Forensic Analysis of Illicit Drugs and Trace Explosives using Ambient Pressure Ionization Mass Spectrometry

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The Science and Technology Directorate of the U.S. Department of Homeland Security sponsored the production of portions of this work under Interagency Agreement HSHQDC-12-X-00024 and HSHQDC-11-X-00420 with the National Institute of Standards and Technology

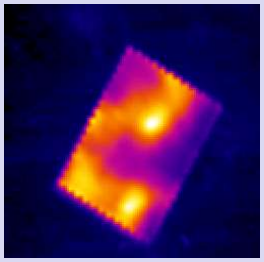
Forensic and Trace Contraband Detection

Goals:

1. Next generation technology for DHS screening
2. Improved technologies for high throughput forensic analysis
3. Standard methods for evaluation of API sources

Contraband Materials
-Organic
-Inorganic
-Nuclear

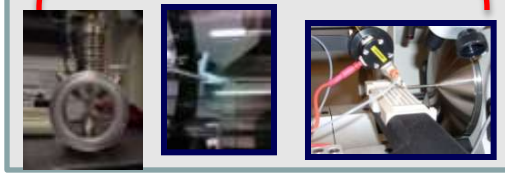
Ambient Desorption and Ionization



Specific Chemical Analysis and Detection

API-MS

Liquid



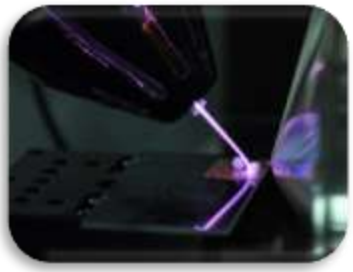
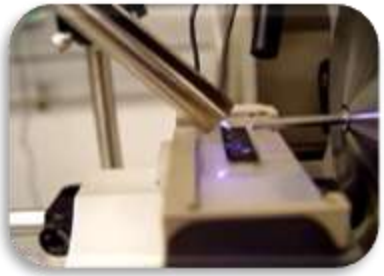
Thermal

Plasma

Photon

API-MS Surface Analysis Methodologies Under Investigation at NIST

- Liquid Based Sources
  - Electrospray Ionization (ESI)
  - Atmospheric Pressure Chemical Ionization (APCI)
  - Desorption Electrospray Ionization (DESI) and (SESI)
  - Desorption Electro-Flow Focusing Ionization (DEFFI)
  - PaperSpray Ionization (PS)
- Plasma Based Sources
  - Atmospheric Pressure Glow Discharge (APGD)
  - Low Temperature Plasma (LTP)
- Thermal Based Sources
  - Atmospheric Pressure Thermal Desorption Ionization (APTDI)
- Laser Based Sources
  - Atmospheric Pressure Matrix-Assisted Laser Desorption Ionization (AP-MALDI)
  - Laser Diode Thermal Desorption (LDTD)

Why API-MS

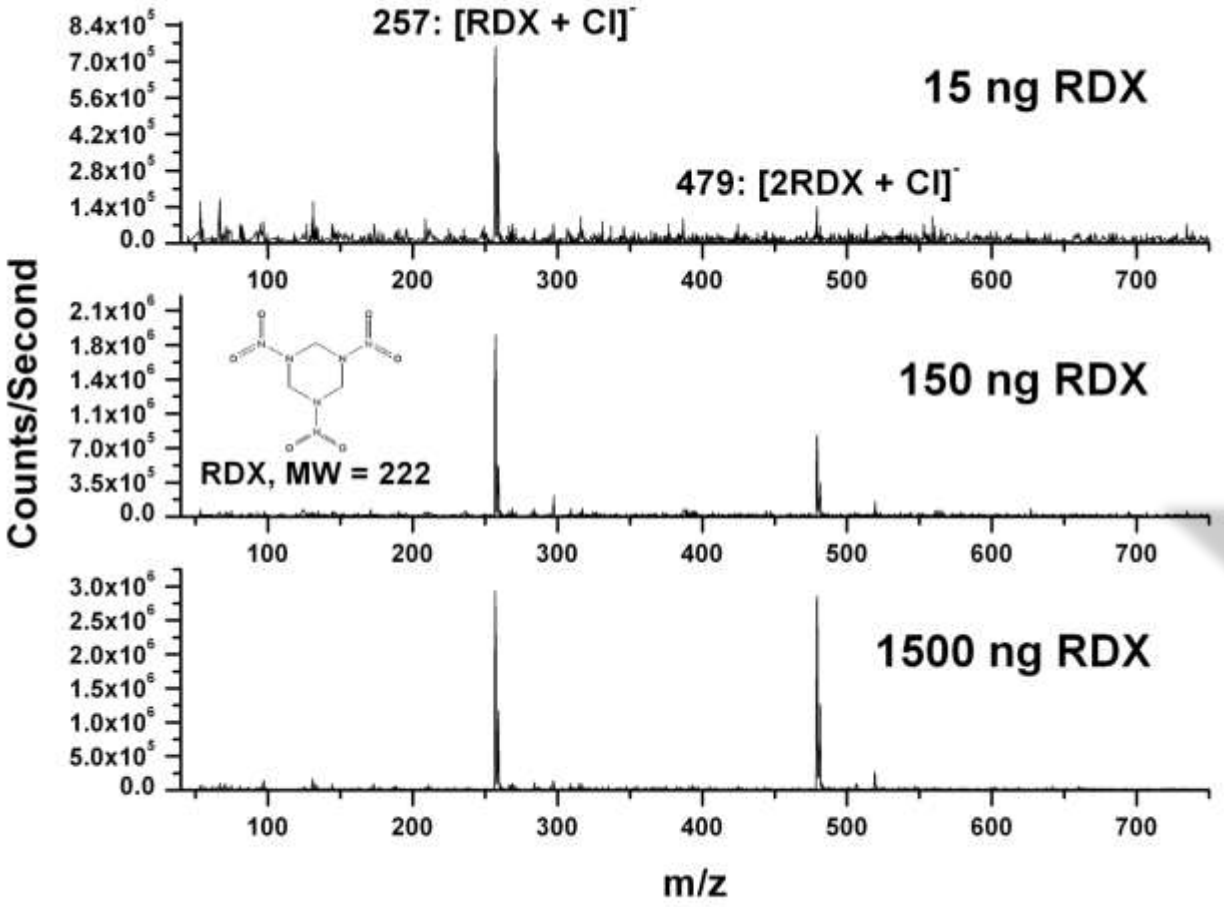
- Fast analysis – high sample throughput

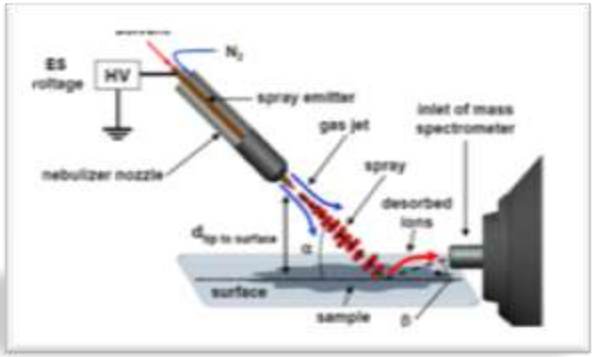
- Multiple sources – maximum flexibility
  - High ionization efficiency
  - Selectivity and flexibility of gas phase and solution phase chemistries

- Sample requirements minimized (direct analysis of wet/insulating/geometric samples or swipes, + vacuum-incompatible surfaces, non planar, non conductive)
  - Can analyze solids, liquids and vapors both positive and negative polarities

- Performance of Mass Spectrometers and MS/MS (chemical speciation *and* identification)
  - No need for chromatographic separation

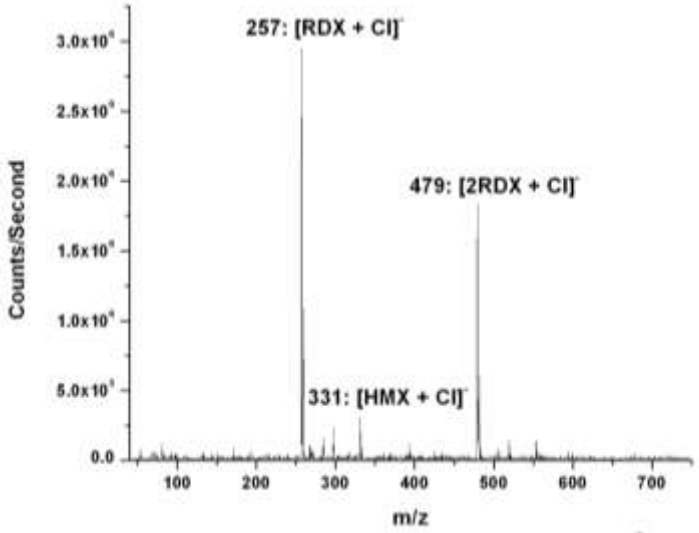
Liquid: DESI Analysis of Explosives Residues

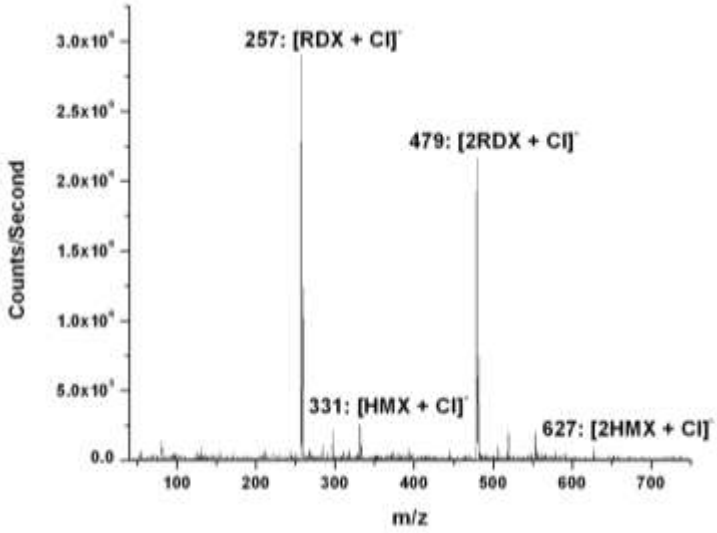


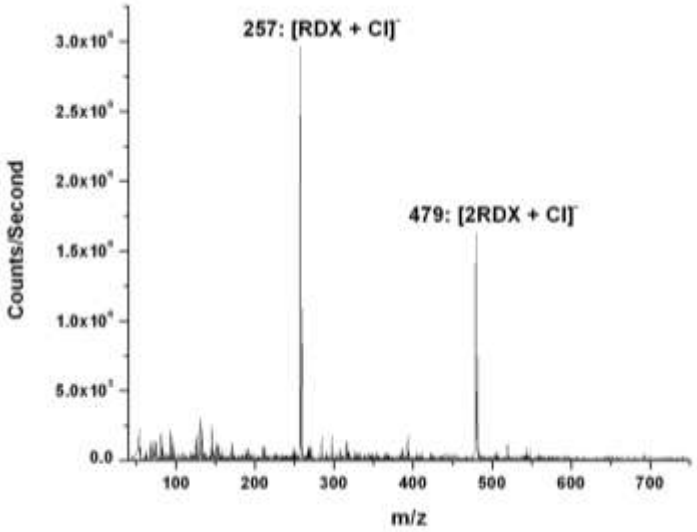


Szakal, C. and Brewer, T.M., *Anal. Chem.*, **2009**, *81*, 5257-5266

Liquid: DESI C-4 Spectra



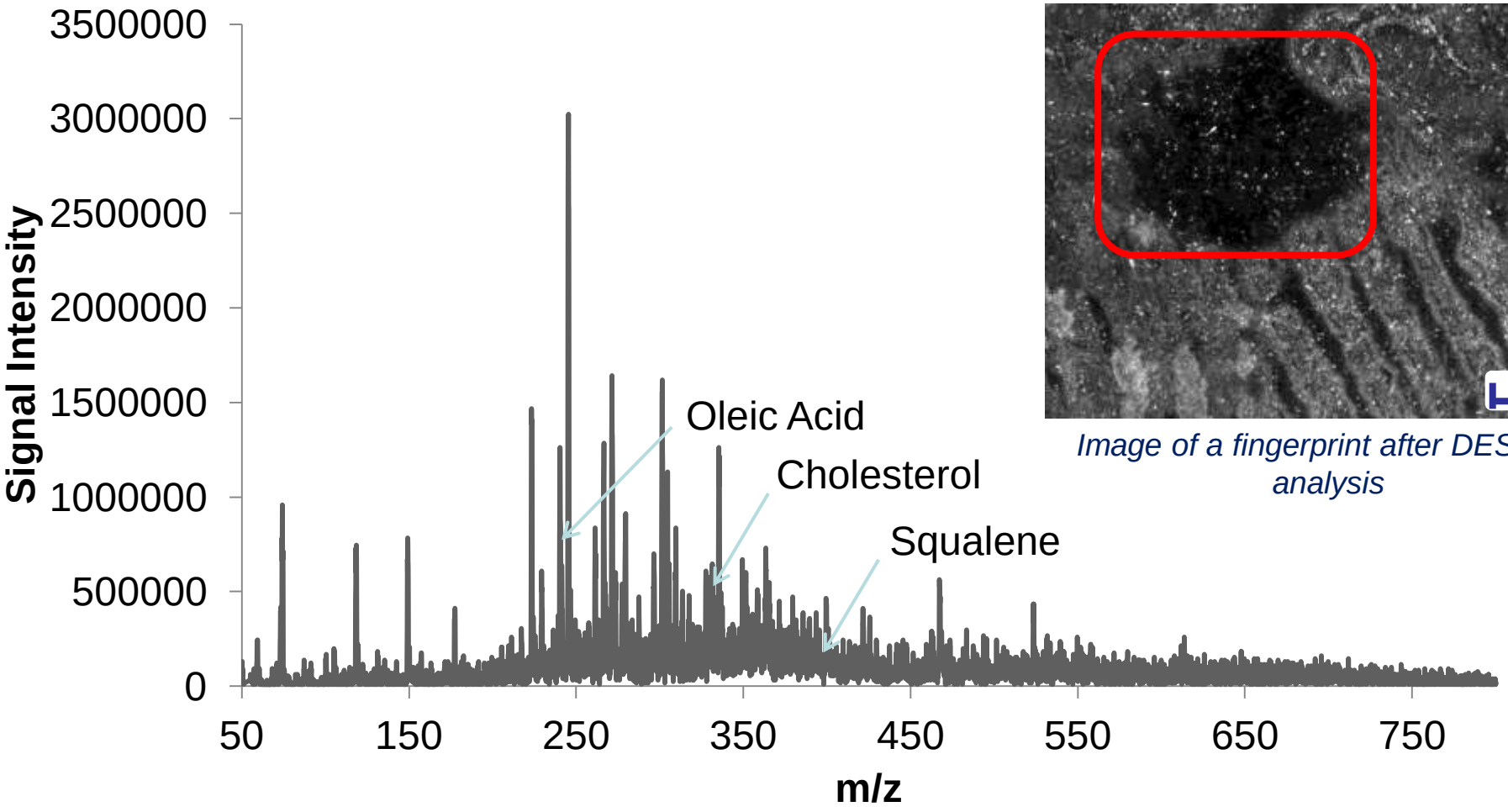




C-4 samples from Montgomery Country bomb squad

Explosives-containing portions of C-4 samples obtained with liquid-liquid extraction in acetonitrile (explosives, polars)

Liquid: DESI Fingerprint analysis



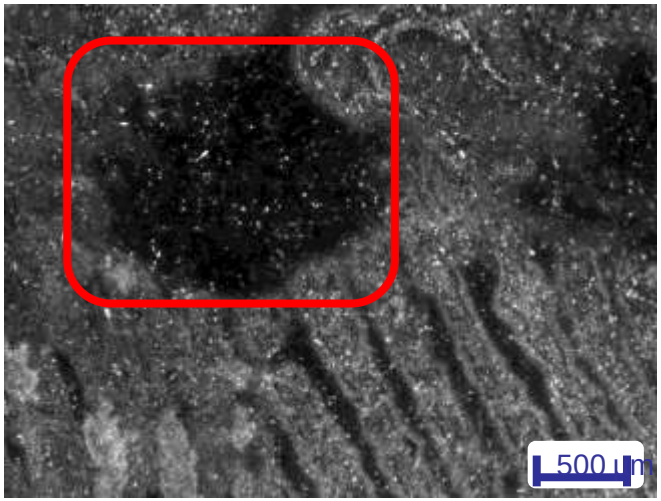
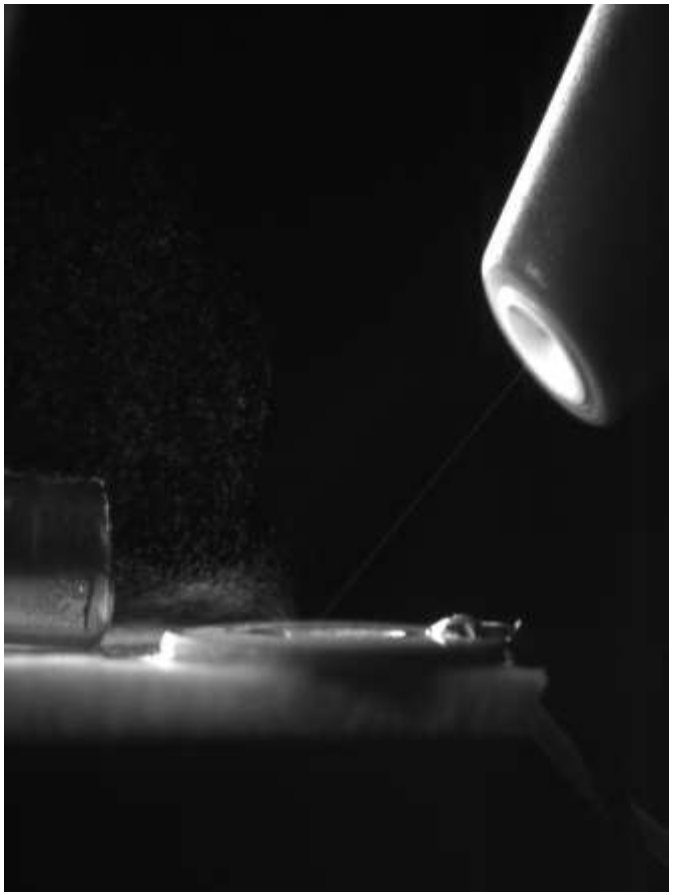


Image of a fingerprint after DESI-MS analysis

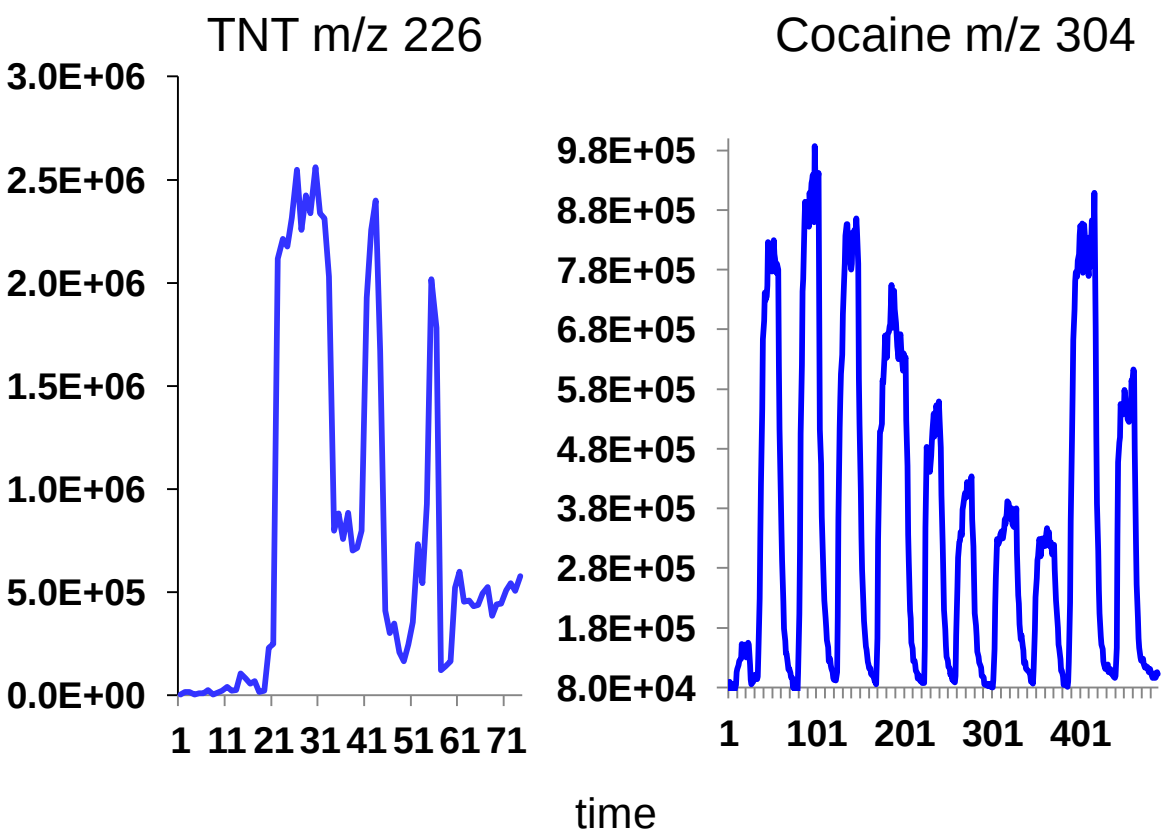
Positive Ion Scan using DESI-MS

Liquid: Nebulizer Assisted DESI



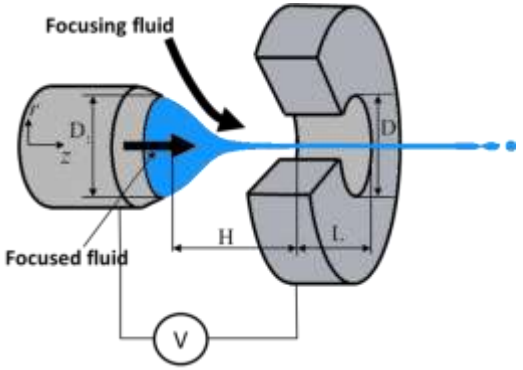
Allows for analysis on metal surfaces

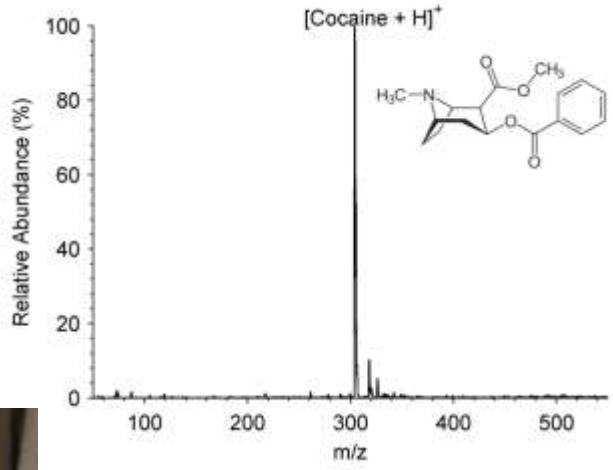
Selected Ion Monitoring vs. Frequency

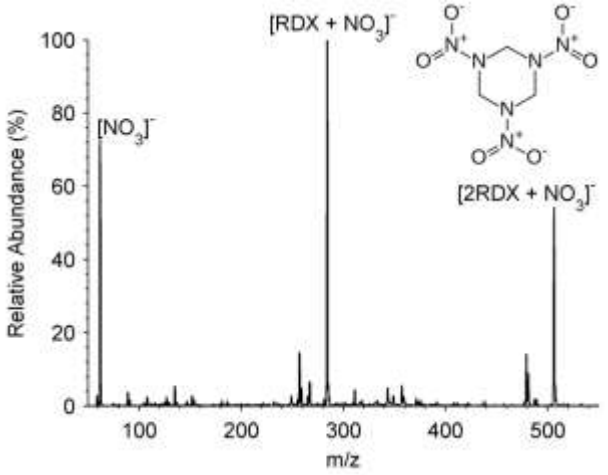


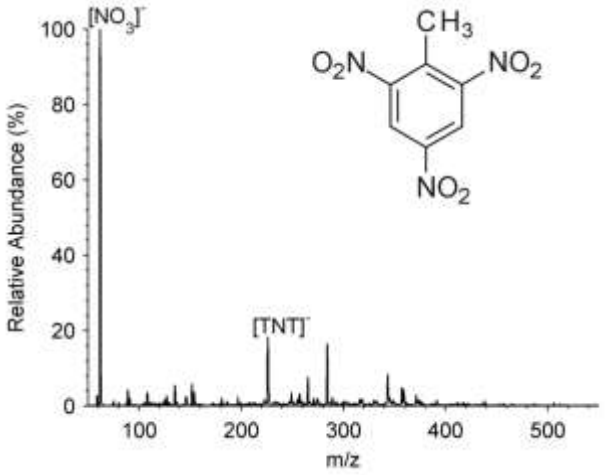
Typical enhancement of 10x but have seen up to 2000x enhancement

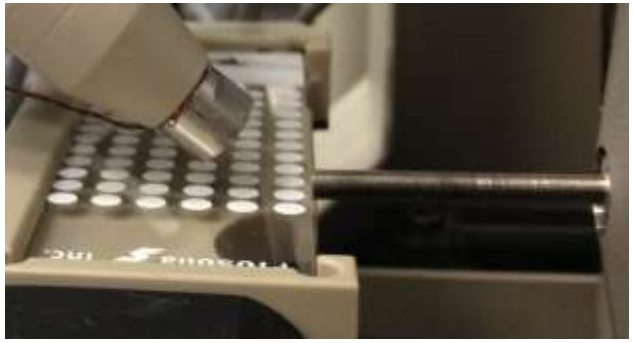
Liquid: Desorption Electro-Flow Focusing Ionization



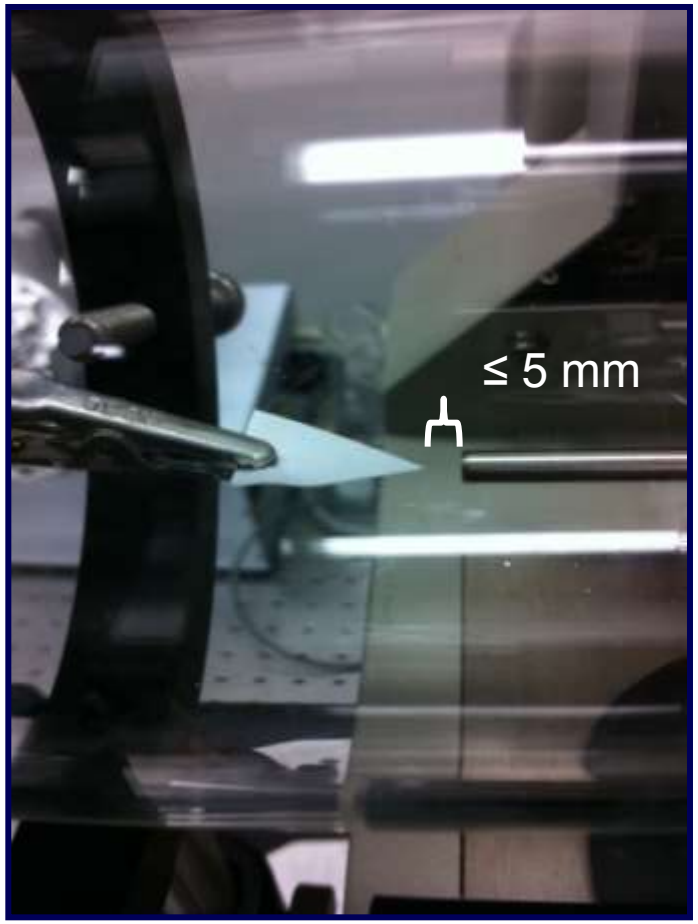


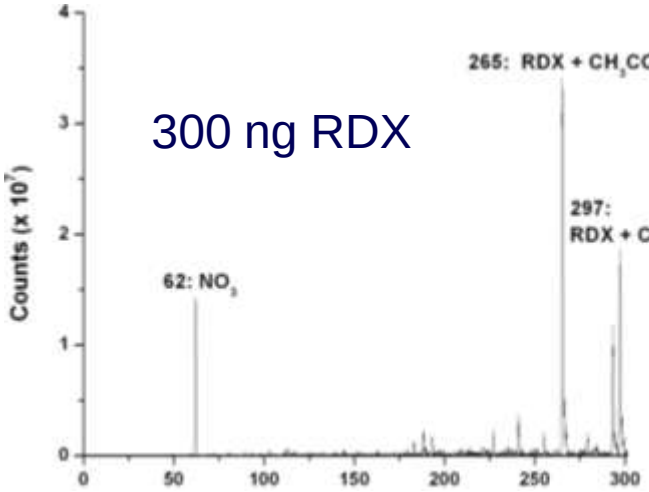


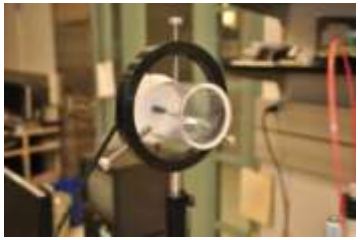


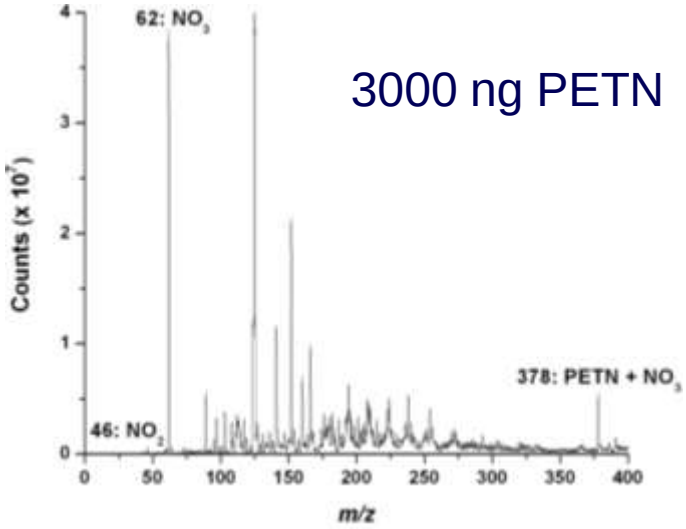


Liquid: PaperSpray –Directly from Swipes



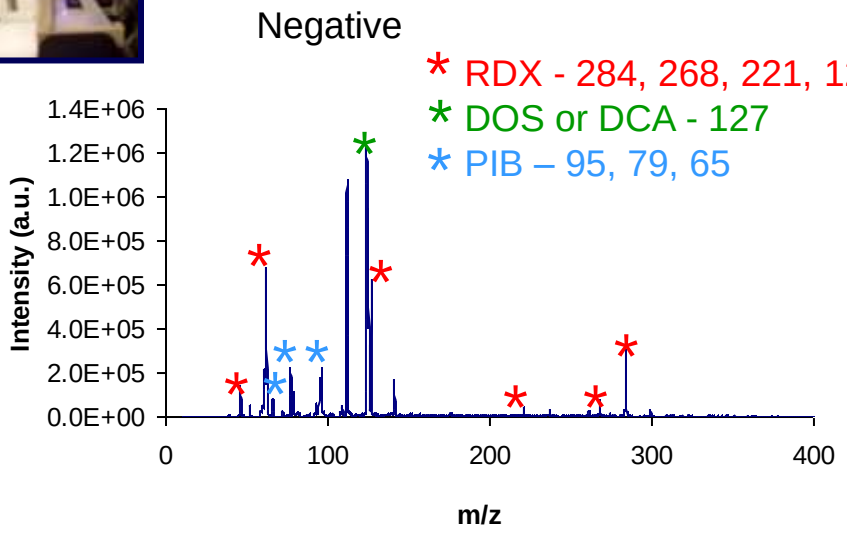


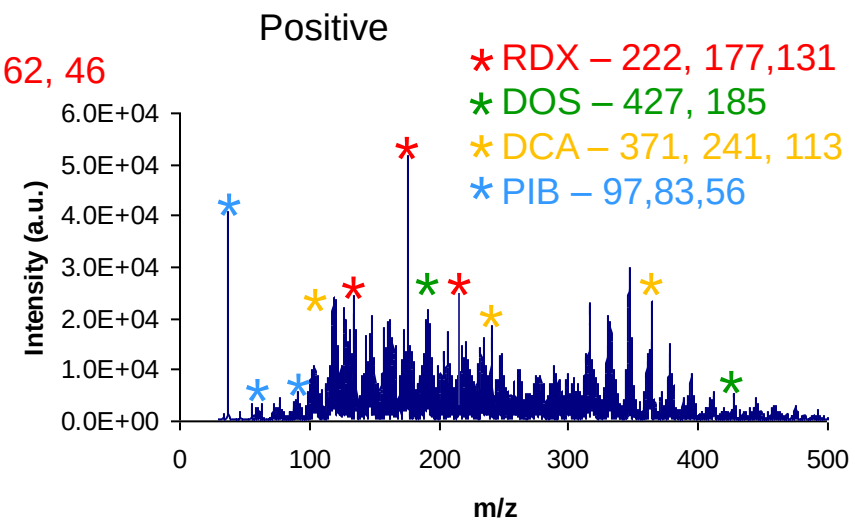


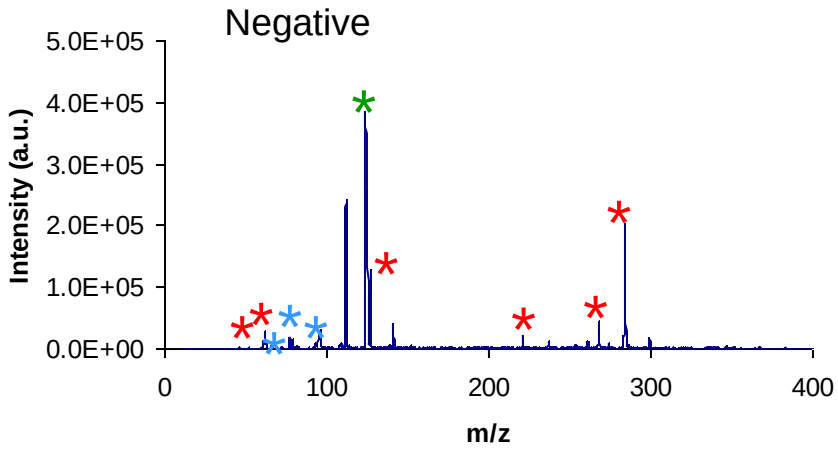


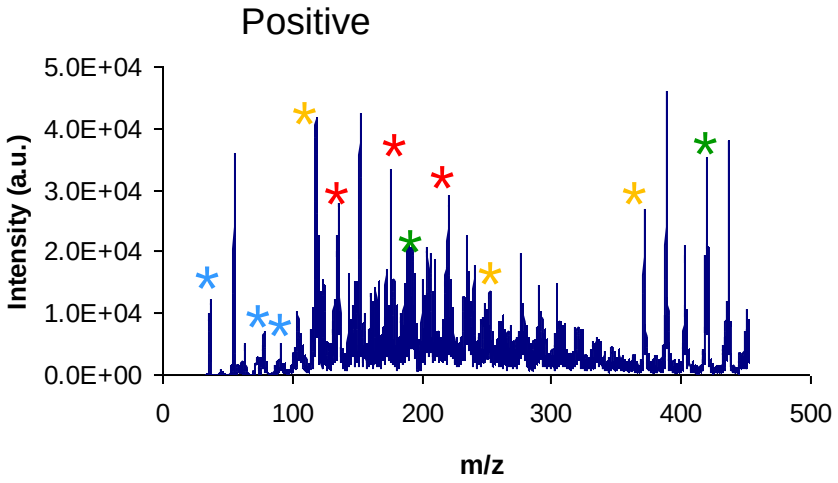
The Swipe is the Ion Source – Little to no Sample Preparation Required

Plasma: APGD Analysis of C-4 Residues





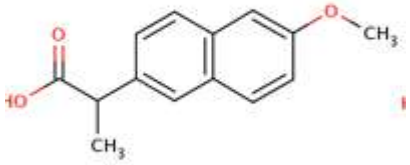




Placed visible amount on explosive swipe. Plasma 75W and 1 L/min He and O 0.1 L/min. No liquid needed for extraction.

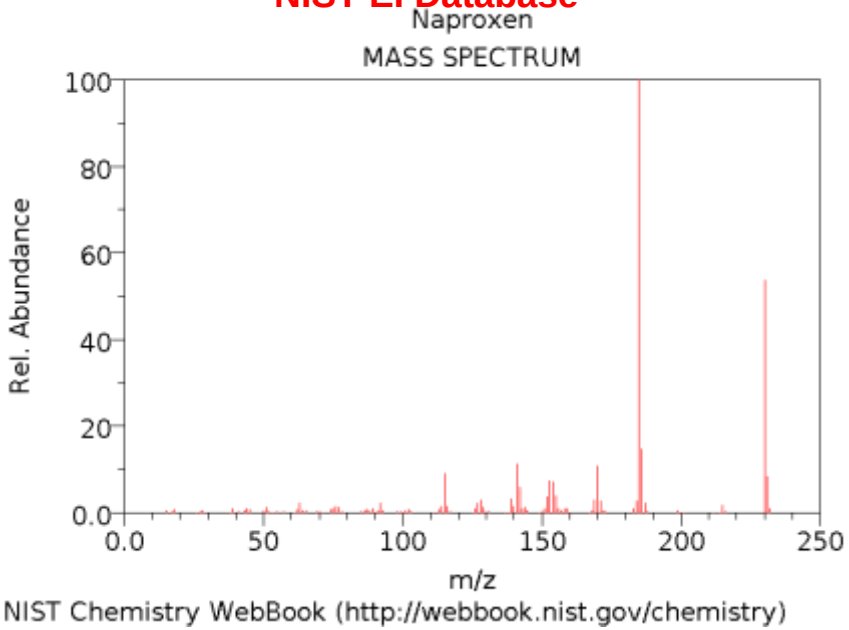
Plasma: OTC Pharmaceutical - Aleve

Active Ingredient – Naproxen

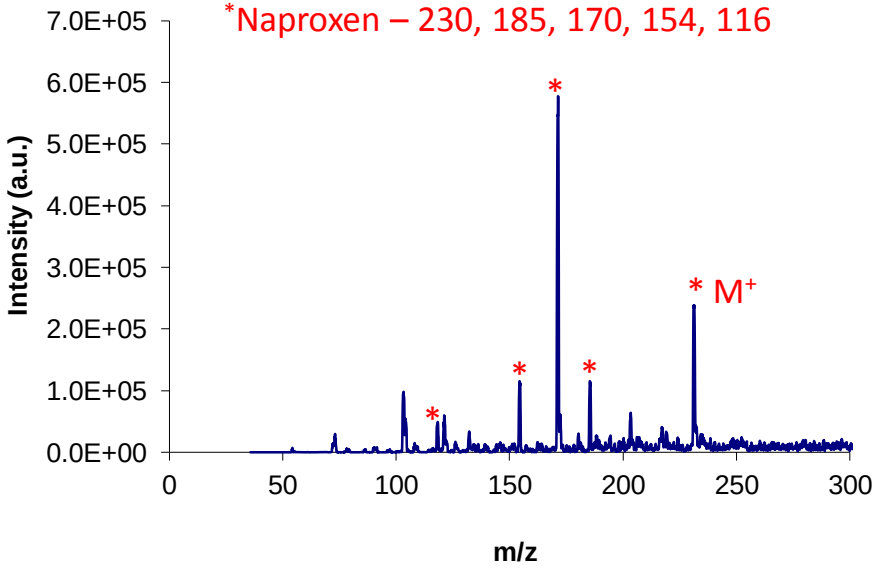


MW = 230

NIST EI Database



Aleve



Molecular ion Signal at m/z 230

EI “like” fragmentation - NIST EI Database Searchable (>200,000 compounds)

APGD-MS spectra of Aleve Pill. Plasma 75W and 1 L/min He and O 0.1 L/min

Plasma: APGD Analysis of Forensic Compounds

Forensic Compounds Characterized by APGD

Narcotics

THC
Cocaine
Heroin
MDMA
Methamphetamine
Hydrocodone

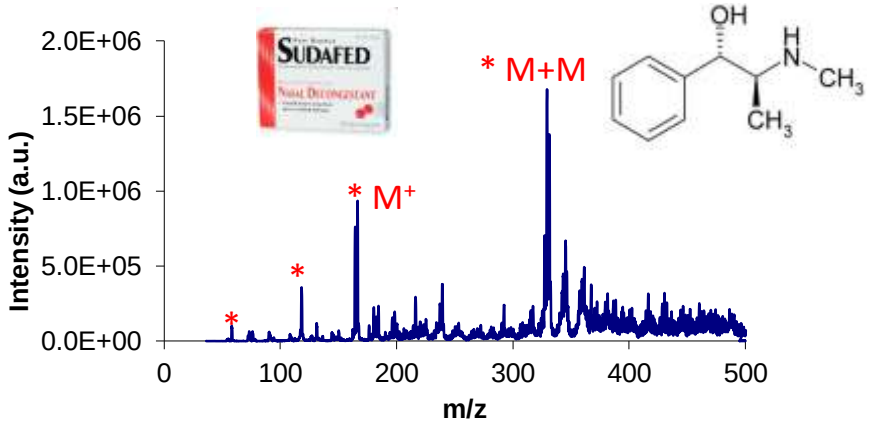
Explosives

C-4
RDX
PETN
TNT
NG
HMX
Semtex H
Semtex A

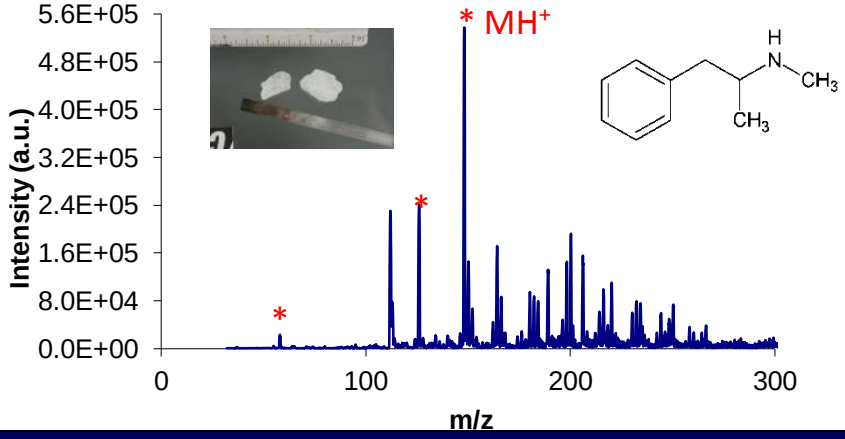
OTC pharmaceuticals

Mucinex DM
Aleve
Sudafed
Alka-Selzter Plus Nightime
Ibuprofen
Tylenol
Asprin

*Pseudoephedrine – 330, 165, 118, 77

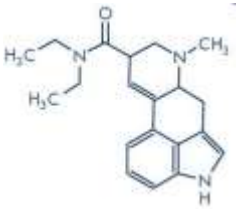


*Methamphetamine – 150, 134, 58

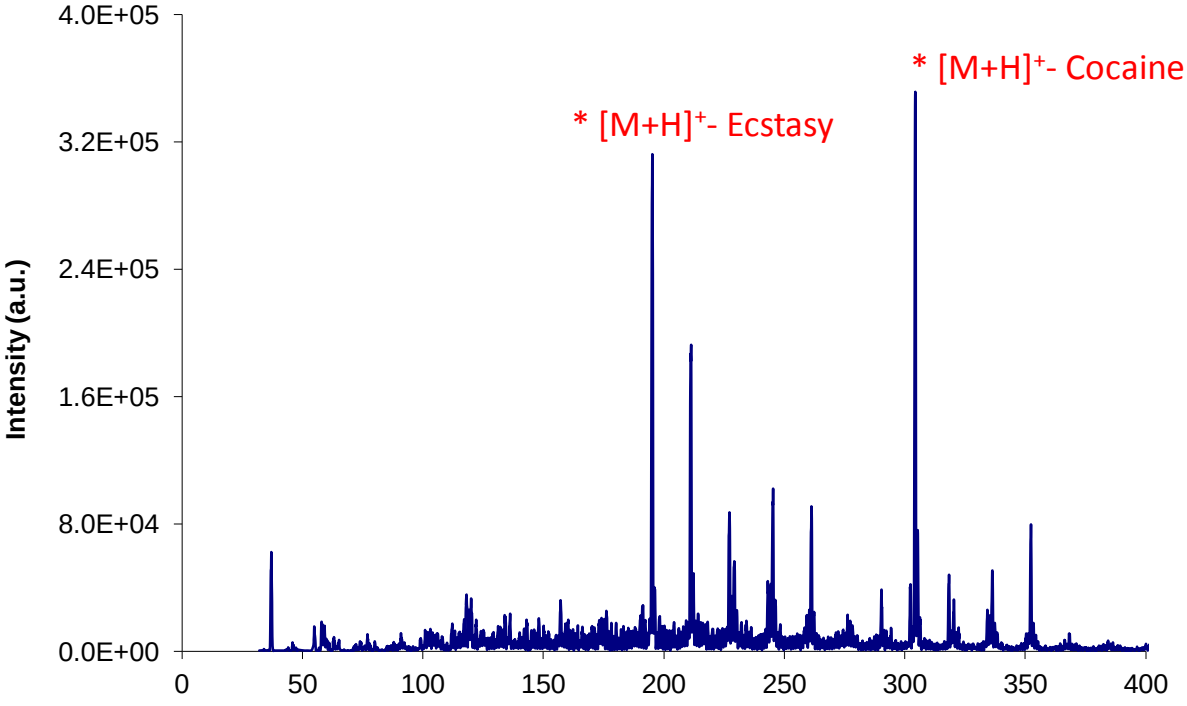


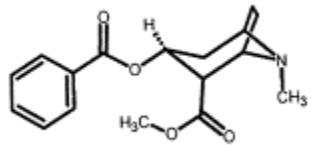
APGD-MS spectra of Musinex DM and Sudafed Pills. Plasma 75W and 1 L/min He and O 0.1 L/min

Plasma: APGD-MS Analysis of Ecstasy and Cocaine Mixture



MW = 193

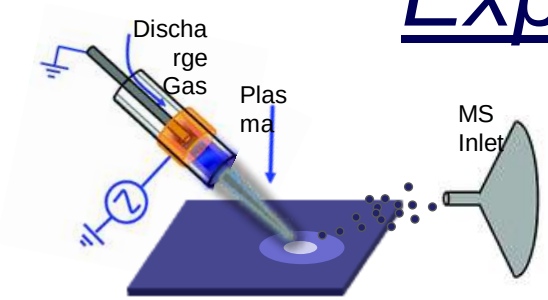


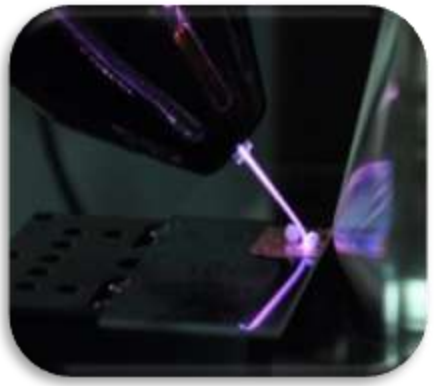


MW = 303

APGD-MS spectra of Ecstasy and Cocaine. Plasma 75W and 1 L/min He fragmentation pattern with O to extensive.

Plasma: Low Temperature Plasma – Explosive Particles

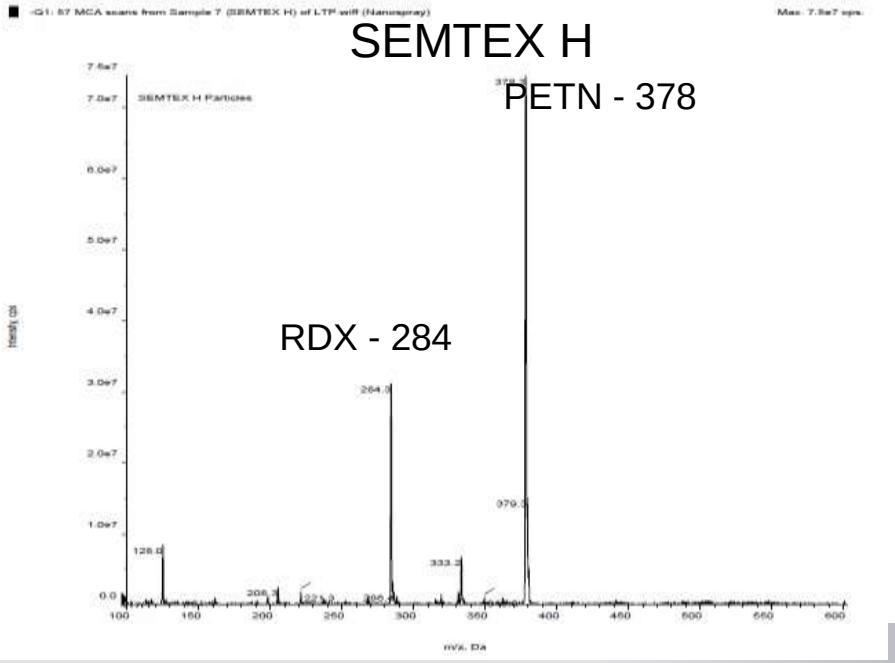




SEMTEX H

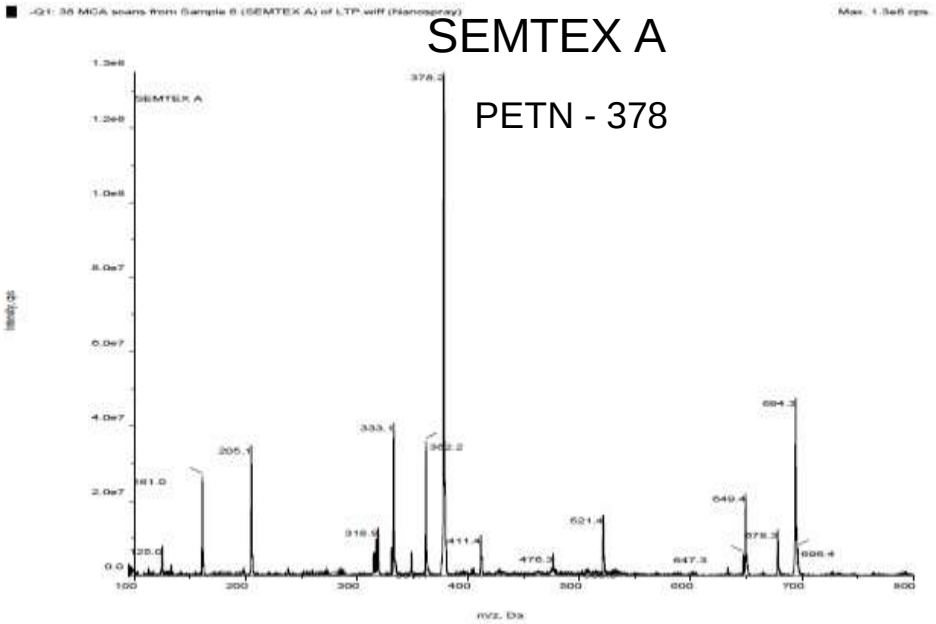
PETN - 378

RDX - 284

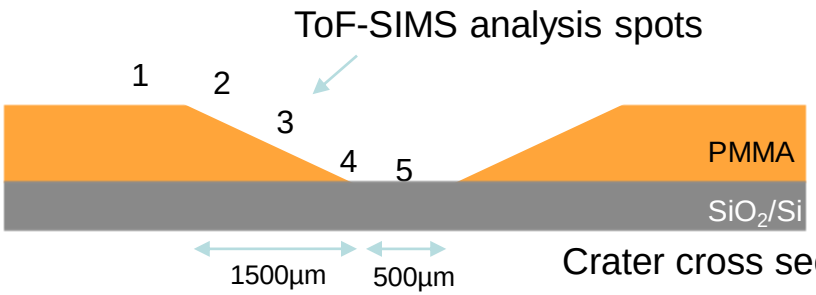


SEMTEX A

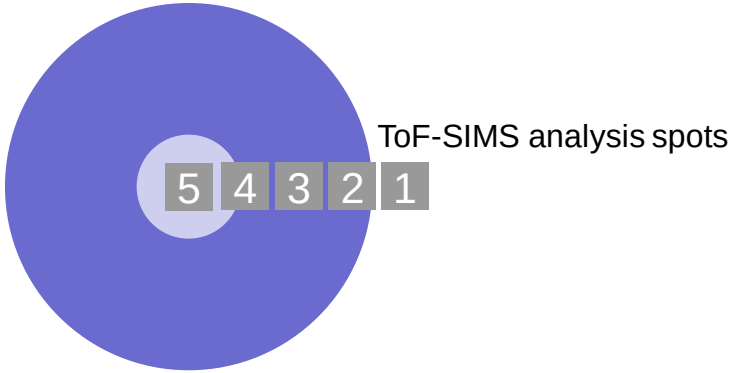
PETN - 378



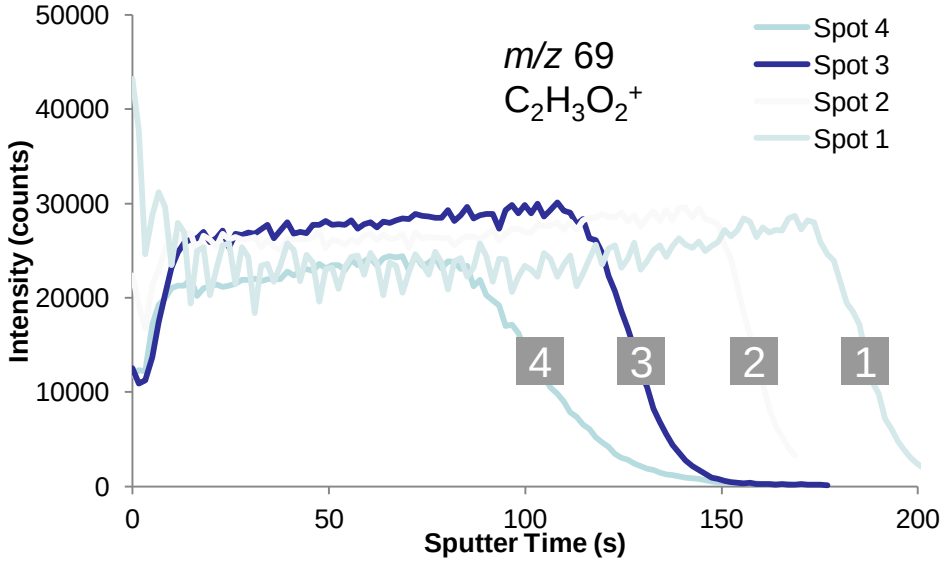
Plasma: LTP Depth Profiling - PMMA



Crater cross section

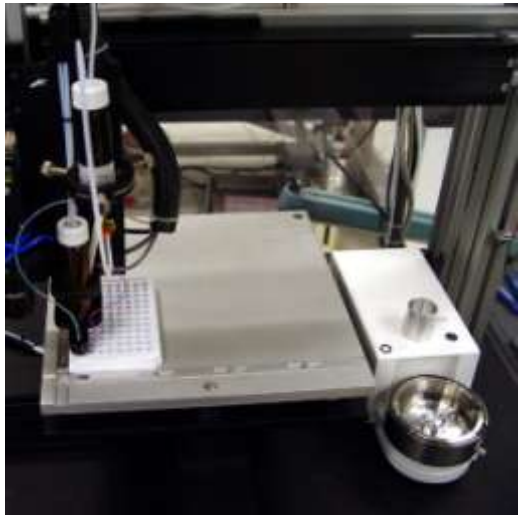


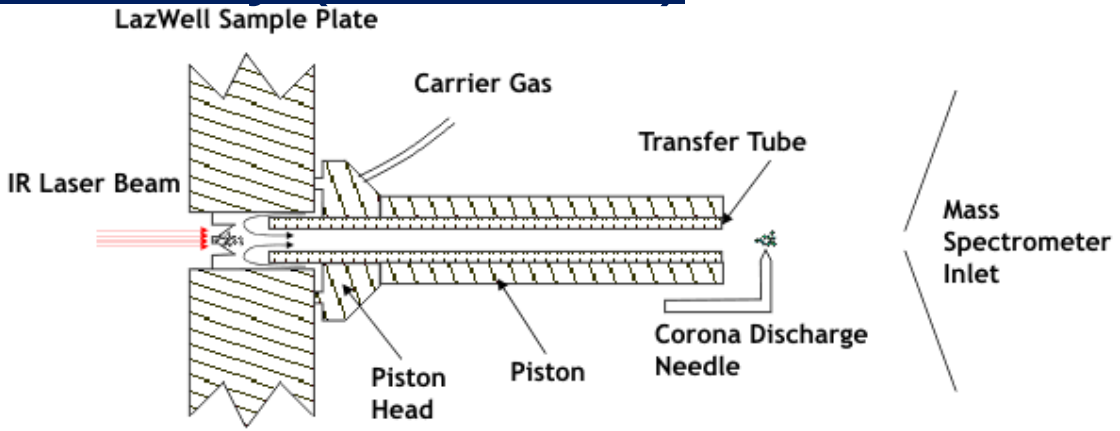
SIMS depth profiling can reveal changes in chemistry along the depth of the film

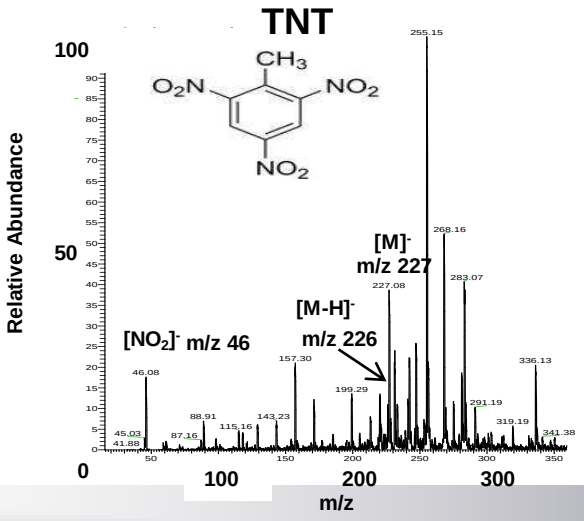


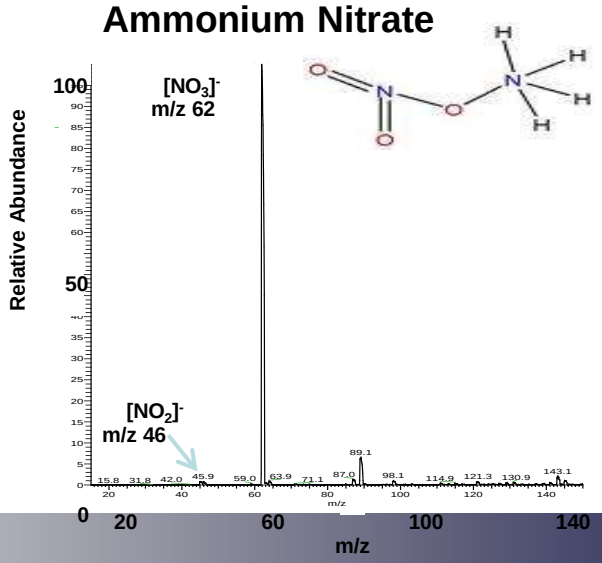
Results suggest damage is localized at the surface, and the extent of damage seems proportional to plasma exposure. In the sub-surface region, the intensity is seen to quickly return to steady state values

Laser: AP Laser Diode Thermal Desorption Mass Spectrometry (LDTD-MS)

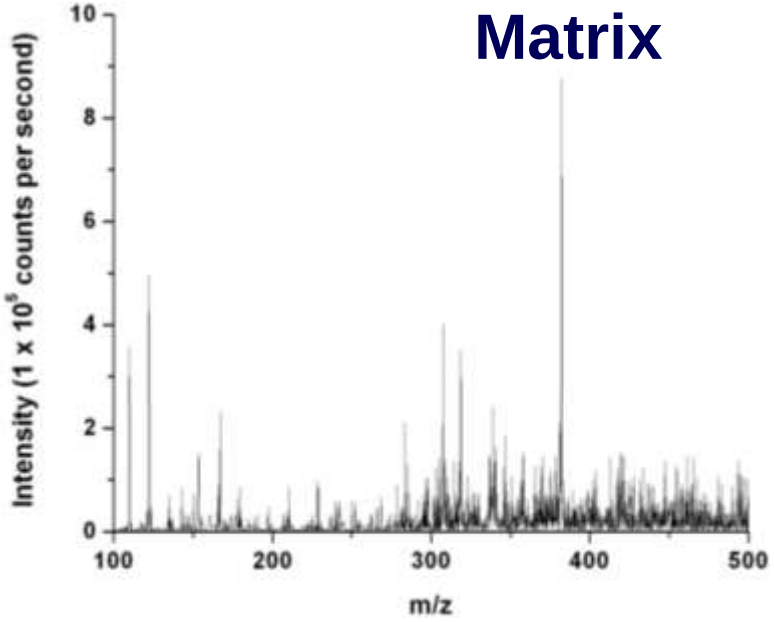


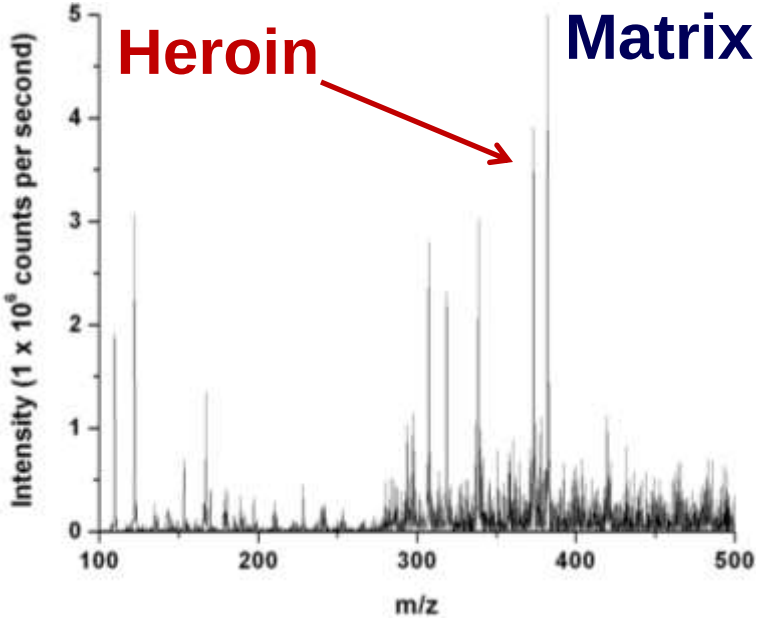






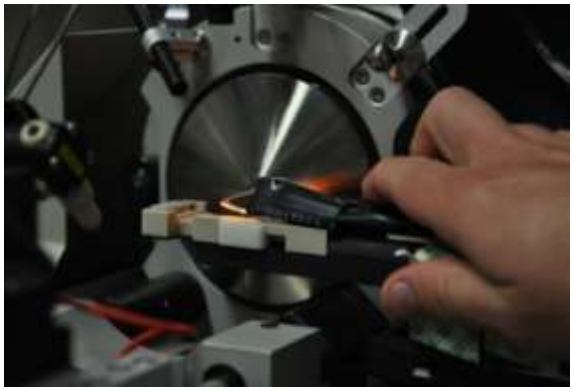
Laser: Narcotics on Currency with AP-MALDI





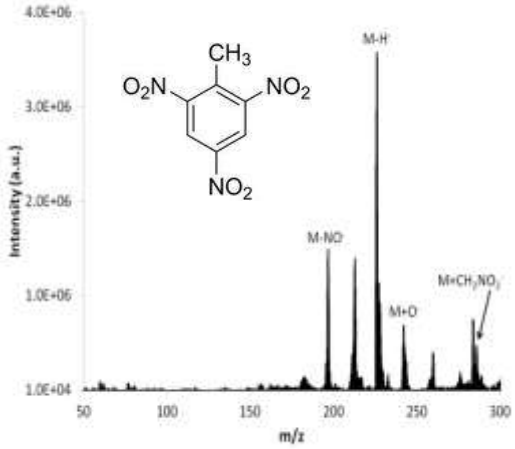
0.5 µL CHCA matrix on US Currency with doped heroin

Thermal: AP Thermal Desorption Ionization - Mass Spectrometry (APTDI-MS)

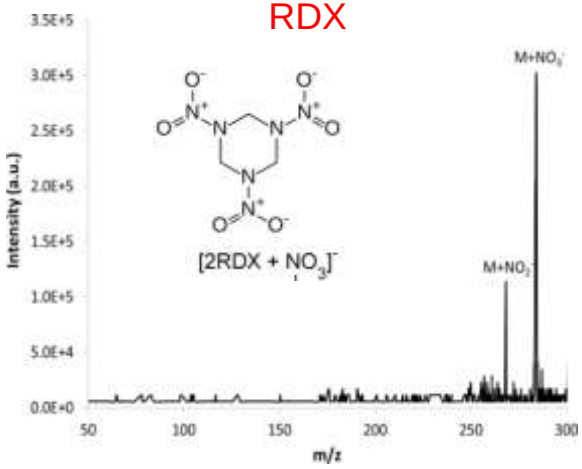


Thermal wire rapidly heated without subsequent ionization technique of both liquids and solids

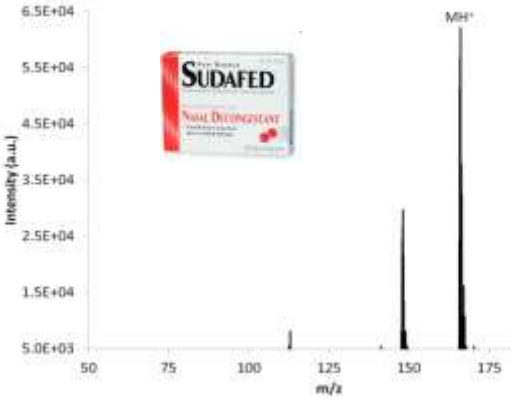
TNT



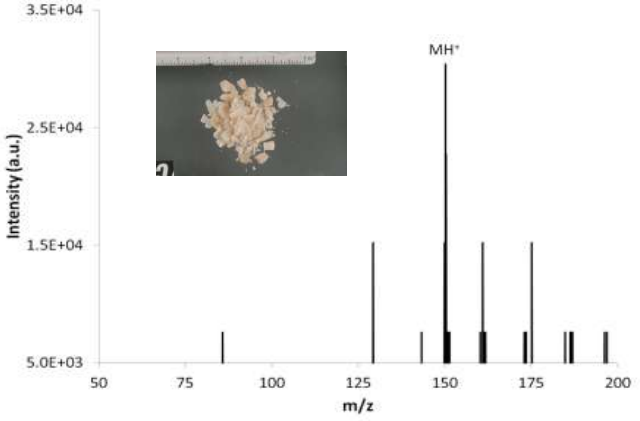
RDX



Pseudoephedrine

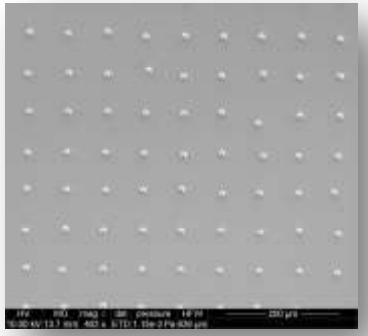


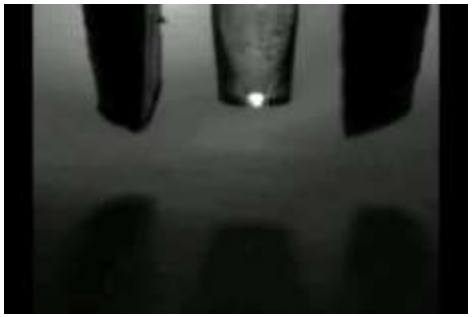
Methamphetamine



How do we evaluate APIMS Systems? - Standard Test Materials

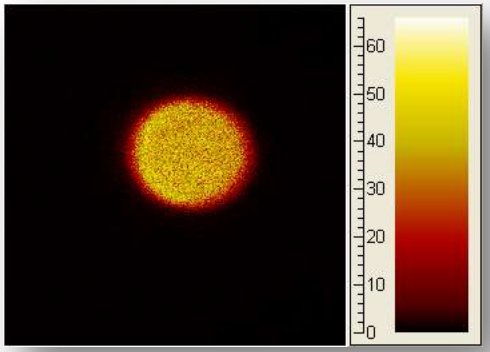
- *Flexible – many different compounds*
- *Rapid*
- *Large dynamic range in mass*
- *Quantifiable*
- *Precise high*
- *Accuracy approximately 5% depending on material and the ability to measure starting material purity*





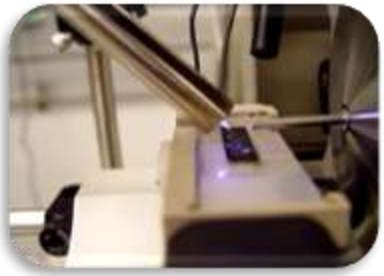
Stability of drop size during ~2 hours of jetting

	mean	SD	RSD
Mass, ng	48.7	0.10	0.2 %
Volume, pL	60.5	0.12	0.2 %

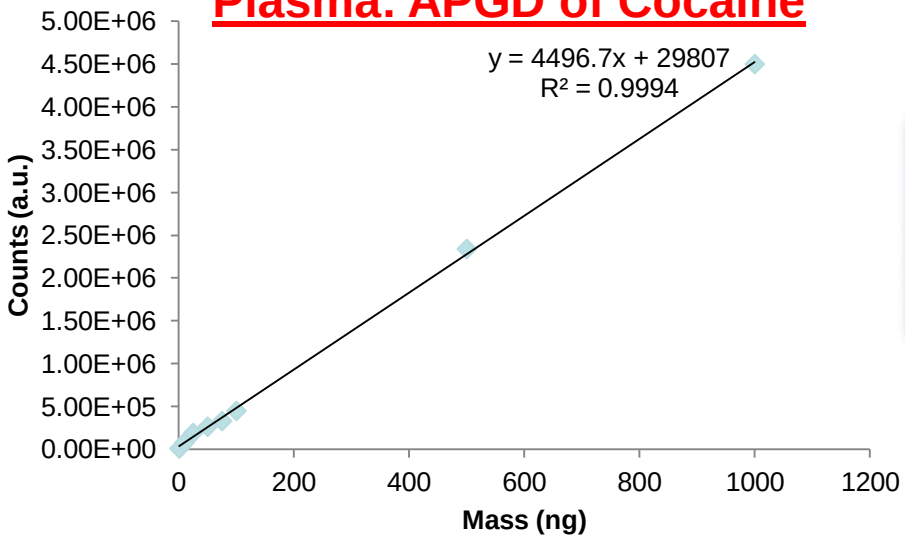


500 μm image field SIMS of single inkjet droplet of cocaine on silicon

Preliminary Quantification with Inkjet Printing

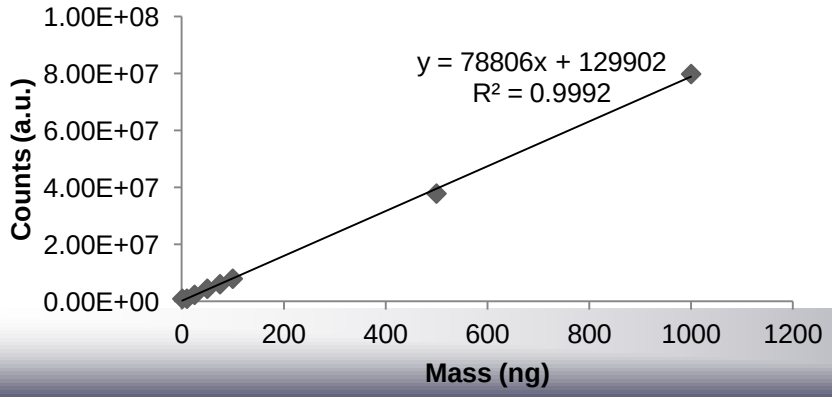


Plasma: APGD of Cocaine

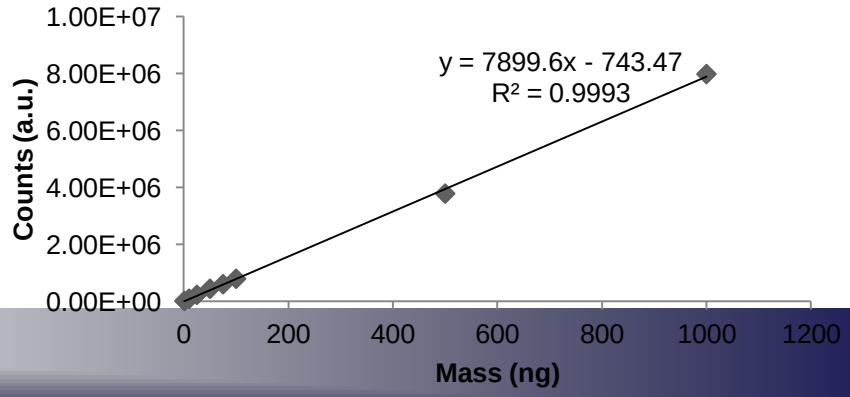


Liquid: DESI of Cocaine and RDX

Cocaine



RDX



Useful Yields for APIMS Analysis

SF_5

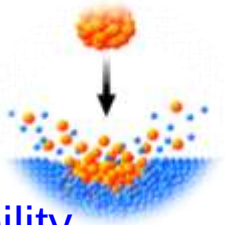
SIMS community have used for years, there is also growing interest in APIMS.

But, how sensitive are these method of analysis? How does sensitivity vary between compounds, ion source type and instrument configurations?

C_{60}

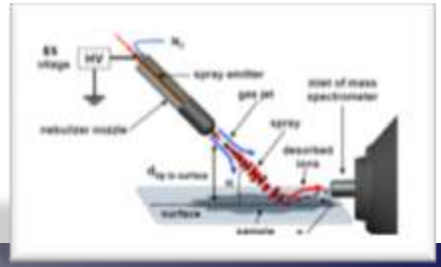
One method for evaluation is to measure the useful yield.

Useful yield = number of molecules detected/molecules in analytical volume.

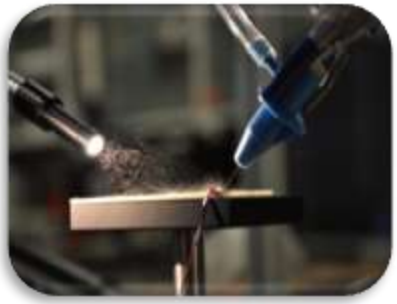
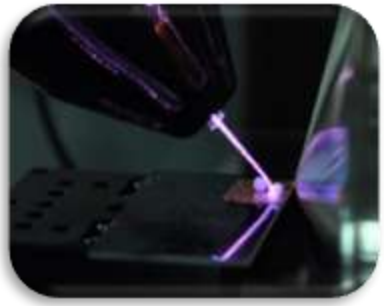
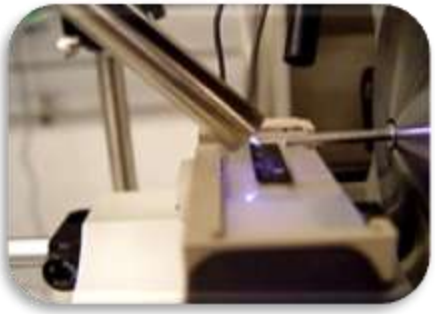


The useful yield takes into account beam induced damage, ionization probability, instrument transmission and detector efficiency. *It is the best measure of the analytical sensitivity for a given molecule under a given set of experimental conditions.*

Useful yields of organic molecules under dynamic SIMS cluster bombardment, Greg Gillen, Christopher Szakal, Tim M. Brewer, Surf. Interface Anal. 43, 376. 2011



Useful Yield Calculations

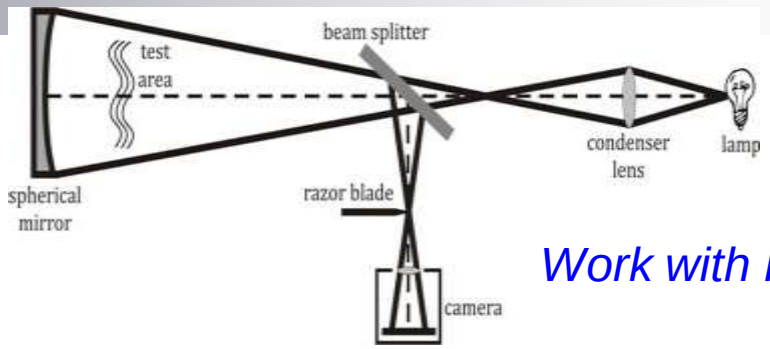




Compound	Ion	m/z	DESI	APGD	LDTD	DEFFI	LTP	APTDI
Cocaine	$(M+H)^+$	304	7.5×10^{-8}	1.8×10^{-8}				2.5×10^{-11}
TNT	$(M-H)^-$	226	6.5×10^{-8}		3.9×10^{-10}		7.7×10^{-7}	3.1×10^{-12}
RDX	$(M+NO_3)^-$ $(M+^{35}Cl)^-$	284 235	2.5×10^{-8} 3.9×10^{-7}	2.5×10^{-8}	3.2×10^{-8}	3.5×10^{-7}		5.2×10^{-12}
PETN	$(M+NO_3)^-$ $(M+^{35}Cl)^-$	378 351	6.8×10^{-8} 1.5×10^{-8}	5.9×10^{-8}	2.5×10^{-9}	6.5×10^{-8}		
AN	$(NO_3)^-$	62			1.5×10^{-10}		7.0×10^{-7}	

Conclusions

- Develop next generation technologies
  - Multi-source approach
  - Mixture analysis without chromatographic separation
- Improved technologies for high throughput forensic analysis
  - Multi-source approach for API-MS of trace and forensic contraband materials allows for fast, chemical surface analysis of a wide range of materials on multiple substrates
  - Characteristic mass spectra for all molecules studied from multiple sampling media
- Objectively evaluate the API sources by leveraging inkjet printing
  - A procedure and test materials have been developed to quantify the difference sources
  - A procedure and test materials have been developed measure useful yields of a range of organic compounds

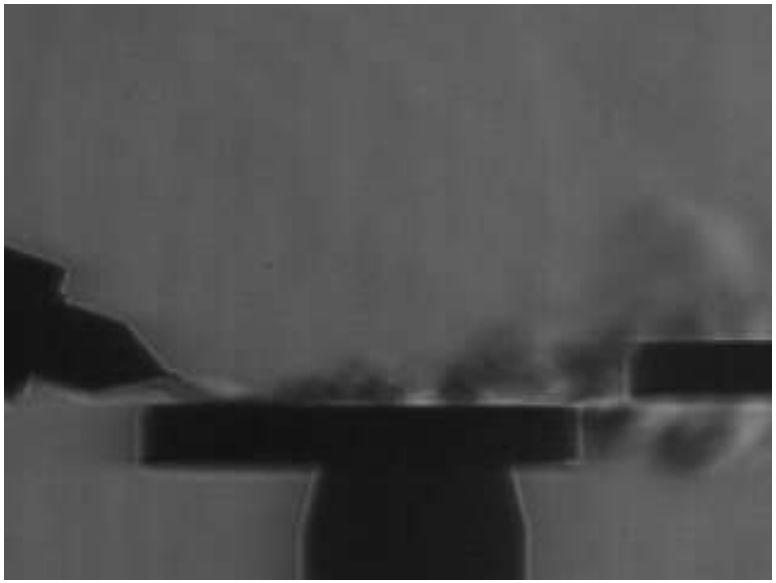
DESI Source Research - Schlieren imaging



Work with Prosolia

High speed videography,
3000 frames per second

20° incidence angle



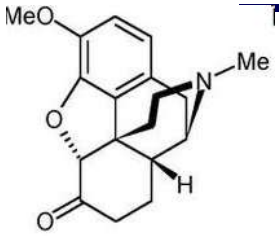
65° incidence angle

Recirculation zone formed from jet entrainment

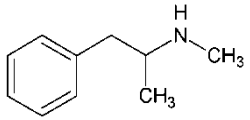
Analysis and mechanisms of cyclotrimethylenetrinitramine ion formation in desorption electrospray ionization.
Szakal C, Brewer TM., Anal Chem. 2009 Jul 1;81(13):5257-66

Flow Visualization Techniques for the Evaluation of Non-Contact Trace Contraband Detectors,
M Staymates, G Gillen and W Smith, ASME, 2010, 203-209,

Plasma: APGD-MS Analysis of Illicit Drugs

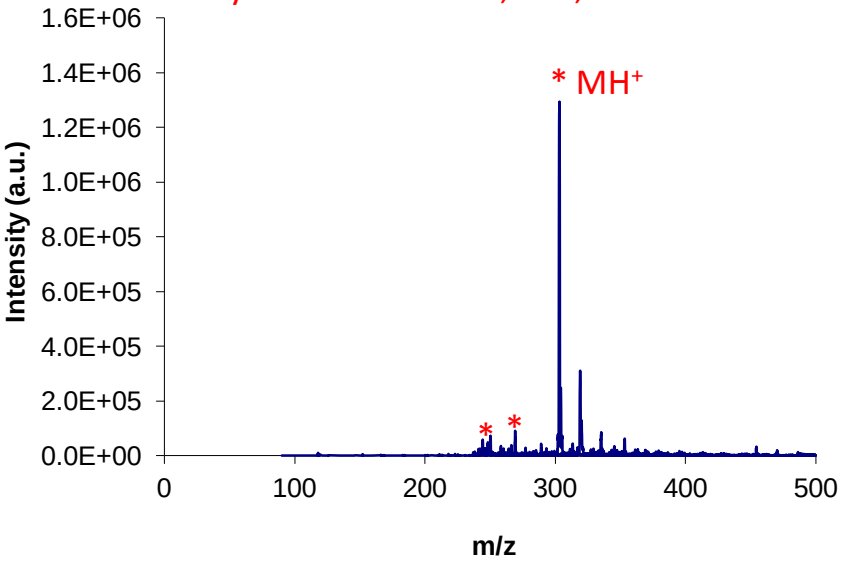


MW = 301

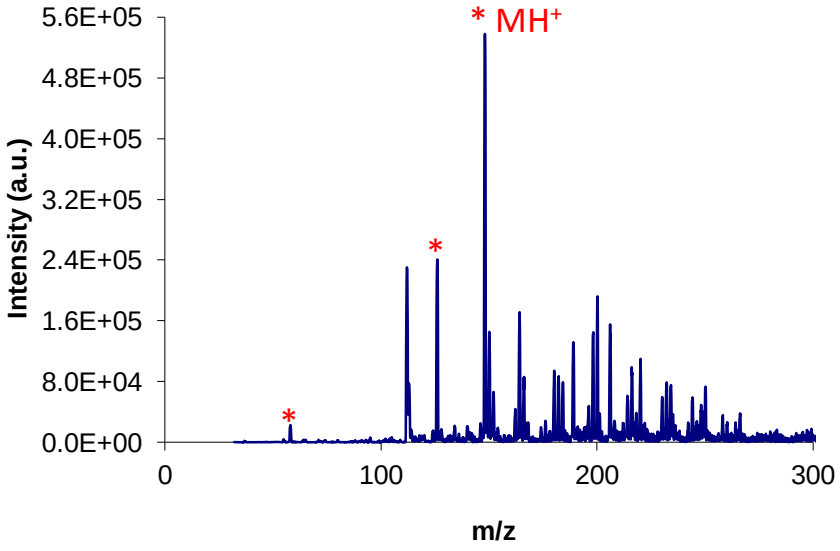


MW = 149

*Hydrocodone – 301, 270, 242

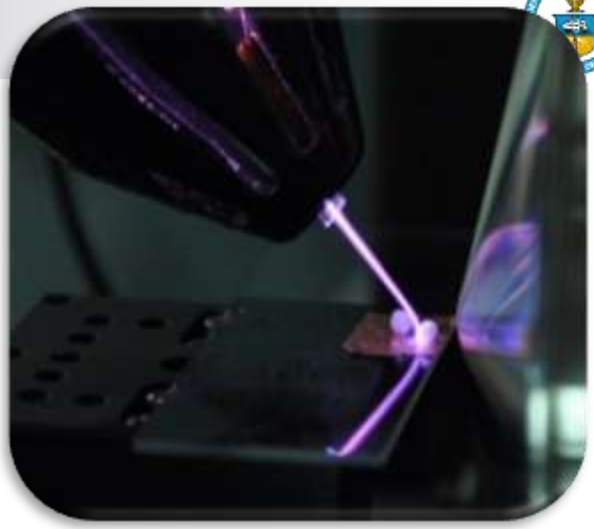


*Methamphetamine – 150, 134, 58

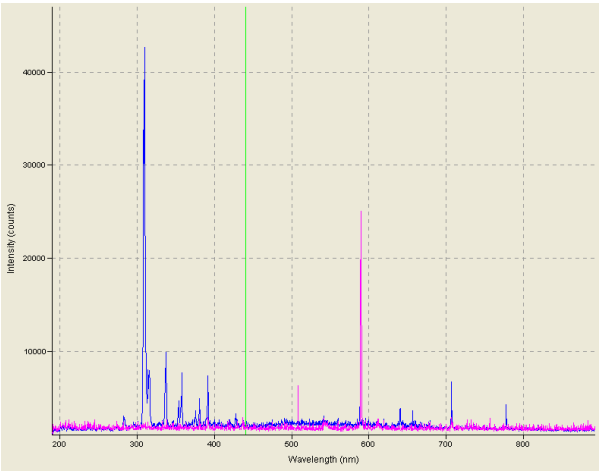


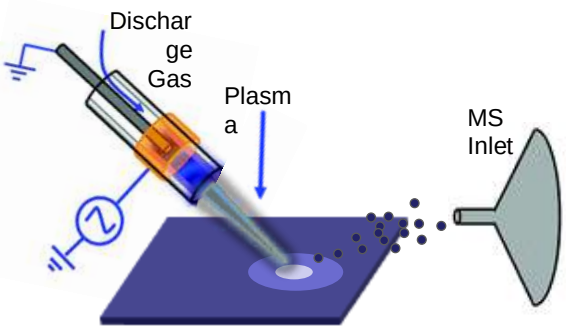
APGD-MS spectra of Hydrocodone and Methamphetamine. Plasma 75W and 1 L/min He and O 0.1 L/min

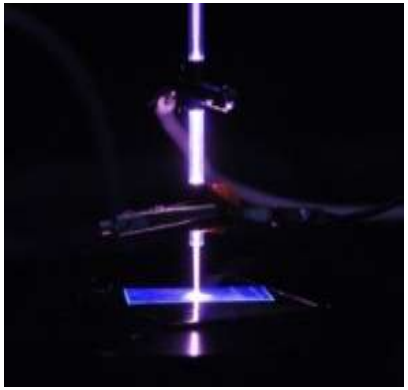
He Low Temperature Plasma



- 20 KV peak-peak , 20-70 KHZ high frequency power supply
- Automated x, y sample stage – lab view
- Multiple gas flow controller
- Heated gas jet
- Sample rotation stage for 2000 RPM depth profiling
- Integrated optical spectroscopy for beam characterization

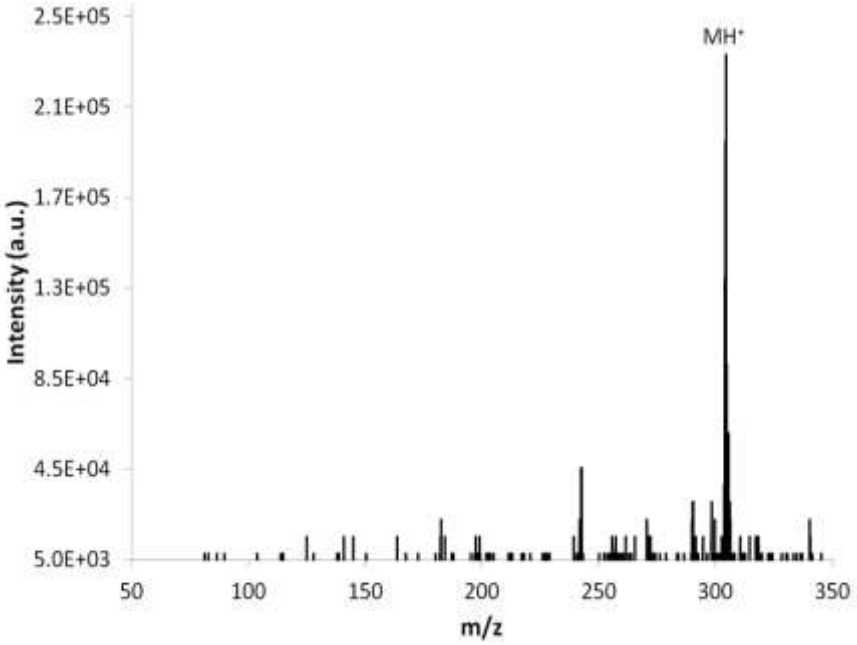




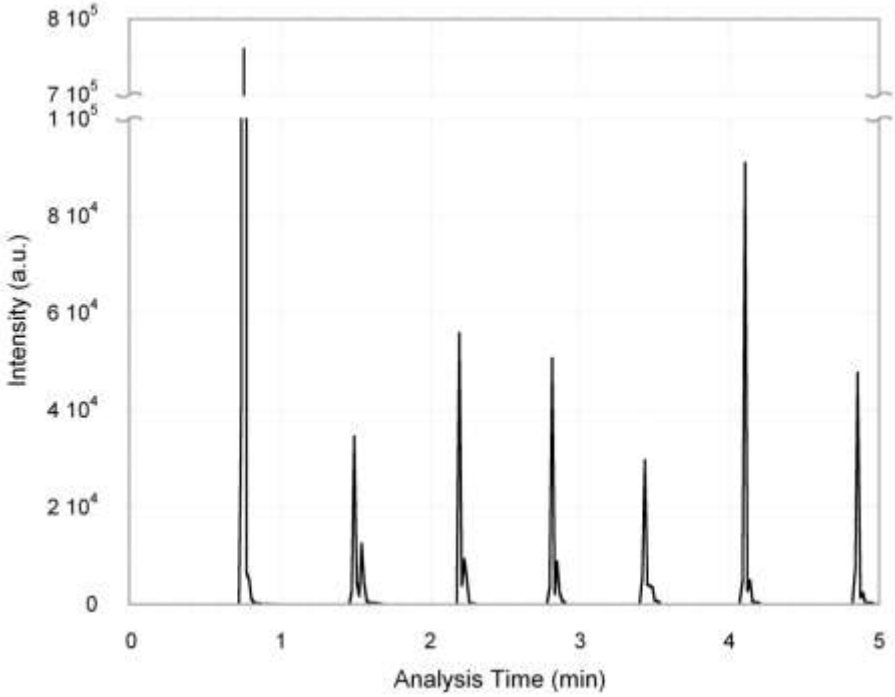


Atmospheric identification of active ingredients in over-the-counter pharmaceuticals and drugs of abuse by atmospheric pressure glow discharge mass spectrometry (APGD-MS)‡ Tim M. Brewer, Jennifer R. Verkouteren, 2011.*

APDTI-MS - Repeatability



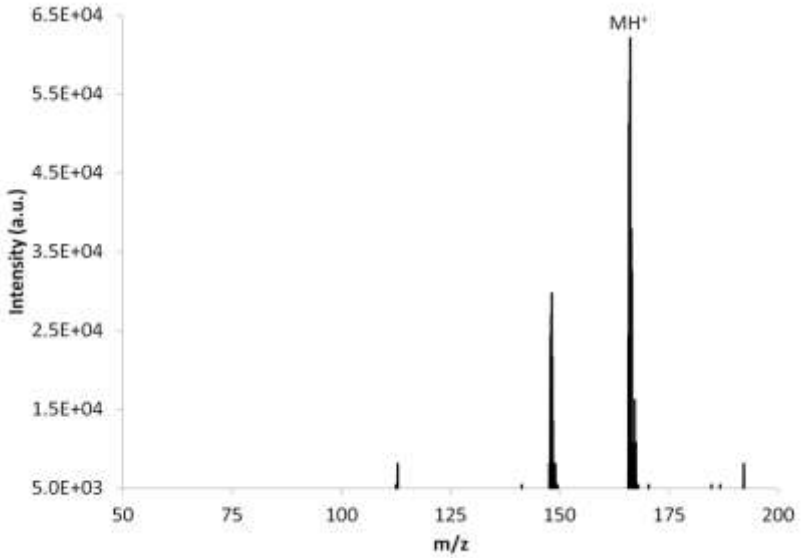
Cocaine



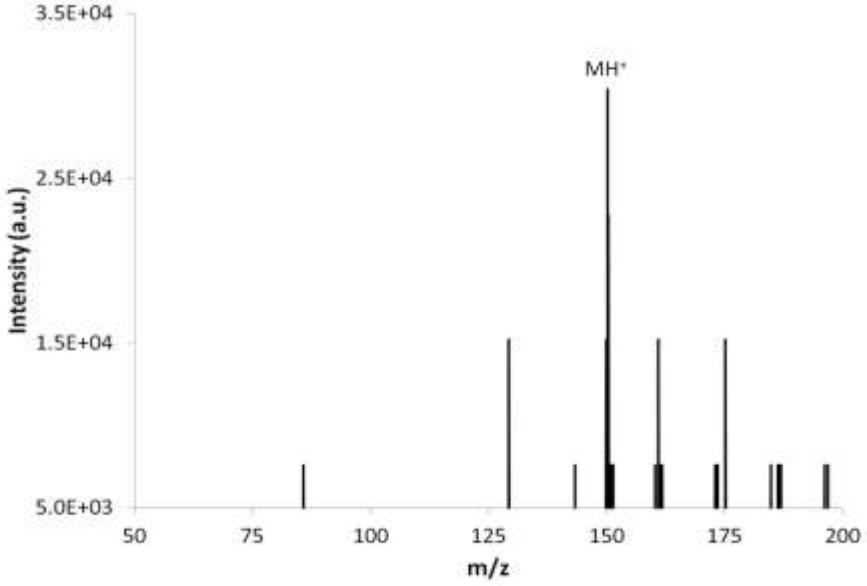
Cocaine repeat analysis

APTDI-MS

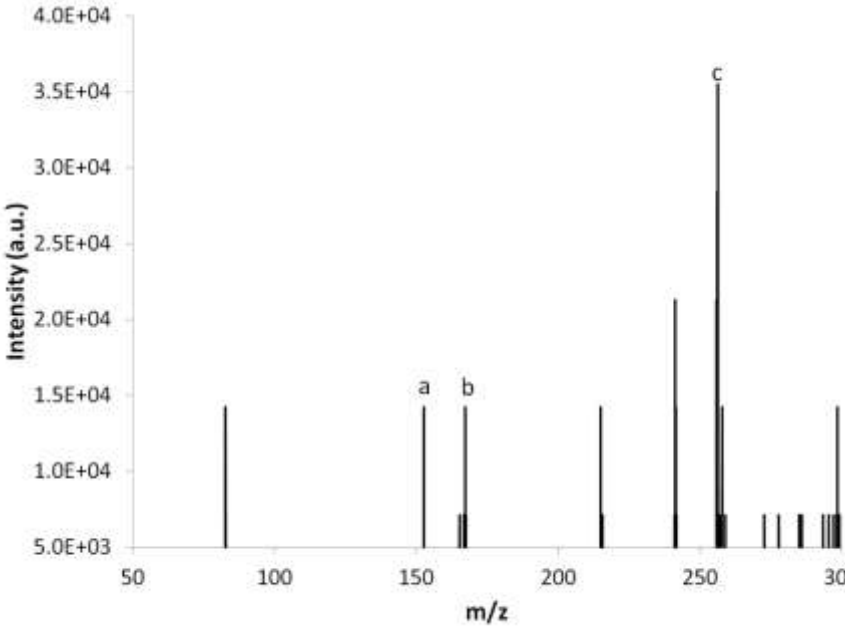
Pseudoephedrine



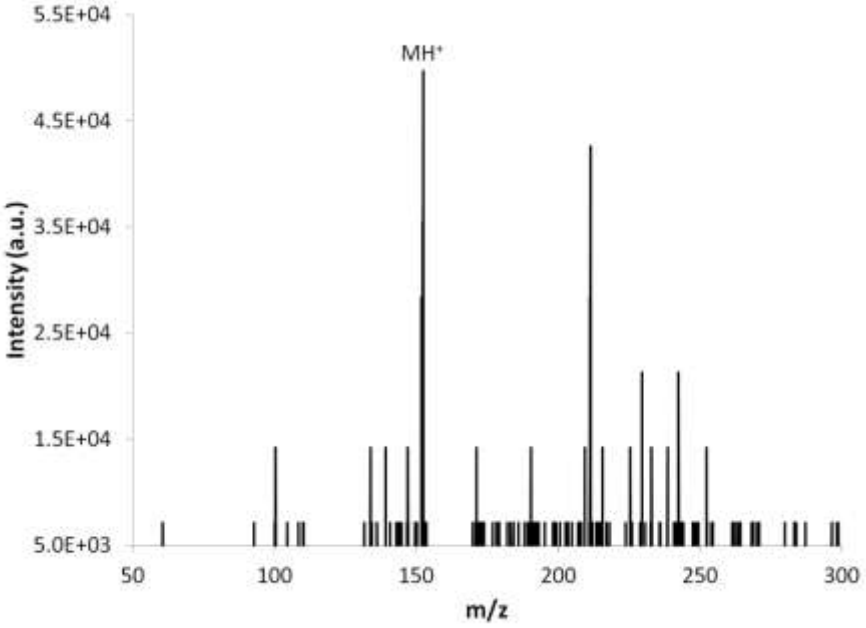
Methamphetamine



APTDI-MS – solid mixture



APTDI mass spectrum of Tylenol Allergy. a) is m/z 151, $M+H^+$ for acetaminophen, b) is m/z 167, M^+ for phenylephrine, and c) is m/z 256, $M+H^+$ for diphenhydramine



APTDI mass spectrum of m/z 151, $M+H^+$ for acetaminophen