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Surface chemical investigation into the cleaning procedures of ancient tapestry materials. Part 1

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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 wool-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 residues adsorption established. © *2004 Kluwer Academic Publishers*

1. 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 tapestries 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 a previous publication [1].

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 [2, 3]. 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 [4].

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. Therefore this study has been undertaken to evaluate the nature of the adsorption of surfactants onto undegraded and artificially aged wool fibre surfaces and establish the presence, or otherwise, of surfactant residues. 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 previously demonstrated to effectively investigate fibre surface modifications and deposition of textile auxiliaries at the fibre surface interface [5, 6]. 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 [7].

In this study the effect of current conservation cleaning methods on "model" wool substrates is investigated and in particular the interaction and substantivity of surfactants with the fibre surface established. In subsequent studies the interactions of the cleaning surfactants

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with the other tapestry components, silk and metal threads (untarnished and corroded), will be reported.

2. Experimental

2.1. Materials

The commercially scoured wool botany serge fabric (220 g/m^2) was purchased from Whaleys, Bradford, UK. Prior to further use the fabric was extracted with excess acetone, 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.

2.2. Cleaning procedure

The pre-cleaned unexposed and photo-oxidised wool fabrics were soaked in either a solution of 1 g/l Synperonic N, 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 wool was soaked in the specified solution for 1 h at 20°C, with occasional gentle agitation, and a wool: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.

2.3. Simulated sunlight exposure

The wool 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 50–150 lux, with an annual exposure period of approximately 3000 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.

2.4. ToF-SIMS analysis

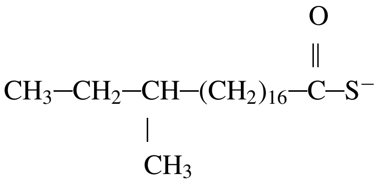
The ToF-SIMS spectra were obtained under *static* conditions using a PHI 7000 instrument with a reflectron analyser, a Cs$^+$ ion source (8 KeV, pulse length 1–25 ns) and a pulsed electron flood source (50–70 eV) for charge compensation. The operating pressure was less than 5.33 μPa (4×10^{-8} torr). 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 $m/z =$ 0–1000$^{+/-}$.

3. Results and discussion

The wool fibre is composed of an inner cortex and an outer cuticle [8]. The cuticle being further differentiated into distinct histological components: an inner endocuticle, an exocuticle and an outer epicuticle. The nature of this outer epicuticle, and even its existence, has been the subject of much discussion, but what is not disputed is the presence of lipids and protein in this surface region [8, 9]. The major lipid is 18-methyleicosanoic acid (18-MEA), which is covalently bound to the keratinous protein via a thioester linkage, though an ester-linked component is also present to a lesser extent [10, 11]. Other lipids, C_{16}–C_{20} fatty acids, are also present at the fibre surface, though the 18-MEA contributes approximately 50–60% to the surface layer [5]. Overall, however, the effect of these covalently bound lipids is to impart water repellency to the keratin fibres.

3.1. Effect of artificial ageing

The ToF-SIMS negative ion spectrum of untreated wool shows the characteristic 18-MEA thioester species at $m/z = 341^-$, Fig. 1. The other lipid species are listed in Table I.



$$\mathrm{CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}(CH_2)_{16}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}S^-}$$

18-Methyleicosanoic Thioester Ion

The effect of artificial sunlight, 404 h in the Xenotest 150S instrument, equivalent to 130 years light exposure in a museum environment, is to remove the 18-MEA surface lipid, Fig. 2. Previous "real" and "simulated" sunlight exposures to automotive upholstery standards" have observed a similar depletion of surface 18-MEA [12, 13]. Another surface chemical change occurring with photo-oxidised wool is the oxidative cleavage of the disulphide bond, giving rise to an anionically charged cysteic acid [14]. This coupled to increased wettability of the fibre will potentially alter the fibres adsorption character. In this case the photo-oxidised wool fabric wets instantaneously while the unexposed fabric remains unwetted after 600 s.

The ToF-SIMS negative ion spectrum of the photodegraded and unexposed wool fabric shows obvious signals at $m/z = 339^-, 325^-, 311^-$ and 297^-. While the latter three signals can be partly attributed to the uncleaved lipids, the $m/z = 339^-$ signal clearly indicates the

TABLE I Negative ion ToF-SIMS spectral assignments of surface lipids at wool fibre surface

Negative ions (A)	SIMS peak m/z
$C_{20}H_{41}COS^-$	341
$C_{20}H_{41}COO^-$	325
$C_{19}H_{39}COS^-$	327
$C_{19}H_{39}COO^-$	311
$C_{18}H_{37}COS^-$	313
$C_{17}H_{35}COS^-$	299
$C_{17}H_{35}COO^-$	283
$C_{17}H_{33}COS^-$	297[a]
$C_{17}H_{33}COO^-$	281
$C_{16}H_{33}COS^-$	285
$C_{16}H_{33}COO^-$	269
$C_{15}H_{31}COS^-$	271
$C_{20}H_{31}COO^-$	255

[a] $C_{18}H_{37}COO^-$ also occurs at $m/z = 297^-$.

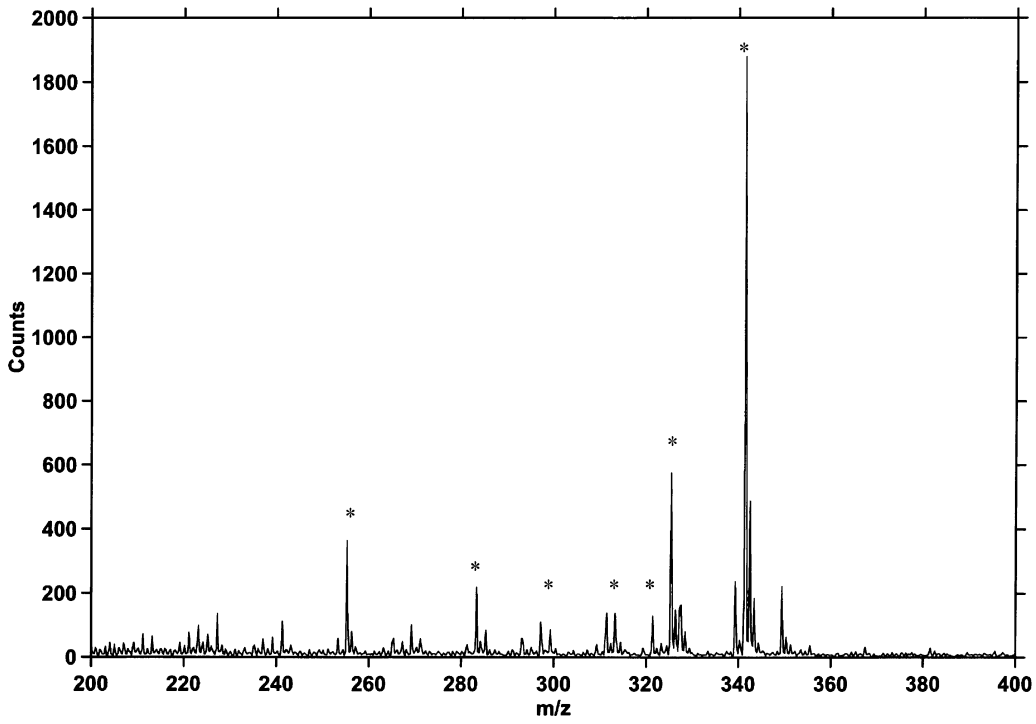


Figure 1 ToF-SIMS negative ion spectrum of untreated wool (*—Wool surface lipids).

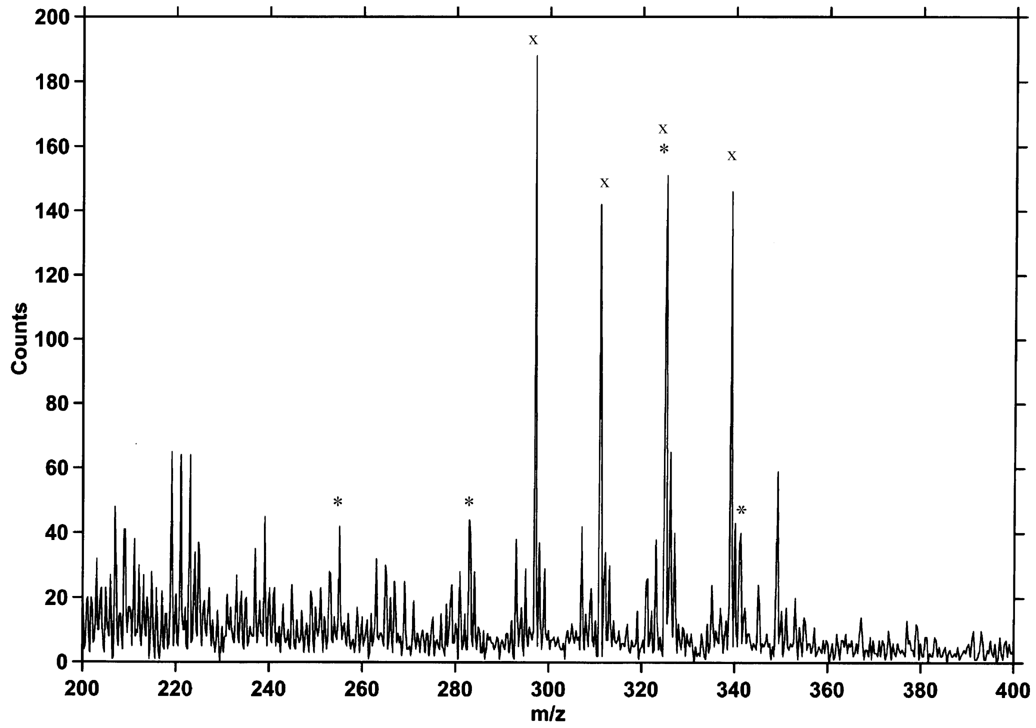
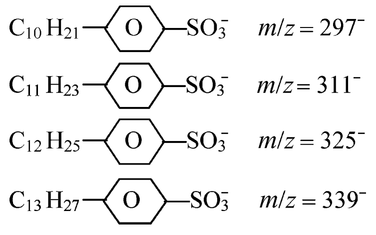


Figure 2 ToF-SIMS negative ion spectrum of photo-oxidised wool (*—Wool surface lipids, x—Linear alkylbenzene sulphonates (LAS)).

presence of residual linear alkylbenzene sulphonates surfactants derived from the commercial pre-scouring, Figs 1 and 2. The alkylbenzene sulphonate species are assigned:



The apparent high intensity of these signals may also be due to the photo-oxidation process revealing these sub-surface surfactant deposits.

3.2. Cleaning of wool in Synperonic N8 solution

Previous ToF-SIMS studies of nonylphenol ethoxylates (NPEO) treatments of textiles provided characteristic positive and negative ion mode spectra, with typically, the sodiated complex observed in the positive ion spectrum [5]. As the surfactant formulation is a

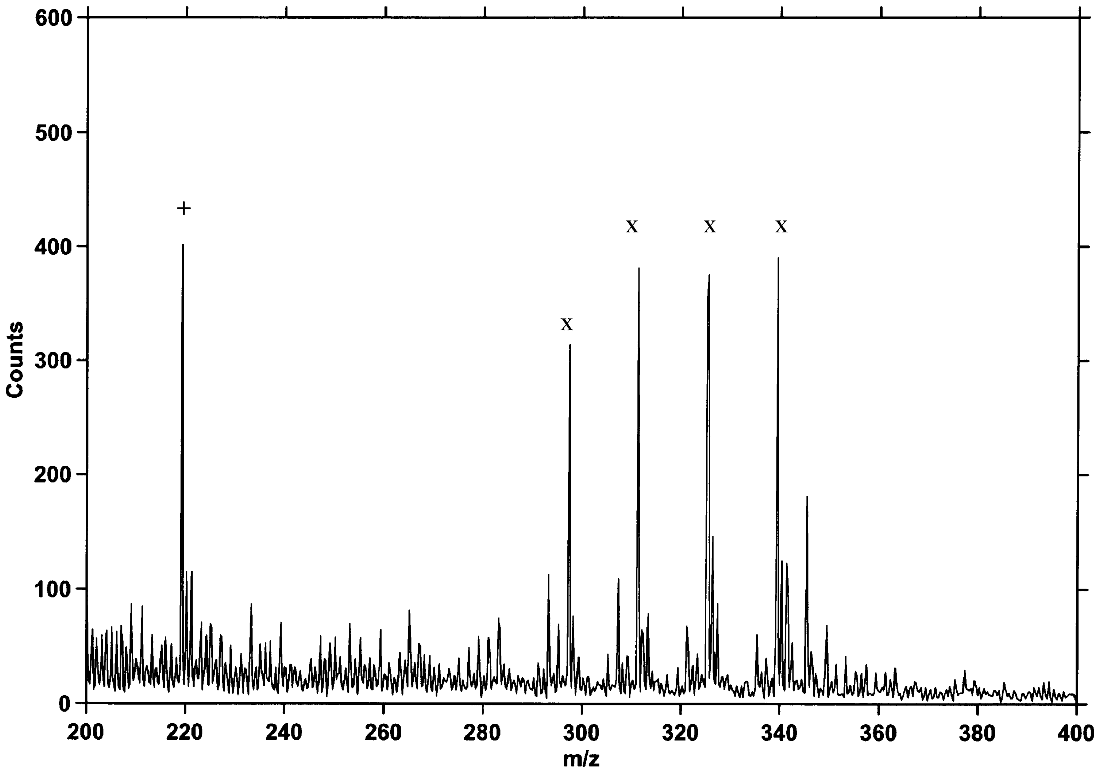
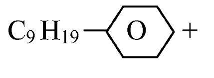


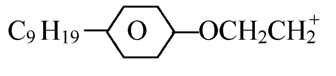
Figure 3 ToF-SIMS negative ion spectrum of photo-oxidised wool washed in aqueous solution of Synperonic N (+— NPE, x—LAS).

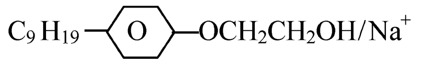
mixture of reaction products a characteristic ethoxymer distribution range is observed with the stated ethoxymer number being the average.

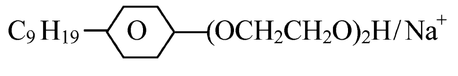
Examination of the ToF-SIMS spectrum of the unexposed wool cleaned in the Synperonic N solution showed little obvious evidence of residual nonylphenol ethoxylates at the fibre surface in either the positive ion or negative ion spectra. In contrast the negative ion spectrum of the cleaned photo-oxidised wool fabric showed the obvious presence of the nonylphenoxide anion species, (NPA), by detection of the signal at $m/z = 219^-$, Fig. 3. The non-ionic surfactant-based cleaning also appears to be ineffective in removing the residual anionic linear alkyl benzene sulphonates from the wool fibre surface.

In addition the positive ion spectrum also showed contrasting behaviour between the photo-oxidised and unexposed washed wool, Figs 4 and 5, where a much greater relative increase in the $HOCH_2CH_2^+$, at $m/z = 45^+$ (indicative of NPEO) is evident for the photo-oxidised sample. Larger molecular NPEO species can also be detected on the photo-oxidised fibre surface and characteristic signals are assigned:


$m/z = 203^+$


$m/z = 247^+$


$m/z = 287^+$


$m/z = 331^+$

Although only a low level of NPEO adsorption is indicated by the detection of low intensity signals of larger molecular ion species, it is apparent that the more hydrophobic shorter ethoxymer chain derivatives are preferentially binding to the fibre surface. In a previous study, the longer chain NPEO species were also observed, with the signal intensities associated with sodiated species greater [5]. However, in this study the aqueous treatment was performed using deionised water, which may suppress ionisation of longer chain ethoxylated species, and the treatment temperature was ambient rather than 60°C. Nevertheless it is apparent that photo-oxidation does appear to increase the adsorption of the non-ionic NPEO.

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].

It is apparent in this study that the $m/z = 45^+$ ion is a sensitive indicator of low levels of ethoxylate adsorption present at the fibre and may therefore provide an indication of ethoxylate adsorption and mixed surfactant system interactions.

Quantification of ToF-SIMS data can present difficulties due to the relatively high proportion of neutral secondary particles produced in comparison to positive and negative secondary ions. However, previous ToF-SIMS studies have successfully monitored the relative surface changes on a number of organic systems using the formula $I_A/(I_A + I_B)$, where I_A and I_B are measured intensities of ions A and B, respectively [5, 17–19]. For the calculations, I_A corresponds to the peak intensity of

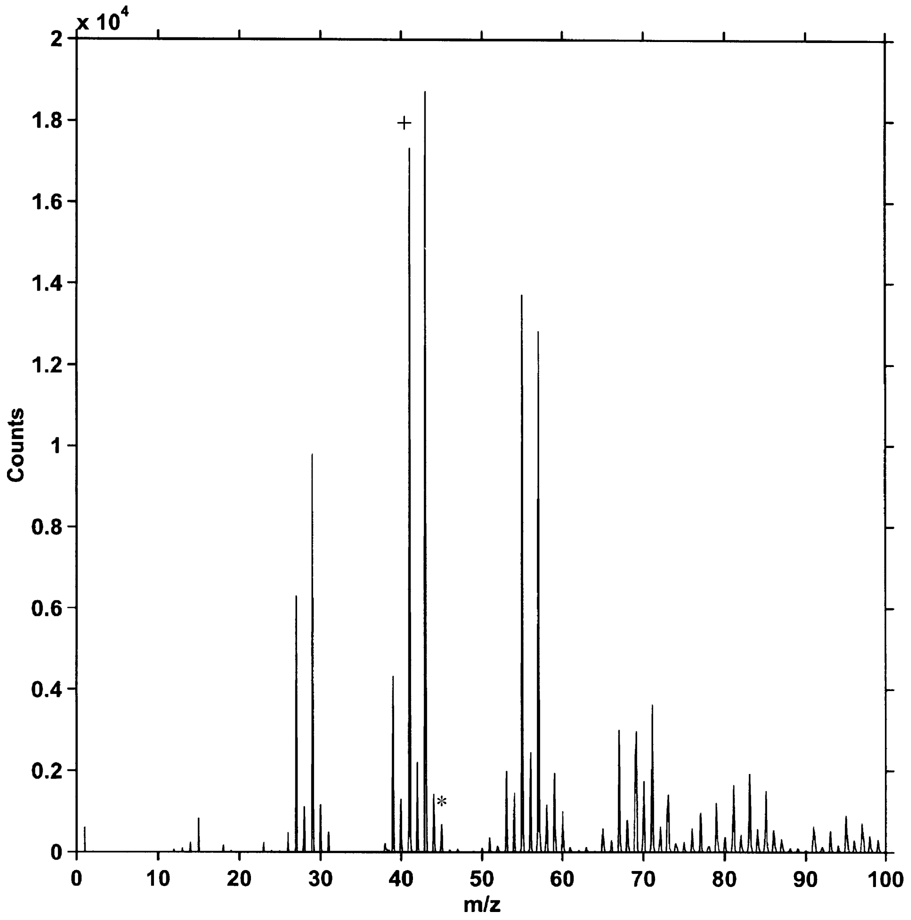


Figure 4 ToF-SIMS positive ion spectrum of untreated wool ($^{+}$—$C_3H_5^+$, $m/z = 41^+$, *—$HOCH_2CH_2^+$, $m/z = 45^+$).

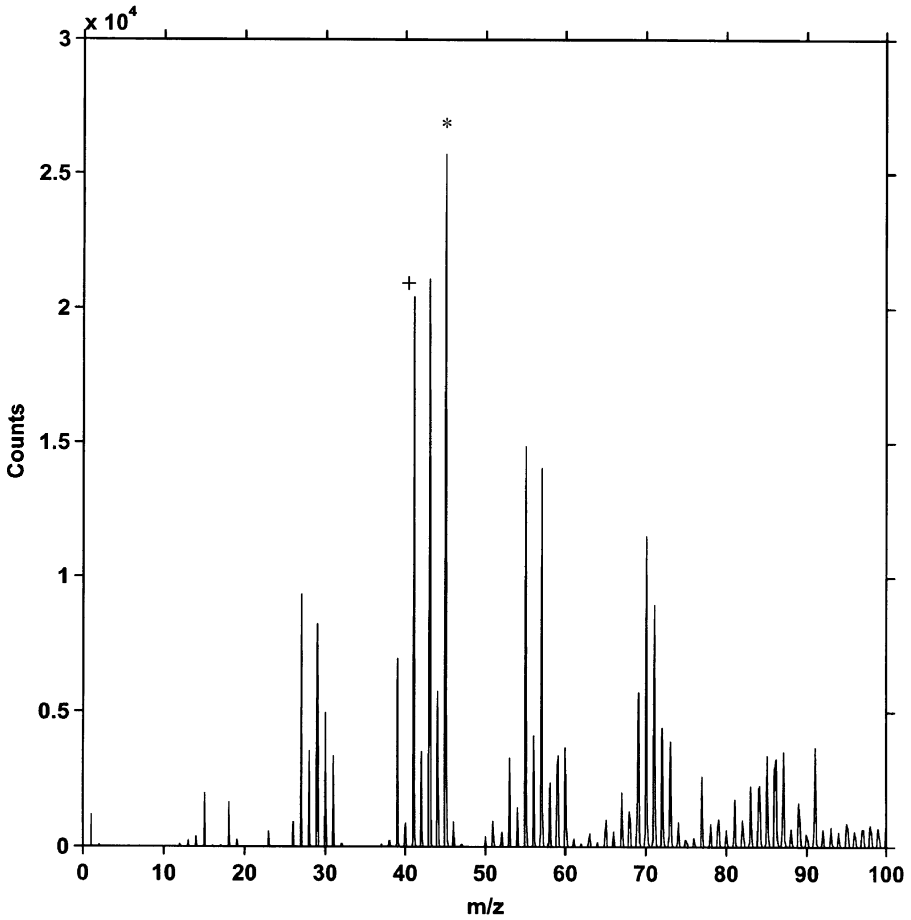


Figure 5 ToF-SIMS positive ion spectrum of photo-oxidised wool washed in an aqueous solution of Synperonic N ($^{+}$—$m/z = 41^+$, *—$m/z = 45^+$).

the $m/z = 45^+$ ion and I_B to the peak intensity of the signal at $m/z = 41^+$ ($C_3H_5^+$), a non-specific ion characteristic of organic surfaces. Analysis of the cleaned wool under identical conditions showed the photo-oxidised wool had a greater level of ethoxylated surfactant on the fibre surface. As an alternative method of monitoring the surface ethoxymer concentration, the ratio of I_A/Total Ion Intensity was also calculated, and again the same relationship was observed with surface ion intensity, indicated by the signal at $m/z = 45^+$, increasing with fibre oxidation.

3.3. Cleaning of wool 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 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 wool in an NPEO/SDS solution produces an obvious change in the ToF-SIMS negative ion spectrum, Fig. 6. The major larger molecular species is the $C_{12}H_{25}OSO_3^-$ ion, $m/z = 265^-$, though other alkyl sulphate components are evident:

$C_{14}H_{24}OSO_3^-$ $m/z = 293^-$
$C_{16}H_{33}OSO_3^-$ $m/z = 321^-$
$C_{18}H_{37}OSO_3^-$ $m/z = 349^-$

ToF-SIMS negative ion analysis of the original SDS detergent film, 2% solution dried on clean aluminium film, indicated that although SDS is by far the largest component, the longer chain species are also present. Using the I_A/I_{TOTAL} equation the surface analyses of the SDS film indicate that the SDS component contributes approximately 97% to the total alkyl sulphate intensity which correlates well with the bulk analyses of above 90% SDS. However it is apparent that the relative proportion of the C_{18} component on the fibre surface is much higher than that observed with the SDS film (0.9% of total alkyl sulphate ion intensity), suggesting the more hydrophobic long chain C_{18} derivative is being preferentially adsorbed onto the fibre surface.

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, the enrichment of the longer alkyl chain derivative, $C_{18}H_{37}OSO_3^-$, $m/z = 349^-$, is less obvious.

Examination of the photo-oxidised wool washed in NPEO/SDS reveals no obvious signal at $m/z = 219^-$ attributable to the nonylphenoxide anion species, Fig. 7. This qualitative observation is supported by the semi-quantitative analysis based on the sensitive $HOCH_2CH_2^+$ ion, $m/z = 45^+$, where again less signal intensity is evident for the ethoxylated species. This reduction in apparent adsorption by the NPEO is probably due to competitive displacement by the SDS.

3.4. Cleaning of wool 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 $m/z = 265^-$ and more particularly at $m/z = 349^-$, Fig. 8. It

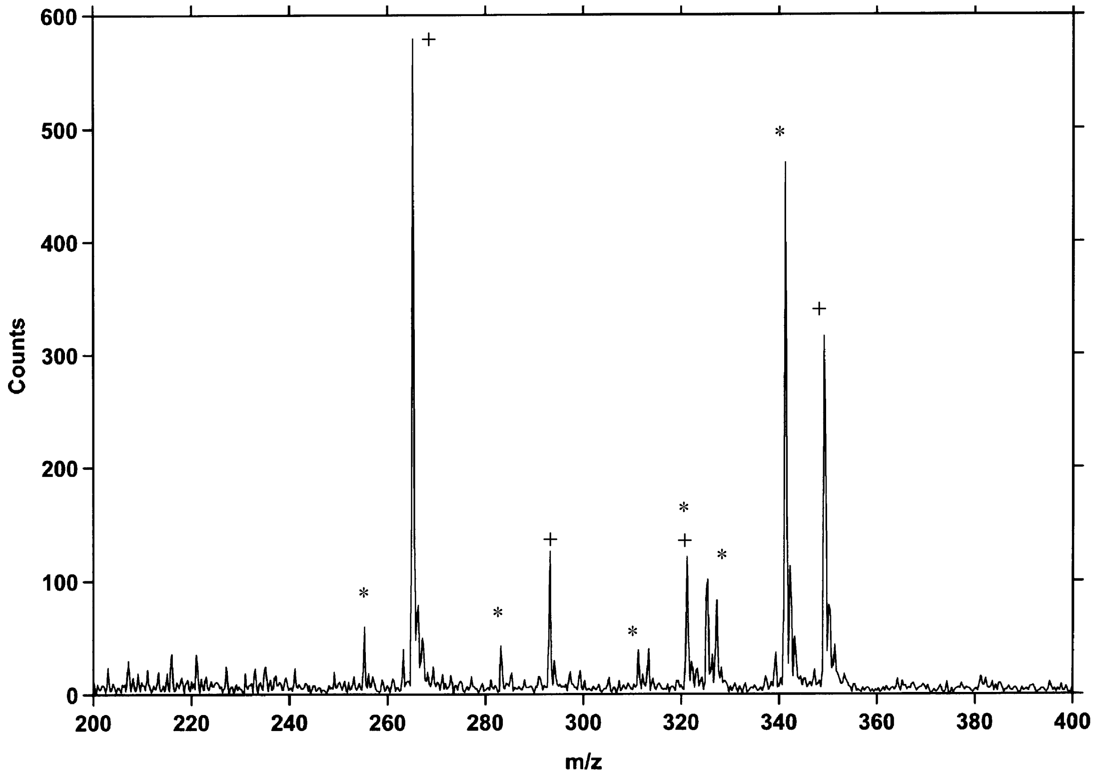


Figure 6 ToF-SIMS negative ion spectrum of untreated wool washed in an aqueous solution of Synperonic N and SDS (+—Alkyl sulphate, *—Wool lipid).

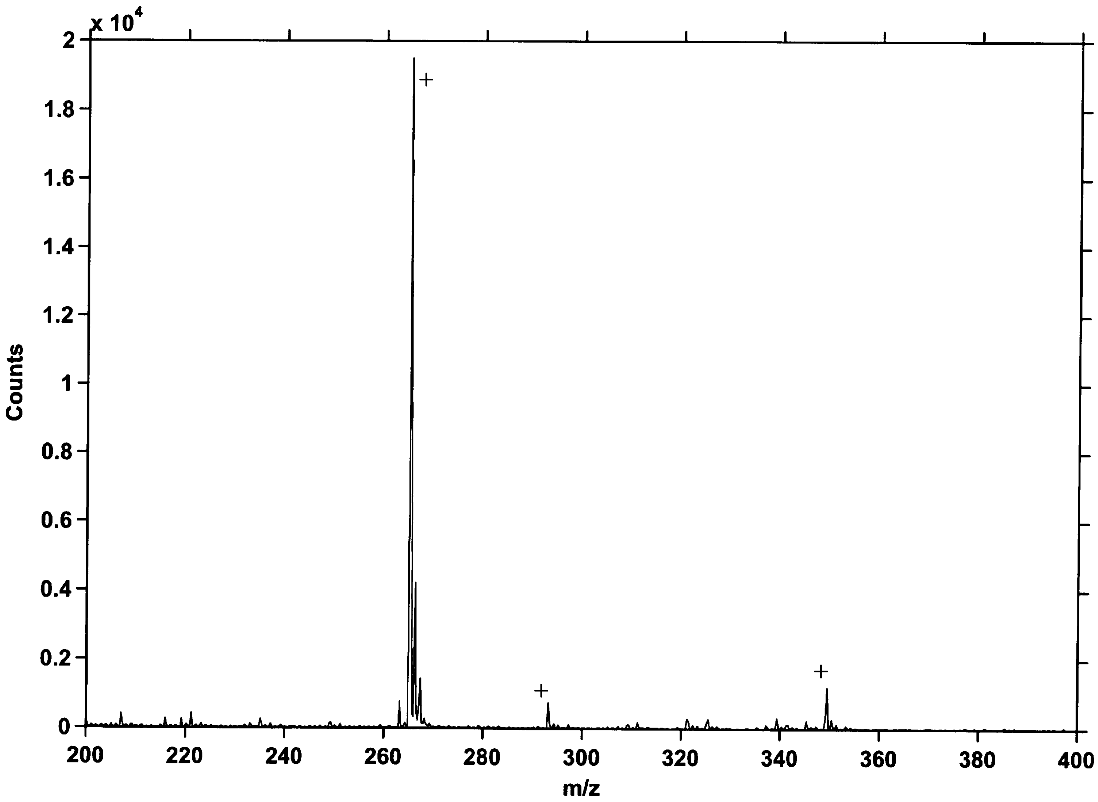


Figure 7 ToF-SIMS negative ion spectrum of photo-oxidised wool washed in an aqueous solution of Synperonic N and SDS (+—Alkyl sulphate).

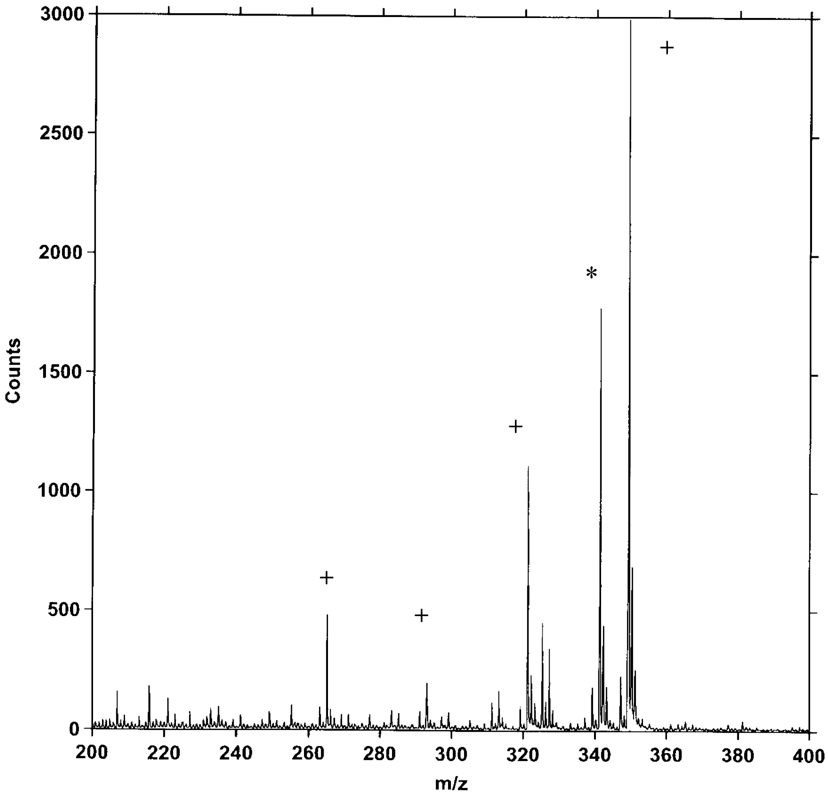


Figure 8 ToF-SIMS negative ion spectrum of untreated wool washed in an aqueous solution of sodium dodecyl sulphate (+—Alkyl sulphate, *—Lipid).

is apparent that the more hydrophobic C18 alkyl sulphate derivative has a relatively stronger affinity for the hydrophobic, lipid-rich wool 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 [20–22].

Treatment of the photo-oxidised wool with the SDS solution again produced an increase in ion intensity at $m/z = 265^-$ and 349^- in the ToF-SIMS spectrum, although again the relative adsorption of the

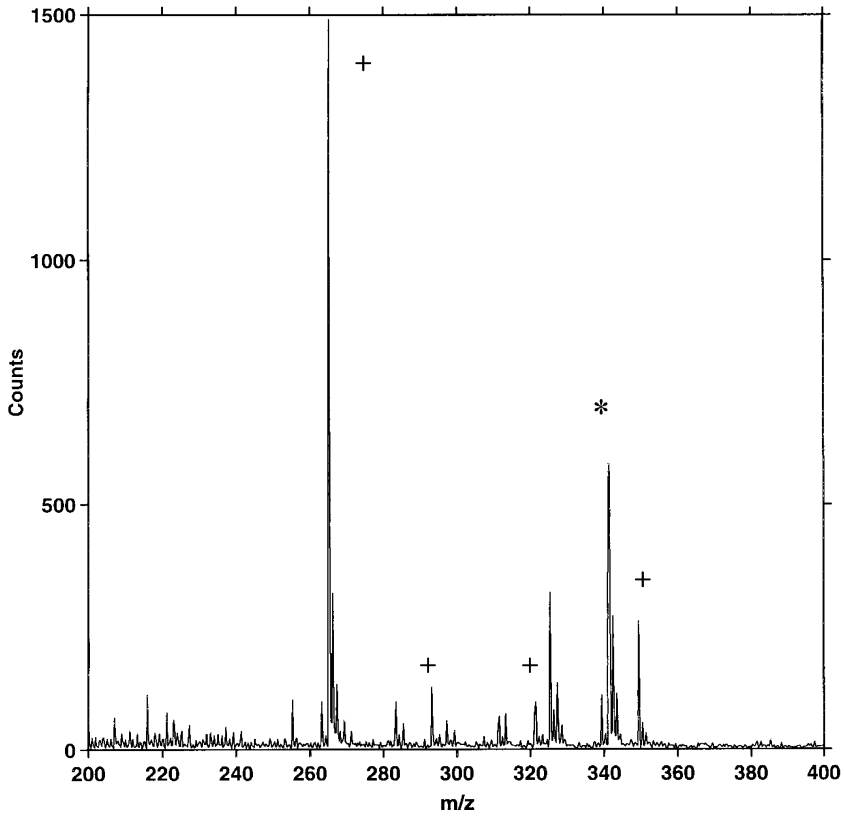


Figure 9 ToF-SIMS negative ion spectrum of untreated wool washed in an aqueous solution of Synperonic A7 and sodium dodecyl sulphate ($^+$—Alkyl sulphate, *—Lipid).

C18 derivative was comparatively less due to the hydrophilic nature of the irradiated fibre surface altering fibre/surfactant substantivity.

3.5. Cleaning of wool 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 positive and negative ion spectra of the wool fabric washed in the Synperonic A7 solutions indicates no obvious larger mass fingerprint signals, which can be assigned to the molecular ions of the non-fragmented aliphatic alcohol ethoxylates. Nevertheless by using the ethoxylate derived ion $HOCH_2CH_2^+$, $m/z = 45^+$, 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 wool surfaces.

The effect of combining the anionic SDS detergent with the Synperonic A7 is again a reduction in the intensity of the $m/z = 45^+$ ion. The magnitude of the reduction suggesting that competitive displacement at both the unexposed and photo-oxidised fibre surfaces rather than just a dilution effect is responsible.

Examination of the negative ion ToF-SIMS spectra of the Synperonic A7/SDS washed wools indicates that similar adsorption behaviour as the Synperonic N/SDS treated wool fabrics has occurred. The $C_{12}H_{25}OSO_3^-$, $m/z = 265^-$, species dominates the higher molecular mass range, but with the $C_{18}H_{37}OSO_3^-$, $m/z = 349^-$, ion showing enhanced spectral intensity on the undegraded fibre surface due to its relatively higher surface substantivity for the unirradiated, intact hydrophobic fibre surface, Fig. 9. 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 wool fibre affecting surfactant substantivity.

4. Conclusions

The surface of the wool fibre has been successfully studied using the surface selective ToF-SIMS technique, and has identified the lipids covalently bound to the protein fibre and residual scouring agents. The effect of simulated sunlight is to remove these hydrophobic lipids, in particular the 18-MEA bound via a thioester linkage, to create a hydrophilic surface.

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

Although only short chain NPEO molecular species were detected, and then only at low intensity, the $HOCH_2CH_2^+$ 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. This effect was more obvious with the intact hydrophobic unexposed wool fibre surface.

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