

A Completely Handheld Ambient Ionization Source for Mass Spectrometry Based on a Low-Temperature Plasma (LTP)

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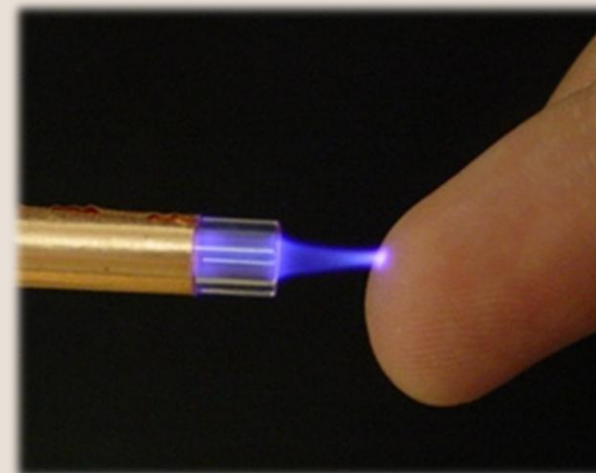
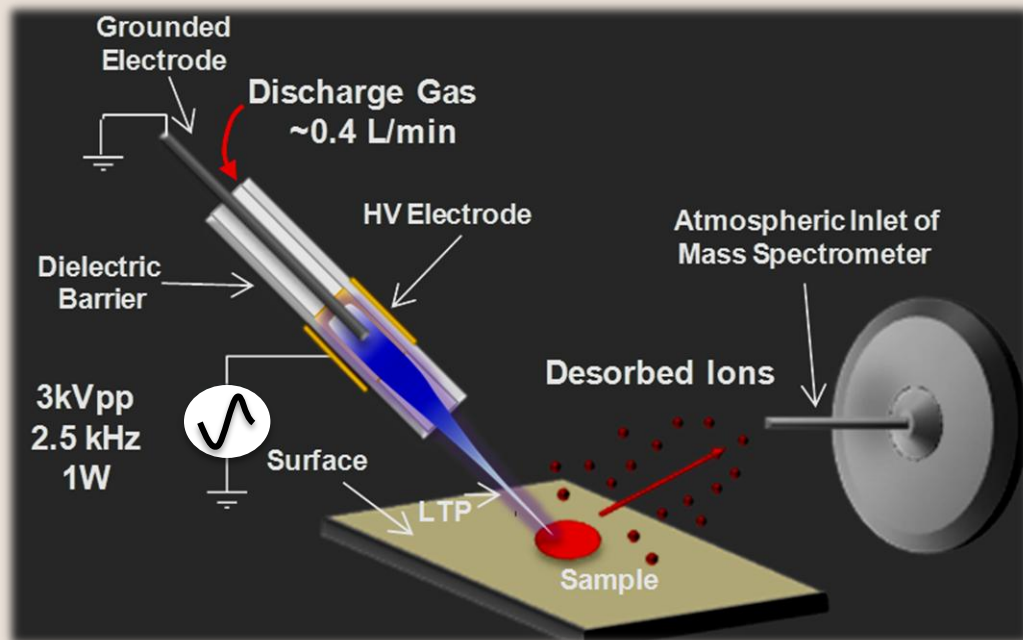
²Dept. of Chemistry, Indiana University, Bloomington, IN 47405



HEMS 2011



Low-Temperature Plasma (LTP) Mass Spectrometry

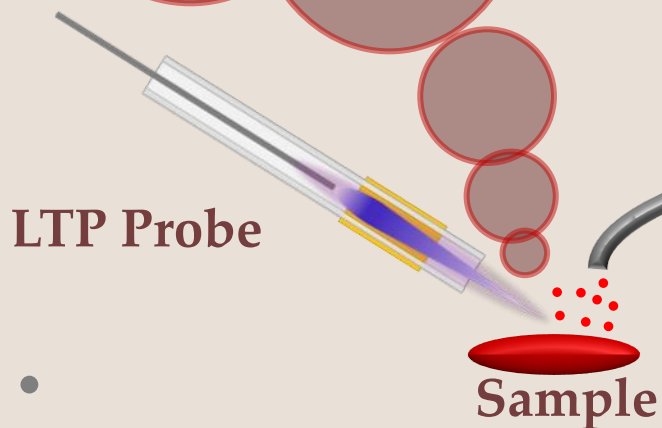


- Based on a Dielectric-Barrier Discharge (DBD)
- Glass Tube: O.D.: 6.35 mm, I.D.: 3.75 mm)
- Grounded electrode (SS, diameter: 1.57mm)
- High Voltage AC: 7 – 15 kV_{p-p}
- Frequency: 2-3 kHz
- Discharge Gas: He, Ar, N₂, Air
- Gas Flow Rate: ~0.4 – 1.2 L/min

Applicability of LTP



- Small molecule detection (<500 Da)
- Potential for in-field analyses
 - Couple with mini-MS
 - Low power and gas consumption
 - Gases, Liquids and Solids
- Minimal sample destruction allows analysis of delicate samples

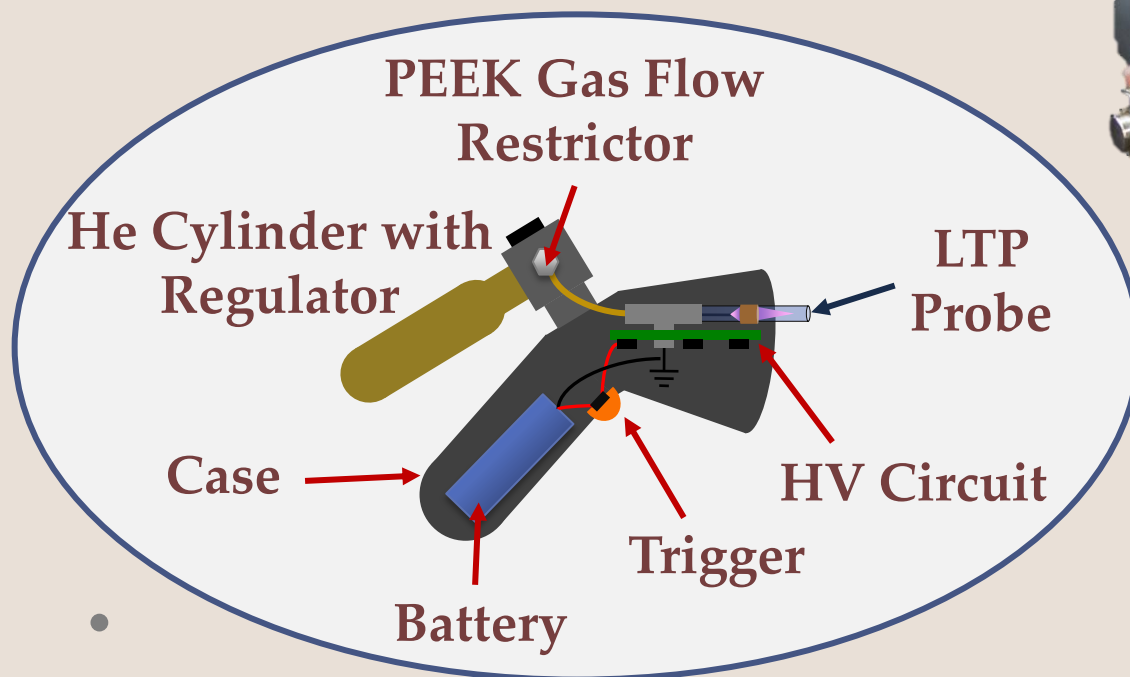


Mini Mass Spectrometer

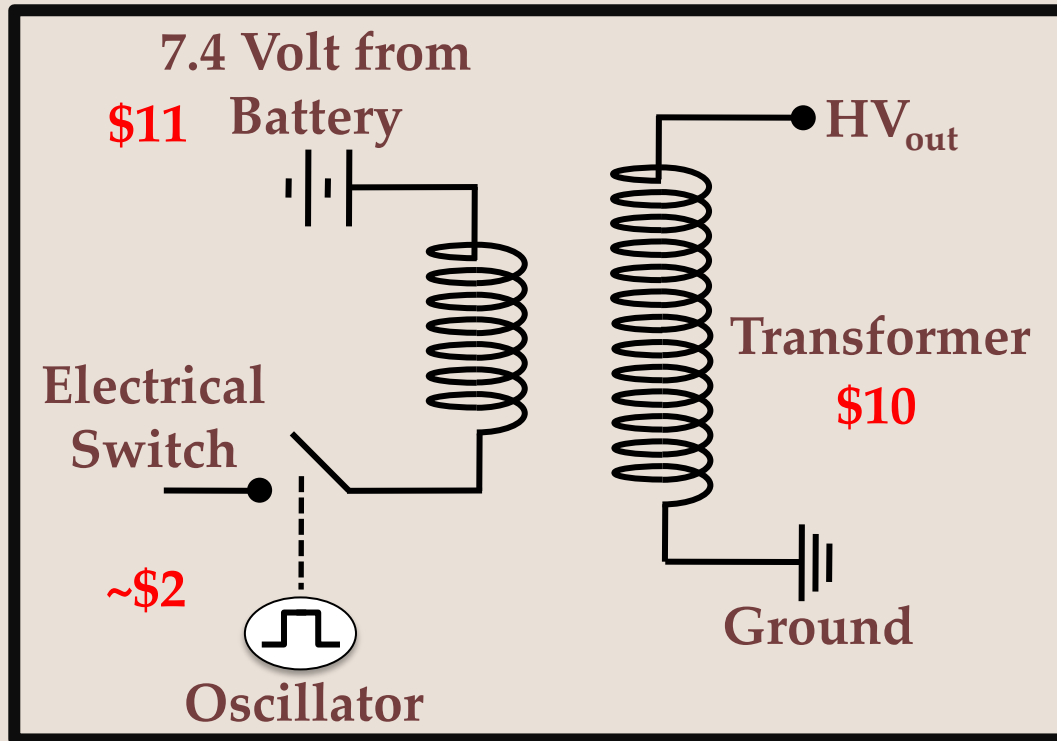
Handheld LTP

Goals of Handheld LTP

1. Enable sample analysis non-proximate to MS inlet
2. Couple to mini MS for *in situ* analysis
 - a) Portable
 - b) Low He Flow
 - c) Decreased Electric Field
3. Maintain capabilities of LTP-MS



Power Supply and Costs for Handheld LTP



Total Cost of Power Supply: **\$23**

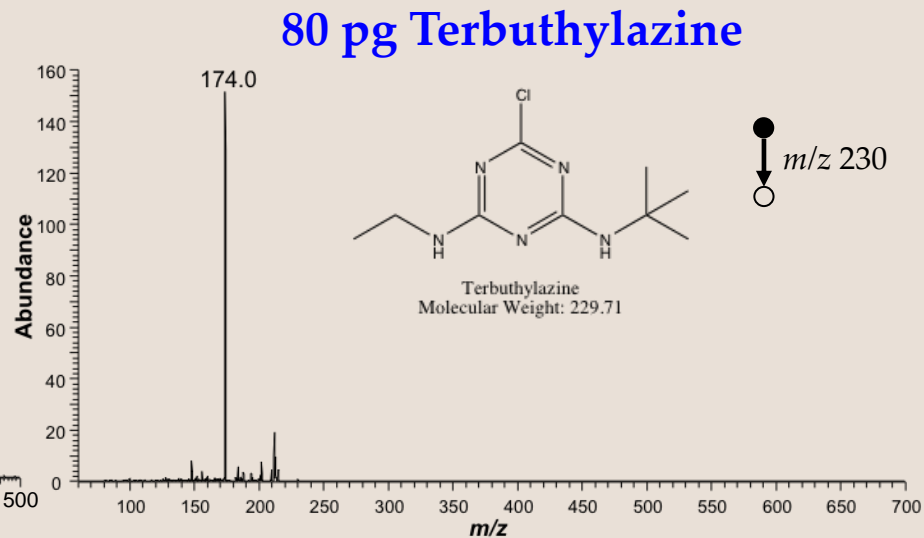
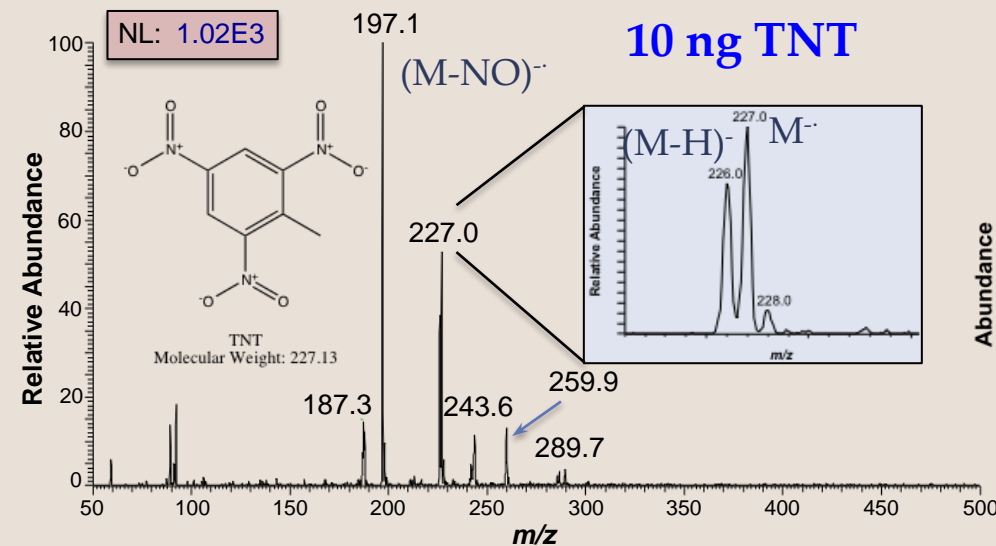
He Cylinders: **\$16**

- Voltage: $\sim 2 \text{ kV}_{\text{p-p}}$
- Frequency: 100 kHz
- Powered by a 7.4 V Li Polymer Battery (900 mAh)
 - Lifetime: ~ 2 Hrs Cont.
- He Flow: $< 100 \text{ mL/min}$
 - Lifetime: ~ 8 Hrs Cont.

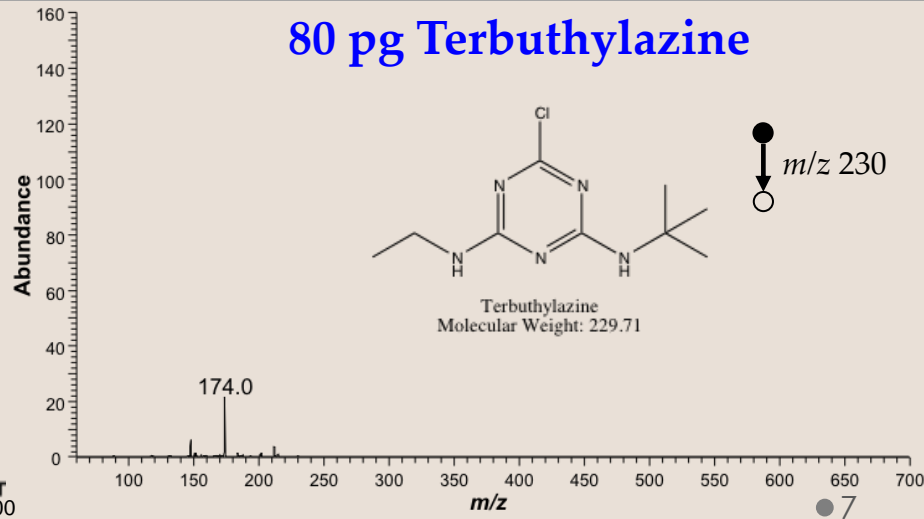
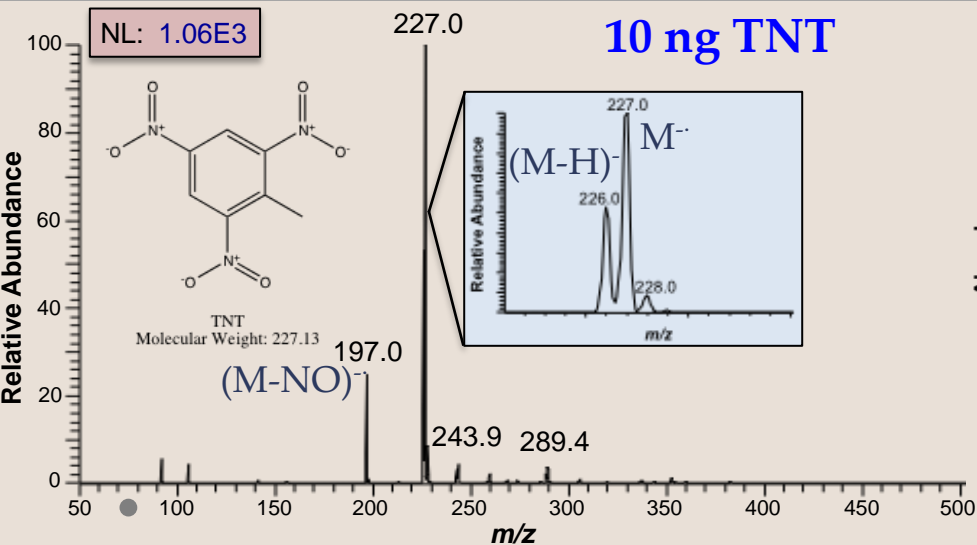
Testing on Bench-Top MS

Comparing Handheld LTP with Conventional LTP

Handheld LTP on Thermo LTQ



Conventional LTP on Thermo LTQ

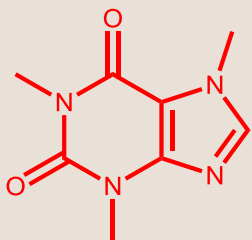


Handheld LTP vs. Conventional LTP on Bench-Top MS

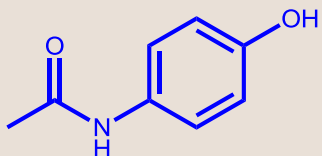
		LODs (ng)			
Analyte Category	Analyte	Air Hand-LTP	He Hand-LTP	Conventional LTP	He Hand-LTP/Mini MS
Pesticides					
	Ametryn	0.024	0.024	0.24	---
	Amitraz	0.12	0.024	1.2	30
	Atrazine	0.024	0.00048	0.24	0.24
	Buprofezin	0.24	0.008	0.24	0.24
	DEET	0.12	0.048	0.6	0.24
	Diphenylamine	0.6	0.0048	0.12	0.24
	Ethoxyquin	300	0.72	10	30
	Isofenphos-methyl	6	0.024	1	0.24
	Isoproturon	0.24	0.048	0.600	6
	Malathion	3	0.24	1.2	1.2
	Paration-ethyl	0.6	0.024	0.24	30
	Terbuthylazine	0.024	0.0008	0.08	0.24
Explosives					
	RDX	0.02	0.02	---	---
	TNT	Not Detected	0.02	---	---
	PETN	0.2	0.05	---	---
	Tetryl	2	2	---	---

- Handheld LTP is 1 – 2 orders of magnitude more sensitive than the conventional LTP probe
- Main difference is smaller geometry and increased frequency for handheld LTP

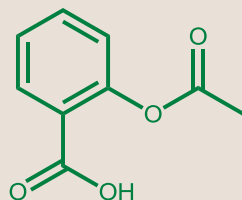
Direct Tablet Analysis: Headache Relief Tablet



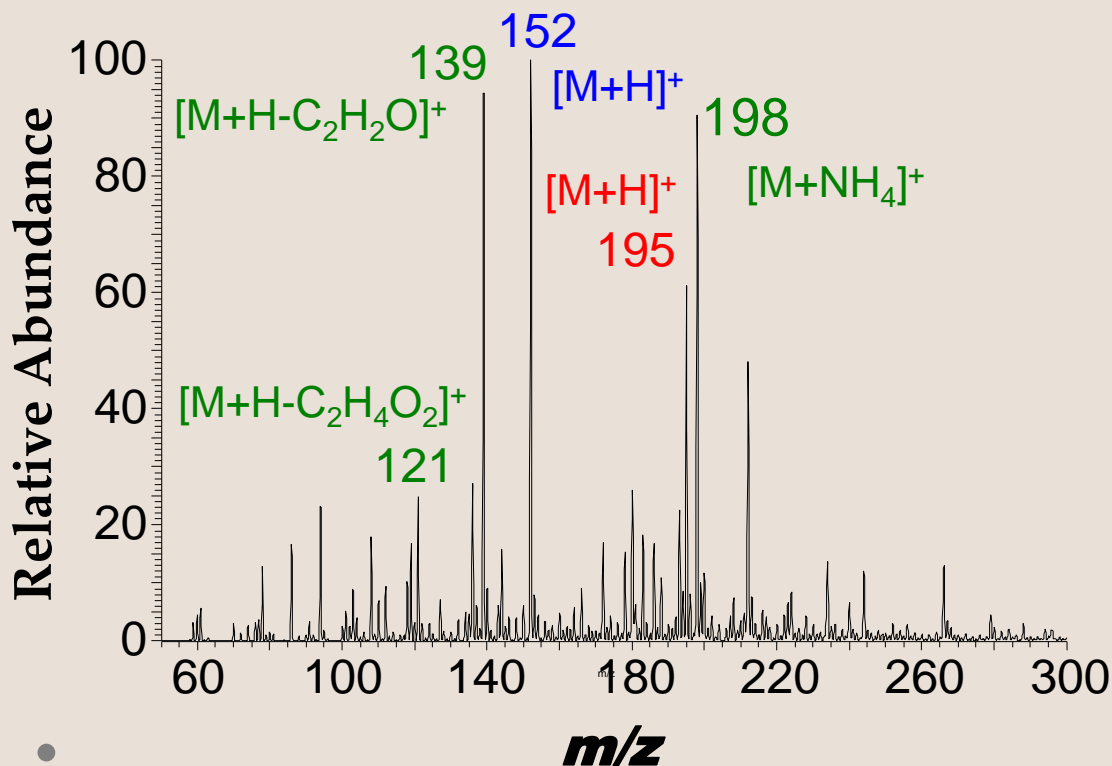
Caffeine
Molecular Weight:
194.1906



Acetaminophen
Molecular Weight: 151.1626



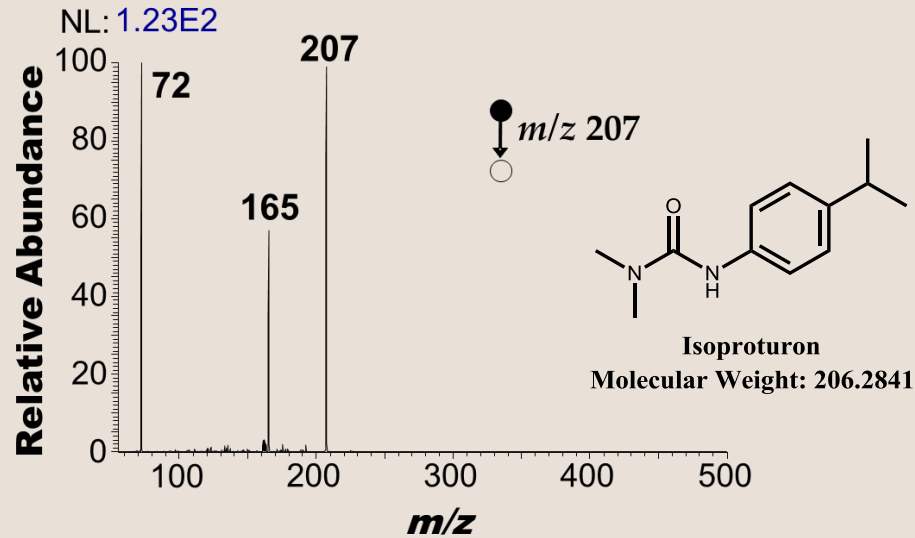
Aspirin
Molecular Weight:
180.1574



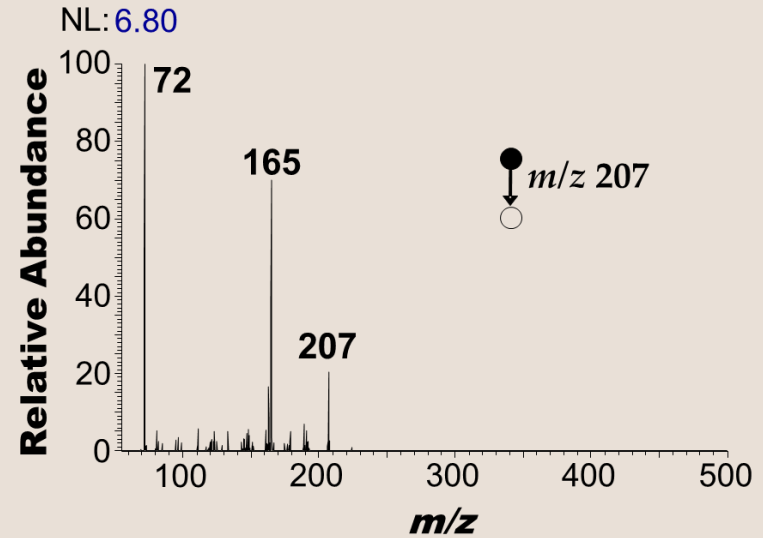
- No sample preparation
- All 3 active ingredients detected
 - Confirmed with tandem MS
- Aspirin also detected in negative mode due to acidic proton
- Spectrum obtained in seconds

Handheld LTP: Air vs. Helium Discharge Gas

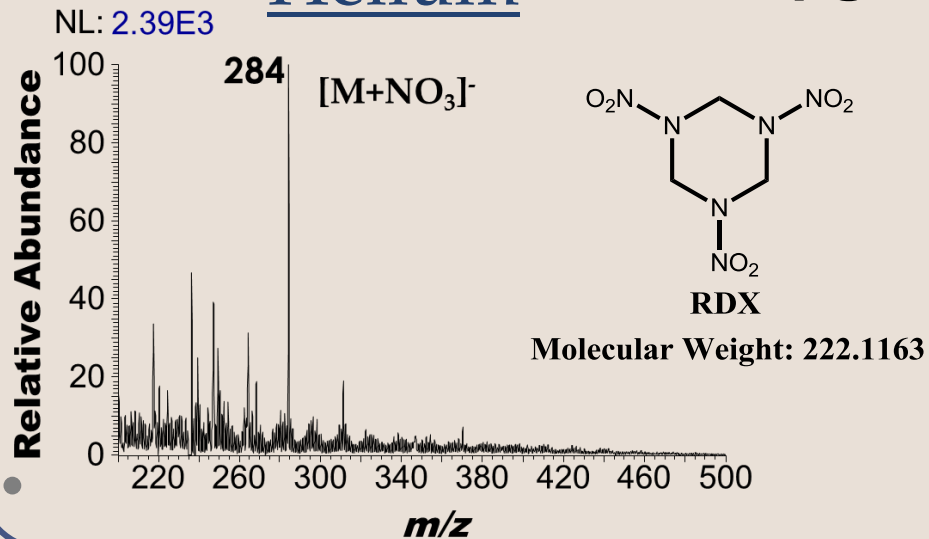
Helium 1.2 ng Isoproturon



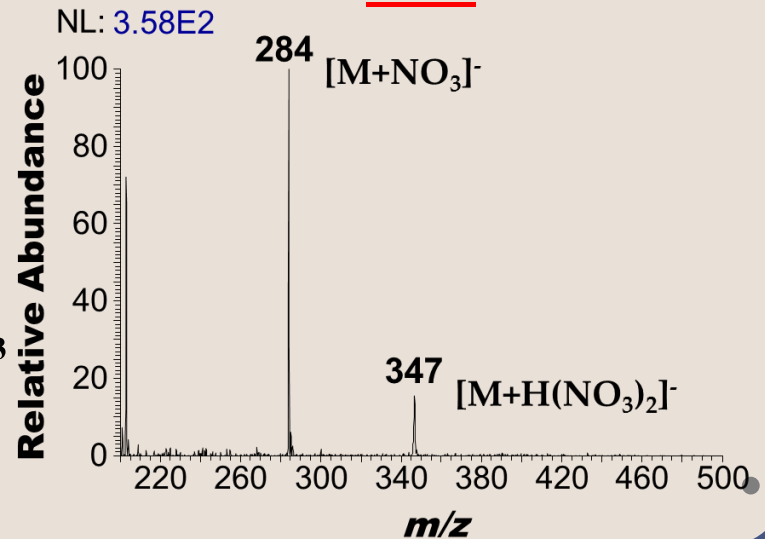
Air



Helium 200 pg RDX



Air



Performance of Air vs. He Discharge Gas

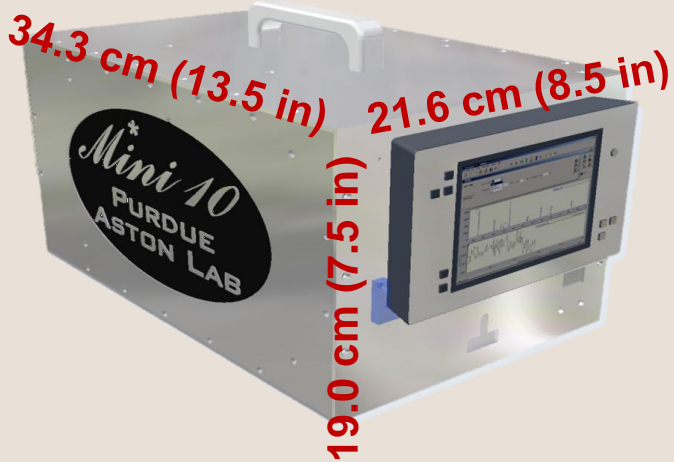
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	Buprofezin	0.24	0.008	0.24	0.24
	DEET	0.12	0.048	0.6	0.24
	Diphenylamine	0.6	0.0048	0.12	0.24
	Ethoxyquin	300	0.72	10	30
	Isofenphos-methyl	6	0.024	1	0.24
	Isoproturon	0.24	0.048	0.600	6
	Malathion	3	0.24	1.2	1.2
	Paration-ethyl	0.6	0.024	0.24	30
	Terbuthylazine	0.024	0.0008	0.08	0.24
Explosives	-----	-----	-----	-----	-----
	RDX	0.02	0.02	---	---
	TNT	Not Detected	0.02	---	---
	PETN	0.2	0.05	---	---
	Tetryl	2	2	---	---

- He yields 1 – 2 orders of magnitude better signal for proton transfer ionization
- He and air yield similar performance for nitrate addition

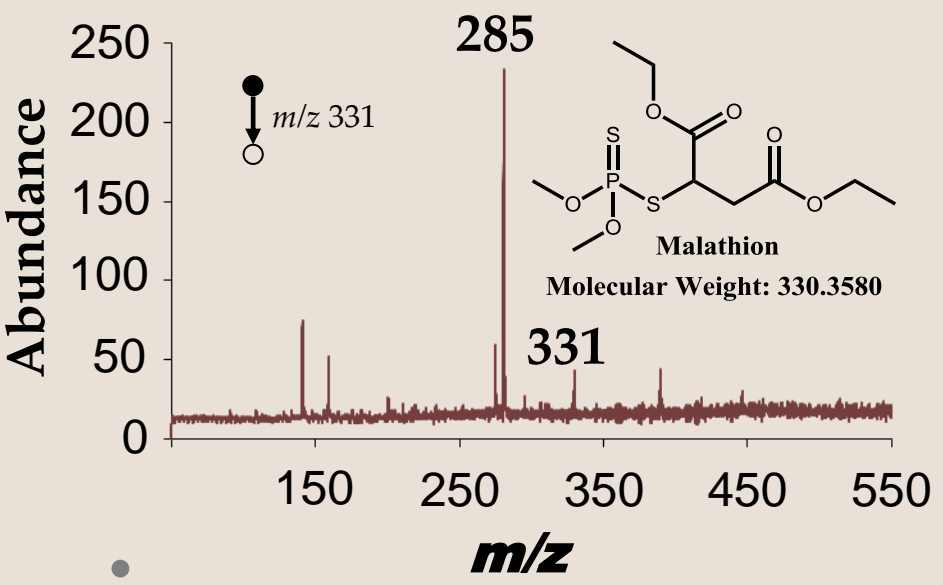
Testing on Mini-10.5 MS

Analysis of Pesticides with Handheld LTP on mini-10.5 MS

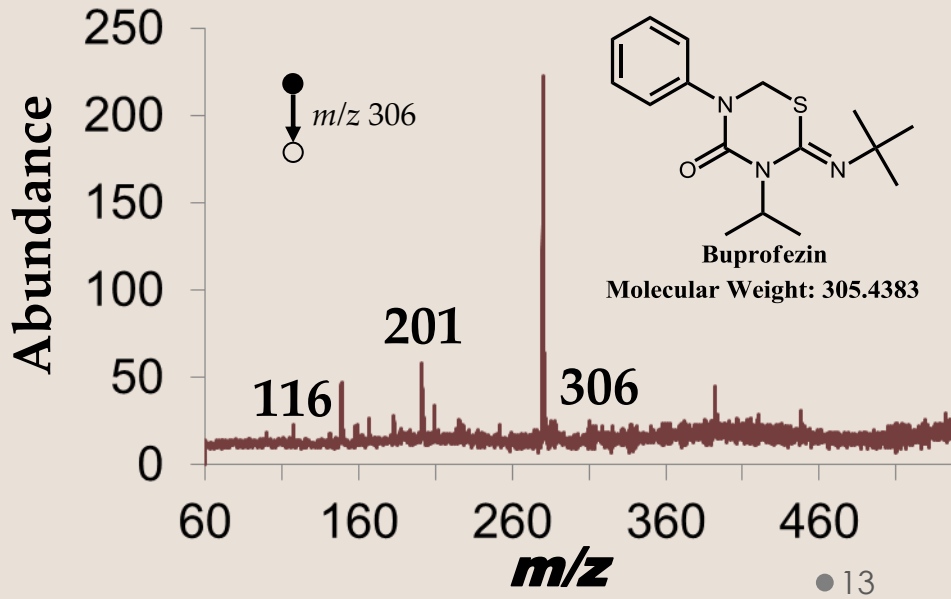
- Mini 10.5: 22 lbs., 0.5 ft³, <75 W and uses rectilinear ion trap (RIT) mass analyzer
- Direct analysis of dried spots on glass slides
- Tandem MS performed using notch broadband isolation and resonant excitation of selected ion



1.2 ng Malathion



1.2 ng Buprofezin

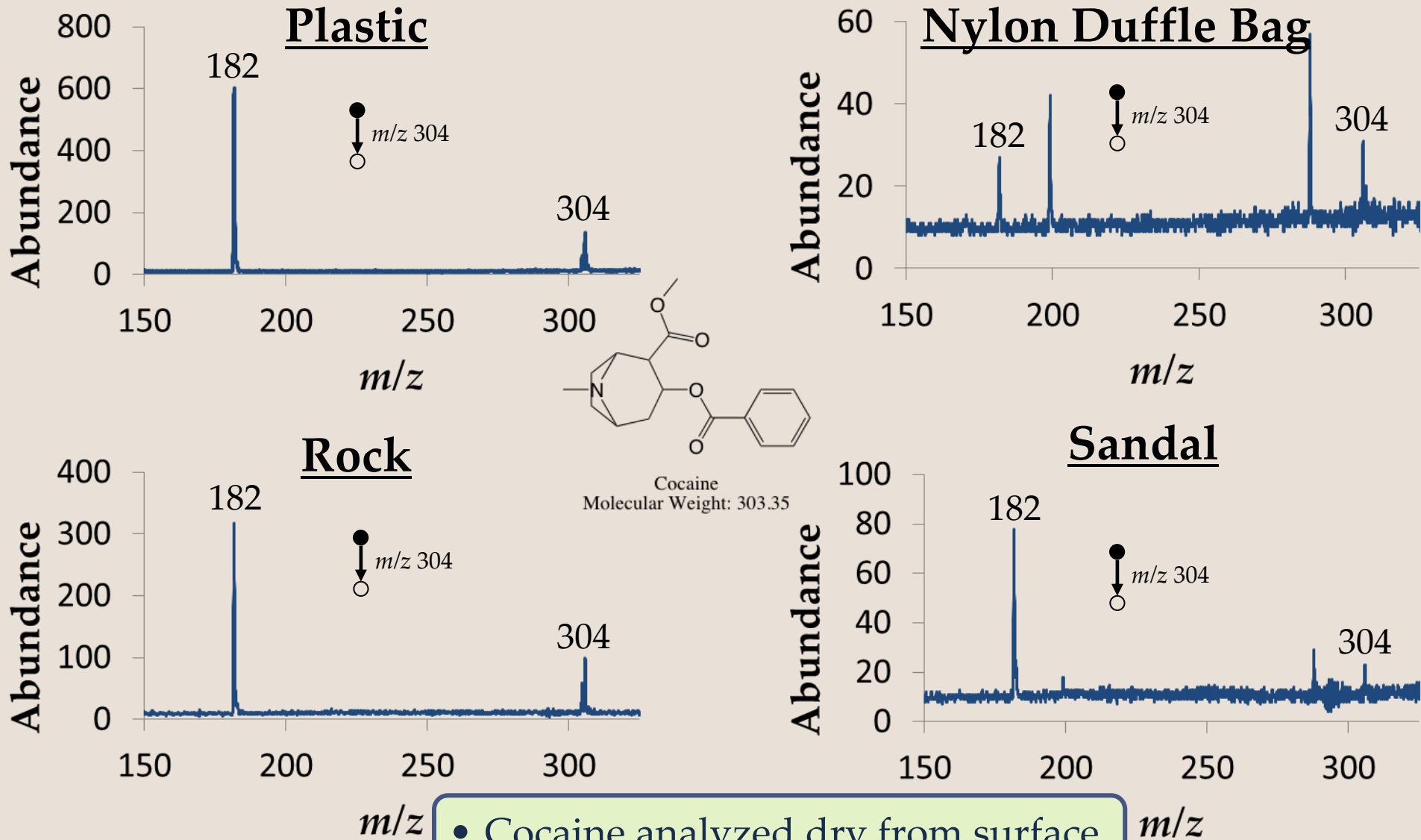


Performance of Handheld LTP on Mini-10.5 MS

Analyte Category	Analyte	LODs (ng)			
		Air Hand-LTP	He Hand-LTP	Conventional LTP	He Hand-LTP/Mini MS
Pesticides	-----				
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	Terbuthylazine	0.024	0.0008	0.08	0.24
Explosives	-----				
	RDX	0.02	0.02	---	---
	TNT	Not Detected	0.02	---	---
	PETN	0.2	0.05	---	---
	Tetryl	2	2	---	---

Sub- to low ng LODs obtained on Mini-10.5 MS

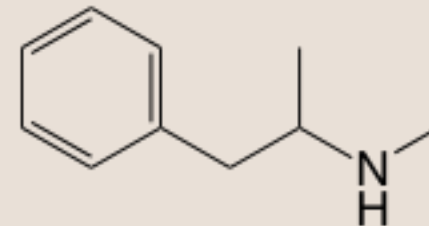
Cocaine from Various Surfaces



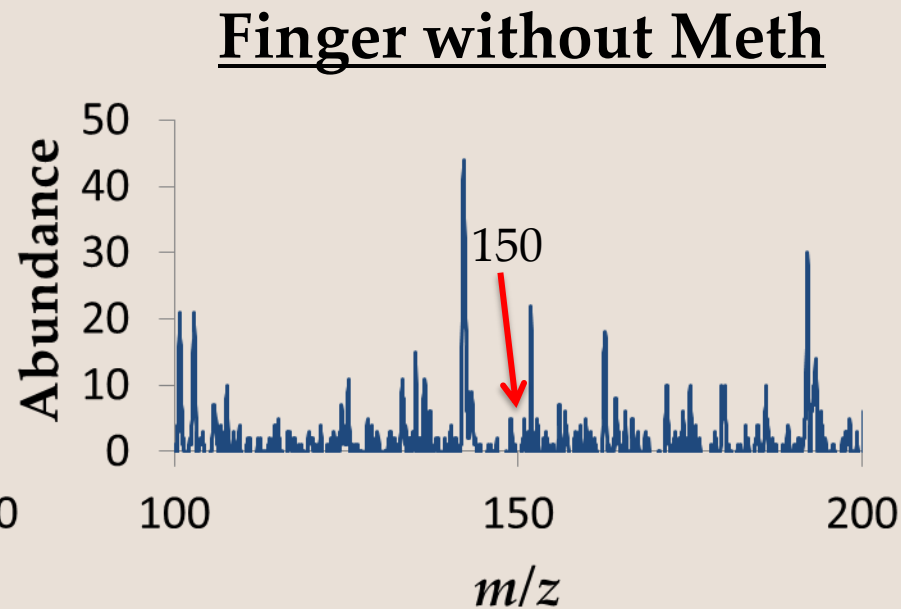
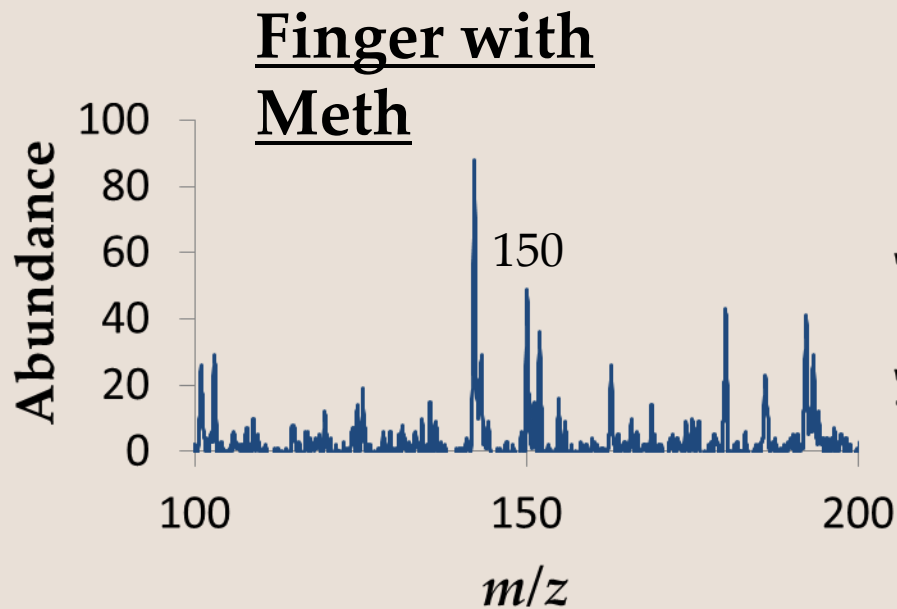
- Cocaine analyzed dry from surface
- Absorptive materials are least sensitive

Methamphetamine Residue from Finger

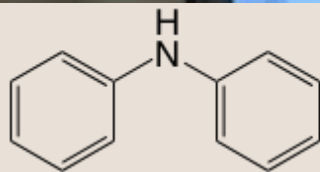
- 1 μg methamphetamine spotted on finger
- Analysis occurred 4.5 hours after application
 - Subject carried on with day as usual



Methamphetamine
Molecular Weight: 149.23



In Situ Analysis of Pesticides



<http://www.purdue.edu/newsroom/research/2011/110608CooksProduce.html>

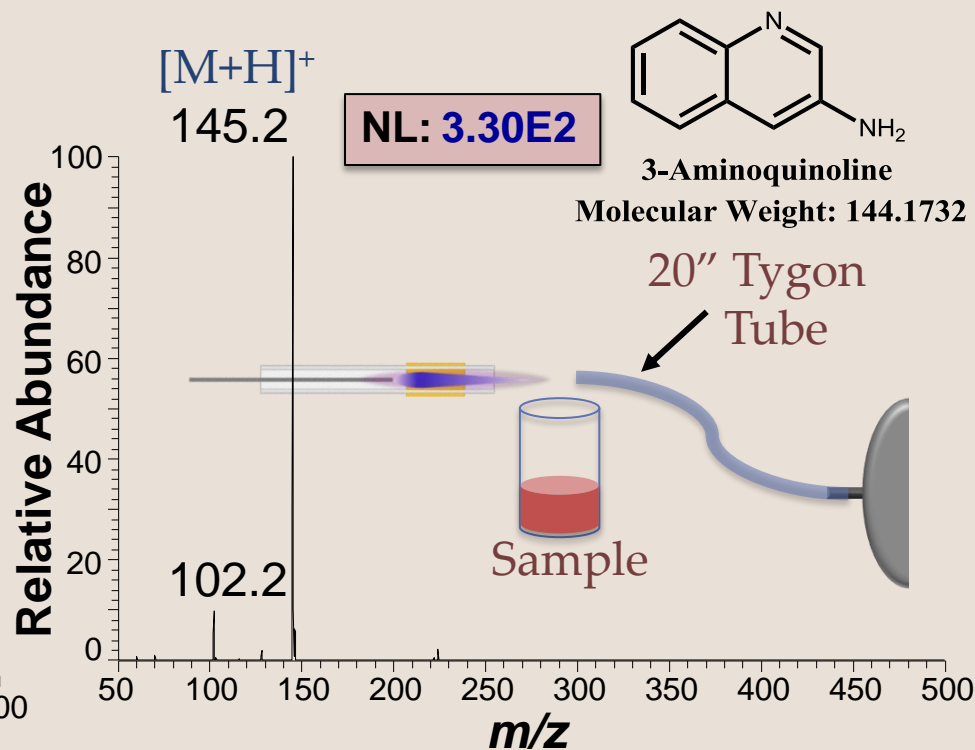
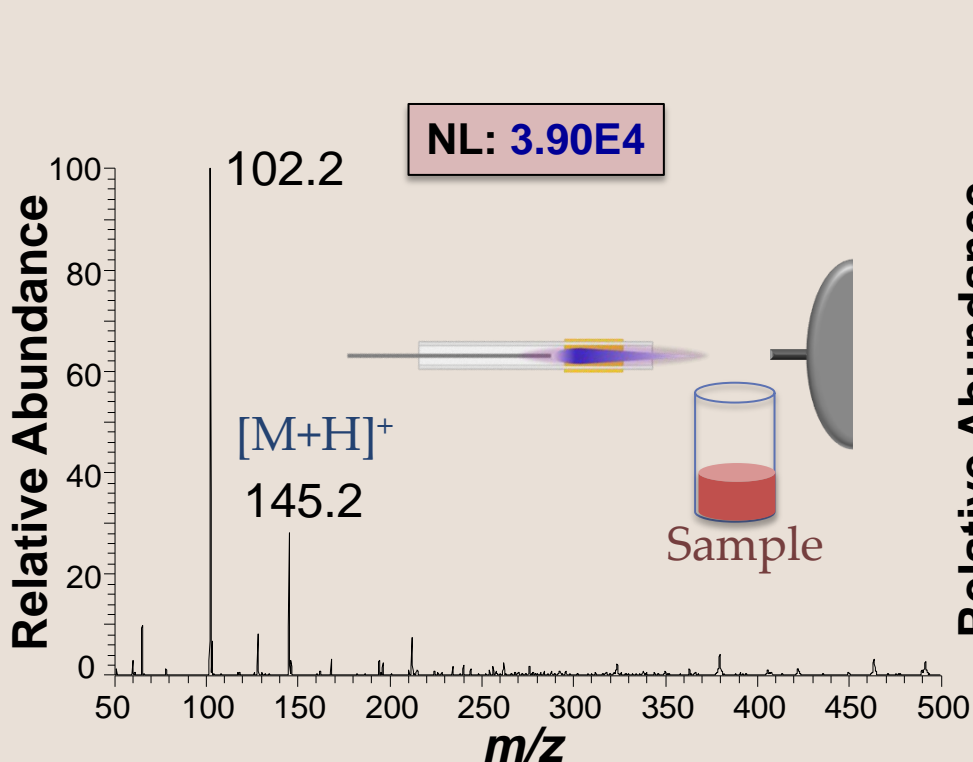
Diphenylamine
Molecular Weight: 169.22

Long Distance Ion Transfer on Bench-Top MS

Long Distance Ion Transfer with Handheld LTP on LTQ

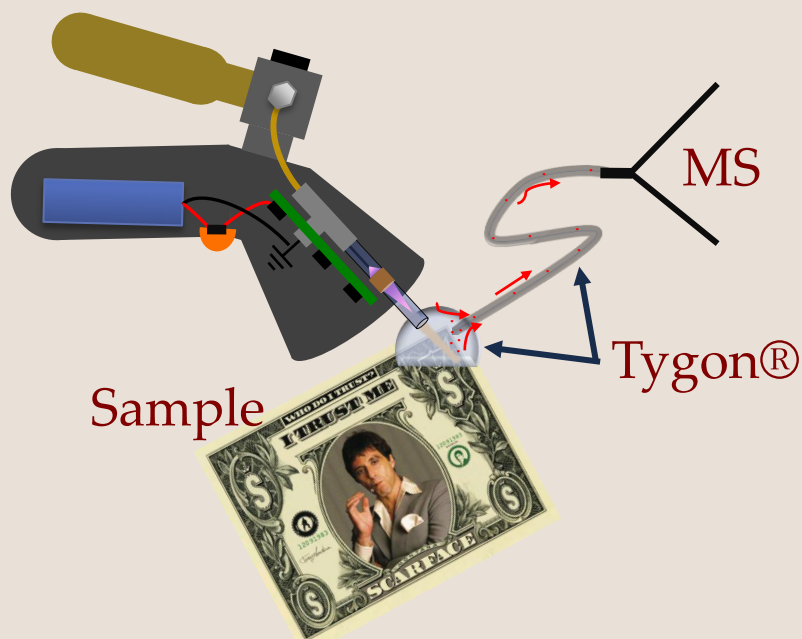
Goal: Analyze samples at non-proximal locations with respect to MS interface using flexible tubing to transport ions

- Use suction from MS inlet to pull ions through Tygon® tube
- Currently losing nearly two orders of magnitude of signal

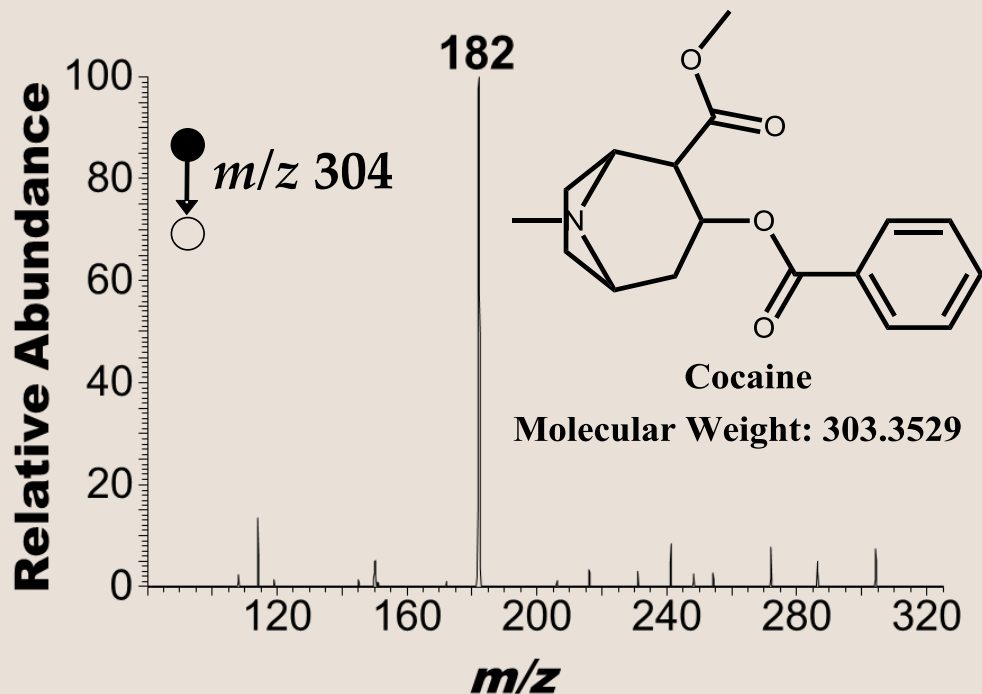


Implementation of Long-Distance Ion Transfer Interface

Long-Distance Ion Transfer Interface



Cocaine from \$1 Bill (Not Spiked)

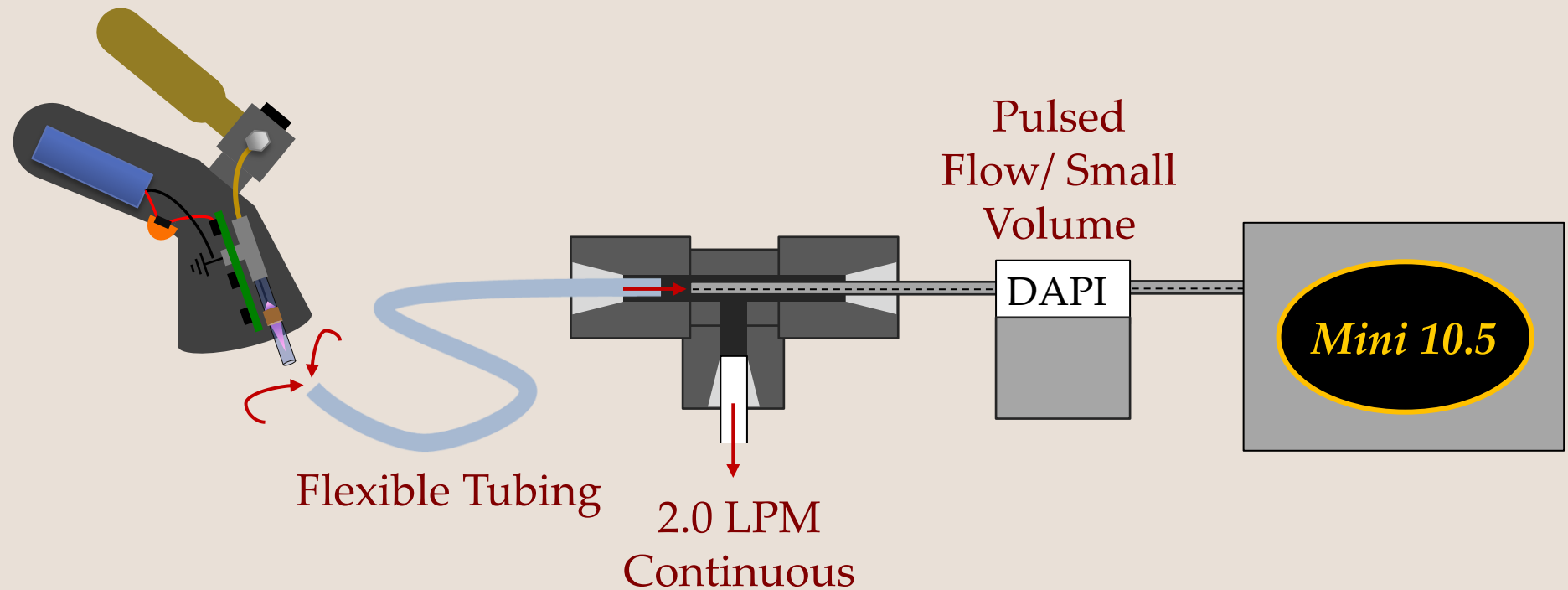


- Again, no supplemental pumping used
- Enclosure around plasma minimizes geometrical fluctuations when holding the source
 - Can be rested against surface of interest

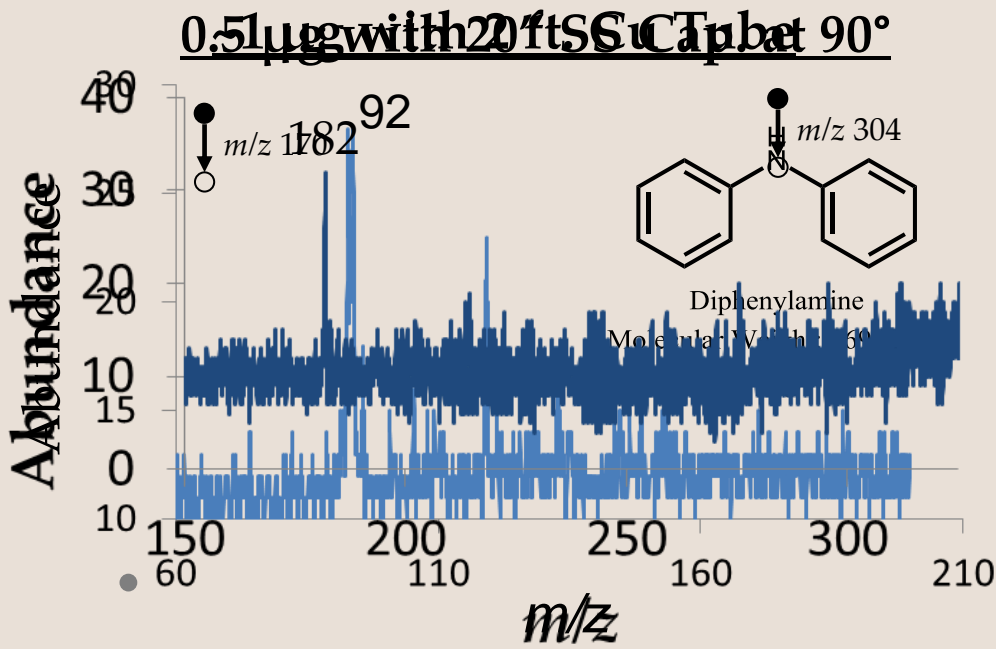
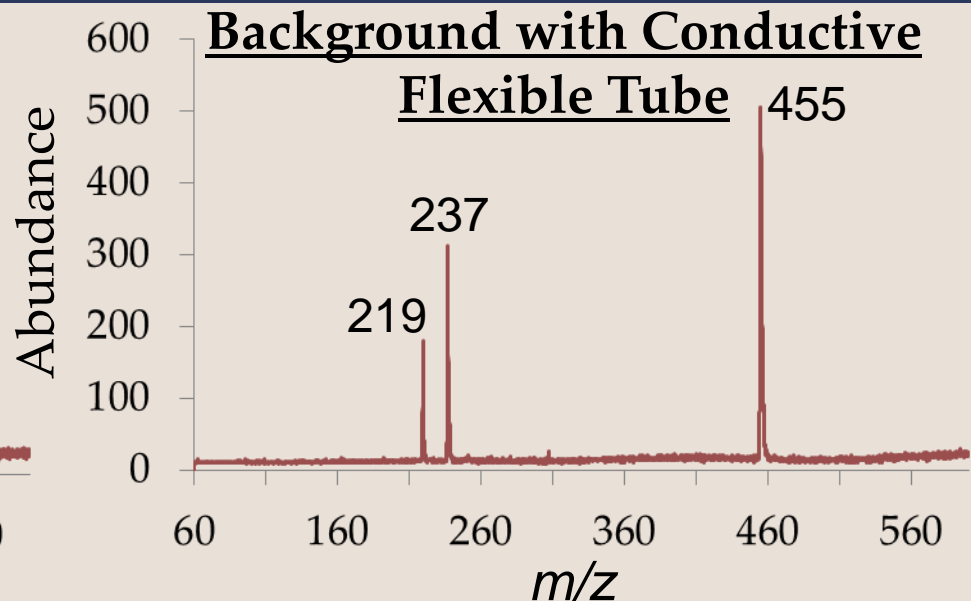
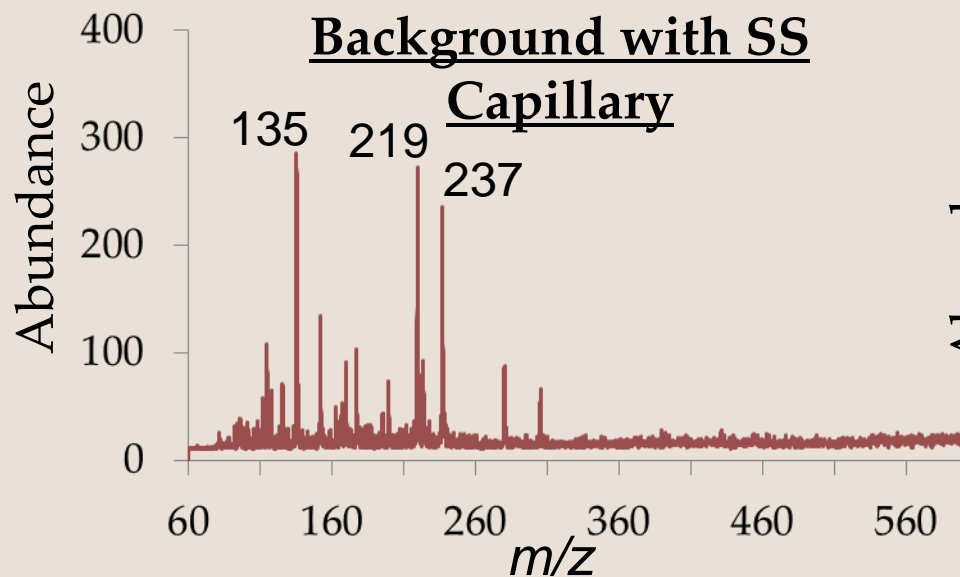
Future Work:
Long Distance Ion
Transfer on Mini-10.5 MS

Long Distance Ion Transfer with Handheld LTP on Mini 10.5 MS

- Short pulses of gas/ions due to DAPI not adequate for long distance transfer of ions on mini-10.5
- Small supplemental pump used for continuous pull of ions to MS inlet



Long Distance Ion Transfer with Handheld LTP on Mini 10.5 MS



- Many background peaks disappear when using rubber tubing
- Diphenylamine detected with 20" semi-flexible steel tube bent at 90° angle
- Working on increasing transfer efficiency

Conclusions

- Increased sensitivity for handheld LTP vs. conventional LTP
- Handheld LTP couples well with mini MS due to portability combined with reduced He flow and electric fields
 - Suitable for in-field analyses
 - Low to sub-ng LODs without supplemental pumping
- Air or He can be used for handheld LTP
 - Helium better for proton transfer; both facilitate nitrate adduction
- Long distance ion transfer possible but needs improved

Acknowledgements

Support/Discussion

Fatkhulla Tadjimukhamedov

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Jason Duncan

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• Dept. of Energy

Dept. of Homeland Security