

# AP-MALDI UHR imaging of sunscreen ingredients in finger marks on an LTQ/Orbitrap instrument

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## INTRODUCTION

AP-MALDI UHR module is a flexible add-on for existing Thermo LC/HRMS equipment.

This Application Note presents a protocol for AP-MALDI imaging workflows based on a Thermo LTQ/Orbitrap Elite instrument.

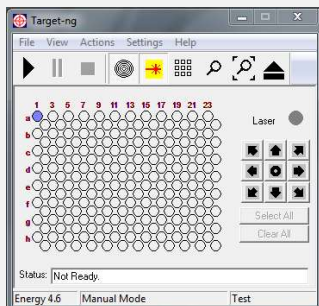
## WORKFLOW

### Sample Preparation:

- 1) Application of sunscreen on skin, and removal of excess using paper handkerchief. Application of of fingermarks on a clean silicon wafer surface
- 2) Matrix deposition with a TM-Sprayer (HTX Technologies) or equivalent to get homogeneous crystals deposition

### Data Acquisition:

- 1) Definition of image parameters (mode, dimension, pixels) in *Target* (Control software)  
 → Parameters are saved as .xml file
- 2) Molecular imaging using AP-MALDI UHR Source (MassTech) with LTQ/Orbitrap Elite (Thermo) high resolution MS.  
 → Data saved as .raw file



### Data Handling:

- 1) Data handling with ImageQuest (Thermo) using native files (xml and raw files)
- 2) Conversion of xml and raw files into imzML file using MassTech imzML Converter
- 3) Data handling with MSI reader, DataCube Explorer, SCILS...



Fig.1: MassTech AP/MALDI UHR add-on

## KEY CHARACTERISTICS AND BENEFITS

- MALDI imaging capabilities down to 10 micron lateral resolution
- Switch from the AP-MALDI configuration to LCMS configuration within 5 minutes.
- Provides MALDI analysis and imaging capabilities to high-end LCMS instruments
- Laser focus can be adjusted from 10 to 30 microns

## Available modes of operation

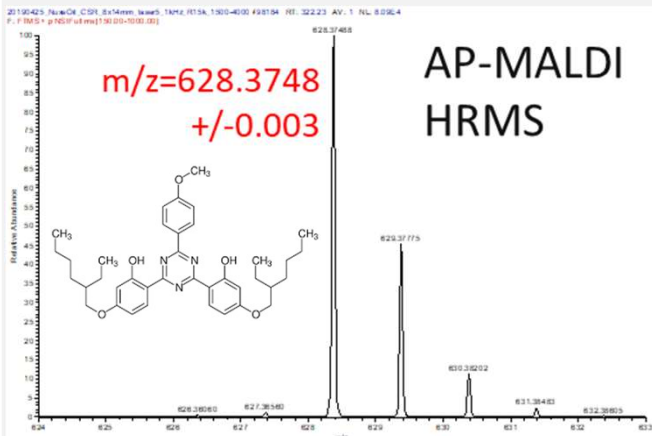
- Sequential MALDI analysis of multiple spot analysis using spiral or raster motion (AB Sciex OptiTOF 192) with tunable parameters
- MALDI imaging using Pixel-Map, with tunable in-pixel motion for multiplexed analysis (HRMS, SRM...).
- MALDI imaging using Constant Speed Raster (CSR) modes for increased pixel rate (MS dependent)

## CASE STUDY:

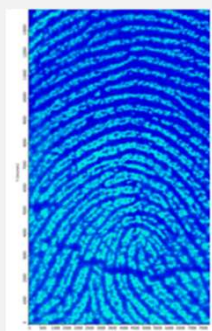
- imaging of sunscreen ingredients in finger marks
- MALDI parameters: 1kHz laser frequency, 10% laser energy
- MS parameters R=60k, Injection time (fixed)=200ms

### AP-MALDI HRMS imaging:

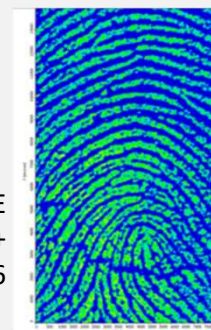
APMALDi Imaging of cosmetic ingredients in fingermarks allows for the detection of intense signals corresponding to UV-filters. In particular, two peaks detected at  $m/z$  628.3748 and 823.51166 are observed. Considering the sub-ppm mass accuracy of the Orbitrap Elite MS measurement (with lock mass = matrix peak), the tentatively assigned formula are  $[C_{38}H_{49}N_{3}O_5+H]^+$ .



This formula is the best fit among tested formula according to  $[C_{30-100}H_{30-100}N_{0-100}O_{0-100}+H]^+$  and potentially correspond to Bemotrizinol (see structure in insert,  $\Delta m/z=0.0003$  Da).



Bemotrizinol  
 $[C_{38}H_{49}N_{3}O_5+H]^+$   
 = 628.37450



ETHYLHEXYL TRIAZONE  
 $[C_{48}H_{66}N_{6}O_6]^+$   
 823.51166

Fig.2: Single pixel mass spectrum showing the signal of tentatively assigned Bemotrizinol UV filter. APMALDI images of bemotrizinol and ethylhexyl triazone from finger marks

### Structural confirmation of UV filters by MS/MS:

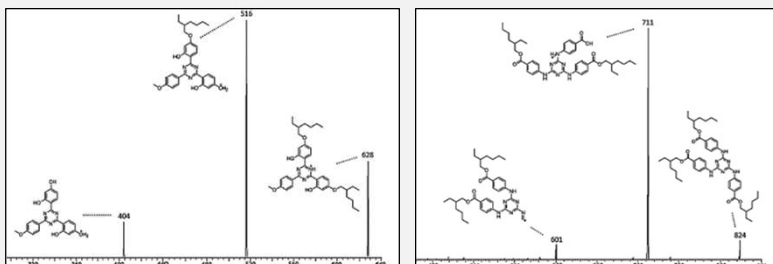


Fig.4: MS/MS data from in Ref [1]

The structural confirmation of the tentatively assigned UV filters is obtained by MS/MS analysis (Collision induced dissociation). The obtained characteristic fragments are consistent with published data [1] and confirm the suspected structures.

AP-MALDI produced ions can be analyzed in hybrid HRMS by fullscan FTMS scans and targeted MS/MS or SRM scans in the ion trap for maximum identification confidence.

#### Conclusion:

AP-MALDI coupled to HR MS Orbitrap instruments allows for confident identification of detected molecules from cosmetic ingredients in finger marks.

[1]:D.N.de Oliveira et al. , In vitro evaluation of Sun Protection Factor and stability of commercial sunscreens using mass spectrometry J.Chromatogr. B 988 (2015) 13–19

MassTech offers a range of analytical ionization sources, accessories and complete instruments for advanced analytical platforms. The AP-MALDI UHR is available exclusively from MassTech.

To request further information, please contact:

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MassTech selected LIST as European Application Lab. [www.list.lu](http://www.list.lu)