

Surface chemical investigation into the cleaning procedures of historic tapestry materials. Part 2

David Howell · Rob Mitchell · Christopher M. Carr

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Abstract Cleaning of invaluable historical artefacts is a major issue for conservators. It is not only what is removed during cleaning, but also what residues are left after cleaning, that is of concern for long-term preservation. In this study, the typical cleaning procedures for silk-based tapestry materials were examined by Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and the nature/influence of the fibre surface on detergent residue adsorption established.

Introduction

Tapestries are uniquely European and are inextricably woven into the fabric of European history and culture. In the 15–17th centuries tapestry manufacture was at its peak and was the definitive symbol of power, wealth and cultural style. The tapestries were predominantly manufactured in Belgium and exported to all parts of Europe to reside in Royal Palaces and wealthy merchants' homes. The tapes-

tries were produced predominantly from wool and silk, with metal threads incorporated into the design to further impart the impression of wealth and to enhance aesthetic impact. The metal threads were composed of silver, gold or silver gilt and have been discussed in previous publications [1, 2].

In the subsequent centuries the tapestries, in general, have been neglected and exposed to sunlight and dirt, which has resulted in the loss of vibrancy and brilliance of the original design. While the sunlight degradation is irreversible, the wet cleaning of ancient textiles is an important tool for conservators in that it allows the original “dirty” artefact to be viewed by the public in a visually enhanced form, and in addition may even retard the chemical degradation of the fibres. Fundamental studies by Hofenk de Graaf developed a range of cleaning protocols depending on water quality, nature of the object and even the financial budget [3, 4]. Derived from this work are cleaning procedures based on the non-ionic surfactant Synperonic N, nonyl phenol ethoxylates, or Synperonic N in combination with sodium dodecyl sulphate, SDS. In contrast to the European conservation practices, cleaning methods in North America are based on purely anionic surfactant systems [5]. However, in recent years the partial withdrawal of Synperonic N surfactants, on the basis of their environmental impact and relatively poorer degradation, has forced conservators to reappraise their cleaning strategy. Conservators are constantly concerned about the effect of the interventive treatments on historical artefacts and the potential for depositing residues, which may accelerate damage to the substrate.

Surfactants by their nature operate at materials surfaces and therefore to probe these regions surface specific and sensitive techniques must be utilised. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) has been

D. Howell
The New Bodleian Library, Oxford University,
Oxford OX1 3BG, UK
e-mail: David.Howell@Bodley.ox.ac.uk

R. Mitchell
CSMA Ltd, Queens Rd., Penkhull, Stoke on Trent ST4 7LQ, UK
e-mail: robmitchell@csma.ltd.uk

C. M. Carr (✉)
Textiles & Paper, University of Manchester, Manchester M60
1QD, UK
e-mail: chris.carr@manchester.ac.uk

previously demonstrated to effectively investigate fibre surface modifications and deposition of textile auxiliaries at the fibre surface interface [2, 6, 7]. This surface-sensitive technique, with its sampling depth of 1–2 nm, provides both elemental and molecular mass spectral data by bombarding the sample surface with a primary ion beam and analysing the masses of the sputtered secondary ions emitted from the surface [8].

In Part 1 of this series the interaction of detergents with unaged and aged wool has been investigated, with clear differences in the adsorption/substantivity behaviour observed [2]. In this study the effect of current conservation cleaning methods on ‘‘model’’ silk substrates is investigated and in particular the interaction and substantivity of surfactants with the fibre surface established. In a subsequent study the interactions of the cleaning surfactants with the other tapestry components, metal threads (untarnished and corroded), will be reported.

Experimental

Materials

The scoured/degummed silk plain weave fabric (220 g/m²) was degummed in the following solutions using a liquor: goods ratio of 20:1:

- 1 g/L sodium carbonate, at 80 °C for 30 min;
- 0.5 g/L sodium carbonate, 0.5 g/L sodium hydrosulphite, 0.8 g/L sodium silicate and 2 g/L alkylbenzene sulphonate based detergent, at 98 °C for 90 min;
- 0.5 g/L sodium carbonate, 0.8 g/L sodium hydrosulphite, 0.8 g/L sodium silicate and 2 g/L alkylbenzene sulphonate based detergent, at 98 °C for 60 min;
- Rinse with water 95 °C for 20 min, 80 °C for 20 min, and 20 °C for 10 min;
- Rinse with 0.5 mL/L acetic acid, at 95 °C for 20 min;
- Finally rinse thoroughly in water and air dry.

Prior to further use the fabric was extracted three times with 50% aqueous isopropanol at 40 °C, then distilled water and finally air-dried. Synperonic N8 and Synperonic A7 were kindly donated by ICI, Wilton, UK. The sodium dodecyl sulphate, SDS, was purchased from BDH Ltd., and was identified as above 90% purity with other primary alkyl sulphates present.

Cleaning procedure

The pre-cleaned unexposed and photo-oxidised silk fabrics were soaked in either a solution of 1 g/L Synperonic N8, or 1 g/L Synperonic A7, or 1 g/L SDS, or 0.5 g/L Synperonic N8 and 0.5 g/L SDS, or 0.5 g/L Synperonic A7 and 0.5 g/L

SDS, respectively. The silk was soaked in the specified solution for 1 h at 20 °C, with occasional gentle agitation, and a silk:liquor ratio of 1:100. The fabric was then rinsed in excess pure (reverse osmosis treated) water for 1.5 h and finally air-dried on a polypropylene coated glass mesh surface.

Simulated sunlight exposure

The silk fabric samples were exposed to simulated sunlight in a Xenotest 150S instrument for 404 h at 20 °C. Average lighting levels present in museums are typically between 50 and 150 lux, with an annual exposure period of approximately 3,000 h. Therefore the simulated sunlight irradiation dosage used in this study was based on an equivalent exposure level of approximately 130 years in a museum environment.

ToF-SIMS analysis

The ToF-SIMS spectra were obtained under *static* conditions using a PHI 7000 instrument with a reflectron analyser, a Cs⁺ ion source (8 KeV, pulse length 1–25 ns) and a pulsed electron flood source (50–70 eV) for charge compensation. The operating pressure was less than 5.33 μPa (4×10^{-8} torr). For each sample analysis, a total primary-ion dose of fewer than 1×10^{12} ions cm⁻² was used, which lies well below the threshold level of 1×10^{13} ions cm⁻² for *static* SIMS. Both positive and negative ion spectra were acquired from areas of 250 μm × 250 μm in the mass range $m/z = 0$ –1,000^{+/-}.

Results and discussion

The silk fibre is typically produced in continuous filament form by the larvae of the silkworm. The raw silk is composed of an inner fibroin filament and an outer protective sericin gum [9]. In commercial processing the raw silk is degummed/scoured to remove the sericin protein and reveal the smooth, soft, lustrous fibroin filament, which can then be subsequently wet processed; for example dyed. Fibroin is mainly composed of glycine, alanine and serine, which are primarily located in the crystalline regions of the fibre. The remaining amino acids are located in the amorphous regions of the fibre due to their relatively large molecular size precluding packing into the crystalline regions. Previous surface chemical studies have indicated that the photosensitive tyrosine amino acid is located in the amorphous region at the fibre surface and that the relatively rapid photoyellowing of silk maybe related to this surface location [10, 11].

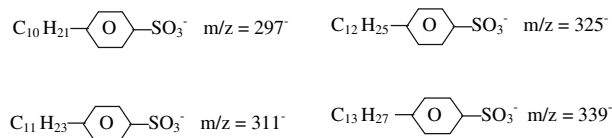
Effect of artificial ageing

The ToF-SIMS positive ion spectrum of untreated silk shows characteristic ion signals associated with the major amino acids, in particular the aliphatic alanine and glycine, and the aromatic phenylalanine and tyrosine species, at $m/z = 44^+$, 58^+ , 120^+ , and 136^+ , respectively, Fig. 1 [12].

The effect of artificial sunlight, equivalent to 130 years light exposure in a museum environment, was to produce an obvious yellowing of the fabric. Previous ‘‘real’’ and ‘‘simulated’’ sunlight exposures have reported a decrease in the tyrosine content and fission of the peptide bond in silk [13, 14]. This amide bond breakage, coupled to oxidation of amino acid side chains produces an increase in polar and charged functionalities such as carbonyls, hydroxyls, amines and carboxyls, which will potentially alter the fibres adsorption character. In the previous ToF-SIMS study of tapestry wool the photo-oxidative process removed the surface lipids, in particular the 18-methyl eicosanoic acid covalently bound via a thioester linkage, oxidised cystine to negatively charged cysteic acid, and changed the character of the fibre surface from non-wetting/hydrophobic to wettable/hydrophilic [2]. With silk the surface chemical structural modifications will be far less obvious due to the absence of surface lipids imparting obvious hydrophobicity. Therefore while an increase in surface oxygen content due to photo-oxidation could be predicted, there is little obvious change in the ToF-SIMS

fingerprint of the photo-oxidised protein fibre surface, with the tyrosine signal at $m/z = 136^+$ relatively unchanged.

The ToF-SIMS negative ion spectrum of both the unexposed and photodegraded silk fabric shows obvious signals at $m/z = 339^-$, 325^- , 311^- and 297^- , Fig. 2. These four signals can be attributed to the presence of residual linear alkylbenzene sulphonates surfactant derived from the commercial pre-scouring. The alkylbenzene sulphonate species are assigned:



It is therefore apparent that the aqueous isopropanol treatment and extensive rinsing, after the commercial scouring/degumming processing, was not completely successful in removing tenaciously bound anionic surfactants from silk.

Cleaning of silk in Synperonic N8 solution

Previous ToF-SIMS studies of nonylphenol ethoxylate (NPEO) treatments of textiles provided characteristic positive and negative ion mode spectra, with typically, the sodioated complex observed in the positive ion spectrum [6]. As the surfactant formulation is a mixture of reaction products, a

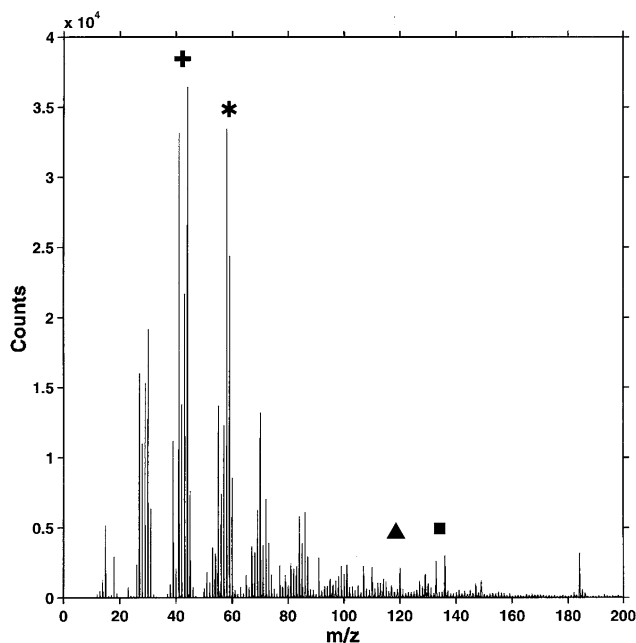


Fig. 1 ToF-SIMS positive ion spectrum of scoured and degummed silk (+, alanine; *, glycine; ▲, phenylalanine; ■, tyrosine)

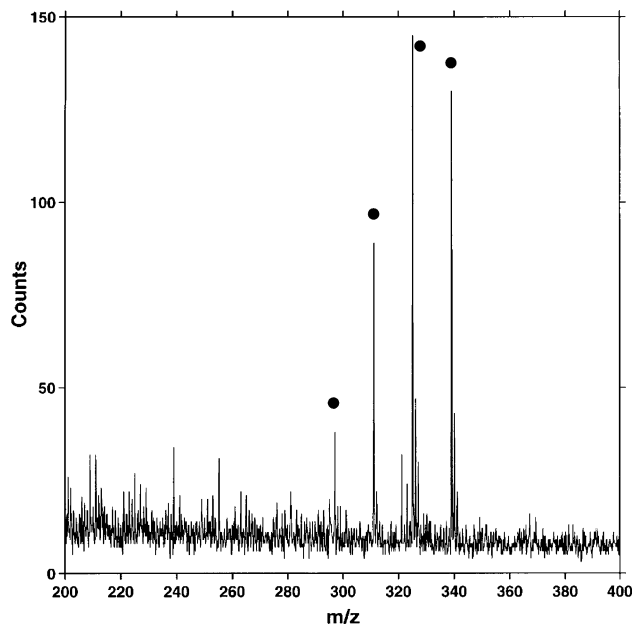


Fig. 2 ToF-SIMS negative ion spectrum of scoured and degummed silk (●, alkylbenzene sulphonate)

characteristic ethoxymer distribution range is observed with the stated ethoxymer number being the average.

Examination of the ToF-SIMS spectrum of the unexposed and photodegraded silk cleaned in the Synperonic N solution showed little obvious evidence of residual molecular nonylphenol ethoxylates at the fibre surface in either the positive ion or negative ion spectra. However in the negative ion spectra of both the silk fabrics the presence of the nonylphenoxide anion species, (NPA), at $m/z = 219^-$, was apparent Fig. 3. In addition while the positive ion spectra show little evidence for molecular NPEO species, the $\text{HOCH}_2\text{CH}_2^+$ ion, at $m/z = 45^+$, clearly shows an increase in intensity after washing in the non-ionic detergent, Fig. 4. Furthermore the increase in the “marker” ion at $m/z = 45^+$ is even greater for the photo-oxidised silk, and this behaviour is apparent for all samples treated with Synperonic N, Synperonic A7, and combinations of the non-ionic surfactants with sodium dodecyl sulphate. It is therefore apparent in this study that the $m/z = 45^+$ ion is a sensitive indicator of low levels of ethoxylate adsorption present at the fibre surface.

In previous non-ionic surfactant studies on wool it has been reported that oxidative chlorination of the fibre can increase NPEO adsorption, and the more hydrophobic short chain ethoxymers have greater substantivity for the wool fibre surface [15, 16]. However it should be noted that this non-ionic surfactant-based cleaning appears to be ineffective in completely removing the residual anionic linear alkyl benzene sulphonates from the silk fibre surface, as indicated by the characteristic ion series, Fig. 3.

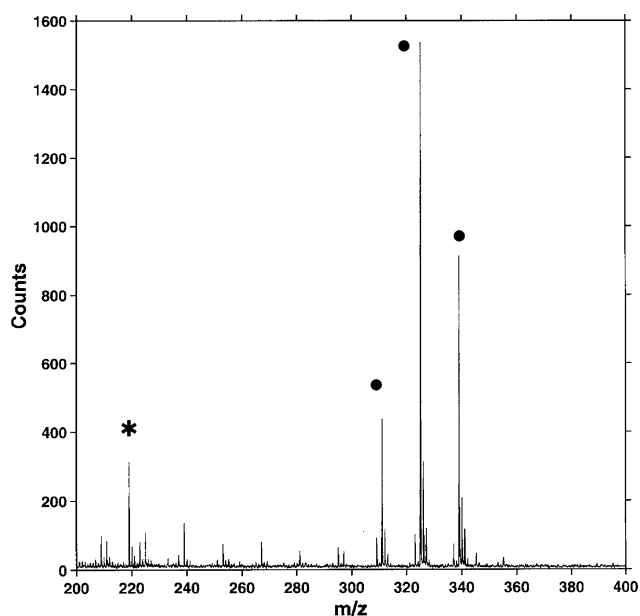


Fig. 3 ToF-SIMS negative ion spectrum of photo-oxidised scoured and degummed silk washed in aqueous solution of Synperonic N (*, NPA; ●, alkylbenzene sulphonate)

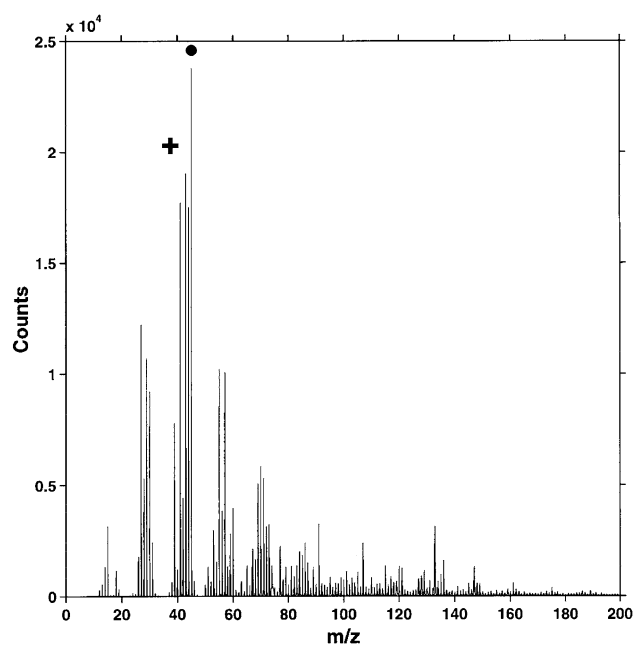


Fig. 4 ToF-SIMS positive ion spectrum of scoured & degummed silk washed in aqueous solution of Synperonic N (+, alanine, $m/z = 44^+$; ●, $\text{HOCH}_2\text{CH}_2^+$, $m/z = 45^+$)

Cleaning of silk in sodium dodecyl sulphate (SDS) solution

Cleaning of unexposed wool fabric in SDS solution alone again led to an obvious increase in the negative ion intensity in the ToF-SIMS spectrum at $m/z = 265^-$ ($\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$), 293^- ($\text{C}_{14}\text{H}_{29}\text{OSO}_3^-$), 321^- ($\text{C}_{16}\text{H}_{33}\text{OSO}_3^-$) and more particularly at $m/z = 349^-$ ($\text{C}_{18}\text{H}_{37}\text{OSO}_3^-$), Fig. 5. It is apparent that the more hydrophobic C18 alkyl sulphate derivative, which is only a minor component (less 1%) in the original SDS surfactant mixture, has a relatively stronger affinity for the silk fibre surface and is not easily removed by water rinsing. In previous studies, not using surface analytical techniques, it has also been proposed that the longer chain, more hydrophobic alkyl sulphates have greater substantivity for the wool fibre [17–19].

Treatment of the photo-oxidised silk with the SDS solution again produced an increase in ion intensity at $m/z = 265^-$ and 349^- in the ToF-SIMS spectrum, Fig. 6. Although the relative adsorption of the C18 derivative was comparatively less, due to the increased hydrophilic nature of the irradiated fibre surface altering fibre/surfactant substantivity.

Cleaning of silk in Synperonic N8 and sodium dodecyl sulphate (SDS) solution

The use of anionic detergents for cleaning historical artefacts is common in North America [4]. In contrast in

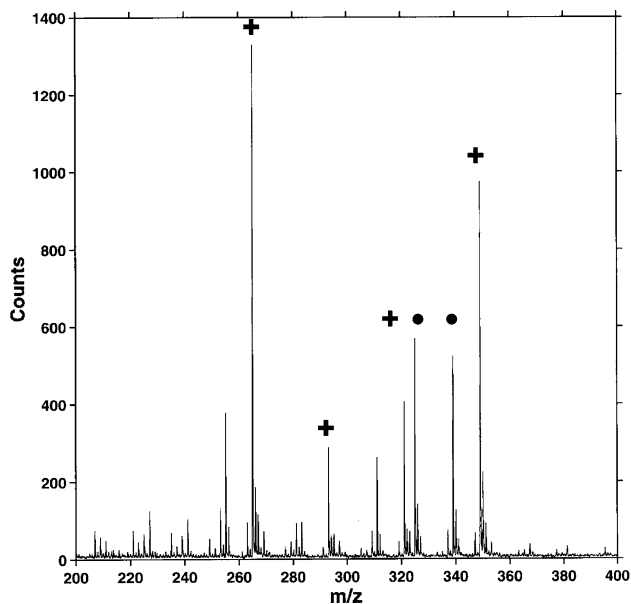


Fig. 5 ToF-SIMS negative ion spectrum of silk washed in an aqueous solution of sodium dodecyl sulphate (+, alkyl sulphate; •, alkylbenzene sulphonate)

Europe the major cleaning protocol utilises non-ionic surfactants alone or non-ionic surfactants in combination with sodium dodecyl sulphate [2, 3]. Cleaning of unexposed silk in an NPEO/SDS solution produces an obvious change in the ToF-SIMS negative ion spectrum. The major larger molecular species is the $C_{12}H_{25}OSO_3^-$ ion, $m/z = 265^-$, though other alkyl sulphate components are still evident.

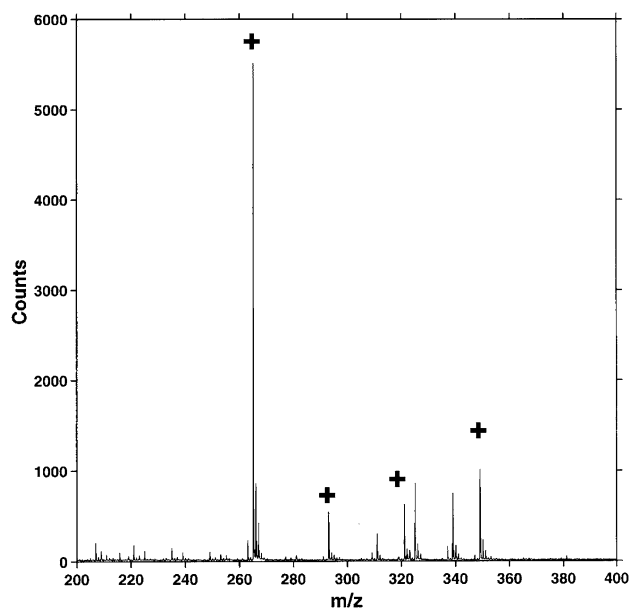


Fig. 6 ToF-SIMS negative ion spectrum of photo-oxidised silk washed in an aqueous solution of sodium dodecyl sulphate (+, alkyl sulphate)

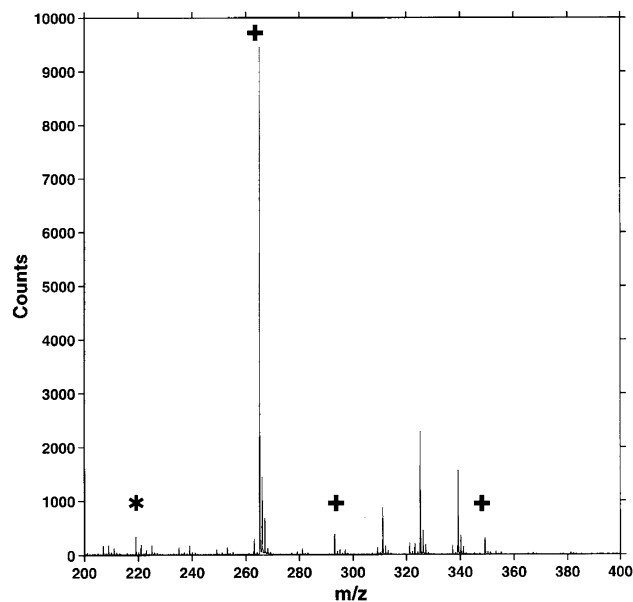


Fig. 7 ToF-SIMS negative ion spectrum of photo-oxidised silk washed in an aqueous solution of Synperonic N8 and sodium dodecyl sulphate (+, alkyl sulphate; *, NPA)

Similarly for the SDS/NPEO cleaning of the photo-oxidised wool the SDS specific signal at, $m/z = 265^-$, dominates the negative ion spectrum, Fig. 7. However, for the combination treatment the enrichment of the longer alkyl chain derivative, $C_{18}H_{37}OSO_3^-$, $m/z = 349^-$, is again less obvious for both the unexposed and photo-oxidised surfaces.

In the washing of the silk with Synperonic N8 solution deionised water was used, which may have the effect of suppressing ionisation of longer chain ethoxylated species, therefore necessitating the monitoring of the surfactant adsorption through the $HOCH_2CH_2^+$ ion. However when washing with SDS present the sodioated surfactant complex is favoured and examination of the positive ion ToF-SIMS spectra of the washed silks shows the characteristic NPEO/ Na^+ series at $m/z = 375^+$, 419^+ , 463^+ , 507^+ , 551^+ , 595^+ , respectively, Fig. 8. Again the surfactant ion intensity in the ToF-SIMS spectra of the photo-oxidised silk was greater than the unirradiated sample.

Examination of the unaged and aged silk samples washed in NPEO/SDS also reveals the presence of obvious signals at $m/z = 219^-$ attributable to the nonylphenoxide anion species.

Cleaning of silk in Synperonic A7 (AEO) solutions

The replacement of Synperonic N8 surfactant systems has focused on the Synperonic A7 alternative, which is based on an ethoxylated (EO) C_{12} – C_{14} aliphatic alcohol with an average EO number of 7. Examination of the ToF-SIMS

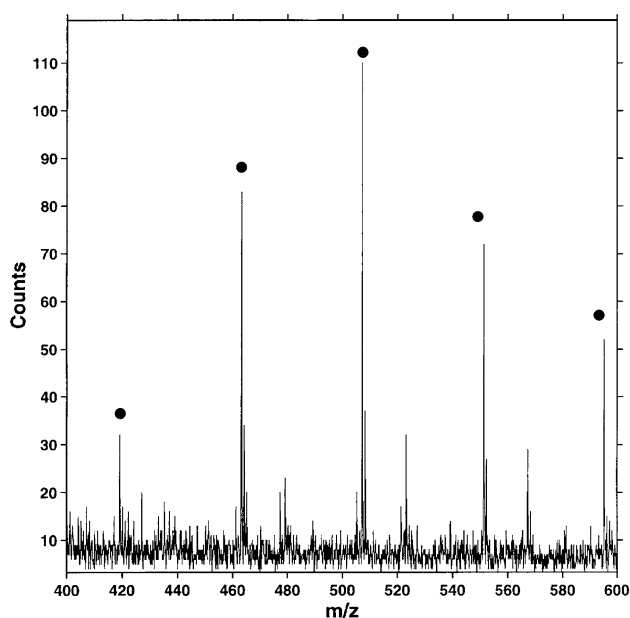


Fig. 8 ToF-SIMS positive ion spectrum of photo-oxidised silk washed in an aqueous solution of Synperonic N8 and sodium dodecyl sulphate (•, NPEO/Na⁺)

positive ion spectra of the silk fabric washed in the Synperonic A7 solutions indicates the presence of low intensity larger mass molecular fingerprint signals, which are characteristic of the molecular ions of the non-fragmented aliphatic alcohol ethoxylates. More obviously taking the ethoxylate derived ion HOCH₂CH₂⁺, $m/z = 45^+$, as a sensitive indicator of low level ethoxylate adsorption, it is evident that adsorption of the non-ionic surfactant occurs at both undegraded and artificially aged silk surfaces, with the photo-oxidised having the relatively greater intensity.

Examination of the negative ion ToF-SIMS spectra of the Synperonic A7/SDS washed silks indicates that similar adsorption behaviour as the Synperonic N/SDS treated silk fabrics has occurred. The C₁₂H₂₅OSO₃⁻, $m/z = 265^-$, species dominates the higher molecular mass range, but with the C₁₈H₃₇OSO₃⁻, $m/z = 349^-$, ion showing enhanced spectral intensity on the undegraded fibre surface due to its relatively higher surface substantivity for the unirradiated fibre surface. In contrast on the photo-oxidised fibre surface the adsorption of the C18 derivative, relative to the main C12 species, is relatively lower and is probably again a reflection of the hydrophilic nature of the photodegraded silk fibre affecting surfactant substantivity.

Conclusions

The surface of the silk fibre has been successfully studied using the surface selective ToF-SIMS technique, and has

identified characteristic amino acids at the protein fibre surface and the presence of residual scouring agents. Exposure of the silk to simulated sunlight had little effect on the ToF-SIMS spectrum associated with the amino acids.

The standard conservation cleaning procedures deposit both non-ionic and anionic surfactants on undegraded and artificially aged silk fibre surfaces, with greater levels of adsorption occurring on the photodegraded fibre surface.

Although only short chain NPEO molecular species were detected, and then only at low intensity, the HOCH₂CH₂⁺ ion derived from the ethoxymer chain can be used as a sensitive indicator of NPEO and AEO adsorbed on the fibre surface. In general ToF-SIMS indicates that greater levels of the anionic alkyl sulphates surfactants were adsorbed onto the fibre surface, with the more hydrophobic, longer chain C18 derivative being preferentially adsorbed onto the fibre surface.

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