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ICP-MS Short Course Participant Materials

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AGENDA

Day One, Tuesday

TIME	Presentation	Speaker
7:45 a.m.	Morning Hospitality	
8:00 a.m.	Welcome to PNNL	Randy Hansen
8:10 a.m.	Introduction and Overview of Inductively Coupled Plasma Mass Spectrometric Techniques	Greg Eiden
8:30 a.m.	Plasma and Ion Sampling Fundamentals in ICP-MS	Martin Liezers
9:30 a.m.	Break	
10:00 a.m.	Mass Separation	Greg Eiden
10:45 a.m.	Sample Introduction Techniques	Charles Barinaga
11:30 a.m.	Overview of Inductively Coupled Plasma Mass Spectrometry for Elemental Analysis	Chris Sorensen
12:15 p.m.	Lunch	
12:55 p.m.	Move to CSF/BSF Lobby	
1:10 p.m.	Poster Session	
2:00 p.m.	Move to EMSL	
2:15 p.m.	Sample Preparation and Protocols	Kellen Springer
3:00 p.m.	Break	
3:15 p.m.	Sample Preparation and Protocols (cont'd)	Kellen Springer
4:00 p.m.	Multi-collector Methods and Examples	Garret Hart
4:45 p.m.	Adjourn	
6:30 p.m.	No Host Dinner at Bookwalter Winery, Richland	

Presentation Abstracts

Introduction and Overview of Inductively Coupled Plasma Mass Spectrometric Techniques

Greg Eiden, Pacific Northwest National Laboratory

This short course is the second in a series of courses sponsored by the U.S. Department of Energy (DOE). DOE seeks to offer training in advanced instrumentation and methods for detection of materials of importance. This training is designed to address the adaptation and operation of instruments that define the state of the art in isotope ratio measurements and to foster communication between laboratories and universities. It is hoped that these short courses will build interest and guide/mentor future generations of mass spectroscopy researchers. The course in 2014 is focused on inductively coupled plasma mass spectrometry (ICP-MS). In 2013, Idaho National Laboratory hosted a meeting and short course focused on thermal ionization mass spectrometry (TIMS) and in 2015, Lawrence Livermore National Laboratory will host a meeting focused on secondary ion mass spectrometry (SIMS).

Plasma and Ion Sampling Fundamentals in ICP-MS

Martin Liezers, Pacific Northwest National Laboratory

In ICP-MS "plasma and ion sampling" can be summarized as: How to form ions and then lose most of them! The ICP is a very effective ion source for elemental/isotopic analysis as can be gauged by the numbers of optical emission and mass spectrometry instruments in use. Much of the explosive development of ICP-MS, which has gone from "a wild idea" in the 1970s to an everyday lab instrument today, has been centered on what goes on in the plasma and the ion sampling interface, which still remains the region where most ions are lost. In spite of the low ion numbers that are actually transmitted into the mass spectrometer, ICP-MS remains one of the most sensitive techniques for elemental and isotopic analysis. Plasma and ion sampling covers the characteristics of the ICP that make it a good ion source, hot-cold plasmas, ion sampling from the plasma, enhanced interface pumping to improve ion transmission, ion energy with mass, and ion acceleration for magnetic sector ICP-MS.

Mass Separation

Greg Eiden, Pacific Northwest National Laboratory

The ICP ion source has been coupled to almost every conceivable kind of mass separator and ion detector, however the most common instruments utilize either a quadrupole mass filter or a magnetic sector field to perform mass-based separation of the ions prior to detection. This talk will provide an overview of the hardware components of these two key mass separators as well as a brief introduction to the physics basis for separation. A few analytical performance metrics of interest such as resolution and sensitivity will also be described.

Sample Introduction Techniques

Charles Barinaga, Pacific Northwest National Laboratory

You've got a sample. You've got an ICP-MS instrument. Now what? All the various types of analytical instrumentation have particular techniques and requirements regarding how a sample is presented to the instrument in order for it to be able to produce meaningful data related to the sample. The two more common sample introduction techniques for ICP-MS, liquid nebulization and laser ablation of solids, will be introduced and briefly discussed. In addition, some alternative sample introduction techniques for different sample types (solids, liquids, and gases) will be presented.

Overview of Inductively Coupled Plasma Mass Spectrometry for Elemental Analysis

Chris Sorensen, Pacific Northwest National Laboratory

Applications of elemental analysis are far reaching, including trace elemental detection in medicine, geology, archeology, semi-conductors, and nuclear energy. Elemental analysis using inductively coupled mass spectrometry can be highly informative even when complex mixtures are analyzed. However, careful experimental design, use of the appropriate standards, and reference materials also need to be considered, prior to data interpretation. These slides highlight important experimental considerations and briefly describe some aspects of calibration and correction of signals from ICP-MS. Highlights from recent publications will be made to illustrate how elemental analysis information can be applied.

Sample Preparation and Protocols

Kellen Springer, Pacific Northwest National Laboratory

Experimental design, sample preparation and interpretation of isotope ratio measurements are presented through an example from isotope geochemistry.

Multi-collector Methods and Examples

Garret Hart, Pacific Northwest National Laboratory

The multi-collector (magnetic sector) inductively coupled plasma mass spectrometer (MC-ICP-MS) provides a powerful tool for the isotopic (and elemental) analysis of many of the elements across the periodic table. The MC-ICP-MS is ideal for high-precision isotope ratio spectrometry because of its flat top peaks, its efficient ion transmission, and its simultaneous detection of the ion beam on either faraday cups or ion counters. In this presentation Dr. Hart will focus on one example of the MC-ICP-MS—the Neptune Plus by Thermo Scientific. He will discuss some key characteristics of this instrument first, including the high-efficiency front-end, the interface pump, the ion energy filters, and the unique collector array designed specifically for U and Pu applications. Second, he will discuss some important parameters used to establish and evaluate the state-of-health of the instrument, including sensitivity, beam coincidence, peak shape, mass calibration, backgrounds, stability, and abundance sensitivity. Finally, Dr. Hart will provide a few example data sets generated with a MC-ICP-MS from his work in geosciences and from work at the lab.

Mass Spectrometry at the National Laboratories: An Overview

Erick Ramon, Lawrence Livermore National Laboratory

The results of a survey of national laboratory mass spectrometry capabilities are presented.

Laser Ablation ICP/MS Topics

Part 1. Laser Ablation – Chemical Analysis

Rick Russo, Lawrence Berkeley National Laboratory

Laser ablation (LA) with mass ICP-MS detection is an excellent technology for direct sample (solid, liquid, or gas) analysis. Benefits of laser ablation include no sample preparation, no consumables, every sample, real-time analysis, standoff (LIBS) measurements, and more. Although the concept of laser ablation sampling is relatively straightforward—a high-power pulsed laser beam on a sample removes a small portion of mass for analysis—the fundamental processes are relatively complex and interdependent. Knowledge of ablation processes, reliable system components, and development of methods has led to excellent performance metrics (accuracy and precision) of this technology for routine chemical analysis. In general, LA-ICP-MS provides ppb elemental analysis and isotopic ratios with per-mil precision. New research shows the ability to perform isotope measurements in the laser plasma at atmospheric pressure to complement ICP-MS measurements. This talk will present a general overview of the governing mechanisms for laser ablation, attributes of LA-ICP-MS, and the ability to simultaneously measure mass and optical emission providing a complete toolbox for rapid elemental and isotopic chemical analysis.

Part 2. Laser Ablation

Andrew Duffin, Pacific Northwest National Laboratory

Laser ablation coupled to inductively coupled plasma mass spectroscopy (LA-ICP-MS) is a versatile and powerful technique for direct elemental and isotopic analysis of solid samples. Advantages of LA-ICP-MS include atmospheric pressure sampling, no dissolutions and therefore no reagent blanks, and no chemical separations. Moreover, LA-ICP-MS can efficiently analyze (high percentage of atoms ablated reach the detectors) materials with micron scale spatial resolution, leading to applications in elemental and isotopic mapping. Of course, the simple sample preparation can also be a disadvantage when the matrix presents isobaric interferences. One of the main drawbacks of LA-ICP-MS is the necessity of dealing with transient signals. These slides give a brief overview of nuances to be aware of during LA-ICP-MS analysis, discuss strategies to deal with transient signals, and present examples of elemental and isotopic analysis.

ICP-MS Instrument Specializations

Charles Barinaga, Pacific Northwest National Laboratory

This presentation is primarily concerned with isobaric interferences in ICP-MS. An isobar is an ion that has the same mass-to-charge (m/z) ratio as an analyte ion. If a mass spectrometer cannot separate it from the analyte, it becomes an interferent in the analysis, i.e., making the intensity of the response at that m/z appear to be greater than would be expected from the analyte alone. The nature and sources of atomic and polyatomic isobaric interferences will be discussed, as will the problems they create. Various techniques (high mass resolution, collision/reaction cell technology, and kinetic energy discrimination) for removing or lessening the effect of these interferences will be presented, including current, commercially available instrumentation that incorporate these techniques. Lastly, two alternative mass separation techniques, time-of-flight (TOF) and distance-of-flight (DOF) will be briefly presented.

Ion Optics Modeling

Chris Zarzana, Idaho National Laboratory

SIMION is an ion optics simulation computer program used to design and analyze charged particle optical systems, from simple electrostatic lenses to complex mass spectrometry instrumentation. The program solves for the electric and magnetic fields produced by a collection of electrodes, and can compute ion trajectories due to those fields. This course presents a broad overview of SIMION, with emphasis on how to perform common tasks. Additionally, features in the newer versions of SIMION are highlighted.

Advanced Detector Technology, Revolutionizing Science Through Better Detection

M. Bonner Denton, University of Arizona

Array detectors have revolutionized many areas of optical spectroscopy. However, until recently the limited array detector technology suitable for the detection of ions has suffered from a variety of problems and limitations. This presentation will present the evolution as well as the current state of the art of a new family of array ion detectors capable of providing high sensitivity, high-stability detection of ions over large dynamic ranges. When coupled with mass analyzers capable of dispersing ions on a spatial focal plane, these detectors provide simultaneous analysis of large mass ranges.

Modes of operation including nondestructive readout, random access integration, and individual pixel gain control and addressing, will be described. Performance, figures of merit including detection capabilities, dynamic range, read noise and dark current will all be presented. Additionally, current and future design considerations will be considered.

Alternative Ion Sources for Trace Inorganic Mass Spectrometry

Doug Duckworth, Pacific Northwest National Laboratory

Why choose one ion source over another for inorganic MS? While the main MS methods considered in this series of short courses (TIMS, ICP-MS, and SIMS) are the workhorses of elemental and (inorganic) isotopic analysis, many other methods are also in widespread use or the subject of ongoing research. Ion source selection is based on many factors including sample size and type, whether the instrument is to be used in a fixed laboratory or is to be portable, and perhaps most importantly, performance trades: sample utilization efficiency (SUE), ionization specificity, and production of background and interfering species. The methods presented and discussed with respect to these performance trades include TIMS, Spark Source MS (SSMS), Glow Discharge MS (GDMS), pulsed glow discharge and RF glow discharge MS, atmospheric sampling glow discharge MS, laser ionization MS, and secondary ion and sputtered neutral MS.

Presenter Biosketches

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Charles Barinaga is a Senior Research Scientist in the Advanced Radioanalytical Chemistry Group of the National Security Directorate at Pacific Northwest National Laboratory. He specializes in research and development of analytical instrumentation, particularly for atomic mass spectrometry in general and ICP-MS in particular. Dr. Barinaga has contributed to several successful projects at PNNL funded by the DOE including Ion Trap ICP/MS (gas phase ion/molecule reactions to reduce polyatomic interferences in ICP-MS) and "All the Signal, All the Time" (successful development of a multichannel-array ion detector). The gas phase ion/molecule work became a component of Collision Reaction Cell (CRC) technology that is a part of nearly every quadrupole ICP-MS sold today. For these and other work Dr. Barinaga has received several national awards, been granted several patents, and wrote several publications and delivered presentations. He received his Ph.D. in Analytical Chemistry from the University of Idaho in 1988.

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M. Bonner Denton received his Bachelor of Science–Chemistry and Bachelor of Arts-Psychology degrees in 1967 from Lamar State College of Technology and his Ph.D. - Chemistry in 1972 from the University of Illinois. Today Denton is a Galileo Professor of Chemistry and Professor of Geological Sciences at the University of Arizona. His research interests include analytical instrumentation, optical spectroscopy, mass spectrometry, separation science, scientific imaging, and forensic analysis.

Over the years Denton and his group have developed methodologies that are today widely used in chemical analysis. He pioneered the development of high resolution array detector technology for both ultra-sensitive spectroscopic analysis and microscopic imaging. The high performance achievable in modern Raman, fluorescence and atomic emission spectroscopies, is directly traceable to contributions made by Denton and his research group. Currently Denton is applying new advanced detector innovations leading to the development of ultra-trace level explosives detection instrumentation capable of detecting small quantities of explosives at over 40 meters standoff distances, and to new detector technology for simultaneous ion detection.

Denton is a Fellow of the Royal Society of Chemistry; Fellow of the American Association for the Advancement of Science; Fellow of the Society for Applied Spectroscopy; and Fellow of the American Chemical Society. He has published over 200 peer reviewed publications and holds 15 patents in the field of chemical instrumentation.

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Douglas Duckworth is a Senior Scientist specializing in nuclear materials analysis at Pacific Northwest National Laboratory. He joined PNNL in 2006 and serves as a Program Manager in the National Security Administration Sector, supporting projects in the DOE's National Nuclear Administration's Office of Nonproliferation and Verification Research and Development (NA-22). He holds a Ph.D. in Analytical Chemistry from Clemson University and began his career at Oak Ridge National Laboratory developing, executing, and managing research programs in isotopic and elemental analysis.

Dr. Duckworth's primary expertise is in mass spectrometry and its application to elemental and isotopic analysis in radiological, nuclear, biological, and chemical analyses. His background includes investigations of fundamental gas-phase chemistry; instrument development and applications for advancing chemical separations and analysis; development and management of research programs in isotopic and elemental analysis; technical support for elemental and isotopic analysis of nuclear, environmental, and materials; and development of light and heavy isotope isotopic signatures. Dr. Duckworth's expertise has been recognized with collaborative research and/or funding from the DOE's Office of Basic Energy Sciences, U.S. Department of Homeland Security, National Institutes of Justice, and the National Nuclear Security Administration. He is the Chair-elect for the Analytical Division of the American Chemical Society.

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Andrew Duffin received his Ph.D. in Physical Chemistry from the University of California, Berkeley in 2010. Since then, he has worked at PNNL as a post-doctoral researcher and now as a staff scientist. His research at PNNL involves the application of fs-laser ablation coupled to multi-collector ICP-MS into a method for rapid, precise, and spatially resolved uranium analysis. In addition to fs-laser ablation, Dr. Duffin works on projects using advanced synchrotron analysis techniques for uranium analysis.

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Gregory Eiden is a Chief Scientist at Pacific Northwest National Laboratory with 25 years' experience in the development of mass spectrometry methods including nearly every type of mass analyzer (time-of-flight, Paul traps, multi-sector field, quadrupole) and ion source (plasma, laser, electron impact) in common use. While at PNNL, Dr. Eiden has focused on how such methods can address applications in national security. He is a co-inventor of "chemical resolution" mass spectrometry, an approach that is now recognized worldwide as a new paradigm in addressing spectral interferences in ICP-MS. This approach earned an R&D 100 Award in 1996, a Federal Laboratory Consortium (FLC) Award in 1997, and the 2004 FLC Award for Excellence in Technology Transfer. His other interests include optical spectroscopic methods (especially resonant photo excitation/ionization-based spectroscopies), the chemistry of gas phase cations, plasma processing etch and deposition for semiconductor fabrication, and surface analysis. Dr. Eiden is the author or co-author of 34 peer-reviewed publications, 80 conference presentations, numerous book chapters, and U. S. and international patents. He has taught short courses in mass spectrometry at key international meetings. Dr. Eiden received his Ph.D. in Physical Chemistry, from the University of Wisconsin-Madison.

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Garret Hart is a Staff Scientist in the Nuclear Materials Analysis Group within the National Security Directorate at Pacific Northwest National Laboratory. Dr. Hart has also worked as a research faculty member in Isotope Geochemistry at Washington State University where was a member of the GeoAnalytical Laboratory for six years. Along with his background in Geology, Dr. Hart has expertise in thermal and plasma source multi-collector mass spectrometry, elemental and isotopic sample characterization by laser ablation, and clean room chemistry procedures. Dr. Hart is working on integrating his experience with mid- to high-mass elements (U, Fe, Cu, Sr, Hf, and Pb) into existing and new research projects and goals. He is the author or co-author of 18 publications and many conference presentations. He received his Ph.D. in Geology from the University of Wisconsin-Madison in 2002.

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Martin Liezers joined the PNNL Radiochemistry group as a Staff Scientist specializing in elemental-isotopic analysis by ICP-MS techniques. Over the past few years he has had opportunity to work on some interesting projects:

- Detection of femtogram levels of ^{135}Cs and ^{137}Cs in groundwater by ICP-MS
- Electrochemical separation/preconcentration of U and Pu using glassy carbon (Pu-239 DL <3 attograms = <7,500 atoms!) by ICP-MS
- Development of Ultrahigh resolution ICP-MS (300,000 res) sufficient to resolve ^{87}Rb from ^{87}Sr (proton versus neutron mass difference)
- Production of surrogate nuclear explosion debris using high power techniques that include the ICP, exploding wires, and high power lasers.

Dr. Liezers received his Ph.D. from the Department of Instrumentation and Analytical Science (DIAS) at the University of Manchester Institute of Science and Technology (UMIST), England. Before joining PNNL in 2006, he was a post-doctoral fellow at UMIST for 3 years based at the Atomic Energy Research Establishment (AERE), Harwell, England. He spent two years as a Higher Scientific Officer at AERE looking at actinide speciation using laser spectroscopy. He joined VG Elemental Ltd, Winsford, England in 1990 as a research scientist working on alternate plasmas to the ICP for Mass Spectrometry applications and improving ICP-MS sensitivity (S-option, Cool Plasma!). During this time he traveled extensively performing installations, service, method development, and customer training on VG ICP-MS instruments, along with presenting numerous conference presentations and authoring scientific publications. Dr. Liezers contributed sections on plasma sampling and ion optics to two ICP-MS books, *Inductively Coupled Plasma Mass Spectrometry Handbook* (Simon Nelms, ed.) and *The Encyclopedia of Mass Spectrometry, Volume 5, Elemental and Isotope Ratio Mass Spectrometry* (Diane Beauchemin and Dwight Matthews, eds.).

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Erick Ramon is a staff chemist at Lawrence Livermore National Laboratory (LLNL). His expertise in analytical chemistry includes elemental and isotopic measurements by plasma source mass spectrometry (ICP-MS), elemental analysis by X-ray fluorescence (XRF) and plasma source emission spectroscopy (ICP-OES), chemical and physical micro characterization by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) and secondary ion mass spectrometry (SIMS). He has also served as principal investigator for several U.S. Government-funded projects. Besides supporting national security programs, he is involved with basic science research at LLNL in the area of cosmochemistry where he uses the NanoSIMS to investigate extinct short-lived radionuclides in meteorites to better constrain the timeframe of early solid formation and planetary differentiation in the solar system.

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Richard Russo is the founder and scientific director of the laser material interactions group at the Lawrence Berkeley National Laboratory. His group pioneered laser ablation for chemical analysis, with over 30 years' contribution to fundamental and applied research. Dr. Russo has an international scientific reputation in chemistry and physics related to nanosecond and femtosecond laser-material-interactions (laser ablation), is co-inventor of the nanowire laser, and developer of a real-time standoff laser ultrasonic sensor, which earned an R&D 100 Award in 2006. He also is co-inventor of a patented process for nano-texturing (ITEX process) thin-films, lead-inventor of the patented ion-assisted pulsed laser deposition (IBAD process), which produced a world record critical current for HTSC materials, and a pioneer in elucidating fundamental laser heating and laser ablation processes for chemical analysis. His research group achieved world record 450nm spatial resolution and a detection limit of 220 attograms using a single femtosecond laser pulse for laser induced breakdown spectroscopy (LIBS) measurements. By pioneering near-field scanning optical microscopy (NSOM) with laser ablation, his group achieved 25nm diameter spatial resolution for sampling and analysis. Most recently, his Berkeley research group, with the assistance of Applied Spectra staff, demonstrated and patented the use of laser plasmas for real-time measurement of isotopes. The new technology has been named LAMIS (Laser Ablation Molecular Isotopic Spectroscopy), which won an R&D 100 Award in 2012. Dr. Russo has over 250 scientific publications; 45 refereed proceedings; 320 (226 invited) presentations-lectures, 10 book chapters and 15 patents. Fourteen students have received their PhD degree under his direction at the University of California, Berkeley. Dr. Russo received his Ph.D. in Chemistry, Laser Spectroscopy from Indiana University, Bloomington in 1981.

Dr. Russo also is founder and president of Applied Spectra, Inc. (ASI). He founded ASI with the assistance of several of his Ph.D. students from Berkeley. Together, they are the world experts in laser ablation chemical analysis using LIBS and Laser Ablation with ICP-OES and ICP-MS. Company core expertise is research, development, and manufacture of laser ablation chemical analysis instrumentation, and analytical measurement services.

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Dr. Christina Sorensen is a scientist in the National Security Directorate at PNNL. She received a Ph.D. in Inorganic Chemistry from the University of Wyoming where she specialized in mass spectrometry with an emphasis on inorganic and bioanalytical characterization. She did her post-doctoral work in Dick Smith's group at PNNL, focusing on multivariate analysis of metabolomics data.

At PNNL, Dr. Sorensen has a number of areas of research including characterization and identification of metals, small compounds, biofuel compounds, oligomers, organometallic compounds, and proteins. She has provided and developed separation and purification methods for a variety of different compounds in different matrices. In addition, she has applied multivariate statistical analysis for metabolic profiles and fuel analysis. She has used mass spectrometry for characterization of compounds of interest for many multifaceted applications in a variety of different groups across the laboratory. One of her specializations has been method development for projects where trace detection of different compounds requires research and development of a standard operating procedure. She has had the opportunity to apply her chemistry knowledge to a wide range of projects in national defense, forensic marker characterization, diabetes markers, peptide and protein markers, small molecule analysis including characterization of synthesis products. Dr. Sorensen has used a broad range of instrumental techniques with different applications for evaluation of characterization methods.

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Kellen Springer is a scientist in the Radiochemical Analysis Group at the Pacific Northwest National Laboratory. Mr. Springer joined PNNL after earning an M.S. in Geology from the University of Houston in 2010 where he studied isotope geochemistry. His thesis research focused on the timing of the Alpine orogenic event as recorded in high-pressure, low-temperature metamorphic assemblages. From these metamorphic assemblages, and associated garnets, Sm-Nd and Lu-Hf geochronometers were used to estimate the duration of the metamorphic event, as recorded in the pro-grade garnet growth. At PNNL Mr. Springer has applied his previous academic experience in clean-room chemistry and trace isotopic analysis to nuclear forensic and nuclear nonproliferation arenas in support of a number of U.S. Government agencies.

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Chris Zarzana received his Ph.D. in Chemistry from the University of Arizona in 2011, under the direction of Professor M. Bonner Denton. His thesis work involved the development and characterization of advanced array ion detectors and their application to dispersive mass spectrometry instrumentation. He was a postdoc at the University of Arizona, where he continued work on using advanced charge amplifier arrays as detectors for mass spectrometers. Dr. Zarzana has been a postdoc at Idaho National Laboratory since 2013, conducting research on electrospray ionization mass spectrometry, with an emphasis on ion formation chemistry.

Presentations

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Introduction and Overview of Inductively Coupled Plasma Mass Spectrometric Techniques

GREGORY C. EIDEN

Pacific Northwest National Laboratory

June 17, 2014

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ICP-MS Short Course Teachers

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- PNNL
  - Charles Barinaga, PhD University of Idaho
  - Doug Duckworth, PhD Clemson University
  - Andrew Duffin, PhD University of California, Berkeley
  - Greg Eiden, PhD University of Wisconsin-Madison
  - Garret Hart, PhD University of Wisconsin-Madison
  - Martin Liezers PhD Manchester (UMIST)
  - Christine Sorensen, PhD University of Wyoming
  - Kellen Springer, MS University of Houston
- Guest Lecturers
  - Professor. M. Bonner Denton (University of Arizona)
  - Dr. Erick Ramon (Lawrence Livermore National Laboratory)
  - Dr. Richard Russo (Lawrence Berkeley National Laboratory)
  - Dr. Chris Zarzana (Idaho National Laboratory)

Introduction: History and Impact

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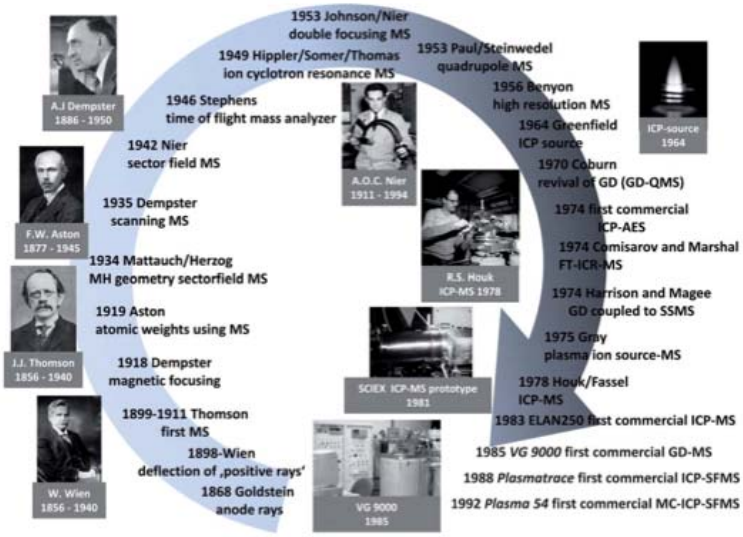

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Comparison of Analytical Methods

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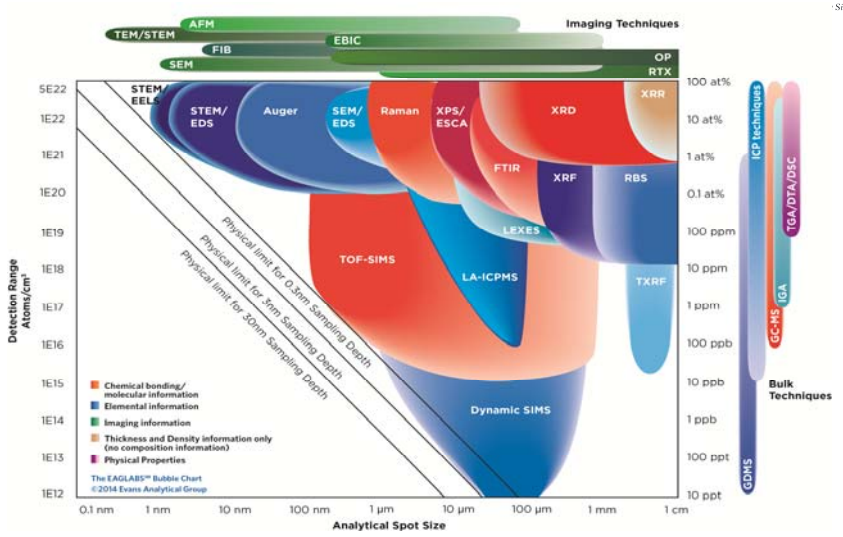

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Comparison of MS Techniques for Trace Analyses

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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)
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	Implantation standards/± 20%	Imaging, depth profiling	Poor detection power
ICP-MS	0.0001-0.1	Using calib soln/± 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 .

5

Short Course Lecture Topics

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- Plasma and Ion Sampling Fundamentals
- Mass Separation (QMS and Magnetic Sector)
- Sample Introduction
- Elemental Analysis
- Sample Prep, Chemistry, Analytical Protocols
- ICP-MS Data Reduction / Isotope Dilution
- MC-ICP-MS Topics
- Mass Spectrometry in the DOE Complex
- LA-ICP-MS Topics
- Instrument Specializations (ToF, DoF and Collision Cell)
- SIMION Modeling
- Advanced Detector Technology from the Denton Group
- Alternative Plasma Source MS /Comparison with TIMS, SIMS and other methods

6

Short Course ICP-MS Hardware

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- Plasma and Ion Sampling Fundamentals
- Mass Separation (QMS and Magnetic Sector)
- Sample Introduction
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Short Course ICP-MS Analytical Methods

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- Plasma and Ion Sampling Fundamentals
- Mass Separation (QMS and Magnetic Sector)
- Sample Introduction
- Elemental Analysis
- Sample Prep, Chemistry, Analytical Protocols
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Short Course ICP-MS Special Topics

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- Plasma and Ion Sampling Fundamentals
- Mass Separation (QMS and Magnetic Sector)
- Sample Introduction
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- Instrument Specializations (ToF, DoF and Collision Cell)
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- Advanced Detector Technology from the Denton Group
- Alternative Plasma Source MS / Comparison with TIMS, SIMS and other methods

9

ICP-MS Roadmap

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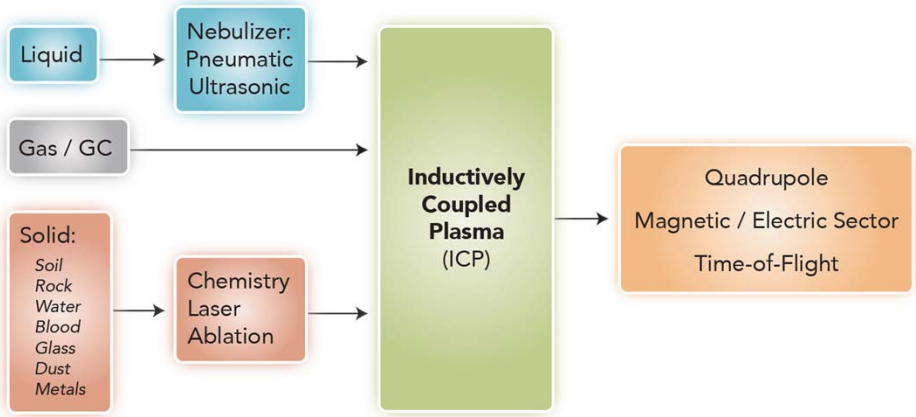

10

ICP-MS Roadmap

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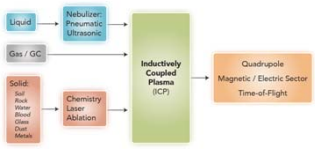
Overall Analytical Plan

Sampling Plan
- samples
- blanks
- standards

Collection and preservation of samples



Ion Detector(s)

Array Detector(s)

Data Reduction

Large Data Sets analysis

Mass Spectrometers
Inductively Coupled Plasma MS (ICP-MS)

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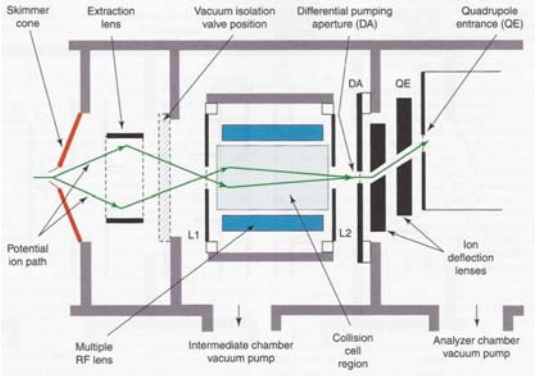
- Robust ion source
- Ions created at ~1atm
- Transfer into high vac
- Broad elemental coverage
- Flexible sample introduction
- 0.1% to 1% precision
- Up to 2% efficiency



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Mass Spectrometers

Inorganic Elemental/Isotopic

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- Sector Field MS
  - Inductively Coupled Plasma MS (ICP-MS)
  - Thermal Ionization MS (TIMS)
  - Secondary Ion MS (SIMS)
- Quadrupole-ICP-MS (Q-ICP-MS)
- Accelerator MS (AMS)
- Mostly Organic/Bio (some elemental/isotopic)
  - Time-of-Flight (TOF), Distance-of-Flight (DOF)
  - Ion traps (RF Quadrupole; Penning)

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Instrument Performance Features

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- Peak shape (flat top?)
  - Response versus mass position (scan)
- Beam stability
  - Static and scanning/"hopping"
- Separation of adjacent peaks
  - Resolution (full-width half-maximum [FWHM] or full width FW at 10%)
  - Abundance sensitivity
  - Efficiency loss at high resolution
- Sample utilization efficiency
- Ion species
  - Atomic, molecular, and polyatomic
  - Singly vs multiply charged
- Detectors
  - single, multiple
  - Ion current (Faraday cup) or ion counting (electron multiplier)

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Peak Shape

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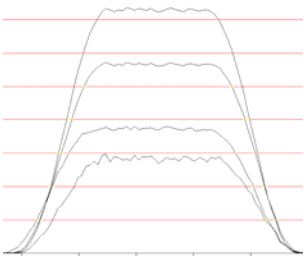
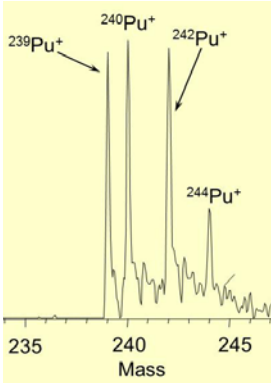
RF Quadrupole Ion Trap

MC-Sector low resolution



Time of Flight*



*Adapted from Mitchell et al., "The Application of Graphite MALDI-TOF-MS For the Detection and Imaging of Actinides in Environmental Samples", 2009 MARC conference.

15

Elemental and Isotopic MS in Nuclear Fuel Cycle Materials Characterization

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- Isotopes/Elements of Interest
  - Nuclear: SNM, fission products, activation products
  - Nuclear process: conversion, enrichment, reprocessing
  - Explosives (trace elements, isotopics)
  - Related materials (packaging, "device" components, etc.)
- Bulk, Minor, Trace levels
- Forensic Interests
  - Material "fingerprint"
  - Provenance: production location or producer
    - Rare earth patterns
    - Sr, Pb, O precision isotopics
    - Process knowledge (elemental/isotopic fingerprints)
  - Age
    - Wide range of chronometers for actinides (^{241}Pu / ^{241}Am, ^{239}Pu / ^{235}U, ^{240}Pu/ ^{236}U, ^{234}U/^{230}Th)

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Instrumental Background
220 – 250 amu

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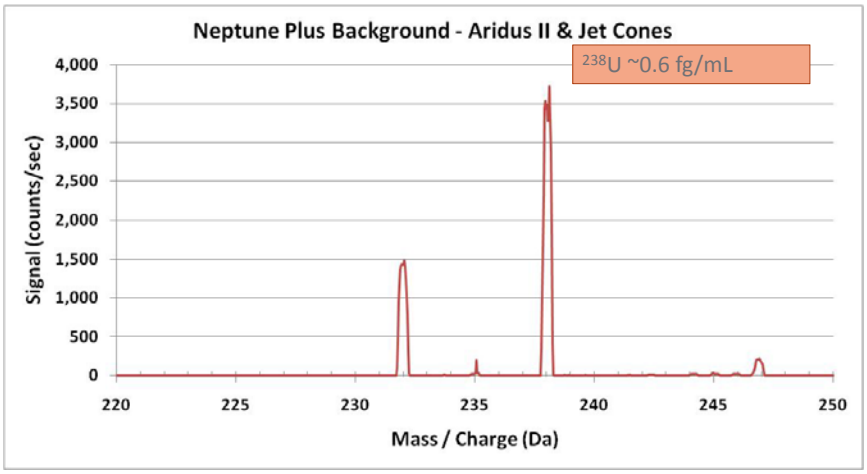

17

Instrumental Background
220 – 250 amu

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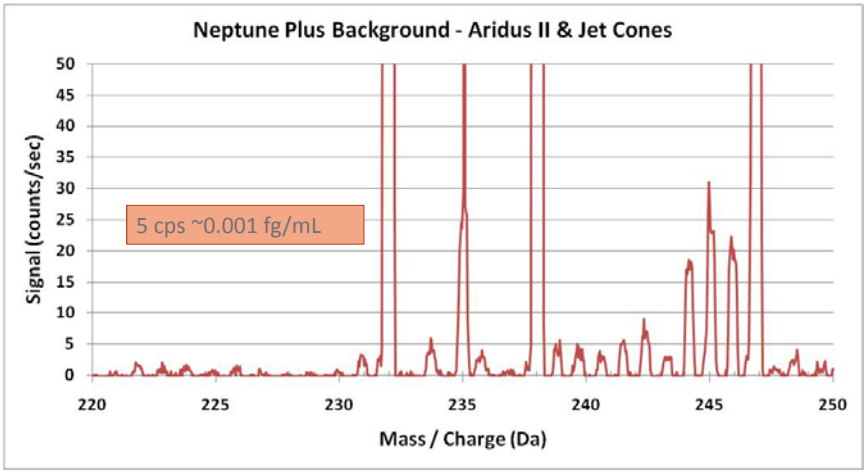

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Short Course Lecture Topics

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- Next: Martin Liezers - Plasma and Ion Sampling Fundamentals
- Mass Separation (QMS and Magnetic Sector)
- Sample Introduction
- Elemental Analysis
- Sample Prep, Chemistry, Analytical Protocols
- ICPMS Data Reduction / Isotope Dilution
- MC-ICPMS Topics
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- SIMION Modeling - Guest Lecture INL
- Advanced Detector Technology from the Denton Group
- Alternative Plasma Source MS /Comparison with TIMS, SIMS and other methods

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Questions?

20

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ICP-MS Short Course

Plasma and Ion Sampling Fundamentals in ICP-MS

MARTIN LIEZERS
Pacific Northwest National Laboratory

June, 17, 2014

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1

Where the Action Happens

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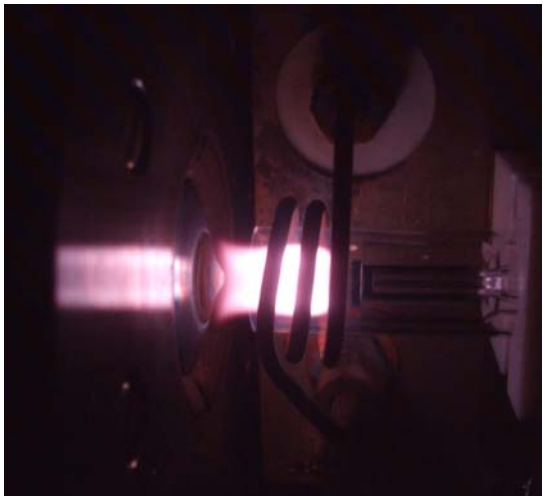

2

Inductively Coupled Plasmas (ICPs)

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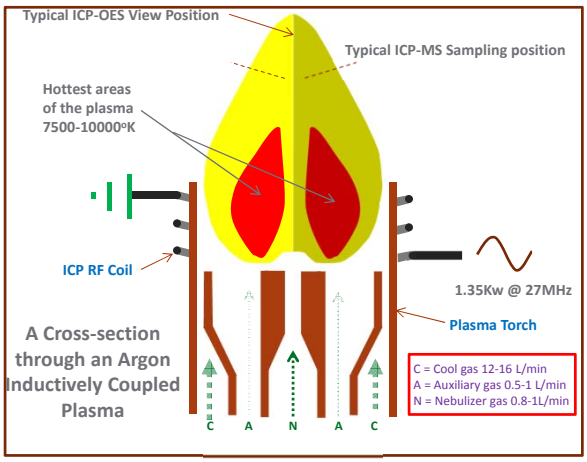
- How do they work?
- What makes them a good mass spec elemental + or - ion source?

Theory



Plasma Torch

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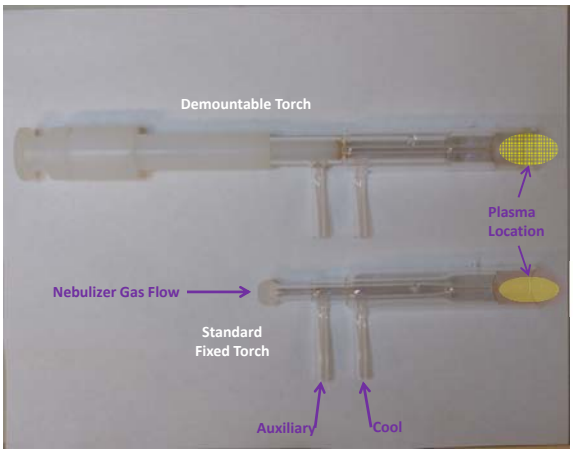
Typical ICP quartz torches



How do ICPs Work and What Makes Them a Good Mass Spec Elemental Ion Source?

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- Very hot atoms and electrons (4500-10000 K) good at vaporization, atomization, and ionization
- High electron number density 1015-1016 cm^{-3}
- Converts most elements into positive ions with 100% efficiency for I.P. <7 eV, modest efficiency for I.P. out to ~12 eV
- Can be used as a negative ion source: F^-, Cl^-, Br^-, I^-
- Formation of doubly charged ions relatively low
- Long Sample-Plasma interaction time ~2-3ms (velocity ~25m/s)
- Relatively inert environment – argon atmosphere
- Can handle solid or liquid aerosols composed of particles <50 um diameter
- Handle aqueous or organic solvents
- Relatively stable, reliable and they require relative little maintenance
- Nothing better has shown up in the last 30+ years

5

Sensitivity versus Robustness

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This can affect the level of interferences and internal standard behavior

Key indicators – formation rates of LaO^+ or CeO^+

$(MO^+ / M^+) \times 100$ (%) <2% Good >5% Poor

6

Plasma Parameters Affecting Sensitivity, Oxides, and Molecular Ions

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- Nebulizer gas flow and to a slightly lesser extent auxiliary gas flow
- Torch - Sample cone distance (wider spacing gives the lowest oxides and lowest internal standard suppression with high matrix samples)
- Plasma Power – higher power will yield lower oxides if gas flow and torch position are not increased
- Sample introduction rate, water loading
- Collision-reaction cell bias (keep negative -5 V to avoid ion clustering when not using gas in the cell)

7

Cool Plasmas: The Pinch Discharge

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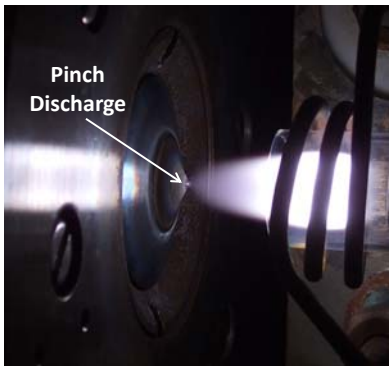

- Caused by capacitive coupling of the rf voltage to the plasma
- Voltage gradient along the rf coil induces charge separation in the plasma elevating plasma potential
- Leads to an ionization kick where the plasma approaches the grounded sample cone aperture, visible as a spark or filament-type discharge

$$Ar^{*} \xrightarrow[\text{Discharge}]{\text{Pinch}} Ar^{+} + \text{electron}$$

8

Cool Plasmas: Eliminating the Pinch Discharge and Suppressing Ar^+ Formation

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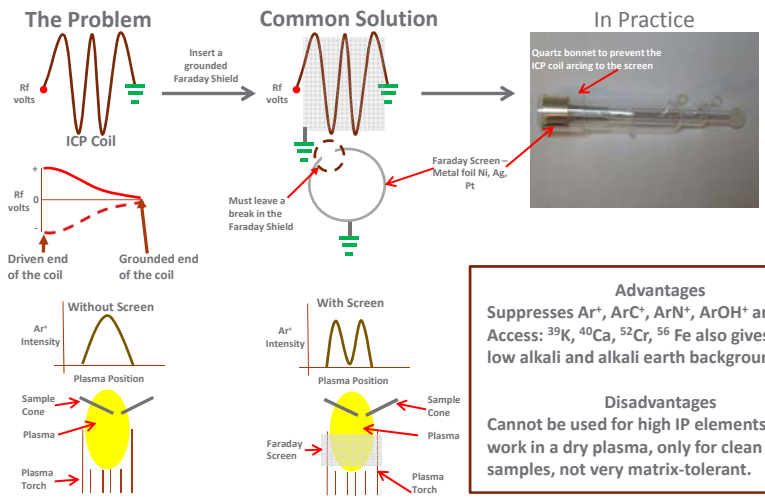

Advantages

Suppresses Ar^+, ArC^+, ArN^+, $ArOH^+$ and $ArAr^+$
Access: ^{39}K, ^{40}Ca, ^{52}Cr, ^{56}Fe also gives very low alkali and alkali earth backgrounds

Disadvantages

Cannot be used for high IP elements, won't work in a dry plasma, only for clean matrix samples, not very matrix-tolerant.

9

Cool Plasmas: Alternate Approaches Used to Minimize a Pinch Discharge

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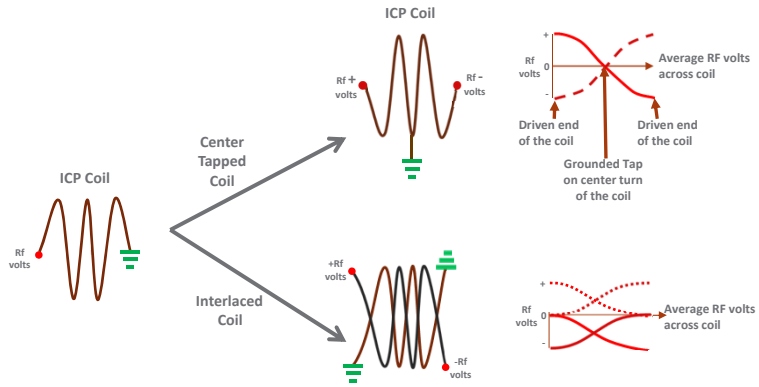

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Cool Plasmas: No Pinch Discharge

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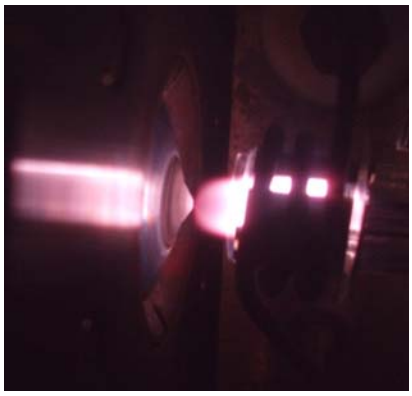

If there is no pinch discharge, the formation of Ar^+ in the central channel of the plasma can be suppressed and tuned out without complete loss of most analyte ion formation.

Additional Benefits of Reduced Plasma Potential

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- Leads to reduced ion energy spread that can lead to better instrument sensitivity which is why screen is often used even under normal high power operating conditions
- Slight drawback—screen absorbs some rf energy so oxides tend to run a bit higher than without the screen

Interesting Cool Plasma Effects

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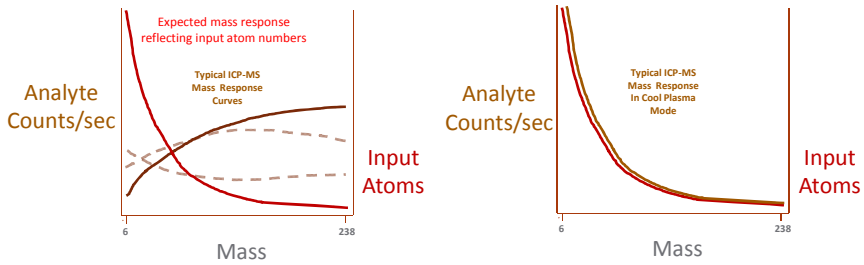
Mass Response v Actual Input Atoms



Important To Remember: 1pg ^{7}Li = 8.6 x 10^{10} Atoms 1pg ^{238}U = 2.5 x 10^{9} Atoms

Ion Sampling the ICP: Extracting Ions from the ICP into the Mass Spectrometer

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- Issues/Problems

1. Analyte ions in a very hot ~5000 K plasma
2. Plasma at ~ 1 atm pressure, mass spec ~ 10^{-10} atm
3. Elemental ion-electron recombination process (neutralization) fast
4. Create a positive ion beam

- Solution: Supersonic Molecular Beam Interface

1. Reduces temperature ~150 K, freezes composition of the plasma
2. First stage reduction in pressure to ~10-7 atm
3. Minimal ion-electron recombination 3 µs transit
4. Creates an effective point ion source

Supersonic Molecular Beam Interface

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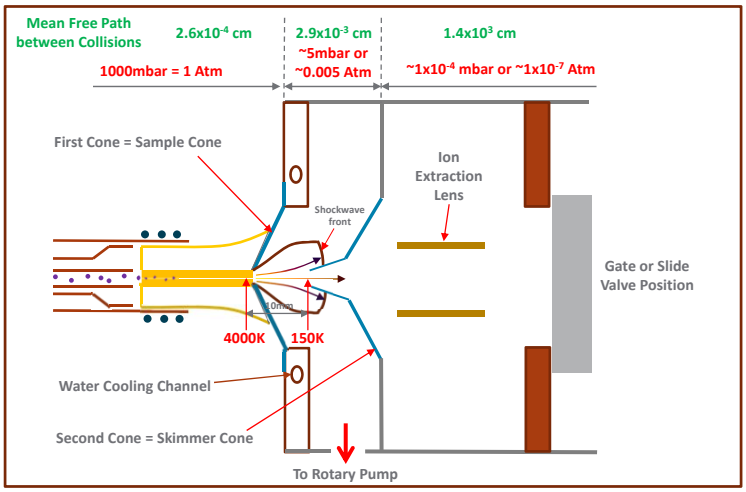

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Adiabatic Free Jet Expansion

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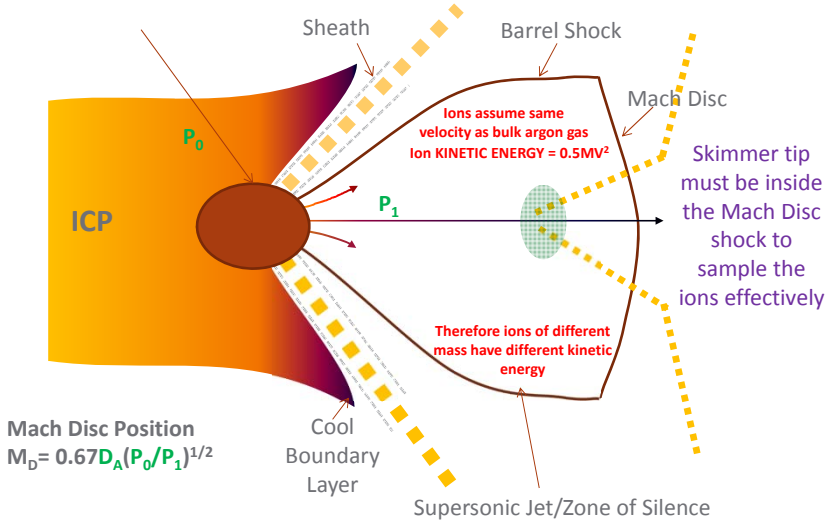

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Thermo X-Series ICP-MS Plasma Sampling Interface

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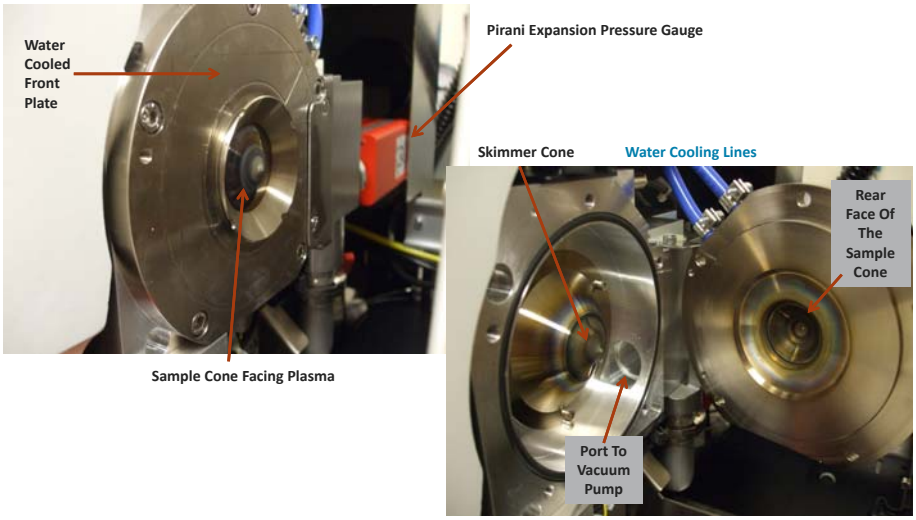

17

Ion Energy as a Function of Mass

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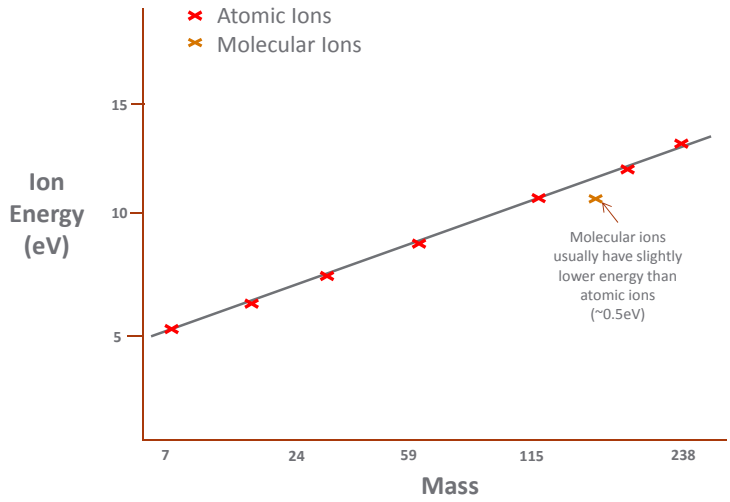

18

S-Option (Improving Sensitivity)

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- Most quadrupole ICP-MS instruments use a small expansion pump 25-30m^3 hr^{-1}, but higher sensitivity can be achieved by using a larger pump 50-100m^3 hr^{-1}. This is the so-called "S-option"
- Used by manufacturers Nu and Thermo on their multicollector ICP-MS instruments to maximize sensitivity
- Benefits improved sensitivity x2-5 for elements heavier than argon (sensitivity reduced for low-mass elements except under cool plasma conditions where sensitivity gains >x10 are possible)
- Will work on quadrupole instruments if the expansion pumping port does not limit gas conductance

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Sample and Skimmer Cone Performance

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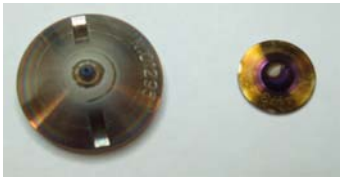
- Common Cone Materials
  - Nickel - Most common cone material for general purpose use
  - Platinum - $$$, best cone lifetime especially with HF, H_2SO_4, H_3PO_4, $HClO_4$
  - Copper - General purpose
  - Aluminum - General purpose especially if you do not want Ni or Cu



- Sample cones - Fairly chunky and robust but they do wear out. Sensitivity effects usually small, large apertures make oxides go up
- Skimmer cones - Aperture tip very fragile, easily damaged during extraction or cleaning. Sensitivity effects large, shape and surface affect backgrounds

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Cone Care

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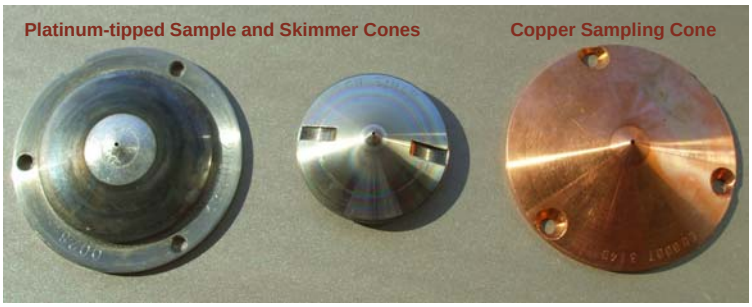
- Avoid cleaning cones in acid, this accelerates sample cone aperture wear
- Most salt deposits will be removed by placing cones in DIW in an ultrasonic bath for 5-10 minutes
- If more aggressive cleaning is required use a mild abrasive that will not scratch the metal surface



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More Cones

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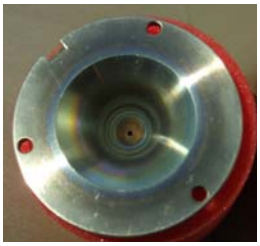

For sample cones concentric heat rings – good
Asymmetric or offset heat rings usually indicate cone damage at aperture – poor performance

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Ion Sampling on Magnetic Sectors

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- Ions have to be traveling fast, much faster than in a quadrupole for a magnetic sector instrument to operate effectively

  Quadrupole ICP-MS ion energy 2-10eV
  Magnetic Sector ICP-MS ion energy 4000-10000eV

- *How do you get ions of these energies from the same ion source to the ICP?*

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How Do You Get Ions of These Energies from the Same Ion Source to the ICP?

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Answer: You have to accelerate the ions somehow.

- Two ways to do it:
  - VG Way
  - Finnigan Way

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Accelerating the ICP Ions

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VG Way

Electrically isolate the plasma sampling interface from ground and electrically bias it at +4000-8000V

Finnigan Way

Keep the plasma sampling interface at ground potential but isolate and float the rest of the spectrometer downstream at -10000V

- Advantages
  - (VG Way) only a small part (interface) of the instrument is at high voltage
  - (Finnigan Way) interface and cones at ground potential
- Disadvantages
  - (VG Way) high voltages and the mbar interface pressures can cause discharge issues
  - (Finnigan Way) most of the spectrometer is at a high voltage

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Accelerating the ICP Ions (contd.)

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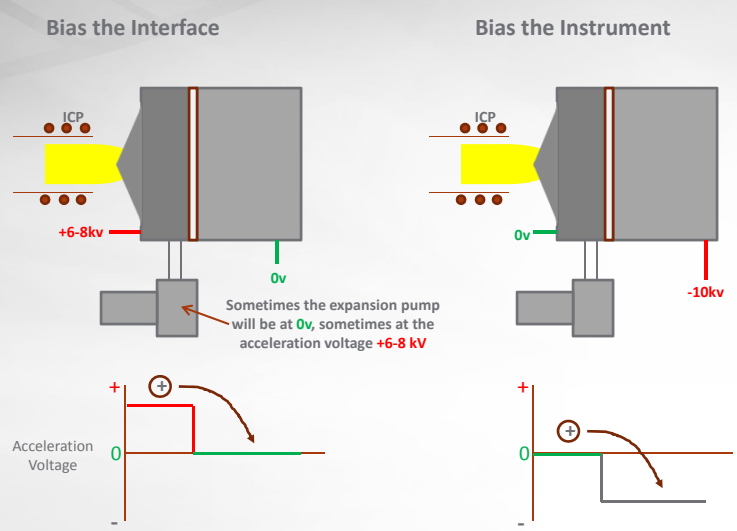

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Questions?

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ICP-MS Short Course
Mass Separation

GREG EIDEN

Pacific Northwest National Laboratory

June 17, 2014

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Mass Separation Topics

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- This Talk
  - Quadrupole Mass Filter (QMF)
  - Magnetic Sector
- Later
  - Time of Flight
  - Distance of Flight
  - Ion Trap
  - Orbitrap

Quadrupole Mass Filter Theory

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- Quick Development of the Mathieu Equation
  - Stability Diagrams
- Peak Shapes
- Resolution/Response tradeoff

- Quadrupole
  - Mass Filter - 2D
  - Ion Trap - 3D
    - Other Traps
    - Psuedo-potential Well
- Ion Injection - ion trapping
- Ion Ejection - mass scanning

3

MS with Quadrupole Mass Filters

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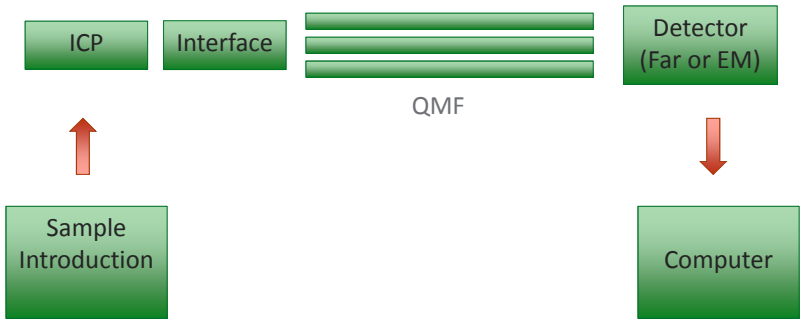
Form ions → Extract into high vacuum → Filter narrow mass range → Detect



4

Quadrupole Mass Filter

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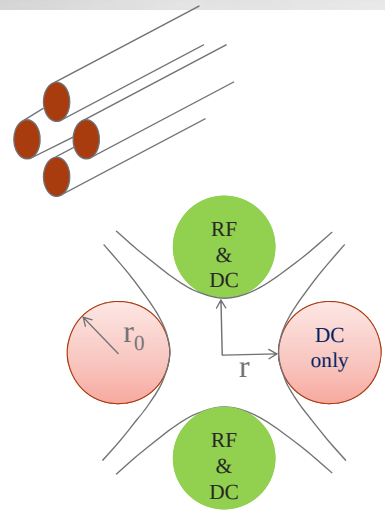
- RF & DC potentials
  - charged species dynamics
- Hyperbolic rods
  - Ideal field
  - r_0 from center to rod apex
- Other Considerations
  - Length of rods
  - Ion Energy
  - RF pre-filters
- Round rods
  - Typical (easier to make)
  - Non-ideal field
  - $r = 1.1487\ r_0$



QMF - Equations of Motion

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Equations of motion

$$m\ddot{x} + 2e[U + V_0\cos(\omega t)] / r_0^2 = 0$$

$$m\ddot{y} - 2e[U + V_0\cos(\omega t)] / r_0^2 = 0$$

U – DC amplitude
V_0 – RF amplitude
ω – RF frequency

Substitute:

$$A = 8eU / (mr_0^2\omega^2)$$
$$Q = 4eV_0 / (mr_0^2\omega^2)$$
$$\xi = \omega t/2$$

$$d^2x/d\xi^2 + (A + 2Q\cos(2\xi)x] = 0$$

$$d^2x/d\xi^2 - (A + 2Q\cos(2\xi)x] = 0$$

Mathieu* Equations

Émile Léonard Mathieu (French Mathematician; 1835 - 1890)
See Dawson or March and Hughes for detailed derivations

QMF-Stability Diagram Region A

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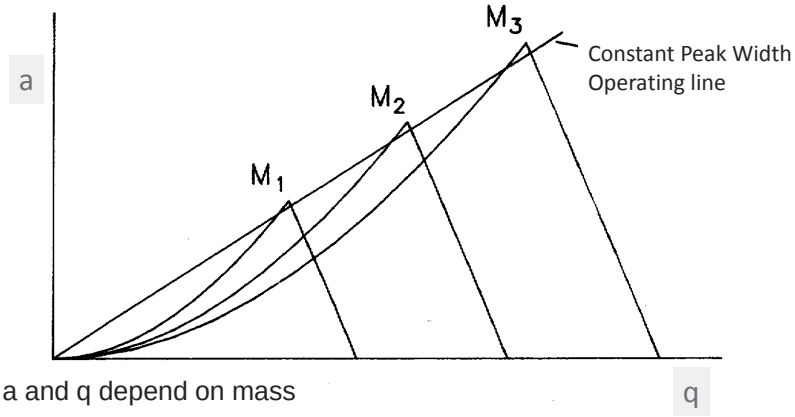

- a and q depend on mass
  - Separate stability region for each mass
- Scan at constant a/q
- Mass positions arrayed along scan line
- Scan at constant resolution or peak width

$a_u = 8eU / (mr_0^2\omega^2)$
$q_u = 4eV_0 / (mr_0^2\omega^2)$

$u = x,y$

adapted from Fig. 2.9, page 48, March and Hughes, Quadrupole Storage Mass Spectrometry, 1989.

7

Quadrupole Peak Shapes

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Permission requested for Figure 2.10 from "ICP Mass Spectrometry Handbook", CRC Press, 2005, Simon Nelms, Ed.

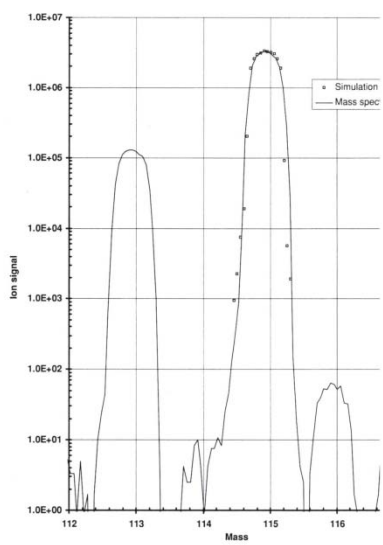

Figure 2.10 Spectrum from a commercially available quadrupole ICP-MS

8

Sensitivity vs Resolution: Trade-offs
energy dependent

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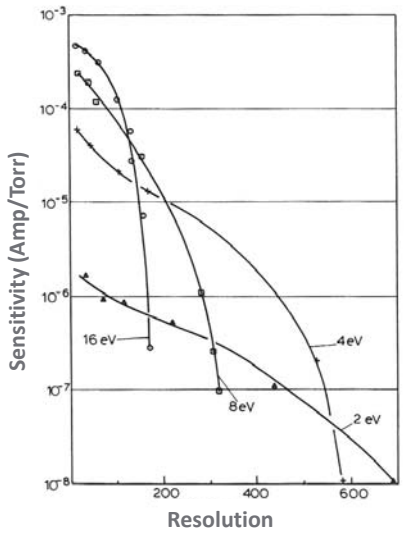
This plot shows the relationship between sensitivity and resolution at various ion injection energies

(adapted from Fig 6.17 in "Quadrupole Mass Spectrometry and its Applications, Peter H. Dawson, Ed., American Institute of Physics Press, 1995)



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Magnetic Sector Field Mass Separators

Simple Magnetic Sector

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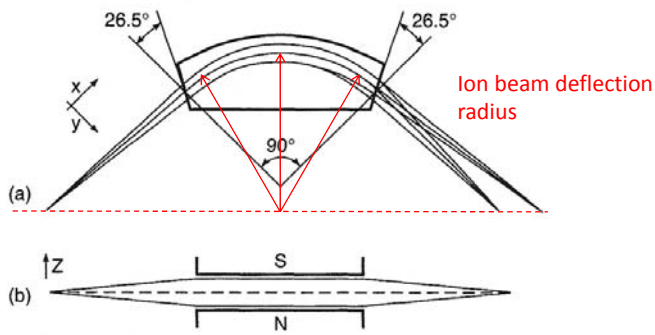

Figure 3.3. (a) Radial and (b) axial focusing of a magnetic sector with oblique ($\epsilon'_m = \epsilon''_m = 26.5°$) beam entrance and exit

Adapted from Chapter 3 in "Applications of Inorganic Mass Spectrometry", John R. de Laeter, John Wiley and Sons, 2001.

Simple Magnetic Sector: Basic Optics Equations

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Accelerate ions to high energy

$$qV = \frac{1}{2} mv^2$$

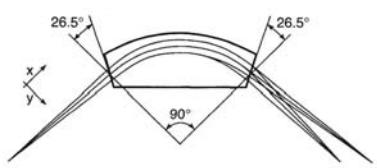
Charged particles move in circular paths through magnetic fields due to magnetic force:

$$F = qvB$$

Magnetic forced balanced by centrifugal force:

$$qvB = mv^2/R$$

So, $m/q = R^2B^2/2V$
$= c\,B^2$

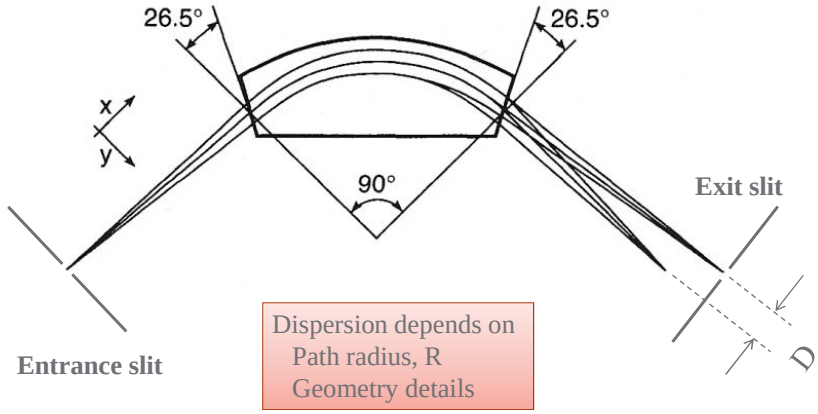


In practical units:
$R = 0.01436 \times (mV)^{1/2} / qB$

[R(cm), m(amu), V(kV), B(tesla)]

m: ion mass V: accel voltage v: ion velocity e: elementary charge
z: charge of the ion B: magnetic field strength r: magnetic field sector radius

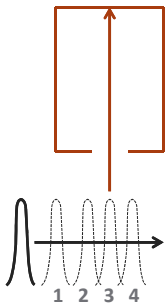
Simple Magnetic Sector: Dispersion



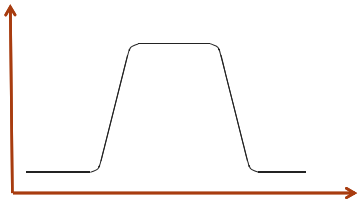
Dispersion depends on
Path radius, R
Geometry details

Adapted from Chapter 3 in "Applications of Inorganic Mass Spectrometry", John R. de Laeter, John Wiley and Sons, 2001.

Magnetic Sector MS Peak Shapes
simple



Sweep (magnetic field)
Peak across detector



Magnetic Field (Gauss)

Pseudo High Res – Thermo Version from NeptunePlus Brochure

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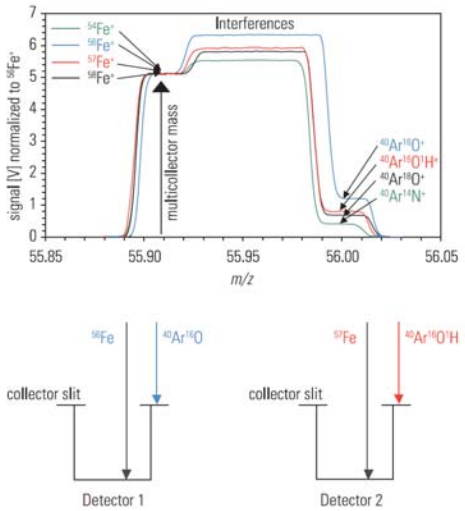

Figure from ThermoFisher "NeptunePlus" brochure (www.thermofisher.com), used by permission.

Performance Figures of Merit

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Parameter	Vendor Spec	Champion
Sensitivity	~1-2%	2-4 % (counts/atom)
Instrument LOD	< 1fg/g	<0.1 fg/g
Det Noise (EM)	<0.2 cps	<5 cpm
Det Noise (Far)	~1 fA**	Same
Precision: single Det	<0.02% RSD	Same
Precision: multi-Det	<0.002% RSD	Same
Mass Resolution	Up to 12000 in commercial instruments	Same

**1 sec integration (Johnson noise limit 0.4 fA)

Trade-offs

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Quadrupoles

Advantages	Disadvantages
Low Cost ($100K-$200K)	Low sensitivity
Speed of analysis	Peaks not “flat-topped”
Automation	

Magnetic Sectors

Advantages	Disadvantages
High mass resolution	High cost ($500K-$850K)
High sensitivity	Loss of sensitivity at high resolution
Excellent isotope ratio precision (“flat-topped” peaks)	Rapid, multi-elemental analysis challenging

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MC-ICP-MS is Mainstream

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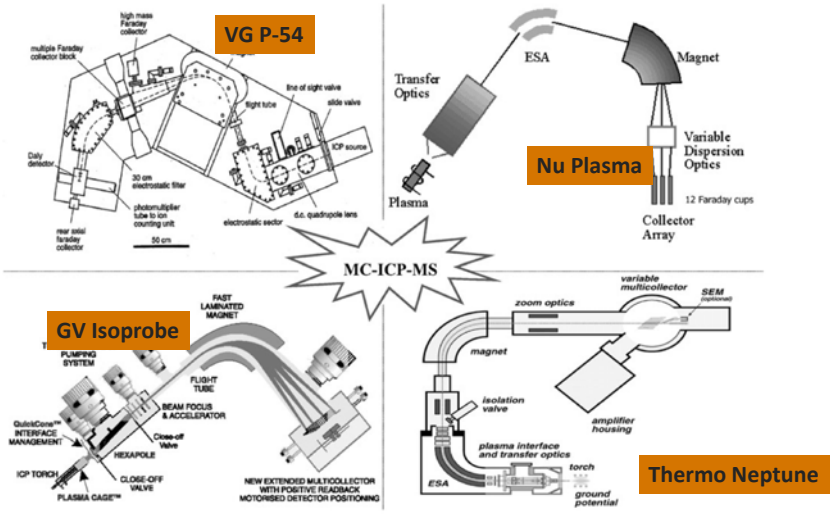

Reproduced by permission of The Royal Society of Chemistry. J.S Becker. 2005.
“Recent developments in isotope analysis by advanced mass spectrometric techniques, Plenary lecture,”
Journal of Analytical Atomic Spectrometry, 20:1173-1184.

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Magnetic Sectors – Commercial Examples

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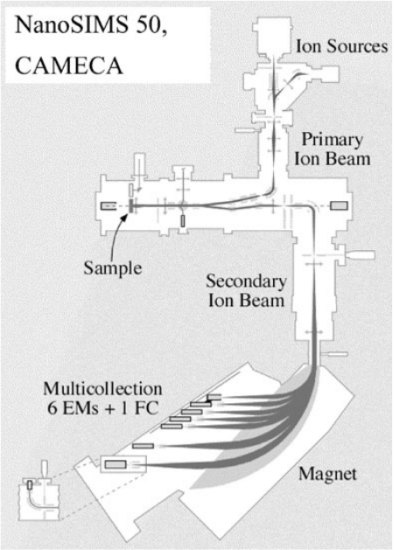

Reproduced by permission of The Royal Society of Chemistry. J.S Becker. 2005. "Recent developments in isotope analysis by advanced mass spectrometric techniques, Plenary lecture," *Journal of Analytical Atomic Spectrometry, 20:1173-1184.*

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Magnetic Sectors – Commercial Examples ThermoFisher "Triton"

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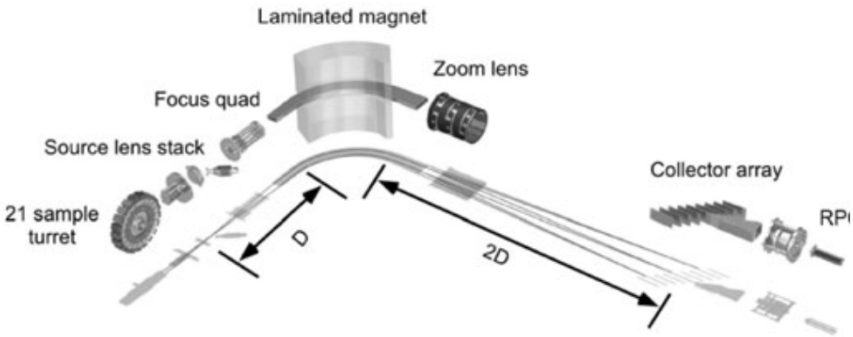

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Questions?

End

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- Fahey, A. J., N. W. M. Ritchie, et al. (2010). "The use of lead isotopic abundances in trace uranium samples for nuclear forensics analysis." *Journal of Radioanalytical and Nuclear Chemistry* **284**(3): 575-581.
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- Varga, Z., M. Wallenius, et al. (2010). "Origin assessment of uranium ore concentrates based on their rare-earth elemental impurity pattern." *Radiochimica Acta* **98**(12): 771-778.
- Varga, Z., M. Wallenius, et al. (2009). "Application of Lead and Strontium Isotope Ratio Measurements for the Origin Assessment of Uranium Ore Concentrates." *Analytical Chemistry* **81**(20): 8327-8334.
- Wallenius, M., K. Lutzenkirchen, et al. (2007). "Nuclear forensic investigations with a focus on plutonium." *Journal of Alloys and Compounds* **444**: 57-62.
- Wallenius, M. and K. Mayer (2000). "Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry." *Fresenius Journal of Analytical Chemistry* **366**(3): 234-238.

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- Weaver, J., S. R. F. Biegalski, et al. (2009). "Assessment of non-traditional isotopic ratios by mass spectrometry for analysis of nuclear activities." *Journal of Radioanalytical and Nuclear Chemistry* **282**(3): 709-713.

Bibliography – Conferences and Short Courses

Pacific Northwest NATIONAL LABORATORY
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- International Conferences
  - Measurements and Applications in Radiochemistry, held every three years, Kona, Hawaii.
  - International Nuclear Materials Management
  - Winter Plasma Spectrochemistry Conference
  - Federation of Analytical Chemistry and Spectroscopy Societies
  - American Geophysical Union
- Short Courses
  - WPC?
  - FACSS?
  - INMM?
  - Other

27

Backup Slides

Quantities of Interest - Uncertainty

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- Significance of comparisons requires method validation and confidence in uncertainty estimates
  - "Signatures" studies must address all sources of uncertainty
  - Address assumptions underlying sampling to data reporting
- Inter-comparability of measured quantities and uncertainties requires carefully prescribed procedures
  - Thorough QA/QC planning and implementation required
- All sources of uncertainty must be assessed
  - Systematic
  - Random – modeled vs measured scatter ("excess" variability)
  - Thorough analysis of uncertainty – understand instrument better

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Quantities of Interest – Measured Values

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- Concentrations or ratios indicative of processes or materials of interest
- Elemental
  - Qualitative composition – "external calibration" – 10% accuracy
  - Quantitative analysis – 1% accuracy or better
    - Absolute concentrations, inter-elemental ratios
    - Requires accurate spike/traced analysis
- Single element isotope ratio
  - Many systematic factors cancel out – highest possible precision
  - Highly purified samples required for accuracy
- Isotopic ratios, multi-elemental (e.g., ^{241}Am / ^{241}Pu)
  - Chemical effects must be "traced"
  - Precision and accuracy worse than single element IRMS

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Example: Sr Isotope Ratios in Yellowcake from Various Sources (Varga *et al*.*)

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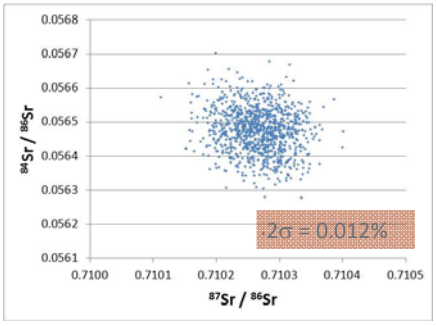
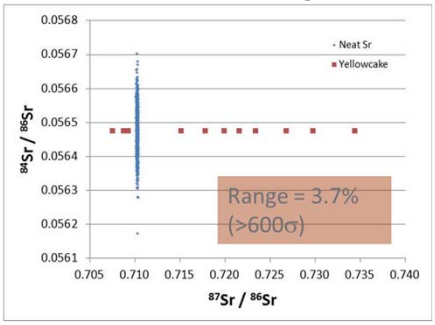
Neat Sr solution
Int. Prec. ~60ppm



Neat solution and
Yellowcake; various origins



Yellowcake data from Z. Varga *et al.,* Analytical Chemistry, Vol. 81, No. 20, October 15, 2009.

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Change in Precision over Time for U030(a)

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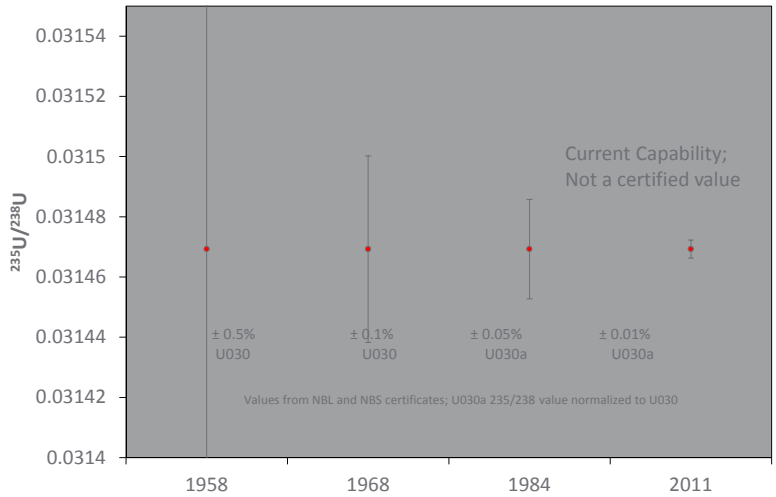

Slide courtesy of Dr. Garret Hart, PNNL.

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A Nonforensic Example: Variation in Natural Uranium $^{238}U/^{235}U$ Ratio** (Natural Fractionation)

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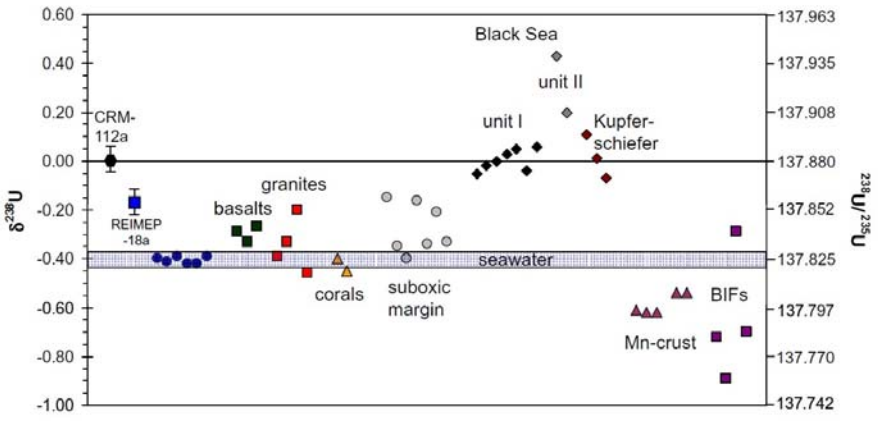

from S. Weyer et al., 2008, "Natural fractionation of $^{238}U/^{235}U$", Geochimica et Cosmochimica Acta **72, pp. 345–359

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PNNL MS Team

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- ICPMS
  - April Carman
  - Doug Duckworth
  - Andrew Duffin
  - Tom Farmer
  - Garret Hart
  - Rich Hanlen
  - Martin Liezers
  - John Robinson
  - Kellen Springer
  - Jesse Ward
- TIMS, SIMS
  - Sara Hager
  - Rich Hanlen
  - Robert Kiddy
  - Ben Naes
  - Steve Petersen
  - Kellen Springer
  - Blandina Valenzuela
  - Ken Wagnon
  - John Wacker
  - David Willingham

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Detectors

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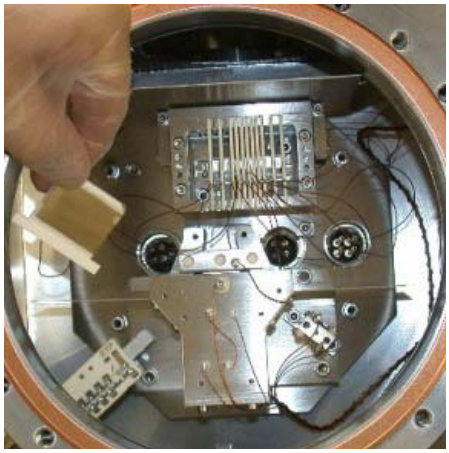
NuPlasma™ detector array

Detector cross-calibration
essential for high accuracy
not trivial!



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Mass Spectrometers Accelerator MS (AMS)

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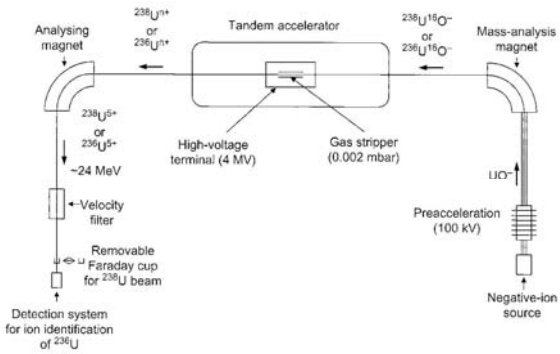
- Highest abundance sensitivity
  - Ratios down to 1E-15
- Low mass detection limit
- High sample throughput
- High capital cost



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Mass Spectrometers
Sector Field MS

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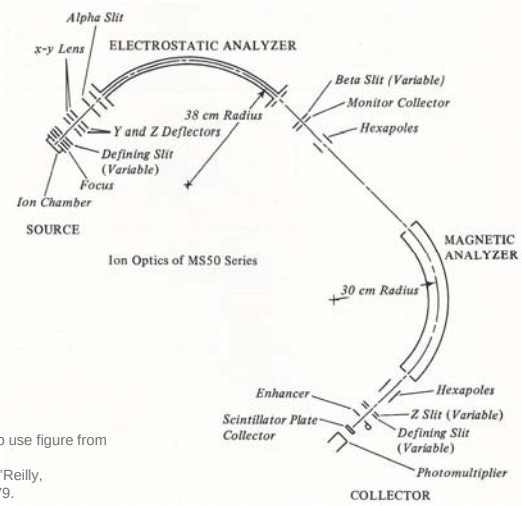
- Thermal Ionization MS (TIMS)
- Inductively Coupled Plasma MS (ICP/MS)
- Secondary Ion MS (SIMS)
- Gas Species and Isotope Ratio

- High Sensitivity
- Excellent precision/accuracy
- Large footprint
- High Cost ($1000K)



Permission requested to use figure from *Instrumental Analysis,* Bauer, Christian, and O'Reilly, Allyn & Bacon, Inc., 1979.

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ICP-MS Short Course

Sample Introduction Techniques

CHARLES J. BARINAGA
Pacific Northwest National Laboratory

June 17, 2014

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PNNL-SA-103257

U.S. DEPARTMENT OF ENERGY

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Introduction

- Brief overview of an ICP
  - Much more detail in subsequent presentations
  - Good general, tutorials by Robert Thomas for ICPMS (and other techniques) in Spectroscopy magazine (www.spectroscopyonline.com)
- More commonly used sample introduction techniques
  - Pneumatic nebulization for liquids
  - Laser ablation for solids
- Alternative sample introduction techniques
  - Gas
  - Liquid
  - Solid

Inductively Coupled Plasma (ICP) Overview

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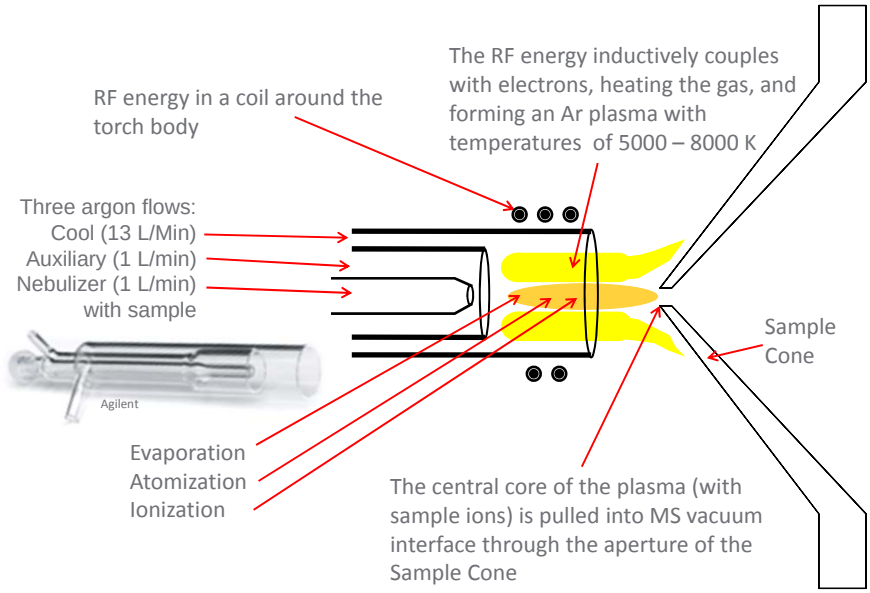

3

Most Commonly Used Sample Introduction Techniques

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- Liquids - nebulize (break-up) into fine aerosol droplets
  - Aqueous solutions of mineral acid(s) and dissolved and/or digested solid or liquid sample
    - Drinking or waste water, fuels, biological fluids, etc.
      - A. Sarmiento-Gonzalez, JM. Marchante-Gayon, JM. Tejerina-Lobo, et al., "ICP-MS multielemental determination of metals potentially released from dental implants and articular prostheses in human biological fluids", Anal. and Bioanal. Chem., 2005, **382**, 1001-1009
    - Digested soil, rocks, biological material, semiconductor, etc.
      - A. Quemet, R. Brennetot, E. Chevalier, et al., "Analysis of twenty five impurities in uranium matrix by ICP-MS with iron measurement optimized by using reaction collision cell, cold plasma or medium resolution", Talanta, 2012, **99**, 207-212
- Solids - laser ablate to produce aerosol particles
  - No digestion, no solution background
    - Rocks, metals, glasses, zircons, etc.
      - A. Duffin, G. Hart, R. Hanlen, et al., "Isotopic analysis of uranium in NIST SRM glass by femtosecond laser ablation MC-ICPMS", J. Radioanalytical and Nuclear Chem., 2013, **296**, 1031-1036

4

Liquid Sample Introduction System

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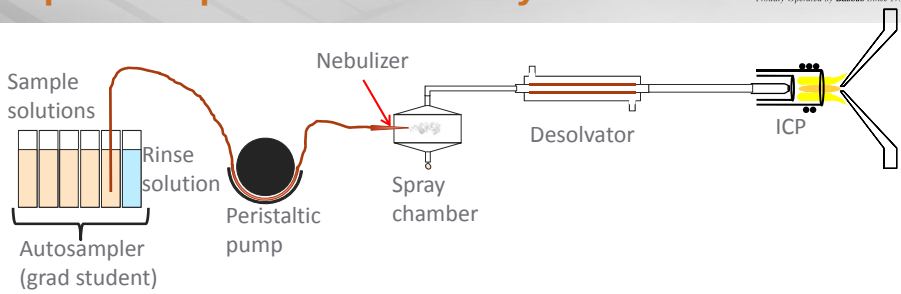

- Sample introduction systems
  - Adopted from earlier techniques:
    - DC Discharge Emission Spectroscopy
    - Atomic Absorption Spectroscopy
    - ICP-Atomic Emission Spectroscopy, etc.
  - Current generation has evolved for lower sample flow rates
    - Less sample
    - Less waste

5

Liquid Sample Introduction System

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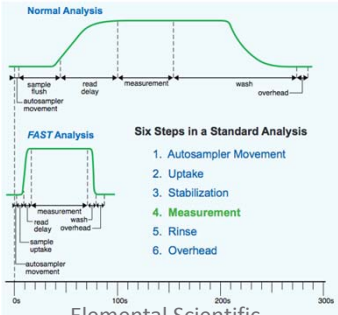
- Autosampler
  - Most common suppliers
    - CETAC Technologies http://www.cetac.com/
    - Elemental Scientific http://www.icpms.com/
  - Most ICPMS instruments interface to these
- Memory or carry-over (signal from previous sample[s])
  - High concentration samples
    - Pre-screen, adjust dilutions
  - "Sticky" elements
    - Select correct materials
  - Poorly swept dead volume in tubing
    - Correct sizes and fittings
- Uptake and washout times
  - Time to flow rinse solution through tubing
  - Software control of pump and solutions can dramatically reduce analysis time



Elemental Scientific

6

Nebulization of Liquids (contd.)

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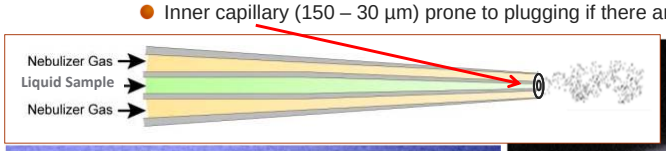
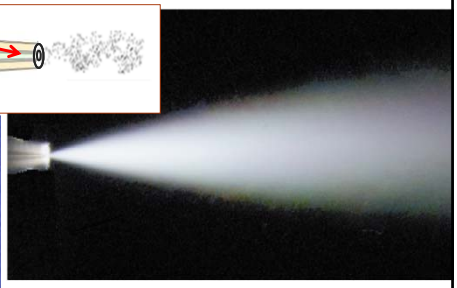
- Nebulize ("to reduce to a fine spray" *Merriam-Webster Online*)
  - Pneumatic – high velocity concentric Ar stream around the central liquid stream shears liquid into aerosol droplets of various sizes
    - Inner capillary (150 – 30 µm) prone to plugging if there are particulates





  - Ultrasonic – rapidly vibrating ultrasonic surface shatters liquid into aerosol

Permission requested

Nebulization of Liquids (contd.)

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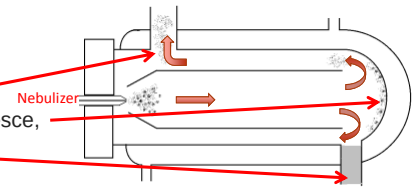
- Aerosol droplet size-separation
  - Larger droplets may not be completely evaporated and atomized by the plasma
    - Sputtering of signal, salt build-up on cones
  - Select the smaller sized particles in a "spray chamber"
    - Double-pass
    - Cyclonic
  - Momentum separation
    - Small droplets flow on to ICP
    - Larger droplets hit the wall, coalesce, and flow out to waste
  - Efficiency
    - Older style at 1mL/min: 1-10% to ICP, rest to waste
    - Newer styles, 100-200 µL/min, 50 – 100% to the ICP, "total consumption", little to no waste



Desolvation of Nebulized Liquids

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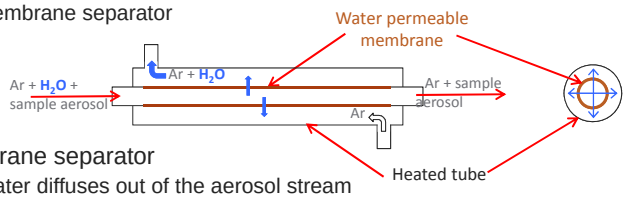
- Plasma "loading"
  - ICP's job: vaporize, atomize, and ionize
    - Vaporizing and atomizing water takes "power" away from analyte and matrix
  - Solution: desolvate - get rid of most of the water
    - Condensers, water cooled
    - Membrane separator



  - Membrane separator
    - Water diffuses out of the aerosol stream
    - Through the permeable membrane
    - Into counter-current argon flow
  - Efficiency
    - Oxygen (from water) containing polyatomics decreased ~10-100X
    - Interfered analyte response increased ~10X
      - Due to decreased "loading" of the plasma

9

Laser Ablation of Solids

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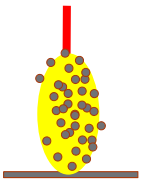
- Much more detail coming up from Andrew Duffin and Rick Russo
- Ablation – the loss of surface material by abrasion, evaporation, melting, etc.
  (think space re-entry vehicle heat-shield)



- Sequence
  - Laser pulses enter sample
  - Rapid heating – plasma formation
  - Thermal expansion (explosion) of material from the surface
  - Fine particles may coalesce, large particles may fall out
  - Particles are entrained in the sweep gas and transported to the ICP

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Laser Ablation of Solids (contd.)

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- Wavelengths
  - IR, visible, and UV have been used
  - Choice depends on sample material characteristics, analytical performance needs, and laser
- Pulse lengths
  - ns, ps, fs are available
  - Choice depends on sample material characteristics, analytical performance needs, laser, and *budget* (!)
- Pulse energy (J/cm^2 per pulse)
  - Need to exceed "damage threshold" for that material
  - Choice depends on sample material characteristics, analytical performance, and laser
- Performance metrics covered soon by A. Duffin and R. Russo
  - Sample utilization efficiency (SUE), precision vs. solution, etc.
  - Fractionation effects, spatial resolution, etc.

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Alternative Sample Introduction Techniques (selected)

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- Gas
  - Gas Chromatograph (usually capillary columns)
    - Few mL/min of carrier gas (H_2 or He) in to the nebulizer stream
    - Samples – volatile molecules containing ICPMS sensitive atoms
      - Organo-tin, -mercury, -arsenic, -selenium, etc.
        - J. Cavalheiro, H. Preud'homme, D. Amouroux, et al., "Comparison between GC-MS and GC-ICPMS using isotope dilution for the simultaneous monitoring of inorganic and methyl mercury, butyl and phenyl tin compounds in biological tissues", Anal. Bioanal. Chem., 2014, **406**, 1258
      - Halogenated organics (Cl, Br, I)
        - C. Peters, S. Pechtl, J. Stutz, "Reactive and organic halogen species in three different European coastal environments", Atmos. Chem. and Phys., 2005, **5**, 3357-3375
  - Direct gases
    - Gas sample stream is mixed with Ar nebulizer flow
      - Impurities in high purity gases
    - Atmospheric air is pumped through a membrane gas-exchanger
      - Removes air components and replaces them with argon
      - Airborne solid aerosols – pollution, exhausts, etc.
        - K. Nishiguchi, K. Utani and E. Fujimori, "Real-time multielement monitoring of airborne particulate matter using ICP-MS instrument equipped with gas converter apparatus", J. Anal. At. Spectrom., 2008, **23**, 1125-1129

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Alternative Sample Introduction Techniques

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- Liquid
  - High Pressure Liquid Chromatography (HPLC)
    - Usually aqueous eluents with some organic modifiers
      - May have to add oxygen or other gas to handle the organic component
      - Nebulize as above
    - Samples
      - Proteins and peptides
        - C. Carazzone, R. Rami, S. Pergantis, "Nanoelectrospray ion mobility spectrometry online with inductively coupled plasma-mass spectrometry for sizing large proteins, DNA, and nanoparticles", Anal. Chem., 2008, **80**, 5812-5818
      - Other organics containing ICPMS sensitive elements
        - R. Juskelis, W. Li, J. Nelson, Jenny; et al., "Arsenic Speciation in Rice Cereals for Infants", J. Agricult. and Food Chem., 2013, **61**, 10670-10676
  - Ion Chromatography
    - Eluent ionic strength may be a problem
      - Eluent cations and/or anions may interfere
      - Nebulize as above
    - Samples – low concentration cations and anions
      - H. Biester, D. Selimovic, S. Hemmerich, S, et al., "Halogens in pore water of peat bogs - the role of peat decomposition and dissolved organic matter", Biogeosciences, 2006, **3**, 53-64

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Alternative Sample Introduction Techniques (contd.)

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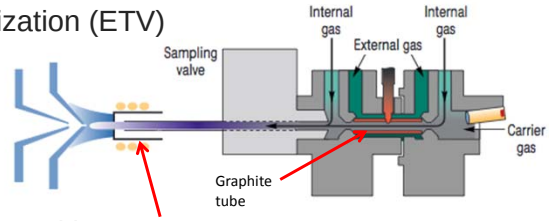
- Solids
  - Electro-thermal vaporization (ETV)

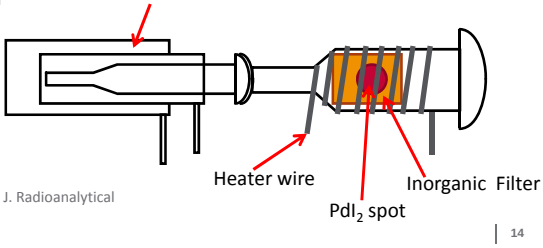
Adapted from R. Thomas, "Beginner's Guide to ICP-MS Part XIV — Sampling Accessories, Part II", Spectroscopy, 2003, **18**(2), 42-53 (www.spectroscopyonline.com)



  - Electro-thermal decomposition

$$2\ HI + PdCl_2 \longrightarrow PdI_2\downarrow + 2\ HCl$$

$$PdI_2 \xrightarrow{360\,^{\circ}C} Pd + I_2\uparrow$$



O. T. Farmer III, C. J. Barinaga, D. W. Koppenaal, J. Radioanalytical and Nuclear Chemistry, 1998, **234**, 153-158.

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Alternative Sample Introduction Techniques (contd.)

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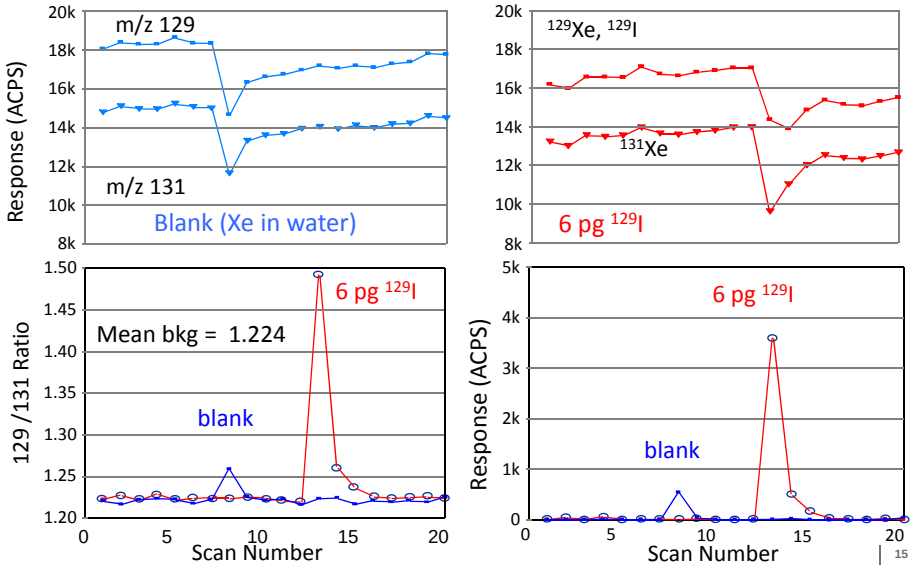

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Alternative Sample Introduction Techniques (contd.)

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- Solids
  - Direct laser ablation in air (no ablation cell)
    - Atmospheric air is pumped through a membrane gas-exchanger
      - Removes air components and replaces them with argon
    - Samples - solid aerosols from laser ablation of solids
      - Objects too large to fit in ablation cell
      - Art work, archeological samples, etc.
    - R. Kovacs, K. Nishiguchi, K. Utani and D. Günther, Development of direct atmospheric sampling for laser ablation-inductively coupled plasma-mass spectrometry, J. Anal. At. Spectrom., 2010, **25**, 142–147
- There are several specialty introduction techniques in the literature but beyond today's scope

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Additional Thoughts

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- Sample memory
  - Elements from previous samples may carry over to the current sample
  - Problem for very low-concentration samples
  - Must always consider the possibility
  - Consider separate components used only for the special analysis (tubing, nebulizer, spray chamber, cones, etc.)
  - E. Paredes, D. Asfaha, E. Ponzevera, et al., "MC-ICPMS isotope ratio measurements using an ultra-low flow sample introduction system", J. Anal. Atomic Spectrom., 2011, **26**, 372-1379
  - J. Clausen, M. Ketterer, A. Bednar, et al., "Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples", Int'l. J. Environ. Anal. Chem., 2010, **90**, 773-783
- Sample introduction techniques
  - Must be considered during the design of an analytical procedure
  - Are materials compatible with sample matrix components?

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Conclusion

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- The growing appreciation of the elemental and isotope ratio analysis power of the ICPMS is driving it into
  - Applications with smaller sample sizes and lower analyte concentrations
  - Many non-traditional, elemental applications
- The trick will be getting your sample to the ICP
  - Here is where your imagination and creativity can find outlet
  - However - if you can imagine it, somebody has probably tried it
  - It is challenging to be first
- Questions

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ICP-MS Short Course

Overview of Inductively Coupled Plasma Mass Spectrometry for Elemental Analysis

CHRISTINA SORENSEN
Pacific Northwest National Laboratory

June 17, 2014

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U.S. DEPARTMENT OF ENERGY

PNNL-SA-103115

Outline

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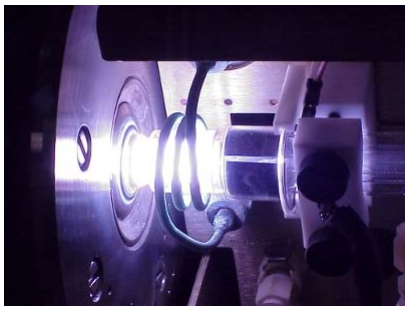
- Introduction
- Quantities of Interest
- Sample Collection and Preparation
- Corrections, Calibration, Statistics
- Instrumentation – Types and Features
- Analytical Examples
- Bibliography



Separation/sample introduction → ICP-MS

Applications of Elemental Analysis

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- Medical
- Environmental
- Geological
- Semiconductor
- Archeology
- Nuclear
- Petroleum
- Food
- Other industry

Photo courtesy of USGS

Photo courtesy of NASA

Additional information in *Applications of Inorganic Mass Spectrometry*, by John R. de Laeter, John Wiley and Sons, 2001.

3

IONIZATION IN ICP

$M^+/(M^+ + M)$ (%)

H 0.1																	He
Li 100	Be 75											B 58	C 5	N 0.1	O 0.1	F 9e-4	Ne 6e-6
Na 100	Mg 98											Al 98	Si 85	P 33	S 14	Cl 0.9	Ar 0.04
K 100	Ca 99,1	Sc 100	Ti 99	V 99	Cr 98	Mn 95	Fe 96	Co 93	Ni 91	Cu 90	Zn 75	Ga 98	Ge 90	As 52	Se 33	Br 5	Kr 0.6
Rb 100	Sr 96,4	Y 98	Zr 99	Nb 98	Mo 98	Tc	Ru 96	Rh 94	Pd 93	Ag 93	Cd 85	In 99	Sn 96	Sb 78	Te 66	I 29	Xe 8.5
Cs 100	Ba 91,9	La 90,10	Hf 96	Ta 95	W 94	Re 93	Os 78	Ir	Pt 62	Au 51	Hg 38	Tl 100	Pb 97,0.01	Bi 92	Po	At	Rn
Fr	Ra	Ac															

Ce 96,2	Pr 90,10	Nd 99*	Pm	Sm 97,3	Eu 100*	Gd 93,7	Tb 99*	Dy 100*	Ho	Er 99*	Tm 91,9	Yb 92,8	Lu
Th 100*	Pa	U 100*	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

$\%M^{+2}$

$T = 7500\ K \quad n_e = 1 \times 10^{15}\ cm^{-3}$

Courtesy of Sam Houk

*These elements also make M^{+2}

Elemental Analysis – Ideal Method Requirements

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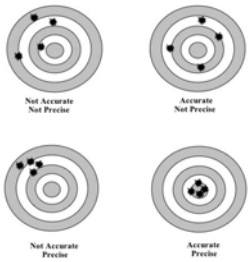
- Comprehensive elemental analysis
  - Quantitative
- Determination over wide & variable concentration range
  - May be instrument dependent
- Matrix matched standard
- Appropriate and frequent "blank" measurements
- No interference
- Analyzes small samples
- Applies to many sample types and matrices
- Rapid analysis
- Good precision and accuracy

Image courtesy of NOAA



5

Real-world Samples

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- Matrix match not possible for all samples
  - Standard addition
  - Internal standard/reference/Isotope ratio (Kellen)
- Interferences in m/z region of interest
  - Magnetic sector for higher resolution
  - Separation/preparation
- Broad concentration range & many analytes present
  - Targeted approach needed?
- What do you do for a true unknown?
  - Dilute/ shoot—address what needed—retry
  - Multi-element standard/ modify method
  - Re-run with optimized method

Photo courtesy of NASA

6

Sample Considerations

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Separation/sample introduction → ICP-MS

- Objectives of study
- Sample state, concentration, matrix
- Preparation/instrument
- Target analytes
  - single, multiple
- Standards needed
- Resolution and accuracy required (instrument performance?)
- Statistical rigor (metrics)
  - robust, reproducible, LOD, sensitive

Adapted from S Nelms, ed. 2005, *ICP Mass Spectrometry Handbook*, CRC Press.

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Sample Collection and Preparation

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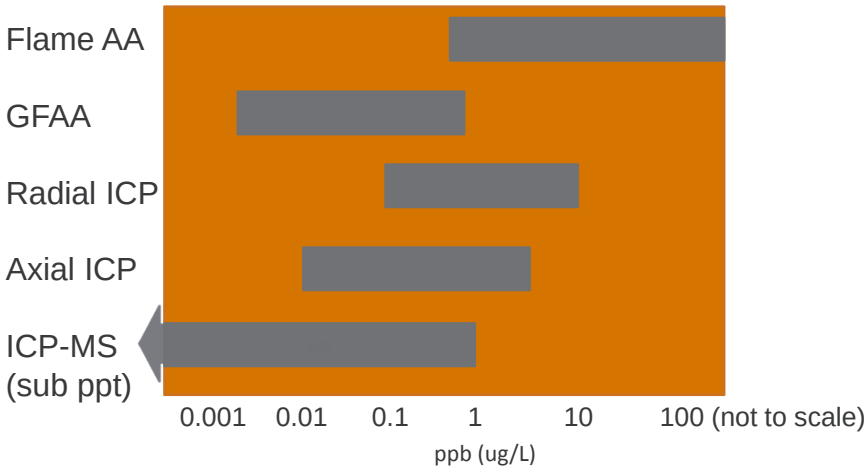
- Collect representative sample(s)
- Ash and digest as required
  - may not completely go into solution
  - volatile species (Se, As) hazard during dissolution
- Group and elemental separations

Separation/sample introduction → ICP-MS

- High accuracy/precision typically requires highly purified sample (only the element[s] of interest present)
  - Nanograms of Pb or Hg can interfere with femtogram level ICP-MS determinations of U and Pu

8

Spectroscopy Detection Limits



ICP-OES versus ICP-MS

ICP-OES

ICP-MS

	ICP-OES	ICP-MS
Sample size:	0.1- 1 g	0.01-0.1 g
Optimum Detection range:	50 ppm- 50%	0.1 ppm- 1% wt
Typical Application:	Precise determination known constituents	Trace and ultra-trace detection impurity studies

Photo and information courtesy of: EAG and Thermo

ICP-MS Capabilities

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Detection Limits	0.1 - 10 ppt routine 10 ppq Some insts. Usually blank-limited
Total Solutes	0.1% usually OK 1% usually problems unless use flow injection
Precision	3% rsd routine 1% good 1% routine w. int. stds.

Accuracy comparable to precision if compensate for interferences

Courtesy of Sam Houk,
Department of Chemistry, Iowa State University

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Interferences (Rel. to ICP-AES)

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- Spectral less frequent than atomic emission spectroscopy (AES)
- Overlap less severe, more predictable, easier to correct
- Matrix effects worse in ICP-MS
  - Plugging
  - Change of signal (usually loss)

Courtesy of Sam Houk,
Department of Chemistry, Iowa State University

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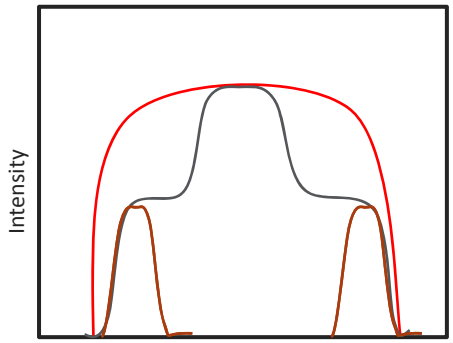
Resolution and Interference



Cartoon for signal

Low mass resolution-
no distinction mass and interference

Medium mass resolution- (Q ICPMS)
undefined regions with overlap

High mass resolution- (MS ICPMS)
mass and interference resolved
-ArO and Fe distinct

Adapted from S Nelms, ed. 2005, *ICP Mass Spectrometry Handbook*, CRC Press.

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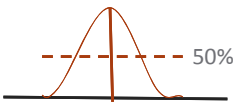
Instrument Performance Features

- Separation of adjacent peaks
  - Resolution (full width half maximum [FWHM] or full-width [FW] at 10%)
  - Abundance sensitivity
  - Efficiency loss at high resolution



Cartoon

- Ion Species
  - Atomic, molecular and polyatomic
  - Singly vs. multiply charged

Resolution	Nuclide	Polyatomic ion
2502	$^{56}Fe^{+}$	$^{40}Ar^{16}O^{+}$
7775	$^{75}As^{+}$	$^{40}Ar^{35}Cl^{+}$

Adapted from Jakubowski, N., J. Anal. At. Spectrom., 2011, 26, 693–726

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Mass Spectrometers
Inductively Coupled Plasma MS (ICP-MS)
– Quadrupole Mass Analyzer

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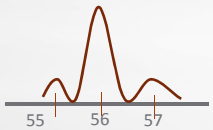
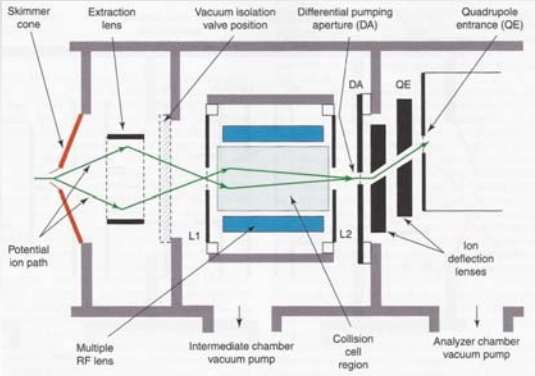
- Broad elemental coverage
- Flexible sample introduction
- 0.1% to 1% precision
- 0.01% efficiency or better
- Small footprint
- Lower cost ($150K)

$^{56}Fe^{+}$ + $^{40}Ar^{16}O^{+}$



Cartoon depiction



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Mass Spectrometers
Inorganic Elemental/Isotopic

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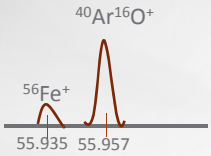
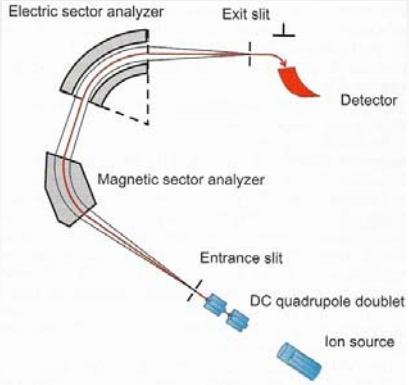
- Sector Field MS-single and multicollector



Cartoon depiction

- High sensitivity/resolution
- Excellent precision/accuracy
- Large footprint
- High cost ($1000K)



Reproduced with permission of Elsevier Science and Technology. Diane Beauchemin and Dwight E Matthews, eds. 2010. *Encyclopedia of Mass Spectrometry*, Volume 5, Elsevier, Amsterdam.

Comparison

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Isotope Ratio	Method	Precision	Sample Size	Efficiency	Reference
*$^{235}U/^{238}U$ ~1	ICP-QMS	0.028%	255 pg	Not Avail	Platzner
*$^{235}U/^{238}U$ ~1	DF-ICP-MS	0.026%	255 pg	Not Avail	Becker
---	---	---	---	---	---
$^{238}U/^{235}U$ = 137.9	ICP-QMS	0.07 %	663 pg	0.13 %	PNNL
$^{235}U/^{234}U$ = 160.5	ICP-QMS	3.8 %	9.42 fg	0.15 %	PNNL

*From: J. Sabine Becker and Hans-Joachim Dietze,
"Precise and accurate isotope ratio Measurements by ICP-MS", *Fres. J. Anal. Chem*. (2000) 368, 23-30.

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Quantities of Interest - Uncertainty

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- Significance of comparisons requires method validation and confidence in uncertainty estimates
  - "Signatures" studies must address all sources of uncertainty
  - Address assumptions underlying sampling to data reporting
- Inter-comparability of measured quantities and uncertainties requires carefully prescribed procedures
  - Thorough QA/QC planning and implementation required
- All sources of uncertainty must be assessed
  - Systematic
  - Random – modeled vs. measured scatter ("excess" variability)
  - Thorough analysis of uncertainty – understand instrument better

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Quantities of Interest – Measured Values

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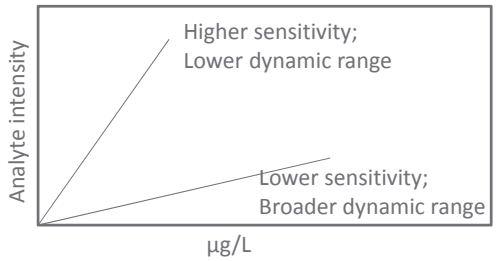
- Concentrations or ratios indicative of processes or materials of interest
- Elemental
  - Qualitative composition – "external calibration" – 10% accuracy
  - Quantitative analysis – 1% accuracy or better
    - Absolute concentrations, inter-elemental ratios
    - Requires accurate measurement/ spike/ standard addition approach



Detector limits sensitivity and influences signals observed

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Calibration Methods

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- Internal standards-blanks and samples have equal amount of standard (not originally present); ratio of analyte intensity to standard used for calibration curve
- Standard addition (useful when no certified material available)—compensates for matrix effects by adding known and increasing amounts of analyte to subsamples; frequently used
- Isotope dilution (refer to the sample preparation and protocols presentation)—robust strategy where the sample is spiked with an enriched isotope for each analyte
- External calibration- when minimal matrix effects exist or qualitative information desired

Additional information in Agatemar, C., Analytica Chimica Acta 706 (2011) 66-83.

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Corrections and Calibration

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- Corrections
  - Spectral Interferences, e.g., $^{238}U/^{238}Pu$, $^{235}UH^{+}/^{236}U$
  - Scattering tails (finite abundance sensitivity)
  - Non-spectral effects, e.g., matrix effect on ionization
  - Corrections using data "internal" to measurement is best
  - Blanks
- Calibration
  - Instrument response vs mass (mass bias)
  - Ion source fractionation (isotope ratio changes during analysis)
  - Multi-detector cross calibration
  - Gain stability of detectors

$$^{236}U \text{ counts} = (236/EMFC) - 235*HR - 238*(236/238)_{natU}$$

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QA/QC Is Expensive
Simplified Analytical Measurement Sequence

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- Acid Blank
- Reference material?
- Mass Bias Standard
- Acid Blank
- Reagent Blank 1

x3

- Acid Blank
- Mass Bias Standard
- Acid Blank
- Procedure Blank 1

x3

- Acid Blank
- Mass Bias Standard
- Acid Blank
- Sample 1 (Unknown)
- Etc.

x10

10 Samples

Total Number of Runs	67
Samples =	10
Acid Blanks =	34
Mass Bias =	17
Procedure Blank =	3
Reagent Blank =	3

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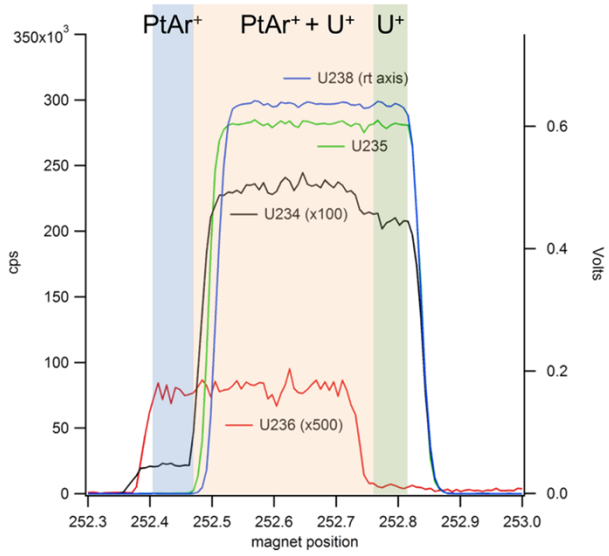
Mass Resolve U from Interference



Medium resolution
↓
No interference

Representative examples

- Nuclear forensics- ICP-OES/ICP-MS in forensics
- Archeology- Finding a matrix match and performing QA/QC

Discovery

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- Safe containing ~400 mg of Pu in glass jug uncovered by WCH during decontamination and decommissioning (D&D) operations in December 2004.

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Nuclear Forensics Example

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- Sample consisted of ~400 mL of a white slurry
- "LaF_3 for Recovery…" written on bottle
- Preliminary field gamma analysis detected only ^{239}Pu (i.e., potentially separated, weapons-grade, Pu)
- ARC Group at PNNL took receipt of half of the liquid and about 4% of the solid in May 2006
- The group characterized the sample in late 2007

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Representative Preparation

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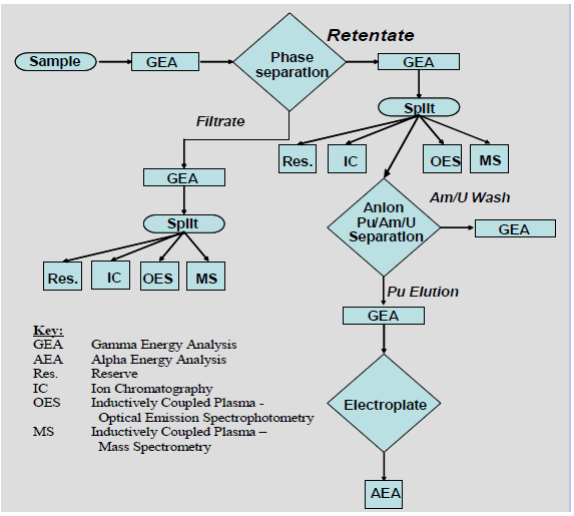

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History of Reprocessing at Hanford

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T-Plant, Hanford, Washington
(World's 1st industrial scale reprocessing facility)

http://www.mbe.doe.gov/me70/history/t_plant.htm

- US Process Methods
  - Bismuth Phosphate (1944-1956)
    - Precipitation
    - Batch
  - REDOX (1951-1966)
    - Solvent Extraction
    - Continuous
  - PUREX (1956- early 1990's)
    - Solvent Extraction
    - Less volatile / better

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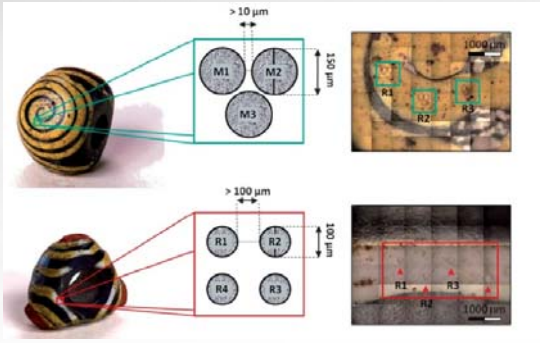
Archeological Application

- Bronze age beads
  - Matrix matching
  - Reproducibility/method robustness
  - Measurement variability



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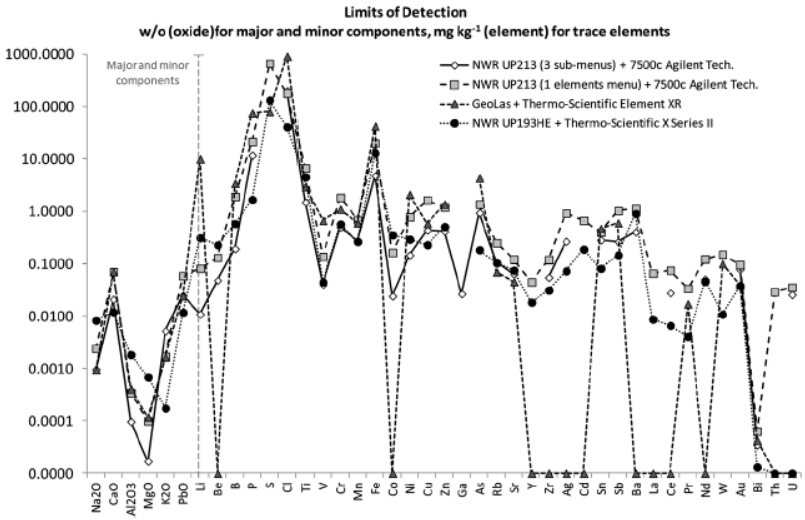
Archaeological Use Example



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Summary

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- Measurement Methods
  - Sample Collection and Preparation
  - Concentrations, ratios, uncertainties, assumptions
  - Corrections and calibration
- Instrumentation
  - Types and Features
- Highlights of applications
  - Examples

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Acknowledgements

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- Jon Schwantes
- Thermo
- EAG
- RSC

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Thank you!

Questions?

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Web Resources

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- Evans Analytical Group www.eag.com
- Perkin Elmer http://www.perkinelmer.com/PDFs/downloads/BRO_WorldLeaderAAICPMSICPMS.pdf
- Spectroscopy online: http://www.spectroscopyonline.com/
- Thermo:http://www.thermoscientific.com/

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Bibliography – Conferences and Short Courses

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- International Conferences
  - Measurements and Applications in Radiochemistry, held every three years, Kona, Hawaii.
  - International Nuclear Materials Management
  - Winter Plasma Spectrochemistry Conference
  - Federation of Analytical Chemistry and Spectroscopy Societies
  - American Geophysical Union
- Short Courses
  - Federation of Analytical Chemistry and Spectroscopy Societies
  - American Society for Mass Spectrometry
  - American Chemical Society
  - Institute of Nuclear Materials Management

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ICP-MS Short Course

Sample Preparation and Protocols

KELLEN SPRINGER

Pacific Northwest National Laboratory

June 17, 2014

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U.S. DEPARTMENT OF ENERGY

PNNL-SA-103061

Questions from YOU! (The Audience)

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- "What should I be aware of during sample preparation?"
- "…I am also interested in learning more about sample preparation, various sample introduction methods, detection limits, and data reduction."

Sample Preparation

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Why bother?

- In the case of a bulk analysis (liquid introduction), sample needs to be a liquid!
- Remove/minimize interferences at masses of interest.
  - Atomic isobars
  - Poly-atomic isobars
  - Reduced sample utilization efficiency due to “plasma loading” effects.
- Inter-element ratios most accurately measured by isotope dilution (addition of a spike).

3

Sample Preparation Can Take Many Different Approaches

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- Largely dependent on the sample matrix and analyte of interest
  - Soils
  - Minerals
  - Whole Rocks
  - Water (seawater, fresh, etc.)
  - Others
- All matrices need to be in a form suitable for introduction to the plasma source

4

Typical Workflow for Isotope Dilution Analysis of Solids in a Geochemical Application

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1. Separation of phases (required for "internal isochron" application, optional for most other purposes)
   1. Crushing
   2. Sieving
   3. Density (heavy liquids, Wilfley table, etc.)
   4. Magnetic susceptibility (Frantz, etc.)
   5. Visual examination
2. Prepare sample(s) for chemical isolation and liquid introduction to plasma source
   1. Ashing (wet or dry, depending on matrix and lab capabilities)
   2. Acid digestion

5

Typical Workflow for Isotope Dilution Analysis of Solids in a Geochemical Application (contd.)

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3. Spike samples *(isotope dilution analysis)*
   - To determine the concentration of an element in a sample isotope dilution is a favored approach
   - The spike is of the same chemical element as the element of interest in the sample, but has distinct isotopic composition
   - A known amount of spike is added to the sample <u>before</u> chemical separations
     - Concentration of the spike must be known
     - Quantity of spike added to the sample must be known
     - Isotopic composition of the spike must be known
   - Chemical equilibration between spike and sample is required
   - Isotopic composition of the element of interest in the sample must be known (measured or known *a priori*)

6

Typical Workflow for Isotope Dilution Analysis of Solids in a Geochemical Application (contd.)

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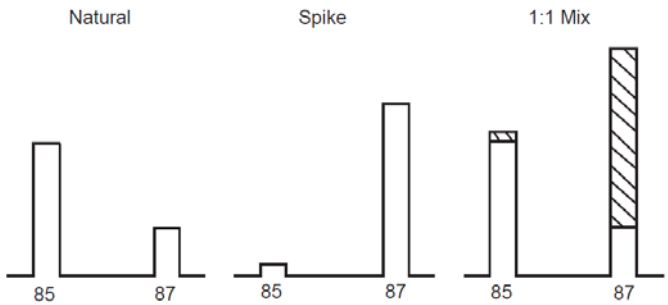
- If concentrative properties are the only values of interest, the quantity of the spike added is planned such that the major isotope in the spike and the major isotope in the sample is near unity (1:1)
- The ID method is a "definitive method" (high accuracy and traceability)



Typical Workflow for Isotope Dilution Analysis of Solids in a Geochemical Application (contd.)

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4. Chemically isolate elements of interest
   - Minimize atomic isobars
     - ^{87}Rb from ^{87}Sr
     - ^{142}Ce from ^{142}Nd
     - ^{204}Hg from ^{204}Pb
     - Any beta decay nuclides!
     - Doubly charged species
   - Minimize molecular isobars
     - Argides
     - Oxides
     - Nitrides
     - Doubly charged species

Typical Workflow for Isotope Dilution Analysis of Solids in a Geochemical Application (contd.)

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5. Transpose to appropriate aqueous matrix for introduction to ICP source
   - 2%-HNO_3 (e.g. lanthanides, group 1 & 2 elements)
   - 2%-HNO_3 + 1%-HF (e.g. HFSE, Ge)
6. Design an analytical method suited for the analysis of the element of interest.
   - Nd requires monitoring both ^{140}Ce and ^{147}Sm.
     - ^{140}Ce, ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{147}Sm, ^{148}Nd, ^{150}Nd
   - Sr requires monitoring ^{85}Rb (not a bad idea to monitor 86.5 on occasion to verify minimal/no doubly charged Yb)
     - ^{84}Sr, ^{85}Rb, ^{86}Sr, ^{87}Sr, ^{88}Sr

9

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Let's take a look at a real "internal isochron" sample preparation scheme

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Parent-daughter Schemes Typically Used for Isochron Age Dating

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- $^{87}Rb \longrightarrow {}^{87}Sr$; $t_{1/2} = 48.8 \times 10^{9}$ years
- $^{147}Sm \longrightarrow {}^{143}Nd$; $t_{1/2} = 1.06 \times 10^{11}$ years
- $^{176}Lu \longrightarrow {}^{176}Hf$; $t_{1/2} = 3.78 \times 10^{10}$ years

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Fundamental Radioactive Decay Equations

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- $$D^* = N\left(e^{\lambda t} - 1\right),$$
$$D = D_0 + N(e^{\lambda t} - 1)$$
$$t = \frac{1}{\lambda}\left[\frac{D - D_0}{N}\right] + 1$$

$D^* = stable\ radiogenic\ daugter\ atoms$

$N = Parent\ atoms$

$D = total\ stable\ daughter\ atoms$

$D_0 = stable\ daugter\ atoms\ initially\ present\ in\ system$

$\lambda = decay\ constant$

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Fundamental Radioactive Decay Equations (contd.)

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- $$D^* = N\left(e^{\lambda t} - 1\right),$$
  $$D = D_0 + N(e^{\lambda t} - 1)$$

This we can measure, but it is difficult (hard to measure quantities of anything to [high] accuracy/precision).

$D^* = stable\ radiogenic\ daugter\ atoms$

$N = Parent\ atoms$

$D = total\ stable\ daughter\ atoms$

$D_0 = stable\ daugter\ atoms\ initially\ present\ in\ system$

$\lambda = decay\ constant$

13

Fundamental Radioactive Decay Equations (contd.)

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- $$D = D_0 + N(e^{\lambda t} - 1)$$

Let's make this a bit more amenable to mass spectrometry

$$\frac{^{143}Nd}{^{144}Nd} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_i + \frac{^{147}Sm}{^{144}Nd}(e^{\lambda t} - 1)$$

$$\frac{D}{S_{Di}} = \frac{D_0}{S_{Di}} + \frac{N}{S_{Di}}(e^{\lambda t} - 1)$$

$S_{Di} = stable, non - radiogenic\ nuclide$

$D^* = stable\ radiogenic\ daugter\ atoms$

$N = Parent\ atoms$

$D = total\ stable\ daughter\ atoms$

$D_0 = stable\ daugter\ atoms\ initially\ present\ in\ system$

$\lambda = decay\ constant$

14

Fundamental Radioactive Decay Equations (contd.)

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$$\frac{^{143}Nd}{^{144}Nd} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_i + \frac{^{147}Sm}{^{144}Nd}\left(e^{\lambda t} - 1\right),$$

$$t = \frac{1}{\lambda} ln\left[\frac{\frac{^{143}Nd}{^{144}Nd} - \left(\frac{^{143}Nd}{^{144}Nd}\right)_i}{\frac{^{147}Sm}{^{144}Nd}} + 1\right]$$

$$\frac{147Sm}{144Nd} = \left(\frac{Sm}{Nd}\right) * \frac{Ab147Sm\ * WNd}{Ab144Nd\ * WSm}$$

$\lambda = decay\ constant$ $\quad WSm = atomic\ mass\ of\ Sm$ $\quad WNd = atomic\ mass\ of\ Nd$

$Ab147Sm = isotopic\ abundance\ of\ 147Sm$

$Ab144Nd = isotopic\ abundance\ of\ 144Nd$

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Fundamental Radioactive Decay Equations (contd.)

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$$\frac{^{143}Nd}{^{144}Nd} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_i + \frac{^{147}Sm}{^{144}Nd}\left(e^{\lambda t} - 1\right),$$

$$t = \frac{1}{\lambda} ln\left[\frac{\frac{^{143}Nd}{^{144}Nd} - \left(\frac{^{143}Nd}{^{144}Nd}\right)_i}{\frac{^{147}Sm}{^{144}Nd}} + 1\right]$$

How do we know this? Cannot be directly measured.

$$\frac{147Sm}{144Nd} = \left(\frac{Sm}{Nd}\right) * \frac{Ab147Sm\ * WNd}{Ab144Nd * WSm}$$

$\lambda = decay\ constant$ $\quad WSm = atomic\ mass\ of\ Sm$ $\quad WNd = atomic\ mass\ of\ Nd$

$Ab147Sm = isotopic\ abundance\ of\ 147Sm$

$Ab144Nd = isotopic\ abundance\ of\ 144Nd$

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Isochron Definition

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- Isochron
  - A "common" technique for age dating events such as crystallization and metamorphism in geologic samples (rocks, minerals)
  - Internal, or mineral, isochrons determine the age of the event on a "hand sample" scale
  - Whole rock isochrons determine the age of the event on a more regional scale

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Isochron in a geologic application

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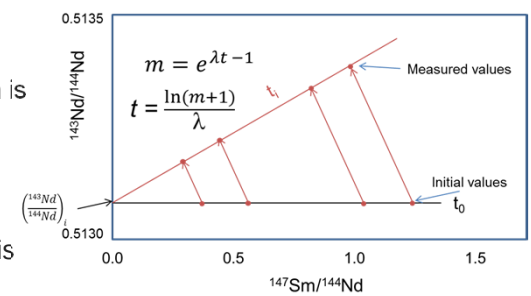
- Slope of the isochron, m, is related to the time elapsed since closure of the system.
- Precision of the isochron is highly dependent on the fractionation between parent and daughter elements at t_0 (need sufficient spread on x axis to define slope)
- In the case of internal (mineral) isochrons sufficient spread on x axis is achieved by clean mineral separations



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Sample Area
Aosta Valley Region, Italy

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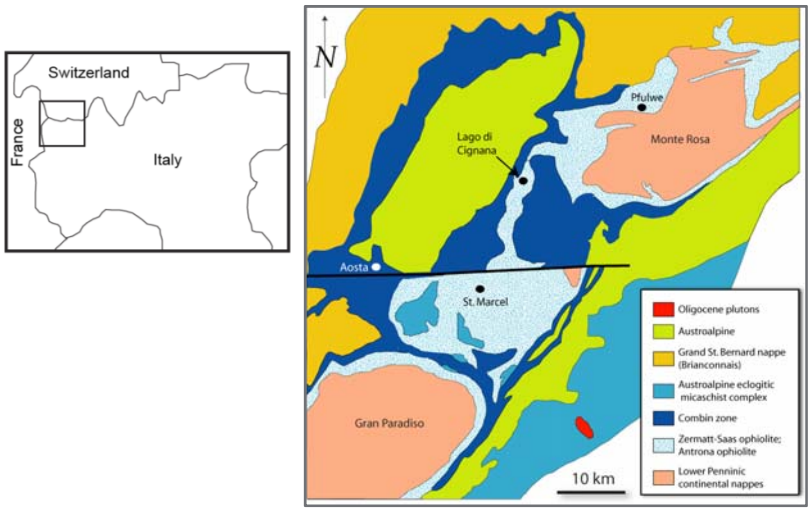

Modified after Dal Piaz, 2001

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Sample Area
Generalized Cross Section

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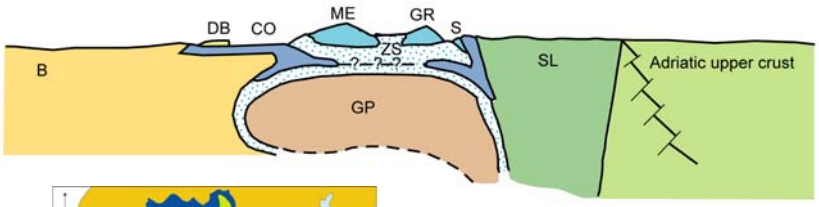

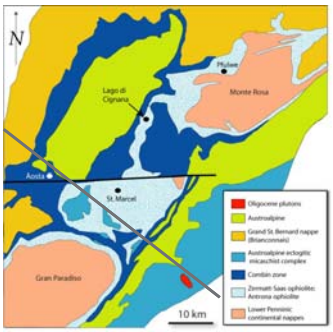

Modified after Dal Piaz, 1999

20

Monte Rosa

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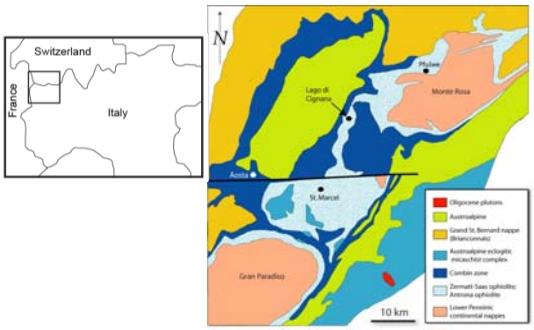

21

Sample Preparation
Garnet Isolation

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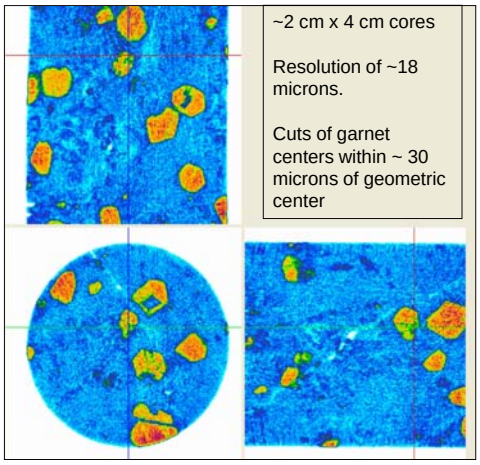
- Central cuts of Garnets aided by X-ray tomography



~2 cm x 4 cm cores

Resolution of ~18 microns.

Cuts of garnet centers within ~ 30 microns of geometric center

22

Clean Mineral Fractions are not Easy to Obtain

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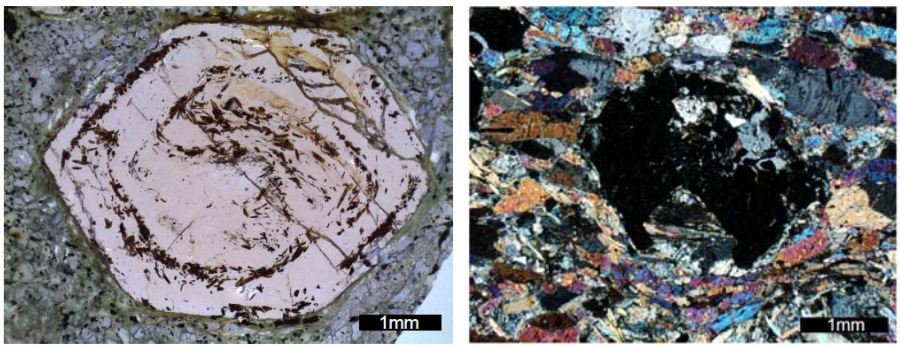

Left: Reflected light photomicrograph of garnet in blueschist (Zermatt-Saas ophiolite). Rutile is the abundant inclusion. Right: Refracted light, XP photomicrograph showing garnet with large inclusion of lawsonite pseudomorphs (paragonite and clinzoisite).

23

Inclusions Formed in Pro-grade Garnet Growth

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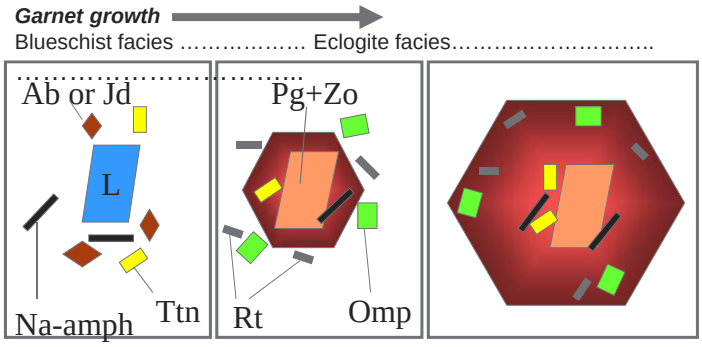
- Garnet growth and incorporation of minerals as inclusions during prograde metamorphism.



24

Laser-ablation ICP/MS for Sample Screening and Mineral Growth History

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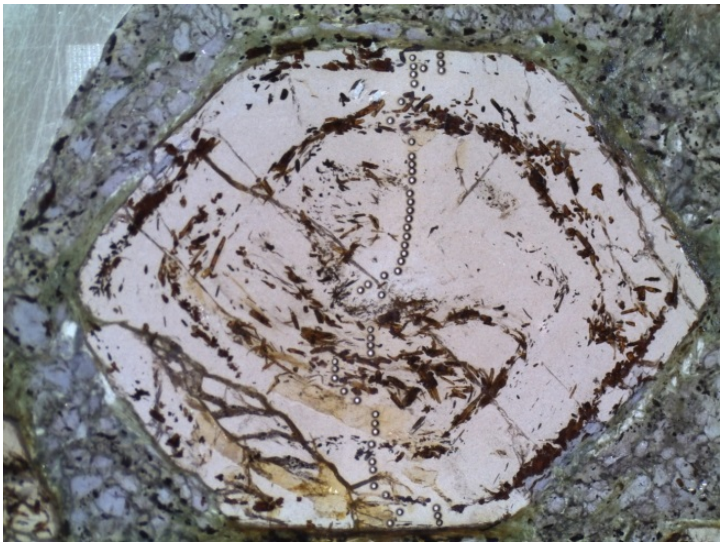

25

Laser-ablation ICP/MS for Sample Screening and Mineral Growth History (contd.)

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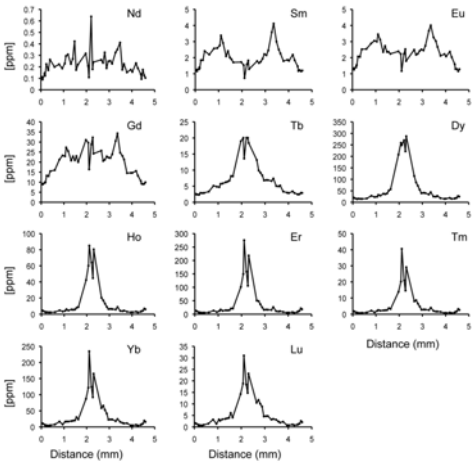
LA-ICP/MS transect across garnet

- Implies a Sm/Nd of ~5!
- If true, isochron could very precise!



26

Two-component Mixing and Effect on Isochron Uncertainty

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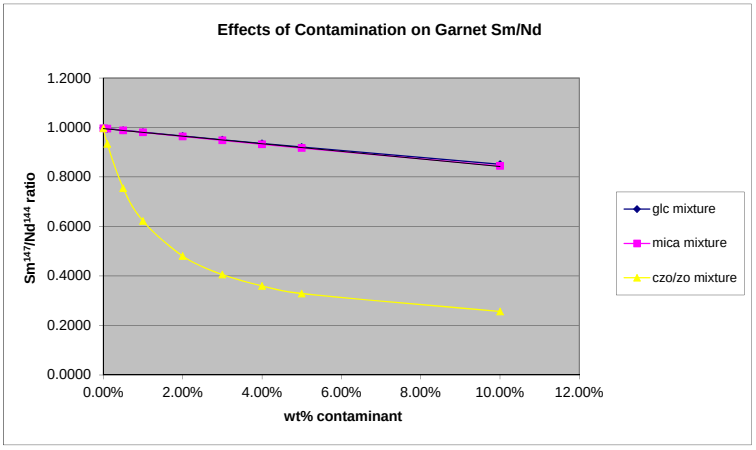

27

Two-component Mixing and Effect on Isochron Uncertainty (contd.)

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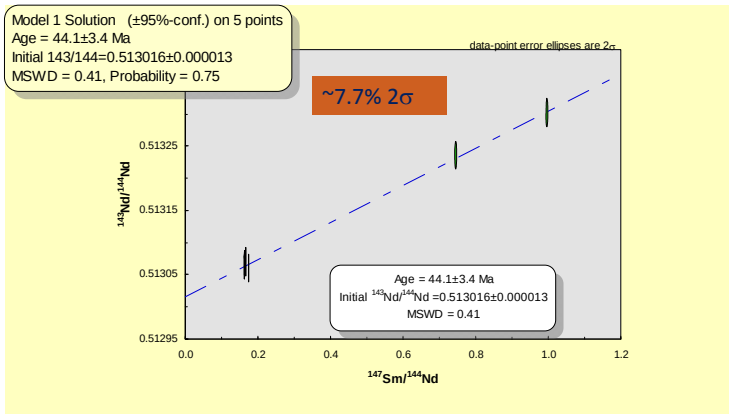

28

Two-component Mixing and Effect on Isochron Uncertainty (contd.)

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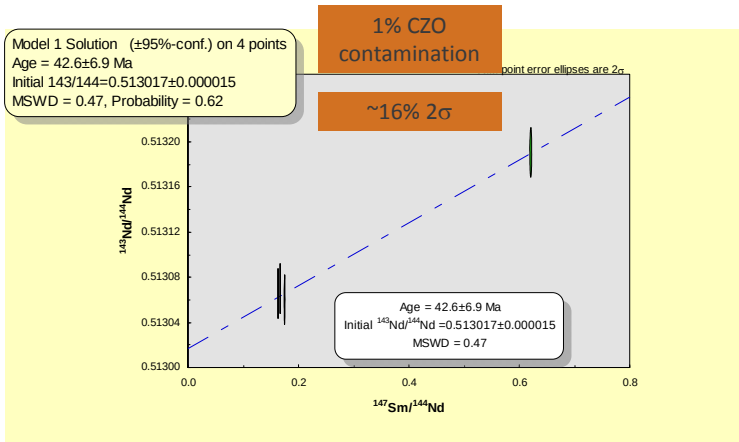

29

Sample Preparation is Very Important!

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- In the present example of an internal isochron on a garnet-bearing metamorphic assemblage, the mineral separation prior to chemical isolation and isotopic analysis is a significant contributor to overall age uncertainty.
- Sample preparation is extremely important!

30

Selective Dissolution of Less "Refractory" Mineral Phases is one Method to Remove Inclusions

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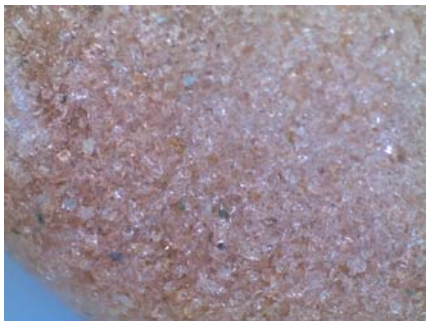
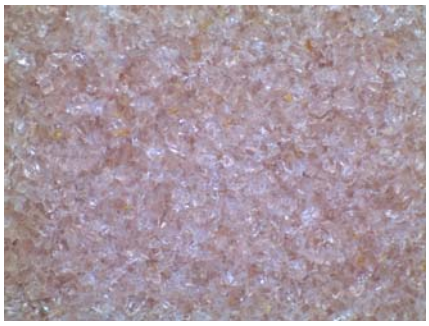


Garnet fraction after 2M-HF leach



Garnet fraction after 29M-HF leach

31

Selective Dissolution of Less "Refractory" Mineral Phases is one Method to Remove Inclusions (contd.)

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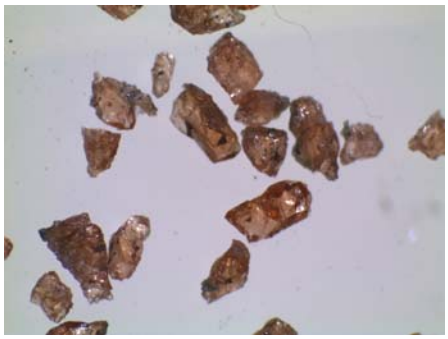
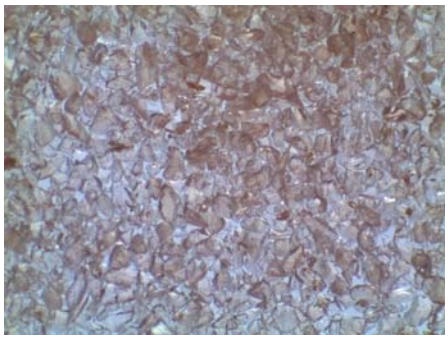


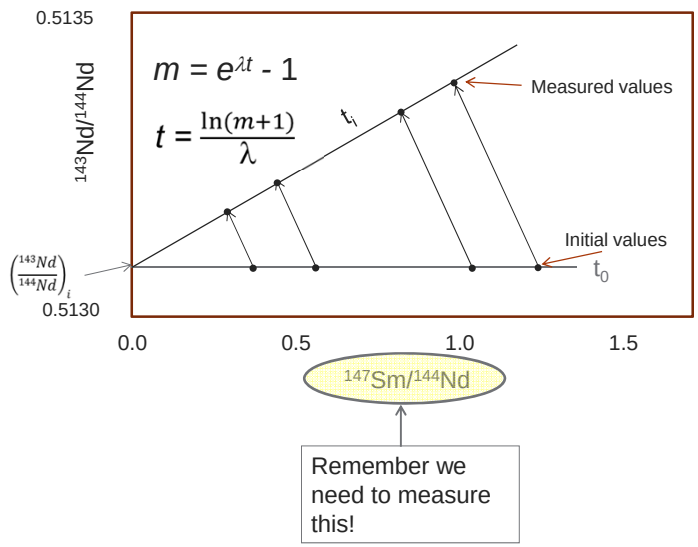
Garnet fraction before acid leach



Garnet fraction after acid leach

32

Sm-Nd Isochron Sample Preparation



Isotope Dilution

- Benefits
  - No "external calibration" curves required
  - Can be very accurate and precise
  - Accuracy of 1% "easy", 0.1% is obtainable
  - Losses during chemical processing do not bias results
- Sources of Uncertainty
  - Non-ideal proportions of sample to spike
  - Weighing uncertainties
  - Incomplete sample/spike equilibration
  - Uncertainties associated with X atoms in spike and isotope ratio

Isotope Dilution (contd.)

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- $N_{sample} = N_{spike} * \left(\frac{R_{spike,\frac{150}{144}} - R_{mix,\frac{150}{144}}}{R_{mix,\frac{150}{144}} - R_{sample,\frac{150}{144}}} \right) * \left(\frac{\Sigma\ of\ all\ isotope\ R_{sample} + 1}{\Sigma\ of\ all\ isotope\ R_{spike} + 1} \right)$

Uncertainty,

$$\frac{Var(Nsample)}{N_{sample}^{\ 2}} = \frac{\sigma_{Nspike}^{\ 2}}{Nspike^2} + \left[\frac{R_{spike}}{R_{spike} - R_{mix}}\right]^2 * \frac{\sigma_{Rspike}^{\ 2}}{Rspike^2} + \left[\frac{R_{mix}}{R_{mix} - R_{sample}}\right]^2$$

$$* \frac{\sigma_{Rsample}^{\ 2}}{Rsample^2} + \left[\frac{R_{mix}(R_{spike} - R_{sample})}{(R_{spike} - R_{mix})(R_{mix} - R_{sample})}\right]^2 * \frac{\sigma_{Rmix}^{\ 2}}{Rmix^2}$$

Maximize ($R_{spike} - R_{mix}$) and ($R_{mix} - R_{sample}$)

Minimize ($R_{spike} - R_{sample}$)

35

Isotope Dilution (contd.)

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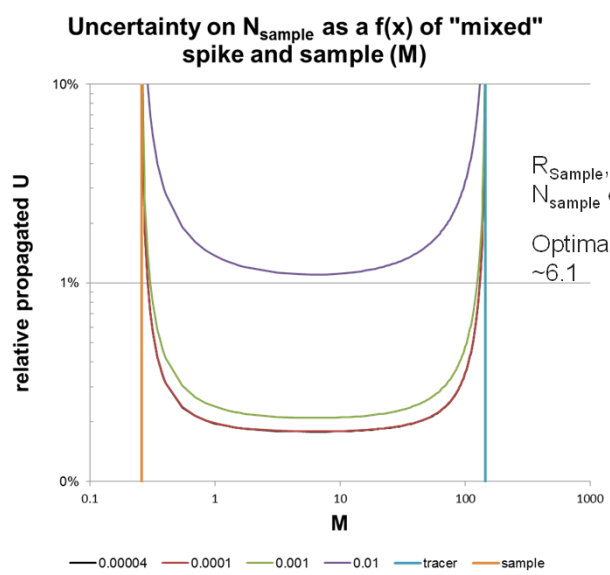

R_{Sample}, R_{Spike} and N_{sample} σ = 0.1%

Optimal "M" = ~6.1

36

Isotope Dilution (contd.)

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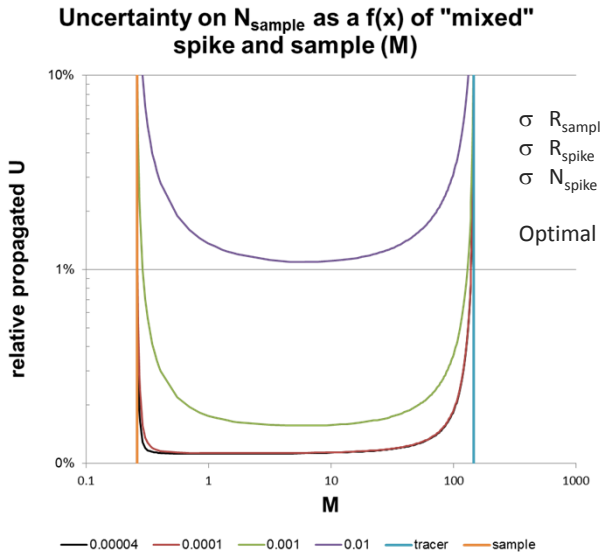

σ R_{sample} = 0.005%
σ R_{spike} = 0.05%
σ N_{spike} = 0.1%

Optimal M = ~1.1

Chemical Isolations

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Chemical separation schemes need to

1. Remove atomic isobars (e.g., ^{142}Ce)
2. Remove poly-atomic isobars (e.g. argides, nitrides, oxides, etc.)
3. Remove elements that (might) doubly charge (e.g. Ln's in Sr fraction)
4. Contribute little to know analyte of interest (chemical process blanks)

Chemical Isolations (contd.)

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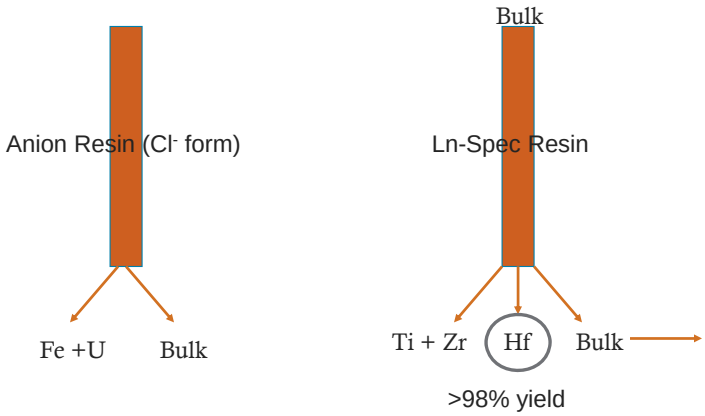
- Procedure developed such that Rb-Sr, Sm-Nd and Lu-Hf can be recovered on same aliquot (serial chemistry).



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Chemical Isolations (contd.)

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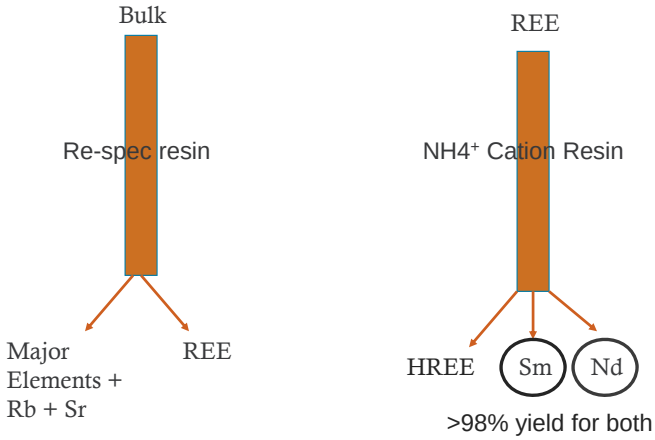
- Procedure developed such that Rb-Sr, Sm-Nd and Lu-Hf can be recovered on same aliquot (serial chemistry).



40

Sm-Nd Sample Preparation Chemical Separations

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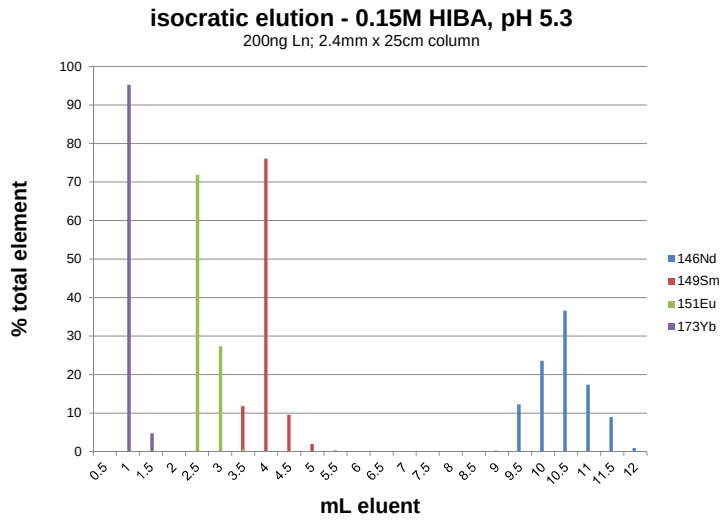

Mass Fractionation

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- Mass fractionation within the mass spectrometer does occur and is a significant obstacle for accurate isotope ratio data.
  - TIMS: Mass fractionation best described by approximations of Rayleigh distallation.
  - In practice, the Exponential law provides the most accurate correction,

$$R_A = r_a * \left(\frac{m_2}{m_1}\right)^{\beta},$$

$$\beta = \frac{ln\left(\frac{R_B}{r_b}\right)}{ln\left(\frac{m_3}{m_1}\right)}$$

R_A = corrected ratio R_B = normalizing ratio
r_A = measured ratio r_B = measured ratio
m_i = atomic mass

Mass Fractionation (contd.)

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- Mass fractionation within the mass spectrometer does occur and is a significant obstacle for accurate isotope ratio data.
  - ICP: ???
    - Varies with operating parameters
    - Space charge effects?
    - Originate in the plasma?
  - For our present example we will use exponential law and *internally* normalize.

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Mass Fractionation (contd.)

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- Internal Normalization
  - Mass bias determined in the sample solution
    - Invariant isotope pair (e.g. $^{146}Nd/^{144}Nd$)
    - Known isotope pair of an element added with similar mass
- External Normalization
  - Isotope ratio of interest measured in a standard solution
  - Standards “bracket” samples
  - Increases analysis time
  - Magnitude of mass bias can vary in the presence of dis-similar sample matrices

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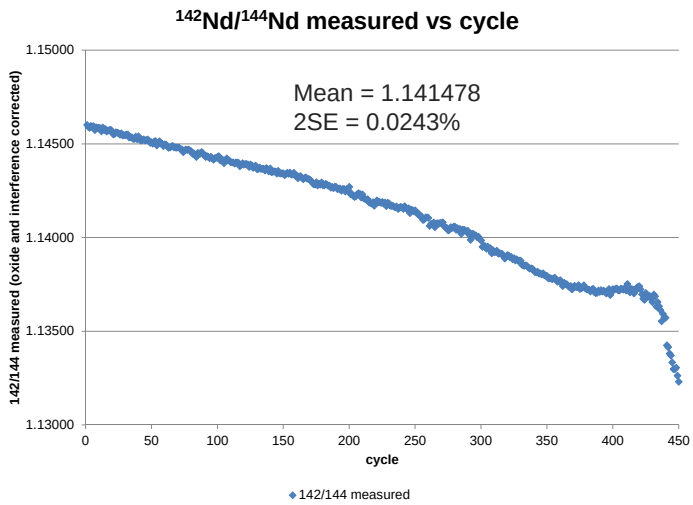
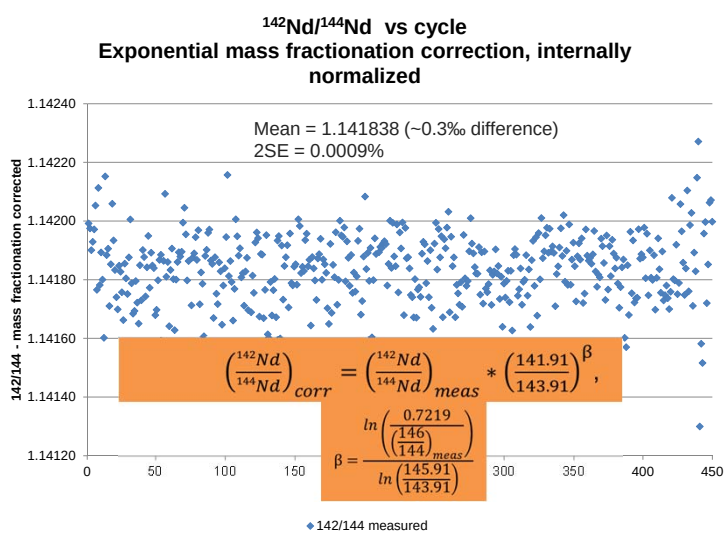
Mass Fractionation, TIMS Data



TIMS = thermal ionization mass spectrometry

Mass Fractionation, TIMS Data (contd.)



Sm-Nd Isochron

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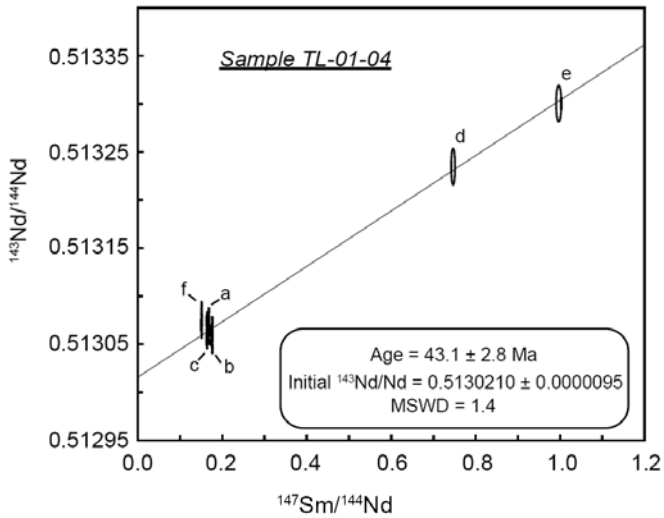
a: paragonite
b: clinozoisite
c: whole rock
d: bombed garnet
e: tabletop garnet
f: glaucophane



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Process Blank Subtraction

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- Process blanks need to accompany sample preparations
  - Minimized through
    - Clean-rooms
    - Ultra-clean reagents
    - Good lab practices!
    - Clean labware!
  - Hopefully small enough (sample:blank) to where blank subtraction is not necessary
- In the case of anthropogenic enrichments, “natural” blanks can become rather significant
- A blank subtraction can be thought of as a special two-component mixing line between sample and process blank.
- Y-intercept = blank subtracted value in atom fraction vs. 1/N space.

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Process Blank Subtraction (contd.)

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- $Ab_S = \left[\frac{N_T Ab_T - N_B Ab_B}{N_T - N_B}\right]$
  - T, S and N represent Total, Sample and Blank
  - N terms represent atom or molar quantities
  - Ab represents the abundance of isotope i (atom fraction).
- $\sigma^2{}_{Ab_S} = \left[\frac{N_B(Ab_B - Ab_T)}{(N_T - N_B)^2}\right]^2 * \sigma^2{}_{N_T} + \left[\frac{N_T}{N_T - N_B}\right]^2 * \sigma^2{}_{Ab_T} + \left[\frac{N_T(Ab_T - Ab_B)}{(N_T - N_B)^2}\right]^2 * \sigma^2{}_{N_B} + \left[\frac{-N_B}{N_T - N_B}\right]^2 * \sigma^2{}_{Ab_B}$

See Hayes, 1983.

49

Process Blank Subtraction (contd.)

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- $N_T Ab_T = N_S Ab_S + N_B Ab_B$
  - T, S and N represent Total, Sample and Blank
  - N terms represent atom or molar quantities
  - Ab represents the abundance of isotope i (atom fraction).
- Rearranging, and substituting $N_S = N_T - N_B$
  - $Ab_T = Ab_S - \left[\frac{N_B * (Ab_S - Ab_B)}{N_T}\right]$
  - Above equation is in the form of a line, $y = a + bx$, where Ab_S is the Y-intercept.

See Hayes, 1983.

50

Blank Subtraction by Linear Regression

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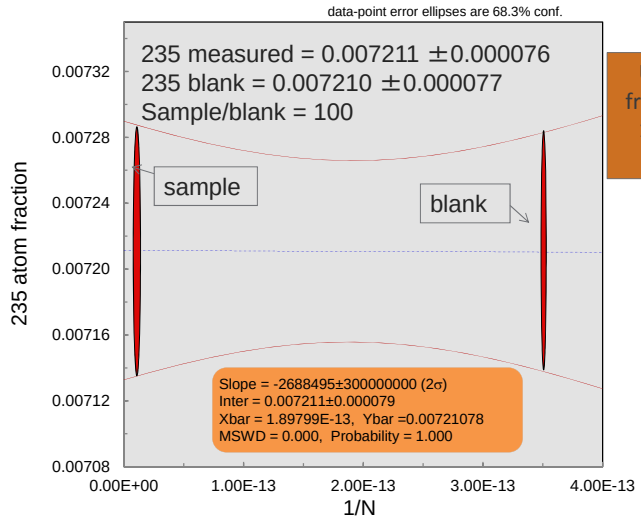

U increases from 1.05% to 1.1% (small increase).

51

Blank Subtraction by Linear Regression (contd.)

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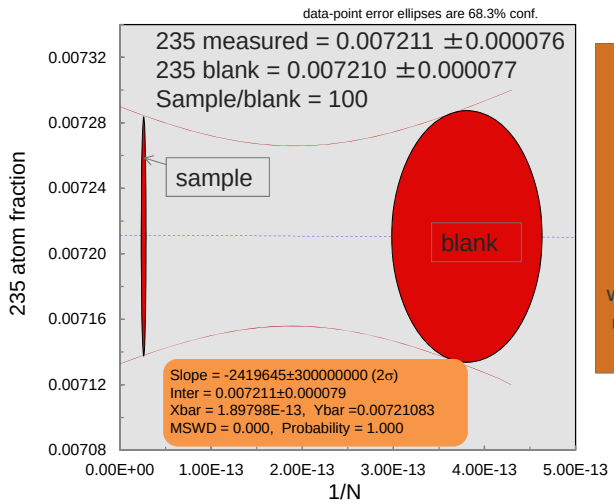

U increases from 1.05% to 1.1% (small increase).

Same as previous example, but with 100x more uncertainty on N_{blank}

52

Blank Subtraction by Linear Regression (contd.)

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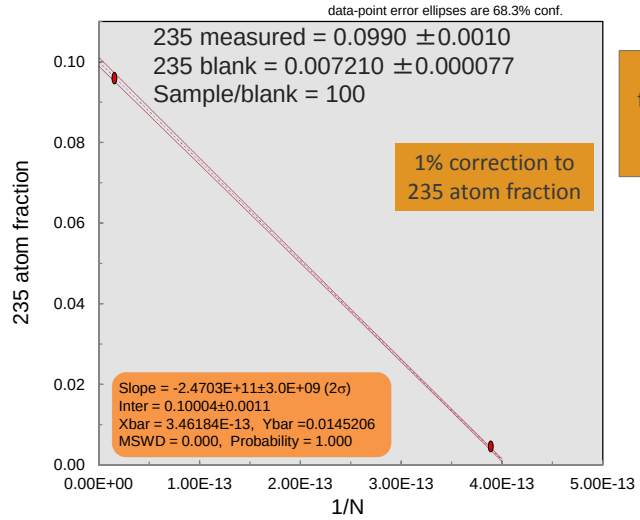

U increases from 1.01% to 1.10% (small increase)

53

Blank Subtraction by Linear Regression (contd.)

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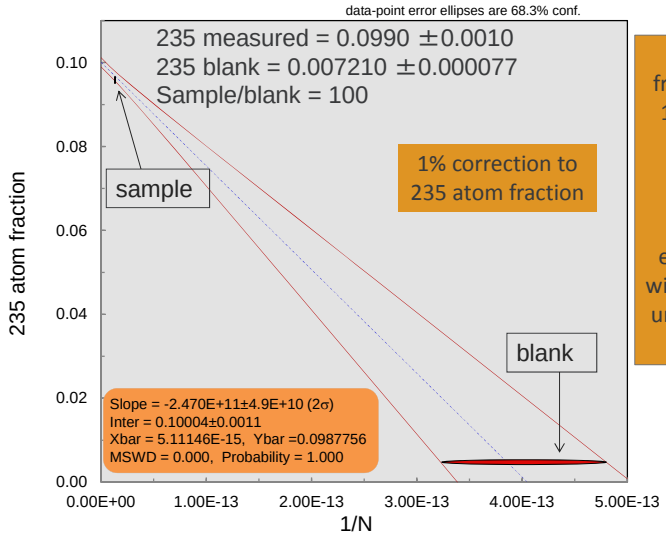
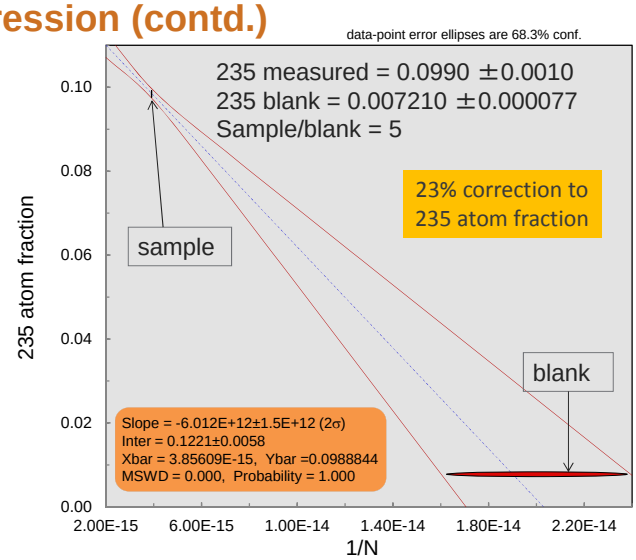


U increases from 1.01% to 1.10% (small increase).

Same as previous example, but with 100x more uncertainty on N_{blank}

54

Blank Subtraction by Linear Regression (contd.)



U increases from 1.01% to 4.75%

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ICP-MS Short Course

Multi-collector Methods and Examples

GARRET L. HART

Pacific Northwest National Laboratory

June 17, 2014

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U.S. DEPARTMENT OF ENERGY

PNNL-SA-103116

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Outline

- ICP-MS Overview
- Detector Setup
- Analytical Method
- Corrections and Calibration
- Analytical Examples

Thermo Scientific NEPTUNE *Plus* MC-ICPMS

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- Launched in 2009
- New multi-ion-counting options
- New jet interface option
- Other hardware revisions

3

PNNL "Neptune*Plus*™"
The first purpose built U/Pu MC-ICP-MS

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Jet cone interface
  - More efficient transfer of ions from plasma into MS
  - High Sensitivity – 2% to 4% sample utilization efficiency
- High precision, stability
  - Small signal precision: 0.1% U015 $^{235}U/^{238}U$ at 10K counts per second (cps)
  - Uranium mass bias stability: ~100 ppm (1-sigma, 1 hour)
  - Sr isotope ratio precision < 20ppm
- Flexible detector array
  - Specialized for U/Pu, broad elemental coverage retained
  - All EM detectors for lowest analyte amounts
  - 235, 238 on Faraday cup (FC) for intermediate analyte amounts
  - Best possible precision for low level actinide analysis

4

Significant New Features

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- High efficiency, Jet sampler cone and X skimmer
  - 4% reported by Thermo
  - 2.2% on site acceptance tests
  - 1.4% in recent PNNL work
- Interface pump: Pfeiffer On Tool Booster 150
  - Track record in semiconductor industry
  - Water cooled; compact (inside instrument)
  - Currently used in many of Thermo's instruments

5

Schematic Overview of the NEPTUNE

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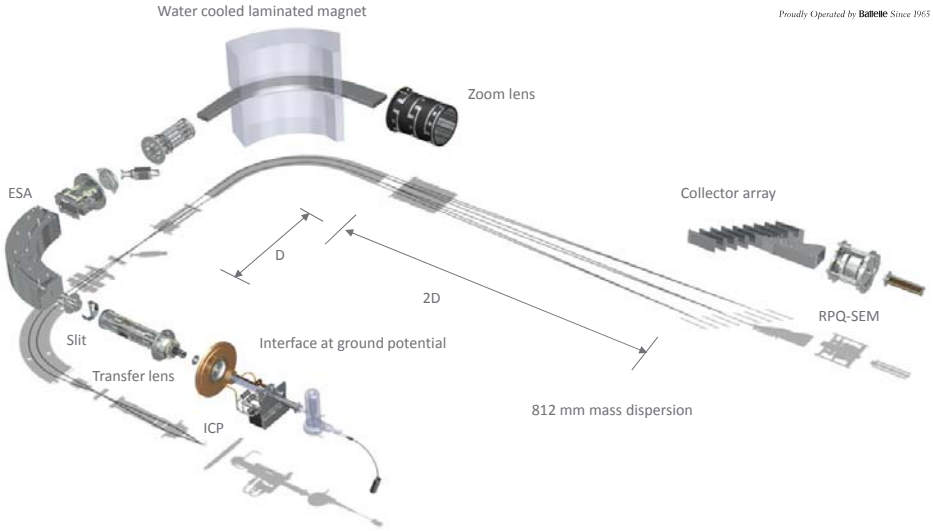

6

Schematic Overview of the NEPTUNE

Pacific Northwest NATIONAL LABORATORY
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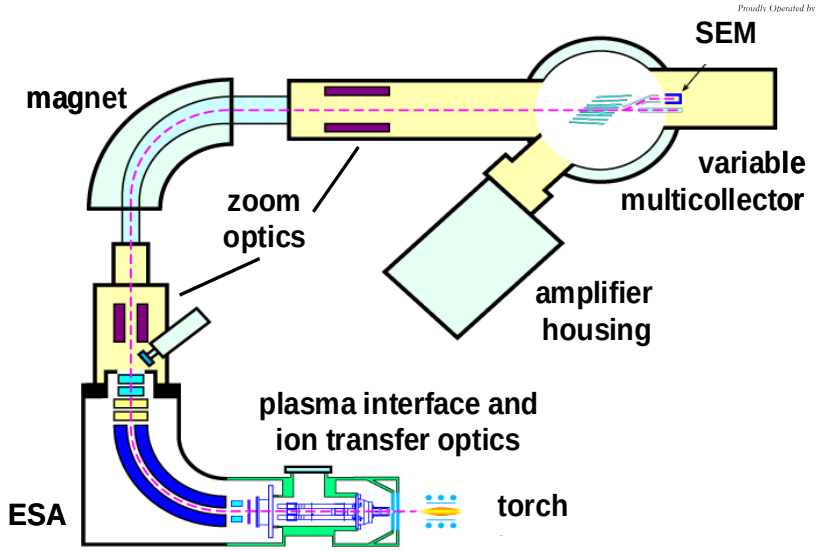

7

Neptune*Plus*™ Detector Array Design Goals, Approach

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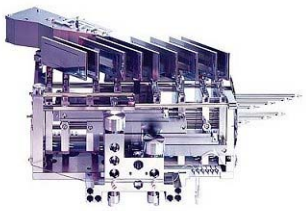
- Match detector choice to ion beam intensities (U amount)
  - <2.5 pg/min total U (natural) all isotopes on EM detectors
  - <350 pg/min total U (natural)238 on FC, other isotopes use EM
  - <35 ng/min total U (natural) 235, 238 on FC; 233, 234, 236 on EM



8

The *Plus* Deflection Platform for U Isotopes

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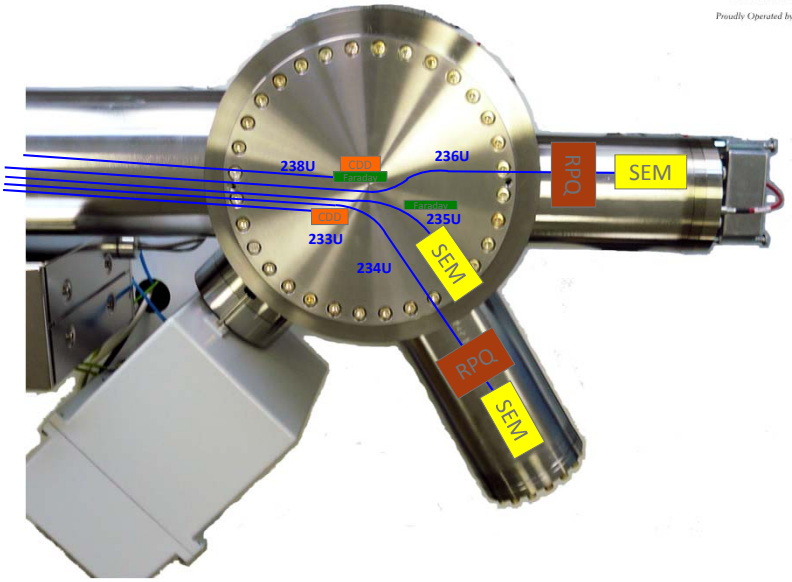

9

Detector Chambers**

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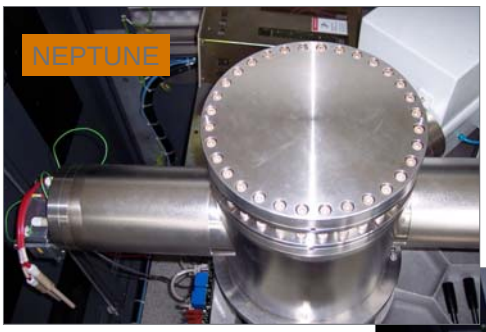
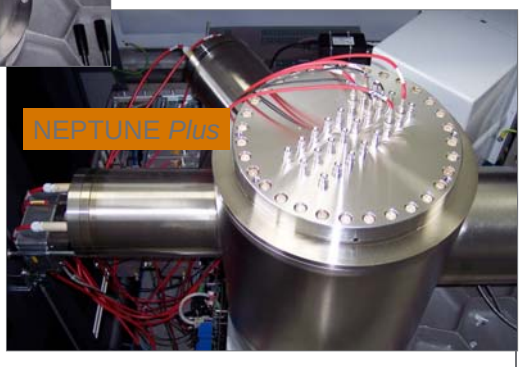
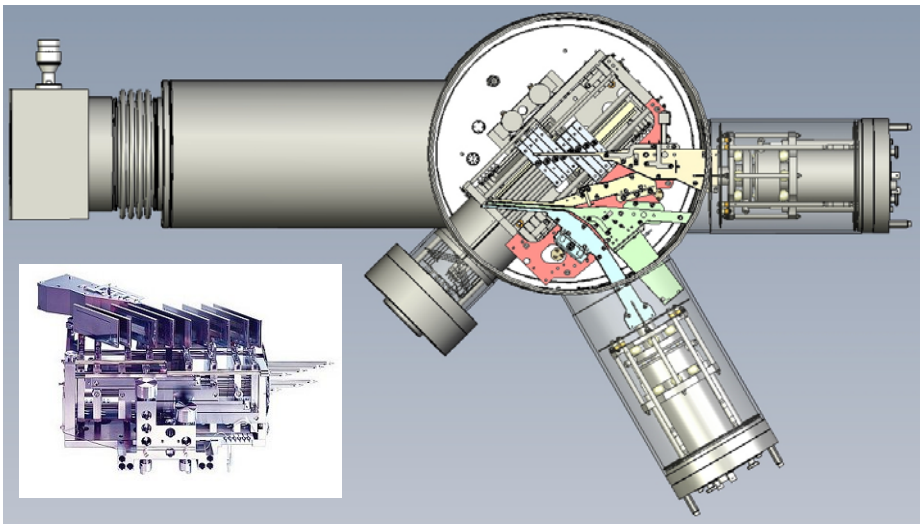




**Photos from "High Precision Uranium Isotope Analysis of Very Small Samples by MC-ICPMS", Adapted from C. Bouman *et al.*, Goldschmidt 2009

10

Multi-collector eDrawing



Detector Array – Structural Elements

- H1 – H4: four movable FC
- Center: RPQ/IC1 C (Masscom) or FC
  - Fixed position
  - Electrostatic selection
- L1 – L2: two movable FC
- L3: IC5 (CDD) + FC, tied together (movable platform)
- L4: single movable FC
- L5:
  - Fixed position array
  - RPQ / IC1 B (deflectors to enable use of center channel RPQ/IC1)
  - L5/IC2, FC (Masscom, electrostatic selection)
  - RPQ / IC3 A (Masscom)
  - L5/IC4 compact discreet dynode (CDD)

PNNL Detector Array

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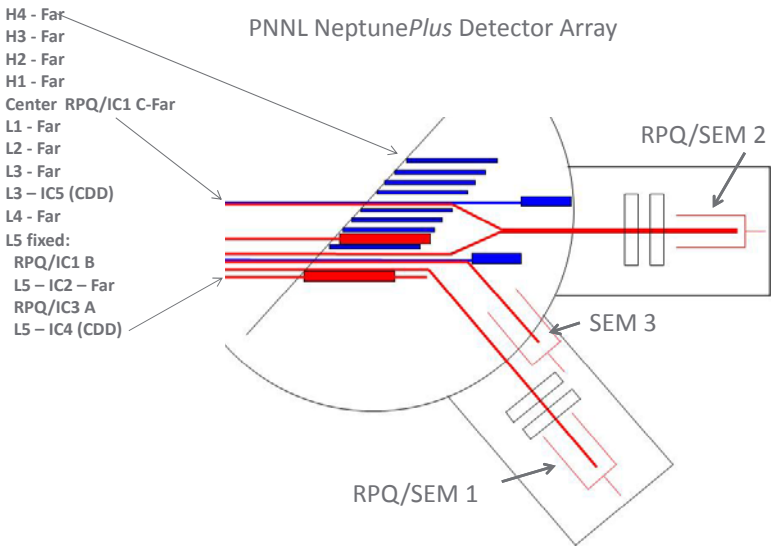

**Figure adapted from Michael Deerberg, ThermoFisher, Bremen, Germany

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PNNL NeptunePlus Detector Array** (contd.)

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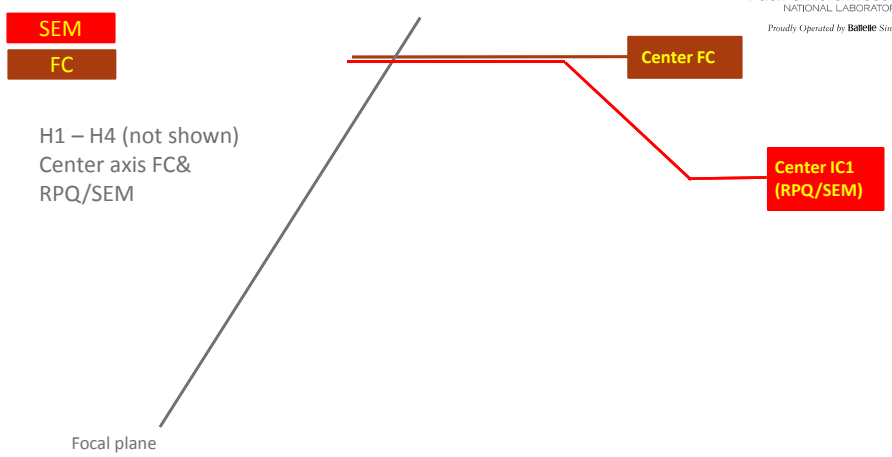

**drawing adapted from Michael Deerberg (ThermoFisher) figure

14

PNNL Neptune*Plus* Detector Array**(contd.)

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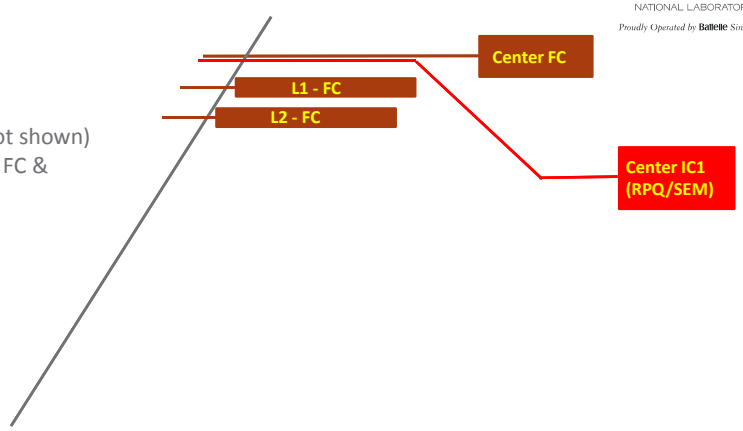
SEM
FC

H1 – H4 (not shown)
Center axis FC &
RPQ/SEM
L1 – L2



Focal plane

**drawing adapted from Michael Deerberg (ThermoFisher) figure

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PNNL Neptune*Plus* Detector Array**(contd.)

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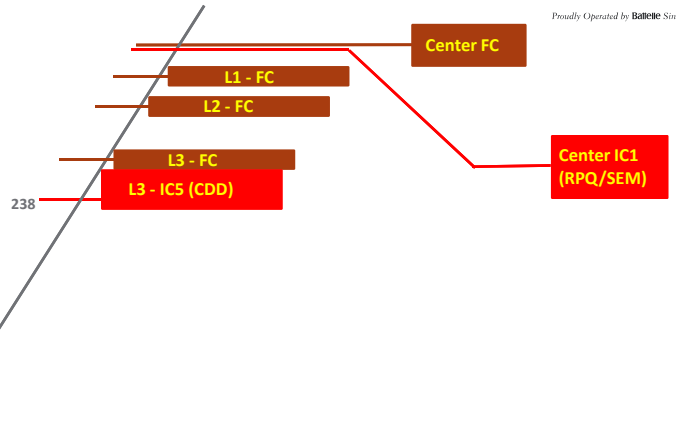
SEM
FC

L3 – FC
L3 – IC5 (CDD)



Focal plane

**drawing adapted from Michael Deerberg (ThermoFisher) figure

16

PNNL Neptune*Plus* Detector Array**(contd.)

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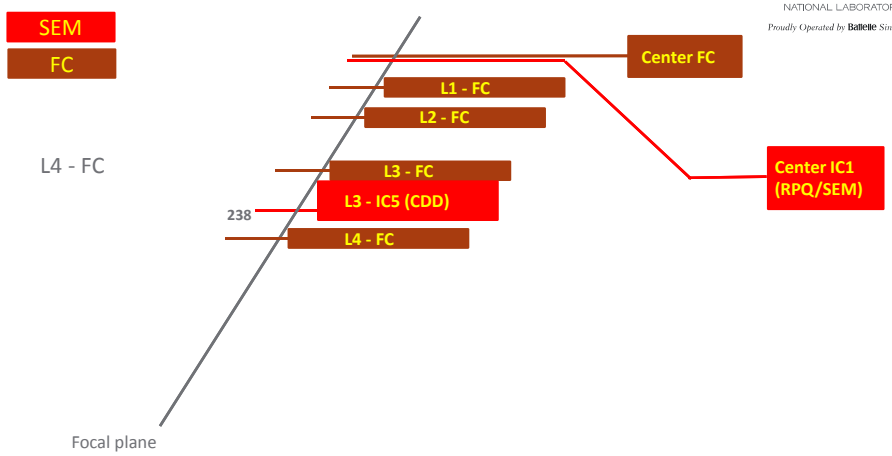

**drawing adapted from Michael Deerberg (ThermoFisher) figure

PNNL Neptune*Plus* Detector Array**(contd.)

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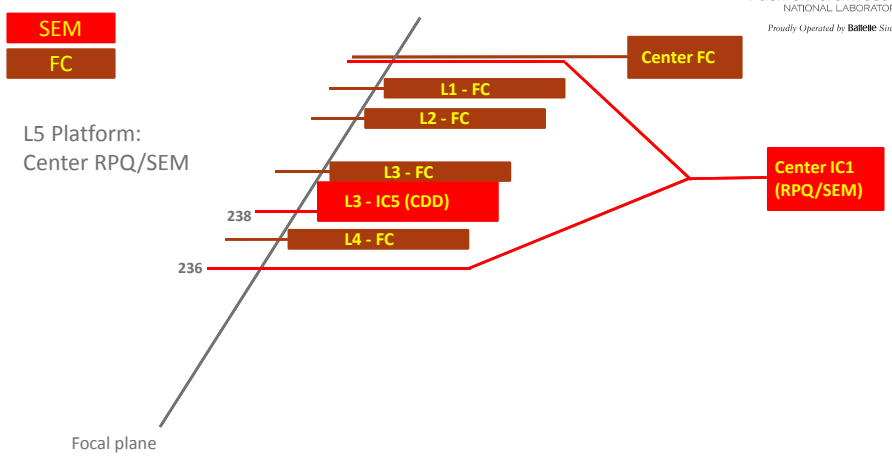

**drawing adapted from Michael Deerberg (ThermoFisher) figure

PNNL Neptune*Plus* Detector Array**(contd.)

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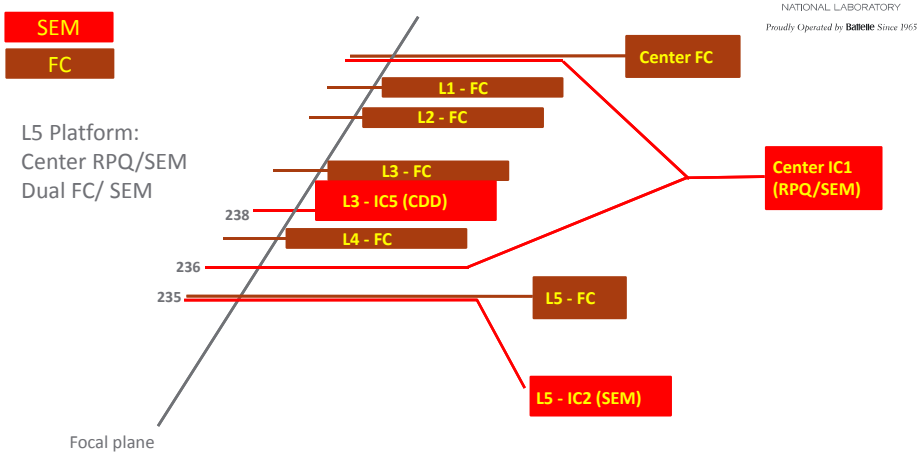

**drawing adapted from Michael Deerberg (ThermoFisher) figure

19

PNNL Neptune*Plus* Detector Array**(contd.)

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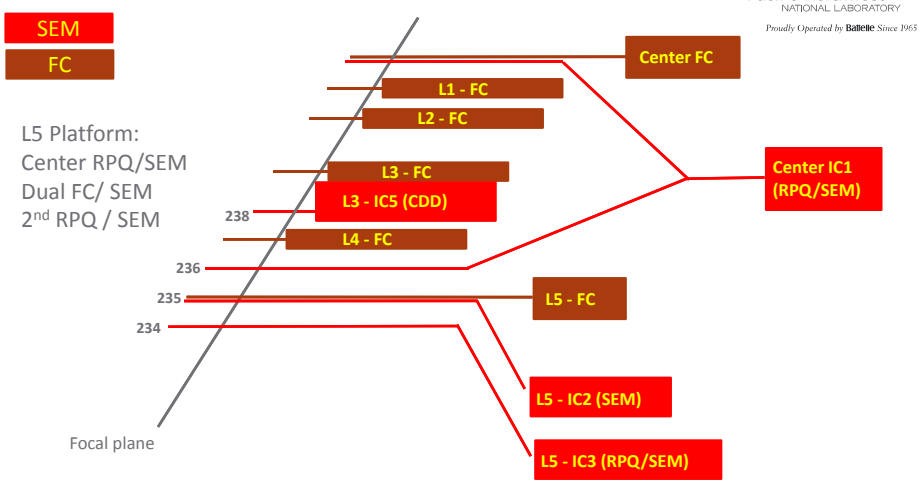

**drawing adapted from Michael Deerberg (ThermoFisher) figure

20

PNNL Neptune*Plus* Detector Array**(contd.)

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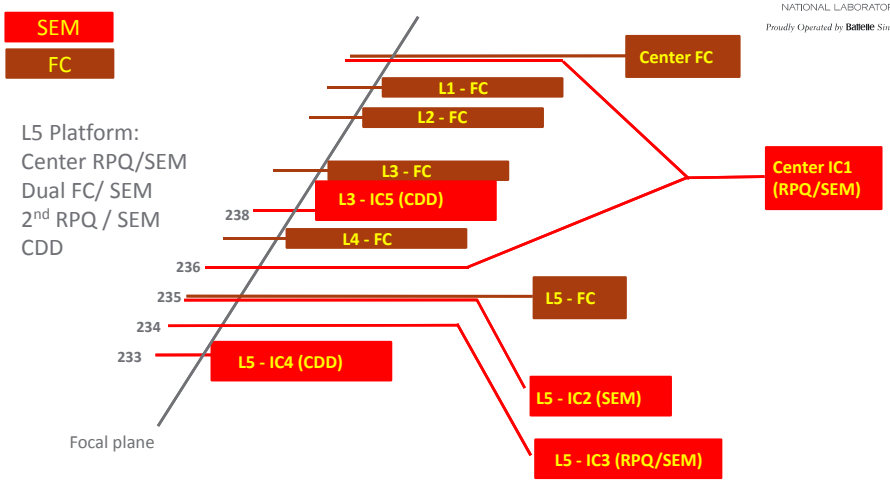

**drawing adapted from Michael Deerberg (ThermoFisher) figure

21

PNNL Neptune*Plus* Detector Array**(contd.)

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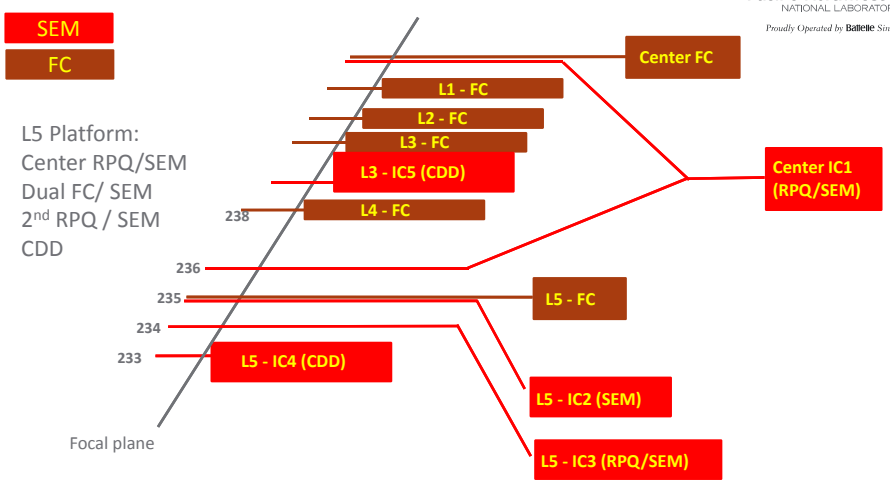

**drawing adapted from Michael Deerberg (ThermoFisher) figure

22

Detector Setup

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Faraday and/or SEM in static mode (most common mode)

Isotope	233U	234U	235U	236U	238U
Config. 1	IC4	IC3	Faraday L5	SEM-2	Faraday L4
Options	CDD	SEM-RPQ		SEM-RPQ	
Config. 2	IC4	IC3	IC2	IC1	IC5
Options	CDD	SEM-RPQ	SEM	SEM-RPQ	CDD

SEM-RPQ = Secondary Electron Multiplier- Retarding Potential Quadrupole
CDD = Compact Discreet Dynode SEM
IC = Ion Counter

Faraday and SEM in peak jump mode

Cup	Faraday L1	Center	Faraday H1	Faraday H2	Faraday H3
Amplifier	10^{11} Ohm	SEM	10^{11} Ohm	10^{11} Ohm	10^{11} Ohm
Line 1		234U	235U		238U
Line 2	235U	236U		238U	

23

Coincident Detection of Uranium Signals

U030, 20 ng/mL

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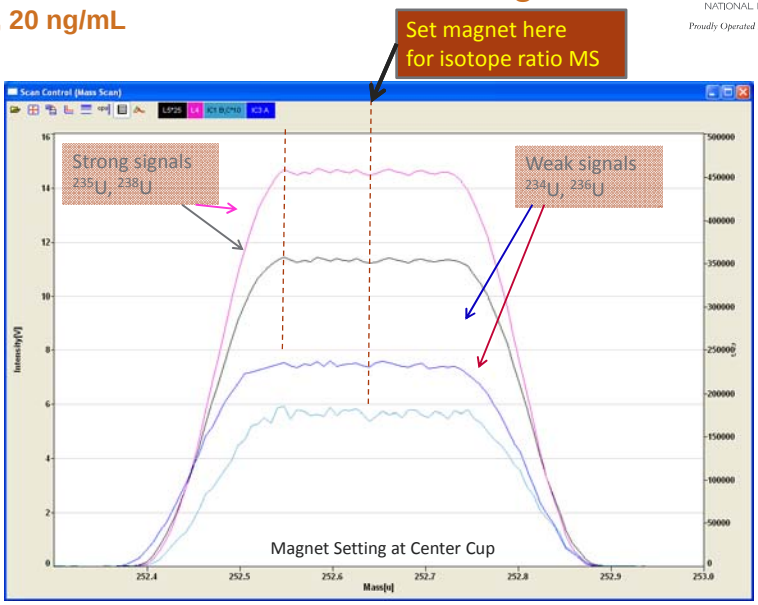

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Instrument Performance Features

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Sensitivity
- Peak shape (flat top?)
- Beam stability
  - Stable, fast scanning
- Mass resolution
  - Efficiency loss at high resolution
- Sample utilization efficiency
- Abundance sensitivity
- Background levels
- Detectors
  - single, multiple
  - Ion current (Faraday cup) or Ion counting (electron multiplier)

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Elemental Sensitivity

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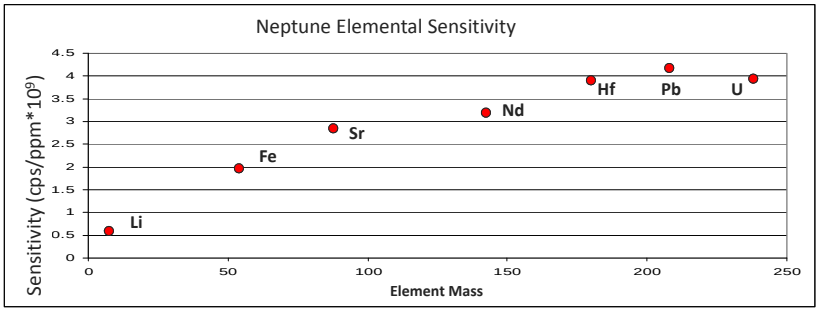

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Mike Schmidt, 08/18/2003

^{238}U Sensitivity
(18 V * 5) / 0.9927 = 90 V / ppm

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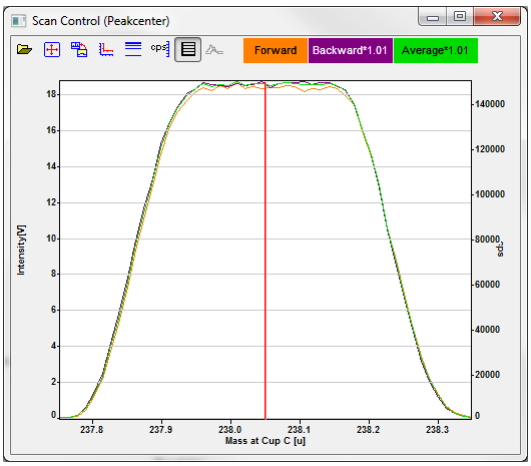

Sensitivity Calculation: (Signal Intensity * Conc. Factor) / Isotopic Abundance = Volts / ppm

^{178}Hf Sensitivity
(5.2 V * 5) / 0.273 = 95 V / ppm

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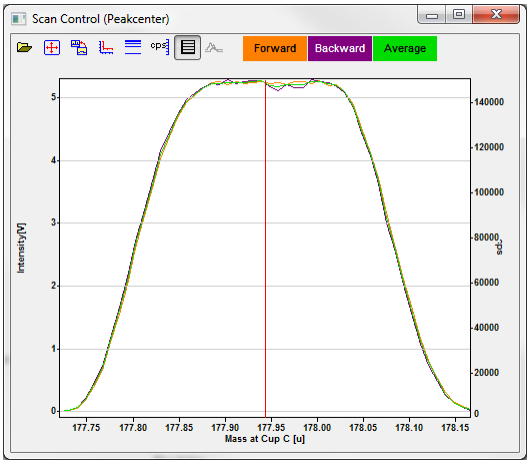

Sensitivity Calculation: (Signal Intensity * Conc. Factor) / Isotopic Abundance = Volts / ppm

^{142}Nd Sensitivity
(4.8 V * 5) / 0.272 = 88 V / ppm

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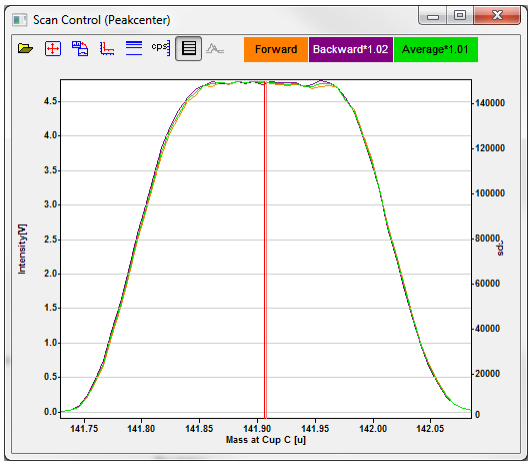

Sensitivity Calculation: (Signal Intensity * Conc. Factor) / Isotopic Abundance = Volts / ppm

^{88}Sr Sensitivity
(11.5 * 5) / 0.826 = 69 V / ppm

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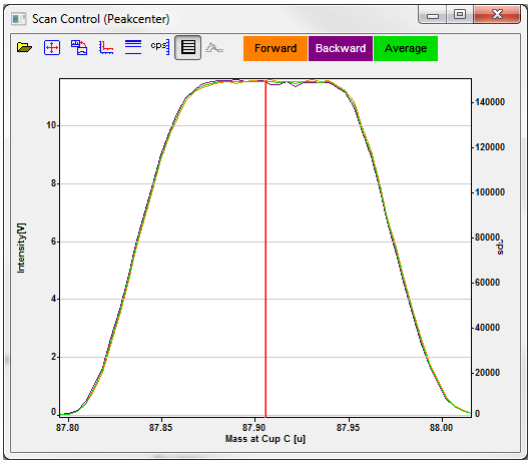

Sensitivity Calculation: (Signal Intensity * Conc. Factor) / Isotopic Abundance = Volts / ppm

Sensitivity:
High-efficiency Interface, Jet cone, Aridus II

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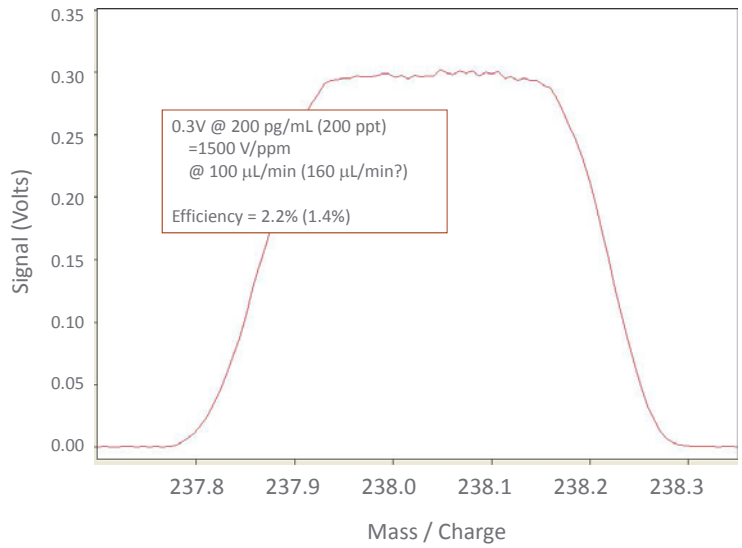

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Mass Bias Stability:
^{238}U / ^{235}U (U030) 1-hour stability

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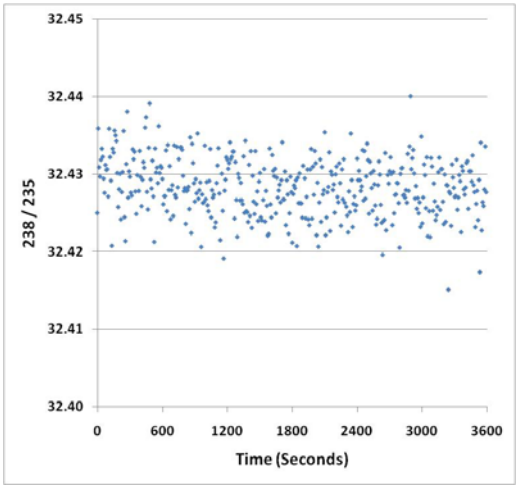
Measure U030 on Faradays
8 sec integrations
1 hour data set
~7 Volts $^{238}U^{+}$

Stability
0.0114% (1-sigma)



32

Mass Bias Stability: U030 Three-isotope Plot, No Skew

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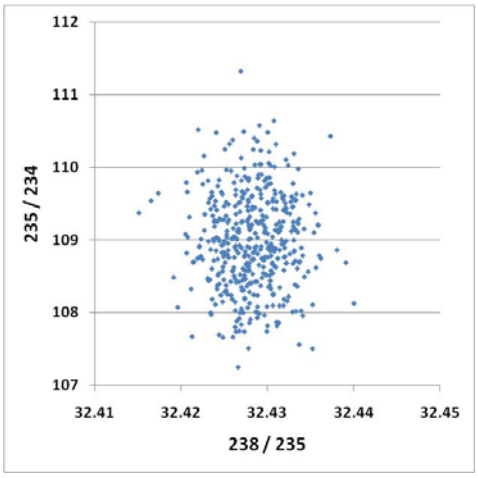

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Yield Stability SEM

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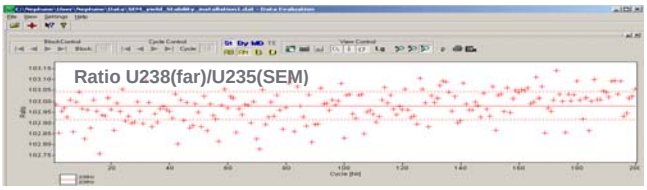
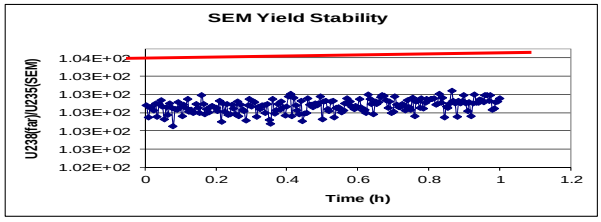


U235 count rate = 120,000 ions/s



Slope: 0.093/h

Yield stability measured: 0.093/103*100% = 0.09%/hour
Yield specified : < 0.2 %/hour

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M. Schmidt, 08/21/2003

Sensitivity (without RPQ)

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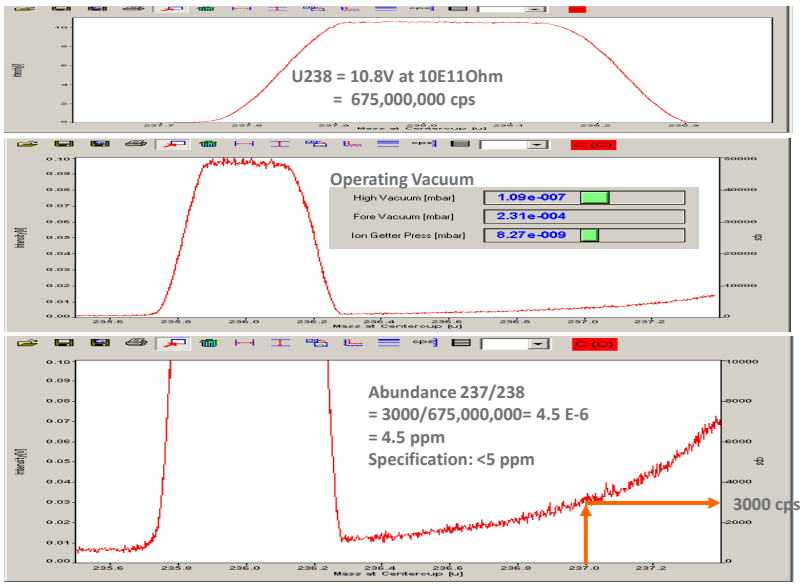

M. Schmidt, 08/18/2003

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Abundance Sensitivity, no RPQ

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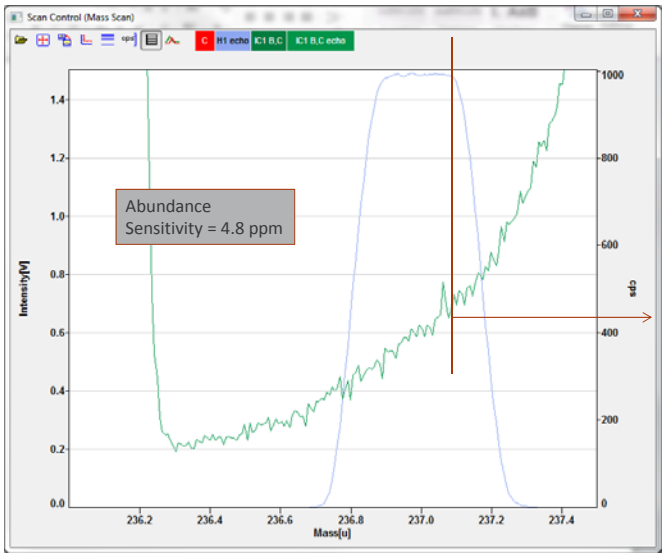

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Abundance Sensitivity with RPQ

Pacific Northwest NATIONAL LABORATORY
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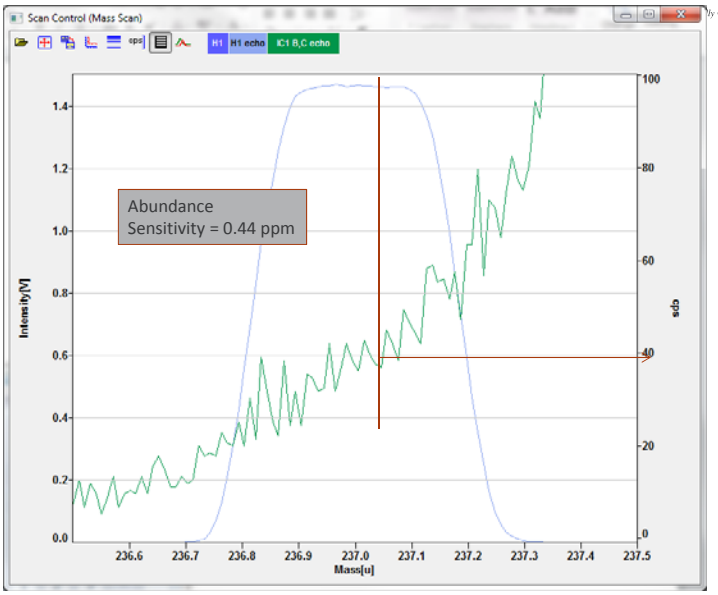

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Instrumental Background
220 – 250 amu

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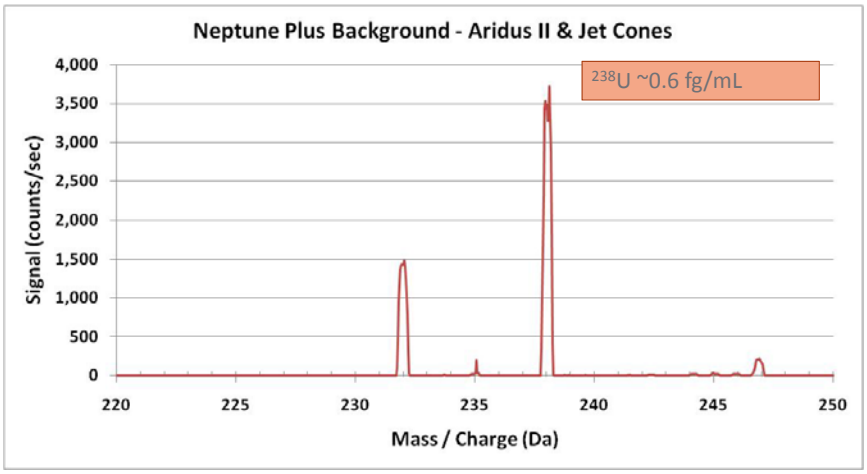

38

Instrumental Background (contd.)
220 – 250 amu

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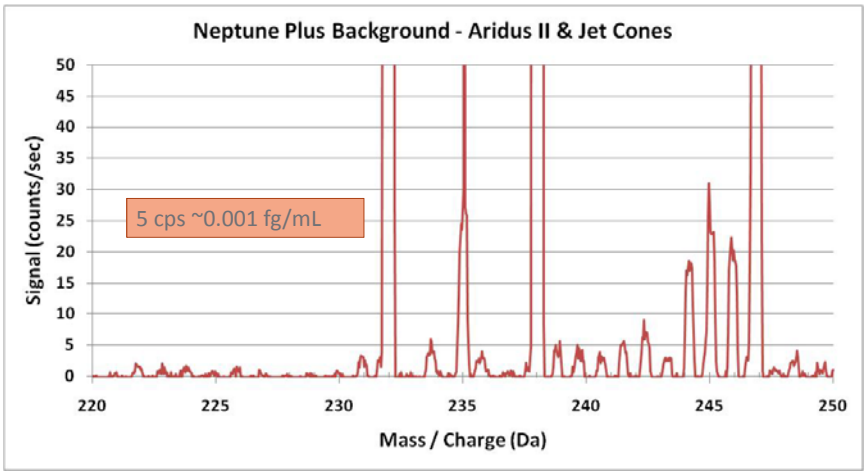

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Mass Calibration

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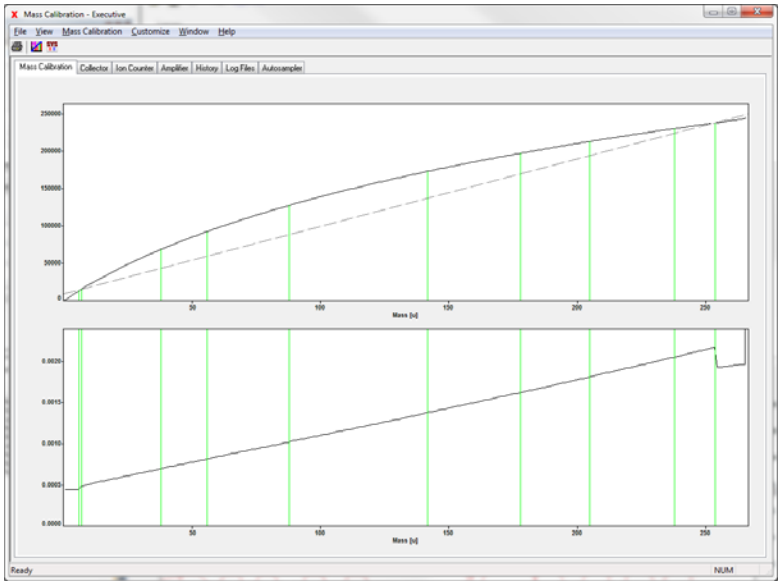

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LR, MR, HR Transmission

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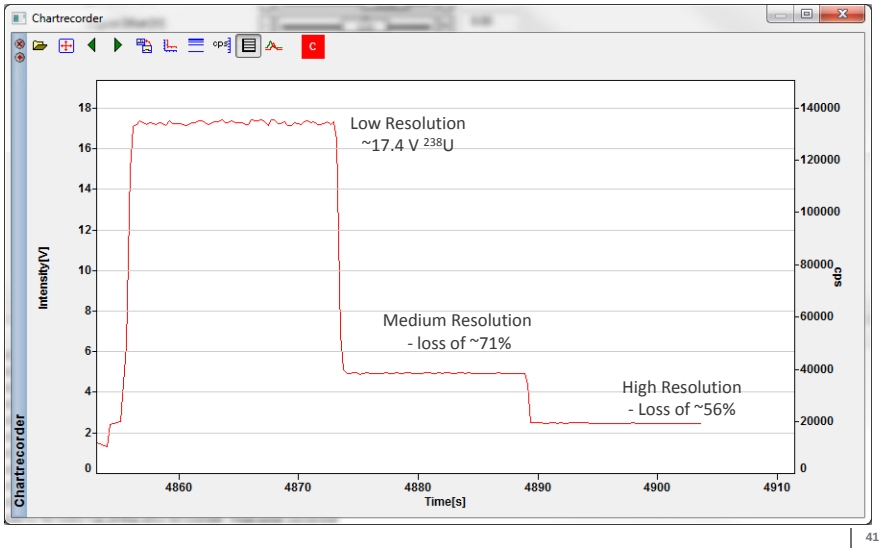

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QA/QC Is Expensive
Typical Analytical Measurement Sequence

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- Acid Blank
- Mass Bias Standard
- Acid Blank
- Reagent Blank 1
- Acid Blank

x3

- Mass Bias Standard
- Acid Blank
- Procedure Blank 1
- Acid Blank

x3

- Mass Bias Standard
- Acid Blank
- Sample 1 (Unknown)
- Etc.

x10

10 Samples

Total Number of Runs	67
Samples =	10
Acid Blanks =	34
Mass Bias =	17
Procedure Blank =	3
Reagent Blank =	3

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Data Processing: Need to Correct for Mass, Bias, Gain, Efficiencies, and Drift

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- **Method 1:** Standard-Sample-Standard Bracketing
  - Standards run before and after a sample, are used to calculate a correction factor for each ratio that is then applied to the bracketed sample
- **Method 2:** Exponential Mass Bias Correction
  - Exponential correction factor determined by bracketing standards
  - All ratios corrected for mass bias (MB) using these parameters
  - The difference between MB corrected $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios from truth due to gain between IC1 and Faradays (H2 and H3)
  - Gain corrections are calculated for these ratios and applied to samples

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Sr Peak Alignment

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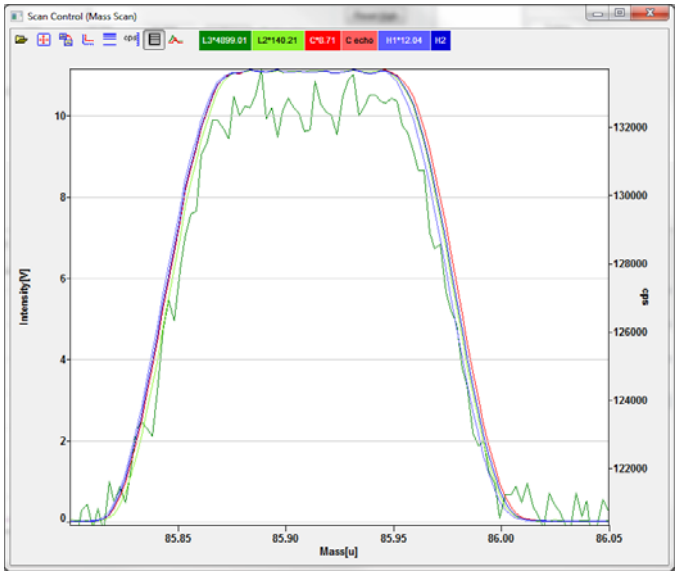

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Sr Isotope Results

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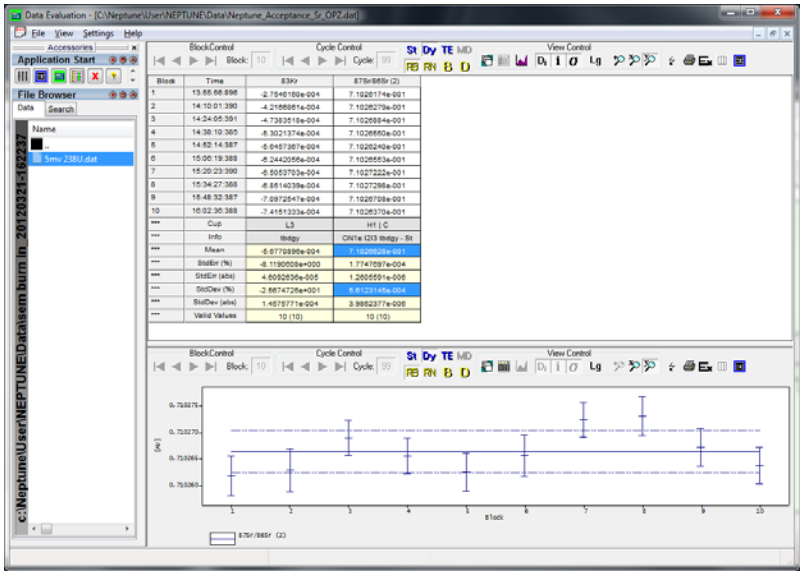

Nd Peak Alignment

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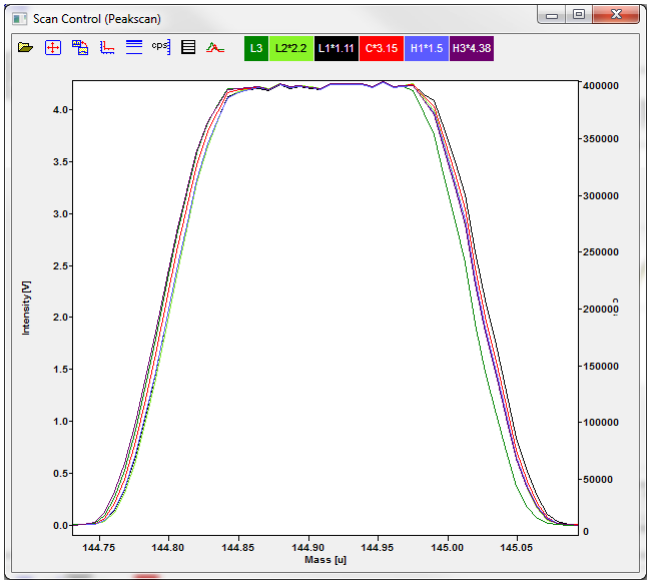

Nd Isotope Results

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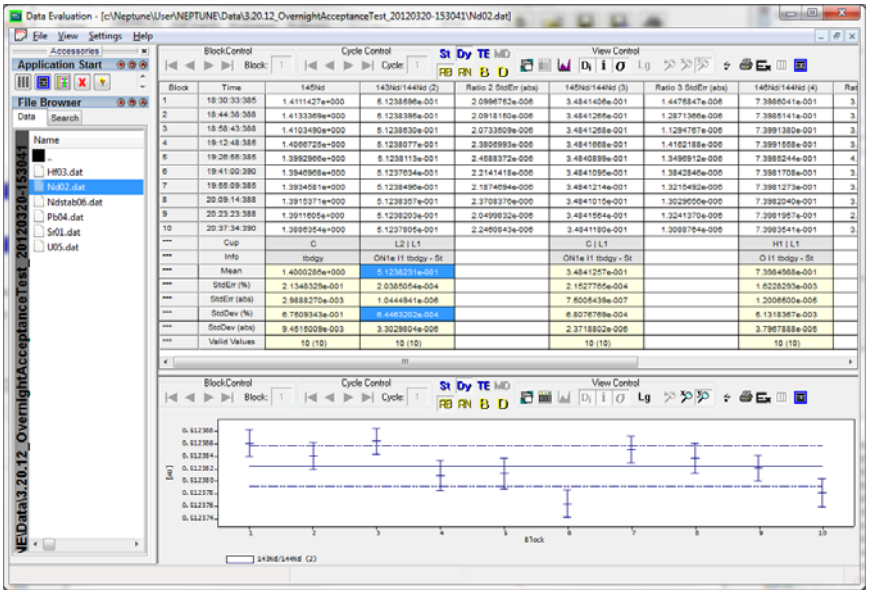

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Pb Peak Alignment

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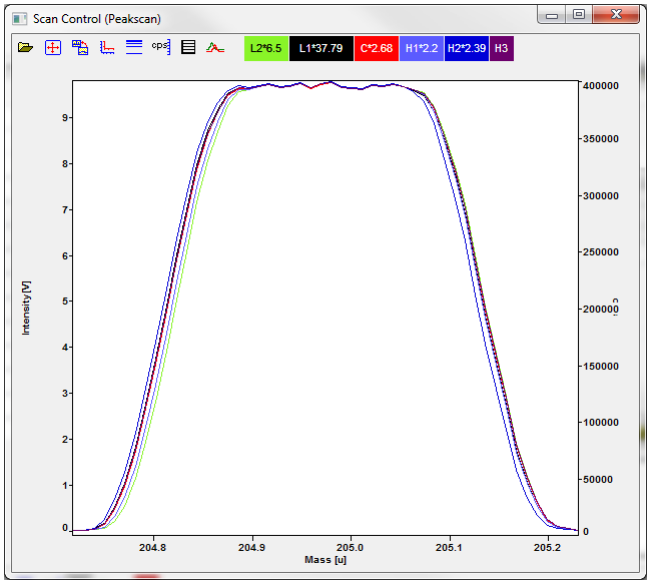

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Pb Isotope Results

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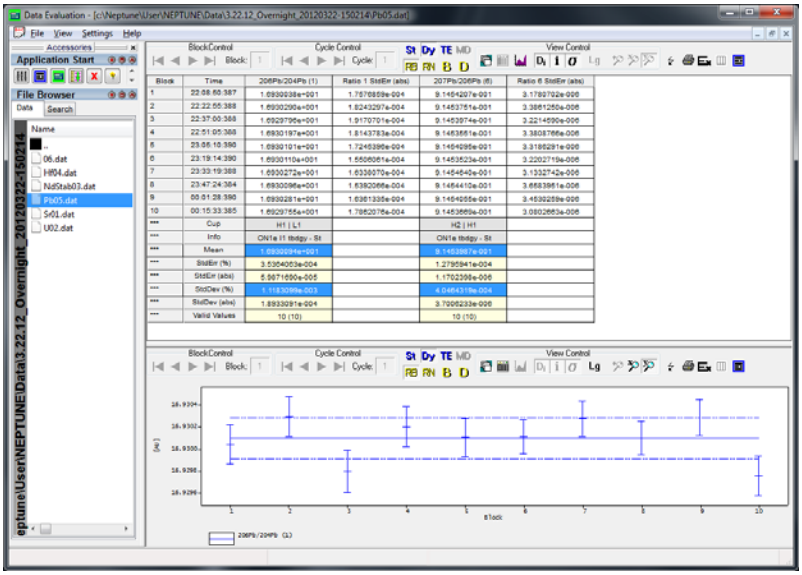

Example: Plagioclase Crystals and Sr isotope variations from Mount St. Helens, WA

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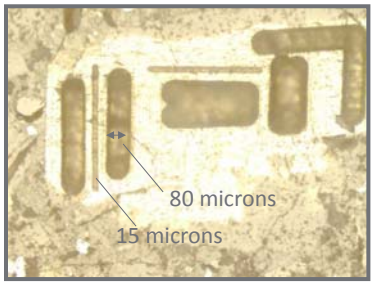
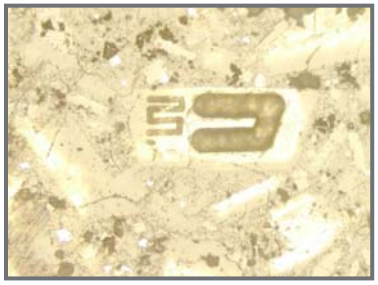
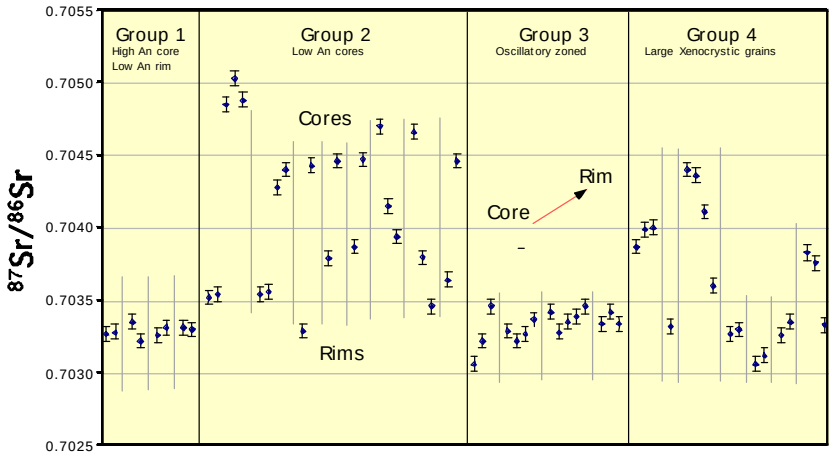


Tracks for isotopic analysis
80 microns wide
300-600 microns long



Tracks for trace element analysis
5 - 30 microns wide
30 - 100+ microns long

Sr Data: Plagioclase



Summary

- MC-ICP-MS allows for a wide variety of configurations
- Collector setup up and alignment is critical for the element of interest
- State of health parameters are important
  - Sensitivity – volts/ppm (millivolts/ppb)
  - Peak alignment – ion beam coincident in the respective collectors
- Methods for running samples depends on desired results
  - Internally mass bias corrected data
  - Externally mass bias corrected data
- Many different applications of MC-ICP-MS

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End

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