

Penetration of cationic conditioning compounds into hair fibers: A TOF-SIMS approach

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Synopsis

Cationic conditioning compounds protect against hair damage caused by cosmetic chemical treatments and grooming practices. They also enhance the retention of moisture. However, the question as to whether they do this superficially by residing on the hair surface or by penetrating into the fiber remains unanswered. In this work, an attempt has been made to show the penetration of a low-molecular-weight cationic conditioning compound into the hair cortex using the time-of-flight secondary ion mass spectrometry (TOF SIMS) method, applied in earlier research to show the penetration of oils into hair. An example of the practical benefit of such penetration into the cortex in greatly improving the fatigue resistance of hair has been discussed.

INTRODUCTION

Cationic conditioning compounds are often used to improve the cosmetic properties of hair, such as manageability, combability, and reduction of static charging, known as “flyaway.” Most of the desirable effects are brought about by the small amounts of conditioner residues left on or in the hair fiber. Earlier studies have shown that these cationic conditioner residues reinforce the cuticle sheath of hair and reduce scale lifting, which occurs as a response of the surface cuticle cell when tensile stress is imposed on the hair fiber during grooming, especially when encountering a snag, or pulling and stretching the hair (1).

Other properties of the hair assembly coveted by consumers and producers of hair care products are abrasion and fatigue resistance and retention of moisture. These attributes of conditioning compounds are often enhanced by the penetration of these compounds into the hair fiber. Although conventional concepts of diffusion doubt the penetration of high-molecular-weight polymer cationics (above a molecular weight of ~1000) beyond the cuticular sheath, claims have been made to the contrary. We, therefore, pursued a study involving penetration of two cationic conditioning compounds, differing in chemistry and molecular weight, using a reliable method of identifying their residues within the hair fiber, especially at low concentration.

Faucher and Goddard (2), using a radiotracer technique, showed the penetration of cationic cellulose-based polymers into the hair fiber. Similar studies were conducted

by Chow (3) and Woodard (4) on the penetration of polyethylenimine conditioners in hair.

This study attempts to map the diffusion of high- and low-molecular-weight cationic conditioning compounds into hair-fiber cross sections. The technique used for this work is time-of-flight secondary ion mass spectrometry (TOF SIMS) (5), adapted earlier to show penetration of oils into hair.

We have used the outcome of this study to interpret the beneficial effects of surface-deposited high-molecular-weight cationic conditioner on cuticle reinforcement and penetrated low-molecular-weight cationic conditioner on extending the fatigue life of single hair-fibers.

EXPERIMENTAL

MATERIALS

Cationic conditioning compounds. The high-molecular-weight cationic conditioning compound was polyquaternium-10 (PQ-10). The low-molecular-weight cationic conditioning compound was cetyl trimethyl ammonium bromide (CETAB). The neat compounds were applied from 0.5% aqueous solutions.

Hair samples. Fourteen-inch-long unaltered, European brown hair from DeMeo Brothers, New York, was used in this work. The top five inches of the root sections were mounted in parallel and identified as #1-20. The fibers were then cut into two segments, with the upper segments measuring two inches and the bottom segments three inches. The top segments served as controls, and the adjacent segments of the corresponding fibers were treated with either the CETAB or the PQ-10 in the form of a 0.5% aqueous solution.

TREATMENTS WITH THE CATIONIC CONDITIONING COMPOUNDS

The conditioner treatments were carried out at 37°C for six hours with slow stirring. The fibers were then briefly rinsed, blotted, and air-dried. The reasoning for the long treatment time was that in earlier work of Faucher and Goddard (2), they observed rapid deposition of large amounts of high-molecular-weight PQ-10 conditioner (in minutes), followed by slow deposition (over hours and days). Based on this information, they proposed that high-molecular-weight polymers can diffuse in the swollen keratin matrix. Therefore, in our studies, the fibers were treated up to six hours to see whether we could observe any penetration into the cortex, especially by the polymeric conditioner.

ANALYTICAL TECHNIQUE

The investigative technique used to map the penetration of low- and high-molecular-weight cationic conditioners into hair was time-of-flight secondary ion mass spectrometry (TOF SIMS) and is described in detail in an earlier publication (5).

SAMPLE MOUNTING

Small amounts of the aqueous PQ-10 and CETAB solutions were deposited on clean silicon wafers and allowed to dry at ambient temperature. The untreated (control) and

conditioner-treated hair fibers were cross-sectioned each time with a clean stainless steel blade and mounted in small holders with the cross sections facing the spectrometer at a slight tilt.

ION MASS SPECTRA

Ion mass spectra were collected to isolate characteristic positive/negative ions of the cationics. Positive and negative static TOF SIMS spectra were acquired from several locations on each of the cationic conditioning compounds and from the surface of the hair-fiber cross section. The sampling depth of TOF SIMS is only ~ 1 monolayer for molecular fragment ions and one to three monolayers for atomic species. Since the sampling depth of TOF SIMS is only approximately one molecular layer, only the low-molecular-weight, highly mobile, components in the surface are detected.

The higher-molecular-weight compounds are more difficult, if not impossible, to ionize with the $^{69}\text{Ga}^+$ 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).

IMAGING

Imaging/mapping the presence of cationics within the fiber cross section. Once the characteristic or unique positive or negative ions (atomic species or low-molecular-weight fractions) of the conditioning compounds were established, their diffusion into the fiber cross section was mapped.

RESULTS AND DISCUSSION

CHARACTERISTIC POSITIVE AND NEGATIVE IONS OF CETAB

Characteristic positive ions of CETAB are $\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z , $(\text{CH}_2)_x\text{NH}_2^+$ at 114, 128, 142, 156, 170, 184, and 198 m/z , and $\text{C}_{19}\text{H}_{42}\text{N}^+$ at 284.33 m/z . Although mass $\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z is relatively intense, it is probably not a good ion for imaging, since it can be formed from a wide variety of amines and may, therefore, not necessarily be indicative of CETAB if other amines exist. The positive ion $\text{C}_{19}\text{H}_{42}\text{N}^+$ at 284.33 m/z is the best ion and will be used for imaging, since it is intense and is likely to be free of mass interference. In combination with this latter ion, imaging of $\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z will support the presence of CETAB as well.

$^{79}\text{Br}^-$ and $^{81}\text{Br}^-$ are characteristic negative ions of CETAB. Because the organic portion of CETAB forms strong positive ions, it tends to form weak negative ions. However, since the presence of sulfates also produces a peak at 81 m/z due to HSO_3^- , that peak is not ideal for mapping CETAB. Therefore, the negative $^{79}\text{Br}^-$ ion seems to be the best for imaging CETAB through the negative ions.

IMAGING CETAB'S CHARACTERISTIC POSITIVE IONS IN UNTREATED HAIR FIBERS (CONTROLS)

To establish the presence of CETAB in the cross section of CETAB-treated hair fibers, the positive ions of $\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z and $\text{C}_{19}\text{H}_{42}\text{N}^+$ at 284 m/z were imaged first in untreated hair fibers and will serve as reference images for comparison (Figure 1). The images in Figure 1 do not show any CETAB activity within the untreated hair fiber.

IMAGING CETAB'S CHARACTERISTIC POSITIVE IONS IN CETAB-TREATED HAIR FIBERS

In contrast to the control fibers, images of CETAB-treated hair fibers at mass numbers 58 and 284 (Figure 2a,b) clearly show that CETAB has penetrated into the fiber interior. The extent of penetration, however, varies from fiber to fiber. In some cases, the CETAB penetration is restricted to the fiber periphery (broad ring) (Figure 2a), while other fibers have been penetrated uniformly throughout the bulk of the hair-fiber (Figure 2b).

These differences in penetration and the amount of CETAB may be due to differences in fiber history and constitution. It is important to note that the similarity of images at the two different mass numbers, 58 and 284, in Figure 2a,b support the idea that these two ions come from fragments of CETAB.

IMAGING CETAB'S CHARACTERISTIC NEGATIVE IONS IN THE CROSS SECTION OF UNTREATED HAIR FIBERS

The negative ion image of CETAB at 79 m/z (Br^-) in an untreated control hair fiber is shown in Figure 3. The $^{79}\text{Br}^-$ image in untreated hair does not show much activity.

IMAGING CETAB'S CHARACTERISTIC NEGATIVE IONS IN THE CROSS SECTION OF CETAB-TREATED HAIR FIBERS

The $^{79}\text{Br}^-$ ion image of the CETAB-treated hair fiber (Figure 4) once again shows partial to complete penetration of CETAB into the bulk of the hair fiber, as was observed in the positive ion imaging.

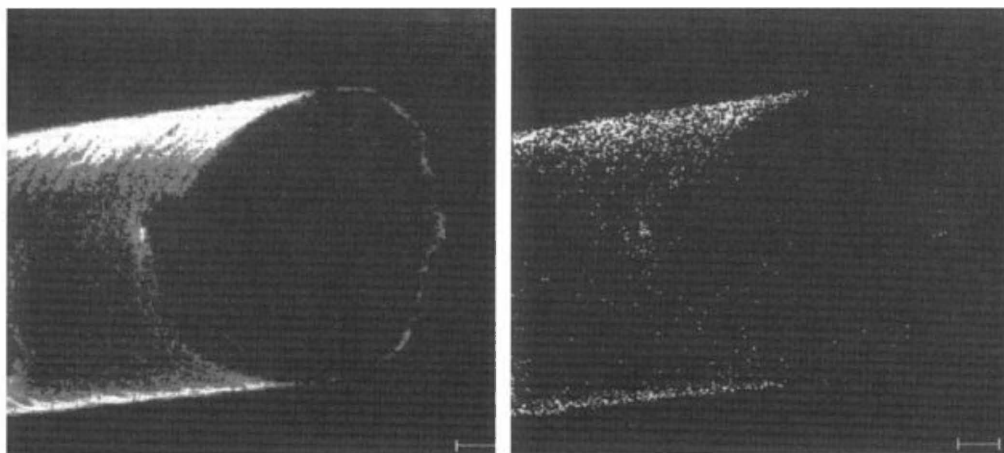


Figure 1. Imaging the presence of two of the characteristic positive ions of CETAB (left: $\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z; right: $\text{C}_{19}\text{H}_{42}\text{N}^+$ at 284 m/z) in the surface of the cross section of an untreated hair fiber (serving as control).

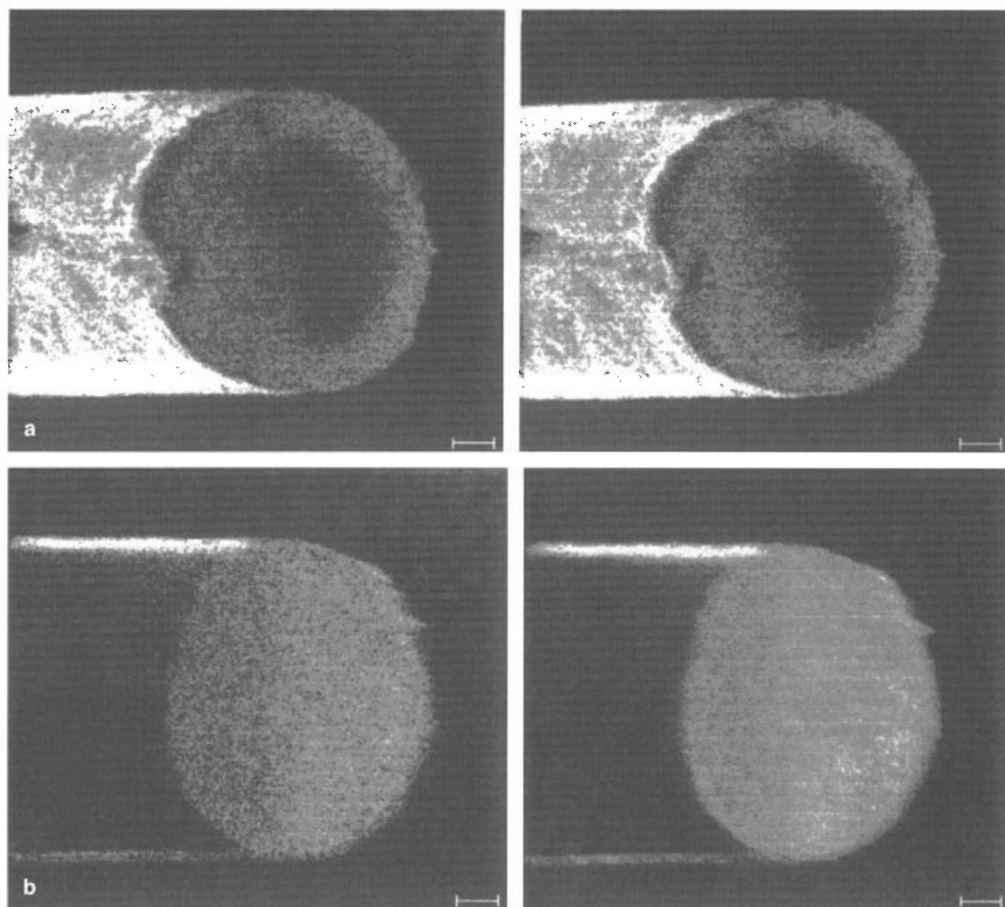


Figure 2. (a) Images of CETAB's characteristic positive ions $C_3H_8N^+$ at 58 m/z (left) and $C_{19}H_{42}N^+$ at 284 m/z (right) in CETAB-treated hair-fiber cross sections clearly show broad peripheral penetration. (b) Images of CETAB's characteristic positive ions $C_3H_8N^+$ at 58 m/z (left) and $C_{19}H_{42}N^+$ at 284 m/z (right) in CETAB-treated hair-fiber cross sections clearly show complete penetration of CETAB throughout the fiber cross section.

CHARACTERISTIC POSITIVE AND NEGATIVE IONS OF PQ-10 IN UNTREATED AND PQ-10-TREATED HAIR

While the low-molecular-weight CETAB could be detected within the hair-fiber cross section via its characteristic positive and negative ions, this study was not able to trace or identify the presence of the high-molecular-weight PQ-10 within the conditioner-treated hair fiber. The positive and negative ion spectra as well as all images of PQ-10-treated hair could not be differentiated from those of the untreated control hair and, therefore, show no evidence of PQ-10 in the cross section of PQ-10-treated hair fibers. This is probably indicative of the lack of penetration of PQ-10 into the hair fiber.

EFFECT OF CONDITIONER PENETRATION ON HAIR FATIGUE RESISTANCE

Combing of hair can be linked to a process of fatiguing. For example, during combing, hair is repeatedly subjected to extension within the Hookean region. In fatiguing, this

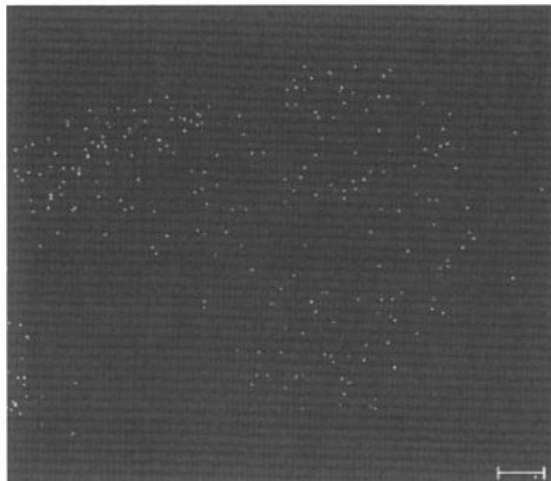


Figure 3. Imaging the characteristic negative ion of CETAB at 79 m/z (Br) in the cross section of an untreated control hair fiber.

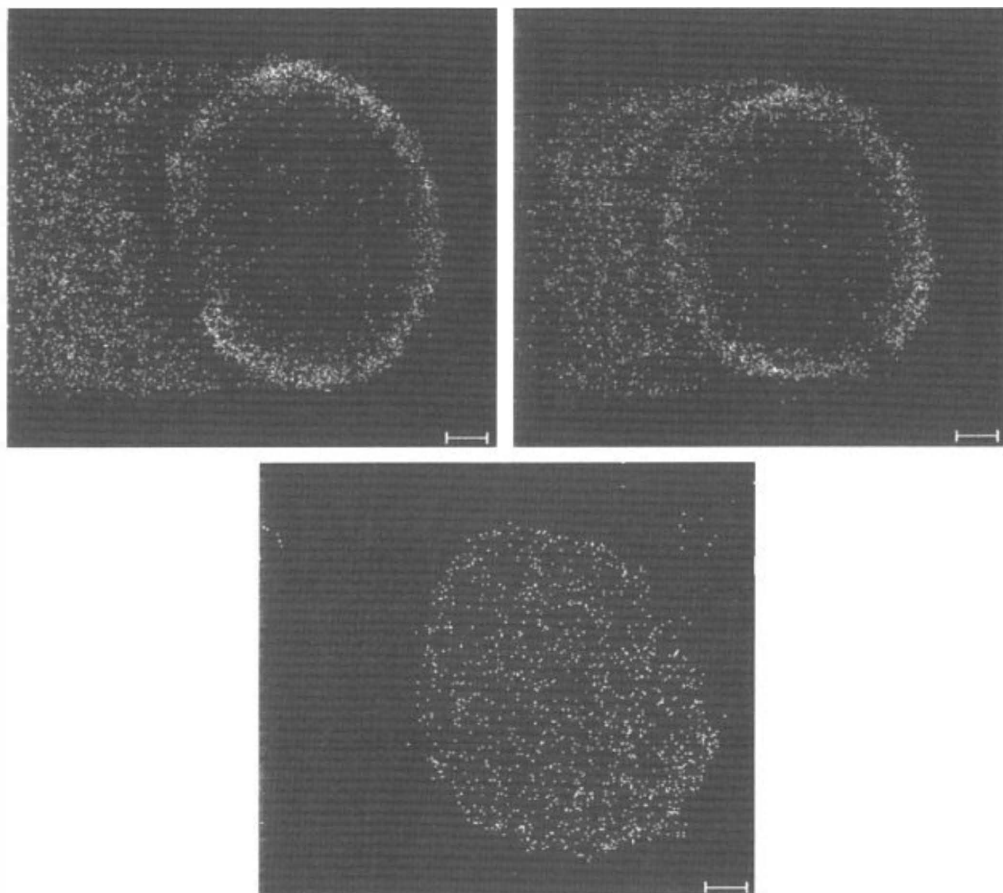


Figure 4. Imaging the characteristic negative ion of CETAB at 79 m/z (Br) in the cross sections of three different CETAB-treated hair fibers.

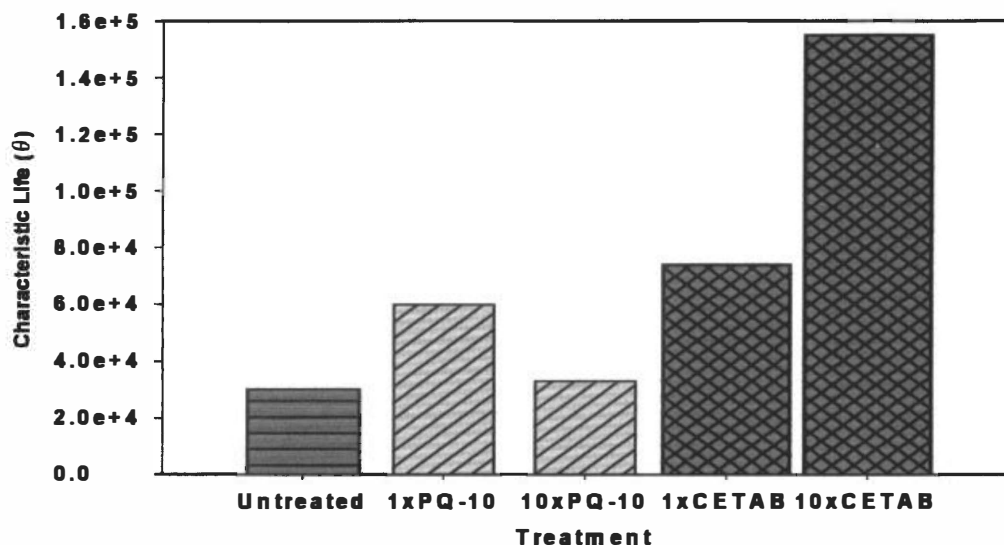


Figure 5. Effect of polymeric and monomeric cationic conditioning compounds on fatigue resistance (characteristic life, θ).

is simulated by repeatedly loading and unloading a single hair with a weight that is close (or slightly lower) to the yield force of the hair. This is done by a machine (TRI "Hair Fatigue Tester") developed by TRI to simulate repeated stretching of hair within the Hookean region by repeated loading and unloading (cyclic fatiguing).

Fatigue resistance is expressed by characteristic life, θ , which represents the number of fatigue cycles necessary to break 63.2% of the total hair population tested. Fatigue resistance depends on the properties of the cortex. Therefore, a decrease in characteristic life is generally indicative of fiber damage, whereas an increase in characteristic life suggests reinforcement of the fiber cuticle and cortex.

Although details of the test and the processing of data cannot be given in detail in this communication, hair fatigue studies at TRI have shown that in comparison to bleached hair without conditioner treatment, fatigue resistance (characteristic life, θ) is greatly improved in bleached hair that had been exposed to multiple treatments with the CETAB (Figure 5). Even a single treatment of bleached hair with the low-molecular-weight CETAB shows an increase in characteristic life, suggesting fiber reinforcement by penetration of the monomeric cationic into the fiber interior. (Hair fibers were fatigued in TRI's "Hair Fatigue Tester" at a rate of ~1 Hertz and a 40 g load.) As shown in Figure 5 as well, treatments with polymeric cationics, such as PQ-10, show moderate or no improvement in fatigue resistance over that of untreated hair, because the cationic polymeric is not capable of penetrating into the cortex.

Since fatigue resistance depends on the properties of the cortex, high-molecular-weight conditioning compounds, which show no penetration into the cortex, may not display (as in this case) significant improvements in fatigue resistance. However, it should be noted that these polymeric conditioning compounds are capable of penetrating, at least for a limited distance, into the outer cuticle layers and "reinforcing" them by gluing. We have shown in an earlier publication (1) that this conditioner-induced "reinforcement" improves the creep resistance of the hair fiber. This can have a small effect on fatigue

measurement. Although cuticle reinforcement may not affect the tensile strength of the fiber, it can reinforce the cuticula, which in turn can affect fiber surface properties as well as the tactile and optical properties of the hair assembly.

CONCLUSIONS

Ion spectra and images clearly identified CETAB within the hair-fiber cross section and on the hair-fiber surface. The penetration of CETAB ranges in depth from 10 μm to penetration of the entire hair-fiber cross section. This is clearly demonstrated by mapping both positive ($\text{C}_3\text{H}_8\text{N}^+$ at 58 m/z and $\text{C}_{19}\text{H}_{42}\text{N}^+$ at 284 m/z) as well as negative ($^{79}\text{Br}^-$) ions.

The higher-molecular-weight compounds are more difficult to ionize. Therefore, one has to look for their low-molecular-weight fragments, which in the case of PQ-10 may not be suitable for mapping because these fragments are not unique to PQ-10-treated hair, since they are also found in untreated hair.

The fact that CETAB is able to penetrate into the hair fiber while PQ-10 is not, manifests itself in improved fatigue resistance of CETAB-treated hair. The greatly extended fatigue life of CETAB-treated hair versus PQ-10-treated hair is, without doubt, due to the ability of the low-molecular-weight CETAB to penetrate into the hair fiber, while PQ-10 is restricted to deposition on the hair surface.

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REFERENCES

- (1) S. B. Ruetsch, Y. K. Kamath, and H.-D. Weigmann, The role of cationic conditioning compounds in reinforcement of the cuticula, *J. Cosmet. Sci.*, **54**, 63–83 (2003).
- (2) J. A. Faucher and E. D. Goddard, *J. Colloid Interface Sci.*, **55**, 313 (1976).
- (3) C. D. Chow, Interaction between polyethylenimine and human hair, *Textile Res. J.*, **41**, 593–603 (1972).
- (4) J. Woodard, Aziridine chemistry—Applications for Cosmetics, *J. Soc. Cosmet. Chem.*, **23**, 593–603 (1972).
- (5) S. B. Ruetsch, Y. K. Kamath, A. S. Rele, and R. Mohile, Secondary ion mass spectrophotometric investigation of penetration of coconut and mineral oils into human hair, *J. Cosmet. Sci.*, **52**, 169–184 (2001).