Post-Detonation Radiological Debris Analysis using Mass Spectrometry

Theresa Evans-Nguyen
C.S. Draper Laboratory
Francy Sinatra
Spiros Manolakos
Kevin Hufford
James Alberti
Erkinjon Nazarov

Robert Cotter
The Johns Hopkins University – School of Medicine
Di Wang
Friso Van Amerom

Kenyon Evans-Nguyen
The University of Tampa
Amanda Quinto
David Glatter
Tiffanie Hargraves
Hilary Brown
Jennifer Speer

Jing Wang
The University of South Florida
Tianpeng Wu
Adrian Avila

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Dirty Bombs - Radiological Dispersal Devices

RDDs:
- Accessible radioisotope
- Conventional explosive

- 1987: Goiânia, Brazil – Cesium-137
- 1995: Moscow – Cesium-137
- 2001: Georgia (FSR) – Strontium-90
- 2002: Kabul, Afghanistan – Cobalt-60

Table 1. Likely RDD Radioisotope Sources

Nuclide	Primary Form	Application
Strontium-90	Ceramic ($SrTiO_3$)	Radioisotopic Thermal Generator (RTG)
Cesium-137	Salt (CsCl)	Irradiator
Cobalt-60	Metal	Irradiator
Iridium-192	Metal	Industrial Radiography
Americium-241	Ceramic (AmO_2)	Well-logging
Californium-252	Ceramic (CfO_2)	Neutron Radiography & Well-logging
Plutonium-238	Ceramic (PuO_2)	RTG
Radium-226	Salt ($RaSO_4$)	Medical Therapy

Program Background/Introduction

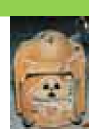
Nuclear Forensics:

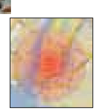
Post-Detonation Radiological Debris Analysis

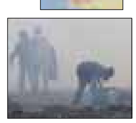
Need: Rapid, accurate, post-detonation analysis of debris from a **radiological** event to decrease the forensics timeline.

Approach: Apply methods in surface sampling, chemical separation, and ion trap mass spectrometry.

Goal: Enable little to no sample preparation, simplify sample collection after an RDD attack







NUCLEAR FORENSICS:
Chemical and isotopic composition to link persons, places, things

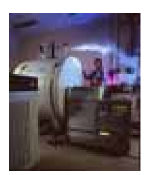
Nuclear Forensic Analysis

Lab Instrumentation

- Sample Collection
- Sample Preparation
  - Digestion/Extraction
- Elemental/Organic Analysis
  - ICP-MS
  - LC-MS

Collection

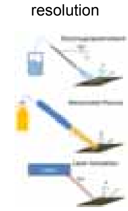
Preparation



MS Analysis

On-site Analysis

- Simultaneous explosive and elemental/isotopic analysis
- Surface sampling in air
- Rapid sample preparation
- MS: Man-portable with isotopic resolution



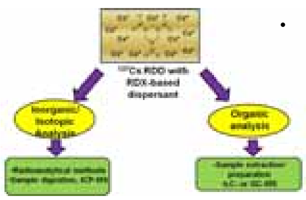
Surface Sampling

Rapid Filtering

Low power MS

Obj.1: Technical Approach - Surface Sampling

- Evaluate various surface sampling techniques on Thermo LTQ
  - Year 1: Desorption Electrospray Ionization (DESI)
  - Year 2: Direct Analysis in Real Time (DART)
  - Year 3: Laser Desorption Ionization (LDI)
- Simulants: Individual samples and mixtures of radioisotopes with explosives



- Limitations and Risks
  - Dual sample optimization compromises sensitivity

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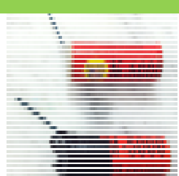
Target analytes

Isotope	Primary decay	Surrogate Analyte
^{137}Cs	^{137m}Ba → ^{137}Ba	Salt ^{133}Cs
^{226}Ra	^{222}Rn	Salt (^{134}Ba, ^{135}Ba, ^{137}Ba, ^{138}Ba)
^{60}Co	^{60}Ni	Metallic ^{59}Co
^{192}Ir	^{192}Pt	Metallic Ir (^{191}Ir, ^{193}Ir)
^{90}Sr	^{90}Y → ^{90}Zr	Ceramic $SrTiO_3$* (^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr)

*Also an effective mimic for ceramics of significant Actinide oxides: $^{241}AmO_2$, $^{252}CfO_2$, $^{238}PuO_2$)

Potential Dispersant Explosive	Examples
Conventional Nitro(organic)	RDX, HMX, PETN, Tetryl, TNT, Nitroglycerine
Peroxide (organic)	TATP
Black Powder IEDs (inorganic)	nitrates, chlorates, perchlorates
Ammonium Nitrate/Fuel Oil	

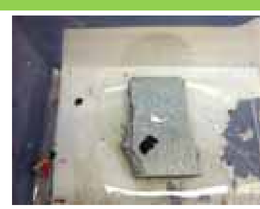
Obj. 1: Results - Simulated Cs/black-powder RDD



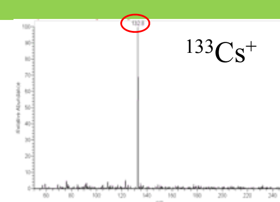
Top: Black powder-based firecracker (primarily perchlorate)

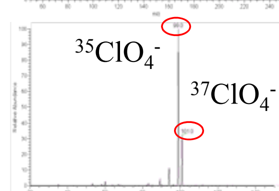
Bottom: Firecracker laced with 5mg ^{133}Cs using electrical tape

Simulated Cs/black-powder RDD

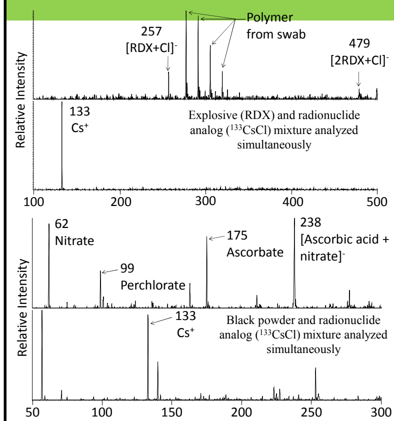


Swab portions of the container with polypropylene mesh



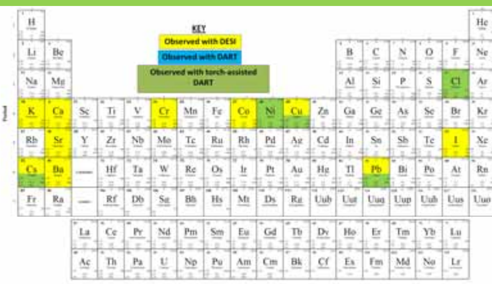


DESI and RDDs



- DESI
  - explosive dispersants
  - soluble radionuclide analogs

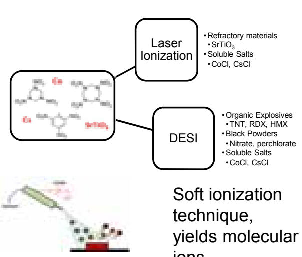
Obj. 1: Data Summary – Tasks 1, 4



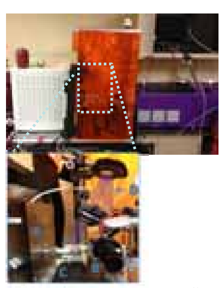
•Organic explosives observed: RDX, TNT, Tetryl, Nitroglycerine
•Inorganic explosive observed (anions): nitrate, perchlorate, nitrite, chlorate
•Actual black powder formulations used in domestic IEDs analyzed for nitrate, chlorate, and perchlorate content

Obj.1: Ambient Sampling

- Evaluate various surface sampling techniques
  - Year 1&2: Desorption Electrospray Ionization (DESI), DART
  - **Year 3: Laser Desorption Ionization (LDI), Hybrid Ionization → Hard, Refractory Materials?**



Soft ionization technique, yields molecular ions



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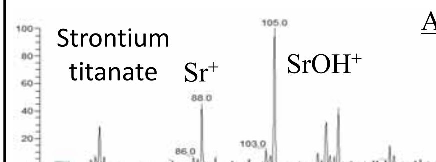
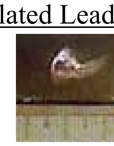
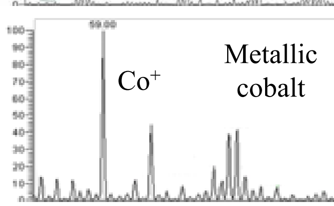
Laser Ionization of Refractory RDD Components



Ablated Lead Foil

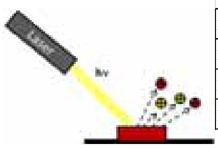




- Strontium titanate and cobalt metal are the typical forms of ^{90}Sr and ^{60}Co
- Strontium titanate is also a chemical analog of actinide oxides
- No signal obtained without helium sheath gas

Laser ion sources for MS of Refractory RDD Components

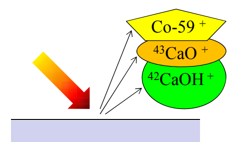
- Low energy laser: laser desorption (vacuum)
  - No signal for insoluble solids/refractory materials
- High energy laser, inert sheath gas: laser ablation
- High energy laser, ambient: laser ionization

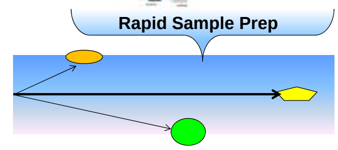


	Organics	Soluble Salts	Refractory Materials
DART	+++	+	-
DESI	+++	+++	-
Laser desorption	++	+++	-
Laser ablation	-	+++	++

Obj. 2: Differential Mobility Separation applied to Radionuclides

- Approach:
  - Sample Preparation by DMS
  - Year 1: Modeling DMS
  - Year 2: Fabricate prototype DMS
  - Year 3: Test analogs





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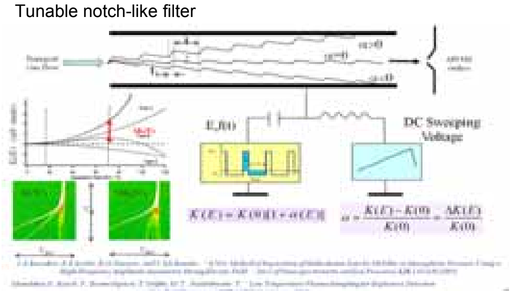
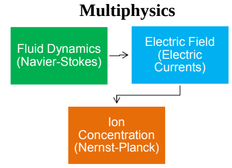
Background & Significance - DMS

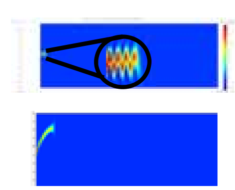
- Rapid Sample Clean-Up (20ms)
- Differential Mobility Spectrometry - separation based on differential mobility, K
  - Factors: Collision cross-section, adduct formation, polarizability
- Tunable notch-like filter

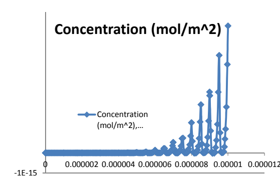


Obj. 2: Results – Task 2. COMSOL DMS Modeling



	Parameters	Values
c	Ion Concentration	42.86 mol
z	Charge	1
N	Number Density (Molecules / Unit V)	2.5e25 m^{-3}
VC	Compensation Voltage	-1.35
D	Diffusion Coefficient	4.97e-6 m^2/s
K_0	Mobility for Low Electric Field	1.94e-4 $m^2/V*s$
α_2		5.09e-6 1/Td^2
α_4		-1.58e-10 1/Td^4





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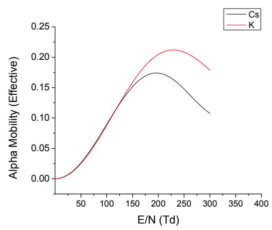
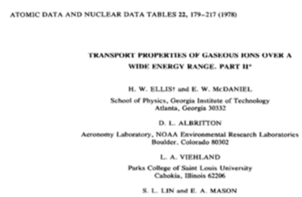
Radioisotope mobility parameters




ATOMIC DATA AND NUCLEAR DATA TABLES 22, 179–217 (1978)

TRANSPORT PROPERTIES OF GASEOUS IONS OVER A WIDE ENERGY RANGE. PART II*

H. W. ELLIS† and E. W. McDANIEL
School of Physics, Georgia Institute of Technology
Atlanta, Georgia 30332

D. L. ALBRITTON
Aeronomy Laboratory, NOAA Environmental Research Laboratories
Boulder, Colorado 80302

L. A. VIEHLAND
Parks College of Saint Louis University
Cahokia, Illinois 62206

S. L. LIN and E. A. MASON

- Prior DMS experiments focus mostly on organic species
- Historical atomic data for ion mobilities in N_2
  - Cesium
  - Potassium

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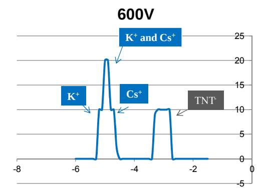
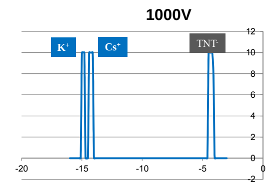
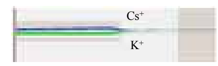
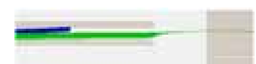
SIMION DMS Modeling

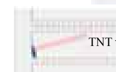
- SIMION modeled electro-optical forces with parabolic flow profile from COMSOL











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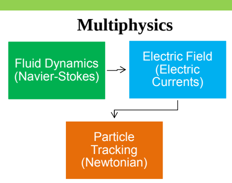
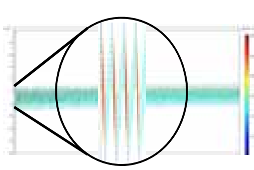
COMSOL DMS Modeling: Particle Tracing Module



Parameters		Values
Ion #	Number of ions Released at Inlet (Uniformly distributed over 0.05mm gap at center of channel)	10
z	Charge	1
N	Number Density (Molecules / Unit V)	$1.5511e^{25}$ m^{-3}
VC	Compensation Voltage	-7.35V
Vac	AC Voltage	750 V
K_0	Mobility for Low Electric Field	2.00934 [$cm^2/V*s$]
α_2	Alpha 2 Parameter	$9.016e^{-6}$ [Td^{-2}]
α_4	Alpha 4 Parameter	$-1.321e^{-10}$ [Td^{-4}]



Multiphysics: Semi-computing intensive

- Particle tracing module
  - Collision frequency E dependence
- Includes Electric and Elastic Collision Forces

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COMSOL: Forces Applied to Ions → Particle Tracing Module

Electric Field Force

$$\mathbf{F} = eZ(-\nabla V)$$

$$V_D(t) = \frac{V_{iD}}{3}\left[2\sin(\omega t) + \sin\left(2\omega t - \frac{\pi}{2}\right)\right] + V_C$$

V_{iD} = 1000 V
V_C = -5V

ω = 1.2 MHz*(2π)

e = Ion charge [C]
V = Electric potential [V]

Ion Collision Force

$$\mathbf{F} = -m_p\nu(\mathbf{v} - \mathbf{u})$$

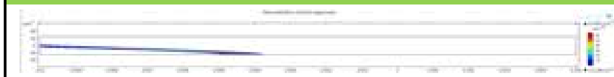
$$\nu = \frac{e}{K * \mu}$$

$$K\left(\frac{E}{N}\right) = K(0)\left[1 + \alpha_2\left(\frac{E}{N}\right)^2 + \alpha_4\left(\frac{E}{N}\right)^4 + \cdots\right]$$

$K_{(0)}$ = 2.00934 [$cm^2/V*s$]
α_2 = $9.016e^{-6}$ [Td^{-2}]
α_4 = $-1.321e^{-10}$ [Td^{-4}]

m_p = Ion mass [kg]
ν = Ion collision frequency [Hz]
v = Neutral gas velocity [m/s]
u = Ion velocity [m/s]
K = Ion mobility [$m^2/V*s$]
μ = Reduced mass [kg]
N = Neutral gas number density [m^{-3}]

Cesium Ion Trajectory
Vrf = 1000V, Vc = 0V

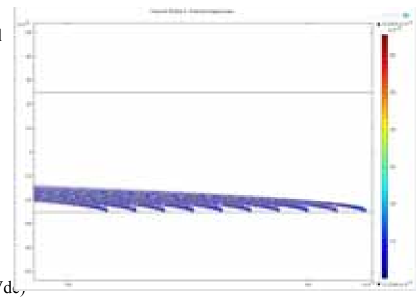


Ion: Cesium
MassCs = 132 g/mol
RadiusCs = 167 pm
10 Ions Released

Pressure = 1atm
Temperature = 25C

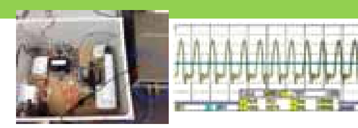
Vrf = 1000V
Vc = 0V
f = 1.2 MHz

Forces Included
Lorentz Force (Vac & Vdc)
Ion Collision Force



DMS Fabrication

DMS Adaptor inlet



- Adapt existing commercial components
  - Sionex DMS to Agilent TOFMS
  - Flow leaking – O-rings
  - Charge saturation – nanospray ionization
  - Sheath gas obstruction – inlet redesign
  - Synchronize control and data acquisition components - Labview

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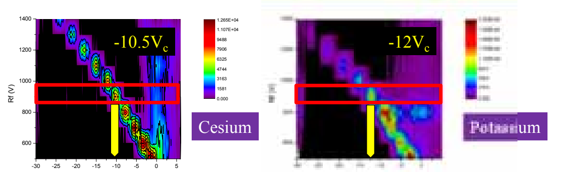
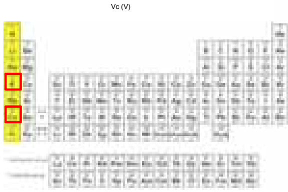
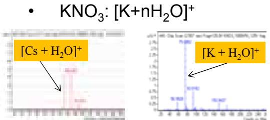
Radiological analog in DMS: between electronic shells, n=4, n=6





- Nanospray of dissolved salts
  - CsCl: $[Cs+nH_2O]^+$
  - KNO_3: $[K+nH_2O]^+$



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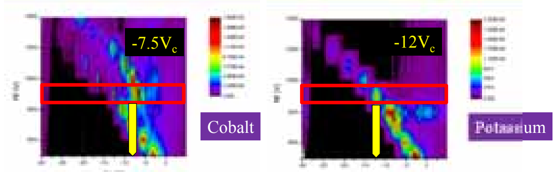
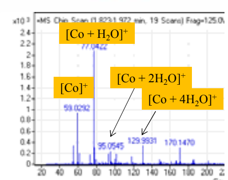
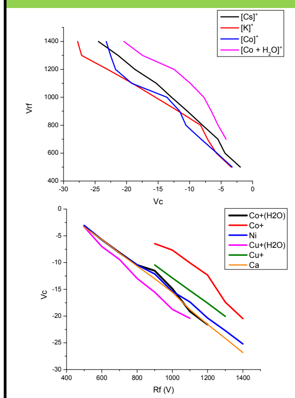
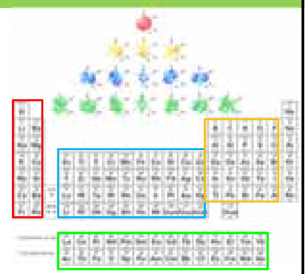
Task 8. Radiological analog in DMS across an electronic shell n=4





Task 8. Fast Elemental Separation by DMS





Method Development

- Pick and choose qualifying voltage pairs as a training set
- Spend 100 ms at each (Vc, Vrf pair)

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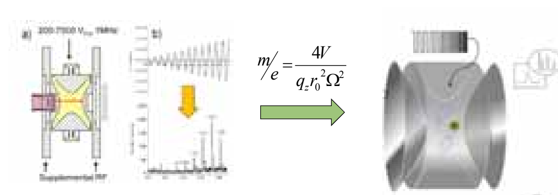
Obj. 3: Portable High Resolution ITMS

- Technical approach:
  - High resolution MS – High vacuum
  - Low resolution Ion Trap MS – Medium vacuum



$$m/e = \frac{4V}{q_z r_0^2 \Omega^2}$$

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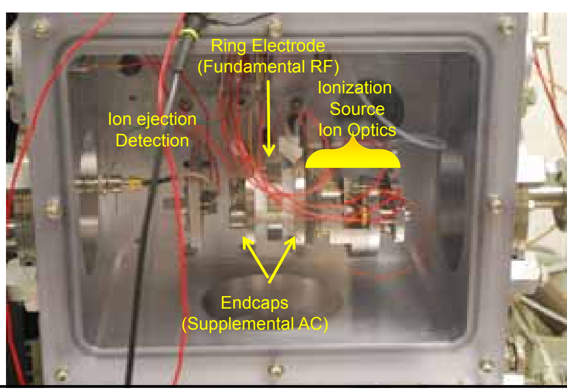
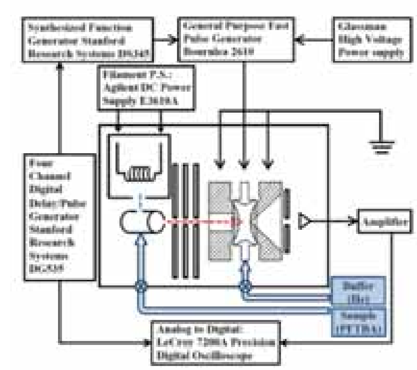
Ion Trap MS Assembly



Block Diagram



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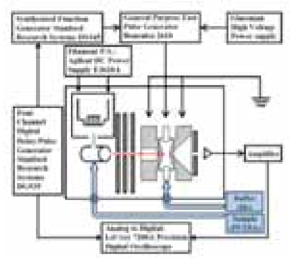
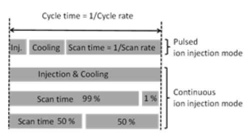
Continuous Ionization Mode



- High emission current
- High pressure trap (1x10^{-3} Torr)
- Fast trap filling
- Frequency scanning
  - Mass instability
  - Resonance ejection
  - β resonance



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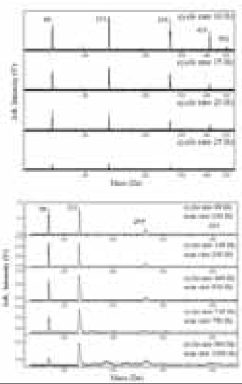
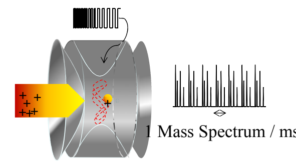
Obj. 3: High Speed Digital Frequency Scanning

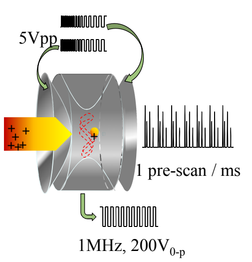


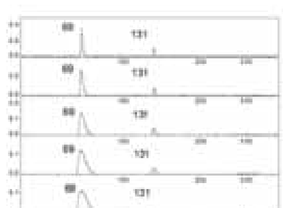
400V amplitude
900-350kHz frequency sweep (log)



- Mass instability scanning at high pressures accommodates continuous ion beam currents

Obj. 3: Digital Frequency Scanning





- Low voltage waveforms provide a low power resonance ejection method suitable to field portable applications
- A combination of digital waveform timing schemes to explore zoom scanning methods through frequency scanning.

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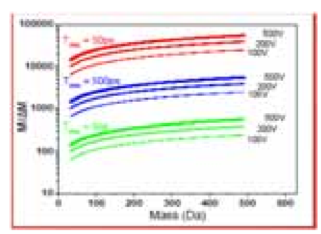
Obj. 3: Digital Frequency Scanning



$$m = \frac{4eV}{q_z r_0^2 \Omega^2}$$

- With current jitter, desired resolution may be attainable with careful consideration for all peak broadening factors.
  - Phase locking may further facilitate resonance ejection
  - Analogous "zoom scanning" methods will be programmed
  - Simultaneous amplitude control

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Conclusions & Future Directions

- IONIZATION:
  - DESI, DART, LDI
  - Multi-mode source configuration, hybridize desorption/ionization processes
- SEPARATION:
  - Computational models inform DMS design
  - DMS separation of isobars and elemental species promising
  - Explore homologous series
- MASS ANALYSIS:
  - Continuous ionization (with semi-continuous injection)
    - Frequency scanning digital waveforms can enable fast MS scanning up to 1000Hz
  - Resonance ejection mode uses higher scan speeds and pressures so better for low power field portable MS?
  - Optimize waveform sync, phase locking, to increase resolution

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