Available online at www.sciencedirect.com
SCIENCE DIRECT
Applied Surface Science 252 (2006) 6761–6764
applied surface science
www.elsevier.com/locate/apsusc

Characterisation of human hair surfaces by means of static ToF-SIMS: A comparison between Ga^+ and C_{60}^+ primary ions

Claude Poleunis [a,*], Emmanuel P. Everaert [b], Arnaud Delcorte [a], Patrick Bertrand [a]

[a] *Université catholique de Louvain (UCL), Unité de Physico-Chimie et de Physique des Matériaux (PCPM), Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium*

[b] *Unilever R&D Port Sunlight, Quarry Road East, Bebington Wirral CH63 3JW, United Kingdom*

Received 12 September 2005; accepted 15 February 2006
Available online 2 May 2006

Abstract

This study deals with the secondary ion yield improvement induced by using C_{60}^+ primary ions instead of Ga^+ ones to characterize human hair surfaces by ToF-SIMS. For that purpose, a bunch of hair fibres has been analysed with both ion sources. A high improvement is observed for the detection of amino acids with C_{60}^+ primary ions as compared to Ga^+ ions. As an example, a yield enhancement factor greater than 3000 is found for the CNO^- peak. A similar gain is observed for the positive secondary ions characteristic of the amino acids. Most of the atomic ions, such as Ca^+, O^- and S^-, constitute minor peaks with C_{60}^+ ions while they often dominate the spectrum in the case of Ga^+ ions. However, with the C_{60}^+ source, a series of inorganic combination peaks with the elements Ca, S and O are observed in the positive spectra (i.e. $HCaSO_4^+$), while they are marginal with the Ga^+ source. For the mass range beyond 100 *m/z* and in both polarities, the hair fingerprints are similar with both sources. In average, for a comparable number of primary ions per spectrum, the C_{60}^+ ion source gives intensities between two and three orders of magnitude higher than the Ga^+ one.

Keywords: C_{60}^+; Amino acids; 18-Methyleicosanoic acid (18-MEA); Keratin; Surfactants; Static ToF-SIMS

1. Introduction

It is well established that the uppermost hair surface, called exocuticule, is mainly composed of lipids bonded to an underlying layer of proteins ([1,2] and references therein). The most abundant hair protein is keratin, which is known to be rich in cysteine amino acids. This underlying keratin layer is covalently bond to the lipids via a thioester linkage [1,2]. The lipid outermost surface layer is mainly constituted by a fatty acid identified as 18-methyleicosanoic acid (18-MEA), a methyl branched 21-carbon fatty acid [1–3].

Among all the available surface techniques, static ToF-SIMS is well suited to probe the human hair. Different publications already underlined the interest of ToF-SIMS to improve our knowledge not only on ''pristine-hair'' but also to study the effect of various treatments of the hair surface [4–6].

Recently, the use of new polyatomic primary ions was shown to highly enhance the secondary ion yields. In the case of C_{60}^+ primary ions, this enhancement could reach two to three orders of magnitude as compared with Ga^+, for various organic materials [7,8]. The advantages to use the C_{60}^+ primary ions have been very well described by Winograd [9].

The aim of this paper is to discuss critically the improvement gained by the use of C_{60}^+ polyatomic primary ions, with respect to Ga^+, to characterize a very complex surface like that of the human hair.

2. Experimental

2.1. Sample preparation

The hairs used for this study are of dark brown Caucasian type (10″ long, from International Hair Importers & Products Inc., Glendale, NY 11385). A hair staple has been measured after a washing process in a sodium laureth sulphate (SLES-2EO) solution at 14% and an abundant rinsing under tap water.

* Corresponding author. Tel.: +32 10 473582; fax: +32 10 473452.
E-mail address: poleunis@pcpm.ucl.ac.be (C. Poleunis).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2006.02.174

An area of a bunch of hair fibres, taken approximately at 5 cm from the hair root, has been analysed with $^{69}Ga^+$ and C_{60}^+ primary ions sources.

2.2. ToF-SIMS measurement

The ToF-SIMS spectra measurements were performed with a PHI-Evans TFS-4000MMI (TRIFT 1) spectrometer [10]. In order to increase the detection efficiency of high-mass ions, a 7 keV post-acceleration was applied at the detector entry. Charge effects were compensated for both ion sources by means of a pulsed electron flood gun (E_k = 24 eV). The electron/primary ions cycle depended on the polarity of the secondary ions and also on the primary ion species. Furthermore, a stainless steel grid (1.5 mm mesh) covered the sample surface.

For the $^{69}Ga^+$ measurements, the samples were bombarded with a FEI (model 83-2) pulsed liquid metal ion source (15 keV, 1.2 nA dc, 11.4 kHz repetition rate and 22 ns pulse width bunched down to 1 ns). The analysed area was either a square of 120 μm × 120 μm for the positive secondary ions or a square of 180 μm × 180 μm for the negative secondary ions. With a 5 min data acquisition time, the total number of primary ions was either 4.4×10^8 Ga^+ for the positive secondary ions or 2.4×10^8 Ga^+ for the negative secondary ions, depending of the used charge compensation cycle. These analytical conditions ensured static analysis conditions [11]. For the present samples and analytical conditions, the mass resolution was about 1000 at $m/z = 41$ ($C_3H_5^+$ peak).

For the C_{60}^+ measurements, the same samples were also bombarded with an Ionoptika (model IOG-C60-20) pulsed ion gun. Further details about this source can be found in ref. [7]. This ion source has been fitted to a PHI-Evans TFS-4000MMI (TRIFT 1) spectrometer, in place of the Cs^+ source. The specific analytic conditions for the conducted C_{60}^+ measurements were: 15 keV, 2.6 pA dc (aperture 300 μm), 10.8 kHz repetition rate, 40 ns pulse width bunched down to 8 ns. The grid voltage was 50 V, giving roughly 20% of C_{60}^{2+} species in the primary beam [12]. These C_{60}^{2+} species were filtered by a double set of blanking plates. The analysed areas were estimated either at 120 μm × 90 μm for the positive secondary ions or at 180 μm × 120 μm for the negative secondary ions. With a 5 min data acquisition time, the total number of primary ions was 1.0×10^6 C_{60}^+ for both secondary ions polarities. These analytical conditions ensured static analysis conditions too [11]. For the present samples and with these analytical conditions, the mass resolution was about 700 at $m/z = 41$ ($C_3H_5^+$ peak).

For both primary ion sources and in both secondary ion polarities, four spectra located at different hair areas have been measured and averaged data are presented.

2.3. C_{60}^+ enhancement factors (EF)

The C_{60}^+ enhancement factor is calculated by the evaluation of the secondary ion (SI) yield ratio:

$$\frac{Y_{C_{60}^+}}{Y_{Ga^+}} = \frac{I_x^{C_{60}}/\phi_{C_{60}}}{I_x^{Ga}/\phi_{Ga}},$$

where $I_x^{C_{60}}$ and I_x^{Ga} are the peak area for a mass "x" in the C_{60}^+ spectrum and in the Ga^+ spectrum, respectively, and $\phi_{C_{60}}$ and ϕ_{Ga} are the number of C_{60}^+ and Ga^+ ions required for the spectrum acquisition, respectively. In our analysis conditions, $\phi_{C_{60}}/\phi_{Ga} = 240$.

3. Results

In the positive spectra (not shown) obtained on the hair surfaces, the different hair components are detected. They mainly consist in hydrocarbon $C_xH_y^+$ peaks at the odd masses and amino acids fragments, coming from proteins such as keratin. Some residues of the previous washings or hair treatments are also detected. They come mainly from silicone oil (masses 147, 207, 221 and 281 m/z) and from cationic conditioners such as hexadecyltrimethyl ammonium (mass 284 m/z) and disteryldimethyl ammonium (masses 522 and 550 m/z).

Although at first sight, the positive spectra look rather similar, a significant enhancement factor is observed for most of the peaks. An averaged enhancement factor of 125 is found for the total positive SI intensity. More specifically, for the above-mentioned washing or hair treatment residues, EF is about 180 for the silicone peaks and about 380 for the cationic conditioner peaks.

A significant EF is found for several peaks at even masses that are related to amino acid fragments, such as NH_4^+, CH_4N^+, $C_2H_6N^+$, $C_3H_8N^+$, $C_4H_8N^+$, $C_2H_4NO_2^+$, $C_4H_6NO^+$, $C_3H_4NO_2^+$ and $C_4H_4NO_2^+$, respectively. The same effect is also found for two odd mass peaks, corresponding to CH_3S^+ and $C_2H_5S^+$, and associated to S-containing amino acids (cysteine and methionine). The EF values for all these amino acid peaks are presented in Fig. 1a.

Variable EFs, with sometimes very high values, are also observed for several aromatic peaks (see Fig. 1b).

The inorganic peak EF values are presented in Fig. 1c. They are rather low for inorganic atomic ion peaks such as Na^+, Mg^+, Si^+ and Ca^+ as compared to the previous values, with an exception for Na^+. However, important intensity increases are observed for the inorganic clusters containing these atoms such as $CaOH^+$, $HCa_2O_2^+$, $HCaSO_3^+$ and $HCaSO_4^+$.

Fig. 2 displays the negative spectra obtained on the hair surfaces with a Ga^+ beam (upper part) and a C_{60}^+ beam (lower part). Only the mass range between 30 and 350 m/z is presented. As for the positive secondary ions, some hair components are well detected. They consist mainly in amino acid species (peak at mass 42 m/z corresponding to CNO^-) and the 18-MEA molecular ion at mass 341 m/z, that corresponds to $C_{21}H_{41}OS^-$. Some residues of the washing treatments are also detected. They come mainly from S-containing surfactants such as sodium laureth sulphate and dodecyl benzene sulphonic acid (masses 183, 265, 279, 293, 309, 321, 325 and 339 m/z).

An averaged enhancement factor of 220 is found for the total negative SI intensity. For these surfactant residues, EF values are illustrated in Fig. 1e.

As shown in Fig. 1d, variable EF values are found for the N-containing peaks, corresponding to amino acids at masses 26,

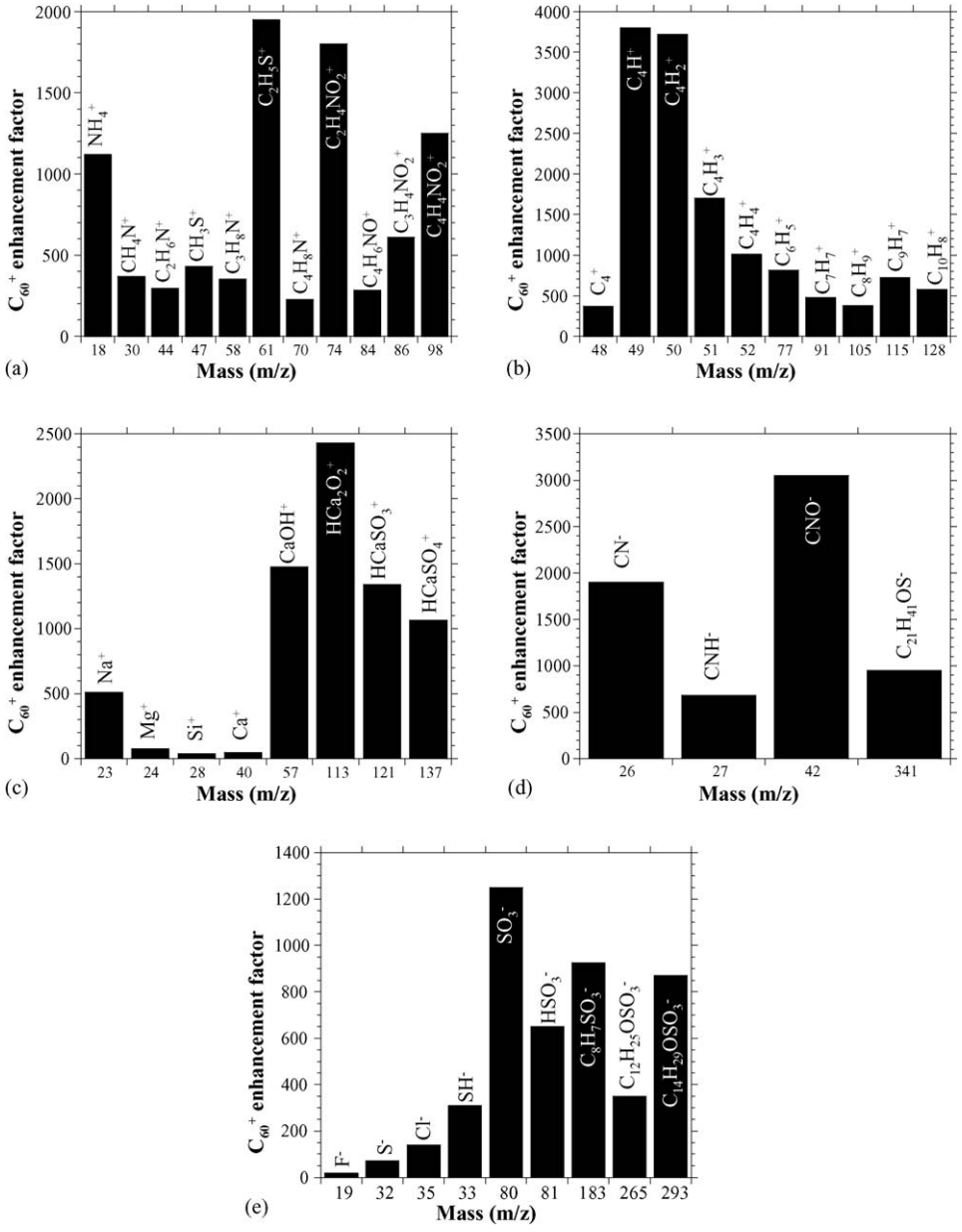

Fig. 1. C_{60}^+ enhancement factors for some positive and negative secondary ions: (a) positive amino acid peaks, (b) aromatic hydrocarbon peaks, (c) positive inorganic peaks, (d) negative amino acid and 18-MEA peaks and (e) negative inorganic peaks.

27 (not shown) and 42 *m/z* and corresponding to CN^-, CHN^- and CNO^-, respectively. An important enhancement factor (EF = 940) is observed for the 18-MEA molecular ion.

The EF values of the atomic inorganic peaks such as F^-, S^- and Cl^- isotopes at 19 (not shown), 32 and 35 and 37 *m/z* are relatively low as compared to the general trend (see in Fig. 1e). However, very important yield enhancement factors are observed for the inorganic SI clusters containing sulphur atom such as SH^-, SO_3^-, HSO_3^- at the masses 33, 80 and 81 *m/z*, respectively.

4. Discussion and conclusion

The EF values found for the amino acid fragments suggest a better detection of the proteins with C_{60}^+ ions (i.e. keratin) towards the hair surfaces. Since the hair protein layer is known to be covered by the lipid outermost layer (18-MEA) [1,2], this suggests a difference information depths between the two beams. EF is found to vary strongly for the amino acid fragments (from 285 up to 1950, in the case of the positive secondary ions). This fact is a bit odd. However, mass interferences with $C_xH_y^+$ clusters coming from the back-scattered C_{60}^+ fragments could occur for SI peaks presenting a very high EF. Indeed, the mass resolution obtained with these hair bunch samples does not allow us to separate isobar ions. This is mainly caused by the important surface roughness. So, mass interferences with C_x^+, C_xH^+, $C_xH_2^+$, ..., could occur, leading to an EF overestimation of several amino acids, i.e. at the masses 61, 74, 86 and 98 *m/z*. Along those lines, it is worth noting that the EF values of aromatic peaks, shown in Fig. 1b, are higher for the fragments at 49 and 50 *m/z* than for the

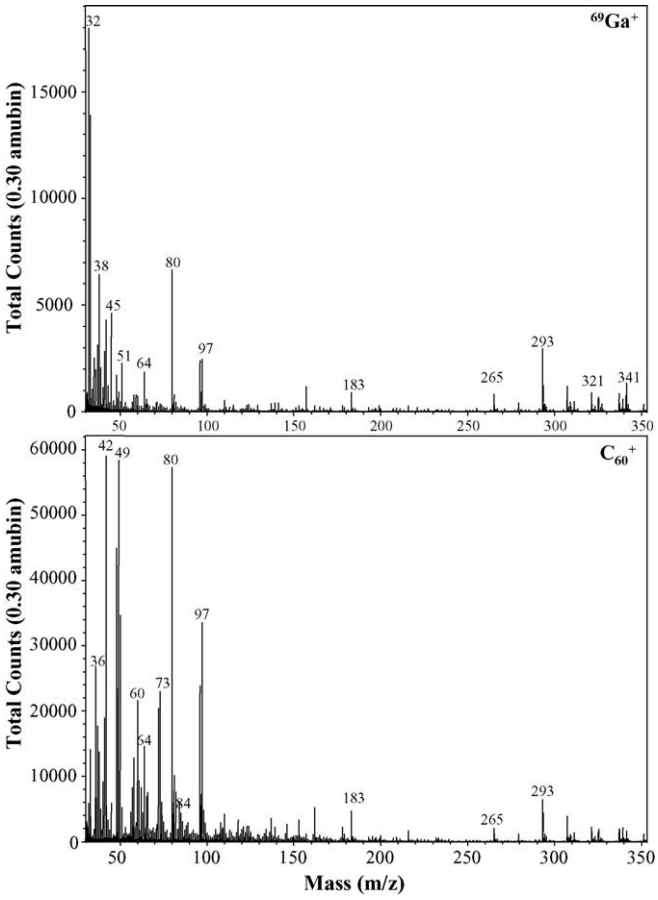

Fig. 2. Negative static ToF-SIMS spectra of human hairs, in the mass range 30–350 *m/z*, measured with $^{69}Ga^+$ and C_{60}^+ primary ion beams.

fragment at 51 *m/z*. To clearly remove this incertitude, a better mass resolution is required, allowing us to check the possible presence of isobar ions. Moreover, kinetic energy distribution measurements could help to identify any difference in the SI emission mechanisms [13]. In the case of the negative SI peaks related to the amino acid, the same kind of remark could be done about possible mass interferences with hydrocarbon for masses 26 and 27 *m/z*. However, there is no possible hydrocarbon interference for the mass 42 *m/z* (CNO^-) although its enhancement factor is very high (EF = 3050). A high EF value (950) is also found for 18-MEA (341 *m/z*), where there is no known mass interference. This clearly shows that mass interference cannot be the only one reason to explain all the very high SI yield improvements seen with C_{60}^+ beam.

Concerning inorganic peaks (in both ion polarities), the detection of atomic ions is less improved by the use of C_{60}^+ than that of clusters containing a combination of several of these atoms. This effect is not yet well understood but it might be related to the difference in energy deposition and emission mechanisms between C_{60}^+ and Ga^+ ions. Recent molecular dynamics simulations suggest that by the C_{60} projectile dissociate directly at the impact, depositing its energy only in the top surface layers and creating an overheated nanovolume that relaxes via collective atomic and molecular motions [14]. Moreover, different ion ionisation processes cannot be excluded too.

In conclusion, the use of C_{60}^+ primary beam is seen to improve the ToF-SIMS efficiency at the surface of natural biological matter such as human hairs. The enhancement factors vary between two and three orders of magnitude. This confirms the similar effect recently found for another protein (human serum albumin) adsorbed on a polycarbonate membrane [15].

Acknowledgement

The authors thank the FRFC of Belgium for the financial support in the acquisition of the C_{60} ion gun.

References

[1] J.M. Maxwell, M.G. Huson, Micron 36 (2005) 127.
[2] A. Harvay, C.M. Carr, A. Pereira, J. Cosmet. Sci. 55 (2004) 265.
[3] J.A. Swift, J.R. Smith, Scanning 22 (2000) 310.
[4] G.S. Groenewold, G.L. Gresham, A.K. Gianotto, R. Avci, J. Trace Microprobe Tech. 18 (1) (2000) 107.
[5] I.M. Kempson, W.M. Skinner, P.K. Kirkbride, A.J. Nelson, R.R. Martin, Eur. J. Mass Spectrom. 9 (2003) 589.
[6] S.B. Hornby, Y. Appa, S. Ruetsch, Y. Kamath, Int. Fed. Soc. Cosmet. Chem. Mag. 8 (2) (2005) 99.
[7] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill, J.C. Vickerman, Anal. Chem. 75 (2003) 1754.
[8] D.E. Weibel, N. Lockyer, J.C. Vickerman, Appl. Surf. Sci. 231–232 (2004) 146.
[9] N. Winograd, Anal. Chem. 77 (2005) 143A.
[10] P. Bertrand, L.T. Weng, Mikrochim. Acta 13 (1996) 167.
[11] D. Briggs, M.J. Hearn, Vacuum 36 (1986) 1005.
[12] Ionoptika Limited (Ed.), IOG-C60-20 Ion Source Operating Manual 99-014 Rev. 1.0, Southampton, UK, 2004, p. 44.
[13] V. Solomko, A. Delcorte, B.J. Garrison, P. Bertrand, Appl. Surf. Sci. 231–232 (2004) 48.
[14] Z. Postawa, B. Czerwindki, N. Winograd, B. Garrison, J. Phys. Chem. B 109 (2005) 11973.
[15] A. Delcorte, C. Poleunis, M. Henry, P. Bertrand, 16th European Symposium on Polymer Spectroscopy, Rolduc Abbey, Kerkrade, NL, May 29–June 1, 2005.