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Surface analysis of permanent wave processing hair using DART-MS

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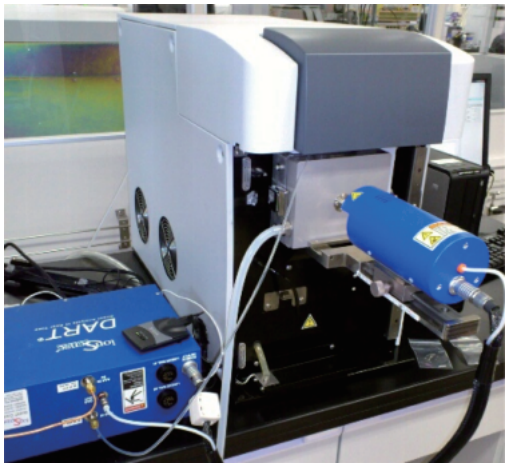
Introduction

Permanent wave processing of hair is carried out at two processes as follows;
(A) Reducing agent (permanent wave 1 agent) makes the bridge construction between the keratin protein molecular chains of hair, especially disulfide (S-S) bond of cystine residue cleaved to thiol (-SH) group and hear results a wave and curl.
(B) Oxidizing agent (permanent wave 2 agent) makes -SH group oxidized to be reproduced S-S bond. As reducing agents used for permanent wave 1 agent, the thing of cosmetics approval, such as cysteamine hydrochloride and a butyrolactone thiol (brand name Spiera, other than quasi drugs, such as ammonium thioglycolate, acetyl cystein, and thiolactic acid, are used.

After hair is applying permanent wave processing and coloring repeatedly, the chemical structure of a keratin molecule and fine structure in the hair have been damaged and it resulted as damage hair. It is thought that hair becomes dryness and twining if the cuticle which covers hair is damaged, so it is important to investigate the surface structure of hair and its chemical structure changing.
DART (Direct Analysis in Real Time), a direct atmospheric pressure ionization source, is capable of analyzing samples directly with little or no sample preparation. Here, analysis of the ingredient which has deposited on the permanent wave processing hair surface was tried using this DART combined with a mass spectrometer.

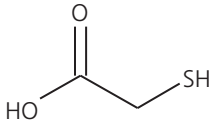


High Speed Mass Spectrometer

Ufswitching
High-Speed Polarity Switching 15msec
Ufscanning
High-Speed Scanning 15,000u/sec

Figure 1 DART-OS ion source & LCMS-2020

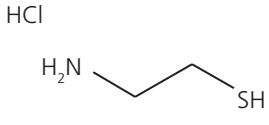
TGA
(thioglycolate)



Fw 92

Wave efficiency is good in a weak alkaline (pH 8 - 9.5)

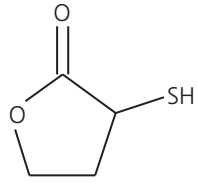
CA
(cysteamine hydrochloride)



Fw 113

Wave efficiency is good in a weak alkaline (pH 8 - 9.5)

BLT
(butyrolactone thiol)



Fw 118

Wave efficiency is good in a weak acid (pH 6)

The chemical state and property were investigated in the surface of the hair which repeated permanent wave processing with these reducing agents.

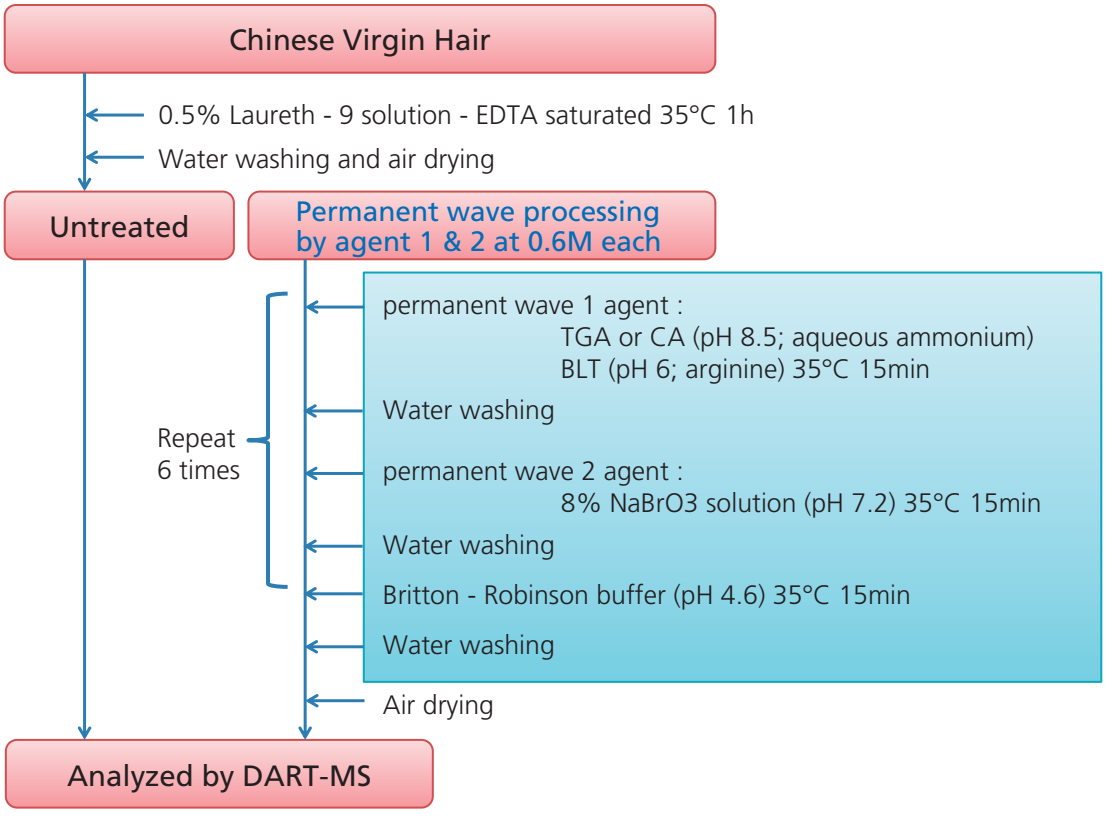
Surface analysis of permanent wave processing hair using DART-MS

Methods and Materials

The Chinese virgin hair purchased from the market was washed with the 0.5% non-ionic surfactant containing saturated EDTA solution, and then it was considered as untreated hair sample. Permanent wave processing of hair was prepared as following; the 0.6M TGA solution and 0.6M CA solution which were adjusted to pH8.5 with aqueous ammonia and the 0.6M BLT solution adjusted to pH6.0 with arginine water, which were used as a reducing agent. After hair sample was reduced for 15 minutes at 35°C using each solvent, it was carried out oxidation treatment at 35°C by being immersed in 8% sodium bromate solution (pH7.2) for 15 minutes.
LCMS-2020 (Shimadzu) was coupled with DART-OS ion source (IonSense) and hear samples were held onto DART gas flow directly, then their surface analyzed.

MS condition (LCMS-2020; Shimadzu Corporation)

Ionization	: DART (Direct Analysis in Real Time)
Heater Temperature (DART)	: 350°C
Measuring mode (MS)	: Positive/Negative scanning simultaneously



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Result

After repeating operation of permanent wave processing 1-6 times using TGA (thioglycollic acid), CA (cysteamine), and BLT (Butyrolactonethiol), hair was immersed for 15 minutes at 35°C and with a flush and air-drying, then permanent wave processing hair was prepared. In order to investigate the ingredient which has deposited on the permanent wave processing hair surface, DART-MS analysis was performed.
DART-MS analysis was conducted in order of #1 Untreated (woman hair), #2 control; ammonia treatment (pH 8.5), #3 0.6M thioglycolic acid (TGA) processing, #4 0.6M butyrolactone thiol (BLT) processing, #5 0.6M cysteamine hydrochloride (CA) processing and #6 control; arginine processing (pH 6).

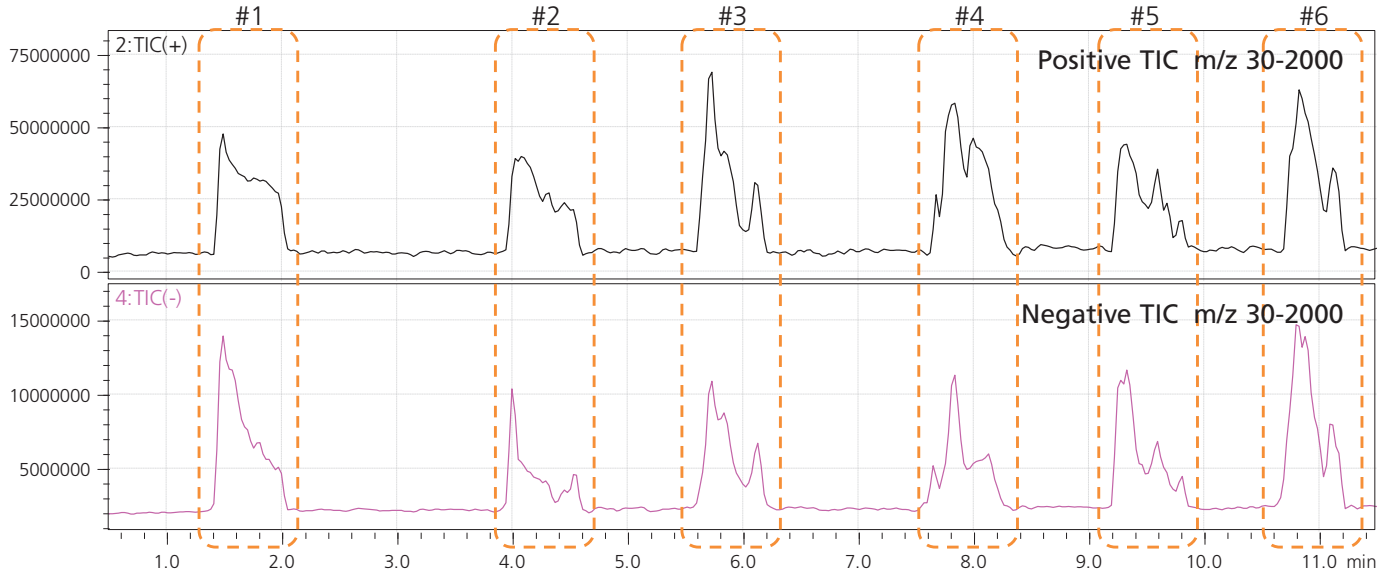

Figure 2 TIC chromatogram of each sample analyzing with DART

In the DART mass spectra of #1 untreated and #6 control, many signals considered as triglyceride and diglyceride were detected in both positive and negative spectra obtained by DART-MS. In #3 0.6M thioglycolic acid (TGA) processing spectra, the signal in particular of TGA origin was not detected.
In #4 BLT processing spectra (Figure 3), the signals considered to be oxidized BLT (3, 3'-dithiobis (tetrahydrofuran2-one), molecular weight 234) were detected at m/z 235 and 252 in the positive mode. The signal m/z 235 is equivalent to [M+H]+ and m/z 252, [M+NH4]+. In the negative mode, the signals, m/z 115, 231 were detected. They were considered the signal equivalent to [M-H]- and [2M-H]- of BLT oxide compound ($C_4H_4O_2S$, molecular weight 116) in which two hydrogen atoms were removed from BLT. Carrying out permanent wave processing by BLT, it was found that the dimer of BLT accumulated on the cuticle surface.
In #5 CA processing spectrum (Figure 5), the signal considered to be the dimer (Fw152) origin in which CA carried out S-S bond in the positive mode was detected at m/z 153.
This is equivalent to [M+H]+.

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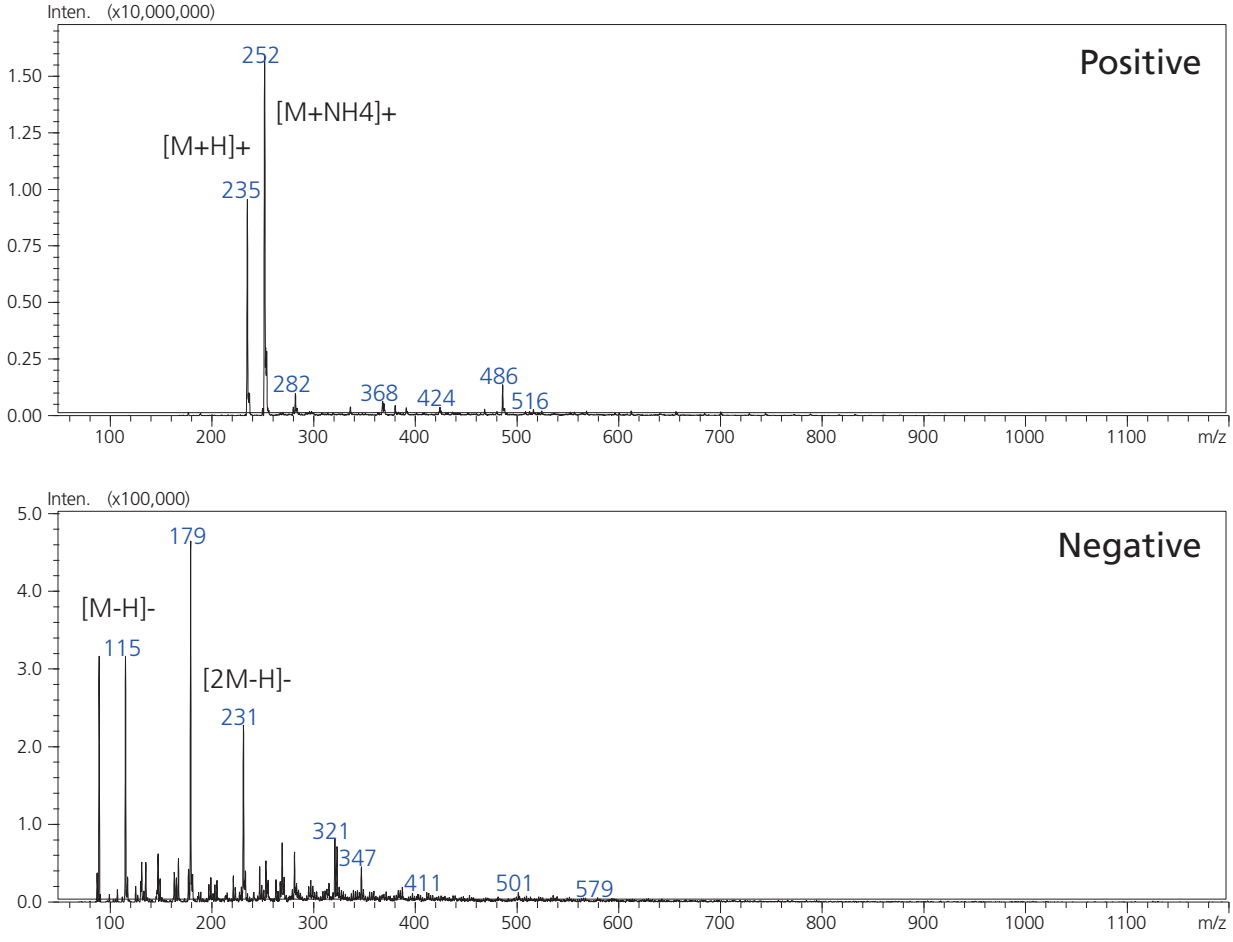

Figure 3 DART-MS spectra of #4 BLT processing
The BLT-related signals were detected from the positive and the negative spectra.

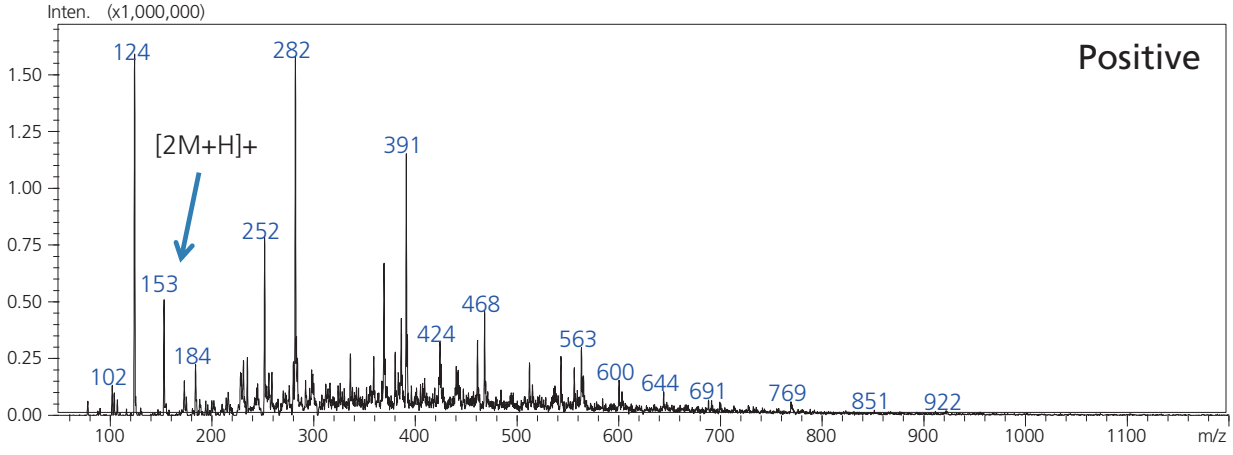

Figure 4 DART-MS spectra of #5 CA processing
The CA-related signal was detected from the positive spectrum

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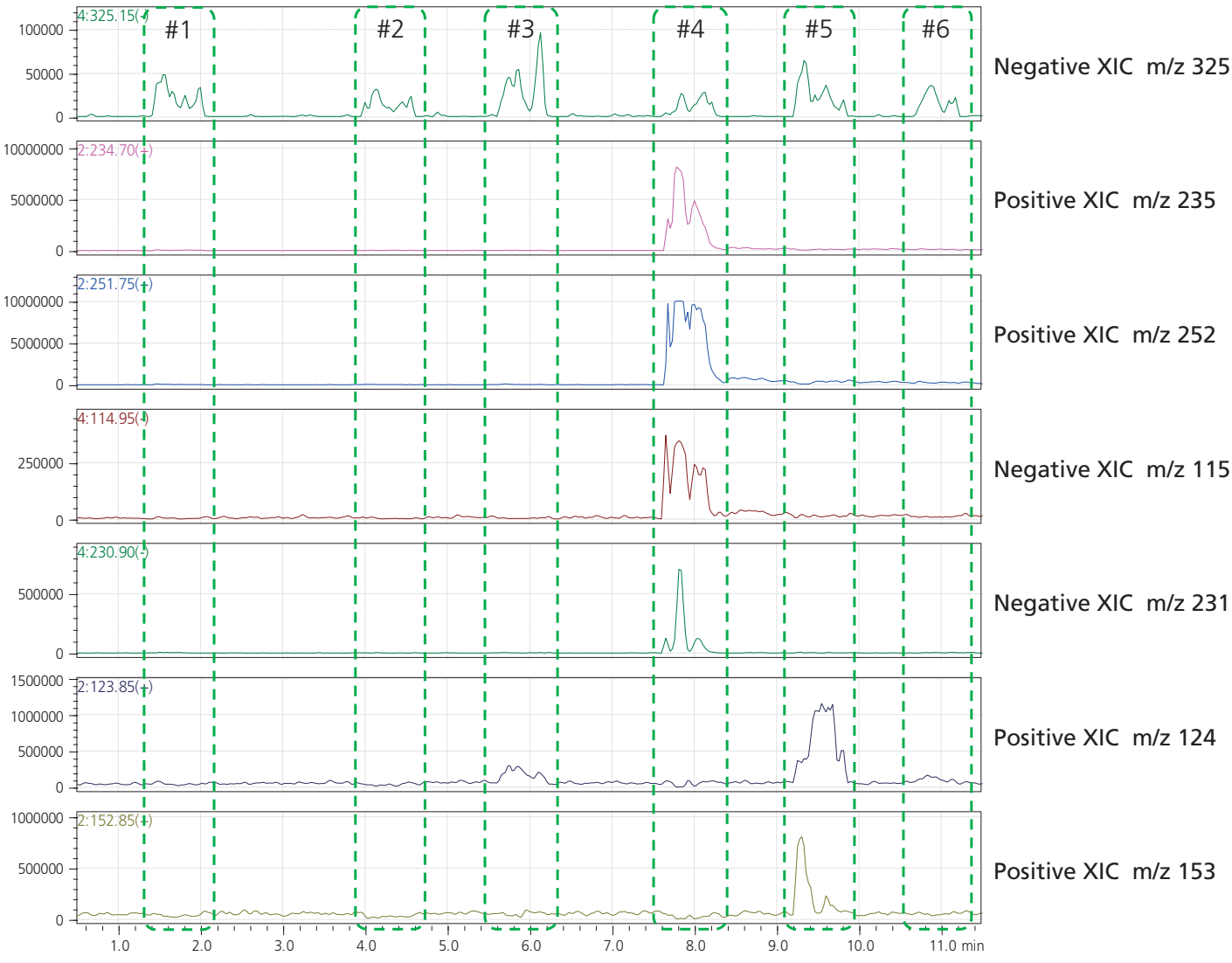

Figure 5 XIC chromatorgam of each sample analyzing with DART

In order to indicate clearly the signals specifically detected in each sample, the extraction chromatograms (XIC) were shown (Figure 5). It turned out that BLT-related signals were detected only in #4 and the CA-related signal in #5.
Moreover, although the signal intensity was weak, the signal at negative m/z 325 was detected from all samples. Negative m/z 325 is equivalent to [M-H]- of 18 methyl eicosanoic acid (18MEA, molecular weight 326). 18MEA is one of lipid components which protect a cuticle. There is no significant difference of this signal in the hair between treated hair and untreated hair. We would like to inquire so that intensity difference can be found out by further verifying the detection technique in the future.

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Conclusions

By direct analysis of the hair by DART-MS, the chemical structure change in the surfaces of hair, such as permanent wave processing, was able to be observed.

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