Photoionization Workshop Summary

"New Developments in Photoionization"

64th ASMS Conference on Mass Spectrometry and Allied Topics, San Antonio, TX
Wednesday, June 9, 5:45 – 7:00 pm, Room 225C
Organized by: Jack Syage and Ralf Zimmermann

Ralf and I opened with a brief overview of the highlights of the year in photoionization and then we introduced four discussion leaders:

- "Implementation of APPI MS for Organometallic Compounds"
  Noam Tal, Tel Aviv University, Israel
- "Compact Laser Desorption/Ionization TOFMS for Planetary Missions"
  Xiang (Shawn) Li, University of Maryland
- "APPI Dopants for DART"
  Chip Cody, JEOL
- "Online Photoionization TOFMS Studies on the Catalytic Pyrolysis of Bituminous Coal"
  Yang Pan, University of Science and Technology, Shanghai, China

The workshop demonstrated continued strong interest in the subject matter as it attracted a large audience (about 60 people), but not as large as last year (about 100 people). We think this may be due to the switch from Mon to Weds evening and also there seemed to be more workshops this year. It may not have helped that for the second straight year the beer dispenser on our floor was not ready by the 5:45 pm start time.

Each of the discussion leaders kept to their 5-10 min allotment of time, which allowed for plenty of discussion. On the whole there was a high quality of audience participation as evidenced by strong and rigorous discussion on the varied topics. We heard positive feedback from many attendees.

I also announced that I will be stepping down as co-chair. We have a couple of highly qualified candidates to replace me.

The briefing material is attached.

New Developments in Photoionization (APPI/PI)

Wednesday, June 9, 5:45-7:00 pm
Room 225C (San Antonio Convention Center, TX)
Organized by Jack Syage and Ralf Zimmermann

Discussion Leaders

- "Implementation of APPI MS for Organometallic Compounds"
  Noam Tal, Tel Aviv University, Israel

- "Online Photoionization TOFMS Studies on the Catalytic Pyrolysis of Bituminous Coal"
  Yang Pan, University of Science and Technology, Shanghai, China

- "APPI Dopants for DART"
  Chip Cody, JEOL

- "Compact Laser Desorption/Ionization TOFMS for Planetary Missions"
  Xiang (Shawn) Li, University of Maryland

Benefits of PI and APPI

- Ionizes a wide range of compounds (polars to non-polars)
  - Wide bandwidth ionizer
- Lower susceptibility to ion suppression than ESI or APCI
  - Simpler clean-ups mean ease and better recoveries
  - Use with faster chromatography and even flow injection analysis
- Large linear dynamic range
  - Great for quantitative analysis

Can APPI and PI be a mainstream technologies or are they best suited for niche applications?

APPI for Explosives and Narcotics Trace Detection

Morpho Detection

IT4DX IMS

MS ETD

Implant Sciences

QS-B220 IMS

1st Detect

Bruker

DE-tector IMS

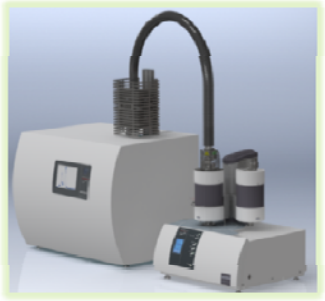
Why not APCI

Discharge sources in air create atmospheric NO_3^- ions that interfere with NO_3^- nitrate ions from nitrate explosives

PI for on-line detection and GC applications

- Many PI-MS applications for on-line detection (Laser- or Lamp-PI) or as detector for gas chromatography or thermal analysis
- Vacuum ionization: No susceptibility to ion suppression but lower sensitivity than EI
- Now systems are becoming commercially available….

Photonion
(TG-PIMS, on-line, GC-PIMS)



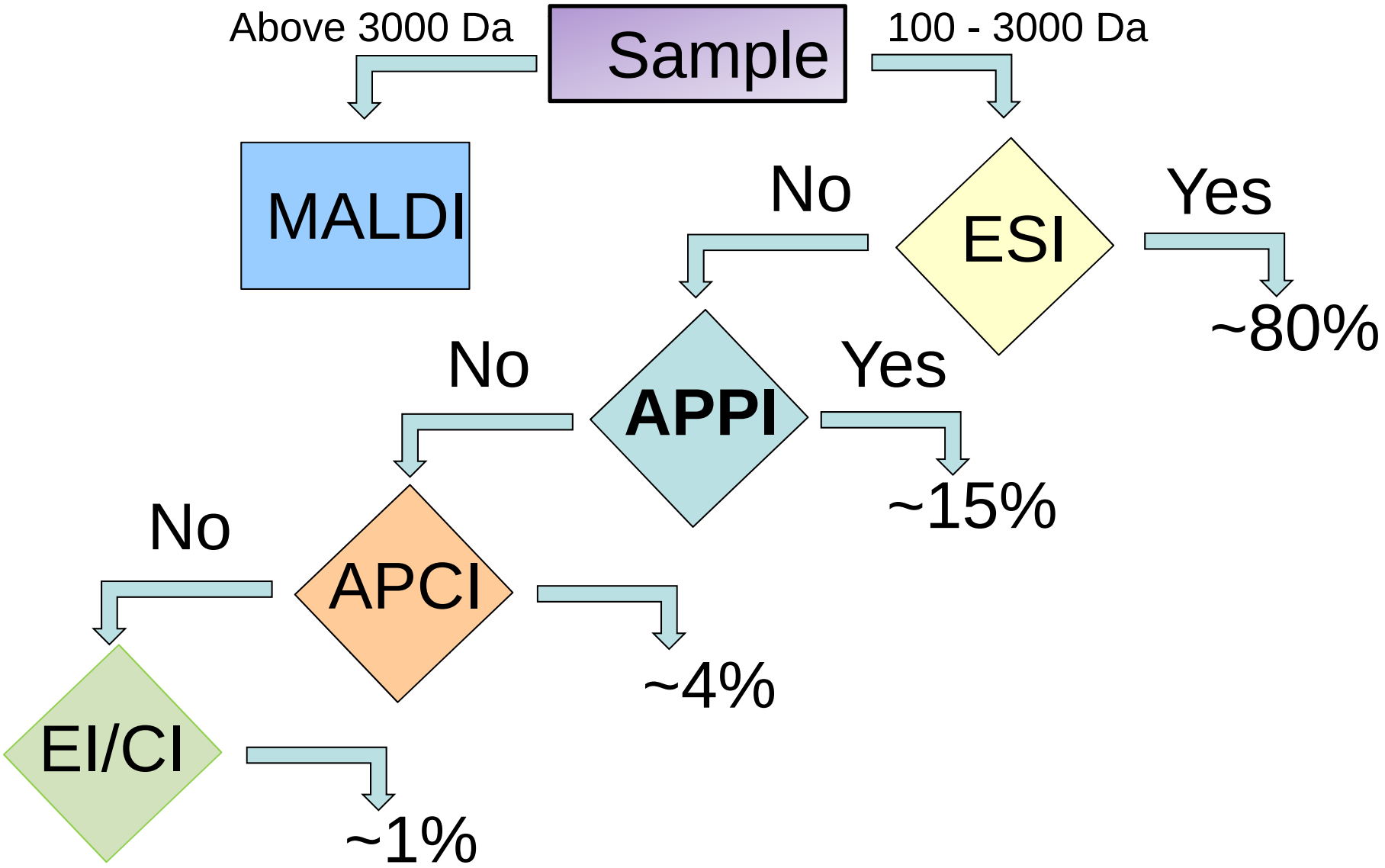
Hexin
(on-line)

Jeol
(GC-PIMS)

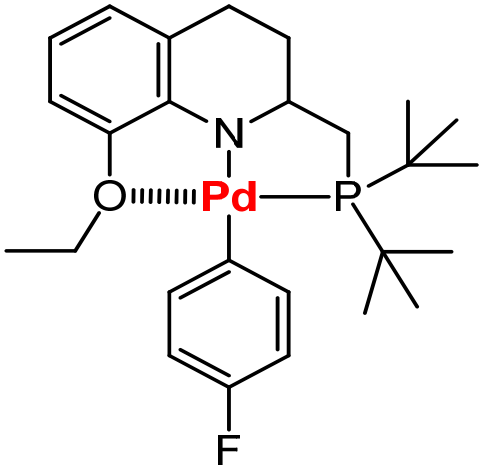
➔ Development of vacuum PI sources for GC-/GCxGC-HRTOFMS Systems

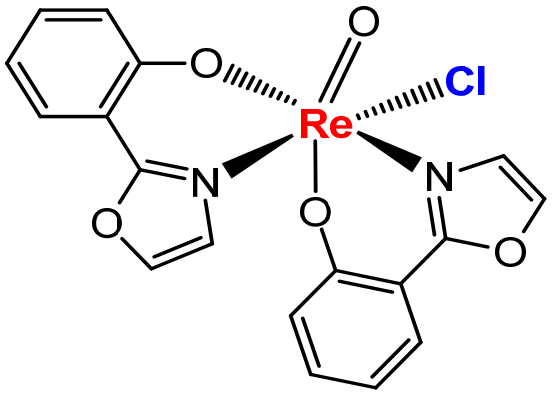
Implementation of APPI for Organometallic compounds

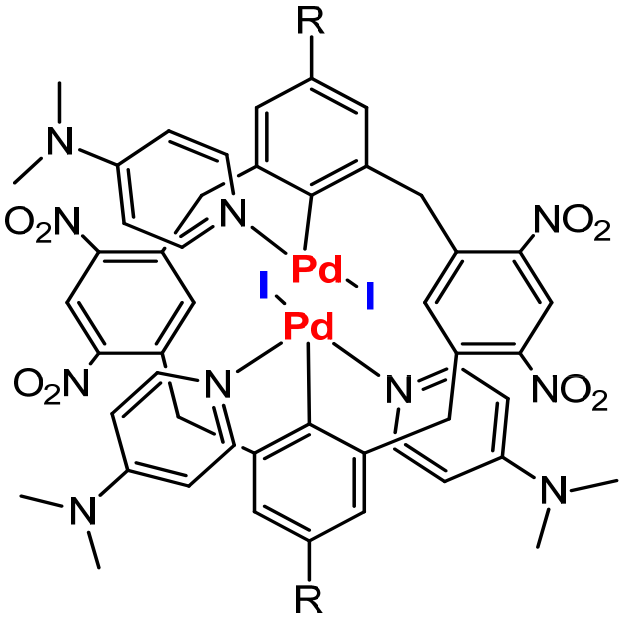
Noam Tal, Tel Aviv University, Israel

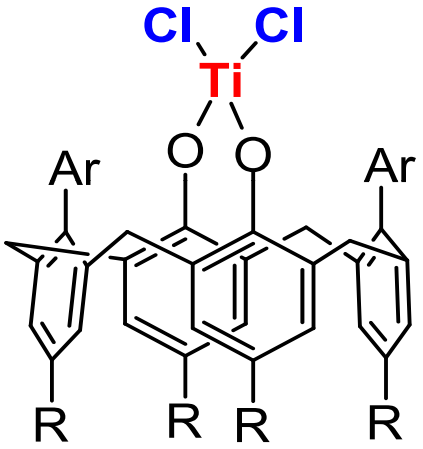

Above 3000 Da
Sample
100 - 3000 Da
MALDI
No
ESI
Yes
~80%
No
APPI
Yes
~15%
No
APCI
~4%
EI/CI
~1%

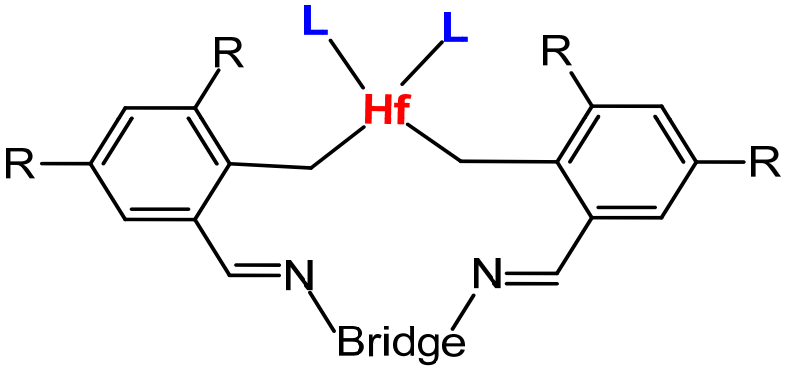
Organometallic compounds





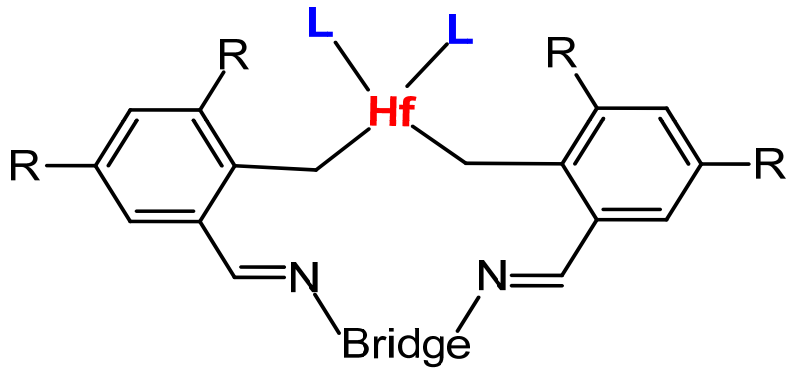






Organometallic compounds

- Hafnium complexes mostly used as catalyst for alpha olefine polymerization resulting industrial polymers such as polypropylene.
- Extremely reactive and sensitive (oxygen, moisture)
- Covalent and coordinative bonds.

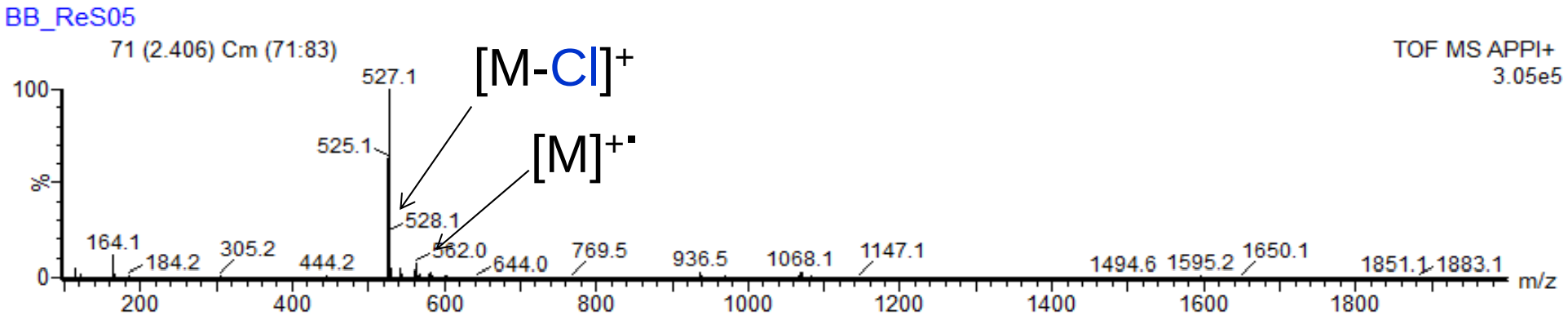


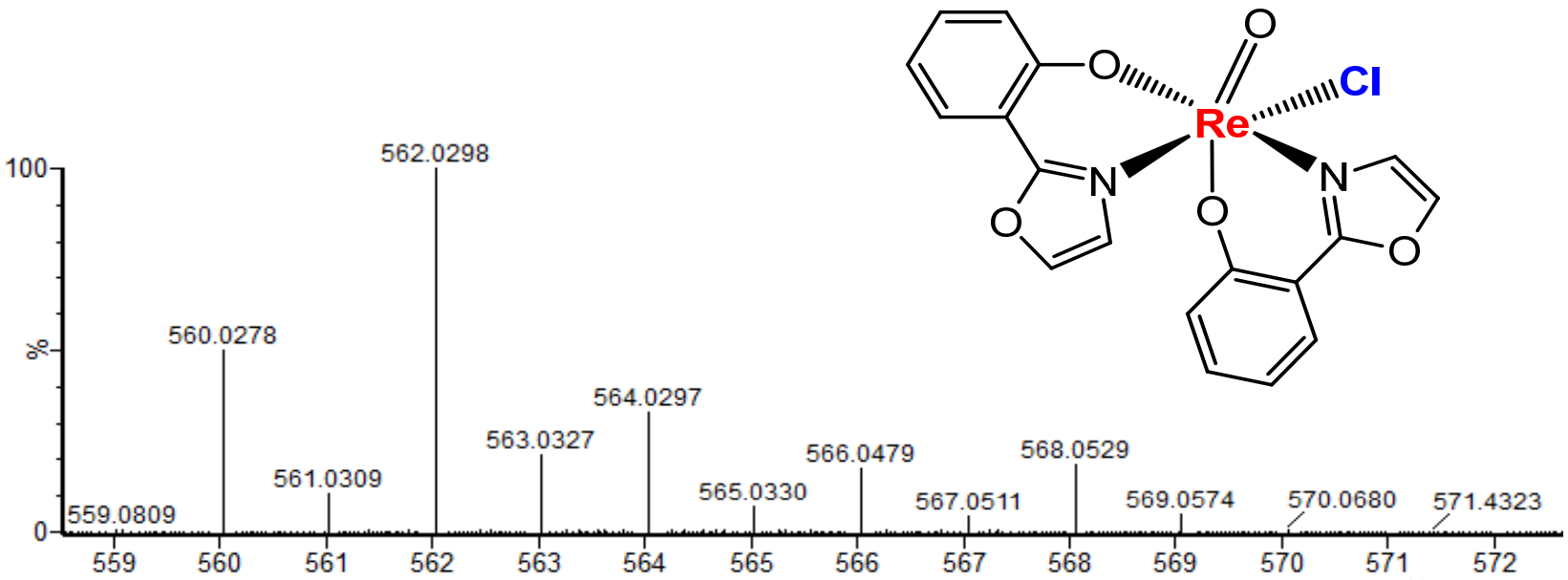
APPI conditions:

- MS: SYNAPT, Waters.
- UV Lamp: Syagen 10.6 ev krypton discharge Lamp
- Repeller 0.8-1.2 KV
- Sampling Cone 40
- Extraction Cone 4
- DCM/MeCN + 1-10%Toluene, Acetone
- Desolvation temp: 300-400 °C

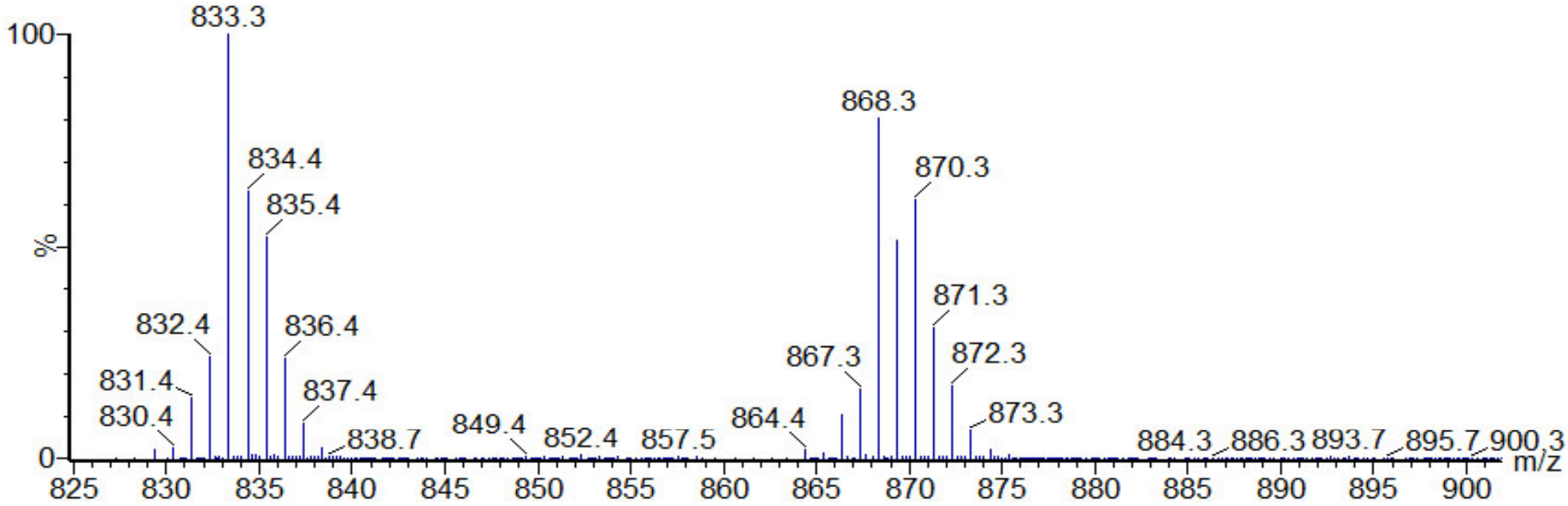
  Flow: 500-750 L/h , 99.9% Dry Nitrogen

Organometallic compounds

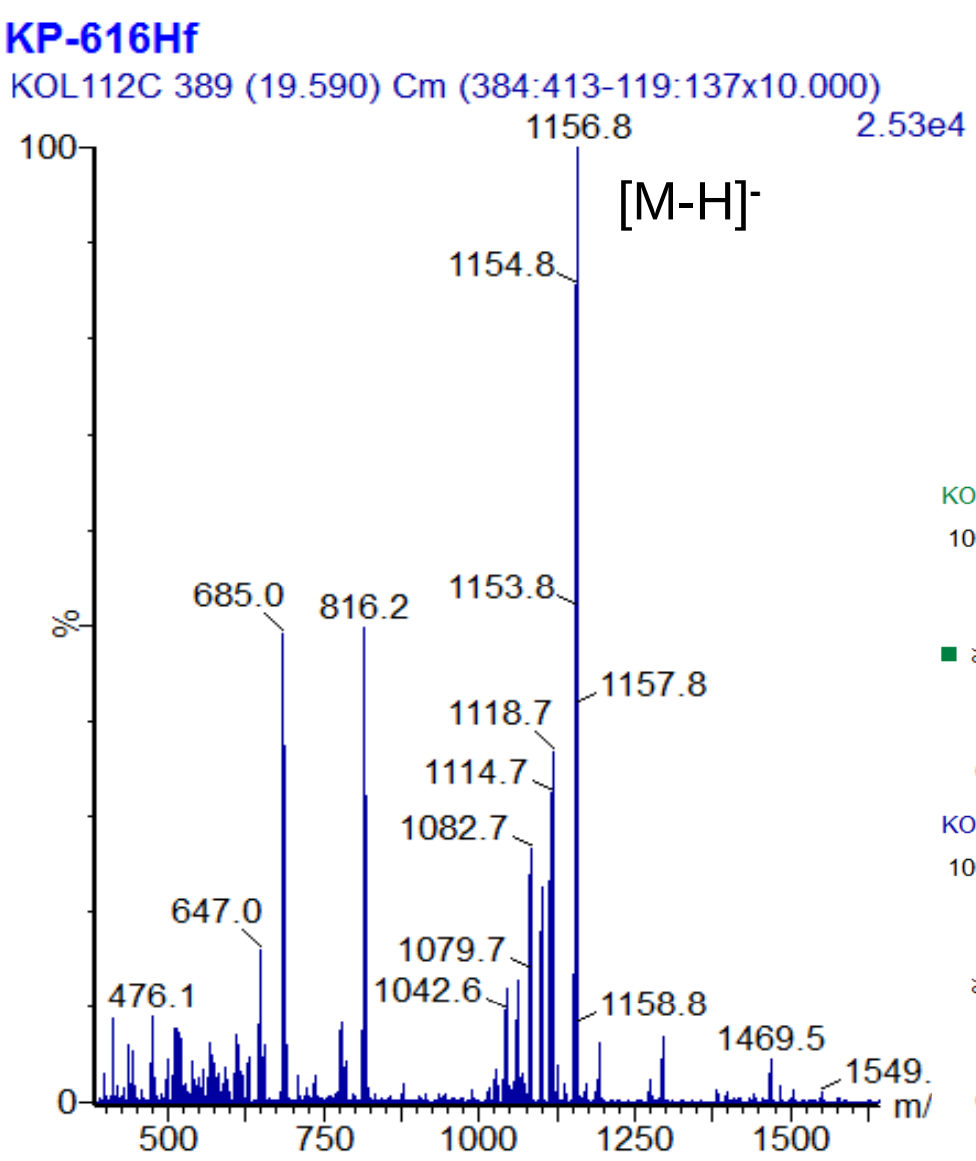


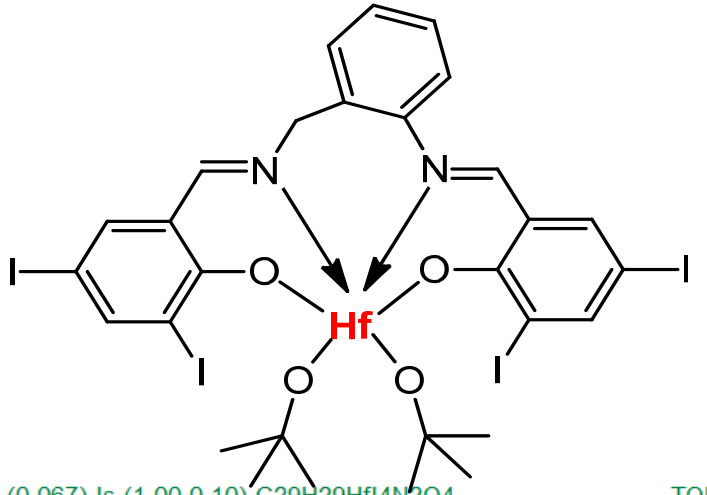


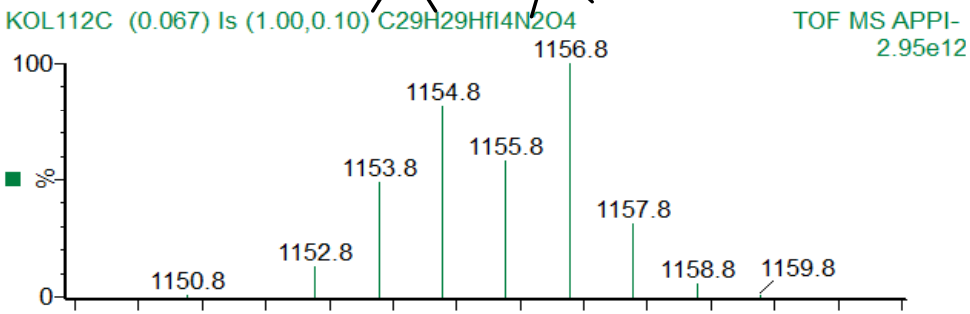
Organometallic compounds

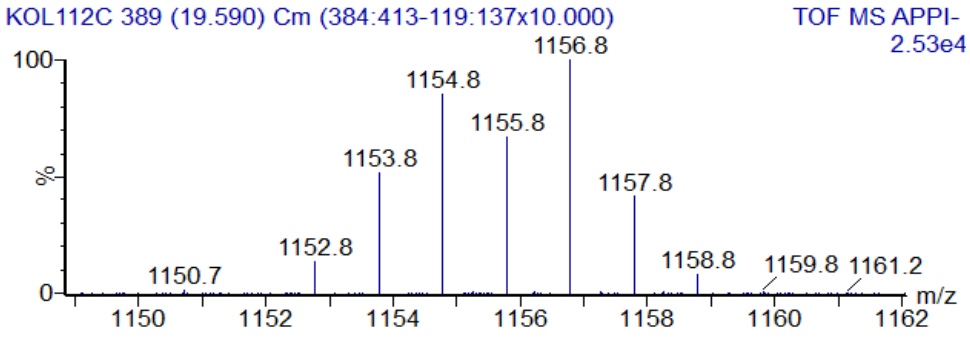


Organometallic compounds

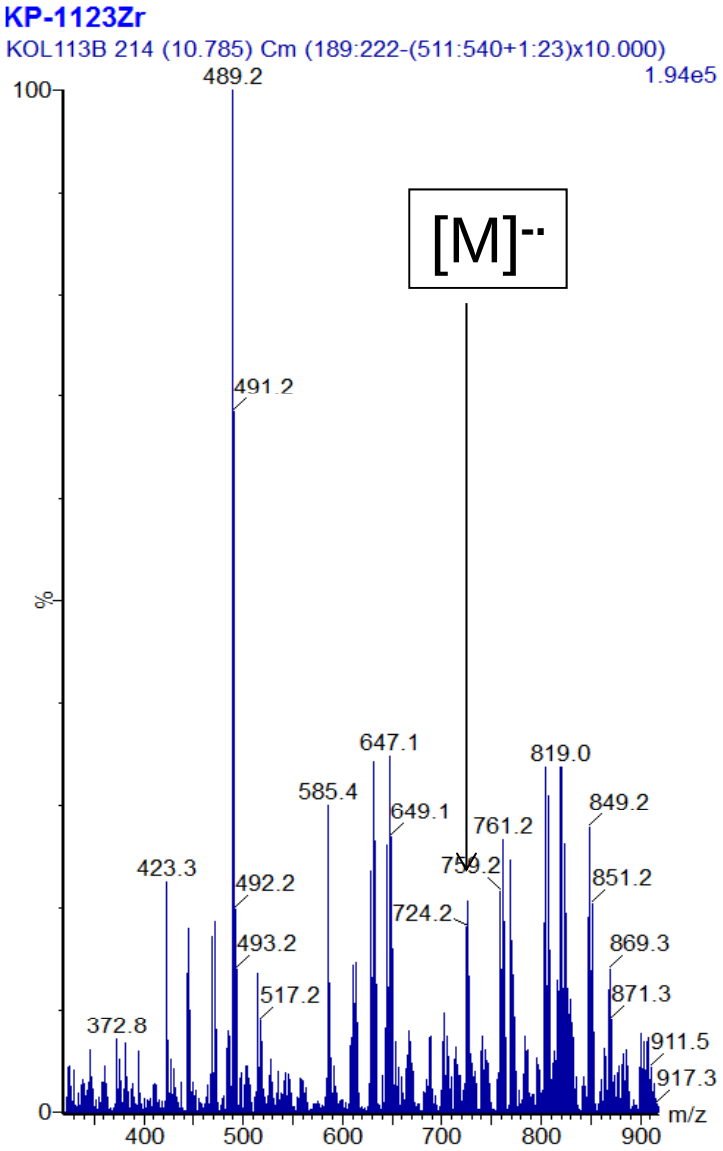


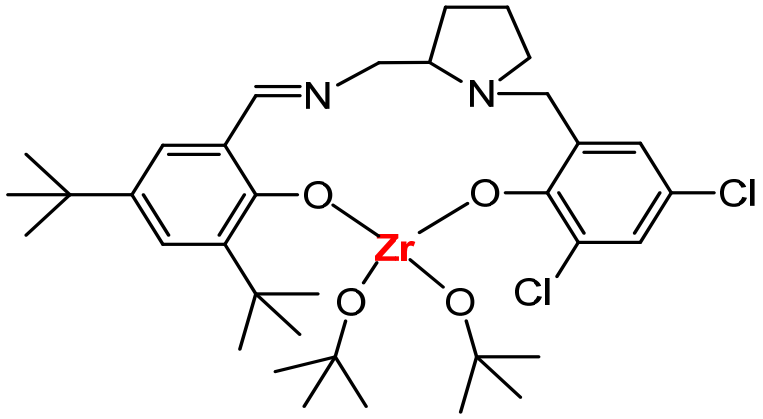


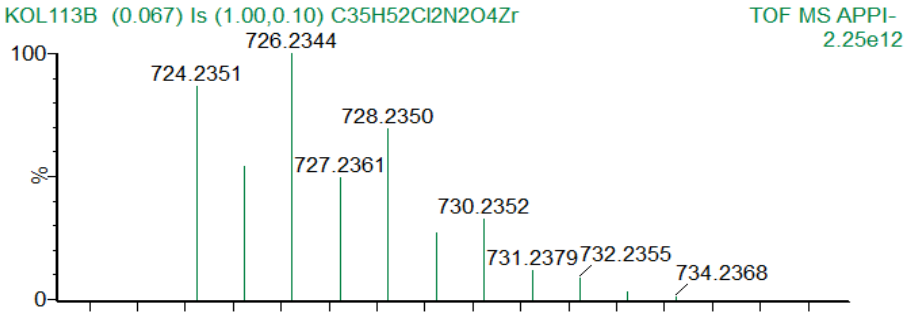


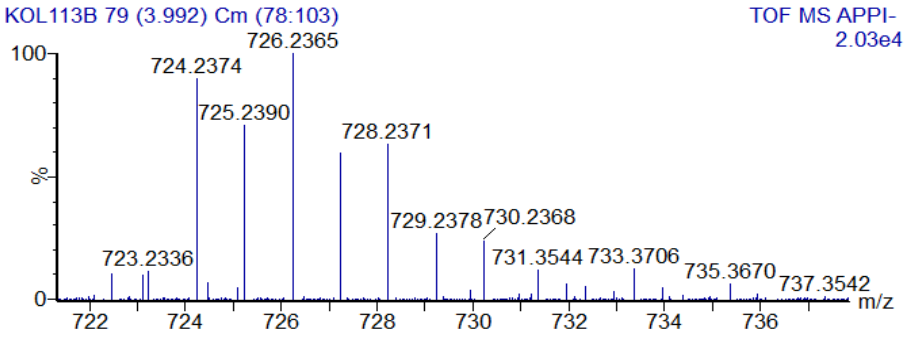


Organometallic compounds

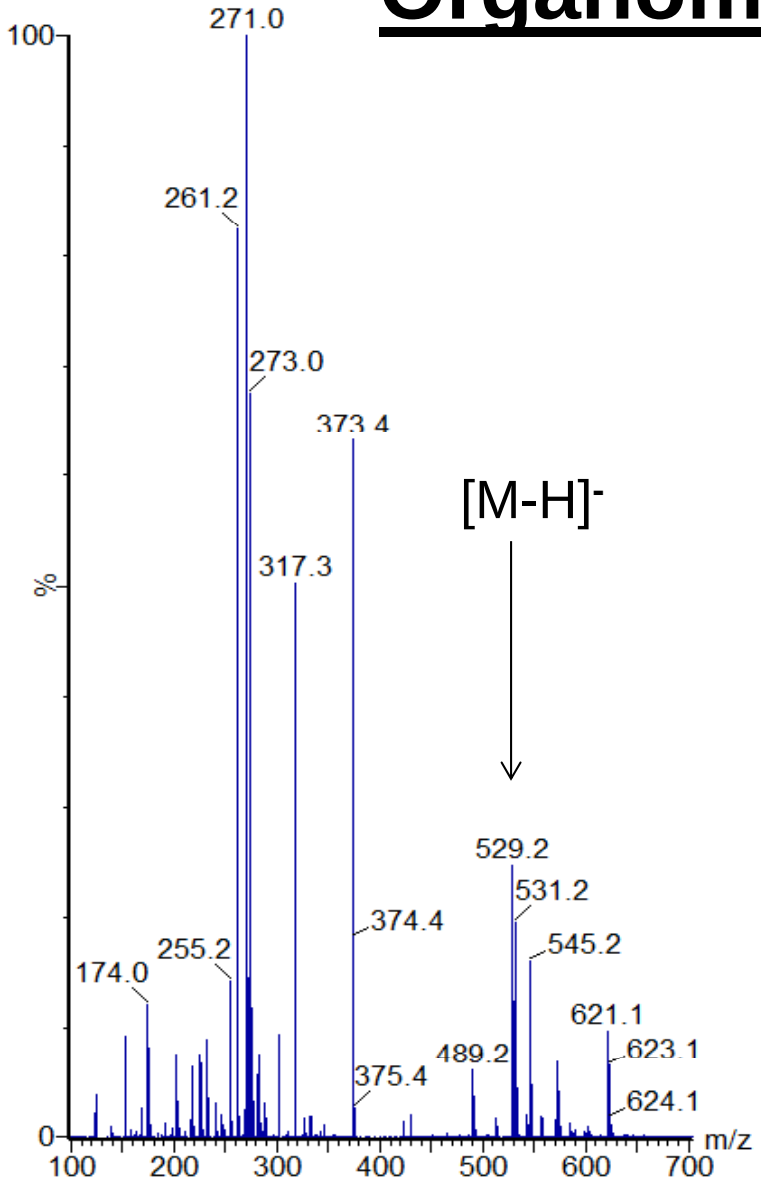


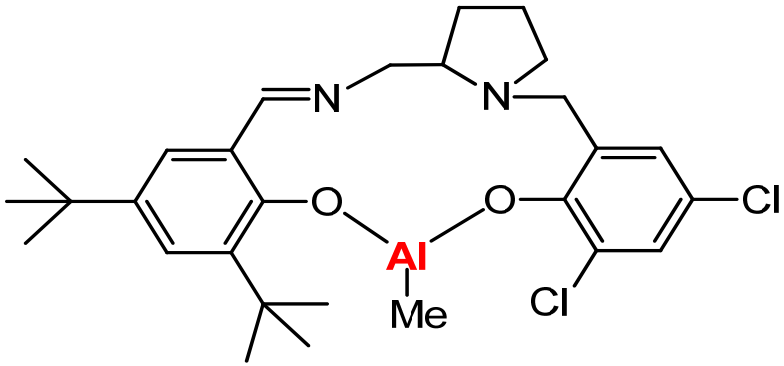






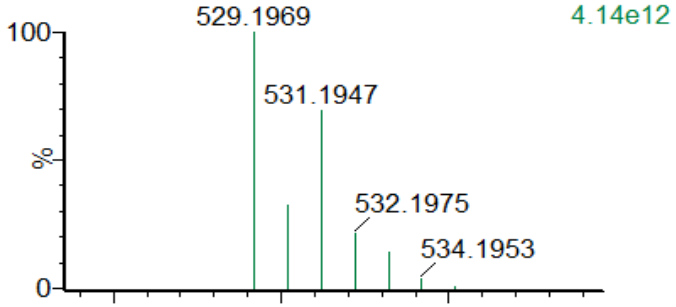
Organometallic compounds



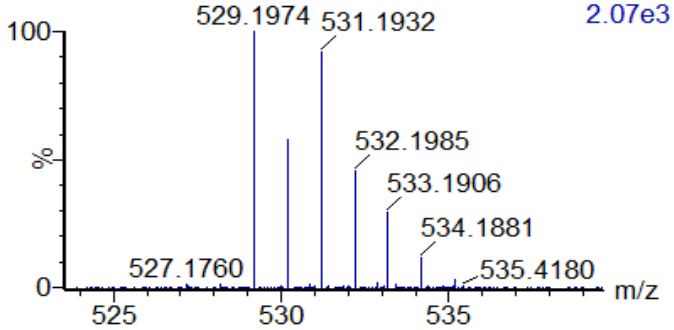


KP-1123AlMe

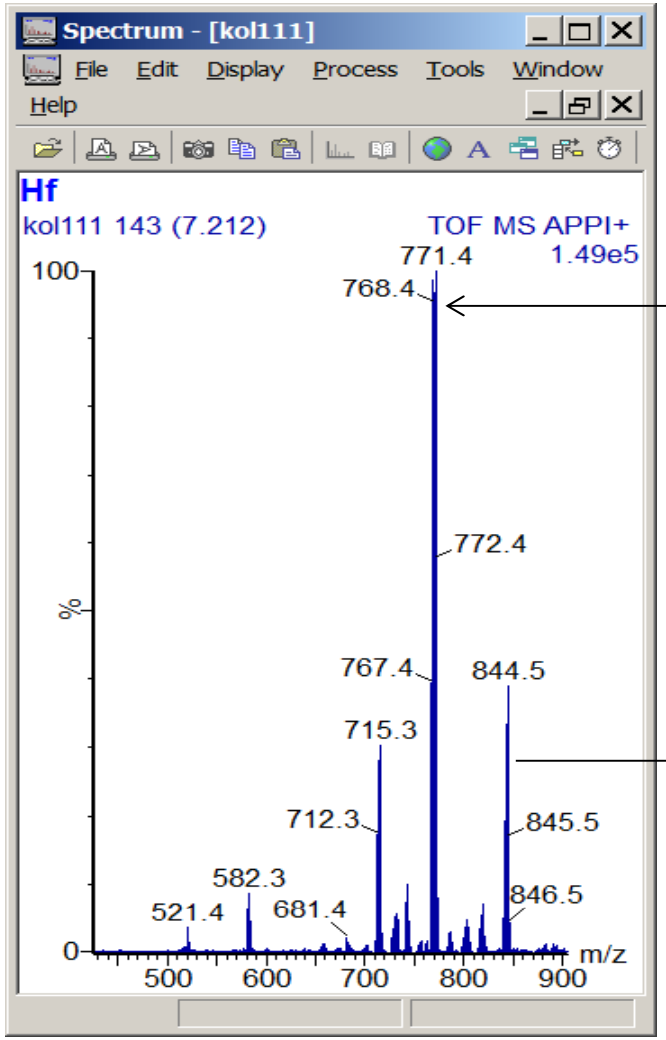
KOL114 (0.067) Is (1.00,0.10) C28H36Cl2N2O2Al 4.14e12

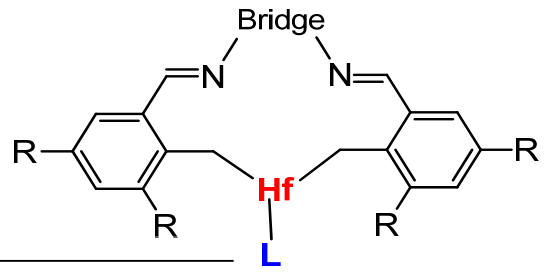


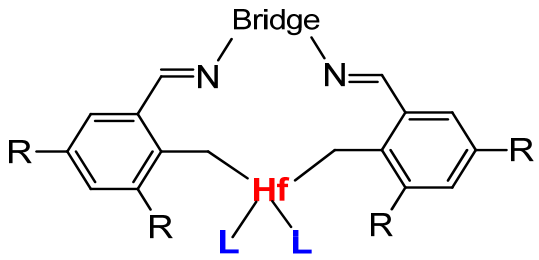
KOL114 616 (31.012) Cm (611:616) TOF MS APPI- 2.07e3

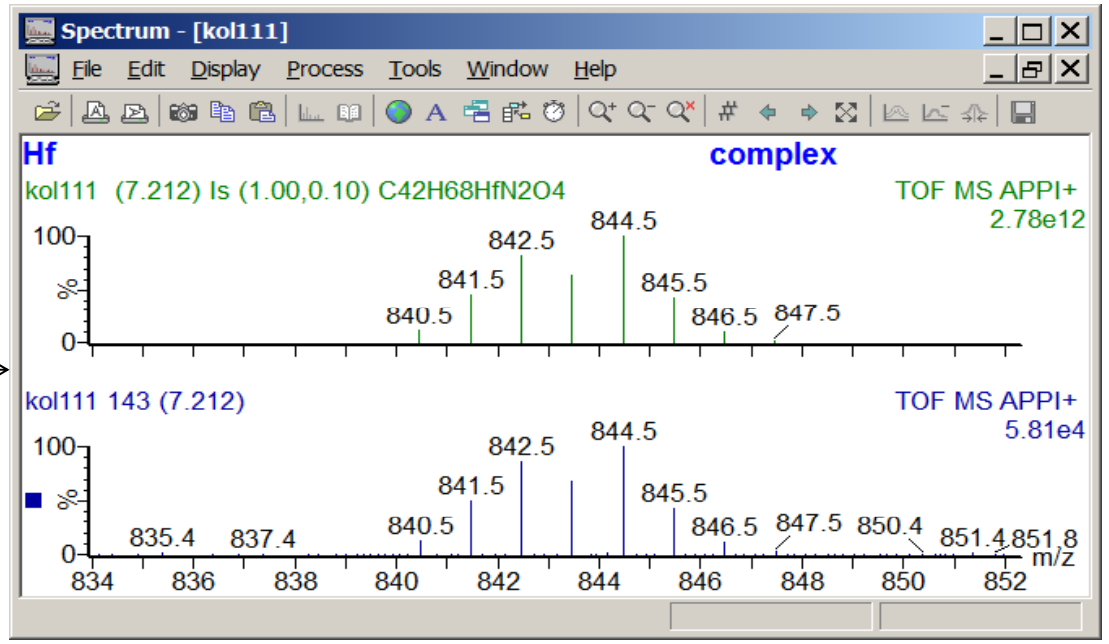


Organometallic compounds









Summary

1. APPI is suitable to organometallic compounds that can't be analyzed using ESI, and decompose in EI.

2. High sensitivity both in positive and negative modes

3. Provides additional information compared to ESI.
   (labile ligands or counter ions)

4. Broaden capabilities of API source.

Photoionization: A Powerful Tool for Mass Spectrometry

Yang Pan

National Synchrotron Radiation Laboratory

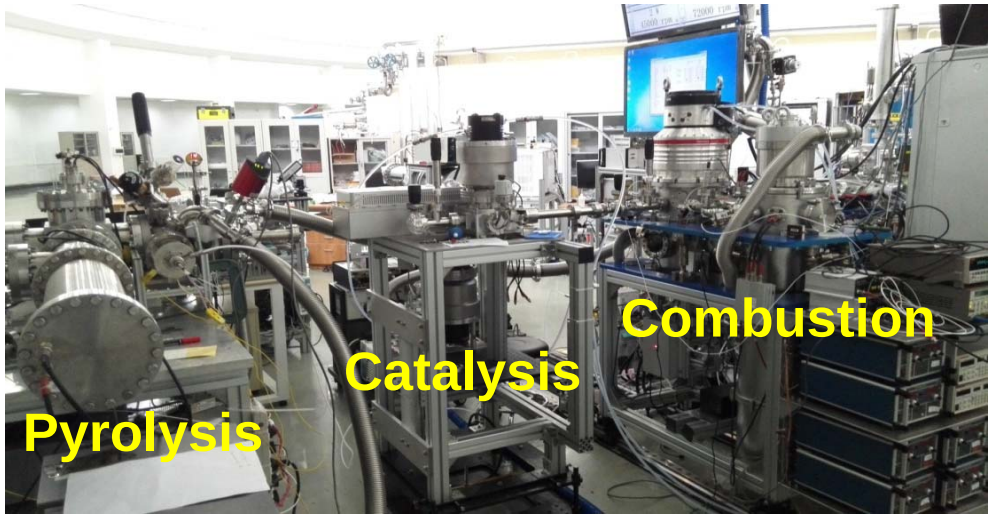
University of Science and Technology of China

06-08-2016

OUTLINE

- **Our recent work**
- **Challenge of Photoionization**

Introduction of NSRL



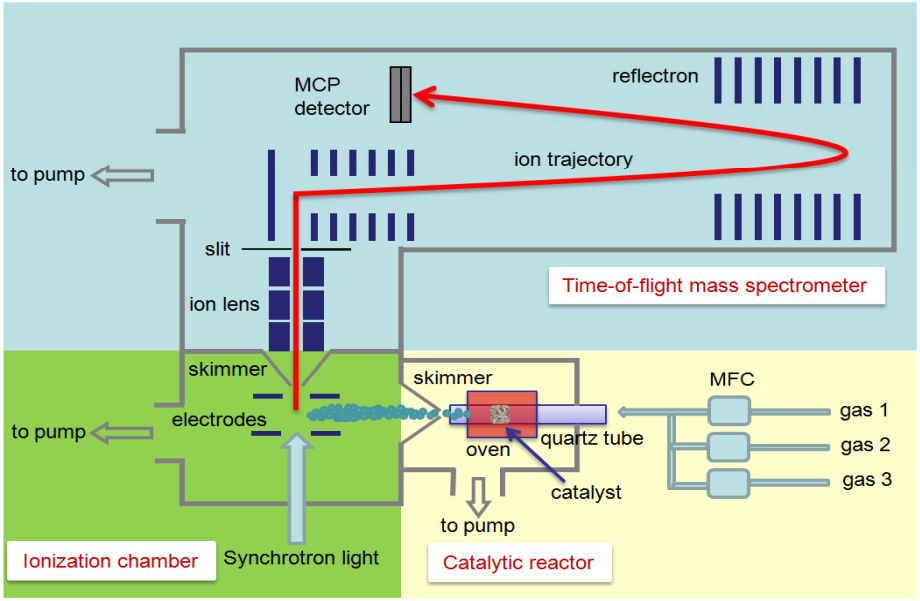
Source	Undulator
Acceptance angle	1(H)×1 mrad² (V)--4Xsigma
energy range	7-20 eV
resolving power	3000 (E/ΔE) @ 15.8 eV
Photon flux	5×10^{12} photons/sec @ 300 mA
spot size	1.6×0.5 mm²

Recent work 1: heterogeneous catalytic reactions

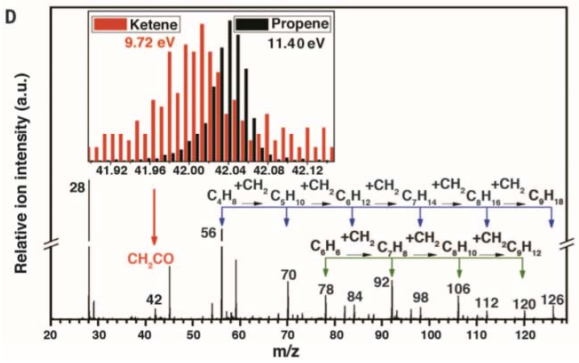
Intermediates?

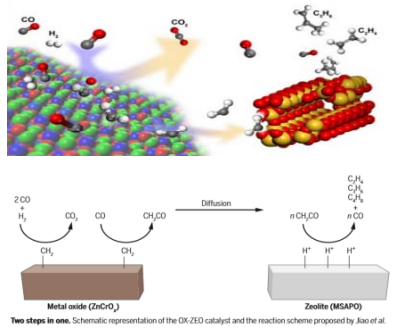
Reactants → **catalyst** → **Products**

- ✓ In situ
- ✓ In real time
- ✓ Multi-products analysis



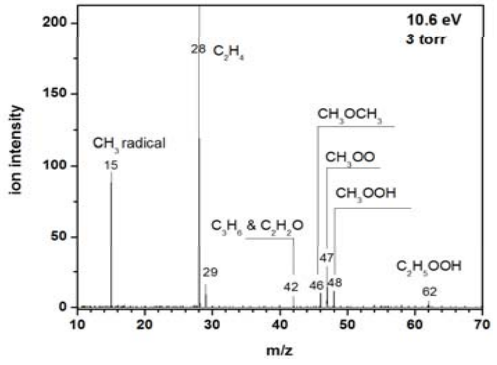
$CO + H_2 \rightarrow$ olefins (Zeolite/ZnCrOx)

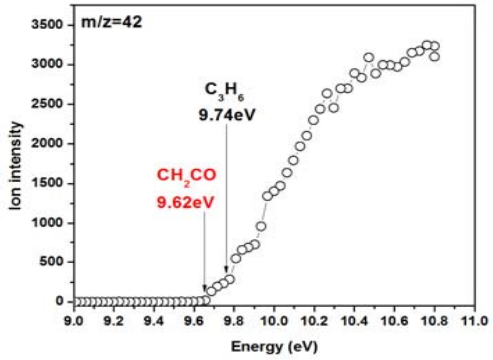




Jiao et al, *Science*, 2016, 351 (6277), 1065-1068

$CH_4 + O_2 \rightarrow C_2H_4$ (Li/MgO)

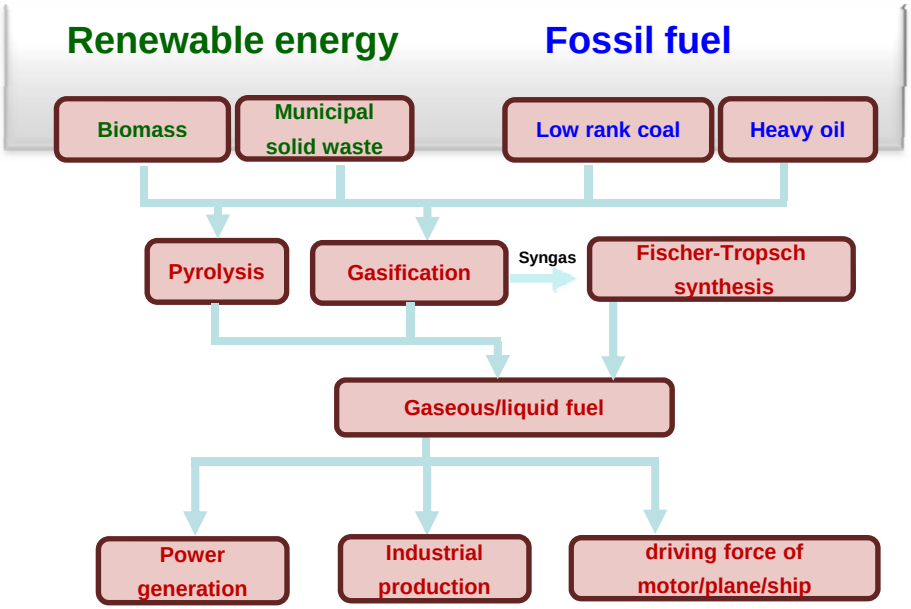




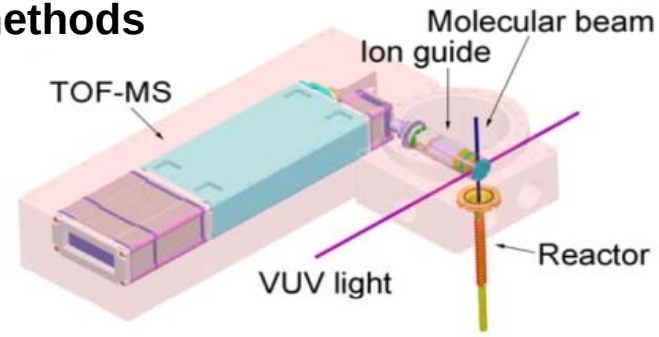
Luo et al, ***submitted***

Recent work 2: pyrolysis of biomass, coal and waste

◆ background



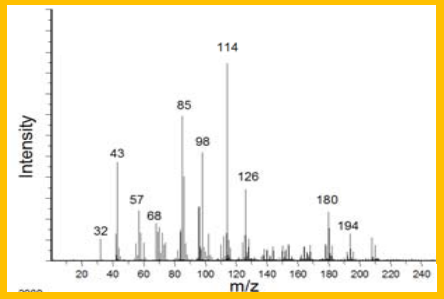
◆ methods



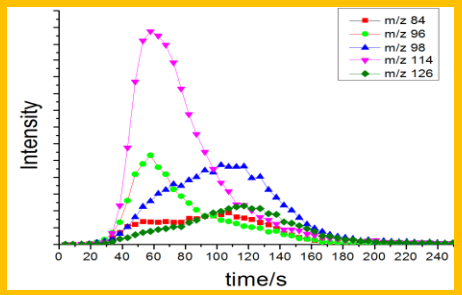
- **molecular beam**
- **fused silica capillary**

◆ results

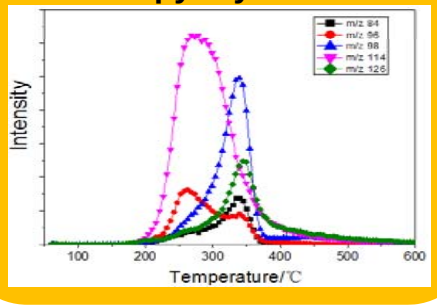
On-line mass spectra



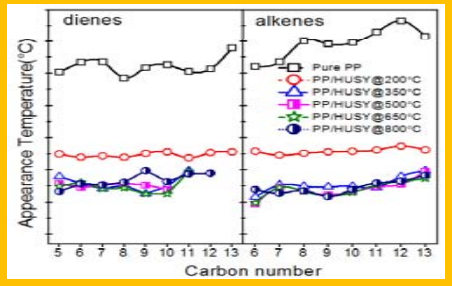
Time-evolved profiles



Temperature-programmed pyrolysis



Temperature-programmed pyrolysis



catalytic pyrolysis of polymer/biomass

Wang et al, *Energy & Fuels*, 2015, 29 (2), 1090-1098

Wang et al, *Energy & Fuels*, 2016, 30 (3), 1534-1543

Zhu et al, *Energy & Fuels*, 2016, 30 (3), 1598-1604

He et al, *Energy & Fuels*, 2016, 30 (3), 2204-2208

Wang et al, *Energy & Fuels*, 2016, accepted

Recent work 3: rapid analysis of chemicals in matrices

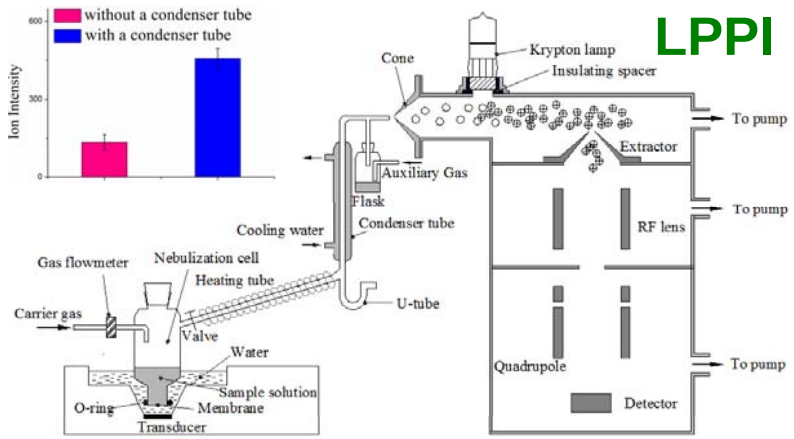
◆ Motivation

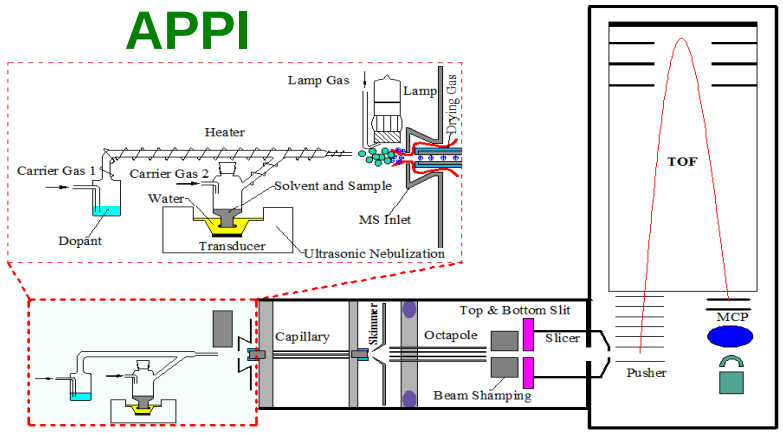
- ✓ Rapid analysis without separation
- ✓ inner part analysis rather than surface analysis

◆ Application

- ✓ Natural products analysis
- ✓ Soil analysis . . .

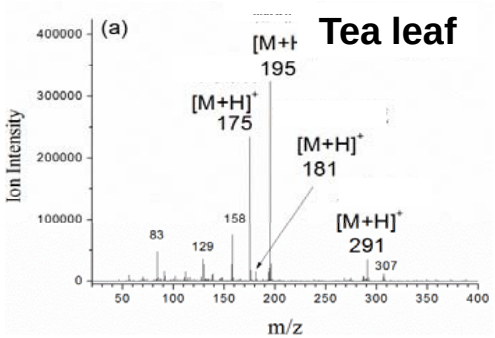
◆ Methods

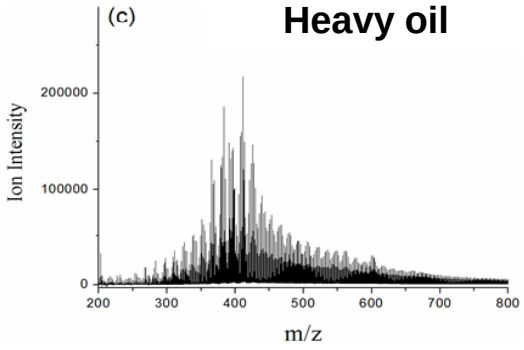


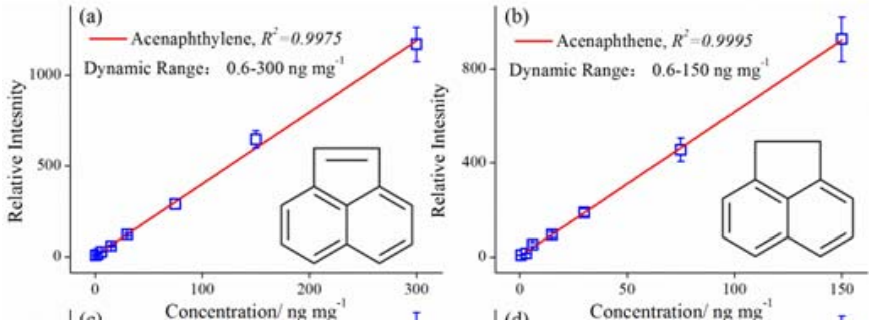


Ultrasonic Nebulization Extraction(UNE)+ Photoionization

◆ Results





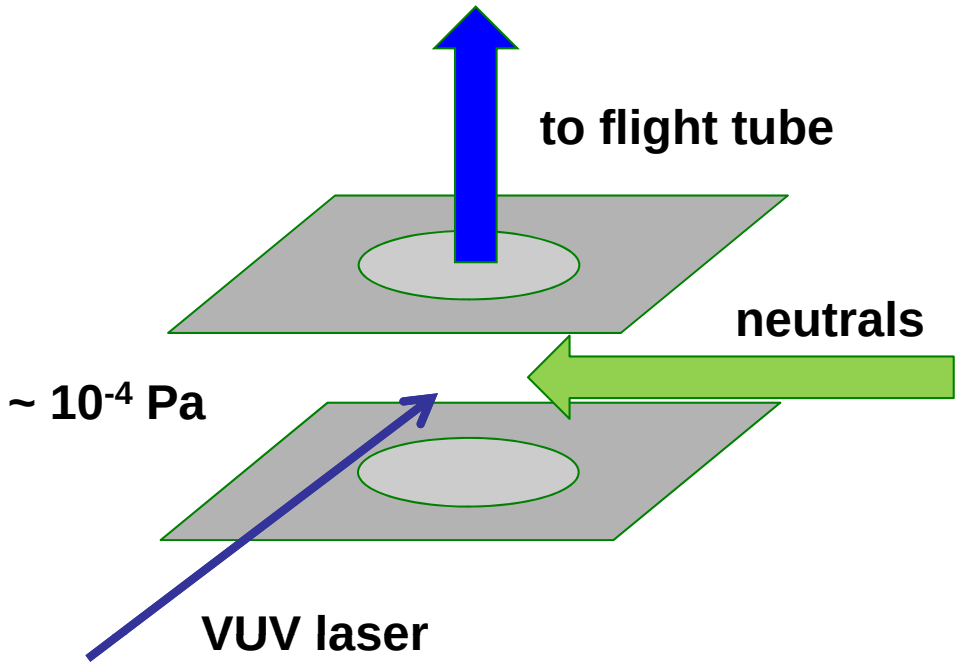


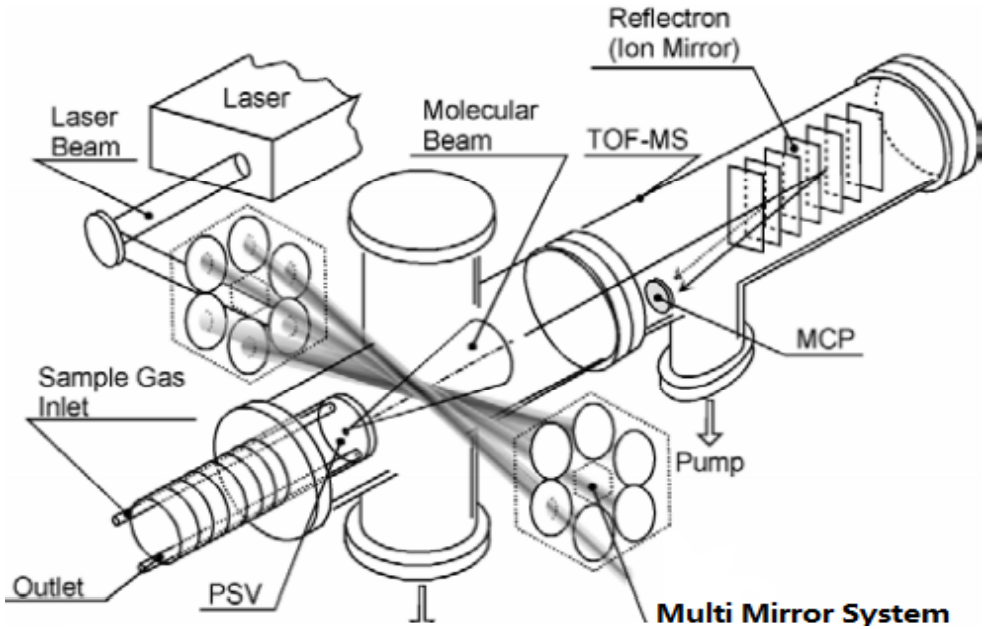
Liu et al, ***Anal. Chim Acta.***, 2015, 891, 203

Liu et al, Submitted

Challenge of PI: Improvement of the sensitivity

Ultratrace analysis with low pressure photoionization

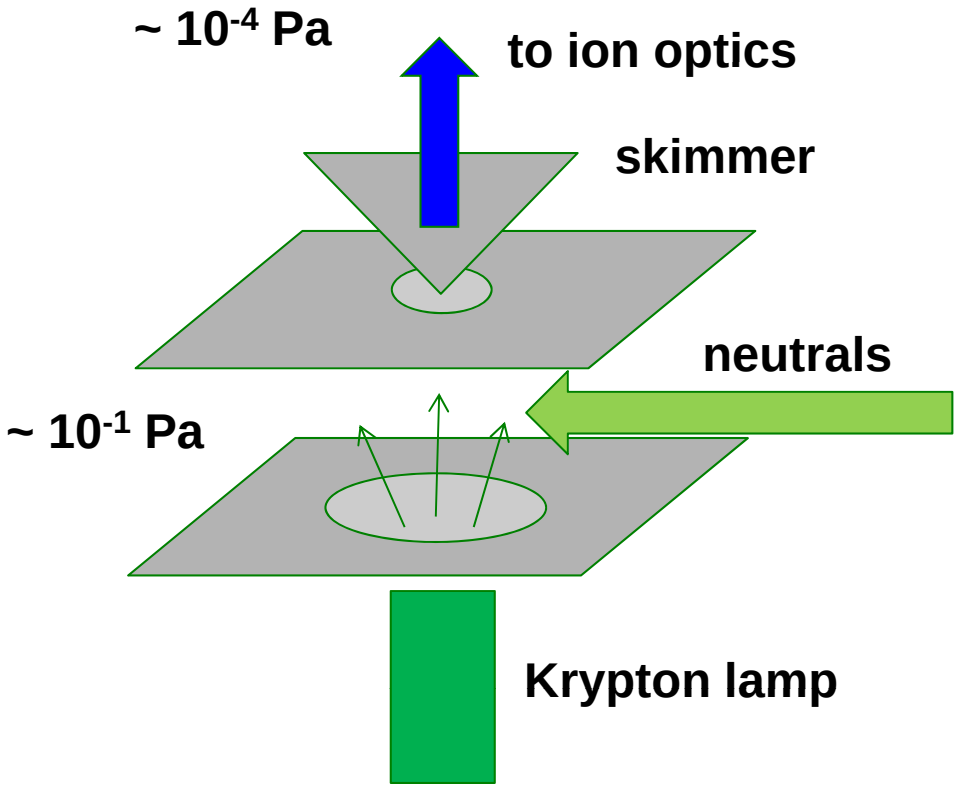


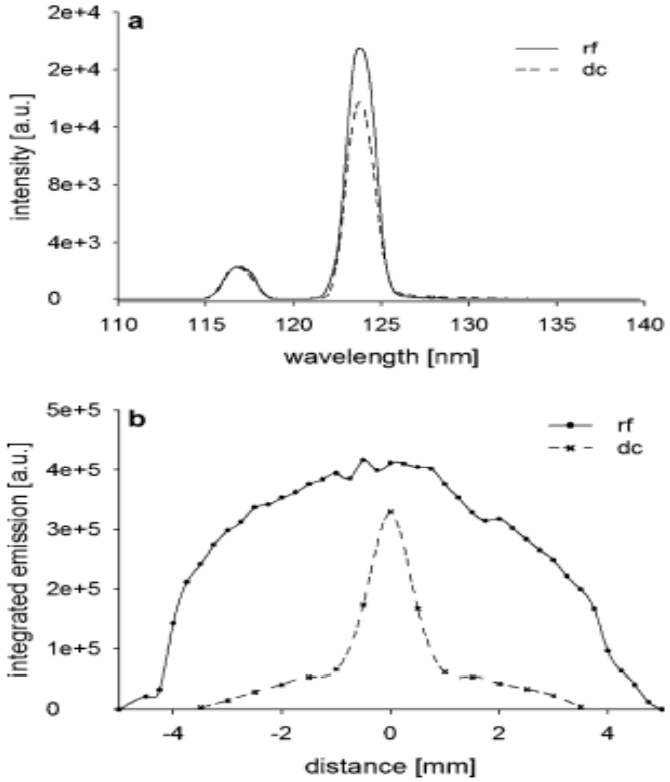


Y. Suziki, Analytical Science, 2001, 17, i563-i566.

Challenge of PI: Improvement of the sensitivity

Ultratrace analysis with low pressure photoionization

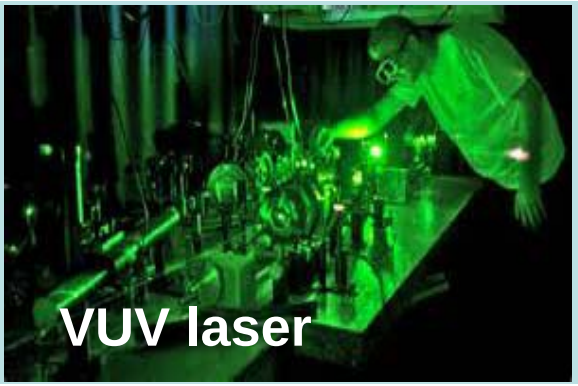




T. J. Kauppila , Analytical Chemistry, 2012, 84, 1408-1415

Challenge of PI

1. Design of new VUV light source

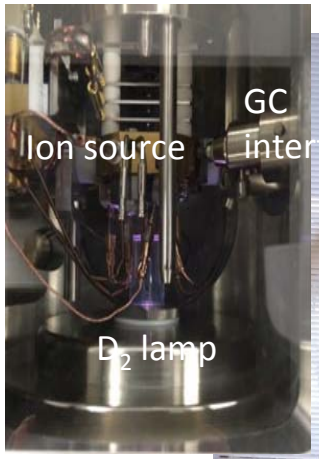
			
Photon Flux	**Low**	**High**	**high**
Tunability	**N**	**partly**	**widely tunable**
Price	**cheap**	**expensive**	**extremely expensive**
portability	**Y**	**N**	**N**

A cheap, portable light source with higher photon flux is critically needed.

Thank you!

Short topic 1: GCxGC/HRTOF with PI source

GC-PI-HRTOFMS system

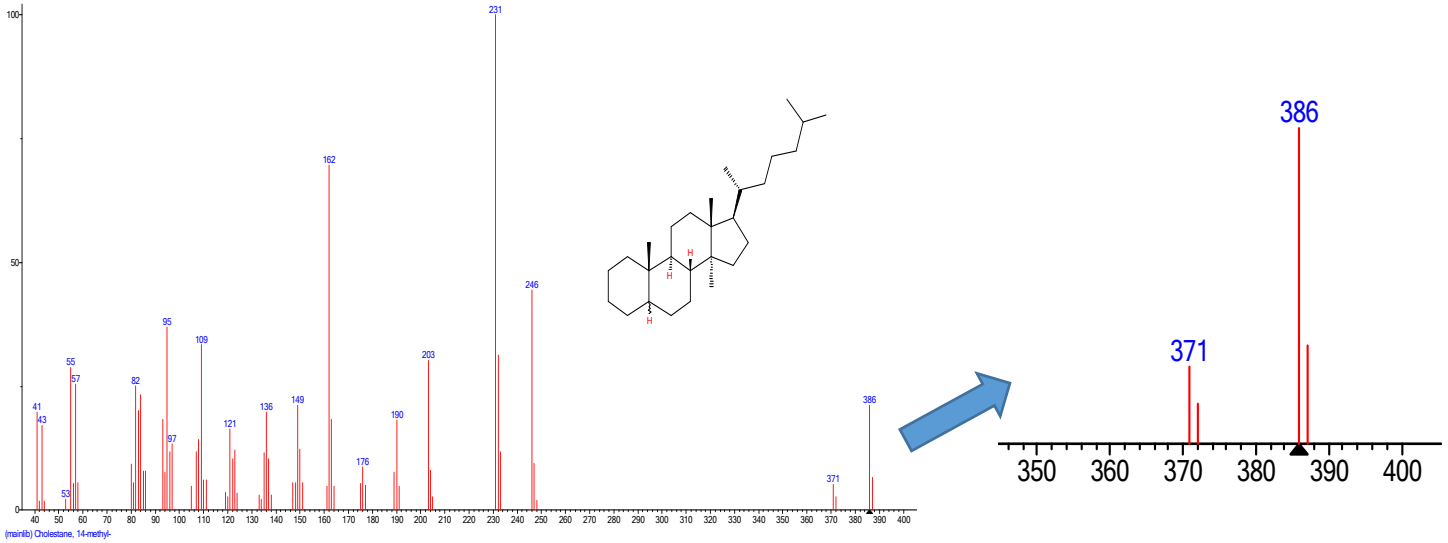


AccuTOF GCv4G + PI (proto type)

Agilent 7890 equipped with Zoex thermal modulator for GCxGC

AccuTOF GCx + PI (product type)

Fragment ions can confuse biomarker analysis, even with GCxGC and HRMS

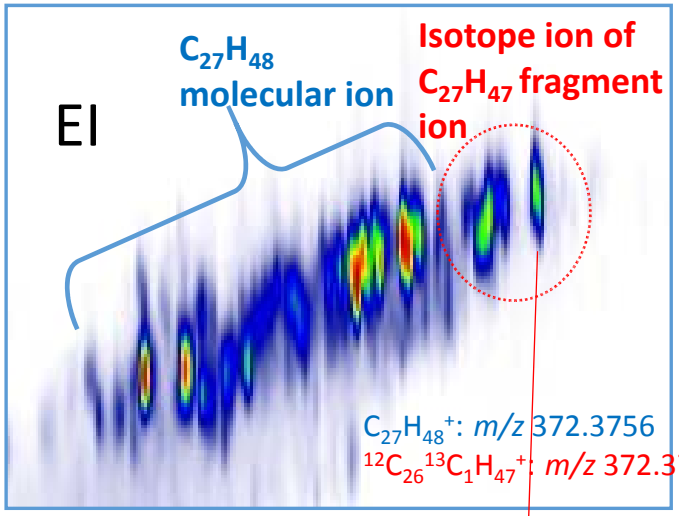


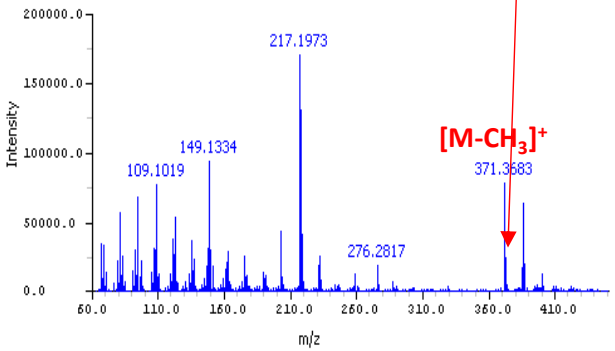
- "...SIM is affected by interference. For example, C_{28} steranes can lose a methyl group (15 amu) during ionization, resulting in a fragment at *m/z* 371. However, some 372 will also result from the C_{28} steranes because heavy isotopes of carbon (^{13}C) or hydrogen (D) are also present."

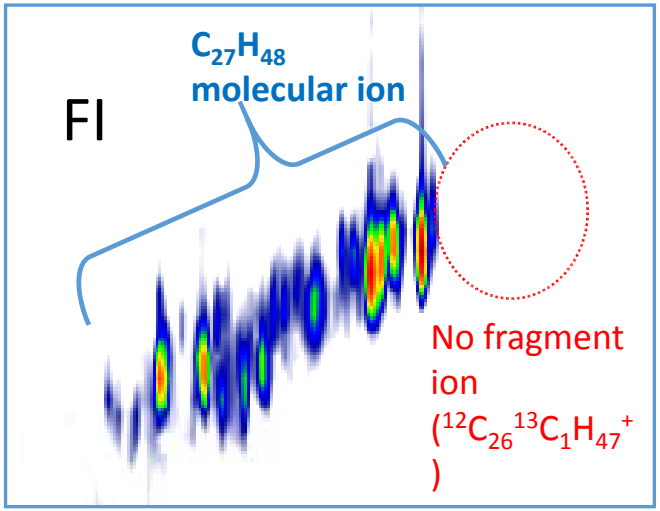
The Biomarker Guide: Volume 1, Biomarkers and Isotopes in the Environment ... By K. E. Peters, C. C. Walters, J. M. Moldowan

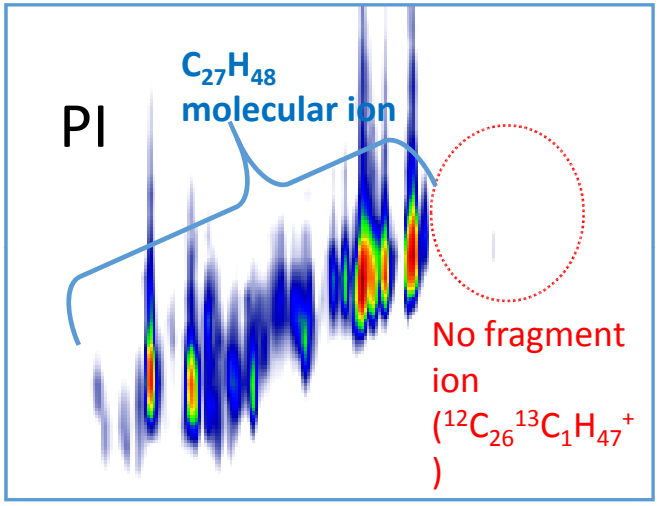
Cambridge University Press, Aug 16, 2007

$C_{27}H_{48}$ (*m/z* 372.3756) extracted ion chromatograms









Using the FI and PI data, the isotopic ion of demethylated fragment ion $C_{27}H_{47}$ interference from $C_{28}H_{50}$ disappeared as a result of FI and PI producing minimal fragment ions in the mass spectrum. The GCxGC/FI and GCxGC/PI EICs made it much easier to interpret the data and correctly assign the biomarker identities in crude oil samples.

GCxGC/PI

- Abundant molecular ions
- More sensitive than FI for some compounds
- Much less fragmentation than EI, but more fragmentation than FI
- Interfering fragments eliminated for biomarker analysis, but characteristic fragment for hopanes, cholestanes etc. allows us created chromatograms for homologues

Short topic 2: Argon DART

“This is a photoionization work
Why is he talking about DAR

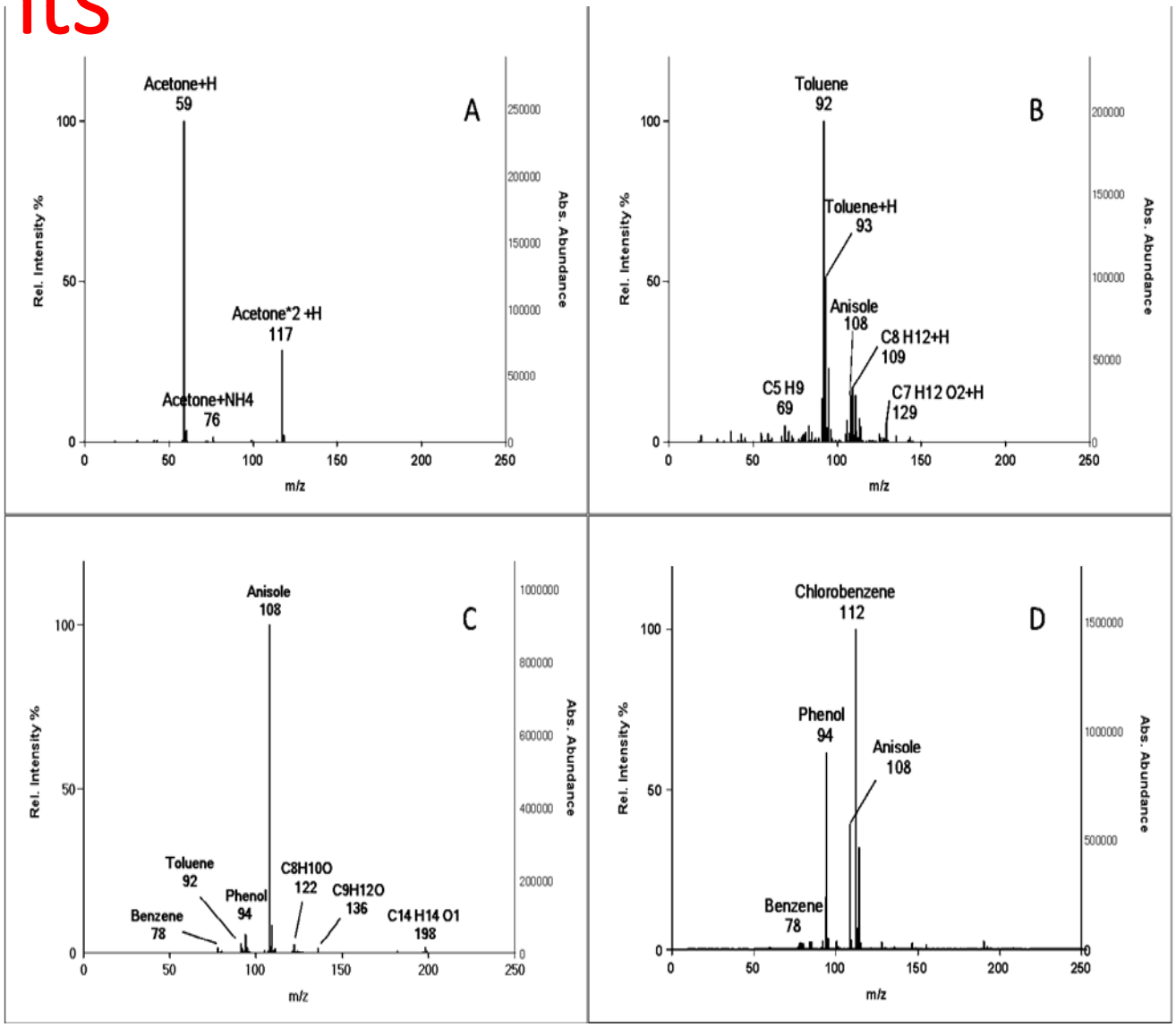
DART is usually done with helium or nitrogen.
What about argon?

- Ar^* doesn't ionize water
- Only 2 papers used argon for DART. Both used proton transfer dopants (AcAc/pyridine, or absolute ethanol)
- PAH's have a low ionization energy, but results were inconsistent.

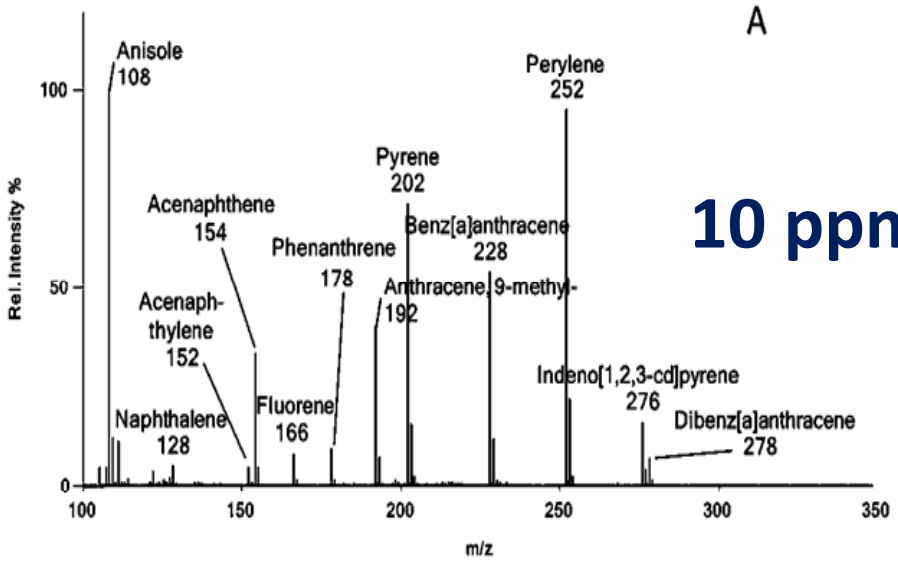
- **The 11.55 eV internal energy of Ar^* is close to the 10.6 eV photon energy of krypton lamps used for atmospheric pressure photoionization (APPI). Use APPI Dopants!**

The 11.55 eV internal energy of Ar^* is close to the 10.6 eV photon energy of krypton lamps used for atmospheric pressure photoionization (APPI). Use APPI Dopants!

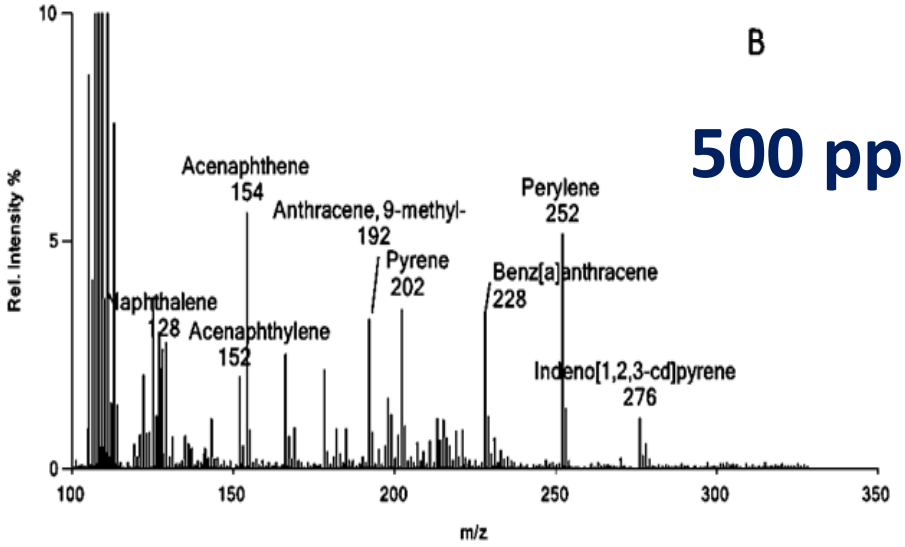
Ar DART mass spectra for common APPI dopants



Ar DART with chlorobenzene dopant produces $M^{+\cdot}$ for PAHs

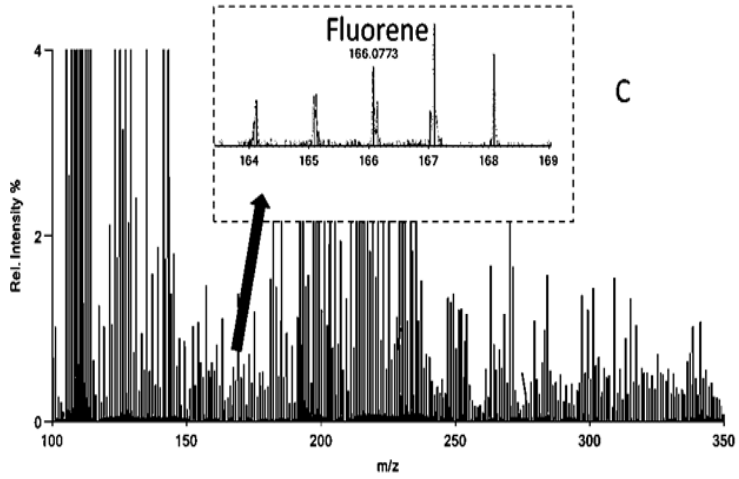


10 ppm

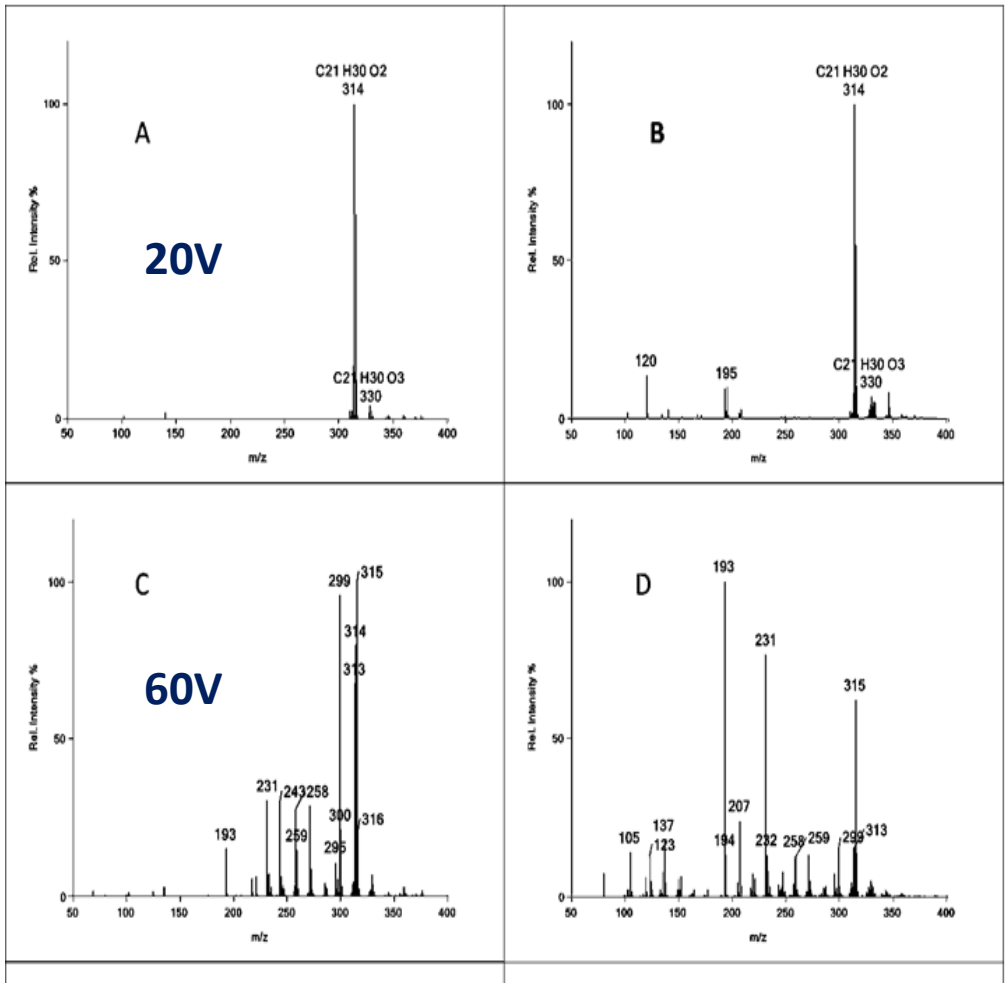


500 ppb

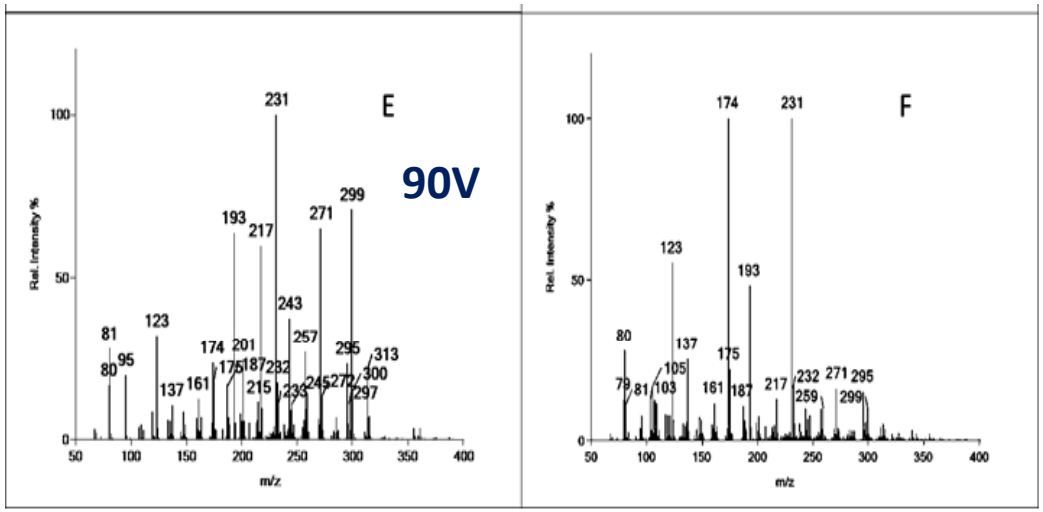
5 ppb



THC CBD



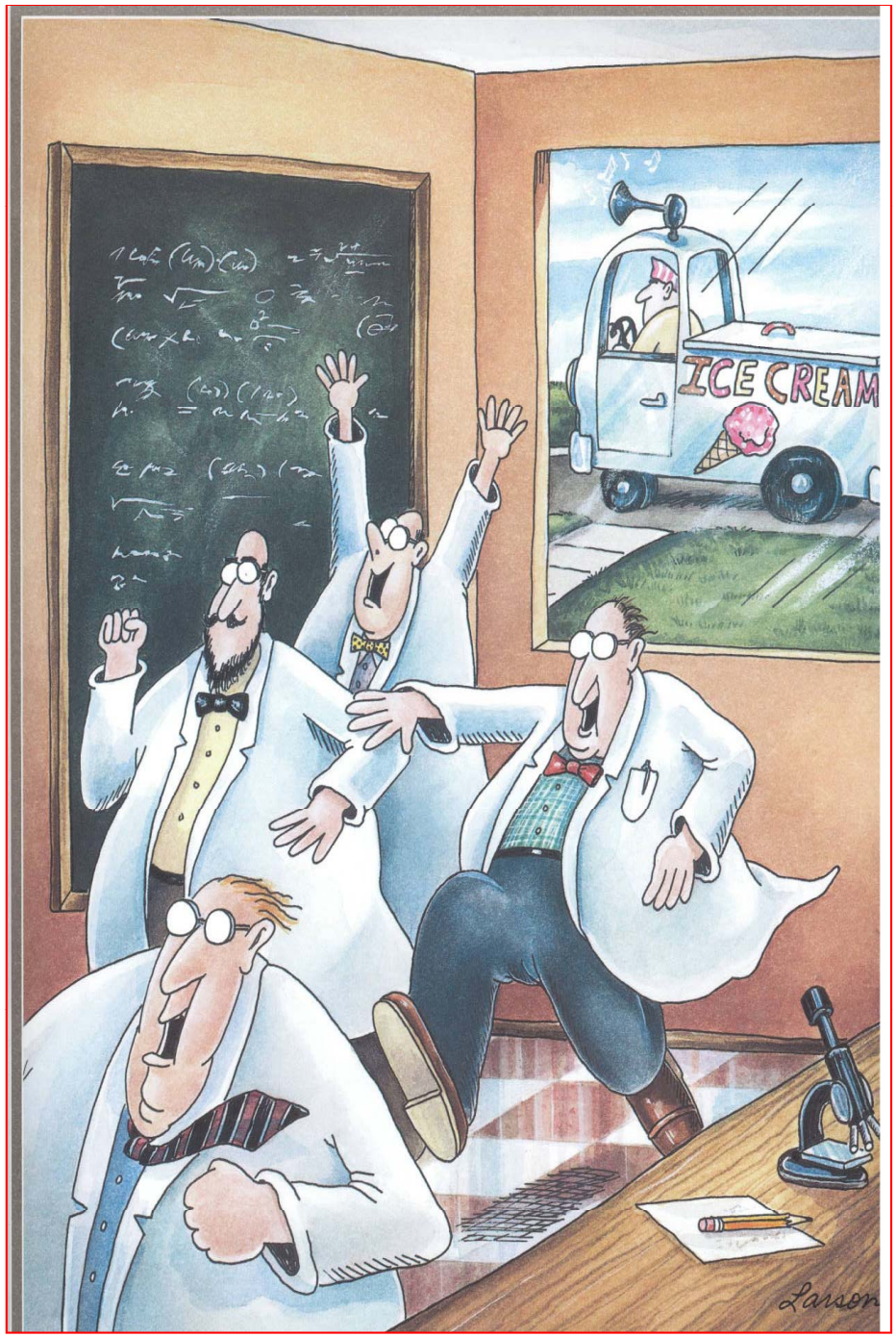
THC CBD



Protonated THC and CBD fragments are identical.
Fragments from $M^{+\cdot}$ Are different!

Analogous to Tiina's APPI results:

T.J. Kauppila, A. Flink, U.-M. Laakkonen, L. Aalberg and R.A. Ketola, *Drug Testing and Analysis*, 5, (2013) 186.



All done!

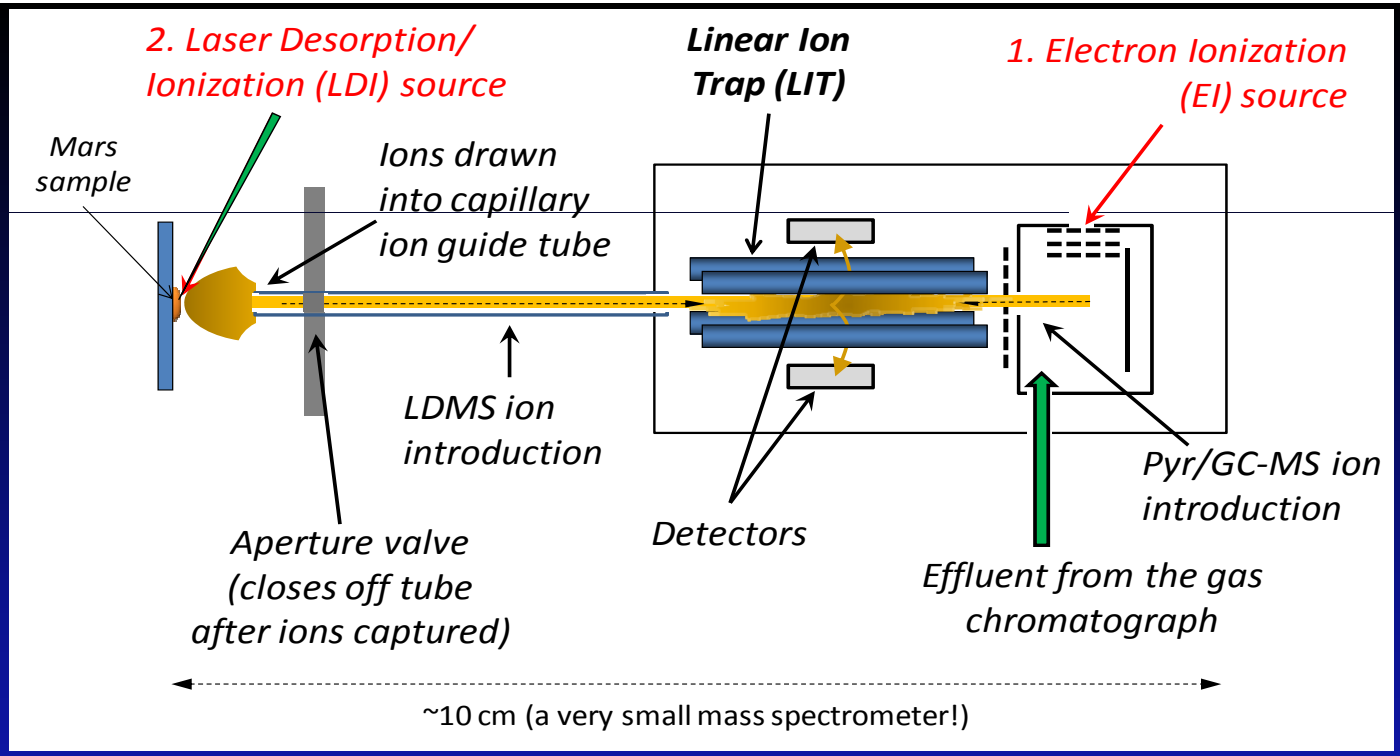
More at poster #001 tomorrow and
R.B. Cody and A.J. Dane, ***Rapid Communications in Mass Spectrometry*****, 30, (2016) 1181.**

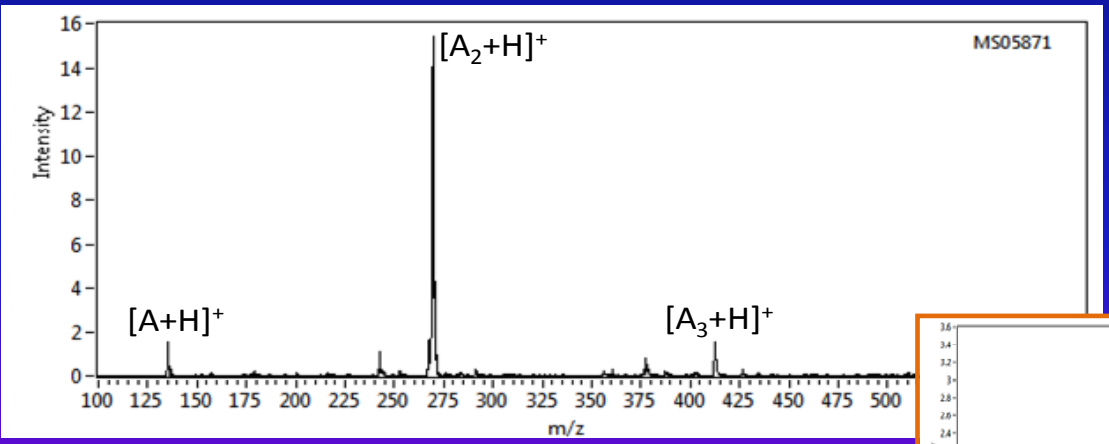
Photoionization workshop: Laser Desorption/Ionization for Planetary Science Applications

Xiang(Shawn) Li

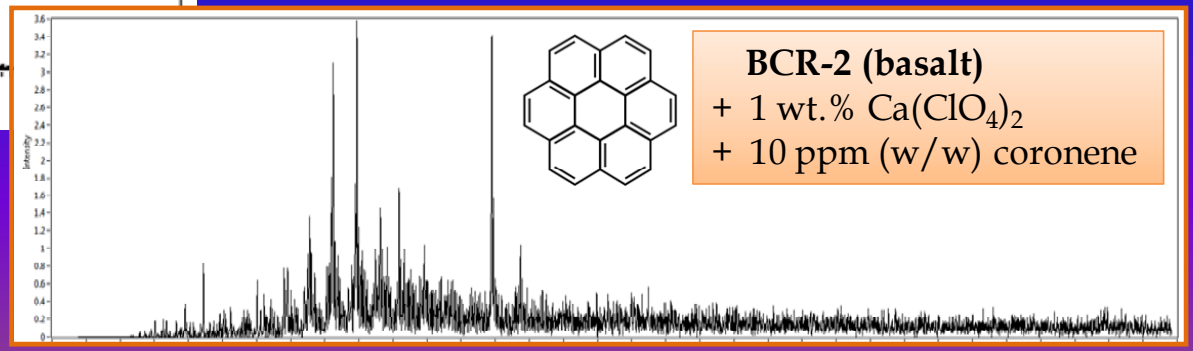
CRESST, UMBC

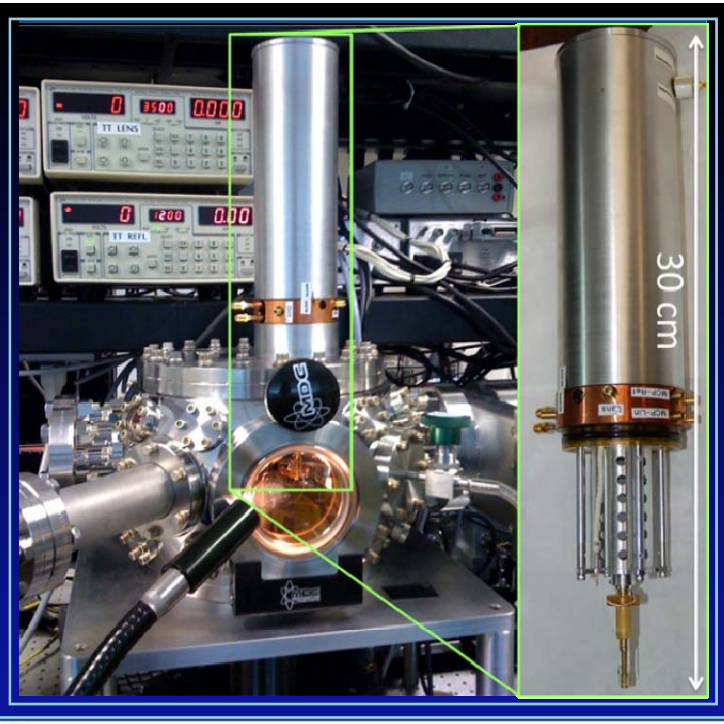
Goddard Space Flight Center

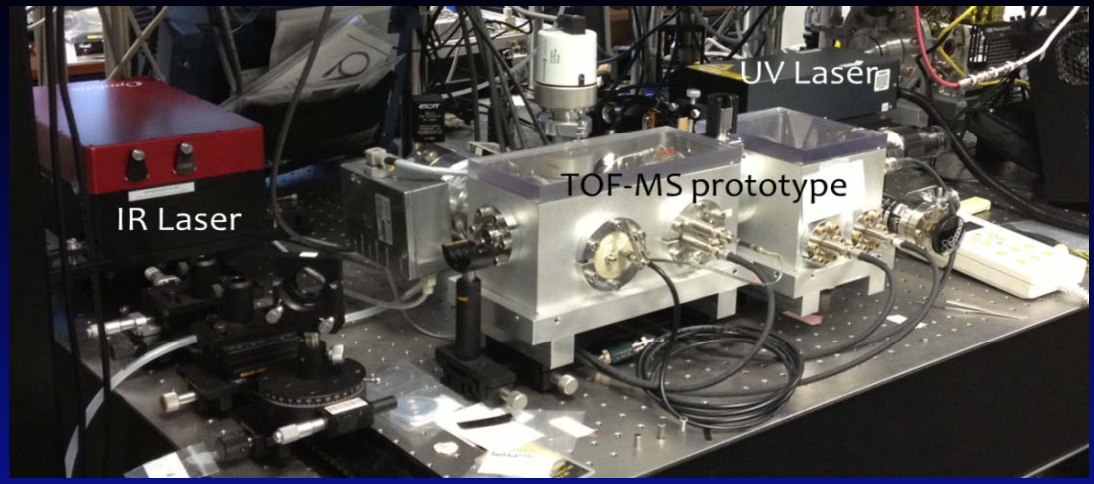


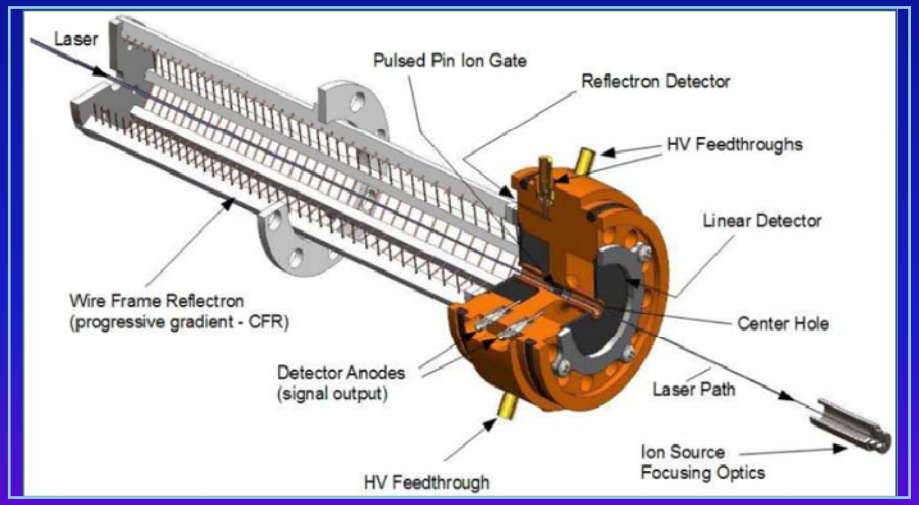


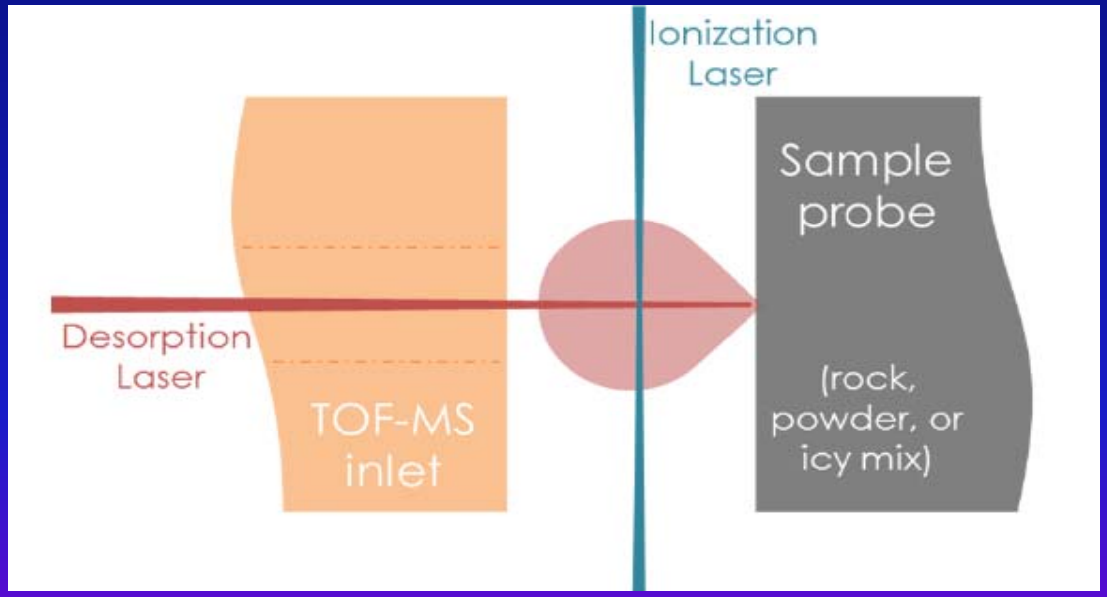
Nd:YAG laser, 266nm, 1ns, up to 150uJ
Target: high mass, non-volatile organics
MPI process





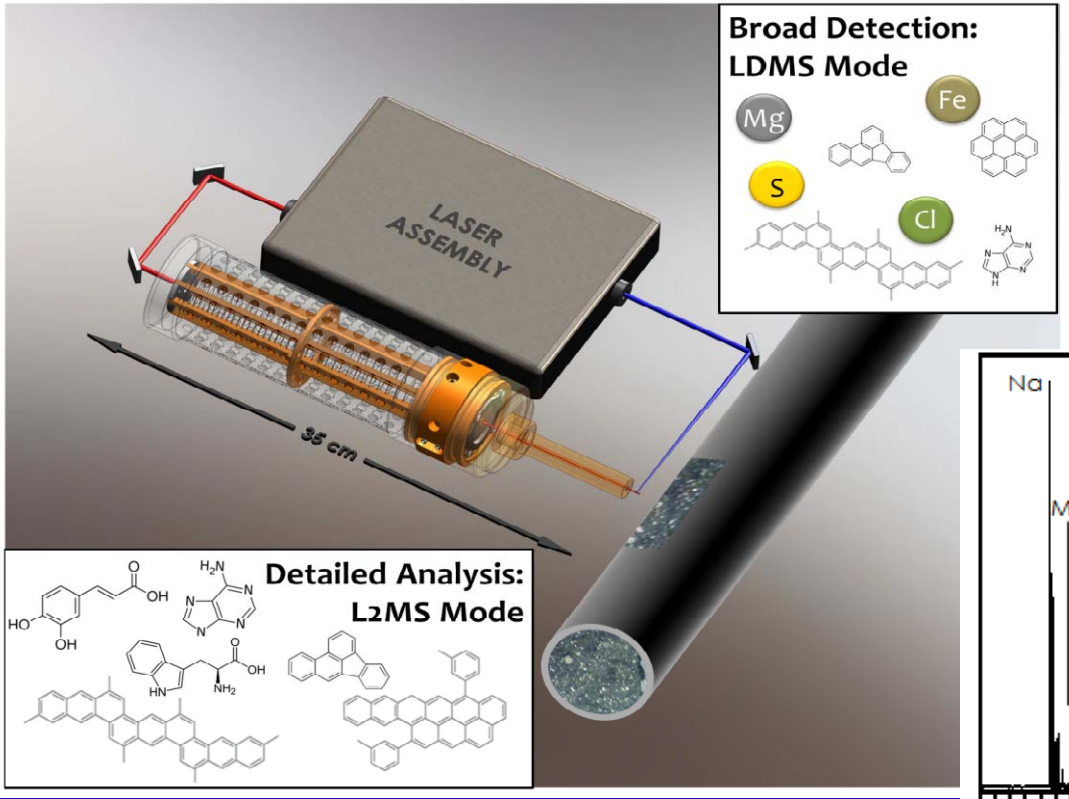


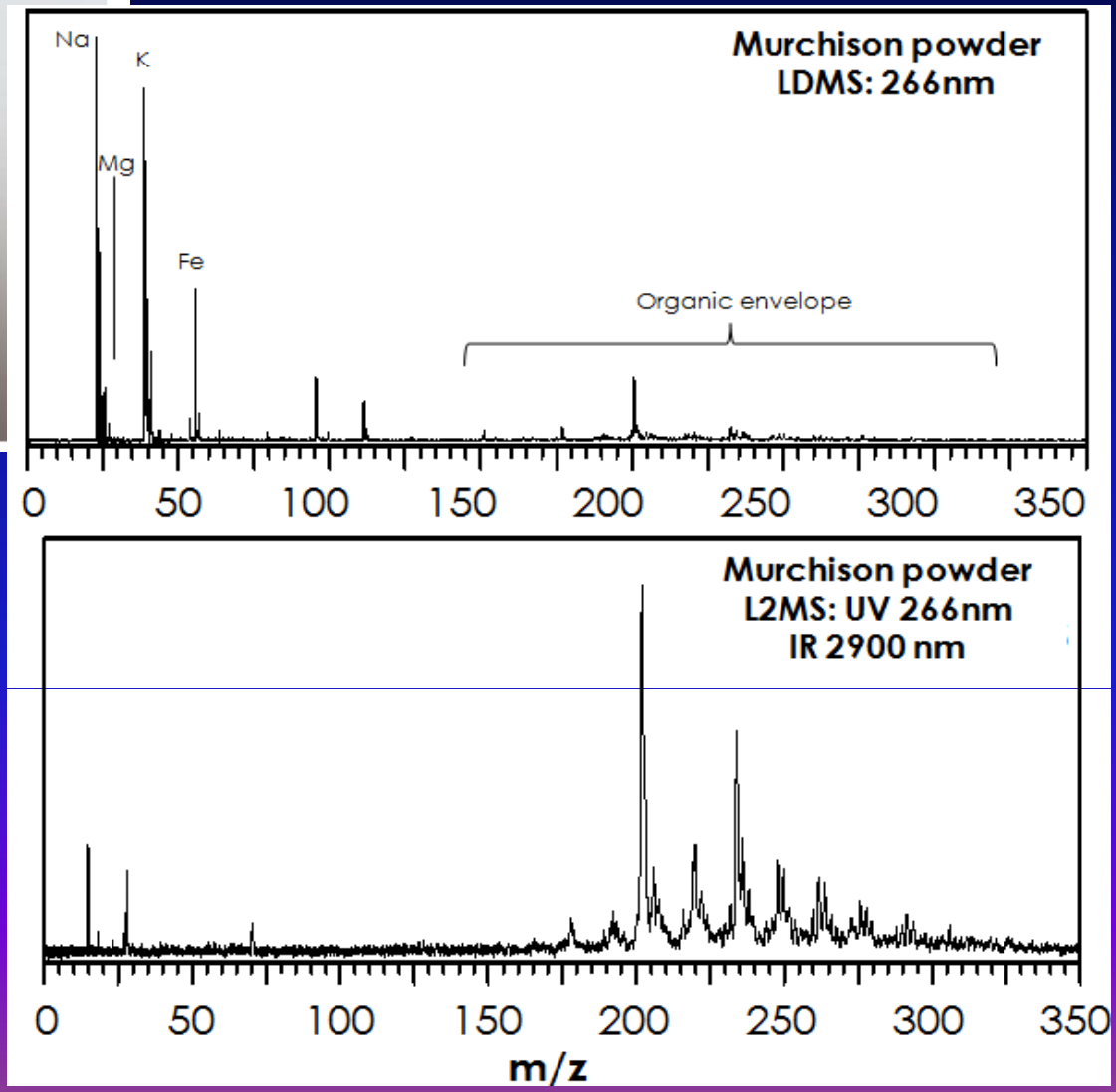




Single laser desorption/ionization
UV: 266nm, 337nm, 355nm
MPI

Two step laser desorption/ionization (L2MS)
IR: 1064nm or 2.7-3.4nm, UV:266nm
REMPI





Selectively ionize PAHs ⟶

- Soft ionization has great potential to be used in future space missions requiring the careful analysis of complex organics in planetary surface materials.
- The ExoMars Rover will carry the MOMA instrument, which will use photoionization as ion source for the first time for in situ analysis of planetary surface chemistry beyond Earth.
- Other photoionization sources can be considered for future instruments, e.g., miniaturized VUV laser or lamp, tunable wavelength laser…… subject to the unique environmental constraints imposed by space flight!

Requirements for space missions

Goal (simplified!)

- Detect intact organic molecules – e.g., by soft ionization mass spectrometry

Instrument itself

- Clean design – compatible with strict contamination and planetary protection requirements
- Compact – low power, low volume, and low weight
- Operable in harsh environments
  - Radiation
  - Temperature extremes – environments range from cold (~ 100 K) to hot (~ 500 C)
  - Dust and particulate challenges