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NATIONAL LABORATORY

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ICP-MS Short Course Participant Materials

Volume 2, Day 2, June 18, 2014

June 2014

U.S. DEPARTMENT OF ENERGY

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AGENDA

Day Two, Wednesday

TIME	Presentation	Speaker
7:45 a.m.	Morning Hospitality	
8:00 a.m.	Welcome to Day Two	Greg Eiden
8:15 a.m.	Mass Spectrometry in the DOE Complex	Erick Ramon
9:00 a.m.	LA-ICPMS Topics - Laser Ablation – Chemical Analysis - Laser Ablation-Multi-Collector ICPMS	Rick Russo Andrew Duffin
10:00 a.m.	Break	
10:30 a.m.	ICP-MS Instrument Specializations	Charles Barinaga
11:30 am.	Lunch	
11:45 a.m.	Student Opportunities at PNNL	Marisela Linares-Mendoza
12:30 p.m.	Ion Optics Modeling	Chris Zarzana, Idaho National Laboratory
1:15 p.m.	Advanced Detector Technology	Bonner Denton, University of Arizona
2:00 p.m.	Break	
2:30 p.m.	Alternative Plasma Sources for Trace Inorganic Mass Spectrometry	Doug Duckworth
3:30 p.m.	Wrap Up	
4:00 p.m.	Adjourn	

Presentations

Mass Spectrometry at the National Laboratories: An Overview

2014 Mass Spectrometry Short Course

Pacific Northwest National Laboratory

June 17-18, 2014

Erick Ramon

Lawrence Livermore National Laboratory

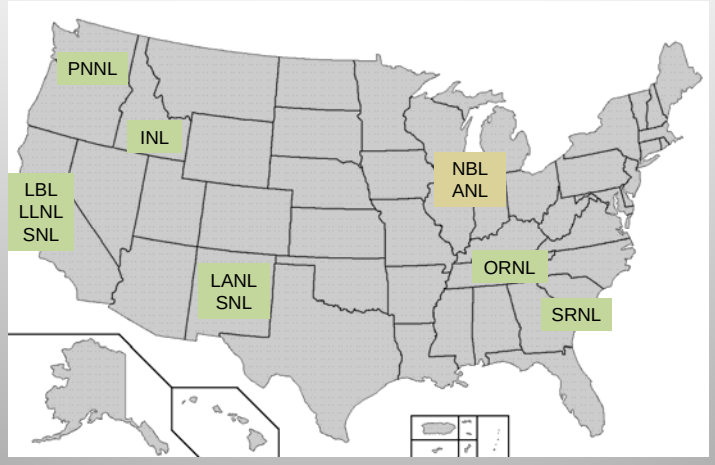
LLNL-PRES-655389

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Survey of Labs in 2011

- Who?
  - Survey involved on-site visits to 9 national laboratories
  - Most laboratories prepared a presentation covering mass spectrometry capabilities
- What?
  - Record of the instruments, personnel, and facilities
  - Identify the application and problem space
  - Solicit input on technology gaps
- Why?
  - Develop an investment roadmap to address technology gaps
  - Provide HQ program managers a snapshot of what we have and what we need

Survey of National Laboratories



Argonne and New Brunswick Lab were never surveyed

Boundaries on the scope

- Only techniques designed to measure **isotope ratios**
  - Excludes elemental analysis MS
- Only inorganic MS
  - Organic MS not as applicable to the sponsor
- Excludes radioactivity counting techniques
- Includes spectroscopy to measure isotope ratio
- Includes sample preparation, instrument accessories, and data reduction

What Did We Look At?

- Yes
  - ICP-MS, TIMS, SIMS, AMS and other atom counting techniques
  - Sample introduction
    - Laser ablation
    - Desolvation
    - Electro-chemistry
  - Sample Preparation
    - Automation
    - Purification
  - Other techniques
    - HR-ICP-OES
    - LIBS
- No
  - Elemental analysis
  - Radiation detection of any type
  - “Soft” ionization
  - Sample collection
  - Data utilization
  - Portable or miniaturized versions
  - Sub-SOTA technology

General Findings

- DOE National Laboratories have formidable mass spectrometry facilities.
  - Very few analogs in the academic community
- Unique blend of operational and research activities.
- Many examples of “home built” instruments specializing in niche measurements
- Aging workforce and dwindling expertise in instrument design and repair.

What is Meant by Formidable?

- Single Facility
  - 4x MC-ICP-MS
  - 6x MC-TIMS
  - MCMS-SIMS
  - TOF-SIMS
  - 3x Stable Isotope
  - 3x Noble Gas
  - 10,000 ft^2 cleanroom
  - 2x laser ablation

Also have non-MS instruments

- Across Complex
  - Over 25K ft^2 cleanroom
  - Hot cell facilities
  - 100+ MS instruments
  - Over 15 different ionization techniques
  - nanometer spatial resolution
  - attogram sensitivity
  - ppm level precision

Together we have almost everything!

Our Challenges are also Formidable

- Diverse sample matrices
- Radioactivity, high explosives, and bio hazards
- Measure trace and bulk on the same sample
- COTS instruments not designed for actinide element measurements
- Accuracy, precision, and throughput important
- Stakes are high. Above all, answer MUST be correct!

The current technology gaps are specific to national labs that often don't represent a large enough "market" for commercial R&D investments.

Identified Gaps

- Pipeline – attracting the next generation of science and engineering students.
- Throughput – How to do more things, just as well, in the same time
- Improvements in instrument and accessory performance.
- Innovation – What's the next great thing?

We want to leverage relationships with commercial and academic partners to address these gaps.

Short Course a Piece of the Solution

- 2013 TIMS Short Course at INL
- 2014 ICP-MS Short Course at PNNL
- 2015 SIMS Short Course at LLNL
- 2016 and beyond to be decided
- Students benefit by expanding their knowledge about MS
- Labs benefit by raising external awareness about opportunities for cooperation and R&D needs

We want to leverage relationships with commercial and academic partners to address the identified gaps.

Thank you for coming in 2014
Hope to see you in 2015!

Laser Ablation - Chemical Analysis

Rick Russo

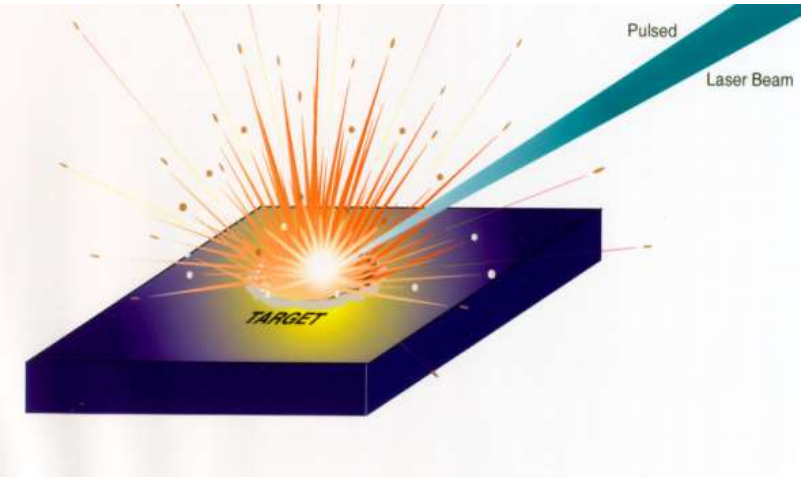
Lawrence Berkeley National Laboratory

ICP-MS Short Course
PNNL
18 June 2014

Laser Ablation - Chemical Analysis

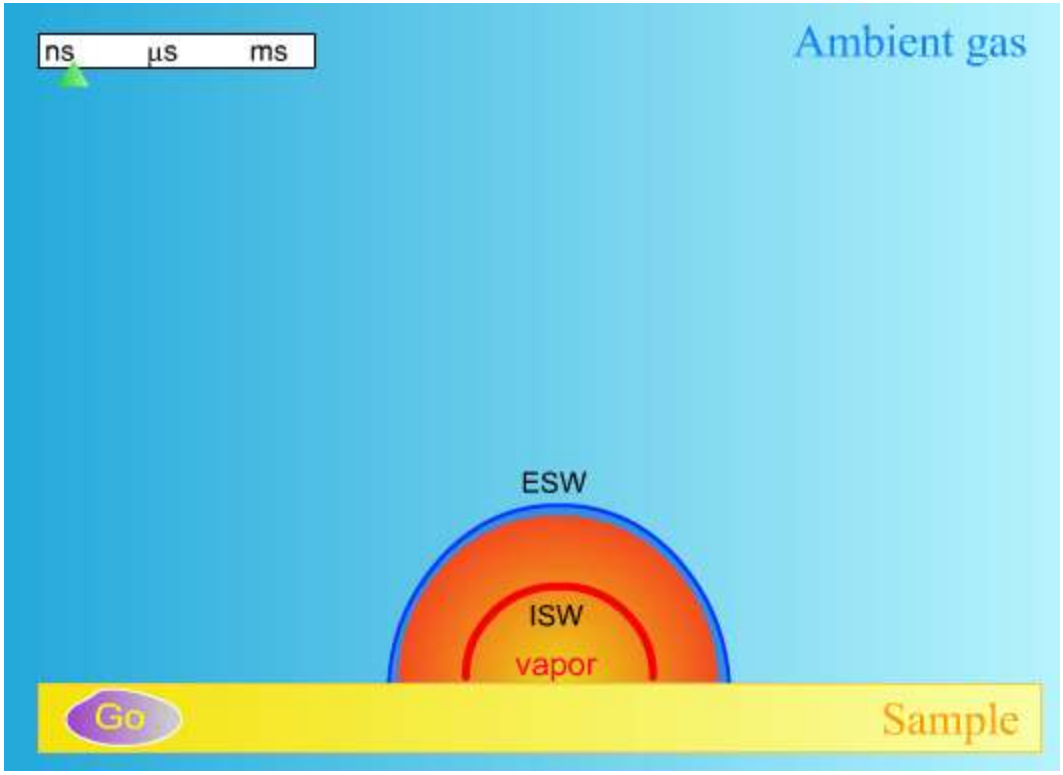
Transform portion of a sample into an optical plasma and aerosol

- **Rapid multicomponent analysis**
- **No sample preparation, consumables or waste**
- **Every element on the periodic chart**
- **Elemental, isotopic and classification**
- **Sample quantity (micro– attograms)**
- **Resolution (micro - nanometers)**
- **Qualitative, quantitative**
- **Laboratory, field, standoff applications**



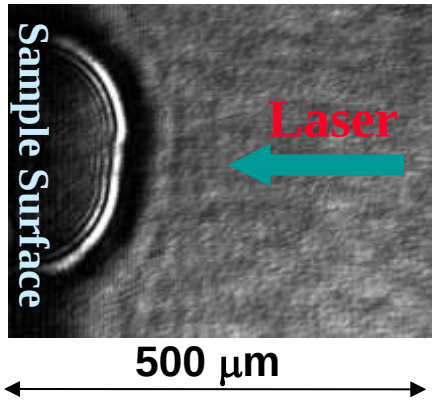
Fundamental Processes

Process simulation based on time-resolved measurements of plasma plume

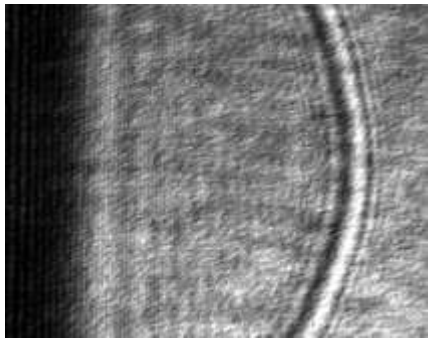


- **ISW = internal shockwave**
  ESW = external shockwave
- **Laser-sample interaction**
  (~few fs to ~few ns)
- **Vapor plume expansion**
  (~few ns to ~1µs)
- **Radiative cooling**
  (~1µs to ~100µs)
- **Vapor plume condensation**
  (~100µs to ~100ms)

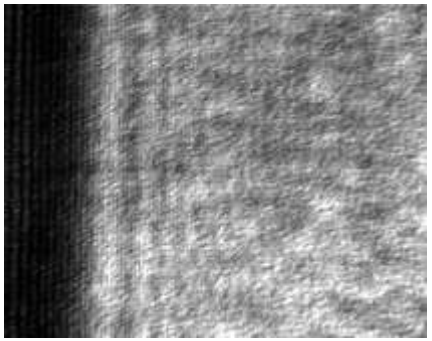
Shockwave and Particle Ejection



5 ns

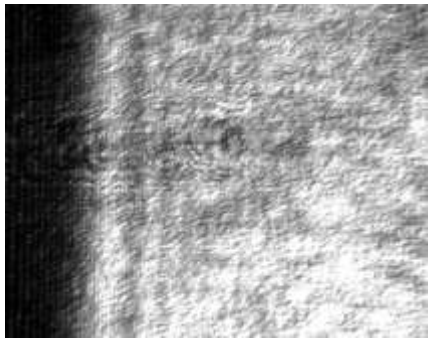


68 ns

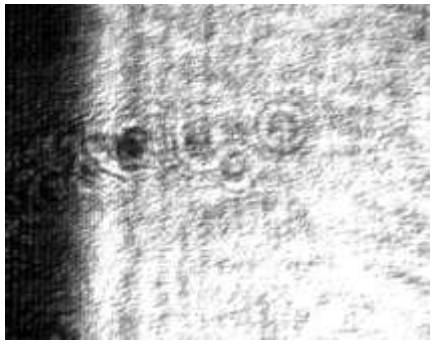


200 ns

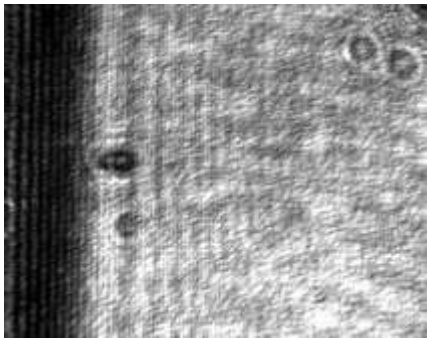
Shock wave propagates in ns



400 ns



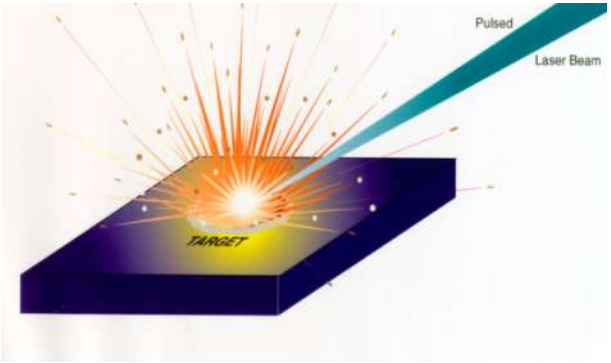
1.3 μs



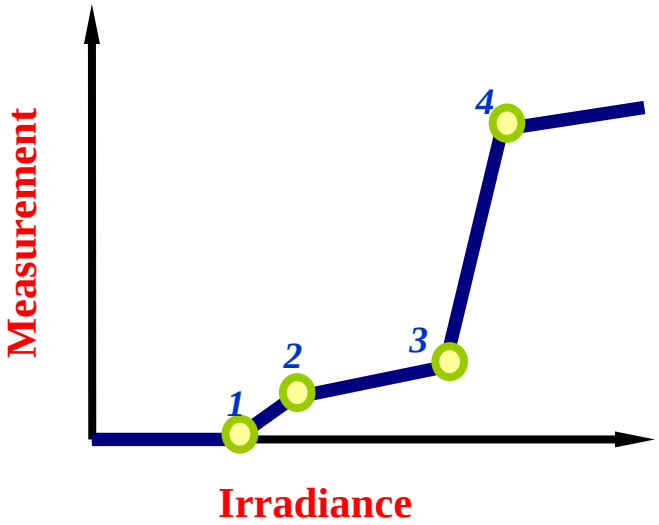
20 μs

Larger particles are ejected after 0.4 μs

Laser Ablation



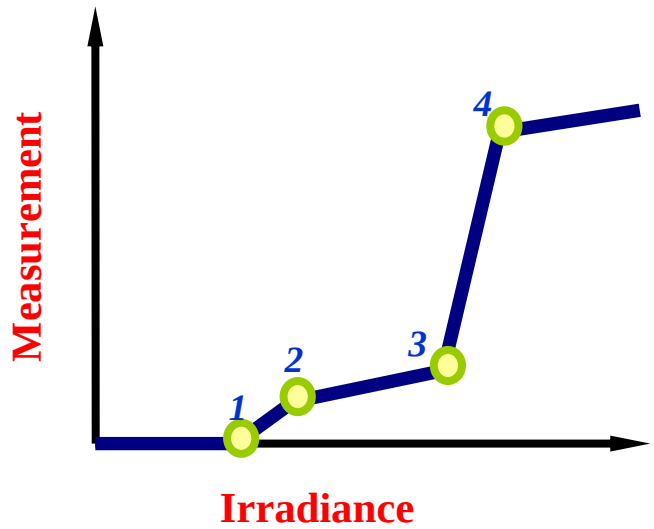
High power pulsed laser beam explodes ‘portion’ of sample

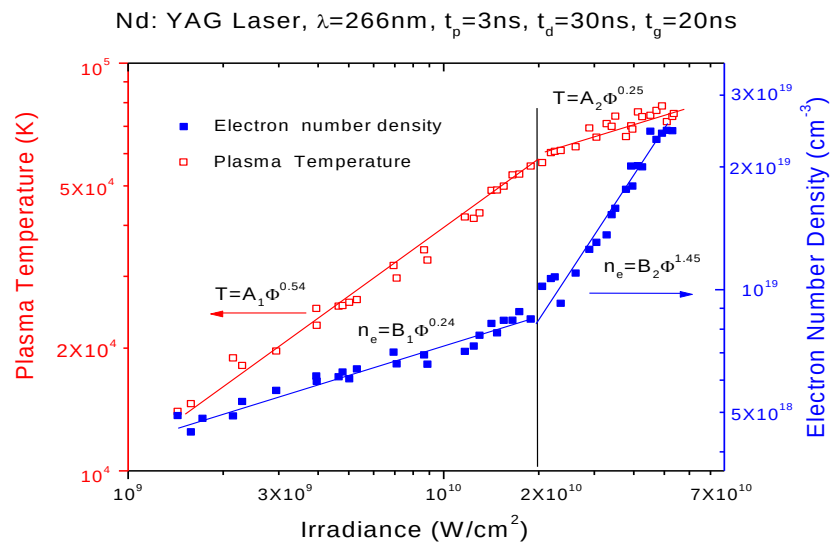


Theory:

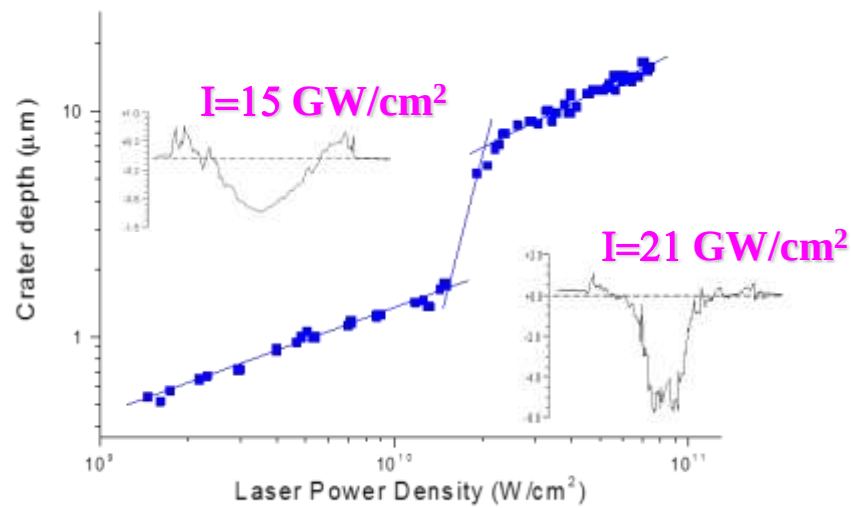
Non-linear processes
Laser material interaction
Laser-plasma interaction
Plasma-sample interaction
Vapor phase processes
Vapor phase chemistry

Dynamic, Non-linear Properties





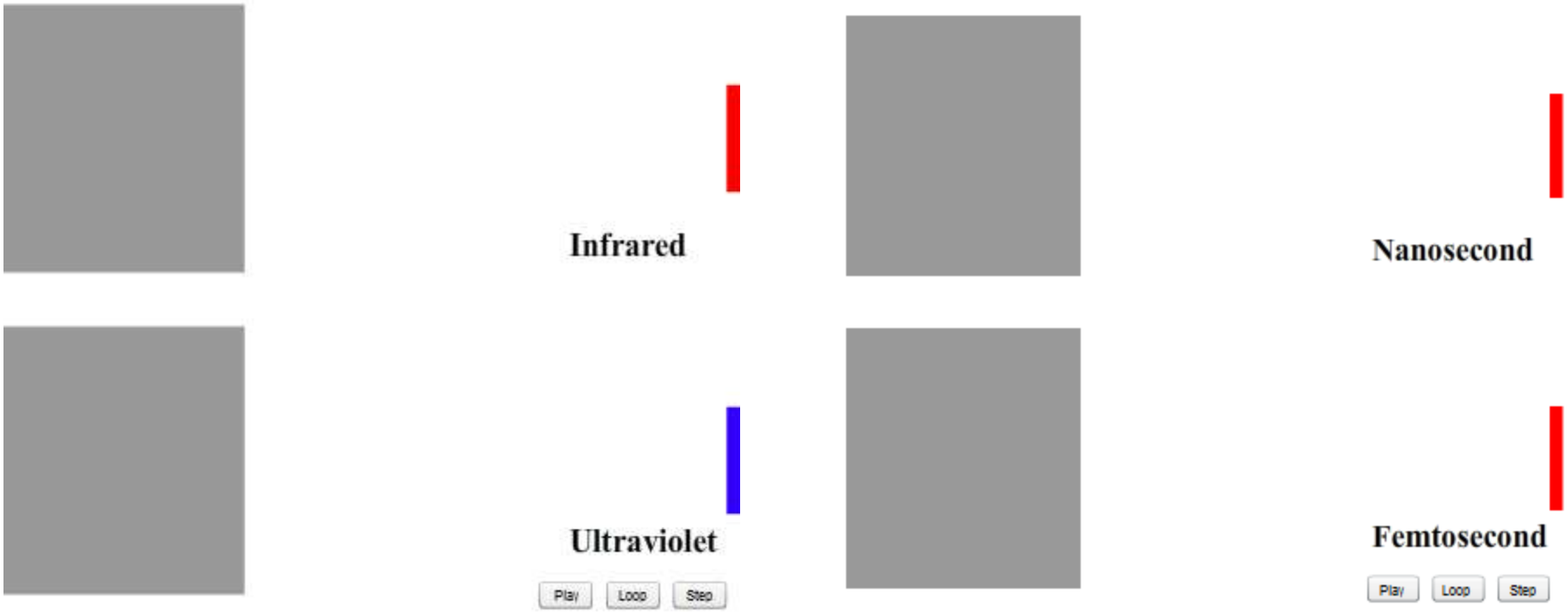
Non-linear processes
Laser material interaction
Laser-plasma interaction
Plasma-sample interaction
Vapor phase physical processes
Vapor phase chemistry



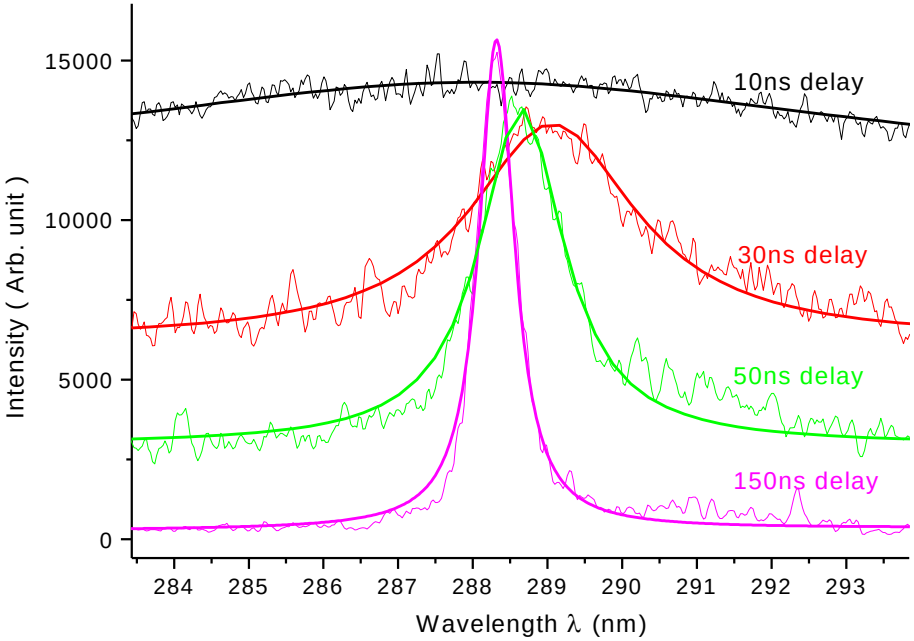
Irradiance – critical parameter

(so is every other parameter)

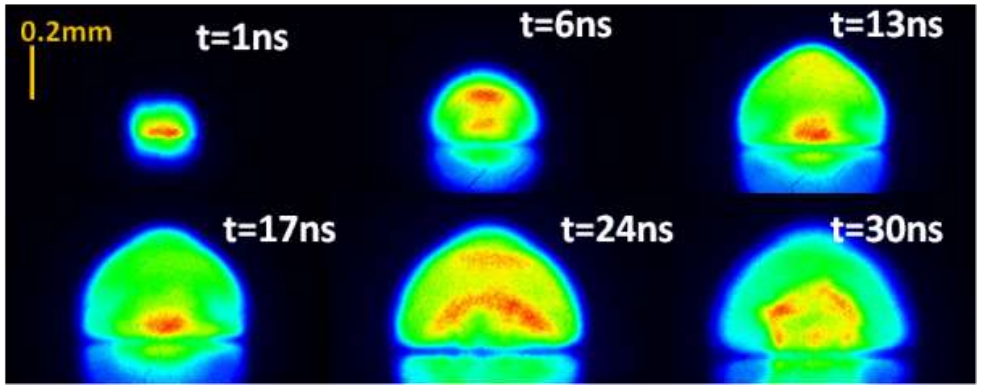
Wavelength and Pulse Duration

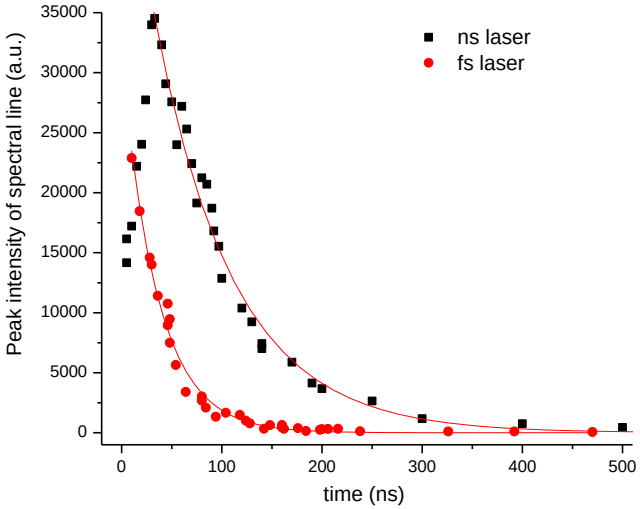


Laser Induced Plasmas

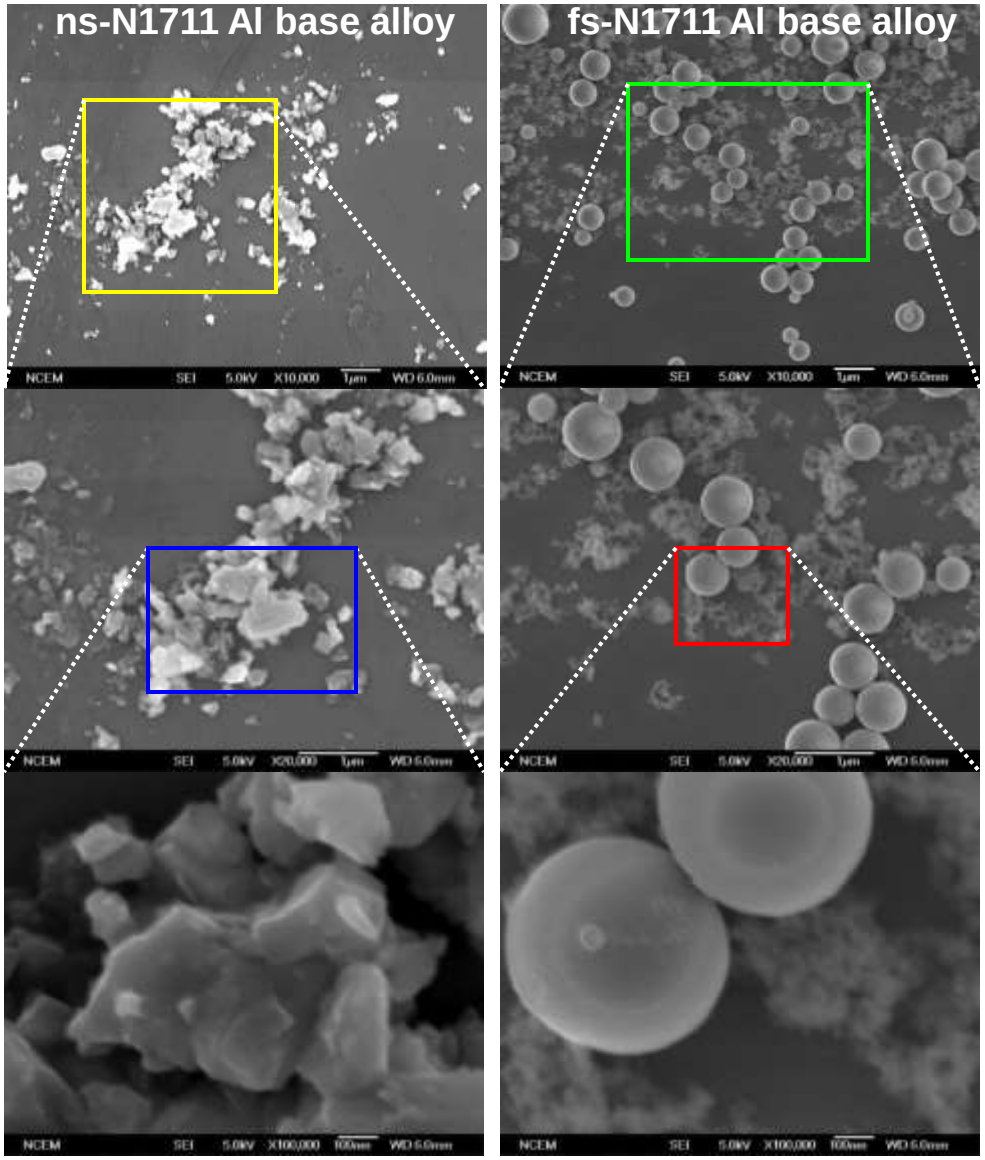


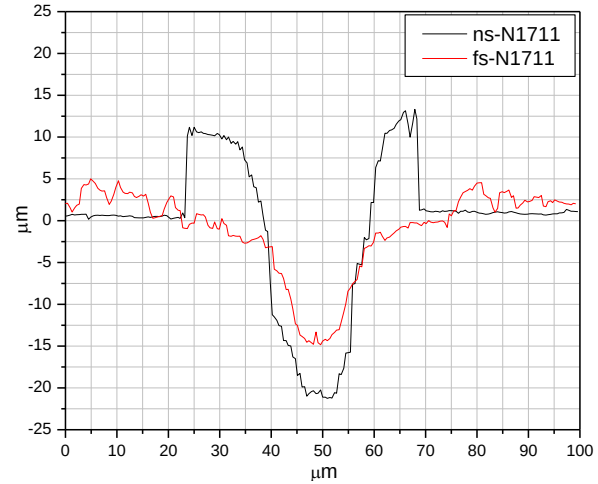
Nanosecond **Femtosecond**



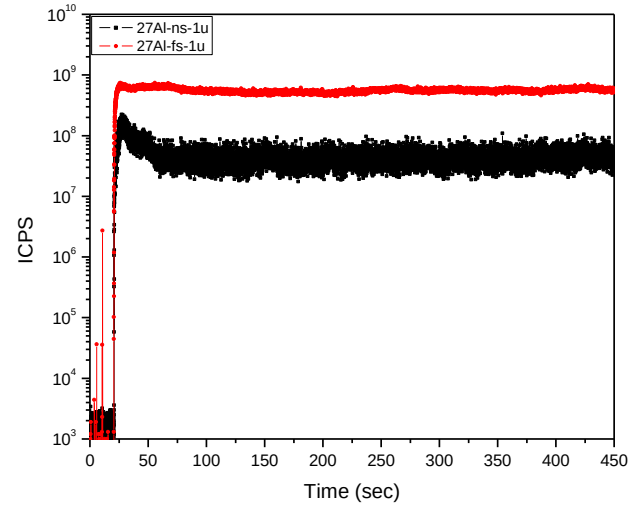


Particles



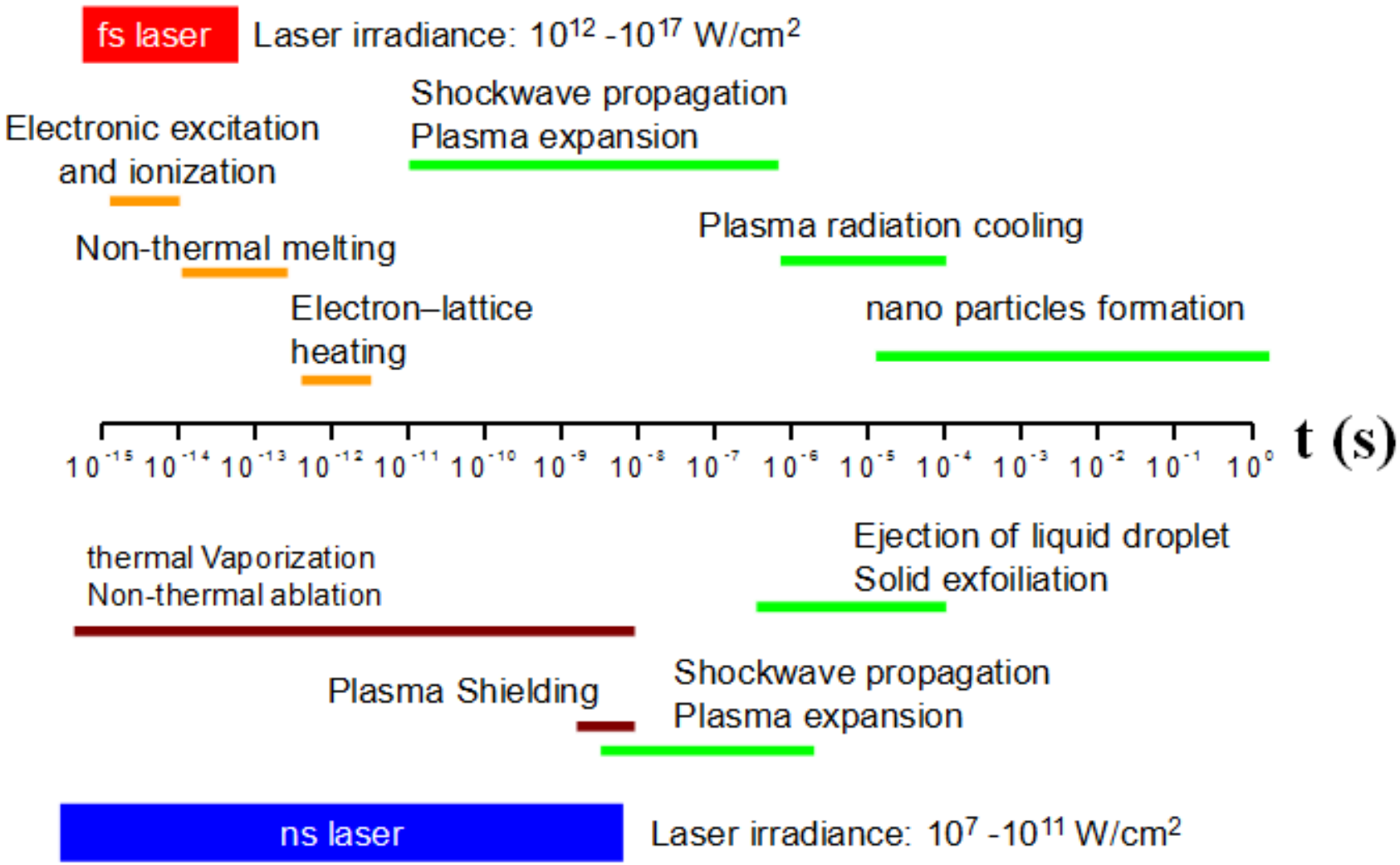


Net volume ratio = 6.6



Integrated ICPMS ratio = 12

Theories


fs laser
Laser irradiance: 10^{12} -10^{17} W/cm^2
Shockwave propagation
Plasma expansion
Electronic excitation
and ionization
Plasma radiation cooling
Non-thermal melting
Electron–lattice
heating
nano particles formation
10^{-15} 10^{-14} 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0}
t (s)
Ejection of liquid droplet
Solid exfoiliation
thermal Vaporization
Non-thermal ablation
Shockwave propagation
Plasma expansion
Plasma Shielding
ns laser
Laser irradiance: 10^{7} -10^{11} W/cm^2

Laser Ablation - Chemical Analysis

Laser Ablation

↓

Optical Plasma ◆ **LIBS, LAMIS**

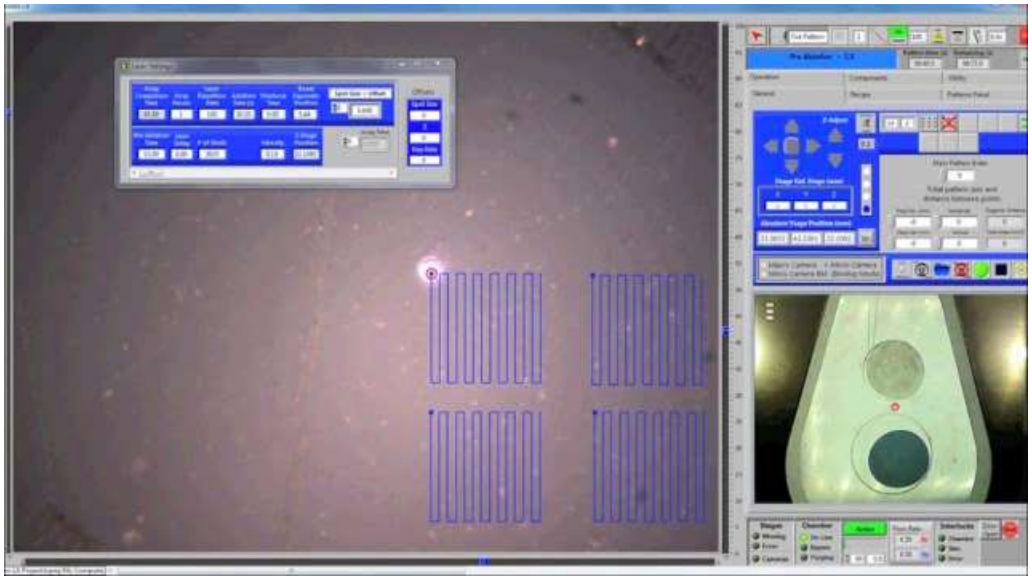
↓

Particles ◆ **ICP-MS**

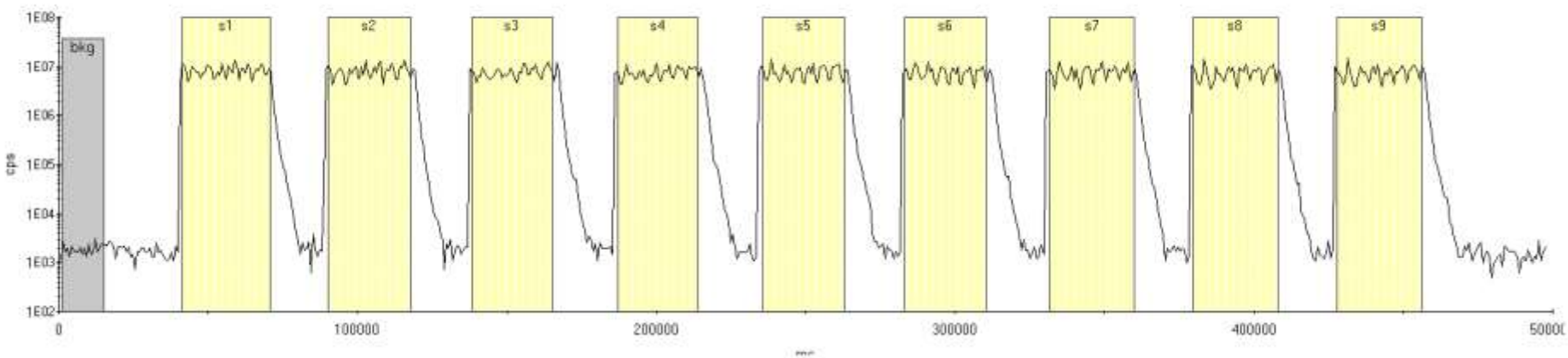
Two ways to do chemical analysis from laser ablation:

1) Measure optical spectra in the plasma:
   - LIBS (Laser Induced Breakdown Spectroscopy)
   - LAMIS (Laser Ablation Molecular Isotopic Spectrometry)
2) Transport particles to a secondary source
   - ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

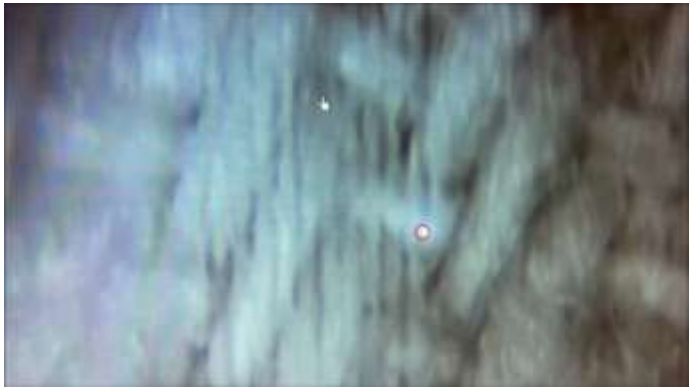
High Repetition Rate fs LA-ICP-MS

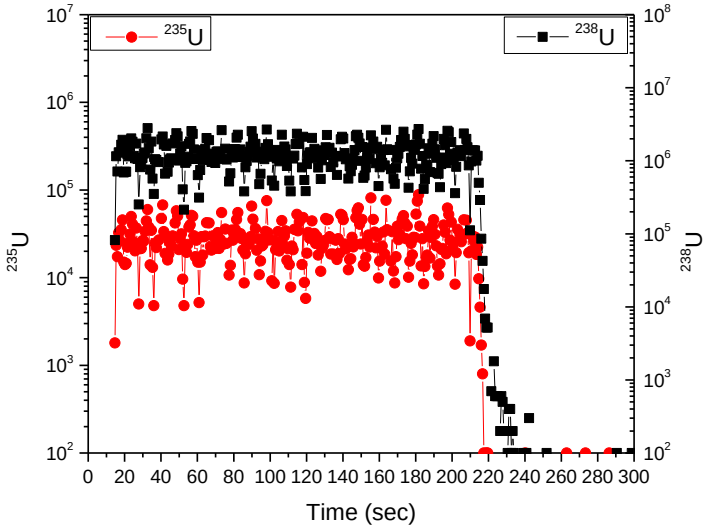


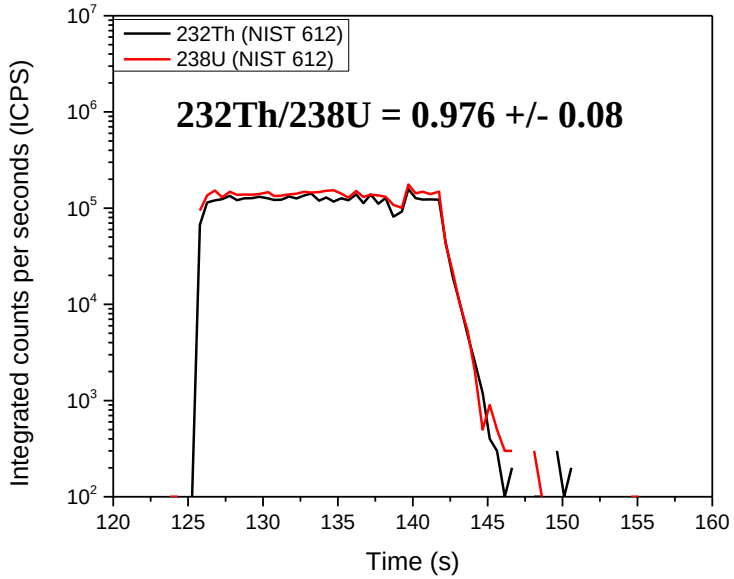
High repetition rate fs laser produces a continuous plasma and a steady stream of particles – <u>direct solid nebulizer</u>

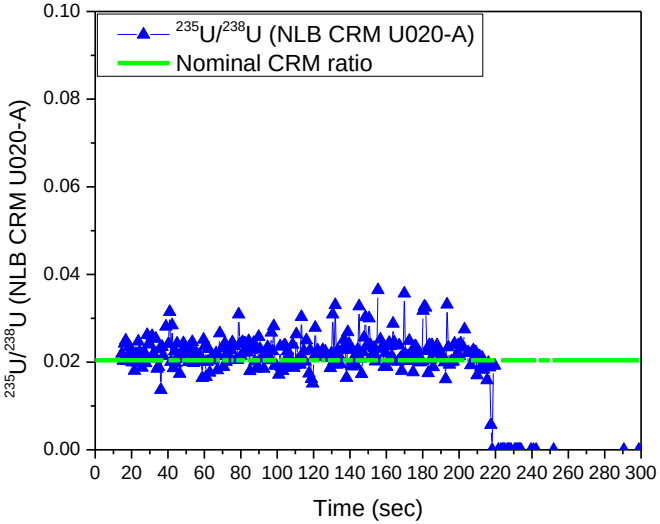


U 235/238



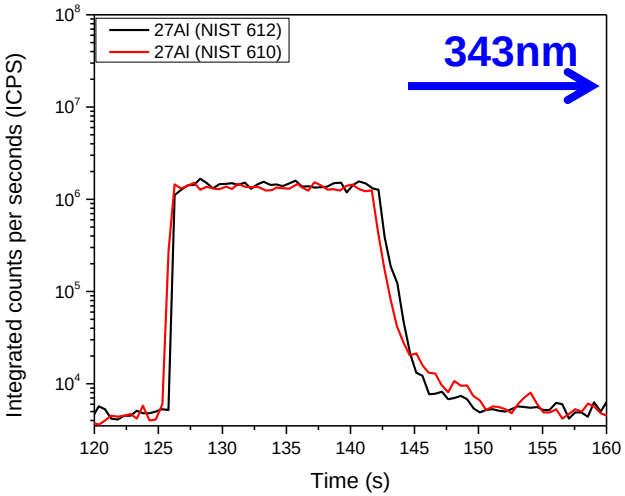


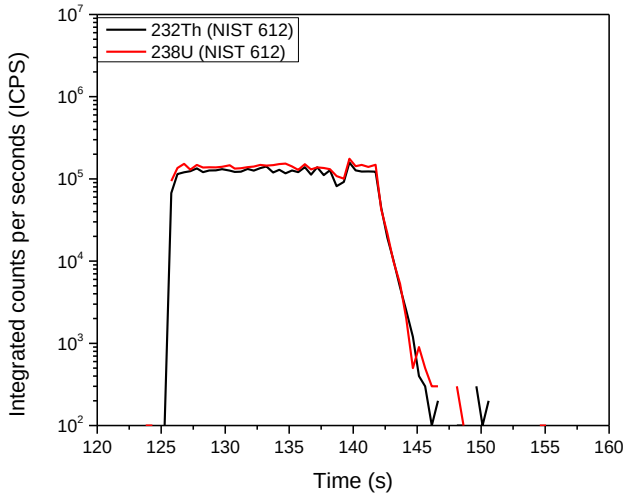




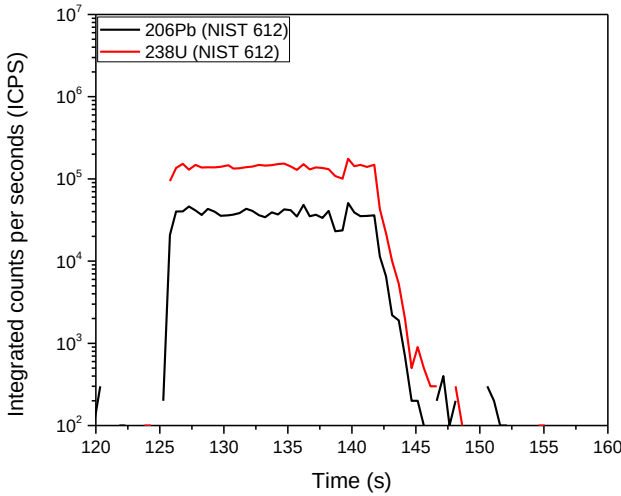
Rapid elemental and isotopic analysis
No sample preparation
Homogeneous and inhomogeneous

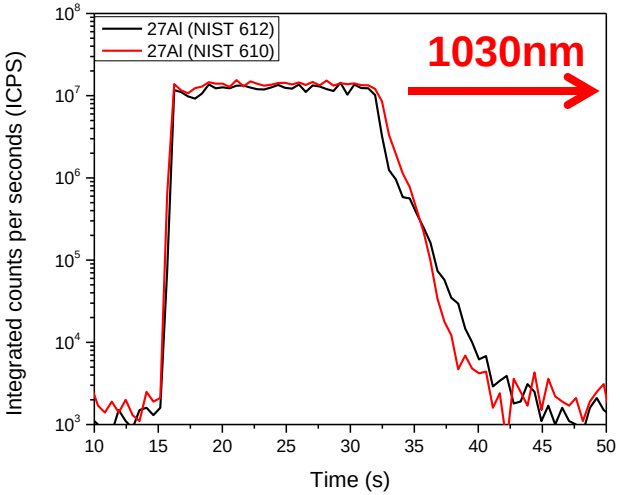
Femtosecond Laser Wavelength - Precision

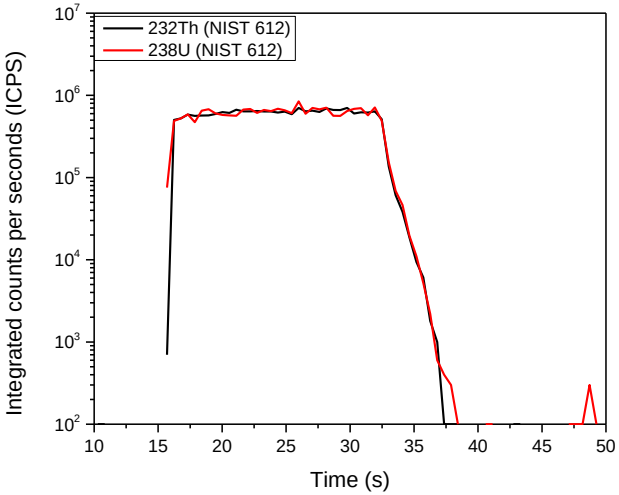




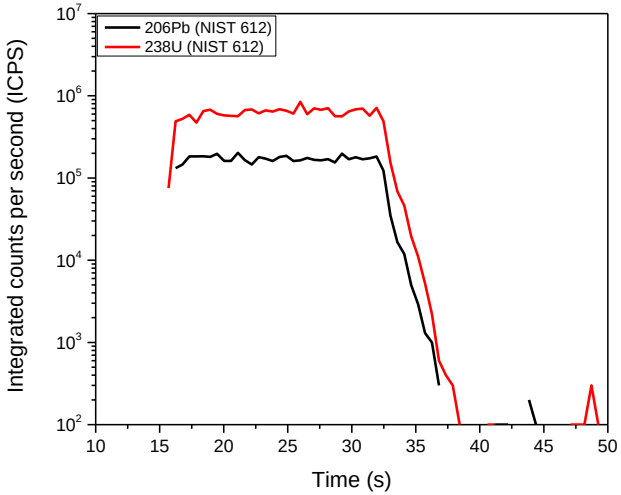
206Pb/238U = 0.282 +/- 0.03





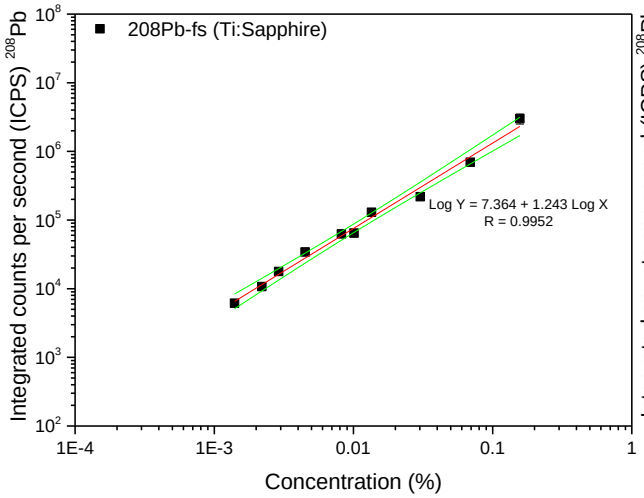


206Pb/238U= 0.286 +/- 0.035

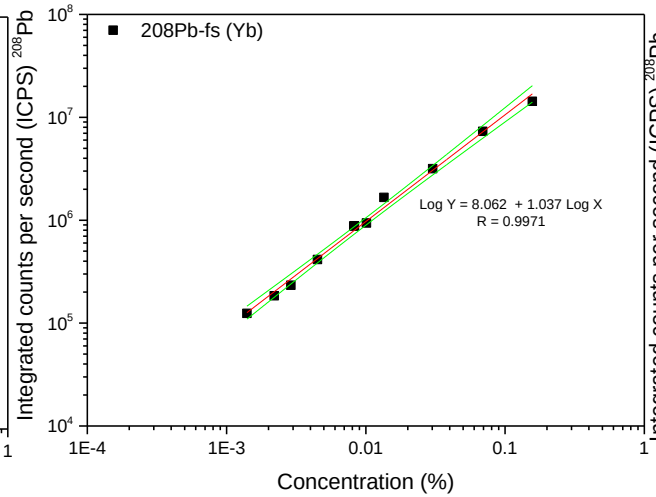


Applied Spectra
A Laser Solutions Company

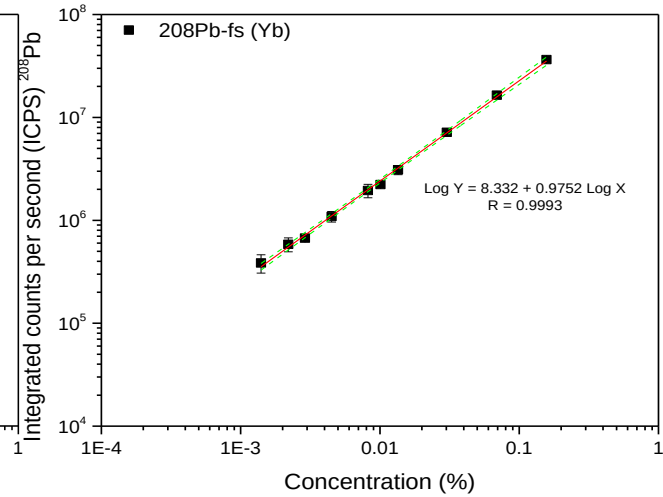
Femtosecond Laser Ablation – Matrix Matching



Ti : Sapphire. Hybrid Spectra Physics laser: 266nm



Yb: diode pump S-Pulse Amplitude laser: 343nm



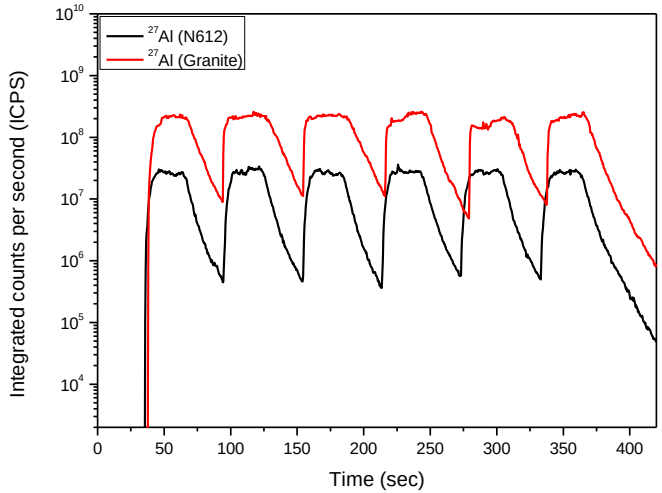
Yb: diode pump S-Pulse Amplitude laser: 1030nm

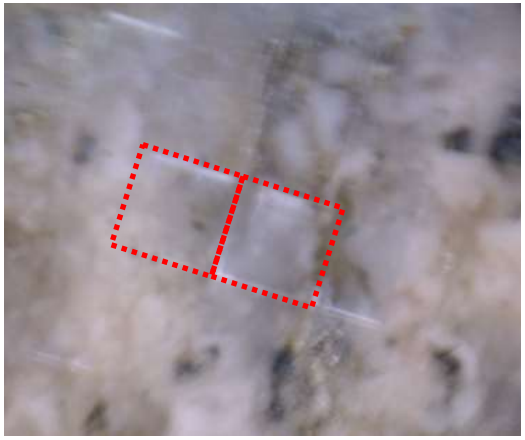
NIST 625-629, Zn base alloy (95%), 11 trace elements
NIST 1737-1741, Zn base alloy (99%), 2 trace elements

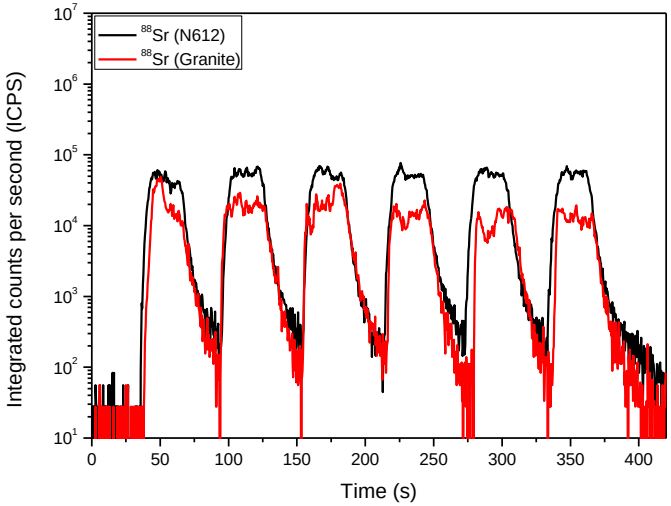
- ❑Wavelength: 1030, 343 and 266nm
- ❑Pulse duration: 200-500 fs
- ❑Laser energy: 100-250uJ
- ❑Repetition rate: 1Hz-20KHz`

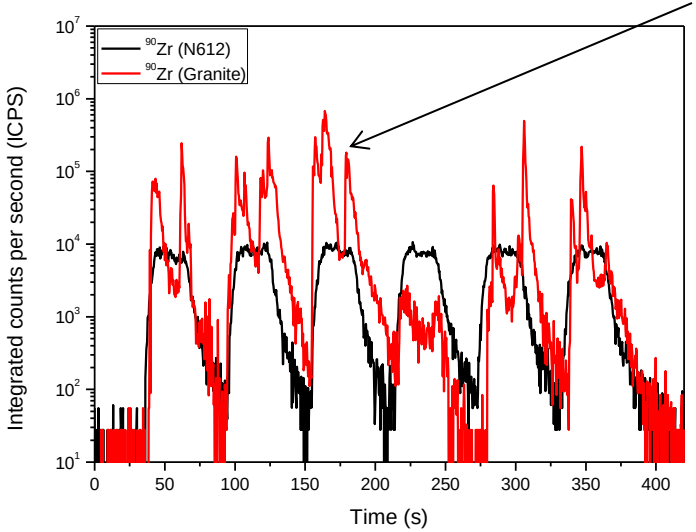
Applied Spectra
A Laser Solutions Company

Rapid Bulk Sampling and Analysis







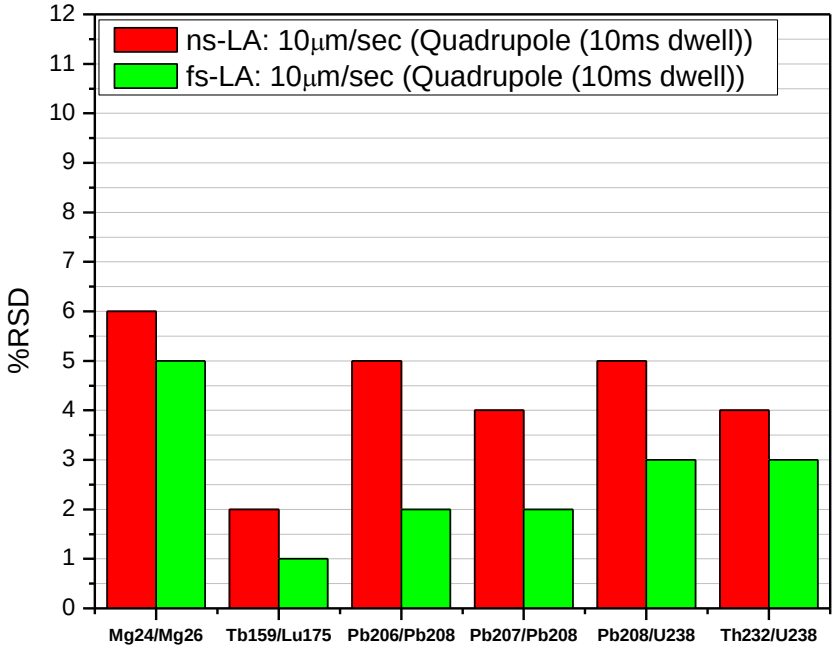


Zn is inhomogeneous in granite

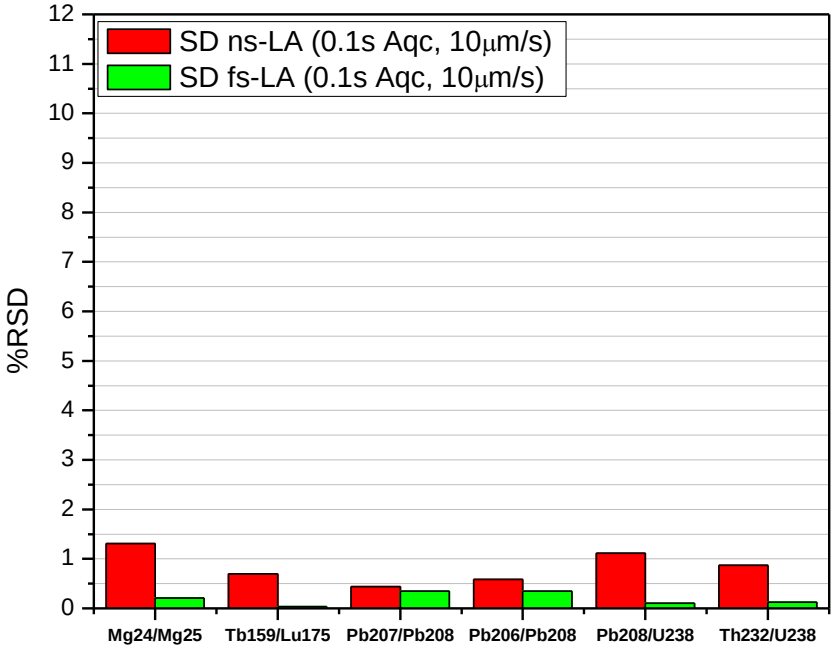
Structure on the signal intensity is related to the homogeneity of the element/isotope in the sample

Femtosecond Laser Ablation – Precision

Quadrupole

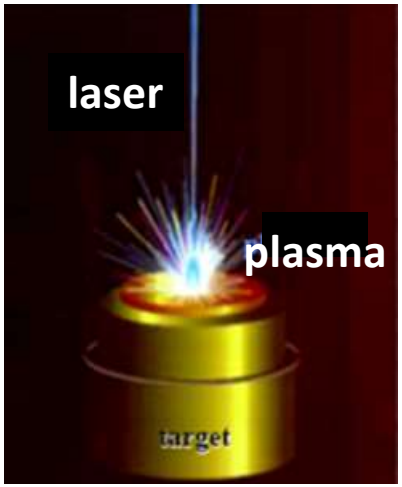


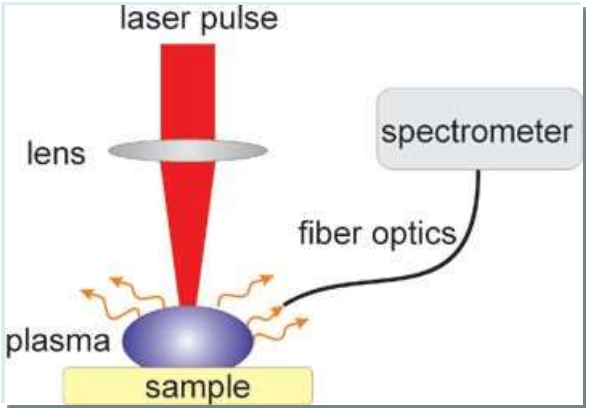
Time of Flight



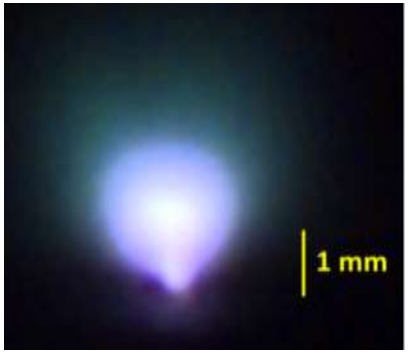
Sample NIST 610

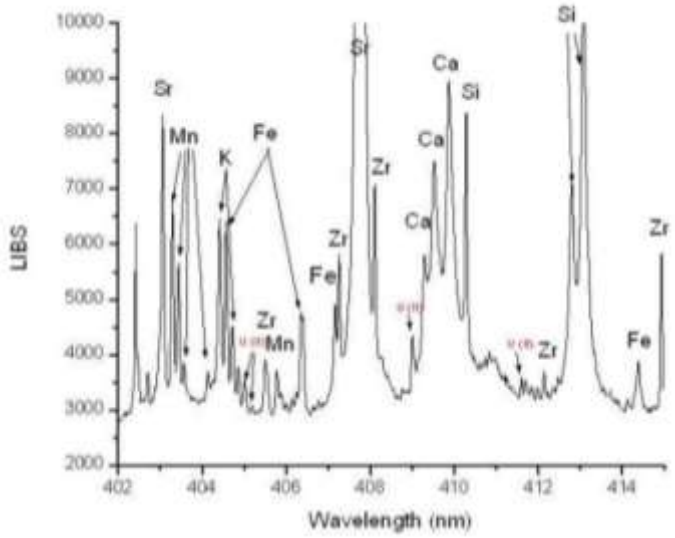
Laser Ablation – Laser Plasma Spectrochemistry





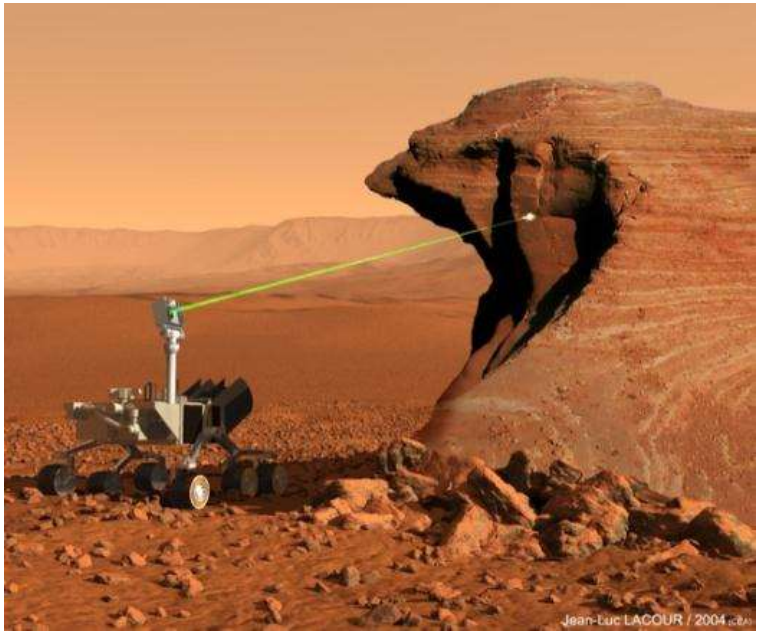
High power pulsed laser beam explodes 'portion' of sample





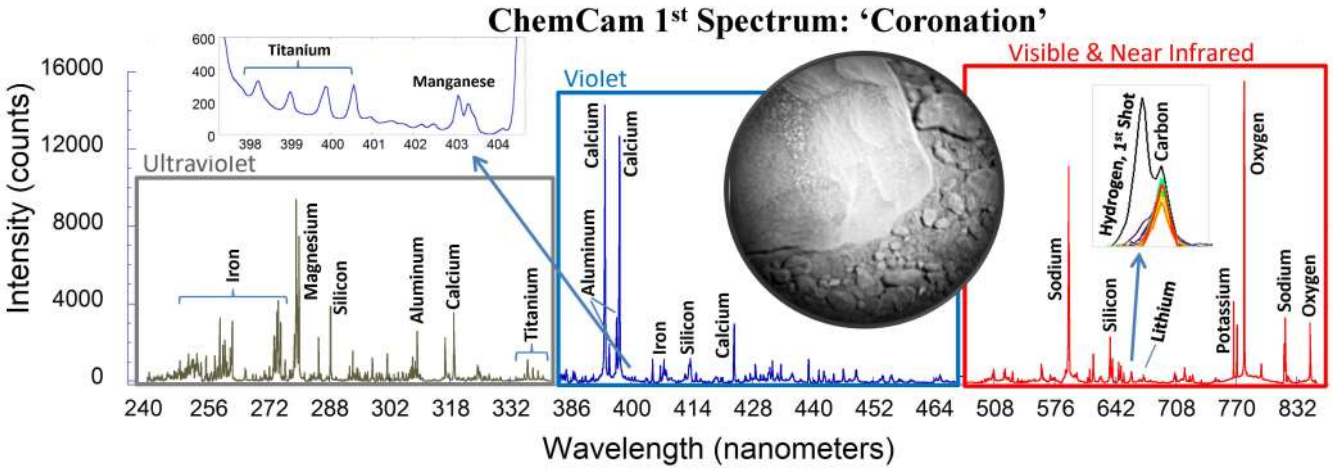
High temperature plasma atomize and excite the sample

Curiosity – NASA Mars Rover



"It is still a matter of wonder how the Martians are able to slay men so swiftly and so silently. Many think that in some way they are able to generate an intense heat in a chamber of practically absolute non-conductivity. This intense heat they project in a parallel beam against any object they choose, by means of a polished parabolic mirror of unknown composition, much as the parabolic mirror of a lighthouse projects a beam of light. But no one has absolutely proved these details. However, it is done, it is certain that a beam of heat is the essence of the matter. Heat, and invisible, instead of visible, light. Whatever is combustible flashes into flame at its touch, lead runs like water, it softens iron, cracks and melts glass, and when it falls upon water, incontinently that explodes into steam."

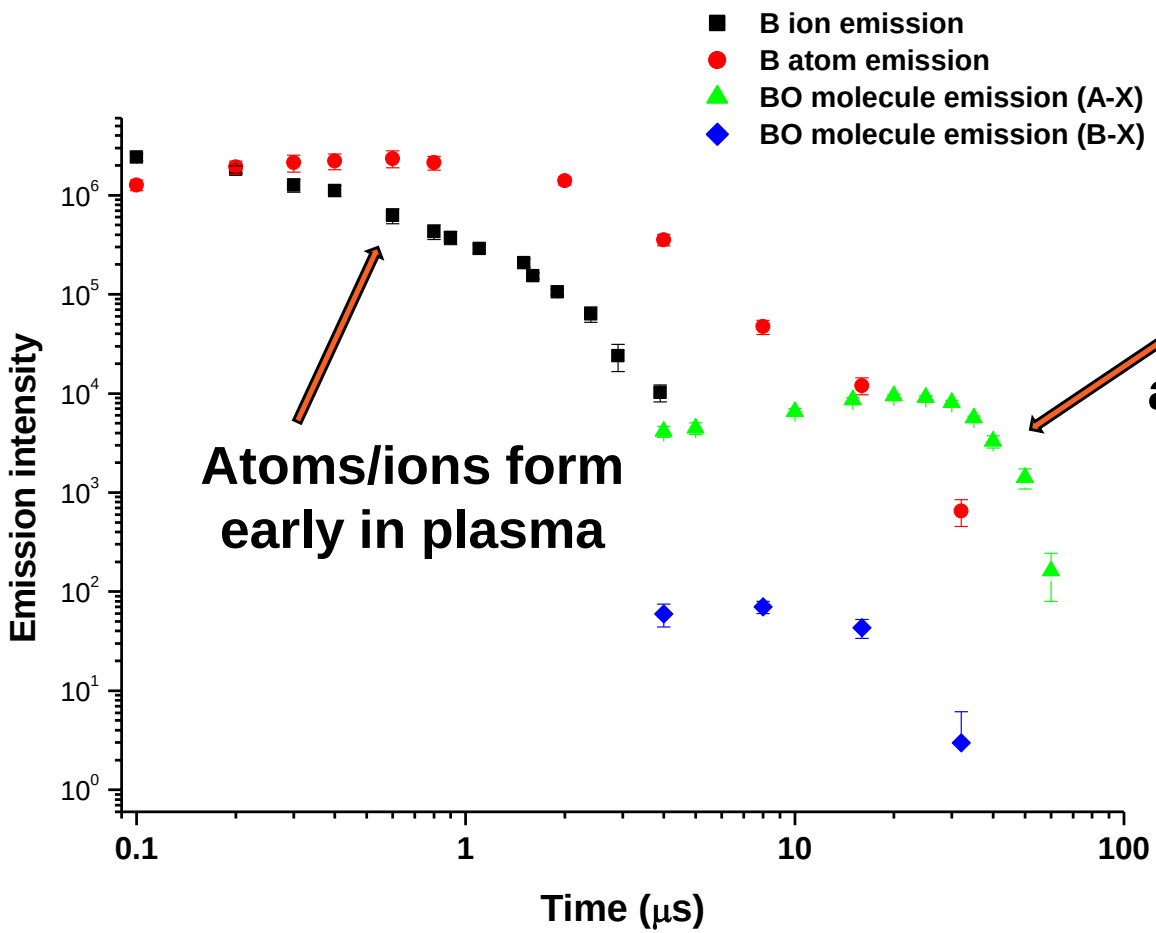
H.G. Wells, *The War of the Worlds* (1896)



ChemCam (LIBS):

- **30 elements at once**
- **Three spectrometers**
- **Analysis time 1-3 min**
- **Standoff range 2-9 m**

Laser Plasma Persistence

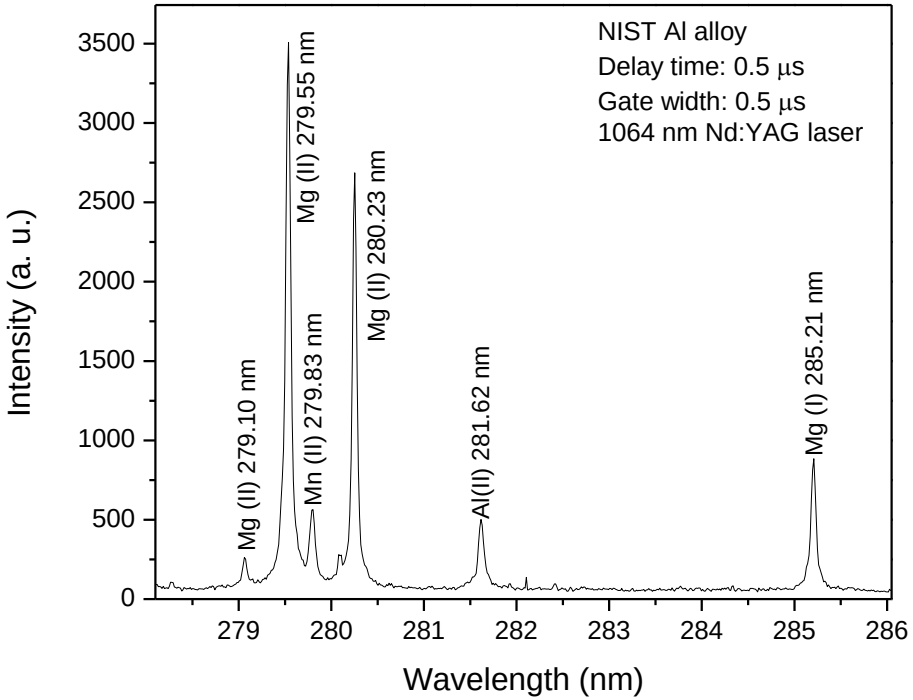


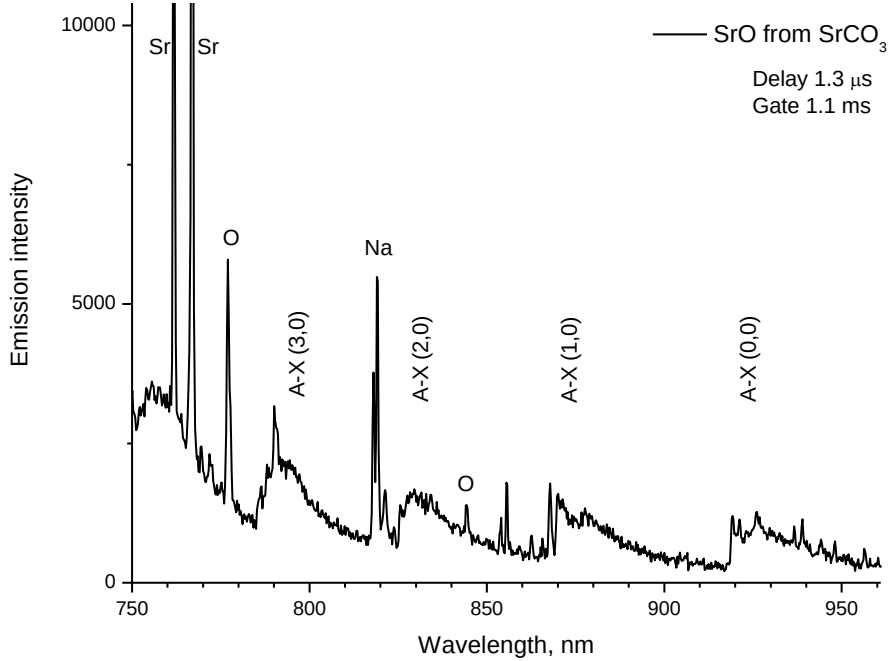
Atoms/ions form early in plasma

Molecules form later in time as plasma cools

Measurement time after ablation!

Laser Plasma Spectra



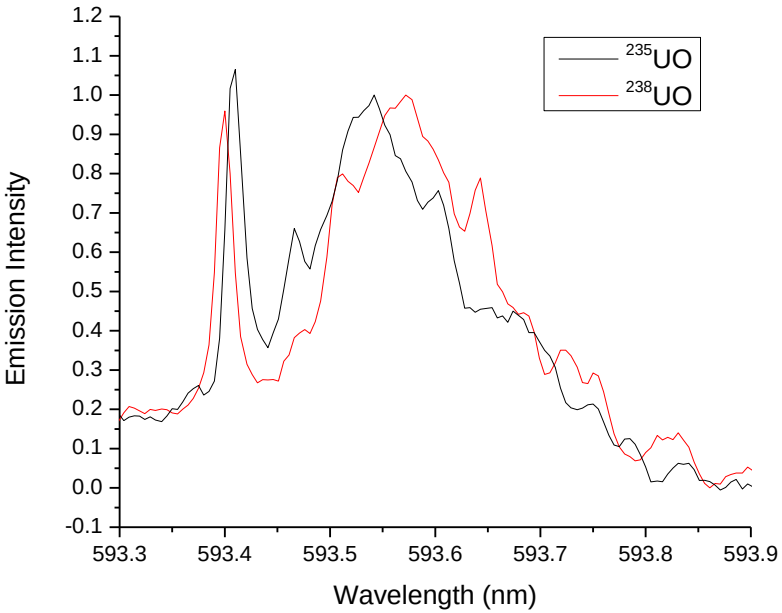


Emission spectrum for Elements

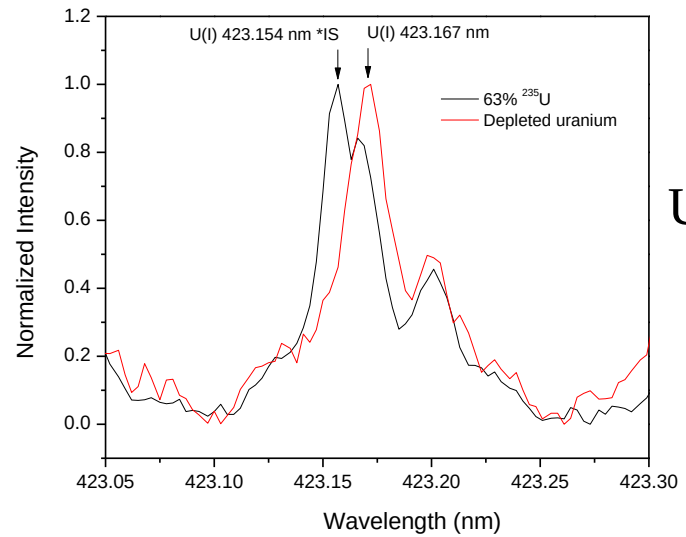
Emission Spectrum for Isotopes

LAMIS: Laser Ablation Molecular Isotopic Spectroscopy

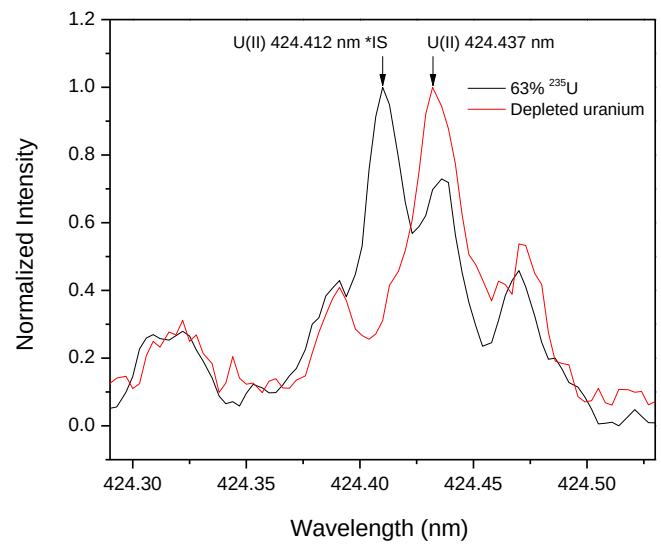
Uranium: LIBS-LAMIS



UO



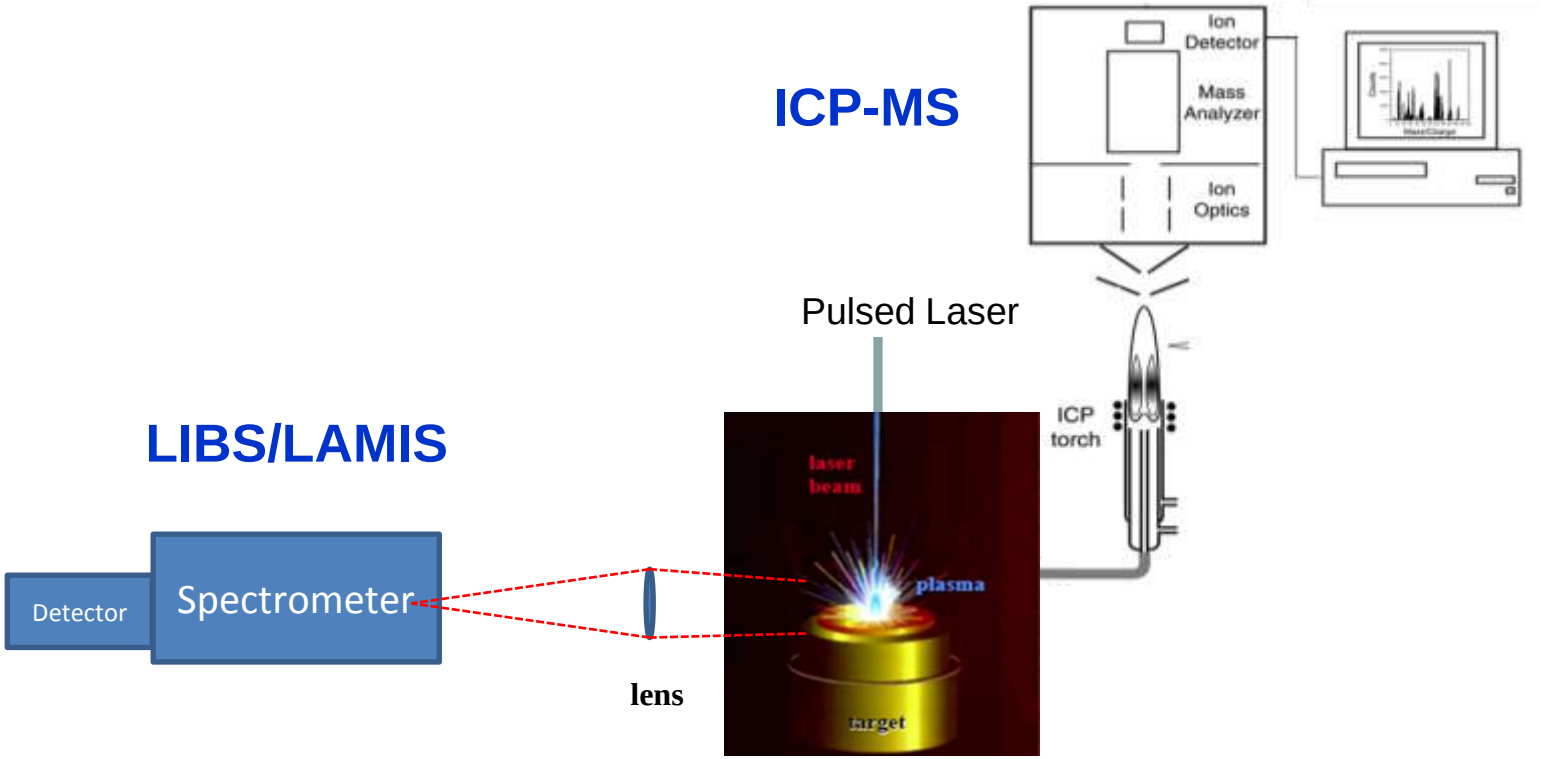
U(I)



U(II)

Provide concentration of element (U) and isotope abundance!

ICP-MS + LIBS + LAMIS



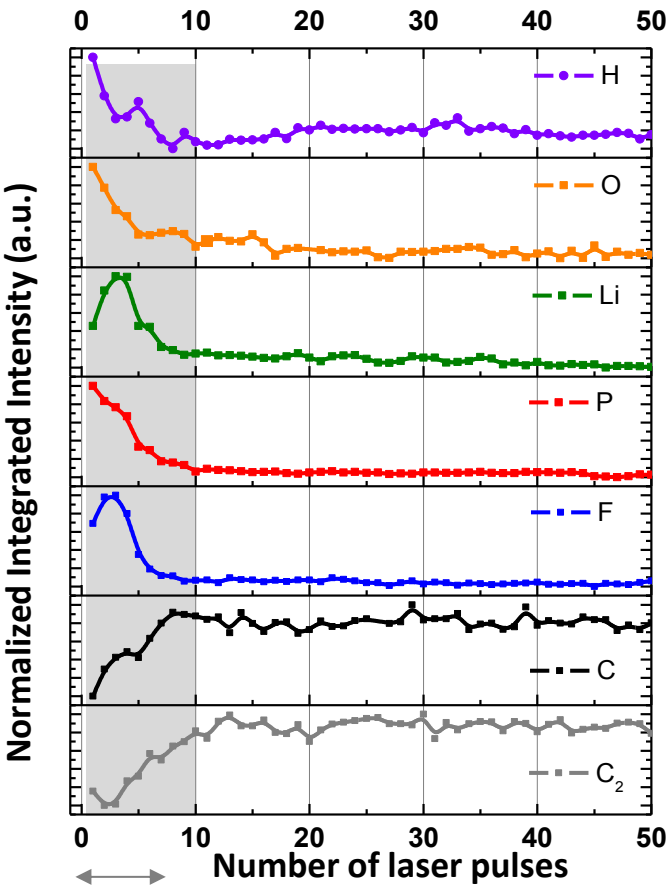
Simultaneous measurements

LA = minor, trace elements and isotopes

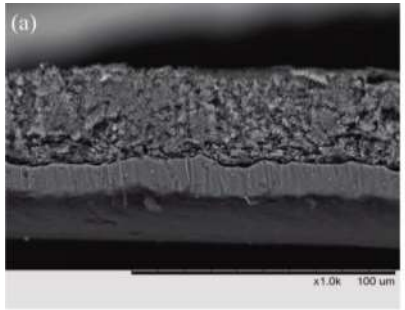
LIBS = light (C, H, N, O, Be, B) and major elements

LAMIS = light element isotopes

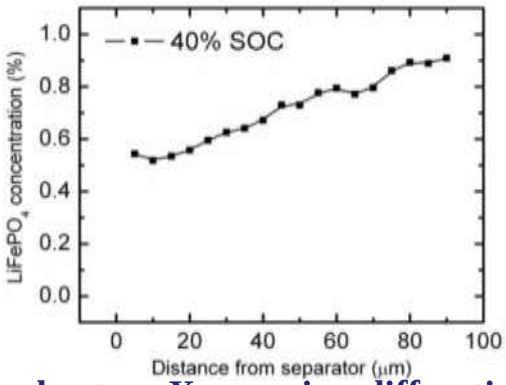
Nanometer Depth Analysis



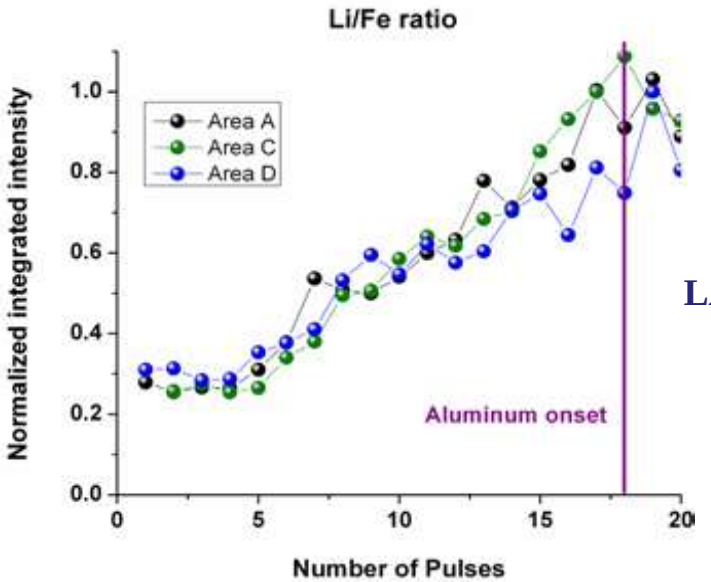
Interface layer



SEM of sample



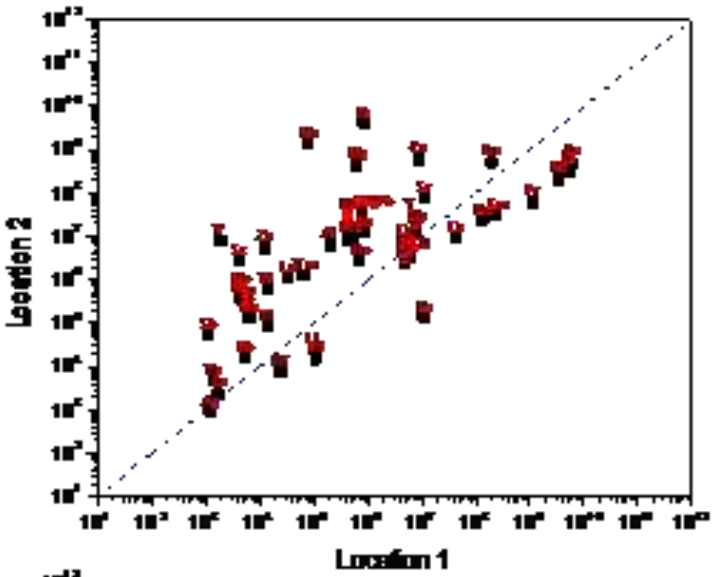
Synchrotron X-ray microdiffraction

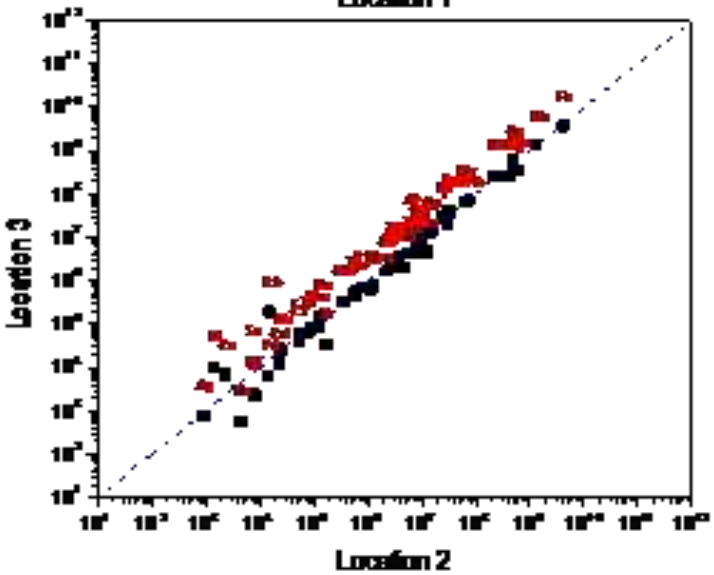


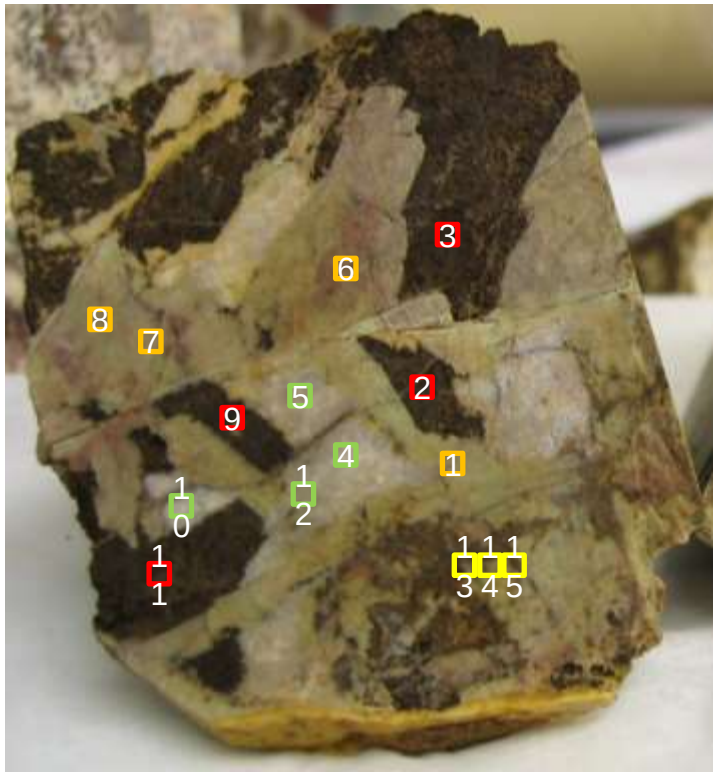
LA-ICP-MS and LIBS

Depth resolution: 7 nm/pulse

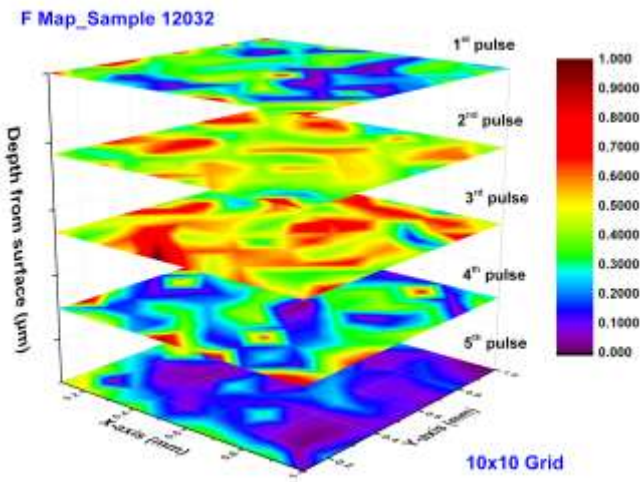
Rapid Identification – Mineral Grains



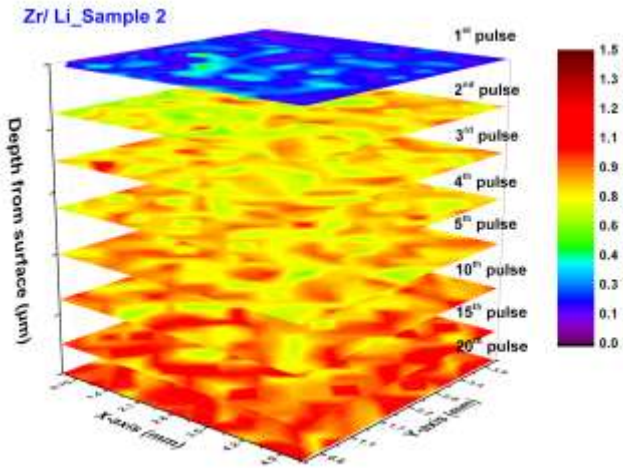




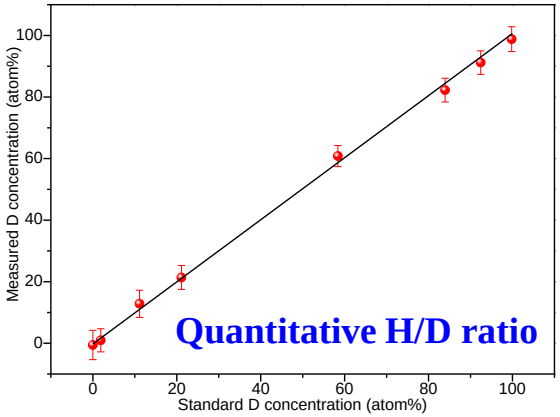
All Elements and Isotopes



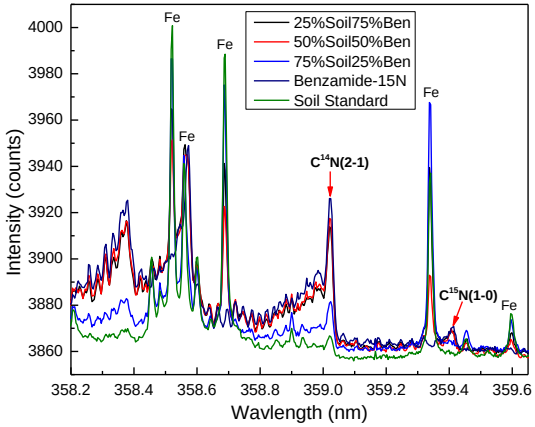
LIBS



LIBS + LA-ICP-MS



LAMIS



LIBS + LAMIS

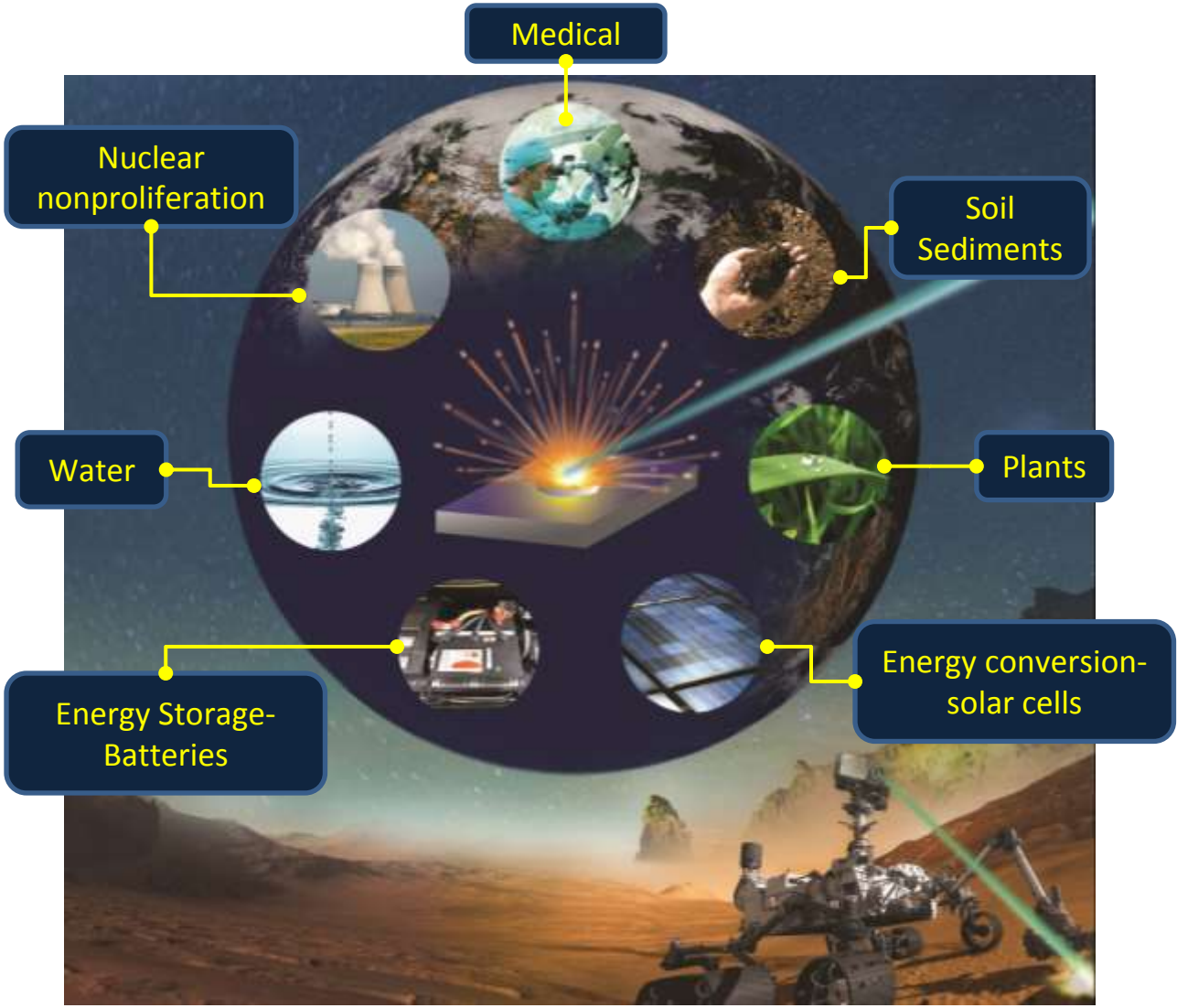
Simultaneous measurements of elements and isotopes, from H to Pu!

Laser Ablation – Chemical Analysis

This technology can be used across the range of sensor technology needs, from fundamental R&D to industrial manufacturing.

Its applications can be directed at a wide range of markets and needs, including:

- ✓ Medical uses such as innovative treatments for cancer and other diseases
- ✓ Climate change research
- ✓ Agriculture and food processing
- ✓ Energy storage and conversion technologies
- ✓ Environmental monitoring
- ✓ Nuclear nonproliferation
- ✓ Advanced materials for clean energy
- ✓ Detection of counterfeit products
- ✓ Pharmaceutical contamination detection



Summary

- **Laser ablation: ICP-MS, LIBS, LAMIS**
- **Elemental and isotopic analysis**
- **Nanometer and micron lateral and depth mapping**
- **High repetition rate analysis**
- **Homogeneous and inhomogeneous samples**
- **Femtogram - attogram absolute mass detection**
- **LAMIS – mass spectrometry without a mass spectrometer! No isobaric interferences**
- **Simultaneous LA-ICP-MS + LIBS + LAMIS**

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ICP-MS Short Course
Laser Ablation

ANDREW DUFFIN

Pacific Northwest National Laboratory

June 18, 2014

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U.S. DEPARTMENT OF ENERGY

PNNL-SA-103044

Laser Ablation Graphical Overview

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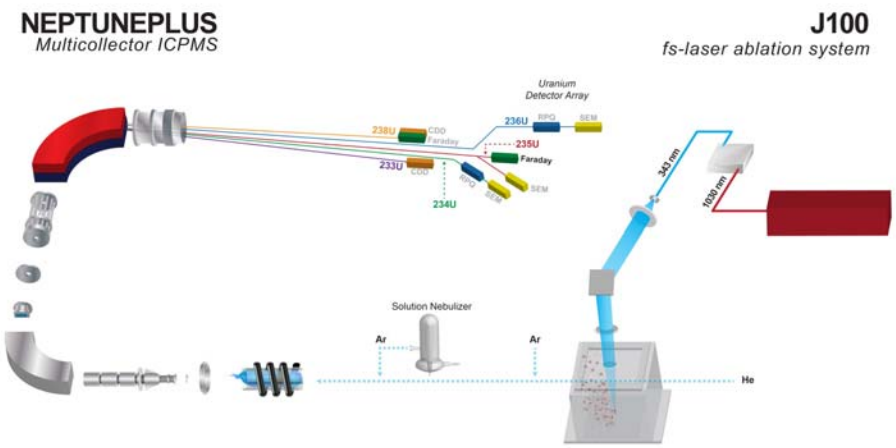

Laser Ablation ICP-MS

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- Advantages:
  - Atmospheric pressure—no waiting for vacuum
  - Sample independent—no conductive coating for insulators
  - No dissolutions, no chemistry (no reagent blanks)
  - Spatially resolved (10-200 μm spots)
  - Efficient sample utilization

Fast, high throughput

- Challenges:
  - No chemistry—isobaric interferences
  - Transient signals

3

Basic Assumptions: Elemental Analysis

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measured intensity, concentration, constant, instrument response, ablation response

$$I = C \cdot K \cdot R \cdot A$$

Standard

$$\frac{I^U_{std}}{I^{Ca}_{std}} = \frac{C^U_{std} \cdot K^U_{std} \cdot R^U_{std} \cdot A^U_{std}}{C^{Ca}_{std} \cdot K^{Ca}_{std} \cdot R^{Ca}_{std} \cdot A^{Ca}_{std}}$$

Unknown

$$\frac{I^U_{unk}}{I^{Ca}_{unk}} = \frac{C^U_{unk} \cdot K^U_{unk} \cdot R^U_{unk} \cdot A^U_{unk}}{C^{Ca}_{unk} \cdot K^{Ca}_{unk} \cdot R^{Ca}_{unk} \cdot A^{Ca}_{unk}}$$

Assume constants, instrument response, and ablation response are the same for both sample and standard

$$\frac{I^U_{unk}}{I^{Ca}_{unk}} = \frac{C^U_{unk} \cdot I^U_{std} \cdot C^{Ca}_{std}}{C^{Ca}_{unk} \cdot I^{Ca}_{std} \cdot C^U_{std}}$$

4

Basic Assumptions: Isotopic Analysis

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measured intensity, concentration, constant, instrument response, ablation response

$$I = C \cdot K \cdot R \cdot A$$

Assume constants, instrument response, and ablation response are the same for both sample and standard

Standard

$$\frac{I_{std}^{U1}}{I_{std}^{U2}} = \frac{C_{std}^{U1} \cdot K_{std}^{U1} \cdot R_{std}^{U1} \cdot A_{std}^{U1}}{C_{std}^{U2} \cdot K_{std}^{U2} \cdot R_{std}^{U2} \cdot A_{std}^{U2}}$$

For solution standard assume ablation response term is unity in the unknown

Unknown

$$\frac{I_{unk}^{U1}}{I_{unk}^{U2}} = \frac{C_{unk}^{U1} \cdot K_{unk}^{U1} \cdot R_{unk}^{U1} \cdot A_{unk}^{U1}}{C_{unk}^{U2} \cdot K_{unk}^{U2} \cdot R_{unk}^{U2} \cdot A_{unk}^{U2}}$$

$$\frac{I_{unk}^{U1}}{I_{unk}^{U2}} = \frac{C_{unk}^{U1} \cdot I_{std}^{U1} \cdot C_{std}^{U2}}{C_{unk}^{U2} \cdot I_{std}^{U2} \cdot C_{std}^{U1}}$$

5

Sample Preparation

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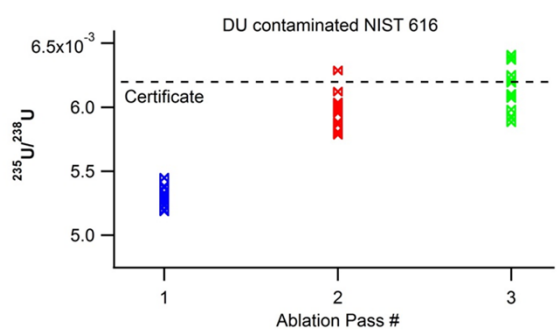
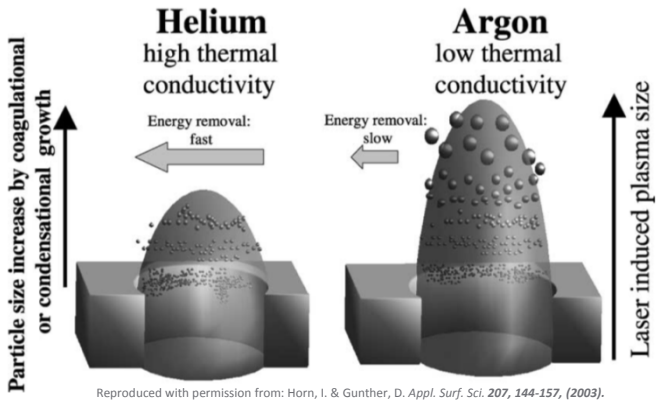
- Keep it clean from contamination
- Fit it in the ablation chamber
  - Embed in epoxy and polish



6

Carrier Gas



Reproduced with permission from: Horn, I. & Gunther, D. *Appl. Surf. Sci.* ***207, 144-157, (2003).***

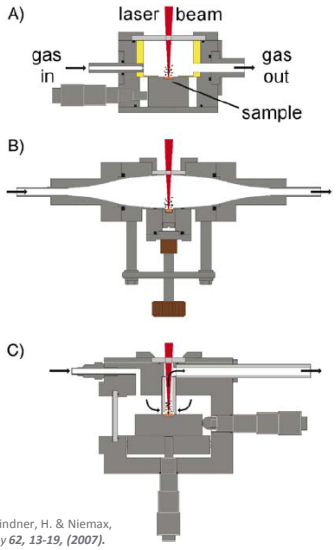
Particle size differences observed after ablation with a 193 nm nanosecond laser are attributed to thermal conductivity of the carrier gas

7

Ablation Chamber

"… the measurement of the mass transport efficiency in fs-LA-ICP-MS using He as gas in the ablation cell was found to be independent of the sampling cell. This holds for cells with strong turbulent flow which should be applied for bulk analysis as well as for cells with sampling tubes which should be used whenever single shot analyses are performed…"

fs-LA: measured a lower limit of 77% aerosol transportation



Reproduced with permission from: Garcia, C. C., Lindner, H. & Niemax, K. *Spectrochimica Acta Part B-Atomic Spectroscopy* ***62, 13-19, (2007).***

8

Sample Utilization Efficiency ns vs. fs

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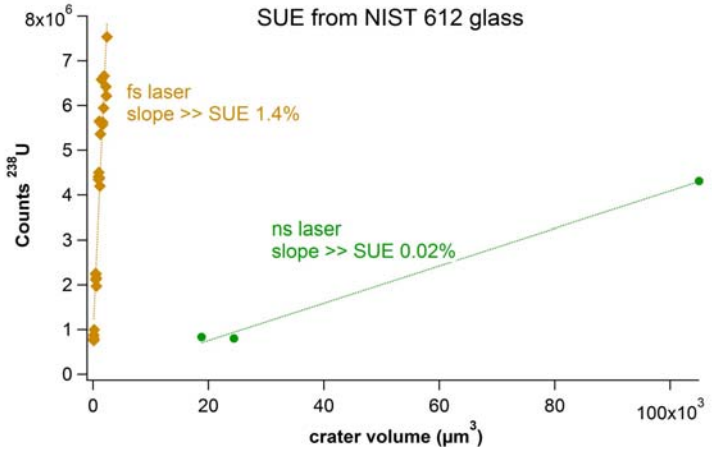

fs-laser ablation offers excellent sample utilization efficiency

9

Make up Gas: Wet or Dry Plasma

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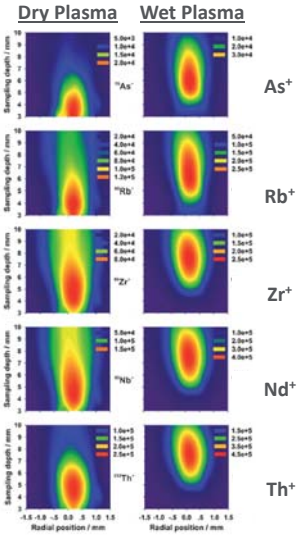
Wet Plasma	Dry Plasma
Convenient introduction of standard	Must use ablation standard
More stable plasma ionization	Less interference from oxide and hydride ions
Enhanced Sensitivity (ca. factor of 2) from most elements	Need to tune to individual element

"The more uniform axis distributions of elements with different physical and chemical properties within the ICP implies that vaporization, atomization and ionization of analytes are enhanced when small amounts of water and/or ethanol vapor are introduced into the central channel of the ICP."



Reproduced by permission of The Royal Society of Chemistry. Liu S.,Z. Hu,D. Gunther Y. Ye, Y Liu, S Gao, and S Hu. 2014. "Signal enhancement in laser ablation inductively coupled plasma-mass spectrometry using water and/or ethanol vapor in combination with a shielded torch." *Journal of Analytical Atomic Spectrometry*, 29:536-544

10

Make up Gas: Wet or Dry Plasma

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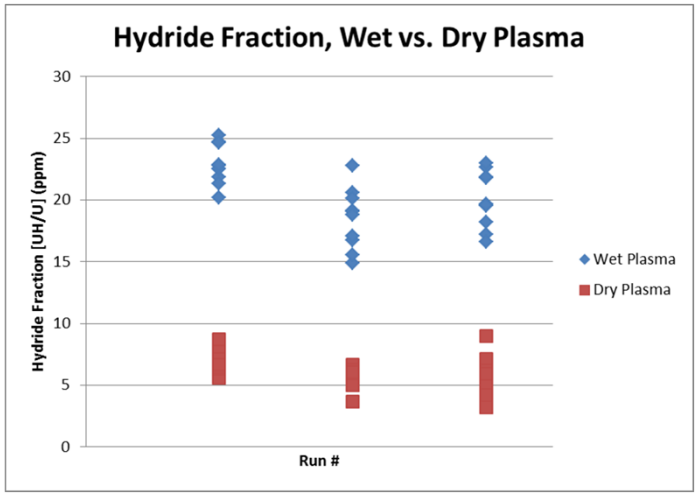
Hydride formation



Plasma Loading

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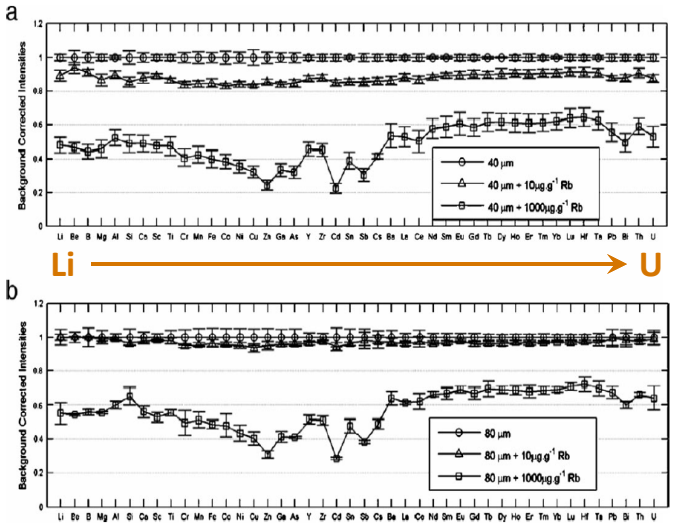

- Signal is depressed with plasma loading
- Inter-element sensitivity changes

Reproduced by permission of The Royal Society of Chemistry. I. Kroslakova and D Gunther. 2007. "Elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry: evidence for mass load induced matrix effects in the ICP during ablation of a silicate glass ." *Journal of Analytical Atomic Spectrometry*, 29:536-544

Mass Spectrometer vs. (Well-behaved) Transient Signal

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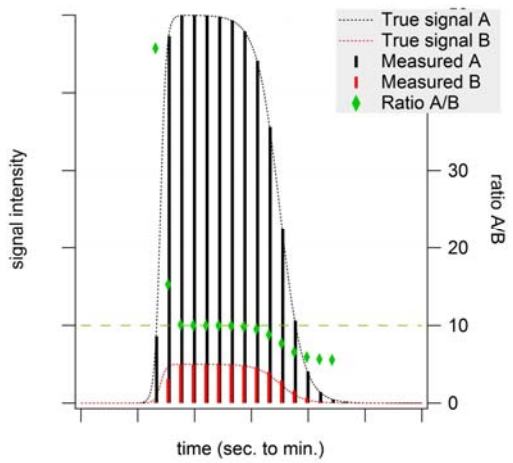

Single Collector Instrument

- Peak hopping with dwell time based on signal level
- Point-by-point ratios are untrustworthy when the signal changes rapidly
- Must create a pseudo-steady-state signal and pick a threshold (arbitrary) for data elimination
- Define region for background subtraction

13

Mass Spectrometer vs. (Well-behaved) Transient Signal (contd.)

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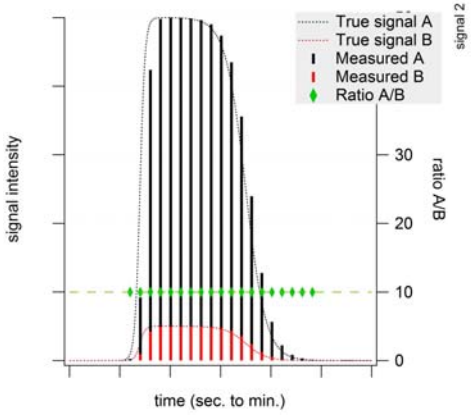

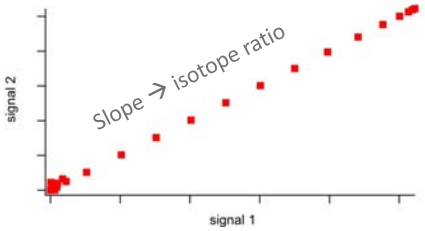

Multiple collector instrument

- Signal and plasma fluctuations are correlated on each detector
- Two isotope plots eliminate need to threshold (arbitrary) and the need to define a region for background subtraction
- Two isotope plots naturally weight higher signals (regression fit)

14

Mass Spectrometer vs. (Well-behaved) Transient Signal (contd.)

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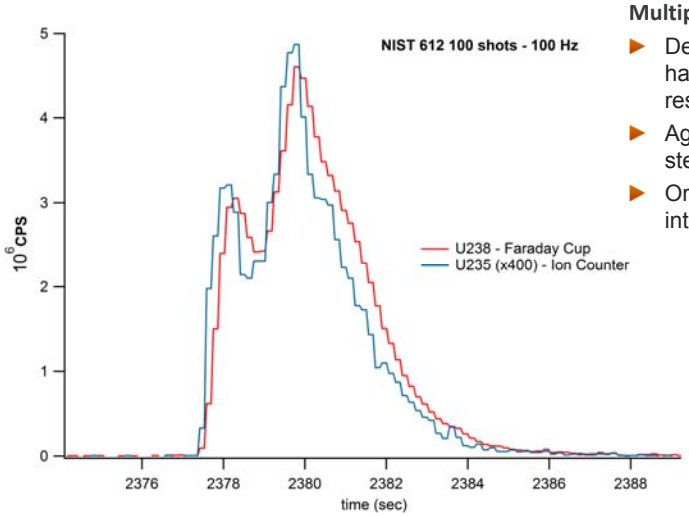

Multiple collector instrument

- Detectors do not always have the same time response
- Again, need pseudo steady-state
- Or, use peak area integration

15

Mass Spectrometer vs. (Well-behaved) Transient Signal (contd.)

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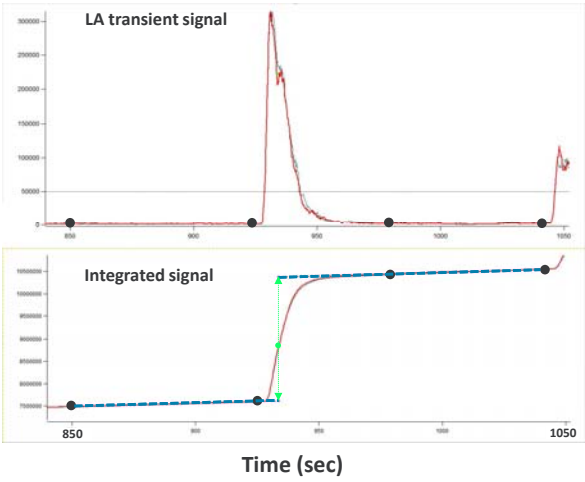

Transient integration

- Extrapolate the integrated signal baselines around a transient
- Vertical distance at inflection is 'background' subtracted, integrated signal

16

Mass Spectrometer vs. (Well-behaved) Transient Signal (contd.)

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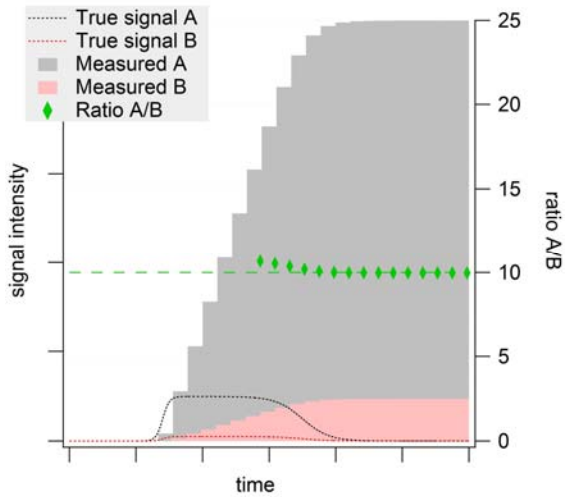

Peak area integration

- Single collectors or mixed detector multicollectors
- Transient signal integration
  - Keep all data points
  - Define region for background subtraction (less arbitrary)

17

Mass Spectrometer vs. (Unruly) Transient Signal

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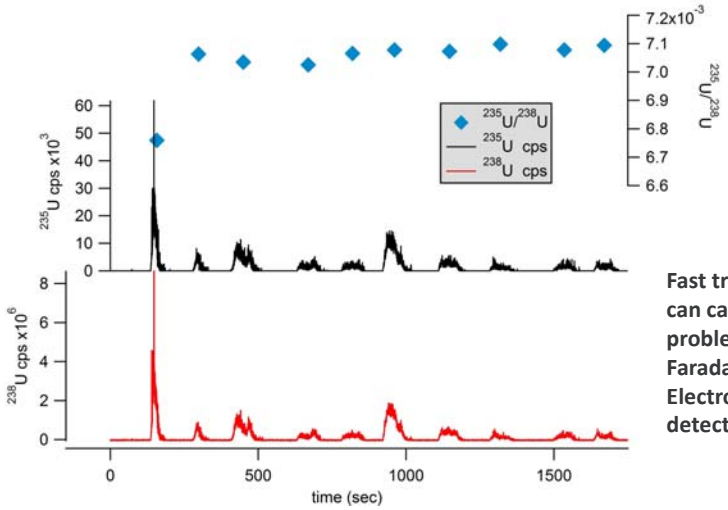

Fast transient spikes can cause detection problems for both Faraday Cup and Electron Multiplier detectors

18

Mass Spectrometer vs. (Unruly) Transient Signal (contd.)

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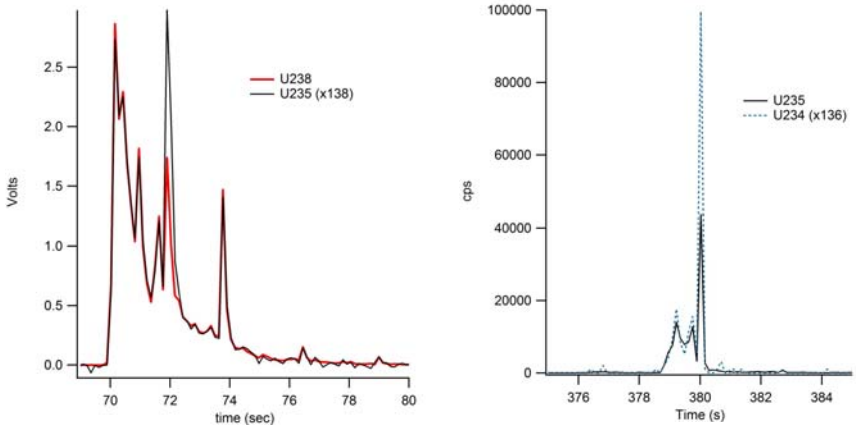
"Even small aerosol particles (1000 total counts) can produce transient signals with peak count rates of 10^7 – outside the typical operating range of SEM detectors"

Reproduced by permission of The Royal Society of Chemistry. J. W. Olesik and P. J. Gray. 2012. "Considerations for measurement of individual nanoparticles or microparticles by ICP-MS: determination of the number of particles and the analyte mass in each particle." *Journal of Analytical Atomic Spectrometry* , 27:1143-1155.



19

Example: Elemental Analysis

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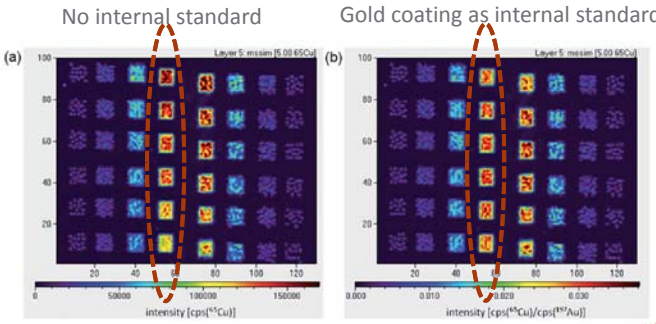
Determination of printed Cu concentration

No internal standard — Gold coating as internal standard



Reproduced by permission of The Royal Society of Chemistry. M. Bonta, H. Lohninger, M. Marchetti-Deschmann, and A. Limbeck,. 2014. "Application of gold thin-films for internal standardization in LA-ICP-MS imaging experiments." *Analyst* 139: 1521-1531.

20

Example: Isotopic Analysis

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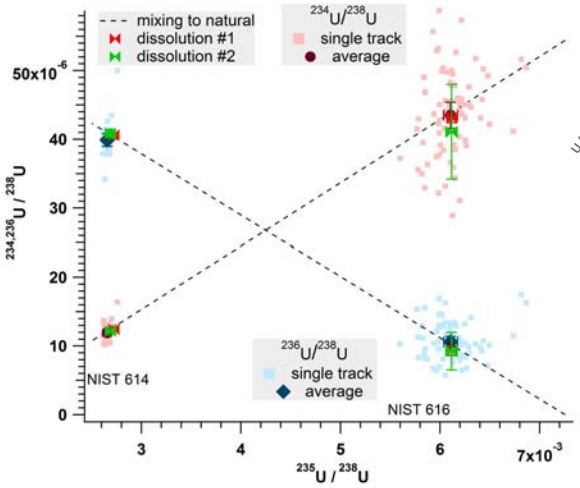
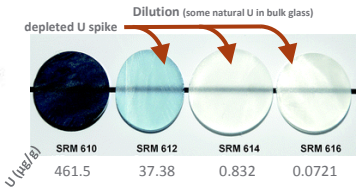
Ideally the standard is as closely matched to unknown as possible





Reproduced by permission of The Royal Society of Chemistry. M. Gaboardi and M .Humayun. 2009. "Elemental fractionation during LA-ICP-MS analysis of silicate glasses: implications for matrix-independent standardization." *Journal of Analytical Atomic Spectrometry* , 24:1188-1197.

However, nebulized solutions can be used as isotopic standards for relatively stable laser ablation signals

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Example: Isotopic Mapping

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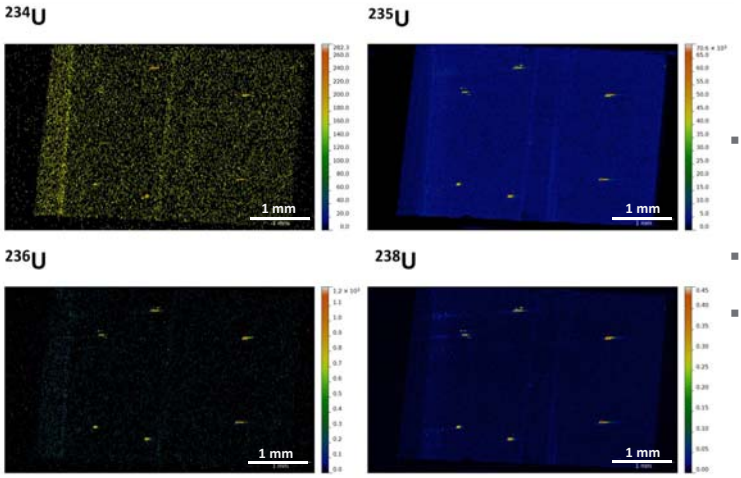

- 20-30 µm NIST 610 particle placed on NIST 616
- ϑ 10^{10} uranium atoms
- ϑ 10^{6} minor isotope atoms (^{234}U, ^{236}U)

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Summary

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- Laser ablation ICP-MS is a convenient and powerful tool for elemental and isotopic analysis of solids

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ICP-MS Short Course

ICP-MS Instrument Specializations

CHARLES J. BARINAGA
Pacific Northwest National Laboratory

June 18, 2014

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U.S. DEPARTMENT OF ENERGY

1

ICP-MS Instrument Specializations: Topics

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- Isobaric Interferences
  - Examples
  - Solutions
- Other types of mass separation
  - Time-of-flight (TOF)
  - Distance-of-flight (DOF)

2

Isobaric Interferences

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- Isobaric Interferences
  - Selected examples
- Solutions
  - High-resolution (HR) ICP-MS
  - Gas phase reaction (collision/reaction cell [CRC] technology)
  - Kinetic energy discrimination (KED)

3

Isobaric Interferences: Sources

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- Argon and argides (argon is the typical plasma support gas)
  (these ions are not stable under ambient conditions)
  - Ar^+, ArH^+, ArC^+, ArO^+, Ar_2^+
  - $NaAr^+$, $ArCl^+$, …
  - MAr^+ / M; 1E-5 typical (when [M] is high relative to the analyte of interest, MAr^+ can be an interference for an isobaric analyte ion)
- Sample matrix
  - Atomic isobars ^{40}Ar / ^{40}Ca
  - Hydrides (from H_2O) usually <100 ppm; UH^+/U^+ ~2E-5
  - Refractory oxides typically <1%
  - Chlorides $^{200}Hg^{35}Cl$ / ^{235}U (ultratrace analyses)
  - Doubly charged Ba^{+2}, Ar^{+2}
- Instrument Background
  - Hydrocarbon ions (chemical ionization by Ar^+, ArH^+, H_3O^+, etc.)
- Sample / skimmer cones
  - Ni, Cu, Al, Pt and sample material from previous, high [samples]

4

Isobaric Interferences: Mass Defect

Definition: actual mass of an isotope minus its integer mass (there are other versions of the definition)

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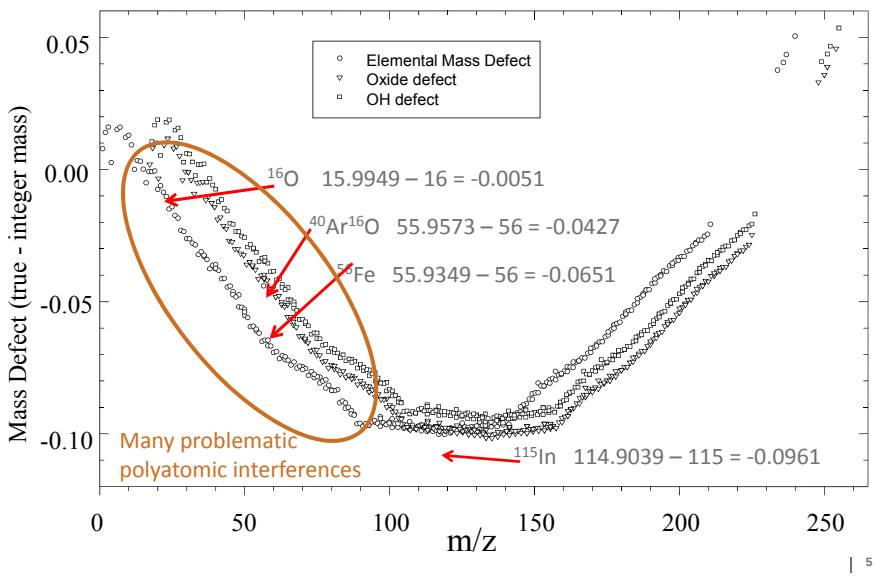

Isobaric Interferences: Examples

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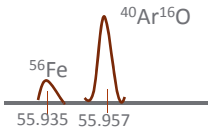
Analyte	Isobaric Interferents	Resolution Required
^{40}Ca	^{40}Ar	190,000
^{51}V	^{35}Cl^{16}O	2,600
^{55}Mn	^{37}Cl^{18}O	2,000
^{56}Fe	^{40}Ar^{16}O	2,500
^{59}Co	^{43}Ca^{16}O	2,900
^{63}Cu	^{40}Ar^{23}Na	2,800
^{64}Zn	^{32}S^{16}O$_2$ ^{32}S$_2$	2,000 4,300
^{75}As	^{40}Ar^{35}Cl	8,000
^{80}Se	^{40}Ar$_2$	9,700
^{90}Sr	^{90}Y ^{90}Zr	154,000 29,600
^{99}Tc	^{99}Ru	315,000
^{107}Pd	^{107}Ag	76,000
^{135}Ba	^{135}Cs	613,000
^{129}I	^{129}Xe	625,000
^{238}Pu	^{238}U	180,000
^{239}Pu	^{238}U^{1}H	37,500

- Mass resolution
  - R = M / ΔM
  - distinguish two peaks of slightly different mass-to-charge ratios ΔM, in a mass spectrum

^{40}Ar^{16}O^{1+} 55.9573 m/z
^{56}Fe^{1+} 55.9349 m/z
ΔM = 0.0224
M = 55.9349
R = 2,500



Cartoon depiction

Solutions to Isobaric Interferences: High-resolution ICP-MS

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- Commercial
  - Magnetic sector instruments (see Greg Eiden presentation)
    - Thermo Scientific – Element 2
    - NU Instruments – Attom
- Non-commercial
  - LTQ-Orbitrap – PNNL research

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Solutions to Isobaric Interferences: High-resolution ICP-MS (contd.)

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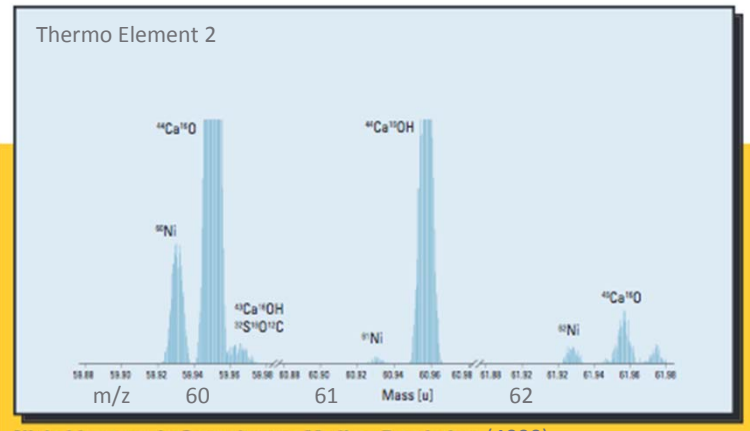

Nickel Isotopes in Groundwater, Medium Resolution (4000)

Example of polyatomic interferences from major elements in the sample. Low to medium resolution commonly costs ~10X in sensitivity.

8

Solutions to Isobaric Interferences: High-resolution ICP-MS (contd.)

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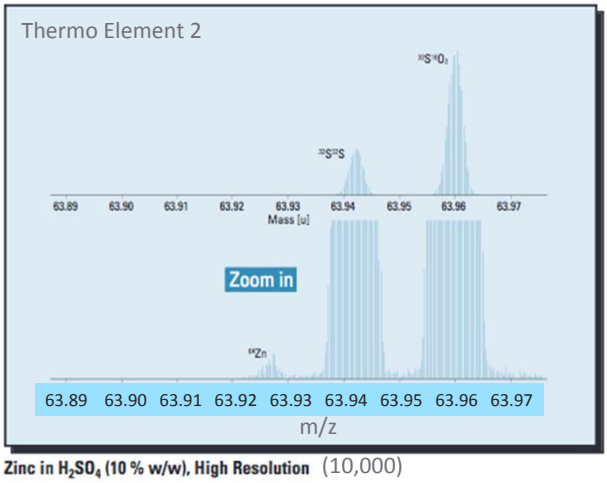

Zinc in H_2SO_4 (10 % w/w), High Resolution (10,000)

Example of polyatomic interferences from acid dissolution matrix.
Medium to High resolution typically costs 5-10X in sensitivity.

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High-resolution ICP-MS: Commercial

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- Thermo Scientific
  - Element 2, HR ICP-MS
  - 300-4000-10,000 resolution
  - $400K – $450K depending on features and accessories
  - http://www.thermoscientific.com/en/product/element-2-icp-ms.html

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High-resolution ICP-MS: Commercial (contd.)

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- NU Instruments
  - The Attom, HR ICPMS
  - 300 to >10,000 resolution
  - $400K – $450K depending on features and accessories
  - http://www.nu-ins.com/index.php/plasma-source/nu-attom

Isobaric Interferences: Magnetic Sector High-resolution ICP-MS Solution

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Analyte	Isobaric Interferents	Resolution Required
^{40}Ca	^{40}Ar	190,000
^{51}V	$^{35}Cl^{16}O$	2,600
^{55}Mn	$^{37}Cl^{18}O$	2,000
^{56}Fe	$^{40}Ar^{16}O$	2,500
^{59}Co	$^{43}Ca^{16}O$	2,900
^{63}Cu	$^{40}Ar^{23}Na$	2,800
^{64}Zn	$^{32}S^{16}O_2$ $^{32}S_2$	2,000 4,300
^{75}As	$^{40}Ar^{35}Cl$	8,000
^{80}Se	$^{40}Ar_2$	9,700
^{90}Sr	^{90}Y ^{90}Zr	154,000 29,600
^{99}Tc	^{99}Ru	315,000
^{107}Pd	^{107}Ag	76,000
^{135}Ba	^{135}Cs	613,000
^{129}I	^{129}Xe	625,000
^{238}Pu	^{238}U	180,000
^{239}Pu	$^{238}U^{1}H$	37,500

- Commercial high-resolution ICPMS
  - Are not high resolution
    - "high" > 50,000
  - But are adequate for isobaric, polyatomic interferences with large mass defect differences with the analyte ions
  - Not adequate for atomic isobars
    - Particular problem for non-natural isotopes
      - Fission yield isotopes

Solutions to Isobaric Interferences: High-resolution Orbitrap MS

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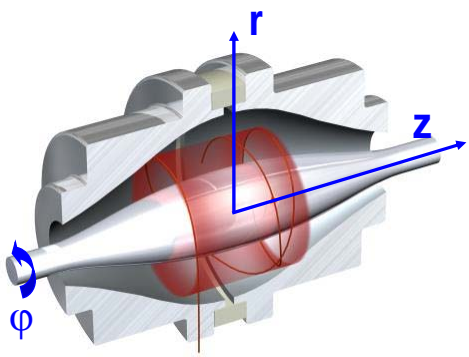
- Characteristic frequencies:
  - Frequency of rotation ω_φ
  - Frequency of radial oscillations ω_r
  - Frequency of axial oscillations ω_z

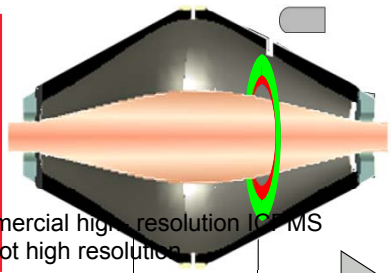
$$\omega_\varphi = \frac{\omega_z}{\sqrt{2}}\sqrt{\left(\frac{R_m}{R}\right)^2 - 1}$$

$$\omega_r = \omega_z\sqrt{\left(\frac{R_m}{R}\right)^2 - 2}$$

$$\omega_z = \sqrt{\frac{k}{m/q}}$$

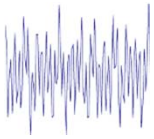


Lord of the ion rings: Part 2- Retainment of the rings



Commercial high resolution ICP MS
Are not high resolution

$$\omega = \sqrt{\frac{k}{m/z}}$$



- Many ions in the Orbitrap generate a complex signal whose frequencies are determined using a Fourier Transformation
- High accuracy m/z determination does not (theoretically) require mass calibration, i.e. m/z derives from frequency measurement. In reality mass standards are used to confirm mass and chromatographic elution time.

Analyze • Detect • Measure • Control™ Thermo ELECTRON CORPORATION

Solutions to Isobaric Interferences: ICP-LTQ-Orbitrap MS

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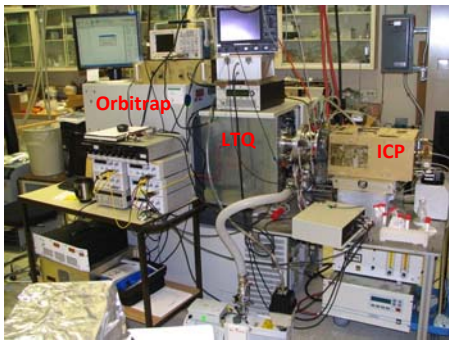
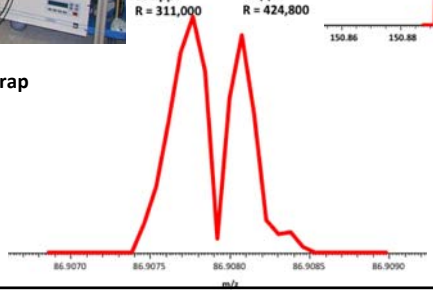
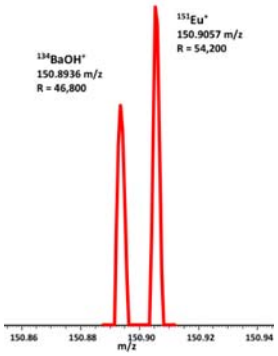


Interface ICP with LTQ-Orbitrap

R ~ 350,000 !





15

Solutions to Isobaric Interferences: ICP-LTQ-Orbitrap MS (contd.)

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- ICP-LTQ-Orbitrap
  - Designed for high mass resolution and mass accuracy
    - Mainly for Electrospray Ionization (ESI) of large biomolecules
      - Peptides, proteins, DNA, nucleotides, etc.
  - Advantages
    - Best demonstrated atomic resolution
  - Disadvantages
    - Space charge effects
      - Limits the number of ions in the trap
      - Limits isotope ratio accuracy
      - Limits abundance sensitivity

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Isobaric Interferences: Orbitrap HR ICP-MS Solution (?)

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Analyte	Isobaric Interferents	Resolution Required
^{40}Ca	^{40}Ar	190,000
^{51}V	$^{35}Cl^{16}O$	2,600
^{55}Mn	$^{37}Cl^{18}O$	2,000
^{56}Fe	$^{40}Ar^{16}O$	2,500
^{59}Co	$^{43}Ca^{16}O$	2,900
^{63}Cu	$^{40}Ar^{23}Na$	2,800
^{64}Zn	$^{32}S^{16}O_2$ $^{32}S_2$	2,000 4,300
^{75}As	$^{40}Ar^{35}Cl$	8,000
^{80}Se	$^{40}Ar_2$	9,700
^{90}Sr	^{90}Y ^{90}Zr	154,000 29,600
^{99}Tc	^{99}Ru	315,000
^{107}Pd	^{107}Ag	76,000
^{135}Ba	^{135}Cs	613,000
^{129}I	^{129}Xe	625,000
^{238}Pu	^{238}U	180,000
^{239}Pu	$^{238}U^{1}H$	37,500

- Prototype ICP-Orbitrap
  - Truly high resolution
    - >>50,000
  - Adequate for most if not all polyatomic, isobaric interferences
  - Adequate for some atomic isobars
  - Abundance sensitivity and isotope ratio accuracy are limiting factors for atomic ion applications

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CRC Introduction: Quadrupoles

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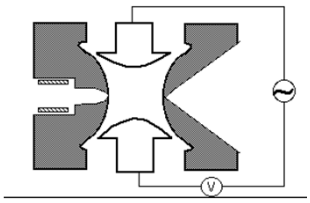
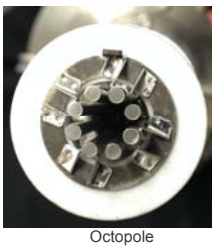
- Non-magnetic quadrupole mass filter
  - Nobel Prize 1989 – Wolfgang Paul and Hans DeMelt
  - Discussed earlier by Greg Eiden
- Manifestations
  - Radiofrequency (RF)/ direct current (DC) linear quadrupole mass filter
  - RF-only linear multipole ion guides and traps
  - RF/DC 3D quadrupole ion trap

ThermoElemental





Octopole

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CRC Technology: Multipoles

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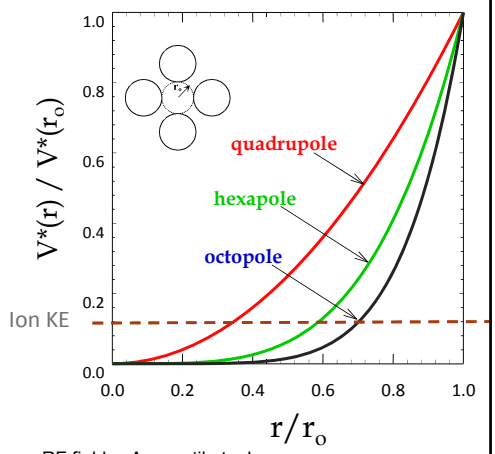
- Linear multipole, RF-only ion traps and guides
  - Quadrupole
    - ion traps and linear filters
    - narrowband storage / transmission
  - Higher order multipoles
    - Hexapoles, octopoles
    - steeper psuedo-potential walls
    - stronger field at center
    - best for broadband ion guide



Adapted from, D. Gerlich, "Inhomogeneous RF fields: A versatile tool for the study of processes with slow ions." *Adv. In Chem. Phys. Series* Vol. 82, Cheuk-Yiu Ng and Michael Baer, eds., pp. 1-172 (1992).

19

CRC Technology: Early ICP-MS Papers on Gas Phase Collisions and Reactions

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- D. J. Douglas, "Some Current Perspectives on ICP-MS", *Can. J. Spectroscopy* **34**, 38-49 (1989)
- J. T. Rowan and R. S. Houk, "Attenuation of Polyatomic Ion Interferences in Inductively Coupled Plasma Mass Spectrometry by Gas-Phase Collisions", *Appl. Spectr.* **43**, 976-980 (1989)
- S.A. McLuckey , G.L. Glish , D.C. Duckworth , R. K. Marcus, "Radio-frequency Glow Discharge Ion Trap Mass Spectrometry," *Anal. Chem.*, **64**,1606–1609 (1992)
- C. J. Barinaga, D. W. Koppenaal, "Ion-trap Mass-spectrometry With An Inductively-coupled Plasma Source," *RCMS* **8**, 71-76 (1994)
- G. C. Eiden, C. J. Barinaga, D. W. Koppenaal, "Selective Removal Of Plasma Matrix Ions In Plasma Source Mass Spectrometry," *JAAS* **11**, 317-322 (1996)
- S.D. Tanner and V.I. Baranov, "A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DRC-MS). II. Reduction of interferences produced within the cell," *JASMS* **10**, 1083-1094 (1999)

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CRC Technology: Early Ion Chemistry in Plasma Source Ion Trap

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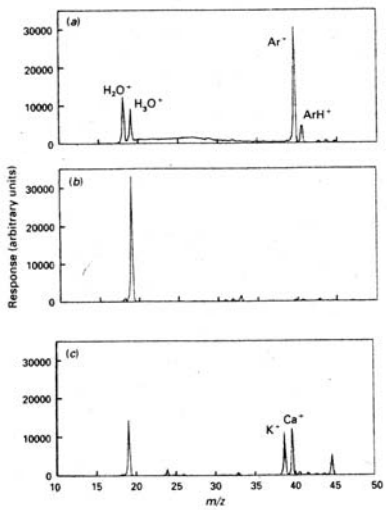
1% HNO_3 blank
0 msec reaction time

1% HNO3 blank
30 msec reaction time

Reactive gas - adventitious water, removes Ar^+ but also reacts with lots of other ions

10 ug/mL K, Ca
30 msec reaction time



D. W. Koppenaal, C. J. Barinaga, M. R. Smith, JAAS **9**, 1053-1058 (1994)

21

CRC Technology: Selective Gas-phase Chemistry with H_2

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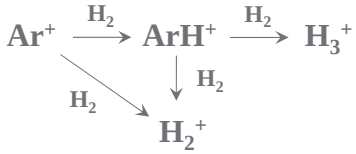
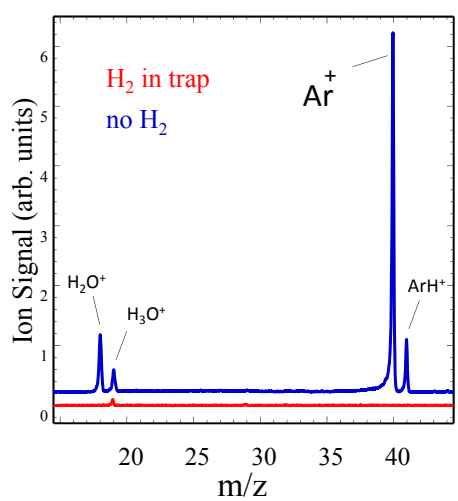
Application:
Separation of ^{40}Ar from ^{40}Ca



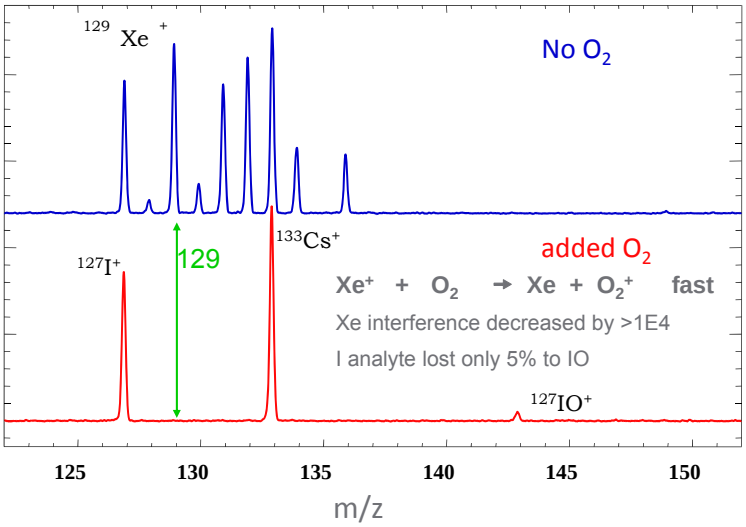


Adapted from G. C. Eiden, C. J. Barinaga, D. W. Koppenaal, JAAS **11**, 317-322 (1996).

22

Solutions to Isobaric Interferences:

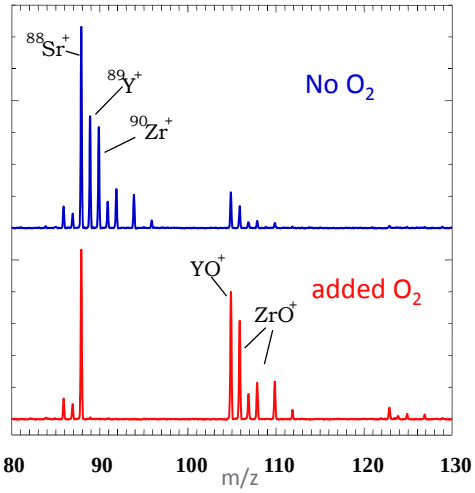
Separation of ^{129}Xe and $^{129}I^*$: CRC with O_2



Necessary instrument R = 625,000

CRC Technology: Selective Reaction with O_2

- Removal of $^{90}Y^*$ and ^{90}Zr Isobaric Interferences on $^{90}Sr^*$
  - Selective Reaction of O_2 with Y^+ and Zr^+
  - Demonstrated with nonradioactive ^{88}Sr and ^{89}Y



Necessary instrument R = 29,600

Isobaric Interferences: CRC Technology Chemical Resolution

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Analyte	Isobaric Interferents	Resolution Required
^{40}Ca	^{40}Ar	190,000
^{51}V	$^{35}Cl^{16}O$	2,600
^{55}Mn	$^{37}Cl^{18}O$	2,000
^{56}Fe	$^{40}Ar^{16}O$	2,500
^{59}Co	$^{43}Ca^{16}O$	2,900
^{63}Cu	$^{40}Ar^{23}Na$	2,800
^{64}Zn	$^{32}S^{16}O_2$ $^{32}S_2$	2,000 4,300
^{75}As	$^{40}Ar^{35}Cl$	8,000
^{80}Se	$^{40}Ar_2$	9,700
^{90}Sr	^{90}Y ^{90}Zr	154,000 29,600
^{99}Tc	^{99}Ru	315,000
^{107}Pd	^{107}Ag	76,000
^{135}Ba	^{135}Cs	613,000
^{129}I	^{129}Xe	625,000
^{238}Pu	^{238}U	180,000
^{239}Pu	$^{238}U^{1}H$	37,500

- Plasma gas and most polyatomic interferences
  - Charge exchange Ar^{+}<>H_2
  - Collisional dissociation
- Atomic isobaric interferences
  - Selective gas phase chemistry
  - Specific reactive gases
    - O_2, NH_3, CH_3OH, etc.
  - May create other interferences

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Solutions to Isobaric Interferences: Kinetic Energy Discrimination

Pacific Northwest NATIONAL LABORATORY
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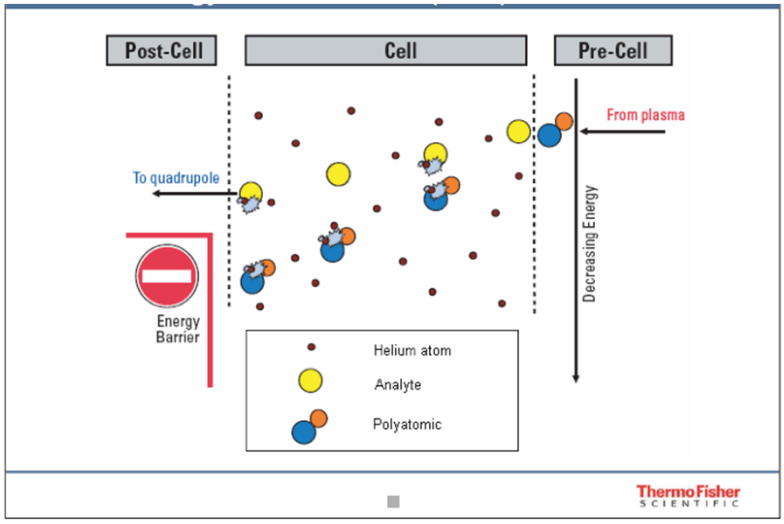
Collisional energy loss



26

Collision/Reaction Cell Technology: ICP-MS Instruments

Pacific Northwest NATIONAL LABORATORY
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- ThermoScientific
  - iCAP Q series
  - CRC and KED
  - http://www.thermoscientific.com/en/product/icap-q-icp-ms.html

- Perkin Elmer
  - NexION series
  - Dynamic Reaction Cell
  - http://www.perkinelmer.com/catalog/family/id/nexion-350-icp-ms-spectrometers

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Collision/Reaction Cell Technology: ICP-MS Instruments (contd.)

Pacific Northwest NATIONAL LABORATORY
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- Agilent
  - 7900 Series
  - CRC and KED
  - http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Atomic-Spectroscopy/7900-ICP-MS/Pages/default.aspx

- Agilent
  - 8800 Series Triple Quad
  - CRC and KED
  - http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Atomic-Spectroscopy/8800-Triple-Quadrupole-ICP-MS/Pages/default.aspx

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Collision/Reaction Cell Technology: ICP-MS Instruments (contd.)

Pacific Northwest NATIONAL LABORATORY
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- Bruker
  - Aurora series
  - Collision/Reaction Inlet
    - He and H_2 are introduced at the skimmer
  - http://www.bruker.com/products/mass-spectrometry-and-separations/icp-ms.html

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Isobaric Interferences: Recap

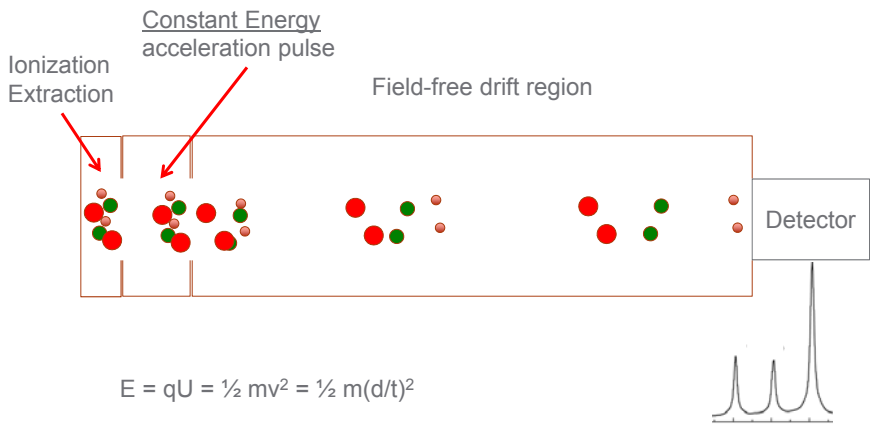
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Isobaric Interferences
  - Selected examples
- Solutions
  - High-resolution ICP-MS
  - Gas phase reaction (collision/reaction cell technology)
  - Kinetic energy discrimination
- No panacea
  - Non-natural (fission product) isotopes especially

30

Time-of-Flight (TOF) MS: Concept

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



$E = qU = ½ mv^2 = ½ m(d/t)^2$

$t = d/ (2U)^{½} \ (m/q)^{½} = k(m/q)^{½}$

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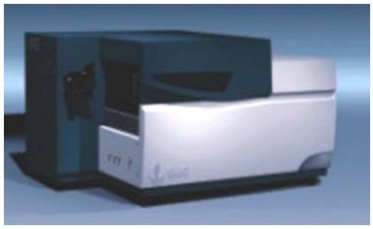
Time-of-Flight ICP-MS

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

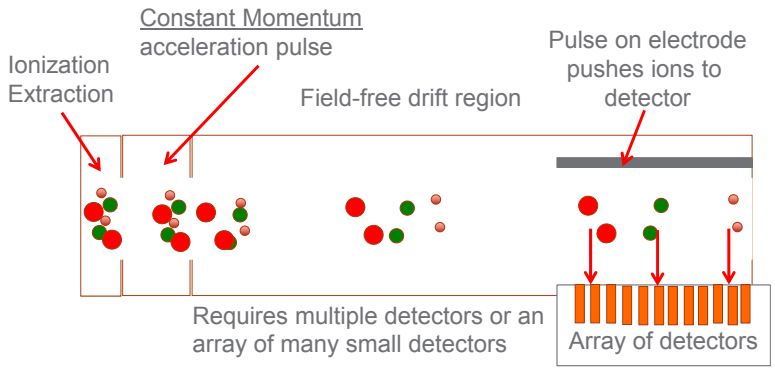
- GBC
  - OptiMass 9500
  - http://www.gbcsci.com/products/icp_tof/optimass.asp
- DVS Sciences
  - CyTOF 2
  - Specifically for cells analysis (cytometry)
    - Rare earth element tagged proteins
    - Element tags identify cell or reaction
    - Can generate huge amounts of data for sets of cells
  - http://www.dvssciences.com/



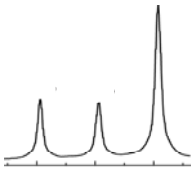
32

Distance-of-Flight (DOF) MS: Concept

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



$L_{FF} = (zE_p\tau/m)(t_{det} - \tau/2) - (s_o + \Delta s_o)$



Enke, C.G., Dobson, G.S., "Achievement of energy focus for distance-of-flight mass spectrometry with constant momentum acceleration and an ion mirror", Anal. Chem,. 2007, **79,** 8650–8661

A. Graham, S. Ray, C. Enke, C. Barinaga, D. Koppenaal and G. Hieftje, First Distance-of-Flight Instrument: Opening a New Paradigm in Mass Spectrometry J. Am. Soc. Mass Spectrom., 2011, **22**, 110–117

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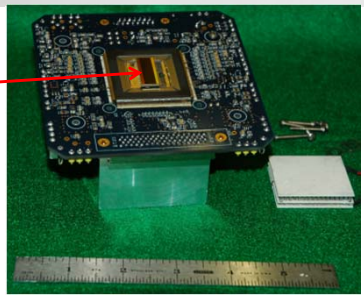
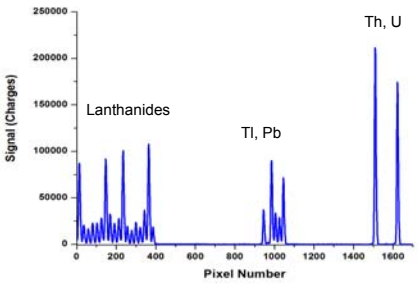
Ion Detector Array Development

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Ion detector array
  - 1696 channels
  - 8.5 μm channel width, 12.5 μm pitch
  - 6-8 channels/mass
- Collaboration
  - PNNL
    - D. Koppenaal, C. Barinaga
  - University of Arizona
    - Bonner Denton et al. – up next
  - Indiana University
    - Gary Hieftje et al.
- Funding
  - National Nuclear Security Administration (NNSA)
    - NA-22





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ICP-MS Instrument Specializations: Conclusions

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Instrumental capabilities for elemental and isotopic analysis have grown significantly over the past 30 years, especially for ICP-MS
- No panacea
  - Careful analytical design, sample preparation, and attention to detail are still required
  - Chemical separation may still be required for certain analytes and/or matrices
- Questions

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Ion Optics Modeling
Presented by Chris Zarzana (INL)

- Build intuition
- Develop some understanding of how our instruments work
- Easily explore new ideas

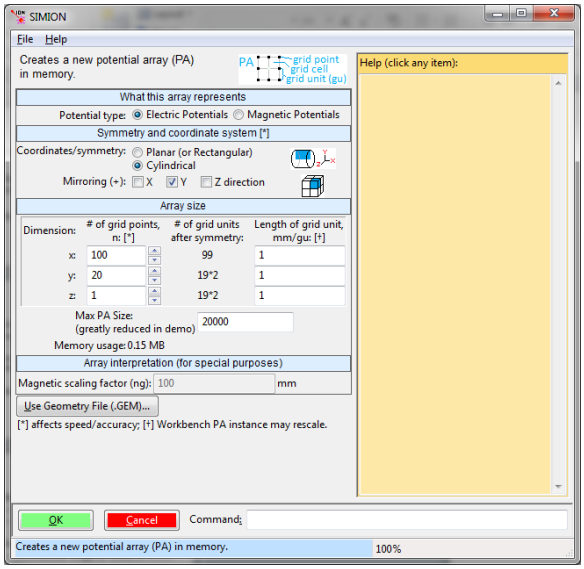
SIMION

- Uses a finite difference method to solve the Laplace equation
  - $\nabla^2 V = 0$
- Calculates charged particle trajectories through electric and magnetic fields
- Read the manual for details

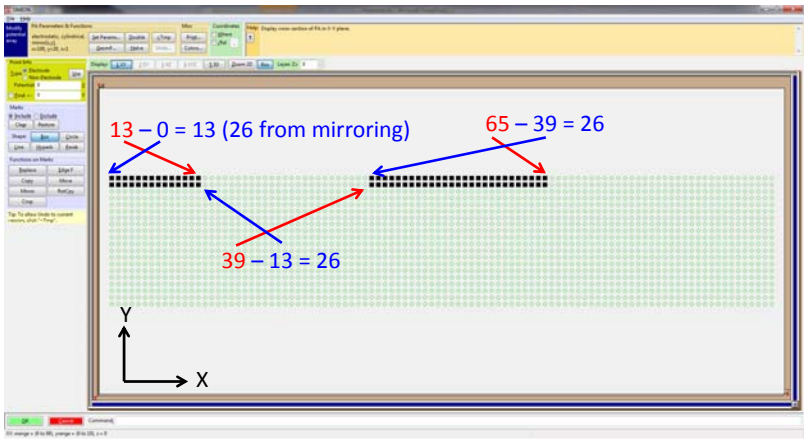
Potential Arrays

- Basic Potential Array (.pa)
  - Define electrode voltages explicitly (i.e. 24.5V)
  - After “Refine”, electrode voltages can be scaled, but not changed independently
- Fast Adjust Definition Array (.pa#)
  - Define electrode voltages as indices (i.e. 1 V, 2 V, etc.)
  - After “Refine” electrode voltages can be changed independently using “Fast Adjust”

Creating a PA

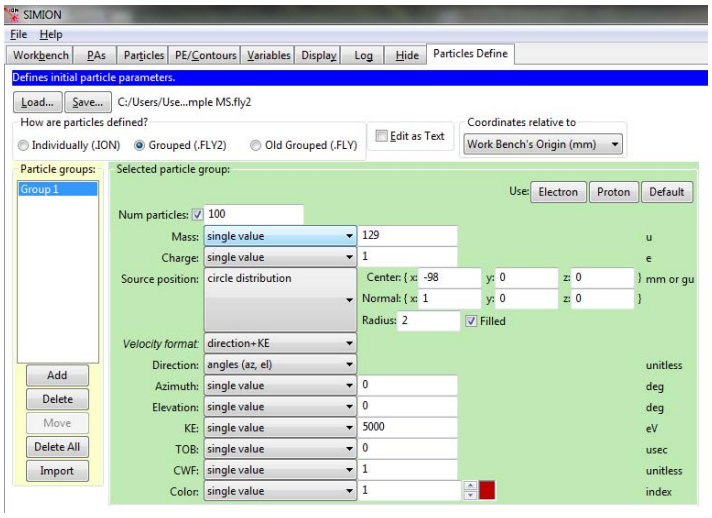


PA Units to Workbench Units



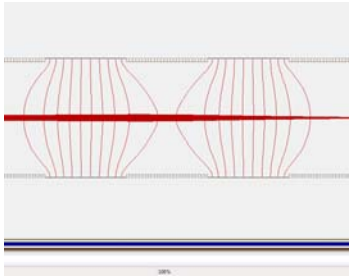
OK to exit, then Refine, then Save

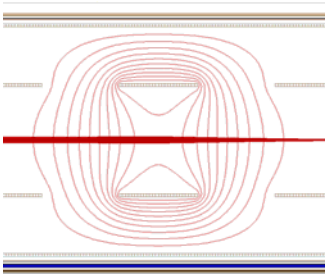
Define Particles



Boundary Conditions

- Non-electrode points on PA edges are always treated as zero Neumann boundary conditions





GEM files

Einzel.GEM

```
; Electrode length in mm
# local length = 26

; Electrode spacing in mm
# local spacing = 26

; Electrode inner radius in mm
# local radius = 18

; Electrode thickness in mm
# local thickness = 1

; empty space before and after the einzel lens in mm
# local x_space = 34

; Define PA dimentions
# nx = math.floor(1.5*length) + spacing + x_space + 1
# ny = radius + thickness + 1
```

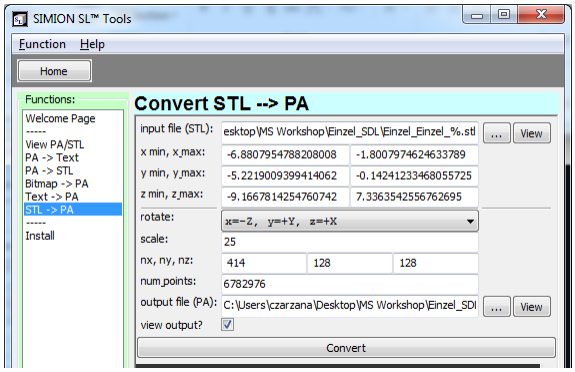
GEM Files

```
; Define array
pa_define($(nx),$(ny),1,cylindrical, X, electrostatic)

locate(0,0,0,1,0,0,0)
{
        electrode(1)
        {
                fill
                {
                        within{box(0,$(radius),$(math.floor(length/2)),$(radius+thickness))
                        }
                }
        }
}

locate($(math.floor(length/2)+spacing),$(radius),0,1,0,0,0)
{
        electrode(2)
        {
                fill
                {
                        within{box(0,0,$(length),$(thickness))
                        }
                }
        }
}
Raw:T-----XEmacs: Einzel.GEM      (Fundamental)----Bot-----------------------------------------
```

STL Import

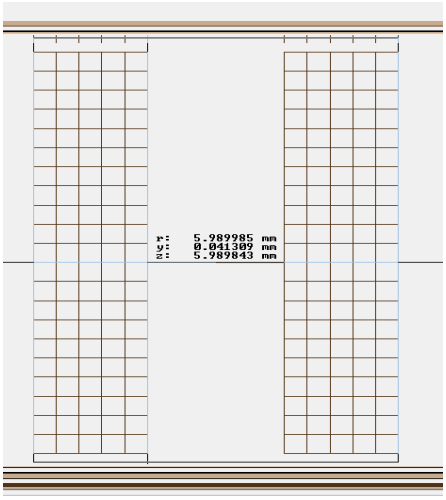


- Use % as wildcard to import multiple STL files

Magnetic PAs

Set ng to magnet gap

ng=6 in this example

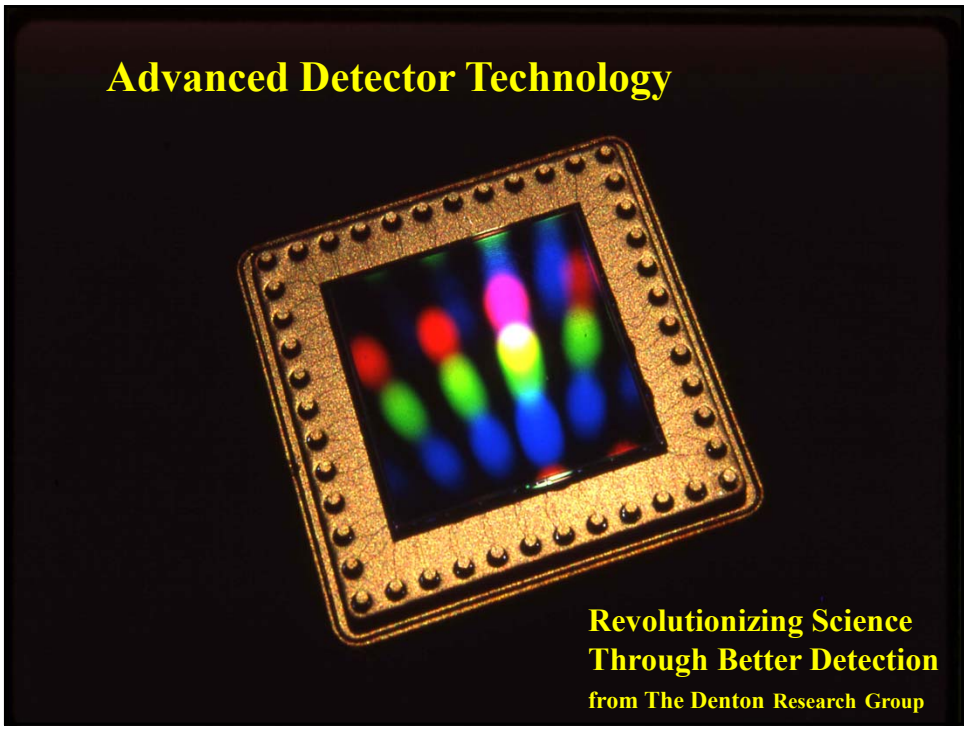


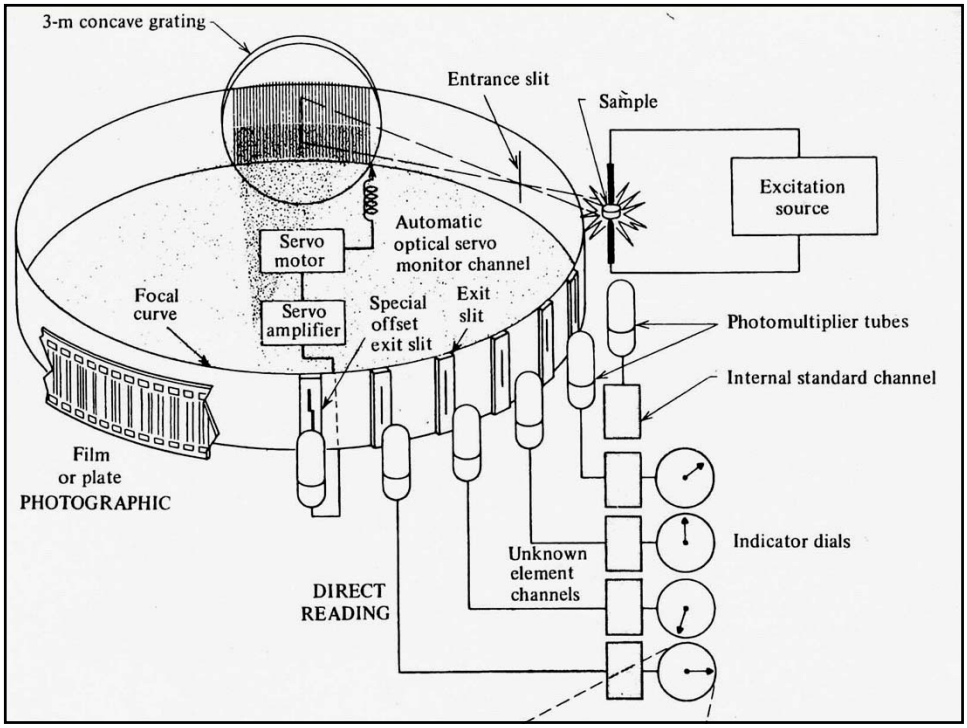
User Programs

- Workbench programs
  - Written in Lua
  - Programs only operate inside Pas
    - Make a 3D PA with no field that is the size of the workbench if you need control at all times.
- Batch programs
  - Convert GEM files to PAs, refine, fly ions
  - SL libraries for C++/Python/Perl/Lua (in 8.1)

Advances in SIMION 8.1

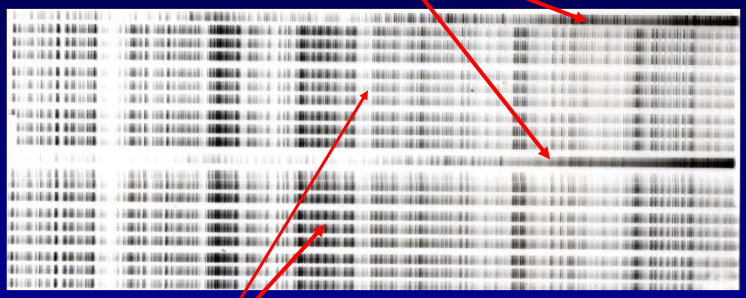
- Large arrays for 64 bit systems
- Multicore “Refine”
- Non-square grid
- Much more


Advanced Detector Technology
Revolutionizing Science
Through Better Detection
from The Denton Research Group


3-m concave grating
Entrance slit
Sample
Excitation source
Automatic optical servo monitor channel
Servo motor
Servo amplifier
Focal curve
Special offset exit slit
Exit slit
Photomultiplier tubes
Internal standard channel
Film or plate
PHOTOGRAPHIC
Indicator dials
Unknown element channels
DIRECT READING

Optical Emission Spectra

DC Arc Calibration Spectra



Spark Spectra 10-24-1967

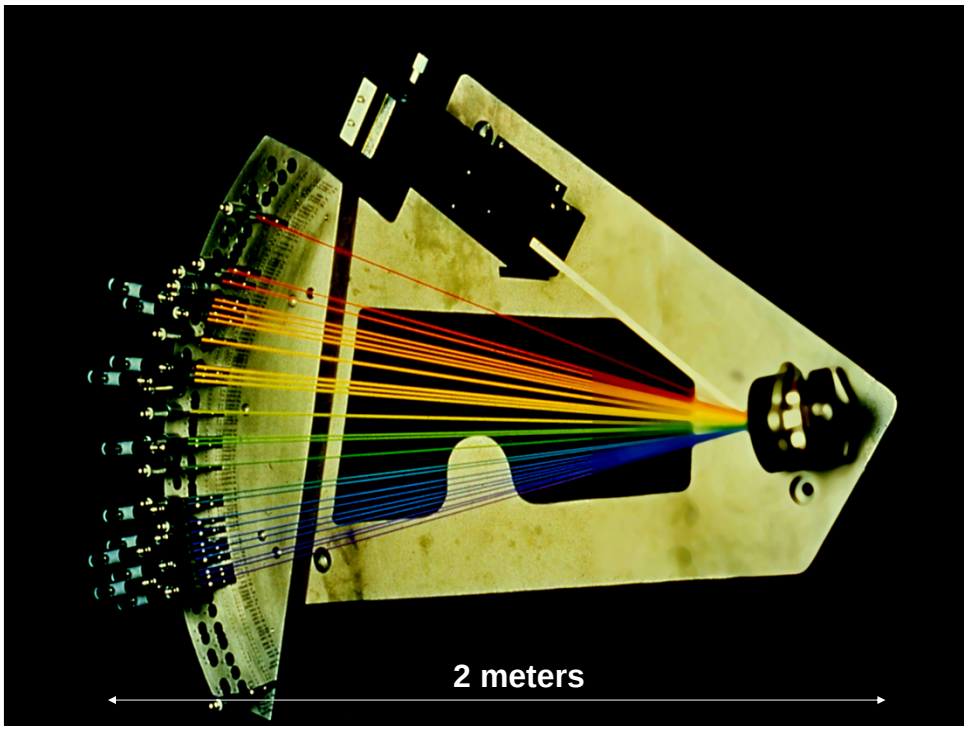
Howard Malmstadt's Spectroscopy Course Univ. of IL

Spark Source Mass Spec Also Can Utilize Photographic Plates

Photographic Plates Characteristics

(For Both Optical & Mass Spectroscopies)

- Capture Large Ranges Of Spectral Data
- Integrate Signal
- Simultaneous
- Can Yield Quantitative Data
- Non Linear- Requiring Calibration
- Require Stringent Developing Procedures
- Readout – Data Reduction Difficult & Time Consuming



NEED Some type of electronic readout which can measure photon flux at all wavelengths (Masses) simultaneously

Various Camera Devices

Vidicons

Intensified Target Vidicons

Plumbicons

Orthicons

Image Dissectors

Photodiode Arrays

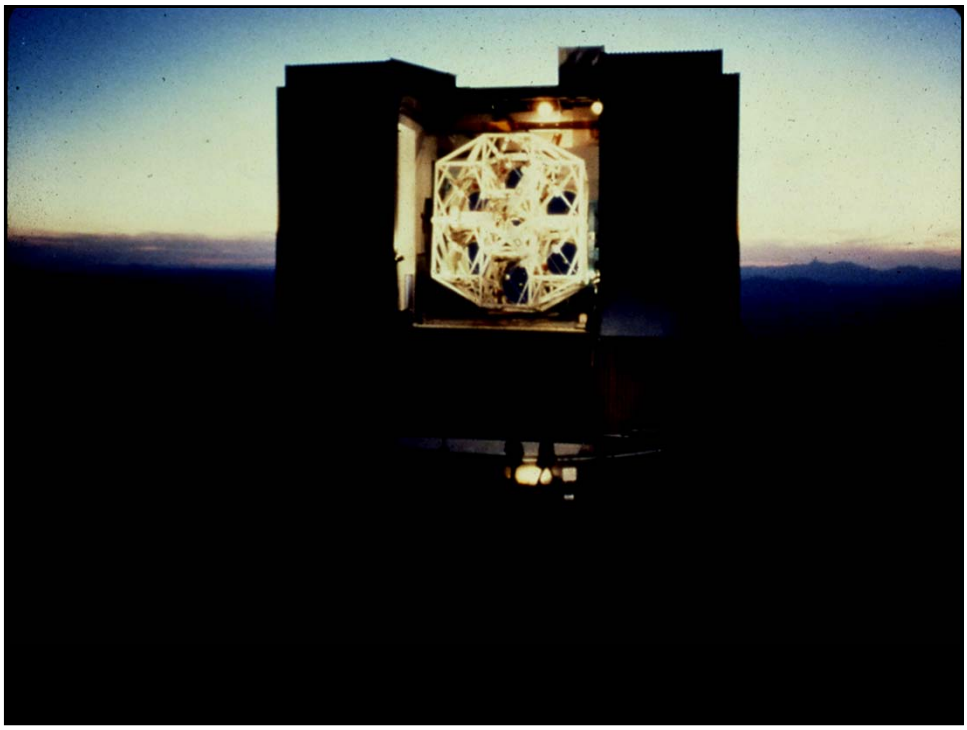
Previously Investigated

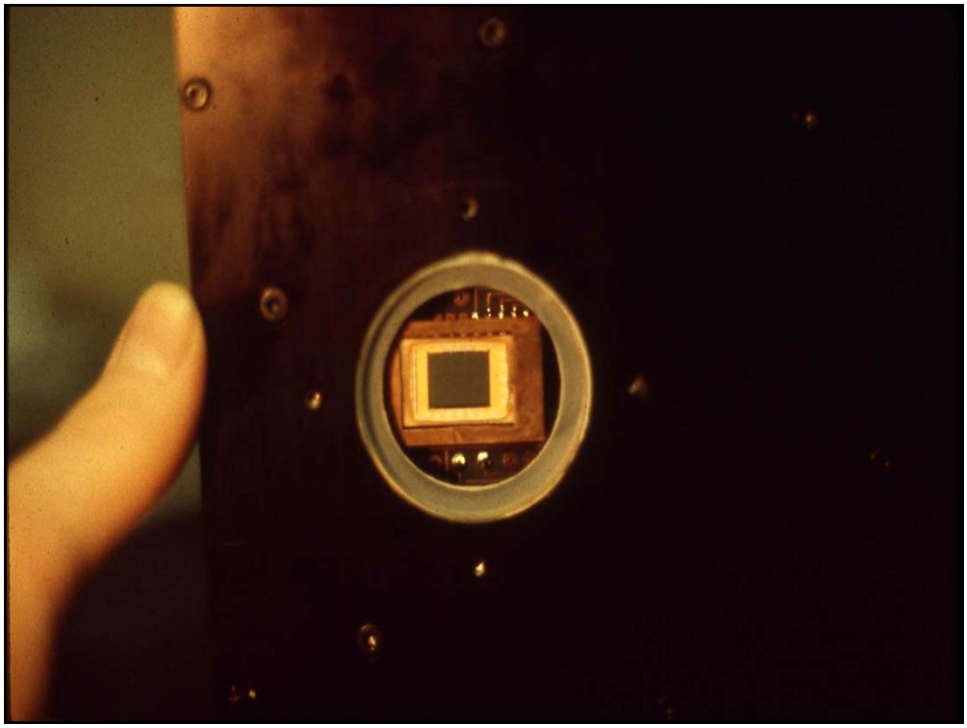
Scientific Charge Transfer Devices

(CCD's & CID's)

" Camera" Techniques Explored to that Date Suffered from one are more of the Following

- Poor dynamic range
- Insufficient spectral range
- Poor reproducibility between detector elements
- Crosstalk between elements - blooming, smearing, etc.
- Insufficient number of resolution elements
- Poor sensitivity (QE)
- High dark &/or read noise
- Inability to integrate photon flux
- Inability to randomly access detector elements
- Poor reliability





It Can't be Done

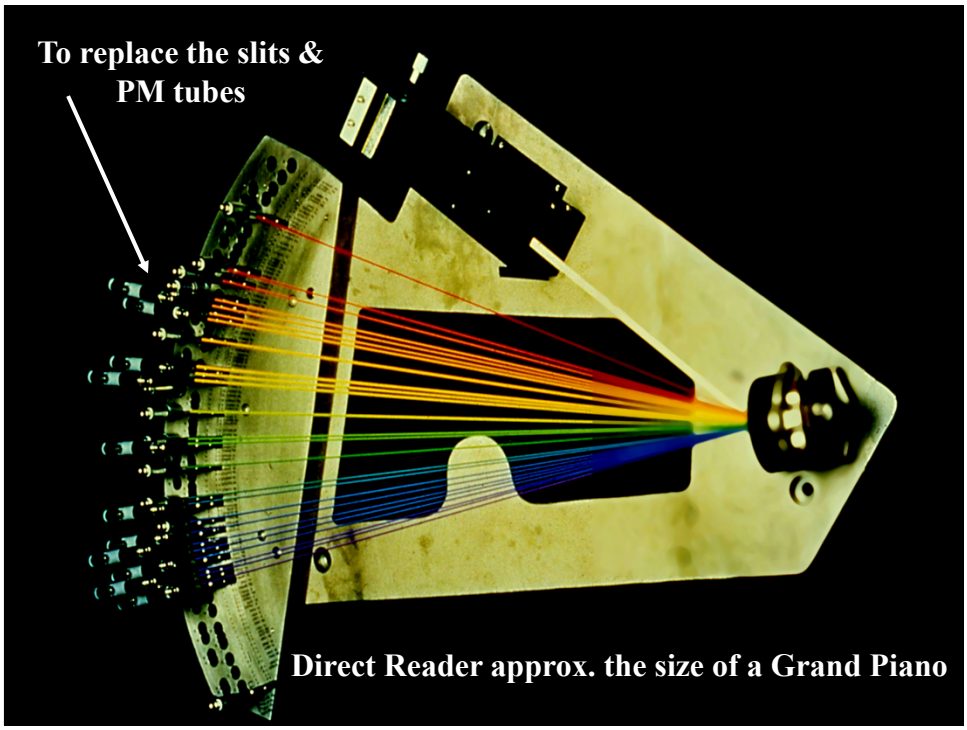
Denton's CCD & CID devices are far
FAR TOO
Small !!!

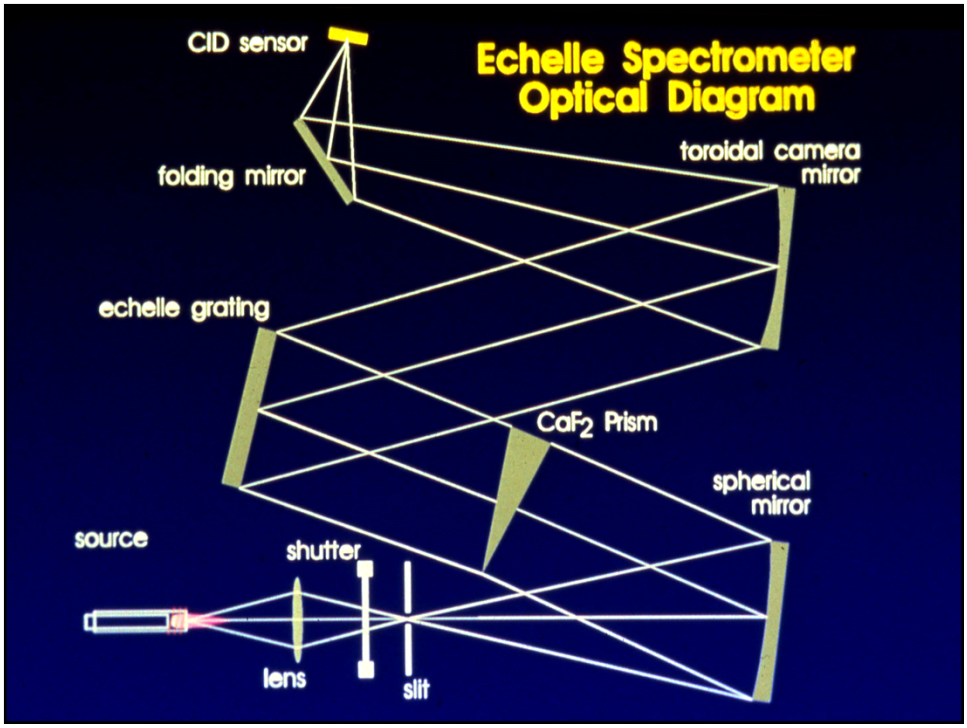
Small
Small
Small
Small
Small

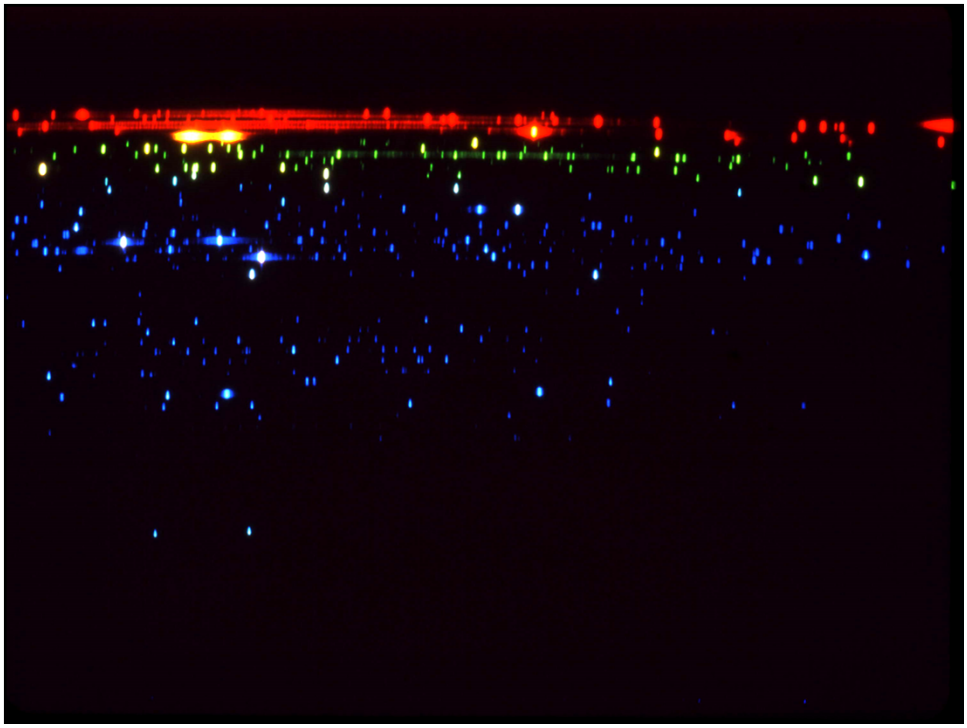
"One requires a sensor 1 to 1.5 Meters Long"

"Curved to fit the focal plane
of a Direct Reading Spectrograph"

"With 3mm tall X 50 to 100 micron wide pixels"


To replace the slits &
PM tubes
Direct Reader approx. the size of a Grand Piano


Echelle Spectrometer
Optical Diagram
CID sensor
folding mirror
toroidal camera
mirror
echelle grating
CaF2 Prism
spherical
mirror
source
shutter
lens
slit



CID Detection Limits

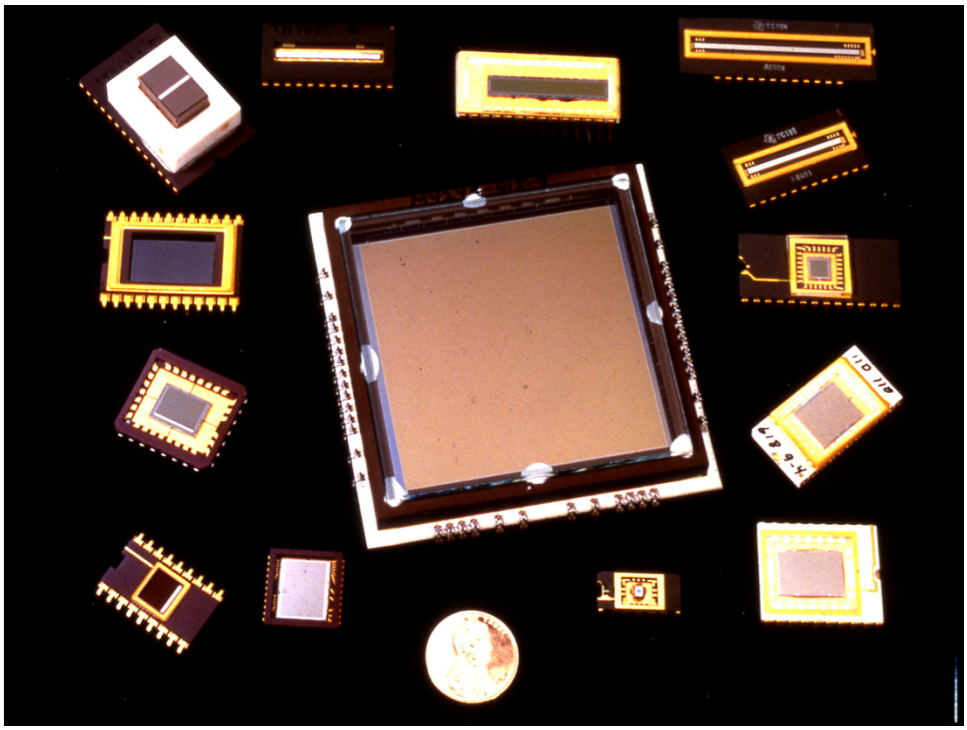
element	wavelength (nm)	Std. D.L. (ng/mL)	Modified D.L. (ng/mL)	improvement factor
Ba	233.5	0.87	0.17	5.1
	493.4	0.20	0.27	0.74
Cd	214.4	1.9	0.20	9.5
	226.5	1.2	0.26	4.6
	228.8	1.5	0.64	2.3
	sum	0.70	0.27	2.6
Co	228.6	1.5	0.56	2.7
	237.8	3.7	0.55	6.7
	sum	1.0	0.33	3.0
Cu	224.7	3.6	1.5	2.4
	324.7	1.3	2.3	0.57
	327.3	3.8	0.66	5.8
K	766.4	140	48	2.9
Mg	279.0	18	3.6	5.0
	279.5	0.10	0.28	0.35
Mn	257.6	0.13	0.036	3.6
	260.5	0.40	0.070	5.7
	sum	0.17	0.030	5.7
Zn	202.5	0.83	0.16	5.2
	206.2	1.2	0.40	3.0
	213.8	0.83	0.30	2.8
	sum	0.47	0.18	2.6

Standard Configuration: cross-flow nebulizer, vertical ICP

Modified Configuration: Meinhard nebulizer, horizontal ICP

Advanced Detector Technology

- Optical Spectroscopy
  - Raman Spectroscopy
  - Atomic Emission Spectroscopy
  - Molecular Fluorescence Spectroscopy
  - Array Infrared Spectroscopy
  - Imaging Spectroscopy
- Mass Spectrometry
  - Magnetic Sector
  - Ion Mobility
  - Secondary Ion Mass Spectrometry
  - Quadrupole
  - Time of Flight
- X-Ray Techniques
  - Diffraction
  - Fluorescence
  - X-Ray Photoelectron Spectroscopy



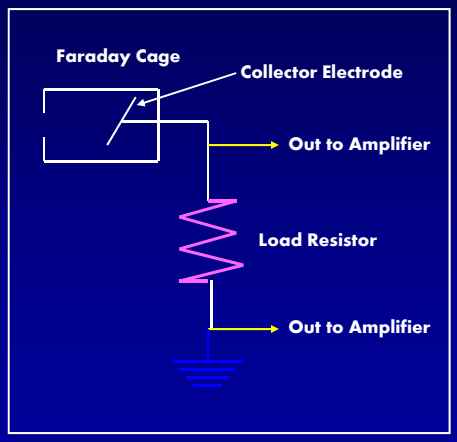
Can We Revolutionize Mass Spectrometry In The Same Manner

Certainly For Mass Analyzers With A Spatial Focal Plane
&
Potentially Even For Certain Applications Using Other Analyzers

New Ion (& Electron) Detectors

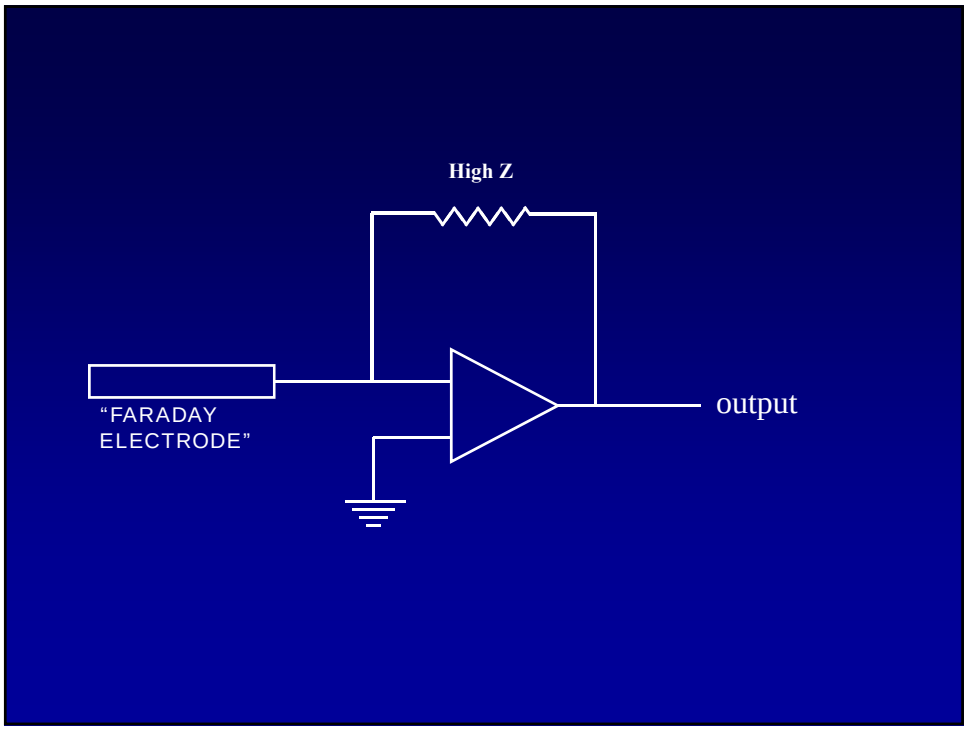
Capable of High Sensitivity Approaching Ion Multipliers
No Gain Drift With Age
Not Damaged By Very High Ion Fluxes
Stability of Faraday Cups
Provide Simultaneous Detection Of Large Mass Ranges
Detects Both Positive & Negative Ions
No Upper Mass Limit
Not Affected By Magnetic Or Electrostatic Fields
Operate at High Pressure (no upper pressure limit)

Present Detector Technology – Faraday Cups

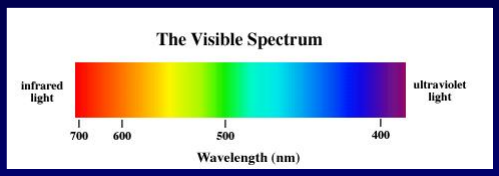


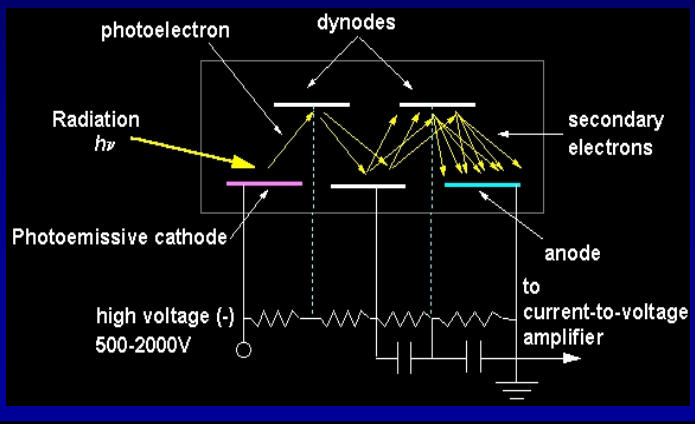
- Gain is stable and precisely known (gain=1)
- Bandwidth is consistent with use in sector-based mass spectrometry
- Useful for $I_{ion} \geq 10^{-15}$ amp (1 ion/sec = 1.6×10^{-19} amps)
- Implies that one needs about 6250 ions/sec for detection by Faraday cup

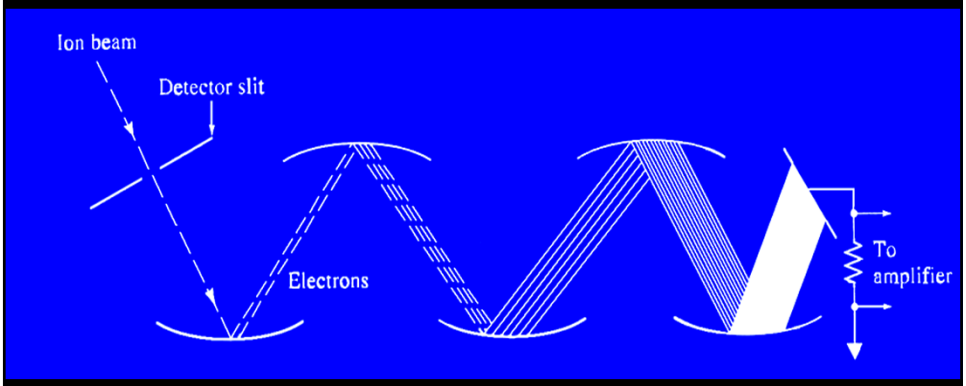
Operates at any pressure !



Photomultiplier Tube

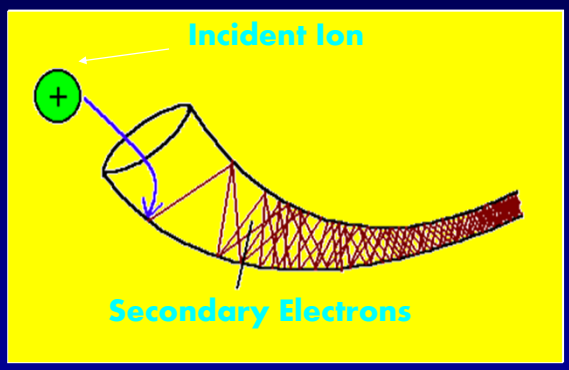




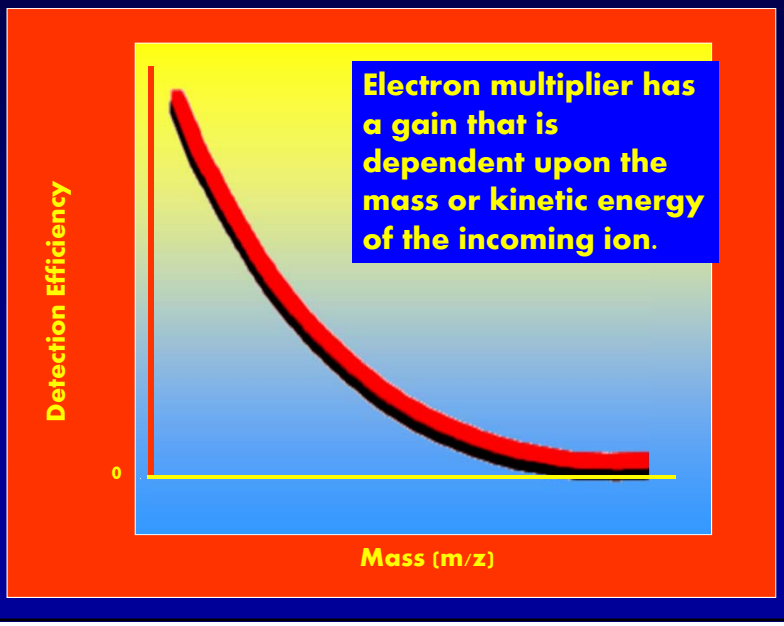


Operates only when free mean path of the electrons is large ie. a high vacuum

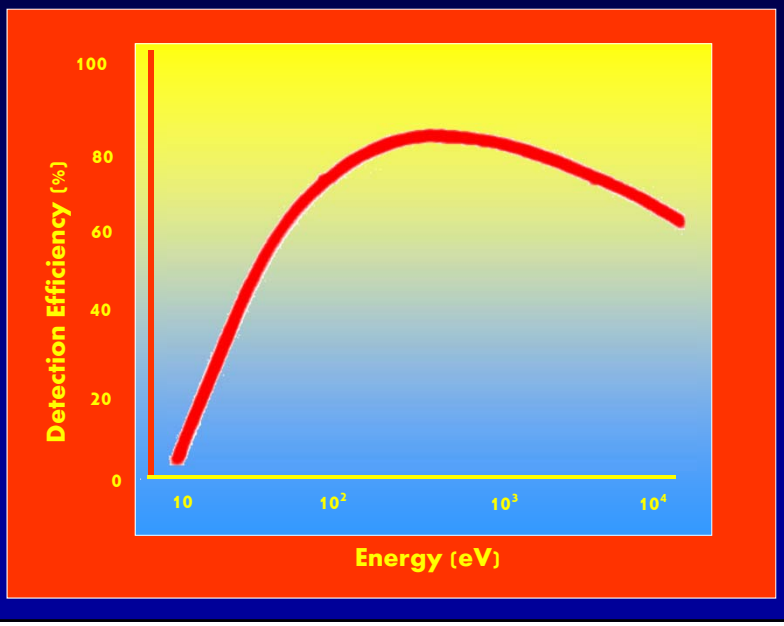
Electron Multiplier Detector



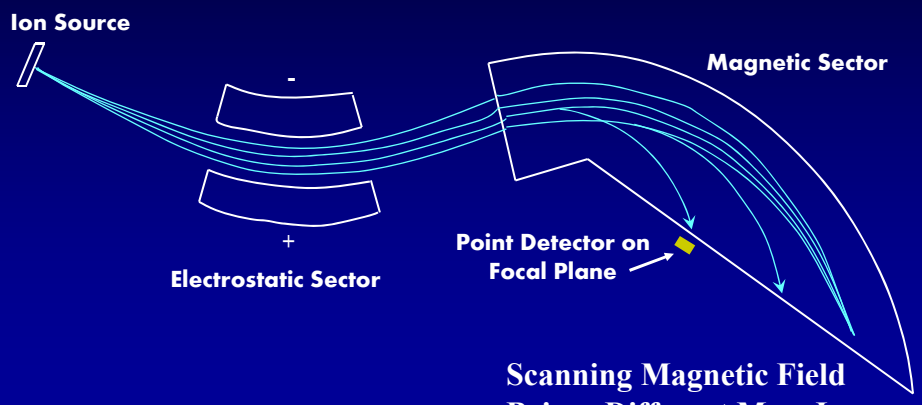
Electron Multiplier Detector



Electron Multiplier Detector

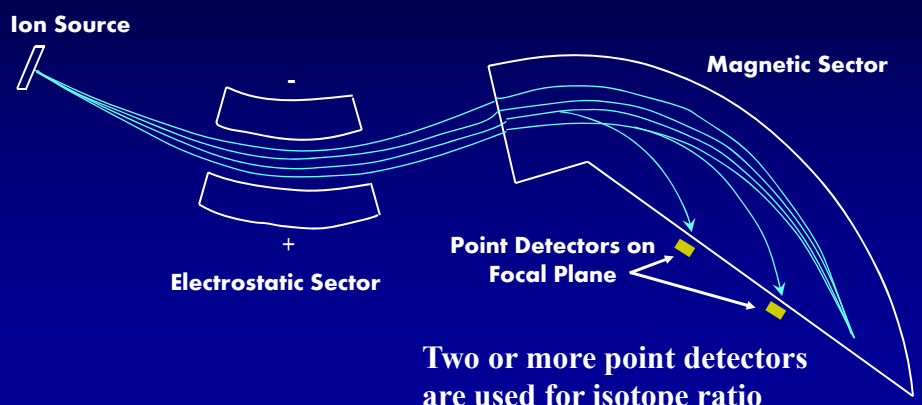


Mattauch-Herzog Mass Spectrometer Geometry



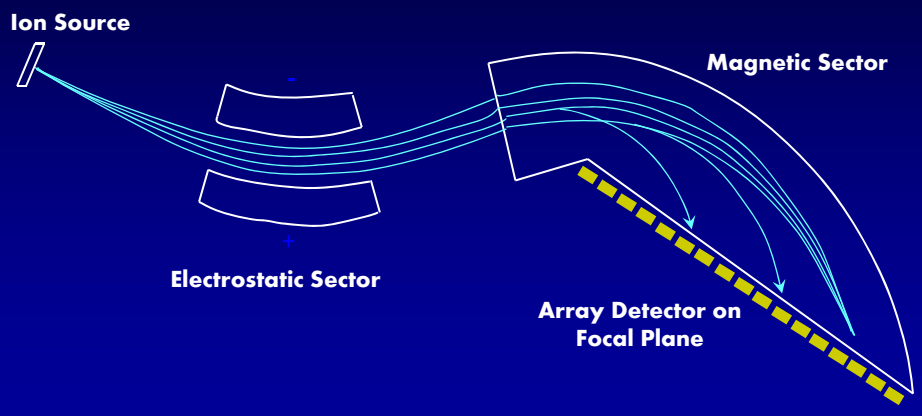
Scanning Magnetic Field Brings Different Mass Ions Onto Detector

Mattauch-Herzog Mass Spectrometer Geometry

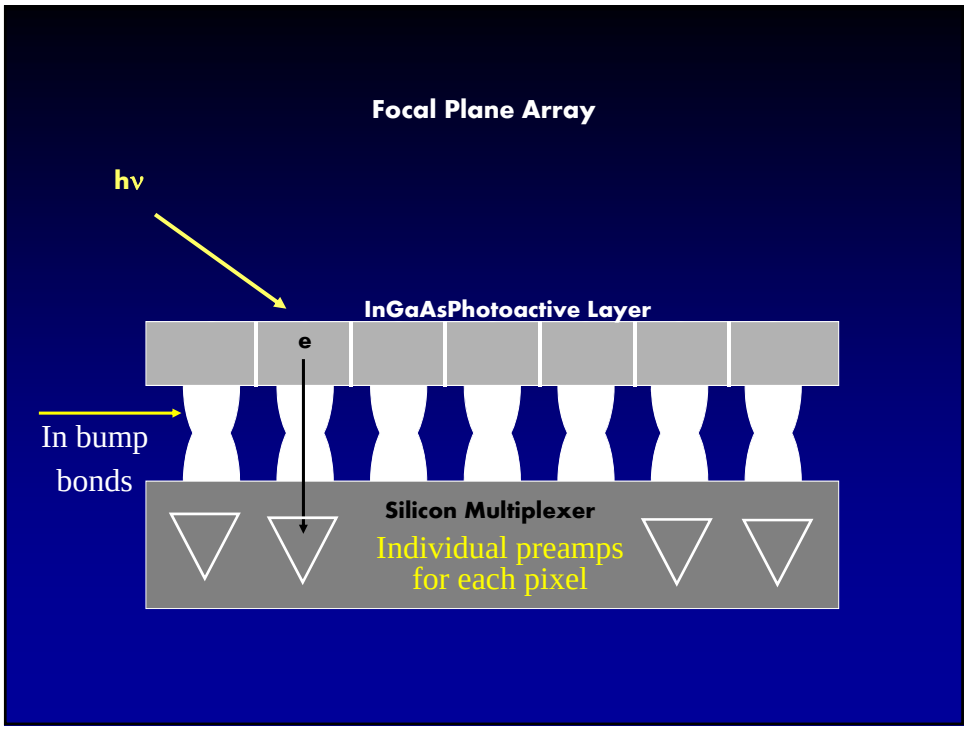


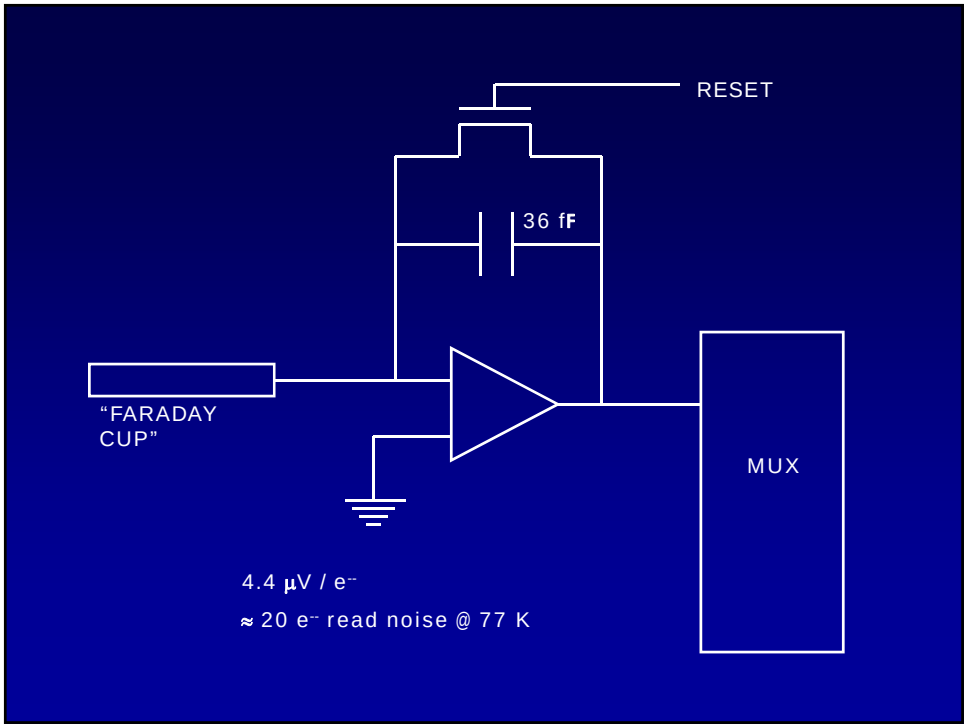
Two or more point detectors are used for isotope ratio analysis

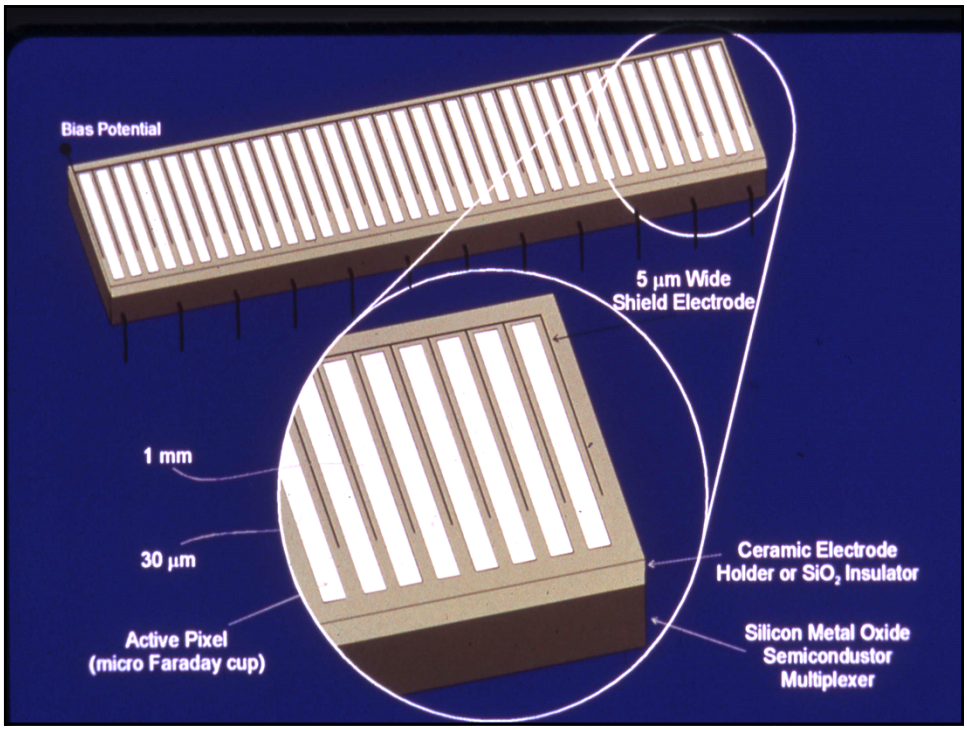
Mattauch-Herzog Mass Spectrometer Geometry



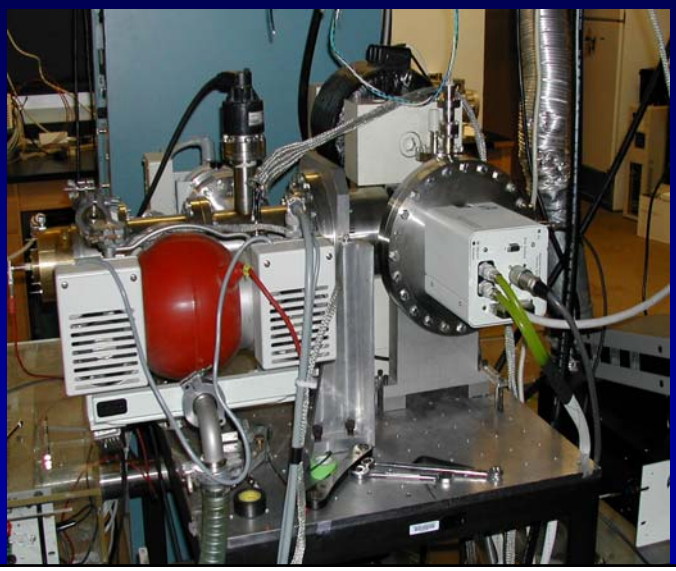
At the 1998 Winter Conference (Scottsdale AZ)
I proposed Adapting Focal Plane Readout Technology for Implementing Array Detectors for Mass Spectrometers

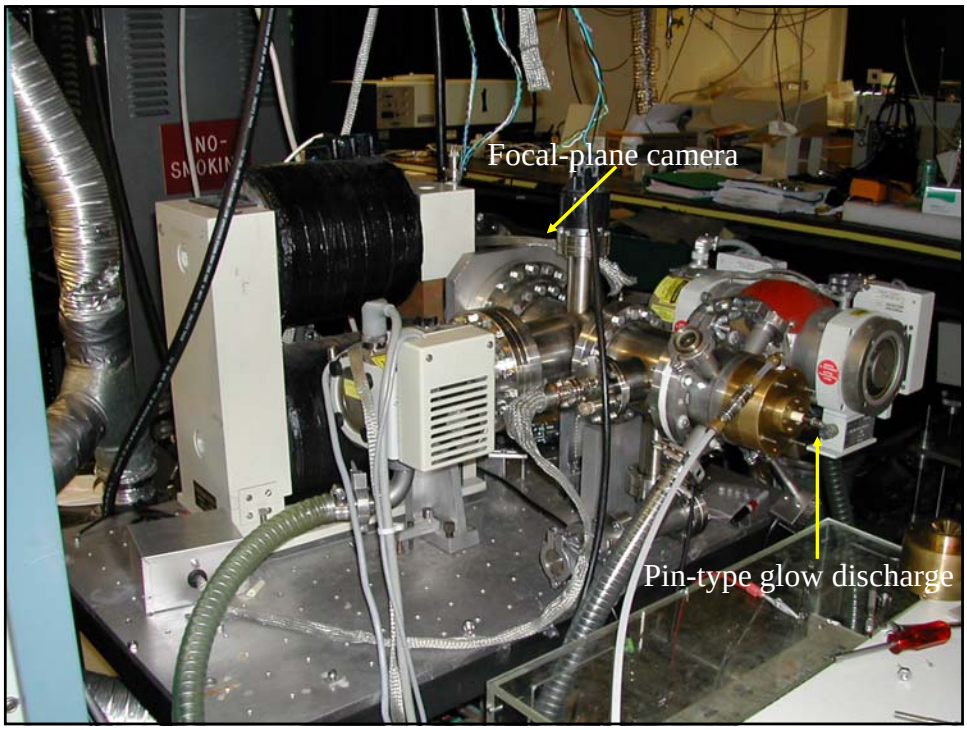

Focal Plane Array
hν
InGaAsPhotoactive Layer
e
In bump bonds
Silicon Multiplexer
Individual preamps for each pixel

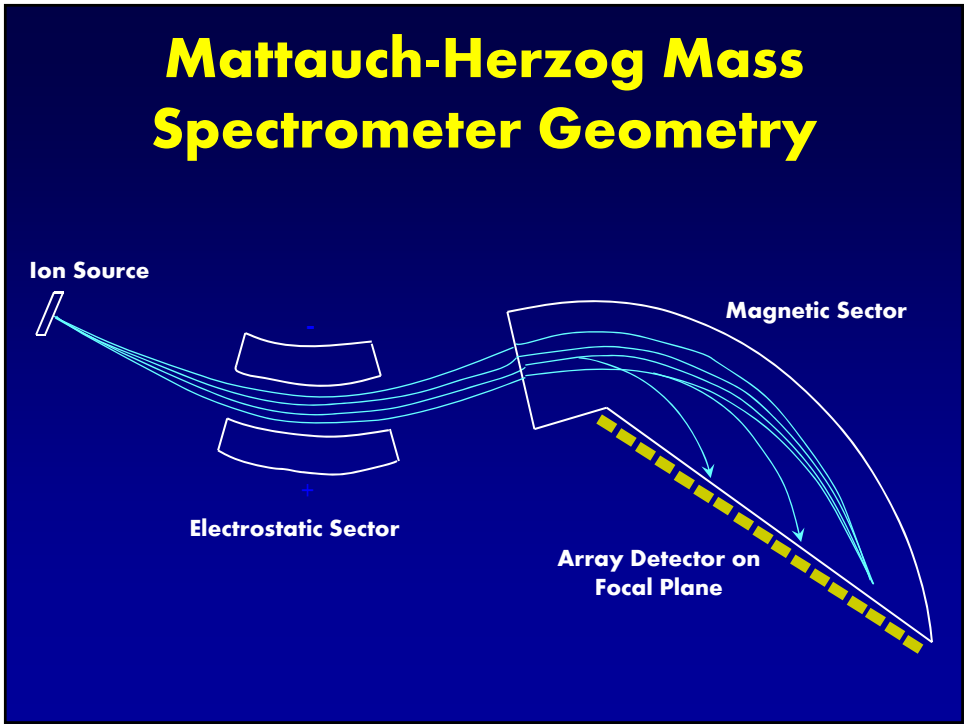

RESET
36 fF
"FARADAY CUP"
MUX
4.4 μV / e⁻
≈ 20 e⁻ read noise @ 77 K



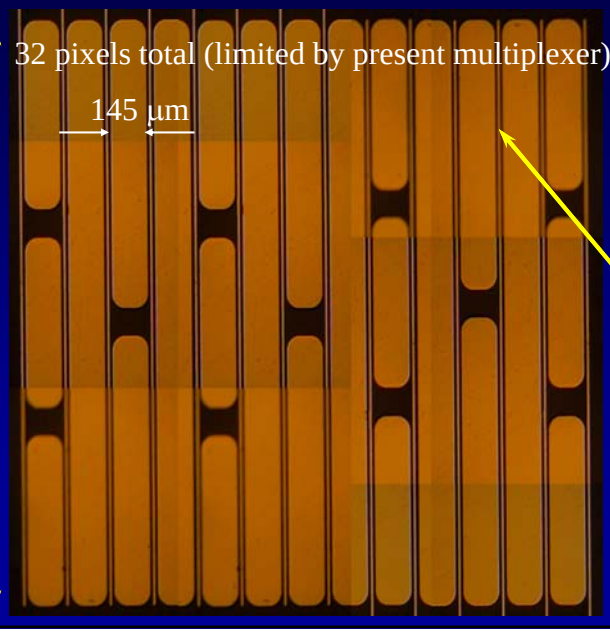
Attachment of Arizona ASAT Camera to G. Hieftje's Mass Spectrometer @ IU



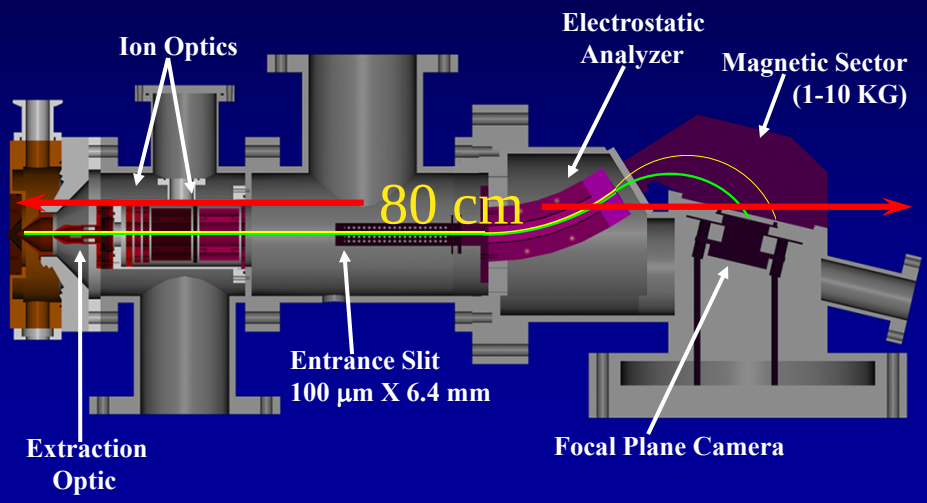

Focal-plane camera
Pin-type glow discharge

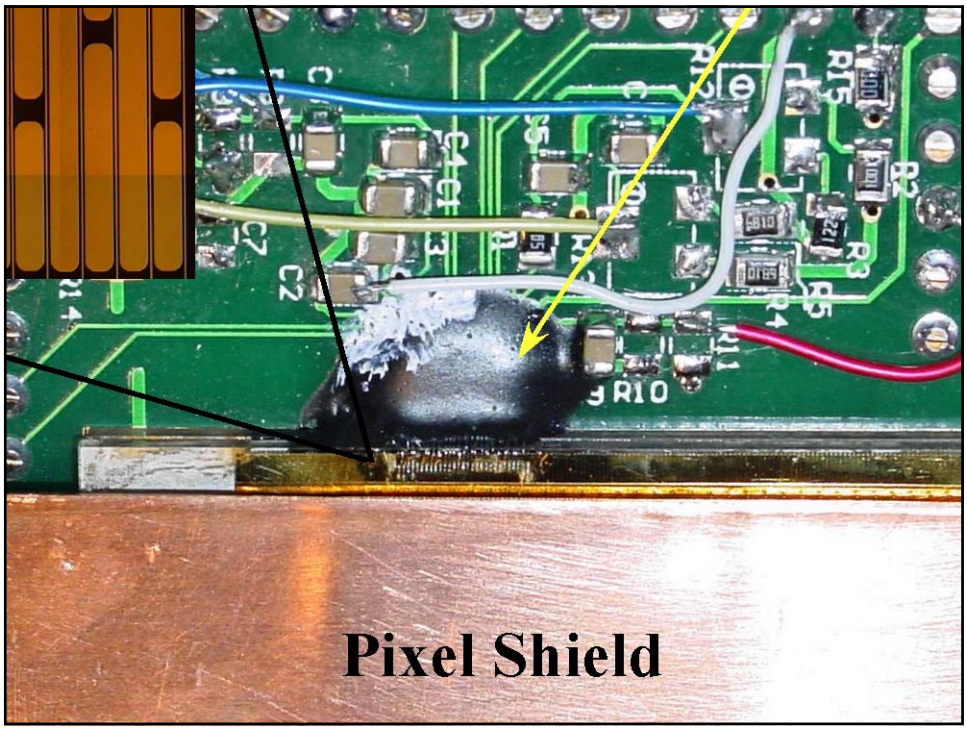

Mattauch-Herzog Mass Spectrometer Geometry
Ion Source
Magnetic Sector
Electrostatic Sector
Array Detector on Focal Plane

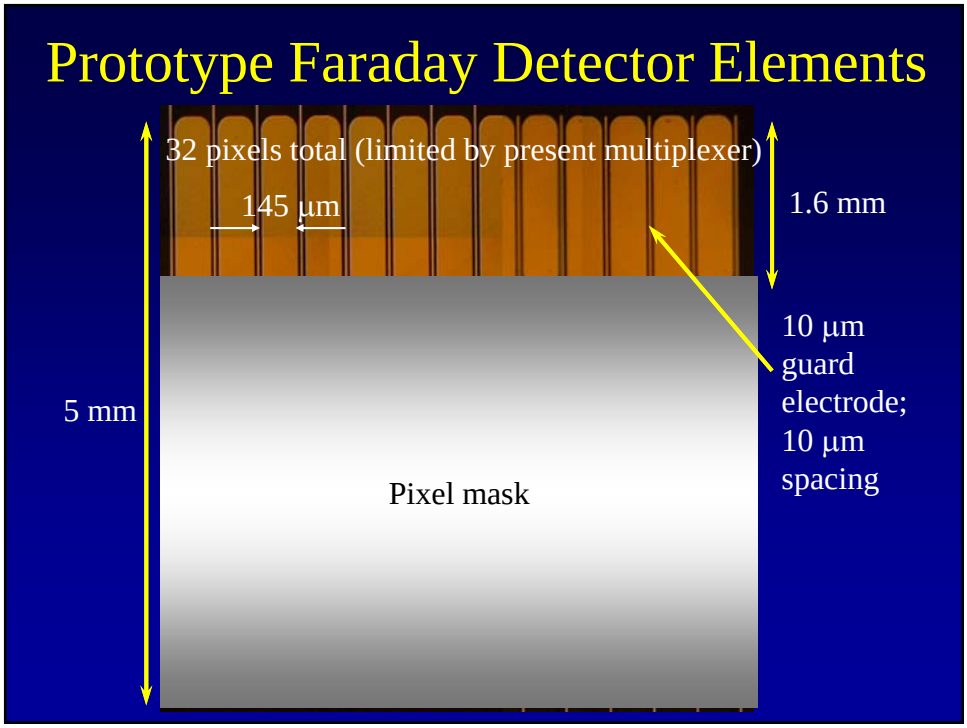
Prototype Faraday Detector Elements



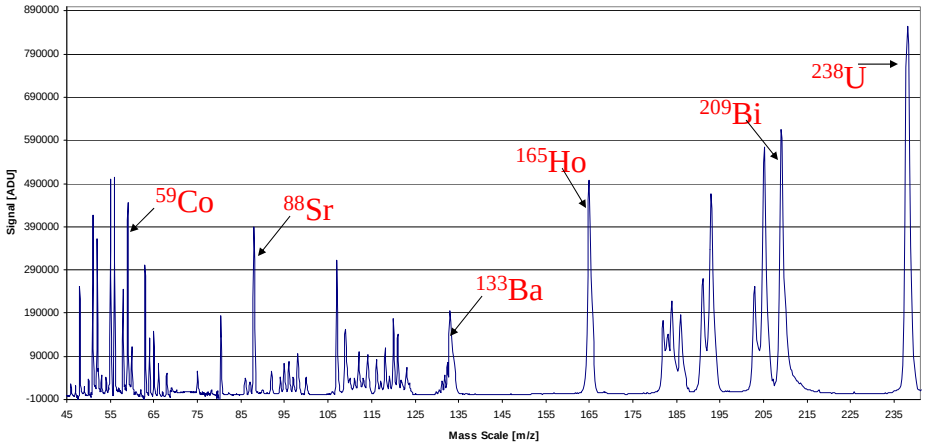
Hieftje's Mattauch-Herzog Mass Spectrograph




Pixel Shield


Prototype Faraday Detector Elements
32 pixels total (limited by present multiplexer)
145 μm
1.6 mm
5 mm
10 μm guard electrode; 10 μm spacing
Pixel mask

Mass Spectrum made from several Mass Windows

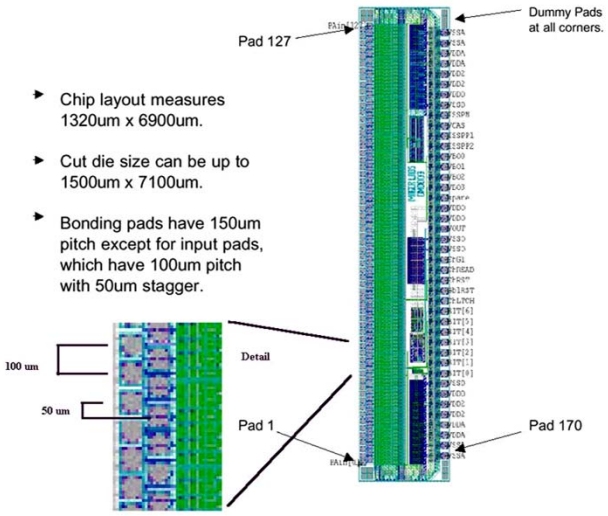


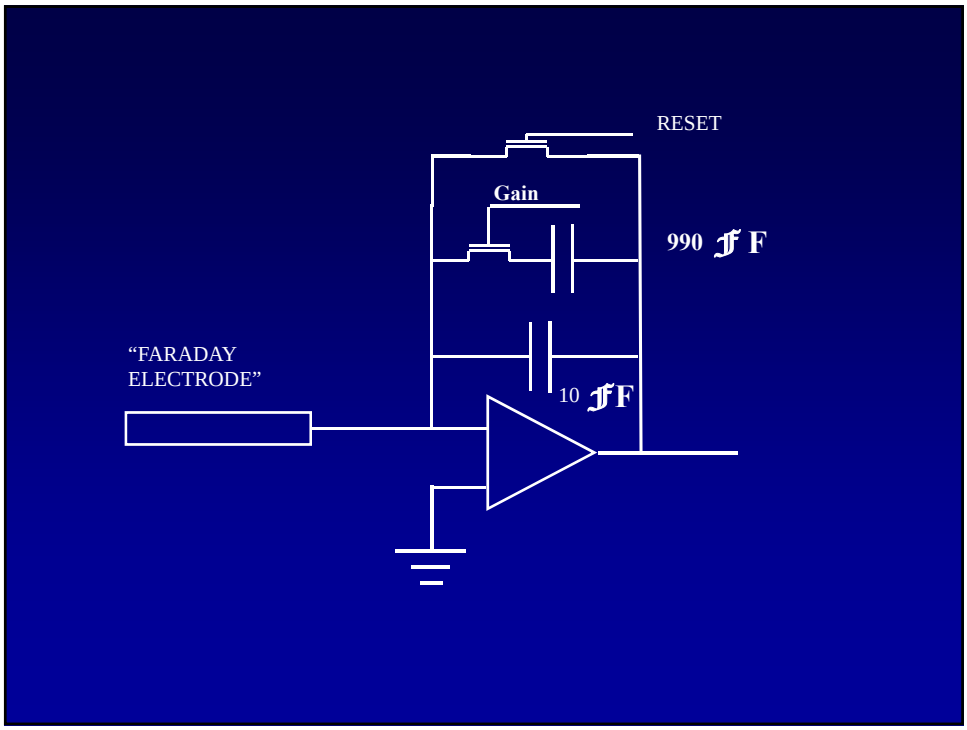
Conditions: 10 ppb multi elemental solutions, 5.011 ms Integration, 100 Reads, 20 replicates, 10.022 s total integration time, 1 ADU = ~2.4 counts

DM0003 Layout

iMAGERLABS

- Chip layout measures 1320um x 6900um.
- Cut die size can be up to 1500um x 7100um.
- Bonding pads have 150um pitch except for input pads, which have 100um pitch with 50um stagger.

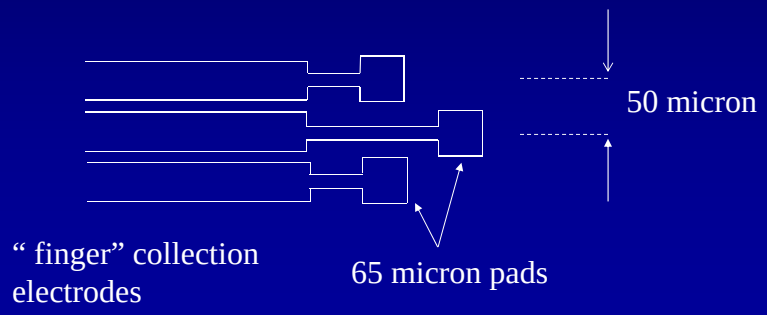


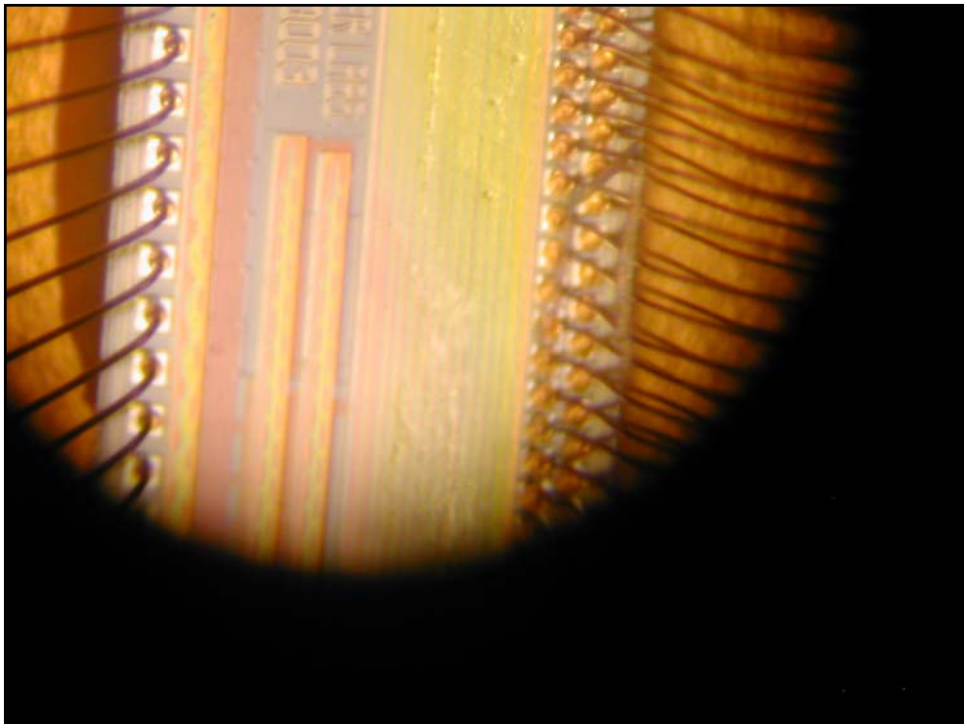


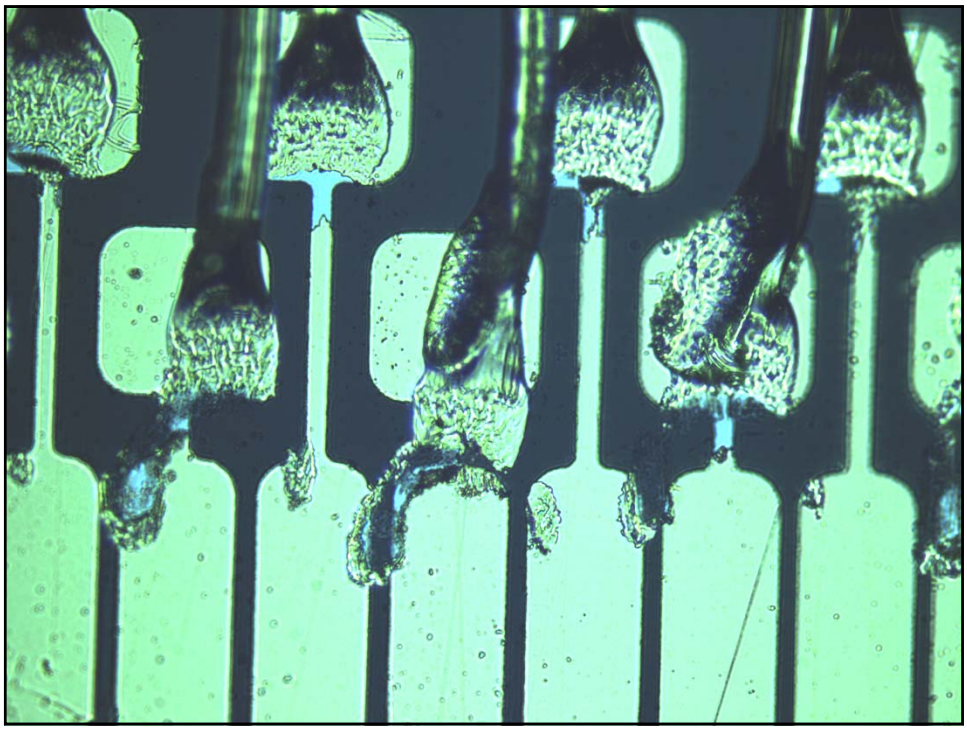
Issues to be Addressed

(1) Pixel Spacing

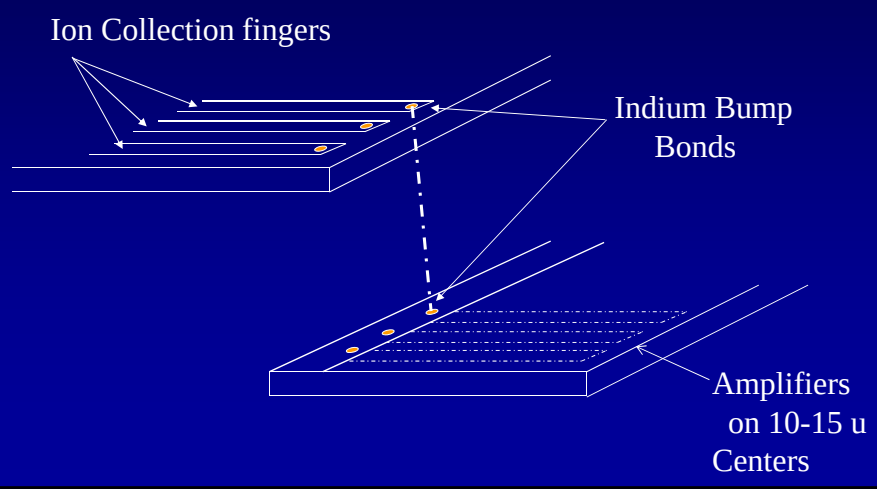
Smallest practical using Wire Bonding Connections is 50 microns



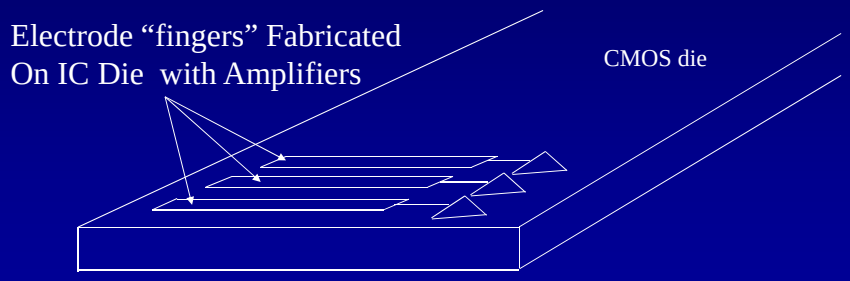




Bump Bonding Allows Connections to as Small as a Few Microns

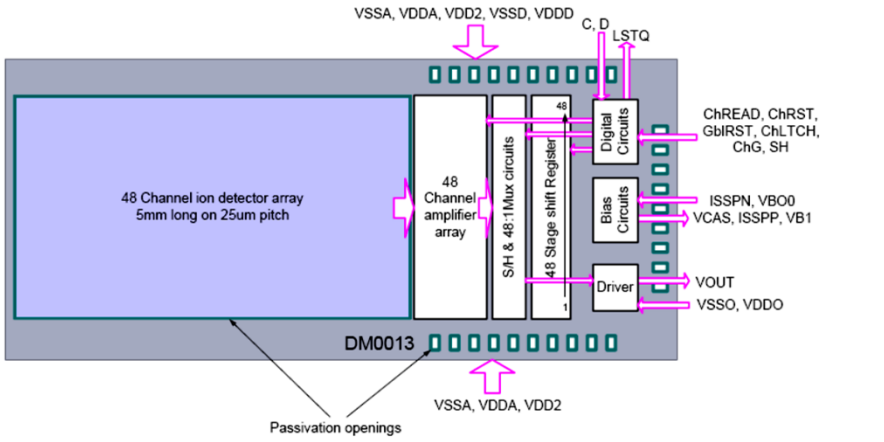


Monolithic Collection Electrodes

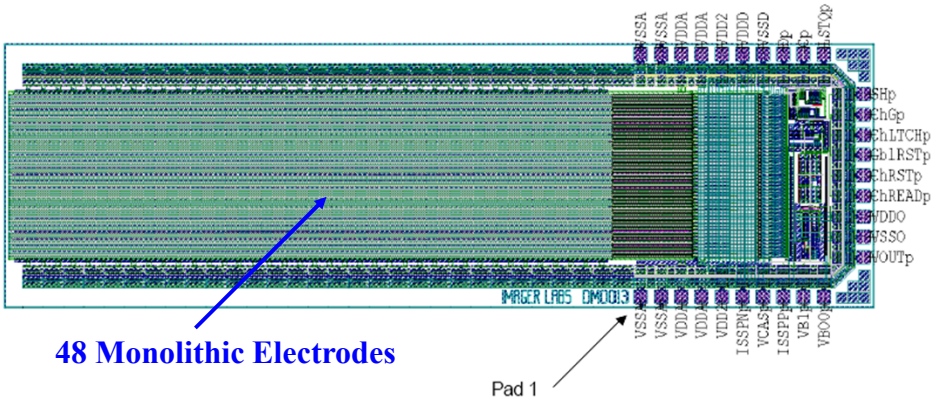


DM0013 Block Diagram / Floor Plan

iMAGERLABS

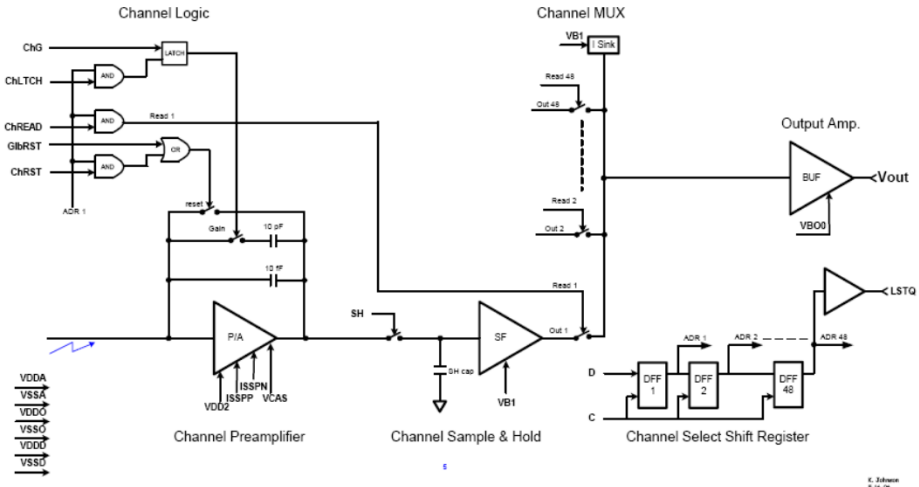


- Chip layout measures 6410um x 1950um.
- There are 29 bonding pads on 150um pitch.
- 48 Detector array is 5mm x 25um.



DM0013 Channel Block Diagram

iMAGERLABS



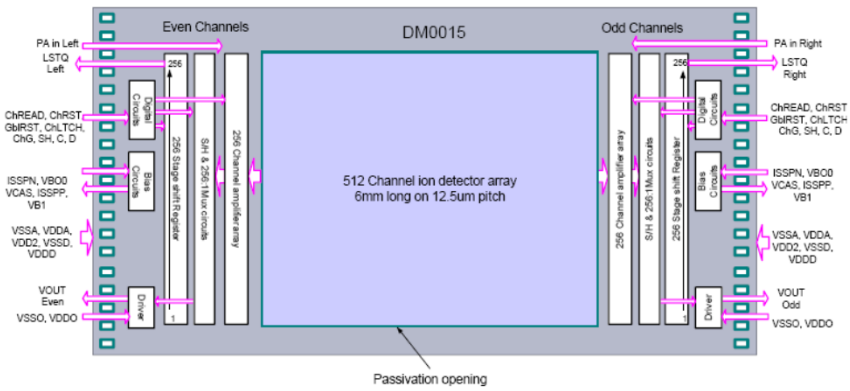
DM0013 Features

iMAGERLABS

- The DM0013 die measures 6.41 mm x 1.95 mm. It is laid out using TSMC CM035 design rules, which is a 3.3 Volt, 0.35um minimum geometry, 2-layer poly, and 4-layer metal process with a linear capacitor.
- The DM0013 is a 48-channel amplifier array chip with integrated ion detectors. It is on a 25um pitch and detectors are 5mm long.
- The 48 channels are muxed down to 1 high-speed output with shift register addressing.
- Preamp will integrate > 1.5 Volts in both positive and negative direction.
- Each of the channels consists of: Low noise preamp with two gain settings.
- Channels can be reset simultaneously with the global reset command, or individually with shift register access. Gain setting and reading channel outputs are also shift register access.
- Refer to "DM0013 Pads" for interface information.
- Chip bandwidth is controlled by current input (ISSPN). Output bandwidth is controlled by current input VBO0.

DM0015 Block Diagram / Floor Plan

iMAGERLABS



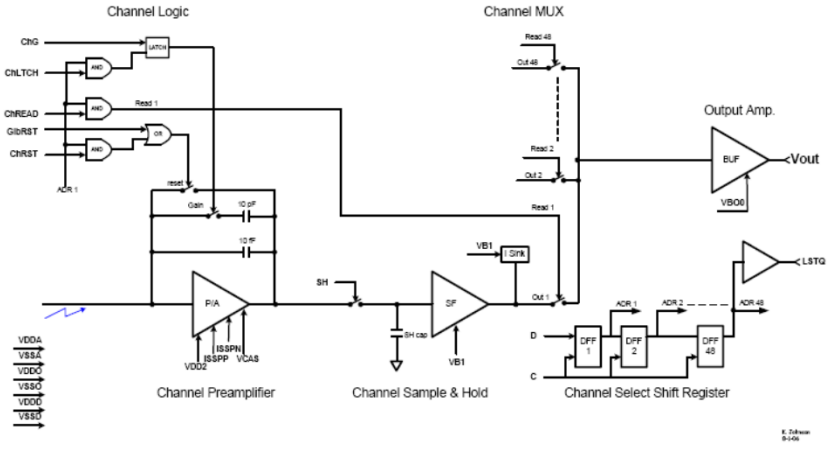
DM0015 Features p1

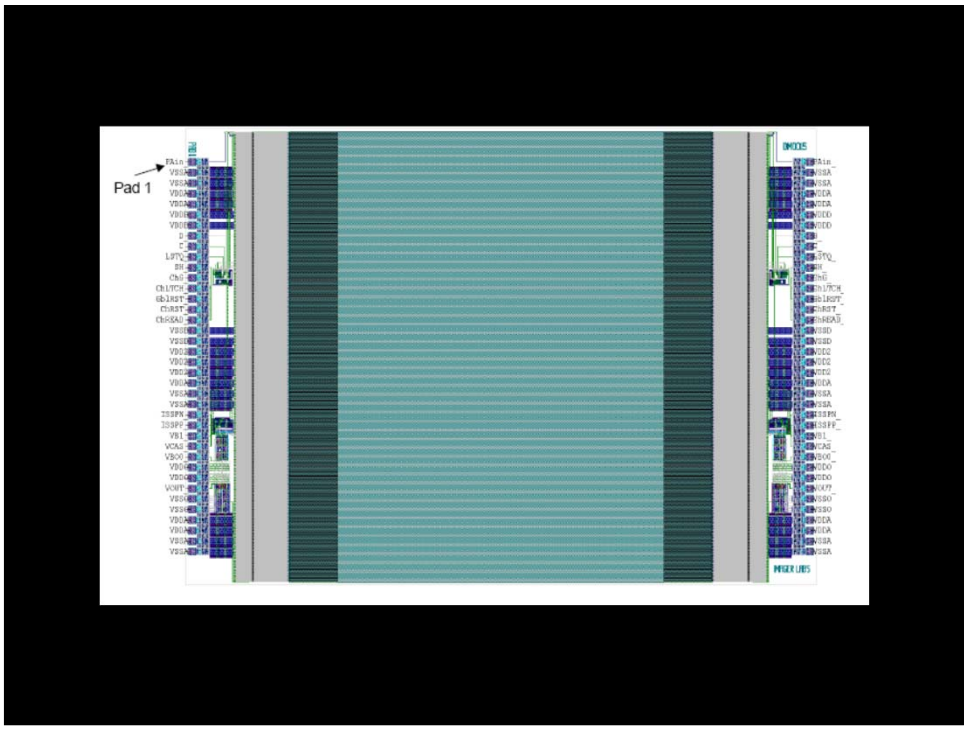
iMAGERLABS

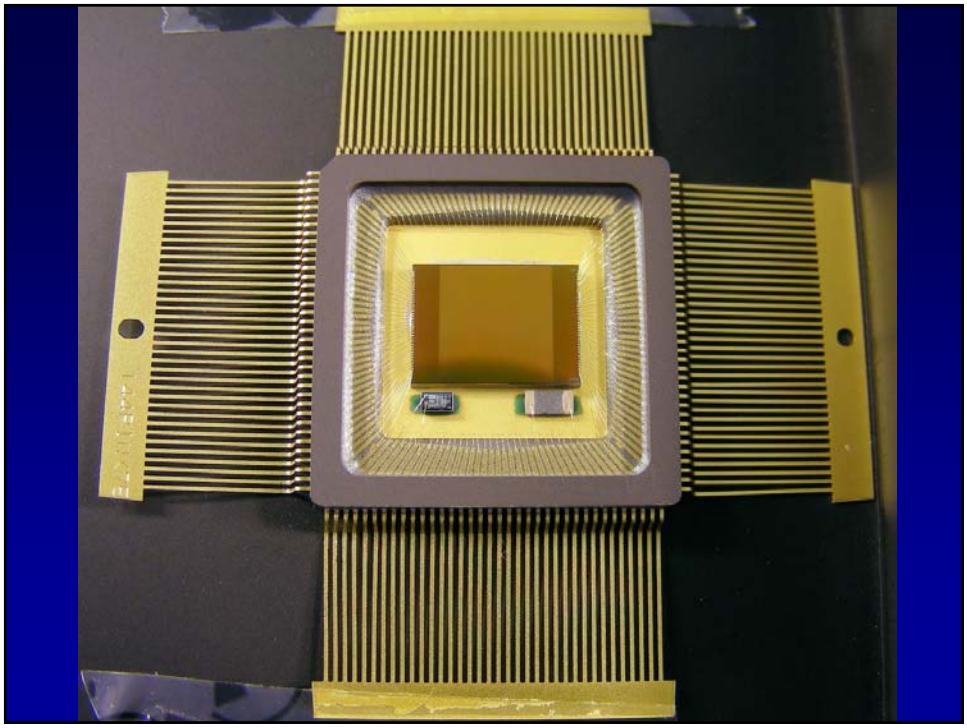
- The DM0015 die measures 9.0 mm x 6.5 mm. It is laid out using X-Fab XH035 design rules, which is a 3.3 Volt, 0.35um minimum geometry, 2-layer poly, and 4-layer metal process with a linear capacitor.
- The DM0015 is a 2 x 256-channel linear amplifier array chip with 6mm long integrated ion detectors in the center of the chip. Amplifier pitch is 25um. Detector pitch is 12.5um.
- The 256 channels on either side of the chip are muxed down to 1 high-speed output on each side with shift register addressing.
- Channel arrays on each side of the chip are independent of each other but can be driven by the same clock and bias inputs.
- Preamp will integrate > 1.5 Volts in either positive or negative direction.
- Each of the channels consists of: Low noise Preamp with two gain settings, Sample & Hold, Output Mux, and Channel logic.

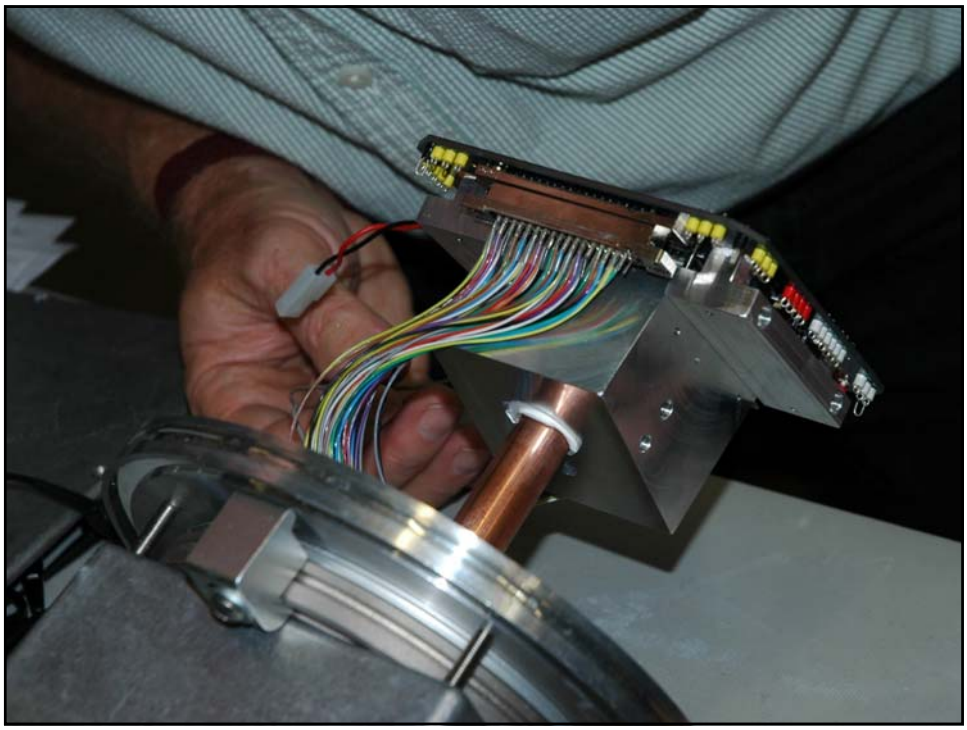
DM0015 Channel Block Diagram

iMAGERLABS

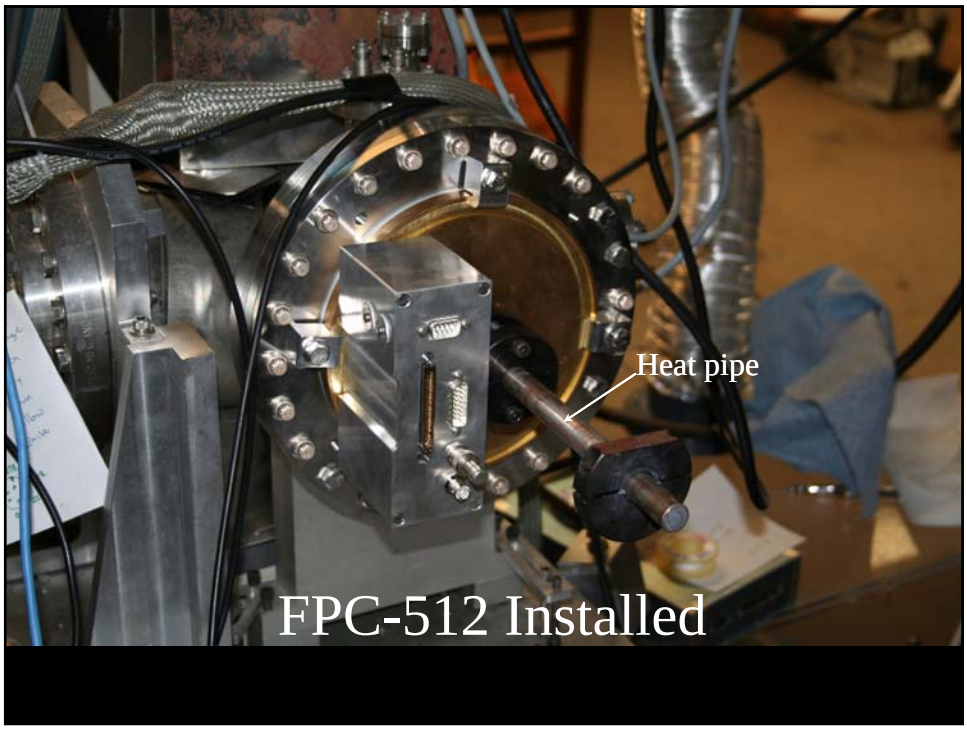


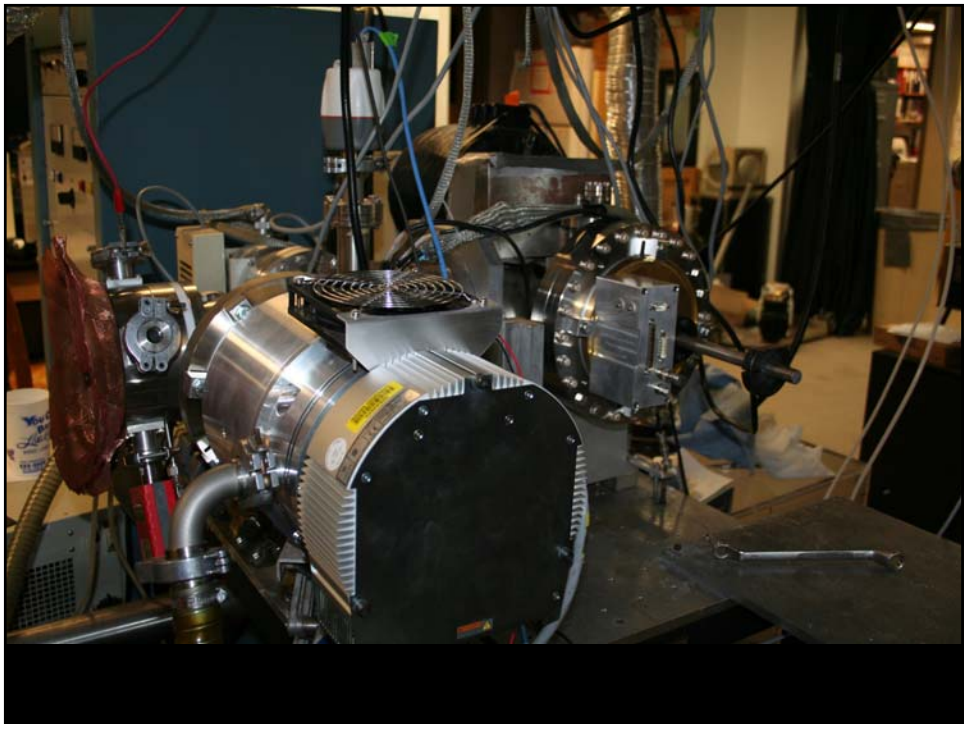

Pad 1



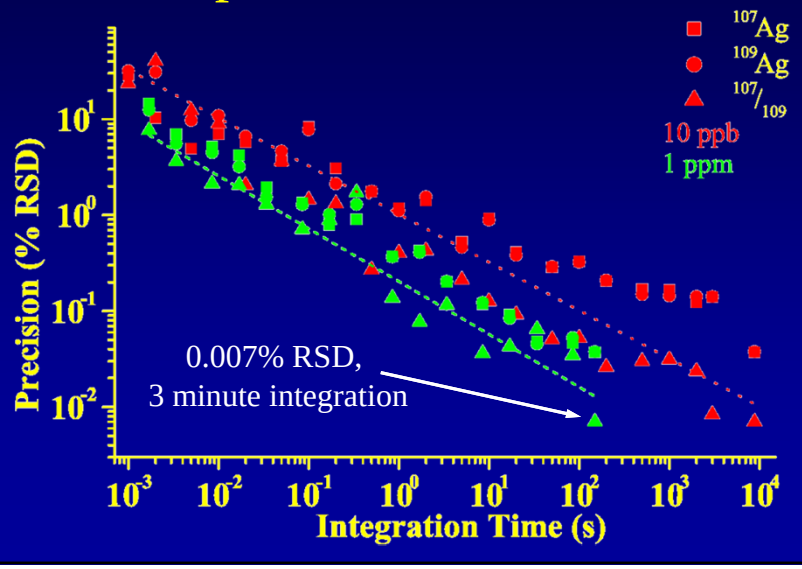


Flange-Mounted FPC-512

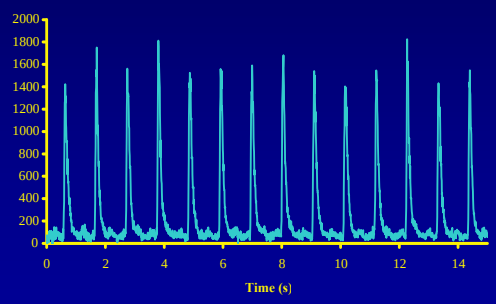

Heat pipe
FPC-512 Installed



Isotope Ratio Precision

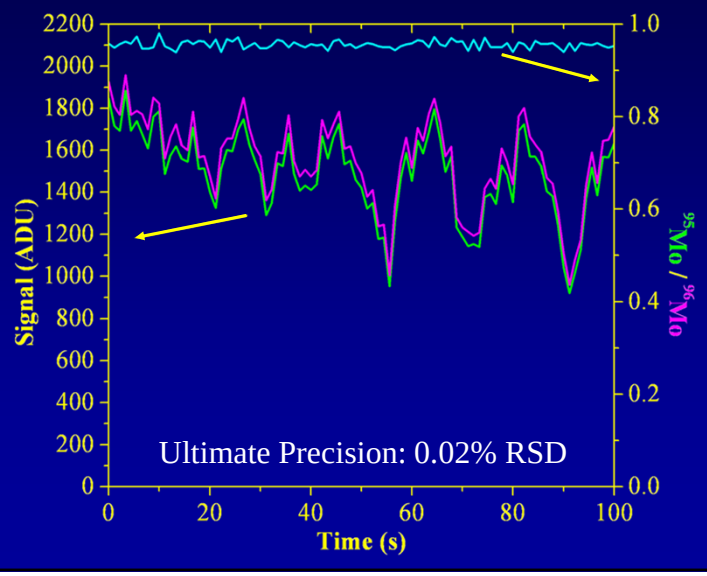


Laser Ablation ICP-ADAMS Shot-to-Shot Reproducibility



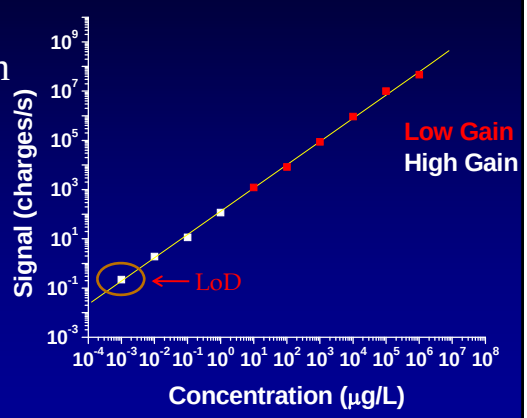
Isotope	%RSD	Isotope	%RSD
^{27}Al	3.3	^{65}Cu	9.5
^{28}Si	7.4	^{93}Nb	8.4
^{52}Cr	11.3	^{100}Mo	6.4
^{55}Mn	9.8	^{120}Sn	5.1
^{56}Fe	9.3	^{186}W	21.5
^{64}Ni	5.8	^{208}Pb	12.2

Laser Ablation Precision

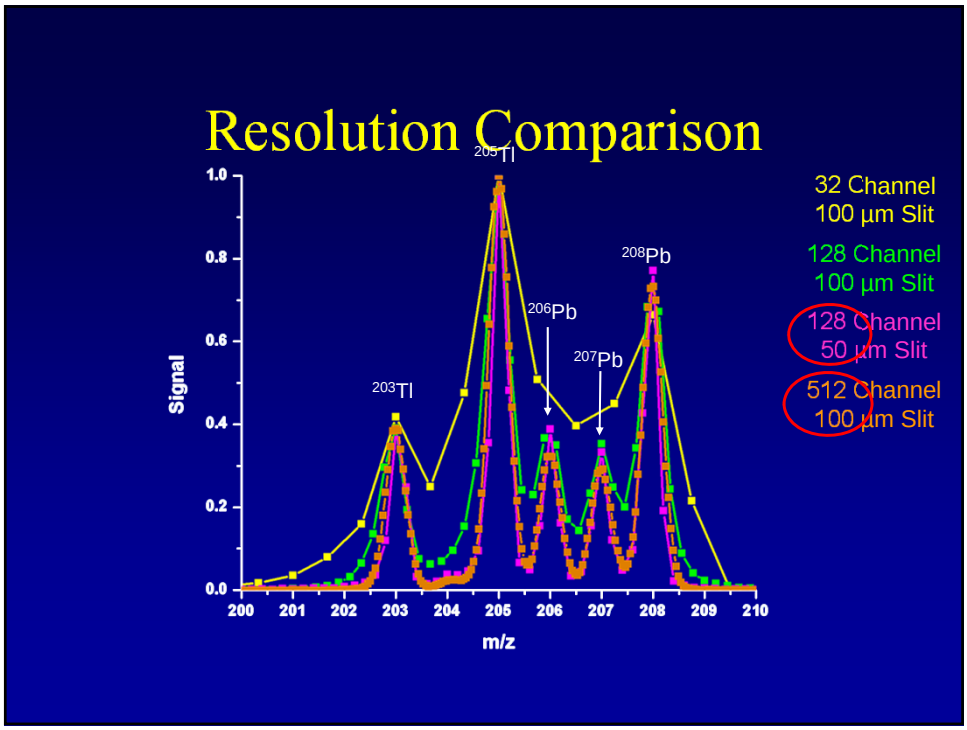


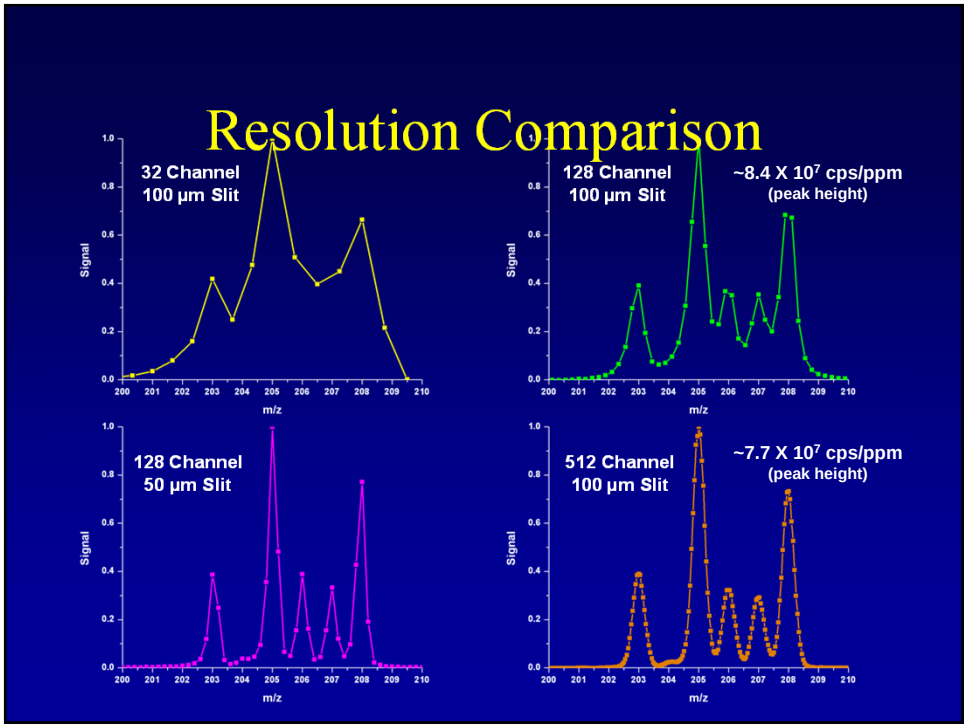
Data run by The Hieftje Research Group @ IU with a Denton Group Array Detector System

- 1 pptr to 1000 ppm Ho at various integration times
- Limit of detection included
- Over 9 orders of magnitude

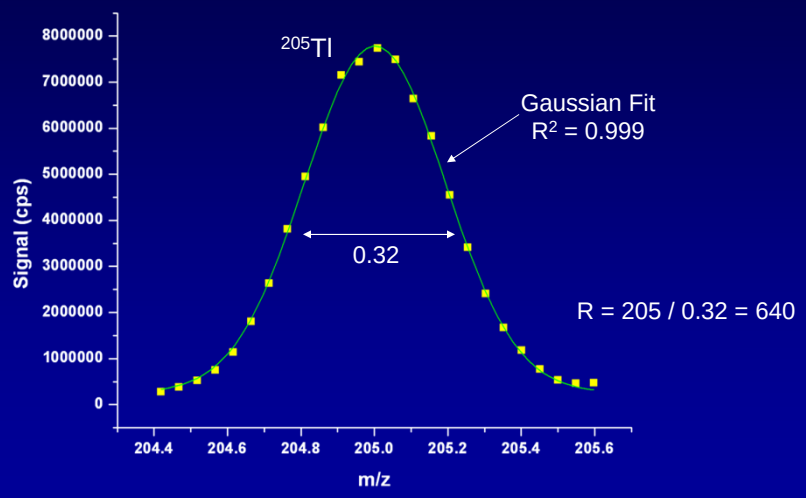


Linear Dynamic Range

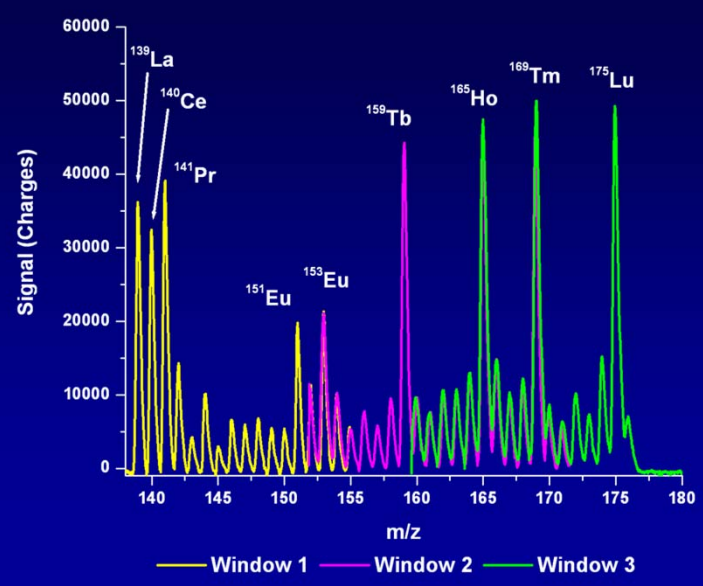

Resolution Comparison
205Tl
208Pb
206Pb
207Pb
203Tl
Signal
m/z
32 Channel
100 µm Slit
128 Channel
100 µm Slit
128 Channel
50 µm Slit
512 Channel
100 µm Slit


Resolution Comparison
32 Channel
100 µm Slit
128 Channel
100 µm Slit
~8.4 X 10^7 cps/ppm
(peak height)
128 Channel
50 µm Slit
512 Channel
100 µm Slit
~7.7 X 10^7 cps/ppm
(peak height)
Signal
m/z

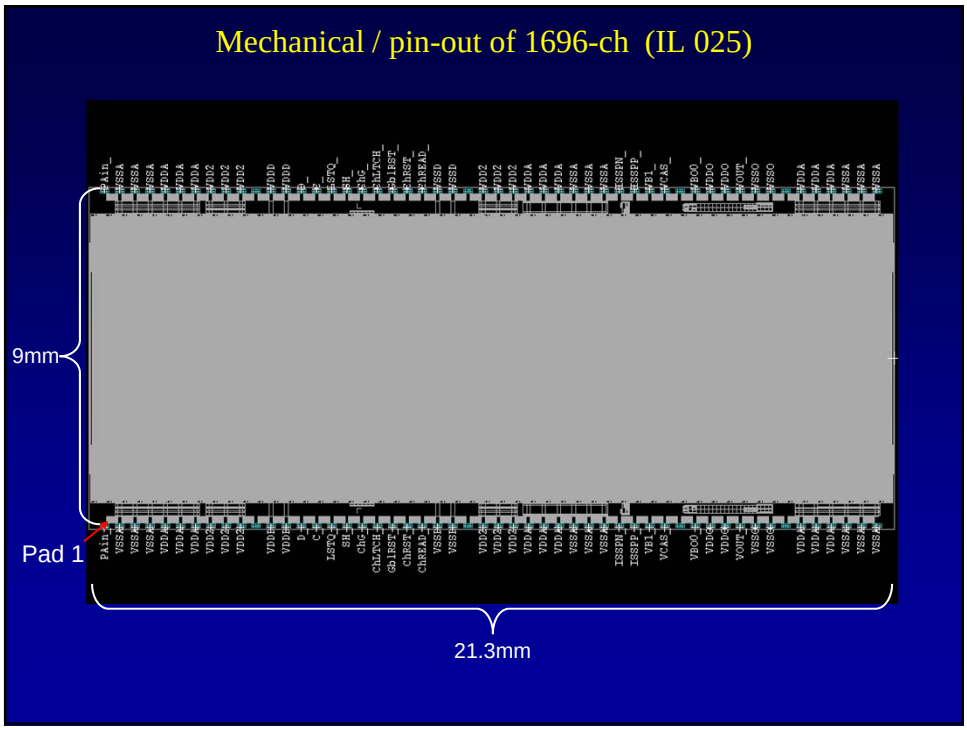
Resolving Power

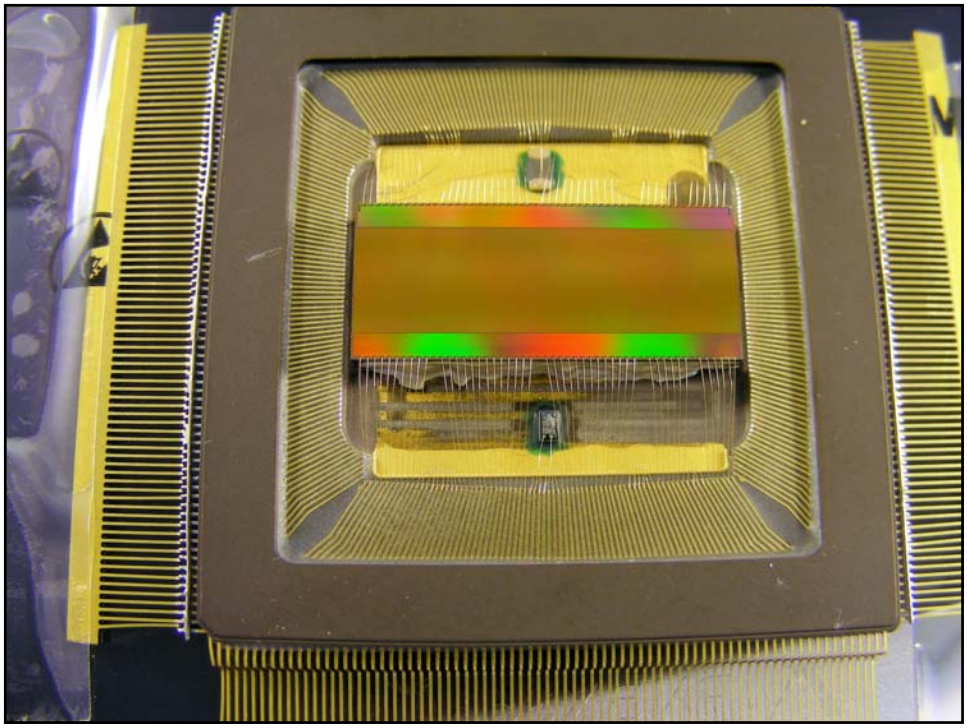


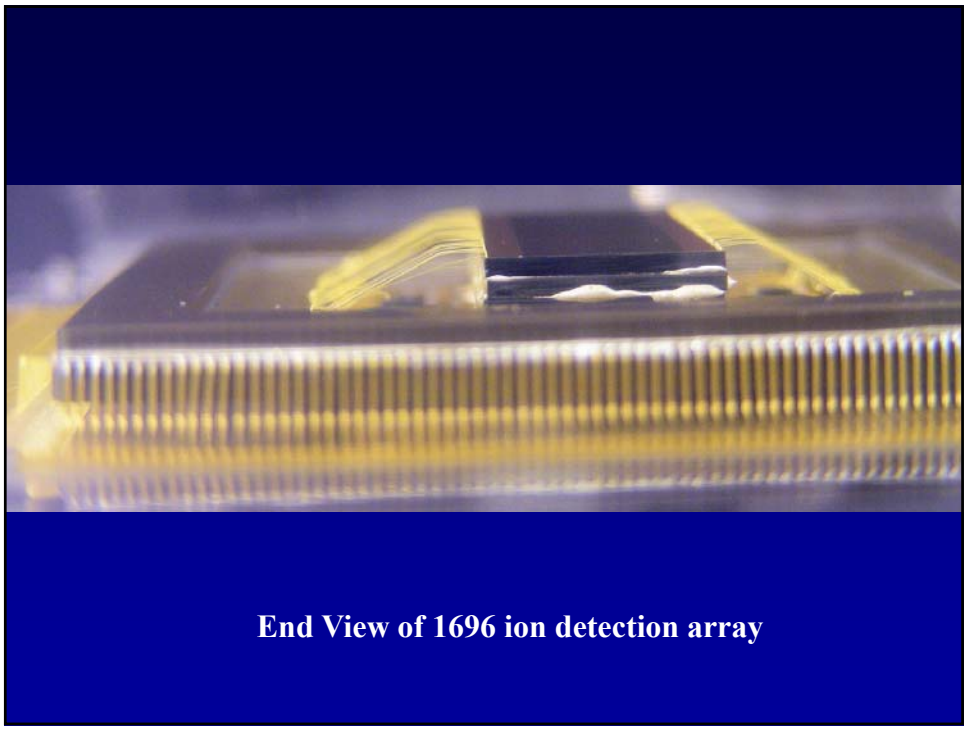
Rare Earth Elements

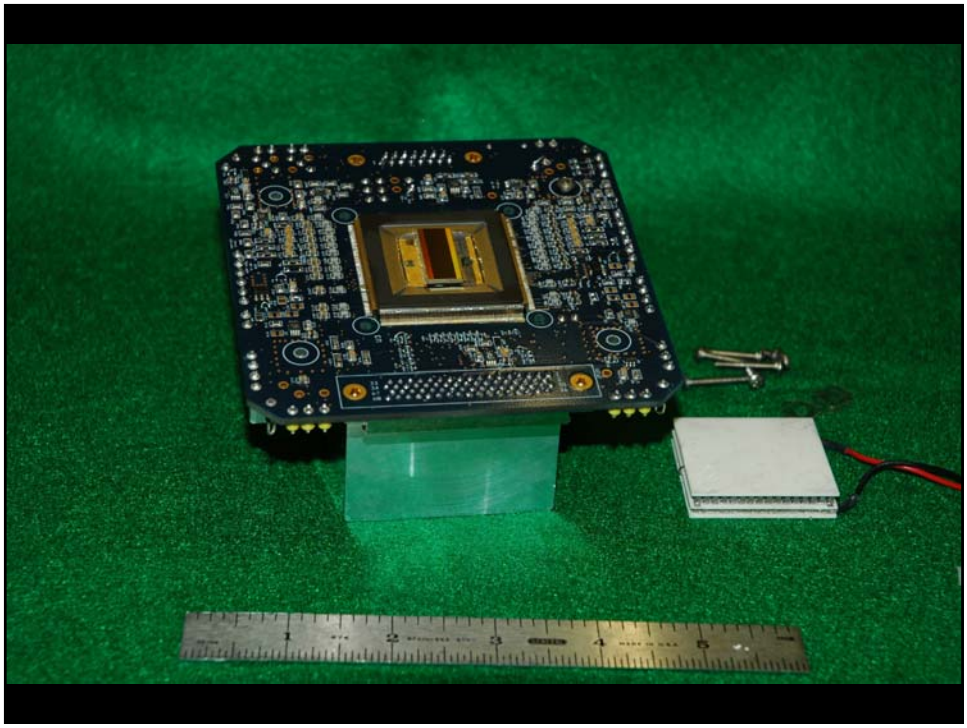


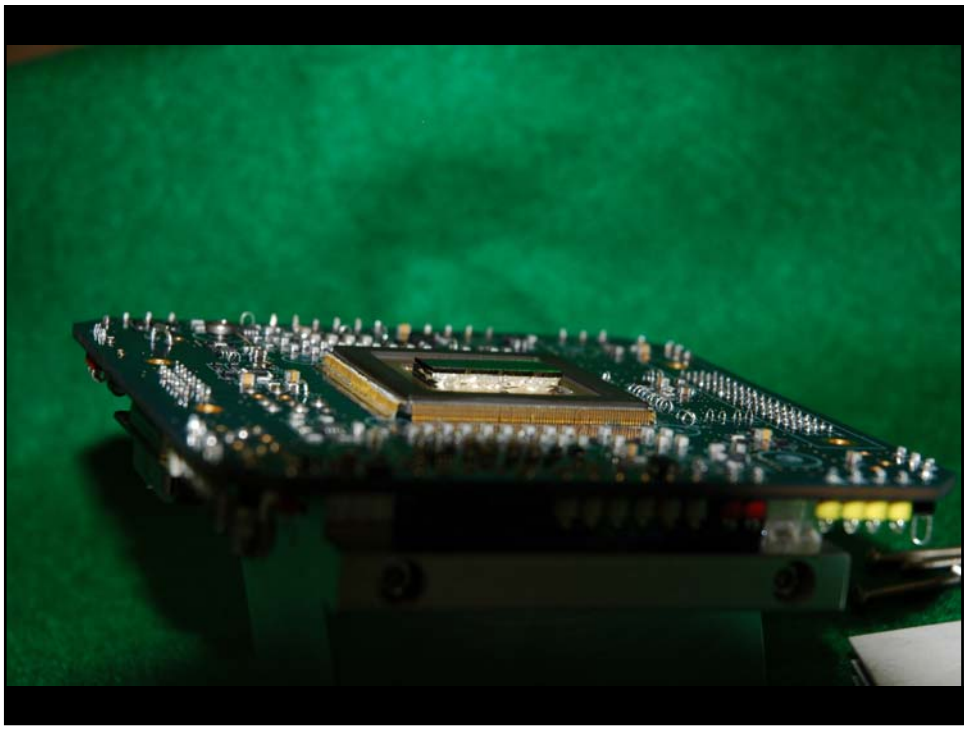
10 ppb multi-elemental solution, 0.5 s Integration Time

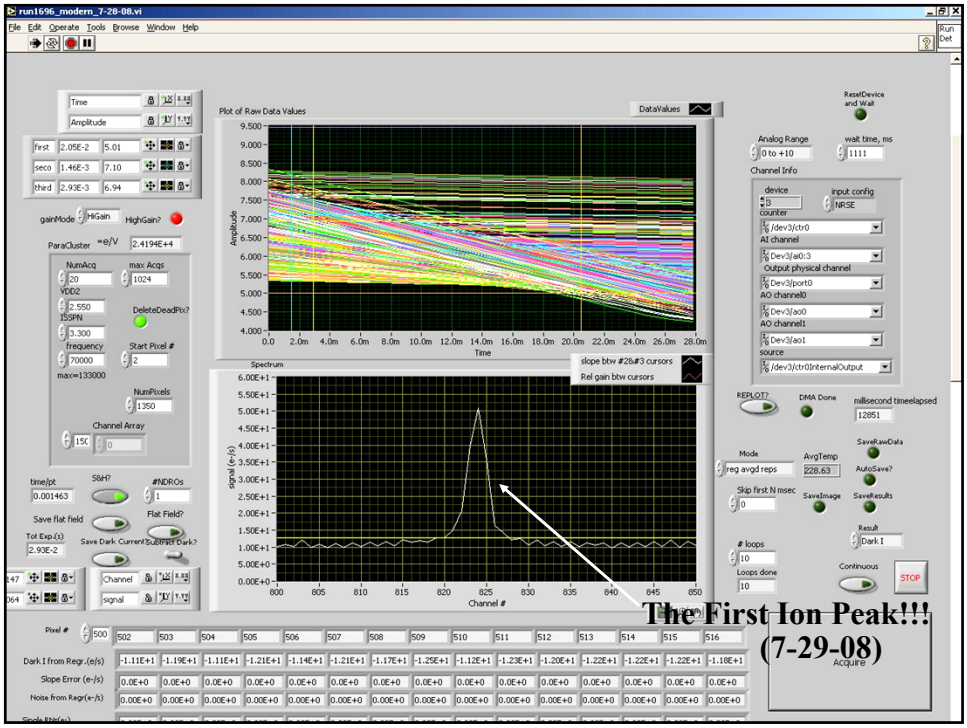

Mechanical / pin-out of 1696-ch (IL 025)
9mm
Pad 1
21.3mm




End View of 1696 ion detection array






run1696_modern_7-28-08.vi
File Edit Operate Tools Browse Window Help
Plot of Raw Data Values
DataValues
Amplitude
Time
Spectrum
slope btw #2&#3 cursors
Rel gain btw cursors
signal (e-/s)
Channel #
ResetDevice and Wait
Analog Range
wait time, ms
Channel Info
device
input config
counter
A1 channel
Output physical channel
AO channel0
AO channel1
source
REPLOT?
DMA Done
millisecond timeelapsed
SaveRawData
AutoSave?
SaveImage
SaveResults
Mode
AvgTemp
Skip first N msec
loops
Loops done
Continuous
STOP
Acquire
gainMode
HiGain
HighGain?
ParaCluster
NumAcq
max Acqs
DeleteDeadPix?
frequency
Start Pixel #
NumPixels
Channel Array
time/pt
S&H?
#NDROs
Save flat field
Flat Field?
Save Dark Current
Subtract Dark?
Channel
signal
Pixel #
Dark I from Regr.(e/s)
Slope Error (e-/s)
Noise from Regr(e-/s)
The First Ion Peak!!!
(7-29-08)

Detection Limit at This Point

1.45 electrons of read noise with NDRO

5 IONS !

Number of Amplifier Channels

Using CMOS 0.35 micron design technology:

Device size is limited to approx. 22mm (0.866in.)

Unless “Stitching” is used to tie together mask “replicates”

Therefore:

Using 50 micron centerlines = 440 channels

Using 10 micron centerlines = 2200 channels

Using Stitching:

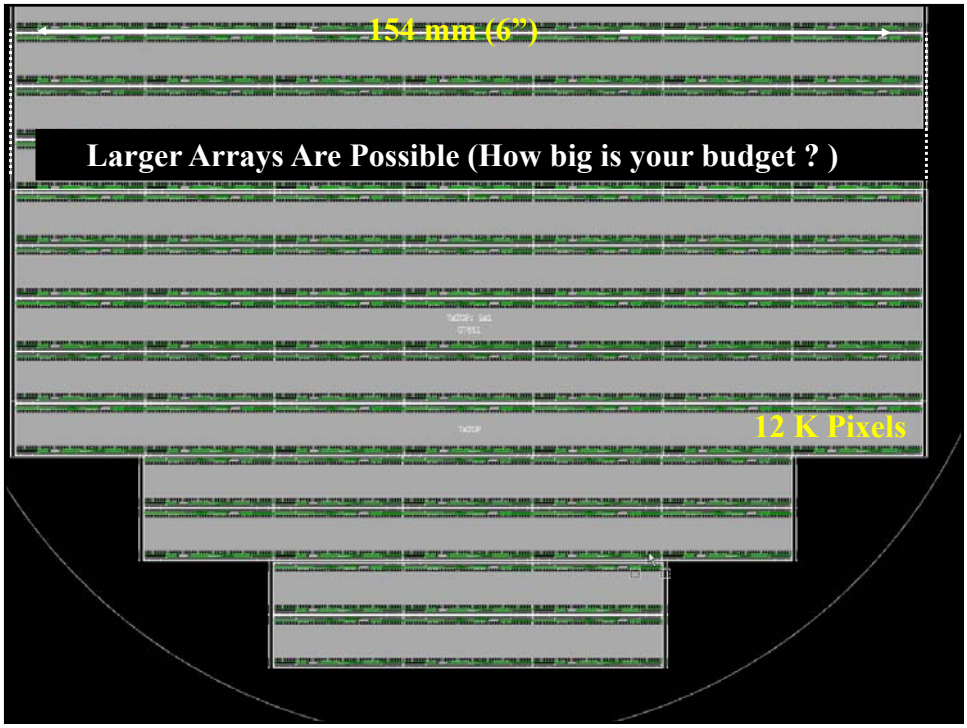
Theoretically – As big & as many channels as you can afford $$$$

But practically 120 mm to 196 mm(4.7in – 7.7in)

Very long thin dies are fragile

Alternatives:

End butting 22 or 44 mm dies can achieve any desired Size Focal Plane
- albeit with a loss of 1 to 4 channels at the seam

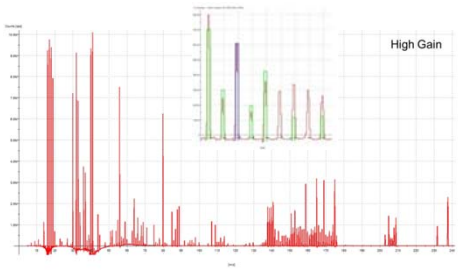


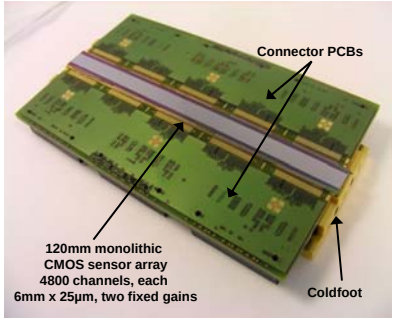
World's First Commercial CMOS Array Detector Based Isotope Ratio Instrument

SPECTRO

SPECTRO MS: Fully simultaneous Mattauch-Herzog ICP-MS

- "ION 120 Direct Charge Detector" (DCD)
  - spatially resolving direct charge detector, active pixel (CMOS)
  - 120mm sensor, 4800 channels with 6mm x 25µm, two fixed gains
  - CDS (Correlated Double Sampling), NDRO (non-destructive read-out)
  - Signal-Adaptive Integration Time: "Threshold Mode"
  - Cooling only to < -10°C required





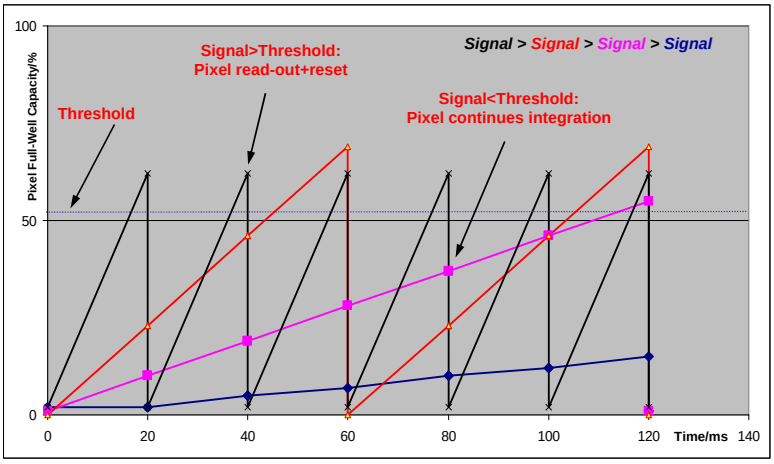
www.spectro.com

AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

DCD-Detector ION-120: CDS, NDRO and Threshold-Mode

- **Correlated Double Sampling (CDS):** lowest reset pedestal noise and FPN
- **Non-destructive Read-Out (NDRO):** signal-adaptive integration time for best SNR



www.spectro.com

AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

What is fully simultaneous ICP-MS (especially) good at?

- "usual" ICP-MS capabilities
  - multi-element method, ultra-trace detection, isotopes, ...
- complete mass spectra analysis
  - retrospective analysis, complete documentation of **each** replicate
  - reverse method development: from sample to calibration
  - fast and precise "semi-quantitative" overview analysis
- fully simultaneous measurement: elimination of ICP "flicker noise"
- precise determination of element and isotope ratios
  - no limits for the fully simultaneously measurable mass range
  - simultaneous determination of concentrations and isotope ratios
- efficient analysis of transient signals
  - hyphenated methods: laser-ablation, chromatography, ETV, ...

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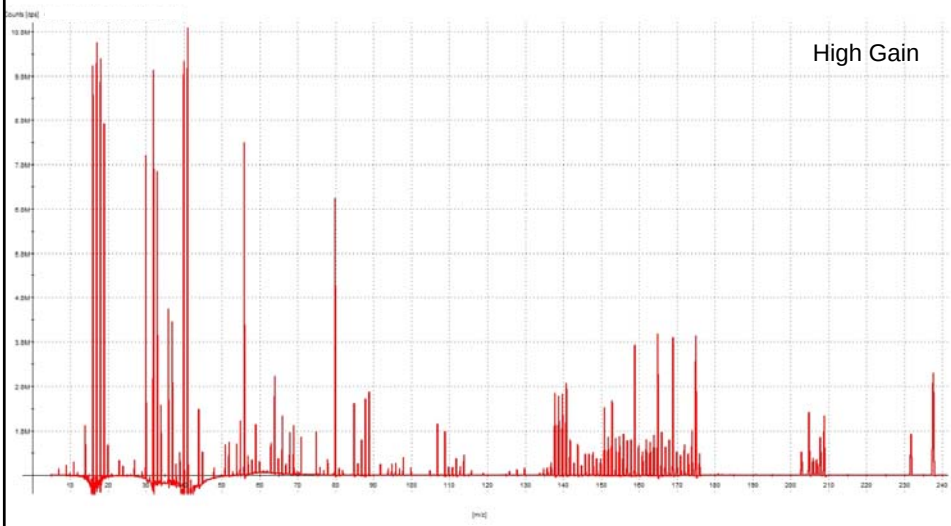
AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

Full periodic table mass spectrum (20ng/ml Merck VI+CMS-1)



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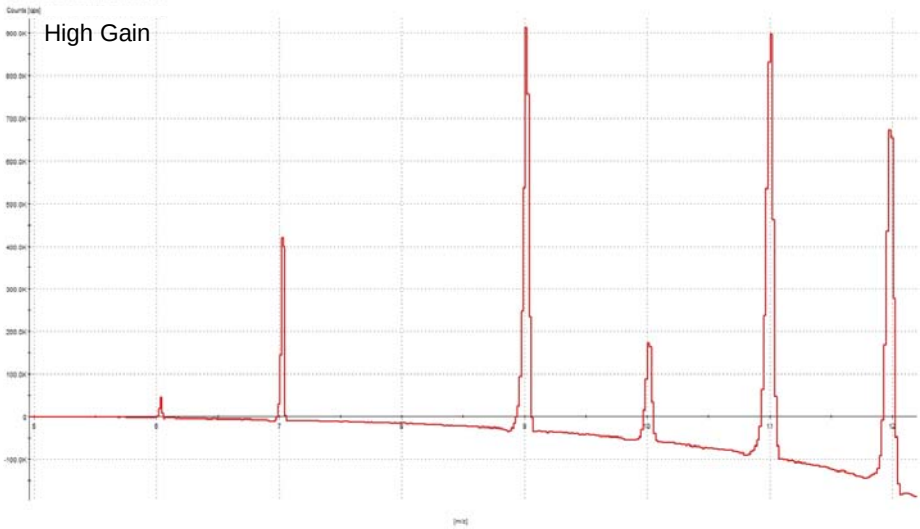
AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

Mass Range 5-12 amu: 20 ng/ml Li, 200 ng/ml Be and B



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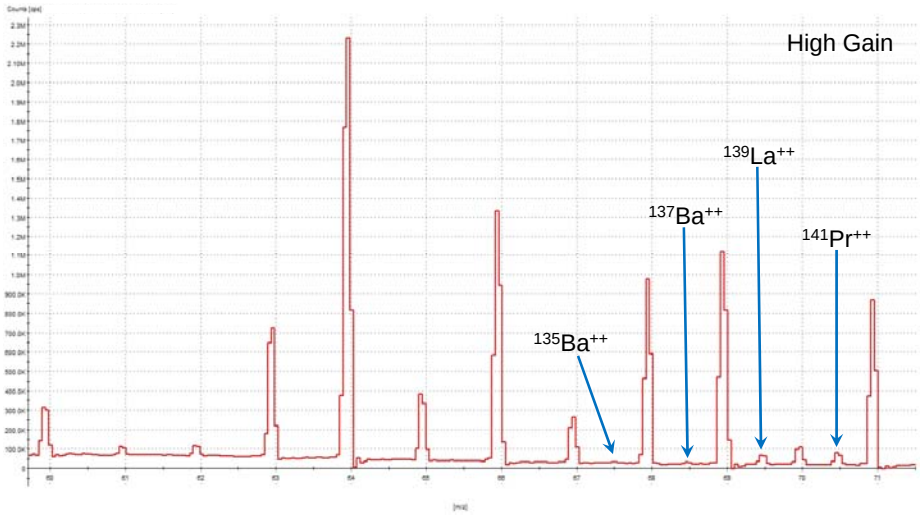
AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

Range 60-71 amu: $^{135}Ba^{++}$, $^{137}Ba^{++}$, $^{139}La^{++}$, $^{141}Pr^{++}$ resolved



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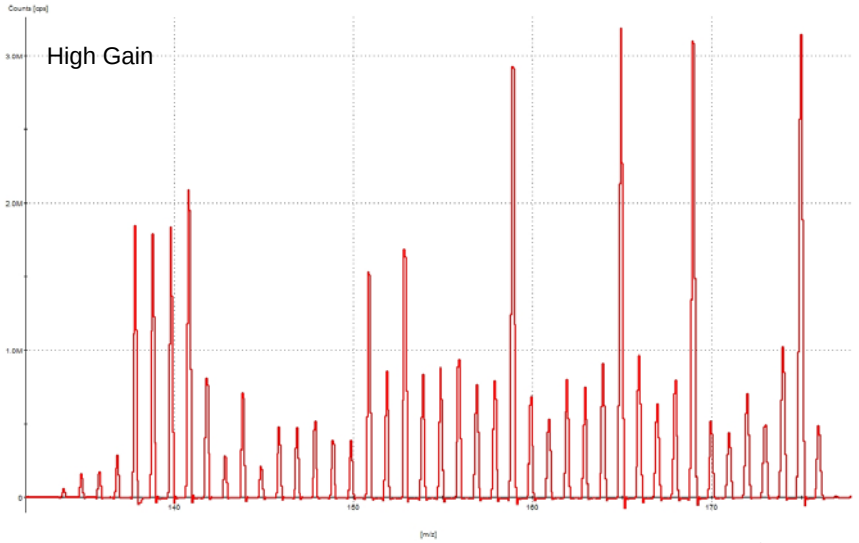
AMETEK MATERIALS ANALYSIS DIVISION

SPECTRO

Rare Earth Elements (REE) Mass Range

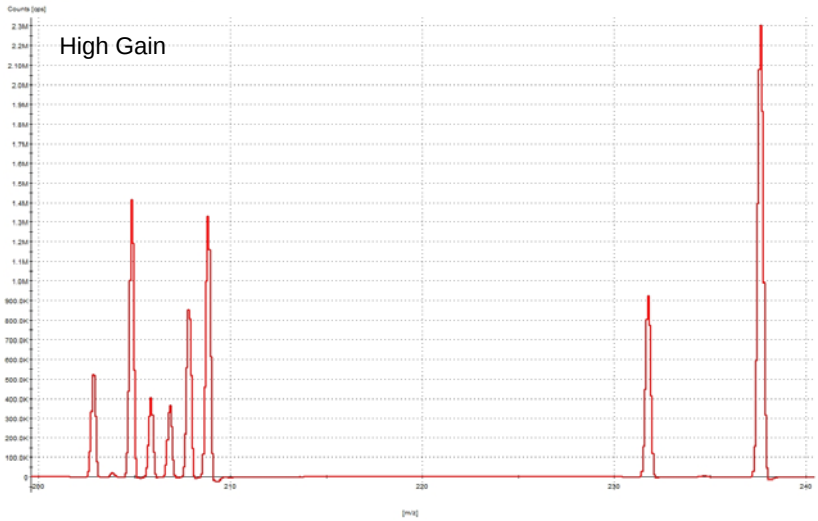


www.spectro.com

AMETEK MATERIALS ANALYSIS DIVISION

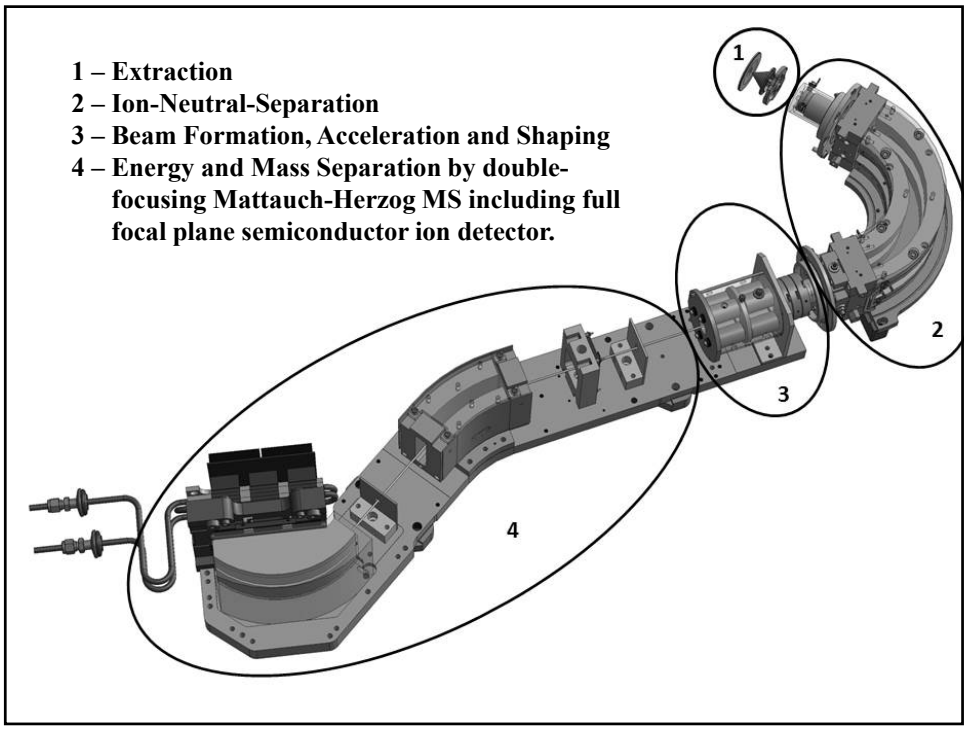
SPECTRO

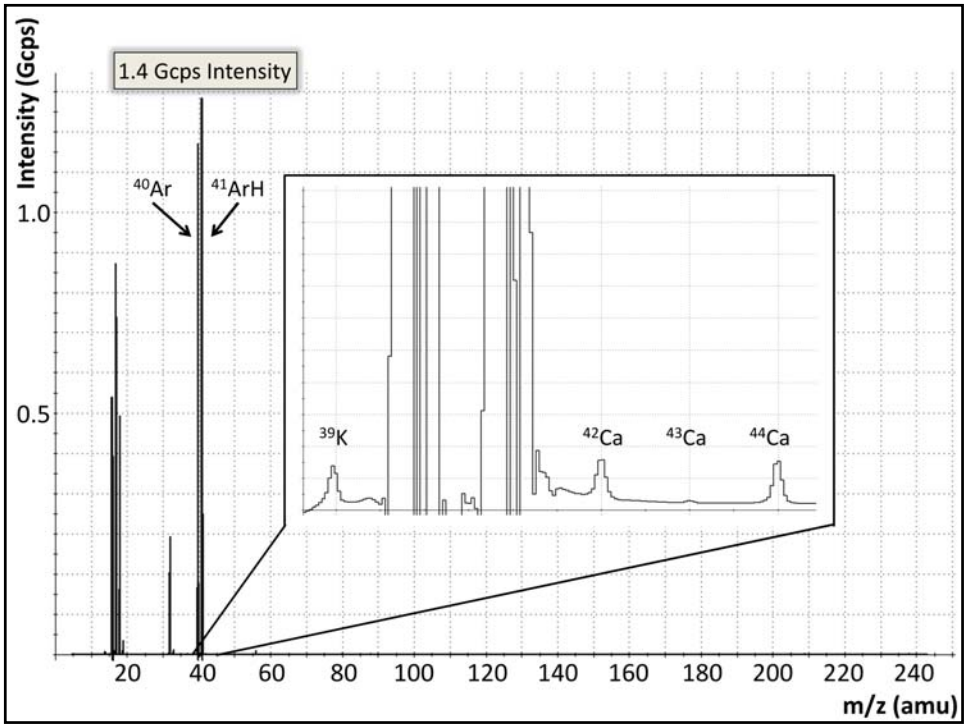
Mass Range 200-238 amu: Excellent Resolution (ca. 700)

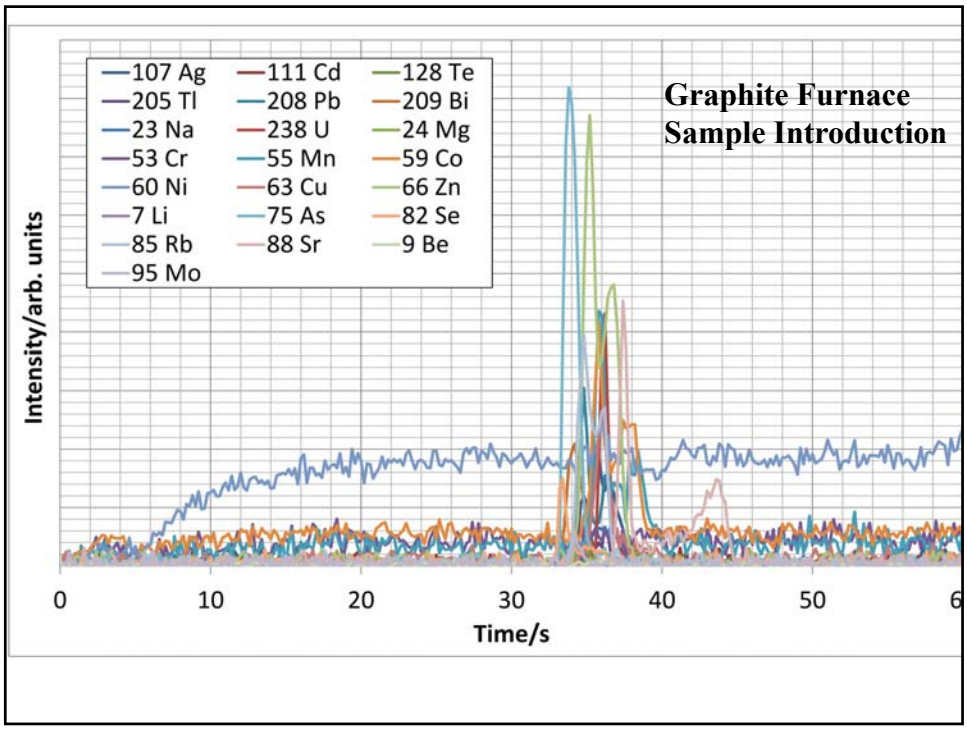


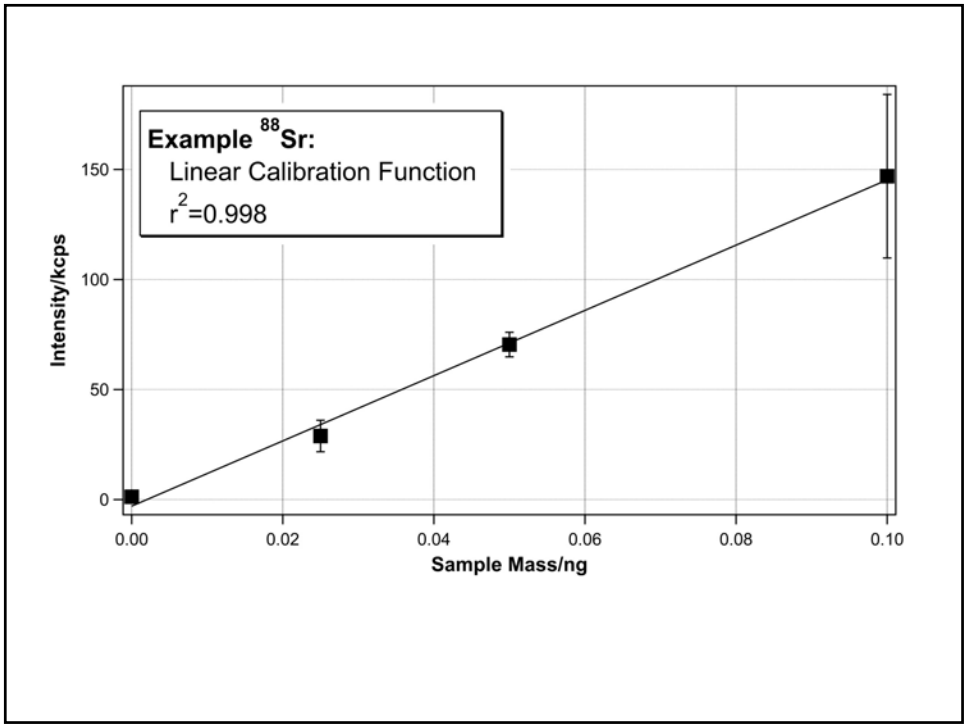
www.spectro.com

AMETEK MATERIALS ANALYSIS DIVISION


1 – Extraction
2 – Ion-Neutral-Separation
3 – Beam Formation, Acceleration and Shaping
4 – Energy and Mass Separation by double-focusing Mattauch-Herzog MS including full focal plane semiconductor ion detector.
1
2
3
4


1.4 Gcps Intensity
Intensity (Gcps)
1.0
0.5
40Ar
41ArH
39K
42Ca
43Ca
44Ca
20
40
60
80
100
120
140
160
180
200
220
240
m/z (amu)

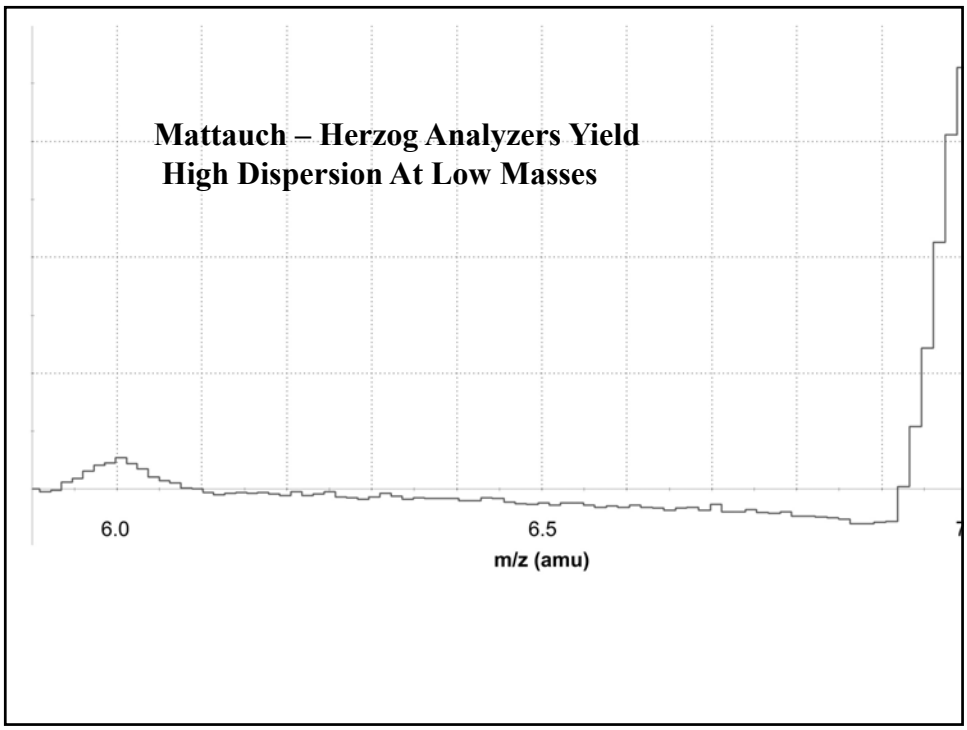

Graphite Furnace
Sample Introduction
107 Ag
111 Cd
128 Te
205 Tl
208 Pb
209 Bi
23 Na
238 U
24 Mg
53 Cr
55 Mn
59 Co
60 Ni
63 Cu
66 Zn
7 Li
75 As
82 Se
85 Rb
88 Sr
9 Be
95 Mo
Intensity/arb. units
0
10
20
30
40
50
Time/s

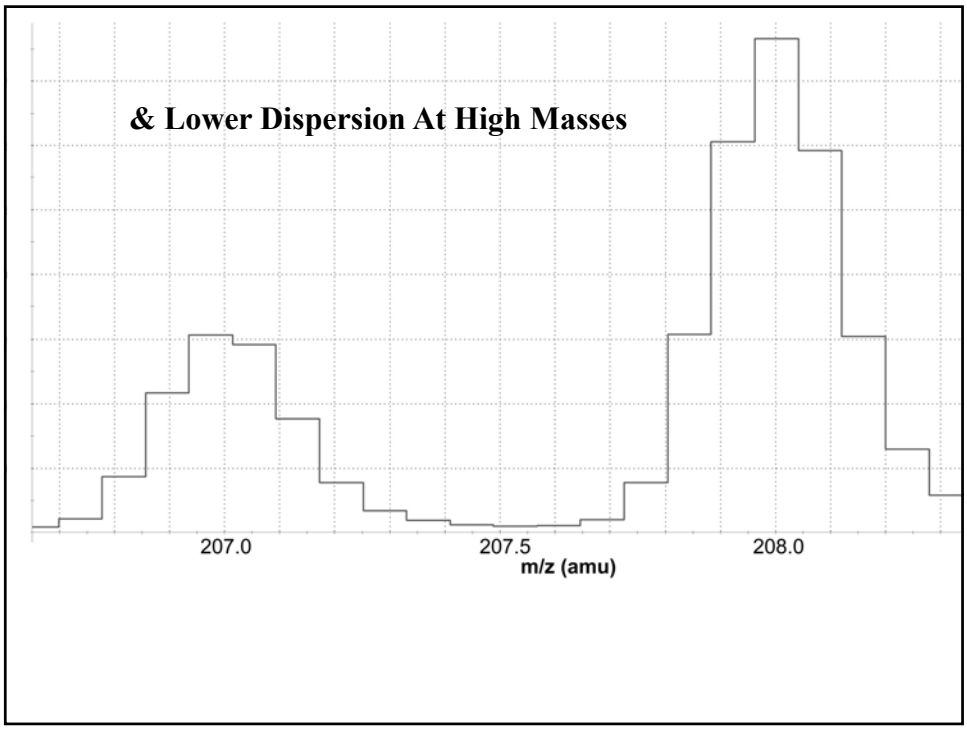

Example 88Sr:
Linear Calibration Function
r2=0.998
Intensity/kcps
0
50
100
150
0.00
0.02
0.04
0.06
0.08
0.10
Sample Mass/ng

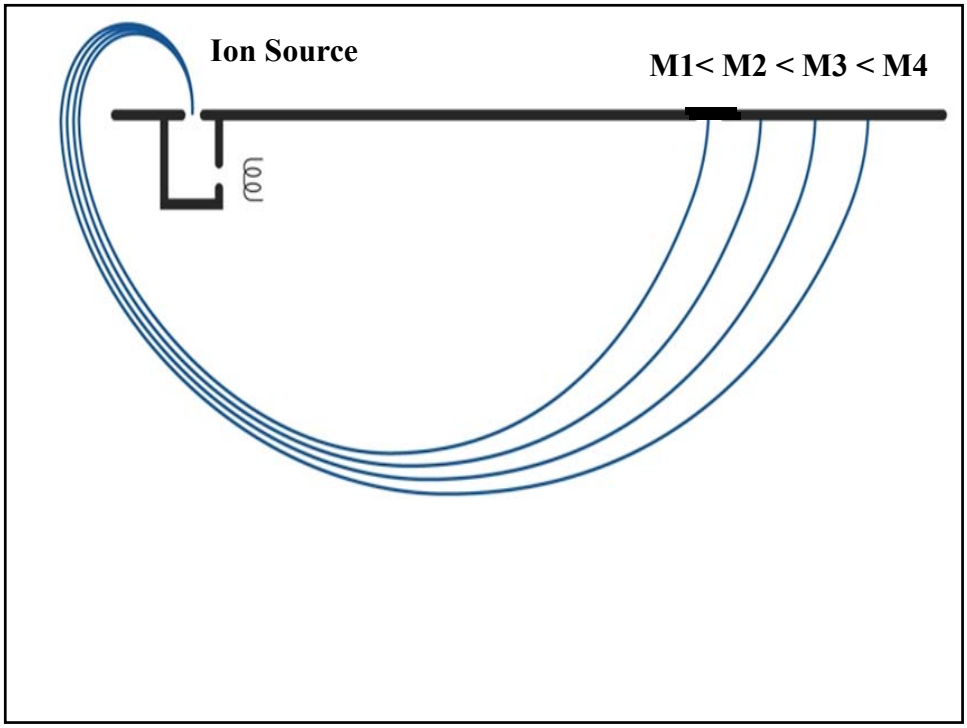
Cycloidal Analyzers

Performance Advantages:

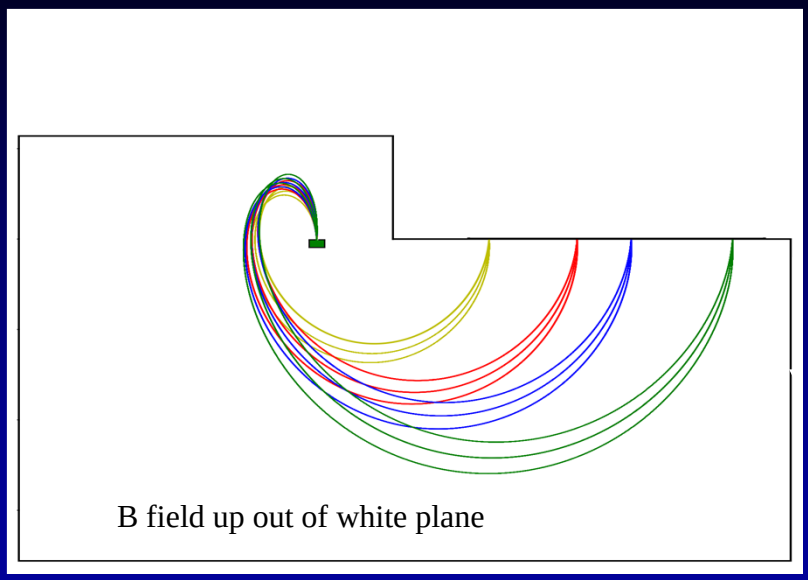
- Compact
- Linear Mass Dispersion
- Rugged. Can operate while in motion.
- Calibration stability
- High accuracy and precision.
- High abundance sensitivity.
- Double focusing.
- Low Cost.
- Low power required - only DC
- Well confined permanent magnets



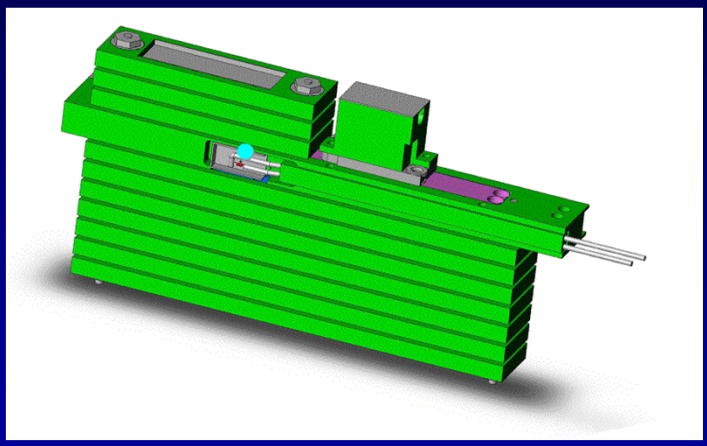

& Lower Dispersion At High Masses
207.0
207.5
208.0
m/z (amu)

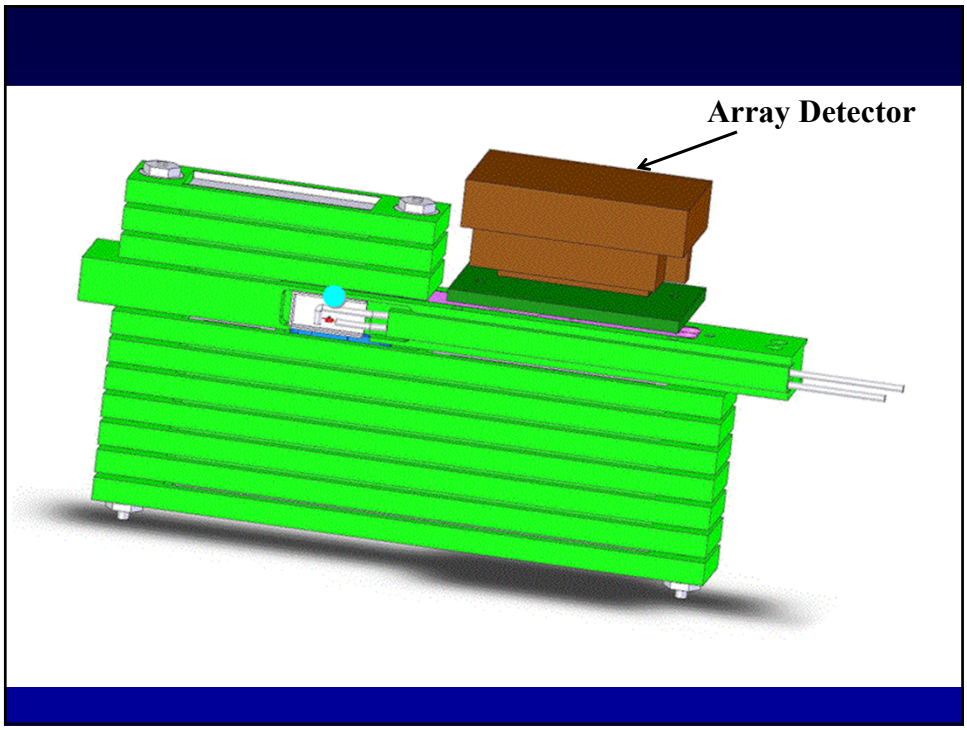

Ion Source
M1< M2 < M3 < M4

Cycloid MS Equipped with an Array



E field

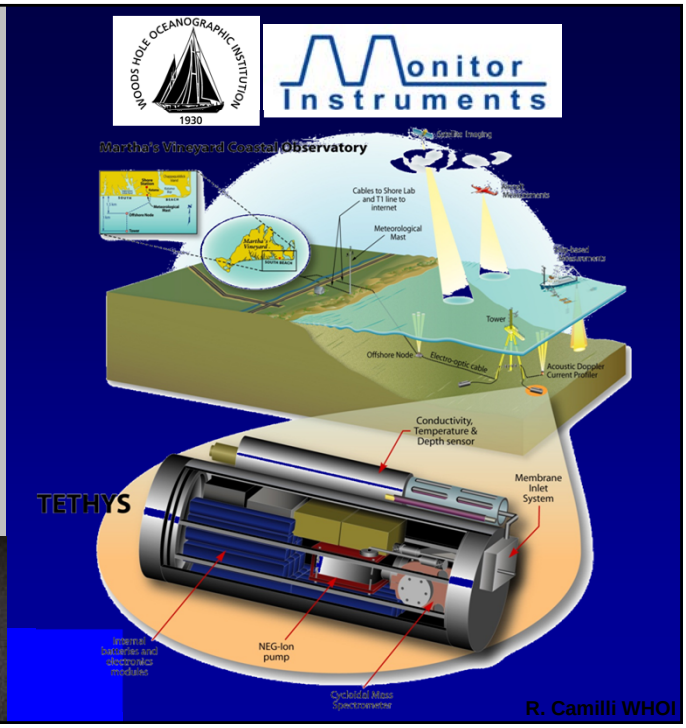


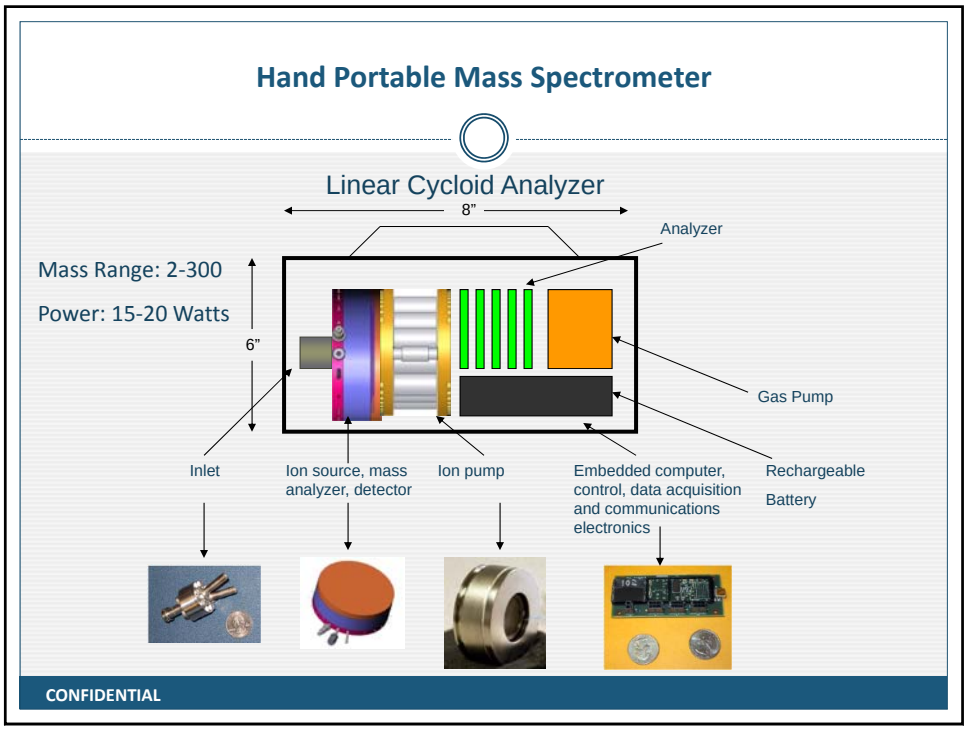


TETHYS

TETHered Yearlong Spectrometer

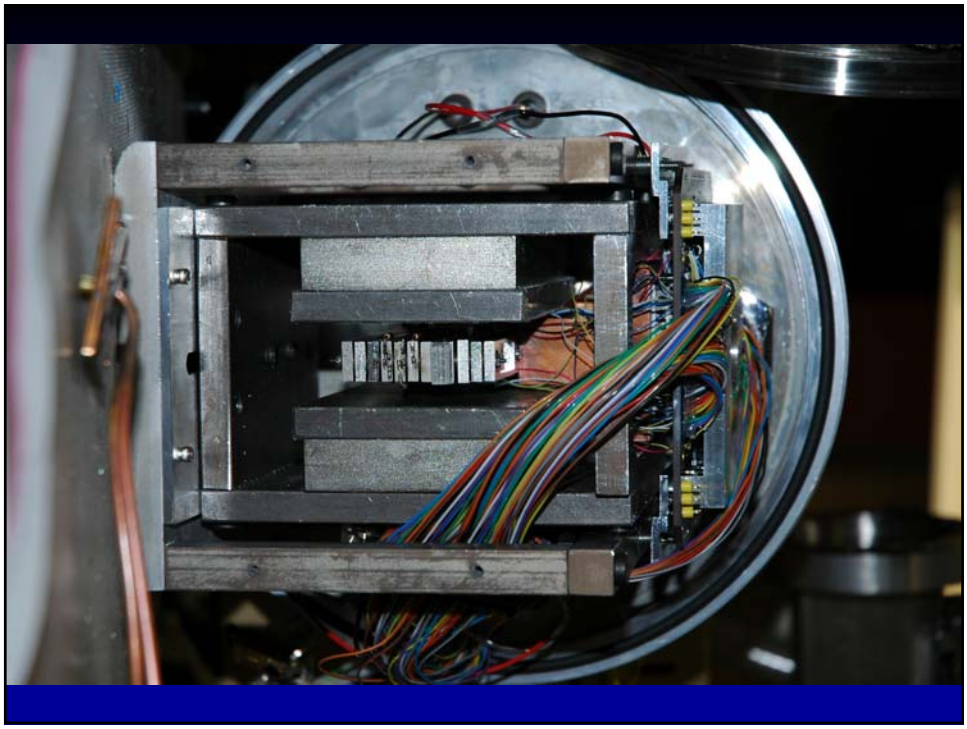
Mass range	1-200amu
Mass resolution	<0.1amu
Power	~15 W
Maximum depth	>5,000m
Endurance	~1 yr
Response time	5 sec
Sensitivity (LOD)	~1 ppb
Weight	<10kg
Displacement	<14 L
Moving parts	none

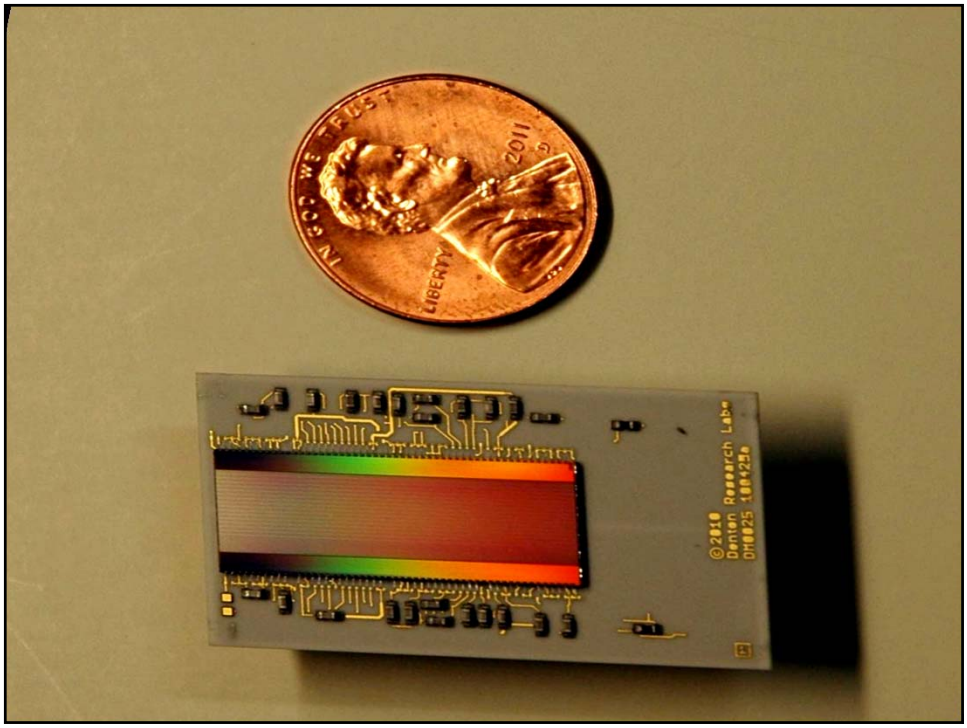




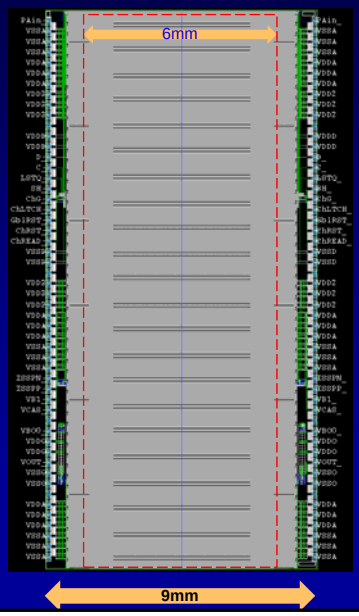
The Focal plane of a Cycloidial Mass Spec. is located down inside the magnet.

Therefore the detector must operate inside a high magnetic field. An ion multiplier will not work since electrons “cyclotron” in a magnetic field.



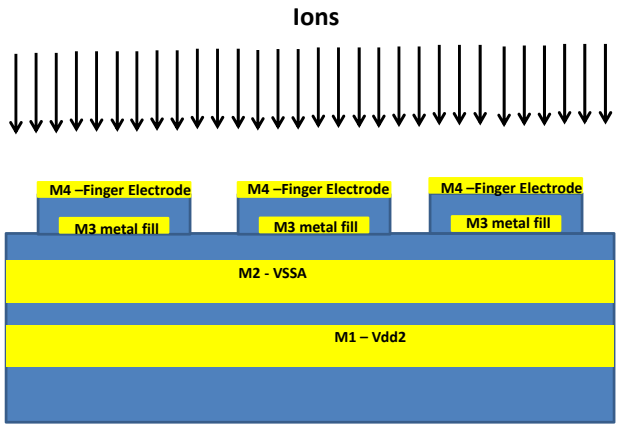

IN GOD WE TRUST
LIBERTY
2011
©2010
Damian Research Labs

1696 Pixel Generation Six Device

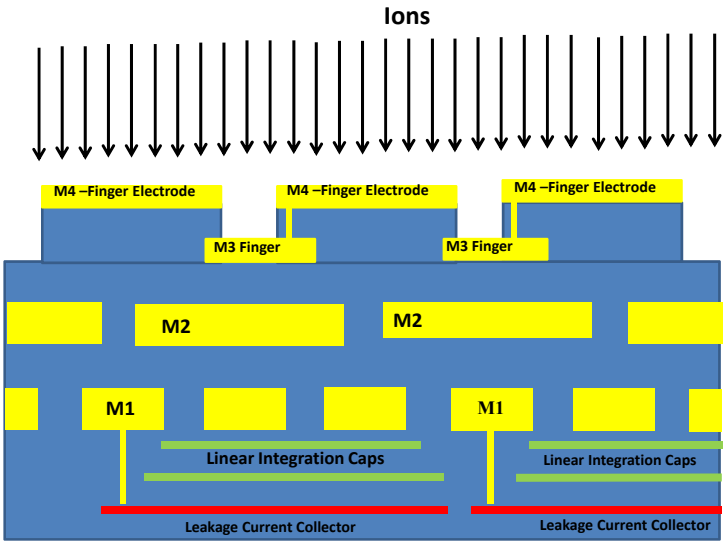


CMOS Ion Detector Technology Under Continued Development

- **Reduced Noise**
  - Redesign Gain & Reset Transistors
  - Optimize Layout
  - Add " Scarfer" Transistors
  - Improved Lower Loss Packaging
  - Input Optimized for Input to Ground Capacitance
- **Optimize Gain Levels**
  - Increase Fullwell Capacity for all Gain Ranges
  - Added Gain Ranges

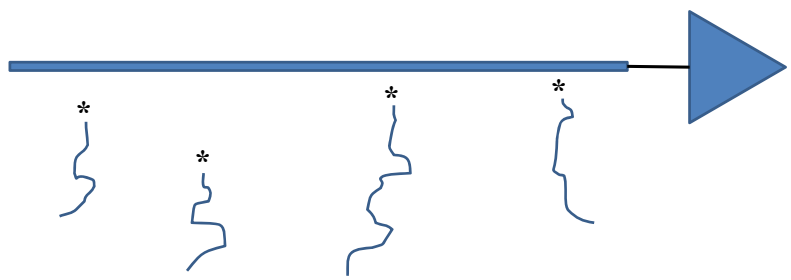


In the 1696 Generation Design 8% of ions fell in open space between finger electrodes



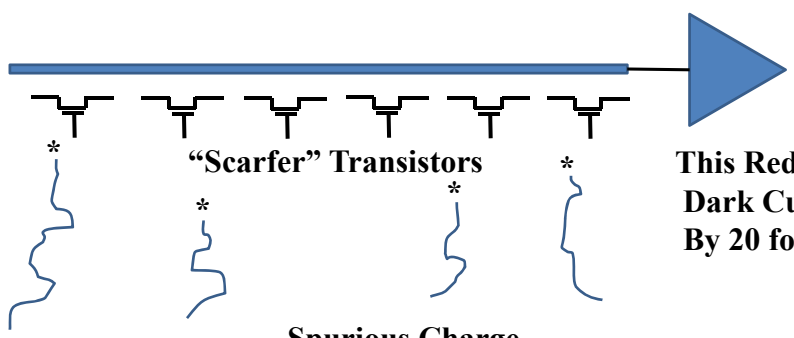
The 1704 Generation Design Achieves 100% Fill Factor
All ions fall on finger electrodes

Remember a 12 micron by 3mm electrode = 3600 microns^2



Spurious Charge

Remember a 12 micron by 3mm electrode = 3600 microns^2

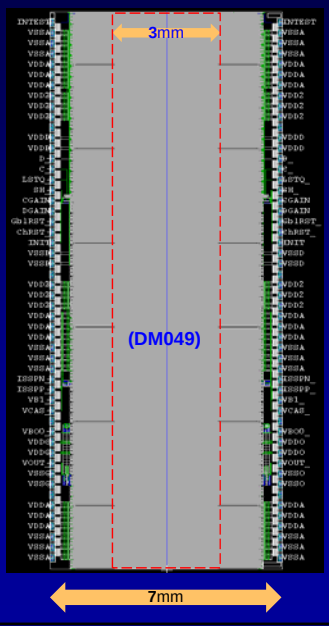


"Scarfer" Transistors

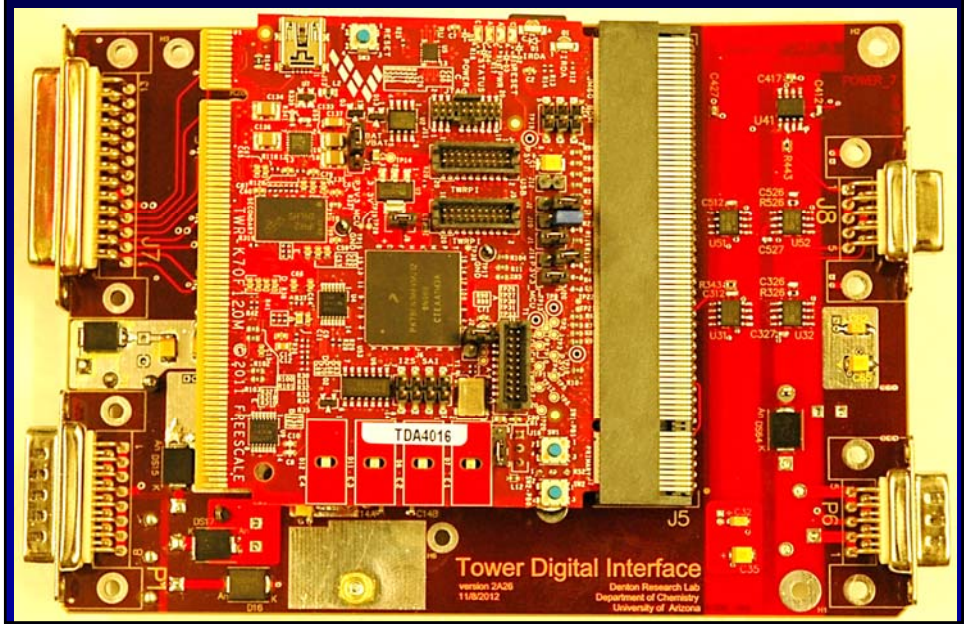
This Reduces Dark Current By 20 fold

Spurious Charge

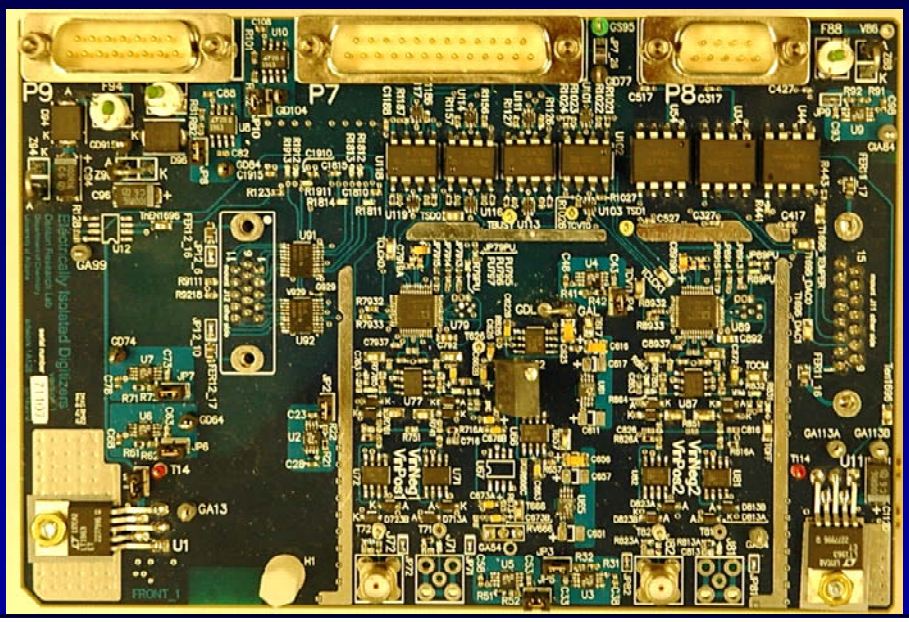
1704 Pixel Generation Device



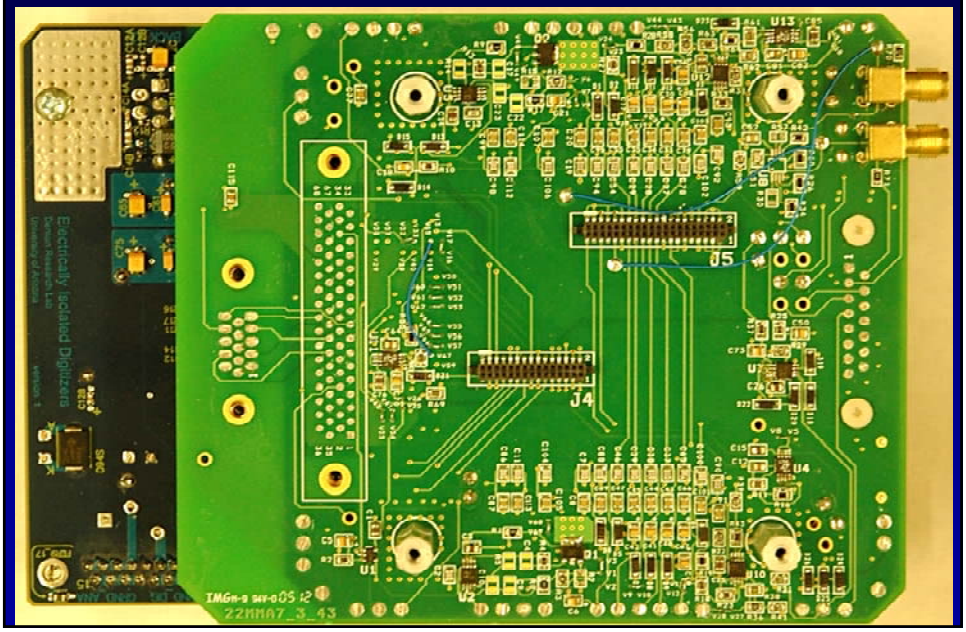
Interface Board



Isolated Digitizer



Detector Support Board



Latest Generation Ion Detectors

100% Fill Factors – All Ions Are Collected

Four Overlapping Gain Ranges

Reduced Dark Currents ≈ 20 fold

Lower Noise Amplifiers

Improved Linearity

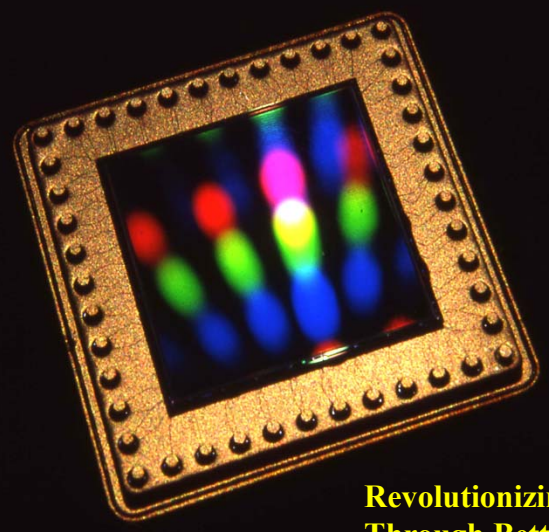
Custom Ion Detection Devices Developed by the Denton Group

- CTIA -1 A 32 channel device adapted from astronomy
- CTIA -2 (DM01) A 4 channel single ended input device – demonstrated high sensitivity - but in handheld IMS's was also highly sensitive to environmental noise
- CTIA -3 (DM03) A 128 channel wire bonded mass spec. detector
- CTIA -4 A 64 channel wire bonded mass spec. detector with novel noise reduction circuitry by ADIC
- CTIA -5 (DM04) A 4 channel differential device designed to reject environmental noise
- CTIA -6 (DM013) A 48 channel monolithic electrode mass spec. detector
- CTIA -7 (DM016) A 4 channel differential device with X1 & X100 gain levels, programmable bandwidth & advanced low noise input FETs
- CTIA -8 (DM 015) A512 channel monolithic electrode mass spec. detector
- CTIA -9 A 512 channel monolithic – fixes clocking problem on CTIA -8
- CTIA -10 A 1696 channel monolithic 12.5 micron pitch mass spec array
- CTIA – 11 A 4 channel differential with 2 to 4 fold increased sensitivity
- CTIA 12 A512 channel monolithic electrode mass spec. with low dark current – low leakage PN junctions
- CTIA 13 A1696 channel monolithic electrode mass spec. with low dark current – low leakage PN junctions
- CTIA – 14 A 4 channel differential with 2 to 4 fold increased sensitivity
- CTIA – 15 A 1704 channel monolithic 100% fill factor mass spec array "scarfer trans"
- CTIA – 16 A 9 device new gen. amplifier test device

New Ion
(& Electron) Detectors

Capable of High Sensitivity Approaching Ion Multipliers
No Gain Drift With Age
Not Damaged By Very High Ion Fluxes
Stability of Faraday Cups
Provide Simultaneous Detection Of Large Mass Ranges
Detects Both Positive & Negative Ions
No Upper Mass Limit
Not Affected By Magnetic Or Electrostatic Fields
Operate at High Pressure (no upper pressure limit)

Advanced Detector Technology



Revolutionizing Science
Through Better Detection
from The Denton Research Group

"New directions in science are launched by new tools much more often then by new concepts. The effect of a concept-driven revolution is to explain old things in new ways. The effect of a tool-driven revolution is to discover new things that have to be explained."

Freeman Dyson, Imagined Worlds
as quoted by Dudley Herschbach, Nobel Laureate in Chemistry

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

ICP-MS Short Course

Alternative Ion Sources for Trace Inorganic Mass Spectrometry

DOUGLAS C. DUCKWORTH

Pacific Northwest National Laboratory

June 18, 2014

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U.S. DEPARTMENT OF ENERGY

PNNL-SA-103259

Approximate Mass Spectrometry Publications: 1960-2013

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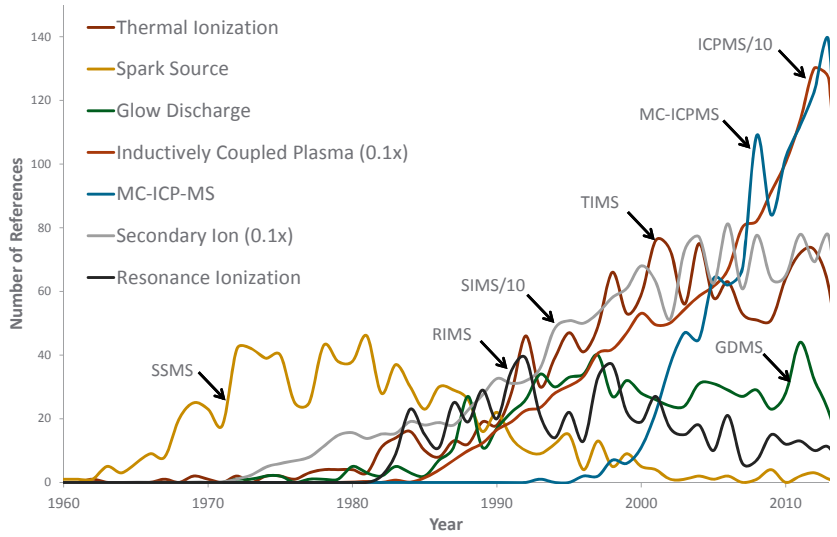

Why Alternative Ion Sources (and MS Pairings)?

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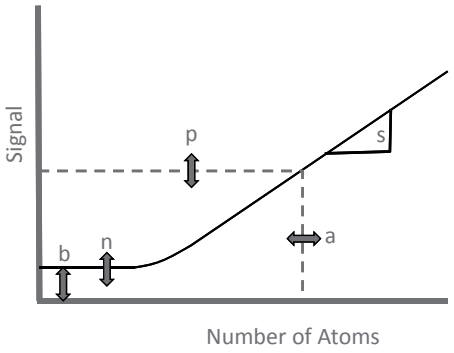
- Type of information required
  - Elemental or isotopic
  - Bulk or ultra-trace
  - Depth or lateral information
  - Oxidation state or molecular form
- Improved analytical performance
  - Sensitivity (s)
  - Signal-to-background (b)
  - Signal-to-noise (n)
  - Accuracy (a)
  - Precision (p)



What Are Your Ion Source Requirements?

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- Sample size and type
  - Solid, liquid, gas
  - Bulk, powder, or particulate
  - Electrically conductive or insulating
- Concept of operation
  - Sample preparation requirement
  - Clean room requirement
  - Field deployment (size, weight, and power)
  - Acceptable performance trades

Your Ion Source Selection Influences Your Mass Spectrometry System

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- Ion source selection has implications for mass separation and analysis
- Ion source characteristics:
  - Ion kinetic energy and energy distribution influences mass resolution
    - Requires energy focusing (kinetic and collisional focusing)
  - Source pressure influences ion extraction efficiency and abundance sensitivity
    - Requires proper vacuum interface and vacuum system design considerations
  - Ion source stability influences measurement precision
    - Requires simultaneous collection systems and analysis methods
  - Relative absolute or temporal elemental ion formation influences calibration
    - Requires appropriate calibrations (matrix matched standards)
    - Or, discrete atomization/ionization steps
    - Pulsed/transient signals require gated simultaneous collection of source ions
  - Ion source chemical backgrounds will influence mass resolution requirements (and sample preparation)

5

Your Ion Source Selection Influences Your Mass Spectrometry System (contd.)

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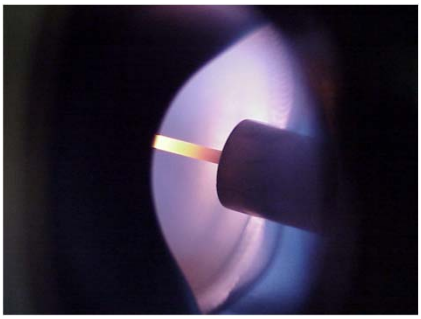
Ion source development requires understanding the chemistry and physics of ion formation its impact on ion separation and ion detection.



rf-powered cavity ion source

6

Inorganic Ion Source Descriptions

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Atomization Process	Integrated Evaporation/Atomization and Ionization	Discrete Evaporation/Atomization and Ionization	Ionization Process
Ion Sputtering	Secondary Ion MS (SIMS)	Sputtered Neutral MS (SNMS)	Electron Impact
			Ion sputtering
		Glow Discharge MS (GDMS)	Argon Plasma
Photons	Laser Ionization MS (LIMS)		Laser Plasma
		Laser Ablation - ICPMS (LA-ICPMS)	Argon Plasma
Electrons	Inductively Coupled Plasma MS (ICPMS)		
	Spark Source MS (SSMS)		Spark Plasma
Hot Filament		Resonance Ionization MS (RIMS)	Resonant Photons
	Thermal Ionization (TIMS)	Thermal Ionization (TIMS)	Hot Filament

7

Thermal Ionization Mass Spectrometry

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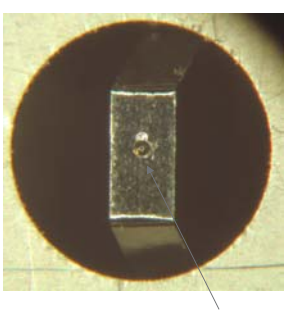
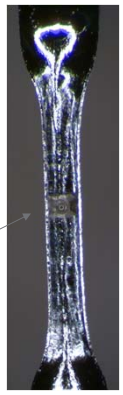
Single Filament

Volatilization and ionization occur simultaneously.





resin bead

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

8

The Efficiency of Thermal Ionization Generally Follows the Saha-Langmuir Equation

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$$\frac{N_+}{N_0} = \exp\left[\frac{(W - I)}{kT}\right]$$

- W is the work function of the filament, filament + matrix or matrix (usually in eV)
- I is the ionization potential of the element being analyzed (also in eV)
- K is the Boltzman constant (approx. 8.62×10^{-5} eV/ K)
- T is the temperature in K
- N_0 is the number of un-ionized atoms of the element of interest in the vapor phase above the filament
- N_+ is the number of singly charged ions of the element in the vapor phase above the filament

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

9

Double and Triple Filaments

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- Separates the process of volatilization from ionization
- Side filament(s) is run at a temperature low enough to provide useful volatilization, while the center filament is run at high temperature to generate ions. This is useful for elements with high ionization potentials where the high temperature needed for efficient ionization would result in high volatilization rates

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

10

Triple Filament

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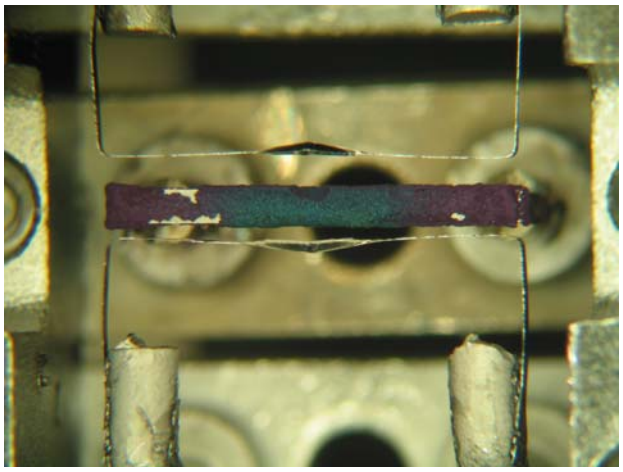

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

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Advantages of Thermal Ionization

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- Many filaments can be prepared and placed in the mass spectrometer at one time
- Nearly all elements that can be put in solid form can be analyzed
- Very high efficiency for some elements
- All of the sample is subject to ionization
- Ions are very mono-energetic
- Mass spectrometer (MS) can be operated at high vacuum
- Accelerating voltage can be high

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

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Disadvantages of Thermal Ionization

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- Some elements have very low efficiencies
- Mass-dependent evaporation (fractionation)
- Sample dissipates as it is analyzed
- Samples can behave erratically because of
  - impurities (which affect ionization efficiency)
  - sample changes during analysis, and
  - the quality of loading
- Filament geometry affects beam intensity (source geometry changes between samples)
- Source must be vented to change samples

Tony Appelhans,"Ionization Methods" in *2013 Mass Spectrometry Workshop, Thermal Ionization Mass Spectrometry (TIMS)*, May 1-2, 2013.

13

Spark Source Mass Spectrometry

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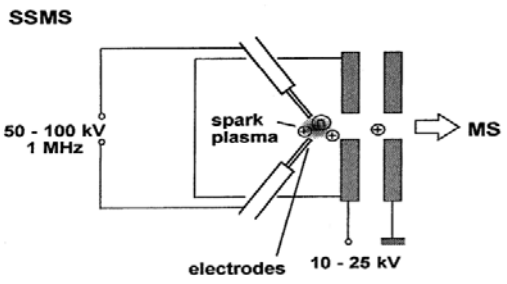
- Atomization
  - Spark Plasma
- Ionization
  - Electrons
- Sample types
  - Solids & Solution Residues



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Spark Ion Source (AEI MS 702; 1970-71)

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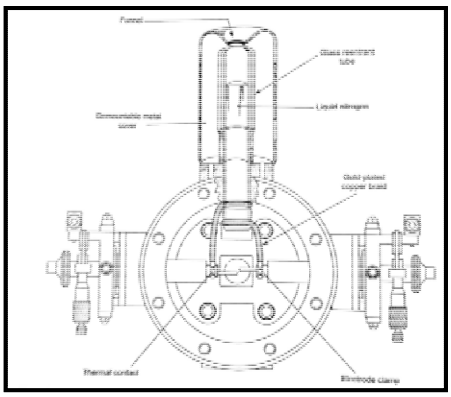
- Two conducting pins
- rf-power supply
  - 10 – 20,000 Hz
  - ≤ 30,000 V
- High vacuum (10^{-6} – 10^{-7} torr)



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15

Spark Source Mass Spectrometer (SSMS)

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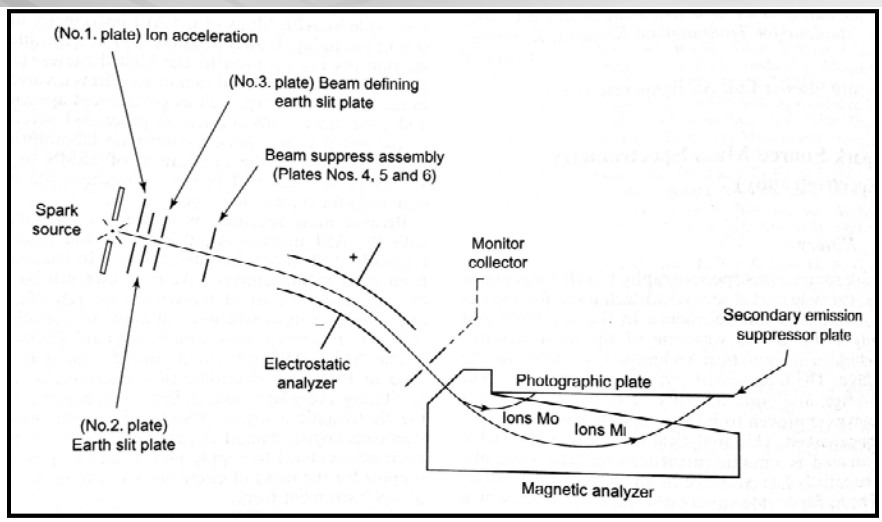

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Photoplate Detection

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1978 SSMS Photoplates

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SSMS Spectra: Stainless Steel (AEI MS702)

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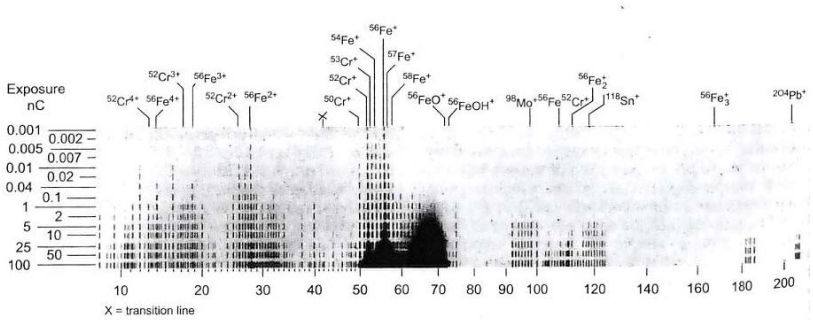

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SSMS Advantages

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- High sensitivity
- Comprehensive element/isotope coverage
- Linear response across elements
- Broad application across sample types
  - Solids and liquid residue (no dissolution)
  - Major and trace concentrations
- Rapid analysis (1-2 hours per sample)
- Simple spectrum relative to SS atomic emission

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SSMS Disadvantages

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- Erratic nature of the spark
  - Complicated scanning
  - Required integrating detectors (photoplates)
- Photoplate detection
  - An art practice by a killed technician
    - Photoplate preparation/development a in dark room
    - Focusing the instrument on the photoplate
    - Reading photoplates (simplified by use of densitometers)
  - Availability of quality photoplates (later years)
- Vacuum tube maintenance (1960-1970s)

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Glow Discharge Mass Spectrometry (GDMS)

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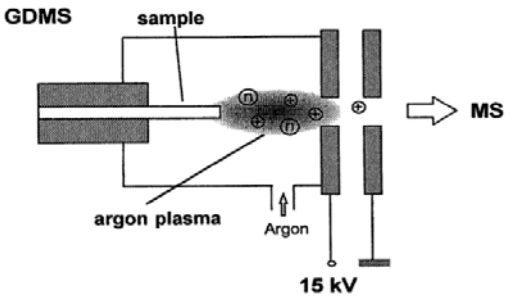
- Atomization:
  - Ar^+ sputtering
- Ionization:
  - Ar plasma
- Sample types:
  - Solids
    - Conducting samples
    - Insulators
  - Solution residues
  - Thin films
  - Vapor detection



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Glow Discharge: a Simple, Diode Discharge Geometry

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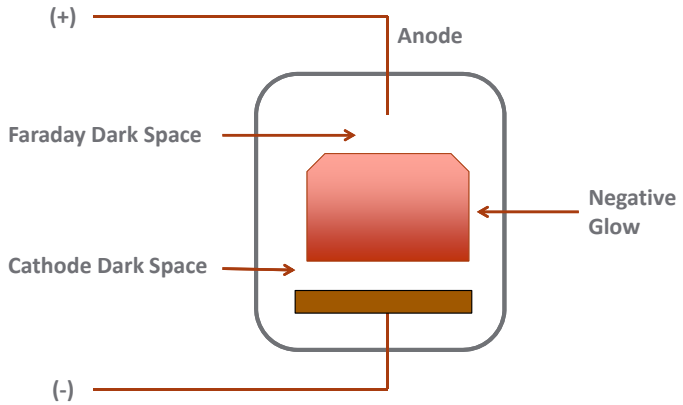

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Schematic of the Grimm-type Glow Discharge

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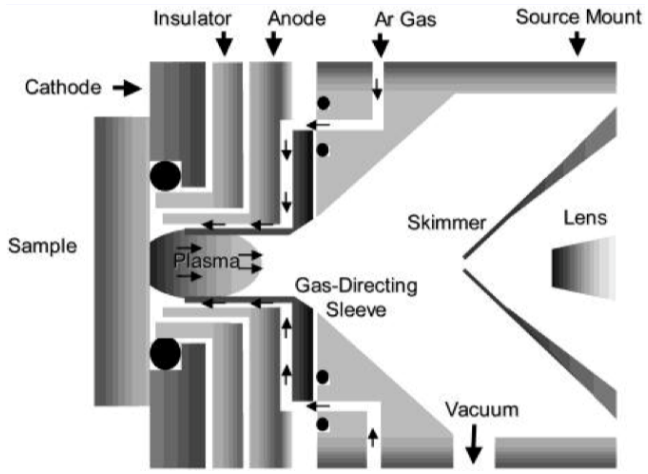

Reprinted with permission from Eric Oxley, Chenglong Yang, Jian Liu, and W. W. Harrison, 2003, "Ion Transport Diagnostics in a Microsecond Pulsed Grimm-Type Glow Discharge Time-of-Flight Mass Spectrometer," Analytical Chemistry, 75:6478-6484 , Copyright 2003, American Chemical Society.

23

Sector Field GDMS with Glove Box Enclosure

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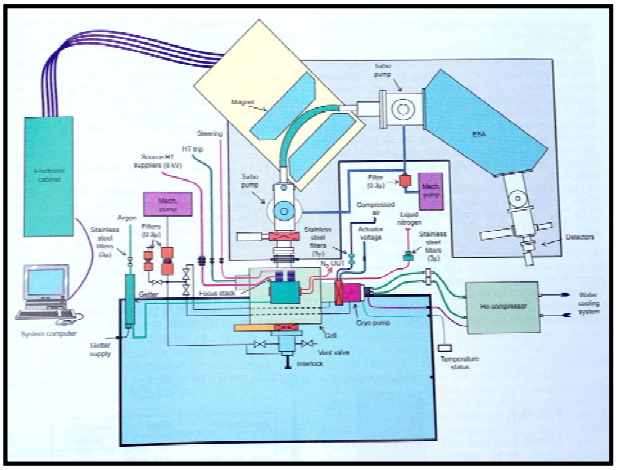

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Glow Discharge Processes

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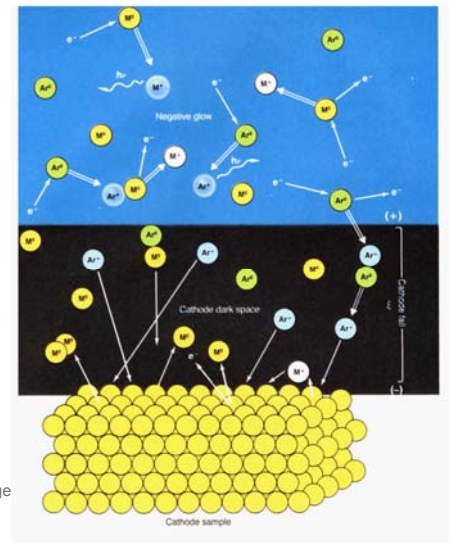
- Ar discharge
  (1 torr, 1 kV, 1-3 mA)
- Atomization via Ar^+ sputter ejection
- Principle ionization mechanism is through collisions with long-lived argon metastable atoms:
  $Ar^m + X \rightarrow Ar + X^+ + e^-$



Reprinted with permission from W. W. Harrison, K.R. Hess, R.K. Marcus, and F.L. King. 1986. "Glow Discharge Mass Spectrometry, *Analytical Chemistry*, 58(2):341A-356A, Copyright 2003, American Chemical Society.

Quantification in GDMS

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- Relative ion yields tend to be uniform across elements and matrices
- Three levels of quantification
  - "Standardless," factor of 3x: based on uniform relative elemental sensitivities

    $C_a = I_a (C_{ref}/I_{ref})$
  - Semi-quantitative: based on the use of pre-defined RSFs

    $RSF = (I_a/C_a) / (I_{ref}/C_{ref})$

    $C_a = (1/RSF)\ I_a (C_{ref}/I_{ref})$
  - Quantitative: using external standards
    - Direct comparison of signal intensities with a matrix matched standard
    - Use of calibration curves form a series of matrix matched standards

Comparison of GDMS and LA-ICP-MS

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Detection limits for trace elements in high-purity platinum (NIST SRM 681)

Element	Detection limit (µg g^{-1})	
	LA-ICP-MS	GDMS
Co	0.05	n.d.
Cu	0.04	0.009
Zr	0.01	n.d.
Rh	0.003	0.006
Ag	0.002	0.01
Pd	0.003	0.005
Hf	0.006	n.d.
Ir	0.001	0.03
Pb	0.003	1
U	0.003	n.d.
R.S.D. (%)	5	5-10
Accuracy (%)	<8	<15
Analysis time (h)	≈1	≈2
n.d. Not determined		

J.S. Becker, H.-J. Dietze. 2003. "State of the art in inorganic mass spectrometry for analysis of high-purity materials." *International Journal of Mass Spectrometry*, 228:127–150.

27

GDMS Depth Profiles (0.2µm CrN/0.75µm TiN/st-3)

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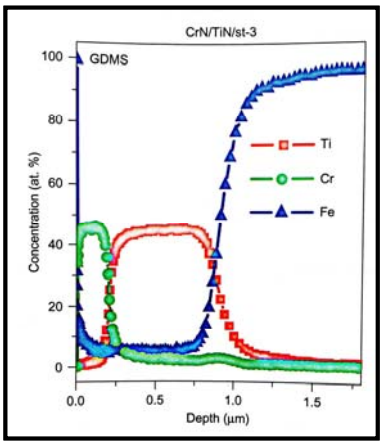
- Performance characteristics:[1]
  - Limit of detection: 0.01-10 ppm
  - Minimum detectable number of atoms: 10^{11} – 10^{14} atoms/cm^2
  - Minimum depth information: 1 nm
  - Sputter rate 0.1 – 10 nm/s
  - Precision 1%–5%

[1] A.Bengston. 1994. "Quantitative depth profile analysis by glow discharge," *Spectrochimica Acta* 49(4):411-429.



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Pulsed Glow Discharge Operation

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- Motivation High instantaneous power
  - High signal intensity
  - Additional sputtering control
  - Improved temporal profile resolution
  - Improve sample utililzation efficiency
- Mass analyzers for pulsed-GDMS
  - Quadrupole and sector with gated detection
  - Ion traps
  - Time-of-flight

Power Characteristic	dc Glow Discharge	µS, Pulsed Discharge
Voltage	800 V	3 kV
Current	3 mA	400 mA
Power	2.4 W	1.2 kW

W.W Harrison, W. Hang, K. Ingeneri, and C. Schilling. 1997. "Temporal Considerations with a Microsecond Pulsed Glow Discharge." *Journal of Analytical Atomic Spectrometry,* 12:891-896.

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Example µS-Pulsed GDMS

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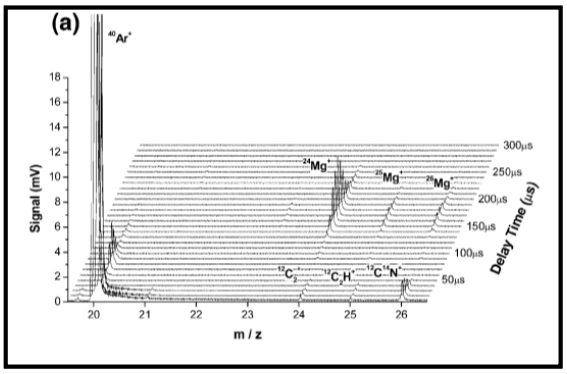

- The temporal resolution Mg (380 µg/g) in cast iron from polyatomic chemical interferences (400 Hz, 20 µS pulse, 2kV, 2.8 torr Ar)
- Ar^+ is present only in initial pulse period

Reprinted with permission from Eric Oxley, Chenglong Yang, Jian Liu, and W. W. Harrison, 2003, "Ion Transport Diagnostics in a Microsecond Pulsed Grimm-Type Glow Discharge Time-of-Flight Mass Spectrometer," Analytical Chemistry, 75:6478-6484 , Copyright 2003, American Chemical Society.

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Millisecond Pulsed GDMS for both Elemental and Molecular Information

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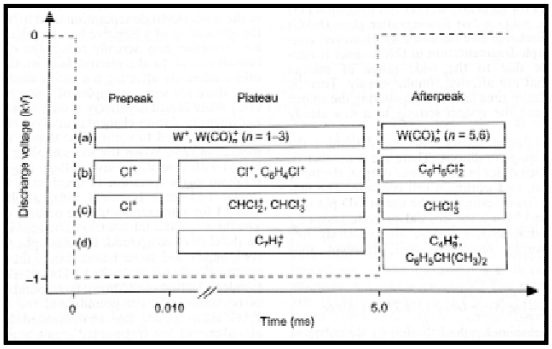

- Gated detection over the pre-peak, plateau, or after-peak regions allows the selection of elemental or molecular information
  a. Tungsten hexacarbonyl, $W(CO)_6$
  b. Dichlorobenzene, $C_6H_4Cl_2$
  c. Chloroform, $CHCl_3$
  d. t-butylbenzene, $C_6H_5C(CH_3)_3$

Reproduced with permission of Elsevier Science and Technology. Diane Beauchemin and Dwight E Matthews, eds. 2010. *Encyclopedia of Mass Spectrometry*, Volume 5., p.305, Elsevier, Amsterdam
See also J.A. Klingler, C.M. Barshick, W.W. Harrison, Anal. Chem. 1991, *63*, 2571.

31

The "Nonconducting" Barrier

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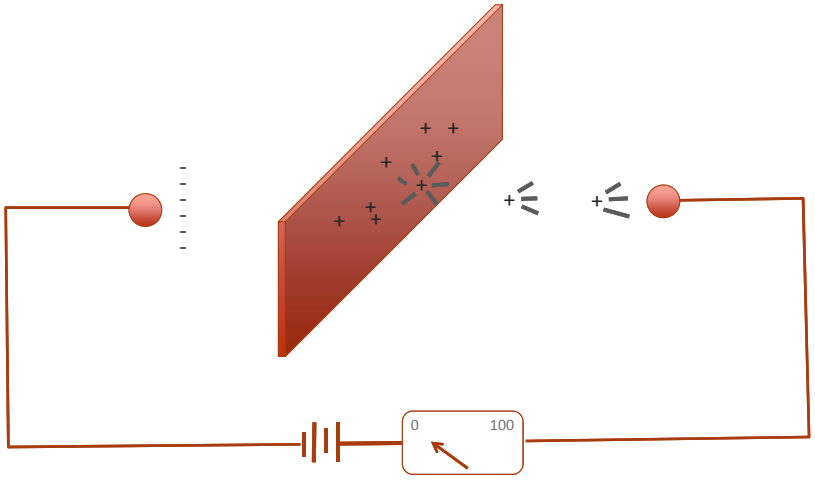

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Sample Preparation for Electrically Nonconductive Samples

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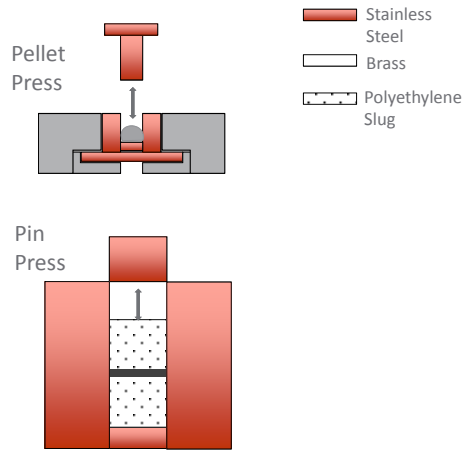
- Make the sample matrix conductive with high purity cathode material
  - Compaction with conducting powder
  - Impaction onto metal surface
    - Indium, silver
  - Sacrificial cathode
- Radio frequency operation to induce a dc bias potential



Die press for powder samples

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Secondary Cathode to Analyze GDMS

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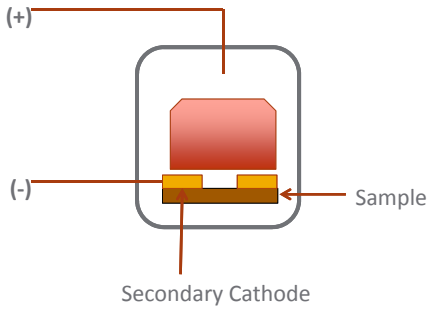

- Secondary cathode lays down a sputtered coating
- Allows direct analysis of non-conducting materials
- Detection limits for NBS Glass ranges from 0.0003 ppm for U to 30 ppm for 1st row transition elements
- Limitation: interferences for cathode material and related polyatomic ions

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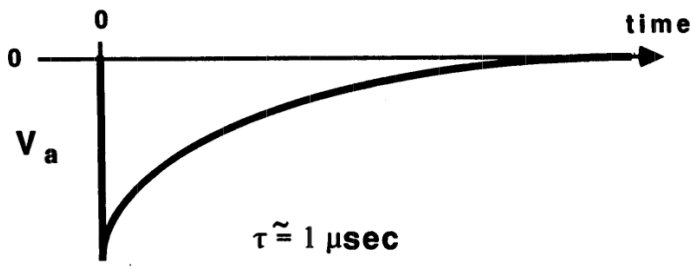
Capacitor-like Response of an Insulating Surface



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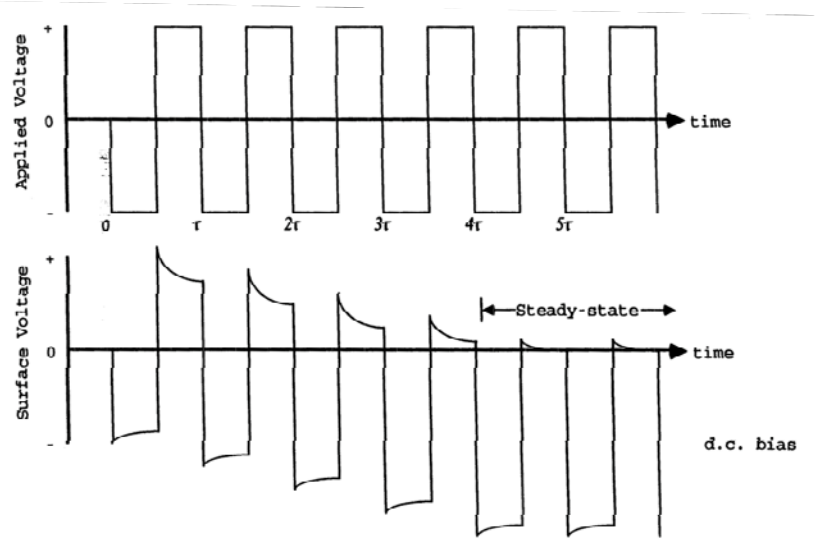
Establishment of an RF Glow Discharge



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RF Glow Discharge Mass Spectrometer with Reverse Nier-Johnson Geometry

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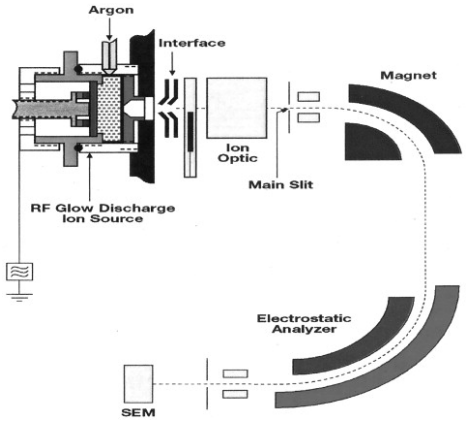

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Detection Limits for RF-GDMS of Glass

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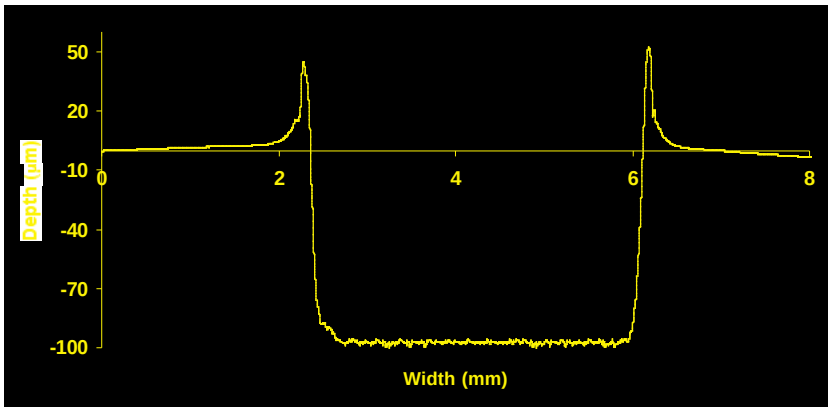
Element	Limit of Detection (ng/g)
Cu	81
Ga	33
Sr	6
Ru	39
Sb	1
Au	6
Pb	280
Th	1
U	3

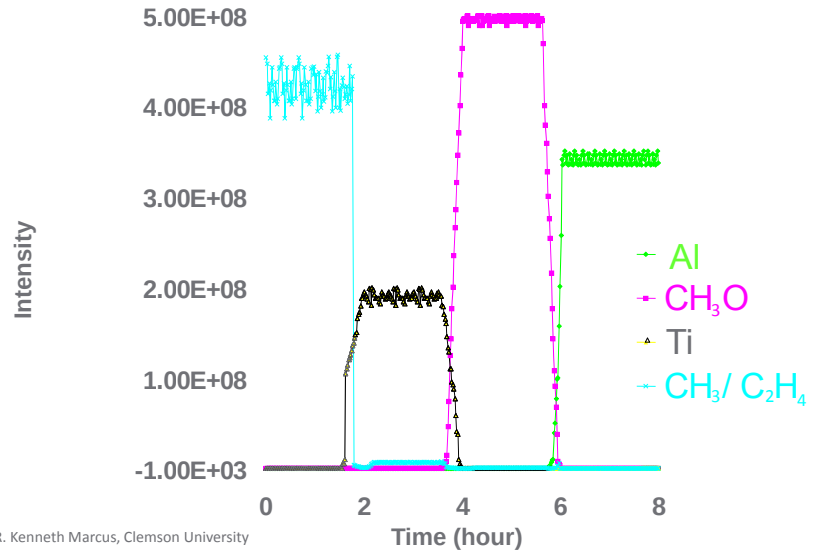
Adapted from C.R. Schick and R. K. Marcus. 1996. "Optimization of Discharge Parameters for a Flat-Type Radio-Frequency Glow Discharge Source Coupled to a Quadrupole Mass Spectrometer System. *Applied Spectroscopy*, 50(4) 445-466.

Crater Profile of Automotive Coating



Dr. R. Kenneth Marcus, Clemson University | 39

RF-GDMS Temporal Profile of Automotive Paint Panel (50W, 0.13 mbar, 6 mm anode)



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Atmospheric Sampling Glow Discharge Quadrupole Ion Trap Mass Spectrometry

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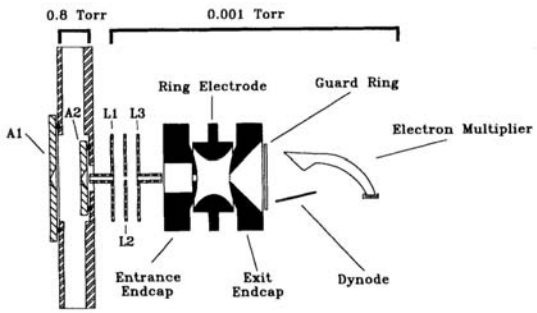

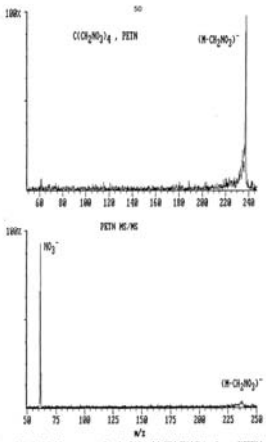

Figure 17. MS/MS spectra of m/z 240, $(M-CH_2ONO_2)_-$ from PETN (top) spectrum of isolated parent ion (bottom) spectrum after resonance

- ASGDI is powerful analytical tool for explosives vapor detection equipment.
  - low to sub- picogram detection limits
  - High efficiency MS/MS provides compound identification

S. A. McLuckey, D. E. Goeringer, K.G Asano, K.J. Hart, G. L. Glish, B.C. Grant, and D.M Chambers. 1993. *Atmospheric Sampling Glow Discharge Ionization and Triple Quadrupole Tandem Mass Spectrometry for Explosives Vapor Detection*. ORNL/TM-12434, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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Miniature Liquid Sampling Atmospheric Pressure Glow Discharge

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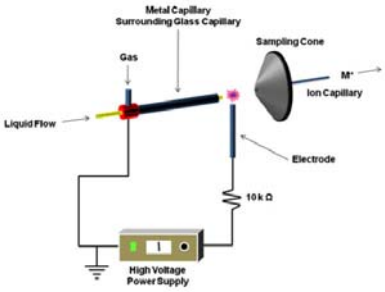

Fig. 1 Diagrammatic representation of the of the liquid sampling–atmospheric glow discharge (LS-APGD) source coupled to the Exactive Orbitrap mass analyzer

Table 1 Elemental response function characteristics

Element	LOD (μg mL^{-1}, 5 μL)	R^2	$y = mx + b$
^{56}Fe	0.67	0.9521	y=6,295.5x+7,116.3
^{58}Ni	1.0	0.9844	y=10,528x+14,751
^{63}Cu	2.2	0.9915	y=2,522.8x+18,756
^{115}In	0.04	0.9931	y=6,161.5x+1,031.4
^{114}Cd	0.60	0.9923	y=5,998.6x+1,003.2
^{133}Cs	0.05	0.9981	y=29,2274x+33,162
^{208}Pb	0.02	0.9862	y=5,076.9x+1,306.1

1 μg mL^{-1} in 5 μL equates to 5 ng absolute mass

Reprinted with permission from Springer. CD Quarles Jr., AJ Carado, CJ Barinaga, DW Koppenaal and RK Marcus. 2012. "Liquid sampling-atmospheric pressure glow discharge (LS-APGD) ionization source for elemental mass spectrometry: preliminary parametric evaluation and figures of merit." *Analytical and Bioanalytical Chemistry*, 402:261–268 .

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Recent Work - New LS-APGD Designs

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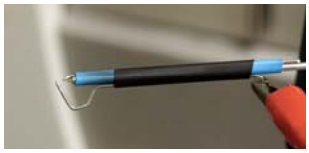
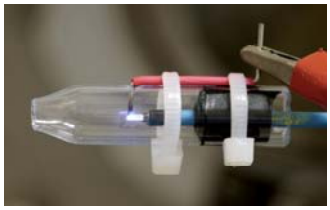
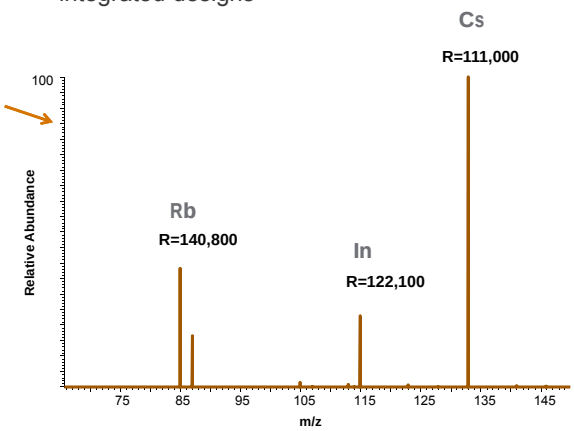




Moving towards compact, linearized, integrated designs



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GDMS Advantages

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- Wide elemental (~70 elements) and isotopic coverage
- Sub-ppb (µg/kg) to ppt (ng/kg) detection
- Uniform element sensitivity and simple calibration
- Thick film analysis
- Ideal for electrically conducting materials
- Ability to analyze ceramics and other insulators with use of conductive matrix, sacrificial cathode, or rf-power
- Depth dependent distribution measurements with high sensitivity (0.01-10 µg/g)
- “Tunable” ion sources provide informative additional operational modes

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GDMS Disadvantages

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- Contamination when preparing non-conducting samples
- Long pre-sputtering periods for stabilization (≥ 1 hr)
- Comprehensive elemental data analysis takes hours
- Matrix matched standards required for best quantification
- Expensive in light of more ubiquitous LA-ICPMS

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Laser Ionization Mass Spectrometry

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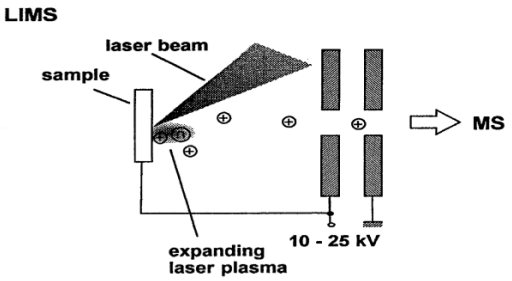
- Atomization:
  - Laser photon
- Ionization:
  - Laser photon
- Application:
  - Broad elemental coverage
  - Particles
  - Gas impurities
  - Particles
  - Aerosols



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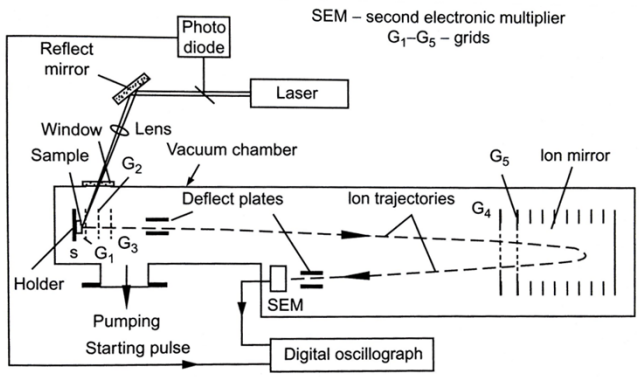
Laser Ionization Mass Spectrometry



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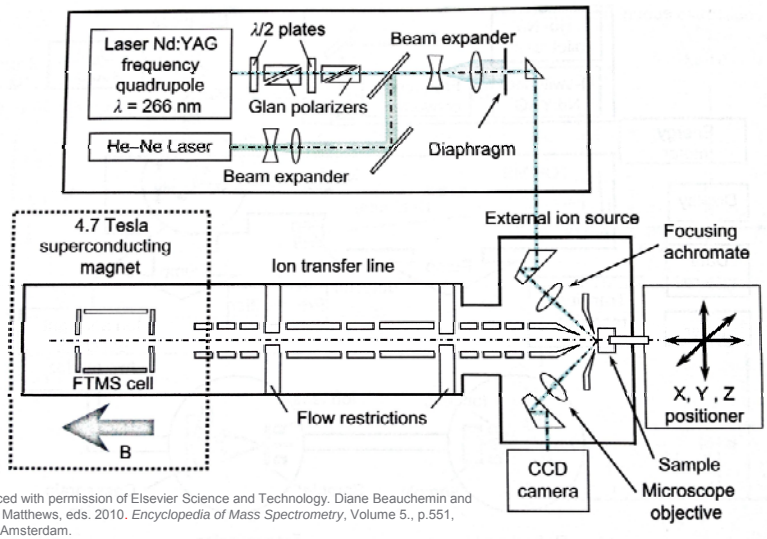
Fourier Transform-Laser Microprobe Mass Spectrometer



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Scheme for Molecular Speciation of Inorganic Compounds using FT-LMMS

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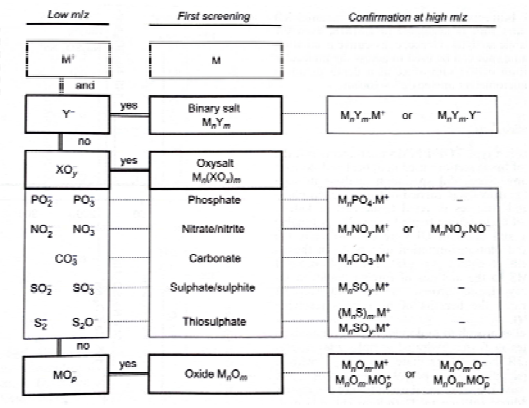

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Diane Beauchemin and Dwight E Matthews, eds. 2010.
Encyclopedia of Mass Spectrometry, Volume 5, Elsevier, Amsterdam.

Aerosol Analysis via Laser Ionization

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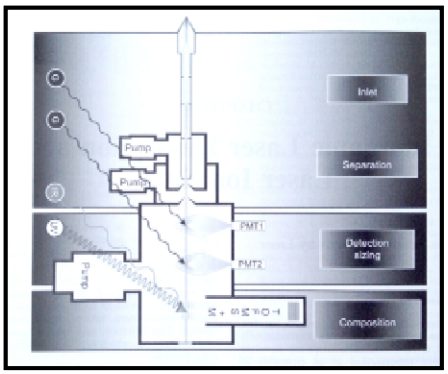
- Aerodynamic lens produces a collimated particle beam
- Light from two visible continuous lasers is scattered and detected by photomultiplier tubes
- IR laser for desorption
- UV laser for ionization
- Time-of-flight mass spectrometer detection



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LIMS Advantages

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- Wide elemental (~70 elements) and isotopic coverage
- No complex sample preparation
- Low material consumption
- Low sources of contamination (no electrodes)
- Local and depth analysis
- Absence of cluster ions
- Aerosol particulate analysis

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LIMS Disadvantages

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- Experimental complexity and cost
- Laser stability
- Analysis of heterogenous samples

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Secondary Ion Source and Sputtered Neutral Ion Source

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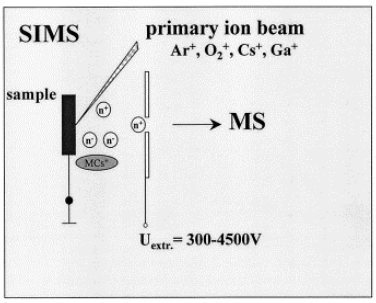

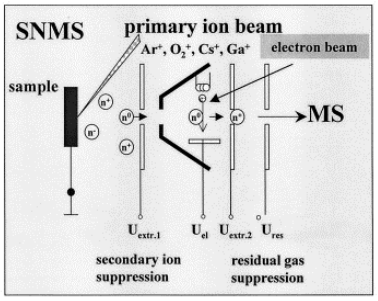

- Atomization:
  - Laser photons
- Ionization:
  - Laser plasma
- Sample types:
  - Solids & Solution Residues
  - Thin films

- Atomization:
  - Laser photons
- Ionization:
  - Electron Impact
  - Plasma ionization
- Sample types:
  - Solids & Solution Residues
  - Thin films

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Schematic Diagram of SIMS Instrument and Analysis Modes

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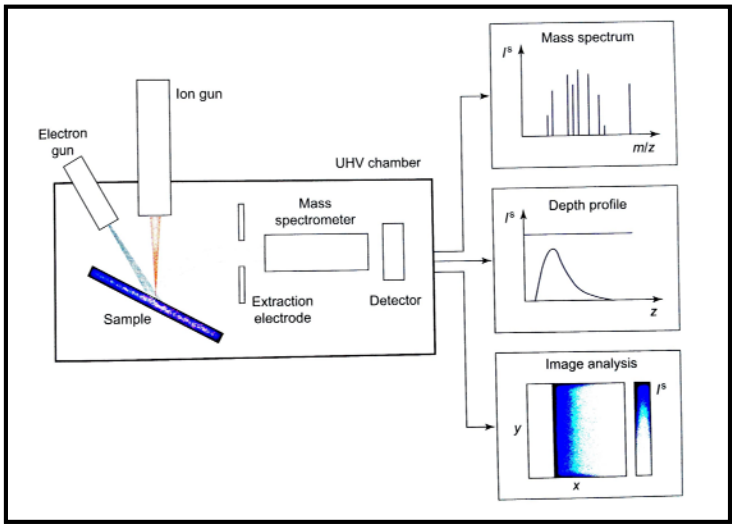

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Comparison: SIMS and SNMS

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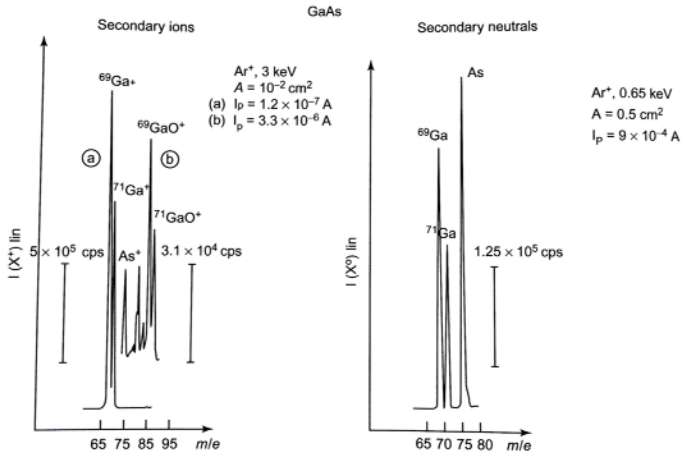

Separation of atomization and ionization events in SNMS provides a spectrum more representative of the sample surface composition than SIMS.

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Main Features of SIMS and SNMS

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	SIMS	SNMS
Evaporation	{ Using primary ions:	Using primary ions: Ar^+, Cs^+, O_2^+, Ga^+
Ionization	{ Ar^+, Cs^+, O_2^+, O^-, Ga^+	Post ionization of neutrals:
		Plasma, e-beam, laser (resonant, nonresonant)
Detection limit	0.001-1 µg g^{-1}	10-100 µg g^{-1}
RSC	10^2-10^6	0.3-3
Depth resolution	<5 nm	<5 nm
Lateral resolution	1-5 µm	1-5 µm
Applications	Depth profiling, imaging, trace analysis	Depth profiling, imaging

[a]Using implantation standards.

Adapted from J. S. Becker and H.-J. Dietze, 2000, "Inorganic mass spectometric methods for trace, ultratrace, isotope, and surface analysis," *International Journal of Mass Spectrometry*, 197:1–35.

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Comparison of Mass Spectrometry Techniques for Trace Analyses

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Method	Detection limit	Calibration/Reproducibility	Strengths of the method	Limitations of the method
SSMS	0.001-0.1	Using SRM/± 20%	High sensitivity	Expensive experimental arrangement
GDMS	0.0005-0.1	Using SRM/± 10%	High sensitivity, good precision	Analysis restricted to electrically conducting samples (dc GDMS)
LIMS (LAMMA, LIMA)	0.001-0.1	Using SRM/± 10-20%	No charge-up effects, high sensitivity	Expensive experimental arrangement
LA-ICP-MS	0.0005-0.5	Using SRM/± 10-20%	No charge-up effects, high sensitivity	Problem with inhomogenous samples
SIMS	0.001-1	Using ion implantation standards/± 30-40%	High sensitivity, imaging, depth profiling	Great variation in element sensitivity, matrix effects
SNMS	10-100	Using ion implantation standards/± 20%	Imaging, depth profiling	Poor detection power
ICP-MS	0.0001-0.1	Using calibration solution/± 10%; isotope dilution/± 0.5%	Good calibration possibility, no problems with inhomogeneity, high sensitivity, good precision	Solution steps necessary, matrix effects
ID-TIMS	0.000005-0.1	± 0.5%	Excellent quantification possibility, highest precision and accuracy	No multi-element capability, trace separation necessary

Adapted from J. S. Becker and H-J Dietze. 1998. "Inorganic trace analysis by mass spectrometry." *Spectrochimica Acta* Part B, 1475-1506 .

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Comparison of Precision and Sample Size for Isotope Ratio Measurements Using Different Mass Spectrometric Methods

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Isotope ratio	Method	Precision	Sample size
$^{235}U/^{238}U \sim 1$	MC-TIMS	0.007%	100 – 200 ng
$^{35}U/^{238}U \sim 1$	ICP-QMS	0.05%	255 pg
$^{234}U/^{238}U \sim 0.01$		0.56%	
$^{235}U/_{238}U \sim 1$	DF-ICP-MS	0.026%	255 pg
		0.2%	0.5 PG
$^{34}S/^{32}S \sim 0.05$	ICP-QMS (hexapole lens)	<0.3%	50 – 250 µg
$^{235}U/^{238}U \sim 0.007$	LA-ICP-QMS	1.7%	Some mg
$^{230}Th/^{232}Th \sim 0.0015$		4%	
$^{182}W/^{183}W \sim 2$	MC-ICP-MS	0.006%	500 – 1000 ng
$^{182}W/^{183}W \sim 2$	MC-LA-ICP-MS	0.009%	Some mg
$^{63}Cu/^{65}Cu$	GDMS	<0.3%	Some mg
$^{107}Ag/^{109}Ag$ (in pure metals)			

Adapted from J. S. Becker and H.-J. Dietze, 2000, "Inorganic mass spectometric methods for trace, ultratrace, isotope, and surface analysis," *International Journal of Mass Spectrometry*, 197:1–35.

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Comparison of Solid State Mass Spectrometric Methods and ICP-MS for Ultratrace Analysis on High-purity Solid Materials

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	Solid state mass spectrometric methods, e.g. SSMS, GDMS, LA-ICP MS, SIMS	ICP-MS
Sample preparation	None or minimal	Dissolution and dilution necessary (expensive if matrix separate required)
Quantification possibility	Matrix matched reference materials required (difficult if no SRM available)	Excellent using aqueous standard solutions
Precision Accuracy	For homogeneous samples: mostly <10%	Isotope dilution: 1 – 5%
Accuracy	Good; only if SRM available	Good
Contamination danger	Low	Enormous
Inhomogeneous sample	Difficult for bulk analysis	No problems if enough homogenized sample materials is dissolved
Time-consuming step	Quantification of analytical results if synthetic laboratory standards must be prepared	Sample preparation steps (mass separation)

Adapted from J. S. Becker and H.-J. Dietze, 2000, "Inorganic mass spectometric methods for trace, ultratrace, isotope, and surface analysis," *International Journal of Mass Spectrometry*, 197:1–35.

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Comparison of Analytical Methods

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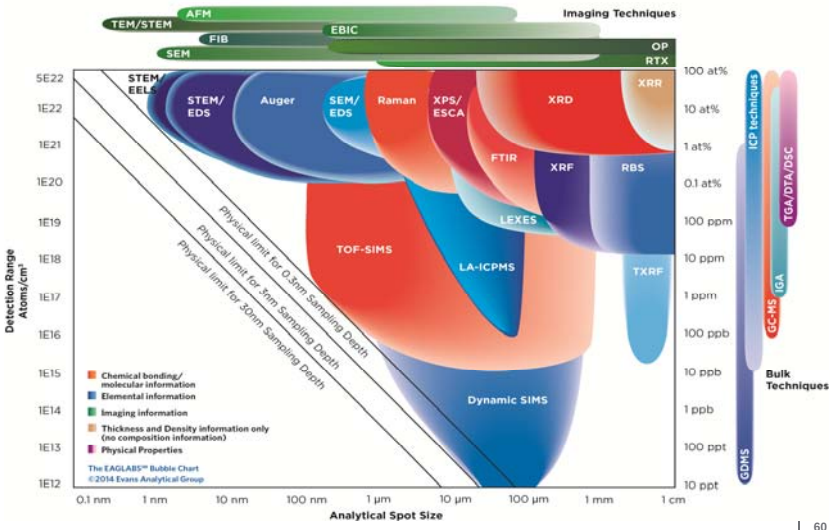

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Science does not know its debt to imagination.

— Ralph Waldo Emerson

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