Miniature Mass Spectrometer Based on the Cylindrical Ion Trap (CIT) and Design and Construction of a Rectilinear Ion Trap (RIT)

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CW and Explosives Monitoring at Trace Levels in Situ

Goal:

Selective, Rapid Detection of Chemical & Warfare Agents in Air or Water

Criteria:

Speed of analysis: < 10 sec

Sensitivity: LOD < 1 pptr

Selectivity: complex mixtures – no false positives

Approach:

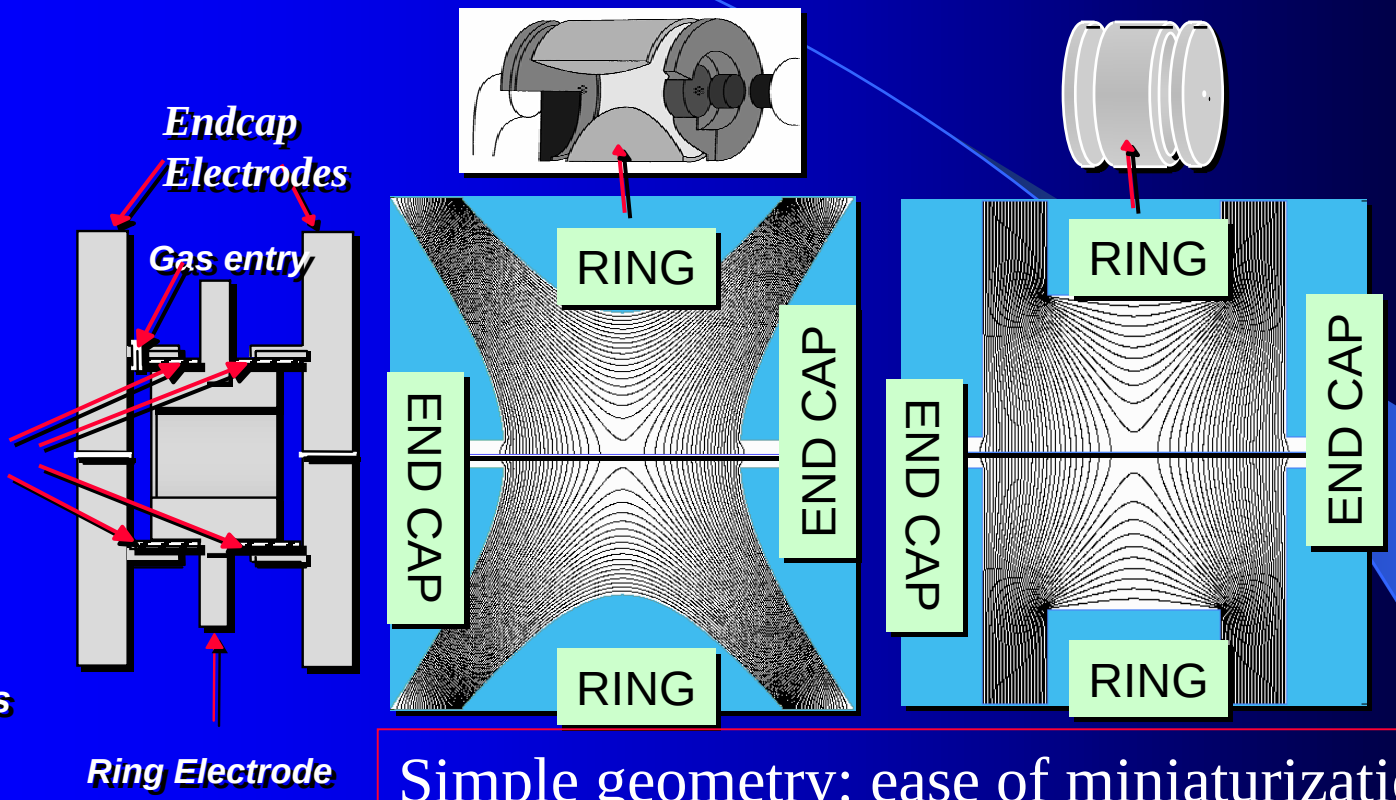
Multiple Stages of Selectivity

Comparing Miniature Mass Spectrometers

Criteria for Judging Miniature Mass Spectrometers (in order of importance)

- Size/ Weight
- Power Consumption/ Battery life
- Specificity – MS/MS capability, selective sampling
- Sensitivity – limits of detection
- Sample cycle frequency – how often can a sample be analyzed
- Ruggedness – ability to reject water (for air or water analysis), ability to be transported
- Recovery time – time from transportation mode to ready for data acquisition
- Mass spectral performance - Resolution, mass range
- Environmental impact (oil and radiation production)
- Need for consumable items in the field (helium tanks, solvents, etc.)

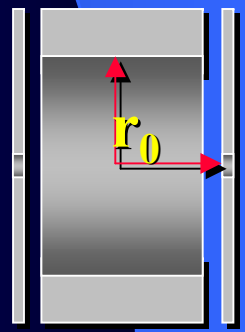
Trapping Fields: Cylindrical Ion Traps



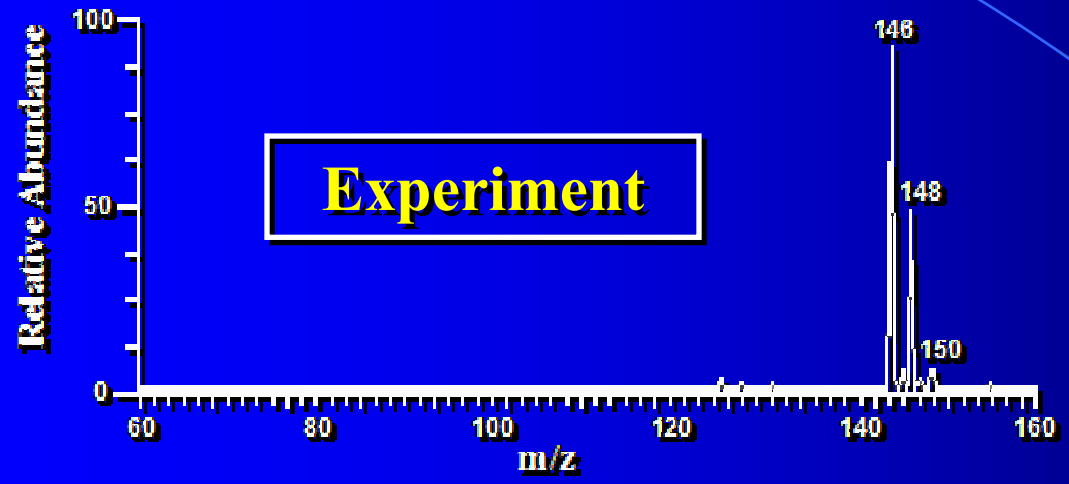
Simple geometry: ease of miniaturization

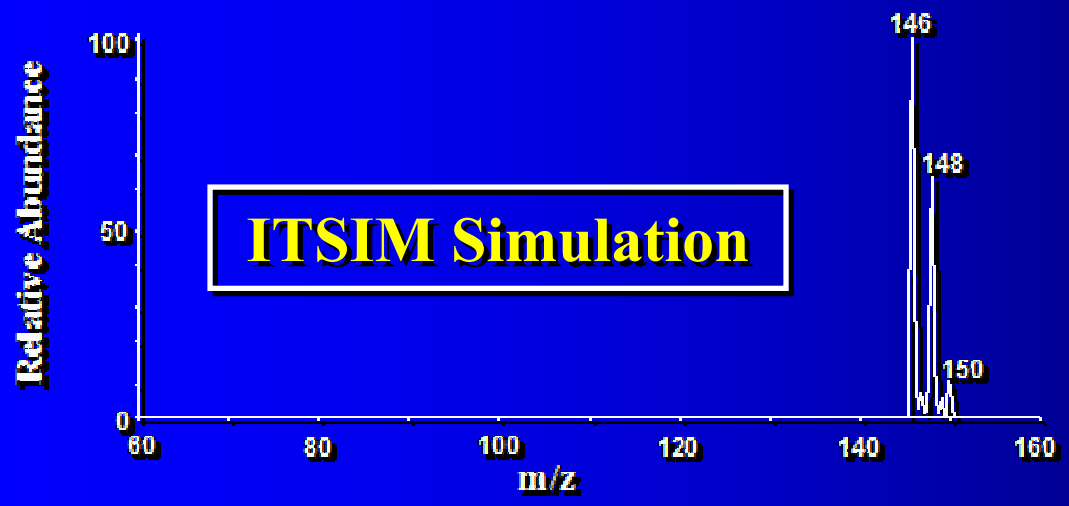
$$(m/z)_{max} = \frac{8V_{max}}{q_{eject}\Omega^2(r_0^2 + 2z_0^2)}$$

Size (r_0 and z_0)	Voltage (V_{max})	Power
$\frac{1}{4}$	$\left(\frac{1}{4}\right)^2$	$\left(\frac{1}{4}\right)^5$

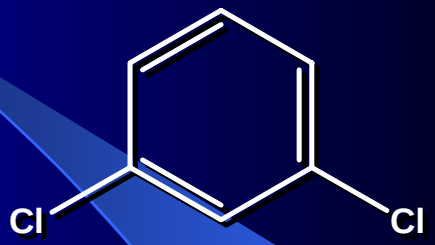


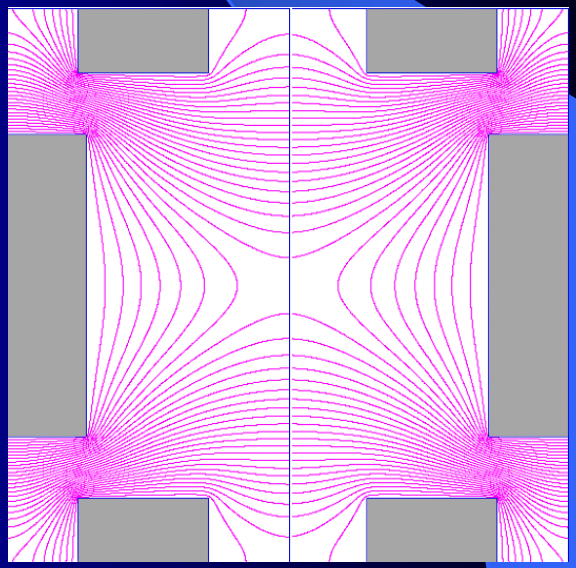
ITSIM: Simulation vs. Experiment





1,3-Dichlorobenzene ions m/z 146-150





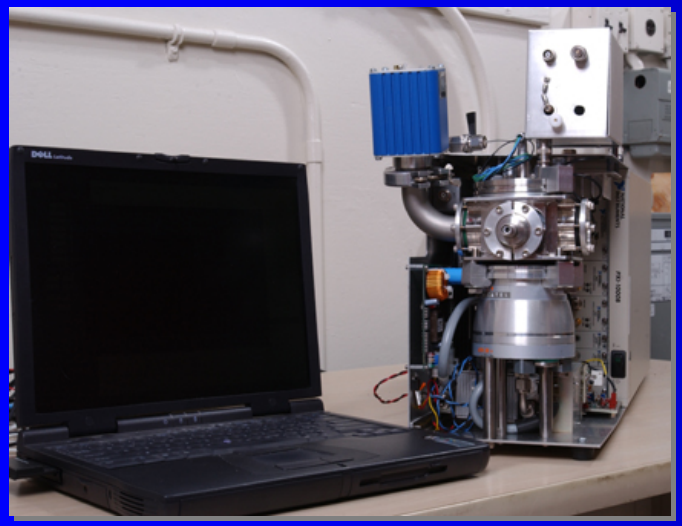
r_o = 2.5 mm

z_o = 2.7 mm

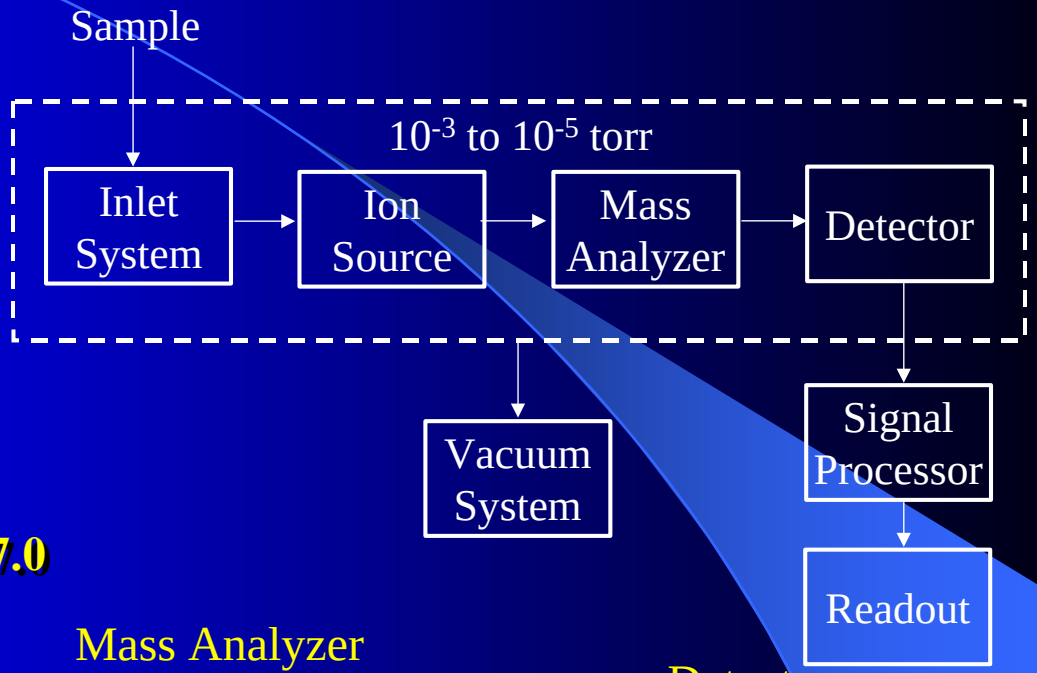
In situ MS/MS Ion Trap

December 2002 –
"Miniature Cylindrical Ion Trap Mass Spectrometer"

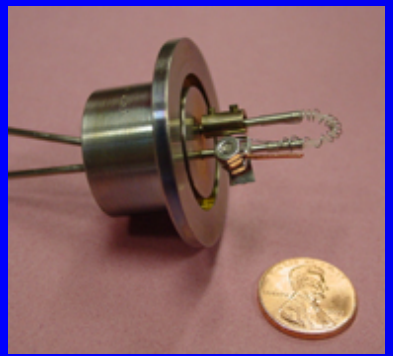
Components of the Mini Mass Spectrometer



Miniature Mass Spectrometer Version 7.0



Inlet System
Membrane Interface



Introduce neutrals

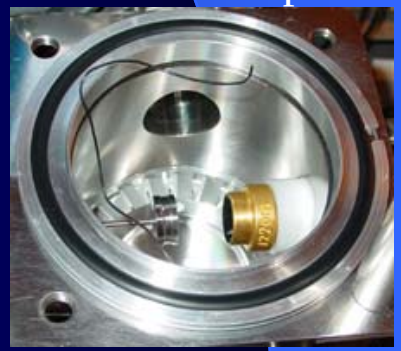
Ion Source
Electron Ionization

Make Ions

Mass Analyzer
Cylindrical Ion Trap

Mass-to-charge analysis

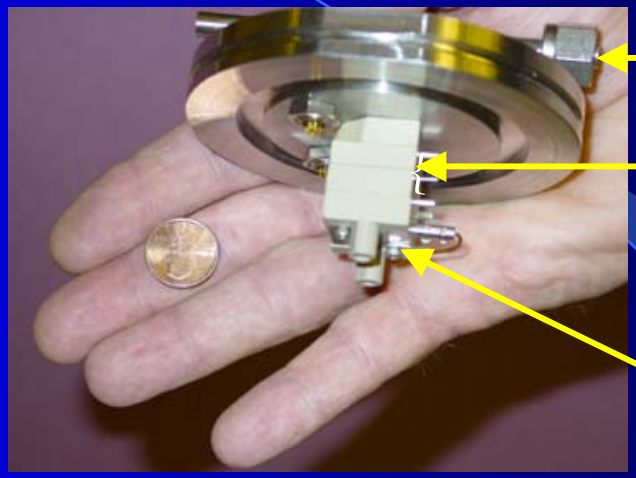
Detector
Dynode and
Electron multiplier

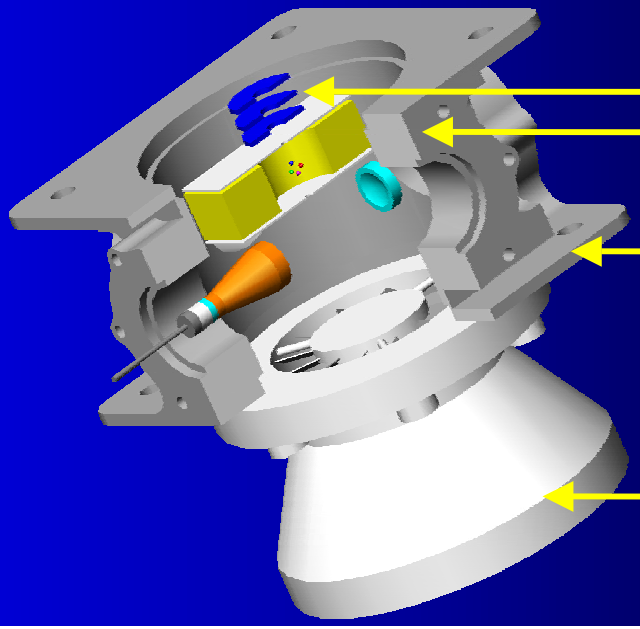


Detect Ions

Miniature Mass Spectrometer (Version 7.0)

- Cylindrical Ion Trap
  - r_0 = 2.5 mm
- Custom vacuum manifold
- Pumps:
  - Backing: KNF Neuburg 2-stage diaphragm
  - Turbo: Alcatel ATH 30+
- Custom power supplies based on 12 V battery
- Weight: 38 lbs
- Power 136 W





Miniaturization of the Quadrupole Ion Trap Mass Spectrometer

m^*

Typical Benchtop Ion Trap MS

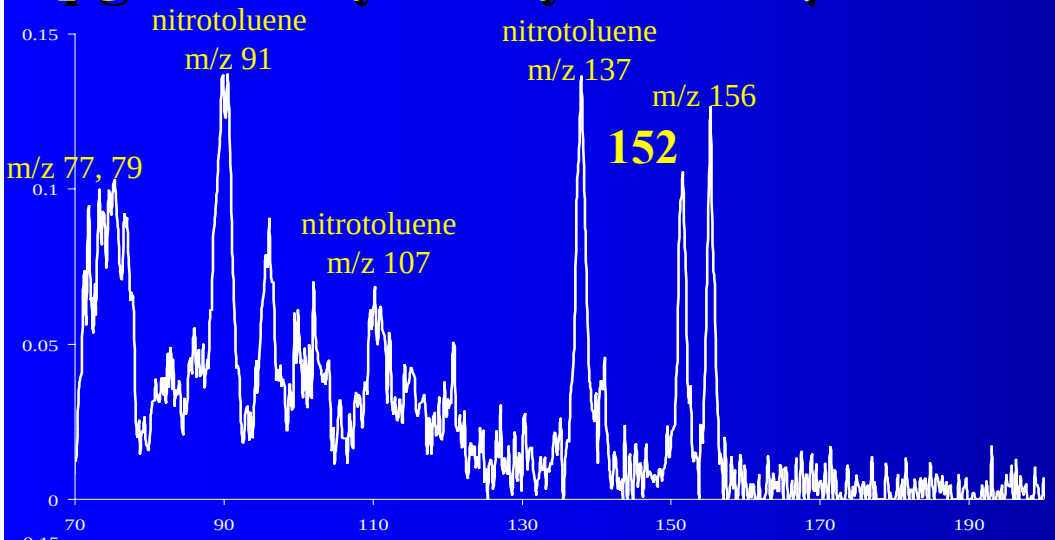
- Operating Pressure: $1x10^{-3}$ Torr
- Mass Range: **2000 amu**
- Max RF Voltage: **7,500 V** $_{(0\text{-}p)}$
- Power: **2400 W**
- Weight:
  - Instrument: 265 lbs.
  - Pumps: 100 lbs.
  - Computer: 85 lbs.
    - Total: **450 lbs**.

Mini cylindrical ion trap MS

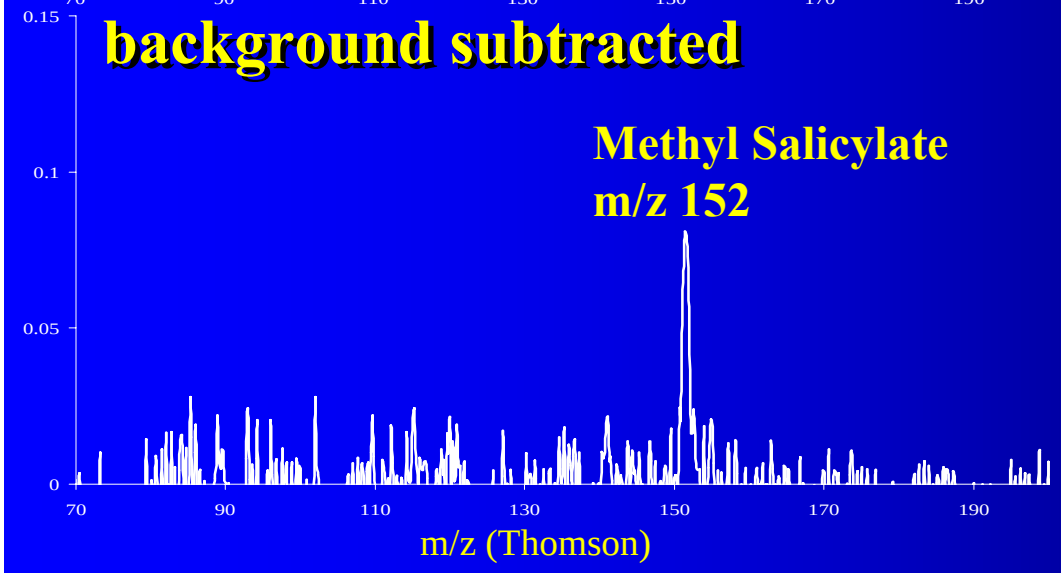
- Operating Pressure: $1x10^{-3}$ Torr
- Mass Range: **500 amu**
- Max RF Voltage: **1,800 V** $_{(0\text{-}p)}$
- Power: **136 W**
- Weight:
  - Instrument: 26 lbs.
  - Pumps: 5 lbs.
  - Computer: 7 lbs.
    - Total: **38 lbs**.

Sensitivity and Resolution

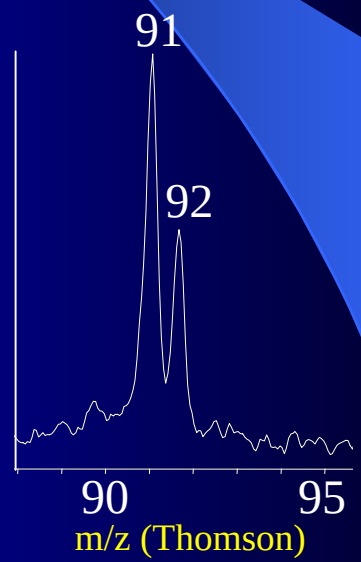
1 pg of methyl salicylate in 1 µL methanol



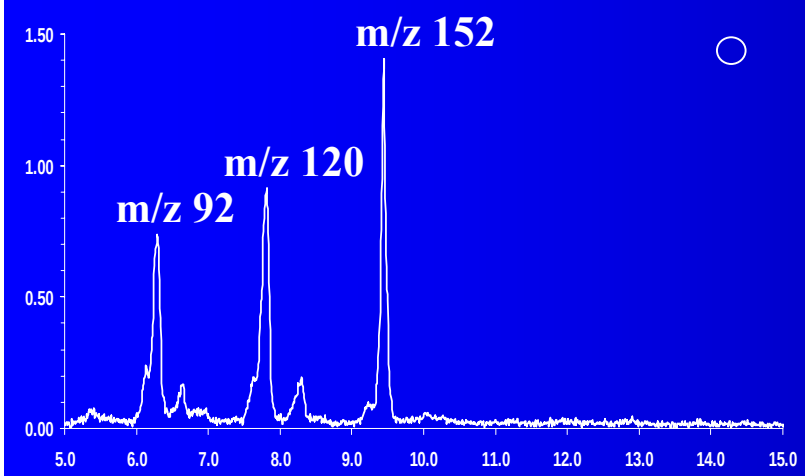
background subtracted

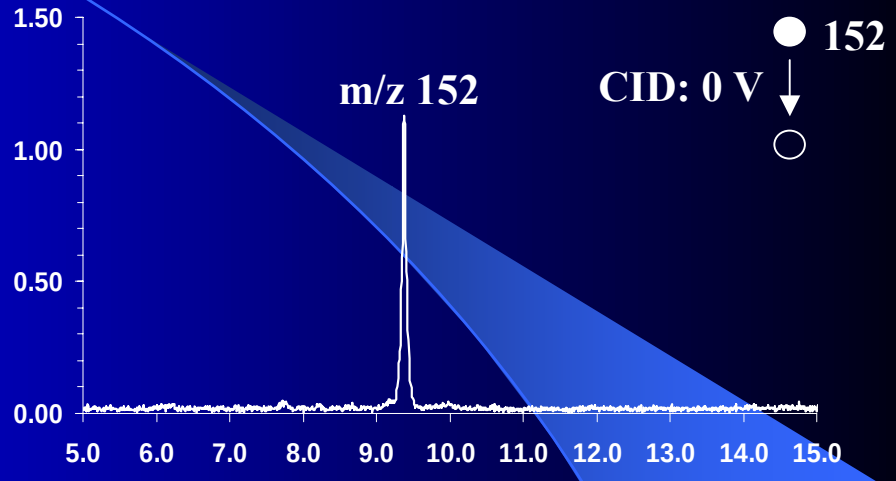


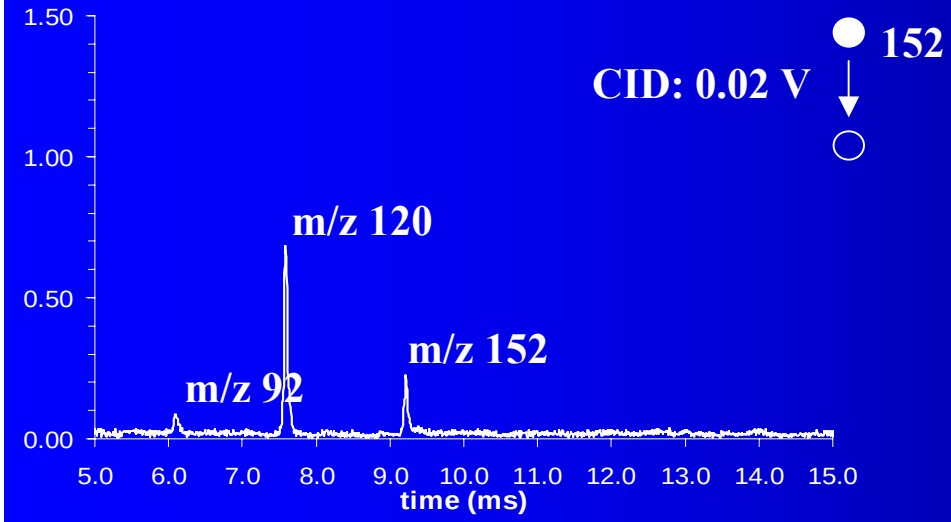
Resolution ~100
Toluene with membrane inlet

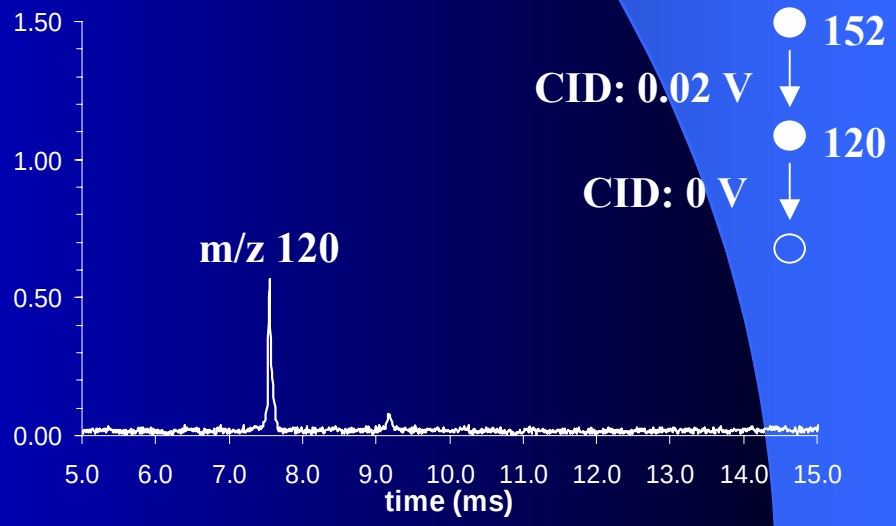


MS/MS of Methyl Salicylate

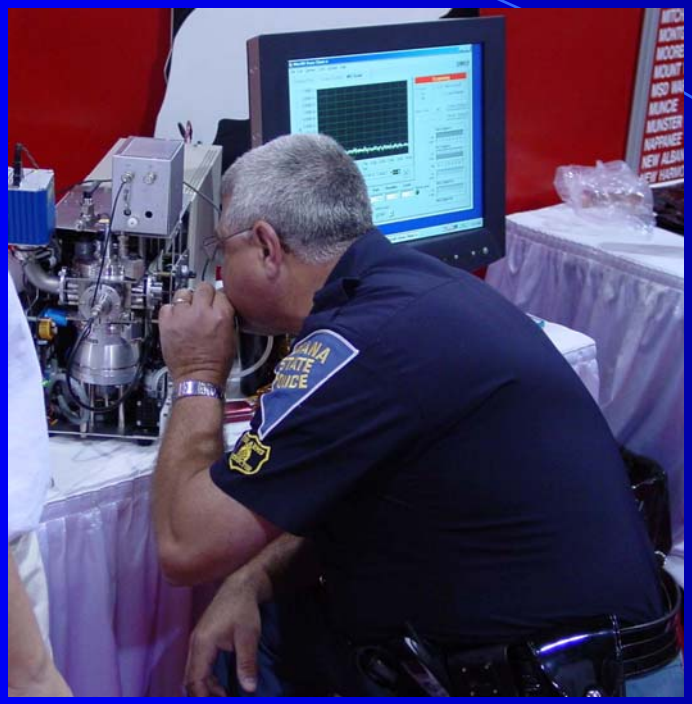


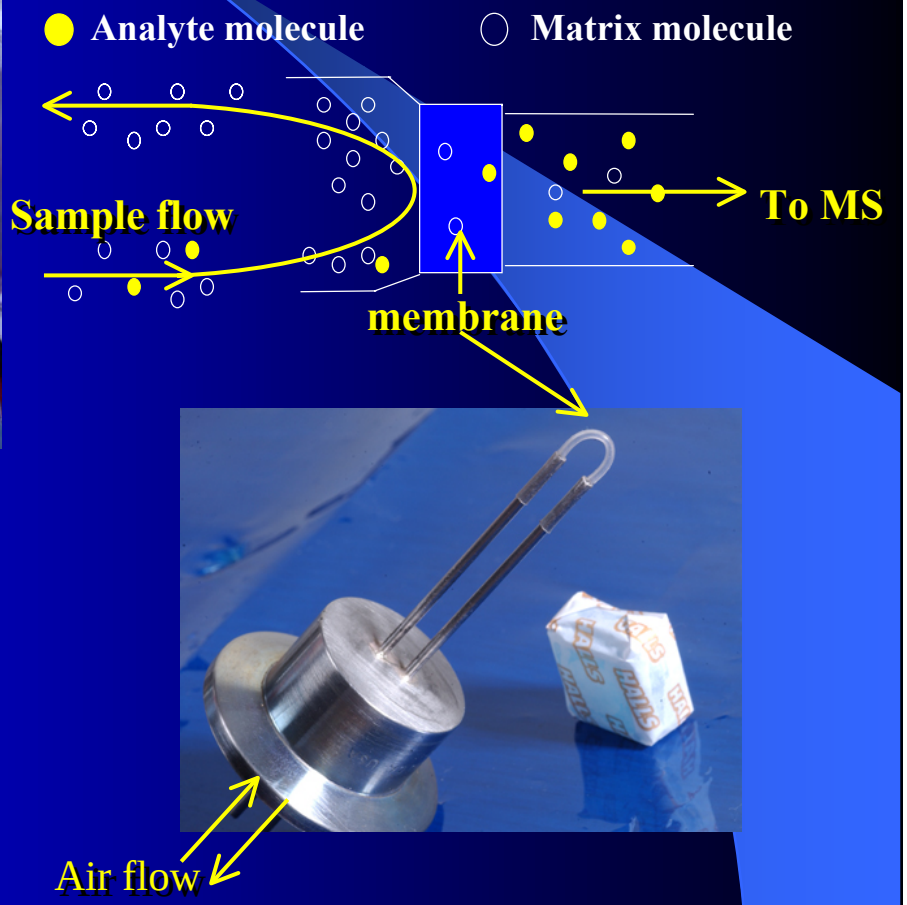






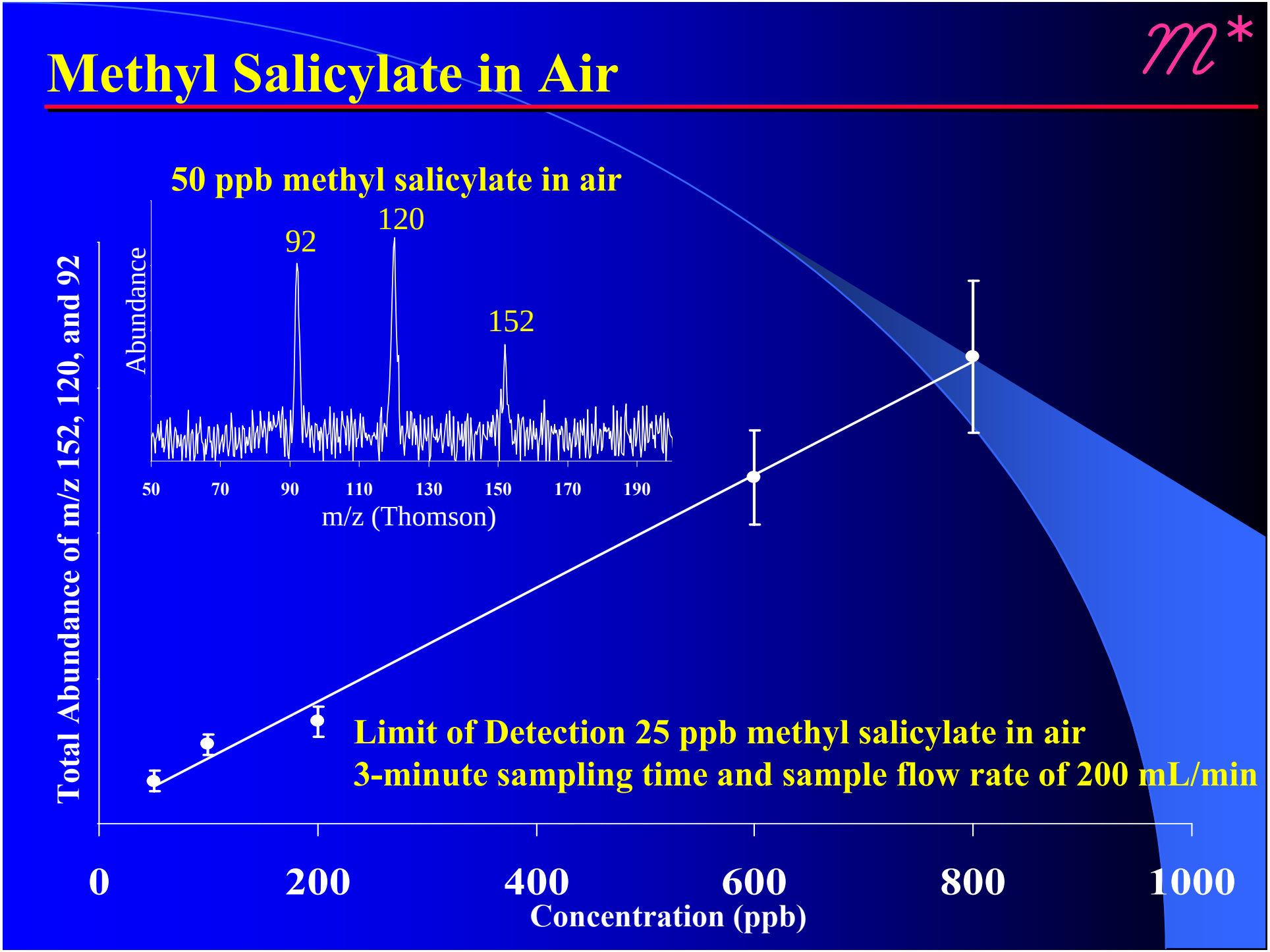
Sampling Methods: MIMS





On-line monitoring of complex samples such as human breath

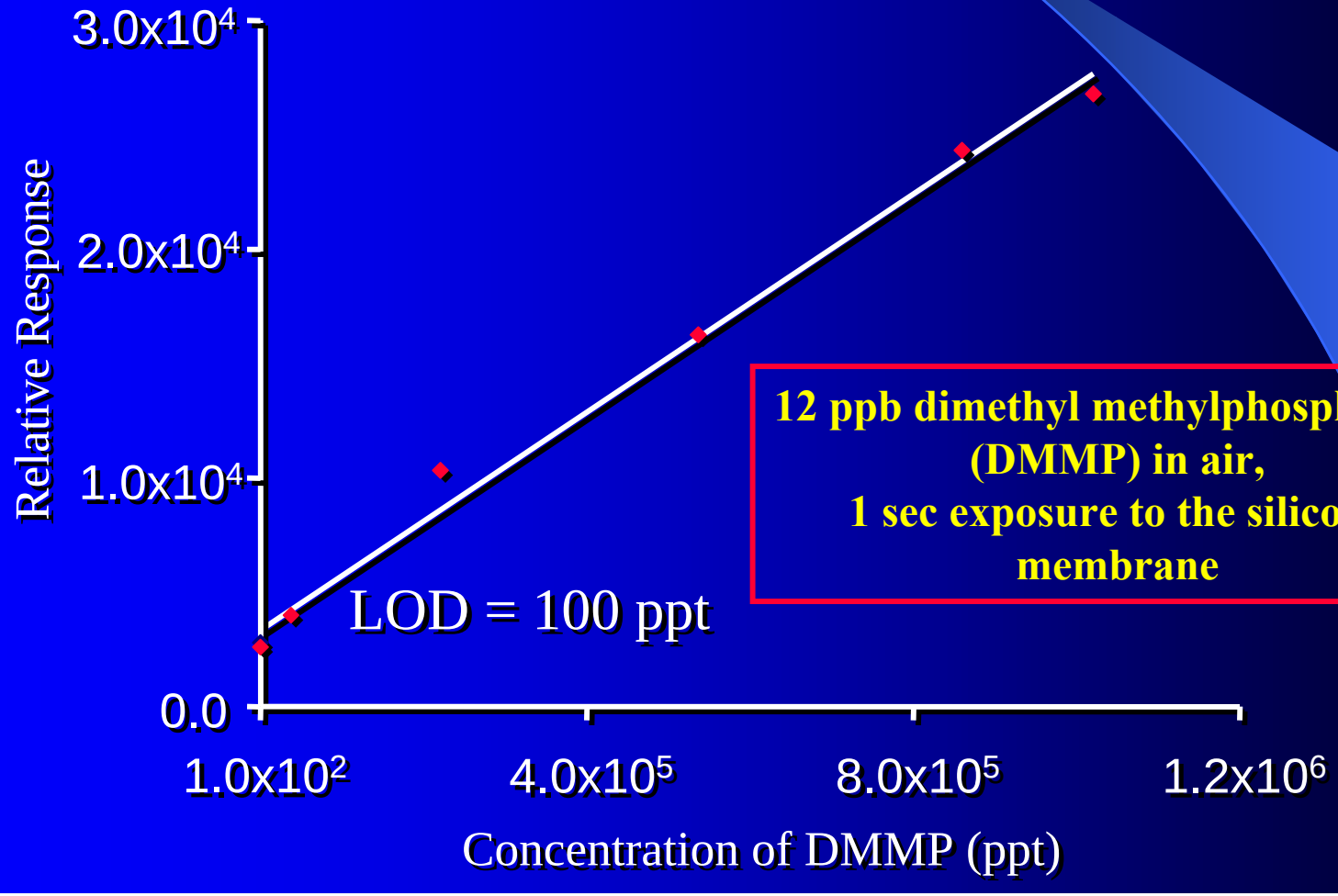
Methyl Salicylate in Air



Linear Response to DMMP in Air

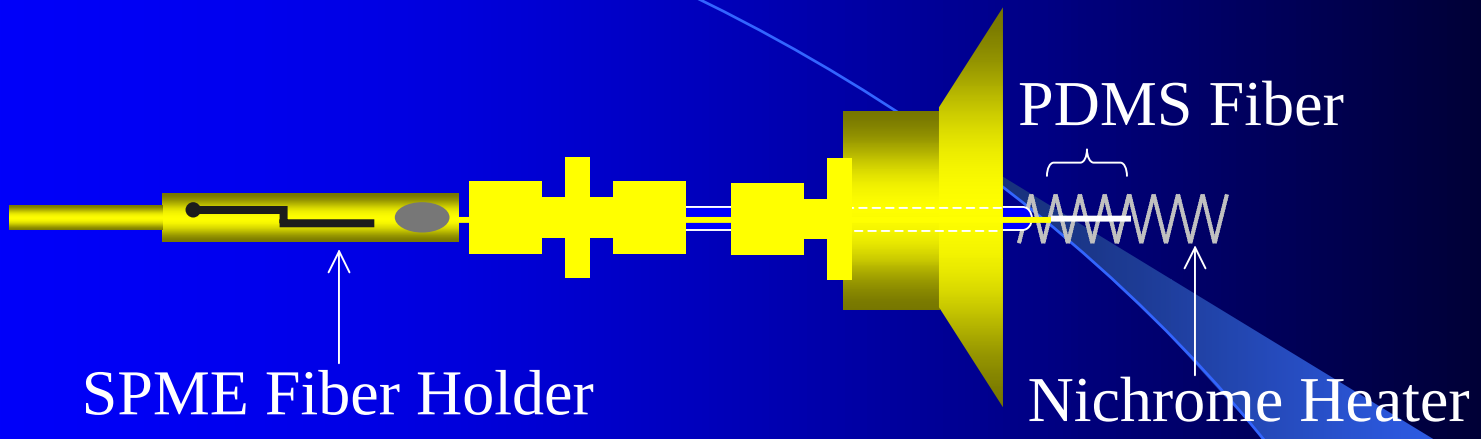
Single-Sided MIMS

SS-MIMS system has a linear response over 4 orders of magnitude



12 ppb dimethyl methylphosphonate (DMMP) in air, 1 sec exposure to the silicone membrane

Single-Sided MIMS solid-phase microextraction (SPME)



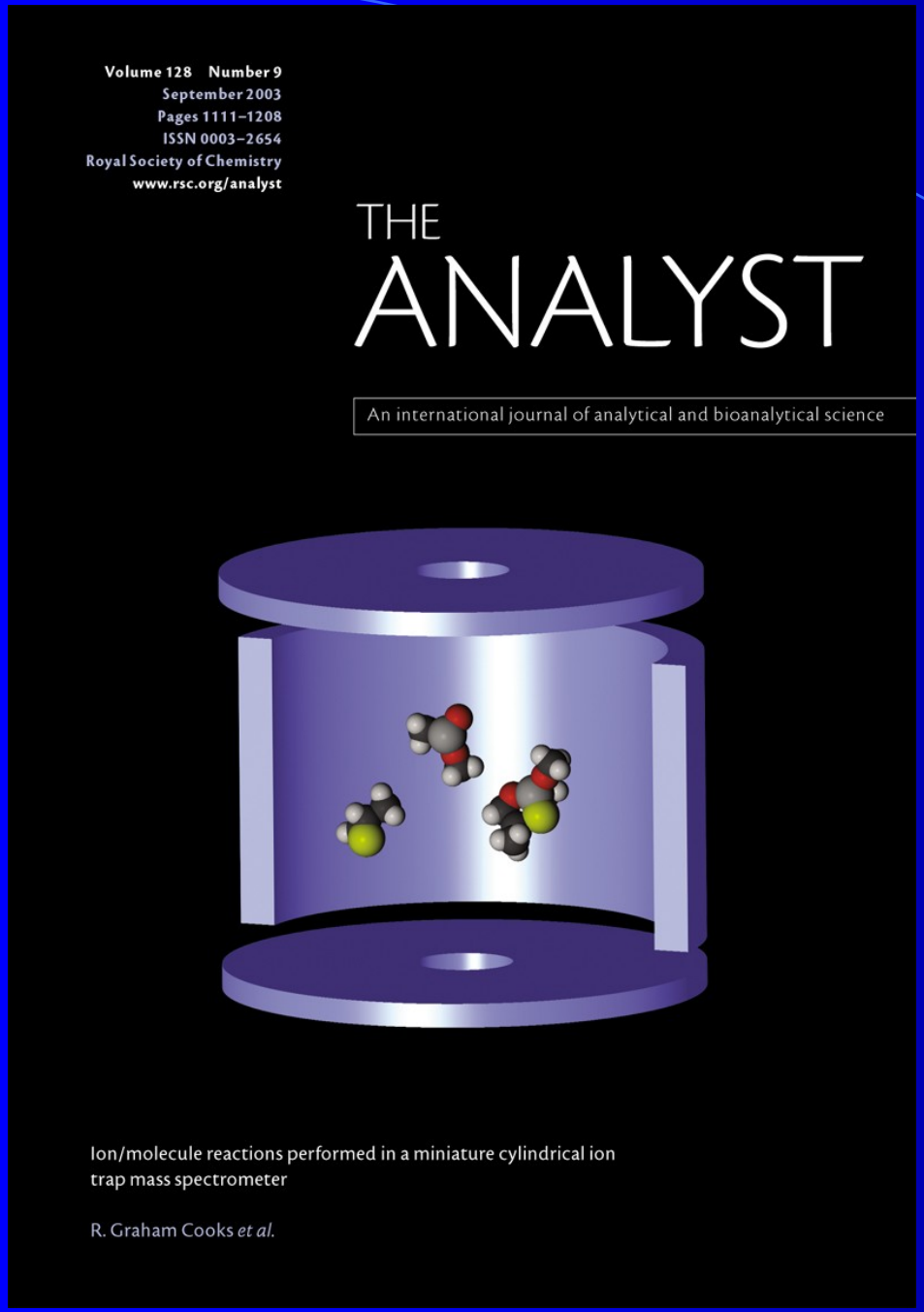
Fiber introduction mass spectrometry (FIMS), a variation of solid-phase microextraction (SPME) and membrane introduction mass spectrometry (MIMS), with a miniature mass spectrometer.

FIMS

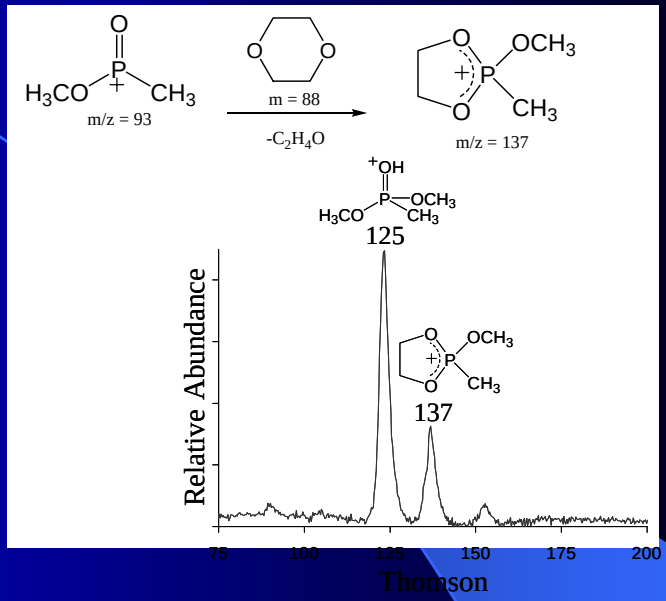
Ruggedness and Field Testing

This instrument has been transported to and has acquired data in a variety of settings

- Outside in both summer and winter (no climate control)
- Transportation by both car and airplane with immediate performance upon arrival
- Repeated sampling of air and breath samples with reliable results
- Battery power for many hours
- Continuous operation for more than 14 hours



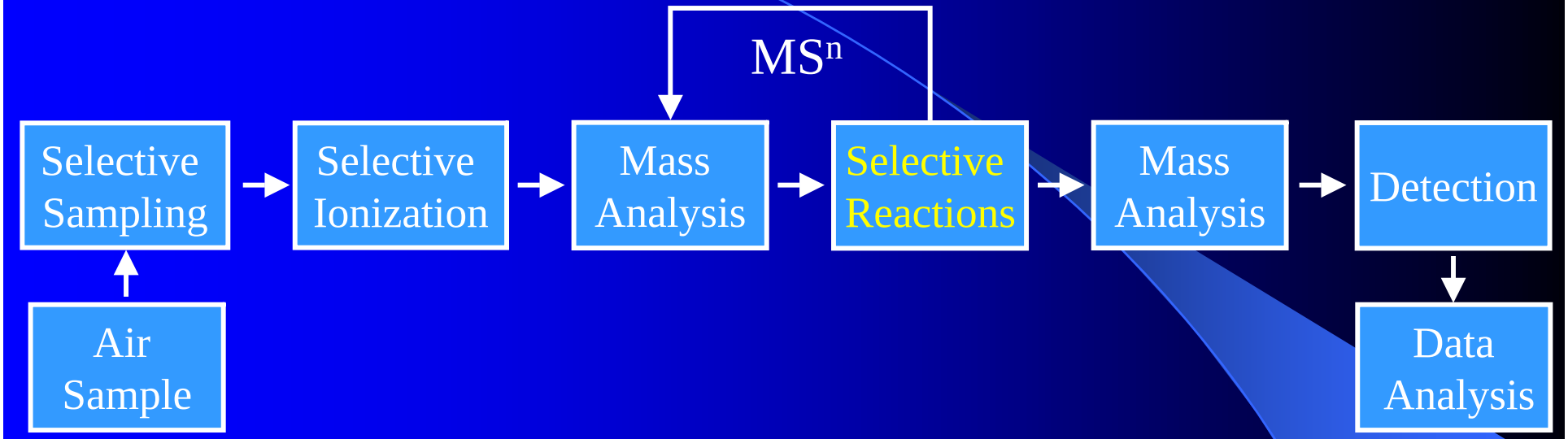
Ion/Molecule Chemistry – Selection of Organophosphorous Warfare Agents



September 2003 -
"Ion/molecule Reactions Performed in a Miniature Cylindrical Ion Trap Mass Spectrometer"

m*

Selective Ion Chemistry

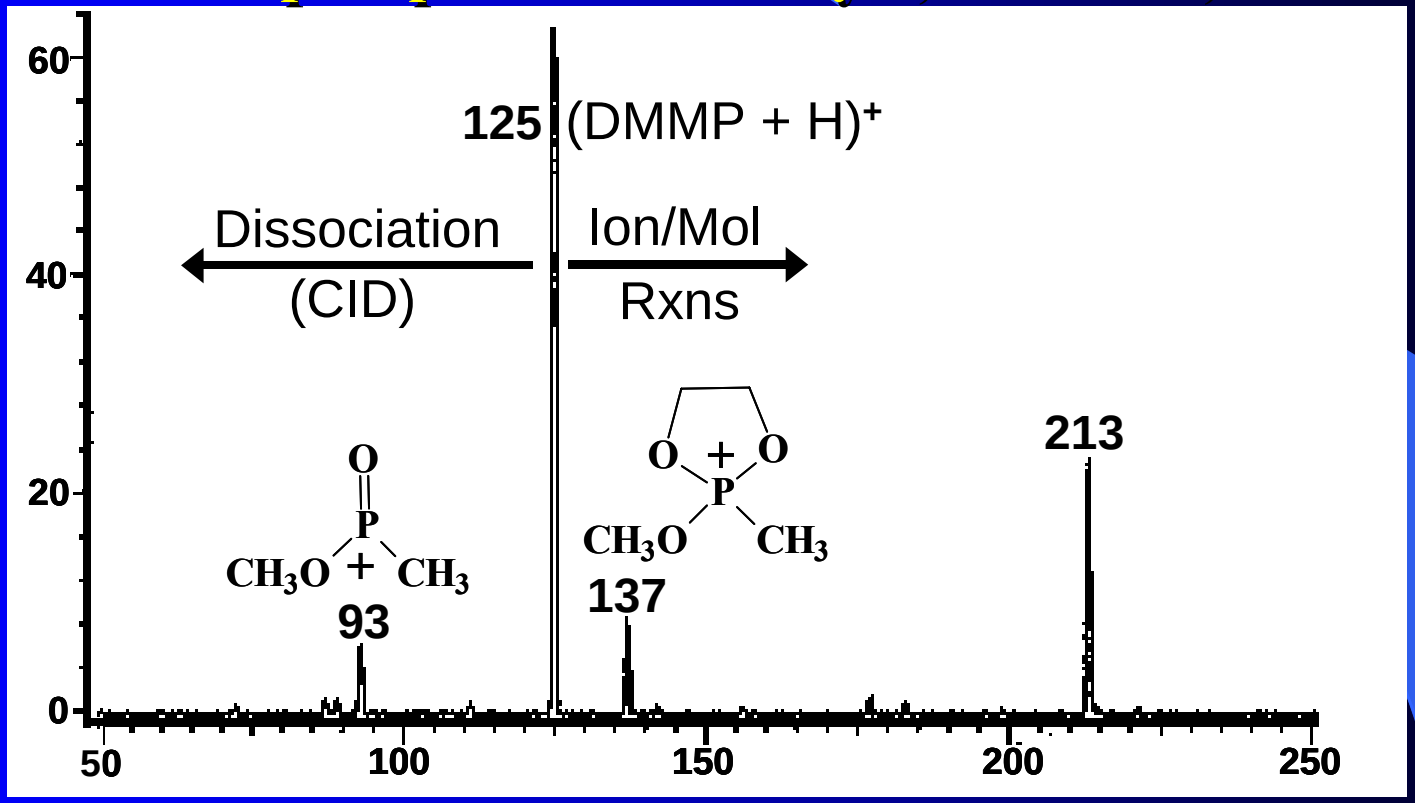


- Additional selectivity can be gained from selective ion chemistry
- Especially useful for mixture analysis as commonly found in field applications.
- The goal of this work is to obtain high selectivity using characteristic ion/molecule reactions as structural probes in a miniature mass spectrometer.

Selective Detection: Ion/Molecule Rxns

DMMP: Chemical agent simulant

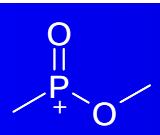
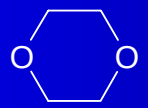
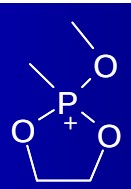
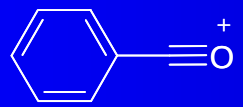
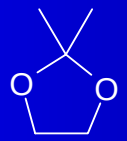
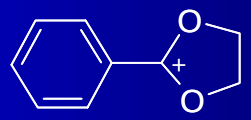
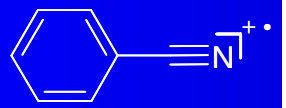
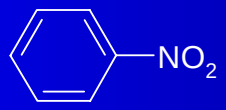
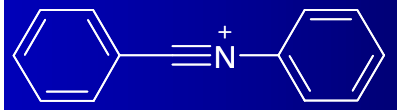
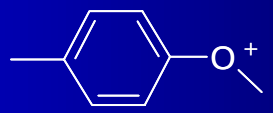
Ketalization of phosphonium ions by 1,4-dioxane; Eberlin Rxn



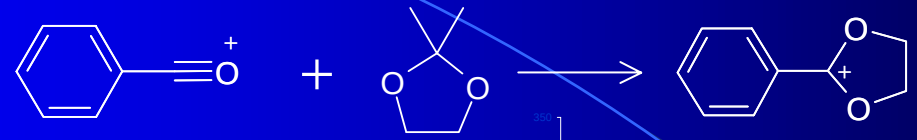
By contrast, acylium ions RC=O$^+$ don't to react with 1,4-dioxane. Such as:

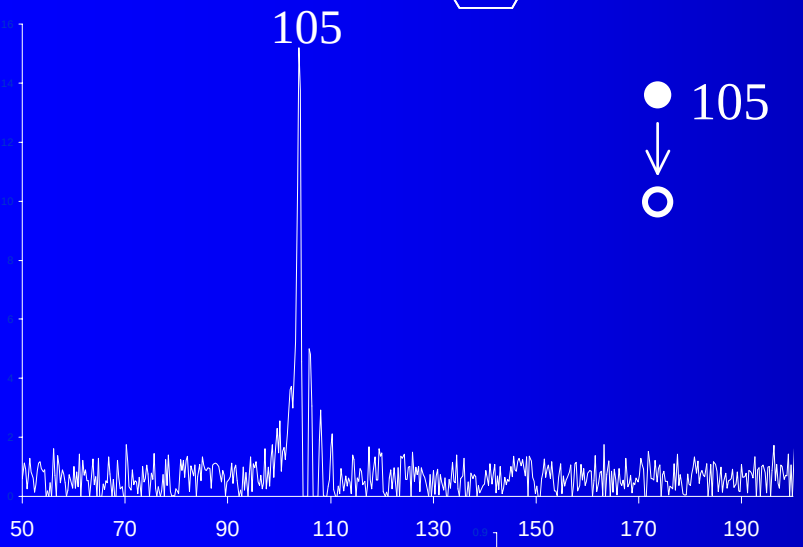
CH_3CO^+ (m/z 43)
CH_3OCO^+ (m/z 59)
$(CH_3)_2NCO^+$ (m/z 72)
$PhCO^+$ (m/z 105)

Ion-Molecule Reaction Summary

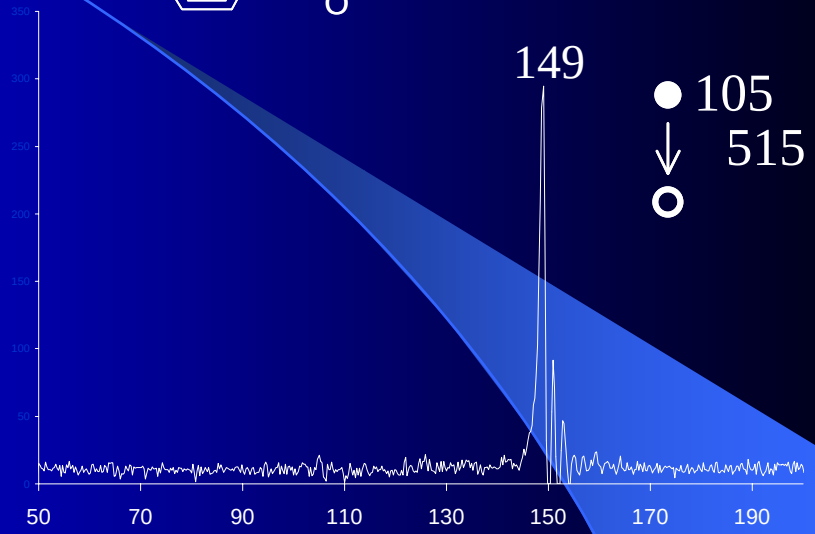
Ionic Reagent	Neutral Reagent	Product Ion	Reaction Type
 m/z 93	 88	 m/z 137	Eberlin
 m/z 105	 102	 m/z 149	Eberlin
 m/z 103	 123	 m/z 180	Addition / NO_2 Elimination
$C_7H_7^+$ m/z 91	—OH 32	 m/z 123	Addition

Eberlin Type Ion-Molecule Reaction

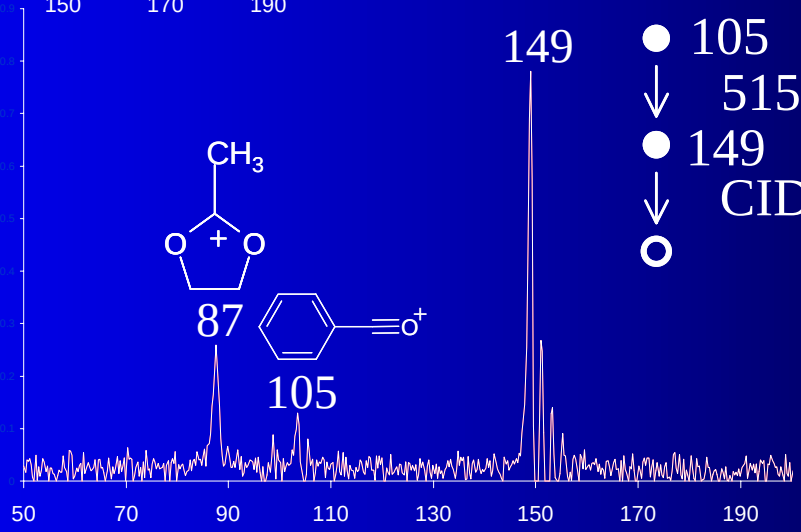




● 105
↓
○



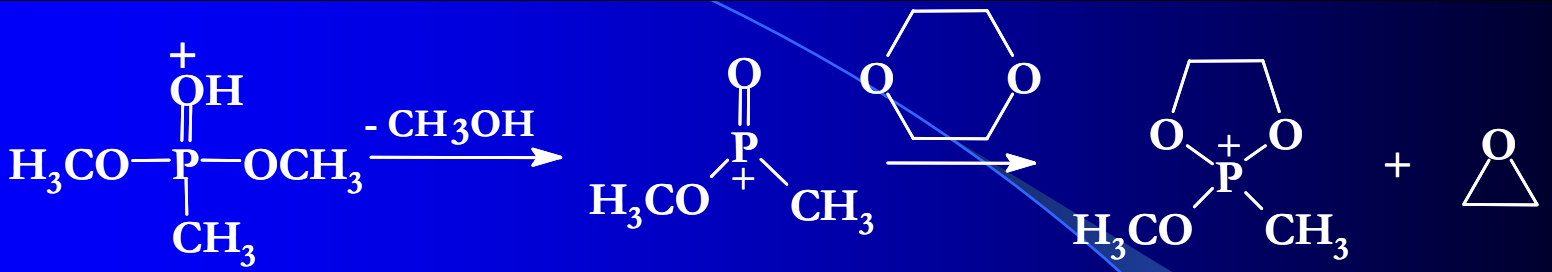
● 105
↓ 515 ms
○



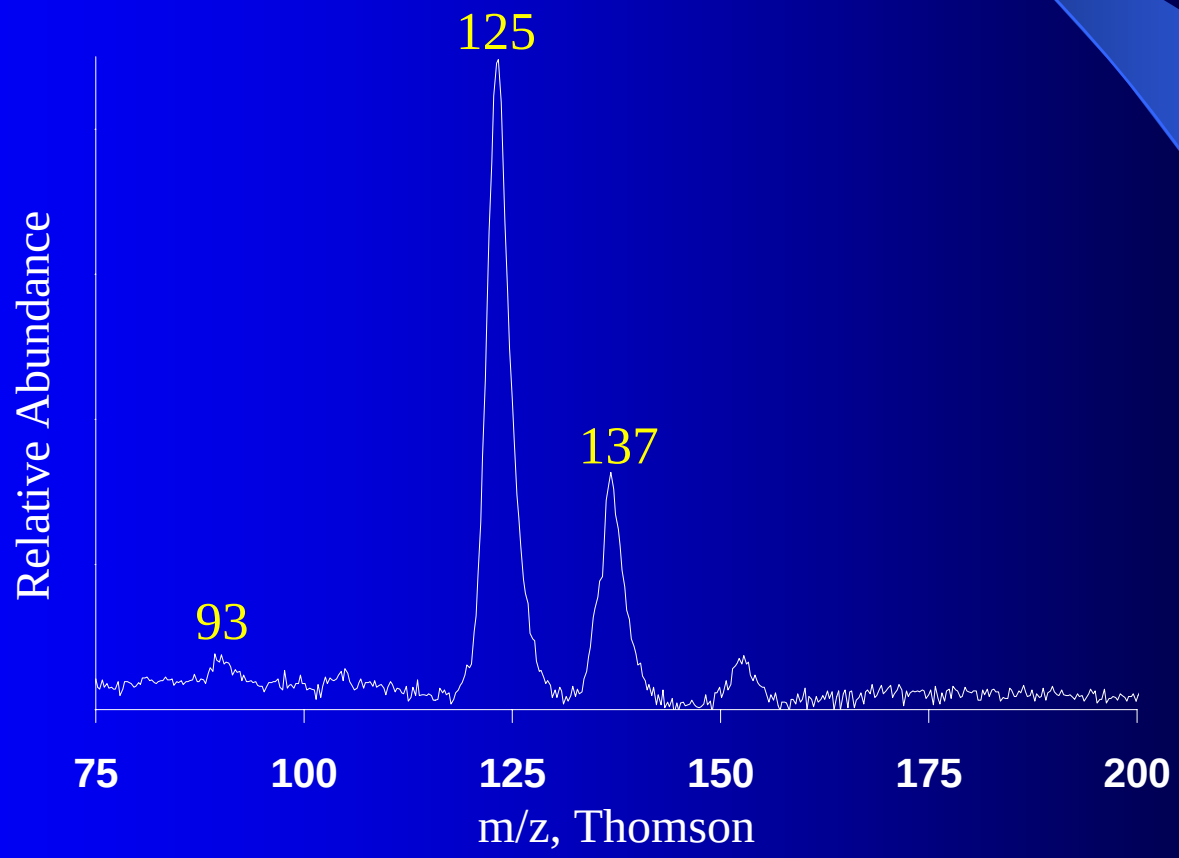
● 105
↓ 515 ms
● 149
↓ CID
○

m/z, Thomson

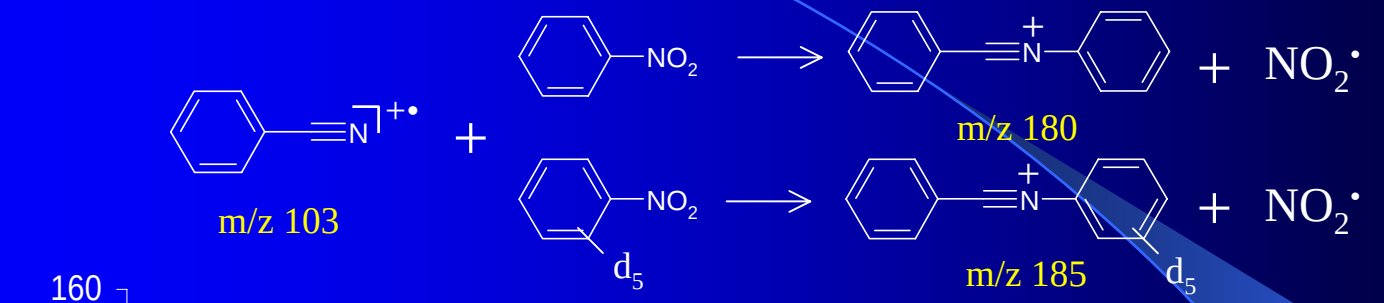
Eberlin Reaction with CW Agent Simulant

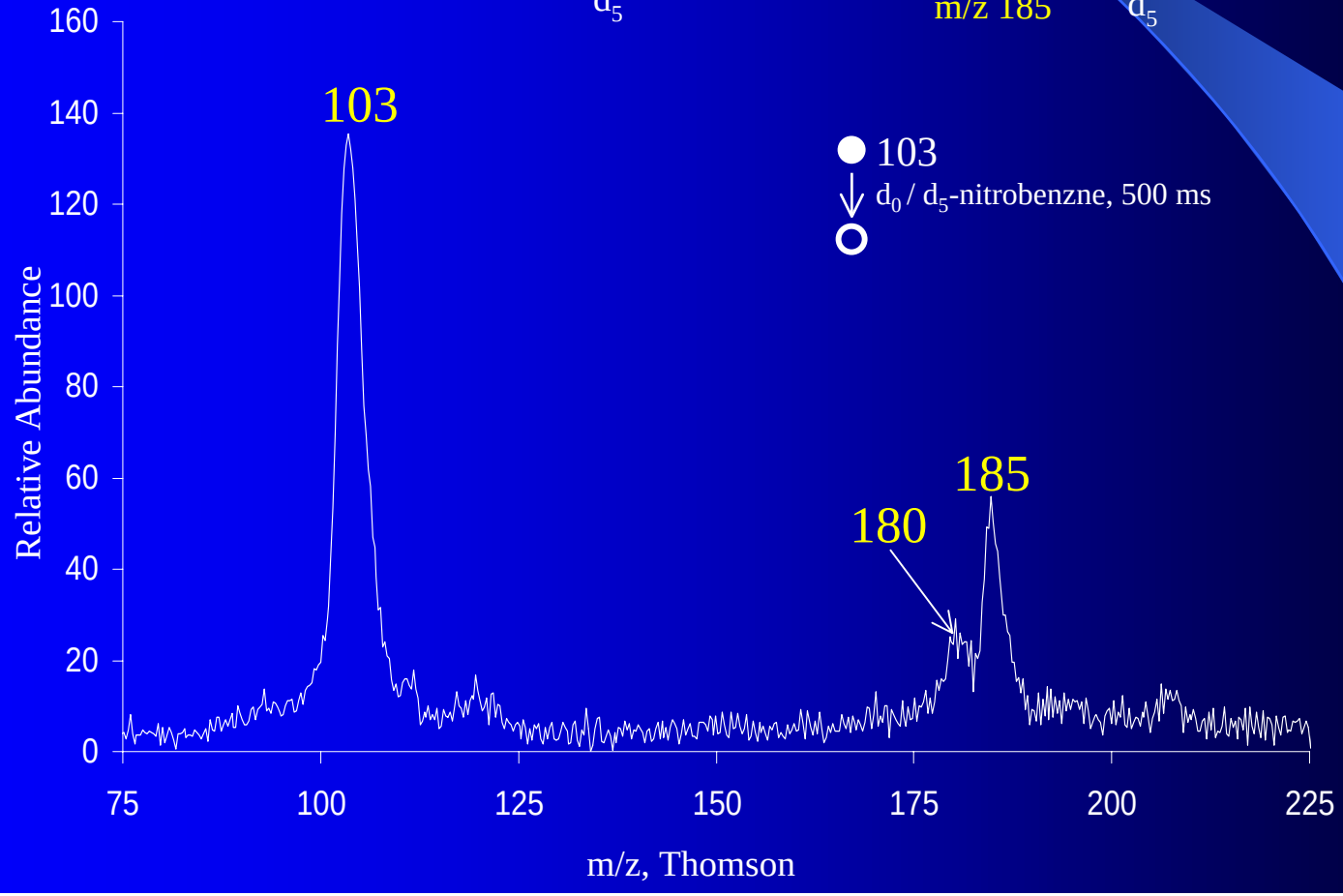


m/z 125 **m/z 93** **m/z 137**



Denitration Reaction for Explosives Detection





Version 7.0 Miniature CIT MS

- The first fully miniaturized (40 lbs.) tandem mass spectrometer
  - based on a cylindrical ion trap (CIT) mass analyzer

- The mini CIT uses lower voltages & less power allowing reduction of ancillary components (not just of the analyzer)

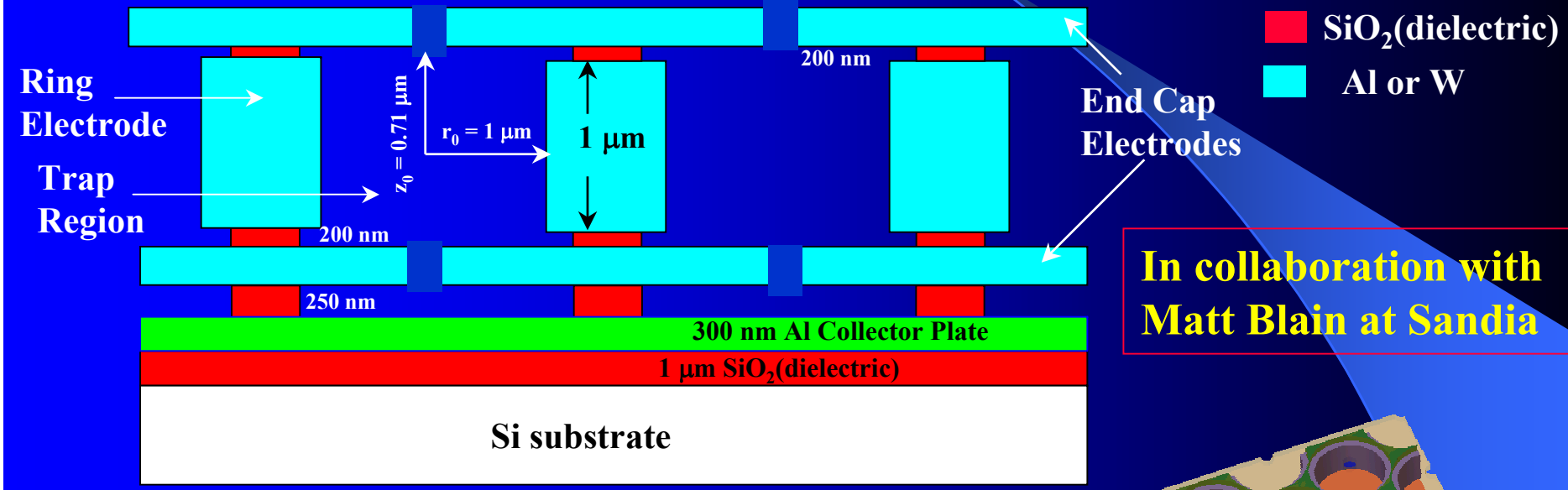
- Preliminary testing :
  - 1 pg methyl salicylate detected
  - 23 ppb toluene in air detected on-line
  - 24 pptr methyl salicylate in air detected (with preconcentration)
  - Resolution 100; mass range 500
  - MS^n (n = 3) for increased selectivity
  - MIMS for on-line monitoring of unprepared air samples

- Additional selectivity gained from selective ion chemistry
- New simpler higher performance designs being tested
- New ultra-small instrument being designed

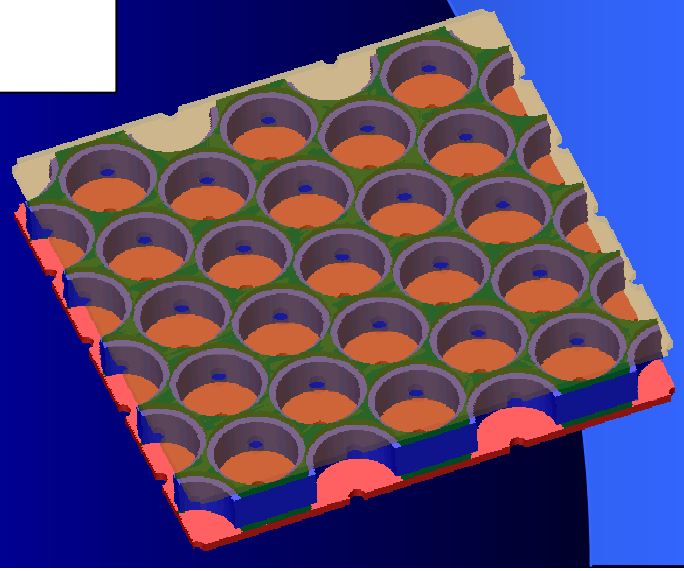
Future Directions

Micro Fabricated Array of Cylindrical Ion Traps

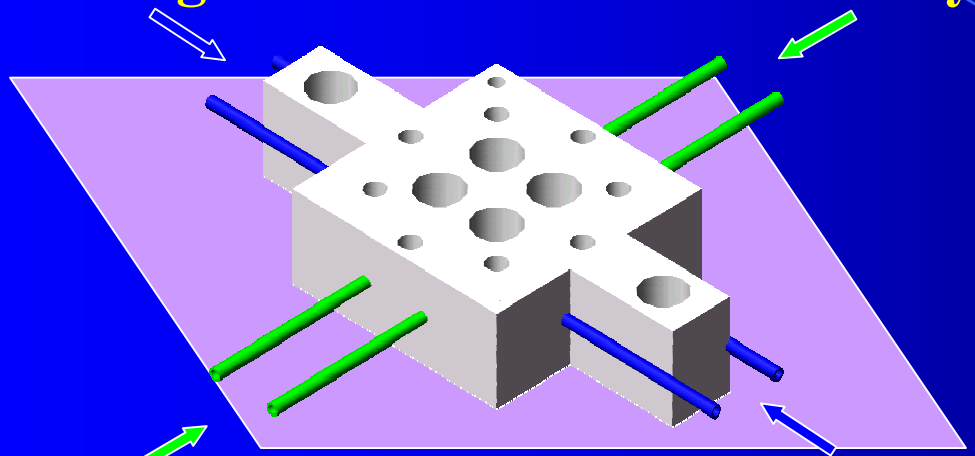
- A cylindrical ion trap array with individual units of r_0 = 1 μm and z_0 = 0.707 μm
- ~10^7 CITs in an array



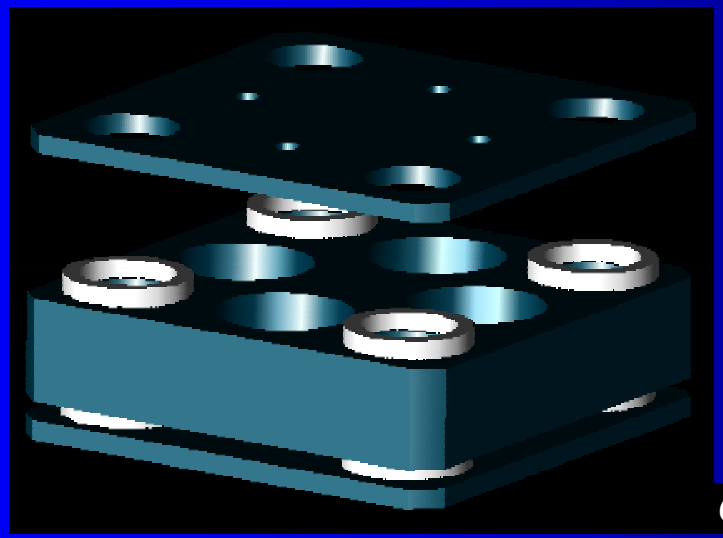
In collaboration with Matt Blain at Sandia



Miniature Cylindrical Ion Trap Arrays



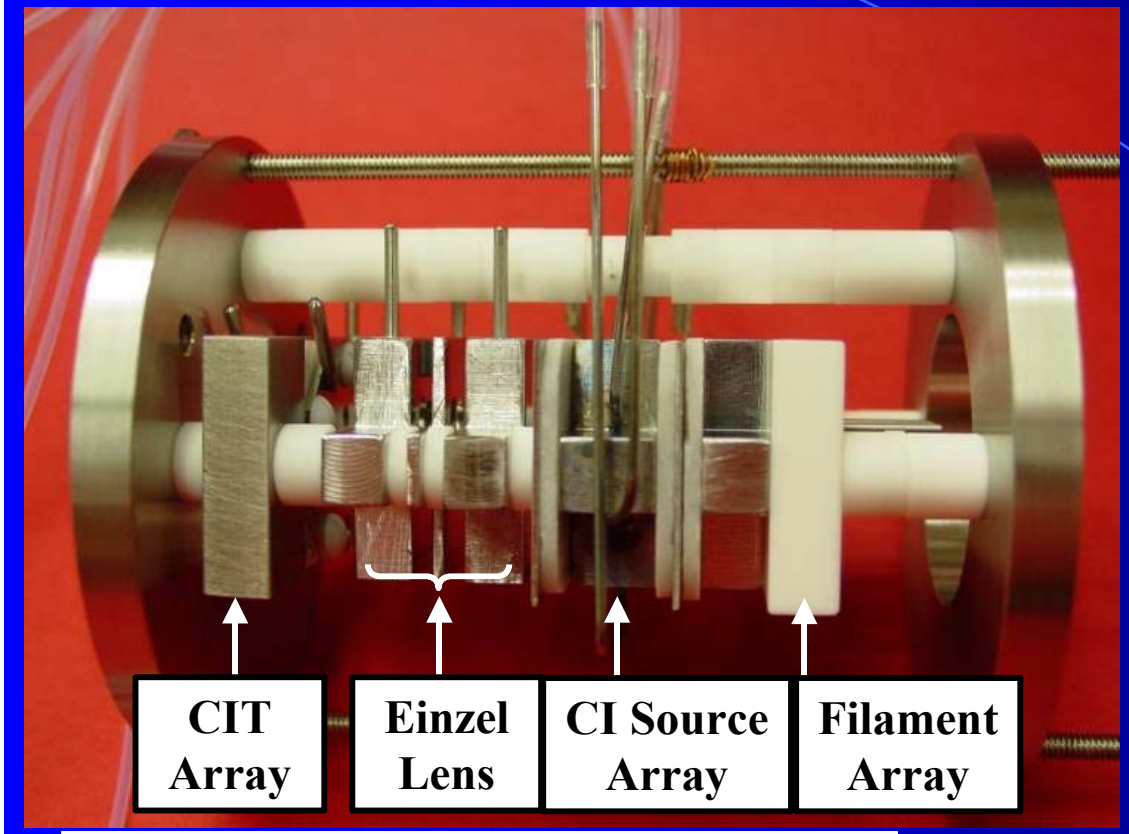
Introduce four separate analytes and up to four different reagent gases

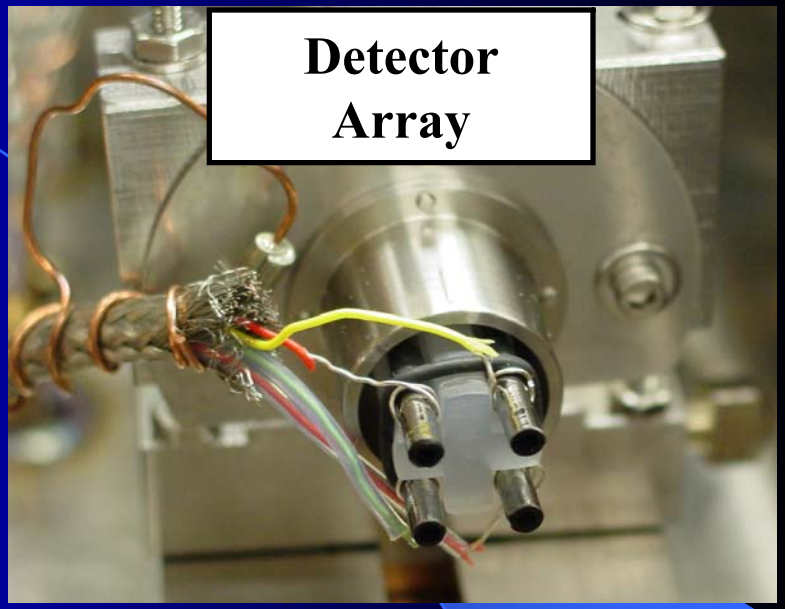


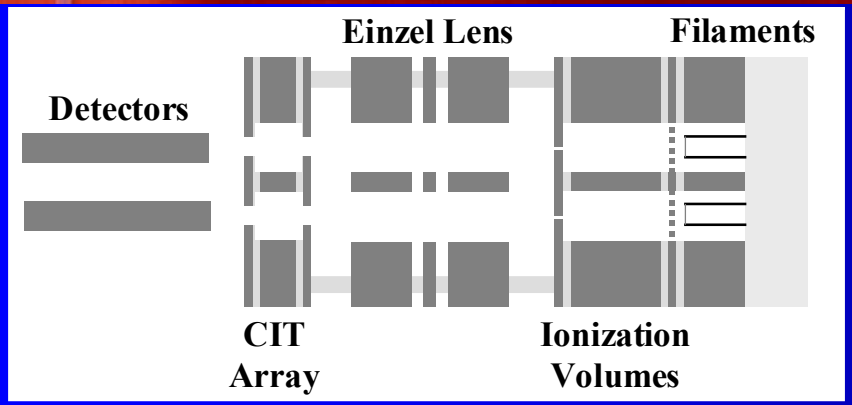
CIT ARRAY

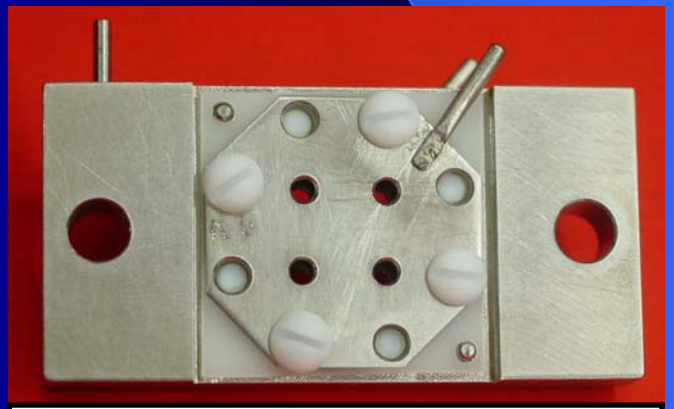
Multiple samples
Multiple detectors

Multiplexed CIT Array Instrument



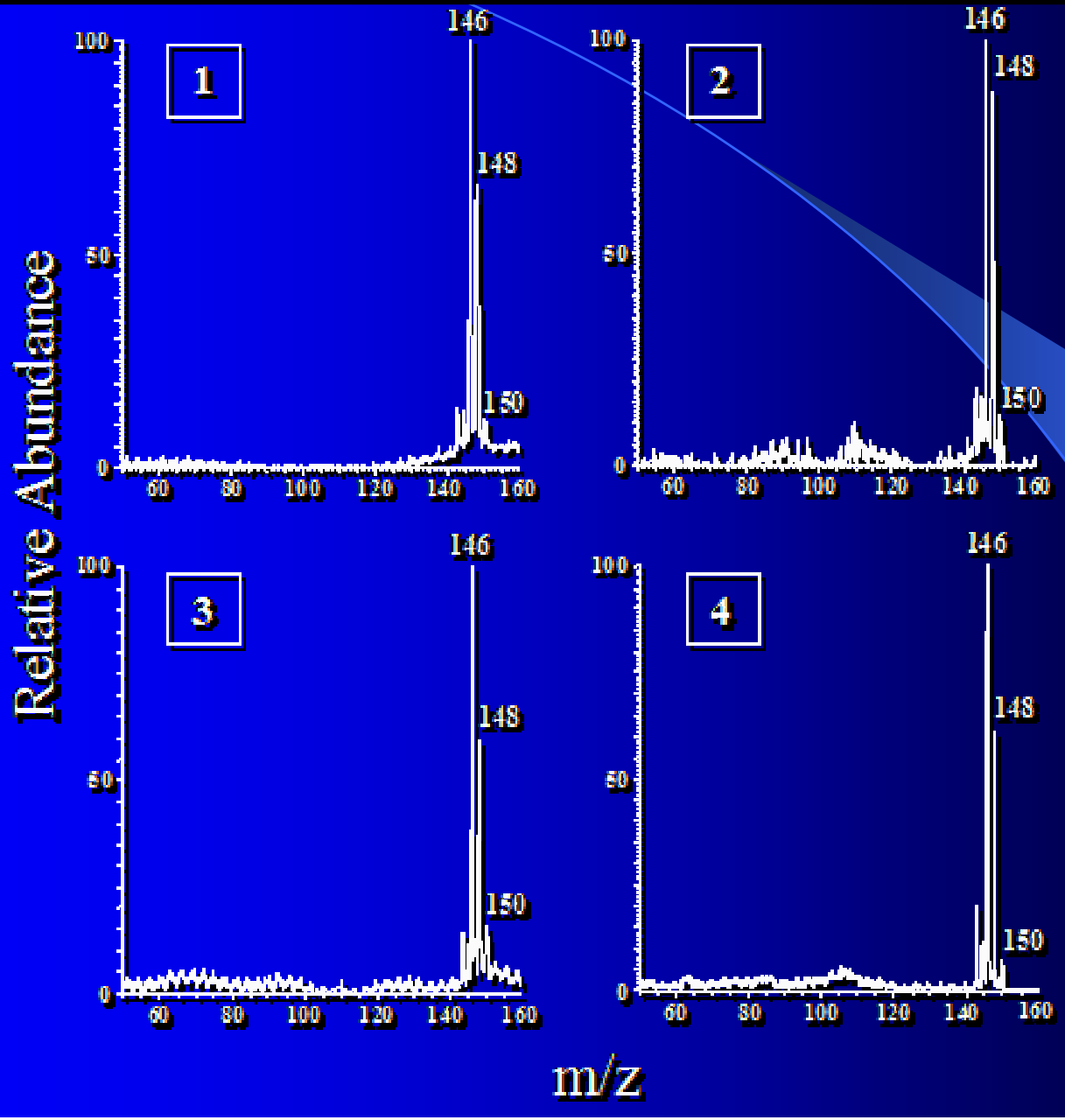




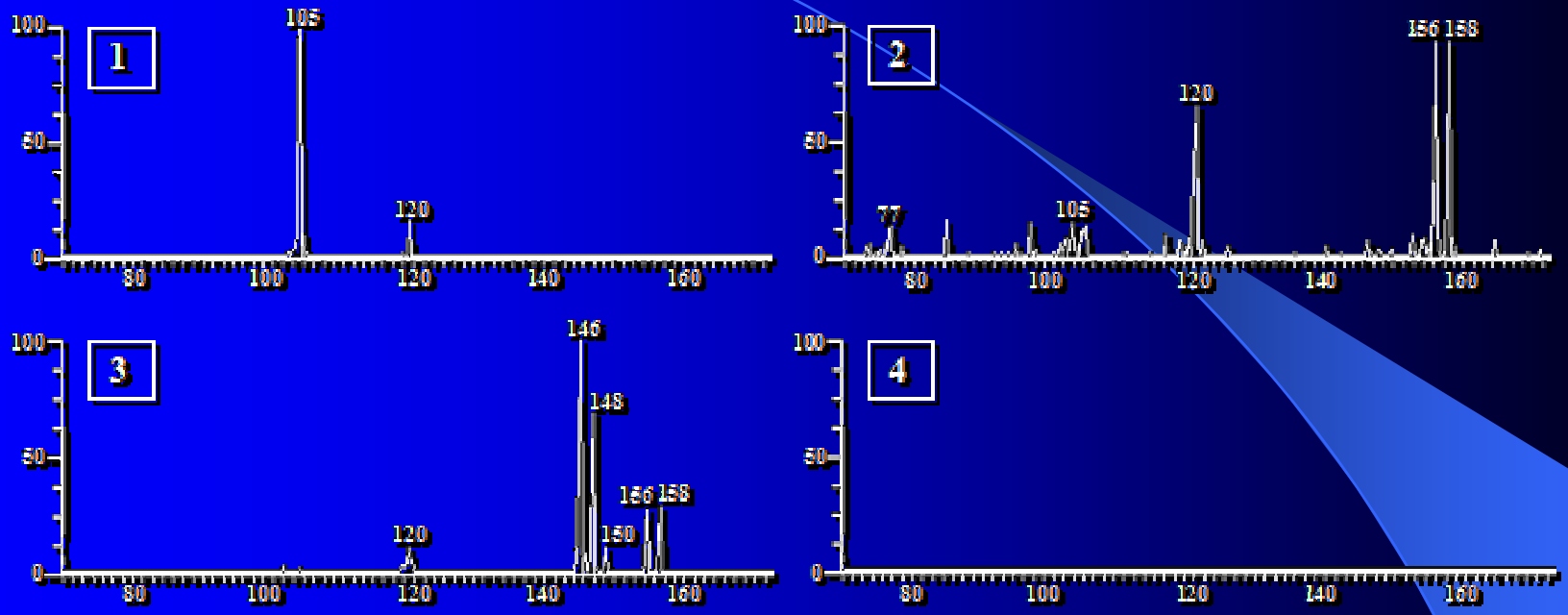


2x2 CIT Array
r_o = 2.5 mm, z_o = 2.7 mm

Four-Channel Mass Spectrometer

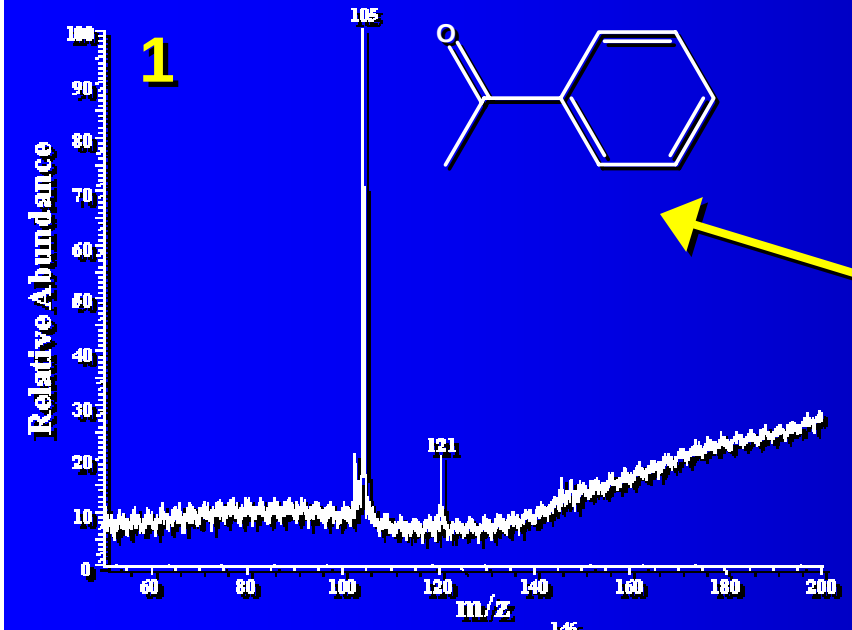


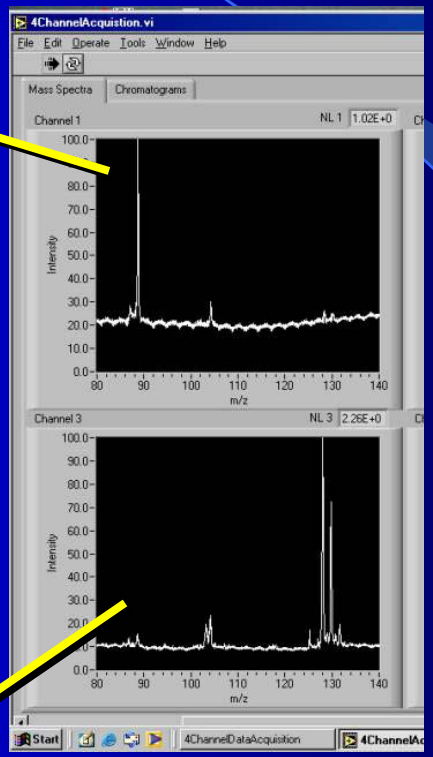
High-Throughput Analysis

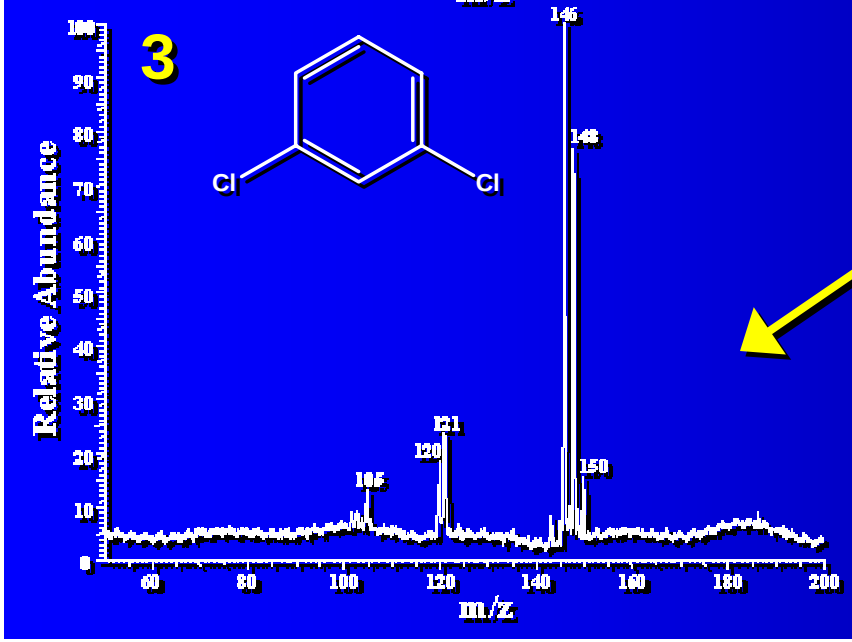


- Acetophenone introduced into channel 1
- Bromobenzene introduced into channel 2
- 1,3-Dichlorobenzene introduced into channel 3

2-Channel EI Experiment



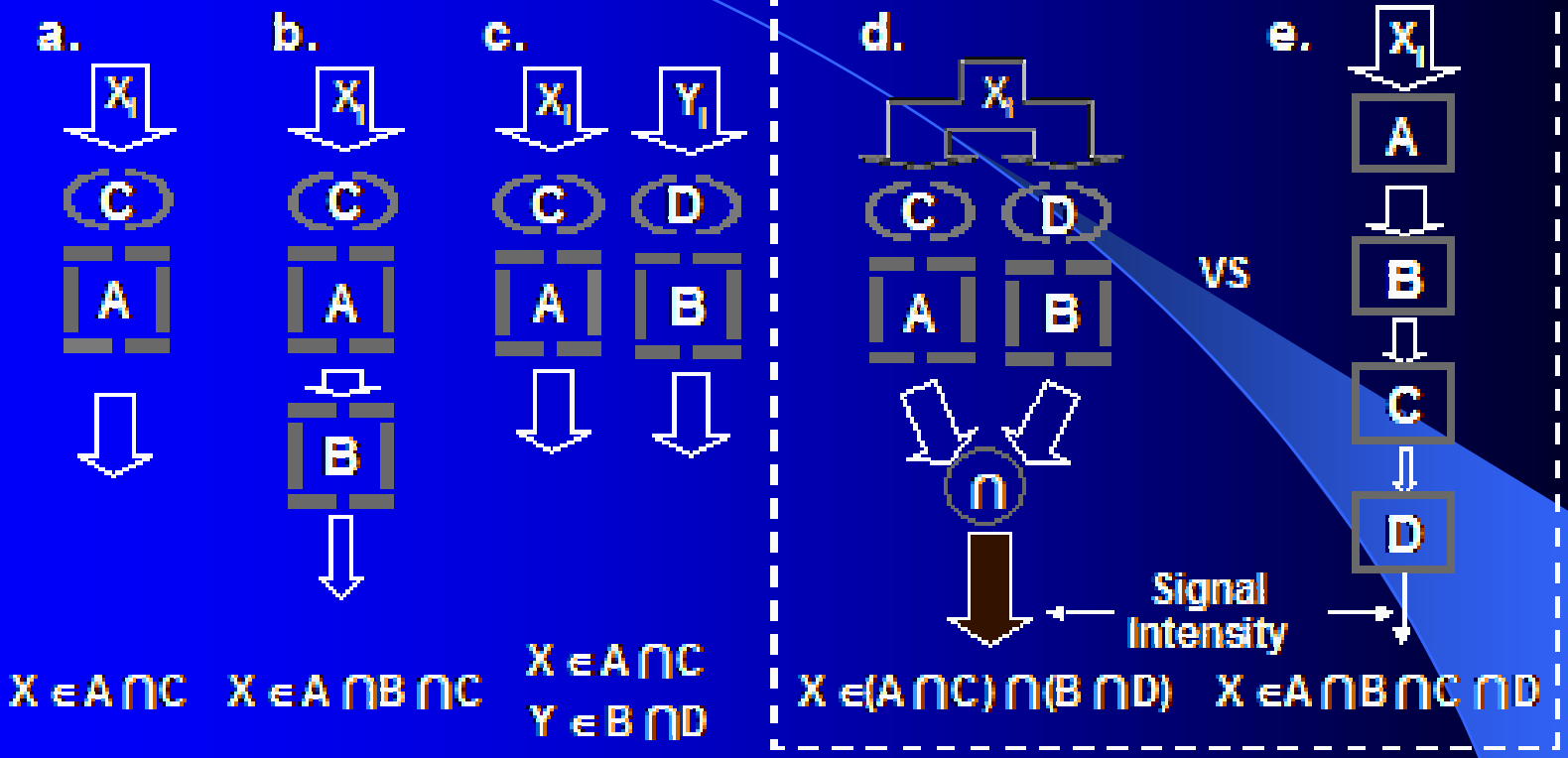




Acetophenone in channel 1

1,3-Dichlorobenzene in channel 3

Multiplexed MS



Pre-MS operation

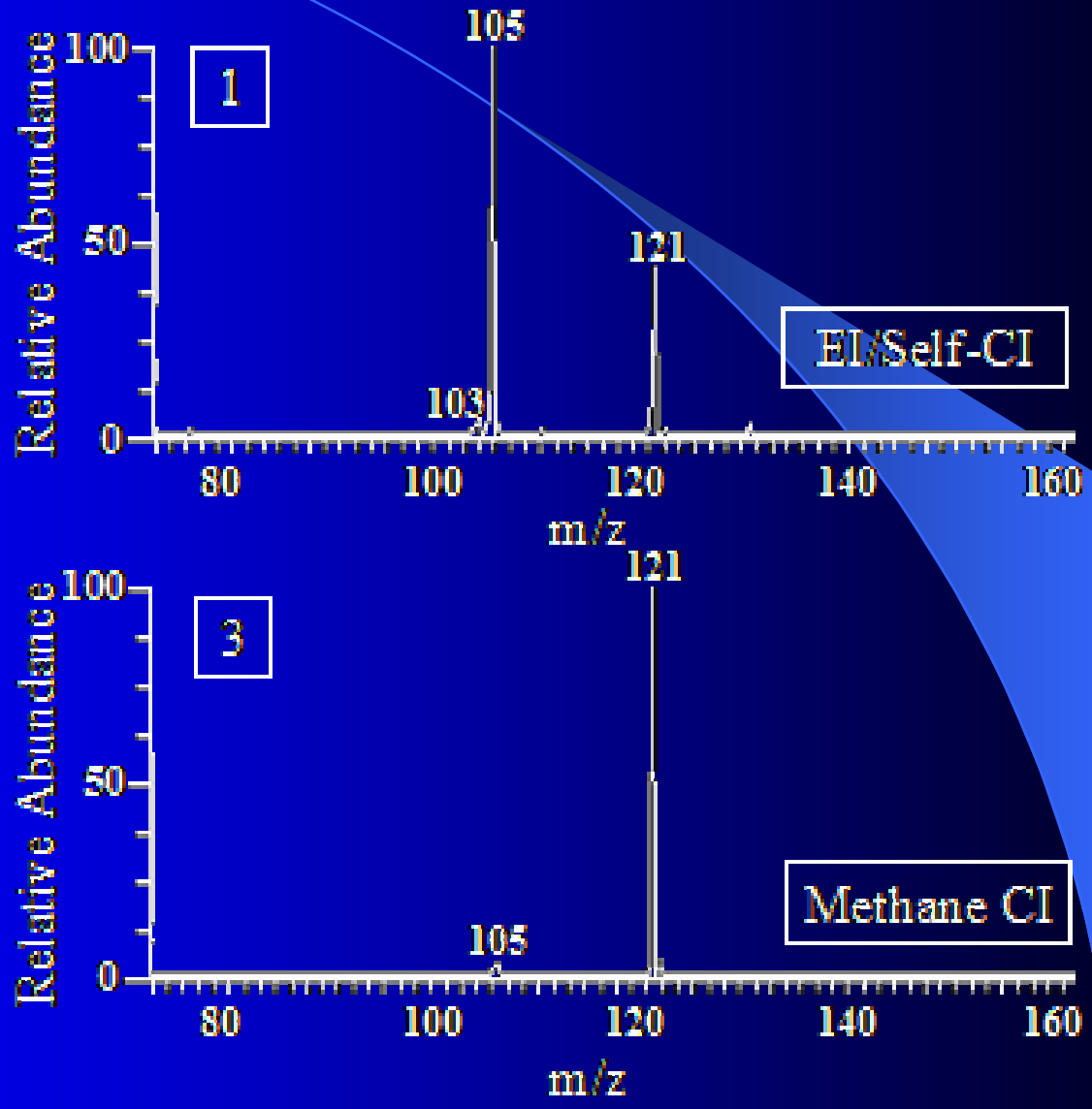
MS operation

Post-MS operation

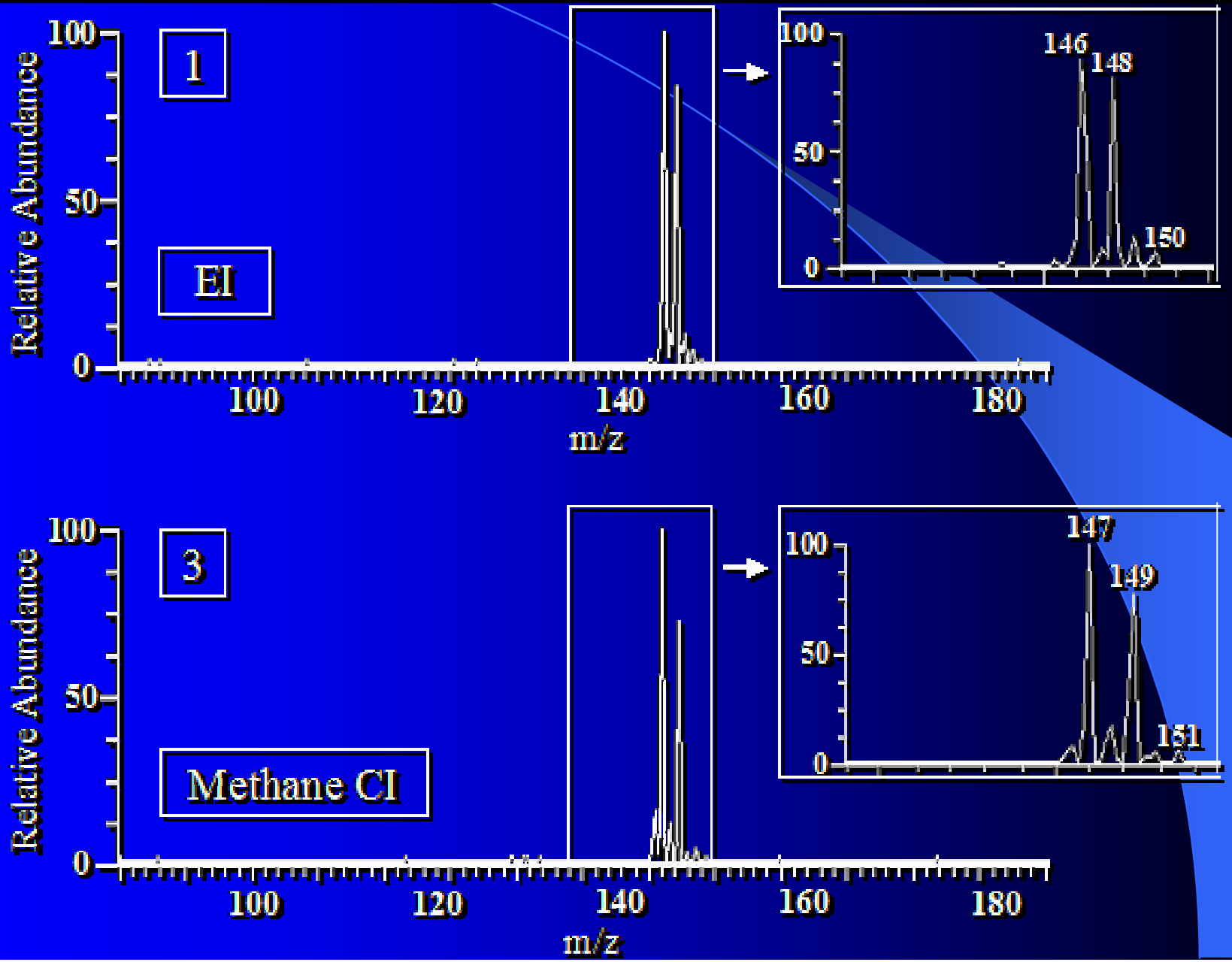
- X_i, Y_i : Analytes
- A, B, C, D : Operation/Set defined by corresponding operation
- Size of Arrows indicates Signal Intensity; NOT size of set

Simultaneous Analysis by EI and CI

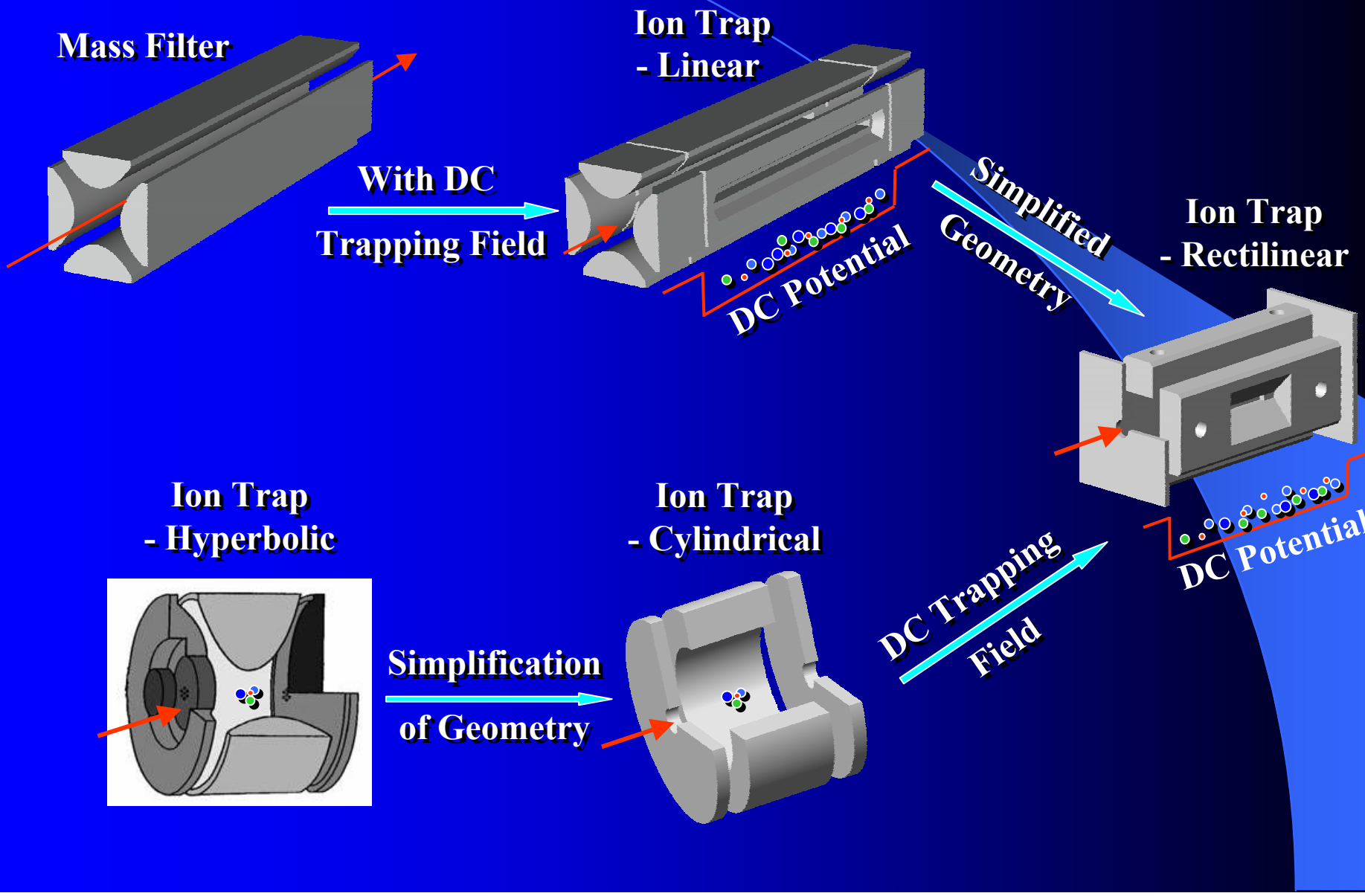
acetophenone



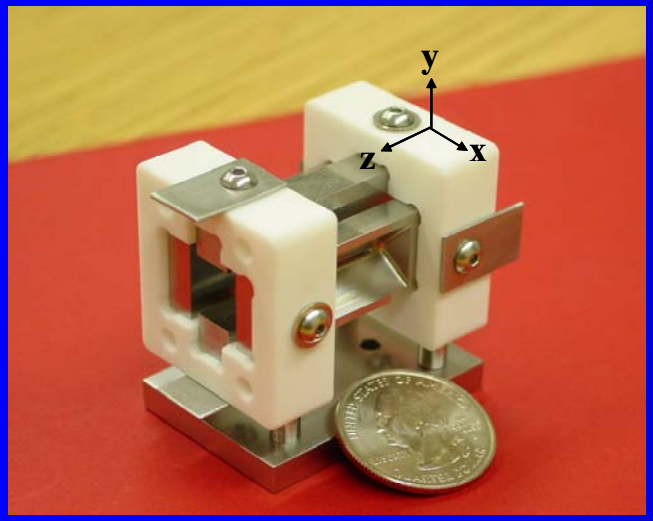
Simultaneous Analysis by EI and CI

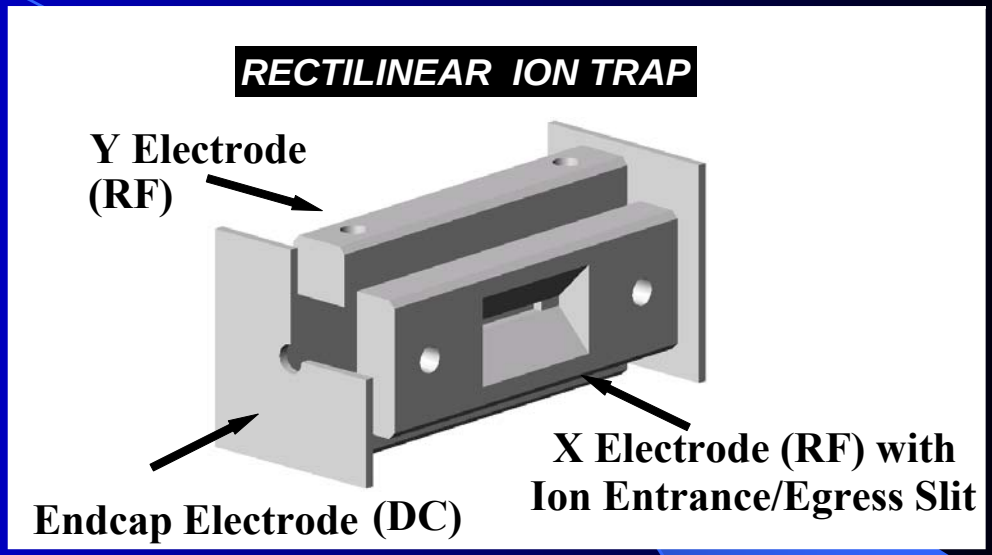


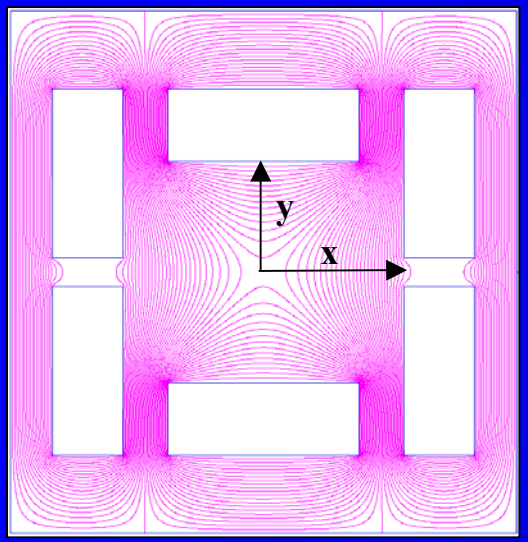
Evolution of the Rectilinear Ion Trap (RIT)



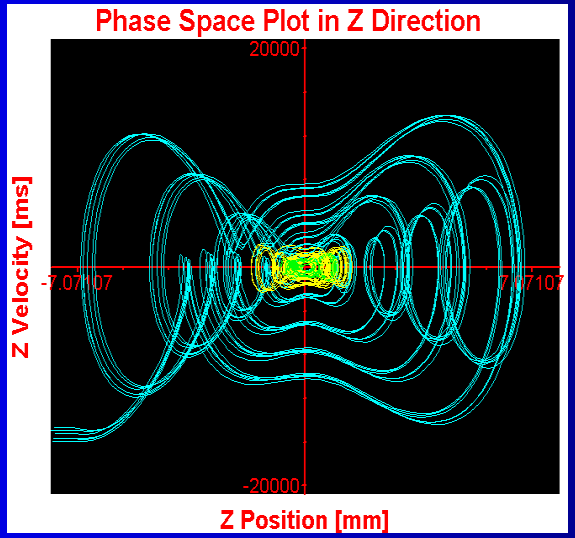
Miniature Rectilinear Ion Trap







Calculated electric field

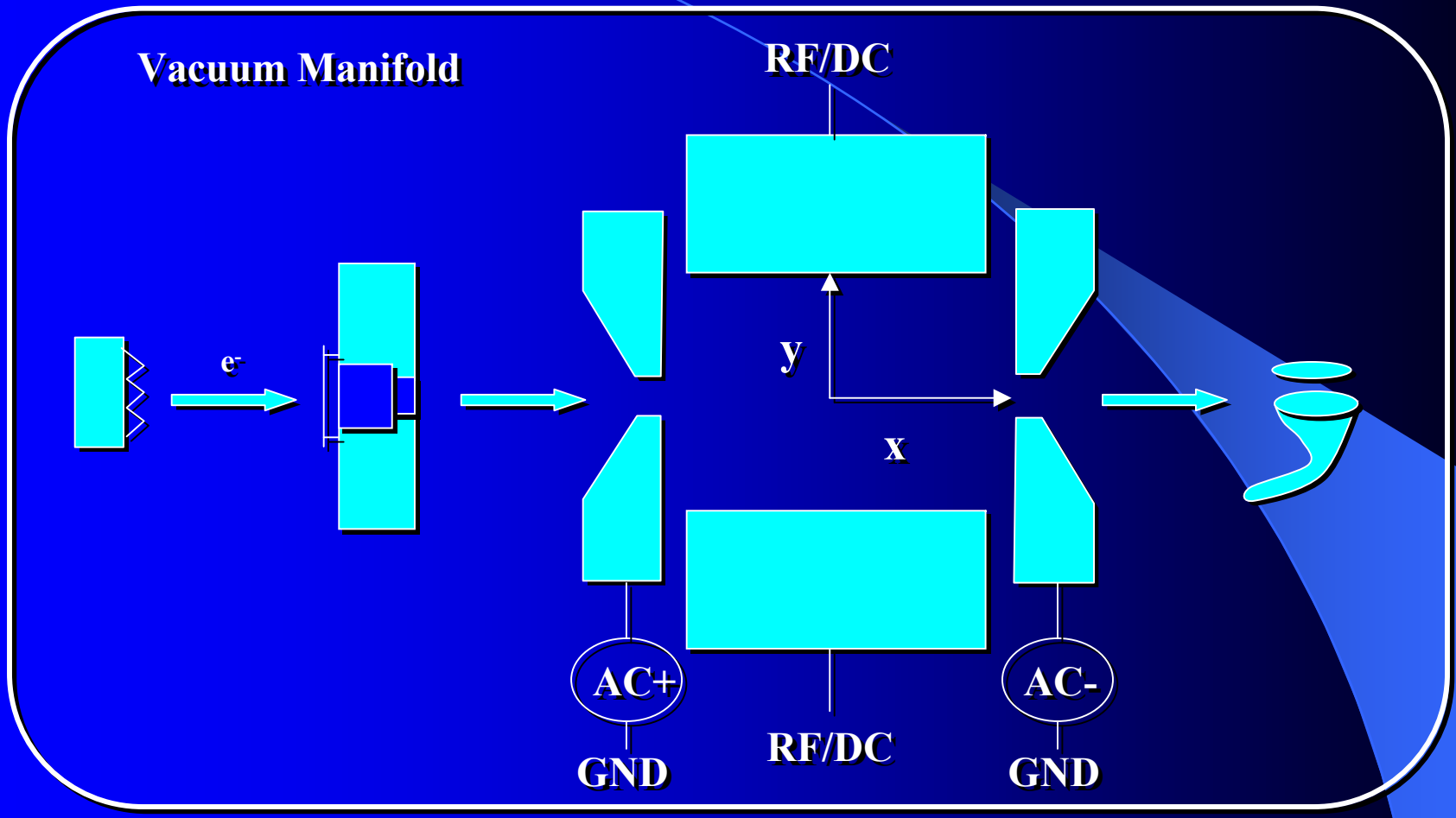


Simulation of ion trajectory

Patent Pending

Elongated Geometry of the RIT enables it to store 100x more ions compared to the CIT. This enables enhanced sensitivity and resolution.

Experimental



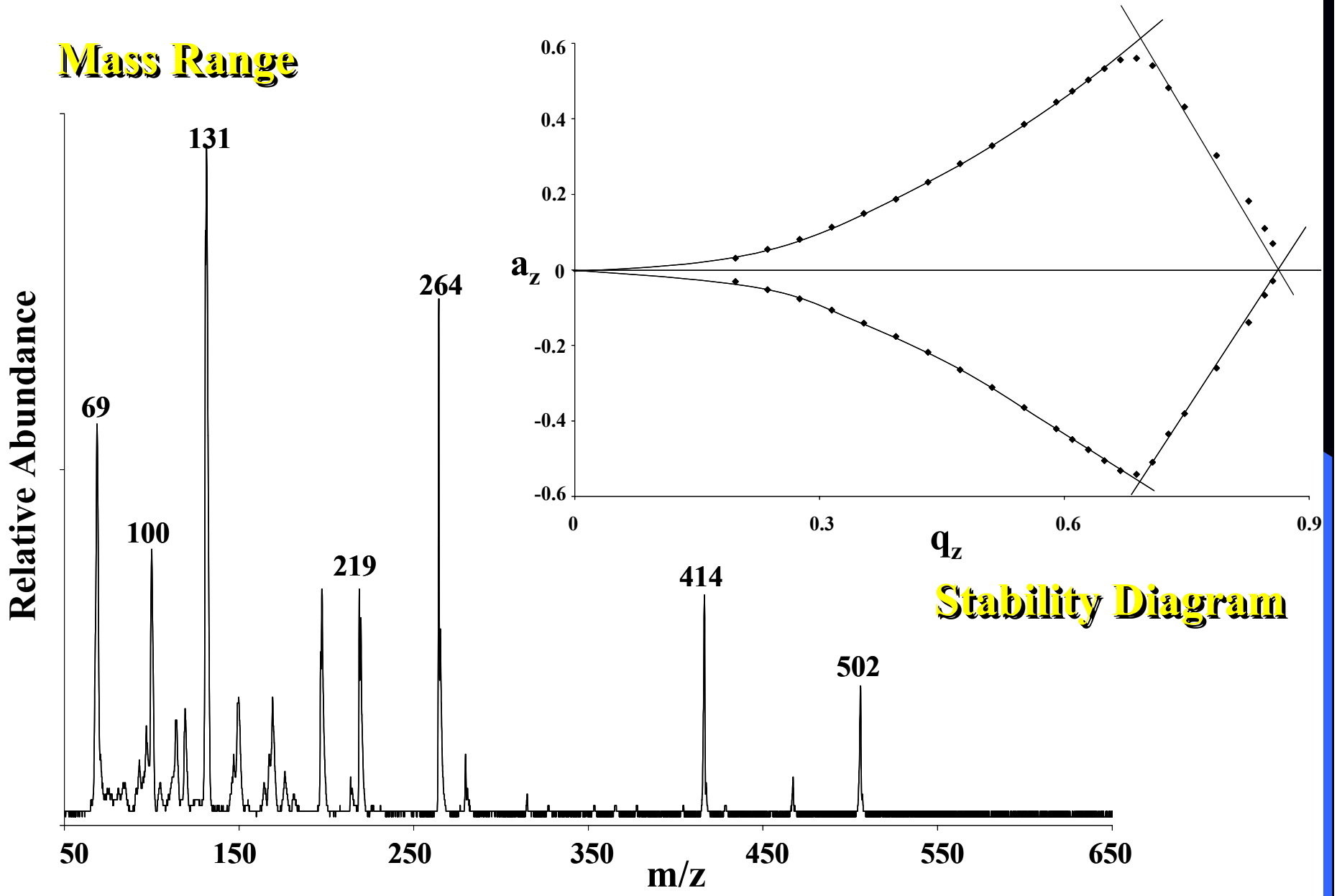
Filaments

Electron Ion Gate

RIT

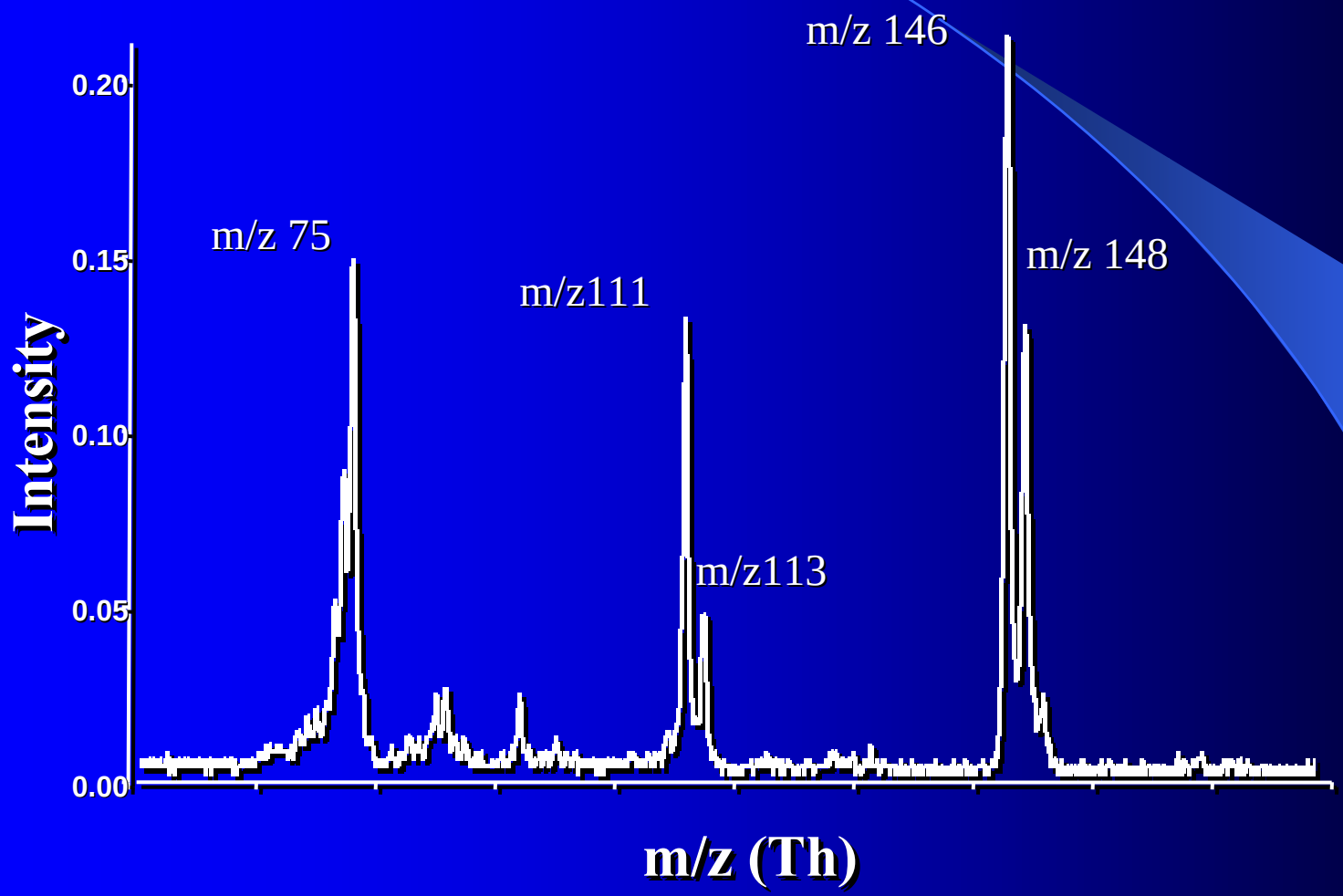
Electron Multiplier

Characterization of the Miniature RIT

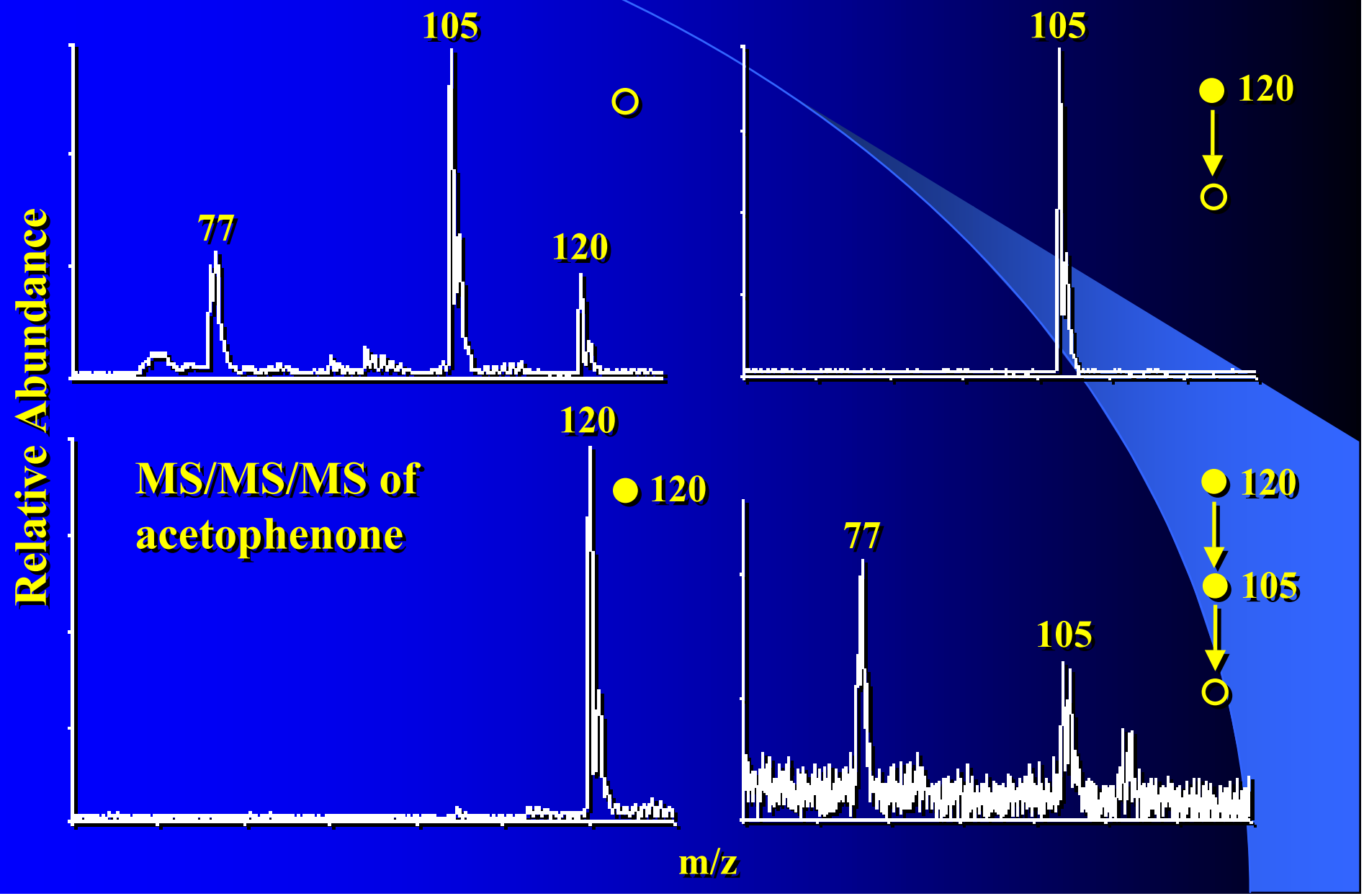


Characterization of the Miniature RIT

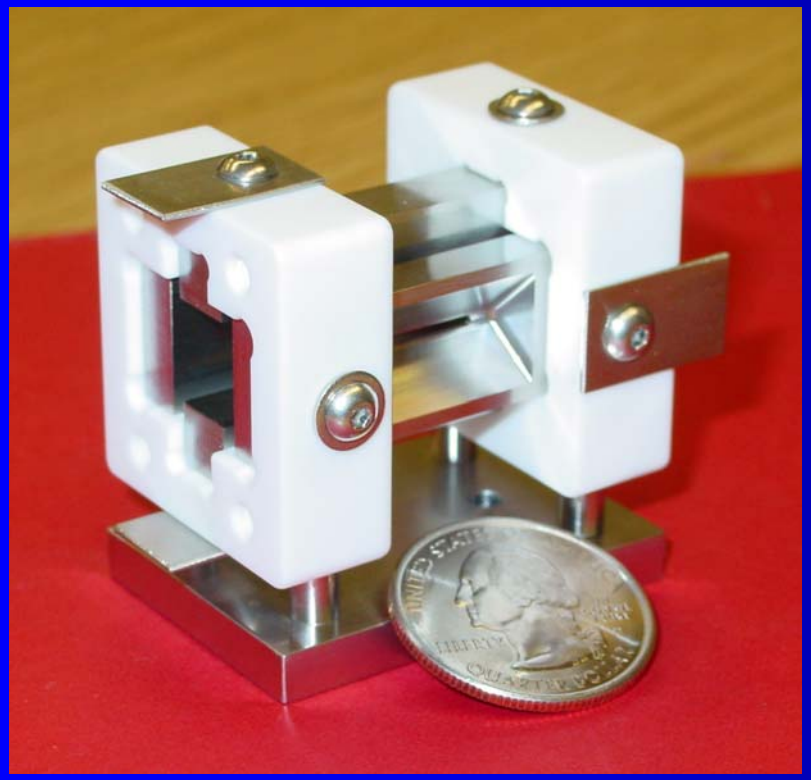
MS Spectrum of Dichlorobenzene – Resonance Ejection

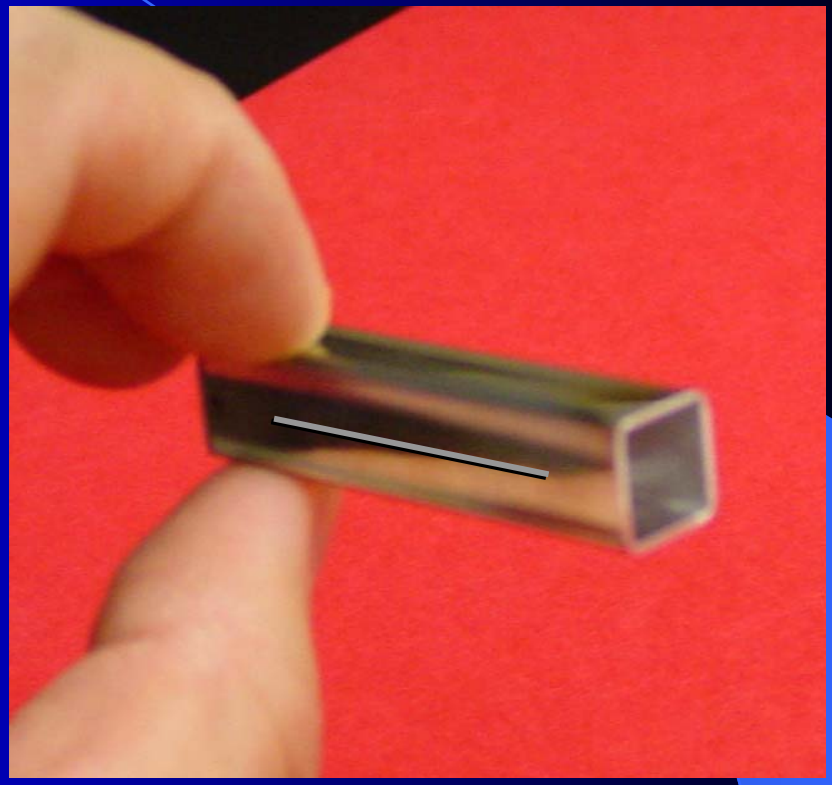


MS^n Capability of the RIT



RIT Configuration





Version 1.0 **Version 2.0**

Towards the 2 lb mass spectrometer system

New Mass Spectrometers

- Miniature Cylindrical Ion Trap (ver. 7.0)
- Multiplexed Ion Trap Array
- Hybrid CIT/Ion Mobility Mass Spectrometer
- Multiplexing & Networking
- Ultra-light MS/MS instrument (RIT)
- Micro-CIT Array

Sampling Systems

- Miniature Membrane Introduction System (MIMS)
- Single-sided Membrane System (SS-MIMS)
- Fiber Introduction Mass Spectrometry (FIMS)

Ionization

- Atmospheric Pressure Corona Ionization

Ion/Molecule Reactions

- Specific Reactions for Phosphate Esters
- Specific Reactions for Nitroaromatics

Aston Lab 2003

Publications

1. Garth E. Patterson, Andrew J. Guymon, Leah S. Riter, Mike Everly, Jens Griep-Raming, Brian C. Laughlin, Zheng Ouyang, and R. Graham Cooks, "A Miniature Cylindrical Ion Trap Mass Spectrometer," Anal. Chem. 2002, 74, 6145-6153.
2. Leah S. Riter, Yanan Peng, Robert J. Noll, Garth E. Patterson, Tenna Aggerholm and R. Graham Cooks, "Analytical Performance of a Miniature Cylindrical Ion Trap Mass Spectrometer," Anal. Chem. 2002, 74, 6154-6162.
3. Leah S. Riter, Brian C. Laughlin, Eugene Nikolaev and R. Graham Cooks, "Direct Analysis of Volatile Organic Compounds in Human Breath using a Miniaturized Cylindrical Ion Trap Mass Spectrometer with a Membrane Inlet," Rapid Commun. Mass Spectrom., 2002, 16, 2370-2373.
4. Eugene Nikolaev, Leah S. Riter, Brian C. Laughlin, Eric Handberg and R. Graham Cooks, "Trace Analysis of Organics in Air by Corona Discharge Atmospheric Pressure Ionization using an Electrospray Ionization Interface," European J. Mass Spectrom., In Press.
5. Hao Chen, Xubin Zheng, R. Graham Cooks, "Ketalization of Phosphonium Ions by 1, 4-Dioxane: Selective Detection of the Chemical Warfare Agent Simulant DMMP in Mixtures Using Ion/Molecule Reactions," J. Am. Soc. Mass Spectrom., 2003, 14, 182-188.
6. Leah S. Riter, Eric S. Handberg, Brian C. Laughlin, Hao Chen, Garth E. Patterson and R. Graham Cooks, "Ion /Molecule Reactions Performed in a Miniature Cylindrical Ion Trap Mass Spectrometer," Analyst, 2003, 128, 1112-1118.
7. Leah S. Riter, Eduardo C. Meurer, Ismael Cotte-Rodriguez, Marcos N. Eberlin and R. Graham Cooks, "Solid Phase Micro-Extraction in a Miniature Ion Trap Mass Spectrometer," Analyst, 2003, 128, 1119-1122.
8. Amy M. Tabert, Jens Griep-Raming, Andy J. Guymon and R. Graham Cooks, "High Throughput Miniature Cylindrical Ion Trap Array Mass Spectrometer," Anal. Chem., In Press.