Wain, Fiona (2015) *An investigation into the effectiveness of using a pH buffer in wet cleaning historical textiles.* [MPhil]

An Investigation into the Effectiveness of using a pH Buffer in Wet Cleaning Historical Textiles

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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, August 2015

Abstract

A pH buffer is used in wet cleaning to control the pH of the wash solution. This research investigates the use and effectiveness of pH buffers for wet cleaning in textile conservation through questionnaires sent to practising textile conservators and by conducting wet cleaning experiments. The most commonly used pH buffers were found to be tri-ammonium citrate and tri-sodium citrate self buffers. Experiments were conducted on naturally aged cotton and silk fabrics using Hostapon T® and Dehypon LS45® respectively, with tri-sodium citrate self buffer and tri-sodium citrate with citric acid and sodium hydroxide with citric acid combination buffers at comparable concentrations. The experiments focused on measurement of the pH of the wash baths, the change in pH of the samples and, to quantify soiling removal, the colour change of the samples. Citric acid in the pH buffer reduced the cloud point of Dehypon LS45®. Tri-sodium citrate was most effective at increasing soiling removal. Tri-sodium citrate in combination with citric acid was found to buffer the pH of the wash solutions most effectively and was also effective at increasing soiling removal.

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Acknowledgements

I would like to thank my supervisor Dr. Anita Quye for her support during this research project. I would like to express thanks to the National Trust Textile Conservation Studio for their support, in particular to Rosamund Weatherall for inspiring me to research pH buffers. Thank you to Frances Lennard, Karen Thompson and Sarah Foskett for their advice and tutoring.

I would like to express thanks to all of the conservators who took the time to reply to the questionnaire, which was a huge help to my project.

Thank you to the Textile Conservation Foundation for their help in finding funding. I am extremely grateful to the South Square Trust, the Anna Plowden Trust, the Coats Foundation Trust and the Cross Trust for their financial support, without which I would not have been able to complete the programme.

Finally, I would like to thank my family and my partner John for their never ending emotional support and encouragement.

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Chapter 1: Introduction

1.1 Introduction

A pH buffer is used in wet cleaning historical textiles in order to prevent sharp changes in the pH of the wash solution. The release of degradation products and soiling, which are usually acidic, into the wash bath cause the pH to drop and can cause further damage to the degraded fibres through hydrolysis. Other reasons for controlling the pH of the wash bath are to prevent or reduce dye bleed from textiles, and for optimal cleaning efficiency.[1]

The subject of pH buffers in wet cleaning was chosen through discussion with colleagues and from investigations for treatments, finding that many of the practical questions on the use of pH buffers are not available or easily accessible. The purpose of this research project is to investigate the current use of pH buffers for wet cleaning in textile conservation practice, and to assess the effectiveness of selected pH buffers in wet cleaning.

This is an initial piece of research that can be built on as further questions arise during the research process, and has been limited to answer a few fundamental questions with regards to the use of pH buffers in wet cleaning.

1.2 Aims

- To identify pH buffers currently used by textile conservators
- To find out why pH buffers are, or are not used in wet cleaning
- To discover the breadth of information and sources available
- To assess the effects of using a pH buffer on the pH of the object and wash solution
- To identify how a pH buffer affects soiling removal

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[1] Ágnes Tímár-Balázsy and Dinah Eastop, *Chemical Principles of Textile Conservation* (Oxford: Butterworth-Heinemann, 1998), 219.

1.3 Objectives

- Send questionnaires on the use of pH buffers in wet cleaning to practising textile conservators
- Analyse results to inform the experimental phase
- Carry out a literature review to highlight gaps in information available on pH buffers
- Conduct experiments using pH buffers monitoring pH and soiling removal from samples
- Analyse results and draw conclusions

1.4 Research Methodology

1.4.1 Questionnaire

The initial phase of research is to gather information on pH buffers by sending questionnaires to practising textile conservators, to gain a snapshot of their use in the UK. This information will influence the experimental phase of the research, including the choice of pH buffers and detergent that will be used in the experiments.

1.4.2 Experiment plan

Experiments will be conducted focusing on stability of pH in the wash bath, change in pH and change in colour of the samples due to soiling removal.

To determine the pH of the samples to be treated, an in-situ measurement will be taken. Aqueous extraction as a method for measuring pH is being taken into consideration, as this can give a more accurate reading. Continuity during the experiments will be paramount, and control samples will be used for comparison of results.

Chapter 2: Literature Review

2.1 Introduction

This literature review will introduce the wet cleaning process before discussing the use of pH buffers and pH measurement in the context of wet cleaning in textile conservation. A short overview of wet cleaning, pH buffers and pH measurement in paper conservation will be included to find similarities and differences in the way treatments are conducted. This review aims to identify gaps in the knowledge on the use of pH buffers for wet cleaning historical textiles, and to find crossover of techniques and materials used in paper conservation.

2.2 Wet Cleaning in Textile Conservation

Wet cleaning is a treatment method that removes water soluble acids and degradation products from textiles.[2,3] Cartwright and Colombini explain that pH is a "prime factor in determining the state of a textile".[4] One of the aims of wet cleaning textiles is to attain a neutral pH within the textile.[5] Eastop *et al.* highlight the damaging effects of acidic soiling on textiles, and that wet cleaning an acidic object will remove acidic soiling.[6] Wet cleaning is an irreversible process and should only be undertaken once all of the benefits and risks to the object involved have been considered.[7]

When undertaking wet cleaning the type of fibre to be treated is taken into consideration. Ideal wet cleaning conditions are slightly acidic (pH4.5-5.5) for protein

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[2] Elizabeth E. Peacock, “Deacidification of Degraded Linen,” *Studies in Conservation* 28, no. 1 (1983): 8-14, http://dx.doi.org/10.1179/sic.1983.28.1.8, 10**.**

[3] Ute Henniges *et al*., “Controversial Influence of Aqueous Treatments on Historic Textiles,” *Polymer Degradation and Stability* 96, no. 4 (2011): 588-594, http://dx.doi.org/10.1016/j.polymdegradstab.2010.12.013, 590.

[4] Helen Cartwright and Alain Colombini, “Detergent Monitoring During the Washing Process at the Textile Conservation Studios, Hampton Court Palace,” In *ICOM CC, 10th Triennial Conference, Washington DC, 22-27 August 1993, Preprints*, ed. Janet Bridgland, 293-298 (LA: Allied Publishers, 2008), 294.

[5] Sheila Landi, *The Textile Conservator’s Manual* 2nd edition (Oxford: Butterworth-Heinemann, 1992) 37.

[6] D. D. M. Eastop *et al*., *The Control of pH in Wet Cleaning and Deacidification of Textiles,* (Original Typescript, 1981) 1.

[7] Patricia Ewer, “Practicalities of Wet Cleaning,” in *The Textile Speciality Group Postprints, Vol. 5: Papers Delivered at the Textile Subgroup Session, 23rd Annual Meeting, St. Paul, Minnesota, June 1995*, ed. Patricia Ewer and Beth McLaughlin, 25-28 (AIC, 1996), 25.

fibres, and for cellulosic fibres are slightly alkaline (pH7-8.5).[8] During wet cleaning multiple wash and rinse baths and running rinses are implemented, with a final rinse in deionised water. Short wash baths have been found to be less damaging to textile fibres than prolonged soaking.[9,10] A darkening of fibres caused by long periods of soaking and a weakening of fibres from incomplete rinsing was found in an investigation by Shashoua.[11]

2.2.1 Surface-Active Agents and Soiling

Surface-active agents (surfactants) reduce the surface tension of water and allow it to penetrate textile fibres with ease; the classes of surfactants used in textile conservation are anionic and non-ionic.[12] The effect of these surfactants on textile fibres has been investigated, concluding that protein fibres should be washed with non-ionic surfactants.[13] Cellulosic fibres can be washed with either anionic, or non-ionic surfactants.[14]

Columbus explains that the choice of detergent is dependent not only on fibre type, but also on soiling type.[15] Soiling types have been categorised (particulate, soluble, insoluble and greasy) and the forces adhering soiling to objects (Van der Waals forces, hydrogen bonding and chemical bonding) have been discussed.[16,17] Surfactant molecules have a hydrophobic tail (hydrocarbon chain) which solubilises greasy substances and a

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[8] David E. Walker, “Surfactants in Textile Conservation,” In *The Textile Speciality Group Postprints, Vol 5: Papers Delivered at the Textile Subgroup Session, 23rd Annual Meeting, St. Paul, Minnesota, June 1995*, ed. Patricia Ewer and Beth McLaughlin, 29-34 (AIC, 1996), 29.

[9] Cartwright and Colombini, 296.

[10] Tímár-Balázsy and Eastop, 209.

[11] Yvonne Shashoua, “Investigation into the Effects of Cleaning Natural Woven Textiles by Aqueous Immersion,” in *ICOM CC, 9th Triennial Conference, Dresden, 26-31 August 1990, Preprints*, ed. Kirsten Grimstad, 313-318 (Dresden: Allied Publishers, 2008), 317.

[12] Tímár-Balázsy and Dinah Eastop, 196-199.

[13] Tarja H. Reponen, “The Effects of Conservation Wet Cleaning on Standard Soiled Wool Fabric: Some Experimental Work,” In *ICOM CC, 10th Triennial Conference, Washington DC, 22-27 August 1993, Preprints*, ed. Janet Bridgland, 321-330 (LA: Allied Publishers, 2008).

[14] Walker, 30-31.

[15] Joseph Vincent Columbus, “Washing Techniques Used at the Textile Museum,” *Bulletin of the American Group: IIC* 7, no. 2 (1967): 14-16, http://www.jstor.org/stable/3178954, 15.

[16] Judith H. Hofenk-De Graaff, “The Constitution of Detergents in Connection with the Cleaning of Ancient Textiles,” *Studies in Conservation* 13, no. 3 (1968): 122-141, http://www.jstor.org/stable/1505317, 122-123.

[17] The Conservation Unit, *Science for Conservators, Volume 2: Cleaning* (London; New York: Routledge, 1992), 13-21.

hydrophilic head which solubilises polar substances. In anionic surfactants the hydrophilic head is negatively charged, and in non-ionic surfactants it is not completely ionic, but soluble in water. The molecules solubilise soiling, forming micelles which hold and suspend soiling in solution. Several authors have explained the action of surfactants swelling fibres, removing and holding soiling in the wash bath.[18,19,20,21]

2.3 pH buffers in Textile conservation

The terms 'de-acidification' and 'neutralisation' are used in textile conservation literature; however it is not always clear if the treatment being described differs from pH buffering. These treatments, including the use of pH buffers, are conducted to remove acidic degradation products and soiling from textiles, while preventing the wash solution pH from dropping to dangerously low levels that could cause damage to the object. Eastop *et al.* explain that colours of dyes may change due to the pH level, and a low pH will have an effect on the efficiency of the surfactant.[22]

Combination (mixed compound) buffers and self-buffers are discussed by Tímár-Balázsy and Eastop, who provide a table of self-buffers used in wet cleaning textiles with concentrations and pH provided.[23] It is not known if all of these self buffers are still in use in textile conservation practice, but the information can be used as a guideline. The design of a pH buffer is explained by Beynon and Easterby, providing equations to calculate pH buffers for specific situations if no prior recipe exists.[24] The language used is easy to understand and the authors go through the steps of pH buffers in a logical manner.

Buffers must be carefully chosen, a pH that is too high would be dangerous for proteins and for degraded cellulose. The most desirable pH in wet cleaning is neutral, or slightly

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[18] Judith H. Hofenk-De Graaff, "Some Recent Developments in the Cleaning of Ancient Textiles," *Studies in Conservation* 27, Supplement 1 (1982): 93-95, http://dx.doi.org/10.1179/sic.1982.27.Supplement-1.93, 338.
[19] Günter Jakobi and Albrecht Löhr, *Detergents and Textile Washing: Principles and Practice* (New York: VCH Publishers, 1987) 7-12.
[20] The Conservation Unit, 80-85.
[21] Tímár-Balázsy and Eastop, 202-204.
[22] Eastop *et al.*, 2.
[23] Tímár-Balázsy and Eastop, 219-221.
[24] R. J. Beynon and J. S. Easterby, *Buffer Solutions: the basics* (Oxford: Oxford University Press, 1996) 46-51.

higher.[25] In practice a pH buffer is usually chosen because it has proved to be successful in past treatments, therefore the methods rarely change.

2.3.1 Control and Monitoring of wash bath pH

Columbus and Rice discuss the importance of controlling the wash solution pH and tailoring it to the specific object.[26,27] However, no detail is given on how the pH of the solution is controlled. In the survey conducted by Ewer it is noted that although buffers are used to balance the wash solution pH, the point at which the additive was used varied between respondents,[28] but no detail is provided.

Two case studies are presented by Tímár-Balázsy and Eastop, using a pH buffer in wet cleaning. The reasons for choosing to use a pH buffer are explained in the context of the objects being treated. In both case studies the same buffer recipe is used: 0.5g/L tri-sodium citrate with $1cm^3$/L (1mL) of 1% citric acid solution. The pH buffer was used, on both occasions, from the first wash bath.[29] This recipe is still used in textile conservation practice; its publication in this go-to text has re-enforced it as safe to use and given it pronounced visibility; however there are no current case studies advocating the use of this recipe.

Mattock explains that when 0.2% of carbon dioxide is absorbed it can lower the pH of a solution by 0.001 units.[30] Therefore the pH of a wash solution that is not stored in a sealed container before use will decrease. This is also true during the wash bath, as it is unlikely and impractical for wet cleaning to be conducted in a carbon dioxide free environment. Decreasing the surface area of the wash bath is one way to reduce the carbon dioxide absorption by the wash solution. However, pH buffers added to the wash

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[25] Eastop, *et al.*, 3-4.
[26] Columbus, 15.
[27] James W. Rice, "Drycleaning Versus Wetcleaning for Treating Textile Artifacts," *Bulletin of the American Group: IIC* 12, no. 2 (1972): 50-55. http://www.jstor.org/stable/3179122, 51-53.
[28] Ewer, 27.
[29] Tímár-Balázsy and Eastop, 255, 370.
[30] G. Mattock, *pH Measurement and Titration* (London: Heywood & Company Lt., 1961) 51.

solution at a high enough concentration can resist the change in pH caused by carbon dioxide.[31]

2.3.2 pH Measurement

Tímár-Balázsy and Eastop, Montague and Tse discuss the pH measurement of objects and solutions using both colorimetric and electrometric methods.[32,33,34] Advice on how to measure the pH of an object is given, making the point that even in-situ testing on an object can cause irreversible damage because the surface must be wetted to take a reading, and the results are representative of the area sampled, not the entire object.[35] In-situ testing can be conducted using pH strips, or a surface pH electrode. If using pH strips, it is important to know if the strips are colourfast, as some bleed when wet. This is particularly important if they are to be used to indicate the surface pH of a textile. Both methods require wetting of the object; this can lead to ring marks on the object where soiling has dissolved and become mobile in the fibres, and should, therefore, be carefully considered before being implemented and be used on a discreet area of the object.

The British Standards Institution provides an industrial standard for determining the pH of a textile through aqueous extraction (EN ISO 3071:2006).[36] Aqueous extraction gives a more reliable reading of the objects pH than a surface reading, by measuring the internal pH of the fibres. The limitation of aqueous extraction in the context of conservation is discussed by Tse, and Montague, as it is a destructive technique that, as for surface measurements, may not be characteristic of the entire object.[37,38] The pH of

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[31] Beynon and Easterby, 49.

[32] Tímár-Balázsy and Eastop, 218.

[33] Meredith Montague, "pH Testing Methods in Textile Conservation." In *The Textile Speciality Group Postprints, Vol. 5: Papers Delivered at the Textile Subgroup Session, 23rd Annual Meeting, St. Paul, Minnesota, June 1995*, ed. Patricia Ewer and Beth McLaughlin, 20-23 (AIC, 1996), 20-21.

[34] Season Tse, "Guidelines for pH Measurement in Conservation," *CCI Technical Bulletin* 28 (2007), http://www.cci-icc.gc.ca/resources-ressources/publications/downloads/technicalbulletins/eng/TB28-GuidelinesforpHMeasurementsinConservation.pdf, 4-7.

[35] Tse,7-11.

[36] "Textiles - Determination of pH of aqueous extract," British Standards Online, https://bsol-bsigroup-com.ezproxy.lib.gla.ac.uk/Bibliographic/BibliographicInfoData/000000000030050606 (accessed through University Library June 7, 2015).

[37] Tse, 10-11.

[38] Montague, 21.

a textile differs throughout the object due to degradation patterns and soiling. To get a true reading for the whole textile, samples must be taken from an area representative of the soiling and degradation of the entire object. Aqueous extraction requires a sample to be removed, and is therefore an irreversible process. It may not always be possible to take samples from historical textiles to implement the extraction procedure. Montague notes that measuring the rinse water pH during wet cleaning provides a more accurate measurement of the objects pH than a surface reading, though it will be less accurate than an extracted reading.[39]

2.4 pH Buffers in Paper Conservation

2.4.1 Wet Cleaning

The procedure for wet cleaning paper is discussed by Hey, and Lienardy and van Damme.[40,41] They explain the reasoning for washing before using an alkaline rinse to de-acidify paper: washing releases degradation products from the paper allowing the alkaline rinse to be effective and can preventing staining to the paper. Hey impresses the importance of wetting out paper, and that de-acidification treatment should be conducted straight after washing, when the paper is still wet. This saves time, as colourfastness tests do not need to be reproduced, and ensures the alkaline solution is able to fully penetrate the cellulose fibres.[42] Washing of aged paper before de-acidification has shown to give final pH measurements that are higher than those obtained by only de-acidification.[43]

2.4.2 pH Buffers

Much of the literature on the conservation of paper concerning pH is regarding de-acidification of cellulose fibres through an alkaline rinse. Stephens *et al*. identify that a reduction of the wash solution pH during treatment conducted in open air laboratory conditions can be caused by absorption of carbon dioxide. Data collected from

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[39] Montague, 21-22

[40] Margaret Hey, “The Washing and Aqueous Deacidification of Paper,” *The Paper Conservator* 4, no. 1 (1979): 66-80, http://dx.doi.org/10.1080/03094227.1979.9638520, 68.

[41] Anne Lienardy and Philippe van Damme, “Paper Washing,” *The Paper Conservator* 14, no. 1 (1990): 23-30, http://dx.doi.org/10.1080/03094227.1990.9638384, 23.

[42] Hey, 68.

[43] Lienardy and van Damme (1990a), 27.

experiments showed that pH8.5 did not cause additional damage to cellulose on a molecular level, and shorter treatments were beneficial.[44] Lienardy and van Damme discuss a range of possible alkaline solutions for use on paper, highlighting that sodium hydroxide can change the colour of inks.[45] This is an important effect to identify; dye bleed tests are always carried out before wet cleaning, as colour change in an object could affect the meaning attributed to it.

2.4.3 pH Measurement

The difference in results of pH readings measured by a surface pH electrode and through aqueous extraction is noted by Joel *et al*., recommending minimum water for surface measurements. Surface pH measurement is a non-destructive method; however, the results must be carefully interpreted as additional materials will affect the pH.[46] Hindhaugh produced a pH map of a textblock by using a template to take surface pH readings from across selected pages. This enabled the author to show how the pH of the paper changed across the sheets.[47]

2.5 Conclusion

While wet cleaning was once a commonplace treatment, it is no longer carried out widely in conservation studios as a matter of routine.[48] The effect of wet cleaning on fibres has been examined and discussed through experimental data and case studies. Control of pH in the wash bath is necessary for various reasons; type and amount of soiling present, to prevent dye loss, suit fibre type, and aid soiling removal. Often the use of a pH buffer in textile conservation is discussed; however, the recipes used and the point of use are not always given, and there is a distinct lack of new case studies published citing the use of a pH buffer in the wash solution. Also, no detail on the extent

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[44] Catherine H. Stephens *et al*., “Assessing the Risks of Alkaline Damage During Deacidification Treatments of Oxidized Paper,” *JAIC* 48, no. 3 (2009): 235-249, http://www.jstor.org/stable/27784670.

[45] Anne Lienardy and Philippe Van Damme, “Practical Deacidification,” *Restaurator* 11, no. 1 (1990): 1-21, http://dx.doi.org/10.1515/rest.1990.11.1.1, 3.

[46] A. Joel *et al*., “The Measurement and Significance of pH in Paper Conservation,” Bulletin of the American Group: *IIC* 12, no. 2 (1972):119-125, http://www.jstor.org/stable/3179136, 123.

[47] Nick Hindhaugh, “A pH Survey of an Acidic Textblock,” *The Paper Conservator* 14, no. 1 (1990): 17-22, http://dx.doi.org/10.1080/03094227.1990.9638383.

[48] Frances Lennard, and Patricia Ewer, “Remedial Conservation,” in *Textile Conservation: Advances in Practice*, eds. F. Lennard and P. Ewer, 141-151 (Oxford: Elsevier, 2010) 142.

to which the buffer prevented changes in the wash solution pH during treatment is given. This leaves the conservator with more questions when there is not always time for additional research.

In paper conservation it has been found that an alkaline rinse is more effective after washing, once coloured degradation products have been fully removed from the object. Similarly in textile conservation the pH buffer can be used after the first wash bath, allowing soiling to be released before controlling the pH of the wash solution. However, guidance on the optimum time to add a pH buffer to the wash solution has not been found in the literature.

Standards for measuring pH have been provided,[49] and useful information on pH measurement in the context of textile conservation has been given, highlighting the most effective and accurate methods.[50,51] It is unfortunate that the most accurate method of measuring the pH of an object is destructive and unlikely to be a possibility for historical textiles. A comparison between aqueous pH extraction and surface measurement methods will be carried out to provide detail on how to interpret the results.

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[49] British Standards Online.

[50] Montague, 21.

[51] Tse, 7-10.

Chapter 3: pH and pH Measurement

3.1 Introduction

In this chapter pH will be defined and the terminology with regard to pH (pK_a and pK_b) will be explained. The different ways pH can be measured, including types of measuring equipment and the accuracy of readings will be discussed. Finally, techniques for measuring the pH of textiles will be outlined, along with their viability for use in textile conservation.

3.2 pH

The measure of hydrogen ions (H^+) in aqueous solution is expressed as pH, which has been reported to stand for 'potenz hydrogen', or 'the power of hydrogen'. However, this association of the 'p' has been disputed, it is now believed that the choice of the letter was arbitrary.[52] Numerically, pH is the negative of the logarithm to the base 10 of the H^+ concentration.[53]

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

The concentration in moles per litre is represented by the square brackets $[H^+]$.[54] The pH scale runs from 0 to 14, with '0' being highly acidic, '7' neutral, and '14' highly alkaline or basic (fig.3.1). The scale is logarithmic; with a reduction/increase in 1 pH unit equating to a ten times increase/reduction in H^+ concentrations.[55]

Water has neutral pH, it is in a constant state of flux, with equal numbers of H^+ and hydroxide ions (HO^-) dissociating and recombining in equilibrium:

$$H_2O \rightleftharpoons H^+ + OH^-$$

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[52] Jens G. Nørby, "The Origin and the Meaning of the Little p in pH," *Trends in Biochemical Sciences* 25, no. 1 (2000): 36-37, http://dx.doi.org/10.1016/S0968-0004(99)01517-0.

[53] Beynon and Easterby, 5.

[54] Tse, 1.

[55] Beynon and Easterby, 5.

Neutral pH corresponds to an equal concentration of H^+ and HO^-. As the concentration of H^+ increases the pH of the solution lowers, conversely, as the concentration of HO^- increases the pH of the solution increases (fig. 1).[56]

In aqueous solutions, acids and bases dissociate and the molecules split into ions. Strong acids and bases dissociate completely in water, whereas weak acids and bases dissociate only partially, and reversibly, reaching equilibrium in solution.[57] The amount of dissociation is measured using the pH scale (fig. 3.1).[58] Acidic compounds are hydrogen ion donators, giving up hydrogen ions into solution which combine with water molecules to form hydronium ions (H_3O^+). Conversely, basic compounds are electron attractors, and attract the H^+ in water molecules, leaving an excess of HO^- from water molecules in solution.

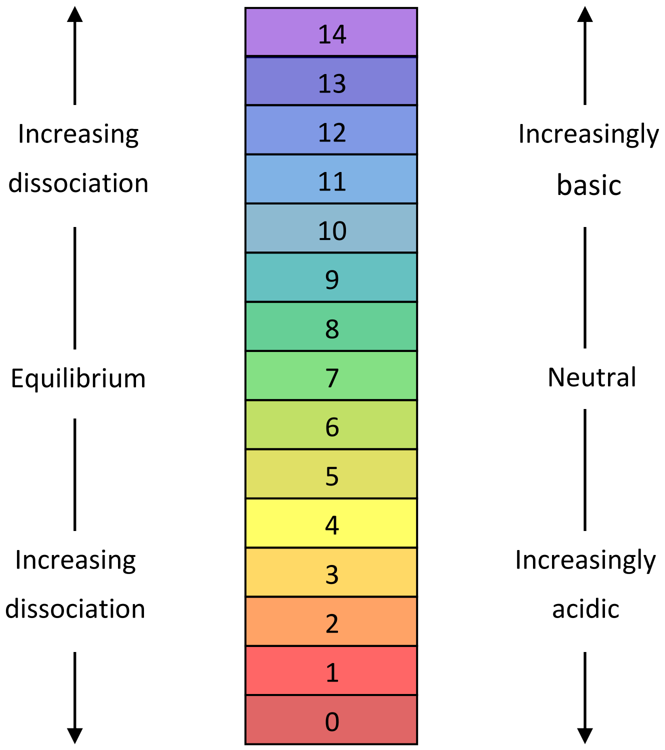

Figure 3.1 The pH scale showing strength increasing with dissociation.[59]

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[56] Tse, 1.

[57] Richard Wolbers, *Cleaning Painted Surfaces: Aqueous Methods* (London: Archetype Publications, 2000) 13.

[58] Tse, 1.

[59] Based on pH scale representation by John Holman and Phil Stone, *Chemistry* 2nd Edition, (Cheltenham: Nelson Thornes, 2001) 160.

The terms conjugate acid or base are used to define the molecules formed when a base receives a proton or an acid donates a proton respectively.[60] The strength of the acid or base is inversely proportional to the strength of the conjugate base or acid.[61] When water dissociates its conjugate acid is H_3O^+, and its conjugate base is HO^-.[62]

The reversible equilibrium reaction of weak acids is characterised by the dissociation constant K_a (where HA is the acid and A^- is the conjugate base):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For bases the reversible equilibrium reaction is characterised by the dissociation constant K_b (where B is the base and BH^+ is the conjugate acid):[63]

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Chemical reactions at equilibrium are defined using an equilibrium constant $K_{c(T)}$ (T represents constant temperature).[64] Equilibrium is dependent on temperature, pressure and concentration. A slight increase in temperature will result in increased dissociation; the point of equilibrium, and therefore the pH, will shift.[65] The generalised equations below (where the italicised lowercase letters represent the coefficients and the brackets represent concentration at equilibrium) show how an equilibrium reaction can be expressed as an equilibrium constant.[66] This is sometimes called the equilibrium law, or the Law of Mass Action.

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{c(T)} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

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[60] Wolbers, 13.

[61] Nivaldo J. Tro *et al*. *Chemistry: a Molecular Approach*. (Upper Saddle River; London: Pearson/Prentice Hall, 2008), 671.

[62] Henry F. Holtzclaw Jr., *et al*, *General Chemistry* Ninth Edition (Toronto; Lexington: D.C. Heath and Company, 1991) 492.

[63] Roger G. Bates, *Determination of pH: Theory and Practice* (New York; London: John Wiley and Sons Inc., 1964) 11-12.

[64] Rob Lewis and Wynne Evans, *Chemistry* 3rd edition (Basingstoke: Palgrave Macmillan, 2006) 267.

[65] Wolbers, 13.

[66] Lewis and Evans, 267-268.

The strength of an acid or base is a molecular property. The strength of an acid or base cannot be determined by the pH of a solution; a dilute solution of a strong acid and a concentrated solution of a weak acid could give the same pH reading. It is useful for conservators to know the strength of an acid or base, as the partial dissociation of weak acids and bases leaves a supply of unionised acid or base available in the solution.[67]

When applying the equilibrium law to acids or bases the equilibrium constants K_a and K_b are used. A high K_a value denotes a strong proton donor ability of the acid, therefore, a strong acid. Similarly, a high K_b value indicates a strong proton acceptance capacity of the base, therefore, a strong base.[68]

The equilibrium constants K_a and K_b are, like pH, expressed in logarithmic notation as pK_a and pK_b respectively.

$$pK_a = \frac{1}{\log_{10} K_a} \qquad pK_b = \frac{1}{\log_{10} K_b}$$

The strength of an acid or base can be expressed by their pK_a and pK_b values; weaker acids have a higher pK_a, as the strength of the acid increases pK_a reduces. For bases the same is true; stronger bases have a lower pK_b, and as the strength of the base decreases, pK_b increases.[69]

The self-ionisation constant for water, K_w is equal to 1.0×10^{-14}, therefore $pK_w = 14.00$. The relationship between K_a and K_b for a conjugate acid and base pair can be expressed logarithmically as:[70]

$$pK_a + pK_b = pK_w$$

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[67] James W. Rice, *Principles of Textile Conservation Science*, Reprinted from the *Textile Museum Journal* 1, no. 1 - vol. 2, no. 4 (1962-1969), (Washington: Textile Museum, 1969) 17.

[68] Lewis and Evans, 289-295.

[69] Wolbers, 13-15.

[70] Holtzclaw *et al*, 497.

3.2.1 pH Buffers

Buffers protect against abrupt changes in acidity or alkalinity, they do not prevent changes in pH but reduce the effects and are effective over a narrow pH range.[71] The result of a pH buffer in a solution is an increase in the amount of acid or base that must be added to the solution to cause a change in pH.[72] The pH of a buffer solution can be calculated from the starting concentration of the buffer components using the Henderson - Hasselbach equation:[73]

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log_{10}\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

A buffering solution works best at a range of 1pH unit either side of its pK_a, and is most effective at a pH equal to its pK_a.[74]

3.3 Measuring pH

Measurement of pH can be carried out in two ways. One uses colorimetric methods - pH strips, pens and indicator solution, where a visible colour, or colour change is read using a defined scale relating colour to pH. The other uses electrometric methods - pH meters with electrodes to measure voltage and electrical current potential which is dependent on the concentration of H^+.[75]

3.3.1 pH Measurement Equipment

Colorimetric pH strips are impregnated with dye that is affected by certain pH levels, triggering a colour change. Paper pH strips are less accurate than electrometric pH measurement, they have a shelf life which can be checked with the manufacturer and should be used only as an indication of the pH of a solution.[76]

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[71] Beynon and Easterby, 1.

[72] D.D. Perrin and Boyd Dempsey, *Buffers for pH and Metal Ion Control* (London: Chapman and Hall, 1974) 1.

[73] Beynon and Easterby, 20.

[74] Tro *et al.*, 731.

[75] Tse, 6.

[76] Montague, 21.

Combination electrodes (fig. 3.2) are filled with an electrolyte solution, usually potassium chloride (KCl); gel filled electrodes are also available. The electrode is silver (Ag) or silver chloride (AgCl) wire within a bulb made of very thin and fragile glass. As this glass can easily be damaged, many combination electrodes have a protective shell to prevent contact with solution containers. The combination electrode contains a reference electrode of Ag/AgCl, which is linked by the KCl solution to the test solution by a semi-porous plug.[77]

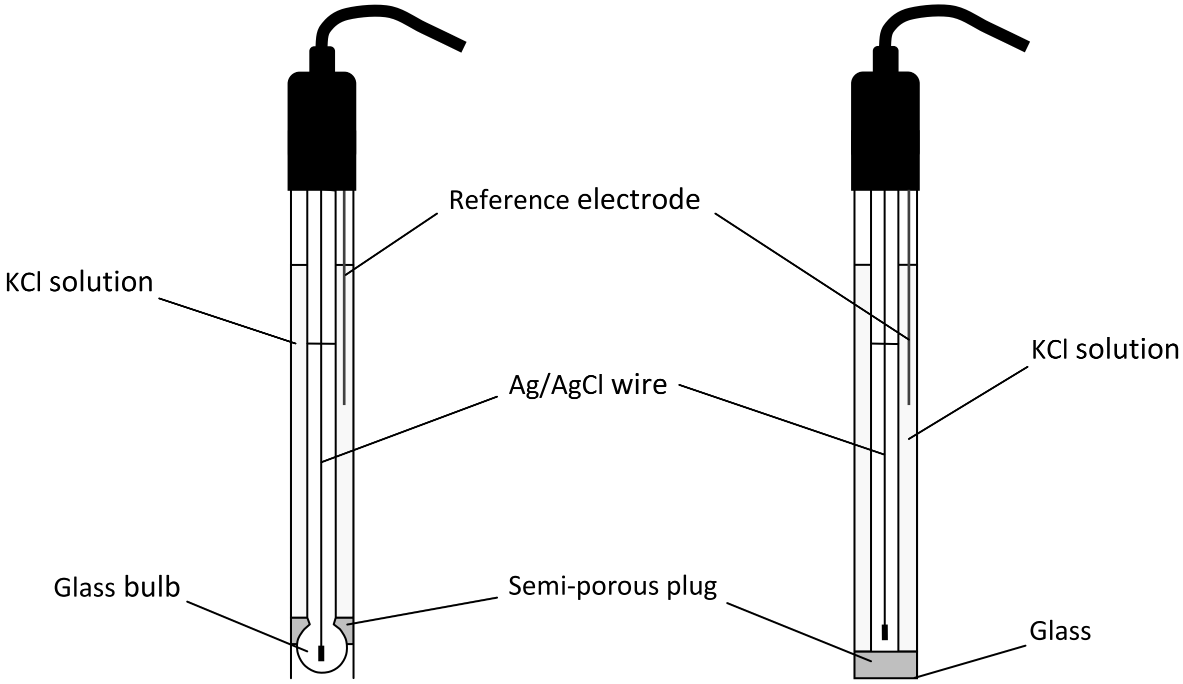

Figure 3.2 Combination electrode (left) and surface electrode (right).[78]

To take a reading the electrode is immersed in the solution, H^+ cover the glass membrane generating a voltage across the glass. This voltage is measured by comparing it to the reference electrode.[79] A pH electrode operates best in a solution that contains

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[77] Beynon and Easterby, 35-36.

[78] Based on Hanna Instruments *Instruction Manual: HI 9023C - HI 9023CN, HI 9024C - HI 9025C, HI 9110 - HI 9210, HI 9210N Portable Waterproof pH Meter*, 1996, http://hannainst.com/manuals/HI902_series.pdf, 26.

[79] Beynon and Easterby, 35-36.

high levels of acid or base, and is slower, or drifts, when measuring deionised or distilled water.[80]

Electrodes should not be allowed to dry out; this minimizes clogging of the semi-porous plug and ensures quick measurement time. They should be stored in supplied storage solution, and never in distilled or deionised water.[81] Combination electrodes become less reliable with age. An electrode that fails to provide a stabilised reading within 10 - 15 seconds may need to be replaced.

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[80] Montague, 20.

[81] Hanna Instruments, 27

Chapter 4: Questionnaire

4.1 Introduction

Important data can be collected from practising conservators; this information can show trends in current conservation practice. A short questionnaire was compiled and sent to practising conservators to identify the current usage of pH buffers in wet cleaning, including which pH buffers are used, and with which detergents. The aim of the questionnaire was also to compile the reasoning for and against using pH buffers in wet cleaning.

In this chapter the choice of questions and format of the questionnaire will be explained. Following this an analysis of the results will be presented, along with reasoning for the experimental choices that have resulted from the questionnaire responses.

4.2 Questionnaire

To maximise the response rate the questionnaire was kept short and used tick boxes where possible, thus reducing subjectivity in the interpretation of the answers provided.

Three key questions were devised, with the conservator needing to answer only two of the three:

1. Do you use pH buffers in wet cleaning?
2. a) Which buffers do you use?
   b) What influences the decision to use a pH buffer?
3. Why do you not use buffers?

Question one had ‘yes’ and ‘no’ options, with additional space for those who answered ‘yes’ to provide details of detergents used with pH buffers. Depending on the response to this question, the respondent was guided to answer either question two, or question three.

Questions two and three had tick box answers and space to provide alternative or additional information. Both questions allowed multiple answers because the reasons for and against using pH buffers can be complex and dependent on different circumstances.

4.3 Questionnaire Results

The expected response rate for the 38 questionnaires sent out was 30%.[82] In this case the response rate was much higher, 47% of questionnaires were returned completed (fig. 4.1). This suggests a possible desire for discourse in the use of pH buffers in wet cleaning within the textile conservation community.

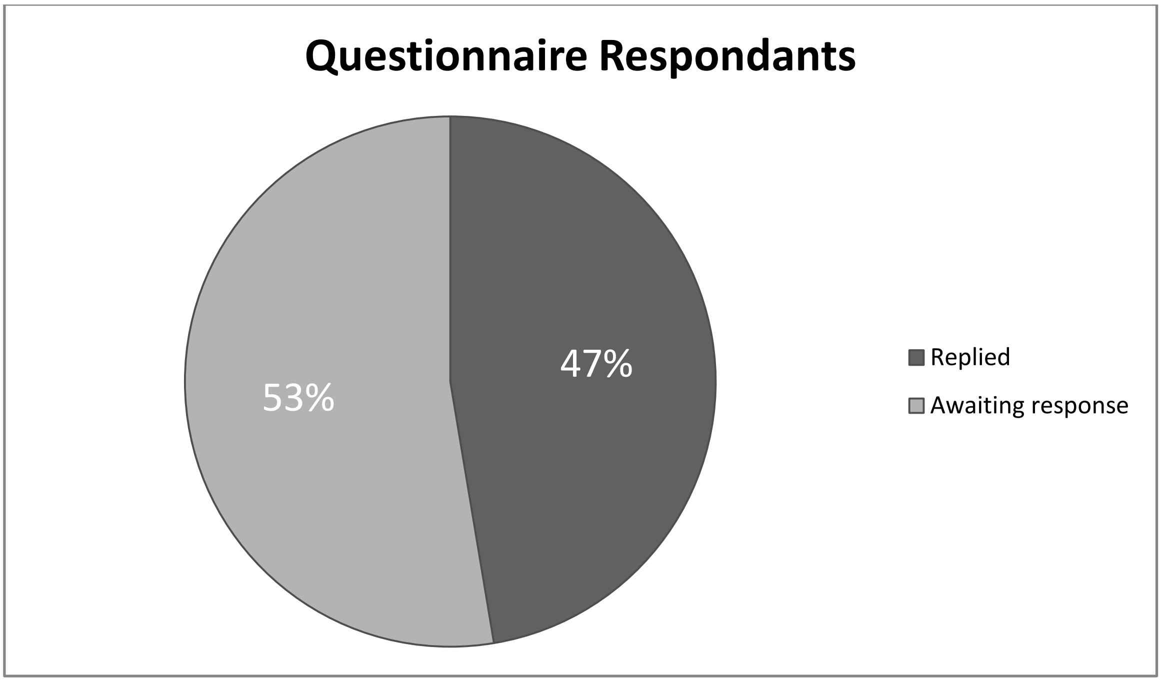

Figure 4.1 Percentage of questionnaire responses.

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[82] Frances Lennard, “Qualitative Research,” *Research Management*, lecture notes, February 17, 2015.

4.3.1 Question One

One third of respondents use buffers in wet cleaning (fig. 4.2). Of the 33% that use pH buffers, 28% of respondents use buffers with detergents and water and an additional 5% use buffers with water only.

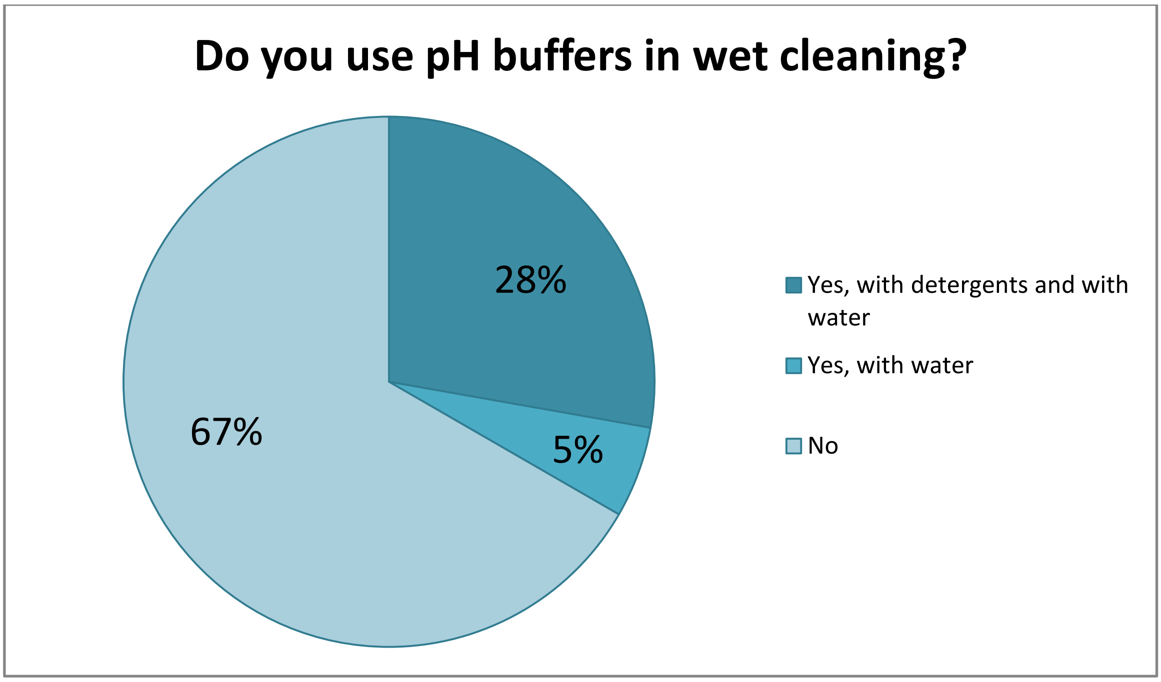

Figure 4.2 Percentage use of pH buffers in wet cleaning.

One respondent specified that they use acetic acid in deionised water to limit dye-bleeding, however this is categorised as an acid rinse and not a buffered solution, so will not be discussed further. The same respondent also described adding a buffer in the final rinse for objects that have been bleached.

A respondent who does not use pH buffers discussed reduction of the acidity of tap water, and questions whether this course of action would rule out a final rinse in deionised water.

The pH buffers used by respondents are (in descending order of prevalence):

- tri-ammonium citrate (4)
- tri-sodium citrate (3)
- tri-sodium citrate with citric acid combination buffer (1)
- sodium hydroxide with citric acid combination buffer (1)
- sodium carbonate used in conjunction with tri-sodium citrate (1)

Tri-sodium citrate with citric acid as a combination buffer was expected to be the most commonly used buffer, due to the recipe published in *Chemical Principles of Textile Conservation*.[83] However, this combination buffer was used by only one of the respondents, as was sodium hydroxide with citric acid combination buffer, which was used at three different pH levels (pH4.5, pH6, and pH7.5) to raise the pH of the object being treated.

The responses received identify that tri-ammonium citrate and tri-sodium citrate have the highest usage. One respondent highlighted the use of these as sequestering agents, because they use them to increase efficiency of cleaning and not to hold buffer pH during wet cleaning. Another respondent identified tri-ammonium citrate as a buffer that they no longer use after being advised to avoid using it on porous objects.

The use of sodium carbonate was identified by one respondent only, who used it in conjunction with tri-sodium citrate as a treatment in a special case.

Respondents who use pH buffers in wet cleaning were also asked which detergents they use with a pH buffer. The results (fig. 4.3) show that all of the respondents have used pH buffers with non-ionic detergents, whereas the use of anionic detergents with a pH buffer is much lower.

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[83] Tímár-Balázsy and Eastop, 255, 370.

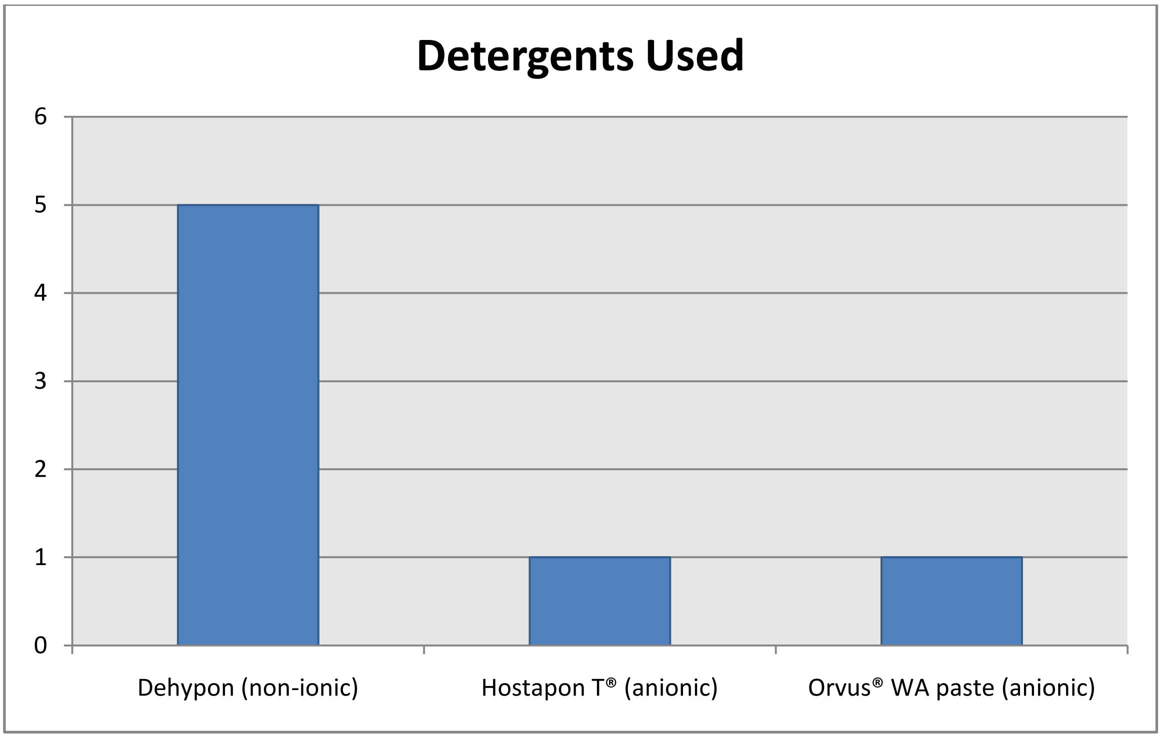

Figure 4.3 Detergents used with pH buffers in wet cleaning.

Both Dehypon LS45® and LS54® non-ionic detergents were named in the questionnaire responses. However, not all respondents specified whether they use LS45® or LS54®. For this reason both types of Dehypon have been grouped together to display the results.

The choice of the detergent used is dependent on the fibre type that is being cleaned. From the responses it is clear that pH buffers are used more often in the wet cleaning of protein fibres, due to the higher percentage of respondents using non-ionic detergents.

4.3.2 Question Two

The determining factors influencing the respondent's decision to use a pH buffer in wet cleaning are shown below (fig. 4.4). Respondents were allowed multiple answers in this question, therefore a single respondent may be present across several categories.

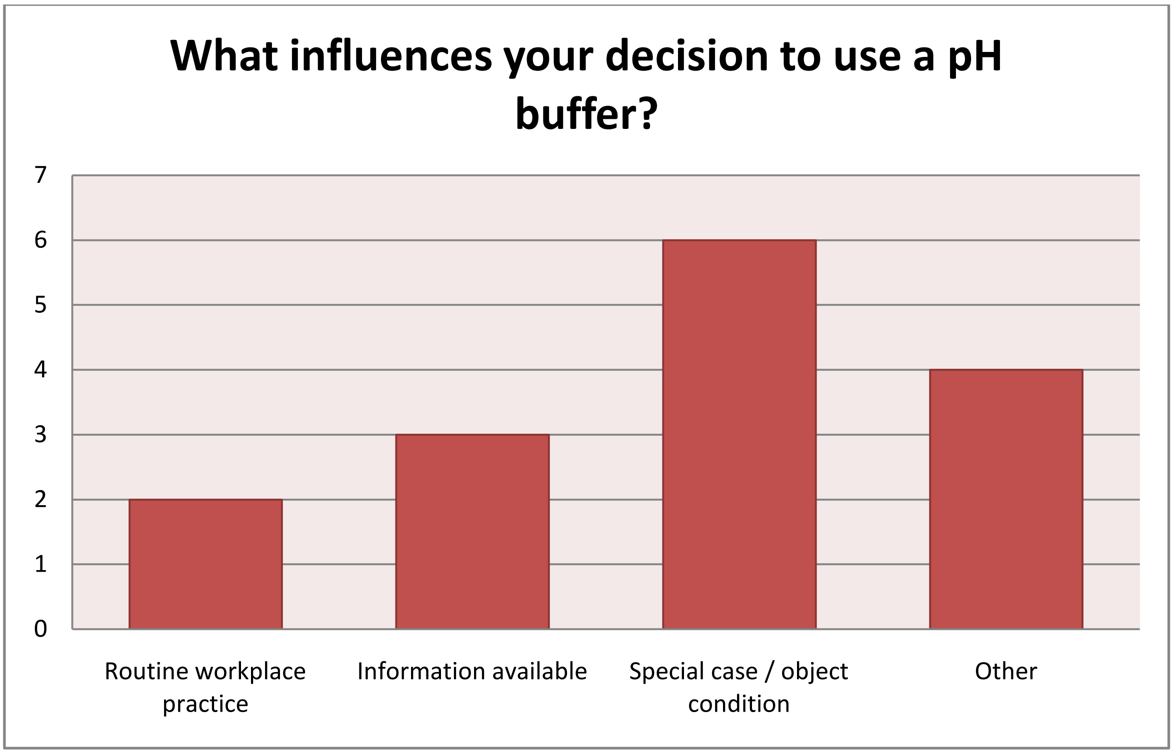

Figure 4.4 Reasons respondents choose to use a pH buffer in wet cleaning.

Of those that use pH buffers in wet cleaning, the decision was most often influenced by the condition of the object or a special case, with all respondents ticking this answer. Half of the respondents who use pH buffers do so because of the information available to them, and for one third it is routine workplace practice.

All of the respondents who answered 'other' mentioned that buffers can also be "used as a sequestering agent in the wash solution to improve soil removal"[84]. One respondent answered:

> "We also use buffers because they are dual purpose and work as chelating agents so if we have very dirty objects we know that it will work for soiling as well as buffering the pH of the wash bath as soiling is released into it."[85]

One respondent highlighted the reason for choosing to use a pH buffer to reduce dye loss.

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[84] Respondent 15.

[85] Respondent 14.

4.3.3 Question Three

The reasons for respondents choosing not to use a pH buffer in wet cleaning are displayed below (fig. 4.5). This question also allowed multiple answers. ‘Not enough information available’ was answered by only 16.67% of respondents, with one respondent observing that “information available for textile conservators is very sparse”[86]. However, the small number identifying a lack of information as a factor suggests that textile conservators feel the information on the use of buffers available is sufficient to carry out a treatment.

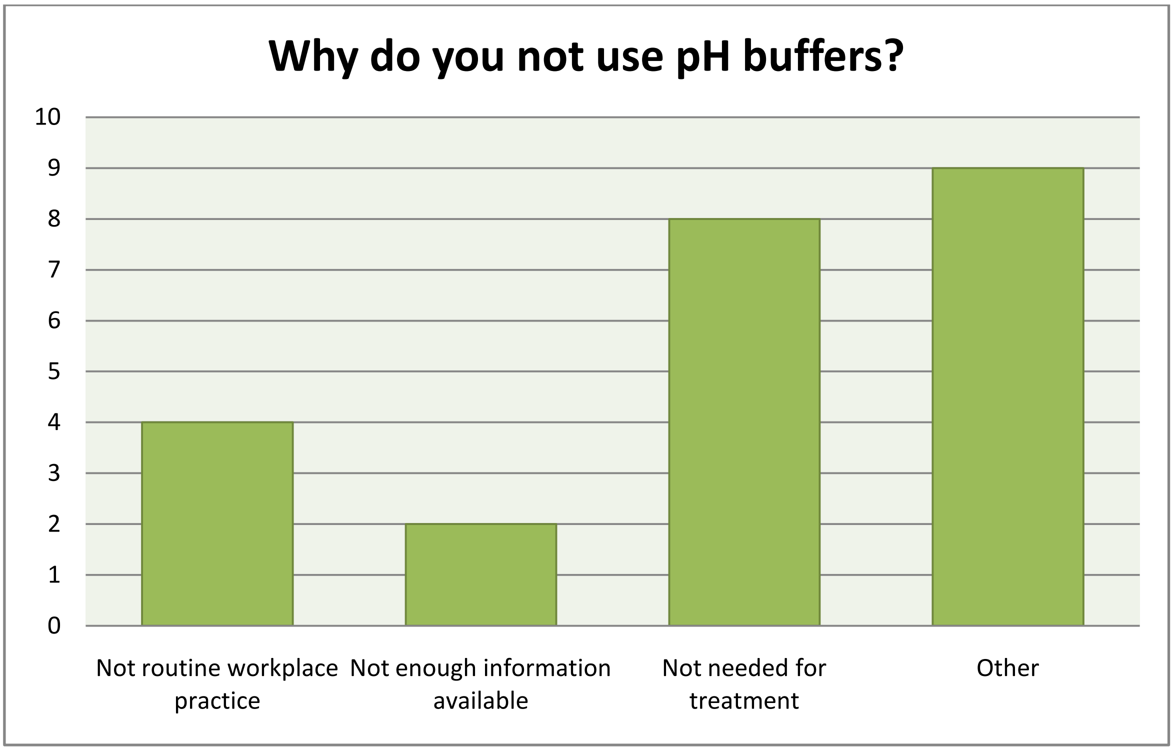

Figure 4.5 Reasons respondents choose not to use a pH buffer in wet cleaning.

Lack of time to carry out experiments and/or fully research the chemicals involved was highlighted as a reason for not using a pH buffer in wet cleaning. One respondent explains:

> “If I am unfamiliar with a treatment I will usually not go ahead with it unless I am confident I have sufficient information. Time is the prominent factor here.”[87]

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[86] Respondent 6.
[87] Respondent 15.

4.4 Summary

The use of pH buffers is not limited to control of the wash bath pH, they are also used to control dye bleeds and increase soiling removal. Replies from the questionnaires show that buffers are not used regularly in practice, and that time for research and testing is not always available. The need for time to conduct research was highlighted throughout the replies, regardless of whether the respondent uses pH buffers in wet cleaning, or not.

Additional questions have arisen from replies, including how to make up molar solutions and the circumstances where certain pH buffers should be used:

> “I took a lot of reading around and research to find practical information on making up molar solutions; the *Chemical Principles* [*of Textile Conservation*] gives some information, but not the practical 'how to' information you need to make a buffered wash solution and what buffer might be suitable for which situation. When you're not a chemist it all has to be much clearer and a bit more prescriptive, as we don't always have the time to do the research and frankly there doesn't seem to be anyone to ask.”[88]

The answers from the questionnaire have resulted in a change of approach to the experiments. Initially cotton fabrics only were going to be used in the experiments; this has been extended to include a protein fibre, in this case silk, due to the number of respondents using non-ionic detergents with buffers. The detergents that have been chosen for the experiments are Hostapon TPHC® anionic detergent, and Dehypon LS45® non-ionic detergent.

From analysing the responses the decision has been made to use tri-sodium citrate self buffer, and tri-sodium citrate with citric acid and sodium hydroxide with citric acid as combination buffers in the experimental phase. Even though it had the highest usage, tri-ammonium citrate has been ruled out because of the information in the questionnaire that advises against its use.

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[88] Respondent 6.

Chapter 5: Experiment Methodology

5.1 Introduction

This chapter builds on the information collected from the questionnaire, designing an experiment that will provide data on the effectiveness of pH buffers in wet cleaning. Sacrificial fabric samples will undergo pH and colour measurement before and after a wet cleaning treatment is conducted. This will give a measure of the degradation products and soiling that have been removed during treatment. Throughout wet cleaning the pH of the wash solutions will be monitored to evaluate the ability of the pH buffer to prevent abrupt changes in pH.

The value of experimental data in conservation cannot be underestimated. Using naturally aged sacrificial fabrics in experiments can help move the understanding of a subject forward, benefitting future treatments and making the data collected easily transferable into workplace practice.

Pre-soiled fabrics for testing have limitations, they are produced for industrial and, therefore, more rigorous testing. They have not degraded naturally, and the type of soiling and the mechanism of its deposition are unlikely to be found on typical objects.[89] It is for this reason that naturally aged fabrics have been sourced for the experiments.

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[89] W. Cooke *et al.*, "The Cleaning of Degraded Linen," *The Conservator* 20 (1996): 3-14, http://dx.doi.org/10.1080/01410096.1996.9995098, 3-4.

5.2 Fabric Samples

Naturally aged soiled cotton and silk fabrics were sourced to be treated during the experiments. The soiling evident on the fabrics is through use and storage of the objects, although the soiling present will not be representitive of all types of soiling found on historical objects. Due to the age of the fabrics selected, there is likely to be degradation of the fibres, providing a more realistic data group.

5.2.1 Cotton Fabric

The cotton fabric chosen for the experiments is an undyed backing to a sampler dated circa 1900 (fig. 5.1). The shape of the brown staining, and dye bleed on the sampler indicates water damage. The fabric has yellowed and has ingrained soiling throughout. There are nail holes and rust stains around the edge of the fabric from the original framing. Extra stitches had been added to the sampler, that were stitched through the backing fabric using a thick purple yarn. These stitches have been removed in order to separate the fabric from the sampler; however the stitch holes are still visible.

Figure 5.1 Front and back views of the cotton fabric after removal from the sampler.

5.2.2 Silk Fabric

The silk fabric available for the experiments was from a red bonnett (fig. 5.2), dated approximately mid to late 19th century, it has been used and retired as a costume piece in theatre productions. The silk is heavily soiled and has very dark staining, most likely from use and storage.

Figure 5.2 Front and back views of the silk fabric.

5.2.3 Preparation of Samples

The rust stained holes round the edge of the cotton fabric were cut off to ensure continuity throughout the samples, as samples cut from the middle of the piece would not have rust stains.

The selvedge of the silk fabric was not used, because of the difference in the weight of the fabric along this edge, the undyed yarn used, and because this edge was cleaner due to the way the bonnet had been constructed.

For continuity of sample size, a paper template was used to cut 24 samples of equal weight measuring 102mm x 71mm from each of the fabrics (fig. 5.3). The template was pinned to the fabrics, and any scrap pieces of fabric were retained.

Figure 5.3 Paper template pinned to silk fabric.

Samples were split into eight groups of three, chosen at random. Eight colours of polyester thread (one for each group) were chosen to identify the groups by a stitch in the top left hand corner. Polyester thread was chosen because the dyes are fast and will not run in the wash process. Within the groups the samples are identified by the direction of the stitch, the first with a vertical stitch, the second diagonal, and the third horizontal. The front and back of each group were photographed documenting the samples before and after treatment.

5.3 Colour Measurement

The colour of the samples was analysed using a chroma meter (Minolta CR-210). Readings were taken using the CIE L*a*b* system. L* corresponds to the level of brightness/darkness, a* gives the balance between red/green, and b* gives the balance between yellow/blue (fig. 5.4).[90]

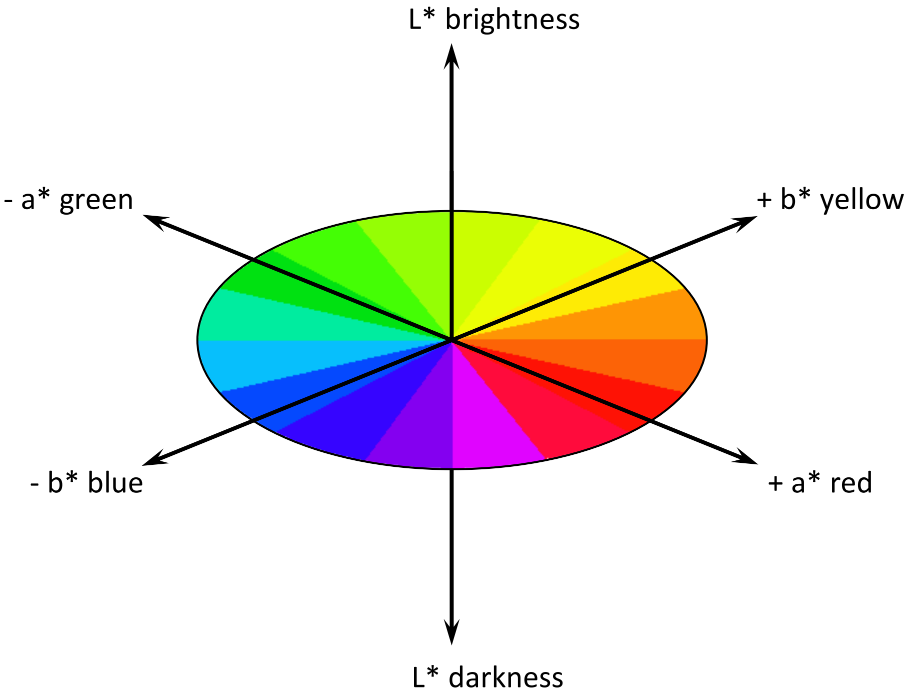

Figure 5.4 The L*, a* and b* axes.[91]

Before use the chroma meter was calibrated using the white calibration tile provided by the supplier (fig. 5.5). The tile was placed behind each sample while readings were being taken to ensure continuity. Three measurements were taken from the centre of each

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[90] N. S. Gangakhedkar, "Colour measurement methods for textiles," in *Colour Measurement: Principles, Advances and Industrial Applications*, ed. M.L. Gulrajani, 221-252 (Cambridge: Woodhead Publishing, 2010), http://dx.doi.org/10.1533/9780857090195.2.221, 224.

[91] Based on a standard colour space representation by Tímár-Balázsy and Eastop, 86.

sample whilst the head was in contact with the sample, for each reading the head of the chroma meter was moved slightly. From the three readings the mean was calculated.

Figure 5.5 Calibration of the chroma meter using the white calibration tile.

5.4 pH Measurement

5.4.1 Surface pH Measurement of Samples

Measuring the pH of the samples before wet cleaning was conducted using a pH meter (Hanna Instruments HI9024C) and a surface electrode. As a non-destructive technique, it was used on each sample before the treatment was carried out. Before, and periodically during analysis, the pH meter with surface electrode was calibrated using calibration solutions (Hanna Instruments) at pH7 and pH4.

To ensure the readings will be taken from the same area on each sample before and after wet cleaning a template was made; a piece of Melinex® (polyester film) was cut to the sample size and, using permanent marker, the top left corner was marked to match the identification stitch. Three circles of 12mm diameter (the diameter of the surface electrode) were cut in the Melinex® (fig. 5.6).

During pH readings the samples were placed on a piece of Melinex®, with the template placed on top matching the marks in the top left corner. Three drops of deionised water were dispensed from a disposable pipette onto each area to be analysed, and left to soak in for three minutes. The template allowed the deionised water to be applied to the specific area to be tested. The electrode was rinsed in deionised water and placed onto the sample through the template (fig. 5.6). Once the pH meter had stabilised a reading was taken. This was repeated for the next two spaces on the template and the samples were allowed to dry naturally before wet cleaning commenced. After the samples had undergone wet cleaning and had dried, the process was repeated.

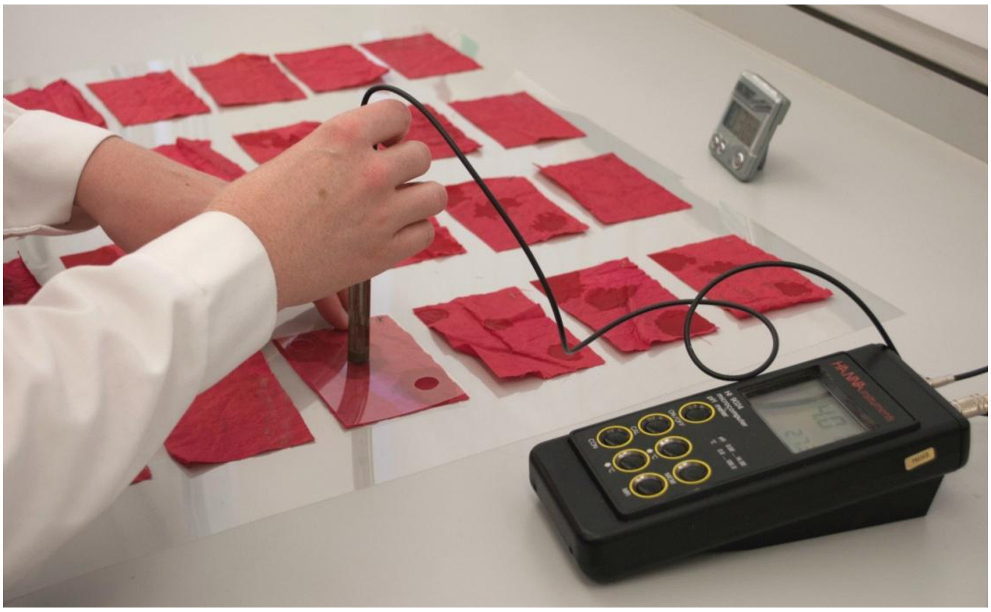

Figure 5.6 Surface pH measurement of silk samples using template.

5.4.2 Extracted pH Measurement of Samples

To determine the bulk pH of the fabrics, aqueous extraction was used following British Standard EN ISO 3071:2006.[92] The standard requires 2g (± 0.05g) samples to be placed in 100mL of extracting solution (deionised water with a pH of 5.0-7.5) in stoppered glass flasks. This size of sample is too large for this application, therefore the sample size and

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[92] British Standards Online.

quantity of deionised water were reduced proportionally to 0.2g (± 0.05g) in 10mL deionised water. An extracted pH representative of the whole piece of fabric was determined by using small samples from across the fabric.

Measurements were taken, using a combination electrode and pH meter which was calibrated as above. Three test samples were weighed out from each fabric to 0.20g and inserted in three test tubes before the deionised water was added, using a volumetric pipette to measure the 10mL, and stoppers were placed on the test tubes which were initially agitated by hand. The British Standard calls for mechanical agitation of the samples for 2 hours (± 5 minutes). This equipment was not available; therefore a mechanical centrifuge was used to create a vortex in the test tubes for 15 seconds every 15 minutes (fig. 5.7).

Figure 5.7 Creating a vortex during pH extraction.

The pH of the solution from the first test tube was measured but, in accordance with the British Standard, not recorded. Without rinsing the electrode between solutions, the pH of the solutions in the second and third test tubes were measured and recorded. The mean of these readings was calculated to give the pH of the fabric.

After wet cleaning, six samples (three of each fibre type) were chosen at random for aqueous extraction, the method was repeated as above. However, due to the lower weight of the silk samples the quantity of fabric tested had to be reduced to 0.1g, with the amount of deionised water proportionally reduced to 5mL.

5.4.3 pH Measurement of Wash solutions

The pH of the wash solutions and rinse baths was measured at the beginning and end of each bath using the pH meter with combination electrode. Before use, and periodically during the wash procedure the electrode was calibrated as above. The reading from each bath was taken once the pH meter had stabilised. Between readings the electrode was rinsed in deionised water.

5.5 Preparation for Wet Cleaning

5.5.1 Wash Solutions

Both the Hostapon TPHC® (Hostapon T®) anionic detergent and Dehypon LS45® non-ionic detergent wash solutions were made up at 3x critical micelle concentration (c.m.c.), chosen as it is the midpoint of concentrations typically used in textile conservation (for detailed preparation of the wash solutions see Appendix D).

The wash solutions were made up using soft water. Soft water differs from deionised water, because it contains dissolved salts; however, unlike hard water it does not contain calcium ions Ca^{2+} or magnesium ions Mg^{2+} and does not produce a scum when used with soap.[93]

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[93] The Conservation Unit, 79-80.

5.5.2 Buffer Solutions

The pH buffer solutions were made up using deionised water (B114 deioniser) and were added to the wash solutions using the recipes detailed in Table 5.1 (for detailed preparation of the buffer solutions see Appendix D). All of the buffers were used at comparable concentrations.

pH Buffer	Components	Quantities
Self buffer	Tri-sodium citrate	0.5g/L
Combination buffer	Tri-sodium citrate	0.5g/L
	1% Citric acid	1mL/L
Combination buffer	1M Sodium hydroxide	0.15mL/L
	0.5% Citric acid	1.85mL/L

Table 5.1 pH buffer recipes.

Titration was used to adjust the pH of the sodium hydroxide with citric acid combination buffer to the required pH6.4 (fig. 5.8).

Figure 5.8 Titration to adjust pH of sodium hydroxide with citric acid buffer.

5.6 Wet Cleaning

To simulate conservation practice, each sample was wet cleaned using three wash baths and rinsed using a mixture of rinse baths and running rinses (table 5.2).

Bath	Time and Details	Wash/Rinse Solution
Wash 1	5 minute soak, 2 minutes sponging each side	Wash solution
Wash 2	2 minutes sponging each side	Wash solution
Wash 3	2 minutes sponging each side	Wash solution
Rinse 1	5 minute soak	Soft water
Running Rinse	5 minutes	Soft water
Rinse 2	5 minute soak	Soft water
Rinse 3	5 minute soak	Soft water
Rinse 4	5 minute soak	Deionised water

Table 5.2 Outline of the wash process.

The pH of the solutions was measured before and after each wash or rinse bath. During wet cleaning (fig. 5.9), sponging was carried out using a synthetic sponge (Ramer® PVA foam sponge). Each wash and rinse bath was measured to 75mL using a 100mL volumetric measuring cylinder (Fisherbrand® class B ±1.0mL).

Figure 5.9 Wet cleaning cotton sample with Hostapon T® wash solution.

Chapter 6: Colour Measurement Results

6.1 Introduction

In this chapter the results from the chroma meter readings will be analysed to quantify the removal of soiling and degradation products from the cotton and silk samples.[94,95]

Readings were taken from the centre of each sample before and after treatment using a chroma meter. The measurements are expressed numerically in terms of brightness and hue using the CIE L*a*b* system, where L* represents the level of brightness (100 = white, 0 = black), a* indicates red if positive and green if negative, and b* indicates yellow if positive and blue if negative.[96] Fibre degradation of cotton and silk causes yellow/brown and yellow discolouration through the formation of water soluble acidic products and chromophores.[97] For this reason a reduction in yellow is expected, as is an increase in brightness from the removal of soiling. The dyed colour of the silk samples and dye loss during treatment will be taken into account.

The overall colour change between two colour readings, or Total Colour Difference (ΔE), is calculated by the equation:[98]

$$\Delta E = \sqrt{[(L_1^*-L_2^*)^2+(a_1^*-a_2)^2+(b_1^*-b_2^*)^2]}$$

This equation will be used to calculate the colour change of the samples from the wet cleaning treatment, identifying the samples that have undergone the most overall colour change.

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[94] John A. Fields *et al.*, “Finding Substitute Surfactants for Synperonic N,” *JAIC* 43, no. 1 (2004): 55-73. http://www.jstor.org/stable/3179851, 59.

[95] Tímár-Balázsy and Eastop, 210.

[96] N. S. Gangakhedkar, 224.

[97] Paul Garside and Paul Wyeth, “Textiles,” in *Conservation Science: Heritage Materials*, eds. Eric May and Mark Jones, 56-91 (Cambridge: RSC Publishing, 2006), 67-83.

[98] David G. Duff, *et al.*, “Light-Induced Colour Changes of Natural Dyes,” *Studies in Conservation* 22, no. 4 (1977): 161-169, http://www.jstor.org/stable/1505832, 164.

For the analysis of results each group has been assigned a code (table 6.1), identifying the wash solution used. Each group contains three samples, denoted by a 1, 2 or 3. The same water codes have been used for the cotton and silk samples; however, when the cotton and silk samples are discussed together the fibre type will be identified.

Wash Solution	**Group Sample Code**
Hostapon T®	H
Hostapon T® with trisodium citrate	HT
Hostapon T® with trisodium citrate and citric acid	HTC
Hostapon T® with sodium hydroxide and citric acid	HS
Water	W
Water with trisodium citrate	WT
Water with trisodium citrate and citric acid	WTC
Water with sodium hydroxide and citric acid	WS
Dehypon LS45®	D
Dehypon LS45® with trisodium citrate	DT
Dehypon LS45® with trisodium citrate and citric acid	DTC
Dehypon LS45® with sodium hydroxide and citric acid	DS

Table 6.1 Sample codes used in results analysis

6.2 Cotton Results

6.2.1 Difference in L* (brightness/darkness)

All of the cotton samples exhibit an increase in brightness (fig. 6.1). The difference in L* is higher for all groups wet cleaned with Hostapon T®, with a larger increase for the groups that included a pH buffer. The largest increase was observed in sample HS2; however, for the groups wet cleaned with water, the largest increase was shown across group WT. The chelating properties of tri-sodium citrate could be a possible reason for this by aiding the removal of metal ions present in soiling.[99] The smallest increase is in group W, and less significant increases are found in group WTC.

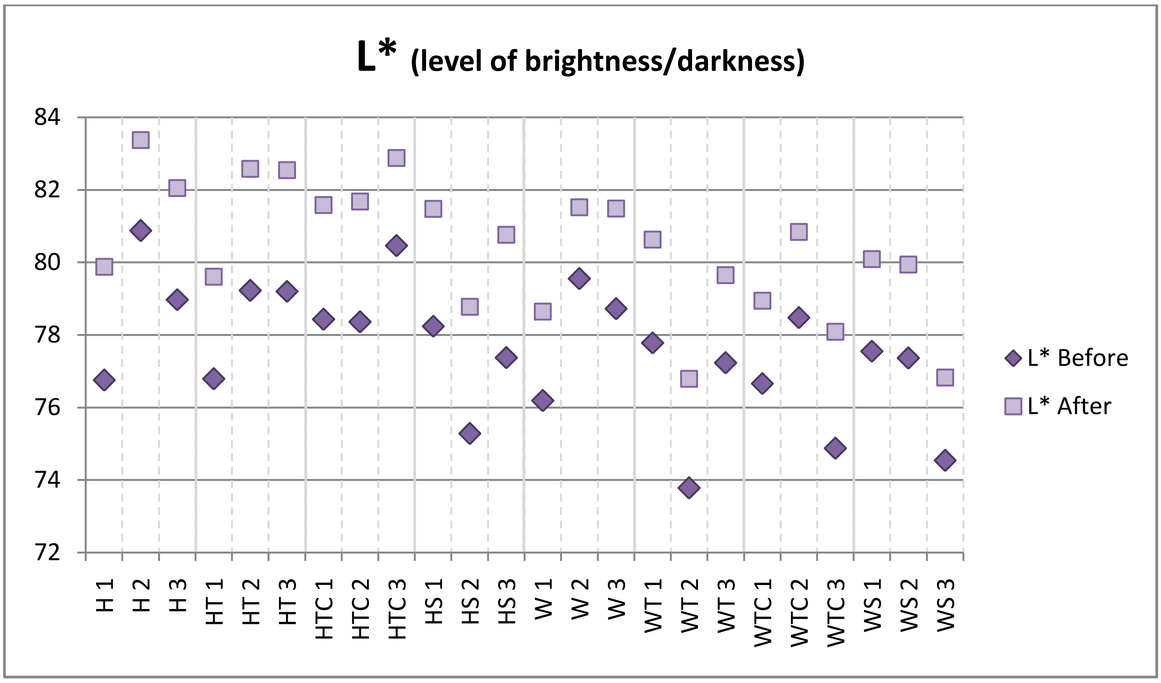

Figure 6.1 Change in level of brightness in cotton samples.

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[99] Tímár-Balázsy and Eastop, 225.

6.2.2 Difference in a* (red/green)

All samples showed a reduction in a*, therefore the redness of all cotton samples decreased (fig. 6.2). The largest reduction is observed in the groups treated with Hostapon T® solutions. Groups H and HS exhibit the greatest overall drop in red, closely followed by groups W and WS. A reduction in red is an indication of removal of the brown staining on the fabric, and of yellow/brown degradation products.[100]

The smallest decrease in a* is observed in group WT; however, this group also contains one of the largest decreases in red. Group WTC also displays small decreases in red, with one larger decrease.

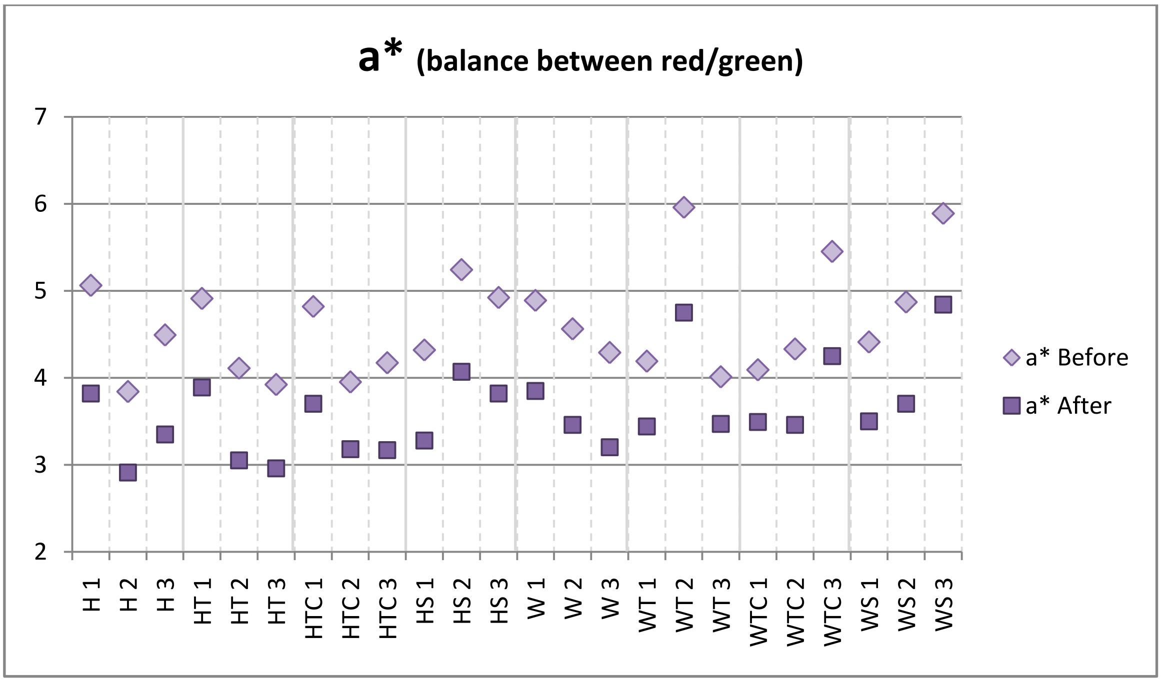

Figure 6.2 Change in level of red/green in cotton samples.

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[100] Garside and Wyeth (2006), 69.

6.2.3 Difference in b* (yellow/blue)

All samples have reduced in yellow, shown through the b* reading (fig. 6.3). The greatest reduction is observed in the groups washed with water solutions, with the greatest reduction in sample WS2. The smallest reduction in yellow is in sample H2. This is, however, not representative of the group as a whole; the other readings show a much greater difference.

A reduction in yellow is an indication of the removal of yellow/brown degradation products from the fibres,[101] and therefore the efficiency of the wash solution.

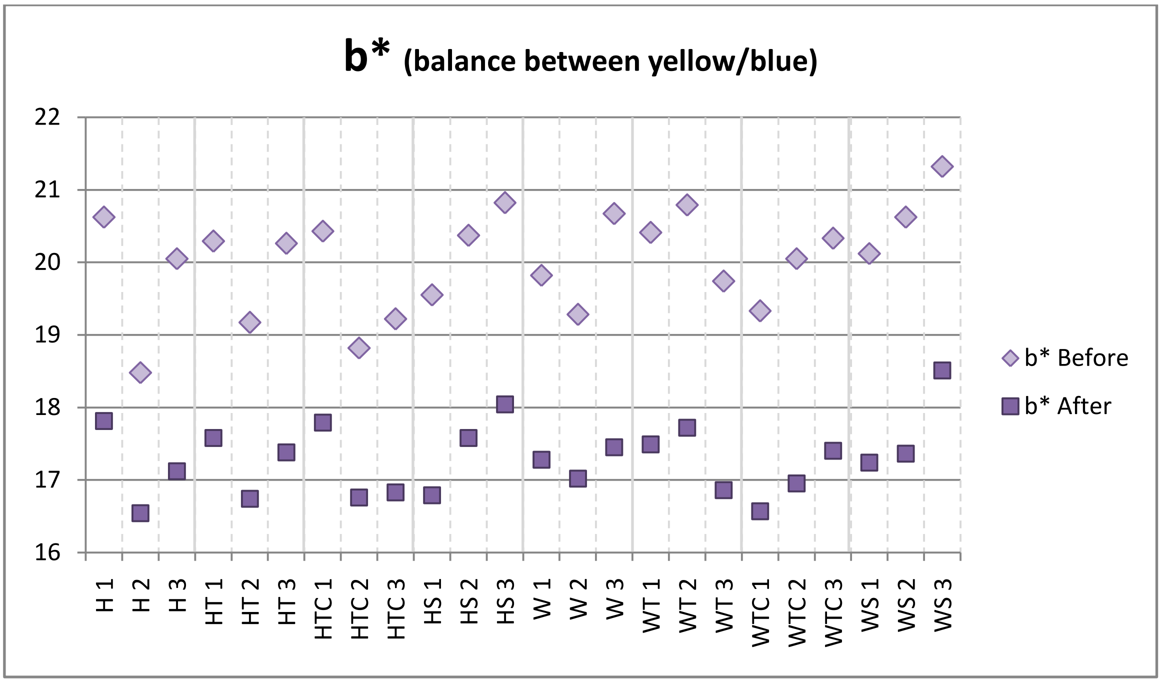

Figure 6.3 Change in level of yellow/blue in cotton samples.

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[101] Landi, 36.

6.2.4 ΔE (Total Colour Difference)

The average ΔE across the groups for cotton (fig. 6.4) shows that the use of detergent in the wash solution had an impact on ΔE, with the exception of the addition of tri-sodium citrate with citric acid in the wash solution. Group HS has a greater average ΔE and the lowest variance, closely followed by group HT.

Within the groups washed with water, group WT exhibits the greatest average ΔE, but the lowest variance is displayed by group WS. Group WTC displays a larger average ΔE than its Hostapon T® counterpart.

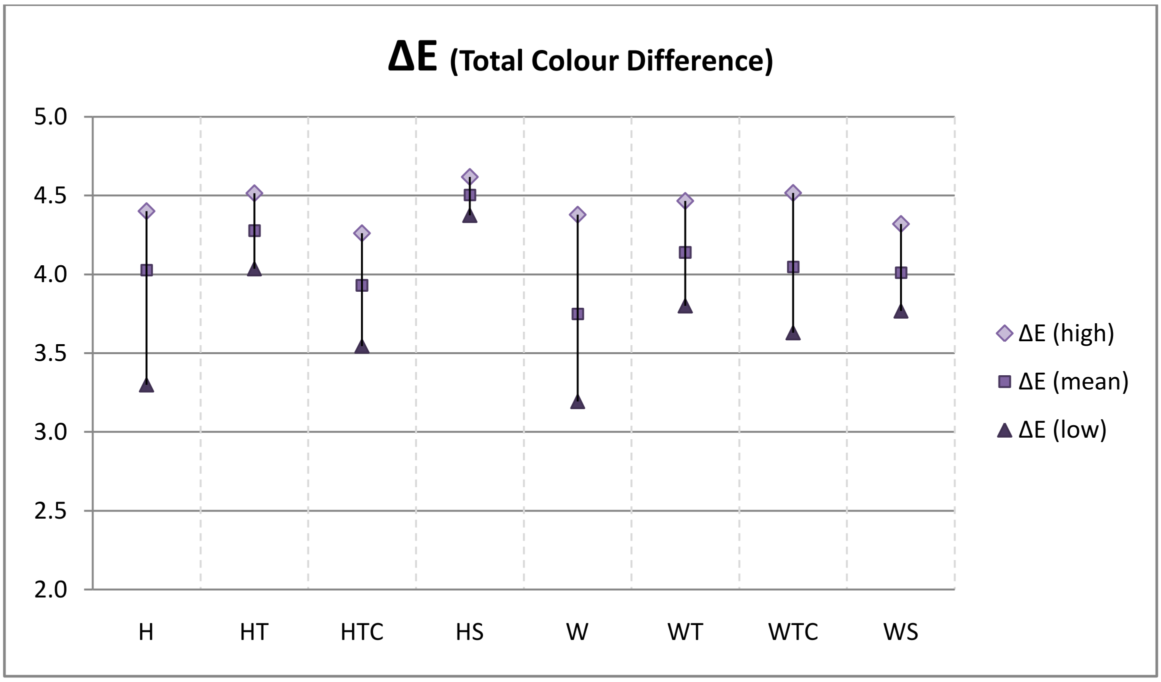

Figure 6.4 Total colour difference in cotton samples.

The range of variance in all of the groups follows the same trend; sodium hydroxide with citric acid has the lowest, followed by tri-sodium citrate, then tri-sodium citrate with citric acid, with no pH buffer in the wash solution displaying the greatest variance.

The addition of pH buffers has boosted average ΔE in the groups washed with water. However, the same is not true for the groups wet cleaned with Hostapon T®, with average ΔE for group HTC being lower than that for group H. The greatest ΔE is in group HS (HS2), and group W (W2) exhibits the lowest ΔE (fig. 6.5). Neither of the two samples displaying the lowest ΔE was treated with a wash solution that contained a pH buffer.

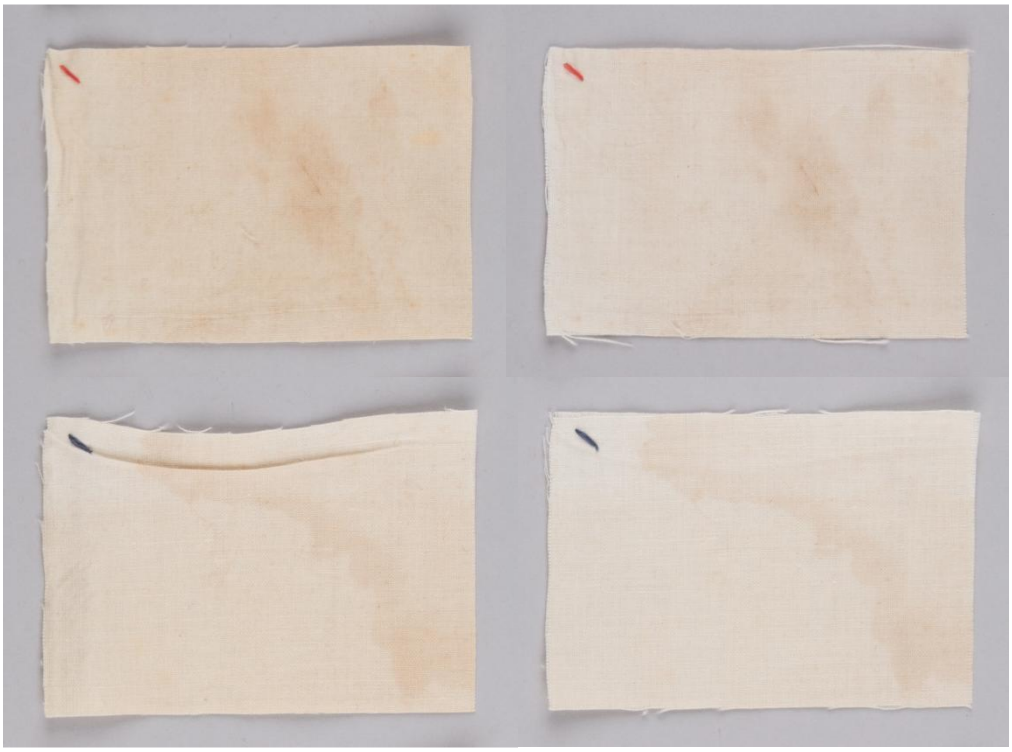

Figure 6.5 Before (left) and after (right) wet cleaning of samples HS2 (top) and W2 (bottom).

The after images display a similar colour between the samples, however, in comparison to the before images it is clear to see that sample HS2 was initially more discoloured and soiled than sample W2. Visually, both samples display an obvious increase in brightness and reduction in yellow and red, however, tide marks from water damage and darker patches are still visible after wet cleaning.

6.3 Silk

All of the silk samples bled dye during wet cleaning. It was evident that this would be an issue from the initial surface pH readings when deionised water caused dye bleed, and during pH extraction there was significant dye loss from the silk, even after wet cleaning. The dye bleed will make the following results difficult to interpret with regard to soiling and degradation product removal.

6.3.1 Difference in L* (brightness/darkness)

The change in brightness of the silk samples was mixed (fig. 6.6); a slim majority darkening. However, this decrease in brightness was not uniform in any group of samples.

The greatest increase in brightness is displayed by sample DS2, and the greatest decrease by sample WTC1. There are no trends visible in any of the groups; this variation in results could be due to inconsistent dye bleed from the samples.

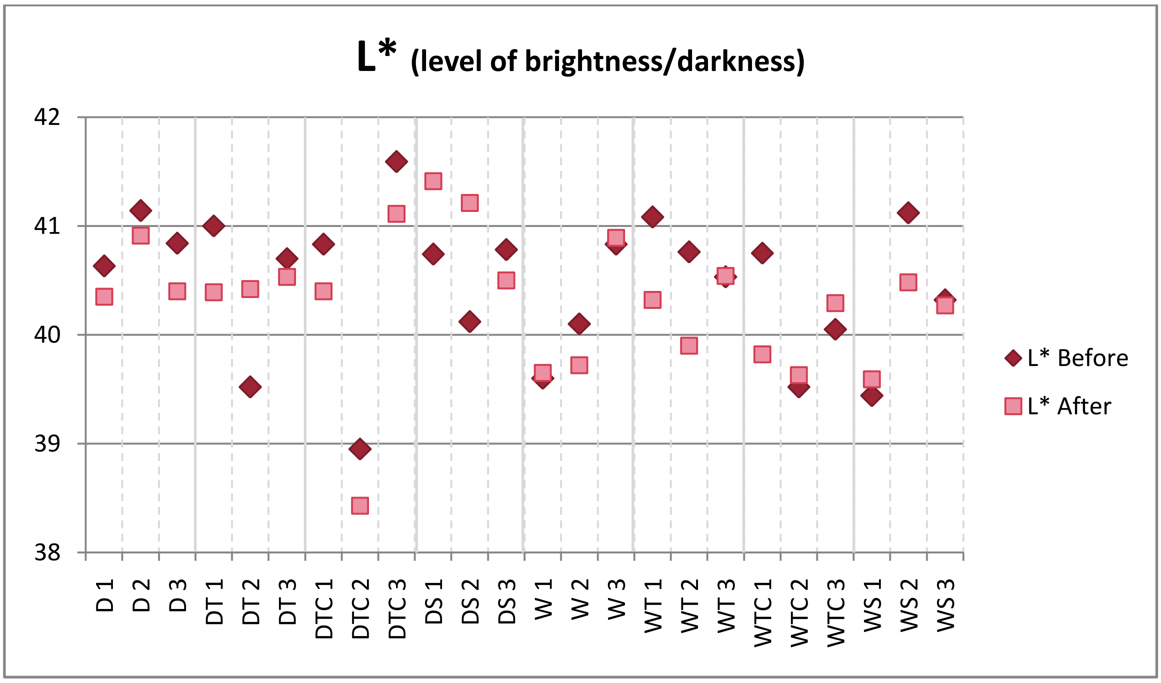

Figure 6.6 Change in level of brightness in silk samples.

6.3.2 Difference in a* (red/green)

The level of a* increased in all of the silk samples after, showing that the samples are redder after wet cleaning (fig. 6.7). This was not expected because the colour of the wash bath showed, in some cases, considerable red dye loss. The greatest increase in red is evident in the groups wet cleaned with Dehypon LS45® solutions, with groups D and DS exhibiting a higher increase compared to the other groups. Within the groups wet cleaned with water, group WS showed the larger increase in red.

The largest increase in red is displayed in sample DS2, which is more than double any other sample, whereas the smallest increase in red is seen in the sample WT1. This difference could be due to the different additives, the soiling present on the sample, or inconsistent dyeing of the fabric.

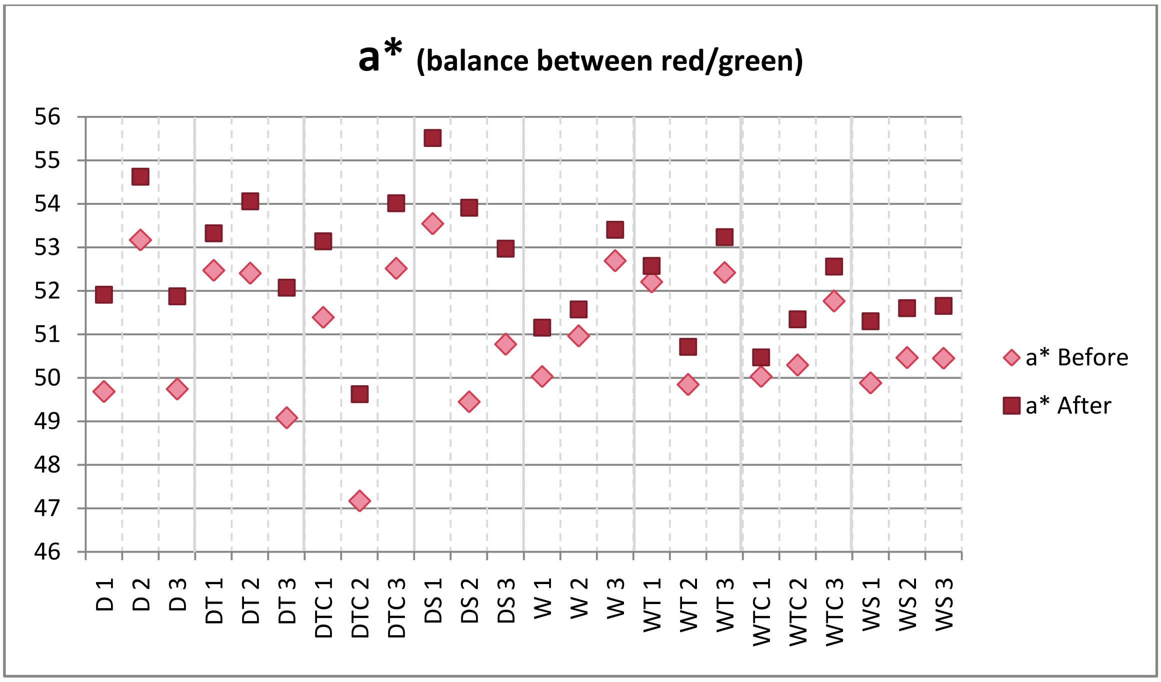

Figure 6.7 Change in level of red/green in silk samples.

6.3.3 Difference in b* (yellow/blue)

The measurement of b* reduced for a large majority of the silk samples after wet cleaning (fig. 6.8). The greatest reduction of yellow is in the groups that were washed in solutions containing tri-sodium citrate, and tri-sodium citrate with citric acid. It is these wash solutions which caused the greatest dye bleed.

Groups D, W, and WS exhibit less of a reduction than the other groups, with the exception of group DS which displays a different trend of an increase in yellow. There was less dye bleed with the addition of sodium hydroxide and citric acid to the wash solution, which could be a factor in the increase or very low reduction in yellow. There is a marked difference in the level of yellow corresponding to the amount of dye bleed during wet cleaning.

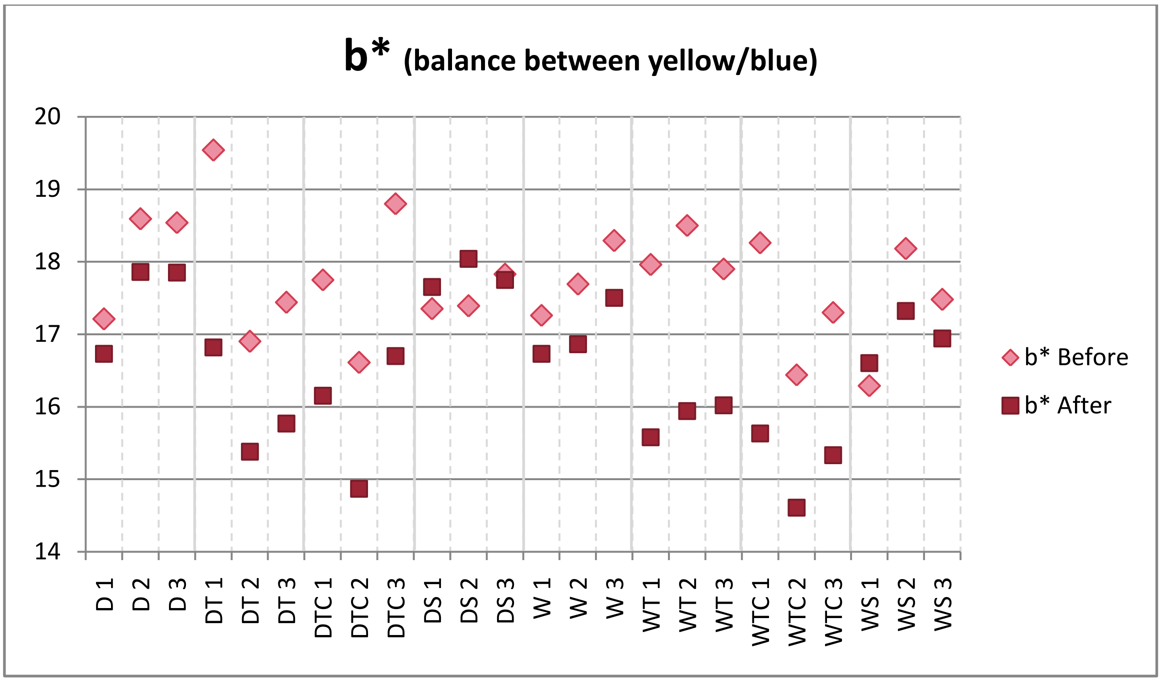

Figure 6.8 Change in level of yellow/blue in silk samples.

6.3.4 ΔE (Total Colour Difference)

In comparison between the samples treated with detergent and those treated with water, the detergent solutions have, overall, had more effect on average ΔE (fig. 6.9). The lowest average ΔE and variance is in group W, closely followed by group WS. These two groups also displayed the least amount of dye bleed and, it is possible that ΔE is reflecting this, as well as removal of soiling and degradation products.

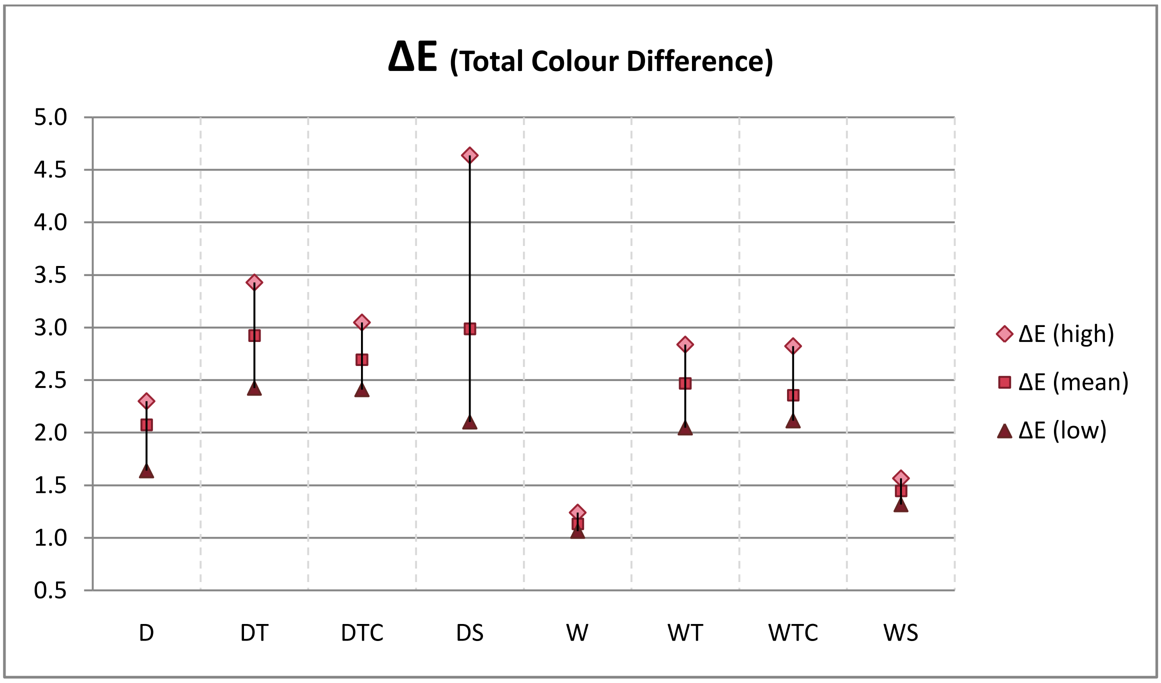

Figure 6.9 Total colour difference in silk samples.

From these results it is clear that the addition of tri-sodium citrate to the wash solution, with or without citric acid, had a larger influence over ΔE. These wash solutions exhibited the most dye bleed; therefore it is very likely that the resulting ΔE has been affected more by dye bleed than soiling removal.

The samples displaying the greatest (DS2) and lowest (W3) ΔE are visually very similar after treatment (fig. 6.10). The most obvious difference in both samples is the reduction in yellow and increase in red, with sample DS2 appearing slightly darker than sample W3.

Figure 6.10 Before (left) and after (right) wet cleaning of samples DS2 (top) and W3 (bottom).

6.4 Discussion

In both groups of samples, those wet cleaned with water only produced the least overall colour change. Although water is a powerful solvent, the use of surfactants and additives in the wash solution provides and improves the ability to remove greasy soiling from historical textiles.[102]

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[102] The Conservation Unit, 80.

The reduction in brightness of the silk samples was unexpected; it is likely that the colour of the samples and dye bleed has had an effect on the outcome of these results. It is also possible that re-deposition of soiling could account for a darkening.[103] The readings from the cotton samples provided results that, as expected, show a brightening of all samples, likely to have been produced by removal of soiling.

Due to the dye loss from the silk, a decrease in red was expected; however all silk samples measured an increase in red. This could be interpreted as the removal of soiling from the samples, from a constituent part of the dye being more soluble, or the pH altering the chromophoric structure of the dye molecule and causing a colour change.[104] In contrast, all of the cotton samples displayed a decrease in red, likely to be from the reduction in brown staining and soiling.[105]

A reduction of yellow was expected, from the removal of soiling and water soluble acidic degradation products from the fibres.[106] Surprisingly, in the case of the cotton samples, there is a slightly bigger decrease in yellow in the samples wet cleaned with water wash solutions compared to those wet cleaned with detergent solutions.

Sodium hydroxide with citric acid combination buffer provided the most acidic wash solutions. These conditions are optimum for non-ionic detergents, and should therefore have been contributed to the effectiveness of Dehypon LS45®. Conversely, the mildly acidic conditions should have made Hostapon T® less effective, as anionic surfactants work best in mildly alkaline conditions.[107] Hostapon T® with tri-sodium citrate was expected to provide good soiling removal because increased alkalinity of the wash solution promotes ionisation of the surfactant, and washing efficiency.[108] However, although tri-sodium citrate displayed a high ΔE, sodium hydroxide with citric acid provided the greatest ΔE of the cotton samples with a mildly acidic wash solution. The

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[103] Fields *et al.*, 64.
[104] Tímár-Balázsy and Eastop,97.
[105] Landi, 36
[106] Garside and Wyeth (2006), 69.
[107] Ágnes Tímár-Balázsy, “Wet Cleaning of Historical Textiles: Surfactants and other Wash Bath Additives, *Studies in Conservation*, vol. 45, no. 1 (2000): 46-64, http://dx.doi.org/10.1179/sic.2000.45.1.46, 55.
[108] Tímár-Balázsy and Eastop, 208.

use of tri-sodium citrate and tri-sodium citrate with citric acid created the larger ΔE in the silk samples, although the dye bleed renders this less conclusive with regard to soiling removal.

The use of an undyed silk fabric would have been beneficial for observing soiling removal; however a marked difference in colour of the wash solutions did identify a difference in the products being removed from the fabric. The colour of the first wash bath was yellower than subsequent baths; possibly due to more soiling and degradation products being present in the initial wash bath, and would account for the reduction in yellow.[109] This was also visible during pH extraction (fig. 6.11).

Figure 6.11 Colour difference between pH extraction solutions before (left) and after treatment (right).

The addition of tri-sodium citrate to the wash solution had the biggest impact on the amount of dye released into the wash bath. Tri-sodium citrate with citric acid combination buffer released slightly less dye into the solution, followed by no pH buffer, and with sodium hydroxide and citric acid releasing the least amount of dye into the

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[109] Garside and Wyeth (2006), 83.

wash bath (fig. 6.12). The affect of tri-sodium citrate on dye release from the silk samples accounts for the high ΔE in the samples treated with tri-sodium citrate in the wash solution.

Figure 6.12 Colour difference between wash solution of silk samples WS2 (top), W1 (centre) and WT1 (bottom).

One interpretation of the effect of tri-sodium citrate on dye bleed is that it produced the most basic wash solution; whereas solutions containing sodium hydroxide with citric acid were the most acidic, and displayed a relatively small amount of dye bleed. This echoes a result found by Hartog in tests on a silk lining.[110] The dye bleed makes the data showing the greatest ΔE in group DS more surprising. However, even though there was dye loss from the silk, the colour change visible in the samples is negligible.

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[110] Frances Hartog, "Costume cleaning conundrums," *V & A Conservation Journal* 56 (2008): 5-7, http://www.vam.ac.uk/content/journals/conservation-journal/issue-56/costume-cleaning-conundrums/.

6.5 Conclusion

Tri-sodium citrate with citric acid proved to be the least efficient with regard to aiding soiling and degradation product removal from the cotton samples, with the Hostapon T® and sodium hydroxide with citric acid group showing the greatest ΔE, and the least amount of variance. Tri-sodium citrate self buffer also proved effective in both Hostapon T® and water wash solutions.

Due to the dye bleed, it is not possible to distinguish soiling and degradation product removal from dye loss. In this case colour measurement has not been effective to quantify soiling removal from the dyed silk fabric.

Chapter 7: Surface pH and pH Extraction Results

7.1 Introduction

The reliability of surface pH electrodes to give accurate readings from textiles will be discussed in this chapter. Surface pH measurements will be compared to aqueous extraction pH measurements. The visual effect on the samples from conducting surface pH readings will also be examined.

Identification of the pH of a textile before wet cleaning gives important information about the state of the textile fibres.[111] The pH of each sample was measured before and after wet cleaning was carried out. To do this, deionised water was applied to the area to be analysed,[112] and a pH meter with surface electrode was used to take readings from three defined points on each sample. Additionally, the pH was determined by aqueous extraction using small samples from the entire piece of each test fabric before treatment, and from three randomly chosen samples of each fibre type after treatment.

7.2 Cotton Samples

7.2.1 Surface pH Results

Before treatment surface pH measurement of the samples (fig. 7.1) places the pH of the cotton between pH4.2 (sample WT2) and pH5.1 (sample HT3). The average pH is very similar in groups H and WS and they display the least variance, whereas HT, W, WT and WTC have the most variability.

After treatment surface pH measurements (fig. 7.2) places the pH of the cotton between pH4.9 (sample W1) and pH6.4 (sample H1). There is much more variability in the measurements after treatment. One possible reason for the greater variance in the pH after wet cleaning could be the difference in pH of wash solutions used.[113]

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[111] Landi, 37.

[112] Tímár-Balázsy and Eastop, 218.

[113] Rice(1962-1969), 17.

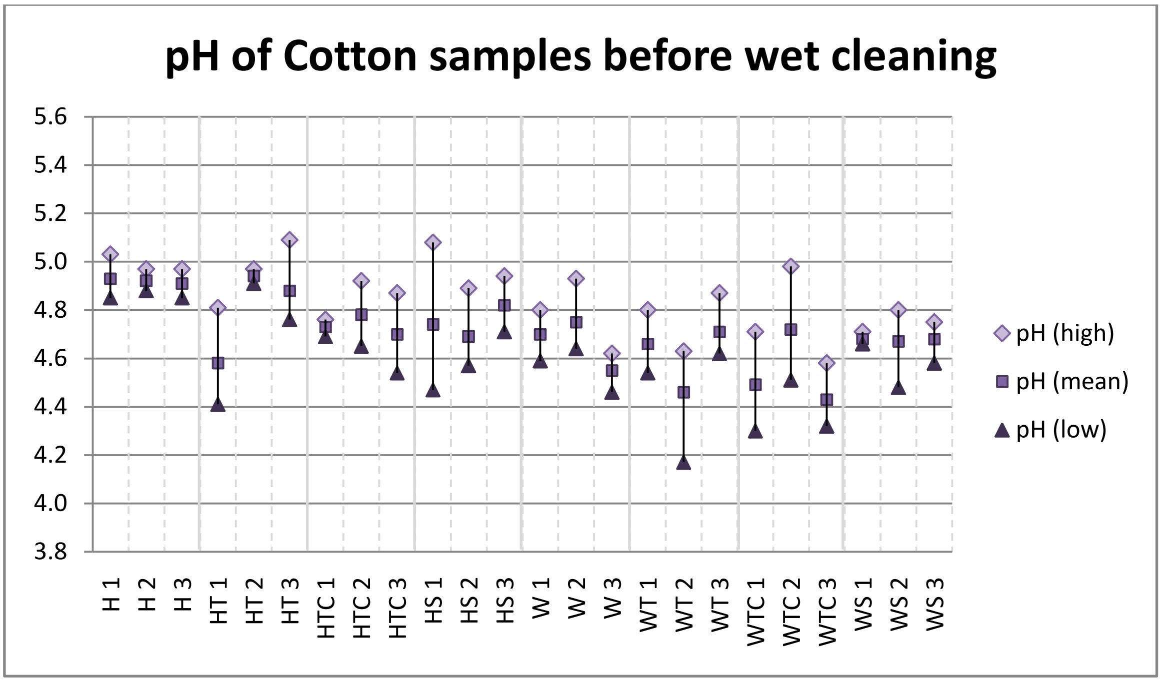

Figure 7.1 Surface pH of cotton samples before wet cleaning.

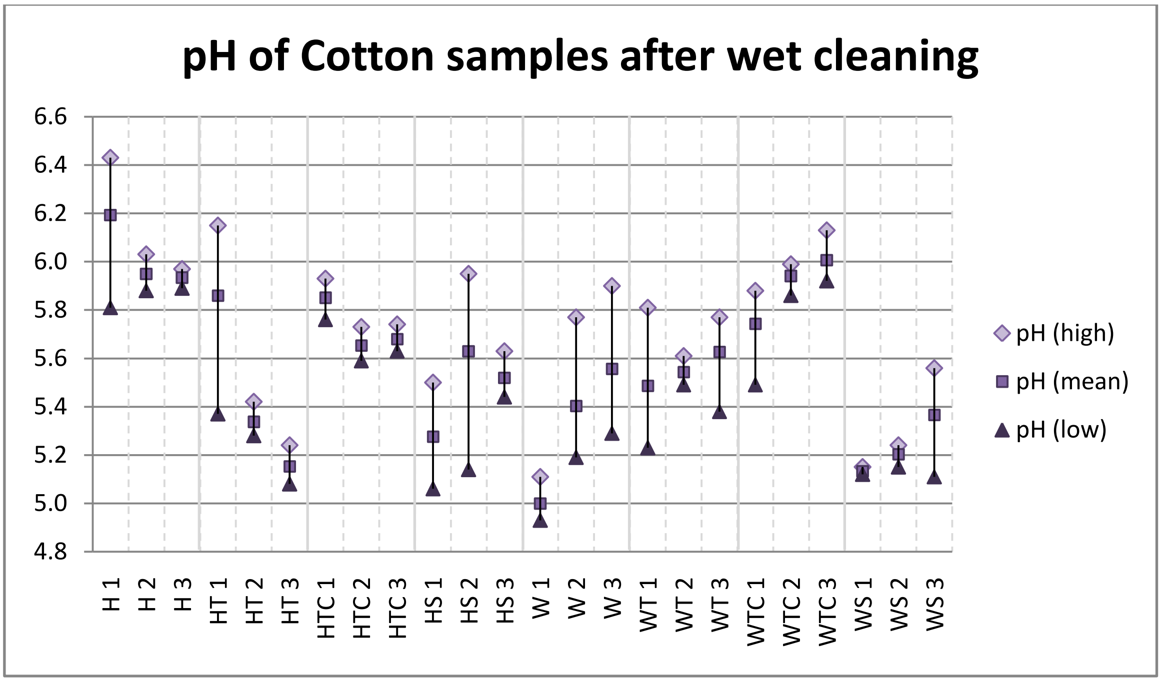

Figure 7.2 Surface pH of cotton samples after wet cleaning.

As expected, the pH of all samples increased from the removal of soiling and degradation products during wet cleaning.

Comparing the mean measurements of the before and after readings (fig. 7.3), only two groups display a rise of over 1pH unit in all three samples: H and WTC. Conversely, only two groups have a rise of less than 1pH unit in all three samples: HS, and WS.

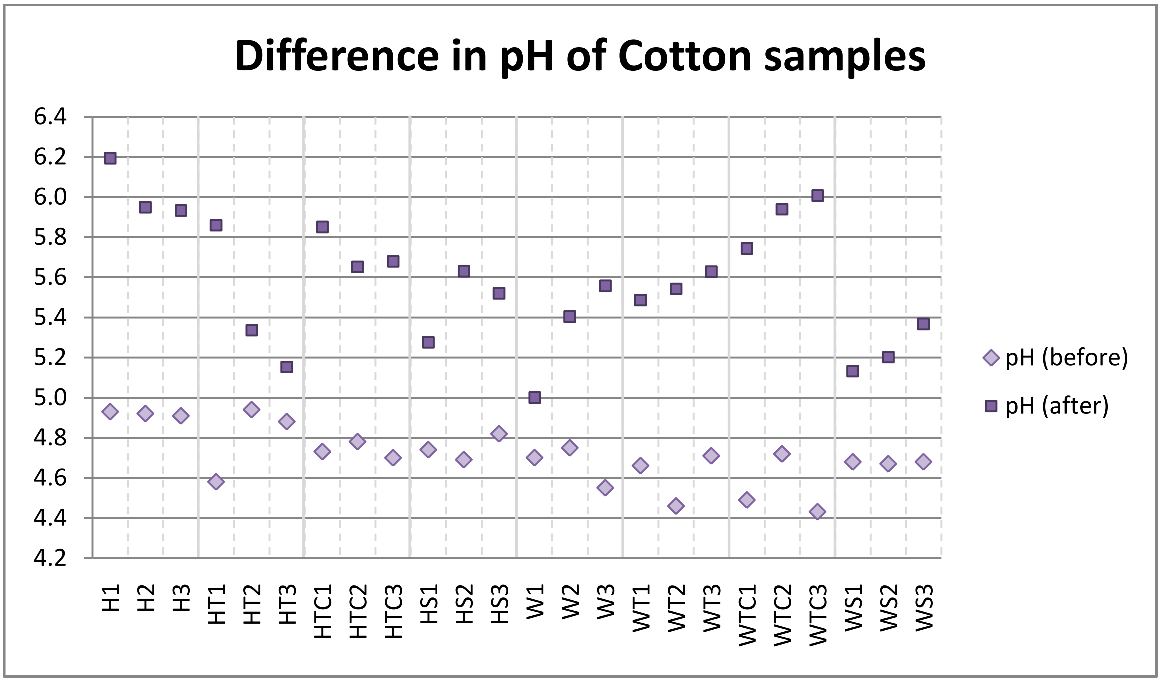

Figure 7.3 Difference in mean surface pH of cotton samples before and after wet cleaning.

The greatest increase is in sample WTC3 and the lowest increase is in sample HT2. The highest increase correlates with the highest overall increase in group WTC, whereas the lowest overall increase is displayed by group WS. This reflects the variance within the groups and lack of any clear trend in the results.

7.2.2 Extracted pH results

After treatment the extracted pH was measured close to neutral (fig. 7.4). Sample HTC3 provided the lowest after reading, with sample WS2 giving the highest reading. A comparison of the before and after wet cleaning extracted pH measurements shows an increase of over 1pH unit; an increase higher than a factor of 10. This increase in pH is beneficial to the textile, showing that there has been a reduction in acidic degradation products from the samples during the wet cleaning process.[114]

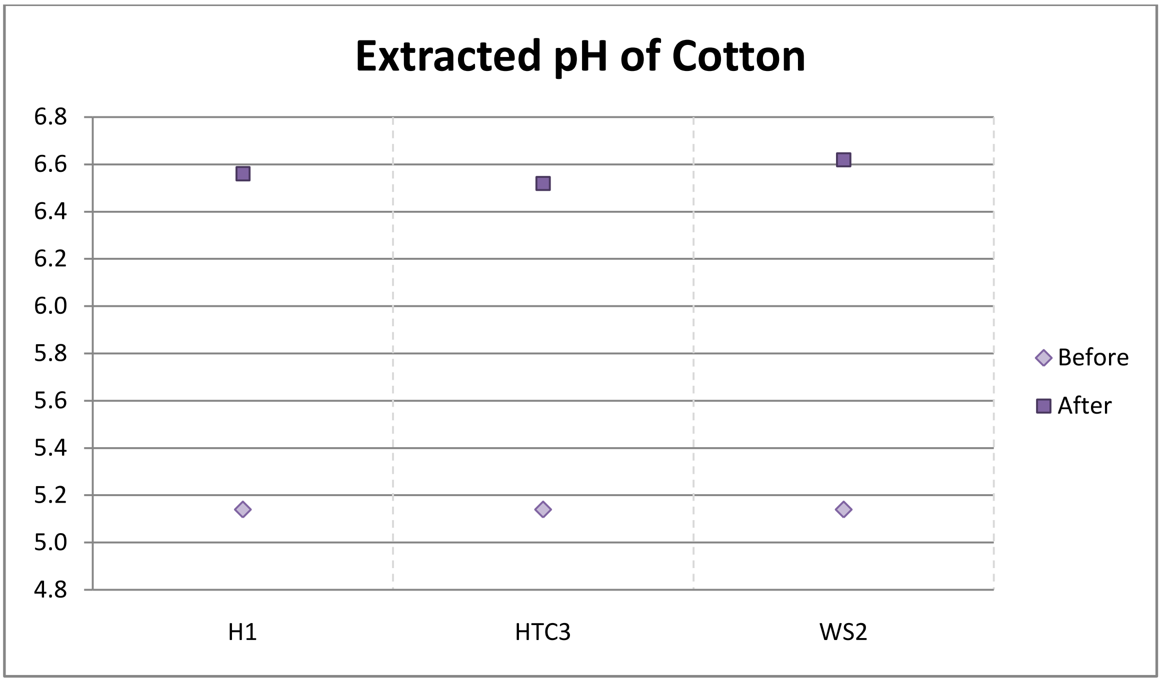

Figure 7.4 Extracted pH of cotton samples before and after wet cleaning.

7.2.3 Comparison of surface pH and extracted pH

The extracted pH measured is higher than the surface pH readings (fig. 7.5). There is a greater difference between the after pH readings. The after results of the surface readings suggest that the samples are still slightly acidic; however, the extracted pH measurements place the samples nearer neutral pH.

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[114] Landi, 37.

The increase in the pH of the cotton has been measured at close to 1.5pH units through extraction. A slim majority of the surface pH readings did not increase by 1pH unit; only one reading provided an increase of over 1.5pH units.

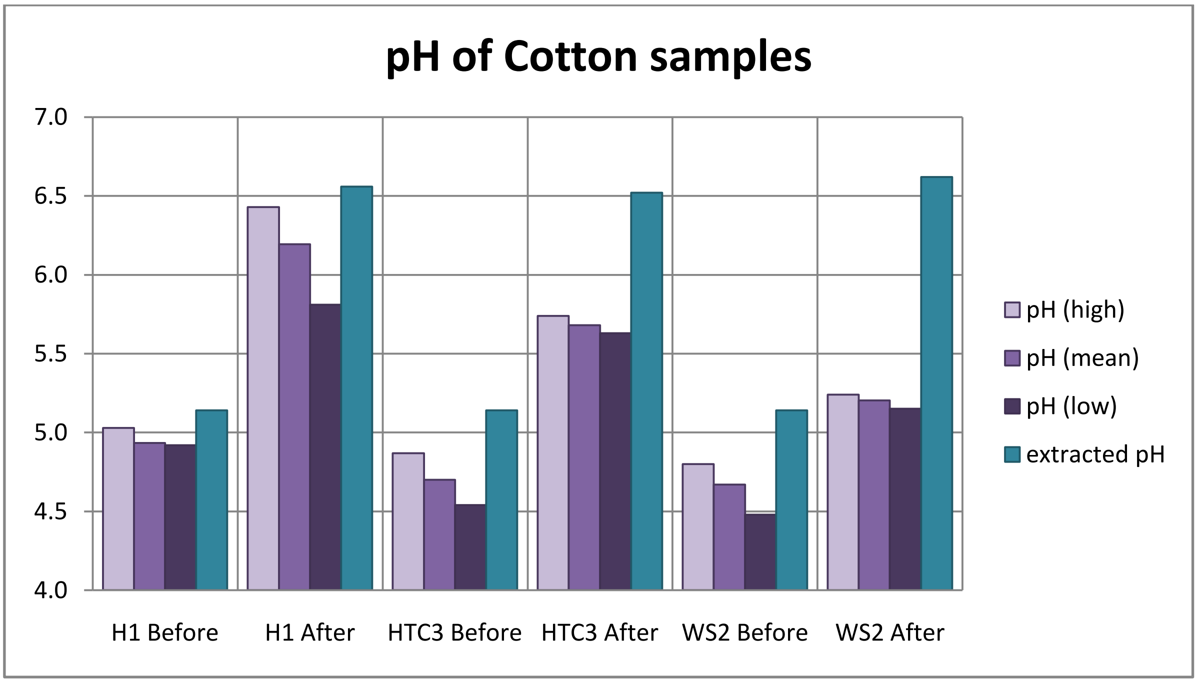

Figure 7.5 Surface and extracted pH of cotton samples before and after wet cleaning.

7.3 Silk Samples

7.3.1 Surface pH Results

Before treatment surface pH measurement (fig. 7.6) places the pH of the silk between pH3.9 (sample D3) and pH4.66 (sample DTC3). There is less variance in the readings of the silk samples compared to the cotton before wet cleaning. The average pH of group WS is very similar, whereas groups D, DT and DTC have the most variability.

After treatment surface pH measurement (fig. 7.7) places the pH of the silk between pH4.9 (sample D2) and pH5.9 (sample DT2). The variability in the surface pH measurements has increased after treatment.

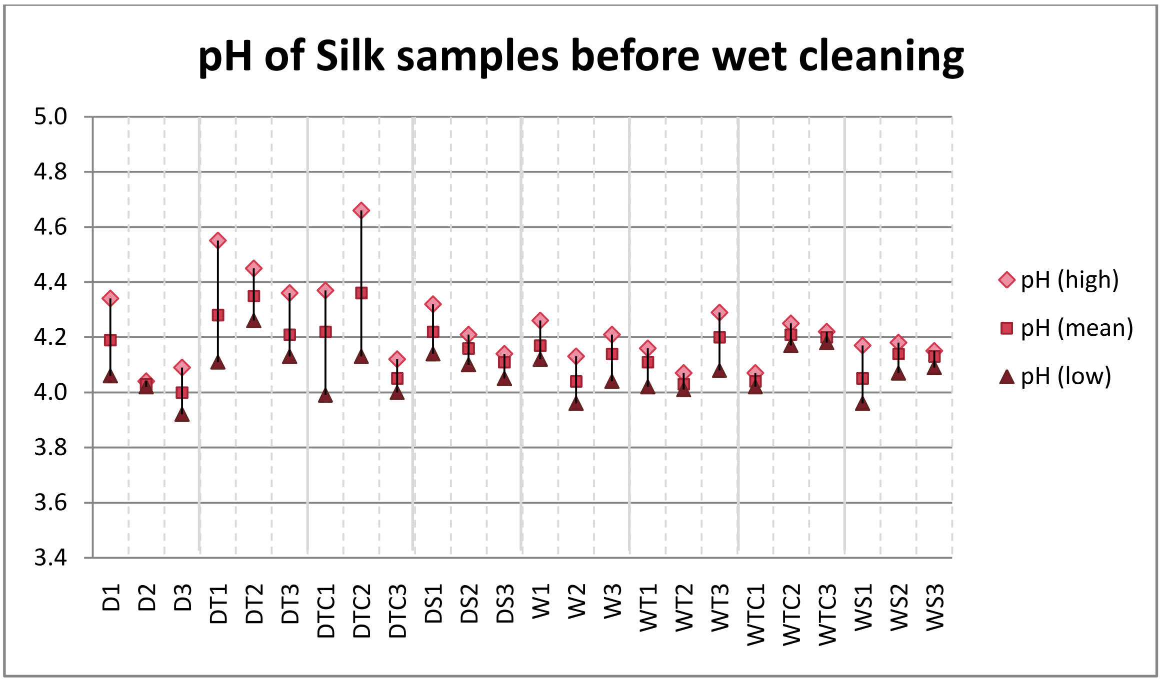

Figure 7.6 Surface pH of silk samples before wet cleaning.

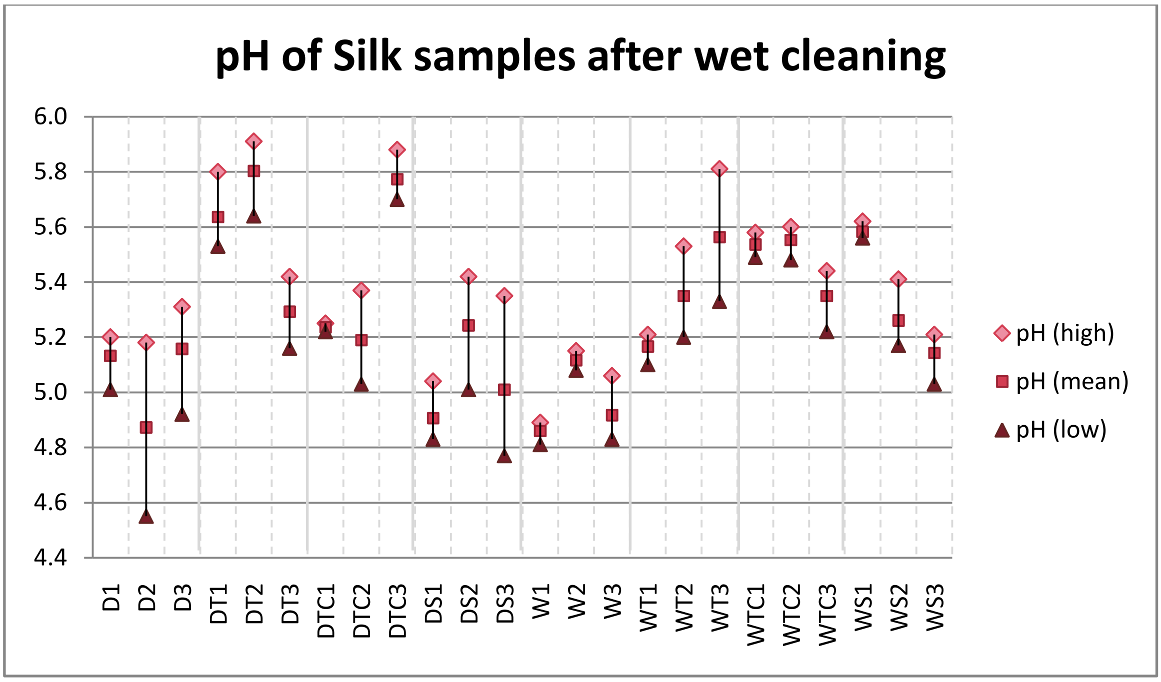

Figure 7.7 Surface pH of silk samples after wet cleaning.

The after pH measurements of the silk samples are, like the cotton, more varied than the before readings. However, the groups of samples are not grouped together with similar pH measurements. This variance could be due to the dye bleed during wet cleaning.

Comparing the mean before and after measurements (fig. 7.8), there is a marked increase in pH in all samples, showing that acidic products have been removed from the silk making it more stable. Four groups have an increase of over 1pH unit in all three samples: DT, WT, WTC, and WS. The greatest increase is in sample DTC3, and the lowest increase is in sample DS1. However, there is a variance in the averages in each group preventing the formation of any conclusive trends with regard to the wash solutions and pH buffers used.

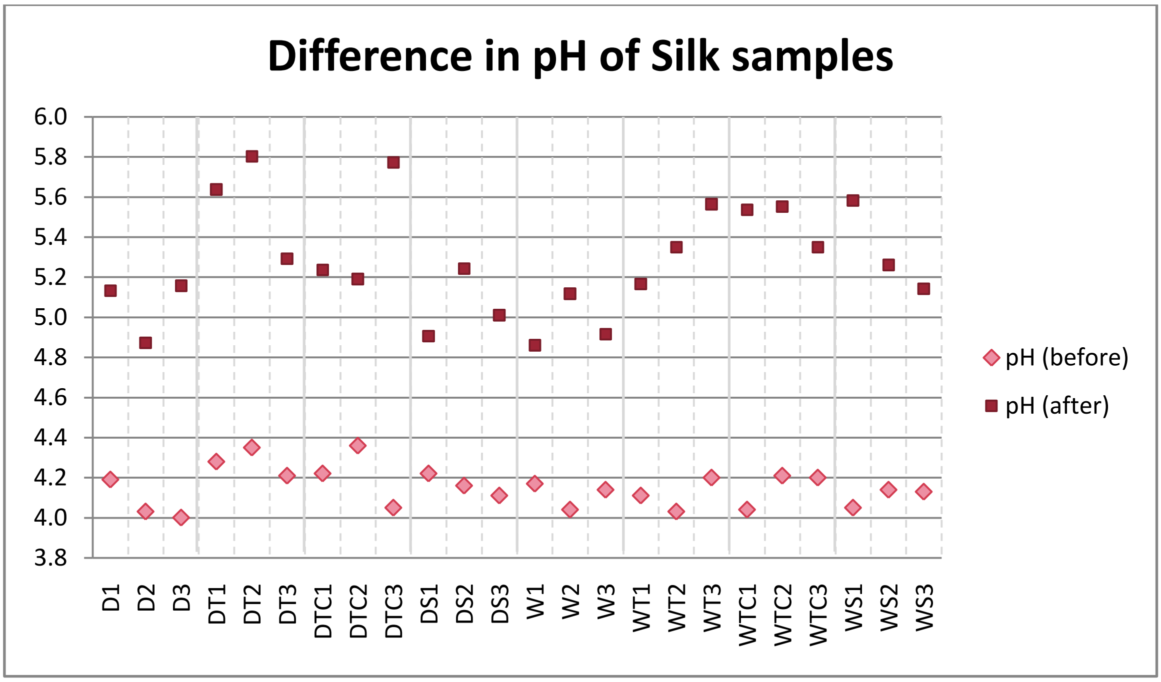

Figure 7.8 Difference in mean surface pH of silk samples before and after wet cleaning.

7.3.2 Extracted pH Results

The extracted pH of the silk samples rose by at least 1pH unit after wet cleaning, a 10-fold increase (fig. 7.9). The results of the extracted pH show that the after pH of sample DT3 is higher than the samples cleaned with water, and that using a pH buffer in water had an impact by raising the pH of the sample significantly further than water as a solvent alone.

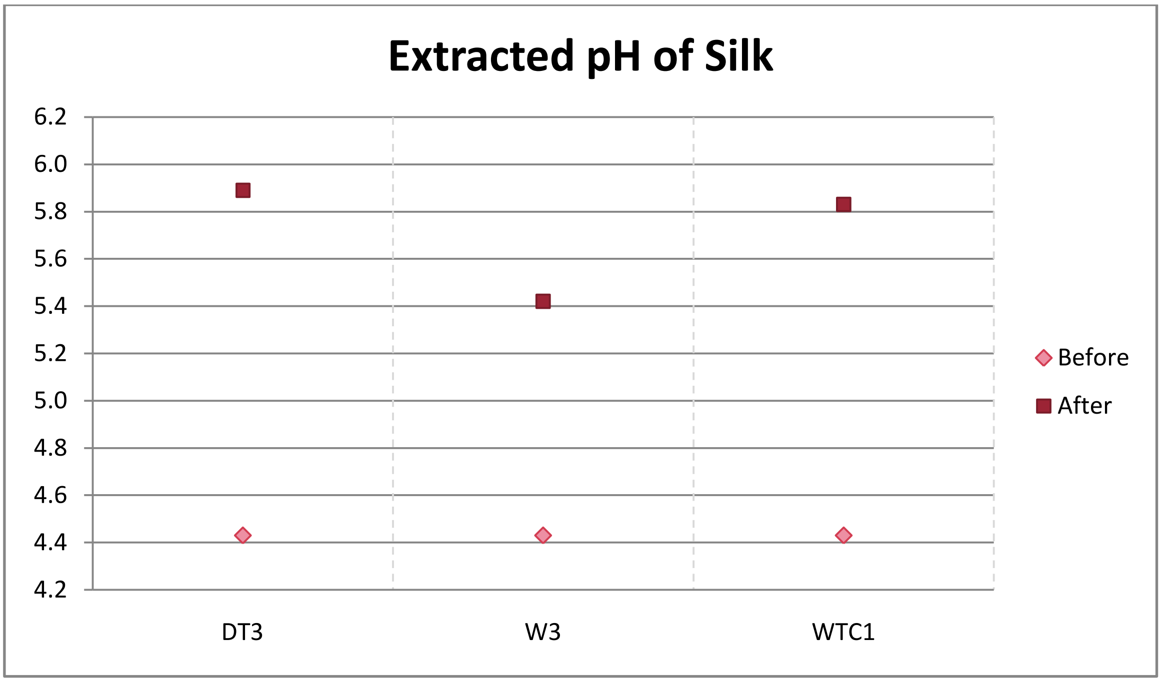

Figure 7.9 Extracted pH of silk samples before and after wet cleaning.

The increase in pH shows that acidic products have been removed from the silk. It is, however, unclear whether this is soiling and degradation products, constituents of the dye, or both.

7.3.3 Comparison of Surface pH and Extracted pH

The extracted pH readings were higher than the surface readings (fig. 7.10). However, the readings differed by less than 1pH unit. The extracted pH of the samples shows that they are still acidic; however the pH has been raised to a safer level. The majority of samples showed a surface pH increase of over 1pH unit.

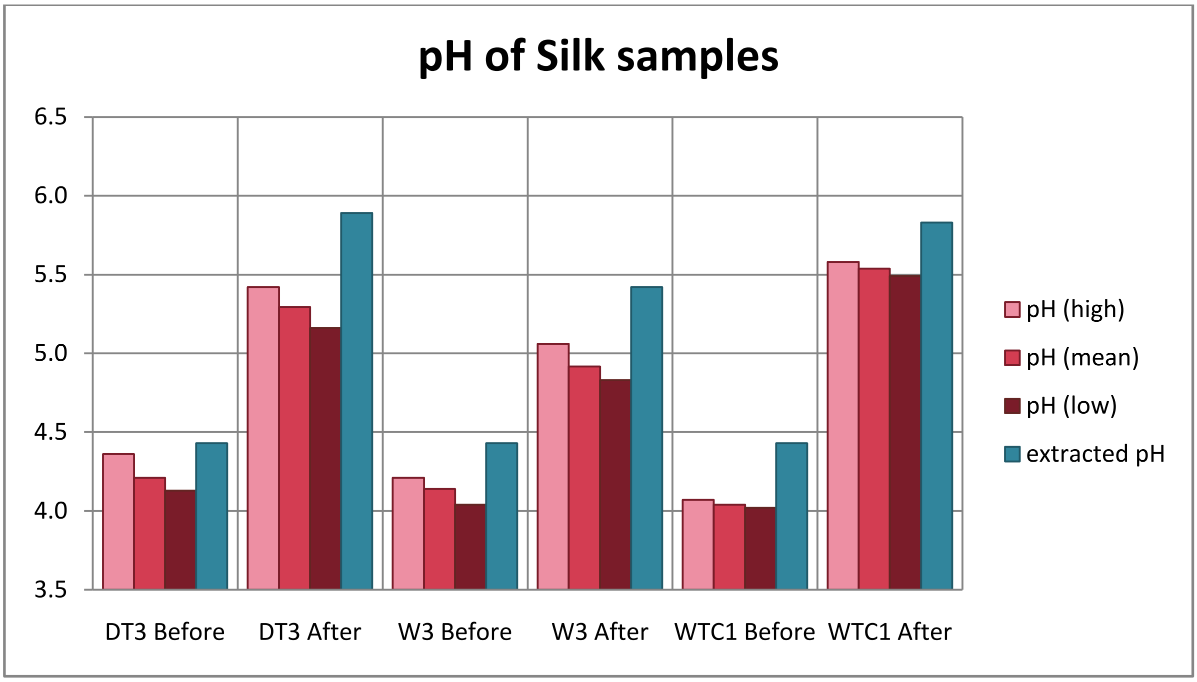

Figure 7.10 Surface and extracted pH of silk samples before and after wet cleaning.

7.4 Discussion

Extracted pH measurement was found to be more accurate than surface pH measurement; the pH reading stabilised faster during pH extraction, whereas the pH reading changed if the surface electrode moved slightly and the deionised water on the textile was difficult to contain or control. The pH meter and surface electrode were slow to stabilise, this was more evident after wet cleaning when the pH of the samples was closer to neutral and is likely to be because the acidic soiling and degradation products, and dye in the fibres had been reduced.[115]

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[115] Montague, 20.

As has been found in paper conservation studies, the extracted pH was higher than the surface readings; however the result did not differ by the same extent of 1-2pH units as was found in the study by Joel *et al*, where it was also noted that the type of paper and additive materials have an effect on the pH measured.[116] It is possible that there is a greater difference in the measurement of cellulosic fibres. The difference between the average surface pH and the extracted pH was greater in the cotton samples than in the silk samples. However, both the extracted and surface readings showed an increase in pH. As long as surface readings are used as a guide, with the knowledge that they are likely to be lower than the actual pH of the object, they can be useful for showing a shift in pH.

The extracted pH of the silk was closer to the surface readings than was found for the cotton samples. The reason for this could be the more acidic nature of the samples, as it is likely that the dye is an acid dye from its reaction to basic wash solutions.[117] The pH electrode was calibrated in pH7 solution followed by pH4 solution; it is possible that a 'memory' effect of the electrode could have affected the readings due to the final calibration at pH4.[118]

Visible ring marks were left on the samples from the before treatment readings. This is possibly due to the amount of water used, and that the samples were left to dry naturally, and not blotted to prevent removal of solubilised soiling prior to wet cleaning.[119] However, the same process for surface pH readings was used after treatment, and ring marks were not visible after readings were taken. This reinforces the reason for the ring marks being the solubilisation and movement of soiling within the samples.[120] If using this technique on an object, the conservator must choose an inconspicuous area for analysis, especially if there is a chance that the object will not be wet cleaned after pH analysis has been carried out.

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[116] Joel *et al.*, 120.
[117] Rice (1962-1969), 57-58.
[118] Montague, 20-21.
[119] Tímár-Balázsy and Eastop, 218.
[120] Tse, 7-11 .

7.5 Conclusion

No clear trends could be identified from the results due to the variability in each of the groups. The increase in pH of all samples shows that acidic products have been removed, be it soiling, degradation products or, in the case of the silk sample, dye. Removing acidic soiling and degradation products benefits the textile, as these products could catalyse degradation of the fibres.[121]

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[121] Landi, 79.

Chapter 8: Wet Cleaning pH Results

8.1 Introduction

The effect of pH buffers on the wash solution during wet cleaning will be examined in this chapter. The pH of the wash and rinse solutions was measured using a pH meter and combination electrode before and after each wash and rinse bath. The pH meter has Automatic Temperature Compensation (ATC),[122] therefore the pH readings taken do not need to be adjusted according to the temperature reading, and results can be directly compared.

The Hostapon T®, Dehypon LS45® and water only samples are controls within the experiment. The most representative pH measurements taken during the wash procedure will be presented and compared below (for full results see Appendix F).

8.2 Wet Cleaning pH Results Cotton

8.2.1 Hostapon T® and Water Only

There is no clear pattern in the pH readings taken during the wash process for these samples. The initial drop in pH of the first wash bath is generally more significant for the W samples, and pH of the final rinse bath was higher for the W samples than the H samples (figs. 8.1 and 8.2). It is possible that the pH of the H solution had a buffering effect, or that more acidic products were released into the W wash baths.

One explanation for this is that the pH of Hostapon T® was more acidic than expected, and because of this it is possible that the detergent did not ionise completely. Anionic surfactants ionise completely in slightly alkaline conditions, improving the efficiency of the detergent.[123] Slightly alkaline conditions are, therefore, the ideal conditions for Hostapon T®, whereas the starting pH of the H solution was mildly acidic.

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[122] Hanna Instruments, 7-8.

[123] Tímár-Balázsy, 55.

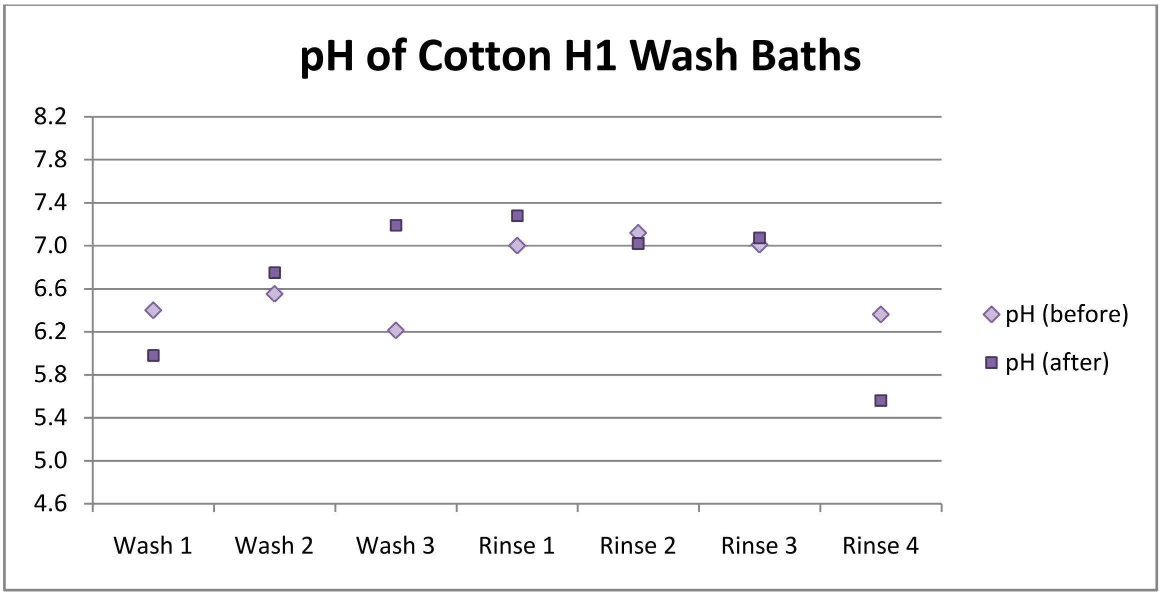

Figure 8.1 Before and after pH of wash and rinse baths for cotton H1.

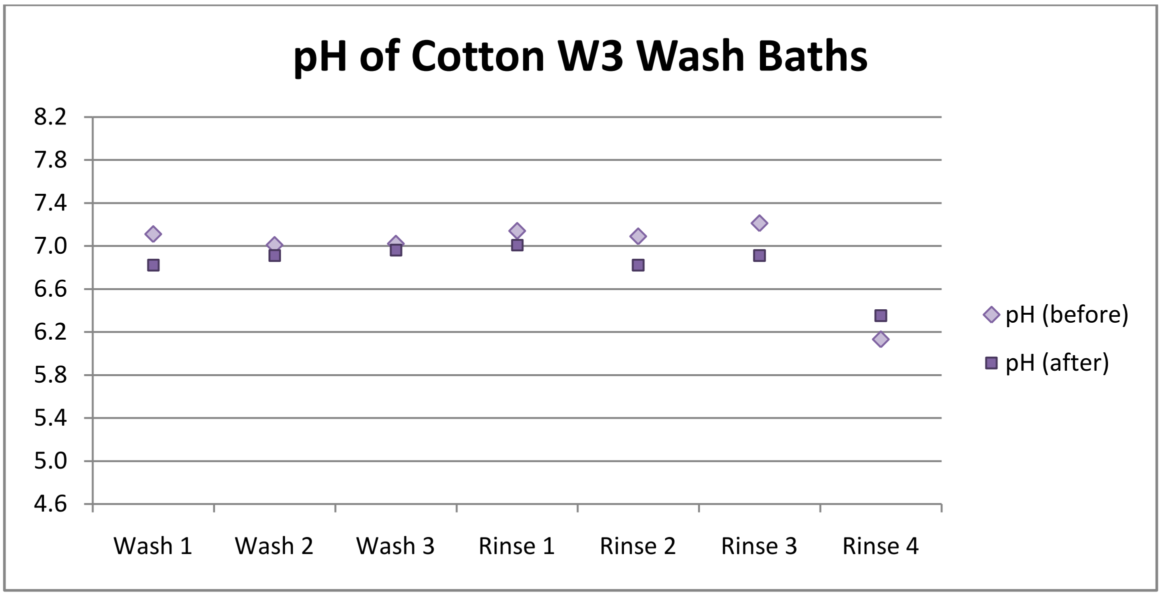

Figure 8.2 Before and after pH of wash and rinse baths for cotton W3.

8.2.2 Tri-sodium Citrate

The addition of tri-sodium citrate to the wash solutions increased the starting pH by up to 1pH unit compared to the controls (figs. 8.3 and 8.4). The after pH of the wash baths stabilised at around the same level, even though the starting pH of the wash solutions differed. The WT wash baths displayed a larger drop in pH than the HT wash baths, where the pH showed less movement after the first wash bath. The final pH of the WT samples was higher than any measured for the other water wash solutions.

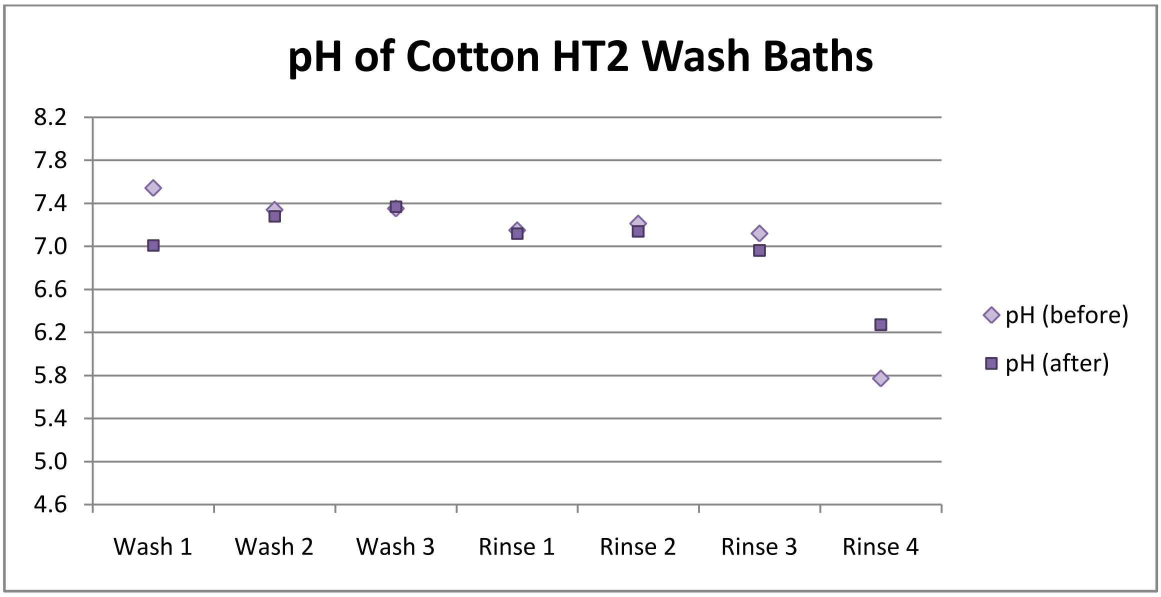

Figure 8.3 Before and after pH of wash and rinse baths for cotton HT2.

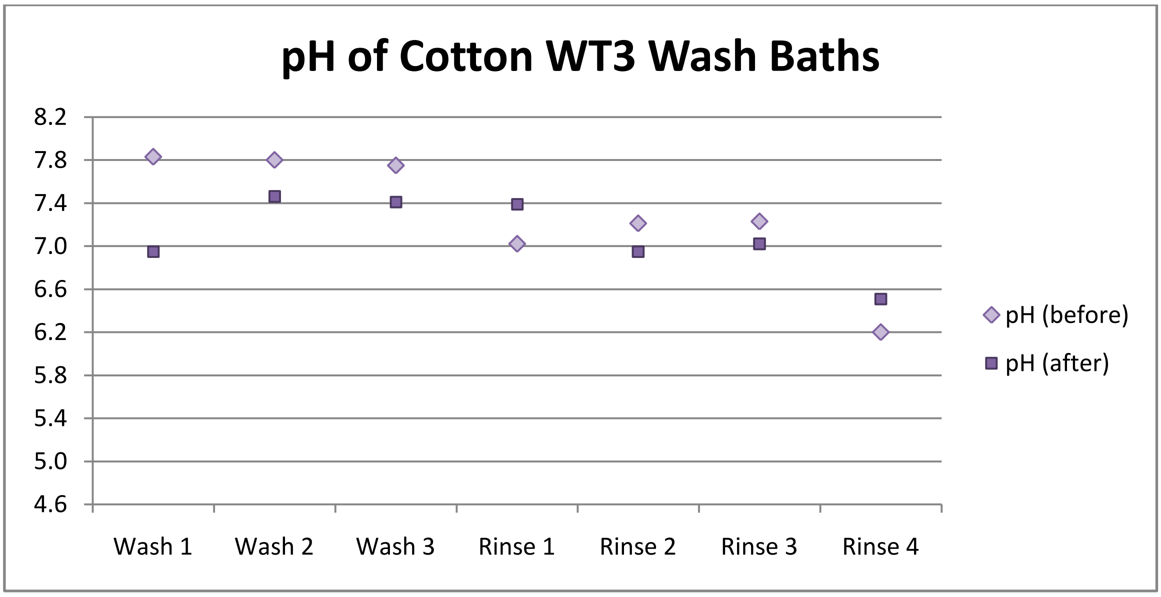

Figure 8.4 Before and after pH of wash and rinse baths for cotton WT3.

8.2.3 Tri-sodium Citrate and Citric Acid

Tri-sodium citrate and citric acid in the wash solution provided a pH that was around neutral, with the WTC pH slightly higher than that of HTC. The pH of the wash baths for both groups stabilised quickly, with slightly more control of pH displayed by the HTC solution (figs. 8.5 and 8.6.). The final pH of the HTC baths was generally higher than the WTC baths.

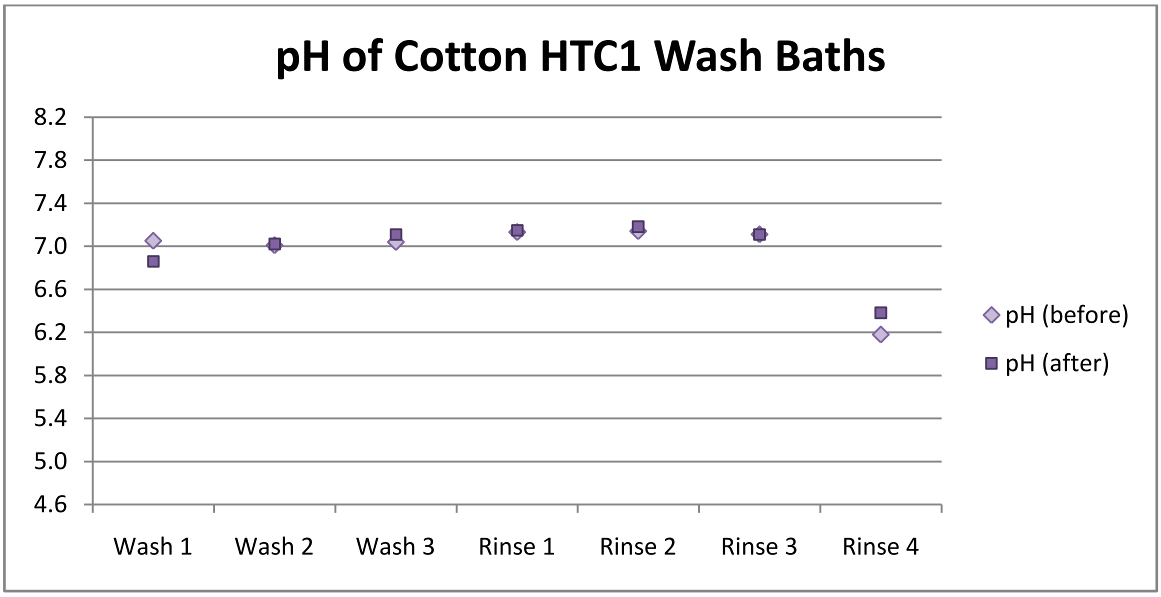

Figure 8.5 Before and after pH of wash and rinse baths for cotton HTC1.

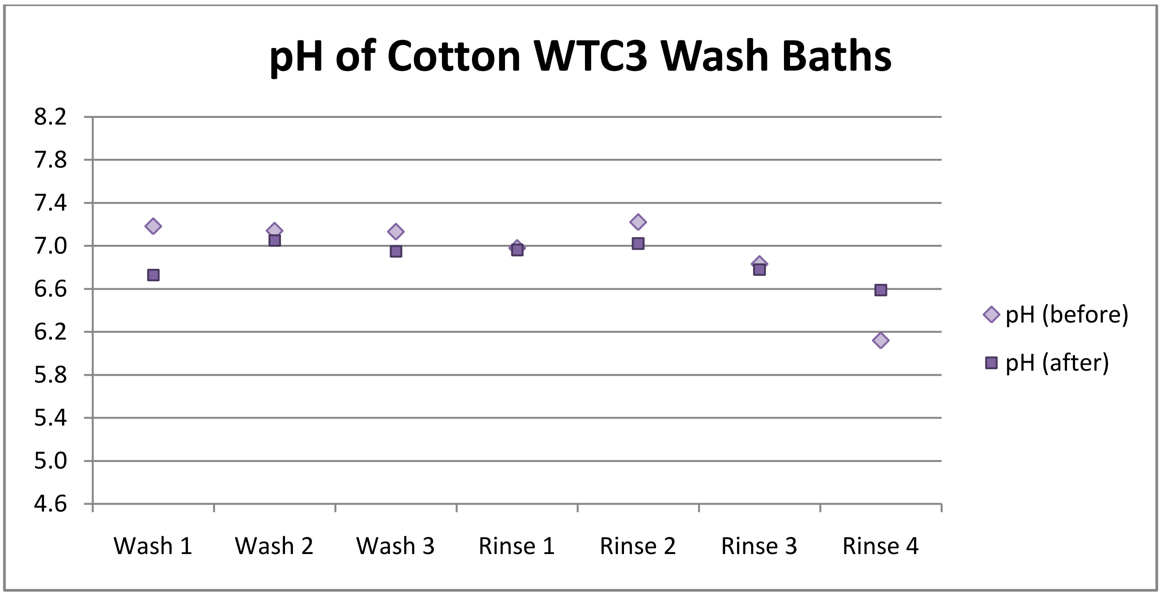

Figure 8.6 Before and after pH of wash and rinse baths for cotton WTC3.

8.2.4 Sodium Hydroxide and Citric Acid

The addition of the sodium hydroxide and citric acid combination buffer provided the most acidic wash solutions of those tested for cotton samples (figs, 8.7 and 8.8). The pH of the HS wash baths increased after the first bath, whereas the pH of the WS wash baths fell. The final rinse bath pH of the HS samples was higher than the WS samples.

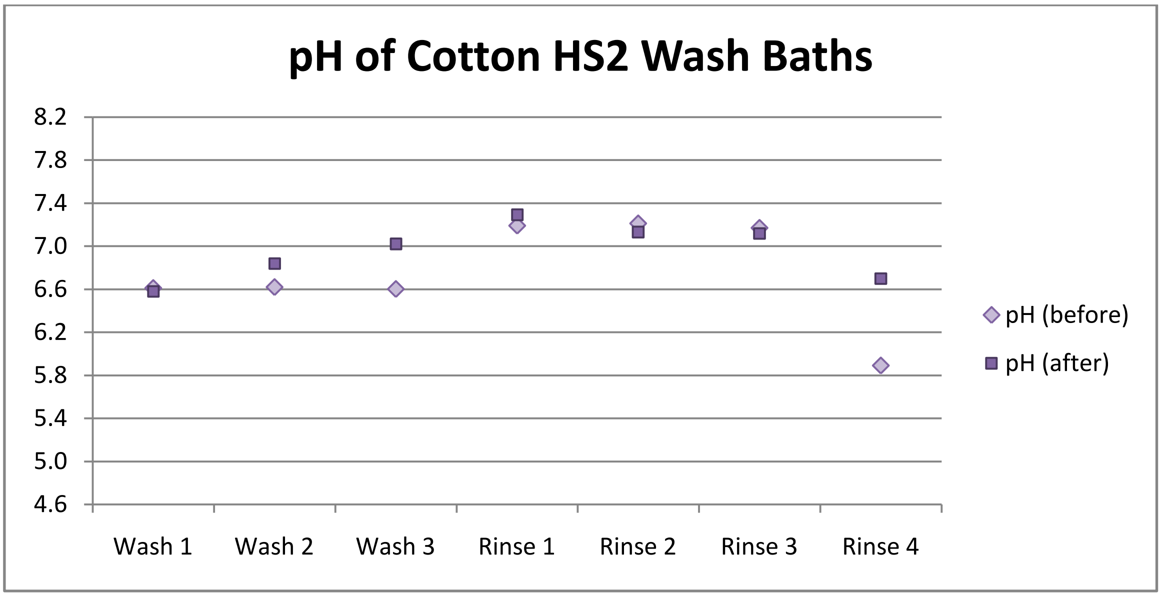

Figure 8.7 Before and after pH of wash and rinse baths for cotton HS2.

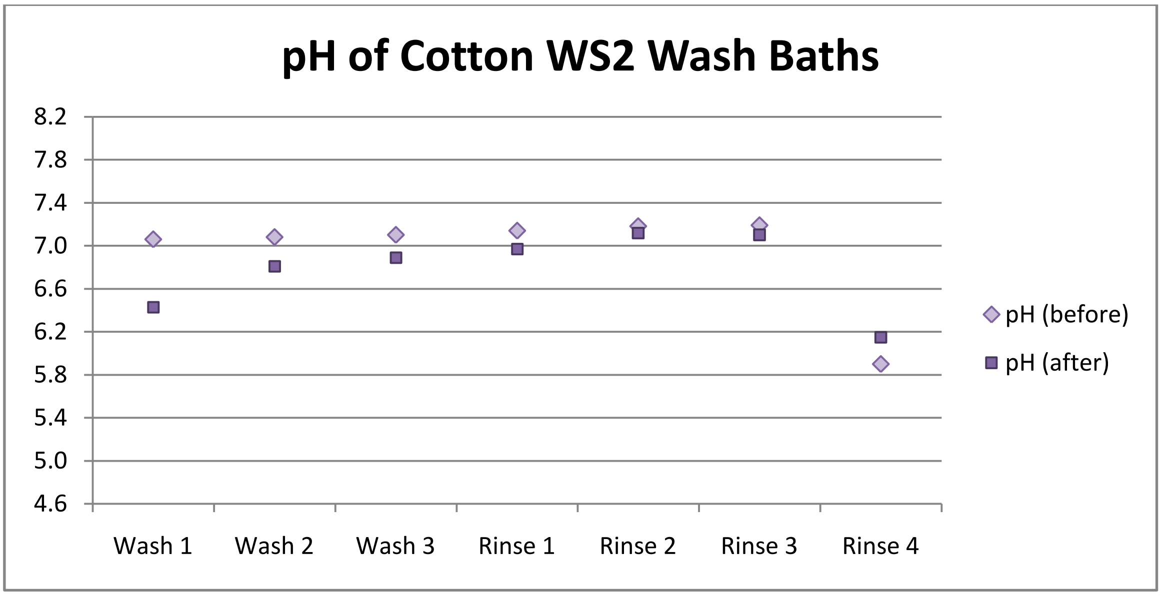

Figure 8.8 Before and after pH of wash and rinse baths for cotton WS2.

8.3 Wet Cleaning pH Results Silk

8.3.1 Detergent and water only

The drop in pH of the first wash bath was significant at approximately 2pH units for both wash solutions (figs. 8.9 and 8.10). The D wash bath pH stabilised more quickly and the final pH reading was higher than the W wash bath.

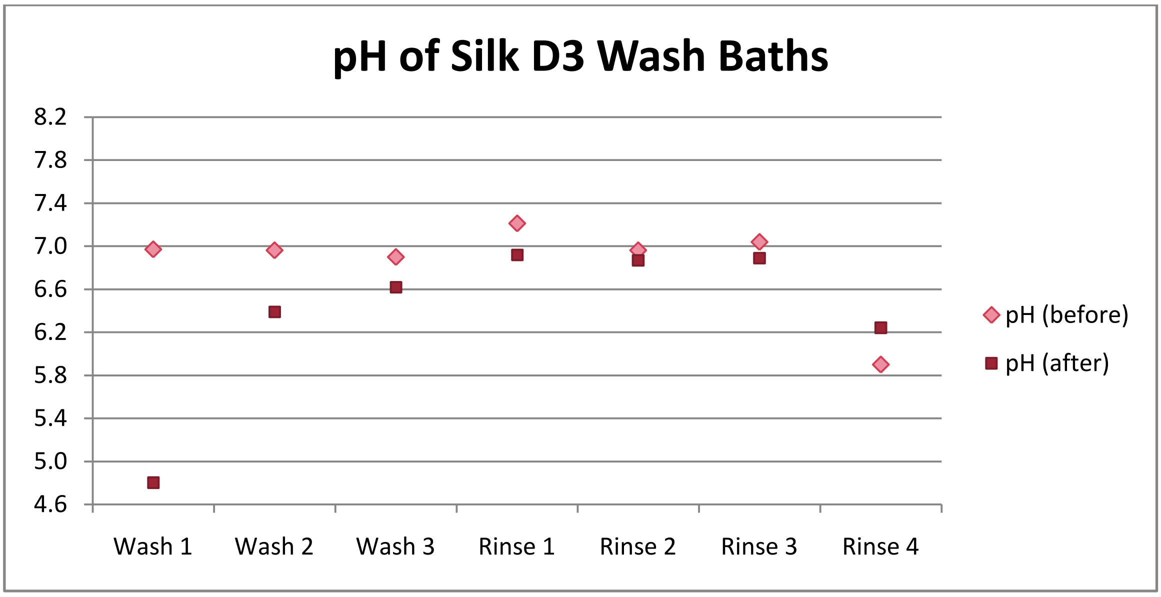

Figure 8.9 Before and after pH of wash and rinse baths for silk D3.

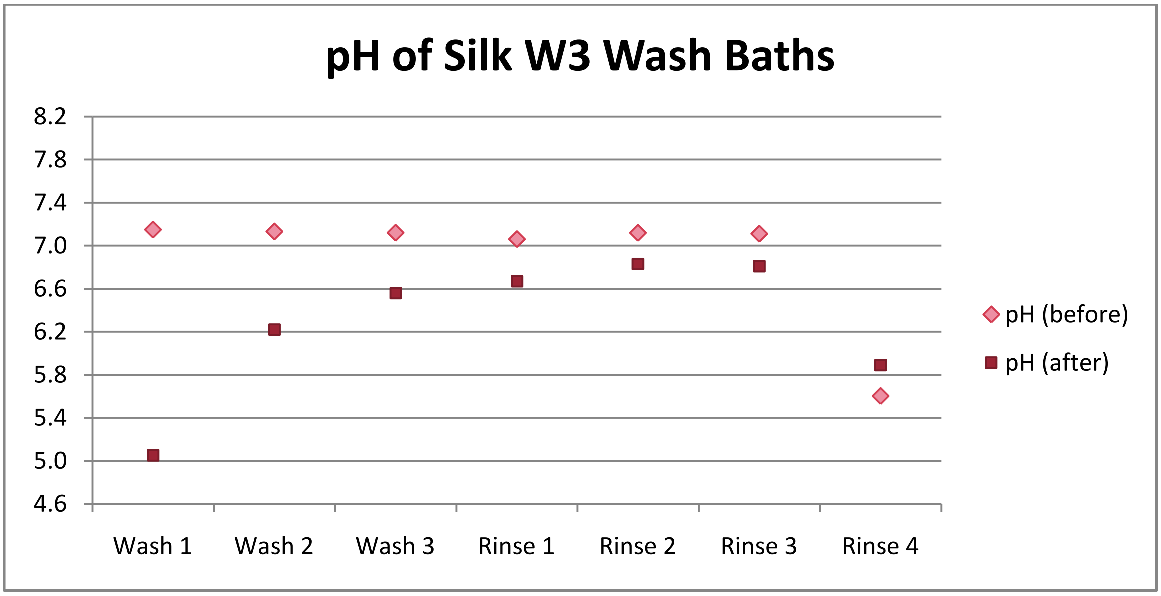

Figure 8.10 Before and after pH of wash and rinse baths for silk W3.

8.3.2 Tri-sodium Citrate

Tri-sodium citrate increased the pH of the wash solutions, making them slightly alkaline (figs. 8.11 and 8.12). The after pH of the DT wash baths is lower than that of WT, the opposite of the before readings. It is possible that the mildly alkaline conditions increased removal of acidic products from the samples, including dye.[124] During rinsing the pH of both groups is stable, but the DT samples have a higher pH after the final rinse.

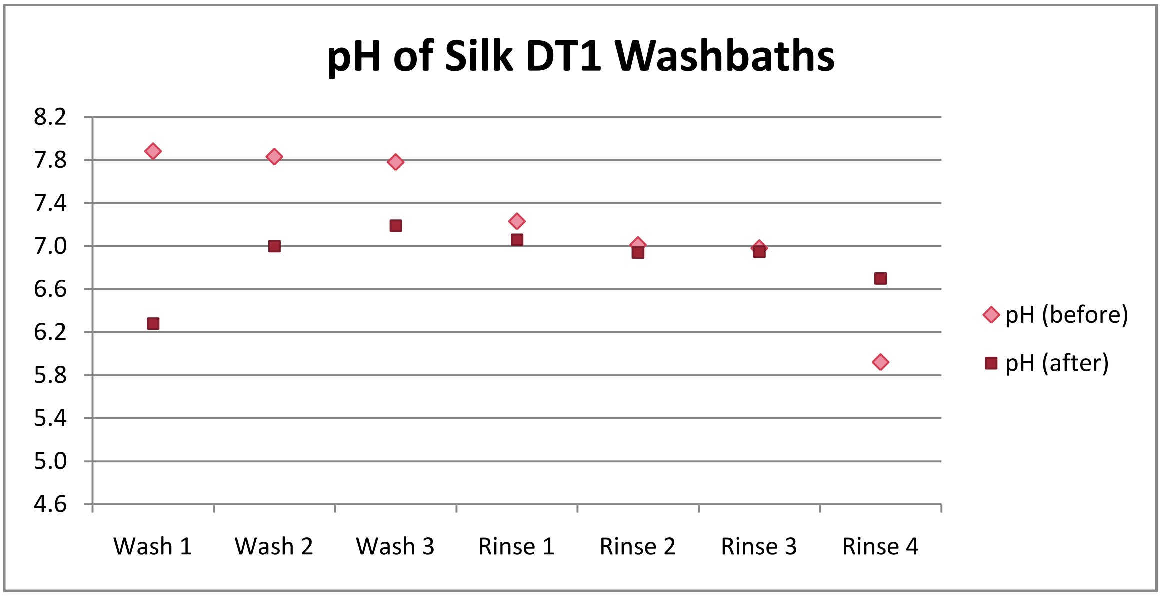

Figure 8.11 Before and after pH of wash and rinse baths for silk DT1.

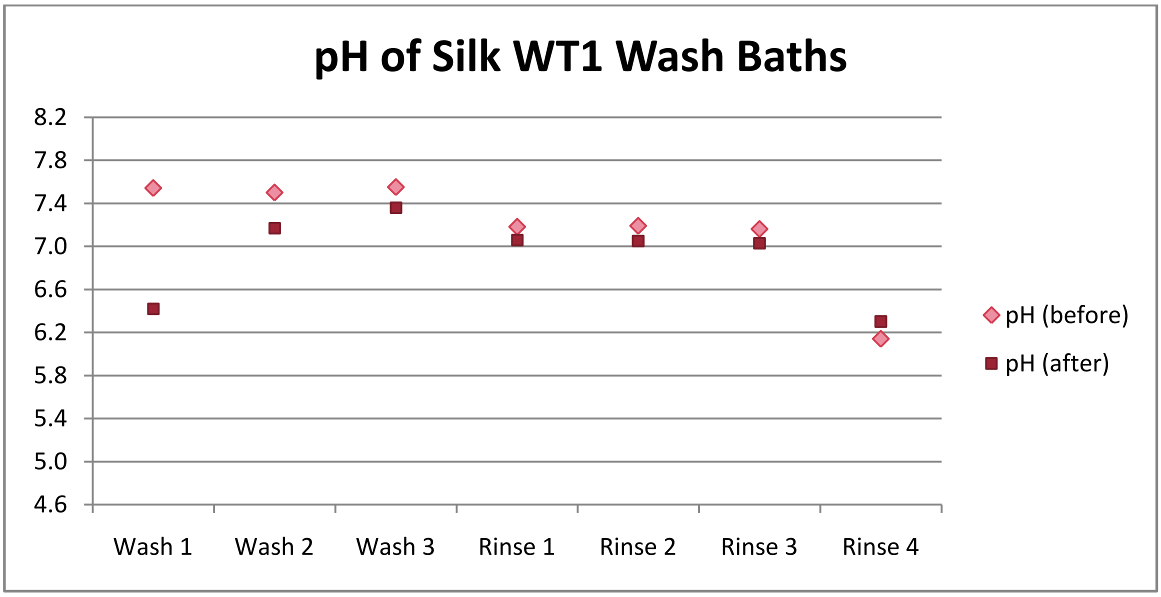

Figure 8.12 Before and after pH of wash and rinse baths for silk WT1.

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[124] Rice (1962-1969), 58.

8.3.3 Tri-sodium Citrate and Citric Acid

The increased alkalinity of the wash baths from the addition of tri-sodium citrate was reduced to nearer neutral by the addition of citric acid (figs. 8.13 and 8.14). The cloud point of Dehypon LS45® was lowered by the addition of citric acid, which is likely to have affected the efficiency of the surfactant.[125] Both wash solutions followed a similar pattern; the main difference being a higher pH of the final rinse for the DTC samples.

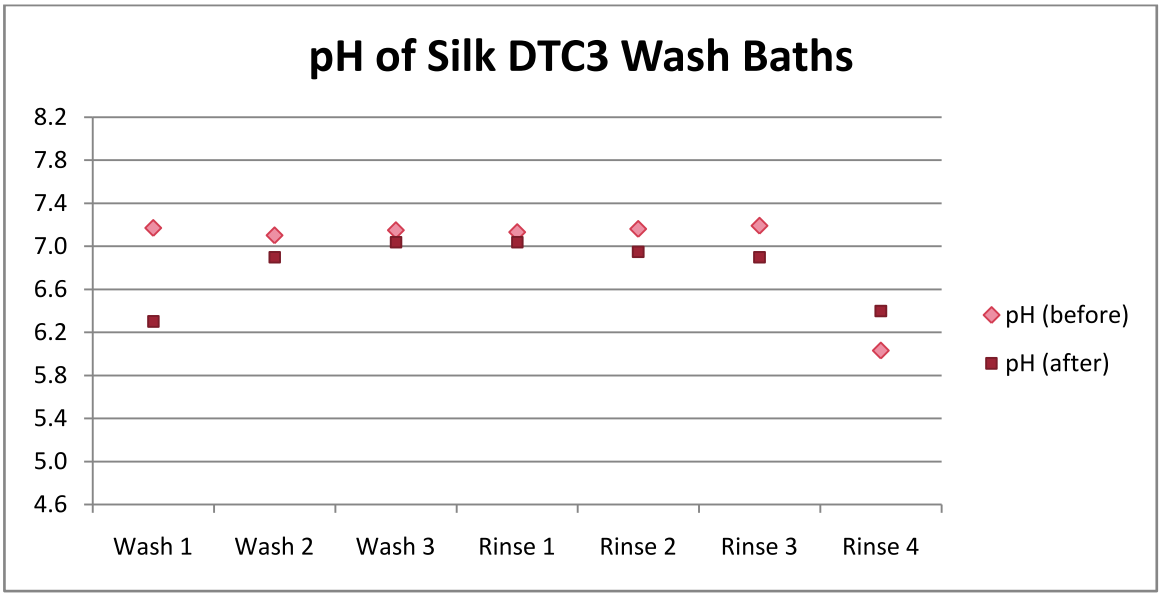

Figure 8.13 Before and after pH of wash and rinse baths for silk DTC3.

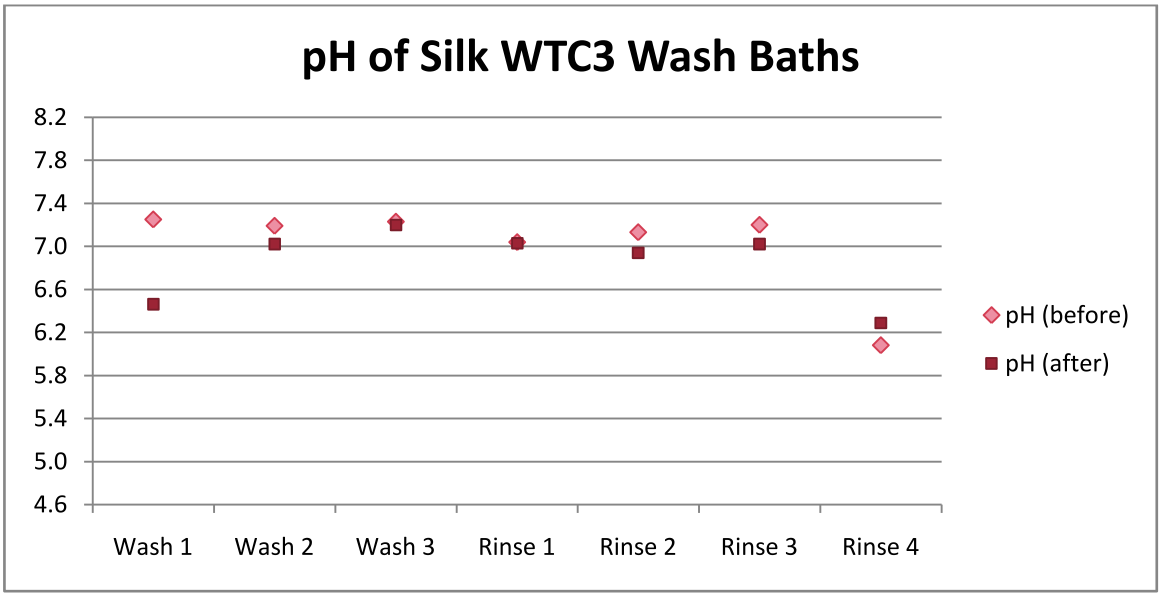

Figure 8.14 Before and after pH of wash and rinse baths for silk WTC3.

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[125] Fields *et al.*, 69.

8.3.4 Sodium Hydroxide and Citric Acid

Sodium hydroxide with citric acid reduced the pH of the Dehypon LS45® wash solution, with that of the water staying near neutral (figs 8.15 and 8.16). Once again, the cloud point of Dehypon LS45® was lowered. Both wash baths show a drop in pH, with the pH reaching near neutral by the third wash bath. The final rinse pH falls for the DS samples, whereas it rises for the WS samples.

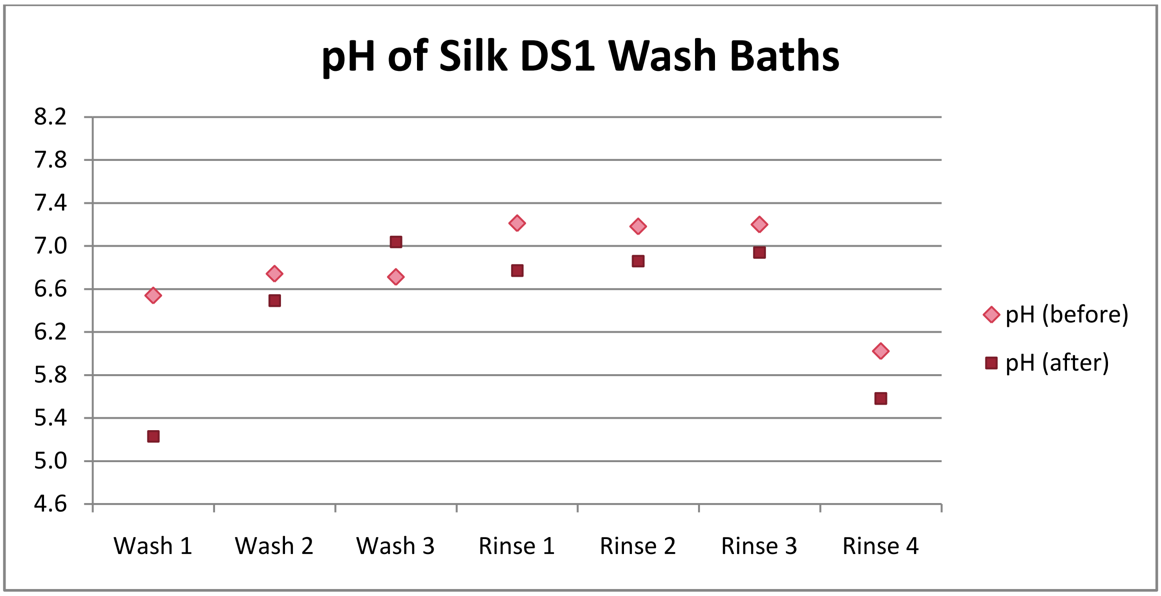

Figure 8.15 Before and after pH of wash and rinse baths for silk DS1.

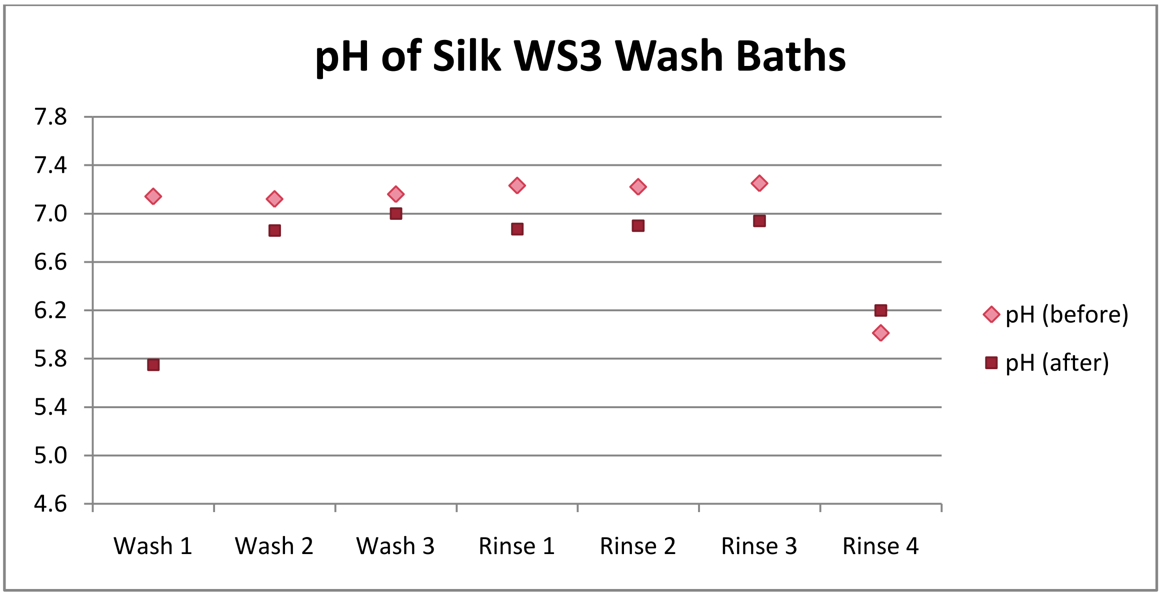

Figure 8.16 Before and after pH of wash and rinse baths for silk WS3.

8.4 Discussion

During wet cleaning of the cotton samples there are some possible anomalous readings. One feasible reason for this is the amount of soiling on the samples varying across the fabric as a whole.[126] However, another factor is the pH electrode used for these measurements was prone to drifting and took a long time to stabilise, possibly due to the age of the electrode. To control drifting the electrode was calibrated frequently throughout the wet cleaning process.[127] The use of this electrode may also account for the lack of a clear pattern during wet cleaning for some of the cotton groups. The electrode was accidentally broken before all of the analyses were completed, and had to be changed. The second electrode was larger than the first and had a protective cover for the glass bulb, it was newer, stabilised faster, and drifting was minimal.

The curve of the after pH readings is, in the majority of cases, very similar between the various wash solutions, with the respective pH buffers, and between the different fibres. The curve displays an increase in pH, with a tendency to drop/dip during rinsing. This shows that the pH of the different wash solutions, though starting at differing pH, follows a similar levelling out during the wash process. Measurement throughout the wet cleaning process is a useful indicator to the changes in pH taking place.[128]

In solution, tri-sodium citrate ranges from pH7.5-pH9.[129] This explains why it provided the most basic solutions as a self buffer. In the silk samples, tri-sodium citrate prevented the wash solutions dropping below pH6.2, and the after pH of the final rinse was higher than solutions with no pH buffer and with sodium hydroxide and citric acid. For the cotton samples, tri-sodium citrate was effective at stabilising the pH of the Hostapon T® solutions, however, the water solutions took longer to stabilise. It is possible that the basic conditions enhanced the surfactant and promoted the release of acidic products.[130]

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[126] Tímár-Balázsy and Eastop, 218.
[127] Tse, 3.
[128] Montague, 22.
[129] Alan Phenix and Aviva Burnstock. "The Removal of Surface Dirt on Paintings with Chelating Agents," *The Conservator*, vol. 16, no. 1 (1992): 28-38 (London: United Kingdom Institute for Conservation, 1992), 29.
[130] Phenix and Burnstock, 30.

Overall, for both the cotton and silk samples, the use of the tri-sodium citrate and citric acid combination buffer had the most buffering effect on both the detergent and water wash solutions. The addition of citric acid to tri-sodium citrate provided more control to the buffer.[131] The pH of all the solutions underwent minimal change and all stabilised after the first wash bath at around neutral pH.

The sodium hydroxide and citric acid combination buffer was trialled at a concentration comparable with the tri-sodium citrate and citric acid buffer. This buffer was not as effective at controlling the pH of the wash baths for the silk samples. It is possible that the concentration of sodium hydroxide was not high enough to be affective, or that the mildly acidic conditions increased efficacy of the surfactant and more acidic soiling and degradation products were released into the wash bath.[132] However, the same concentration proved more successful for the cotton samples, stabilising the pH of the WS baths quickly and displaying an increase in pH of the HS baths. This could be because the cotton samples were not as acidic as the silk samples, or possibly the strength of the base. The concentration of sodium hydroxide needs to be minimal, as it is a strong base and can dissolve degraded cellulose fibres.[133]

The addition of citric acid as part of a combination buffer to the Dehypon LS45® wash solutions caused a change in cloud point (usually 20-22°C). Non ionic surfactants are most effective just below cloud point, but this reduces above cloud point because the surfactant becomes less active.[134] The wash solution was kept refrigerated; however, once measured out for wet cleaning the solution started to become more opaque at approximately 19°C. Because of this the temperature was difficult to control, even though the wash bath size was small and the solution was kept cold; during the wash baths the temperature quickly rose, which is likely to be due to the sponging action.

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[131] The Conservation Unit, 102-103.

[132] Tímár-Balázsy, 55.

[133] Tímár-Balázsy and Eastop, 25.

[134] Fields *et al.*, 69.

8.5 Conclusion

The pH buffer that provided the most control during wet cleaning for all wash solutions and fibres was the tri-sodium citrate with citric acid combination buffer. The pH remained close to neutral, and it displayed the least dramatic drop in pH during the first wash bath. The largest single drop in pH of the first wash bath for both fibre types was displayed by samples wet cleaned in water only.

Chapter 9: Conclusion

The aims of this research project were to identify pH buffers that are currently used by textile conservators, to find out why pH buffers are, or are not used in wet cleaning, to assess the effects of using a pH buffer on the pH of object and wash solution, and to identify if a pH buffer affects soiling removal. To answer these aims questionnaires were sent to practising conservators and experiments were conducted using pH buffers identified through the questionnaire.

The questionnaire results provided useful information on pH buffers that are currently used in textile conservation practice. The most commonly used pH buffers are tri-ammonium citrate and tri-sodium citrate as self buffers, followed by tri-sodium citrate with citric acid, sodium hydroxide with citric acid and sodium carbonate with tri-sodium citrate combination buffers. These results provided a snapshot of the use of pH buffers in the UK; however the use of pH buffers in other countries may differ.

The use of pH buffers in wet cleaning is object dependent, and is not commonplace, with some conservators using them frequently, and some rarely. The most pressed point was the need for time to test pH buffers before use in order to understand their effects on the objects requiring treatment. A pH buffer can have a dual purpose in the wash bath, stabilising pH and acting as a chelating agent to aid soiling removal.

Cotton and silk samples treated using a pH buffer in the wash solution exhibited a greater total colour difference, suggesting that soiling removal was increased by their addition. However, in the case of the silk samples it is not as clear due to the dye bleed during wet cleaning. Tri-sodium citrate produced the most alkaline wash solutions and the most dye bleed. This suggests that it is an acid dye, because acid dyes have reduced wash fastness in alkaline conditions.[135] It is unlikely that the dye is mordant, as although it would explain the increase of dye loss with the chelating agent tri-sodium citrate in the wash bath,[136] it does not explain the dye bleed when this additive is not present.

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[135] Rice (1962-1969), 57-58.

[136] Tímár-Balázsy and Eastop, 225.

The pH of all samples increased, showing that acidic products which could catalyse degradation of the fibres had been removed during wet cleaning.[137] Surface pH readings were lower and less accurate than aqueous extraction pH measurements, with large variance in the readings. However, surface pH is a useful starting point and, used as a guide, can be a valuable marker of the condition of the object. Due to the required size of samples, even when reduced to 0.1g, pH extraction is not practical. Sample size would have to be reduced dramatically to make the process viable for textile conservation.

A pH buffer in the wash solution helped to prevent the sharp drop in pH observed in the first bath of the surfactant and water only solutions. The pH of all of the wash baths stabilised during wet cleaning, however, the use of a pH buffer brought this about earlier in the process. Tri-sodium citrate with citric acid proved most successful for both fibres. All of the pH buffers were used in comparable amounts. It is possible that the amount of sodium hydroxide with citric acid should have been increased in order to buffer the pH of the wash solution more effectively. However, the concentration of sodium hydroxide, a strong base that ionises completely in water, should be minimal for treating historical textiles as it can dissolve wool and degraded cellulose fibres through hydrolysis.[138]

The addition of citric acid caused the cloud point of Dehypon LS45® to drop. The wash solution was kept refrigerated, however, the wash solution started to turn opaque at approximately 19°C while being measured out. During the wash baths the ambient temperature and agitation from sponging caused the temperature of the wash solution to increase further.[139] This will have had an effect on the efficiency of the detergent.

Although tri-sodium citrate with citric acid proved the most successful pH buffer, it was not as effective at soiling removal. In all samples wet cleaned with water solutions, tri-sodium citrate and tri-sodium citrate with citric acid affected the greater total colour difference. For the cotton samples wet cleaned with Hostapon T® solutions, it is sodium hydroxide with citric acid that causes the greatest total colour difference.

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[137] Eastop *et al.*, 2.
[138] Tímár-Balázsy and Eastop, 217.
[139] Fields *et. al*, 69.

Using a pH buffer in the wash solution did not appear to have any adverse effects on the samples. Further testing addressing tensile strength and analysis of the fibres would need to be carried out to address this issue. The main effect of the pH buffers on the silk fabric was the dye loss.

The results from the experiments reinforce the prevalence in the literature of the use of tri-sodium citrate with citric acid combination buffer. It provided the best buffering capability, and although it did not remove the most soiling, it was not far behind the highest soiling remover and was more successful than surfactant or water alone.

Further Research

The next step for this research is to identify the effect that these pH buffers have in the textiles at a micro-fibre level.

Further questions that have formed from this research include:

- How dilute can a pH buffer be in order to still be effective at regulating the pH of the wash bath?
- What effect do pH buffers have on different dye stuffs?
- What effect does citric acid have on the cloud point of Dehypon LS54®?

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Appendices

Appendix A: Materials and Suppliers

pH Buffer Chemicals:

Trisodium citrate;

Citric Acid;

Sodium Hydroxide (Acros Organics)

Fisher Scientific UK Ltd
Bishop Meadow Road, Loughborough. LE11 5RG
Tel: 01509 231 166
Web: http://www.fisher.co.uk/

Surfactants:

Hostapon TPHC®

Chemlink Specialities Ltd
Gladstone House, 26-30 Station Rd, Urmston, Manchester. M41 9JQ
Tel: 0161 6292129
Web: http://www.chemlink.co.uk/

Dehypon LS45®

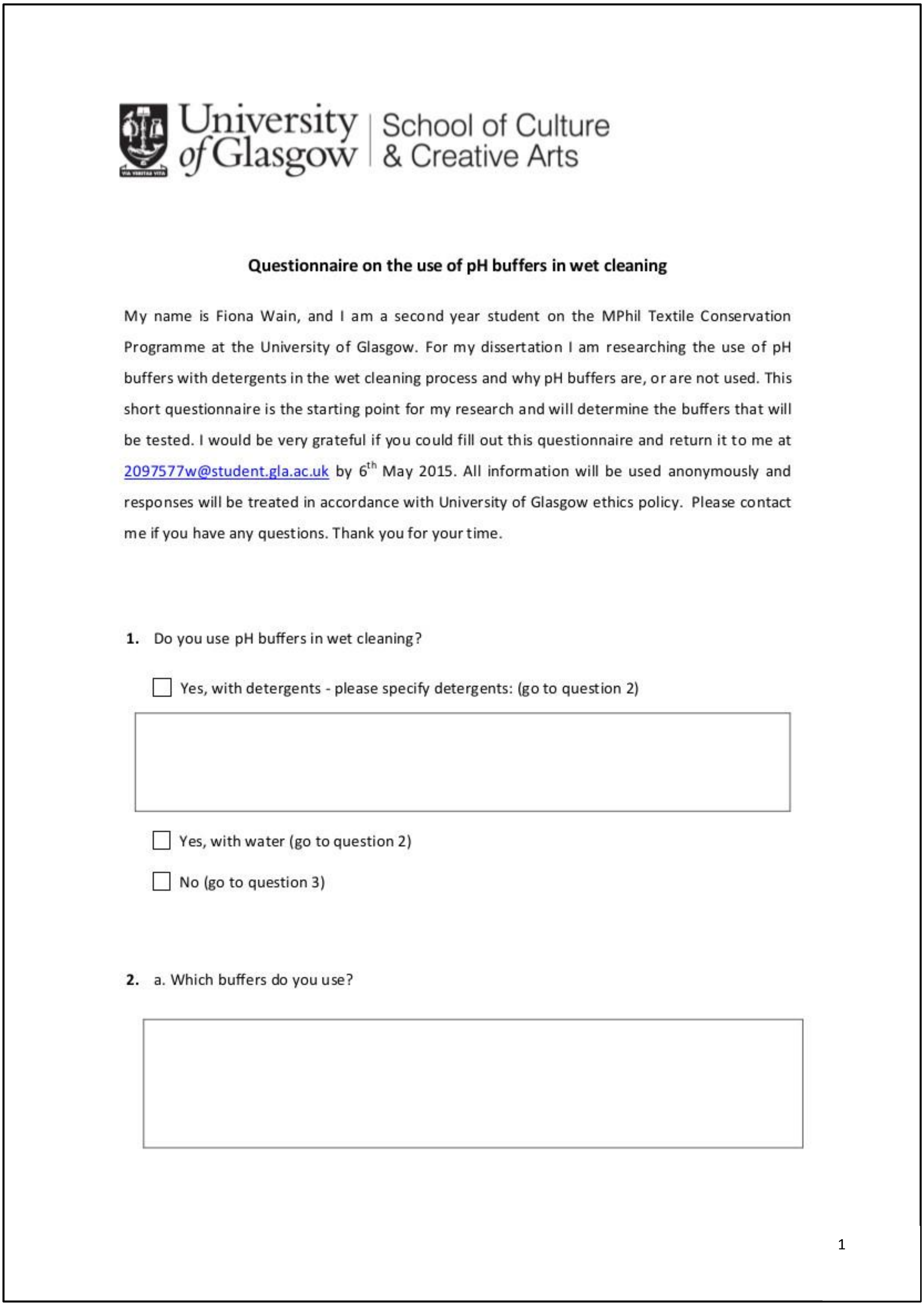
Conservation By Design
Timecare Works, 5 Singer Way, Kempston, Bedford. MK42 7AW
Tel: 01234 846300
Web: http://www.conservation-by-design.com/

Sponge:

Ramer® sponge

Boots UK Ltd
1 Thane Road West, Nottingham. NG2 3AA
Tel: 0345 070 8090
Web: http://www.boots.com/

Appendix B: Questionnaire



University of Glasgow | School of Culture & Creative Arts

Questionnaire on the use of pH buffers in wet cleaning

My name is Fiona Wain, and I am a second year student on the MPhil Textile Conservation Programme at the University of Glasgow. For my dissertation I am researching the use of pH buffers with detergents in the wet cleaning process and why pH buffers are, or are not used. This short questionnaire is the starting point for my research and will determine the buffers that will be tested. I would be very grateful if you could fill out this questionnaire and return it to me at 2097577w@student.gla.ac.uk by 6th May 2015. All information will be used anonymously and responses will be treated in accordance with University of Glasgow ethics policy. Please contact me if you have any questions. Thank you for your time.

1. Do you use pH buffers in wet cleaning?

☐ Yes, with detergents - please specify detergents: (go to question 2)

☐ Yes, with water (go to question 2)

☐ No (go to question 3)

2. a. Which buffers do you use?

2. b. What influences the decision to use a pH buffer? (Please check all that apply)

☐ Routine work place practice

☐ Information available (e.g. in literature / case studies)

☐ Special case / condition of the object

☐ Other, please specify:

3. Why do you not use buffers? (Please check all that apply)

☐ Not routine work place practice

☐ Not enough information available

☐ Not needed for treatment

☐ Other, please specify:

Thank you for taking the time to fill out this questionnaire. I would like to include quotes and the survey responses in my dissertation, please check the box if you agree to this. ☐

Appendix C: Fibre Analysis

Cotton Fabric

The warp and weft of the fabric were both identified as cotton under 200x magnification using an optical microscope; the fibres were flat and twisted (fig. C.1), and fluorescent through 360° in the dark field.

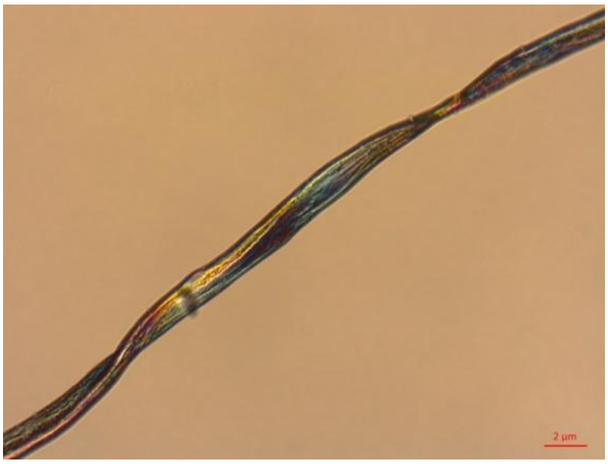


Figure C.1 Cotton fibre from the backing fabric at 200x magnification.

Silk Fabric

Analysis of the fibres in longitudinal orientation at 200x magification using an optical light microscope was inconclusive, however, a cross section of the fibres showed a triangle shape (fig. C.2), identifying the fibres as silk.

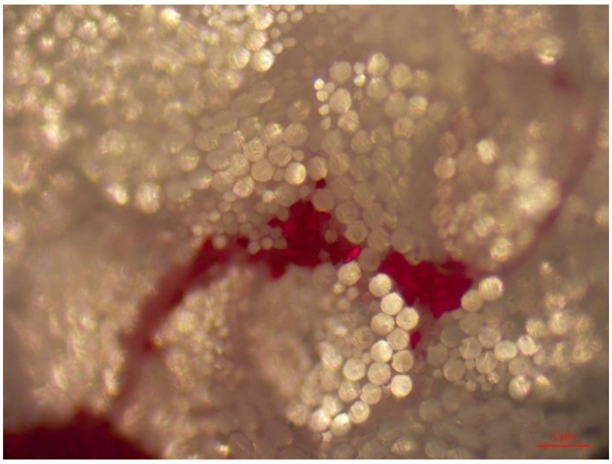


Figure C.2 Cross section of the red silk fibres from the test fabric at 200x magnification.

This was confirmed by Attenuated Total Reflectance Fourier Transform Infrared (ATR FTIR) spectroscopy an analytical technique that can provide precise identification of materials by using an infrared beam to penetrate the sample and produce a spectrum. The spectrum shows the absorption peaks of the infrared, which characterise the chemical composition of the sample.[140] The analysis result was compared to known standards, confirming silk (fig. C.3).

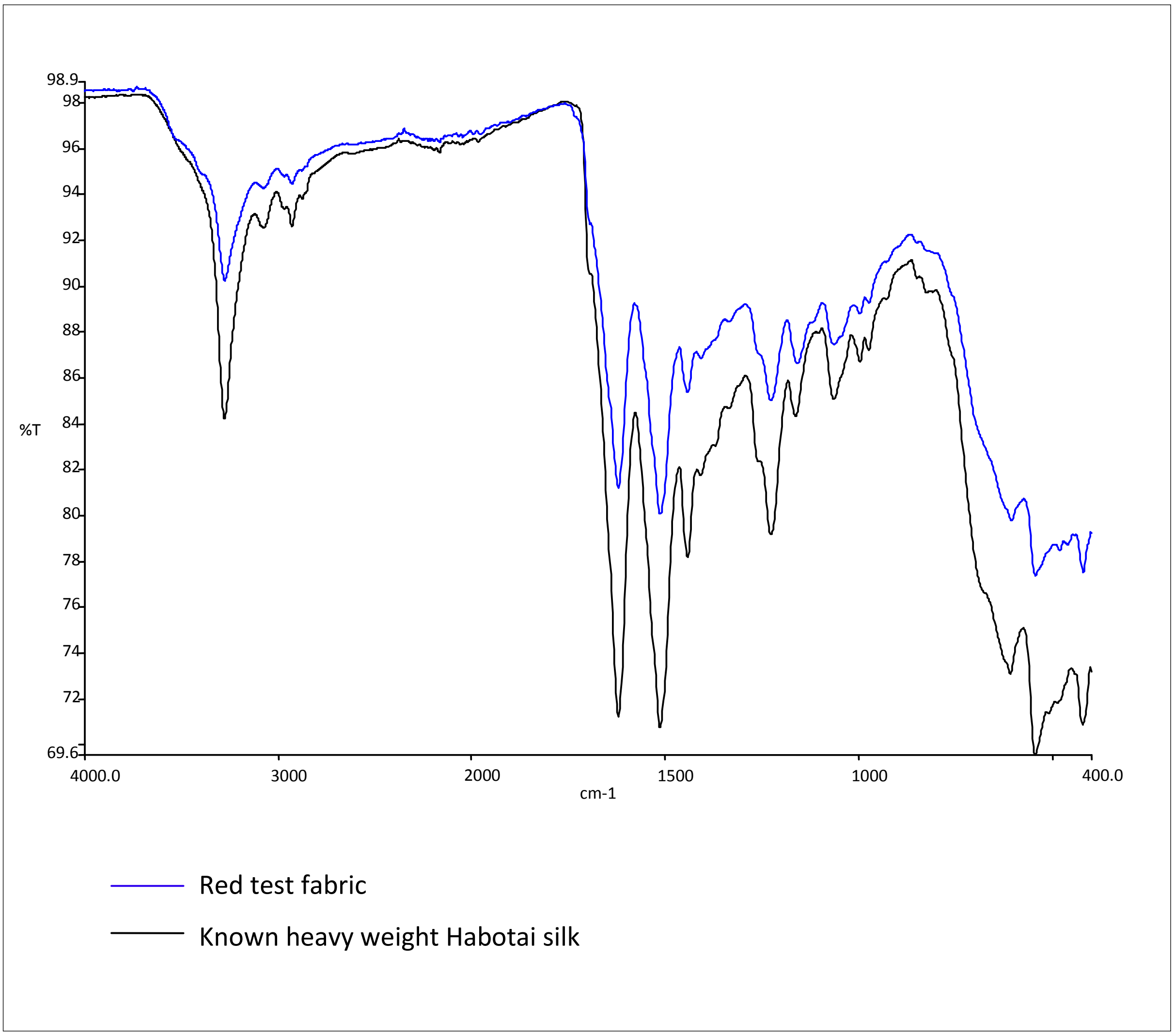


Figure C.3 ATR FTIR spectrum of red silk test fabric and known silk standard.

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[140] Paul Garside and Paul Wyeth, “Identification of Cellulosic Fibres by FTIR Spectroscopy: Thread and Single Fibre Analysis by Attenuated Total Reflectance,” *Studies in Conservation* 48, no. 4 (2003): 269-275, http://www.jstor.org/stable/1506916, 270.

Appendix D: Preparation for Wet Cleaning

Glassware

In preparation for making up and storing the wash and pH buffer solutions the glassware (fig. D.1) was washed in laboratory detergent (Decon 90), and thoroughly rinsed with tap water, with a final rinse in deionised water (B114 deioniser). To ensure that there was no contamination in the glassware it was then rinsed out with acetone which was allowed to evaporate.

Wash Solutions

The dimension of the wash bath was 154mm x 98mm, and a 5mm depth of wash solution was calculated: 15.4 x 9.8 x 0.5 = 75 mL. Each sample was given three wash baths; therefore 675mL of wash solution was required for each set of samples. The wash solution required to complete the experiments for four sets of samples in each fibre type was 2.7L. As a contingency, 300ml was added to this. A total of 3L of wash solution was made for each of the detergents in single batches using a 500mL volumetric flask (Fisherbrand® class A ±0.25mL) for accurate measurement, and measured out for the buffer solutions to be added.

Buffer Solutions

Tri-sodium citrate was weighed out to 0.75g to be dissolved in 1500mL of wash solution (enough for two sets of samples). The tri-sodium citrate was dissolved by pouring the wash solution into the beaker used to measure the tri-sodium citrate and allowing it to dissolve. In preparation for the addition of the 1% citric acid solution 700mL of the wash solution with tri-sodium citrate was measured out into a separate container (fig. D.1), and 0.7mL removed using a volumetric pipette, leaving 699.3mL of wash solution.

A 1% solution of citric acid was prepared using a 25mL volumetric flask (Fisherbrand® class A ±0.04mL). Deionised water was added to a beaker, filling it part way, before 0.25g of citric acid was added. This was mixed and once the citric acid was fully dissolved the solution was moved to the volumetric flask, which was then topped up with deionised water until the centre of the concave meniscus was on the 25mL line. The citric acid solution was measured to 0.7mL using a 2 mL volumetric pipette (Fisherbrand® class B ±0.02mL) into the 699.3mL wash solutions requiring citric acid.

The combination buffer of sodium hydroxide with citric acid was prepared to 'Wolbers recipe A'.[141] A solution of 0.5% of citric acid was prepared using the technique outlined above with 0.5g citric acid made into a 100mL solution with deionised water in a 100mL volumetric flask (Volac class A ±0.08mL). Using titration, a 1M solution of sodium hydroxide was added to the citric acid solution, using a volumetric burette, until the pH of the solution increased from pH2.4 and measured pH 6.4. This resulted in 8mL of the sodium hydroxide solution being added to 100mL of the 0.5% citric acid solution.

Figure D.1 Glassware used in the preparation and storage of wash solutions and pH buffers, and to measure out each wash bath.

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[141] Personal communication with Richard Wolbers.

Appendix E: A note on molar solutions

Molar solutions were highlighted in the questionnaire responses as an area that requires more explanation. The recipes used above use percentage solutions, however, if a molar solution was to be prepared the details below are of use. One mole of an element contains 6 x 10^{23} (Avogadro's number) atoms, which is equal to the relative atomic mass of the element in grams.[142] A molar solution is measured in moles per dm^3 (1 dm^3 = 1000mL).[143] This can also be interpreted as g/L.

The relative atomic masses of the elements are found in the periodic table, those for the elements that are in the pH buffers used in the experiments are (number used in calculations in brackets):

- sodium, Na: 22.990 (23)
- carbon, C: 12.011 (12)
- hydrogen, H: 1.008 (1)
- oxygen, O: 15.999 (16)

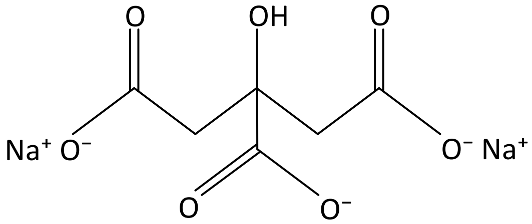
Sodium Hydroxide (NaOH)

A one mole (1M) solution of sodium hydroxide contains: 23 + 16 + 1 = 40g/L. This can be reduced proportionately to 4g/100mL to produce a one mole solution.

Tri-sodium Citrate ($Na_3C_6H_5O_7$)

A 1M solution of tri-sodium citrate contains:

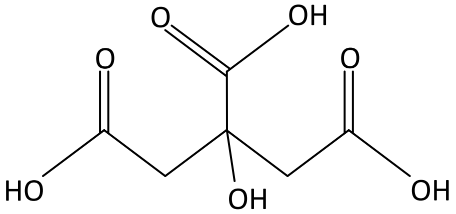
(23 x 3) + (12 x 6) + (1 x 5) + (16 x 7) = 258g/L.



Citric Acid ($C_6H_8O_7$)

A 1M solution of citric acid contains:

(12 x 6) + (1 x 8) + (16 x 7) = 192g/L.



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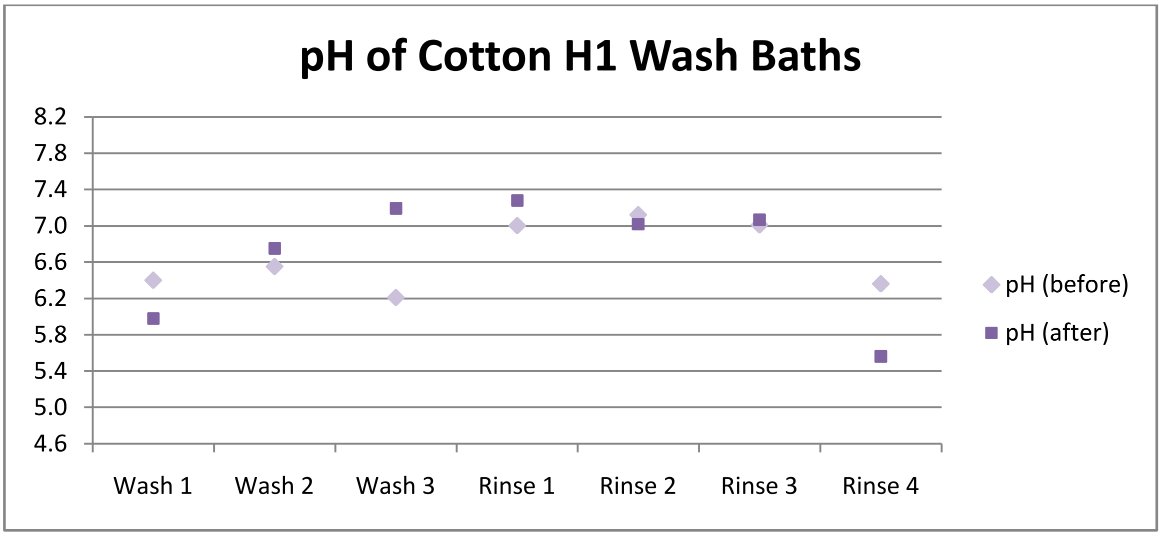
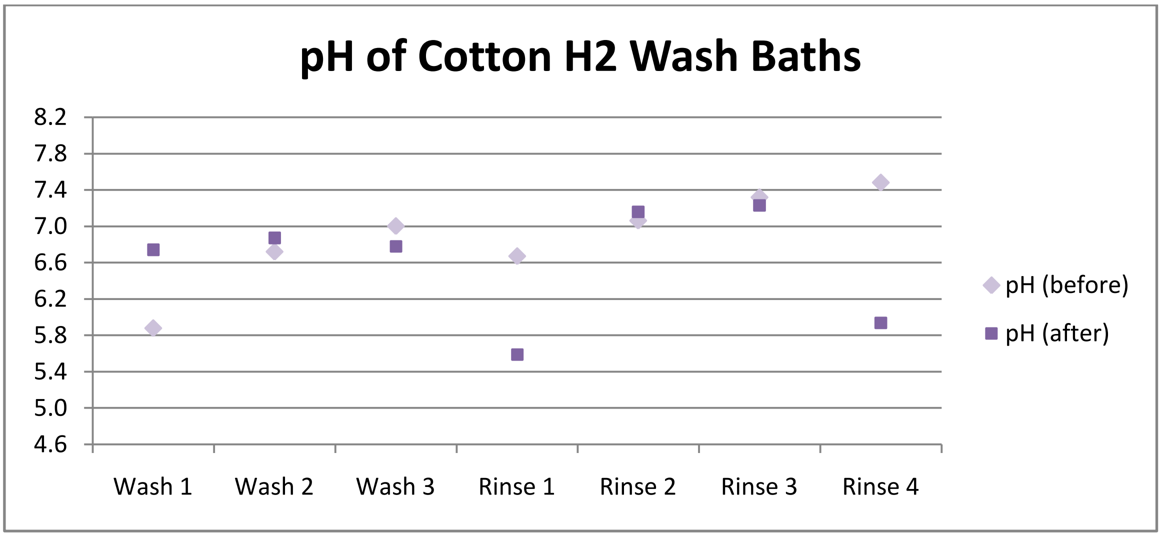
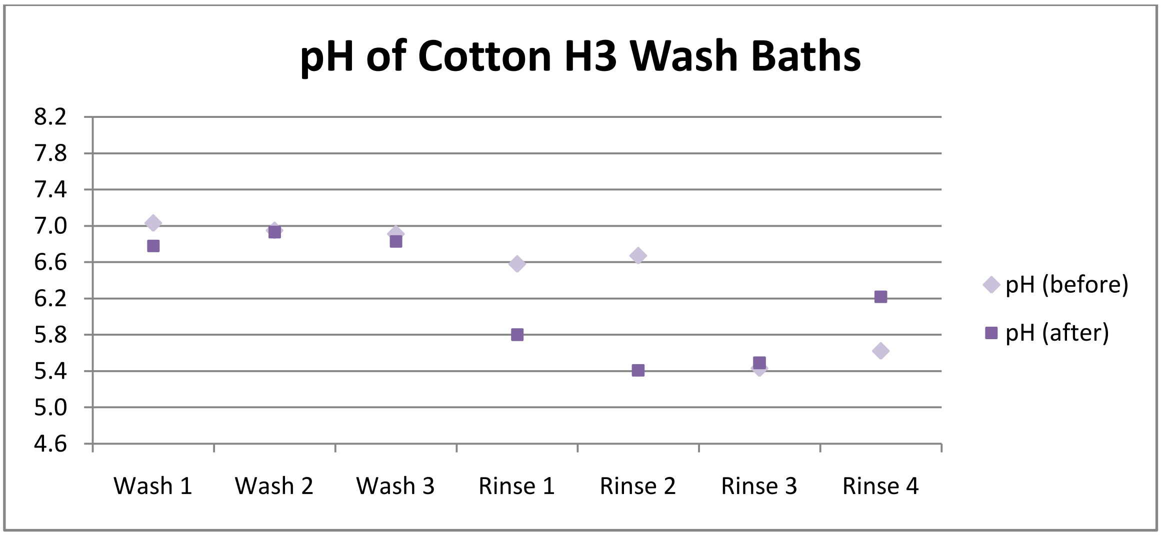
[142] John Holman and Phil Stone, *Chemistry* 2nd Edition, (Cheltenham: Nelson Thornes, 2001) 71.

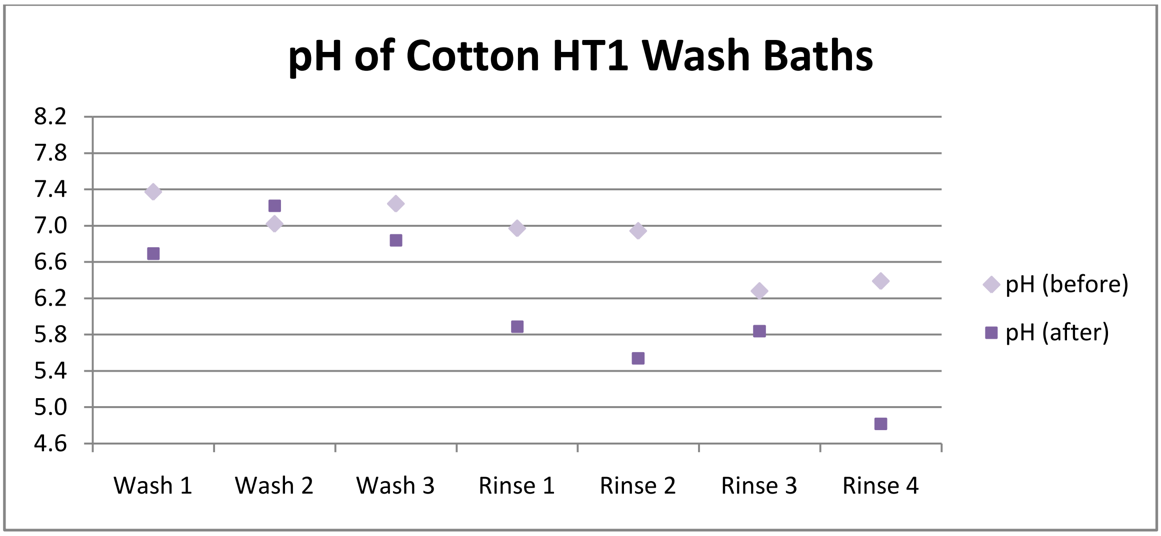
[143] Holman and Stone, 79.

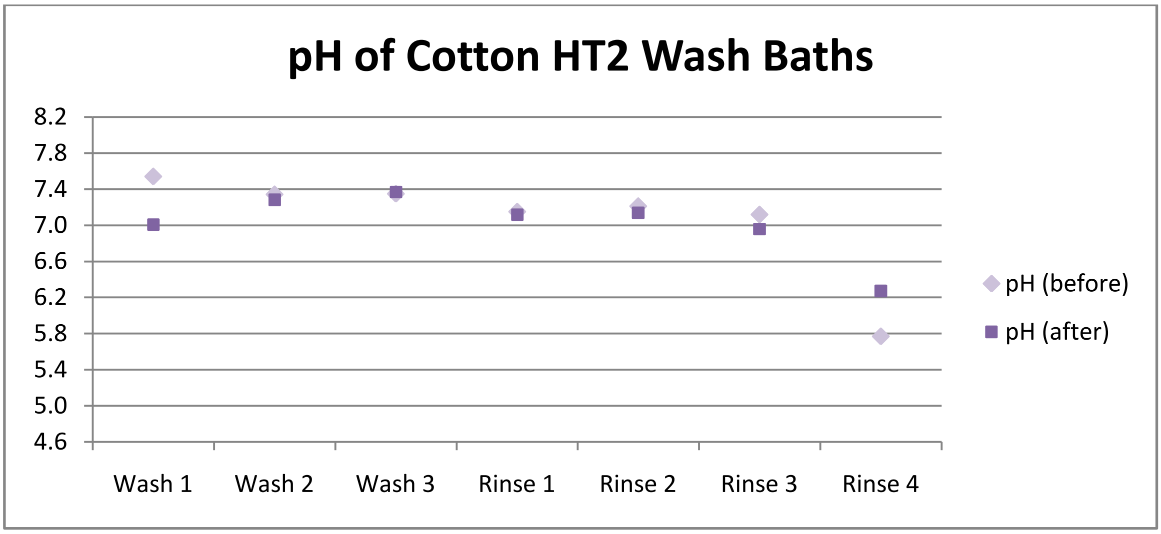
Appendix F: Full Results from Wet Cleaning








pH of Cotton HT1 Wash Baths
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Cotton HT2 Wash Baths
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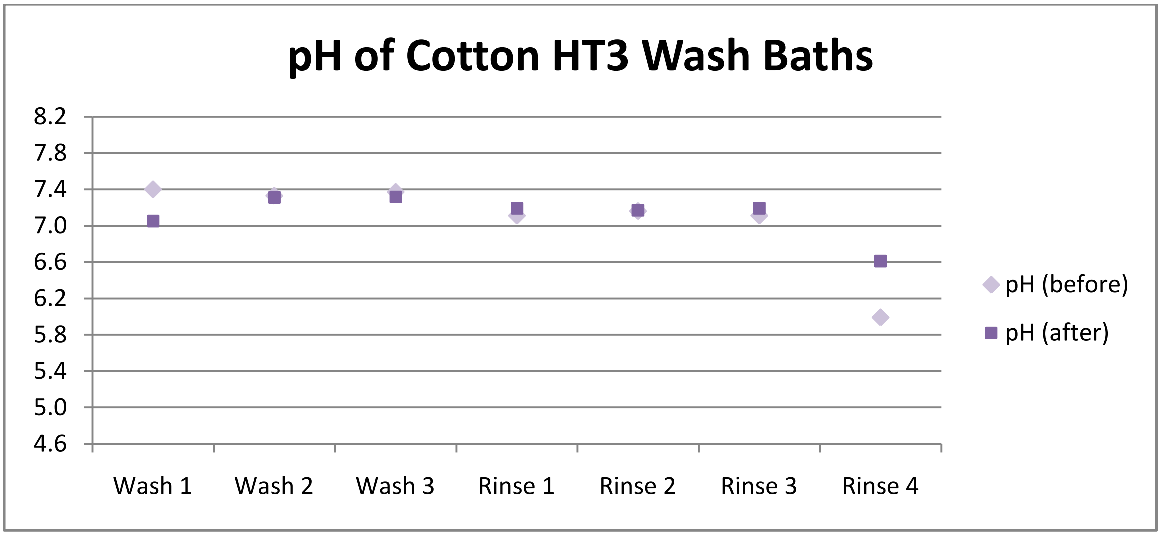
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Cotton HT3 Wash Baths
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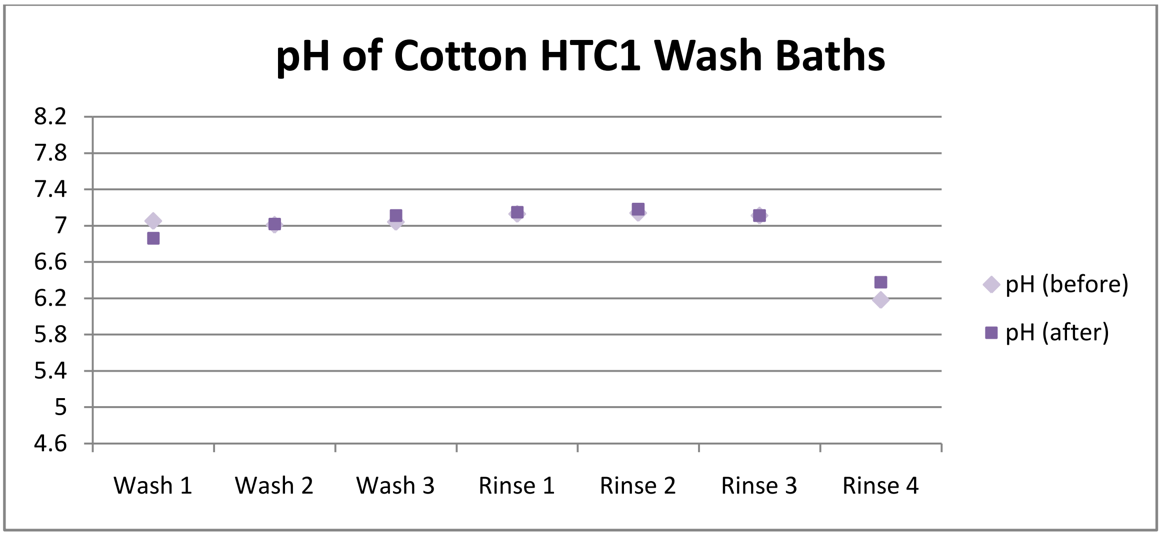
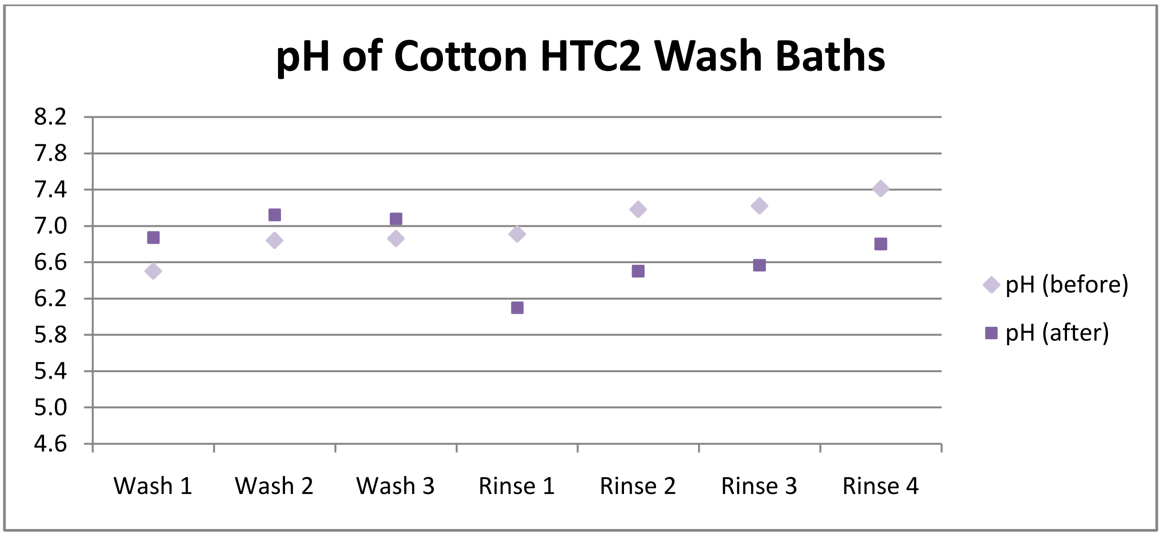
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Cotton HTC1 Wash Baths
8.2
7.8
7.4
7
6.6
6.2
5.8
5.4
5
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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7.4
7.0
6.6
6.2
5.8
5.4
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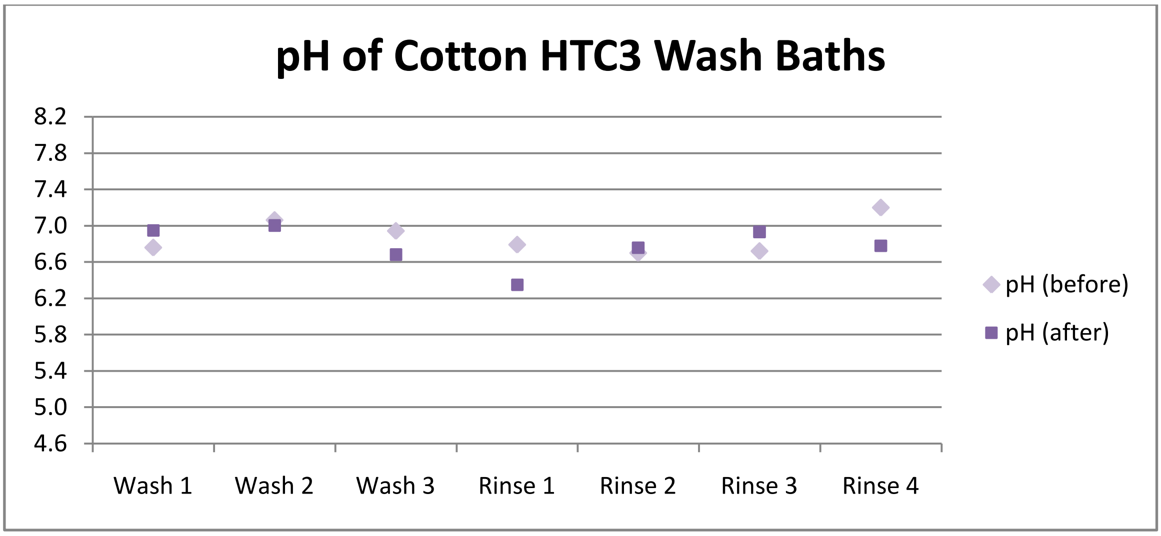
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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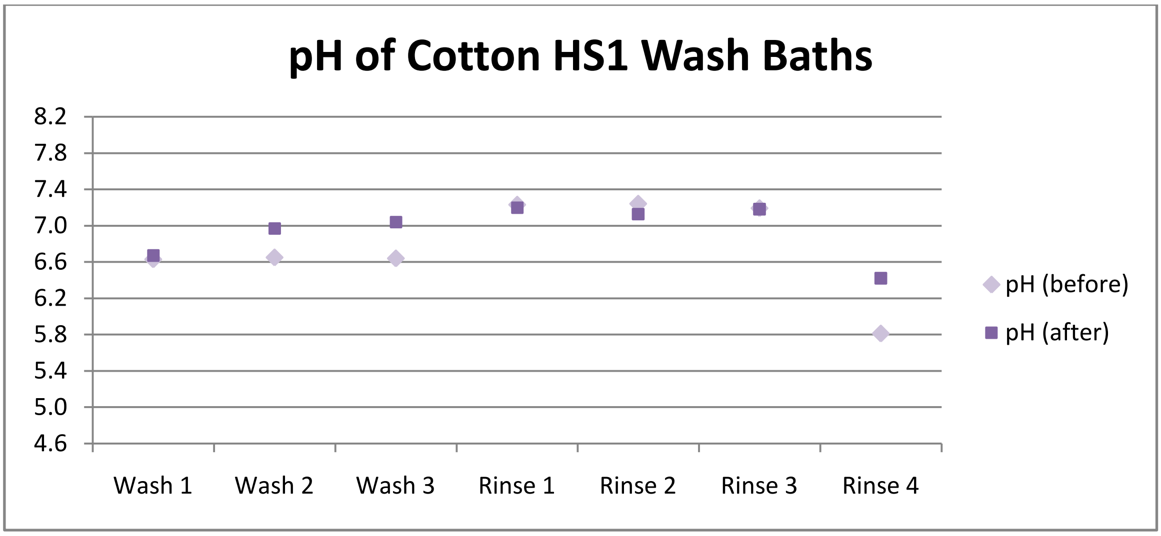
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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7.4
7.0
6.6
6.2
5.8
5.4
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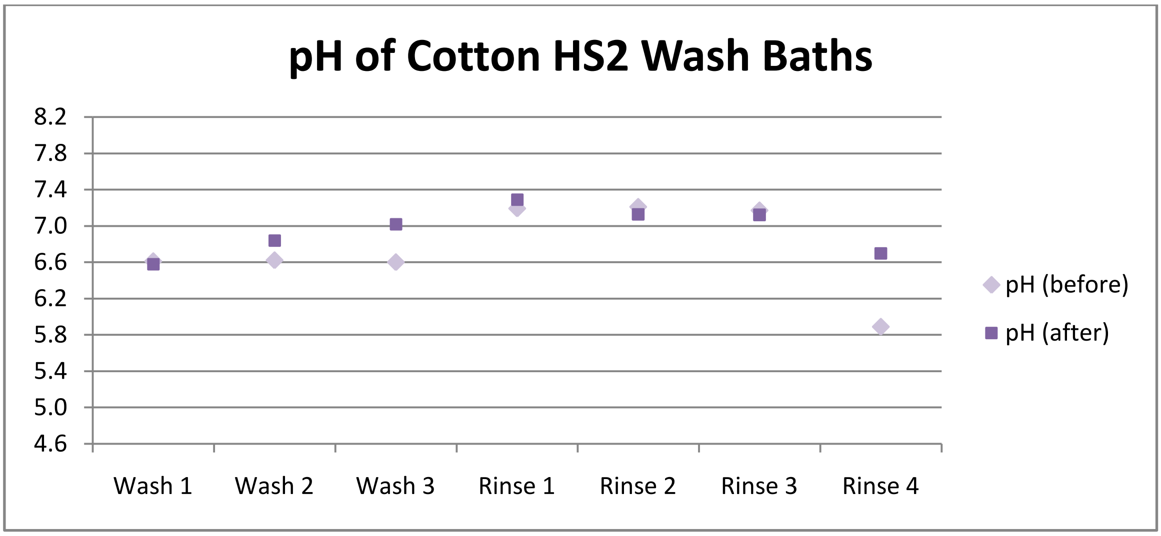
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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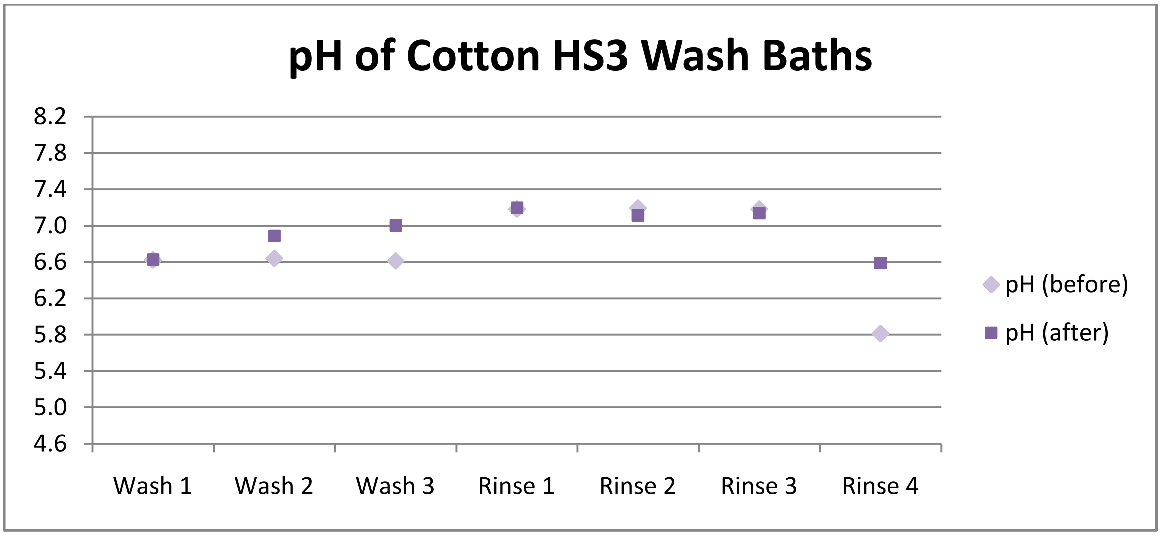
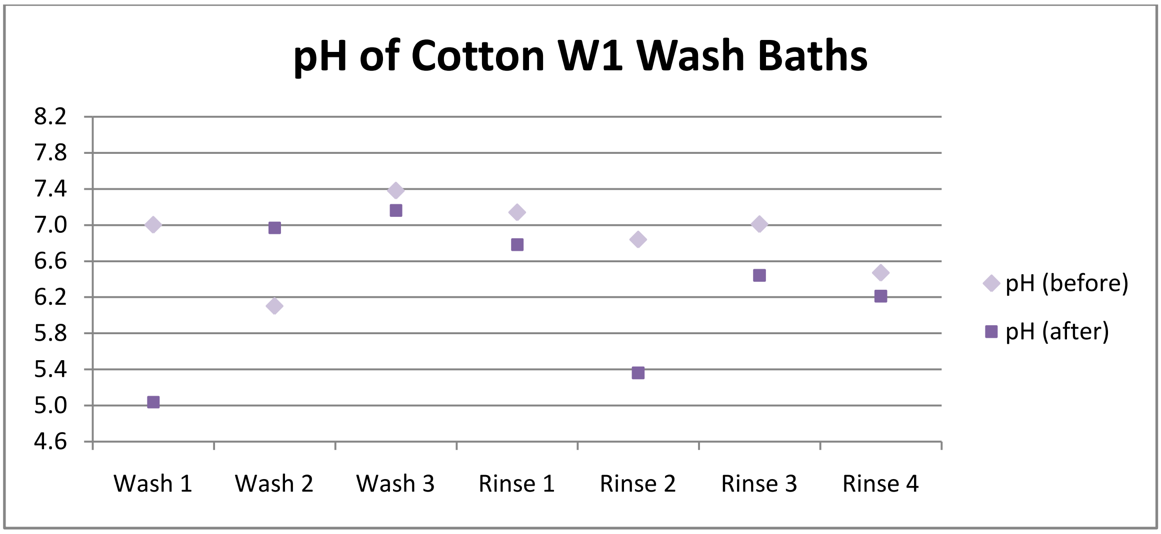
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Cotton HS3 Wash Baths
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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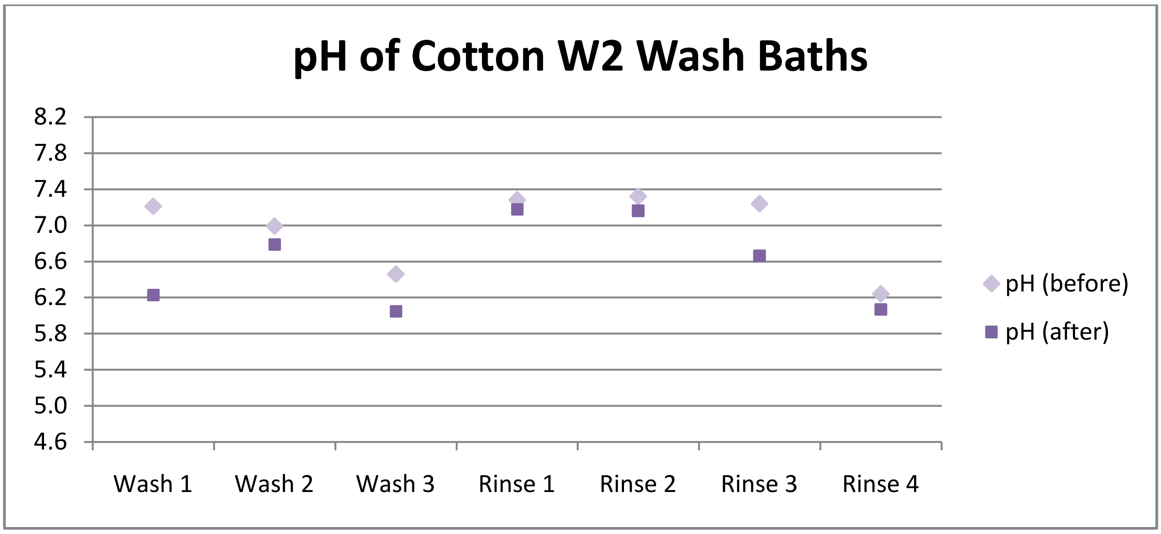
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.6
6.2
5.8
5.4
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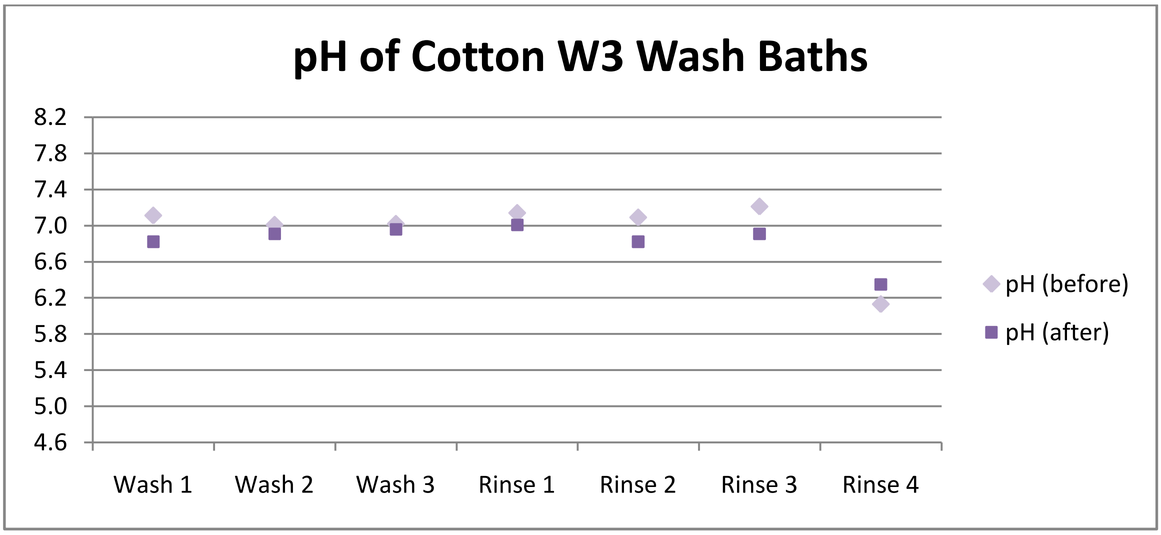
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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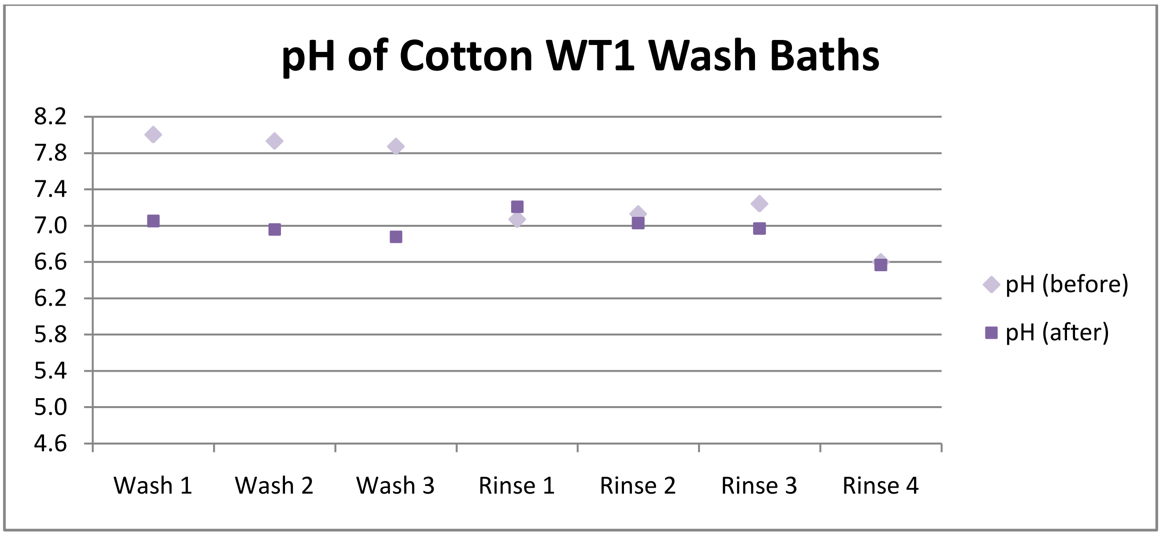
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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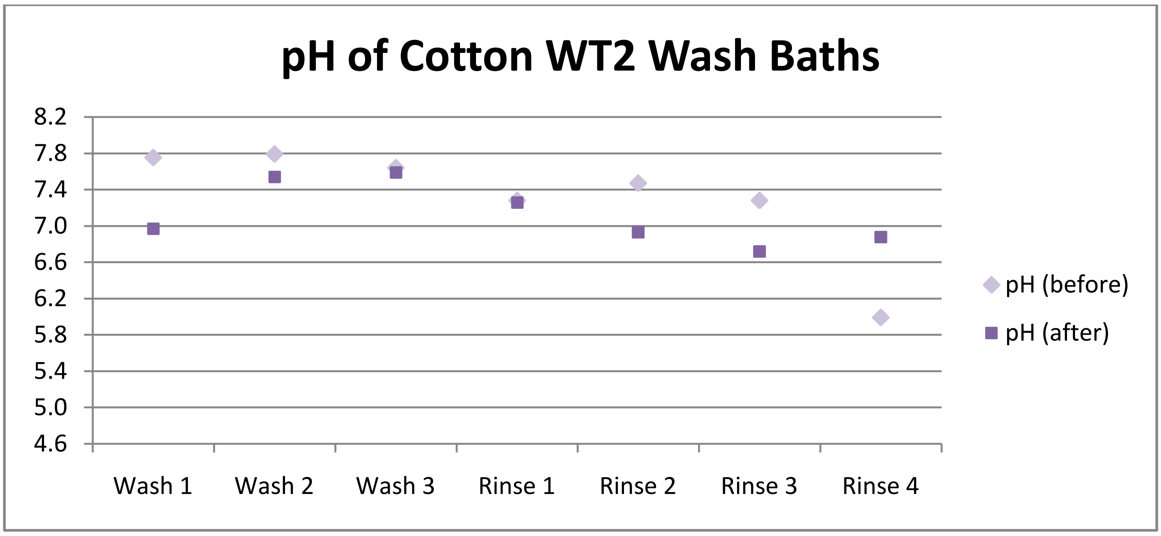
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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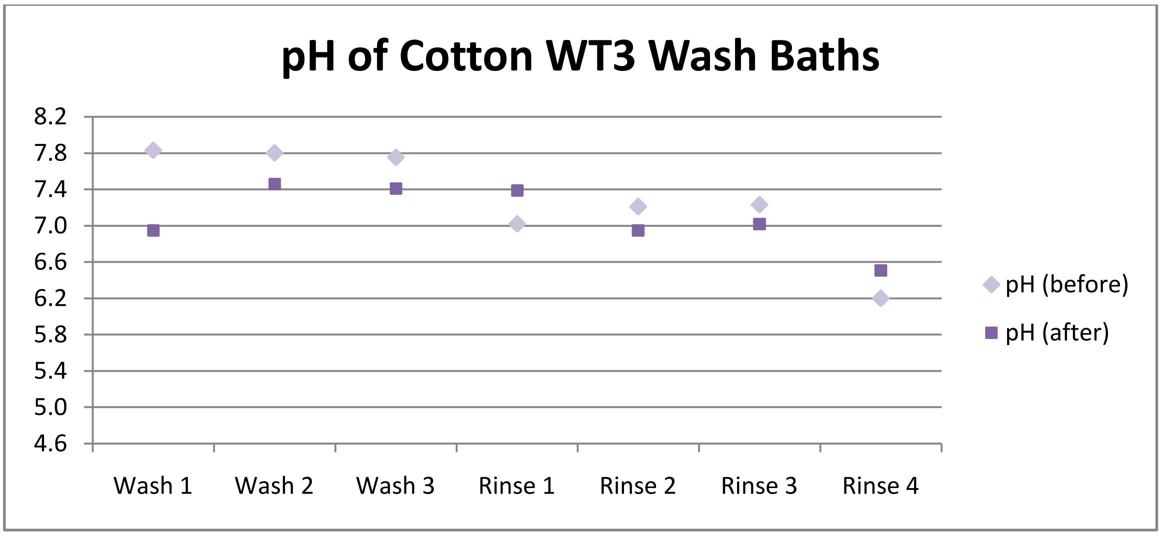
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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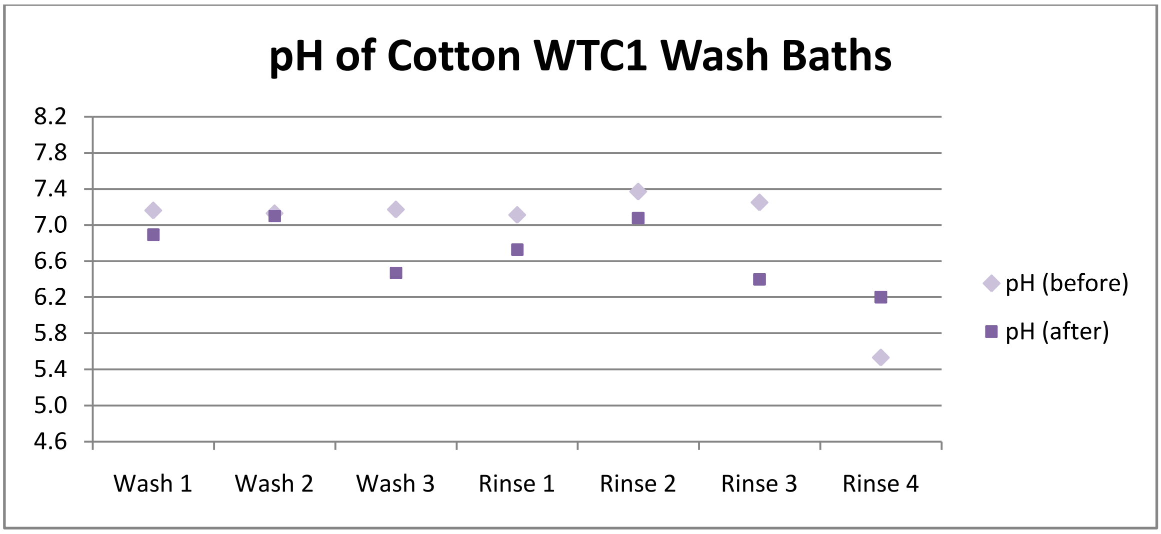
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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6.6
6.2
5.8
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5.0
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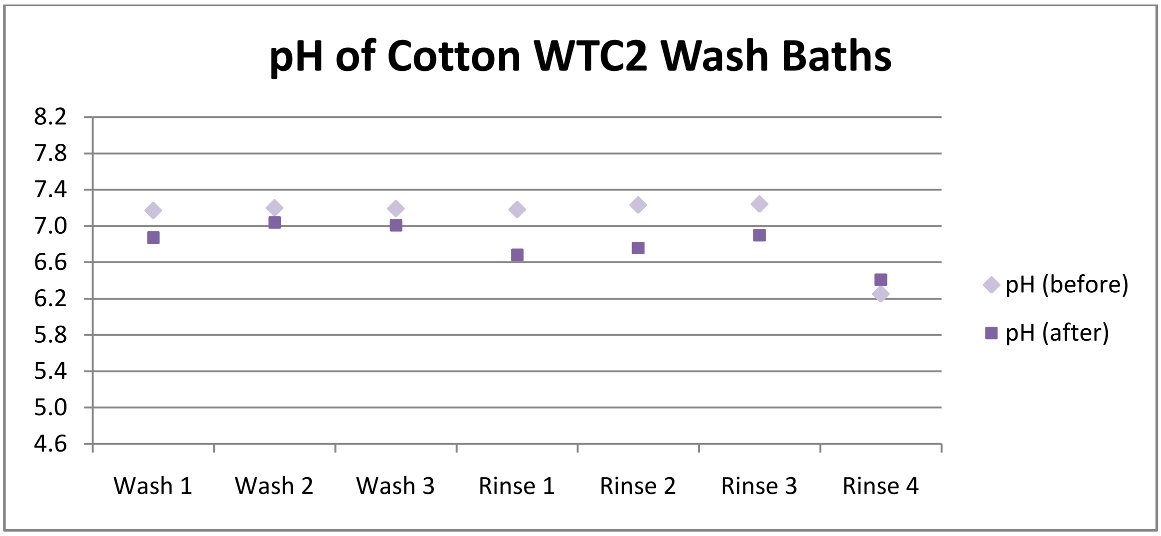
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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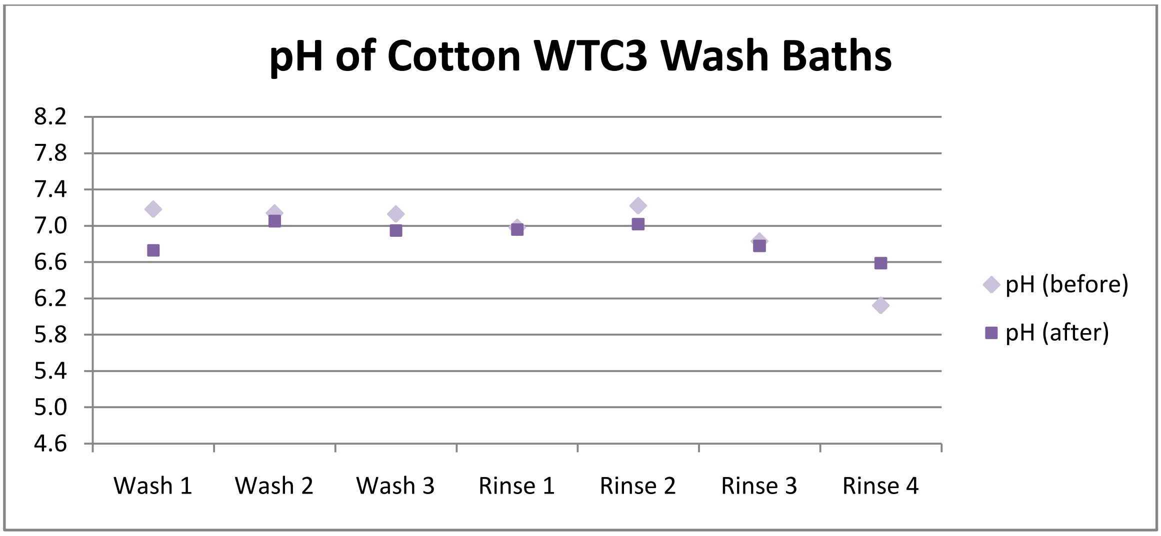
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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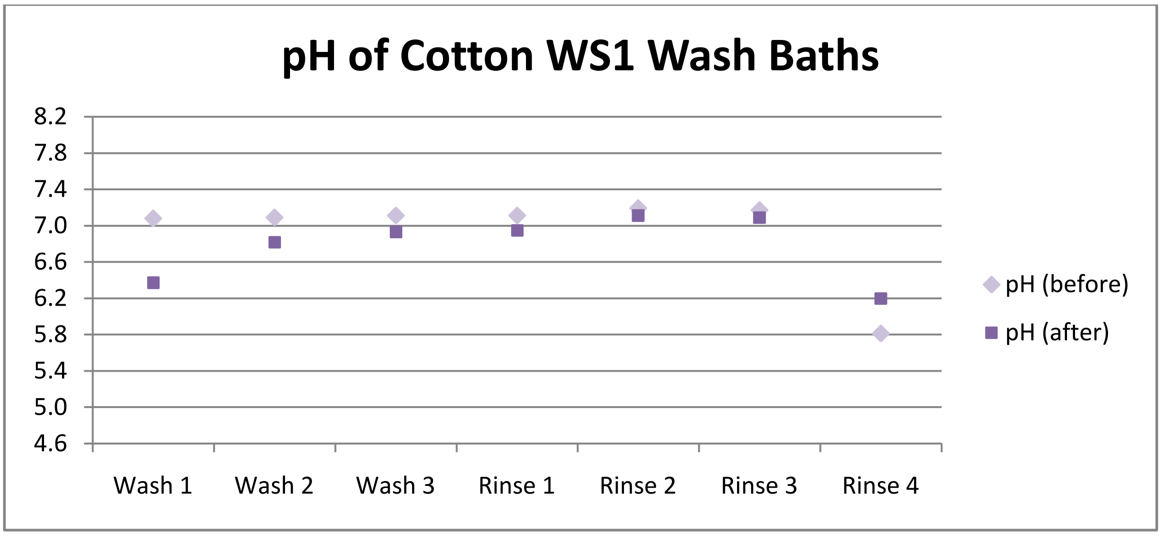
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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7.0
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6.2
5.8
5.4
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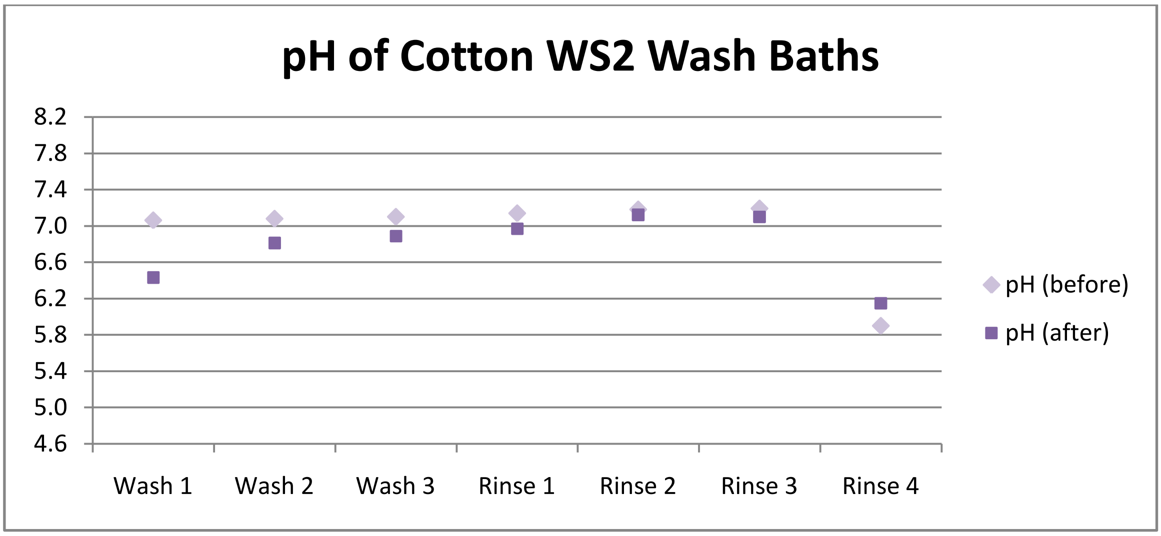
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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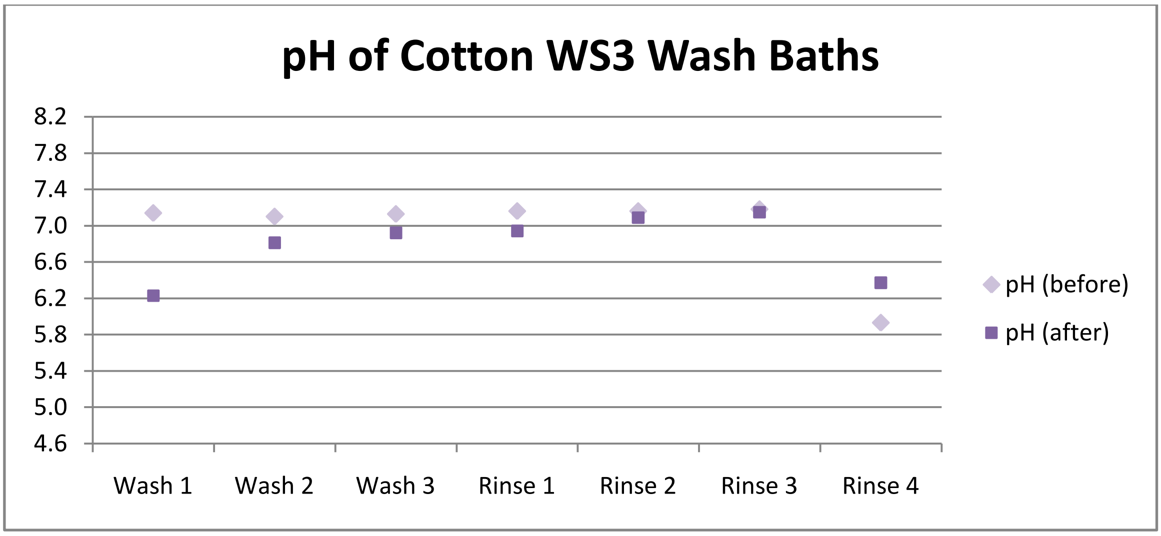
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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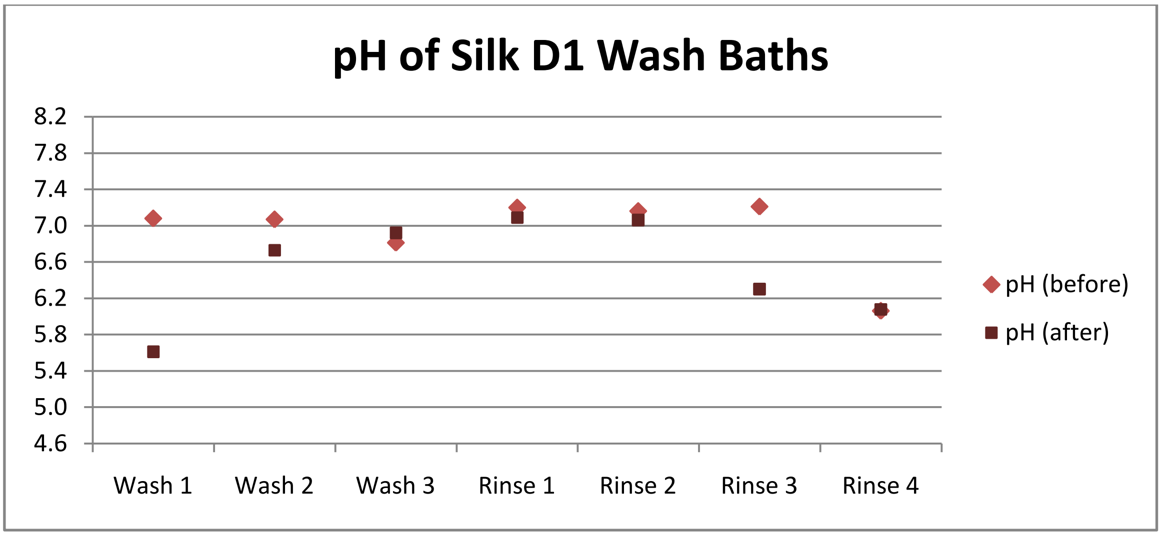
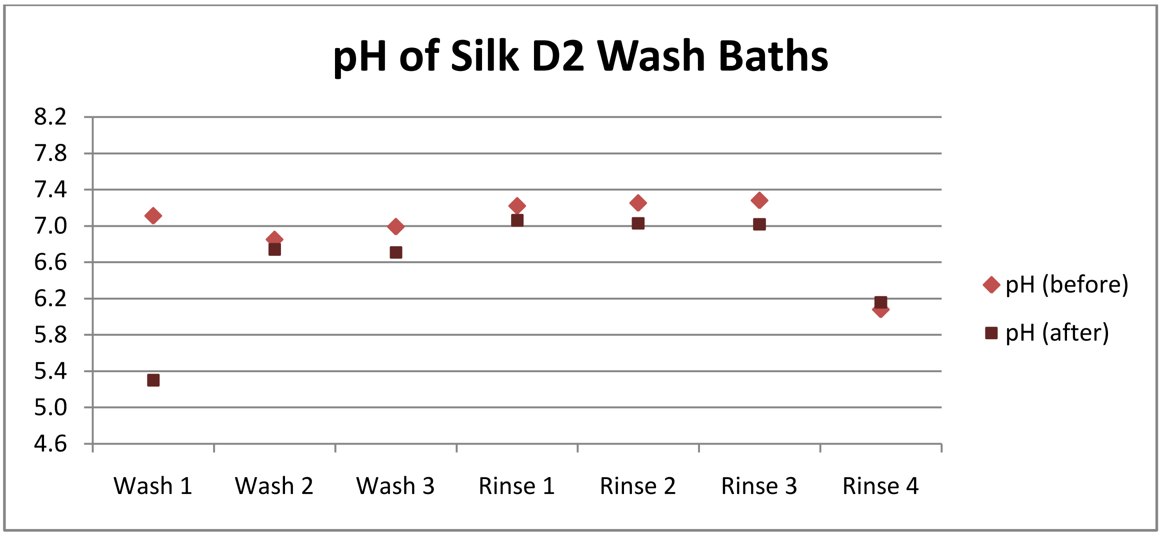
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk D1 Wash Baths
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk D2 Wash Baths
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7.8
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6.6
6.2
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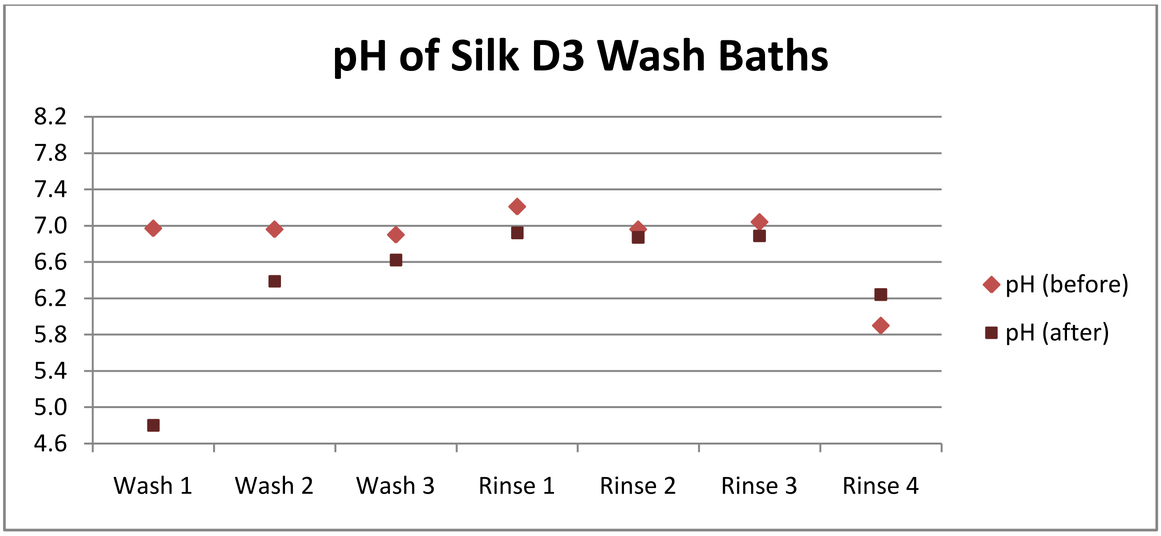
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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6.2
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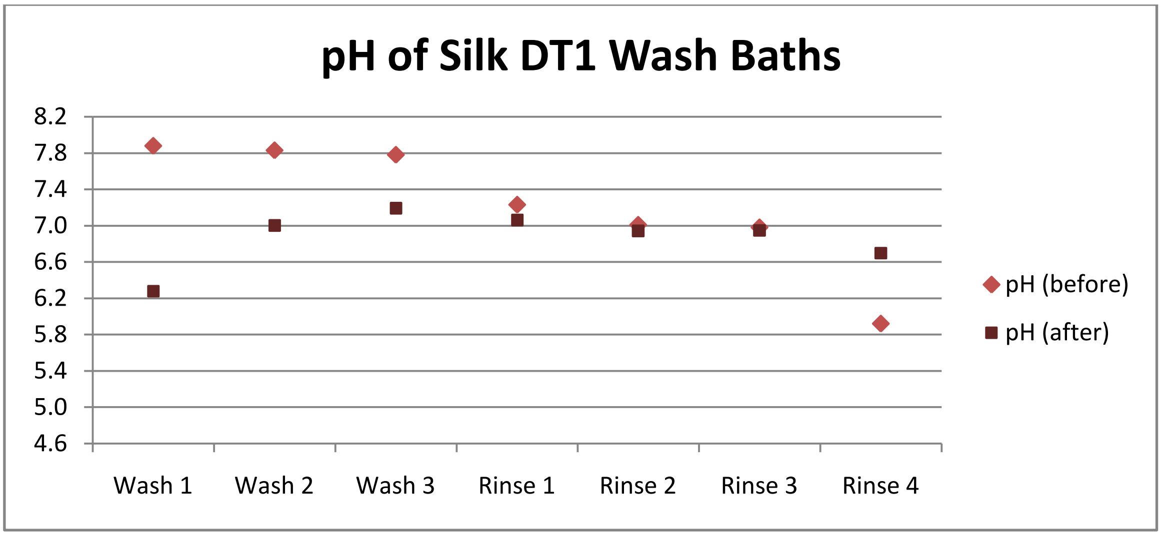
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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6.2
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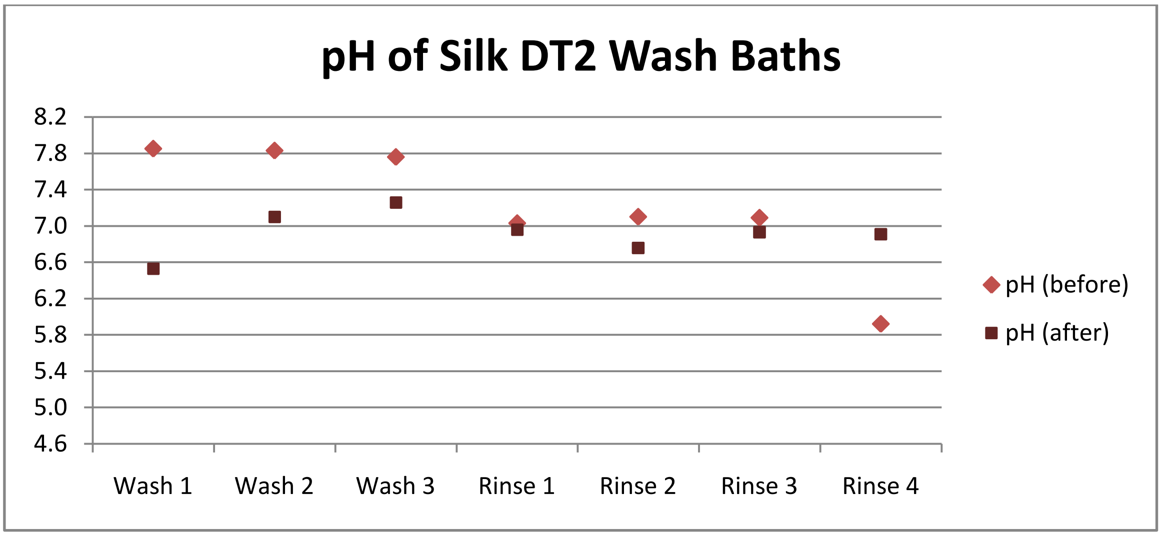
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.6
6.2
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5.4
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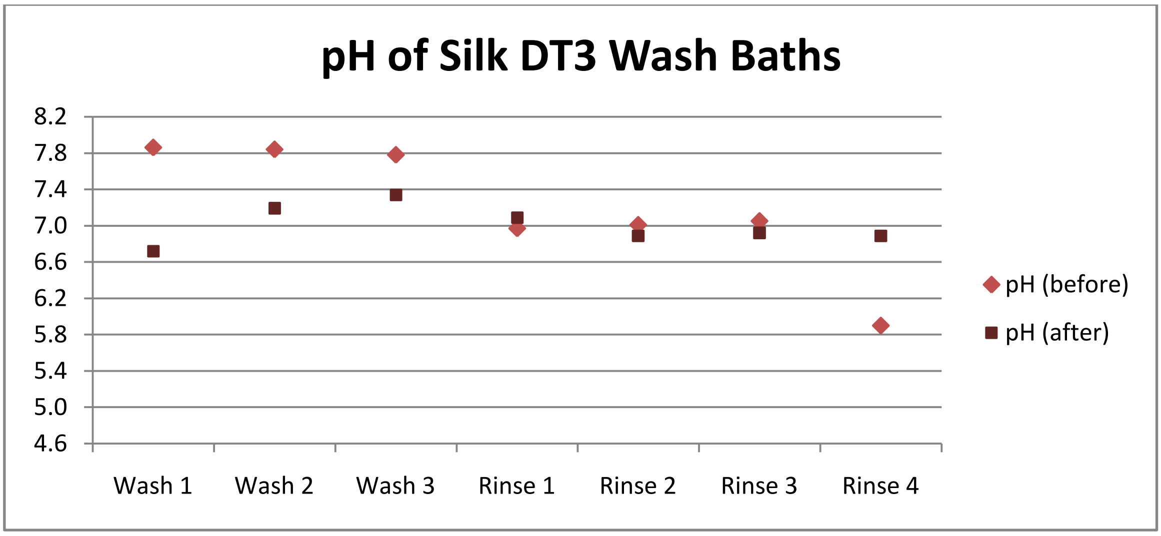
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk DT3 Wash Baths
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7.4
7.0
6.6
6.2
5.8
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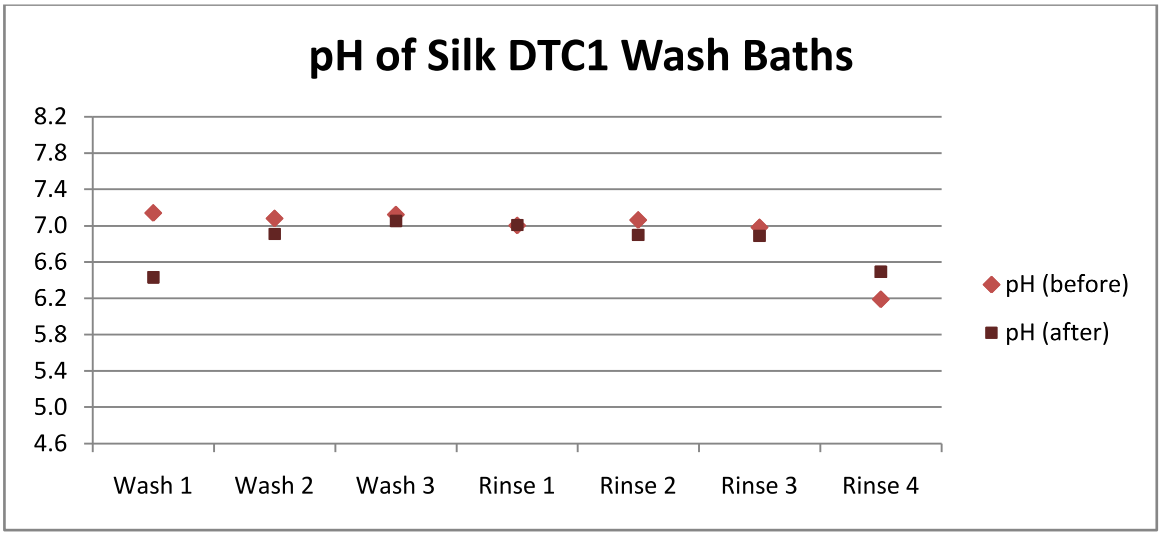
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.6
6.2
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5.4
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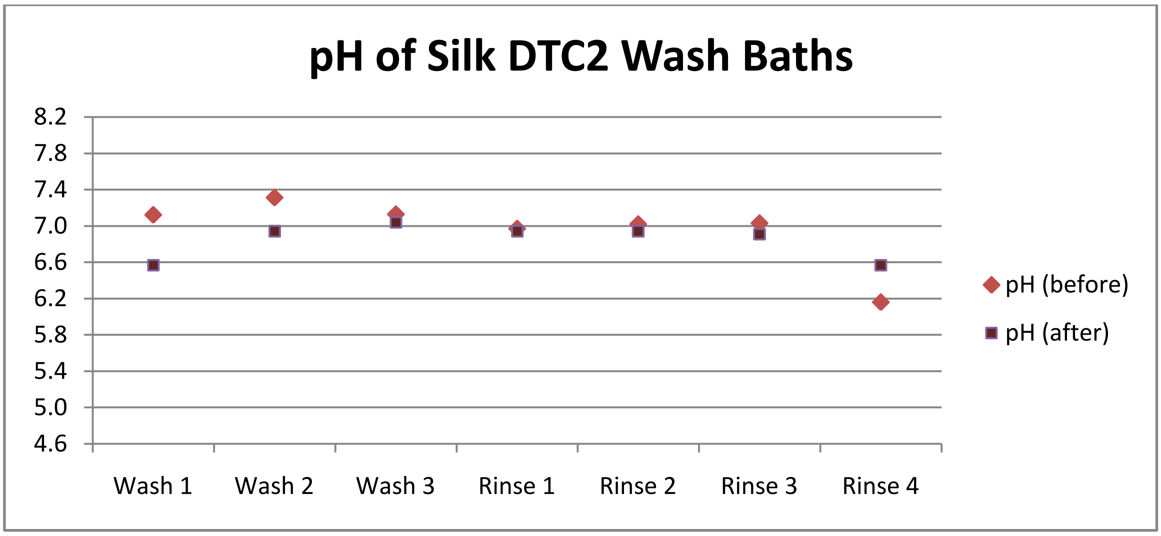
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.2
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5.4
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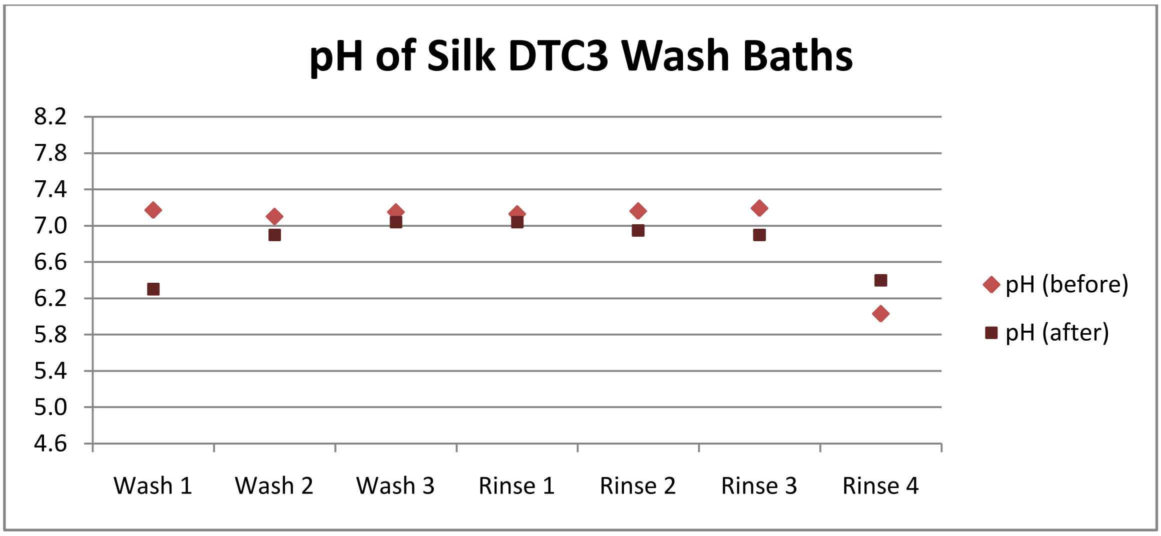
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.2
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5.4
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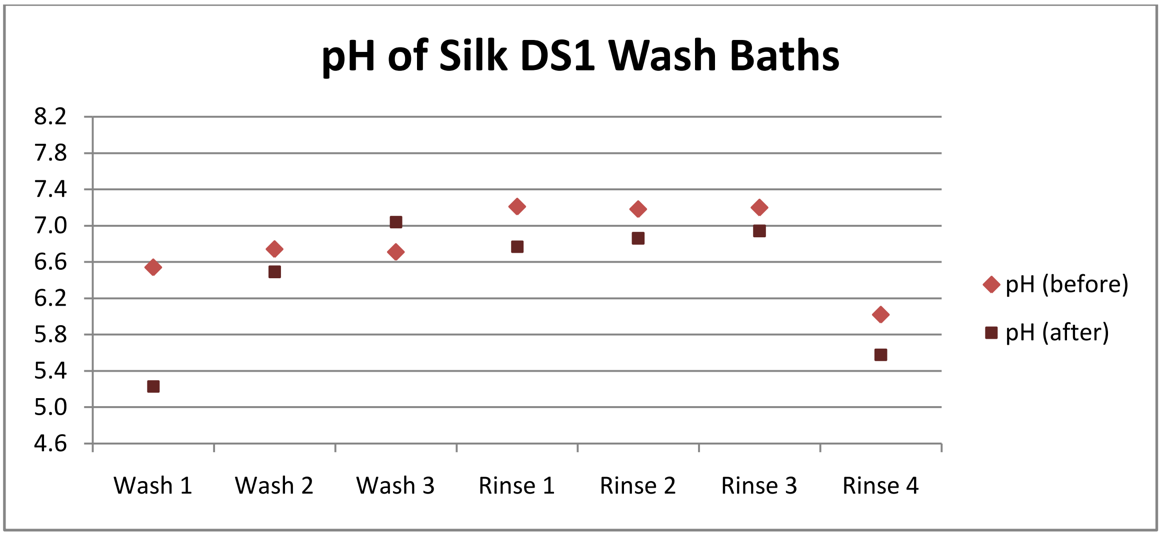
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)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6.2
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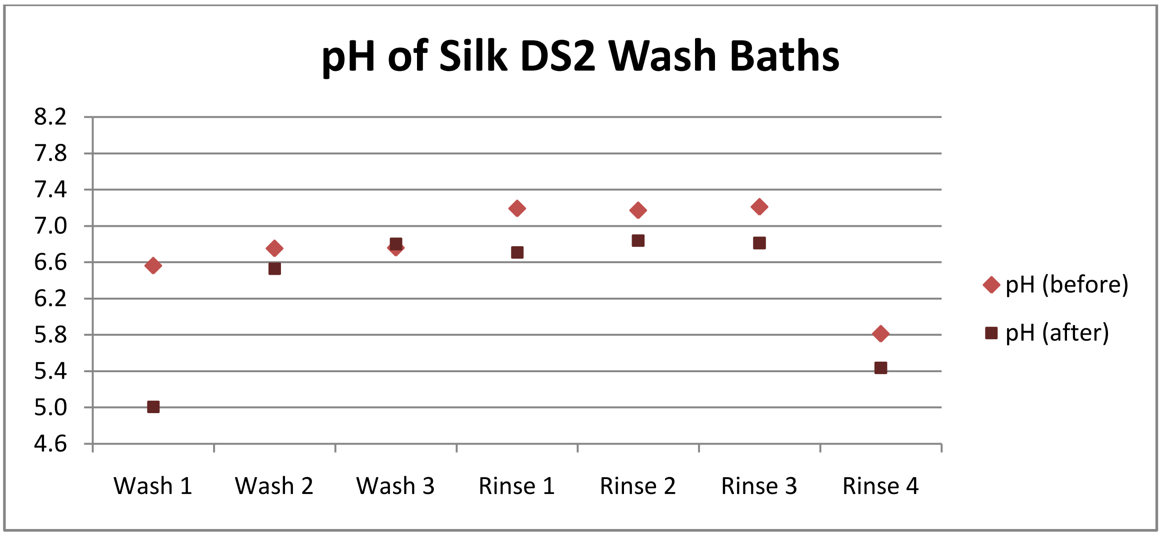
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk DS2 Wash Baths
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6.2
5.8
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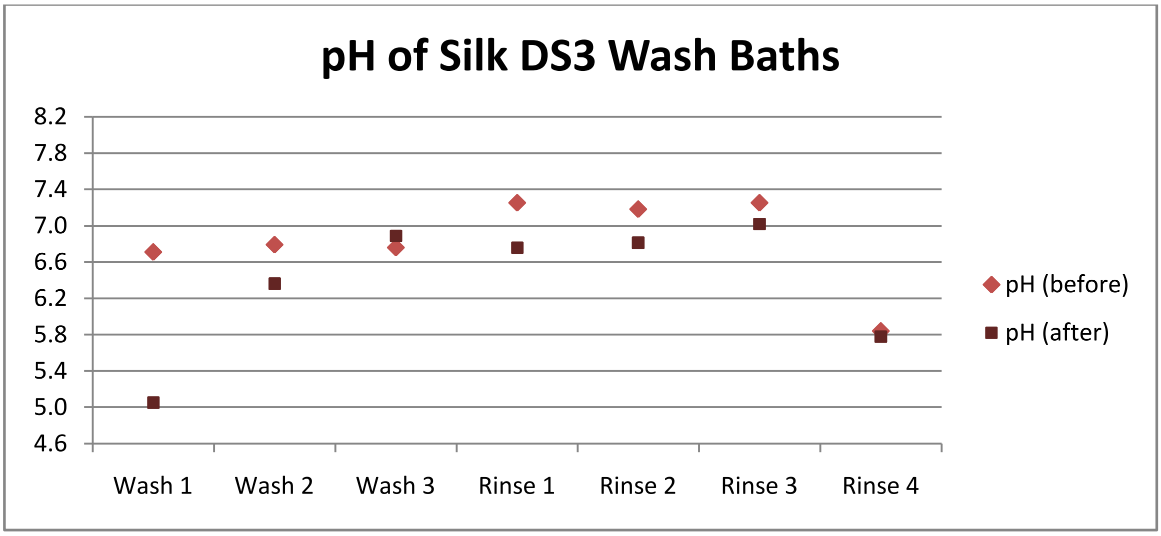
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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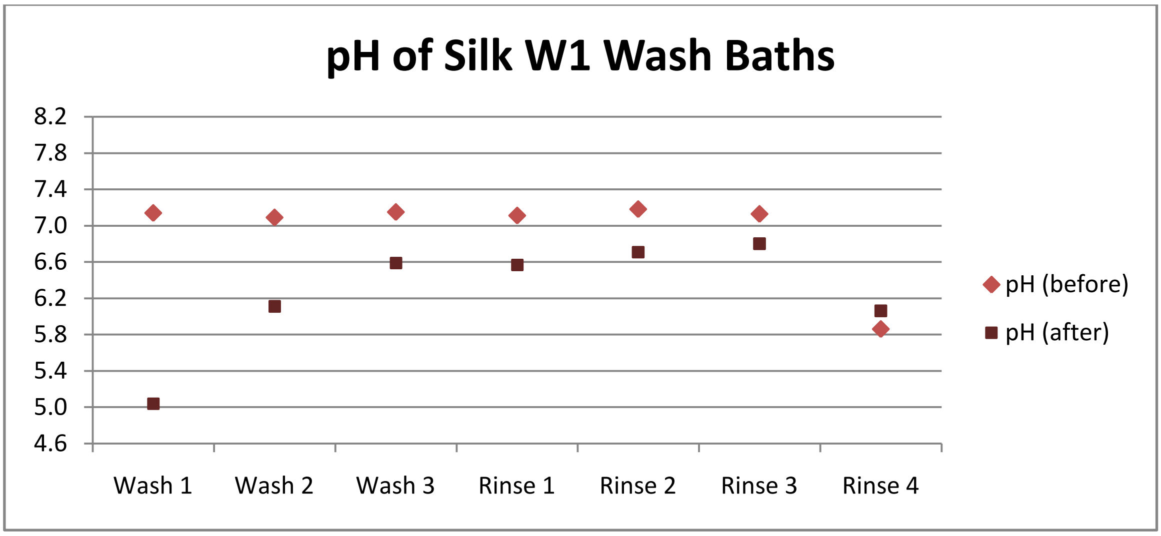
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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5.4
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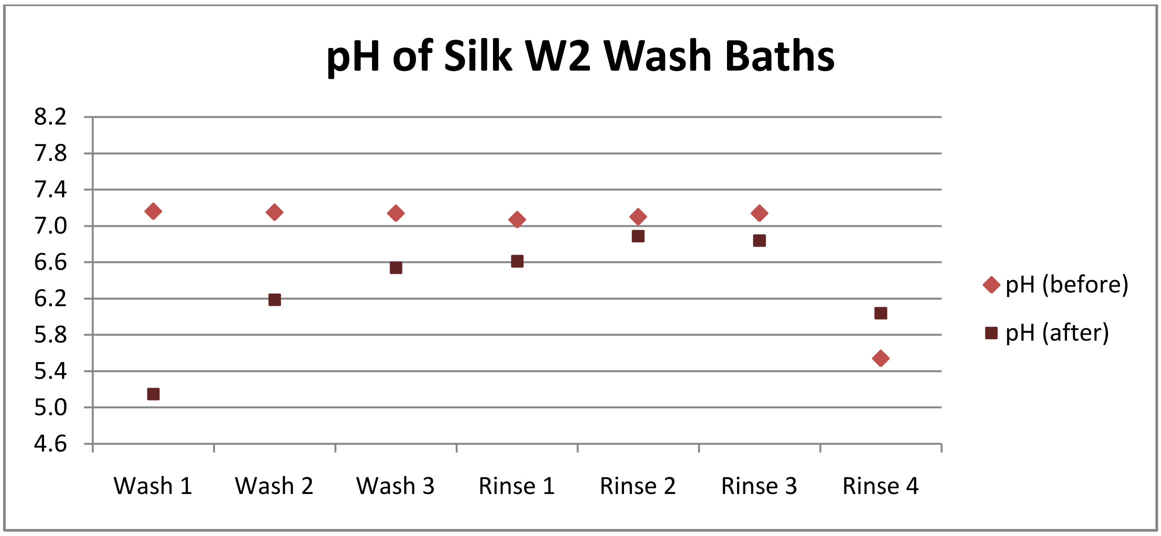
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk W2 Wash Baths
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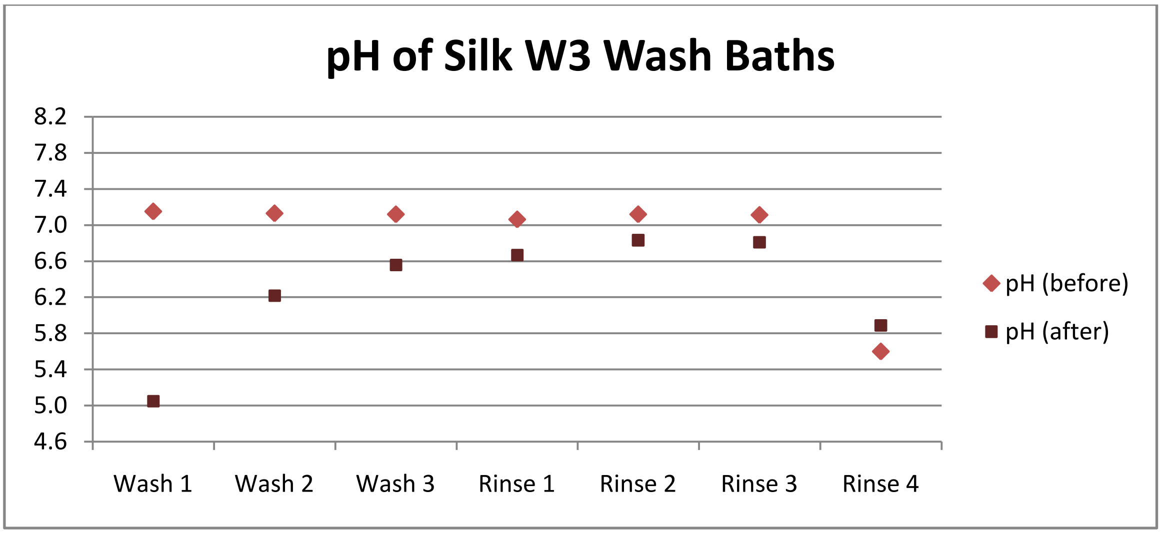
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk W3 Wash Baths
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7.4
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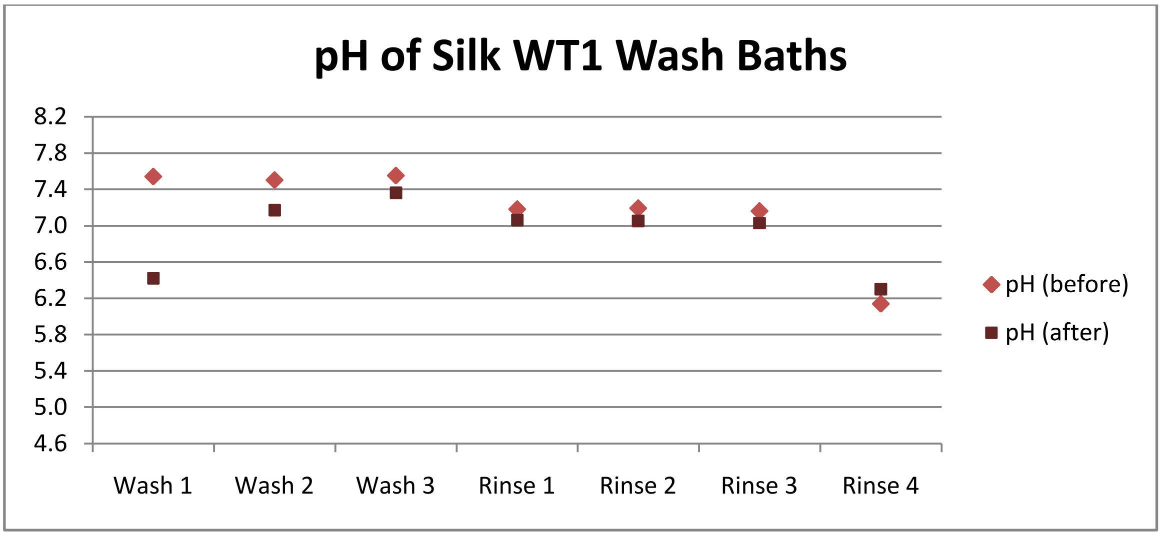
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk WT1 Wash Baths
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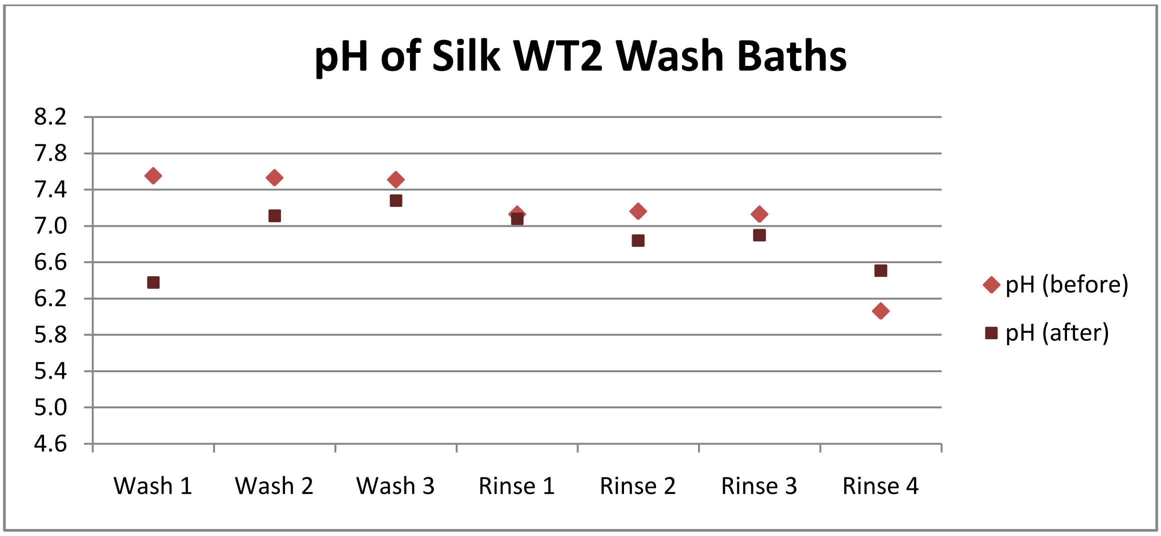
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk WT2 Wash Baths
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7.0
6.6
6.2
5.8
5.4
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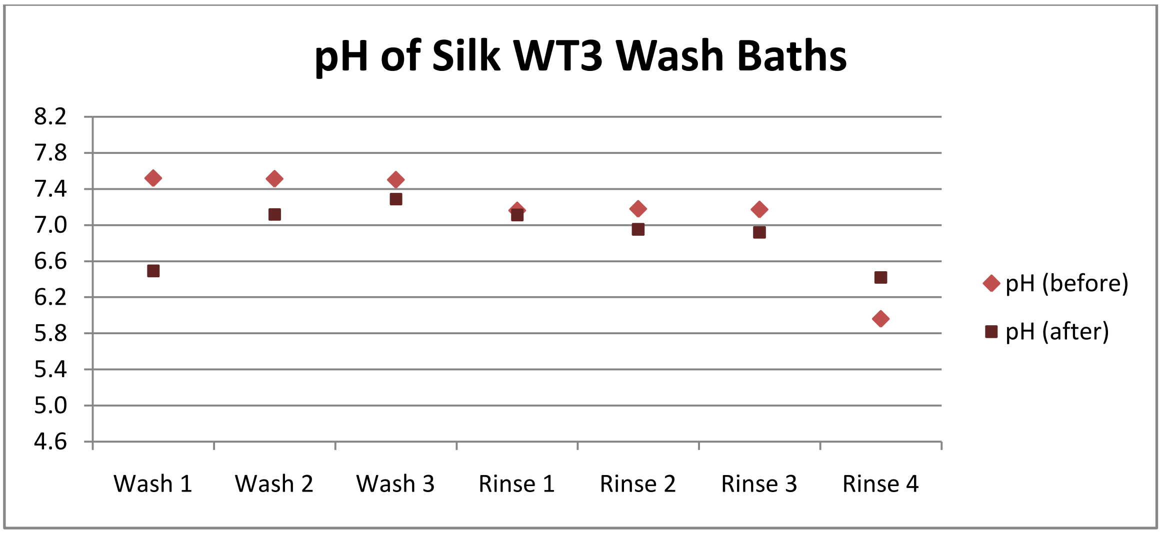
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)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6.6
6.2
5.8
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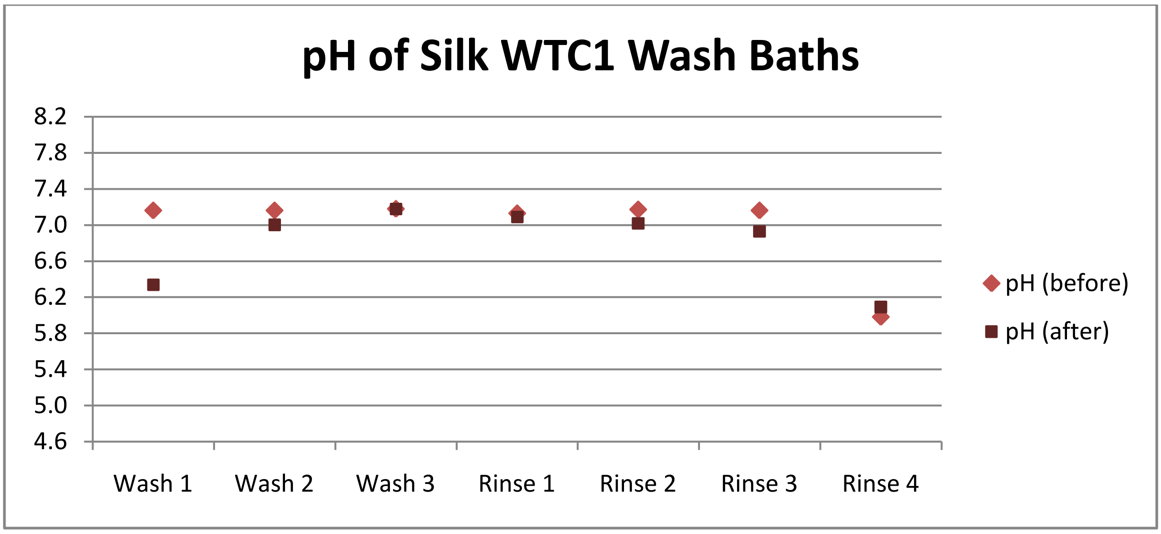
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk WTC1 Wash Baths
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6.6
6.2
5.8
5.4
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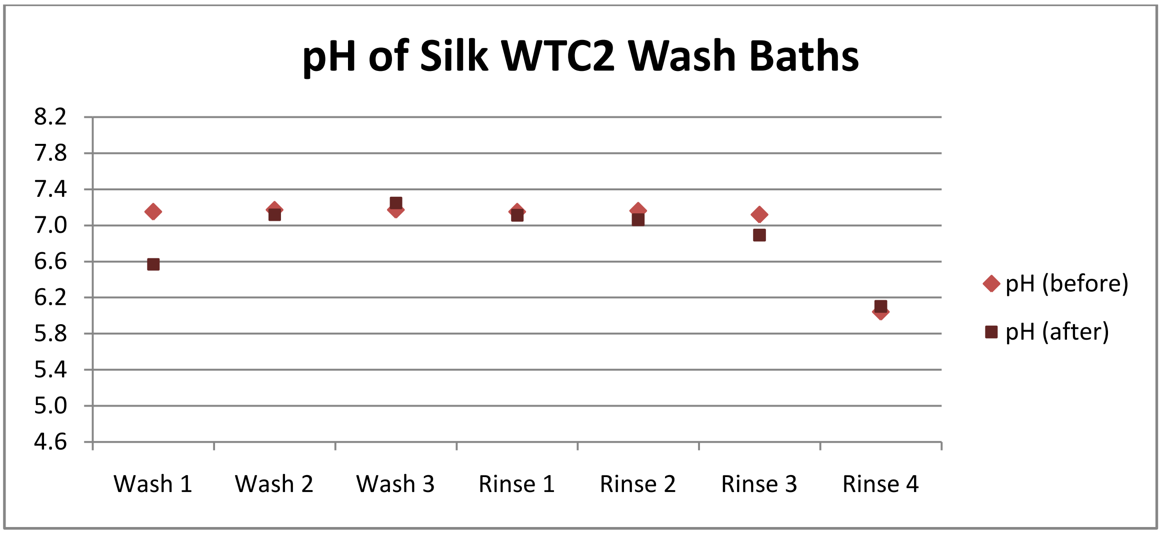
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk WTC2 Wash Baths
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7.4
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6.6
6.2
5.8
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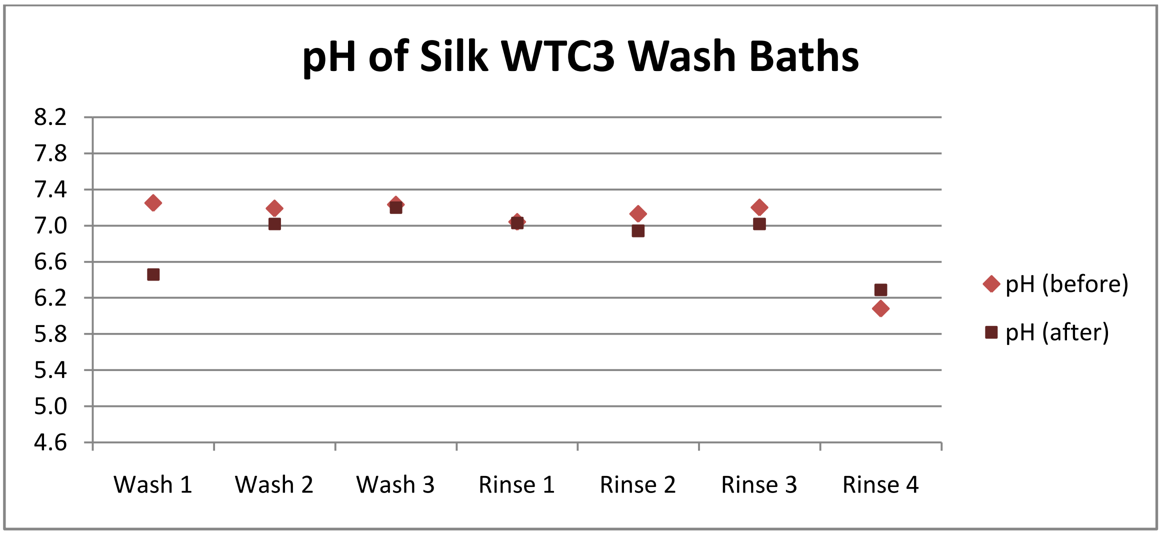
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk WTC3 Wash Baths
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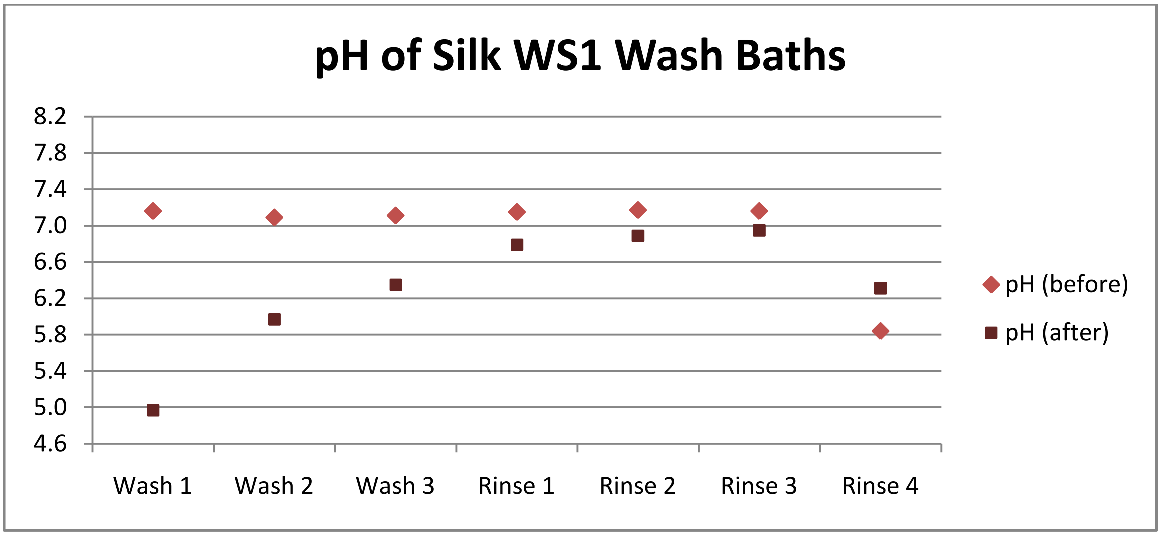
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
pH (before)
pH (after)


pH of Silk WS1 Wash Baths
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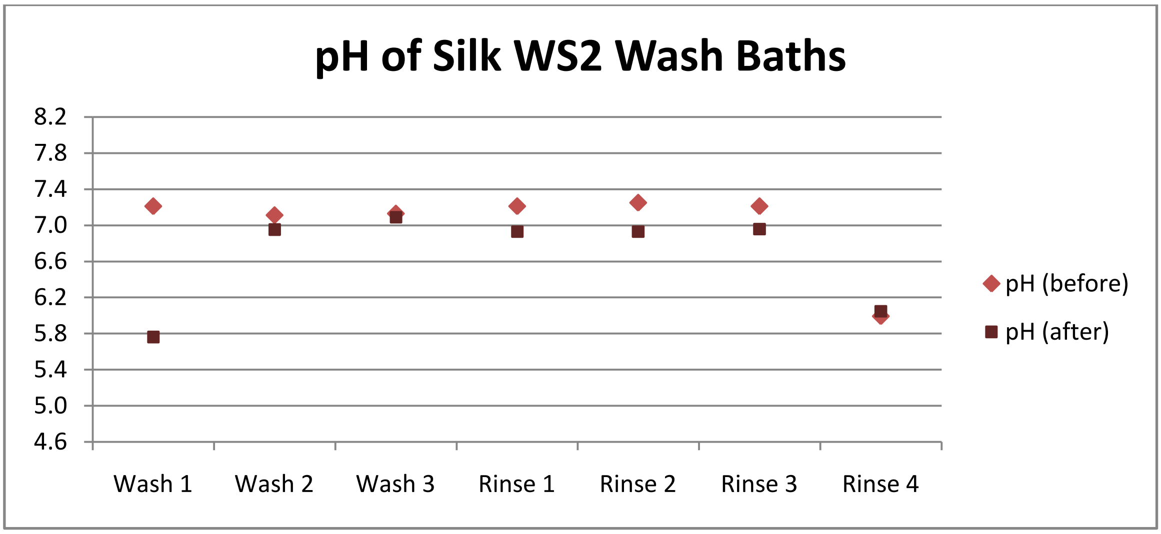
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk WS2 Wash Baths
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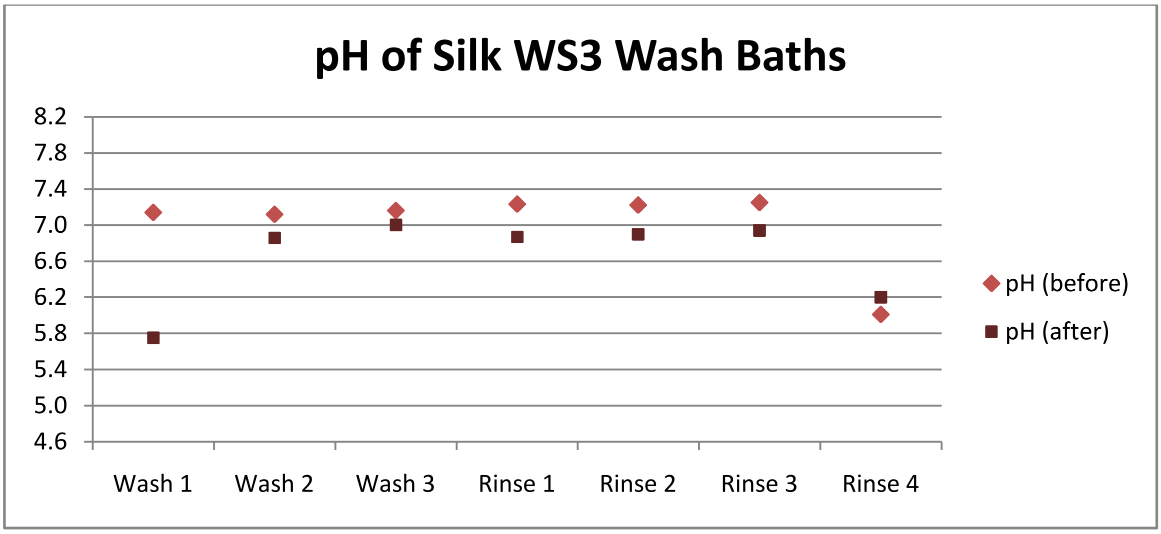
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)


pH of Silk WS3 Wash Baths
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7.4
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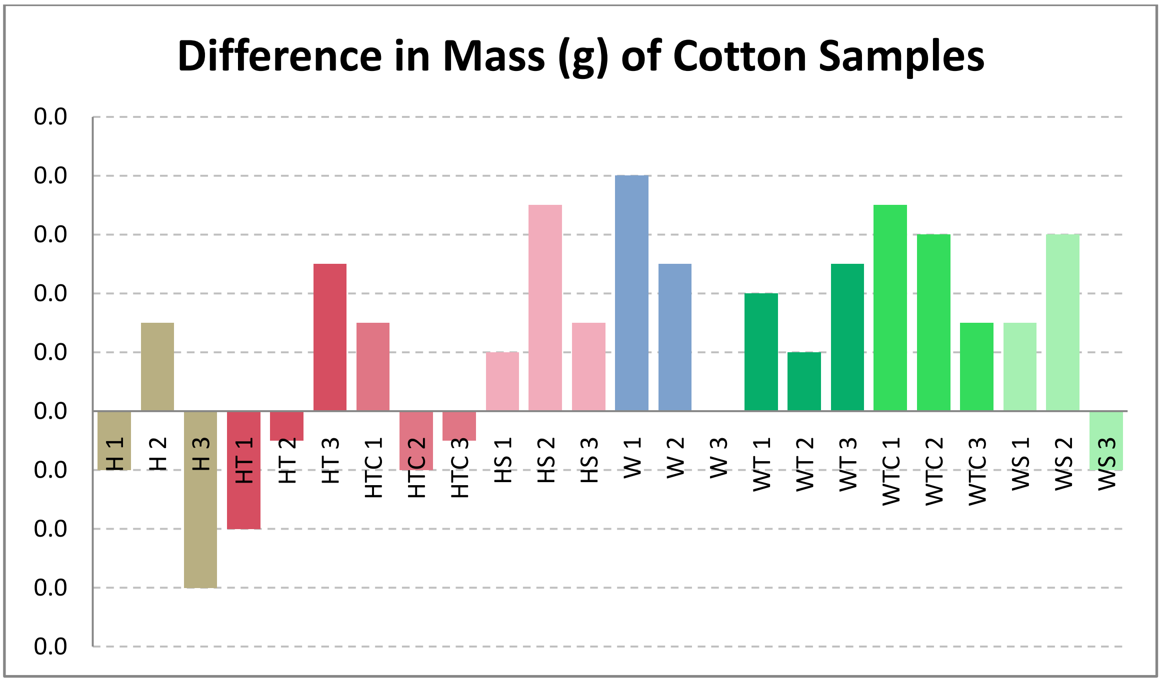
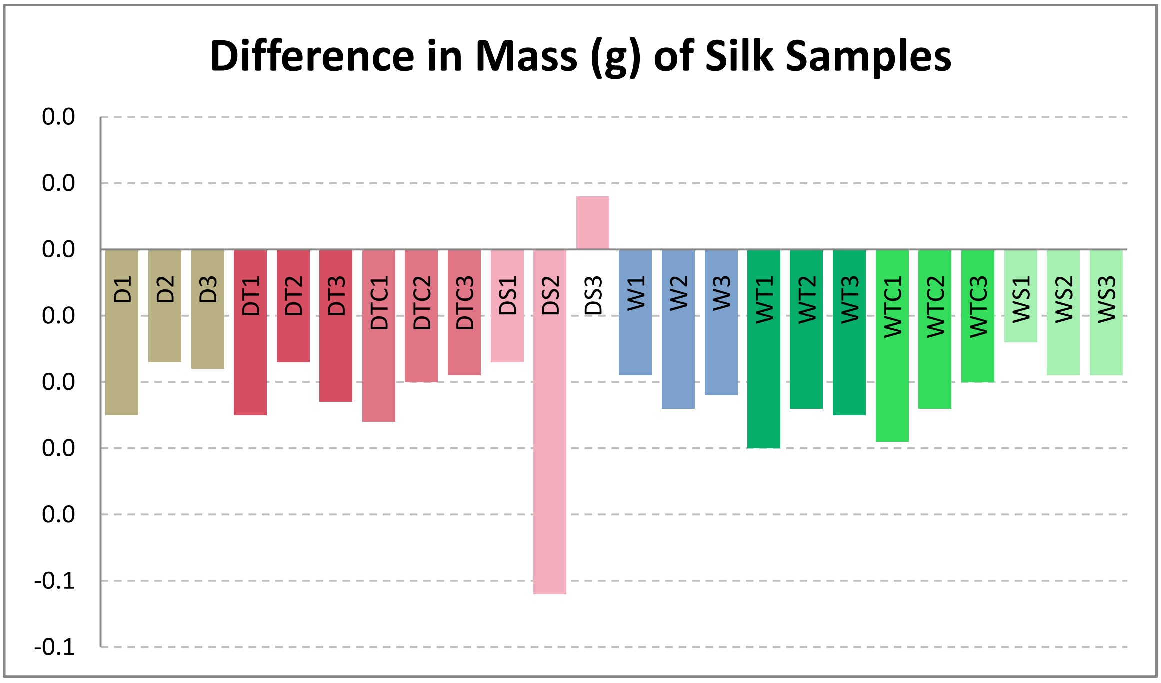
6.6
6.2
5.8
5.4
5.0
4.6
Wash 1
Wash 2
Wash 3
Rinse 1
Rinse 2
Rinse 3
Rinse 4
◆ pH (before)
■ pH (after)

Appendix G: Weight Measurement of Samples





Appendix H: Before (left) and After (right) Images

Samples H1, 2 and 3

Samples W1, 2 and 3

Samples HT1, 2 and 3

Samples WT1, 2 and 3

Samples HTC1, 2 and 3

Samples WTC1, 2 and 3

Samples HS1, 2 and 3

Samples WS1, 2 and 3

Samples D1, 2 and 3

Samples W1, 2 and 3

Samples DT1, 2 and 3

Samples WT1, 2 and 3

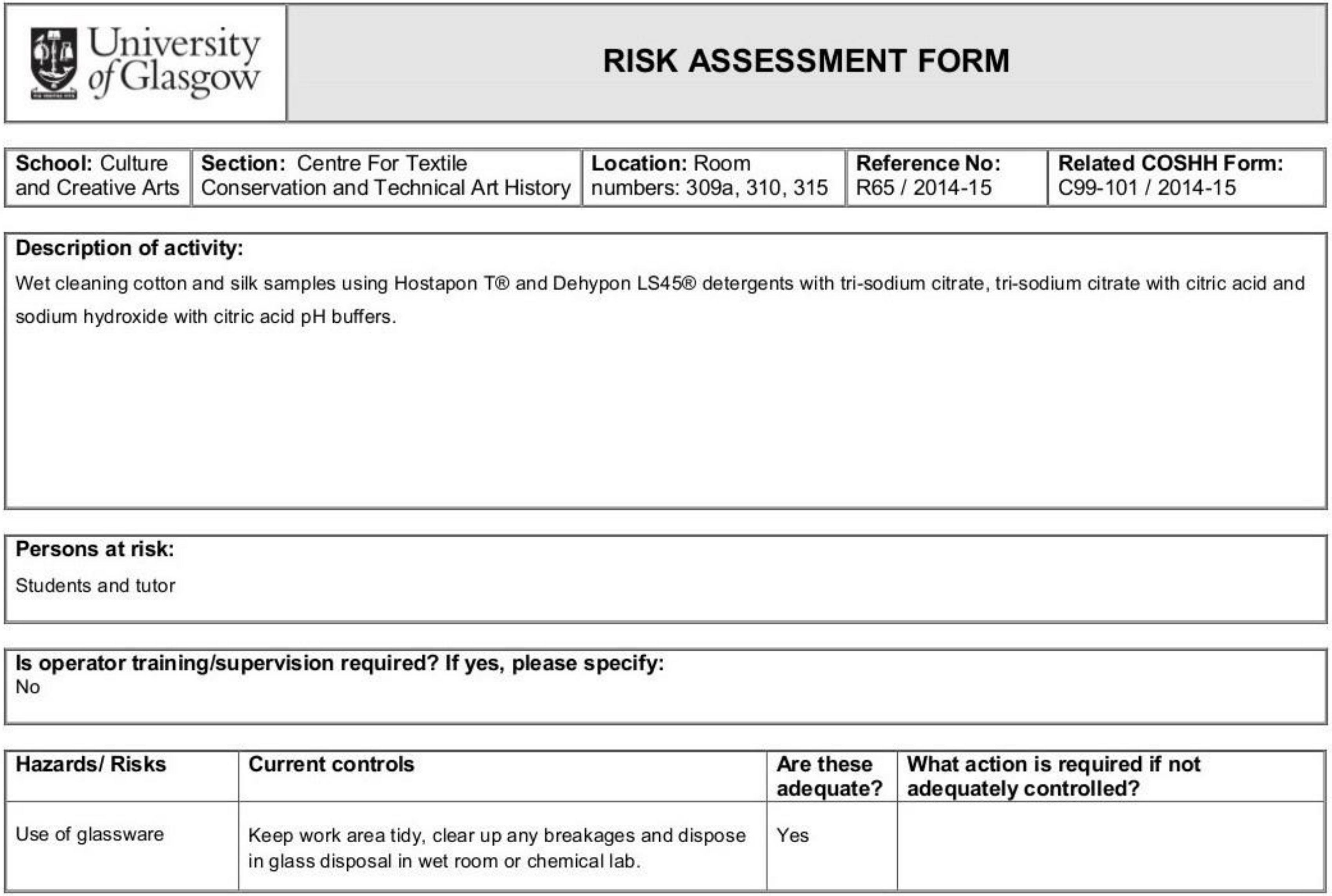
Samples DTC1, 2 and 3

Samples WTC1, 2 and 3

Samples DS1, 2 and 3

Samples WS1, 2 and 3

Appendix I: Risk Assessment and COSHH forms



RISK ASSESSMENT FORM

School: Culture and Creative Arts	**Section:** Centre For Textile Conservation and Technical Art History	**Location:** Room numbers: 309a, 310, 315	**Reference No:** R65 / 2014-15	**Related COSHH Form:** C99-101 / 2014-15

Description of activity:

Wet cleaning cotton and silk samples using Hostapon T® and Dehypon LS45® detergents with tri-sodium citrate, tri-sodium citrate with citric acid and sodium hydroxide with citric acid pH buffers.

Persons at risk:

Students and tutor

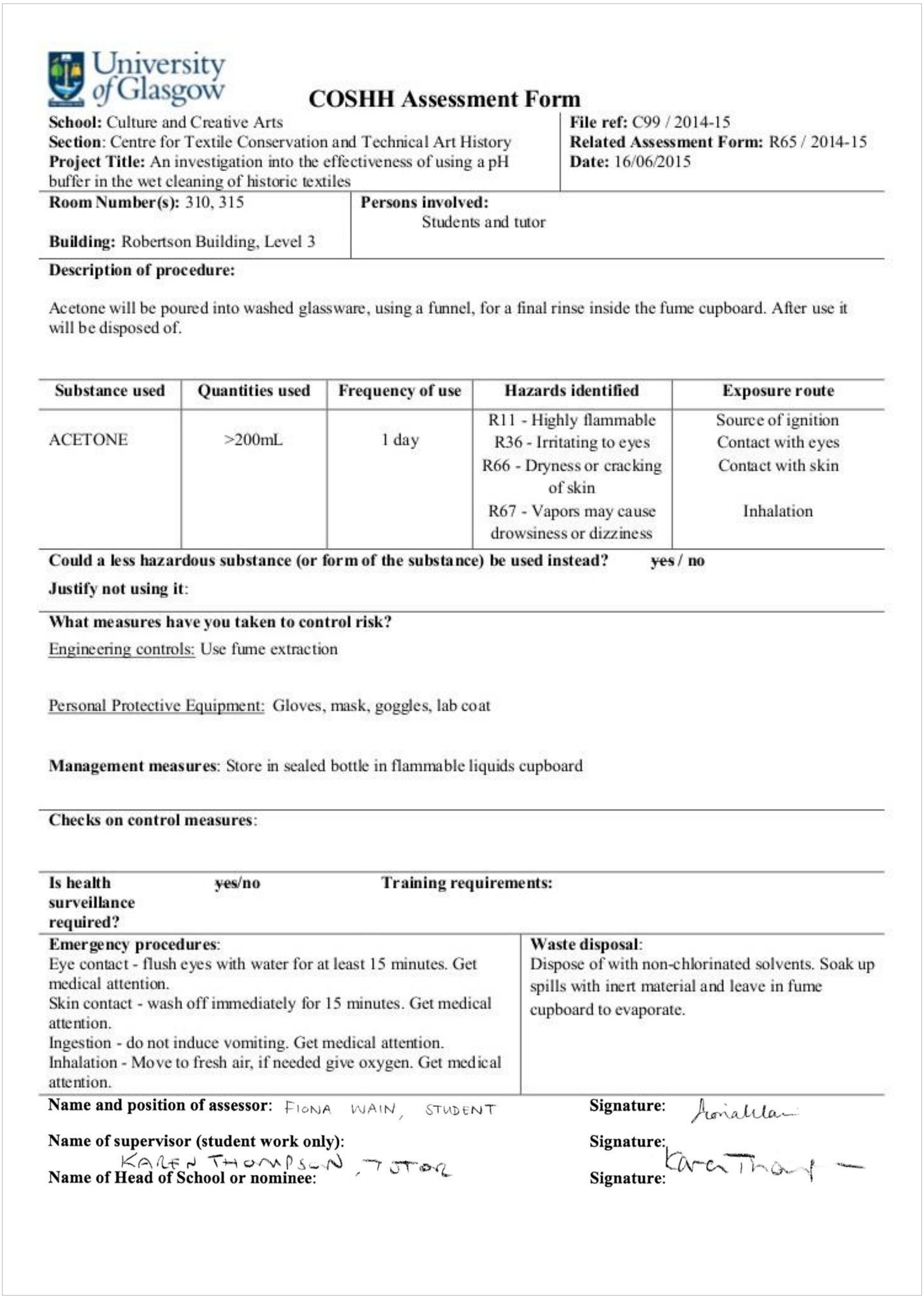
Is operator training/supervision required? If yes, please specify:

No

Hazards/ Risks	Current controls	Are these adequate?	What action is required if not adequately controlled?
Use of glassware	Keep work area tidy, clear up any breakages and dispose in glass disposal in wet room or chemical lab.	Yes	

Spillages	Inform others, clean up spillage and dispose of appropriately.	No	Check COSHH forms
Measuring powders	Wear PPE - mask, goggles, gloves, lab coat.	Yes	
Use of electrical equipment	Keep cables and work area tidy. Unplug when not in use.	Yes	
Use of chemicals to make up buffer solutions and clean glassware	Wear PPE - mask, goggles, gloves, lab coat. Use fume hood and sealable bottles. Transport bottles in bottle holder. Clean up any spillages and dispose of appropriately.	No	Fill out COSHH forms
Use of sharp implements and tools	Take care when handling, know location of first aid kit (wet room or office). Dispose of old blades in sharps box in chemistry lab.	Yes	
R.S.I. from use of electrical centrifuge	Take regular breaks. Do not use for an extended period of time.	Yes	

Completed by (print name and position, and sign): FIONA WAIN, STUDENT	**Date:** 16/06/2015
Approved by (print name and position, and sign): KAREN THOMPSON, TUTOR, Karen Thompson	**Date:** 16.6.2015



University of Glasgow

COSHH Assessment Form

School: Culture and Creative Arts
Section: Centre for Textile Conservation and Technical Art History
Project Title: An investigation into the effectiveness of using a pH buffer in the wet cleaning of historic textiles

File ref: C99 / 2014-15
Related Assessment Form: R65 / 2014-15
Date: 16/06/2015

Room Number(s): 310, 315

Building: Robertson Building, Level 3

Persons involved:
Students and tutor

Description of procedure:

Acetone will be poured into washed glassware, using a funnel, for a final rinse inside the fume cupboard. After use it will be disposed of.

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
ACETONE	>200mL	1 day	R11 - Highly flammable R36 - Irritating to eyes R66 - Dryness or cracking of skin R67 - Vapors may cause drowsiness or dizziness	Source of ignition Contact with eyes Contact with skin Inhalation

Could a less hazardous substance (or form of the substance) be used instead? **~~yes~~ / no**

Justify not using it:

What measures have you taken to control risk?

Engineering controls: Use fume extraction

Personal Protective Equipment: Gloves, mask, goggles, lab coat

Management measures: Store in sealed bottle in flammable liquids cupboard

Checks on control measures:

Is health surveillance required? **~~yes~~/no**

Training requirements:

Emergency procedures:
Eye contact - flush eyes with water for at least 15 minutes. Get medical attention.
Skin contact - wash off immediately for 15 minutes. Get medical attention.
Ingestion - do not induce vomiting. Get medical attention.
Inhalation - Move to fresh air, if needed give oxygen. Get medical attention.

Waste disposal:
Dispose of with non-chlorinated solvents. Soak up spills with inert material and leave in fume cupboard to evaporate.

Name and position of assessor: FIONA WAIN, STUDENT **Signature:**

Name of supervisor (student work only): KAREN THOMPSON, TUTOR **Signature:** Karen Thomp

Name of Head of School or nominee: **Signature:**

University of Glasgow

COSHH Assessment Form

School: Culture and Creative Arts **Section**: Centre for Textile Conservation and Technical Art History **Project Title:** An investigation into the effectiveness of using a pH buffer in the wet cleaning of historic textiles	**File ref:** C100 / 2014-15 **Related Assessment Form:** R65 / 2014-15 **Date:** 16/06/2015
Room Number(s): 309a, 310, 315 **Building:** Robertson Building, Level 3	**Persons involved:** Students and tutor

Description of procedure:

Weighing out required quantity and adding to deionised water to produce 0.5% solution. The solution will be used to produce a pH buffer which will be added to wash solutions.

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
CITRIC ACID	>20g	10 day	R36 - Irritating to eyes	Contact with eyes

Could a less hazardous substance (or form of the substance) be used instead? **yes / no**

Justify not using it:

What measures have you taken to control risk?

Engineering controls:

Personal Protective Equipment: Gloves, mask, goggles, lab coat

Management measures: Keep locked in acids cabinet

Checks on control measures:

Is health surveillance required? **yes/no** **Training requirements:**

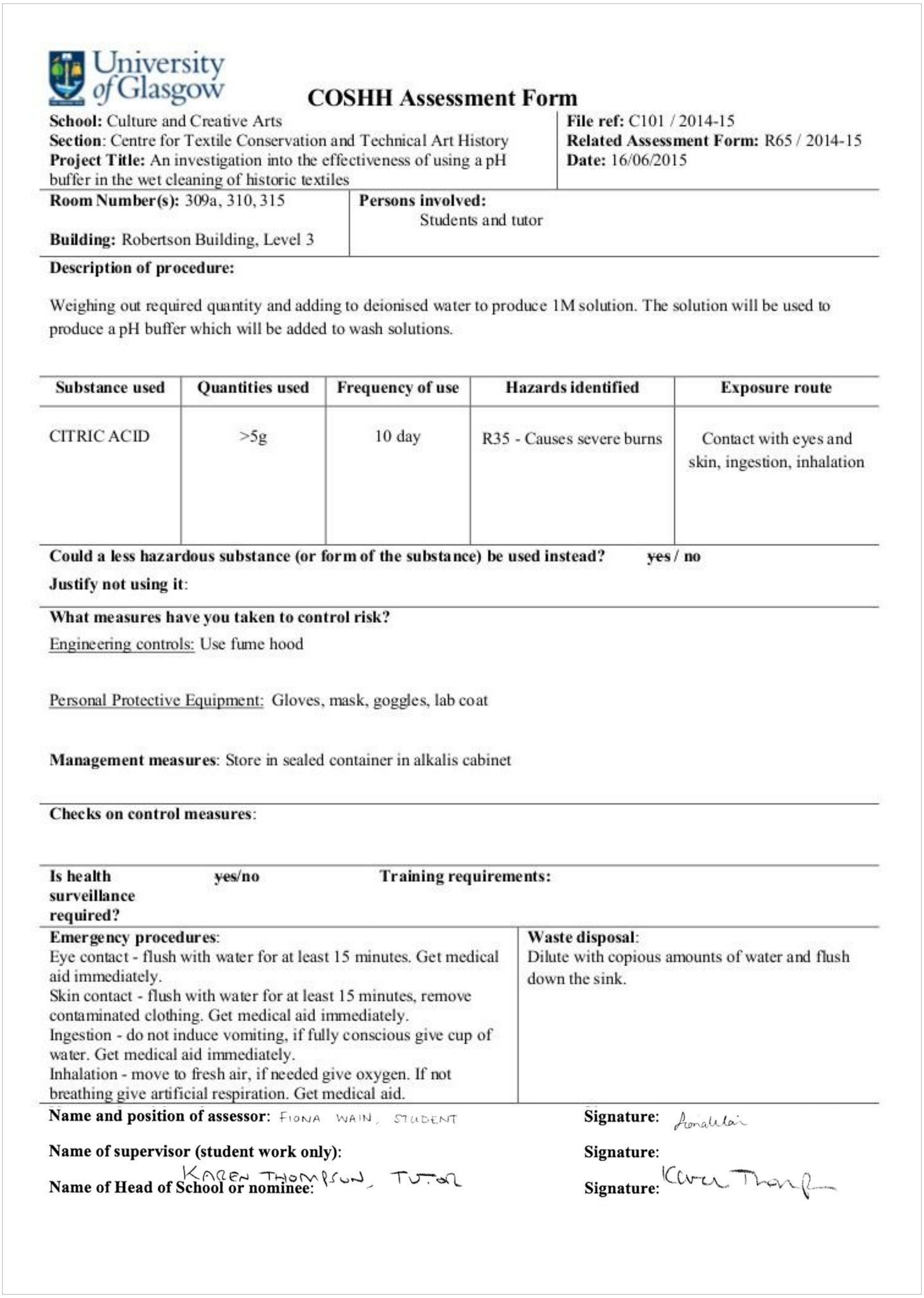
Emergency procedures: Eye contact - rinse thoroughly for at least 15 minutes. Consult a doctor. Skin contact - wash off with soap and water. Consult a doctor. Inhalation - move to fresh air. If not breathing give artificial respiration. Consult a doctor. Ingestion - if conscious rinse mouth with water. Consult a doctor.	**Waste disposal**: Small quantities can be flushed down the sink with plenty of water.

Name and position of assessor: FIONA WAIN, STUDENT **Signature**:

Name of supervisor (student work only): **Signature**:

KAREN THOMSON, TUTOR

Name of Head of School or nominee: **Signature**:



University of Glasgow

COSHH Assessment Form

School: Culture and Creative Arts
Section: Centre for Textile Conservation and Technical Art History
Project Title: An investigation into the effectiveness of using a pH buffer in the wet cleaning of historic textiles

File ref: C101 / 2014-15
Related Assessment Form: R65 / 2014-15
Date: 16/06/2015

Room Number(s): 309a, 310, 315

Building: Robertson Building, Level 3

Persons involved: Students and tutor

Description of procedure:

Weighing out required quantity and adding to deionised water to produce 1M solution. The solution will be used to produce a pH buffer which will be added to wash solutions.

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
CITRIC ACID	>5g	10 day	R35 - Causes severe burns	Contact with eyes and skin, ingestion, inhalation

Could a less hazardous substance (or form of the substance) be used instead? **~~yes~~ / no**

Justify not using it:

What measures have you taken to control risk?

Engineering controls: Use fume hood

Personal Protective Equipment: Gloves, mask, goggles, lab coat

Management measures: Store in sealed container in alkalis cabinet

Checks on control measures:

Is health surveillance required? **~~yes~~/no** **Training requirements:**

Emergency procedures:
Eye contact - flush with water for at least 15 minutes. Get medical aid immediately.
Skin contact - flush with water for at least 15 minutes, remove contaminated clothing. Get medical aid immediately.
Ingestion - do not induce vomiting, if fully conscious give cup of water. Get medical aid immediately.
Inhalation - move to fresh air, if needed give oxygen. If not breathing give artificial respiration. Get medical aid.

Waste disposal:
Dilute with copious amounts of water and flush down the sink.

Name and position of assessor: FIONA WAIN, STUDENT **Signature:**

Name of supervisor (student work only): **Signature:**

Name of Head of School or nominee: KAREN THOMPSON, TUTOR **Signature:**

Appendix J: Table of Abbreviations

Abbreviation	Full Form
AIC	American Institute for Conservation of Historic and Artistic Works
CCI	Canadian Conservation Institute
ICOM CC	International Council of Museums Conservation Committee
IIC	International Institute for Conservation of Historic and Artistic Works
JAIC	Journal of the American Institute for Conservation

Appendix K: Fabric Samples

Fabric samples used in the experiments (listed below) are submitted in the copy of this dissertation held by the University of Glasgow.

Cotton Samples			**Silk Samples**		
H1	H2	H3	D1	D2	D3
HT1	HT2	HT3	DT1	DT2	DT3
HTC1	HTC2	HTC3	DTC1	DTC2	DTC3
HS1	HS2	HS3	DS1	DS2	DS3
W1	W2	W3	W1	W2	W3
WT1	WT2	WT3	WT1	WT2	WT3
WTC1	WTC2	WTC3	WTC1	WTC2	WTC3
WS1	WS2	WS3	WS1	WS2	WS3