of pH measurement technique.

The pH of the textile was measured by pipetting five drops of DI water onto the textile when it was dry, allowing the water to penetrate the fabric for two minutes, and using finger pressure to hold the fabric against the probe through a Melinex® barrier to ensure sufficient contact.

3.5.4 Bathophenanthroline

Visual evidence is not sufficient proof that a rust stain has been removed because colourless iron (II) ions can re-oxidise after treatment, causing colour reversion and continuing cellulose chain scission. Tests detecting the presence of iron ions before and after treatment can confirm if a stain has been fully removed. Chemical indicators can detect the presence of iron ions. The indicator bathophenanthroline is specifically reactive with iron (II) ions and can also detect iron (III) ions.¹³⁵ It is purchased commercially as Iron Gall Ink Test Paper from Preservation Equipment Ltd. (Appendix D). The Canadian Conservation Institute has developed a scale that helps to estimate the amount of iron present in parts per million (ppm) based on the colour of the indicator with a lower limit of 10 ppm.¹³⁶ An efficient reducing agent should remove all iron ions so this scale was not used. Only the presence of iron ions was noted.

Only the stained samples were tested with the bathophenanthroline indicator paper strips because it was presumed that iron would not present in the new, unstained fabric. DI water was used to minimise metal ion contaminants in the water that could affect testing. Testing was carried out in the lower right corner of each sample despite the variation in the staining because an effective reducing agent should remove all rust.

The testing procedure followed the instructions included with the bathophenanthroline strips. The strips were cut into 10 mm x 10 mm pieces. To test for iron (II) ions, a drop of DI water was placed

¹³⁴ Tímár-Balázs and Eastop, *Chemical Principles*, 218.

¹³⁵ Neevel and Reißland, "Bathophenanthroline Indicator Paper," 31.

¹³⁶ Jan Vuori and Season Tse, "A Preliminary Study of the Use of Bathophenanthroline Iron Test Strips on Textiles," in *ICOM Committee for Conservation 14th Triennial Meeting the Hague 12-16 September 2005*, 2005, 991.

on the test strip and blotted with blotter paper so that it was damp. The strip was held with finger pressure on the testing area through a Melinex® barrier for 30 seconds, removed, and placed on a larger piece of Melinex® to allow the result to develop for five minutes. The development of a bright magenta colour indicated the presence of iron (II) ions. Historical iron nails were also tested as comparisons of rust. Controls with DI water were tested because past tests of the laboratory supply had indicated iron ion contaminants.

To check for the presence of water-insoluble iron (III) ions, a 1% w/v solution of ascorbic acid (1 g in 100 mL of DI water) was prepared according to the Iron Gall Ink Test Paper instructions. A deeper magenta colour indicates iron (III) ions. A single drop of ascorbic acid solution was dropped onto each sample and the papers were allowed to develop for five minutes.

3.5.5 Spectrophotometry

Spectrophotometry measures the wavelengths of light reflected or transmitted from an object. The human eye perceives based on a tristimulus (three colour: red, green, and blue) system.¹³⁷ The Commission International de l'Eclairage (CIE) has developed the CIE-LAB system to characterise the three colour components: lightness or value (L^*), red-green (a^*), and yellow-blue (b^*).¹³⁸ A spectrophotometer measures and plots the coordinates of these measurements to characterise a colour.¹³⁹ Specific iron oxides can be characterised by their colours, so spectrophotometry can be used to characterise the staining.¹⁴⁰ It can also quantitatively measure the colour change of samples to determine if iron oxides have been removed.

An effective reducing agent should have no harmful effects on the fibres, such as causing yellowing - an indicator of the cellulose degradation product oxycellulose.¹⁴¹ Spectrophotometry can also be used to monitor the possible development of yellowing on unstained samples since the staining could obscure some yellowing. Mild bleaching effects caused by SDT have been reported, which can also be monitored by spectrophotometry.¹⁴²

A Konica Minolta CM-2600d spectrophotometer with a 3 mm measurement area was used. Because of the variation in the staining between each sample, only one colour was chosen to be measured

¹³⁷ Cornell and Schwertmann, *Iron Oxides*, 131–32.

¹³⁸ *Ibid.*, 132.

¹³⁹ Tímár-Balázs and Eastop, *Chemical Principles*, 86–87.

¹⁴⁰ Cornell and Schwertmann, *Iron Oxides*, 133–34.

¹⁴¹ Tímár-Balázs and Eastop, *Chemical Principles*, 26.

¹⁴² Selwyn and Tse, "Sodium Dithionite," 69.

throughout testing. Visually, the medium orange areas most resembled rust found on historical iron nails that were used as comparisons. The spectrophotometer was used to identify these areas (marked on each sample's Melinex® template), which typically corresponded to the measurements listed in Table 2. Goethite and lepidocrocite can be identified using CIE lab measurements. Goethite typically corresponds to $a^* = 5-13$ and $b^* = 22-48$. Lepidocrocite typically corresponds to $a^* = 13-24$ and $b^* = 34-45$.¹⁴³ A variation of ± 2 was allowed which kept the measurements within the colour range for goethite.

Four measurements were taken at each location by turning the spectrophotometer to each compass point to compensate for stain deposition differences. The data was collected and averaged by the Konica Minolta Spectramagic NX software. Measurements should also be taken 3 times (with the average of four readings) at each site to compensate for instrument error, but this was not done due to time restrictions and the small measurement areas. Spectrophotometry measurements were taken of each stained and unstained sample to compare colour changes caused by the test treatments. Measurements for all unstained samples were taken in the same location.

Measurement	Values ± 2
L*	56
a*	22.5
b*	43.5
c*	49
h	62
Gloss	1
Standard deviation	< 2.0

Table 2 Spectrophotometry measurements BT

3.5.6 Microscopy

Physical damage to cotton fibres can occur through swelling and shrinkage of the fibres during treatment or through chemically induced chain scission.¹⁴⁴ Ideally, monitoring changes using SEM would have been ideal but was outside the budget for this project. Tensile testing was also

¹⁴³ Cornell and Schwertmann, *Iron Oxides*, 132.

¹⁴⁴ Tímár-Balázsy and Eastop, *Chemical Principles*, 23–25.

considered but was beyond the time limit of this research. Optical microscopy was used instead. Dino-Lite Optical Microscopes are hand-held microscopes with magnifications of 250x (model AM-4013ZT4) or 500x (model AM-3013T) which can allow for close optical monitoring of the cotton yarns. Though it is not as powerful as SEM, any observed damage would be a clear indication that a reducing agent was an inappropriate option. Fibre widths can also be measured using optical microscopy imaging software, so dimensional changes to fibres can be monitored as well. Cotton fibres were examined using a Carl Zeiss™ Axiolab optical microscope at 10x and imaged using an 105 color Axiocam. As with the bathophenanthroline indicator testing, examination and samples were taken from the lower right corner of each sample. All stained and unstained samples were examined and imaged before and after treatment. Yarns and fibres were examined for splitting, swelling, and breakage of the fibres caused by treatment with the reagents.

3.6 Historical Object Treatment Case Study

After the results of the sample treatment testing are examined, the most effective concentration of each reagent was determined based on completeness of stain removal and the solution's effects on the fibres. This solution was used to reduce rust stains on an historic object. It was examined before and after treatment using the procedures described above for spectrophotometry, bathophenanthroline indicator paper, microscopy, and pH measurements of the solutions and fabric. Melinex® templates were created to ensure consistent testing locations.

4. Testing Results and Discussion

4.1 Introduction

The results are presented from the test treatments using SDT, SMB, and AA on rust stained and unstained cotton using the procedures described in Chapter 3: Testing Procedures. Although not specifically noted in subsequent discussions and illustrations, the 5% TAC chelator was added to each SDT, SMB, and AA solutions. Each method of analysis will be described separately. Stained sample treatments were performed first, which informed the choice of the most effective concentration chosen for further analysis on unstained fabric. Conclusions were drawn about each reagent's overall effectiveness as an iron stain reduction treatment.

4.2 Stained Samples

4.2.1 Visual Analysis

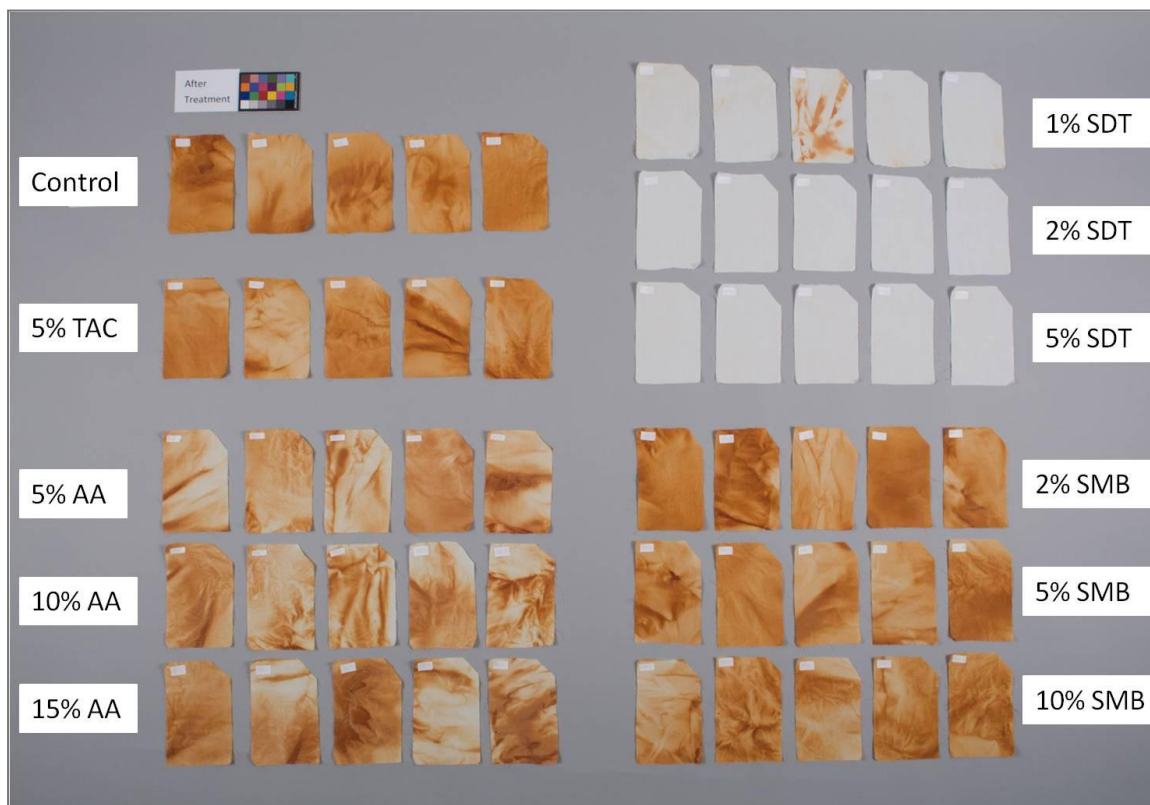


Fig. 6 All stained samples AT

All SDT treatments removed most of the visible staining (Fig. 6). The darkest staining on the samples treated with 1% SDT were not entirely removed possibly because there was not enough SDT in solution to fully reduce the extensive staining (Figs. 7-8).



Fig. 7 1% SDT samples BT



Fig. 8 1% SDT samples AT

The lightest staining was slightly reduced on all of the SMB samples, with 10% removing the most staining (Figs. 9-10). The AA treatments reduced more, but not all, staining as the concentration increased, especially the lightest (presumably lepidocrocite) staining, (Figs. 11-12). The 5% TAC and DI water control samples staining did not appear to change after treatment. See Appendix G for all before and after treatment images.



Fig. 9 10% SMB samples BT



Fig. 10 10% SMB samples AT



Fig. 11 15% AA samples BT



Fig. 12 15% AA samples AT

4.2.2 Working Properties

The working properties (treatment time, pH, cost, observations, and health and safety) of the test treatments are discussed below and summarised in Table 3.

Treatment Time

The SDT worked fastest (10 to 20.2 minutes) to remove the staining of all the reagents. The treatment time decreased with increasing concentration. None of the other reagents fully removed the staining so the treatments were concluded after 60 minutes. Further treatment time may have produced different results, but would not necessarily be representative of treatments in practice.

Solution pH

The pH of every solution decreased except the 10% and 15% AA solutions, which negligibly increased. The general pH decrease was likely partly due to the release of acidic iron staining, though even the control samples' pH decreased 0.1 pH unit when treated in DI water. In SDT and SDM samples, the pH decrease could also be due to the degradation of the reagents in solution. SDT solutions had larger pH decreases over a shorter time when compared to SMB, underscoring its short working life.

Treatment Cost

Costs were calculated using the amount of reducing agent and TAC used in the 70 mL baths and do not include reagent shipping, VAT, or DI water (Appendix I). AA treatments were the most expensive, while the same concentrations of SMB and SDT had similar costs.

Health and Safety

SDT and SMB have similar health and safety concerns, but SDT had a stronger smell when the reagent bottle was opened for treatment.^{145, 146} AA and TAC are safer to use.^{147, 148}

Observations

Some observations could affect the reagents' use in practice. TAC's large crystals take vigorous stirring to dissolve which can aerate solutions so SDT was added after the TAC was dissolved to limit the SDT decomposition.

The SMB solutions all yellowed during treatment (slower with increasing concentration), as was reported by Irwin.¹⁴⁹ The yellowing could be the result of sulfurous decomposition products which have also been reported with SDT.¹⁵⁰ Unlike SDT, a sharp pH decrease was not noted - though the solutions were more acidic (pH 5 to 6) in general.

All AA solutions turned reddish during treatment, becoming darker and occurring faster with increasing concentration, but did not correspond with a visual change in the staining. This did not occur during initial tests with less heavily stained samples. The 15% AA samples had developed a napped surface after drying, indicating some fibre degradation caused by the acid. They were the lowest pH samples and at the pH limit of 4 for cellulose degradation. The AA was increasingly difficult to dissolve as the concentration increased.

¹⁴⁵ Fisher Scientific, "Sodium Hydrosulfite Safety Data Sheet," 2014, https://www.fishersci.co.uk/chemicalProductData_uk/wercs?itemCode=10274490&lang=EN.

¹⁴⁶ Fisher Scientific, "Sodium Metabisulfite Safety Data Sheet," 2016, https://www.fishersci.co.uk/chemicalProductData_uk/wercs?itemCode=10223970&lang=EN.

¹⁴⁷ Fisher Scientific, "L(+)-Ascorbic Acid Safety Data Sheet," 2015, https://www.fishersci.co.uk/chemicalProductData_uk/wercs?itemCode=10055800&lang=EN.

¹⁴⁸ Alfa Aesar, "Ammonium Citrate Tribasic Safety Data Sheet," 2014, <https://www.alfa.com/en/content/msds/british/A16973.pdf>.

¹⁴⁹ Irwin, "Comparison," 42–44.

¹⁵⁰ Selwyn and Tse, "Sodium Dithionite," 68.

Reagent	Average treatment time (min)	Average solution pH BT	Average solution pH AT	Cost (£)	Observations	Health and safety
1% SDT	20.2	7.03	6.15	0.45	Inconsistent stain removal	SDT only: <ul style="list-style-type: none"> • Adequate ventilation needed (strong sulfurous fumes) • Self heating in air exposure and may cause fires • Liberates toxic gas [sulfur oxides] on contact with acids. • Harmful if swallowed
2% SDT	17	6.89	6.13	0.55	Most treatment time variation: 10 to 28 min	
5% SDT	10	6.84	5.74	0.71	Consistent stain removal and treatment time	
2% SMB	60	6.07	5.74	0.52	Solution yellowed at 35 min. Only lightest staining removed	SMB only: <ul style="list-style-type: none"> • Adequate ventilation needed (sulfurous fumes) • Liberates toxic gas [sulfur oxides] on contact with acids and when heated. • Harmful if swallowed • Causes serious eye damage
5% SMB	60	5.72	5.42	0.62	Solution yellowed at 5 to 15 min Lightest stains whitened around 25 min	
10% SMB	60	5.37	5.27	0.80	Solution yellowed at 10 min Lightest stains whitened around 15 to 25 min	
5% AA	60	4.97	4.90	1.13	Lightest stains whitened around 30 min Solutions pinkish after 60 min	AA only: <ul style="list-style-type: none"> • No special precautions, use good laboratory practice
10% AA	60	4.28	4.37	1.81	Vigorous stirring to dissolve AA Solution dark red in 3 min Lightest staining whitened around 20 min	
15% AA	60	3.97	4.01	2.49	3 to 4 min vigorous stirring to dissolve AA Solution dark red in 3 min Lightest staining whitened from 5 to 15 min	
5% TAC	60	7.40	7.10	0.45	No changes observed	TAC only: <ul style="list-style-type: none"> • Skin and eye irritant • May cause respiratory irritation
Control (DI water)	60	5.62	5.52	---	No changes observed	---

Table 3 Test treatment working properties

TAC Buffering

TAC has some buffering capacity.¹⁵¹ Reducing abilities of each reagent are pH dependent, so the buffered range must be a compromise between acidic conditions ideal for iron reduction and near-neutral conditions for cellulosic treatments.

The solutions' pH without 5% TAC clearly demonstrated TAC's buffering of the solutions to a safer pH range for cellulosic treatments (Table 4). The buffered solution pHs recorded in Table 3 may have reduced the solutions' effectiveness - especially AA which has been proven to be most effective at unbuffered pH ranges.¹⁵²

Reagent	pH without 5% TAC
1% SDT	6.48
2% SDT	6.40
5% SDT	6.38
2% SMB	4.49
5% SMB	4.17
10% SMB	4.04
5% AA	2.32
10% AA	2.11
15% AA	1.94

Table 4 pH of treatment solutions without TAC

4.2.3 Surface pH

Most samples' surface pH decreased during treatment (Fig. 13). The exception was for the 1% SDT samples: the increase of 0.03 pH units was insignificant. The control samples' surface pH also decreased, so some decrease may be attributed to the mildly acidic DI water. The AA samples' pH decreased the most: over 1 pH unit for all samples. Though the 10% AA had a lower average pH after treatment, they did not appear as degraded as the 15% AA samples.

¹⁵¹ Phenix and Burnstock, "Removal," 29.

¹⁵² Elmagirbi, Sulistyarti, and Atikah, "Ascorbic Acid," 13–15.

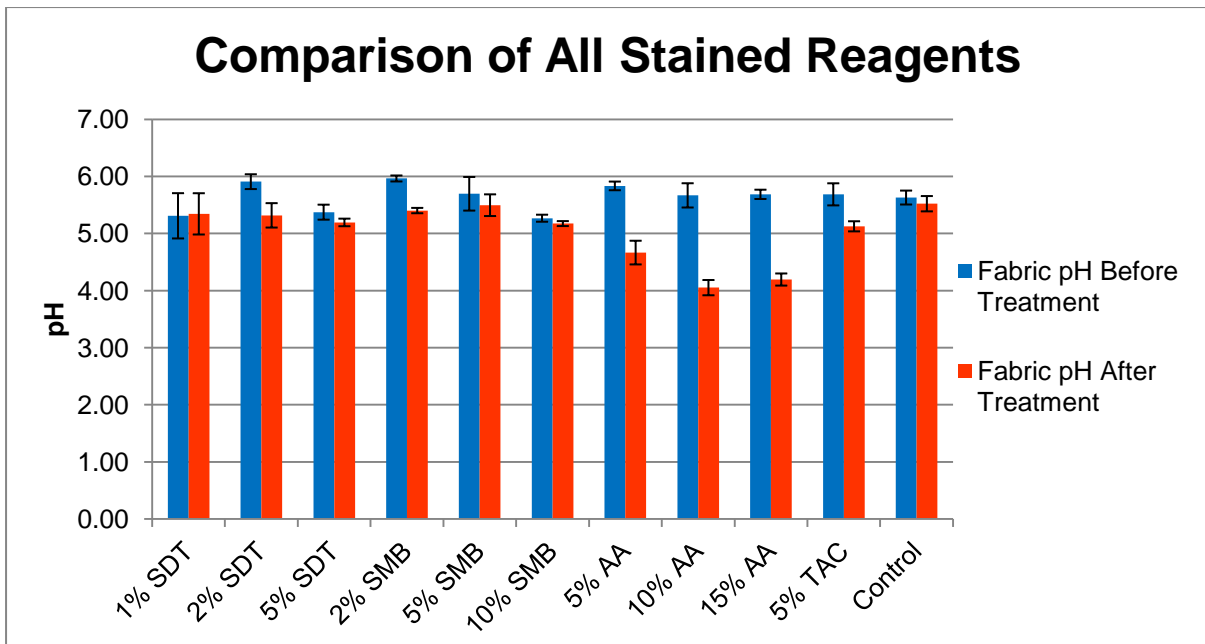


Fig. 13 Surface pH results for all treated stained samples. Mean values of the five replicates have been used. Error bars represent ± 1 standard deviation.

4.2.4 Bathophenanthroline Indicator Test Strips

Positive results for iron (II) stains were indicated by the development of a magenta colour on the test strips that took the exact shape of the staining. Iron (III) results were darker magenta, as was clearly observed with the historical corroded iron nail samples (Figs. 14-15). Result data are in Appendix K. Negative results were noted with no development of the magenta colour indicating no iron present or iron content the indicator's 10 ppm detection limit.

Testing with DI water produced pinpoint sized positive results for both iron (II) and iron (III) ions. This indicated iron ion contamination in the DI water. Any pinpoint results were noted but interpreted as negative results (Fig. 16).

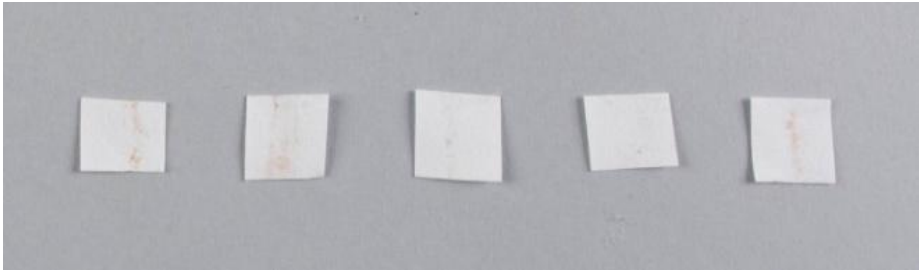


Fig. 14 Positive iron (II) ion results for historical nails

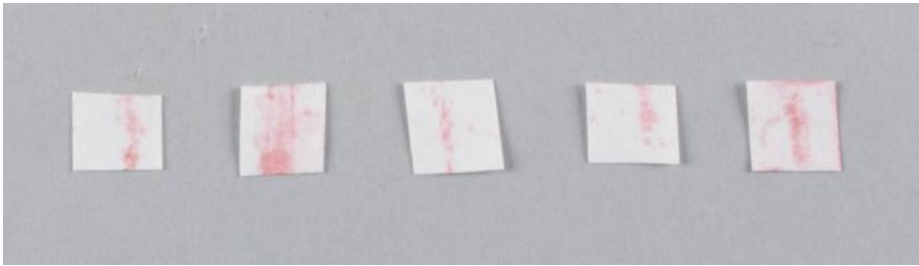


Fig. 15 Positive iron (III) ion results for historical nails

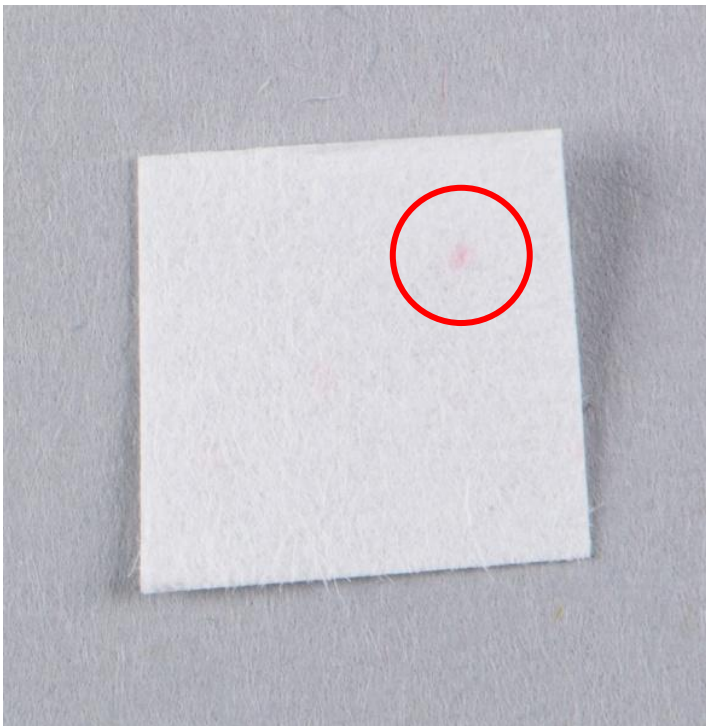


Fig. 16 Pinpoint positive result for iron (II) ions

Before Treatment

Only three of the 55 stained model samples produced a positive result for iron (II) ions BT. There are two possible reasons: rinsing during the sample preparation likely removed the majority of soluble iron (II) ions; and/or iron (II) ions were below the bathophenanthroline test paper's detection limit. Fourteen of the 55 samples returned a positive result or iron (III) ions. Vuori also found negative bathophenanthroline results on new linen that had been stained with rusty nails despite analytical confirmation of iron, so the negative results cannot be confidently interpreted as an absence of iron ions without further analysis.¹⁵³

After Treatment

All SDT samples were negative for both iron (II) and iron (III) ions.

Four of five 2% SMB samples were positive for iron (II) ions, two of five were positive for the 5% SMB samples, and none of the 10% SMB samples were positive for iron (II) ions. All samples were positive for iron (III) ions. This could indicate an incomplete reaction of the SMB and possibly insufficient rinsing, though one sample from each concentration set was re-rinsed and retested three times without any change in the results.

All of the AA samples were positive for iron (II) and iron (III) ions after treatment, similarly to the SMB samples. One sample from each concentration set was rinsed and tested three additional times to check for insufficient rinsing, but no change in the results was observed despite the expected outcome of removing some of the soluble iron (II) staining. These results could indicate that the incomplete reduction led to a transformation of the iron oxides to one with insoluble bound iron (II) ions.

4.2.5 Spectrophotometry

The spectrophotometer takes measurements for both specular component included (SCI) and specular component excluded (SCE). SCI measurements compensate for surface effects like surface roughness and gloss to record the true colour. SCE measurements record what the eye more

¹⁵³ Vuori and Tse, "Preliminary Study," 993.

naturally perceives.¹⁵⁴ SCI measurements were examined to exclude surface effects like fibre damage that may have occurred during test treatments.

Delta E (ΔE or dE) values quantify the total colour change. dE values of 1 to 3 are perceived as colour differences by the human eye - the values depending on the colour.¹⁵⁵ An upper limit of 3 was used as the perceptible limit. The instrument also calculates two different dE values using two different algorithms: dE^*ab and $dE00$. Delta E 2000 (or $dE00$) better accounts for differences in lightness between hues, and is currently the most accurate formula for true colour measurement.¹⁵⁶ The $dE00$ values were averaged. All raw data is in Appendix J.

SDT had the largest recorded colour change. The SMB samples caused some colour change despite not appearing to be very effective. The 5% SMB samples were slightly more effective than the 10% based on the dE^* data, but the 0.36 difference in the values was not visually perceptible. Also despite not appearing to change colour, both 5% TAC and the DI water controls resulted in some colour change although below the perceptible limit.

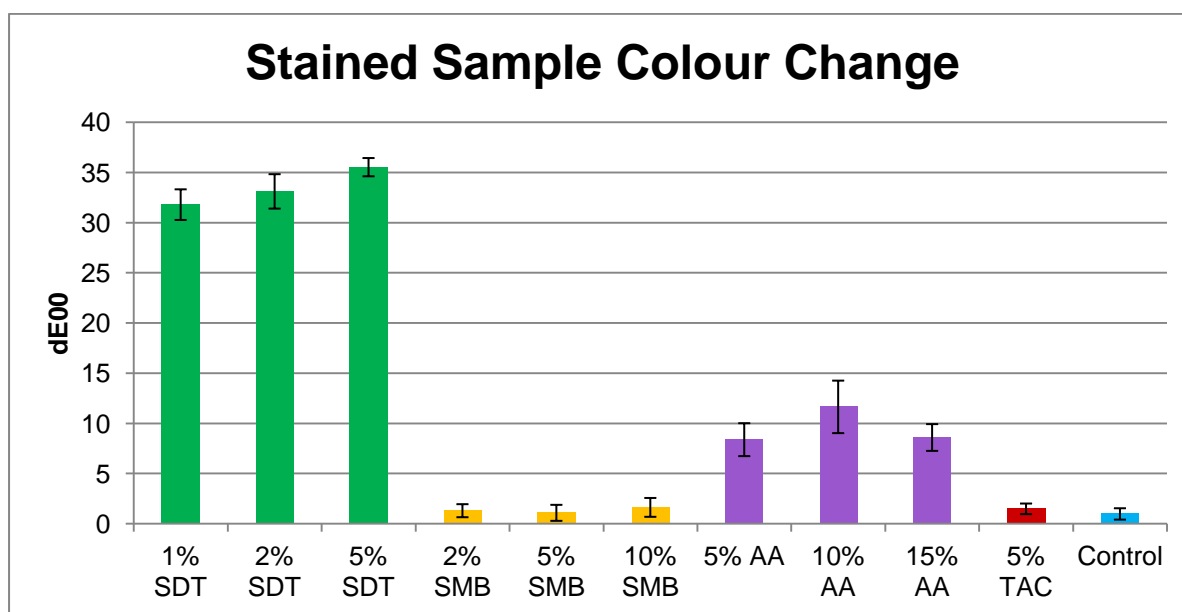


Fig. 17 Colour change caused by treatment of stained samples. Mean values of the five replicates have been used. Error bars represent ± 1 standard deviation. Outliers have been excluded from the 5% and 10% SMB data sets.

¹⁵⁴ Konica Minolta, "Specular Component Included (SCI) vs. Specular Component Excluded (SCE)," accessed July 7, 2017, <http://sensing.konicaminolta.us/2014/02/specular-component-included-vs-specular-component-excluded/>.

¹⁵⁵ SpectraCal Inc., "Visual Color Comparison," 7.

¹⁵⁶ Haisong Xu, Hirohisa Yaguchi, and Satoshi Shioiri, "Testing CIELAB-Based Color-Difference Formulae Using Large Color Differences," *Optical Review* 8, no. 6 (2001): 493, doi:10.1007/BF02931740.

4.2.6 Microscopy

Fabric surface examination was expected to reveal fibre breakage and clear fibre dimensional changes if the reagents caused any fibre degradation.

All samples showed some warp and weft yarn swelling of less than 0.1 mm when examined using the 500x Dinolite, which could be attributed to the aqueous immersion. This increased effect did not result in visual distortions of the fabric.

Fibres were also examined using optical and polarised light microscopy at 10x to look for cracks and fractured fibres that could indicate fibre degradation. Some cracks were observed on the 15% AA samples which confirmed the visual observation of a napped surface after treatment that may have indicated fibre degradation (Fig. 20). No signs of physical damage to the fibres were observed on any of the other samples (Figs. 18-19).

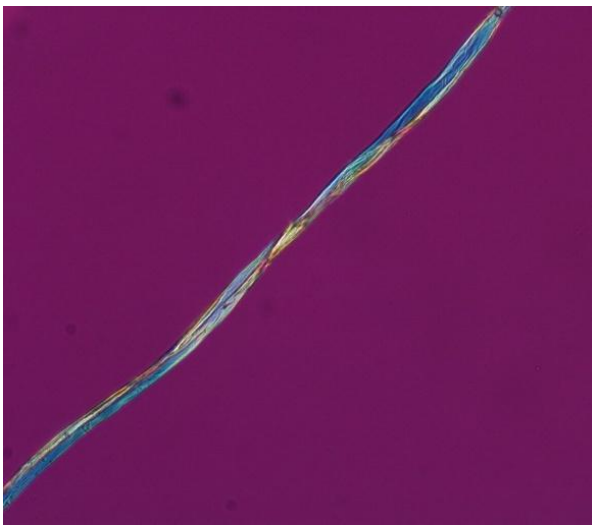


Fig. 18 Stained control sample AT

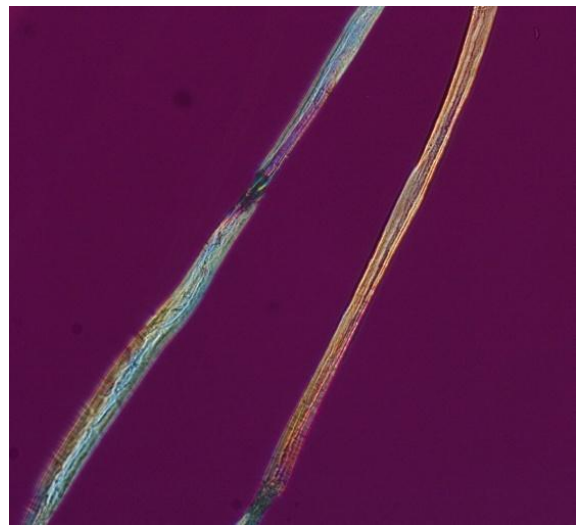


Fig. 19 Stained 5% SDT sample AT



Fig. 20 Stained 15% AA sample AT. Note the fine perpendicular cracks along the fibre.

4.3 Unstained Samples

The most visually effective concentrations of each reagent were chosen to determine if the reagents caused any colour or physical changes on new unstained cotton.

The highest concentration of SDT (5% with 5% TAC) removed the most staining and had the most consistent treatment times, possibly indicating a more stable solution.

All of the SMB samples were largely ineffective at removing most staining, so the highest concentration of SMB was chosen to evaluate its potential maximum effect with the cotton fibres.

The 15% AA was not tested because it caused fibre damage. 10% AA removed a similar amount of staining but without the same level of degradation.

The same treatment times as the stained sample testing were used to simulate the reaction conditions. The samples were evaluated using visual analysis, pH measurements, spectrophotometry, and microscopy. Bathophenanthroline testing was not performed on the unstained samples due to time constraints.

4.3.1 Visual Analysis

Yellowing could indicate some cellulose degradation caused by the reagents, but no yellowing or dimensional changes were observed on the unstained new cotton samples.

4.3.2 Working Properties

The pH measurements of all of the solutions are recorded in Table 5. Their cost and health and safety information are the given in Section 4.2.2. The solutions' pHs were similar to the stained samples, though the AA solutions marginally decreased rather than increased during this testing. The 5% SDT solution pH decreased nearly one pH unit over the course of 10 minutes, illustrating its rapid degradation in water regardless of the presence of iron staining.

Reagent	Treatment time (min)	Average solution pH BT	Average solution pH AT	Observations
5% SDT + 5% TAC	10	6.66	5.77	No changes observed
10% SMB + 5% TAC	60	5.37	5.35	No solution yellowing
10% AA + 5% TAC	60	4.39	4.33	No changes observed
5% TAC	60	7.42	7.21	No changes observed
Control (DI Water)	60	5.81	5.80	No changes observed

Table 5 Unstained sample working properties before and after treatment

4.3.3 Surface pH

Like the stained samples, the pH of almost all unstained samples decreased during treatment, except for TAC's negligible 0.04 decrease (Fig. 21). Similarly to the stained testing, the AA samples' pH dropped over one pH unit to an acidic pH 4.39. The decreases caused by the other reagents are relatively small: less than 0.5 units.

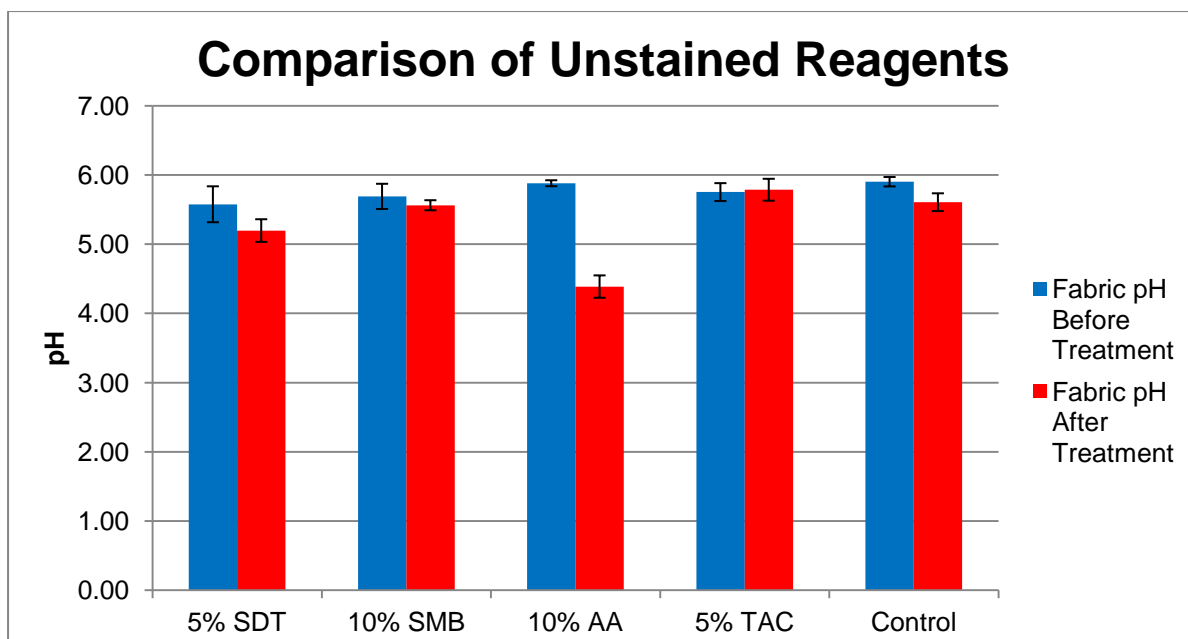


Fig. 21 Surface pH of treated unstained samples. Mean values of the five replicates have been used. Error bars represent ± 1 standard deviation.

4.3.4 Spectrophotometry

All dE values were below the perceptible lower limit of 1, so no colour changes were produced (Fig. 22). This testing was done on new cotton so the effects of aged fibres which may be more sensitive to chemical interactions were not measured. Aged fibres may respond differently, but artificial ageing was beyond the time limit of this research.

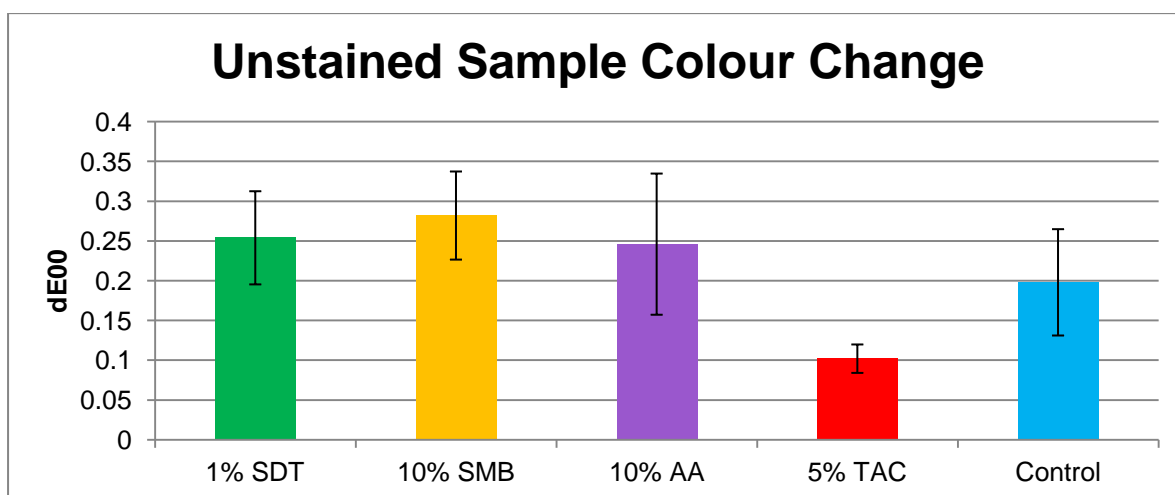


Fig. 22 Unstained sample colour change AT. Mean values of the five replicates have been used. Error bars represent ± 1 standard deviation.

Although dE encompasses all colour components, looking at individual components can be useful. Cellulose degradation products result in a yellowing of cotton fabric.¹⁵⁷ Yellowing is measured by db*. The values were well below 1 unit and therefore imperceptible (Table 6). Water soluble cellulose degradation products may have been removed during treatment.¹⁵⁸ Surprisingly, the samples became marginally darker (dL*) as well despite reported brightening effects caused by reducing agents like SDT (Table 6).

Sample	Average db*	Interpretation	Average dL*	Interpretation
5% SDT + 5% TAC	-0.238	Less yellow	-0.160	Darker
10% SMB + 5% TAC	-0.268	Less yellow	-0.122	Darker
10% AA + 5% TAC	-0.274	Less yellow	-0.028	Darker
5% TAC	0.040	Yellower	-0.190	Darker
Control	-0.082	Less yellow	-0.098	Darker

Table 6 Delta b and delta L results for treated unstained samples

4.3.5 Microscopy

Microscopic examination of the yarns and fibres did not reveal any significant changes from those observed in the control samples. The reagents do not appear to have an effect on the fibres at these concentrations.

4.4 Conclusion

Overall, the SDT solutions produced the best stain removal results. The 5% SDT + 5% TAC solution produced the most consistent and full rust stain removal results. They were the only samples to return negative bathophenanthroline results after treatment for all samples, indicating that the iron staining was removed and the sample was sufficiently rinsed or that the iron content was below the indicator's detection limit.

¹⁵⁷ Tímár-Balázs and Eastop, *Chemical Principles*, 158.

¹⁵⁸ *Ibid.*, 194.

Despite reported results of SDT's potential brightening effects, none were recorded during testing, though the use of new white cotton may have obscured any brightening from being recorded.¹⁵⁹ The rapid pH decrease of each SDT solution used to treat stained and unstained samples reinforces the need to prepare fresh solutions frequently. The SDT treatments were also the fastest and least expensive treatments (multiple fresh solutions can increase the cost). The health and safety concerns can be mitigated using proper extraction and the fast reaction time helps to limit the conservator's exposure.

The alternatives were less successful than the SDT. The SMB solutions produced imperceptible colour changes. The AA solutions visually removed more staining than SMB, but their low pH readings, even with the slight buffering capacity of TAC, were the lowest of the reagents and approached the lowest safe pH threshold for non-damaging treatment of cellulose.

The slight decrease in pH that was recorded for the SDT and SMB treatments may be considered acceptable for removing more highly acidic iron staining but should be a consideration when undertaking immersive treatments where unstained areas may be affected by the reagents. Microscopic analysis confirmed that 15% AA damages new cotton. Both SMB and AA removed the lightest staining best, presumably lepidocrocite, but not darker goethite staining, confirming observations in soil science literature at higher temperature and longer reaction times.¹⁶⁰

Bathophenanthroline indicator tests suggested that the SMB and AA treatments caused incomplete reduction, transforming the staining to an iron oxide with bound iron (II) ions because additional rinsing did not change the results. The model rust sample staining method may not be a perfect approximation of rust staining because the indicator testing would be expected to simulate the staining results found with the historical nails, but further analysis using quantitative techniques would be needed to draw firm conclusions.

DI water and 5% TAC caused imperceptible colour changes. The reagents did not appear to have any substantial effects on the unstained fibres. However testing was carried out on new fabrics, so aged fibres may respond differently and will be explored in the case study.

¹⁵⁹ Bede, "Wright Flyer," 22.

¹⁶⁰ Houben, "Iron Oxide Incrustations," 953.

5. Case Study

5.1 Introduction

The concentration and rapid formation of chemically produced staining was not representative of natural stains which can form more ordered crystals that dissolve less easily.¹⁶¹ The most efficient reagent concentrations were tested with naturally aged rust stains on an historical sampler to determine if the reagents had similar effects (Fig. 23). Efficiency was defined as the highest concentration of each reagent that produced the most visual and measured colour change, the least pH change, and the least effects on the fibres. When the surface pH of the sampler was tested (more in Section 5.4.3) it was lower than the average test fabric pH (4.34 vs. 5.63). This was expected from the aged acidic staining. Though 10% AA produced slightly more colour change than the 5% AA (dE00 of 3.27 units, in the just-perceptible range of 3 units), its solution pH was 4.27 - below the sampler's surface pH. The 10% AA sample surface pH after treatment was lower than with 5% AA in testing. It was decided that a possibly less effective treatment with 5% AA was acceptable to prevent or minimise acid catalysed degradation of the sampler's cotton fibres.

The following solutions were therefore selected for the treatment:

5% SDT + 5% TAC

10% SMB + 5% TAC

5% AA + 5% TAC

The sampler is part of the Karen Finch Reference Collection at the Centre for Textile Conservation (Fig. 23). The sampler is not dated but a handwritten tag suggests that it is from the 19th century. A modern cotton support fabric is sewn around its edges and has a window cut in the reverse. The sampler was chosen for this treatment because it is edged with 10 mm plain weave cotton tape with ingrained orange-brown staining surrounding holes and losses along all sides. Rust was confirmed using ultraviolet light examination (UV): the stains appeared characteristically dark black.¹⁶²

¹⁶¹ Selwyn et al., "Iron Stain Removal," 34.

¹⁶² Selwyn and Tse, "Sodium Dithionite," 69.



Fig. 23 Karen Finch Reference Collection sampler BT

5.2 Testing Preparation

As in previous chapters 5% TAC was added to every solution, though not specifically mentioned hereafter.

A minimum of three areas were needed to test each reagent, but cutting the sampler into multiple testing sites or replicates was not permitted. However, the lower edge tape was only attached to the rest of the sampler at the lower left corner of the tape and stitched to the support fabric along one edge. It was agreed that this lower edge could be detached from the backing fabric for testing by clipping the support stitching. The rest of the sampler was protected from contact with the reagents

by rolling it on a Melinex® tube sealed with Tyvek® (flash-spun high density polyethylene) tape and wrapping it in polyethylene sheeting. A small cut was made in the polyethylene sheeting to draw the detached tape through for testing (Fig. 24).



Fig. 24 Preparation of the sampler for treatment

Separate testing sites were needed. The inert wax cyclododecane (CDD) is used in textile conservation to mask areas in aqueous treatments and sublimates in a few days or weeks.¹⁶³ CDD is melted and then applied to the fabric surface using an electric egg decorating tool called a *kistka*, allowing for precise and controlled application. The CDD was tested for any interaction with the reagents by immersing new cotton samples with applied CDD in the test solutions. No changes in the CDD, fabric surface, or solution occurred so it was deemed safe to use.

The pattern of the losses allowed for three evenly sized testing sites (about 1/3 of the tape), each with one 2 to 3 mm stain in the middle. The CDD was applied in the middle of losses bordering these testing sites to minimise CDD masking. CDD was also applied as two rows on the left edge of the tape border to prevent any solution from wicking onto the main body of the sampler if the lower edge CDD failed (Fig. 25).

¹⁶³ Katherine Sahmel et al., "Removing Dye Bleed from a Sampler: New Methods for an Old Problem," *Textile Speciality Group Postprints, American Institute for Conservation, 40th Annual Meeting, Albuquerque, New Mexico, May 2012 22* (2012): 82.

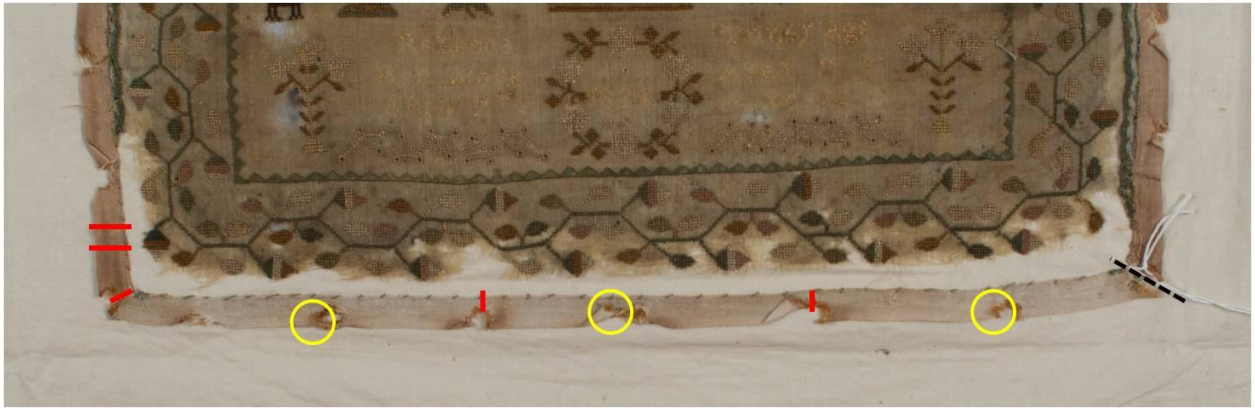


Fig. 25 Sampler testing: solid red lines indicate CDD application, yellow circles indicate the testing sites, and the black dotted line indicates where the tape was already detached.

5.3 Testing Procedure

The treatments and testing were carried out using the same procedures described in Chapter 3 for working properties, pH measurements, bathophenanthroline indicator, spectrophotometry and microscopy, including the Melinex® overlay. Though it would have been useful to note how DI water alone affected the stain removal, no DI water controls were used in this treatment.

The detached sampler tape was too small to fit into the plastic trays used for the model test treatments so a small glass Petri dish was used instead. Due to the size of the sampler, testing was carried out on the workbench under an extraction trunk rather than in the fume cupboard.

5.4 Results

5.4.1 Visual Analysis

The sampler treatment results were similar to the test treatment results. The 10% SMB did not appear to remove any staining (Figs. 26-27). Only the 5% SDT fully removed the staining. It also brightened the stained area (Figs. 28-29). The 5% AA reduced the lightest staining but some staining remained (Figs. 30-31). The CDD failed and the SDT treatment bled to the other sides of the masked stains, removing some nearby staining but not affecting testing sites. The sampler did not appear to have been previously wet cleaned, so gray soiling was released, brightening the tapes.



Fig. 26 10% SMB and 5% TAC BT



Fig. 27 10% SMB and 5% TAC AT



Fig. 28 5% SDT and 5% TAC BT



Fig. 29 5% SDT and 5% TAC AT



Fig. 30 5% AA and 5% TAC BT



Fig. 31 5% AA and 5% TAC AT

5.4.2 Working Properties

The SDT treatment worked rapidly but took two minutes longer than the test treatments despite the decreased amount of staining, possibly because they are more crystalline than the chemical stains (Table 7). The colour changes observed in the SMB and AA testing solutions did not occur. They were likely an effect of the high staining concentration. SDT was the most effective reagent.

Reagent	Treatment time (min)	Solution pH BT	Solution pH AT	Observations
5% SDT	12	6.21	5.83	Lightest stains removed in 3 to 4 minutes
10% SMB	60	5.43	5.39	No solution yellowing
5% AA	60	4.80	4.73	No reddish solution as in testing Most stain removal occurred in first 15 minutes

Table 7 Working properties of the reagents during the sampler treatment

5.4.3 Surface pH

The surface pH increased in all treatments regardless of the level of staining removed (Fig. 32). Simultaneous removal of soiling in the fibres and acidic cellulose degradation products may have caused this pH increase rather than only the rust staining removal.

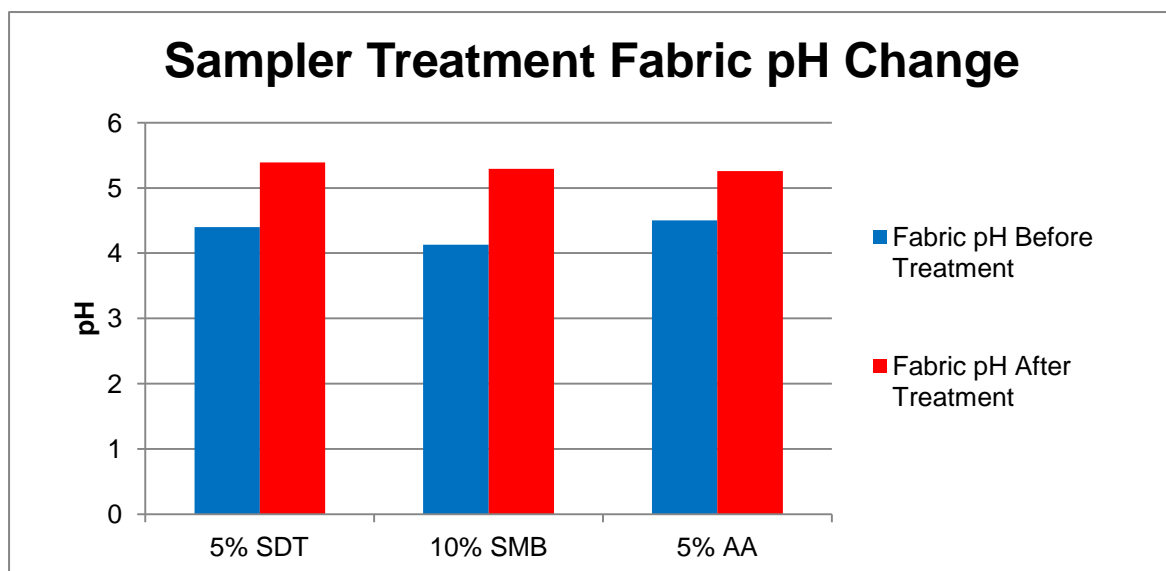


Fig. 32 Fabric surface pH measurements before and after treatment

5.4.4 Bathophenanthroline

The treated stains tested positive for iron (II) and iron (III) ions both before and after treatment (Figs. 33-36). It was thought that two minutes of rinsing was insufficient, but as in the SMB and AA test treatments, repeated rinsing did not remove all detectable iron ions. This result was surprising for the SDT treated area where the staining appeared to be completely removed. The staining may have been transformed and/or not sufficiently removed with a single bath. The staining colour may revert with time.

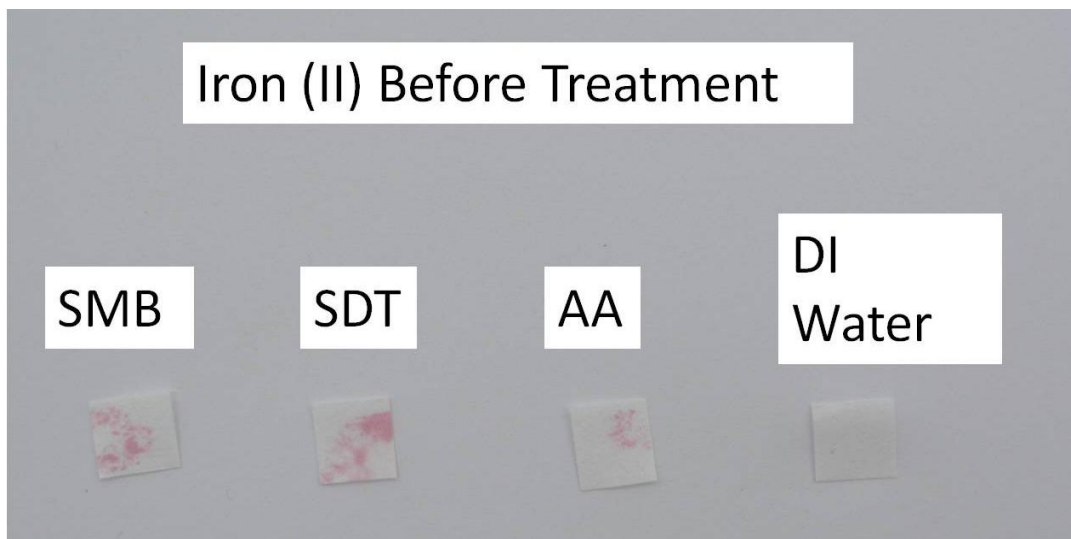


Fig. 33 Iron (II) bathophenanthroline test BT

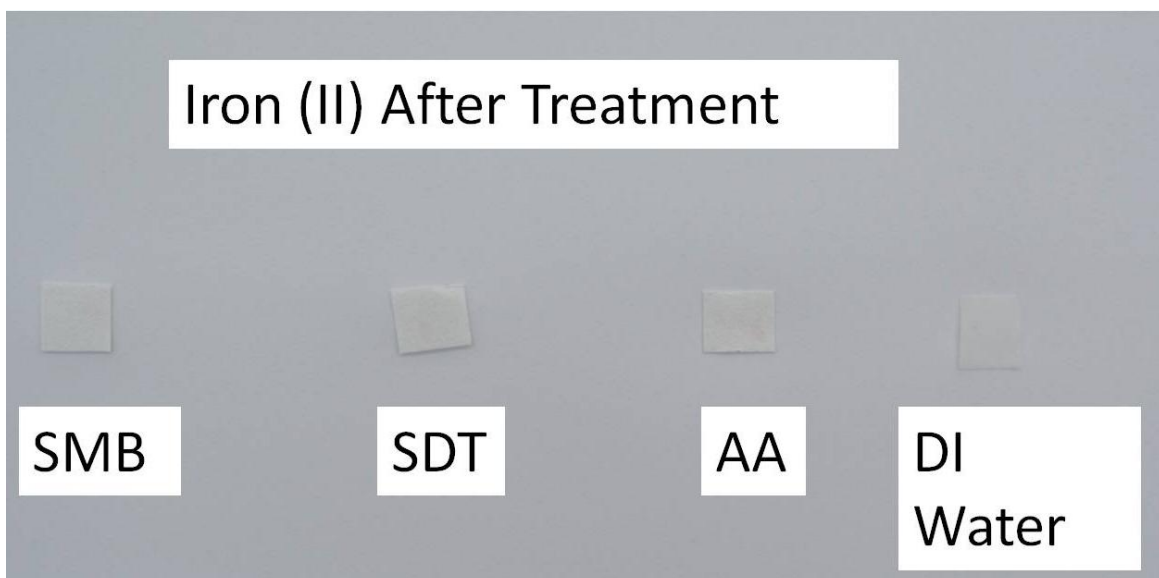


Fig. 34 Iron (II) bathophenanthroline test AT

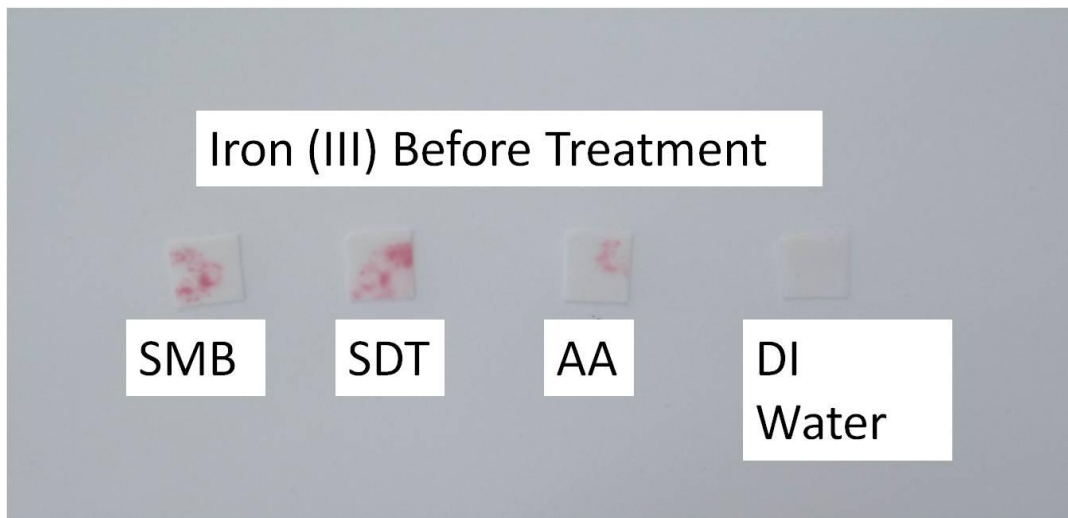


Fig. 35 Iron (III) bathophenanthroline test BT

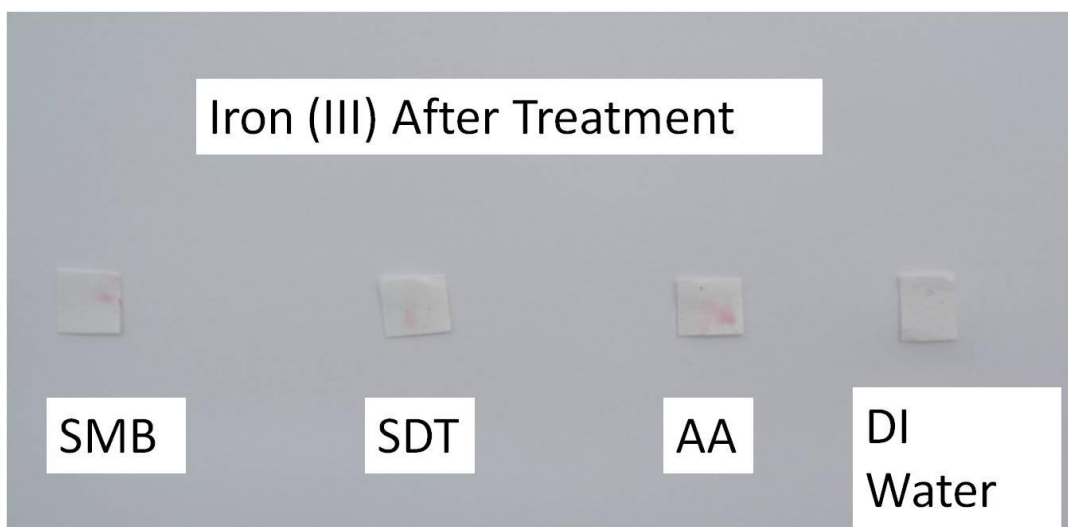


Fig. 36 Iron (III) bathophenanthroline test AT

5.4.5 Spectrophotometry

The SMB treatment colour change was perceptible according to the spectrophotometry measurements despite no visual evidence (Fig. 37). The stains did not entirely fill the target area so some of the whiter unstained areas may have affected the results. These measurements were likely affected by the noticeable soiling removal in each treatment. da^* measurements - the change in the red-green axis - were examined as a better representation of staining removal. A negative da^* value indicates a decrease in red and a positive da^* value indicates an increase in red. The data reflected

the visual observations: the SMB treatment became imperceptibly redder whereas the SDT and AA treatments reduced the reddish staining (Table 8).

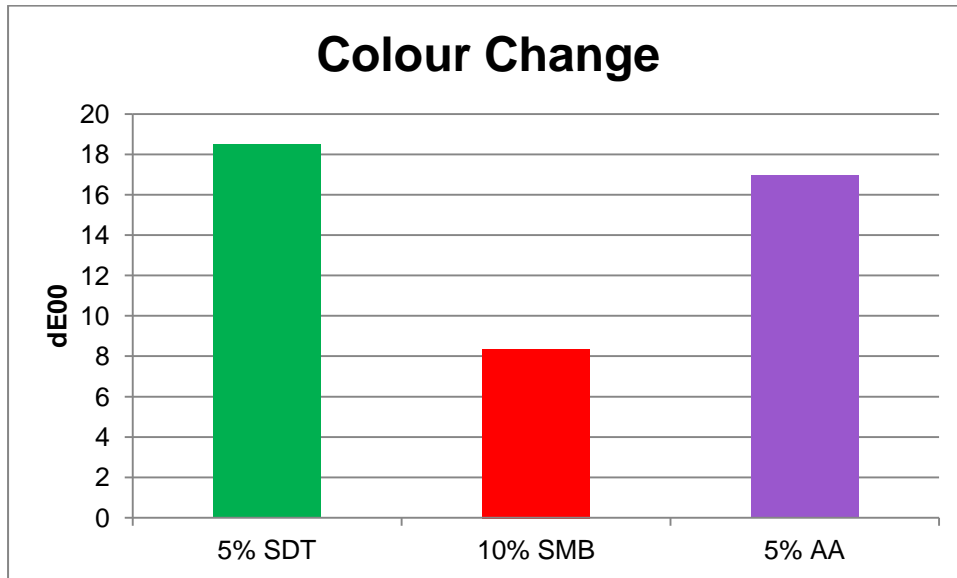


Fig. 37 Overall colour change (dE) caused by treatment

Reagent	da*	Interpretation
5% SDT	-6.02	Less red
10% SMB	0.62	Redder
5% AA	-6.36	Less red

Table 8 da* data measured AT

5.4.6 Microscopy

Images taken with the 250x Dinolite clearly showed the partial removal of staining from the AA samples, some faint staining remaining from the SDT treatment, and the lack of change from the SMB treatment (Figs. 38-43).



Fig. 38 BT



Fig. 39 After 5% AA treatment



Fig. 40 BT



Fig. 41 After 5% SDT treatment



Fig. 42 BT



Fig. 43 After 10% SMB treatment

At 500x, the yarns did not appear to be further damaged in any of the treatments. This was confirmed using optical and polarised light microscopy at 20x: no cracking or fractures were observed.

5.5 Conclusion

Treatment results of naturally aged stains were similar to those observed during the test treatments. 5% SDT and 5% TAC removed the most visual staining, but bathophenanthroline tests showed incomplete rust staining removal. It is possible that the rust was transformed or partially removed and some colour reversion may occur with time as the iron ions re-oxidise. The SDT also appeared to bleach the previously stained area.

The 5% AA and 5% TAC treatment removed the lighter, possibly lepidocrocite staining, but did not remove the darker goethite stains, confirming test treatment observations. Surprisingly, the acidic AA did not lower the pH of the fabric after treatment. The SMB treatment was ineffective, but caused a red colour change that could indicate some stain removal.

None of the reagents appeared to cause fibre or yarn degradation and therefore appear to be safe for use on aged cellulosic textiles.

In conclusion, SDT was the most effective reducing agent for rust staining even though it did not entirely remove the iron ions. A second SDT bath may have removed all bathophenanthroline detectable staining. The alternative reducing agents were much less effective: AA is only effective on a single oxide and SMB does not appear to be an effective rust stain removal reagent using the parameters of this testing.

6. Conclusion

Sodium dithionite (SDT) is the primary reducing agent used in textile conservation to treat rust stains in cellulosic textiles, but its rapid degradation in solution and health and safety concerns make it a less than ideal treatment method. This research aimed to answer one central question: Is there an effective alternative reducing agent to sodium dithionite for iron corrosion product (rust) staining removal from historic cotton fabric? Potential alternative reducing agents were successfully identified through a review of paper conservation, soil science, and historic stain removal literature. Sodium metabisulfite (SMB) and ascorbic acid (AA) were selected. Including a chelator is often recommended in the SDT treatment literature, so tri-ammonium citrate (TAC) was identified as an iron-preferential chelator efficient at the acidic to neutral solution pHs observed in this research.

Testing of three concentrations of each reagent on chemically created staining on new cotton fabric, each with 5% TAC, helped determine the most effective concentration of each reagent, which were examined using visual analysis, fabric surface pH measurements, spectroscopy, and microscopy to determine that none of the final solutions caused any significant changes to the cotton fibres.

5% Sodium dithionite (SDT) proved the most effective rust stain treatment of both chemically produced and historical stains by removing all the visual staining. However, one bath was insufficient for full stain removal because some iron ions were detected after treatment of historical rust stains. 1% SDT did not completely remove the staining in the test treatments and 2% SDT produced inconsistent working times. The SDT solutions' pH measurements decreased rapidly, indicating its short working life in aqueous solutions.

Ascorbic acid was identified as a possible reducing agent from examinations of soil science and historic cleaning suggestions. It was slightly successful as an alternative reducing agent. 15% AA was too acidic and damaged cellulosic fibres. Lower concentrations (5% and 10%) had higher pHs and removed some staining, presumed to be lepidocrocite, but did not remove darker goethite staining as was suggested by the literature. It was the most expensive reagent tested, though it had the least health and safety concerns. The low pH and incomplete reduction do not make it a viable alternative to SDT for treatment of cellulosic materials.

Sodium metabisulfite has been used in paper conservation, but was an ineffective iron reducing agent on both model sample and historical rust stains. SMB did not appear to cause any damage to the cotton fibres and produced little to no observable colour change. The bathophenanthroline tests for iron (II) and iron (III) ions indicated some partial reduction or transformation of some staining

though. An effective reducing agent should fully solubilise iron stains and minimise re-oxidation, so SMB is not recommended as an alternative reducing agent to SDT. Neither alternative was more successful at stain removal than SDT, so optimised conditions cannot be recommended for their treatment of cotton textiles.

6.1 Recommendations for Sodium Dithionite Use

Despite sodium dithionite's health and safety concerns and rapid aqueous degradation, it was the most effective reducing agent tested in this research. Recommendations in the literature vary extensively and can be quite vague, but this research reached useful conclusions for working with SDT:

- Dissolve additives in water first with minimal stirring to prevent water aeration that will accelerate the SDT's degradation
- To anticipate the working life of the solution, make a test solution of the SDT to be used and monitor the time that it takes for the pH to decrease, especially if the SDT is stored in a container that has been opened, i.e. aerated. Fresh solutions should be made just prior to their application to the object.
- Bathophenanthroline test strips should be used to check for complete removal of iron stains even if they appear to have been completely removed.
- Chelators should be chosen that function best in the near neutral range to balance the need for acidic rust reduction conditions and a neutral pH to slow SDT's degradation in water. A chelator that is also a buffer can help moderate SDT's rapid pH decreases in solution.

6.2 Recommendations for Further Research

Further research is recommended in the following topics to help improve conservators' understanding of iron corrosion staining and the optimal use of SDT:

- A survey of historical iron corrosion stains to characterise the iron oxides present, which can help identify alternative reducing agents best suited to the dissolution of those oxides.
- Further exploration of other chelating agents such as HBED (N, N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid) or calcium phytate that may be more efficient at iron ion sequestering.

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Appendices

A. Abbreviations

AA: Ascorbic acid

AT: After treatment

BT: Before treatment

DHEG: Dihydroxyethylglycine

DI: De-ionised

DTPA: Diethylenetriaminepentaacetic acid

EDTA: Ethylenediaminetetraacetic acid

ED-XRF: Energy dispersive x-ray fluorescence

HBED: N, N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid

NH₄OH: Ammonium hydroxide

SDT: Sodium dithionite

SEM: Scanning electron microscopy

SMB: Sodium metabisulfite

STPP: Sodium tripolyphosphate

TAC: Tri-ammonium citrate

TSC: Tri-sodium citrate

B. Sample Set Guide

Stained Samples

Set Label	Reducing Agent	Reducing agent concentration (w/v)	Chelator concentration
SDT 1-5	Sodium dithionite	1%	5% (w/v) Tri-ammonium citrate used in each solution
SDT 6-10		2%	
SDT 11-15		5%	
SMB 1-5	Sodium metabisulfite	2%	
SMB 6-10		5%	
SMB 11-15		10%	
AA 1-5	Ascorbic acid	5%	
AA 6-10		10%	
AA 11-15		15%	
TAC 1-5	Tri-ammonium citrate	5%	No additional chelator added
C 1-5	None - tested only in DI water		

Unstained Samples

Set Label	Reducing Agent	Reducing agent concentration (w/v)	Chelator concentration
SDT 1-5	Sodium dithionite	5%	5% (w/v) Tri-ammonium citrate used in each solution
SMB 1-5	Sodium metabisulfite	10%	
AA 1-5	Ascorbic acid	10%	
TAC 1-5	Tri-ammonium citrate	5%	No additional chelator added
C 1-5	None - tested only in DI water		

C. Sodium Dithionite Treatments in Textile and Paper Conservation

Material	Type of literature	Concentration/ molarity	Additional reagents	Treatment method	Treatment time	Notes	Author
Cotton and silk, dyed and undyed	Case study	5%	1% NH ₄ OH at pH 6.5	Localised: blotter paper		Calls SDT a reductive bleach. Warmed solution to 45°C, followed with detergent washings. Dyes were not affected.	Feniak (1981)
Cotton and barkcloth	Dissertation	2% 5% 10%	0.1 M disodium EDTA and alone (except 10% not alone)	Immersion	1 hour	Liquor ratio of 100 mL/sample. Heated SDT solutions to 45-50°C. Highest concentration with EDTA caused most change in percent reflectance.	Häkäri (1992)
Cotton	Dissertation	1% (pH 3.5 and 6) 2.5% (pH 7) 5%	Alone and with 1% disodium EDTA at pH 4.3 and 6 Alone and with 1% disodium EDTA at pH 4.3 and 6	Immersion	15 min 10 min 15 min	5% SDT + 1% EDTA caused most stain removal	Fredette (1998)
Cotton	Case study	2%	0.1 M EDTA adjusted to pH 7-8 with 5% NaOH	Localised: methylcellulose gel	One hour	Applied twice	Bede (2002)
Cotton	Dissertation	2% (w/v) / 0.015 M	0.05 M tri-sodium citrate, 0.1% Synperonic A5, and 0.1% SDS	Immersion	15 minutes	The pH of test solutions was adjusted to 6, 7, or 8. Ultrasonic baths were used as agitation for 1 minute every 5 minutes. Most effective visually at pH	Margariti (2002)

		0.2% (w/v) 0.0015 M	0.05 M tri-sodium citrate, 0.1% Synperonic A5, and 0.1% SDS	Immersion	Up to one hour	6. Same as above. Most effective visually at pH 6.	
		0.2% (w/v) 0.0015 M	0.05 M tri-sodium citrate/tri-ammonium citrate/di-sodium EDTA, 0.1% Synperonic A5, and 0.1% SDS	Immersion	30 minutes	pH adjusted to 7. Tested three different chelators and showed that TAC is the most effective.	
		0.15 M	0.05 M tri-sodium citrate, 0.1% Synperonic A5, and 0.1% SDS at pH 6	Immersion and localised: cotton wool covered in polythene	15 minutes	Treatment of an 1810 sampler with rust stains. The immersion treatment was sponged every five minutes and removed more staining than the localised treatments.	
		0.15 M	0.05 M tri-sodium citrate, 0.1% Synperonic A5, and 0.1% SDS at pH 7	Localised: as above	15 minutes		

Cotton	Research	7.5% 2.5, 5, and 10% 5%	0.1M EDTA and 5-10% TAC, pH kept at 8 5% TAC 2.5, 5, and 10% TAC	Localised: variety of poultice materials	5-60 minutes	SDT and TAC in Laponite was most effective Most effective at 5% Maximum effectiveness at 5% TAC	Potter (2003)
Paper	Case study	10% 2% 2% 2%	 2% Versene 100 (tetrasodium ethylenediaminetetraacetic acid) 2% Versenex 80 (pentasodium diethylenetriaminepentaacetic acid)	Immersion	15 minutes	10% SDT most effective, though formed an insoluble metal sulphide on iron, tin, and lead	Hawley, Kawai, and Sergeant (1981)
Paper	Conference Research	0.2 M 0.2 M 0.2 M	0.2 M STPP 0.2 M DTPA 0.2 M DHEG	Immersion		Most colour change from iron removal when using SDT with STPP	Lockwood (1984)

Paper	General guide	2% (w/v) recommended but can go up to 4% especially for localised treatments	Suggests 0.1 M EDTA adjusted to pH 7-8 and maybe 0.1 M phosphate salt to buffer			Specific section devoted to iron stain removal. Warns about decolourising dyes. Warns against higher concentrations (4%) because little testing done at that time.	Burgess (1991)
Paper/Photograph	Case study	2% 8%	0.1 M disodium EDTA (pH adjusted to 6.5) 0.1 M disodium EDTA (pH adjusted to 8.5)	Immersion	20 min 22 hours	Using the 8% SDT + 0.1 M EDTA, approximately 80% of the iron was removed along with all calcium and zinc fillers in paper.	Gent (1994)
Paper	Case study	2 and 4%	Alone and with 2 and 4% EDTA	Immersion	1.5 hrs	Decreased folding strength when using SDT	Suryawanshi (2005)
Paper	Case study	2.5, 5, and 10%	Same % of EDTA	Immersion	2.5%: 8 hrs and second bath, 5 and 10%: 4-6hrs	pH fell from 9 to 6 (probably because of the EDTA). 5 and 10% caused most stain removal.	Irwin (2011)
Paper	Research for case study	10% 10%	1%, 2%, and 4% disodium EDTA 2% and 4% Na ₅ DPTA 2% and 4% sodium DHEG	Immersion	45 minutes (no pH adjustment) and 30 minutes (pH 5)	Most effective with 1% EDTA and tested using reflectance. Showed that most effective at room temperature rather than 35-44 °C and when not exposed to air. Compared to other rust removers as well.	Selwyn et al. (2013)

D. Supplies and Suppliers

Sodium Dithionite, Extra Pure, SLR, Fisher Chemical
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
500 g
£38.40

Sodium Metabisulfite, Extra Pure, SLR, meets analytical specification of Ph.Eur., BP, Fisher Chemical
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
500 g
£25.15

L(+)-Ascorbic Acid, Reagent ACS $\geq 99\%$, ACROS Organics™
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
100 g
£19.50

Ammonium citrate tribasic, $>97\%$, Alfa Aesar™
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
500 g
£63.60

Iron(II) sulfate heptahydrate, 99.5%, for analysis, ACROS Organics™
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
250 g
£15.50


Ammonia Solution, 35%, Certified AR for Analysis, d=0.88, Fisher Chemical
Fisher Scientific UK Ltd
Bishop Meadow Road
Loughborough
LE11 5RG
1 litre
£19.65

Iron Gall Ink Test Paper
Preservation Equipment Ltd
Vinces Road
Diss
Norfolk
IP22 4HQ
Package of 100 strips
£19.85

White Cotton Lawn 96 cm, approx. 86 gsm
Whaley (Bradford) Ltd
Harris Court, Great Horton
Bradford, West Yorkshire
BD7 4EQ
£10.35/metre

E. Health and Safety Documentation

E.1. Risk Assessment

 RISK ASSESSMENT FORM				
School: Culture and Creative Arts	Section: Centre For Textile Conservation and Technical Art History	Location: Room number(s) <u>309A +310</u>	Reference No: <u>R 70</u>	Related COSHH Form (if applicable): <u>C 64/2017</u>
Description of activity: Dissertation research experimentation to include: <ul style="list-style-type: none"> • Creating artificially rust stained fabric by making solutions of 5% (w/v) ferrous sulphate and 10% (v/v) ammonium hydroxide and immersing the cotton fabric • Testing three different reducing agents on rust stained cotton fabric samples. The solutions will be created as follows: 1%, 2%, 5% (w/v) sodium dithionite; 2%, 5%, 10% (w/v) sodium metabisulphite; and 5%, 10%, 15% (w/v) L-ascorbic acid (possibly combined with 5%, 10%, 15% (w/v) sodium ascorbate to create a buffer). Three different percentages will be tested of each reducing agent. The chelator 5% (w/v) triammonium citrate will be added to each solution. • Measuring pH of the solutions and cotton samples using a pH meter • Measuring the presence of iron (II) and iron (III) ions on the cotton samples using bathophenanthroline indicator paper and 1% (w/v) L-ascorbic acid • Measuring colour change of the samples using a spectrophotometer • Treating historic rust stains using the most efficient reducing agent combined with the chelator <p>All experimentation and solution preparation will occur in the Chemical Laboratory to control spills and contain artefact contamination. Experimentation will take place from 29 May to 7 July 2017.</p>				
Persons at risk: Students, staff				
Is operator training/supervision required? If yes, please specify: Yes - Anita Guye				

Hazards/ Risks	Current controls	Are these adequate?	What action is required if not adequately controlled?
Handling chemicals	Use smallest amounts needed. Use good lab hygiene and appropriate PPE: lab coat, nitrile gloves, safety glasses, fume cupboard.	No	Refer to COSHH form
Spills	Clean up spill with paper towels or spill kit in chem lab. Dispose in bin.	No	Refer to COSHH form
Transporting large amounts of chemicals	Use chemical carriers	Yes	
Glass breakage	Clear up shards using a dust pan and brush. Dispose in glass disposal box in chemical lab or wet lab.	Yes	
Trip hazards	Keep spaces and walkways clear. Use good lab hygiene.	Yes	
Using electric equipment	Check for recent PAT testing, frayed wires, and loose connections. Use spark/explosion-proof motors.	Yes	
		Yes	

Completed by (print name and position, and sign): *Bella Knight, Student*





























Approved by (print name and position, and sign): *ANITA OWE, SENIOR LECTURER (CON. SCI)*

Date: *21/6/17*

Date: *7 June 2017*

Antonia Owe









E.2 COSHH Form

		<h1>COSHH Risk Assessment</h1>			Ref No: CW9/2017																													
School/Service/Unit Centre for Textile Conservation			Unit Safety Coordinator/Supervisor: Karen Thompson																															
Describe the activity or work process. <i>(Inc. how long/how often this is carried out and quantity substance used)</i>		Creating artificially rust stained fabric: <ul style="list-style-type: none"> • 5% (w/v) ferrous sulphate • 10% (v/v) ammonium hydroxide Testing reducing agents to solubilise rust stains: <ul style="list-style-type: none"> • sodium dithionite [1%, 2%, 5% (w/v)] • sodium metabisulphite [2%, 5%, 10% (w/v)] • L-ascorbic acid [5%, 10%, 15% (w/v)] • sodium ascorbate [5%, 10%, 15% (w/v)] • triammonium citrate [5% (w/v)] Reducing rust on bathophenanthroline indicator paper to iron (II): <ul style="list-style-type: none"> • 1% (w/v) ascorbic acid 																																
Location of process being carried out?		Robertson Building Rms 309 A and 310																																
Identify the persons at risk:		Employees <input checked="" type="checkbox"/>	Students <input checked="" type="checkbox"/>	Public <input type="checkbox"/>																														
Name the substance(s) involved in the process <i>(Attach data sheets to this assessment)</i>		ferrous sulphate ammonium hydroxide sodium dithionite sodium metabisulphite L-ascorbic acid sodium ascorbate triammonium citrate																																
GHP Classification <i>(state the category of danger)</i>																																		
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Gas	Vapour	Mist	Fume	Dust	Liquid	Solid	Other (State) _____																											
Route of Exposure																																		
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>																														
Inhalation	Skin	Puncture	Ingestion	Other (State) Eyes _____																														
Workplace Exposure Limits (WELs) <i>please indicate n/a where not applicable</i>																																		
Long-term exposure level (8hr TWA): ferrous sulphate: 1 mg/m ³ sodium metabisulphite: 5 mg/m ³ N.B. Small amounts used and limited exposure time will not breach exposure limits.			Short-term exposure level (15 mins): ferrous sulphate: 2 mg/m ³ sodium metabisulphite: 15 mg/m ³																															

What are the risks to Health from the process /tasks? (look at the H and P codes on the data sheet)

Self-heating, may catch fire: sodium dithionite (category 1)
 Skin irritant: ferrous sulphate (category 2), triammonium citrate (category 2)
 Skin corrosion: ammonium hydroxide (category 1B)
 Eye irritant: ferrous sulphate (category 2), sodium metabisulphite (category 1), triammonium citrate (category 2)
 Eye corrosion: ammonium hydroxide (category 1B), sodium metabisulphite (category 1)
 Harmful if swallowed: ferrous sulphate (category 4), ammonium hydroxide (category 4), sodium dithionite (category 4), sodium metabisulphite (category 4)
 Respiratory irritant: ammonium hydroxide (category 3), triammonium citrate (category 3)
 Toxic to aquatic life: ammonium hydroxide (category 1)
 Contact with acids liberates toxic gas: sodium dithionite, sodium metabisulphite

What Personal Protective Equipment is used ? (state type and standard)

 <input checked="" type="checkbox"/>	Paper dust mask	 <input type="checkbox"/>	
Dust mask		Visor	
 <input checked="" type="checkbox"/>	Fume extraction	 <input checked="" type="checkbox"/>	Safety goggles
Respirator		Eye wear	
 <input checked="" type="checkbox"/>	Nitrile gloves	 <input checked="" type="checkbox"/>	Lab coat
Gloves		Overalls	
 <input checked="" type="checkbox"/>	Closed toe shoes	 <input type="checkbox"/>	
Footwear		Other	

Assessment of the process/task

(List the summary of controls already in place and identify any gaps)
 Wear appropriate PPE (especially a dust mask when handling powders), handle in small quantities, use extraction for fumes, be aware of nearby portable electronic equipment. Store sodium dithionite and sodium metabisulphite away from acids

Note rate the overall rating with the controls you have listed

High Medium Low

List the new controls that need to be in place to give adequate control (consider the need for monitoring as well as changes to the task or substitution of chemicals used)

Final check: Has the risk rating been reduced to as low as possible with the new controls?

yes Note any monitoring that may be needed.....

Emergency Plans and procedures (this will apply to carcinogens, mutagens or similar health risks)

Are plans in place to deal with spillages or emergencies? Yes N/a
 Clean up spill with paper towel or spill kit in chem lab.
 Let dry in fume hood and dispose in bin.

Refer to any first aid emergency that should be noted in this assessment
 If inhaled, move person to fresh air.
 If skin contact, rinse with water for at least 15 minutes.
 If eye contact, rinse with water for at least 15 minutes.
 If swallowed, do not induce vomiting. Call a poison centre for sodium dithionite and sodium metabisulphite.

Has waste disposal been considered and established Yes N/a
 Waste can be flushed down sink with copious amounts of water because the concentrations are so dilute.
 Ammonium hydroxide waste should be stored in the non-oxidising waste container.

F. Preliminary Rust Stained Model Sample Testing

In these recipes, the general theme is that ferrous sulphate is applied to the substrate then exposed to air. Then twice or half the amount of a basic solution is used compared to the ferrous sulphate to precipitate an iron oxide. The exact mechanism could not be found because product formation can vary depending on reaction conditions such as pH, reaction time, temperature, and ratio of iron to base.¹⁶⁴ Cornell and Schwertmann's extensive text on iron oxides contains an overview of the many methods that can be used to synthesize iron oxides in a laboratory, but none match the recipes used in conservation texts.¹⁶⁵ Ferric chloride recipes were excluded because different iron oxides will form.¹⁶⁶

Author	Method	Artificial (Thermal) Ageing
Bede (2002): 21	Cotton wrapped around piece of iron left wet for several days	--
Tímár-Balázs and Gyork Matefy (1993): 331	Cotton wrapped around piece of iron left wet for seven days	--
Potter (2003): 42-45	No explanation published	--
Adler and Eaton (1995): 70	No specifics given -soaked samples in "iron solutions"	--
Hawley, Kawai, and Sergeant (1981): 17 Recipe taken from Hawley's 1979 dissertation	Paper immersed in 5% ferrous sulfate (FeSO ₄) solution for 5 minutes, air dried, and immersed in 10% v/v concentrated ammonium hydroxide (NH ₄ OH) solution for 10 minutes	Oven drying at 50 °C for two days
Morton (2012)	Linen immersed in 5% FeSO ₄ for 10 minutes, air dried, immersed in 10% v/v NH ₄ OH solution for 20 minutes	Oven drying at 50 °C for two days
Häkäri (1992): 29	Cotton immersed in 5% FeSO ₄ for 5 minutes, air dried, immersed in 10% v/v NH ₄ OH solution for 10 minutes	Oven drying at 100 °C for 19 hours
Margariti dissertation (2002): 26	Cotton immersed in 1 M FeSO ₄ for 10 minutes, air dried, then immersed in 0.05 M sodium hydroxide (NaOH) for 5 minutes	

Methods of artificially creating rust stains in conservation texts

¹⁶⁴ M. Tajabadi and M.E. Khosroshahi, "Effect of Alkaline Media Concentration and Modification of Temperature on Magnetite Synthesis Method Using FeSO₄/NH₄OH," *International Journal of Chemical Engineering and Applications* 3, no. 3 (2012): 206.

¹⁶⁵ Cornell and Schwertmann, *Iron Oxides*, 528-540.

¹⁶⁶ *Ibid.*, 530–34.

Preliminary samples were made using on 80 x 120 mm pieces of undyed cotton lawn fabric. Morton, Håkäri, and Margariti's recipes were tested. Results of testing Morton, Håkäri, and Margariti's recipes are detailed here. None of the samples were initially oven dried. Iron oxides can be transformed at temperatures exceeding 100 °C (not used in the recipes) so it is unlikely that the recipes were significantly altered by excluding this step.¹⁶⁷

Margariti's recipe sample was white after immersion in the 0.1 M FeSO₄, but it the fabric turned black when immersed in the 0.5 M NaOH. This likely indicated the formation of magnetite which typically forms when iron oxides are forced to form at high pH.¹⁶⁸ The sample slowly turned an even light yellow-orange colour while it was rinsed and allowed to dry. Magnetite can transform to the light orange lepidocrocite when it is allowed to further oxidise slowly.¹⁶⁹

Both Håkäri and Morton have similar recipes with Morton leaving the samples in solution for twice the amount of time. Håkäri is the only author to publish the amount of solution used: 500 mL of 5% FeSO₄, but no exact volume or calculations were provided for the NH₄OH. NH₄OH is often sold as a diluted solution (ex. 28% or 35% concentrated from Fisher Scientific), but neither Morton nor Håkäri discuss whether these dilutions were compensated for in their recipes. It was assumed that there were no compensation calculations since the recipes list the percentages as v/v and do not specify that the solutions were concentrated, so solutions for testing were created using 10% based on volume of the solution from the supplier, rather than 10% NH₄OH in solution. This likely resulted in discrepancies between the recipes since the concentration of the stock solutions used in the recipes was unknown. For the each initial sample, 5 g of FeSO₄ in 100 mL of DI water was used for the first bath and 10 mL (of 35% concentrated) NH₄OH in 100 mL of DI water for the second bath. Both samples were stained mottled orange, yellow-brown colours. The use of NH₄OH at room temperature likely created both lepidocrocite (orange) and goethite (yellow-brown), though they were stained less evenly than Margariti's samples.¹⁷⁰ This was deemed acceptable since a variety of rust staining would more accurately model a rust stain than even desposition of a single iron oxide. Morton's recipe produced more heavily stained samples, so her recipe was used for testing.

¹⁶⁷ Cornell and Schwertmann, *The Iron Oxides*, 528-540.

¹⁶⁸ Renaud Daenzer, Thomas Feldmann, and George P. Demopoulos, "Oxidation of Ferrous Sulfate Hydrolyzed Slurry-Kinetic Aspects and Impact on As(V) Removal," *Industrial and Engineering Chemistry Research* 54, no. 6 (2015): 1738, accessed 23 July 2017, doi:10.1021/ie503976k.

¹⁶⁹ *Ibid.*, 1739.

¹⁷⁰ E. Yu. Karateena et al., "Effect of Synthesis Conditions on the Size and Aspect Ratio of Acicular Iron(III) α-Oxyhydroxide Particles Prepared in the FeSO₄-H₄-O₂-H₂O System," *Inorganic Materials* 37, no. 1 (2001): 39, doi:10.1016/S0167-577X(03)00508-1.

G. Before and After Sample Treatment Images

Key

AA: Ascorbic acid

SDT: Sodium dithionite

SMB: Sodium metabisulfite

TAC: Tri-ammonium citrate

G.1 Stained Samples



1% SDT + 5% TAC before treatment



1% SDT + 5% TAC after treatment



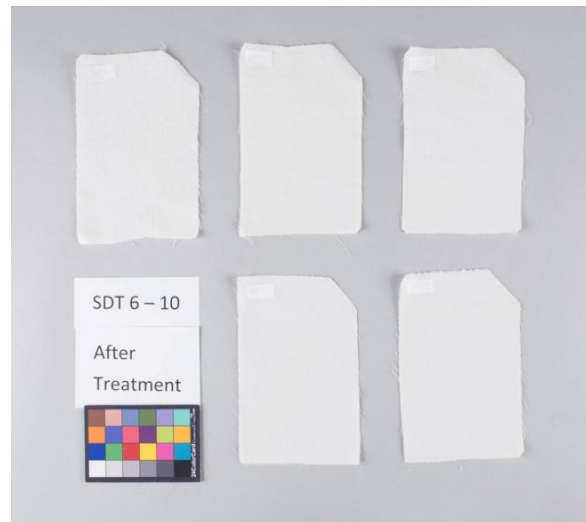
2% SDT + 5% TAC before treatment



2% SDT + 5% TAC after treatment



5% SDT + 5% TAC before treatment



5% SDT + 5% TAC after treatment



2% SMB + 5% TAC before treatment

2% SMB + 5% TAC after treatment



5% SMB + 5% TAC before treatment

5% SMB + 5% TAC after treatment



10% SMB + 5% TAC before treatment



10% SMB + 5% TAC after treatment



5% AA + 5% TAC before treatment



5% AA + 5% TAC after treatment



10% AA + 5% TAC before treatment



10% AA + 5% TAC after treatment



15% AA + 5% TAC before treatment



15% AA + 5% TAC after treatment



5% TAC before treatment



5% TAC after treatment



De-ionised water controls before treatment



De-ionised water controls after treatment

G.2 Unstained Samples



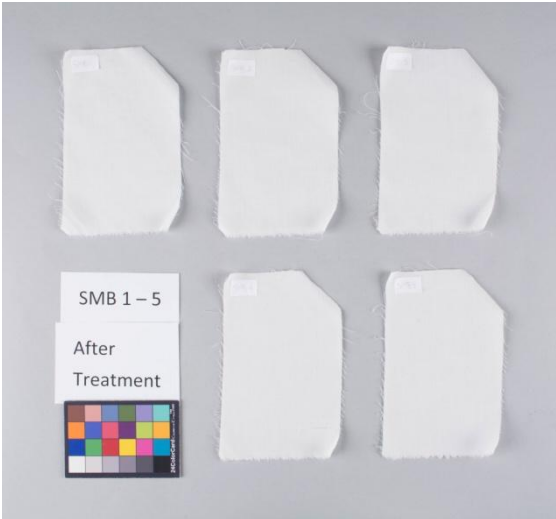
5% SDT + 5% TAC before treatment



5% SDT + 5% TAC after treatment



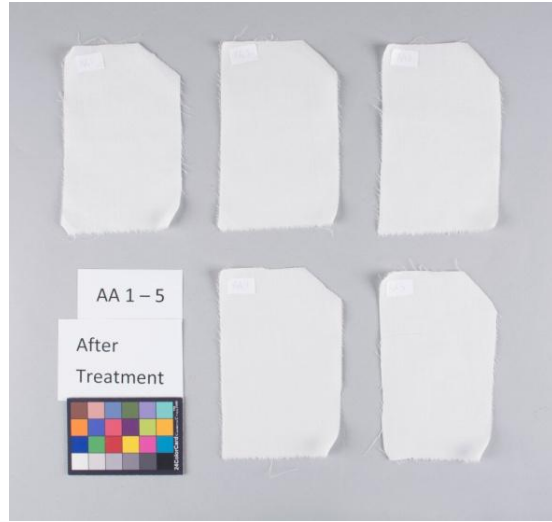
10% SMB + 5% TAC before treatment



10% SMB + 5% TAC after treatment



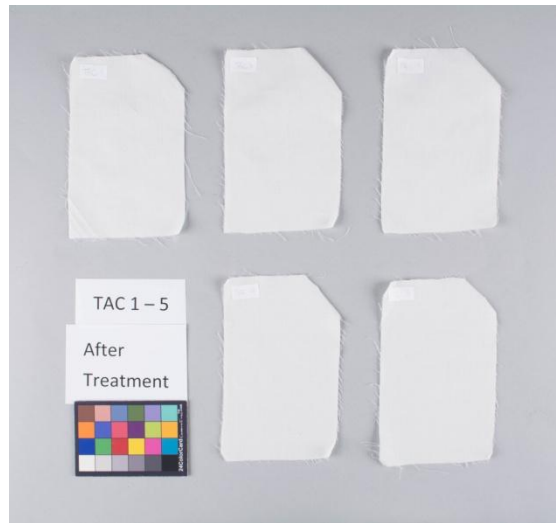
10% AA + 5% TAC before treatment



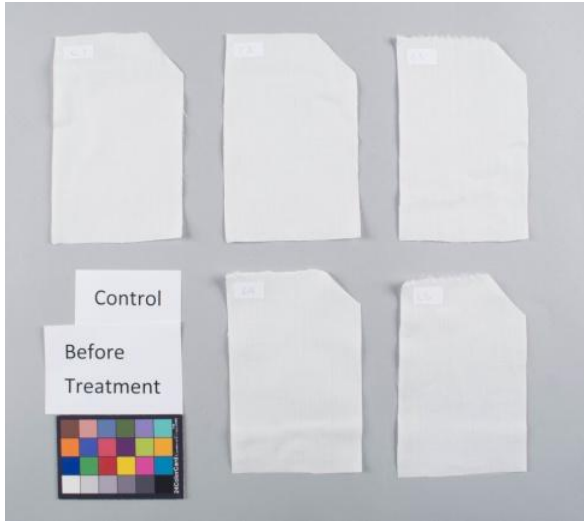
10% AA + 5% TAC after treatment



5% TAC before treatment



5% TAC after treatment



De-ionised water controls before treatment



De-ionised water controls after treatment

H. Samples

All samples have been treated unless otherwise noted.

Key

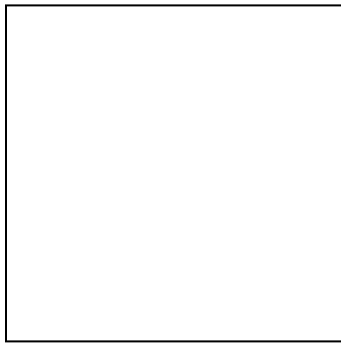
AA: Ascorbic acid

SDT: Sodium dithionite

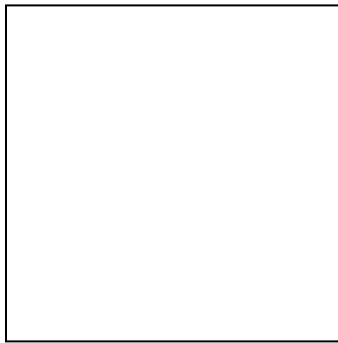
SMB: Sodium metabisulfite

TAC: Tri-ammonium citrate

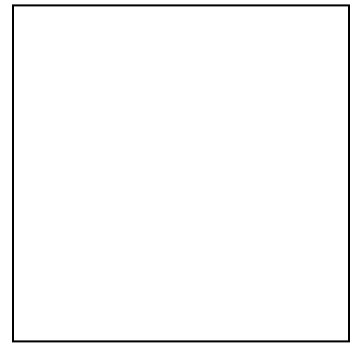
H.1 Stained Samples



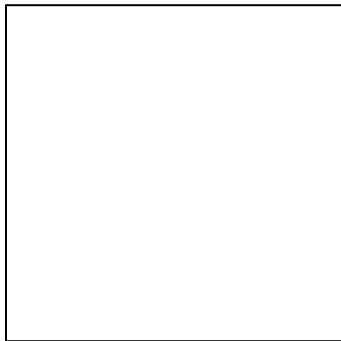
1% SDT + 5% TAC



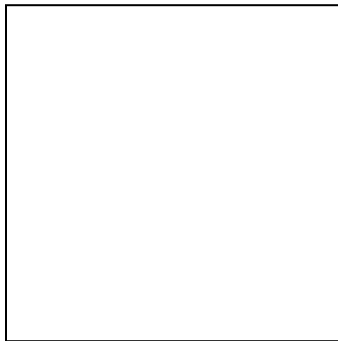
2% SDT + 5% TAC



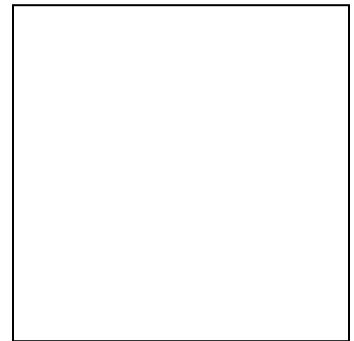
5% SDT + 5% TAC



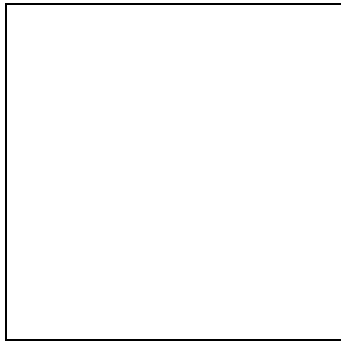
2% SMB + 5% TAC



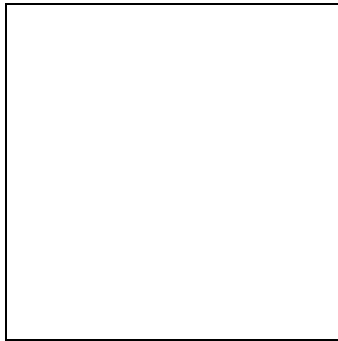
5% SMB + 5% TAC



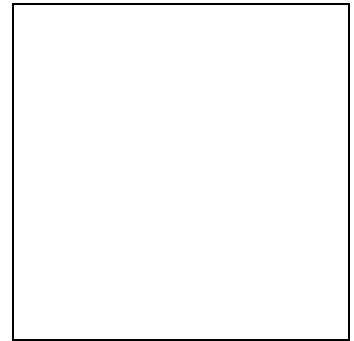
10% SMB + 5% TAC



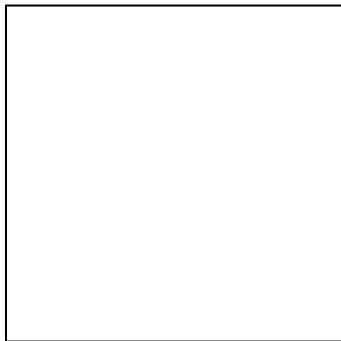
5% AA + 5% TAC



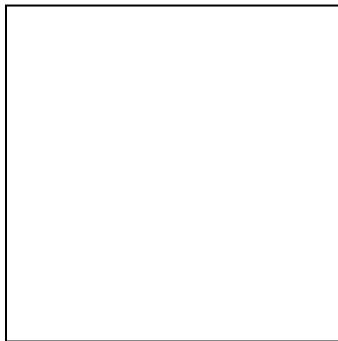
10% AA + 5% TAC



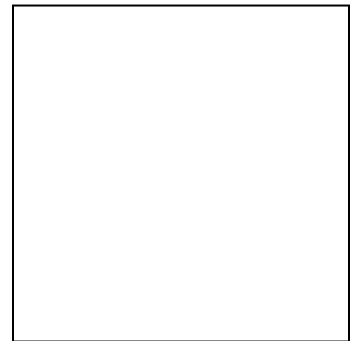
15% AA + 5% TAC



Untreated

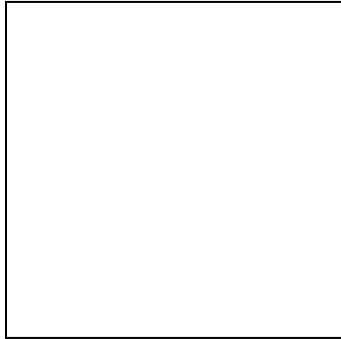


5% TAC

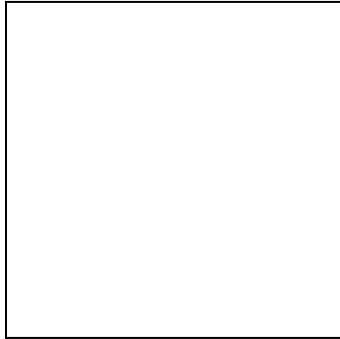


De-ionised water control

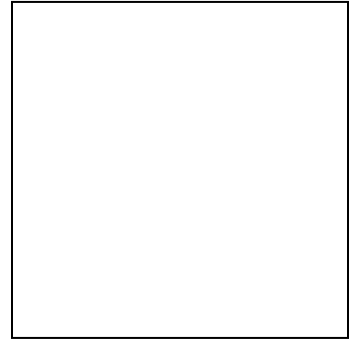
H.2 Unstained Samples



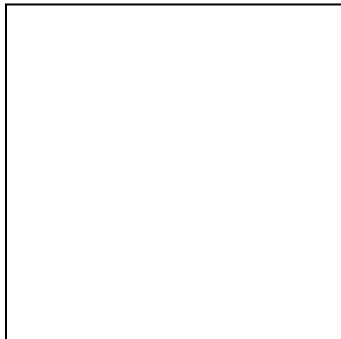
5% SDT + 5% TAC



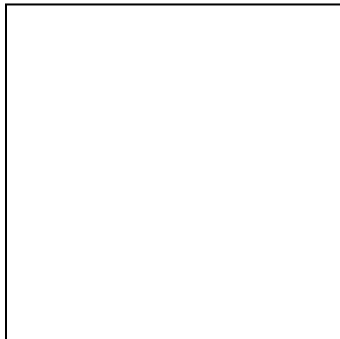
10% SMB + 5% TAC



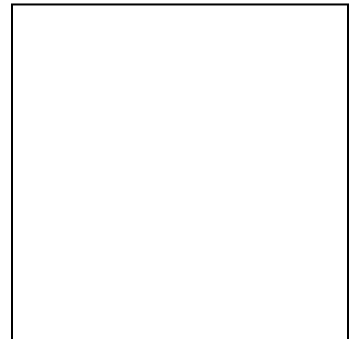
10% AA + 5% TAC



Untreated



5% TAC



De-ionised water control

I. Cost Calculations

The treatment costs were calculated using the following equations:

$$\text{SDT} = \text{reagent g}/500\text{g} \times \text{£}38.40$$

$$\text{SMB} = \text{reagent g}/500\text{g} \times \text{£}25.15$$

$$\text{AA} = \text{reagent g}/100\text{g} \times \text{£}19.50$$

$$\text{TAC} = \text{reagent g} / 500\text{g} \times \text{£}63.60 = 3.5/500 \times \text{£}63.60 = \text{£}0.45$$

The amounts used are in the table below. The £0.45 for TAC was added to each treatment total.

Reagent concentration	Mass in 70 mL DI water (g)
1%	0.7
2%	1.4
5%	3.5
10%	7
15%	10.5

Mass of reagent used based on concentration

J. Spectrophotometry Data

All measurements are after treatment. The first set of measurements for each sample are specular component included (SCI) and the second set are specular component excluded (SCE).

J.1 Stained Sample Treatments

Data Name	L*	a*	B*	C*	h	dL*	da*	db*	dC*	dH*	dE*ab	dE00
[Mean]AA 1	68.04	18.45	42.02	45.89	66.29	11.39	-5.81	-3.82	-5.97	3.56	13.34	10.18
[Mean]AA 1	67.95	18.44	41.98	45.85	66.28	11.34	-5.81	-3.89	-6.04	3.53	13.32	10.15
[Mean]AA 2	69.32	17.58	41.77	45.32	67.17	10.93	-5.79	-4.23	-6.27	3.46	13.07	9.65
[Mean]AA 2	69.25	17.57	41.73	45.28	67.17	10.91	-5.79	-4.28	-6.32	3.45	13.07	9.64
[Mean]AA 3	66.03	19.69	40.62	45.15	64.14	9.54	-4.12	-2.63	-4.23	2.45	10.72	8.53
[Mean]AA 3	66	19.68	40.6	45.12	64.14	9.55	-4.13	-2.67	-4.27	2.44	10.74	8.54
[Mean]AA 4	67.4	18.71	40.89	44.97	65.41	8.49	-3.92	-3.51	-4.87	1.99	9.99	7.45
[Mean]AA 4	67.33	18.7	40.86	44.93	65.41	8.48	-3.91	-3.54	-4.89	1.98	9.99	7.45
[Mean]AA 5	64.01	20.23	41.37	46.05	63.94	6.8	-3.06	-2.88	-3.95	1.43	7.99	6.14
[Mean]AA 5	63.94	20.21	41.35	46.02	63.95	6.78	-3.08	-2.94	-4.02	1.41	8	6.13
[Mean]AA 6	65.49	19.72	41.05	45.54	64.35	8.67	-3.57	-2.2	-3.58	2.18	9.63	7.74
[Mean]AA 6	65.44	19.69	41.02	45.51	64.36	8.65	-3.58	-2.24	-3.62	2.17	9.62	7.73
[Mean]AA 7	71.63	16.42	41.4	44.54	68.37	12.55	-6.65	-3.86	-6.26	4.46	14.72	10.93
[Mean]AA 7	71.55	16.41	41.36	44.5	68.35	12.54	-6.64	-3.91	-6.3	4.43	14.71	10.92
[Mean]AA 8	71.27	16.14	41.31	44.35	68.66	14.64	-7.96	-3.94	-6.91	5.57	17.12	13
[Mean]AA 8	71.19	16.14	41.28	44.32	68.64	14.61	-7.95	-4	-6.97	5.54	17.11	12.99
[Mean]AA 9	72.36	15.41	39.82	42.7	68.85	16.81	-7.84	-2.88	-5.93	5.89	18.77	14.76
[Mean]AA 9	72.29	15.4	39.79	42.66	68.84	16.78	-7.85	-2.94	-5.98	5.88	18.76	14.74
[Mean]AA 10	67.99	20.62	46.1	50.5	65.9	12.98	-6.22	0.27	-2.61	5.66	14.4	11.85
[Mean]AA 10	67.91	20.62	46.05	50.46	65.88	12.96	-6.23	0.22	-2.66	5.63	14.38	11.84
[Mean]AA 11	68.23	17.44	40.49	44.09	66.7	10.45	-5.9	-3.34	-5.57	3.86	12.46	9.41
[Mean]AA 11	68.17	17.43	40.45	44.05	66.69	10.44	-5.89	-3.4	-5.63	3.83	12.46	9.4
[Mean]AA 12	61.33	20.13	40.3	45.05	63.46	7.65	-3.52	-1.41	-2.91	2.44	8.54	7.24

[Mean]AA 12	61.29	20.11	40.28	45.02	63.47	7.64	-3.53	-1.46	-2.95	2.43	8.54	7.24
[Mean]AA 13	62.53	20.19	40.36	45.13	63.43	8.04	-3.96	-2.74	-4.28	2.22	9.37	7.51
[Mean]AA 13	62.48	20.17	40.35	45.11	63.44	8.04	-3.98	-2.8	-4.34	2.21	9.4	7.52
[Mean]AA 14	67.42	17.8	40.24	44	66.14	9.23	-5.92	-4.99	-7.07	3.16	12.05	8.43
[Mean]AA 14	67.37	17.79	40.21	43.97	66.14	9.22	-5.93	-5.03	-7.11	3.14	12.06	8.43
[Mean]AA 15	68.01	16.9	40.1	43.51	67.14	11.46	-6.87	-5.69	-8.07	3.79	14.52	10.44
[Mean]AA 15	67.93	16.89	40.07	43.49	67.14	11.42	-6.87	-5.74	-8.12	3.77	14.5	10.42
[Mean]SMB 1	57.91	23.59	44.57	50.43	62.11	0.16	0.65	-0.31	0.03	-0.72	0.74	0.51
[Mean]SMB 1	57.87	23.58	44.58	50.43	62.13	0.17	0.65	-0.32	0.01	-0.73	0.75	0.52
[Mean]SMB 2	59.35	24.27	47.18	53.05	62.77	1.71	0.36	1.15	1.18	0.21	2.09	1.58
[Mean]SMB 2	59.3	24.26	47.17	53.05	62.78	1.7	0.34	1.12	1.15	0.21	2.07	1.58
[Mean]SMB 3	60.9	22.35	44.28	49.6	63.22	1.77	-0.24	-0.08	-0.18	0.17	1.79	1.57
[Mean]SMB 3	60.85	22.34	44.27	49.59	63.22	1.79	-0.24	-0.11	-0.21	0.16	1.81	1.58
[Mean]SMB 4	59.94	22.55	43.89	49.34	62.81	2.35	-0.19	0.17	0.06	0.25	2.36	2.11
[Mean]SMB 4	59.9	22.53	43.9	49.34	62.83	2.35	-0.2	0.15	0.04	0.25	2.37	2.12
[Mean]SMB 5	56.35	22.4	40.99	46.71	61.34	0.84	0.01	-0.17	-0.15	-0.09	0.86	0.79
[Mean]SMB 5	56.31	22.4	40.99	46.71	61.35	0.84	0.02	-0.2	-0.17	-0.11	0.86	0.79
[Mean]SMB 6	68.57	17.16	41.25	44.68	67.42	11.91	-7.17	-4.39	-7.05	4.59	14.58	10.84
[Mean]SMB 6	68.5	17.16	41.23	44.65	67.4	11.9	-7.17	-4.44	-7.08	4.57	14.58	10.83
[Mean]SMB 7	56.42	23.67	42.8	48.91	61.06	0.78	0.76	0.49	0.8	-0.43	1.2	0.83
[Mean]SMB 7	56.39	23.66	42.82	48.92	61.08	0.78	0.75	0.48	0.78	-0.43	1.19	0.82
[Mean]SMB 8	56.9	23.75	42.91	49.05	61.03	1.04	0.46	0.29	0.48	-0.26	1.17	0.99
[Mean]SMB 8	56.85	23.74	42.91	49.04	61.04	1.03	0.44	0.26	0.44	-0.26	1.15	0.99
[Mean]SMB 9	57.72	25.41	45.84	52.41	61	1.65	0.23	0.93	0.93	0.25	1.91	1.55
[Mean]SMB 9	57.67	25.4	45.86	52.42	61.02	1.67	0.23	0.93	0.92	0.25	1.92	1.57
[Mean]SMB 10	58.95	24.01	45.33	51.3	62.09	2.3	0.23	1.04	1.03	0.29	2.53	2.12
[Mean]SMB 10	58.9	24	45.35	51.31	62.11	2.29	0.23	1.05	1.03	0.29	2.53	2.12
[Mean]SMB 11	57.96	23.05	42.42	48.28	61.48	2.18	0.39	0.44	0.58	-0.14	2.26	2.01
[Mean]SMB 11	57.93	23.04	42.43	48.28	61.5	2.2	0.39	0.44	0.57	-0.13	2.27	2.03
[Mean]SMB 12	60.58	23.75	45.57	51.39	62.47	2.23	-0.02	0.63	0.55	0.32	2.31	1.99

[Mean]SMB 12	60.54	23.74	45.58	51.39	62.49	2.23	-0.03	0.64	0.55	0.32	2.32	2
[Mean]SMB 13	59.81	24.12	45.52	51.51	62.08	2.04	0.26	0.57	0.63	0.04	2.13	1.83
[Mean]SMB 13	59.75	24.1	45.5	51.49	62.09	2.03	0.25	0.54	0.59	0.03	2.12	1.83
[Mean]SMB 14	60.54	23.97	45.76	51.65	62.35	2.65	0	0.83	0.73	0.38	2.78	2.38
[Mean]SMB 14	60.48	23.94	45.75	51.63	62.37	2.64	-0.01	0.79	0.69	0.38	2.76	2.38
[Mean]AA 15	61.93	23.61	46.49	52.14	63.08	6.74	-0.95	3.4	2.54	2.45	7.61	6.32
[Mean]AA 15	61.88	23.59	46.48	52.13	63.09	6.74	-0.97	3.37	2.51	2.45	7.6	6.33
[Mean]TAC 1	59.44	23.55	44.65	50.48	62.19	0.89	0.46	0.84	0.96	-0.02	1.31	0.85
[Mean]TAC 1	59.39	23.54	44.65	50.47	62.2	0.89	0.45	0.81	0.93	-0.02	1.29	0.84
[Mean]TAC 2	57.33	24.02	44.35	50.43	61.55	1.28	0.08	0.24	0.25	0.04	1.3	1.18
[Mean]TAC 2	57.29	24.01	44.35	50.43	61.57	1.28	0.07	0.21	0.22	0.04	1.3	1.18
[Mean]TAC 3	58.42	22.98	43.86	49.52	62.34	2.25	0.06	0.6	0.56	0.23	2.33	2.07
[Mean]TAC 3	58.38	22.97	43.88	49.53	62.37	2.25	0.05	0.58	0.54	0.23	2.32	2.07
[Mean]TAC 4	60.85	24.21	48.63	54.32	63.53	1.54	0.33	0.98	1.02	0.14	1.86	1.39
[Mean]TAC 4	60.78	24.2	48.62	54.31	63.54	1.54	0.32	0.97	1.01	0.14	1.85	1.39
[Mean]TAC 5	59.17	24.35	47.06	52.99	62.64	2.12	0.12	1.5	1.38	0.59	2.6	2
[Mean]TAC 5	59.12	24.33	47.06	52.98	62.66	2.13	0.12	1.5	1.38	0.6	2.61	2.01
[Mean]Control 1	57.32	22.84	43.68	49.29	62.39	0.29	0.87	1.05	1.33	-0.29	1.4	0.54
[Mean]Control 1	57.27	22.83	43.7	49.3	62.41	0.29	0.86	1.05	1.33	-0.28	1.39	0.53
[Mean]Control 2	58.68	23.23	44.85	50.51	62.62	-0.91	0.86	0.29	0.65	-0.64	1.29	0.94
[Mean]Control 2	58.63	23.21	44.85	50.5	62.64	-0.91	0.85	0.29	0.64	-0.62	1.27	0.94
[Mean]Control 3	56.02	22.77	41.47	47.31	61.23	-1.82	0.53	-1.65	-1.21	-1.24	2.51	1.92
[Mean]Control 3	55.98	22.76	41.48	47.32	61.24	-1.81	0.53	-1.64	-1.2	-1.24	2.5	1.91
[Mean]Control 4	56.56	24.89	45.78	52.11	61.47	1.03	0.31	0.92	0.96	0.17	1.42	1.01
[Mean]Control 4	56.52	24.88	45.81	52.13	61.49	1.04	0.3	0.93	0.96	0.18	1.42	1.02
[Mean]Control 5	55.29	24.65	44.61	50.96	61.08	0.37	0.77	1	1.25	-0.19	1.31	0.53
[Mean]Control 5	55.23	24.64	44.62	50.97	61.1	0.37	0.75	0.96	1.21	-0.2	1.28	0.53
[Mean]SDT 1	91.03	-0.42	11.36	11.37	92.11	32.26	-23.42	-33.57	-39.11	12.09	52.12	30.45
[Mean]SDT 1	90.85	-0.38	11.42	11.42	91.89	32.13	-23.37	-33.51	-39.05	12.02	51.98	30.37
[Mean]SDT 2	91.27	-0.37	10.35	10.36	92.05	34.8	-23.57	-33.2	-38.99	11.74	53.56	32.27

[Mean]SDT 2	91.1	-0.33	10.41	10.42	91.81	34.66	-23.52	-33.14	-38.92	11.68	53.41	32.18
[Mean]SDT 3	89.86	0.61	15.53	15.54	87.75	33	-22.96	-27.67	-33.67	12.61	48.8	29.95
[Mean]SDT 3	89.7	0.65	15.57	15.58	87.61	32.88	-22.92	-27.64	-33.63	12.56	48.68	29.87
[Mean]SDT 4	91.36	-0.39	10.81	10.81	92.09	36.04	-24.41	-34.52	-40.48	12.19	55.55	33.31
[Mean]SDT 4	91.17	-0.35	10.86	10.87	91.86	35.91	-24.37	-34.48	-40.44	12.13	55.43	33.23
[Mean]SDT 5	91.67	-0.44	9.35	9.36	92.67	35.69	-23.71	-33.72	-39.6	11.46	54.53	33.05
[Mean]SDT 5	91.49	-0.39	9.42	9.43	92.39	35.55	-23.66	-33.65	-39.52	11.4	54.37	32.95
[Mean]SDT 6	92.74	-0.5	5.26	5.29	95.39	38.03	-25.39	-39.04	-45.53	9.78	60.13	35.79
[Mean]SDT 6	92.57	-0.46	5.36	5.37	94.87	37.88	-25.35	-38.96	-45.45	9.72	59.96	35.68
[Mean]SDT 7	92.53	-0.47	5.38	5.4	94.98	37.52	-23.77	-36.92	-42.89	9.4	57.76	35.09
[Mean]SDT 7	92.35	-0.43	5.46	5.48	94.48	37.37	-23.73	-36.86	-42.83	9.33	57.61	34.98
[Mean]SDT 8	92.78	-0.57	5.67	5.7	95.72	38.33	-24.24	-36.77	-42.9	9.98	58.39	35.64
[Mean]SDT 8	92.6	-0.53	5.76	5.79	95.25	38.18	-24.2	-36.7	-42.83	9.91	58.22	35.53
[Mean]SDT 9	92.64	-0.52	5.39	5.42	95.47	39.76	-25.02	-36.26	-42.91	9.98	59.35	36.82
[Mean]SDT 9	92.44	-0.47	5.47	5.5	94.95	39.6	-24.99	-36.2	-42.86	9.92	59.19	36.72
[Mean]SDT 10	92.58	-0.55	5.73	5.75	95.49	36.62	-23.59	-36.53	-42.38	9.75	56.85	34.36
[Mean]SDT 10	92.39	-0.51	5.81	5.83	94.97	36.49	-23.54	-36.46	-42.31	9.67	56.7	34.26
[Mean]SDT 11	91.36	-0.35	9.42	9.43	92.11	33.99	-23.43	-35.07	-40.7	11.09	54.17	31.93
[Mean]SDT 11	91.19	-0.31	9.49	9.5	91.85	33.86	-23.39	-34.99	-40.62	11.03	54.02	31.85
[Mean]SDT 12	92.09	-0.47	7.69	7.71	93.47	36.08	-24.79	-37.14	-43.3	10.91	57.41	33.9
[Mean]SDT 12	91.91	-0.42	7.77	7.78	93.1	35.93	-24.74	-37.07	-43.23	10.84	57.25	33.8
[Mean]SDT 13	91.66	-0.34	8.59	8.6	92.27	35.44	-23.45	-33.44	-39.36	10.88	54.07	32.9
[Mean]SDT 13	91.48	-0.3	8.66	8.67	91.98	35.29	-23.4	-33.4	-39.32	10.82	53.93	32.8
[Mean]SDT 14	91.96	-0.55	7.83	7.85	94.04	32.49	-23.17	-36.91	-42.28	10.56	54.36	31.28
[Mean]SDT 14	91.78	-0.51	7.91	7.93	93.71	32.37	-23.13	-36.85	-42.22	10.49	54.22	31.19
[Mean]SDT 15	91.95	-0.52	7.84	7.86	93.83	38.98	-23.91	-32.45	-38.73	11.18	56.08	35.63
[Mean]SDT 15	91.76	-0.48	7.92	7.93	93.47	38.85	-23.87	-32.4	-38.68	11.11	55.94	35.54

J.2 Unstained Sample Treatments

Data Name	L*	a*	b*	C*	h	dL*	da*	db*	dC*	dH*	dE*ab	dE00
[Mean]AA 1	93.01	-0.28	2.7	2.72	95.9	-0.35	0.21	-0.16	-0.19	-0.18	0.44	0.39
[Mean]AA 1	92.8	-0.24	2.81	2.82	94.83	-0.33	0.21	-0.16	-0.18	-0.19	0.42	0.39
[Mean]AA 2	93.22	-0.35	2.69	2.71	97.46	-0.13	0.12	-0.03	-0.04	-0.12	0.18	0.19
[Mean]AA 2	93.02	-0.31	2.79	2.8	96.39	-0.11	0.12	-0.03	-0.05	-0.12	0.17	0.19
[Mean]AA 3	93.25	-0.4	2.74	2.77	98.32	-0.06	0.05	-0.18	-0.18	-0.02	0.19	0.17
[Mean]AA 3	93.05	-0.36	2.83	2.86	97.21	-0.03	0.05	-0.18	-0.19	-0.02	0.19	0.18
[Mean]AA 4	93.26	-0.43	2.8	2.83	98.67	-0.14	0.04	-0.28	-0.28	0	0.32	0.27
[Mean]AA 4	93.05	-0.39	2.9	2.93	97.56	-0.12	0.04	-0.28	-0.29	0	0.31	0.26
[Mean]AA 5	93.26	-0.39	2.71	2.74	98.11	-0.12	0.08	-0.17	-0.18	-0.06	0.23	0.21
[Mean]AA 5	93.06	-0.35	2.8	2.83	97.01	-0.1	0.08	-0.17	-0.18	-0.06	0.21	0.2
[Mean]SMB 1	93.27	-0.39	2.65	2.68	98.28	0	0.12	-0.38	-0.39	-0.06	0.4	0.37
[Mean]SMB 1	93.07	-0.34	2.75	2.77	97.13	0.03	0.12	-0.37	-0.38	-0.06	0.39	0.36
[Mean]SMB 2	93.27	-0.46	2.7	2.74	99.6	-0.11	0.08	-0.3	-0.31	-0.03	0.32	0.29
[Mean]SMB 2	93.07	-0.41	2.79	2.82	98.43	-0.08	0.08	-0.29	-0.3	-0.04	0.32	0.29
[Mean]SMB 3	93.31	-0.42	2.71	2.75	98.84	-0.09	0.08	-0.24	-0.25	-0.04	0.27	0.24
[Mean]SMB 3	93.1	-0.38	2.8	2.83	97.69	-0.07	0.08	-0.25	-0.25	-0.04	0.27	0.25
[Mean]SMB 4	93.19	-0.4	2.58	2.61	98.74	-0.19	0.09	-0.25	-0.26	-0.05	0.33	0.28
[Mean]SMB 4	92.99	-0.36	2.67	2.69	97.62	-0.16	0.09	-0.25	-0.26	-0.05	0.31	0.27
[Mean]SMB 5	93.15	-0.41	2.64	2.68	98.74	-0.22	0.07	-0.18	-0.19	-0.04	0.29	0.23
[Mean]SMB 5	92.94	-0.37	2.74	2.77	97.61	-0.21	0.07	-0.18	-0.18	-0.04	0.28	0.22
[Mean]SDT 1	93.39	-0.43	2.63	2.66	99.31	0.05	0.06	-0.28	-0.28	-0.01	0.29	0.26
[Mean]SDT 1	93.19	-0.39	2.72	2.75	98.18	0.07	0.05	-0.28	-0.28	-0.01	0.29	0.26
[Mean]SDT 2	93.43	-0.43	2.71	2.75	99.06	0.06	0.05	-0.22	-0.22	-0.02	0.23	0.21
[Mean]SDT 2	93.22	-0.39	2.81	2.83	97.96	0.07	0.05	-0.22	-0.22	-0.02	0.24	0.21
[Mean]SDT 3	93.31	-0.44	2.7	2.73	99.25	-0.04	0.08	-0.28	-0.29	-0.03	0.29	0.27
[Mean]SDT 3	93.1	-0.4	2.79	2.82	98.14	-0.02	0.07	-0.28	-0.28	-0.03	0.29	0.26

[Mean]SDT 4	93.38	-0.44	2.52	2.56	99.94	0.05	0.04	-0.37	-0.38	0.03	0.38	0.34
[Mean]SDT 4	93.18	-0.4	2.62	2.65	98.73	0.06	0.04	-0.37	-0.37	0.02	0.38	0.34
[Mean]SDT 5	93.03	-0.41	2.77	2.8	98.52	-0.26	0.06	-0.04	-0.05	-0.06	0.27	0.19
[Mean]SDT 5	92.81	-0.38	2.86	2.89	97.47	-0.26	0.06	-0.05	-0.05	-0.05	0.27	0.18
[Mean]C 1	93.19	-0.43	2.87	2.9	98.61	-0.23	0.06	0.06	0.05	-0.07	0.24	0.18
[Mean]C 1	92.98	-0.39	2.97	2.99	97.51	-0.22	0.07	0.06	0.05	-0.07	0.23	0.17
[Mean]C 2	93.26	-0.42	2.77	2.8	98.62	-0.19	0.11	-0.18	-0.2	-0.08	0.29	0.25
[Mean]C 2	93.07	-0.38	2.87	2.89	97.46	-0.16	0.12	-0.18	-0.2	-0.09	0.27	0.25
[Mean]C 3	93.08	-0.41	2.77	2.81	98.51	-0.32	0.06	-0.06	-0.07	-0.05	0.33	0.22
[Mean]C 3	92.88	-0.37	2.87	2.89	97.39	-0.31	0.06	-0.07	-0.08	-0.05	0.32	0.21
[Mean]C 4	93.32	-0.43	2.91	2.94	98.34	0	0.06	0.01	0	-0.06	0.06	0.09
[Mean]C 4	93.12	-0.38	3	3.03	97.31	0.02	0.06	0.01	0	-0.06	0.07	0.09
[Mean]C 5	93.21	-0.44	2.71	2.75	99.23	-0.21	0.04	-0.24	-0.24	0	0.32	0.25
[Mean]C 5	93.01	-0.4	2.81	2.84	98.1	-0.19	0.03	-0.24	-0.24	0	0.31	0.24
[Mean]TAC 1	93.15	-0.44	2.92	2.96	98.58	-0.15	0.04	0.02	0.01	-0.04	0.15	0.11
[Mean]TAC 1	92.96	-0.4	3.02	3.04	97.51	-0.12	0.04	0.02	0.01	-0.04	0.12	0.09
[Mean]TAC 2	93.25	-0.41	2.74	2.77	98.41	-0.14	0.04	0.09	0.08	-0.05	0.17	0.13
[Mean]TAC 2	93.05	-0.36	2.84	2.86	97.32	-0.12	0.04	0.09	0.08	-0.05	0.15	0.12
[Mean]TAC 3	93.36	-0.42	2.76	2.8	98.58	-0.02	0.06	0	-0.01	-0.06	0.06	0.09
[Mean]TAC 3	93.17	-0.38	2.86	2.89	97.48	0	0.06	0	-0.01	-0.06	0.06	0.08
[Mean]TAC 4	93.28	-0.45	2.85	2.89	98.95	-0.11	0.02	0.05	0.05	-0.03	0.13	0.09
[Mean]TAC 4	93.08	-0.41	2.95	2.97	97.87	-0.1	0.02	0.05	0.05	-0.03	0.12	0.08
[Mean]TAC 5	93.25	-0.44	2.82	2.86	98.78	-0.07	0.05	0.04	0.04	-0.05	0.09	0.09
[Mean]TAC 5	93.05	-0.39	2.92	2.95	97.68	-0.02	0.05	0.04	0.03	-0.05	0.07	0.08

J.3 Historical Sampler Treatments

Data Name	L*	a*	b*	C*	h	dL*	da*	db*	dC*	dH*	dE*ab	dE00
[Mean]Right AT (5% AA)	74.22	4.84	16.77	17.45	73.91	19.15	-6.36	-8.12	-9.84	3.1	21.76	16.94
[Mean]Right AT (5% AA)	74.08	4.86	16.79	17.48	73.85	19.07	-6.37	-8.13	-9.85	3.09	21.68	16.89
[Mean]Middle AT (5% SDT)	76.55	4.06	14.53	15.08	74.39	21.39	-6.02	-8.6	-10.15	2.7	23.83	18.53
[Mean]Middle AT (5% SDT)	76.35	4.08	14.54	15.11	74.32	21.25	-6.03	-8.61	-10.16	2.7	23.71	18.45
[Mean]Left AT (10% SMB)	60.2	12.94	30.85	33.45	67.24	8.8	0.62	3.16	3.14	0.69	9.37	8.35
[Mean]Left AT (10% SMB)	60.08	12.97	30.9	33.51	67.23	8.72	0.61	3.17	3.15	0.7	9.3	8.29

K. Bathophenanthroline Data

Key

0 = Negative result (no iron ions or below the detection limit)

1 = Positive result

s = Pinpoint result (water contaminants interpreted as negative results)

Reagent	Sample ID	Before Treatment		After Treatment	
		Iron (II) Test	Iron (III) Test	Iron (II)	Iron (III)
1% SDT	SDT 1	0	s	0	0
	SDT 2	0	0	0	0
	SDT 3	0	1	0	s
	SDT 4	s	s	0	s
	SDT 5	0	0	0	0
2% SDT	SDT 11	0	s	0	s
	SDT 12	s	s	0	s
	SDT 13	0	0	0	s
	SDT 14	0	0	0	s
	SDT 15	0	1	0	s
5% SDT	SDT 6	0	s	0	s
	SDT 7	0	s	0	0
	SDT 8	0	s	0	s
	SDT 9	0	0	0	s
	SDT 10	0	s	0	s
2% SMB	SMB 1	0	0	1	1
	SMB 2	0	0	0	1
	SMB 3	0	s	1	1
	SMB 4	0	0	1	1
	SMB 5	0	0	1	1
5% SMB	SMB 6	1	1	1	1
	SMB 7	1	1	0	1
	SMB 8	0	0	1	1
	SMB 9	0	0	0	1
	SMB 10	0	s	0	1
10% SMB	SMB 11	1	1	0	1
	SMB 12	0	0	0	1
	SMB 13	0	1	0	1
	SMB 14	0	1	0	1
	SMB 15	0	s	0	1
5% AA	AA 1	0	1	1	1
	AA 2	0	0	1	1
	AA 3	0	1	1	1
	AA 4	0	0	1	1
	AA 5	0	1	1	1

10% AA	AA 6	s	s	1	1
	AA 7	0	s	1	1
	AA 8	0	s	1	1
	AA 9	0	s	1	1
	AA 10	0	0	1	1
15% AA	AA 11	0	1	1	1
	AA 12	s	1	1	1
	AA 13	0	s	1	1
	AA 14	s	1	1	1
	AA 15	0	1	1	1
5% TAC	TAC 1	0	s	1	1
	TAC 2	0	s	1	1
	TAC 3	0	0	1	1
	TAC 4	0	0	1	1
	TAC 5	0	0	1	1
DI water immersed samples	C 1	0	s	0	0
	C 2	0	s	0	0
	C 3	0	s	0	0
	C 4	0	0	0	0
	C 5	0	s	1	0
DI water immersed samples	W 1	s	1	0	0
	W 2	0	0	s	s
	W 3	0	0	0	0
	W 4	0	0	0	0
	W 5	0	0	0	0
Historical Rusty Nails	N 1	1	1	1	1
	N 2	1	1	1	1
	N 3	1	1	1	1
	N 4	1	1	1	1
	N 5	1	1	1	1