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Secondary ion mass spectrometric investigation of penetration of coconut and mineral oils into human hair fibers: Relevance to hair damage

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Synopsis

An attempt has been made to show the difference in the penetrability of coconut oil and mineral oil in human hair. We have used secondary ion mass spectrometry (SIMS) in combination with a time-of-flight (TOF) mass spectrometer. Characteristic ions formed by the pure components when bombarded with gallium ions have been identified with their m/z values. The distribution of the ion, characteristic of the particular treatment, has been established in the cross sections of hair treated with coconut and mineral oils. The results show that coconut oil penetrates the hair shaft while mineral oil does not. The difference may be due to the polarity of the coconut oil compared to the nonpolar nature of the mineral oil. The affinity of the penetrant to the protein seems to be the cause for this difference in their behavior. This study also indicates that the swelling of hair is limited by the presence oil. Since the process of swelling and deswelling of hair is one of the causes of hair damage by hygral fatigue, coconut oil, which is a better penetrant than mineral oil, may provide better protection from damage by hygral fatigue.

INTRODUCTION

In an earlier study (1) the beneficial effect of coconut oil used as a pre-wash conditioner was investigated. Use of coconut oil was found to significantly reduce cuticular damage during combing. This was attributed to the hydrophobicity of the oil, which reduced the swelling of the cuticle that otherwise would have damaged the scale structure, especially in wet grooming. The lubricating effect of the oil further contributed to the reduction in damage.

In Asian and African countries, vegetable oils are extensively used as hair dressings, and are known to reduce hair damage. Anecdotal accounts also suggest that the beneficial effects of oils accrue from the penetration of oils into hair and skin. Although conventional concepts of diffusion doubt the penetration of high-molecular-weight compounds such as polymeric conditioners (above a molecular weight of ~1000) beyond the cuticular sheath, claims have been made (2) to the contrary. However, in the case of coconut

oil, which is principally a lauric acid triglyceride, the molecular weight is likely to be well below 1000 Da and, therefore, diffusion into the hair is a distinct possibility. What has been lacking is a study involving diffusion of compounds as a function of molecular weight, and a reliable method of identifying them in the fiber, especially at low concentrations.

Recently, mineral oils have been promoted for use as hair dressings. Although the external effect of these oils is essentially one of lubricating the hair surface, their penetrability into the cortex of hair is likely to be different because of the differences in the polarity of the two materials, namely coconut and mineral oils.

This study attempts to demonstrate the penetration of coconut and mineral oils by mapping their presence in the hair fiber cross section. The technique used for this work is time-of-flight secondary ion mass spectrometry, TOF-SIMS for short (Figure 1).

The TOF-SIMS method makes use of the secondary ion mass spectra, which are obtained when the sample surface is bombarded with a positively charged gallium ion beam. The positive/negative ion mass spectra are obtained by the time-of-flight method. First, characteristic positive/negative ions (peaks) are isolated in the mass spectra of the pure materials, namely neat coconut and mineral oils (reference spectra) used for treatment. The observed characteristic positive/negative ions, which are unique for the pure compounds, are then traced/mapped in cross sections of untreated and oil-treated hair fibers.

EXPERIMENTAL

MATERIALS

Pure coconut oil (Parachute brand from Marico Industries Ltd., Mumbai, India) and mineral oils (viscosity ~ 1P) were used for this study. The hair sample was black Indian hair obtained from individuals who did not use coconut or mineral oils as hair dressings.

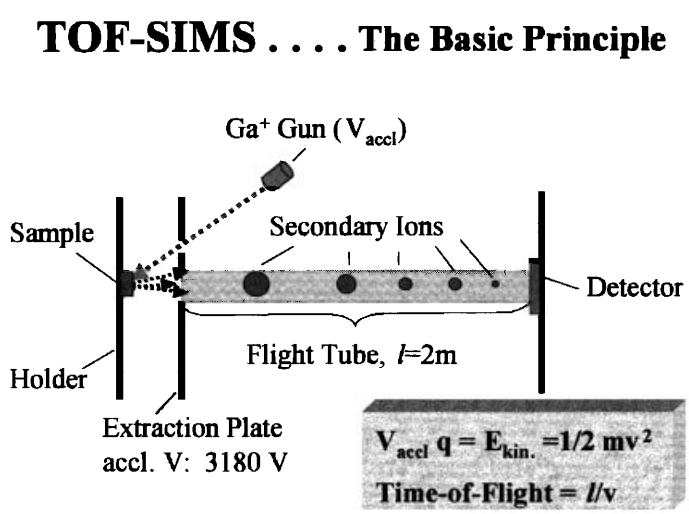

Figure 1. Schematic representation of the basic principle of TOF-SIMS.

HAIR TREATMENTS

The oils were used at a level of 0.2 ml/2.5–3 g tresses. The drops of oil were placed on hair swatches and were spread onto the hair fibers with a fine-tooth comb. The samples were stored overnight, and then the oil remaining on the surface was washed with a 20% solution of sodium laureth sulfate and the swatches were rinsed thoroughly, air-dried, and stored at room temperature. Control samples were treated in a similar way, except for treatment with the oils.

ANALYTICAL TECHNIQUE: CONCEPT AND BASIC PRINCIPAL

The gallium gun emits a pulsed primary ion beam (accelerating voltage of 25 kV). The primary ions impact/bombard the sample surface and ionize atomic species or small fragments of low- and high-molecular-weight molecules. These ionized species, referred to as secondary ions, are highly mobile and volatile, and become easily extracted by an extraction plate and propelled at high speed into a 2-m-long flight tube. A detector at the end of the flight tube detects and records the secondary ions as they arrive at the end of the tube. The velocity (kinetic energy) of the secondary ions depends on their mass:

$$E_{kin.} = \tfrac{1}{2}\, mv^2$$

The smaller the ionized species, the greater their velocity:

$$\text{Velocity} = (\text{length of the tube})/(\text{time-of-flight in the tube})$$

Typical primary ion doses used in this work were on the order of 10^{12} ions/cm^2 for the analysis. This assures that the data is collected within the static limit, i.e., less than 1% of a monolayer was sputtered. Thus, all molecular fragments are indicative of species existing on the surfaces (along the length and in the cross section of the fiber) under investigation prior to analysis. Under these conditions, the sampling depth of TOF SIMS is only ~1 monolayer for molecular fragment ions and 1–3 monolayers for atomic species. Since the sampling depth of TOF SIMS is only approximately one molecular layer, only the low-molecular-weight, highly mobile, surface-active components are detected.

The higher-molecular-weight compounds are more difficult, if not impossible, to ionize with the $^{69}Ga^+$ liquid metal ion gun. Therefore, one has to look at the low-molecular-weight fragments of the high-molecular-weight compounds. Detecting the fragments, in turn, is indicative of the presence of high-molecular-weight compounds.

Positive and negative mass spectra are plotted as the number of secondary ions detected (y-axis, counts) versus the mass-to-charge ratio of the ions (x-axis, m/z).

Instrumental conditions. The work was done at a local surface analytical laboratory, under contract. The specific analytical conditions and instrumentation used for this work are listed below in detail:

Instrumentation	Physical Electronics, PHI TFS-2000
Primary ion beam	$^{69}GA^+$ liquid metal ion beam
Primary beam voltage	25 kV
Primary ion current (DC)	600 pA
Nominal analysis region	$(80\ \mu m)^2$
Charge neutralization	yes
Post acceleration	8000 V
Masses blanked	None
Energy filter/Contrast diaphragm	no/no

SAMPLE PREPARATION FOR TOF-SIMS

Oils. Small amounts of the pure coconut and mineral oils were deposited on clean silicon wafers at ambient temperature to establish the characteristic positive and negative ions from the mass spectra of the oils for their mapping in the hair cross sections.

Untreated and oil-treated hair fibers. The untreated (control) and oil-treated hair fibers were cross-sectioned with a clean stainless steel blade and mounted in small holders with the cross sections facing the spectrometer.

OBTAINING ION MASS SPECTRA: ESTABLISHING CHARACTERISTIC POSITIVE/NEGATIVE IONS

Positive and negative static TOF SIMS mass spectra were acquired from several locations on each of the oils and from the "interior" cross-sectioned surface of the untreated and oil-treated fibers.

In this study, the raw spectra from the pure oils and the fiber "interior," that is, from the surface of the cross-sectioned untreated and oil-treated fibers, were collected and compared. This was done to establish the characteristic positive and negative ions of the pure oils, and to "spectrally" establish their absence or presence in the untreated (control) and oil-treated hair fibers. Since the goal of this study was to establish penetration of the oils into the fiber interior, special attention was directed to mapping the presence of these compounds within the fiber cross section.

RESULTS AND DISCUSSION

I. Penetration of Coconut Oil

ION MASS SPECTRA

Coconut oil on a silicon wafer. As the first step, the positive and negative characteristic ions of pure coconut oil, resulting from ion bombardment, have to be established. It is shown that the positive and negative TOF-SIMS spectra of coconut oil contain several characteristic ions that can serve as markers for the coconut oil within the hair fibers.

Characteristic positive ions of pure coconut oil. Characteristic positive ions are at 127, 155, 171, 183, 211, 257, 411, 439, and 467 m/z. The positive ion at 127 (126.67) m/z may be the best ion for the imaging of coconut oil, since it is intense and is likely to be free of mass interference. Figure 2 shows the mass spectra of the characteristic positive ions for coconut oil.

Characteristic negative ions of pure coconut oil. Characteristic negative ions of pure coconut oil are at 41, 58, 71, 143, 171, 199, and 227 m/z. The individual peaks have not been identified, but many are due to fatty acids such as lauric and oleic acids. Obviously, some of these may be resulting from mixed triglycerides present in minor quantities in coconut oil. Because the coconut oil forms strong positive ions, it tends to form weak negative ions. Therefore, the positive ion at 127 (126.67) m/z will be used for imaging coconut oil in the cross section of the hair fiber (see Figure 3 for the mass spectra of the negative ions for coconut oil).

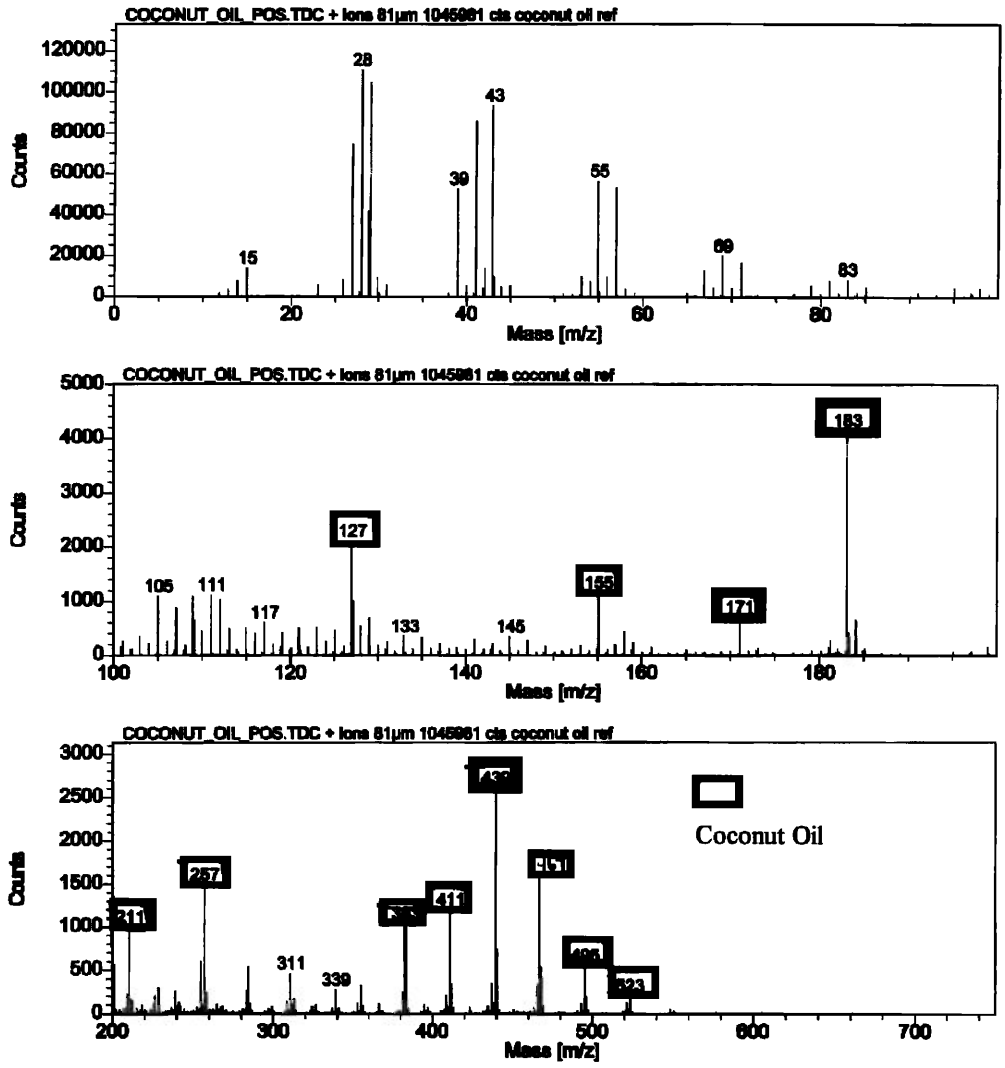

Figure 2. Spectra of positive ions of coconut oil deposited on a silicon wafer, including the highlighted characteristic positive ions of coconut oil.

Characteristic positive ions of untreated hair: controls for coconut-oil-treated hair. The TOF-SIMS spectra were obtained from the surface of the cross sections of untreated hair fibers. These spectra are very different from those obtained for the pure coconut oil. The spectra contain hydrocarbon and Na^+ peaks (Figure 4). The spectra do not contain any of the high-mass peaks observed in the coconut oil mass spectra.

Characteristic positive ions of coconut-oil-treated hair. The positive TOF-SIMS spectra were obtained from the surface of the cross sections of hair fibers treated with coconut oil. As can be clearly seen, these spectra of the coconut-oil-treated fibers have intense peaks at 127, 183, 257, 383, 411, 493, 467, and 495 m/z (Figure 5). These peaks match those of the coconut oil mass spectra, that is, these peaks are unique to the coconut oil. This comparison of the ion mass spectra suggests that coconut oil has indeed penetrated into

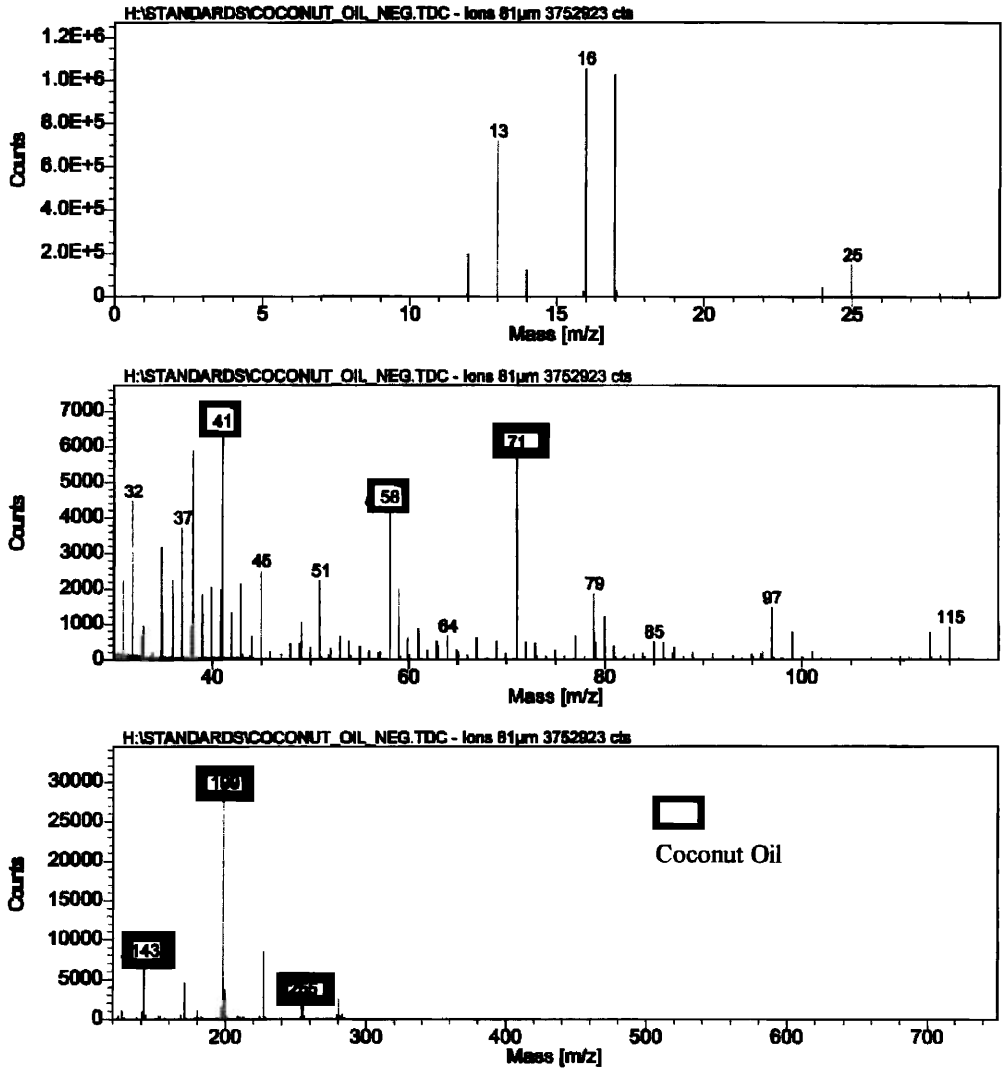

Figure 3. Spectra of negative ions of coconut oil deposited on a silicon wafer, including the highlighted characteristic negative ions of coconut oil.

the hair fiber interior. Mapping/imaging coconut oil in the fiber cross section via one of its unique ions (the positive ion at 127 (126.67) m/z) will confirm this conclusion.

TOF-SIMS IMAGING OF COCONUT OIL IN HAIR

The positive ion images at mass number 126.67 map the distribution of coconut oil in cross sections of an untreated control (Figure 6a) and coconut-oil-treated hair fibers (Figure 6b–d). The image of the untreated control hair fiber at mass number 126.67 in Figure 6a does not show much activity, suggesting essentially the absence of coconut oil.

However, ion images at the same mass number of the coconut-oil-treated hair fibers clearly show partial (Figure 6d) to complete (Figure 6b,c) penetration of the coconut oil into the bulk of the hair fiber. Figure 6d shows only partial and unsymmetrical pen-

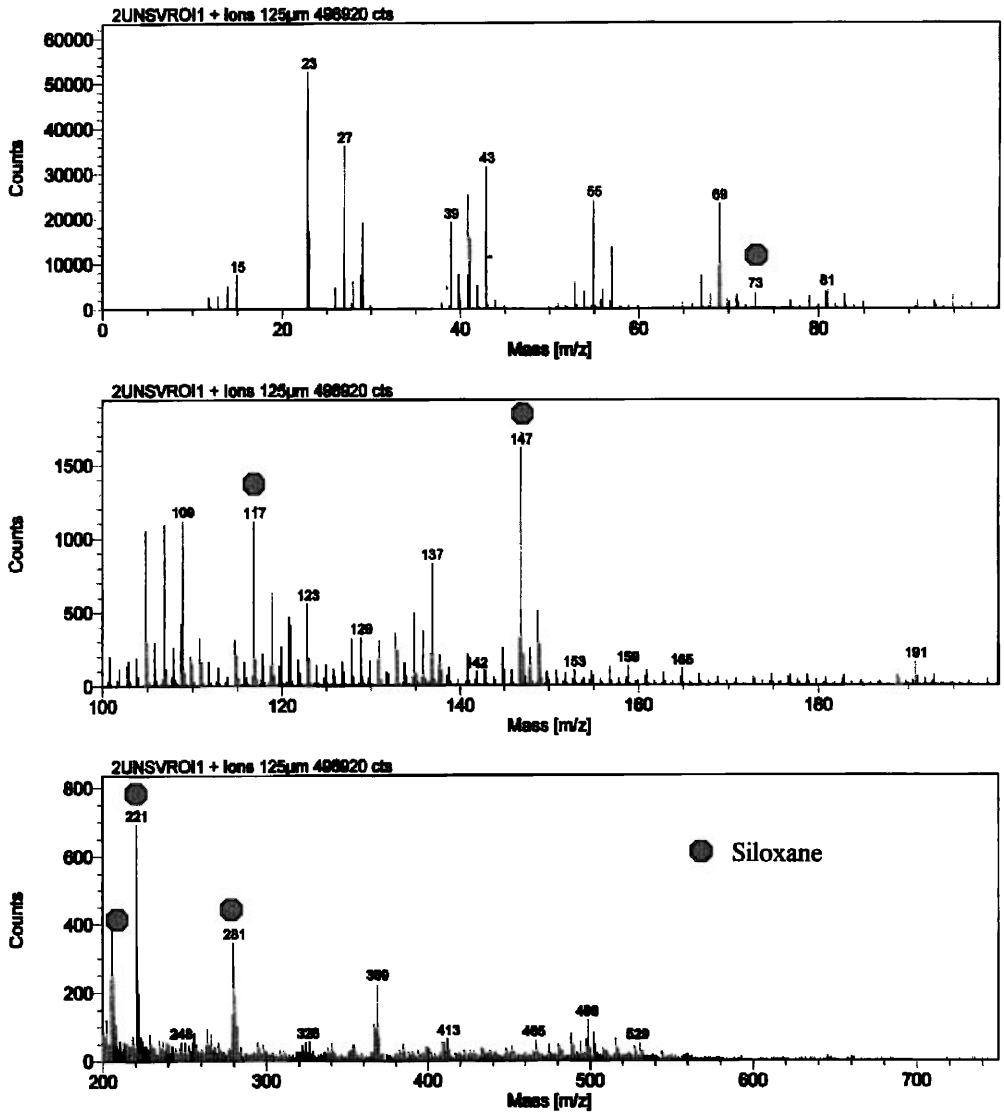

Figure 4. Spectra of positive ions found on the surface of cross sections of an untreated hair fiber (serving as control). No characteristic positive ions of coconut oil were detected within the interior of untreated hair.

etration of the oil. The oil has penetrated into the fiber center from one side, but is restricted to the periphery on the other side. Ion images of cross sections in Figures 6b,c show complete penetration of the coconut oil, even though penetration is non-uniform. There is more oil in the periphery than in the fiber center. The intensity of color reflects relative amounts, but does not give exact amounts. The exact quantification requires calibration with known quantities of oil in the hair. Even then it may not be exact, because penetration of the beam over the sample surface may be non-uniform. Therefore, this method can give information only on penetration and relative distribution patterns of materials, but not on the exact amounts present in a given fiber.

The same format was used to investigate penetration of mineral oil into the hair shaft.

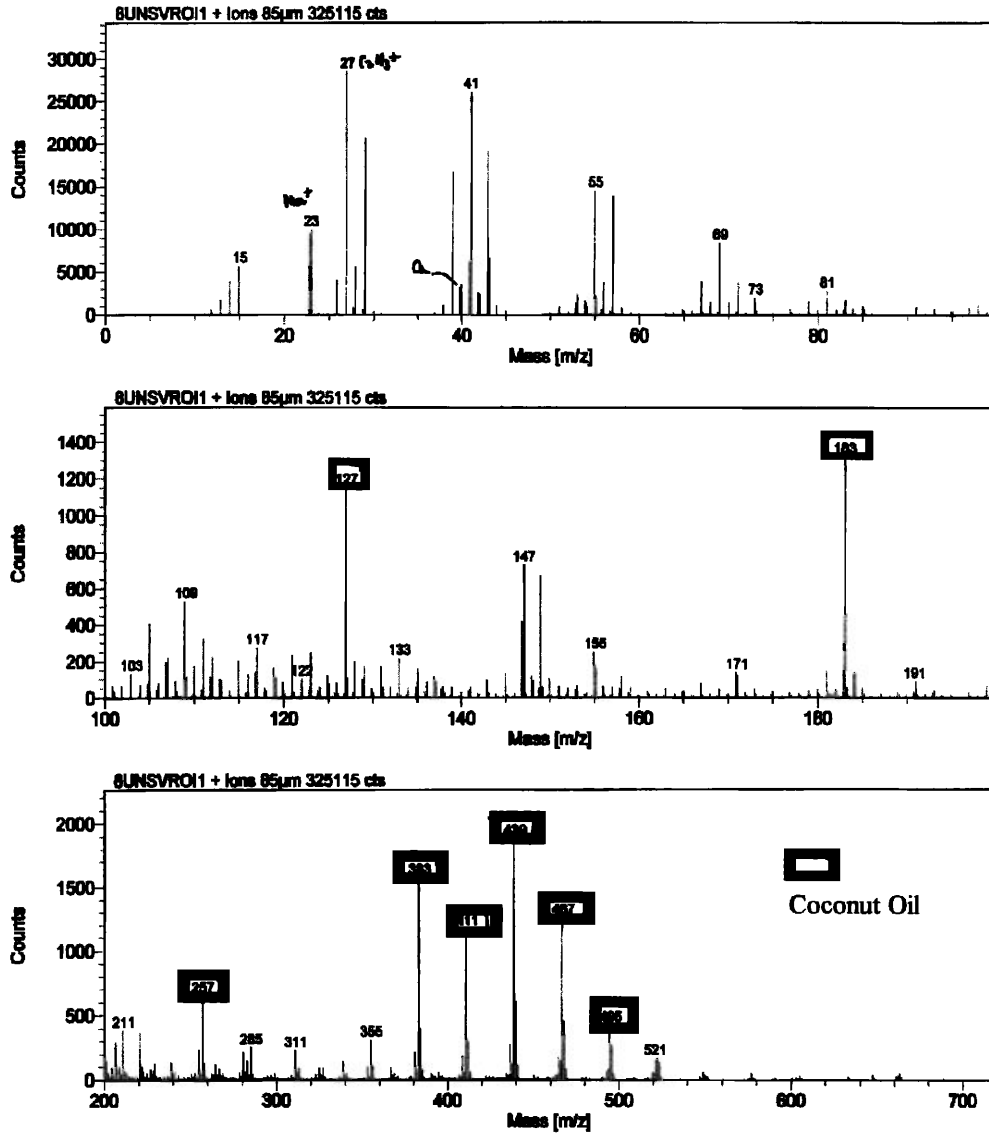

Figure 5. Spectra of positive ions from the surface of a cross section of coconut-oil-treated hair fibers. Clearly, a high count of (highlighted) positive ions characteristic of coconut oil was established within the interior of coconut-oil-treated hair fibers.

II. Penetration of Mineral Oil

ION MASS SPECTRA

Characteristic positive ions of pure mineral oil. The characteristic positive TOF-SIMS spectra are dominated by hydrocarbons that are not unique for mineral oil. However, a series of peaks with 14Da intervals were observed in the high-mass range of 300–400 m/z. These peaks can be used to map the mineral oil within the hair fiber, since these peaks are not found in the positive spectra of untreated hair. The positive ion at 361 (361.26) m/z will be used for imaging of mineral oil in the hair fiber (Figure 7a).

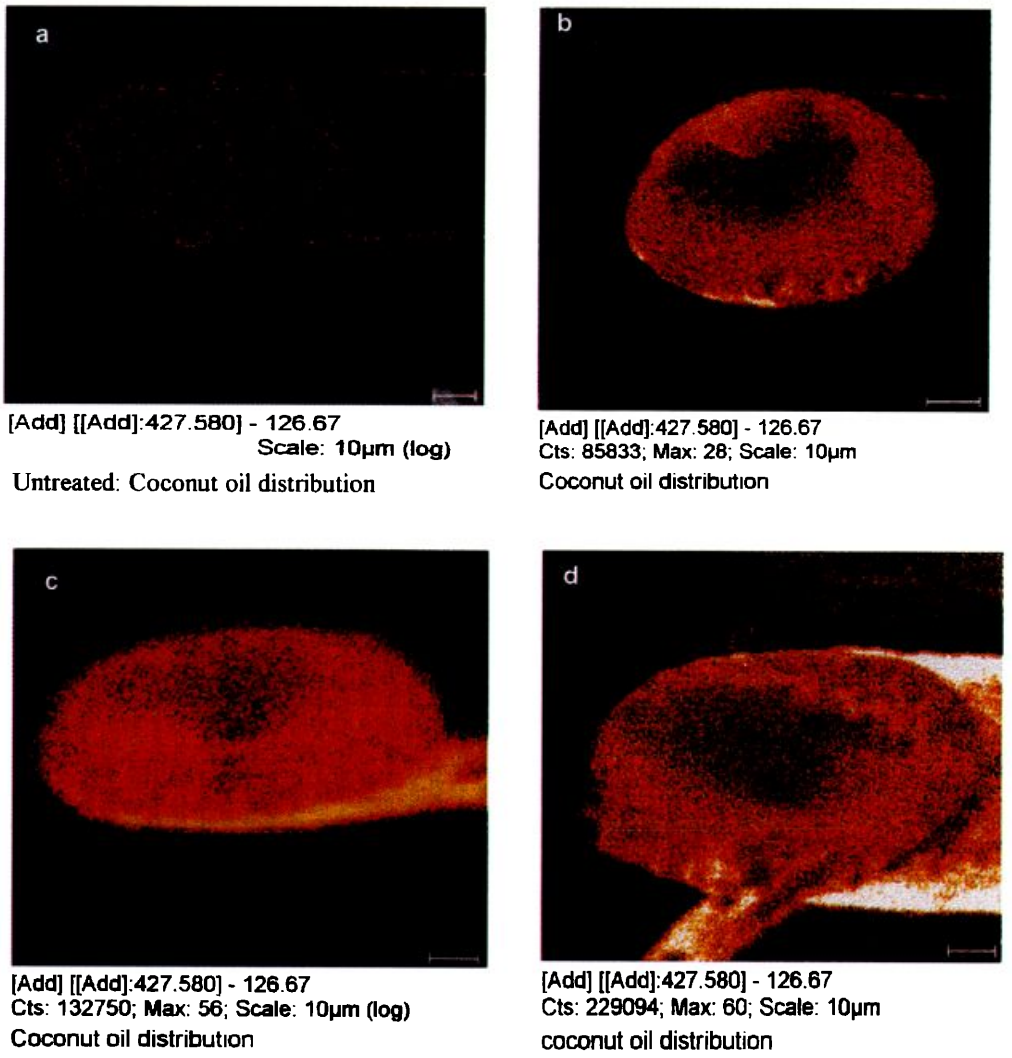

Figure 6. Imaging the presence of coconut oil at mass number 126.67 m/z (one of the characteristic positive ions of coconut oil) in the surface of (a) untreated and (b–d) coconut-oil-treated cross-sectioned hair fibers.

Characteristic negative ions of pure mineral oil. The negative spectra also contain a series of peaks with a 14Da interval in the mass range above 100 m/z. A representative negative ion mass spectrum of mineral oil is shown in Figure 7b.

Mass spectra of characteristic positive ions of untreated hair: controls for coconut-oil-treated hair. The TOF-SIMS spectra were obtained from the surface of the cross sections of untreated hair fibers and showed no peaks corresponding to the mineral oil. The spectra were dominated by hydrocarbon and sodium peaks and showed contamination from coconut oil and polydimethysiloxane (Figure 8). The spectra do not contain any of the high-mass peaks observed in the coconut oil mass spectra.

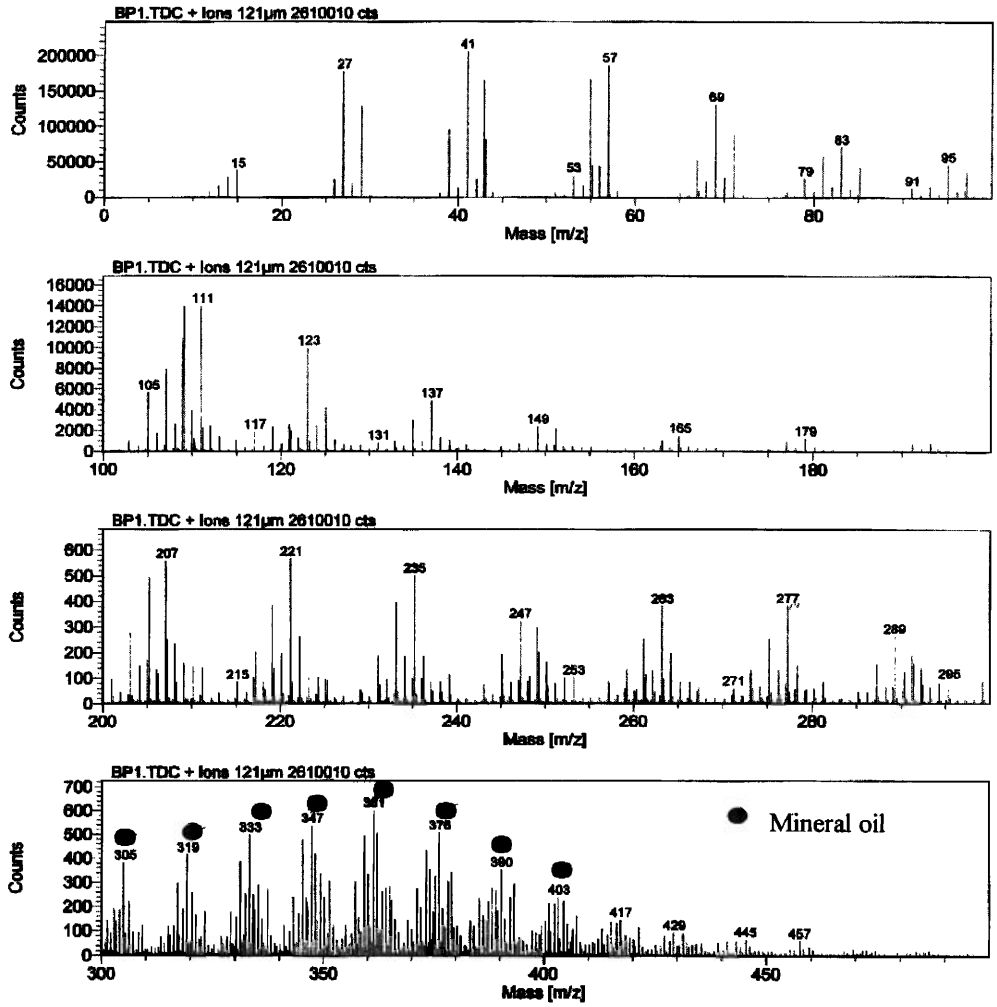

Figure 7a. Spectra of positive ions of mineral oil deposited on a silicon wafer, including characteristic positive ions of mineral oil.

Characteristic positive ions of mineral-oil-treated hair. The positive spectra obtained from the surface of the cross sections of hair fibers treated with mineral oil are similar to the spectra of the untreated hair (Figure 9). No mineral oil was detected in the treated hair. However, coconut oil and polydimethylsiloxane peaks were observed in the high-mass range, similar to observations made for the untreated hair fiber. This indicates that these hair fibers had been exposed to coconut oil as well as silicones and surfactants.

TOF-SIMS IMAGING OF MINERAL OIL IN HAIR BY CHARACTERISTIC POSITIVE IONS

The positive ion at mass number 361.26 is unique to mineral oil, and was used to map its distribution in cross sections of untreated and mineral-oil-treated hair fibers (Figure 10a,b). The image of the untreated hair fiber (Figure 10a) shows essentially nothing. For the mineral-oil-treated fiber cross section, there is a slight increase in the number of

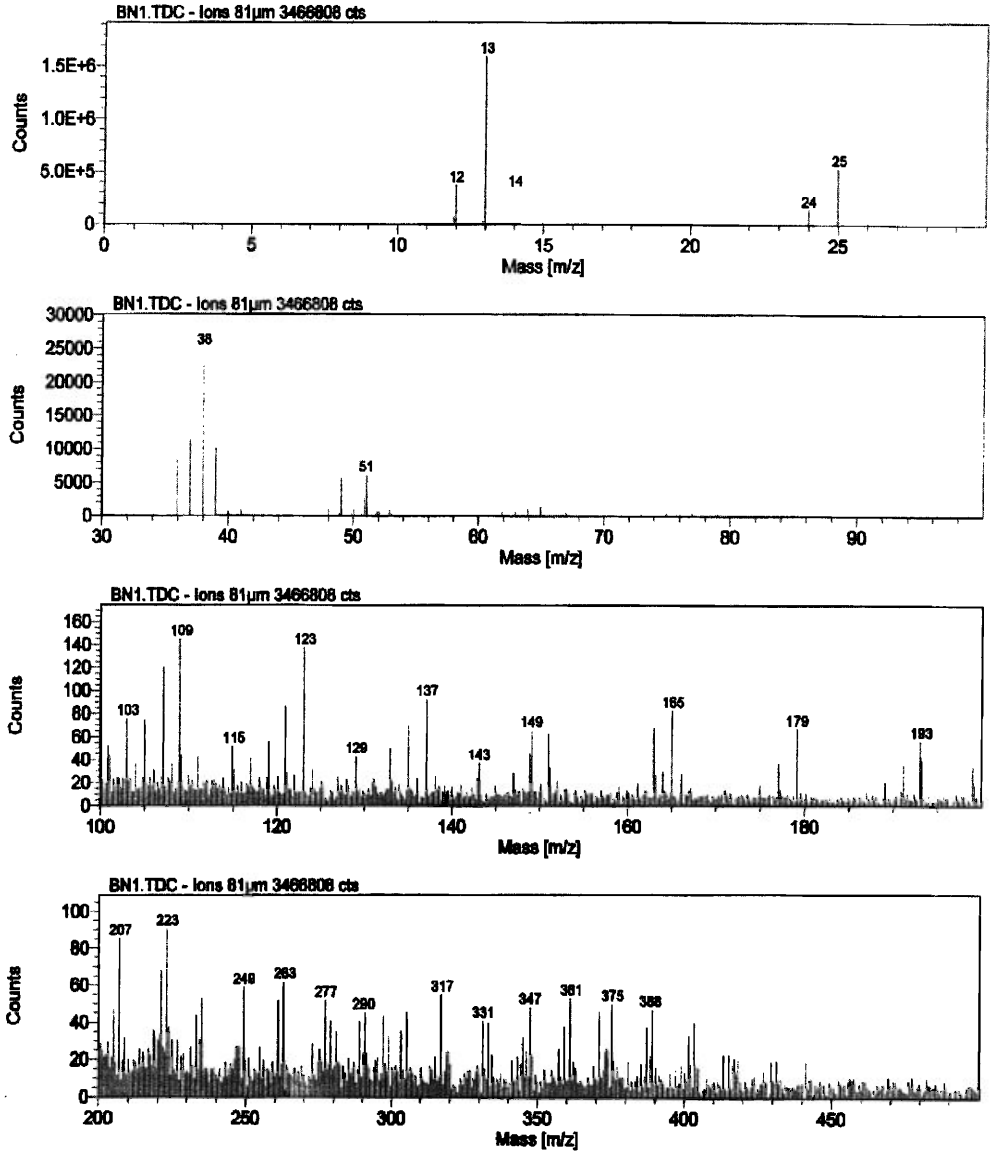

Figure 7b. Spectra of characteristic negative ions of mineral oil deposited on a silicon wafer.

dots, but there is not much activity, suggesting it is quantitatively close to zero. The evidence is quite conclusive that mineral oil does not penetrate hair. This is not quite unexpected, since mineral oil is nonpolar and the cortex of hair is polar and, therefore, has no affinity for mineral oil.

COMPARISONS BETWEEN COCONUT AND MINERAL OIL PENETRATION

Ion spectra and images clearly identified coconut oil within the hair fiber cross section. The diffusion of coconut oil ranges in depth from partial to complete penetration of the

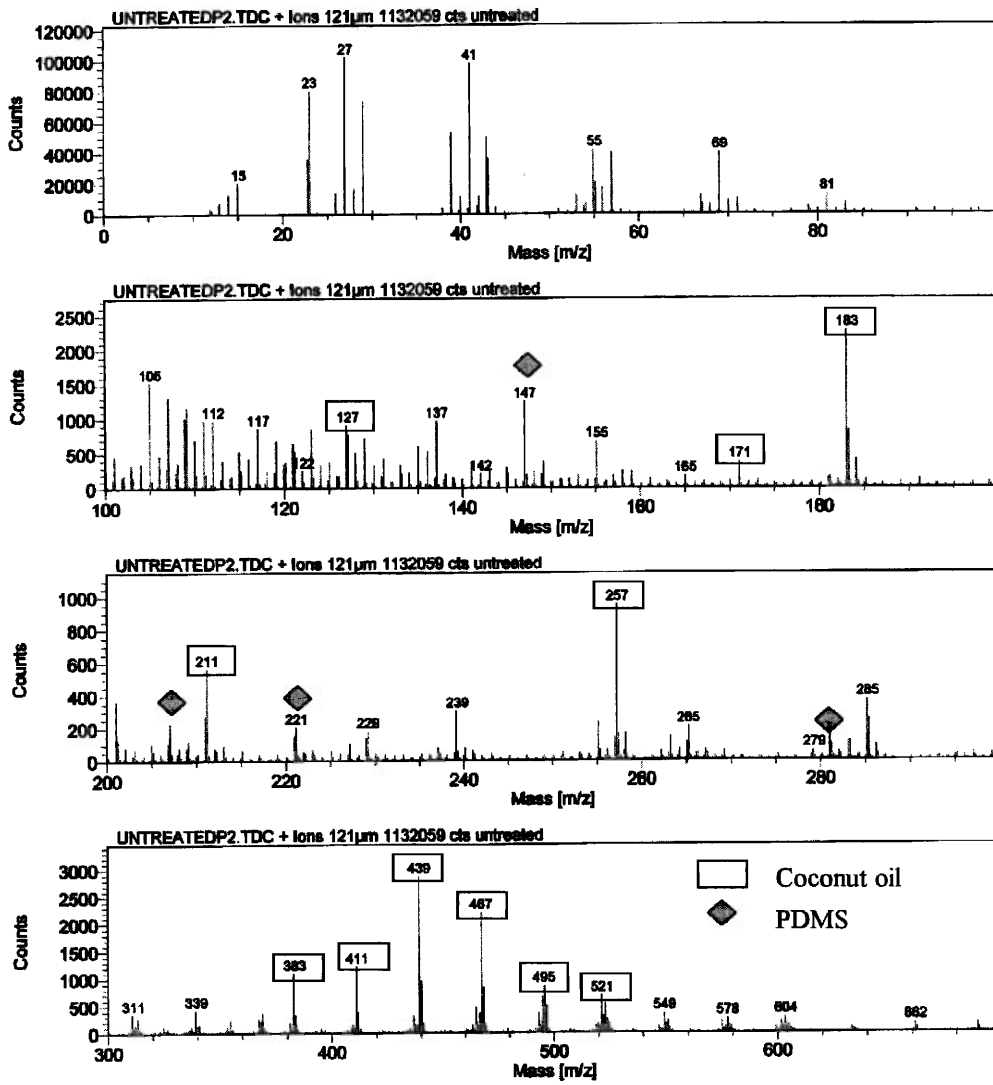

Figure 8. Typical spectra of positive ions from the surface of a cross section of an untreated hair fiber. No characteristic positive ions of mineral oil were detected within untreated hair fibers. However, there is contamination from coconut oil and polydimethylsiloxane surfactants.

entire hair fiber cross section, even though penetration is non-uniform. There is more oil in the periphery than in the fiber center. This is clearly demonstrated in the images obtained by mapping positive ions of mass number 126.67 m/z. It is important to point out that the intensity of color in these images reflects relative amounts of the materials mapped but does not give exact amounts. However, valid and reliable comparisons of the relative distribution patterns can be made.

Mineral oil, on the other hand, was not detected within the hair fiber cross section. This is clearly shown in the positive ion images carried out at mass number 361.26 m/z, which is unique to mineral oil. Both the images of untreated and mineral oil-treated hair

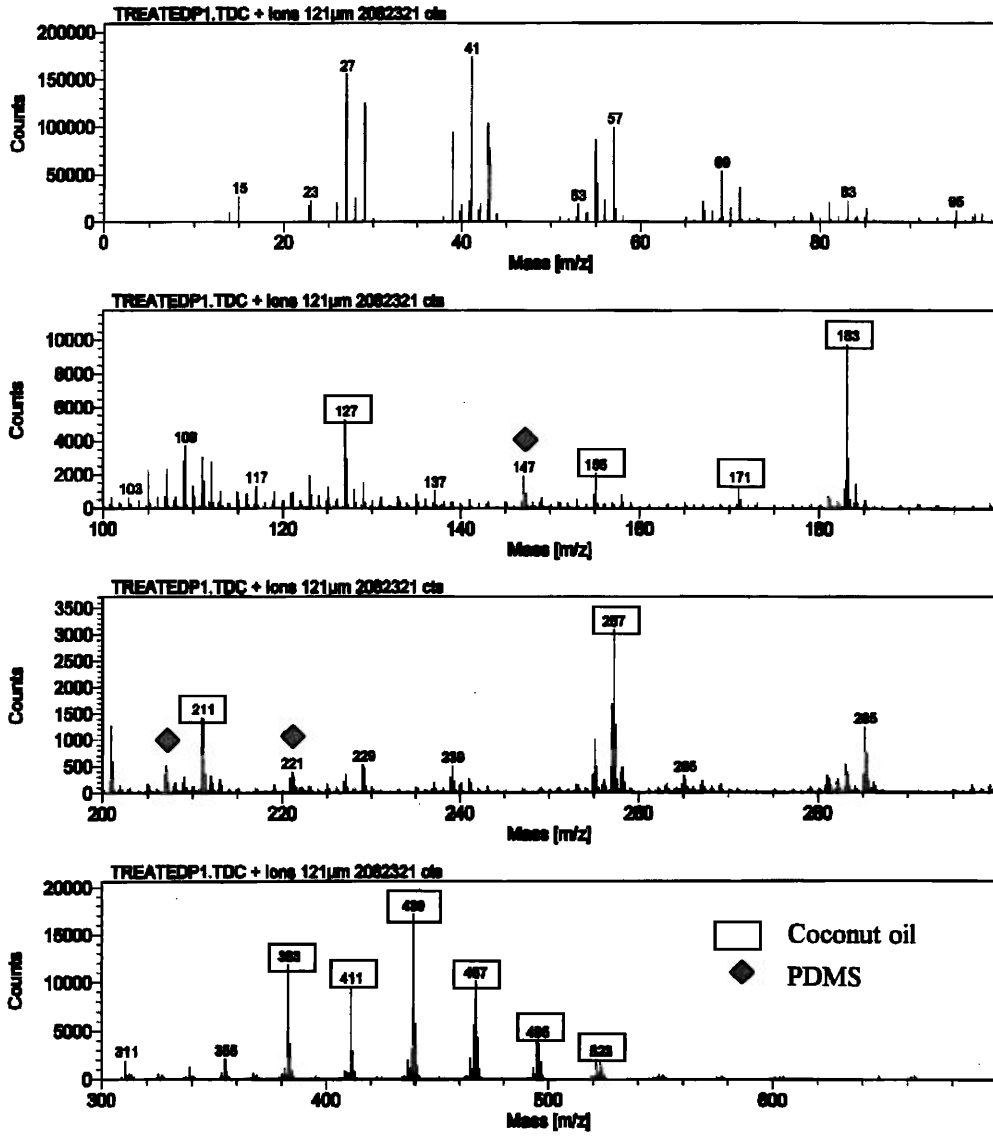

Figure 9. Spectra of positive ions from the surface of a cross section of mineral-oil-treated hair fibers. No characteristic positive ions of mineral oil were detected within mineral-oil-treated hair fibers. However, there is contamination from coconut oil and polydimethylsiloxane surfactants.

fiber cross sections show little activity, suggesting that the penetration of mineral oil into hair is negligible.

The difference seems to be the polarity of the two oils. Coconut oil, being a triglyceride, is polar compared to the nonpolar mineral oil. Therefore, coconut oil has a greater affinity for the cortex of hair, which is also polar in character.

III. Effects of Oil Penetration on Swelling

Untreated, unaltered hair is known to swell up to 16% in the diametral dimension but

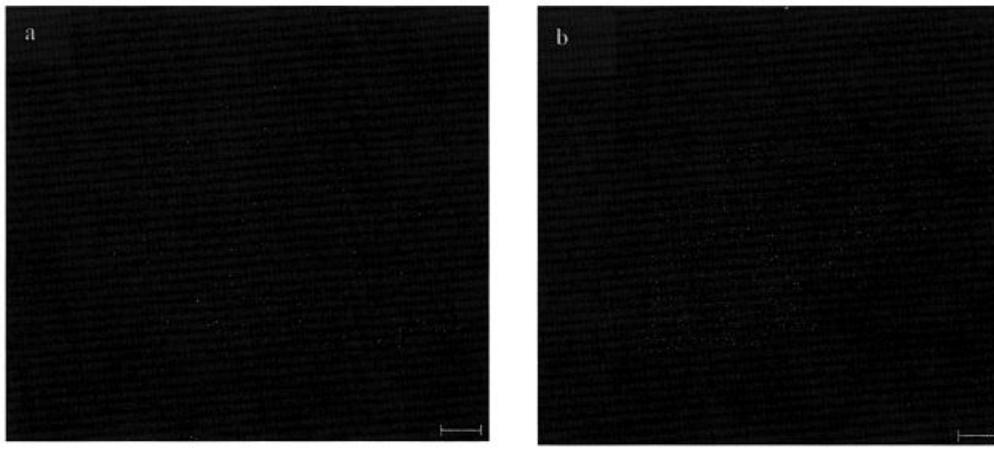

Figure 10. Imaging the characteristic positive ion of mineral oil at mass number 361.26 m/z in the cross section of (a) untreated and (b) mineral-oil-treated hair fibers. No activity was observed, which suggests that mineral oil has not penetrated into the hair fiber interior.

only 2% in length upon immersion in water (3,4). This is due to swelling of the globular keratin-associated proteins (KAPs) surrounding the intermediate filament (3,4), as well as of the non-keratinous domains such as the CMC, the endocuticular layer of the cuticle cell, the intermacrofibrillar material, and nuclear remnants (5). The CMC and endocuticular domains are known to be the pathways for diffusion of molecules into the hair shaft (5).

Oils are known to repel water. Since both the coconut and mineral oils are uniformly coating the hair fiber surface, repulsion of the water molecules upon immersion in water is expected, which, in turn, will inhibit swelling. This is expected to be the case at least during short-term immersion in water. However, during long-term immersion in water, some of the oil molecules may become dislodged by the water, and water molecules will find a passageway into the hair shaft. Since TOF-SIMS clearly identified coconut oil also within the hair fiber cross section, it is expected that the affinity of the protein for the water molecules is reduced, resulting in significantly lower levels of swelling. However, a slightly increased swelling may occur in the case of hair fibers treated with mineral oil because the oil is mainly present on the fiber surface and not in the interior, as established by TOF-SIMS.

To confirm this assumption, untreated hair fibers and fibers treated with coconut and mineral oils were mounted on microscope slides. The fibers were straightened and fastened at both ends, but without tension. Fiber diameters were measured at three marked locations along each fiber. The slides with the fibers were then immersed in DI water in small glass tanks for one hour at ambient temperature. After one hour of immersion in water, the slides with the fibers were removed from the tanks, the bottoms of the slides were blotted, a cover glass was placed on the wet fibers, and the diameters were measured at the same three marked locations along each fiber. The three readings for each fiber were averaged and increases in fiber diameter were calculated.

The water-induced swelling observed in untreated fibers was, as expected, significantly reduced in the oil-treated specimens. Figure 11 shows the increase in fiber diameter during immersion in water for each individual fiber and clearly indicates a significant

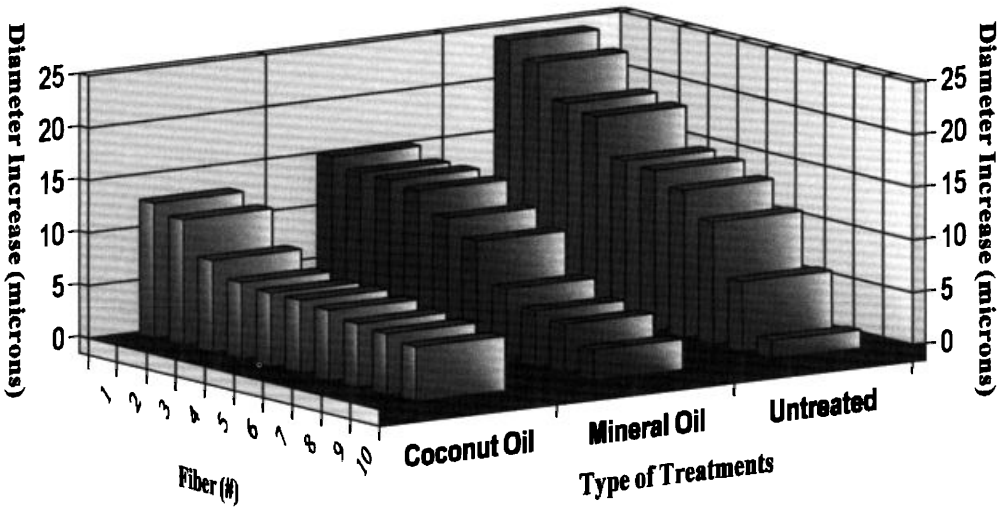

Figure 11. Increases in fiber diameter in untreated and oil-treated hair fibers during one-hour immersion in water, demonstrating the protective action of oils.

decrease in swelling behavior as a result of the oil treatment. Figure 12 shows the inter-fiber averages. While both oil-treated categories show a significant decrease in swelling, it is slightly greater for the coconut-oil-treated fibers than the mineral-oil-treated specimens. In coconut- and mineral-oil-treated specimens, swelling is reduced by 48% and 33%, respectively. This strongly suggests that the fiber is protected from damage by hygral fatigue (swelling and de-swelling).

It should be emphasized that the reduction in moisturization of the fiber does not make the fiber rigid because of the plasticizating action of the absorbed coconut oil.

CONCLUSIONS

This work has shown that the TOF-SIMS technique can be used to study the penetration

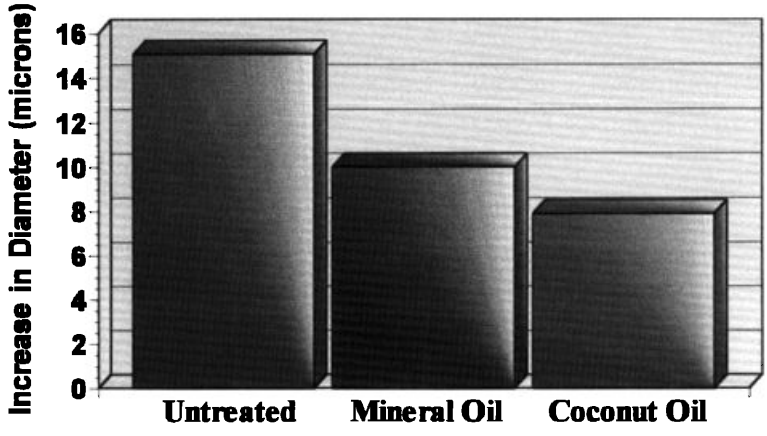

Figure 12. Averaged increases in fiber diameter in untreated and oil-treated hair fibers during one-hour immersion in water, demonstrating the protective action of oils.

of small diffusible molecules into the cortex of hair. Due to its polarity and affinity for the protein, coconut oil was found to penetrate into the hair cortex. Mineral oil, on the other hand, did not penetrate the fiber. The reason is likely to be its lack of affinity for the protein.

Penetration of oils seems to reduce the hydrophilicity of the protein, as indicated by the lower amount of swelling observed in hair fibers treated with coconut oil. Mineral oil also shows lower levels of swelling compared to the untreated fiber, suggesting that it may have penetrated into the cuticular regions, thereby preventing further penetration of water into the hair shaft during the swelling experiment.

Significant reduction in swelling suggests that this will prevent swelling and de-swelling (hygral fatigue) of the fiber. Hygral fatigue can lead to cuticular damage as well as damage to the cortex, which can, in turn, affect the mechanical properties. These results support the beneficial effects of coconut oil to the hair observed in earlier work (1).

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