



Hand-Portable GC-TMS
Instrument for Measurement of
Chemical Agents and Hazardous
Compounds in
Harsh Environments

The 6th Workshop on Harsh
Environment Mass Spectrometry
Cocoa Beach, Florida
September 20, 2007

- Harsh environments and trends in field measurement analyses.
- Choosing a field measurement technique.
- Why mass spectrometry?
- The GUARDION-7™:
 - SPME fiber sample introduction
 - low thermal mass gas chromatograph
 - toroidal ion trap mass spectrometer
 - simple graphical user interface
- GC-TMS Performance Data:
 - chemical agents
 - explosives
 - hazardous chemicals

- HEMS Booklet– Welcome Page
 - Mass spectrometry in:
 - Space
 - Earth's oceans
 - Battlefield scenarios
 - *Author's input: any non-traditional laboratory setting*
 - Common features in MS deployment:
 - High reliability
 - Small size
 - Low power requirements
 - *Author's input: reduce cost burden per analysis*

- Prominent analyses trends analytical measurements in the field:
 - *Faster and faster analysis methods*
 - *Increase measurement sensitivity*
 - *Increased measurement selectivity*
 - *Increase productivity*
 - *Reduce labor costs*



Choosing a Field Measurement Technique

| | |
|-----------------------------------|---|
| Analyte to be detected | Determination of agents most likely to be encountered |
| Sensitivity | Lowest concentration of target analyte that results in positive response; ideally, lower than levels necessary for injury to personnel |
| Resistance to interference | Factors such as smoke, moisture, or other chemicals that prevent the device from accurately providing a response |
| Response time | Time to collect, analyze, and provide feedback |
| Start-up time | Time to assemble and deploy the device |
| Detection status | Vapor, liquid, and/or aerosols |
| Alarm capability | Audible, visual, or both |
| Portability | Ease of transport, which encompasses weight and dimensions |
| Power capabilities | Battery versus alternating current |
| Battery needs | Quantity and type of batteries |
| Operational environment | Extremes of conditions under which the device operates |
| Durability | Amount of abuse the device withstands |
| Procurement costs | Cost per device needed |
| Operator skill level | Skill involved in using the device |
| Training requirements | Number of hours and type of educational background required for operation |

- **Detection Paper**
 - Sensitive (spot diameter & density)
 - Inexpensive
 - Long response time (15-30 min)
 - Poor specificity – false positives (brake fluid, antifreeze, insect repellent)
- **Colorimetric Tubes**
 - Sensitive – 0.005 mg/m^3 (length colored zone in tube)
 - Tube required for each chemical (must know target analyte)
 - Poor specificity – false positives
 - Chip measurement system (pump, flow controller, optical reader 10 capillaries in 20 s)

- Chemically selective coated piezoelectric crystal (measures change in resonant frequency)
- Specific coatings for specific chemicals or chemical types
- Good sensitivity
- Hand portable
- Easy to use
- Poor selectivity

- Used for vapor or solid samples
- Various types of detectors
 - Photoacoustic (modulated IR → absorbed light → heat → gas expansion → signal)
 - Filter-based
 - Differential absorption (vapor cloud)
(2 laser beams – one absorbed, the other not)
 - Passive (vapor cloud)
- Poor sensitivity
- Poor selectivity
 - Broad spectral bands
 - Easily affected by contamination

- Requires adsorption on specially prepared surface
- High sensitivity
- Moderate selectivity
- Hand-portable
- Easy to operate
- Can detect through transparent container

- Sensitivity depends on detector
- Good selectivity
 - Characteristic retention times
 - Improved with selective detectors
- Variety of detectors
 - Flame photometric (sulfur, phosphorus)
 - Chemiluminescence (sulfur, nitrogen)
 - Thermionic ionization (nitrogen)
 - Photoionization
 - Mass spectrometry
- Requires carrier gas supply & detector gases or reagents
- Can be miniaturized (low power)

- Soft ionization, drift time in buffer gas
- Sensitive – 0.03 mg/m³
- Simpler than MS (no vacuum system)
- Hand-portable
- Moderate selectivity – false positives
 - Poor resolution
 - Easily contaminated (reactive ion chemistry)
 - Can be greatly improved with GC
- Can be used for many different chemicals (i.e., chemical agents, explosives, drugs)

- GC/MS is the legal and laboratory standard for chemical identification
- High sensitivity and high selectivity (especially using GC inlet)
 - High Sensitivity \Rightarrow Low false negative rates
 - High Selectivity \Rightarrow Low false positive rates
- Much higher selectivity than spectroscopic techniques or ion mobility spectrometry (i.e., molecular weight, fragment ions, relative intensities vs. one ion mobility value)

Why Ion Trap MS?

- Simple, rugged design (no critical alignment of ion optics)
- Less stringent vacuum requirements (requires 1 mtorr operating pressure)
- High duty cycle \Rightarrow high sensitivity
- Low power (especially with small ion trap mass analyzers)

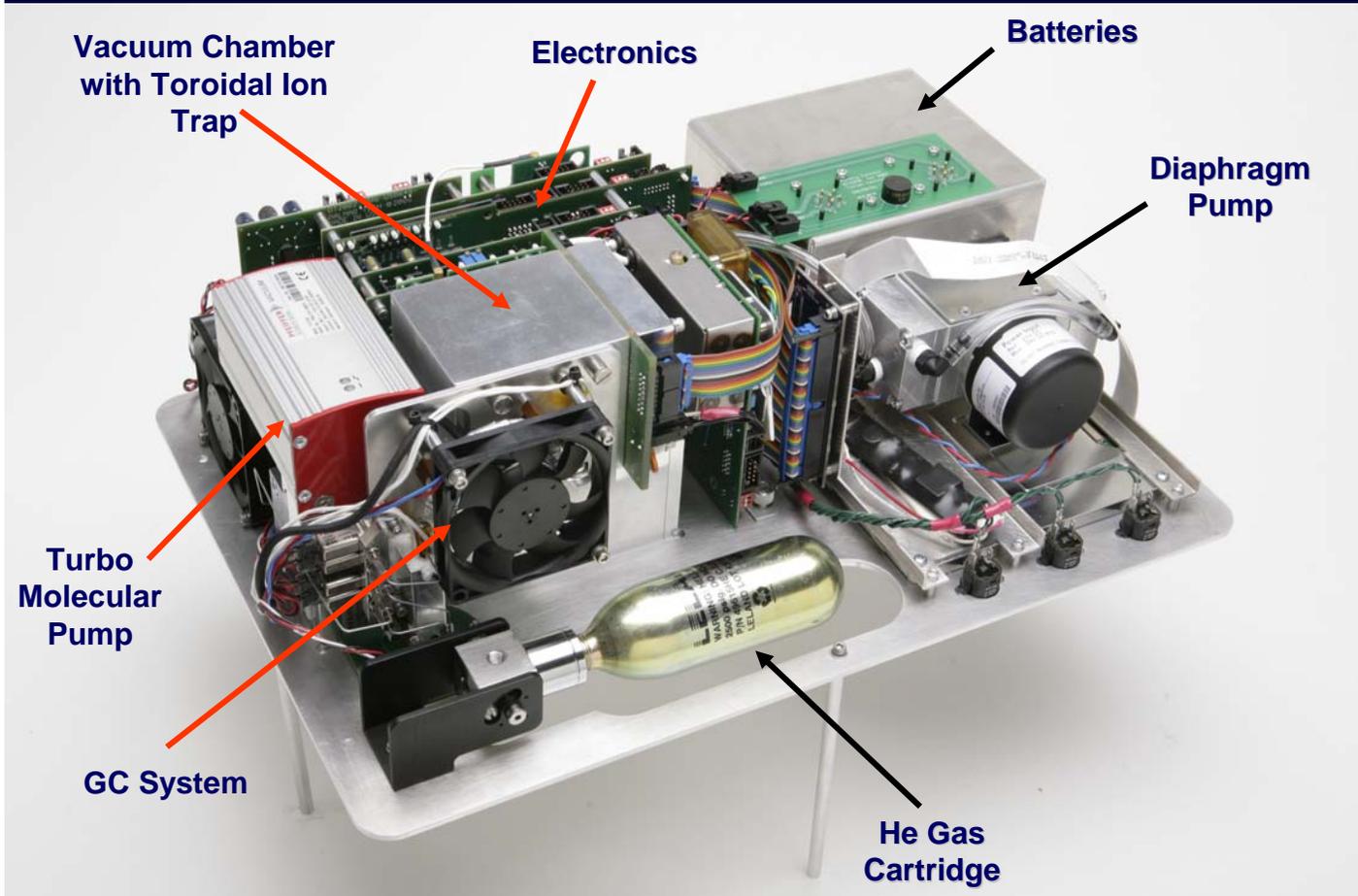
Portable—Fast—Reliable—Easy

Specifications

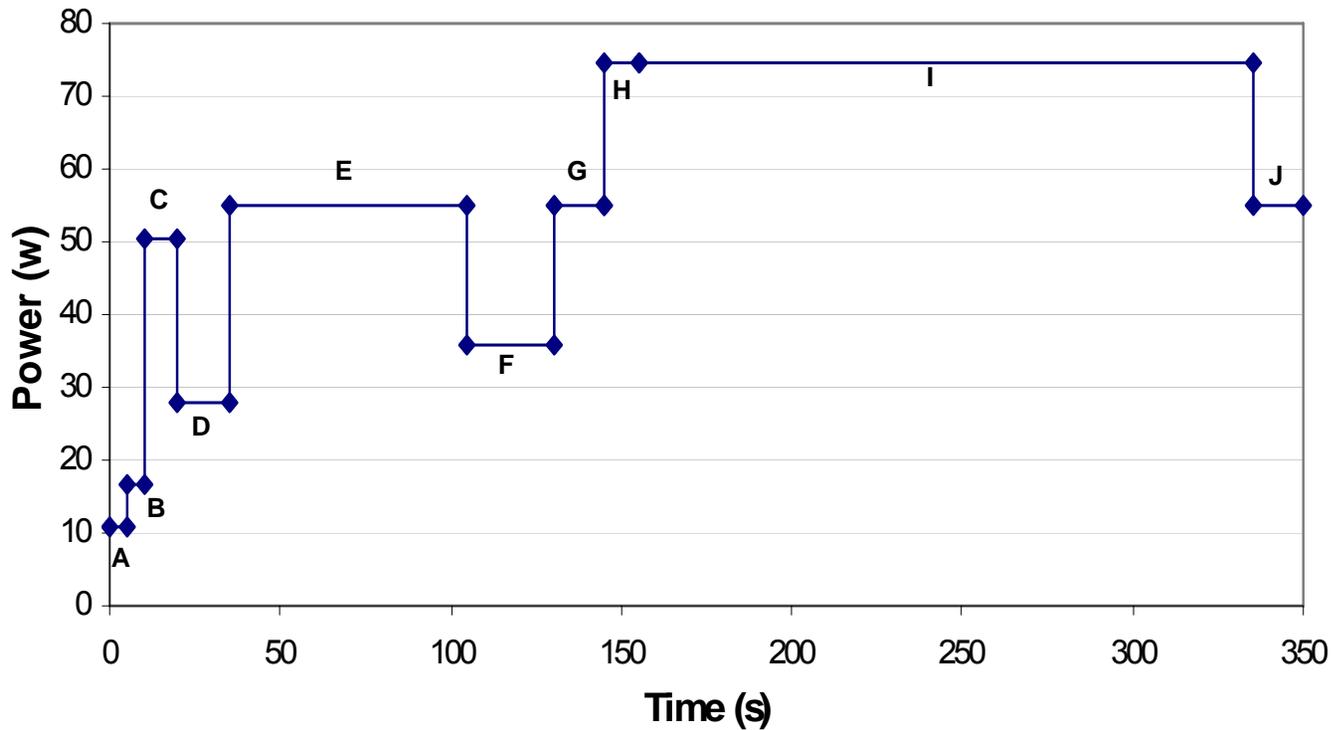


- **Dimensions:** 47 cm x 36 cm x 18 cm
- **Weight:** <11 kg or 25 lbs (including batteries)
- **Peak Power:** ~ 80 W
- **Sample Introduction:** SPME
- **GC:** RTX-5, 5 m x 0.1 mm x 0.4 μ m
- **TMS:** Toroidal Ion Trap
- **Mass Range:** 45 to 500 Daltons
- **Resolution:** < Unit mass
- **Vacuum:** turbo molecular and roughing pumps
- **~50 Analysis:** battery power
- **~100 Analyses:** cartridge He gas supply

Portable



CB007 Power Consumption Profile / Run



Events

- A Start
- B LCD Screen On
- C Roughing Pump On
- D Stable Roughing Pump
- E Turbo Pump On
- F Stable Turbo Pump
- G Heating Injector + Transferline
- H SPME ready
- I Start GC-MS Run
- J Start Analysis Time



Battery Characteristics

24 volts, 7.5 Ah lithium/sulfur dioxide (LiSO₂)

GC-TMS Run Time

5 min (including cooling and data analysis)

Total Power/GC-TMS Run

63.5 W

Number of GC-TMS Runs per Battery

~50 (the GC-MS was on for 4.5 h)



Cylinder characteristics

90 cc stainless steel cylinder at 2500 psig

GC gas flow conditions

Column head pressure: 25 psig

Column maximum flow: 0.7 scc/min @ 20°C

Split-splitless injection: Split ratio 20

GC-TMS run time

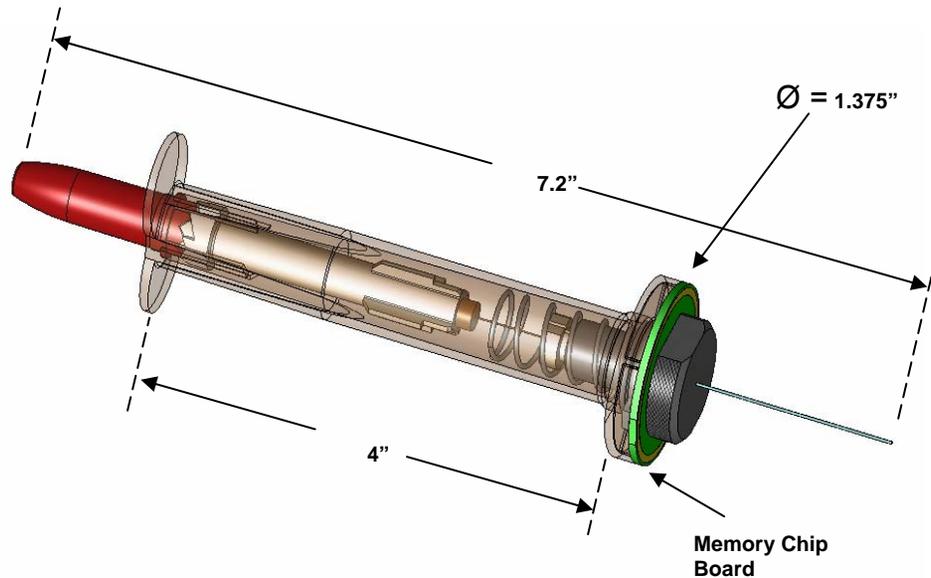
5 min (including cooling and data analysis)

Number of GC-TMS runs/cylinder charge

~100 runs



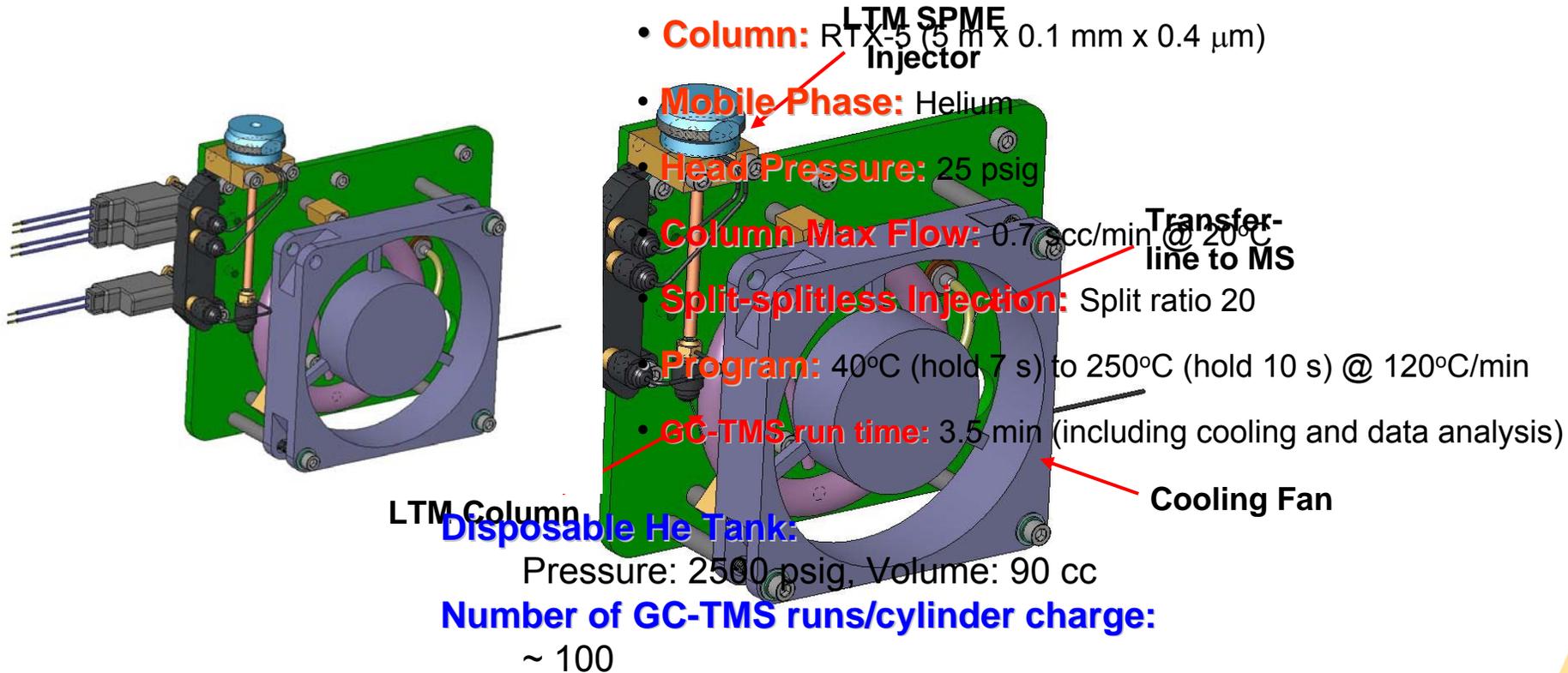
SPME Fiber Sampling Syringe

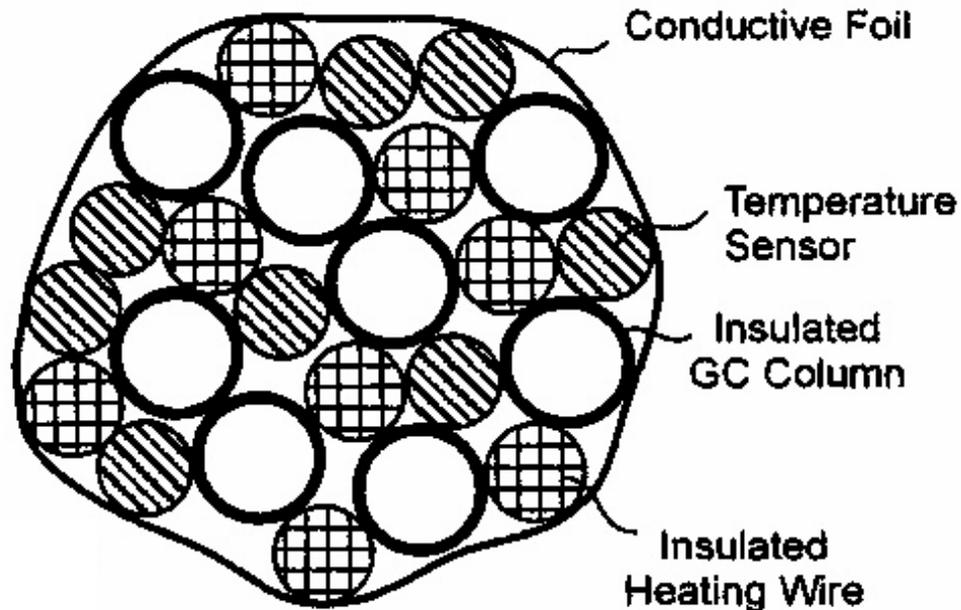


- One hand operation
- Exposes and retracts sampling fiber in and out of a protective sheath
- Contains memory chip board for recording sample information for chain of custody purposes



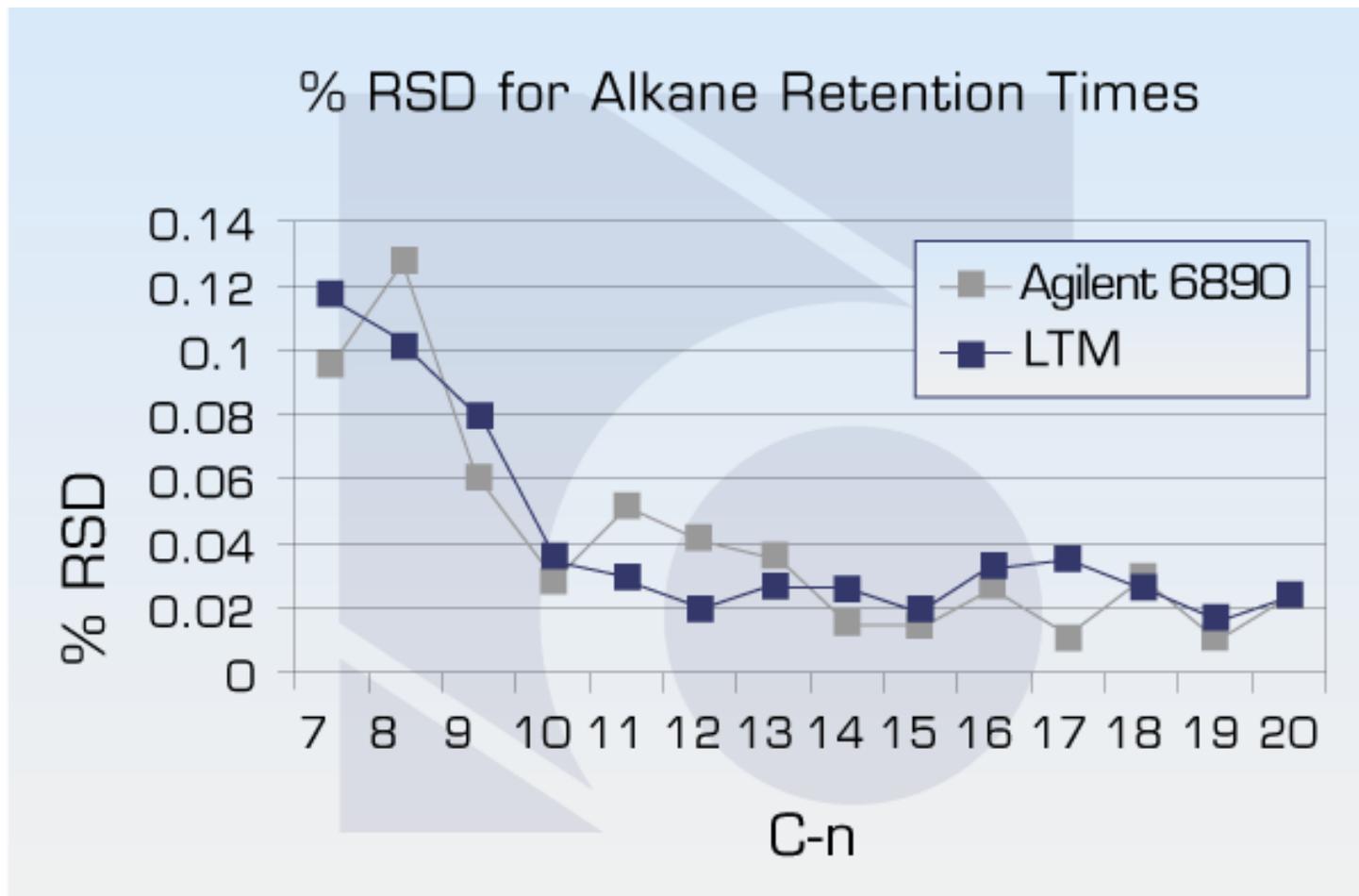
Low Thermal Mass Capillary GC System





Cross Section of Toroid

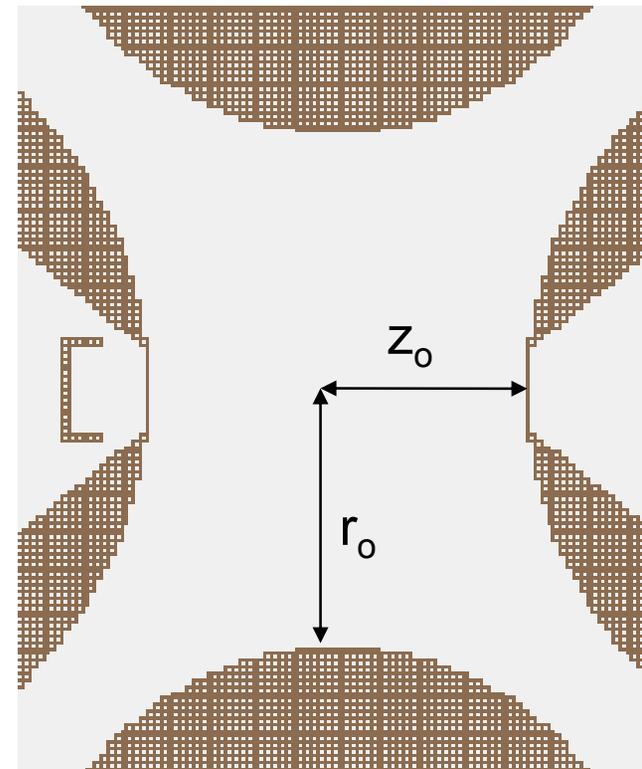
Courtesy RVM Scientific

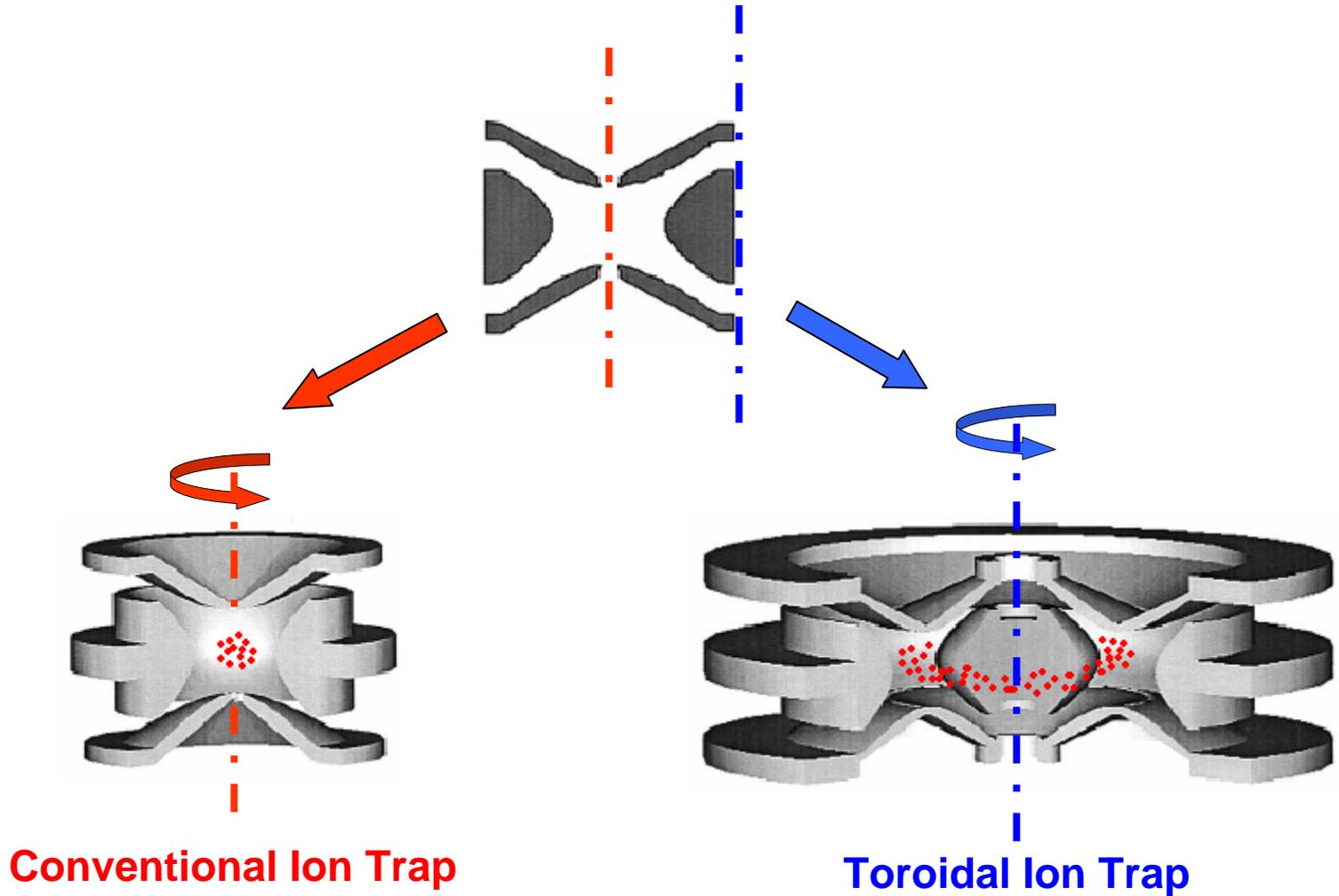


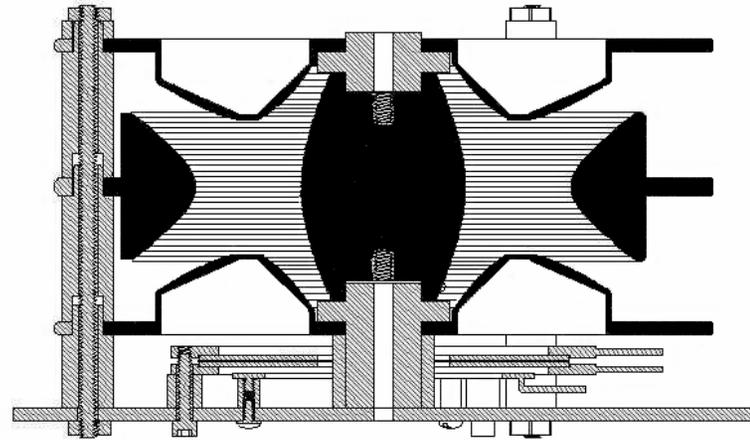
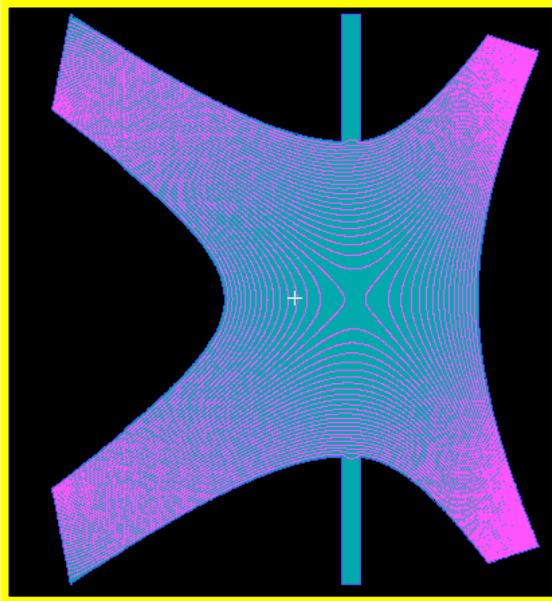
Sloan, K.M., et al., Field Anal. Chem. Technol. 5, 288-301 (2001)

- 3-D ion trap is an “ion bottle” with somewhat fixed relative dimensions (r_o vs. z_o)
- Ion-ion repulsion (space charge)
- Commercial traps optimized at $r_o = 1$ cm, ~ 16 kV_{p-p}
- Further increase in r_o not practical due to arcing of rf high voltage
- Decrease of r_o yields lower rf power, but will lead to earlier onset of space charge

$$q = \frac{-8eV}{m(r_o^2 + 2z_o^2)\Omega^2}$$







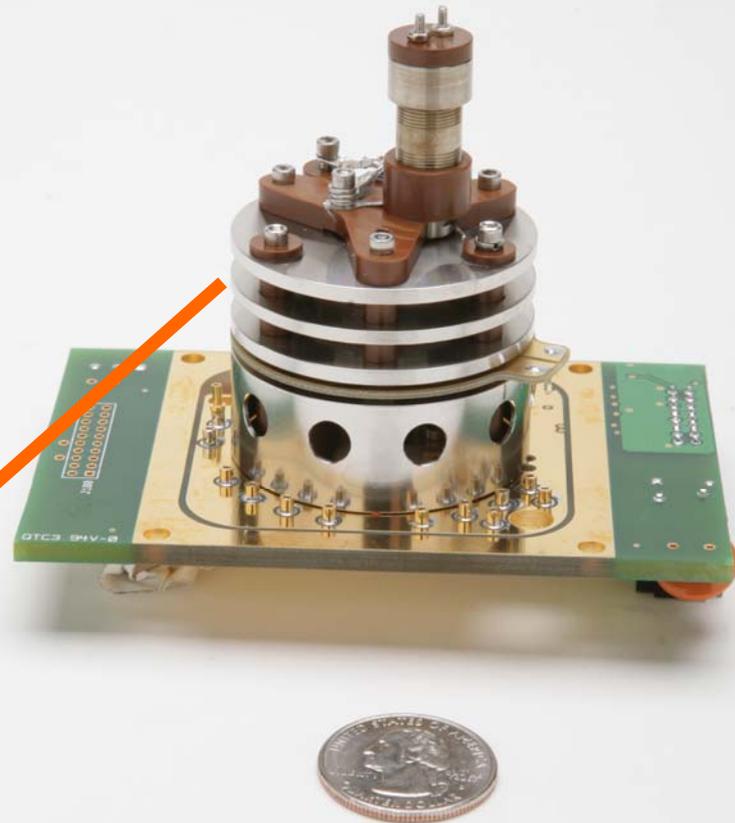
Asymmetric Corrections

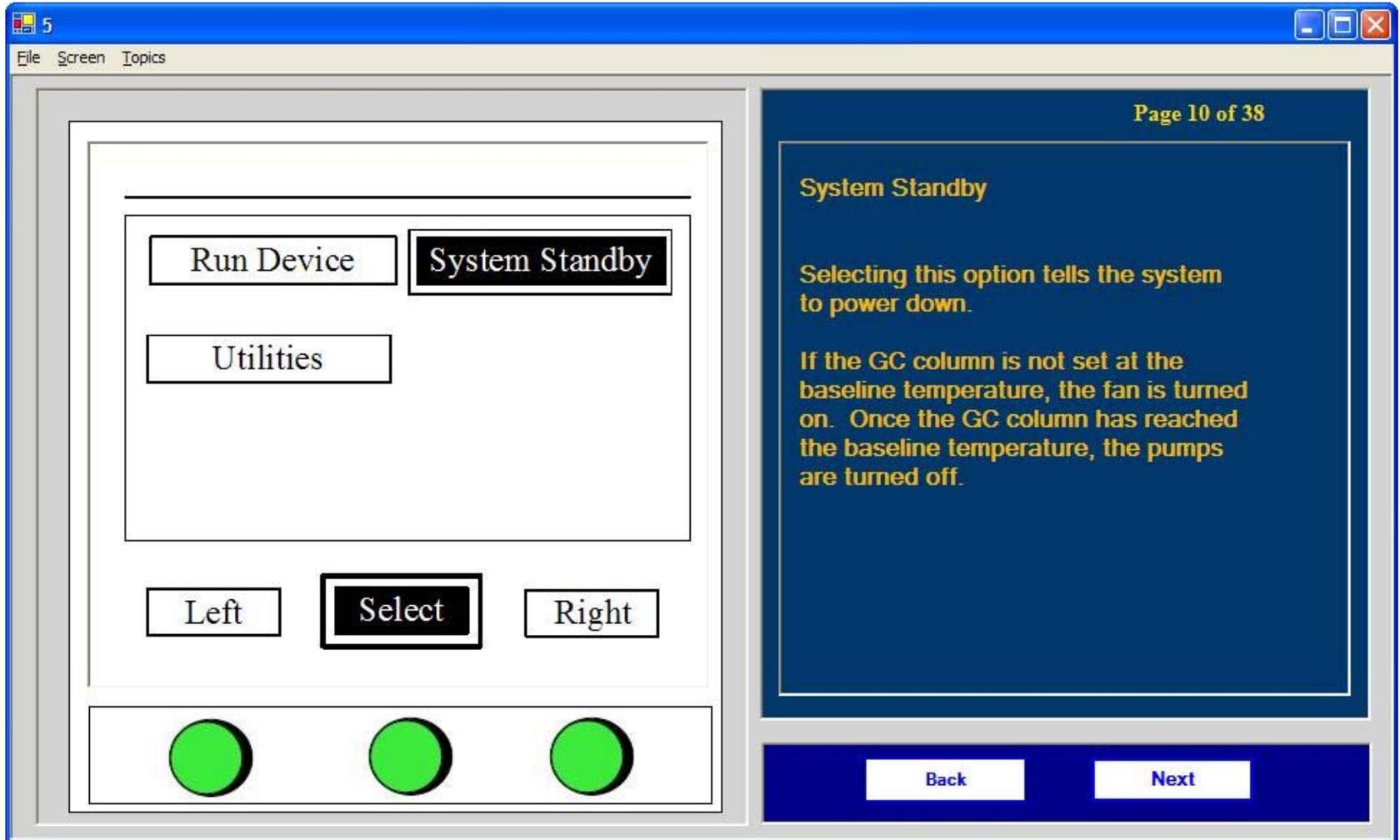
S.A. Lammert et al., Int. J. Mass Spectrom. 212, 25-40 (2001)



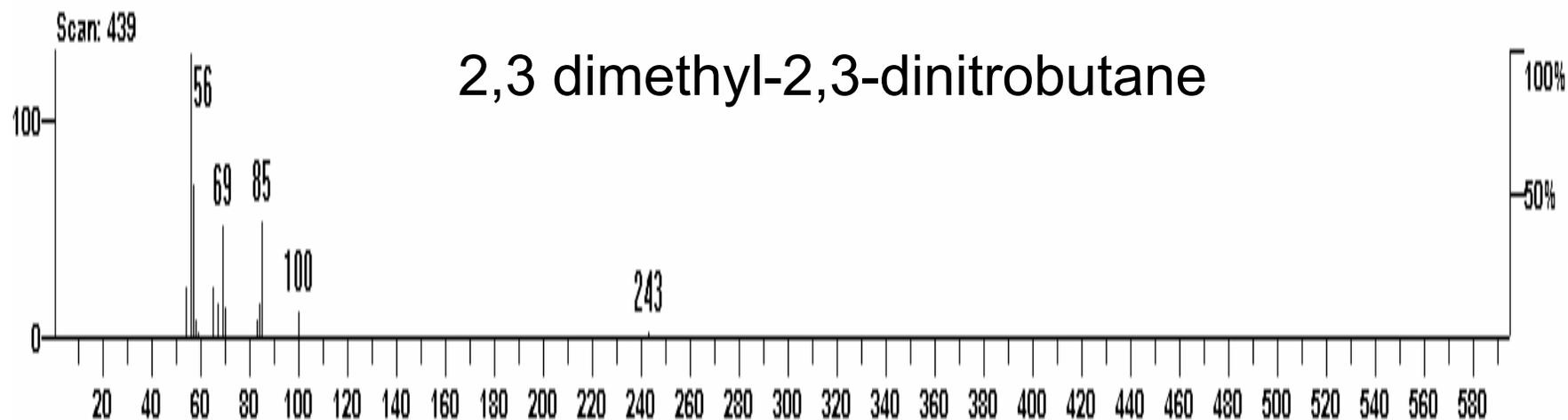
Miniaturized Toroidal Ion Trap Mass Spectrometer

- RF Trapping Field:
 - ~ 3 MHz
 - ~ 800 (max) V_{p-p}
- Resonance Ejection:
 - ~3.5 MHz - 65 KHz
 - ~5 V amplitude
- Pressures:
 - Sample: 1×10^{-6} to 4×10^{-5} mbar
 - He buffer gas: $\sim 2-4 \times 10^{-4}$ mbar



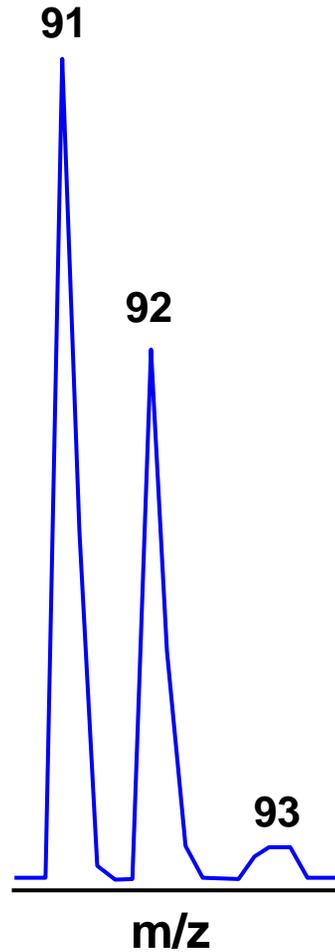


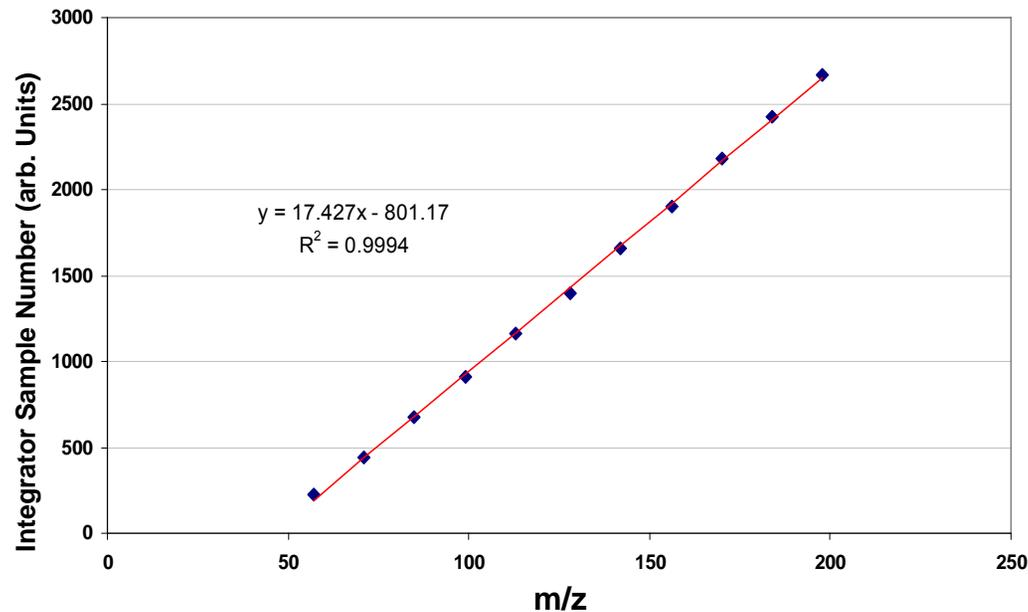
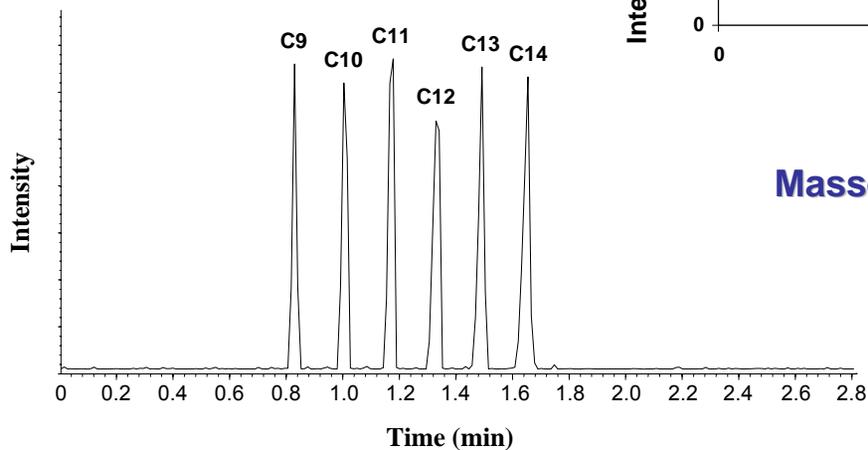
Performance Data



- Inter-system Comparability: GC Parameters on 7 Systems
 - GC retention time %RSD:
 - high = 8.88%(BZ)
 - low = 5.45% (DEP)
 - GC retention time %RSD relative to Naphthalene
 - high = 2.63% (BZ)
 - low = 0.36% (NBB)
 - GC peak area % RSD:
 - high = 165% (BZ)
 - low = 155% (DEP)
 - GC peak area %RSD relative to Naphthalene
 - high = 89.1% (DEP)
 - low = 14.3.%(CN)

Molecular Ion Region of Toluene



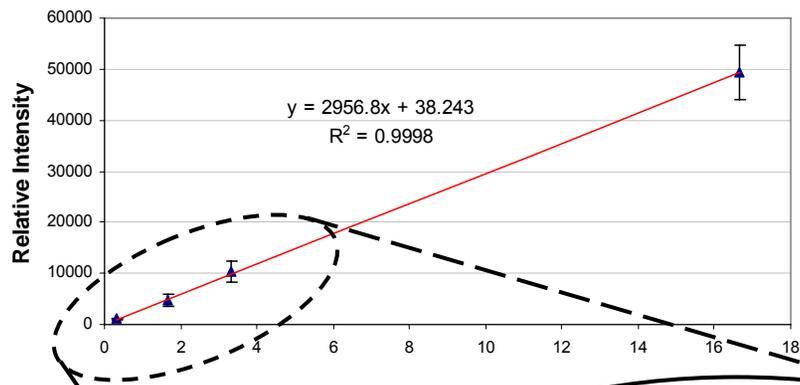


Masses Employed:

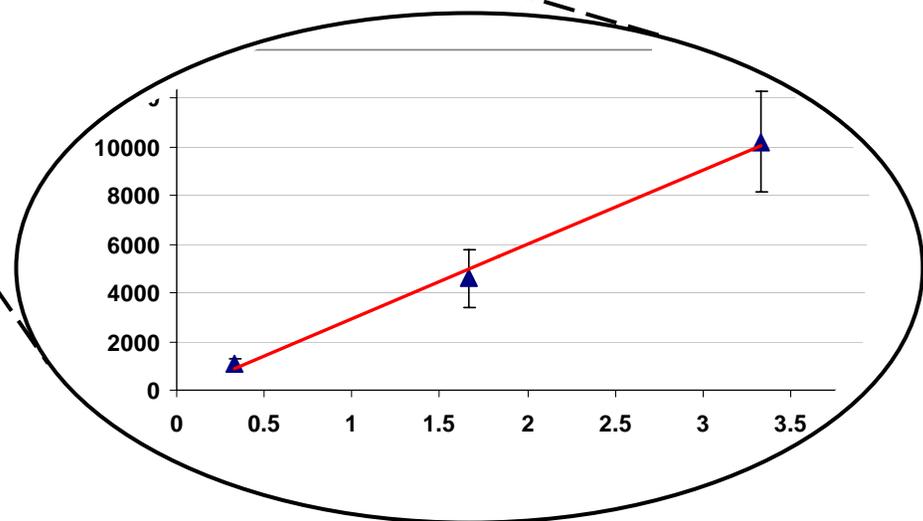
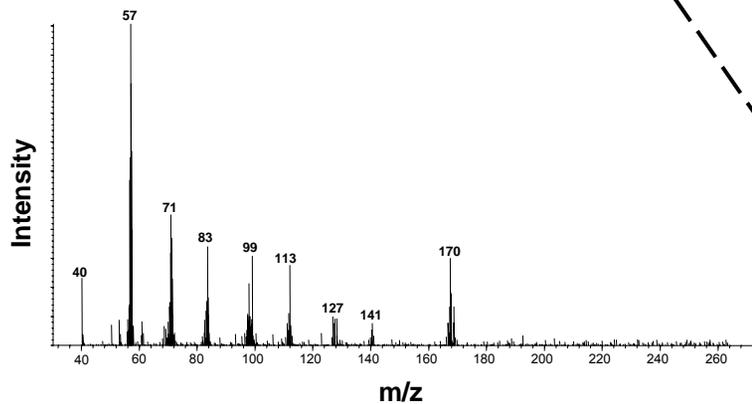
Fragments: **57, 71, 85, 99, 113**

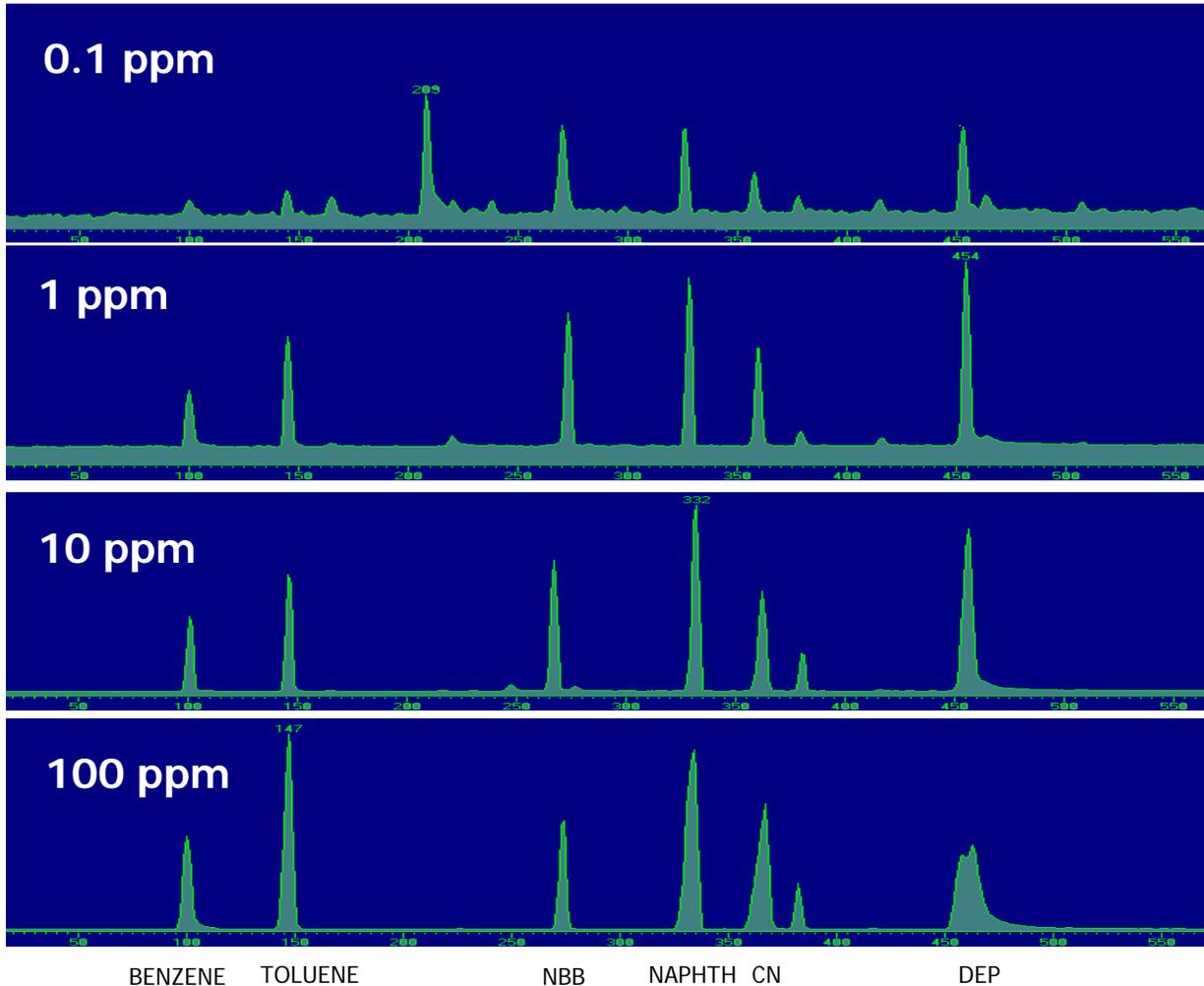
Molecular Ions: **128, 142, 156, 170, 184, 198**

LOD: 250 pg

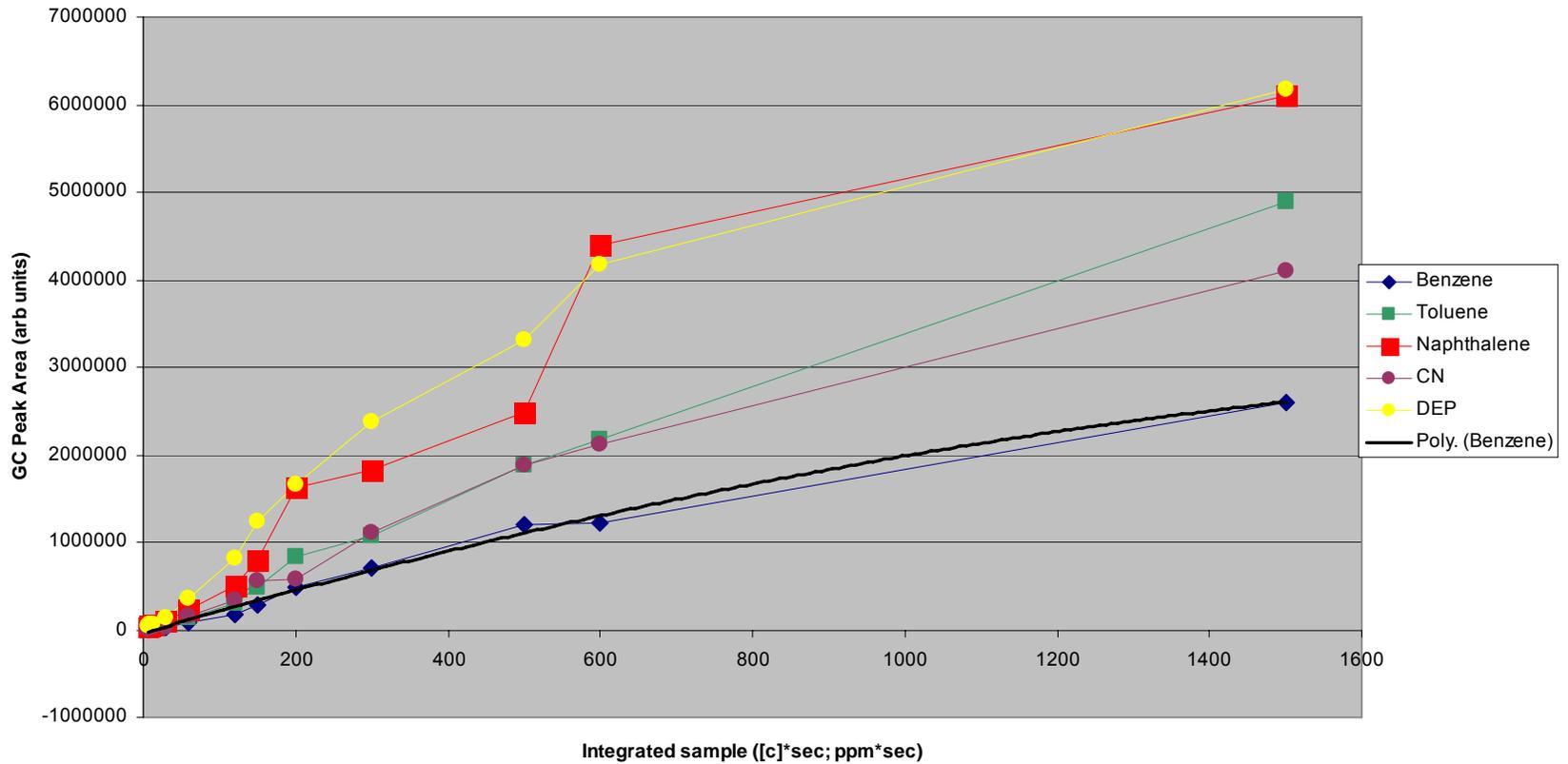


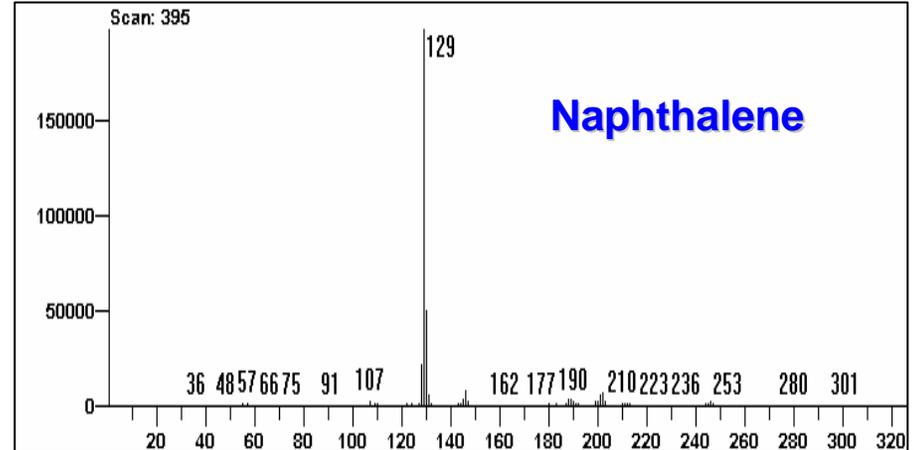
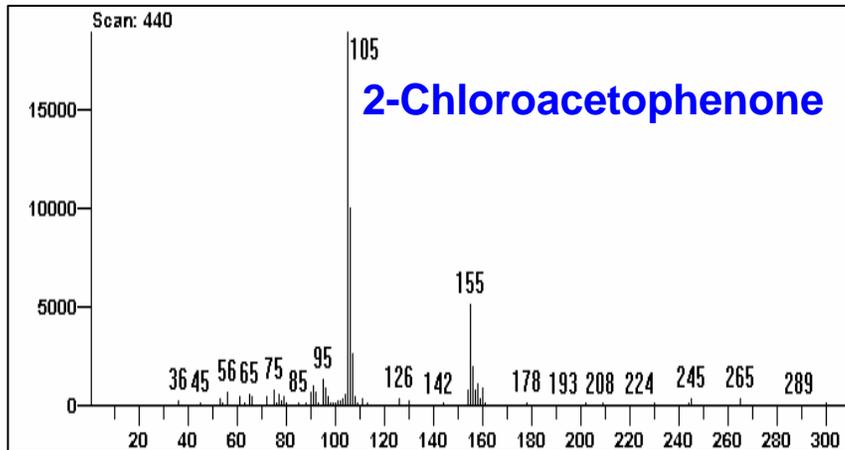
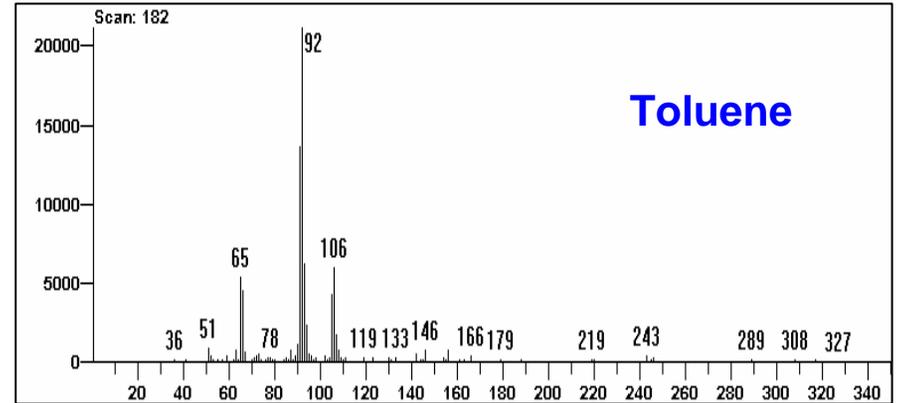
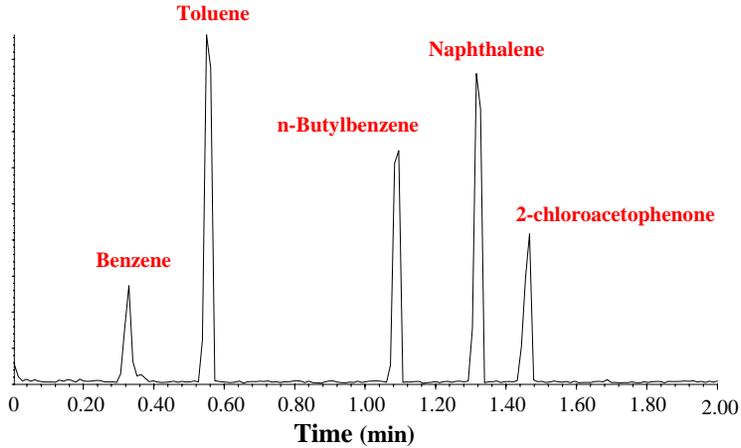
***n*-Dodecane (C₁₂) Spectra**



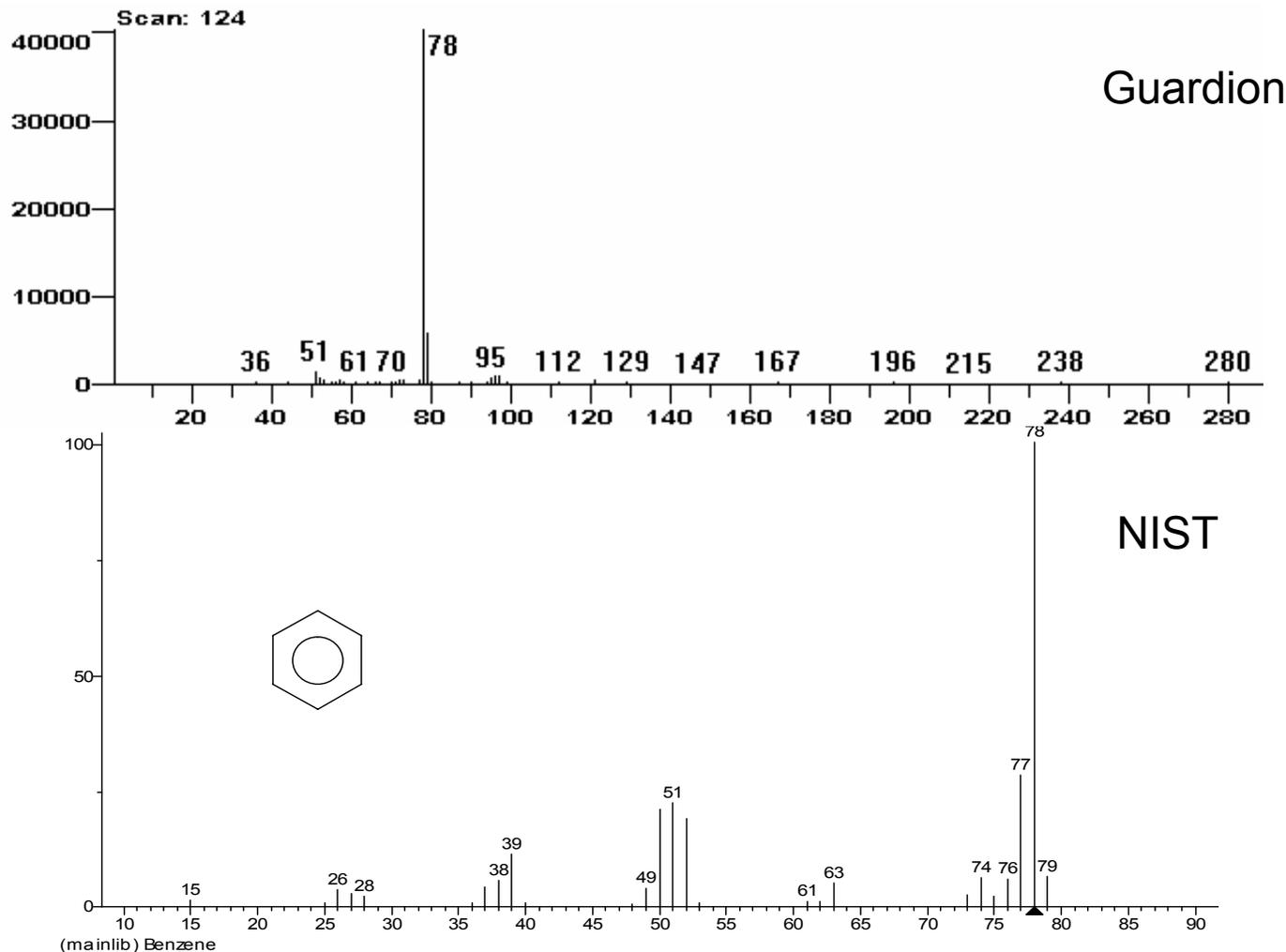


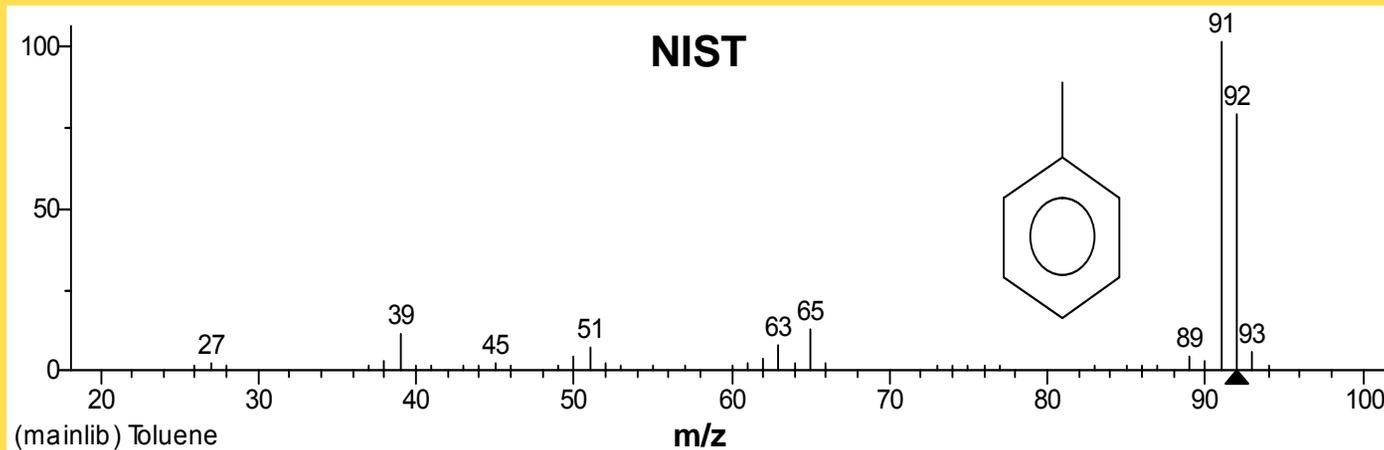
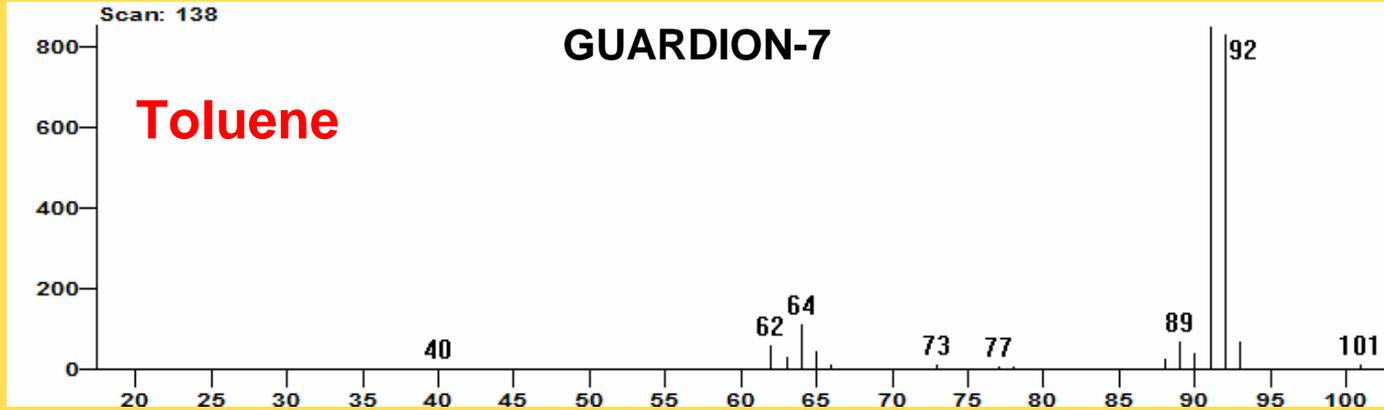
Concentration Study - Six-mix Test Solution
 (three replicates of four concentrations 0.1,1,10,100 ppm with 3 exposure times for each)



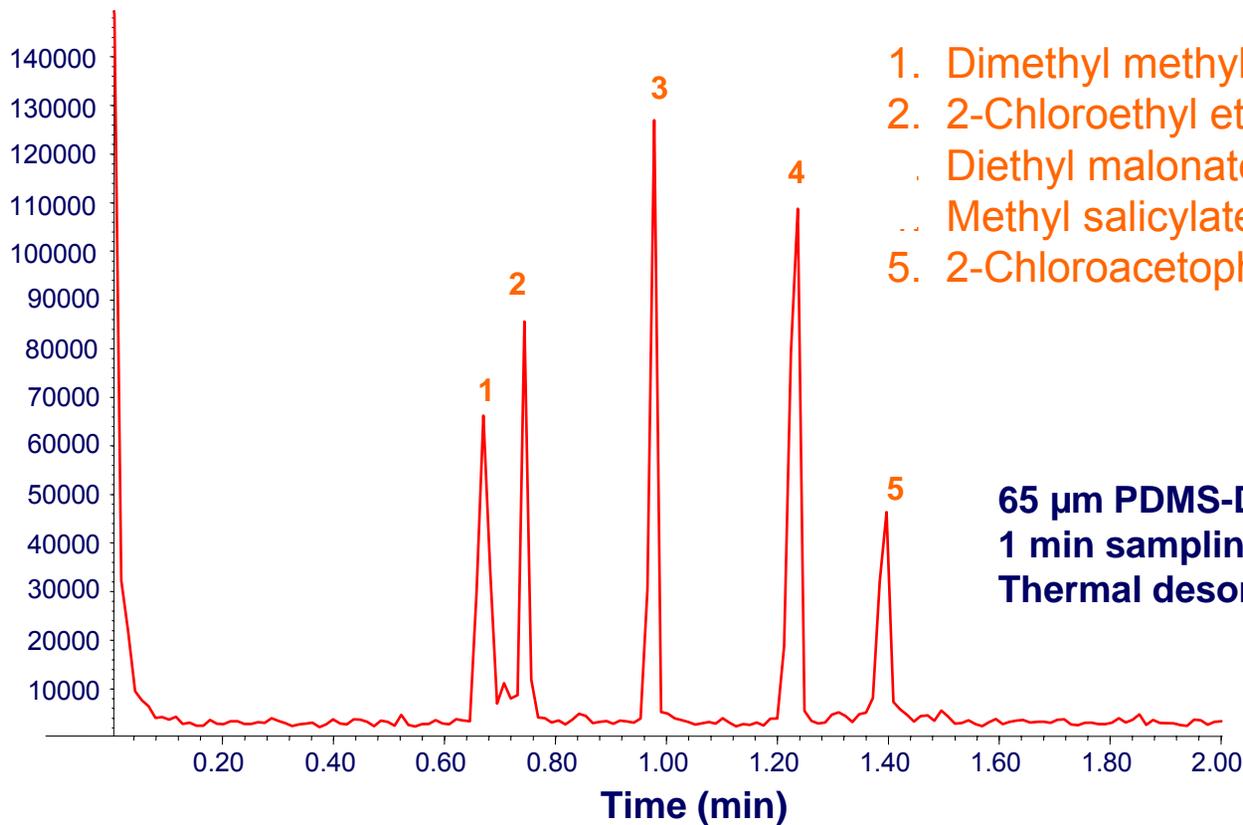


Benzene TMS-NIST Comparison



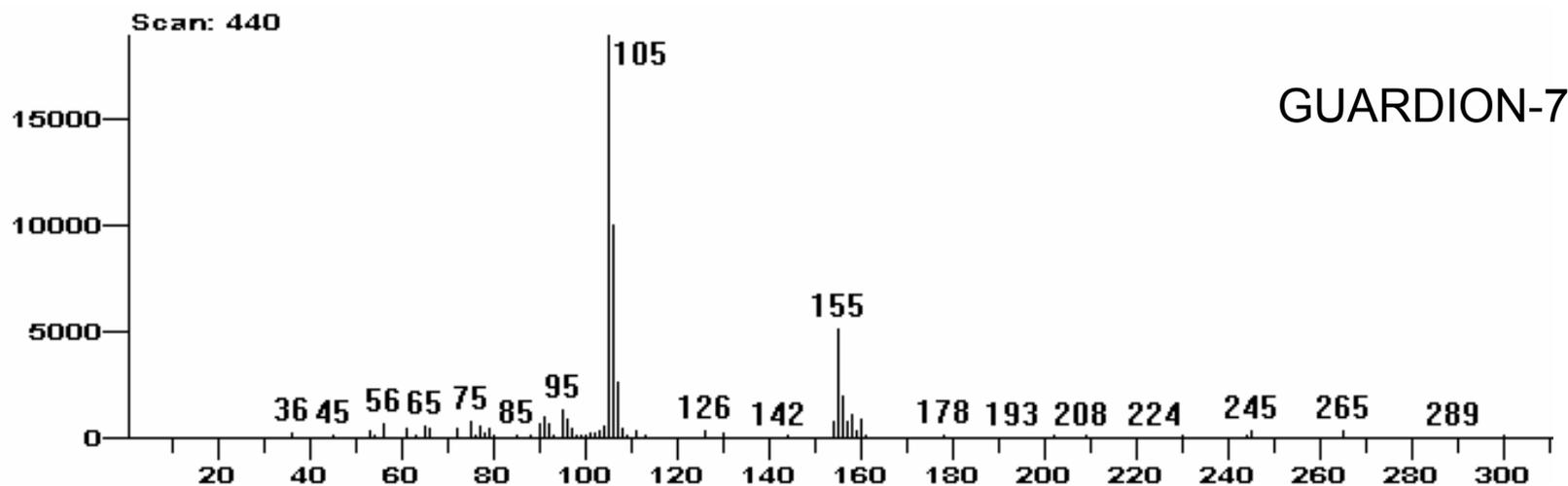


Environmental Contaminants

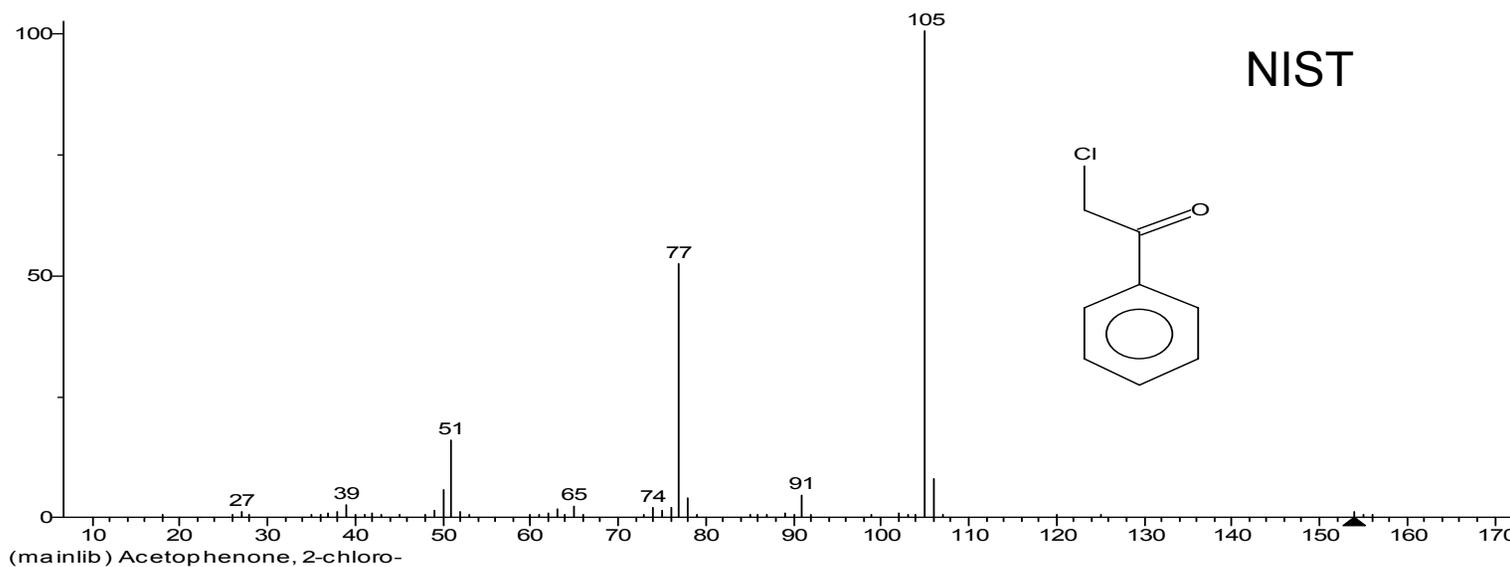


1. Dimethyl methyl phosphonate (DMMP)
2. 2-Chloroethyl ethyl sulfide (1/2 HD)
3. Diethyl malonate (DEM)
4. Methyl salicylate (MES)
5. 2-Chloroacetophenone (CN)

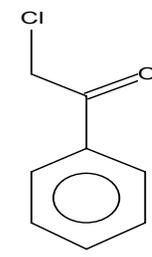
65 μ m PDMS-DBV SPME fiber
1 min sampling from MeOH solution
Thermal desorption @ 250°C for 3 s



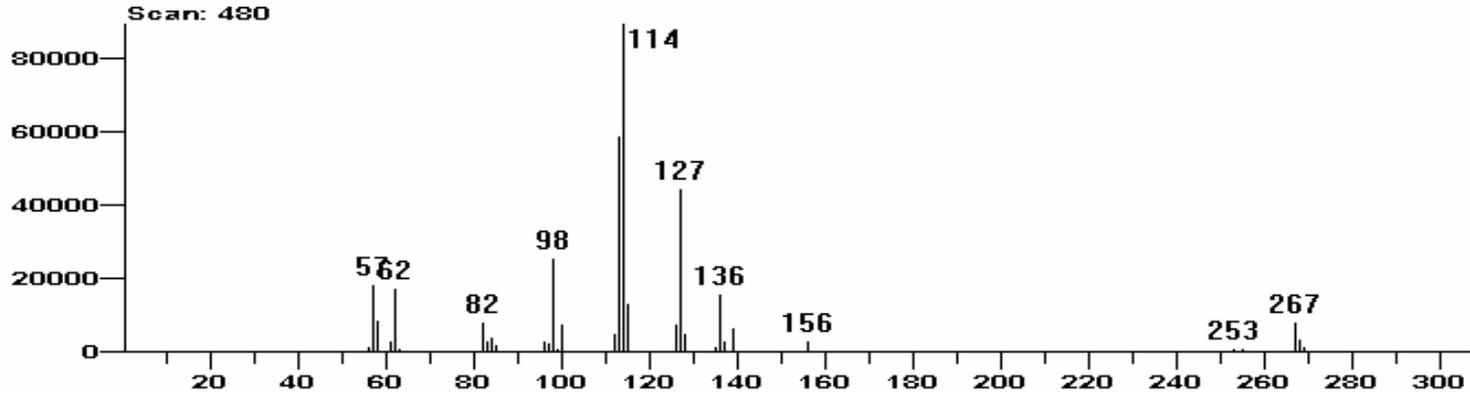
GUARDION-7



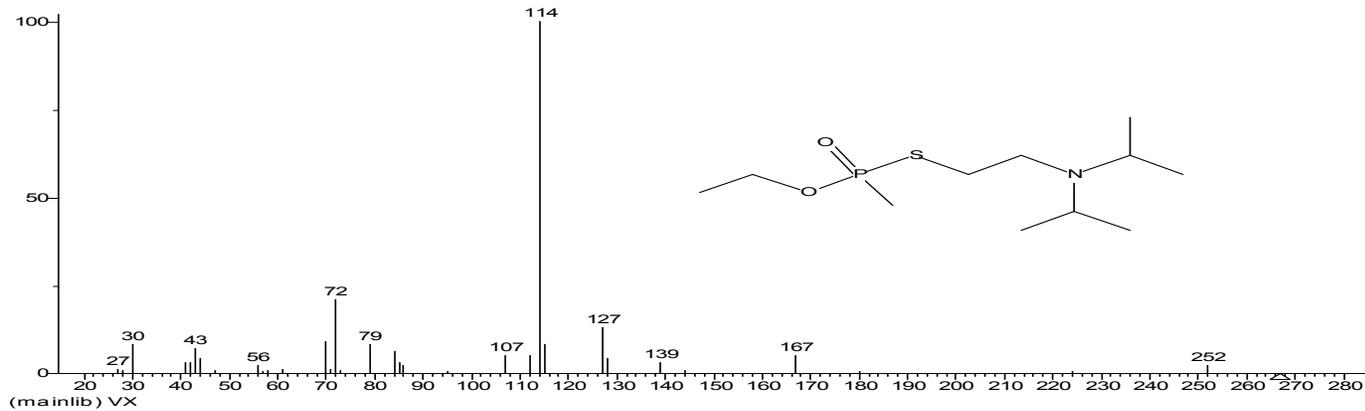
NIST



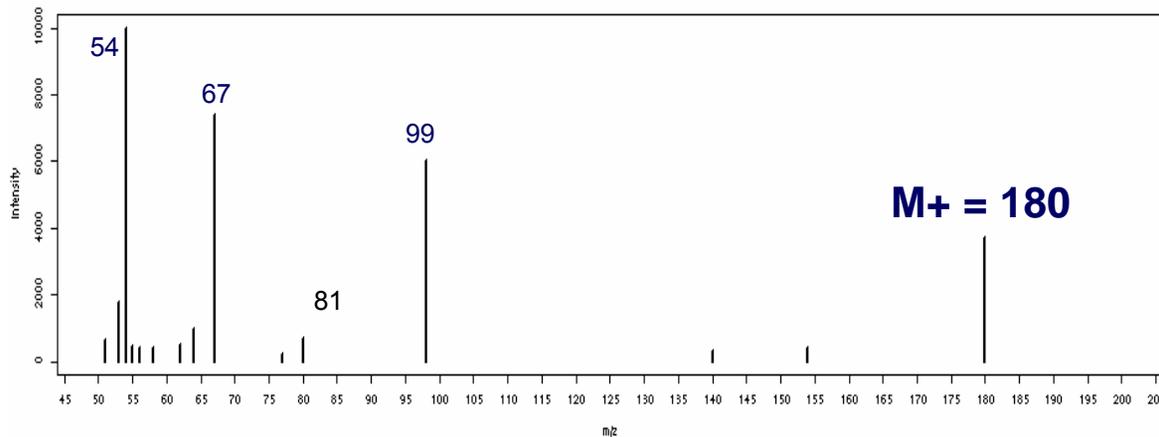
G-7



NIST

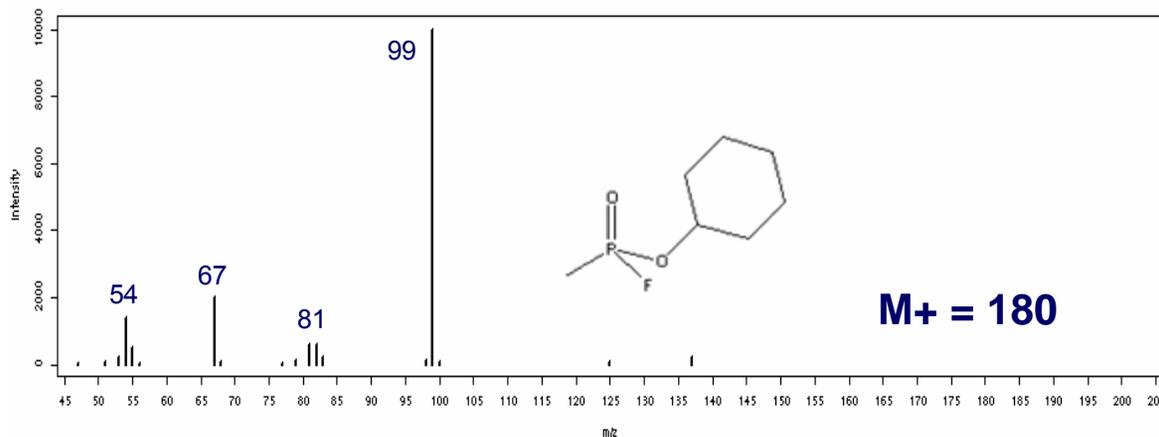


GUARION-7

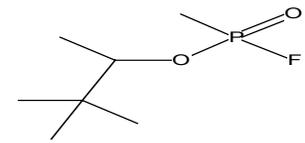
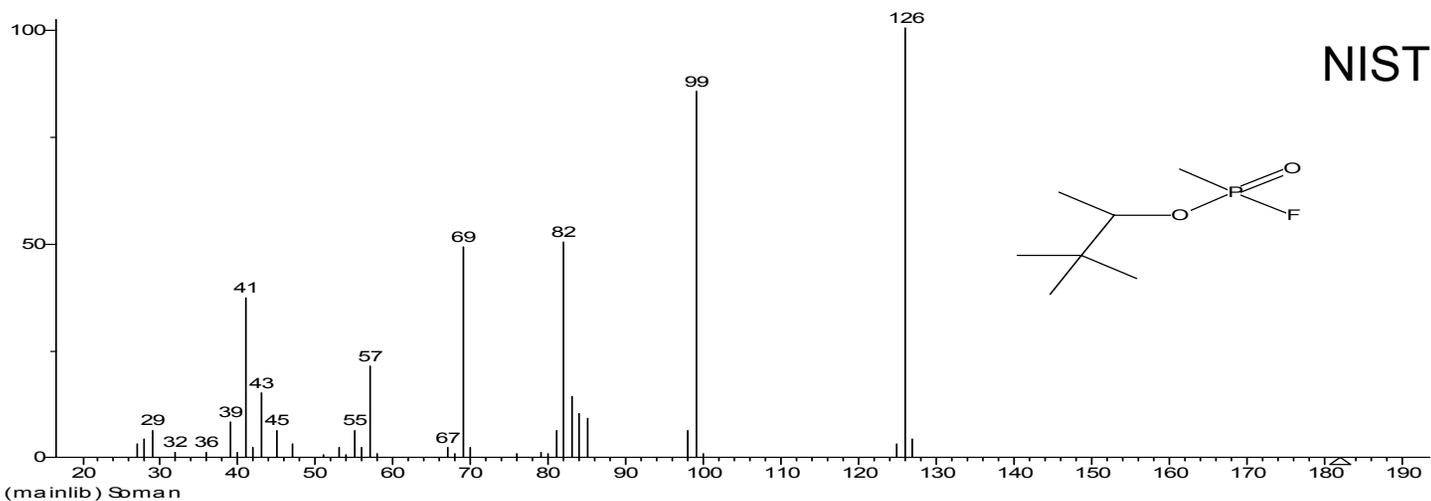
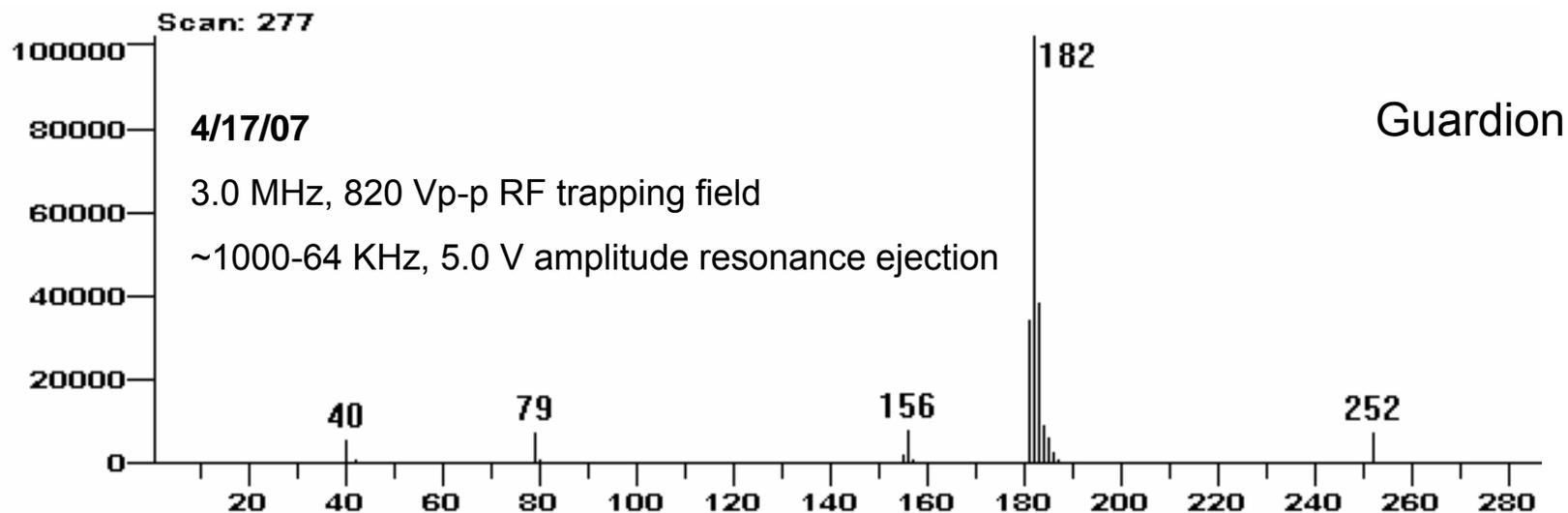


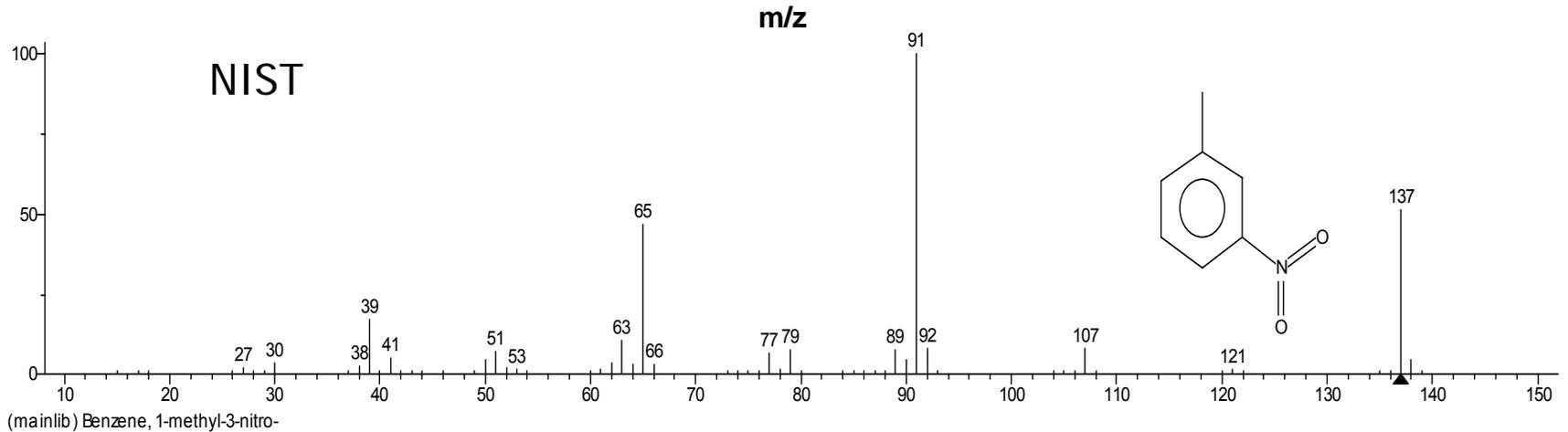
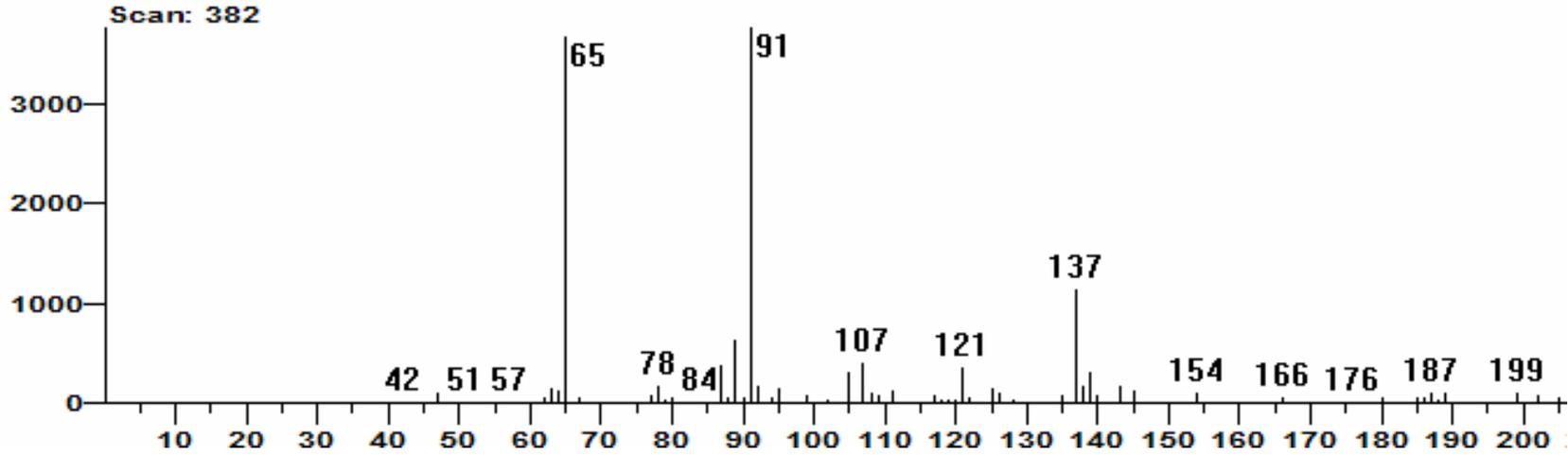
GF NIST

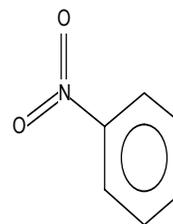
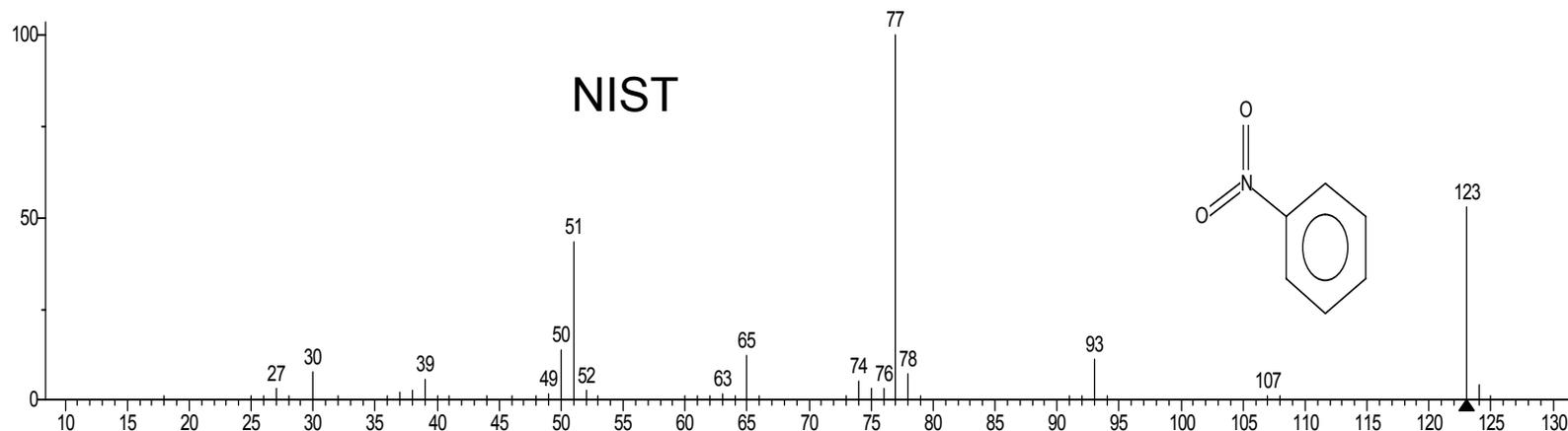
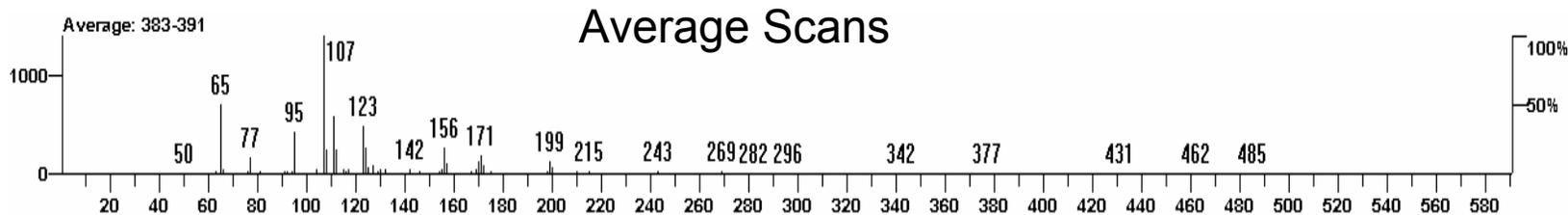
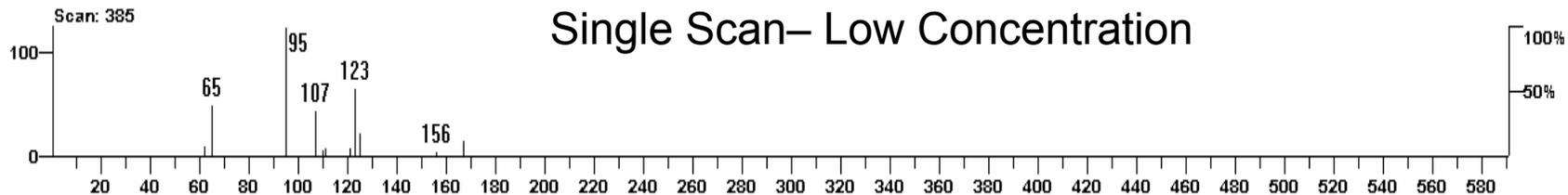
NIST



GD Spectral Comparison

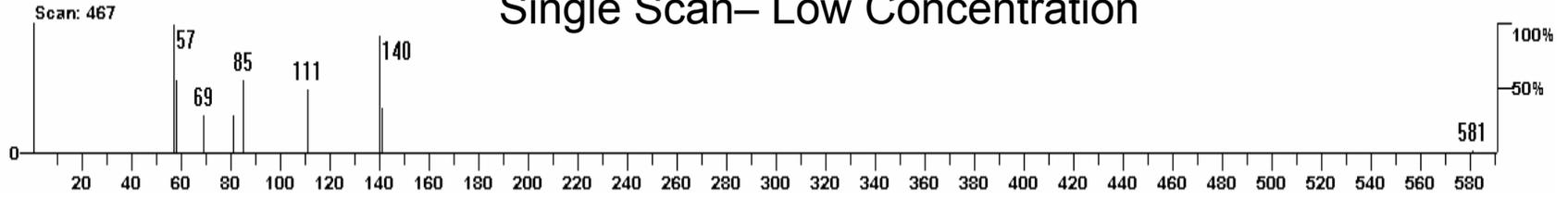




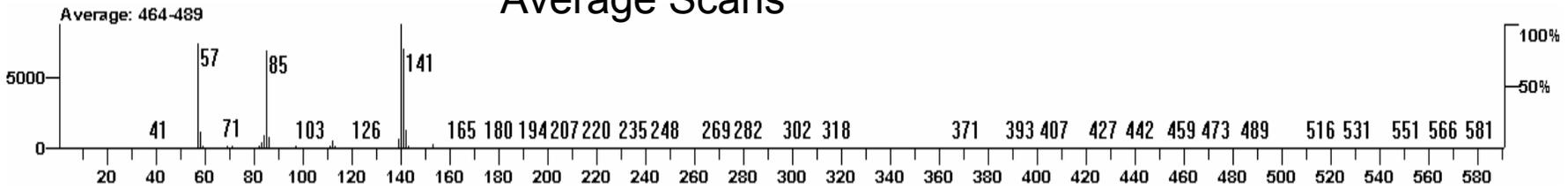


(mainlib) Benzene, nitro-

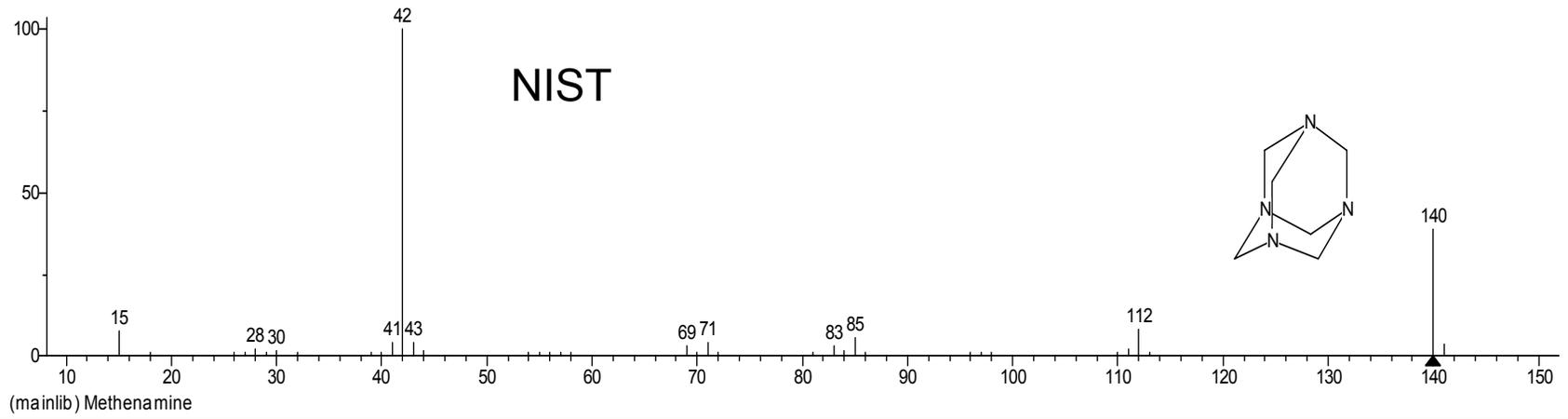
Single Scan– Low Concentration



Average Scans



NIST



May 25, 2007

| Instrument | Runs | Blanks | Identified | Percent |
|------------|------|--------|-----------------|--------------|
| C12 | 7 | 6 | 40/42 | 95.2% |
| C13 | 5 | 5 | 30/30 | 100% |
| C03 | 5 | 5 | 29/30 | 96.7% |
| C08 | 5 | 5 | 30/30 | 100% |
| | | | Average: | 97.7% |

Runs were performed with the 6-mix standard only

June 22 – 25, 2007

| Instrument | Runs | Blanks | Identified | Percent |
|------------|------|--------|-----------------|--------------|
| C03 | 6 | 7 | 29/31 | 93.6% |
| C04 | 6 | 7 | 30/30 | 100% |
| C06 | 6 | 6 | 29/31 | 93.6% |
| C07 | 8 | 7 | 43/43 | 100% |
| C08 | 6 | 6 | 29/30 | 96.7% |
| C11 | 7 | 7 | 22/23 | 96.6% |
| C13 | 6 | 6 | 34/34 | 96.7% |
| C14 | 6 | 7 | 28/32 | 87.5% |
| | | | Average: | 96.1% |

Runs were a combination of 2-mix and 6-mix standards

- Coauthors
 - Milton Lee, Brigham Young University
 - Jesse Contreras, Brigham Young University
 - Jacolin Murray, Brigham Young University
 - H. Dennis Tolley
 - Stephen A. Lammert, Consultant
 - Samuel Tolley, Torion Technologies
 - Edgar Lee, Torion Technologies
- Funding
 - DoD, Defense Threat Reduction Agency
 - DoD, Dugway Proving Ground