Recent Topics in TOF-SIMS Instrumentation at ULVAC-PHI

ULVAC-PHI Inc., Analytical Laboratory

Shin-ichi IIDA

The 18th Scientific International Symposium on SIMS Related Techniques Based on Ion-Solid Interactions (SISS)

23th July, 2016

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Outline

- Company Introduction
- Introduction of PHI nanoTOF II
- Applications
    1) FIB-TOF-SIMS
    2) MS/MS
- Summary

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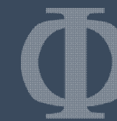
About ULVAC-PHI -The World Leading Manufacturer of Surface Analysis Instruments-



XPS

PHI *Quantera II*

PHI *VersaProbe III*

PHI *X-tool*

AES

PHI *710*

PHI *4800*

SIMS

PHI *nanoTOF II*
Time-of-Flight SIMS

PHI *ADEPT-1010*
Quadrupole SIMS

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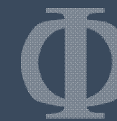
PHI New Products



PHI VersaProbe III

✓Scanning micro focus X-ray source

✓High sensitivity

✓Ultimate depth resolution

✓Various types of options

PHI 4800

✓SCA analyzer enables us to obtain the AES spectrum with high sensitivity, and high energy resolution

✓Detailed AES chemical map

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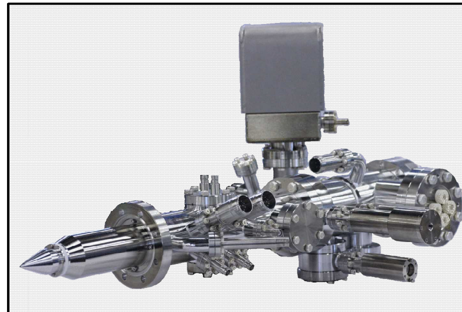
Introduction of PHI nanoTOF II

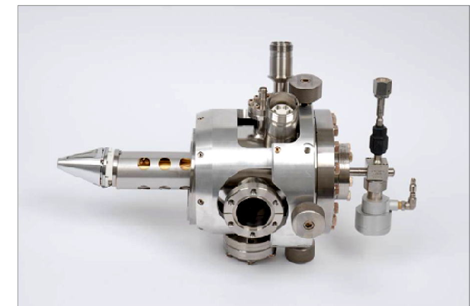
After releasing PHI nanoTOF in 2006, we have provided many components.

Ar gas cluster ion gun

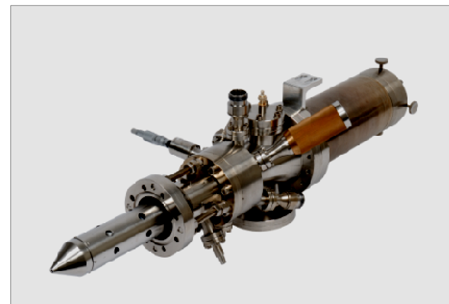
FIB gun



Ar/O_2 ion gun



C_{60} ion gun



Cs ion gun

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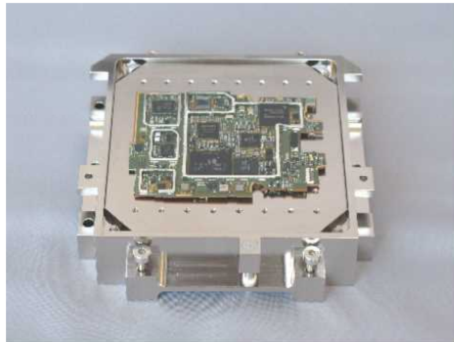
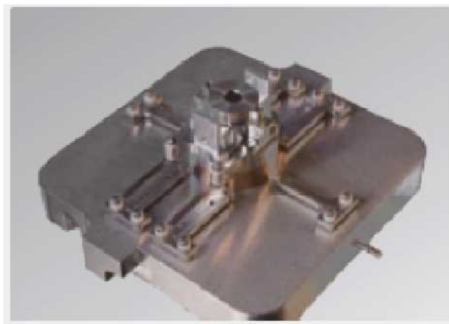
Specimen Stage Options

Specimen Stage (standard)



Transfer Vessel

Cold Stage
(-150～+150 ℃)



Hot Stage
(RT ～ +600 ℃)

Zalar Rotation

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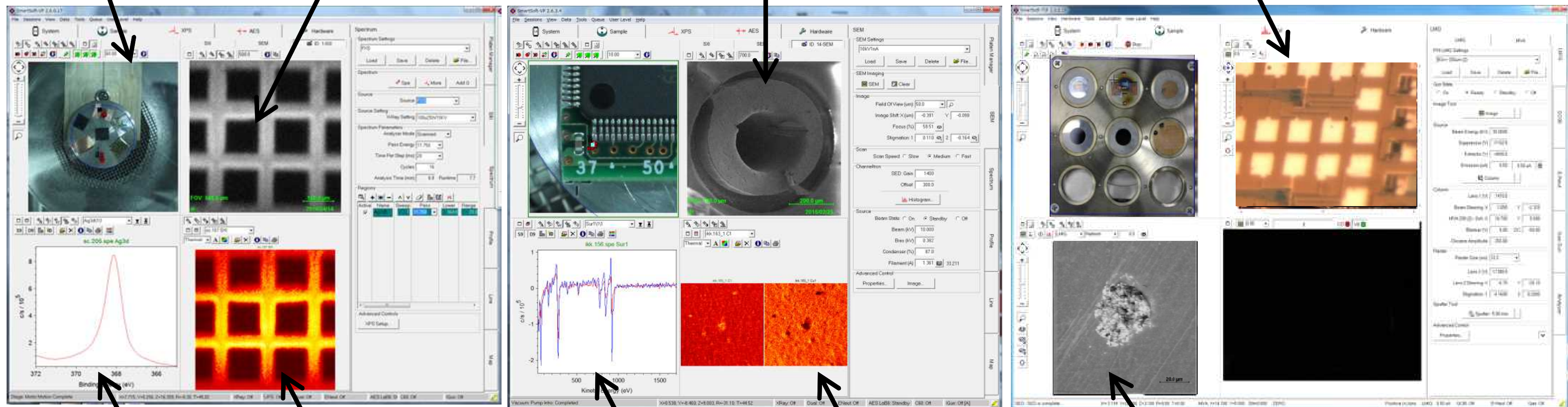
Common Operation Software "SmartSoft"

XPS

AES

TOF-SIMS



We provide "SmartSoft™" for all types of our instruments.
The same software interface makes us easy to master the operation of all PHI instruments.

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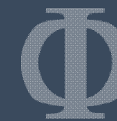
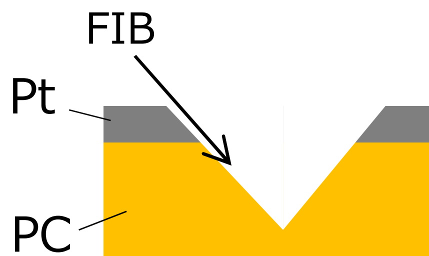
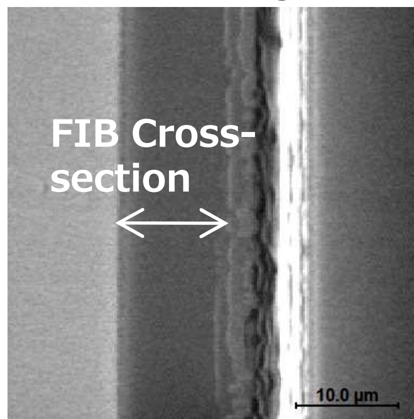
FIB Fabrication of Inorganic/Organic Material



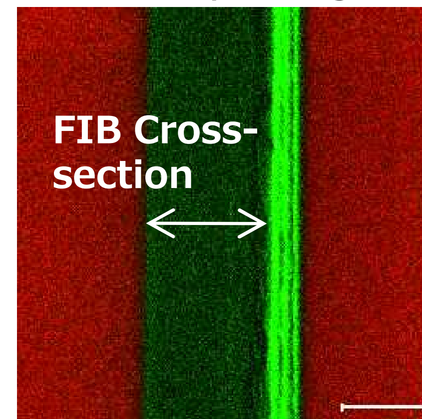
Sample: Pt/Polycarbonate



SIM Image

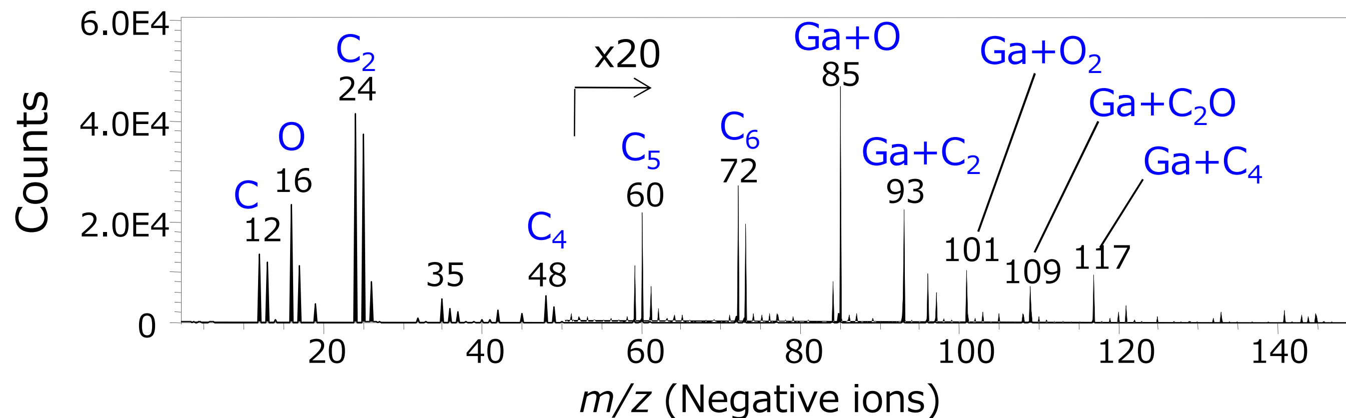


Overlay Image



R : Pt^-
G : C_2^-

Negative ion spectrum from FIB cross-section



FIB causes damage on the cut surface and leads to no chemical information.

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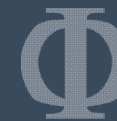
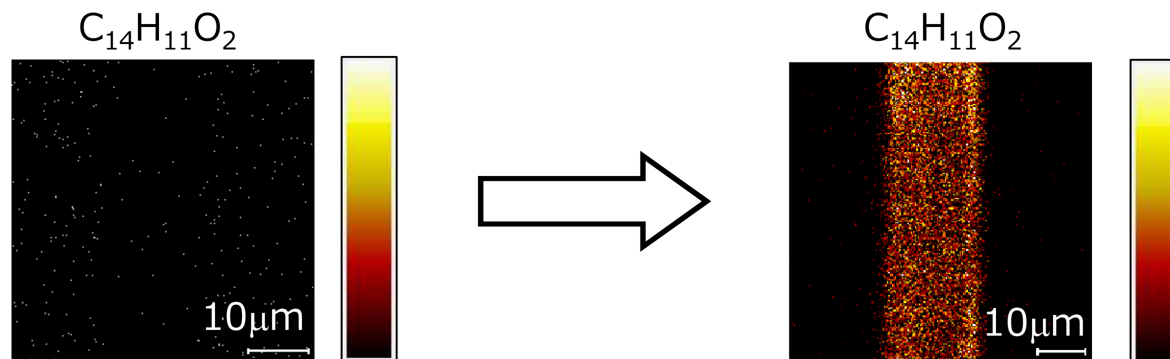
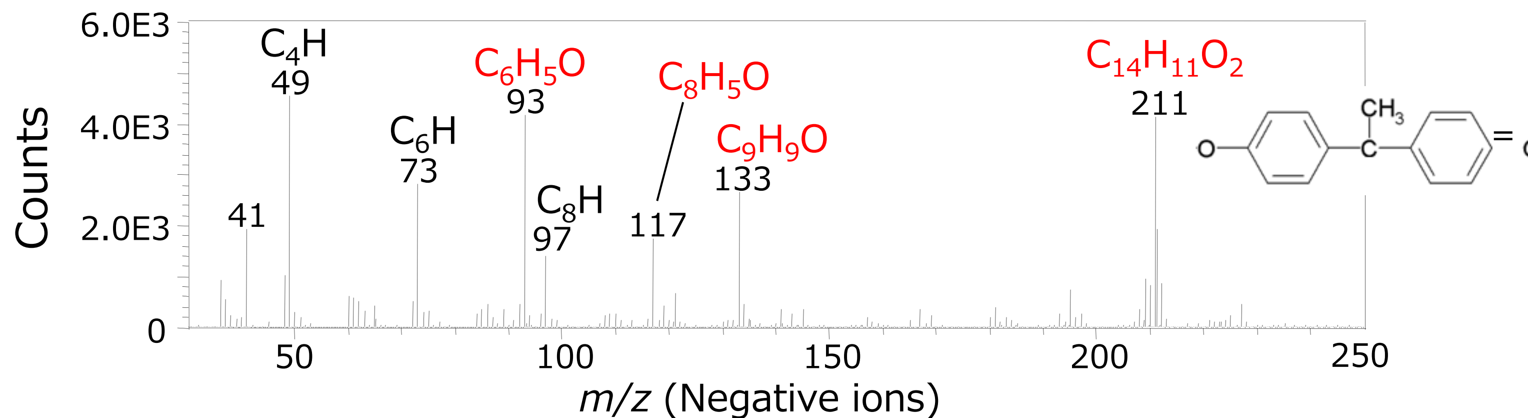
Removal of FIB Induced Damaged Layer



After removing the damaged layer by Ar-GCIB...



Negative ion spectrum from FIB cross-section



Combination of FIB and Ar-GCIB enables us to discover the chemical information underneath the metal layer.

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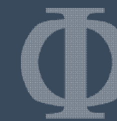
Introduction -Why is MS/MS needed?-



Interpretation of a TOF-SIMS spectrum→ Quite difficult !

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(1) Unpredictable fragment pattern

Need to take a spectrum of standard sample in advance.

(2) Commercial use of cluster ion beam

Sensitivity of high mass molecular ions are dramatically enhanced.
Many peaks are observed at high mass region.

(3) Conventional TOF-SIMS instrument

For molecular ions > 200 Da, difficult to determine the chemical formula from measured mass.

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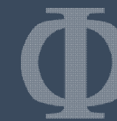
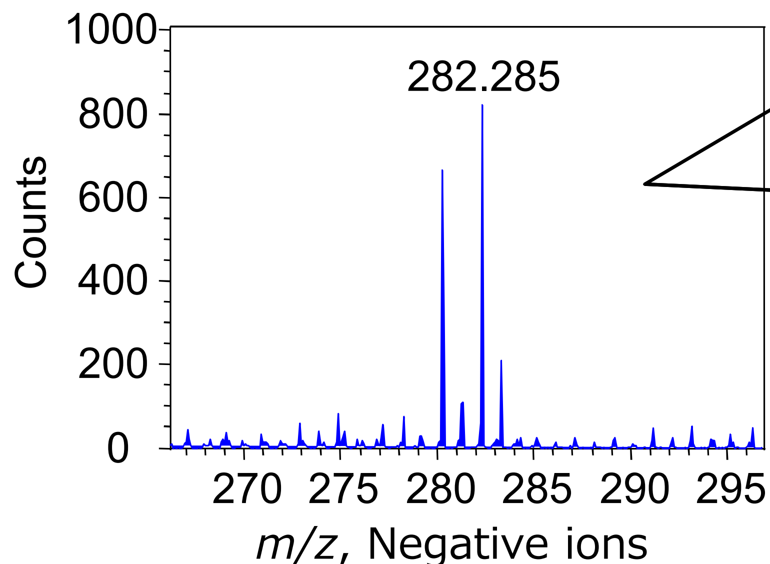
Introduction -Why is MS/MS needed?-



Peak Identification in TOF-SIMS



Possible Chemical Formula (C,H,N,O)

Formula(e)		Mass [amu]	Dev [mamu]
$C_{18}H_{36}NO$	P	282.27949	5.57
$C_{17}H_{36}N_3$	P	282.29073	-5.67
$C_{16}H_{34}N_4$	P	282.27816	6.90
$C_{19}H_{38}O$	P	282.29206	-7.00
$C_{17}H_{34}N_2O$	P	282.26692	18.14
$C_{18}H_{38}N_2$	P	282.30330	-18.24
$C_{15}H_{32}N_5$	P	282.26559	19.47
$C_{18}H_{34}O_2$	P	282.25568	29.38

MS/MS system in TOF-SIMS enables us to overcome the difficulty of the peak identification.

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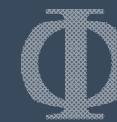
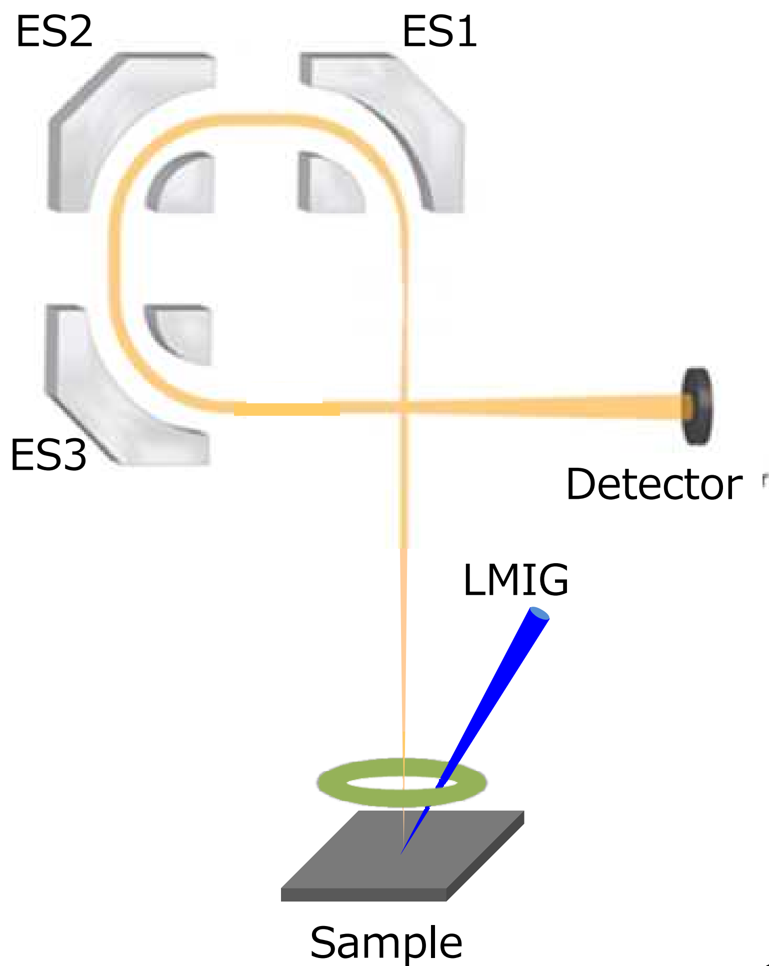
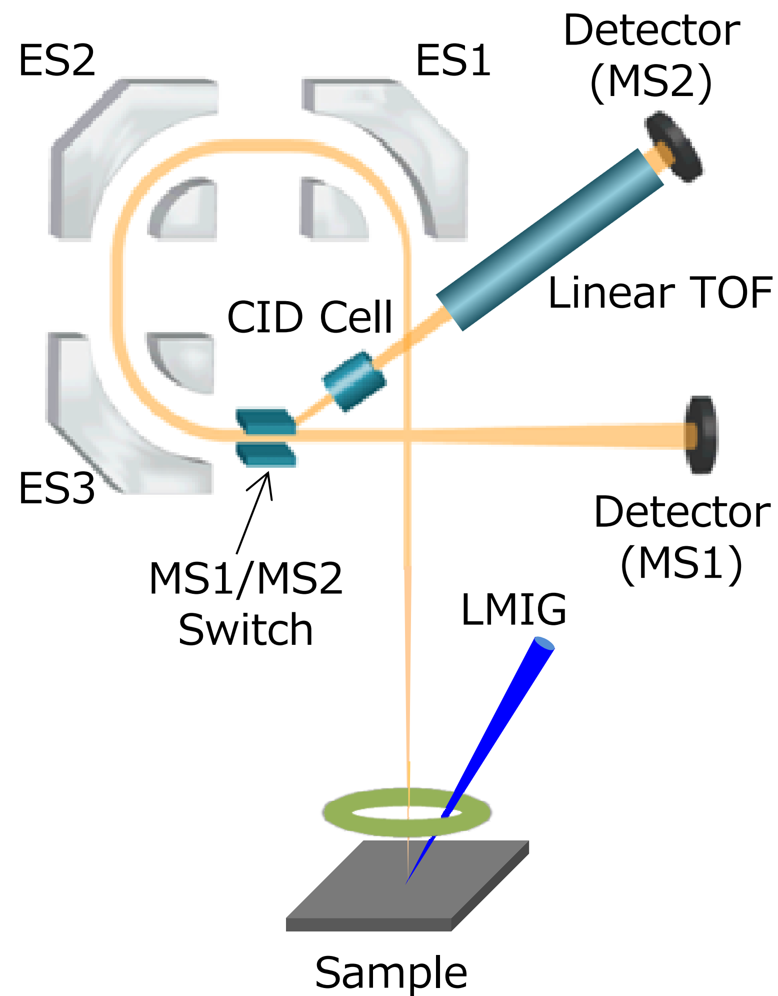
MS/MS in TOF-SIMS







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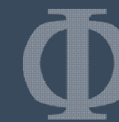
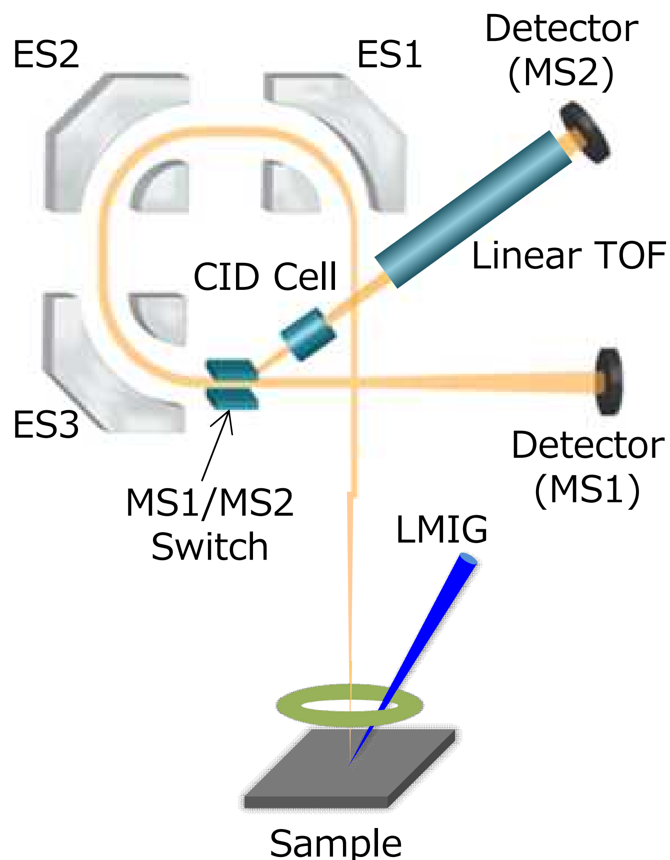
Features of the MS/MS in TOF-SIMS





1) Parallel detection
   Collect both MS^1 and MS^2 data
   from the same area simultaneously.

2) Width of mass selection within 1 Da

3) Easy operation
   Only input the mass number into the software.

4) High speed acquisition
   Maintain the TOF-SIMS repetition rate

5) Simple MS^2 spectrum

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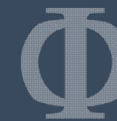

For further information on the applications of parallel imaging MS/MS,

please see the presentation by G.L.Fisher, Physical Electronics

on Friday at 2:50 pm

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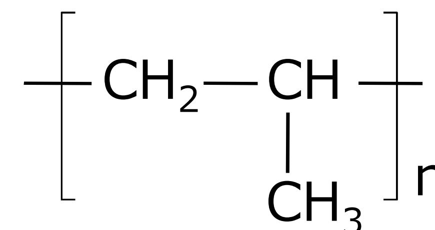
Sample

- Sample

  Several unknown additives in PP

Polypropylene (PP)



- Analysis Conditions
  - Primary ions: 30 keV Bi_3^+
  - Measurement time: 8 min
  - PIDD: 7.6×10^{11} ions/cm^2

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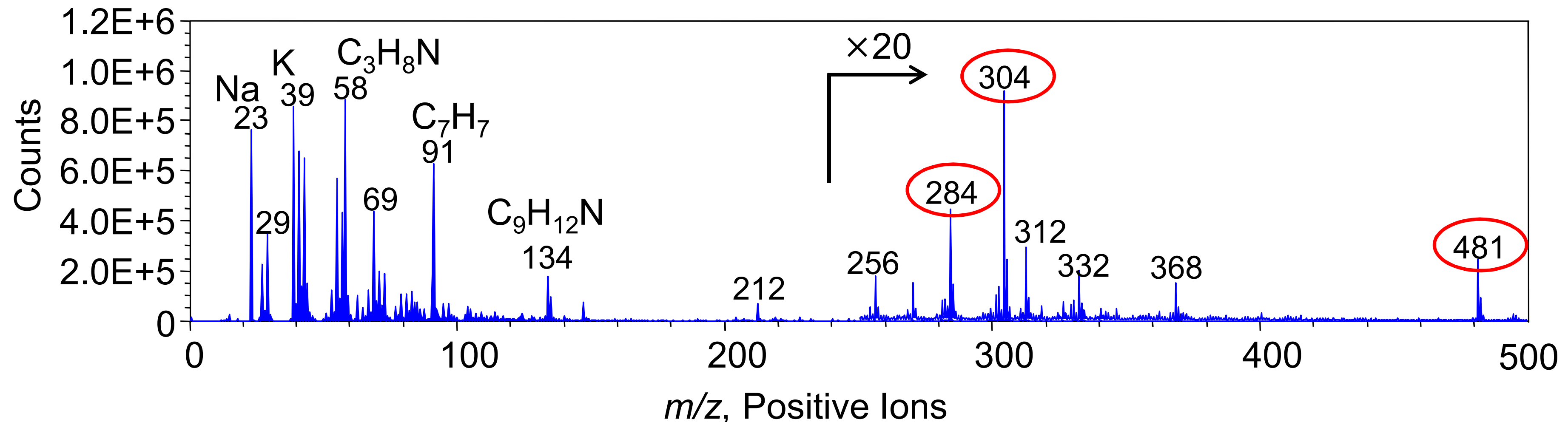
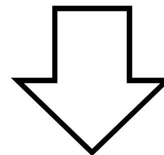
Conventional TOF-SIMS Spectrum

MS[1] (conventional TOF-SIMS) spectrum from PP surface



Spectrum was complicated, and difficult to determine the chemical formula for compound identification.



To reveal the details of them,

MS^2 spectra of *m/z* 304, 284 and 481 were acquired.

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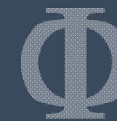
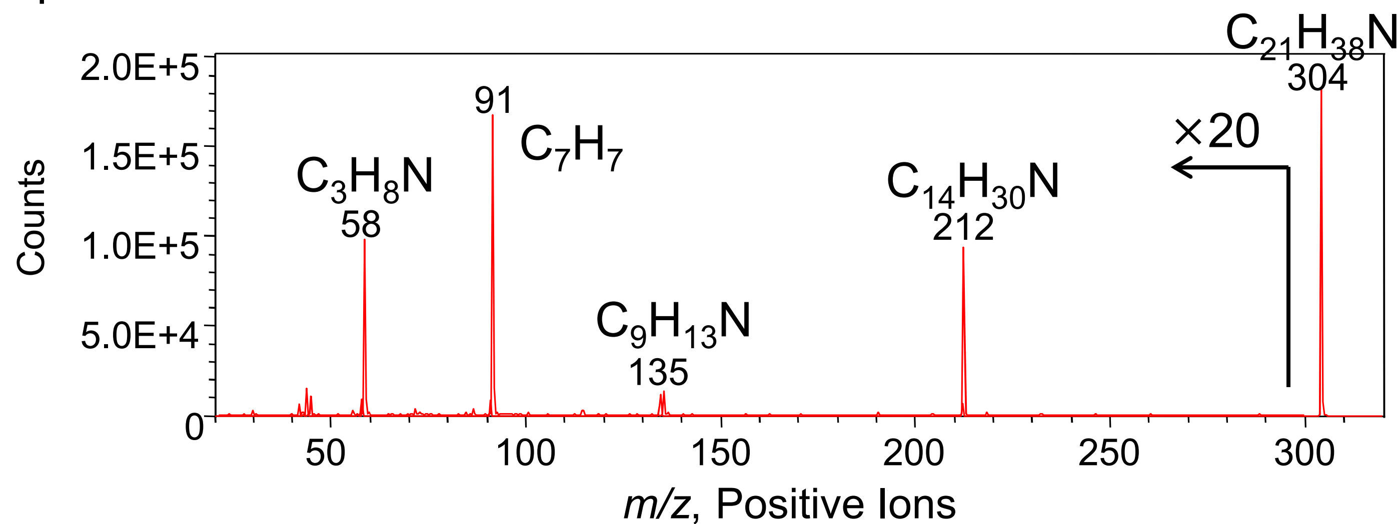
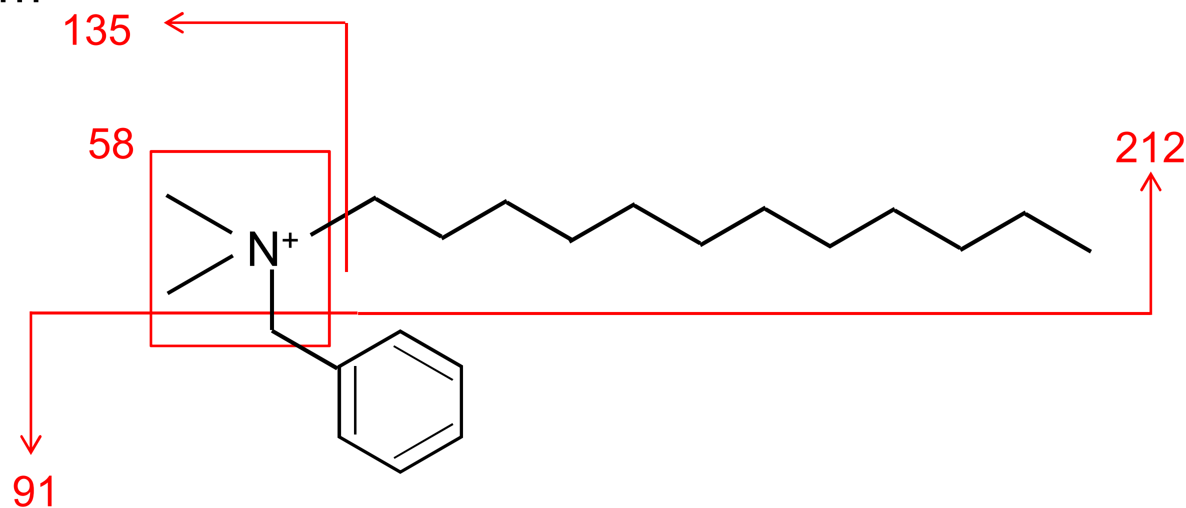
Chemical Structure Analysis of *m/z* 304



MS^2 Spectrum of *m/z* 304



Benzalkonium



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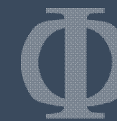
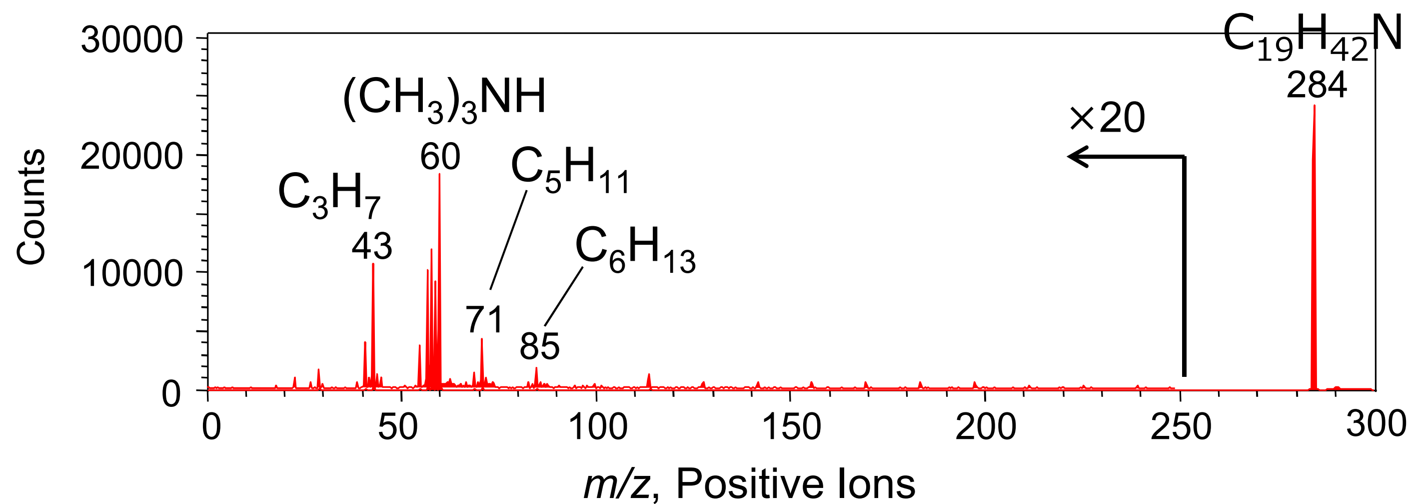
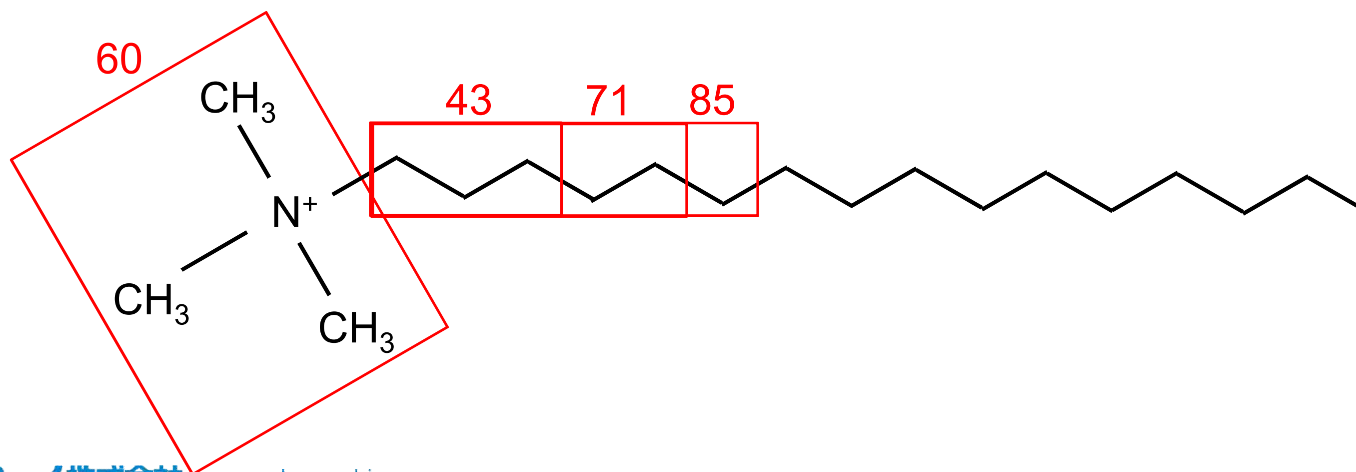
Chemical Structure Analysis of *m/z* 284



MS^2 Spectrum of *m/z* 284



Hexadecyltrimethylammonium



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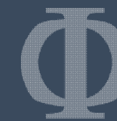
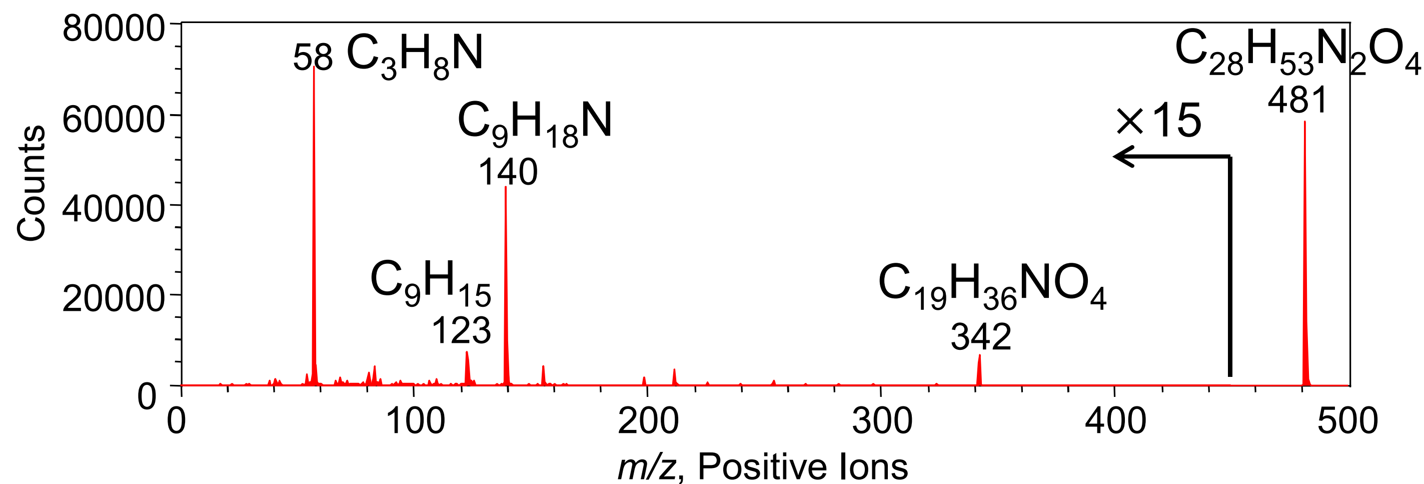
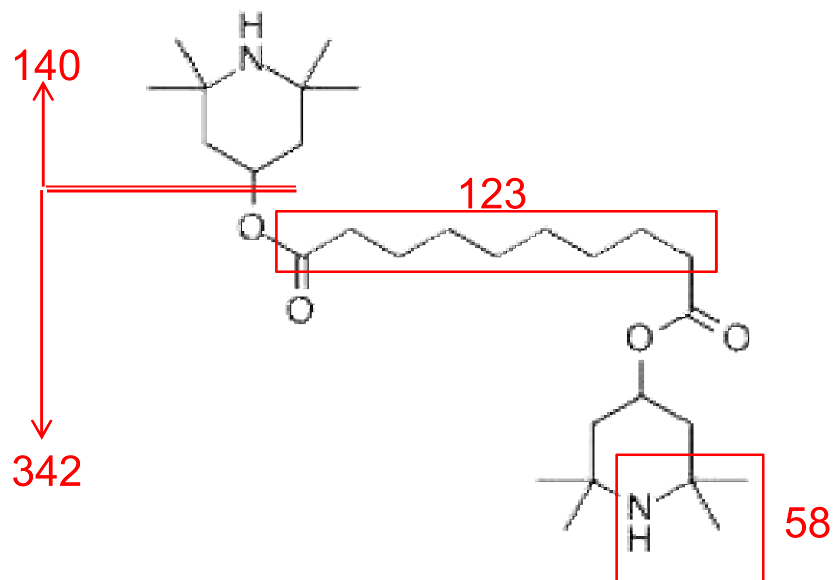
Chemical Structure Analysis *m/z* 481



MS[2] Spectrum of *m/z* 481



Tinuvin770



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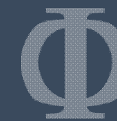
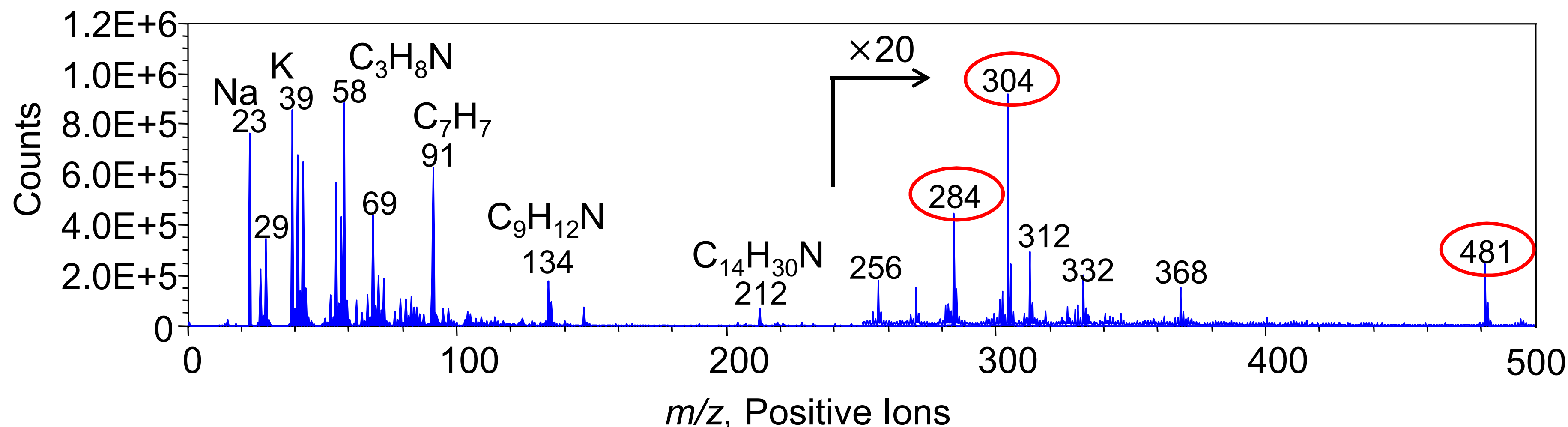
Identification of the Compounds



MS[1] spectrum from PP surface



Mass weight (u)	Chemical formula	Compound name
284	$C_{19}H_{42}N$	Hexadecyltrimethylammonium
304	$C_{21}H_{38}N$	Benzalkonium
481	$C_{28}H_{53}N_2O_4$	Tinuvin770

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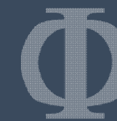
Summary



In this presentation, we introduced our latest options and applications of *nanoTOF* II.

FIB-TOF-SIMS
<Cross-section imaging of organic/inorganic material>

It was possible to remove the damaged layer by Ar-GCIB.
Combination of FIB and Ar-GCIB enables us to discover the chemical information underneath the metal layer.

MS/MS
<Identification of unknown additives on polymer surface>

From the MS^2 spectrum analyses, we can obtain the detailed information on chemical structure, and identify the compound.

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