[POSTER NOTE]

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DEMONSTRATING THE APPLICABILITY OF DESI IMAGING COUPLED WITH ION MOBILITY FOR MAPPING COSMETIC INGREDIENTS ON TAPE STRIPPED SKIN SAMPLES

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OVERVIEW

- DESI-IM-MS was used for the analysis of tape stripped skin samples.
- Different types of cosmetic creams were applied to the forearms of volunteers.
- Data were compared in HDMS™ Compare software and visualized in High Definition Imaging (HDI) Software.
- Key differences between samples were observed.
- Species belonging to different cosmetics and to skin were observed.

INTRODUCTION

Cosmetics and Personal Care (CPC) has become a multi-billion dollar industry.[1] To ensure the safety and efficacy of their products, CPC manufacturers carry out increasingly sophisticated analyses of their products.[2] In particular, the ability of key cosmetic ingredients to permeate the skin's surface is of specific interest.

Tape stripping of the *stratum corneum* is a well accepted method by which the penetration of surface applied dermal preparations can be assessed.[3] The analysis of successively stripped layers of skin, post application of a cosmetic formulation, reveals information about the penetration of ingredients into the skin.

In this work we evaluate the applicability of DESI coupled with ion mobility MS for the analysis of ingredients in cosmetic creams applied to the skin.

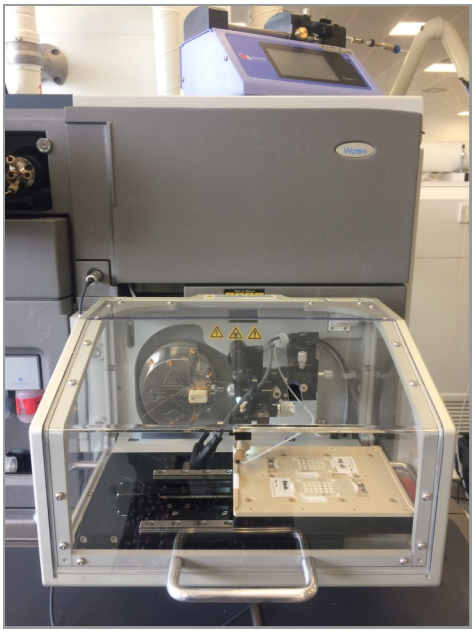

Figure 1. DESI source mounted on a SYNAPT G2-Si HDMS instrument.

METHODS

MS conditions

MS system: SYNAPT™ G2-S*i* HDMS

A Desorption ElectroSpray Ionization (DESI) source (Prosolia) was installed on a SYNAPT G2-S*i* HDMS instrument (Waters Corporation) (Figure 1*)*.

DESI and ion mobility-MS conditions were optimized as follows:

- Ionization mode : DESI+
- Capillary voltage : 3.0 kV
- Cone voltage: 50 V
- Source temp.: 120 °C
- IMS Wave velocity: 1000-350 m/s (ramp)
- IMS Wave height: 40 V
- IMS cell pressure: 3.3 mbar
- DESI spray solution: 98:2 MeOH:H_2O v/v + 0.1% Formic acid + 250 pg/µL Leucine enkephalin
- DESI spray solution flow rate: 3 µL/min
- DESI gas pressure: 7 bar
- DESI sprayer angle: ~85^o
- MS inlet angle: ~10^o

Sampling procedure

Tape stripping of the forearm (ventral) (Figure 2) was carried out using D-Squame sampling discs (CUDERM). A typical methodology was followed whereby 20 acquisitions were made, using a single sampling disc, from similar skin regions on three volunteers after topical application of a cosmetic cream (sunscreen on left arm, anti-wrinkle moisturizer on right arm).

Two 3 cm x 3 cm square regions were marked on the volunteers' forearms. A measured amount (~1 mL) of cosmetic cream was applied using a syringe and gently rubbed onto the skin using a gloved finger. After approximately 10 min. post application the marked areas were sampled.

Data acquisition and processing

Samples were mounted on glass slides using double-sided sticky tape. Individual spots on each sample type were acquired for optimization and survey purposes. Rectangular regions were imaged on each sample type, as shown in Figure 3. Imaging pixel size was 100 µm x 100 µm, acquisition rate was 200 µm/sec., scan time was 0.485 sec., total acquisition time was 50 min.

DESI-IM-MS datasets were acquired using MassLynx™ Software (v.4.1) and examined using MassLynx and DriftScope™ Software (v.2.8). Subsequently, data were processed and visualized using HDMS Compare Software (v1.1) and High Definition Imaging (HDI) (v.1.4) informatics.

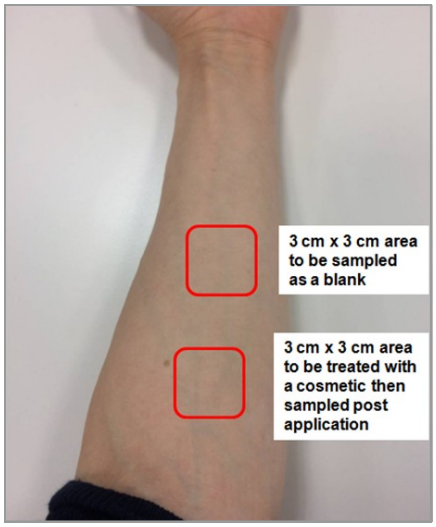

Figure 2. Regions of left ventral forearm used for blank skin sampling and cosmetic application followed by skin sampling post application.

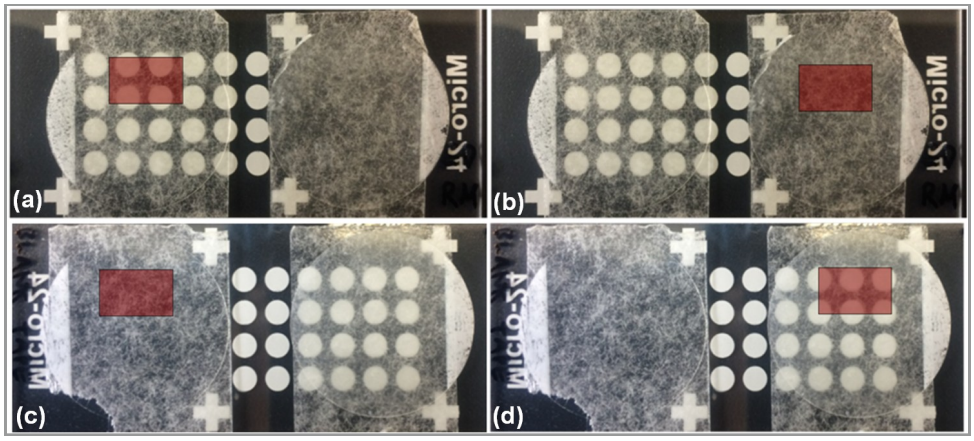

Figure 3. Rectangular regions were selected for imaging: (a) left forearm sunscreen sample, (b) right forearm anti-wrinkle moisturizer sample, (c) blank D-Squame sample tape, (d) blank skin sample.

RESULTS & DISCUSSION

A proof-of-principle approach was taken to demonstrate the utility of DESI-IM-MS for analysing tape stripped skin samples.

Comparisons were made between blank D-Squame tape samples (3 replicates) and blank skin samples (3 replicates) to identify components that were unique to the skin samples. Comparisons were made using HDMS Compare software. An example of the result from a comparison is shown in Figure 4.

When the same data were reviewed in DriftScope software skin-relevant components were seen to separate from background ions related to solvent or tape components, as seen in Figure 5. This shows that ion mobility can be used for spectral cleanup and deconvolution.

Comparisons were also made between blank skin samples and skin with applied cosmetic samples (sunscreen and anti-wrinkle moisturizer).

Figure 6 shows the spectral comparison between blank skin and skin with sunscreen applied.

Figure 7 shows the spectral comparison between blank skin and skin with anti-wrinkle moisturizer applied

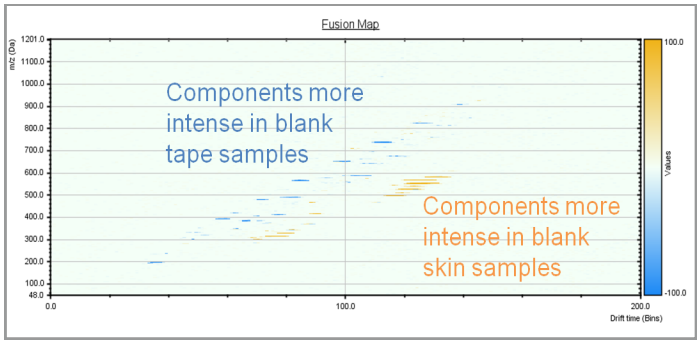

Figure 4. Comparison between blank D-Squame tape samples and blank skin samples were made using HDMS Compare software. Ions that are more intense in the blank tape sample are shown in blue and ions that are more intense in the blank skin sample are shown in orange.

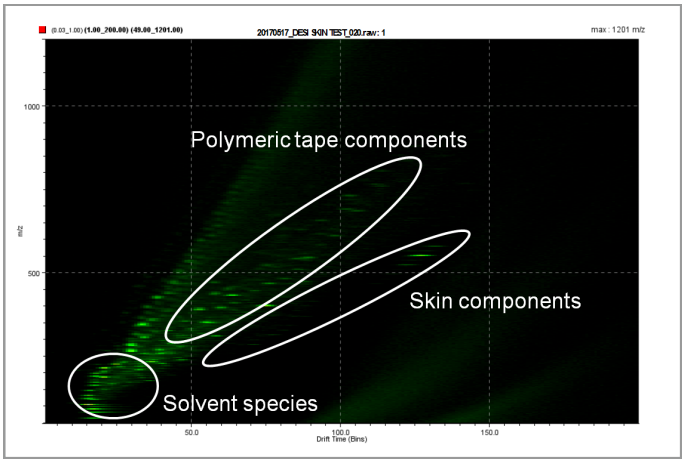

Figure 5. Separation in the ion mobility dimension clearly differentiates skin components from background ions indicating that ion mobility can help with spectral cleanup and deconvolution.

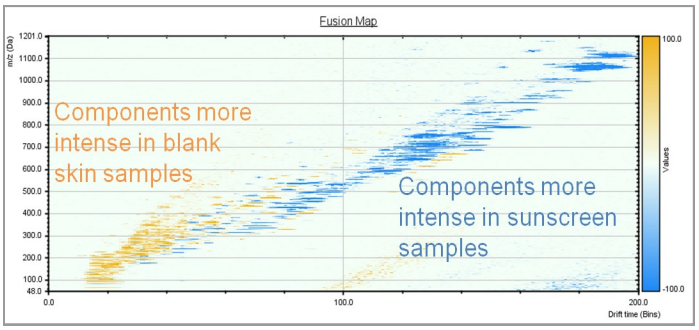

Figure 6. Comparison between blank skin samples (ions shown in orange) and samples from areas of skin with sunscreen applied (ions shown in blue).

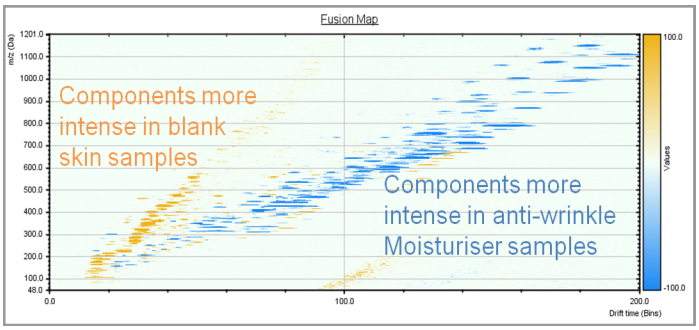

Figure 7. Comparison between blank skin samples (ions shown in orange) and samples from areas of skin with anti-wrinkle moisturizer applied (ions shown in blue).

The spectral comparison data in Figure 6 and Figure 7 show that both the sunscreen and the anti-wrinkle moisturizer contain a large number of characteristic higher mass components. Furthermore, the anti-wrinkle moisturizer has many more polymeric species than the sunscreen, indicated by regularly spaced ions. The mass difference between the regularly spaced ions represents the mass of the monomer species.

Use of the selection tools in DriftScope Software allows the identification of polymeric species. Figure 8 shows the selection of a series of higher mass ions in the anti-wrinkle moisturizer that are 74 Da apart, which represents a section of polydimethylsiloxane (PDMS) polymer.

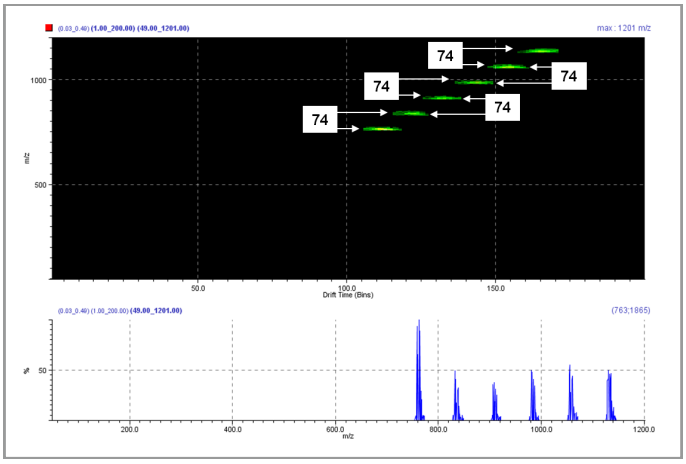

Figure 8. Selection of a related series of ions from the anti-wrinkle moisturizer sample reveals that the monomer mass is 74 Da, which indicates the presence of a PDMS polymer.

Using High Definition Imaging (HDI) software enabled key ions to be imaged across the blank tape, blank skin, sunscreen and anti-wrinkle moisturizer samples. Figure 9 shows images for a representative skin ceramide, 24:0 (2S-OH)ceramide [N-(2'-(S)-hydroxylignoceroyl)-D-*erythro*-sphingosine] with *m/z* 666.64.

Figure 9 illustrates that the skin ceramide is absent from both the blank tape sample and the skin sample with anti-wrinkle moisturizer applied, whereas the ceramide is most clearly detected in the blank skin sample and can also be seen at a lower intensity in the skin sample with sunscreen applied. This suggests that the anti-wrinkle moisturizer does provide a effective barrier on the skin.

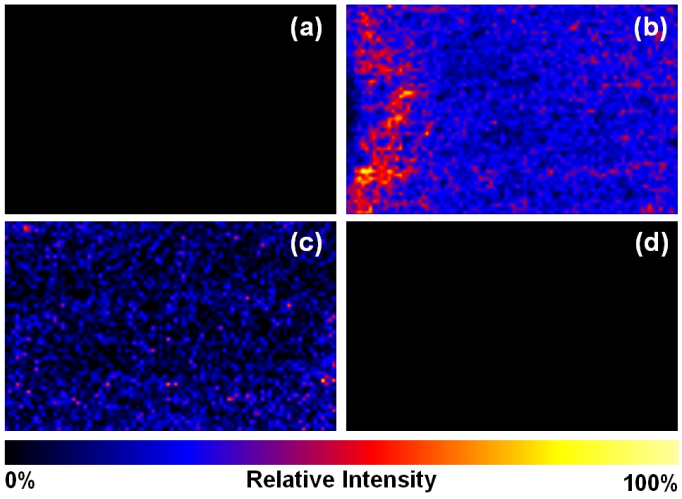

Figure 9. TIC normalized images of a typical skin ceramide with m/z 666.64 for (a) blank tape sample, (b) blank skin sample, (c) skin with sunscreen applied, (d) skin with anti-wrinkle moisturizer applied

Imaging of the four sample types also enabled identification of some common components in both the sunscreen and anti-wrinkle moisturizer that were absent from both the blank tape and blank skin samples. An example of such a common component, with *m/z* 785.36, is shown in Figure 10. The arced distribution of the ions is likely to be because of the way pressure was applied during the manual sampling method used.

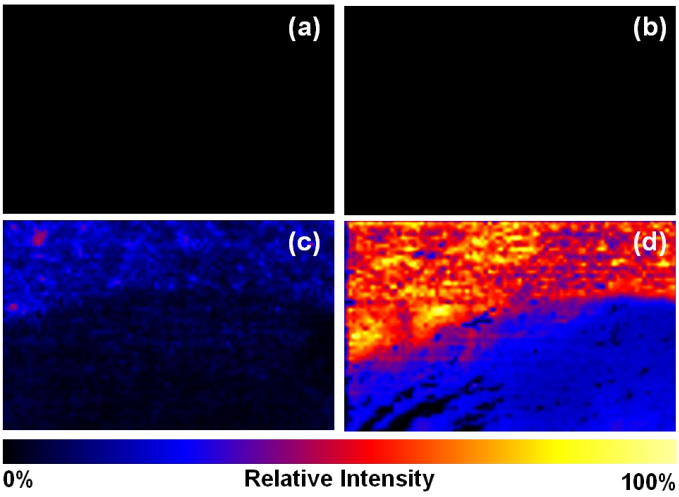

Figure 10. TIC normalized images of component with m/z 785.36 that is absent from (a) the blank tape sample and (b) the blank skin sample, but is common to (c) the skin with sunscreen applied and (d) the skin with anti-wrinkle moisturizer applied.

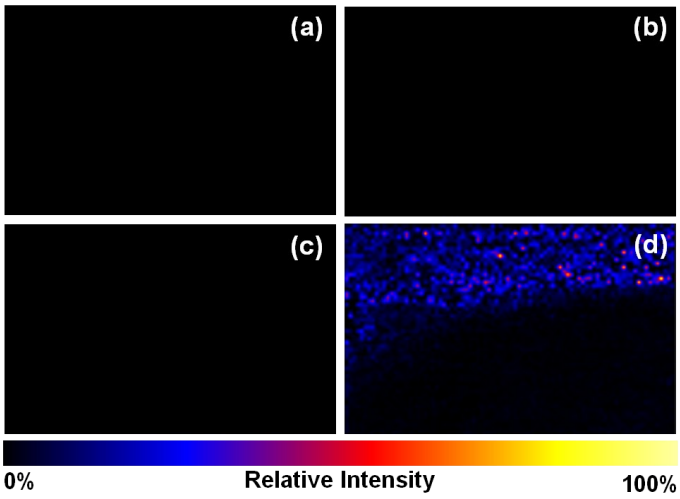

Figure 11. TIC normalized images of ion m/z 1147.38 which is unique to the anti-wrinkle moisturizer sample: (a) blank tape sample, (b) blank skin sample, (c) skin with sunscreen applied, (d) skin with anti-wrinkle moisturizer applied.

As seen in the HDMS Compare plots, the anti-wrinkle moisturizer had more high mass ions than any of the other samples. Many of these high mass ions are unique to that sample. Figure 11 illustrates an example of one of the unique ions, *m/z* 1147.38.

CONCLUSIONS

- **DESI coupled with ion mobility mass spectrometry (DESI-IM-MS) has been demonstrated to be applicable for the analysis of tape-stripped skin samples with cosmetic formulations applied.**
- **DESI-IM-MS data can be interrogated in a number of different ways using ion mobility specific software to illustrate different aspects of the data.**
- **DriftScope Software can be used to provide a global overview of the ions present and can be used to facilitate spectral cleanup and deconvolution.**
- **HDMS Compare Software offers a rapid route to binary comparison of ion mobility data. Images illustrate ions that are more significant in one sample compared with another but do not indicate the distribution of those ions across the sample surface.**
- **High Definition Imaging (HDI) informatics enables full imaging of the tape-stripped samples including component distribution and intensity.**
- **The proposed methodology was successfully used to investigate components of cosmetic formulations (sunscreen and anti-wrinkle moisturizer) applied to skin.**
- **The proposed methodology illustrates the efficacy of the anti-wrinkle moisturizer as a barrier to protect components of the skin from external abrasion (tape-stripping).**

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References

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