Meet the Presenter...

Dr. Rebecca Thomas is a mass spectrometrist at the Department of Energy’s New Brunswick Laboratory (NBL), which is the United States’ certification authority for nuclear reference materials. During her 12-year career at NBL, Dr. Thomas has worked on uranium and plutonium reference materials for quality control of nuclear safeguards and environmental analysis. Prior to working for the DOE, Dr. Thomas’ experience was in geochemistry. She earned a BA in geology and chemistry from Williams College in 1996, and completed her Ph.D. in Geochemistry at the University of Minnesota in 2004. For her Ph.D., she studied uranium and its short-lived daughter isotopes (thorium-230, protactinium-231, and radium-226) as geochronometers, and in volcanic rocks as tracers of melting processes. From 2009 through early 2013, Dr. Thomas worked at the International Atomic Energy Agency (IAEA) in Vienna, Austria, supporting the IAEA’s international network of analytical laboratories in analysis of both environmental and nuclear safeguards samples. Her work included support for the qualification of new member laboratories, and working with others to develop analytical criteria and evaluation of the candidate laboratories. Dr. Thomas’ work/research interests include mass spectrometry of inorganic elements, analysis of trace elements in nuclear and environmental samples, practical applications of ion exchange and extraction chromatography techniques, trouble-shooting sample preparation and mass spectrometry analyses, and quantifying sources of uncertainty in mass spectrometry measurements.

Contact Information
Phone: (+1) 630-252-2464
Email: rebecca.thomas@ch.doe.gov
Mass Spectrometry

Rebecca B. Thomas, PhD

National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE
Introduction

A. O. Nier with the flight tube for his magnetic mass spectrometer used to separate $^{235}\text{U}$ in the Manhattan Project

$^{20}\text{Ne}$ and $^{22}\text{Ne}$ measured by J.J. Thompson on parabola mass spectrograph (1913)
Outline

• The Mass Spectrometer
  – Ion Source
  – Mass Separation
  – Detectors

• Isotope Dilution Mass Spectrometry

• Some corrections:
  – Detector Corrections/Calibrations
  – Abundance Sensitivity
  – Interferences
  – Blanks (Filament, Plasma, etc.)
  – Mass Fractionation/Mass Bias

• Uncertainty
Before Mass Spec Analysis...

• Sample preparation!

• Some samples may require minimal preparation. For example, analysis to perform a survey of elements may merely require dissolution and dilution of the sample.

• Some samples will require significant preparation. For example, analysis for isotope composition and/or concentration of minor elements will require chemical purification no matter the mass spectrometry method used.
Before Mass Spec Analysis...

- Purification usually involves the use of ion chromatography or ion extraction resins

- Depending on the sample, this step can consume from a couple of hours to several days

Various commercially available ion exchange and ion chromatography columns (Eichrom)
Mass Spectrometry

- In mass spectrometry, the ions are sorted by their mass to charge ratio \( \frac{m}{z} \).
- In the source of the mass spectrometer, the sample is converted to ions (usually +1).
- Before entering the mass separator the ions are accelerated by a potential voltage drop.
- Ideally, all ions have the same kinetic energy in the mass separator.
- Ions are sorted based on their behavior in electric or magnetic fields.
Schematic of a Mass Spectrometer

Ion Source
- Thermal (TIMS)
- Inductively Coupled Plasma (ICP-MS)
- Gas

Mass Analyzer (Ion Separation)
- Quadrupole
- Magnetic Sector
- Magnetic Sector with Electrostatic Analyzer
- Time of Flight

Ion Detection (Detectors)
- Faraday Cup
- Ion Counter
Ion Source - Inductively Coupled Plasma

- The sample solution (e.g., 1M HNO$_3$ or 1M HNO$_3$ + 0.01M HF) is introduced to the plasma through a nebulizer.
- The nebulizer creates a fine aerosol.
- The aerosol passes through a spray chamber that is designed to separate the larger drops from the fine drops.
Ion Source - Inductively Coupled Plasma

Schematic of ICPMS nebulizer and spray chamber\textsuperscript{6}

Spray chamber attached to Thermo Scientific Neptune\textsuperscript{7}
Nebulizer described (Meinhard-type):
- May have flow rates from ~100 uL/min to 1 mL/min
- Roughly 1 – 5% of the sample solution will exit the spray chamber

Micronebulizers:
- Flow rates of 10 – 300 uL/min
- Less sample consumed
- Higher efficiency (more sample to plasma)
- Fewer memory effects
- Do not handle samples with complex matrices well

Desolvation nebulizers:
- Can be up to 20 times more sensitive than a 1 mL/min Meinhard-type
Ion Source - Inductively Coupled Plasma

- Plasma gas is usually a high-purity argon gas
- Plasma is maintained in an oscillating magnetic field that is controlled by a radio-frequency generator
- Plasma is at atmospheric pressure
- Plasma temperature is in the range of 6000 – 8000K
- Everything is ionized in the plasma
Ion Source - Inductively Coupled Plasma

Detailed schematic of plasma torch, RF coil, and ICPMS interface
Ion Source - Inductively Coupled Plasma

- Electrostatic (or capacitative) coupling between the RF load coil and the plasma discharge can cause arcing at the sampling cone, resulting in:
  - Production of doubly charged ions
  - Wider spread of kinetic energies for the sample (lower resolution)
  - Ions from the sampling cone

- Solution: Add some form of grounding at the load coil, e.g., guard electrode

ICP torch assembly with guard electrode

Close-up of working plasma torch with guard electrode not in place. The electrode is inserted between the RF coil and plasma prior to sample analysis.
Ion Source - Thermal Ionization

- Typical filament materials:
  - Rhenium
  - Tungsten
  - Tantalum

- Sometimes, especially for very small environmental samples, a carbon modifier (e.g., graphite) is used on the filament

- Increases the work function of the filament, allowing the sample to evaporate and ionize off of a single filament
Ion Source - Thermal Ionization

- **Double filament geometry** (some instruments use triple filament geometry)

- **Evaporation filament** (with sample): low temperature, so that sample does not evaporate too quickly

- **Ionization filament** (across from evaporation filament): high temperature, to ionize the sample vapor that is coming from the evaporation filament

Schematic of double filament geometry. The sample is the dark blob on the evaporation filament.
Ion Source - Thermal Ionization

- **Problem:** double filament geometry is inefficient for very small samples (~ <1 ng)

- **Solution:** single filament geometry and use of a carbon activator (e.g., graphite load, filament carburization, resin bead load)

- Increases the work function of the filament, allowing the sample to evaporate and ionize off the filament
Ion Source - Comparison

• Inductively coupled plasma
  – Frequently has higher ionization efficiencies
  – Most of the sample and plasma are ionized
  – Wider energy dispersion = lower resolution
  – Polyatomic interferences
  – Samples introduced as solutions ... can be modified for other sample types

• Thermal ionization
  – Lower ionization efficiencies, but more selective ionization
  – Sample is dried onto a filament, and put into a vacuum
  – Number of samples in a batch limited to turret size
  – Low background
  – High resolution/sensitivity
Mass Analyzers

- Quadrupole analyzer (ICP)
- Magnetic sector (TIMS)
- Magnetic sector + electrostatic analyzer (ICP)
Mass Analyzers - Quadrupole

- Maintained at vacuum of $10^{-6}$ Torr
- Composed of four rods to which AC and DC current are applied
- When the current is properly set, the ion of choice will be stable within the field and will pass through the rods
- Other ions will be unstable, and their paths will lead out of the quadrupole through the rods, or will collide with the rods

Schematic of quadrupole mass analyzer. The analyzer is optimized for ions (M1). Ions M2 and M3 exit between the rods or collide with the rods and are not measured.
Mass Analyzers - Magnetic Sector

- A stable magnetic field is used to separate the ions

Schematic drawing of forces acting on an ion in a magnetic sector mass analyzer\(^\text{18}\)

Schematic drawing of ion behavior in a magnetic sector mass analyzer (with multiple Faraday cup detectors)\(^\text{19}\)
Mass Analyzers - Magnetic Sector

- The masses are separated in the magnetic field by
  \[ \frac{m}{z} = \frac{eB^2r^2}{2V} \]

- During a single measurement:
- Magnetic field, charge, and acceleration voltage are constant.
- The mass to charge ratio \((\frac{m}{z})\) and the radius \((r)\) will change.
- In a stable magnetic field, ions with greater \(m/z\) will travel a path with a larger radius, ions with a smaller \(m/z\) will curve inward more sharply.
Mass Analyzers - Magnetic Sector + Electrostatic Analyzer

Used in most ICPs

- The dispersion of ion energies is greater in a plasma compared to a thermal source

- Thus, the ion focus can be more diffuse than in a thermal instrument (lowering resolution and sensitivity)

- Solution: add a second mass/energy filter that will further sort the ions, to minimize interferences with the m/z of interest

- An electrostatic analyzer will focus the ions between two curved plates of opposite charges
Mass Analyzers - Magnetic Sector + Electrostatic Analyzer

- Nier-Johnson geometry

**Advantages**
- High resolution
- Abundance sensitivity
- Multi-collector capability

**Disadvantages**
- Magnet controls mass scan
- Scanning over large mass ranges is slower than quadrupole or reverse Nier-Johnson geometry

Line drawing of Thermo Scientific Neptune\(^{21}\)
Mass Analyzers – Magnetic Sector + Electrostatic Analyzer

- Reverse Nier-Johnson geometry

<table>
<thead>
<tr>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faster scanning over large mass ranges</td>
</tr>
<tr>
<td>High resolution</td>
</tr>
<tr>
<td>Abundance sensitivity</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single collector only</td>
</tr>
<tr>
<td>Slower than quadrupole</td>
</tr>
</tbody>
</table>
Mass Analyzers - Comparison

- **Quadrupole**
  - Can quickly scan across multiple masses
  - Resolution/abundance sensitivity lower than magnetic sector

- **Magnetic Sector**
  - Mass selective – can jump between certain elements, ignore others
  - Scan over a wide mass range is slow compared to a quadrupole

- **Magnetic Sector + ESA**
  - High-resolution
  - Magnetic sector – ESA provides compromise between fast scans and high resolution, only single collector
  - ESA – Magnetic sector has very high resolution, allows for multiple ion collectors, but has the slowest scanning speed
Dynamic range of Faraday and SEM detectors with typical signal intensities for uranium nuclear measurements\textsuperscript{23}
Detectors - Faraday Collector

Simplified schematic of a Faraday cup$^{24}$ in which positively charged ions are deposited. The deposition of the charged ions induces an electron current, which is amplified and recorded by the mass spectrometer.

An open Faraday cup in a Thermo Scientific Triton mass spectrometer. The black graphite cup inside the metal frame is the Faraday cup.$^{25}$
## Detectors - Faraday Collector

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Can measure large ion beams (up to 40V signals on newer instruments)</td>
<td>• Effects of noise become significant sources of error when the ion current is $&lt;\sim 3$ mV</td>
</tr>
<tr>
<td>• Do not need to be replaced often</td>
<td>• May need to correct data for tailing from adjacent isotopes</td>
</tr>
<tr>
<td>• Can measure multiple ion beams at the same time, if multiple detectors are installed in the instrument</td>
<td></td>
</tr>
</tbody>
</table>
Detectors - Electron Multipliers

aka: secondary electron multipliers (or SEM)

- Two types

1. **Discrete Dynode**
   - Schematic drawing of a discrete dynode electron multiplier\(^{26}\)

2. **Continuous Dynode**
   - Schematic drawing of a continuous dynode electron multiplier\(^ {27}\)
## Detectors - Electron Multipliers

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Very sensitive</td>
<td>• Multiplier may not be linear at higher ion currents</td>
</tr>
<tr>
<td>• Low noise</td>
<td>• No energy filter for the multiple ion detector array</td>
</tr>
<tr>
<td>• May follow an energy filter (which reduces peak tailing)</td>
<td>• Can handle limited signal intensities</td>
</tr>
<tr>
<td>• Some continuous dynode multipliers are small enough that they can be stacked together to form a multi-collector array</td>
<td></td>
</tr>
</tbody>
</table>
## Multiple Detector Methods

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• All of the isotopes are measured all of the time</td>
<td>• Must calibrate and correct for yield and gain on all detectors</td>
</tr>
<tr>
<td>• Stability of the ion current is not important</td>
<td></td>
</tr>
</tbody>
</table>
Scan of NBL U-500 across multiple Faraday cups. Note the flat-topped peak shape. This was a test to verify cup alignment for a multiple cup analysis. The factors by $^{234}\text{U}$ and $^{236}\text{U}$ adjust the peaks for easier visual alignment.\textsuperscript{28}
## Single Detector Methods

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Do not need to calibrate between detectors</td>
<td>• When one isotope is measured, the others are not</td>
</tr>
<tr>
<td>• When equipped with an energy filter (RPQ), will not need to correct for</td>
<td>• Analysis can take longer than multiple collector</td>
</tr>
<tr>
<td>tailing of nearby isotopes (or minimal correction will be required)</td>
<td>methods</td>
</tr>
<tr>
<td></td>
<td>• Best with a very stable ion current</td>
</tr>
</tbody>
</table>
Isotope Dilution

- Isotope dilution mass spectrometry (IDMS) is a technique for quantifying the amount of an isotope in a sample by mass spectrometry.

- Under certain circumstances, with the use of a double spike, can also be used to correct for mass fractionation.

Cartoon of IDMS sample preparation

Sample → Add spike → Homogenize → Chemical Purification → Analysis
Isotope Dilution

• What makes a good spike?
  – Ideally, a spike contains an isotope that is NOT in the sample (e.g., $^{233}$U is often used to spike uranium samples)

  – Sometimes spikes contain isotopes that are in the sample, but then it is necessary to know the isotopic composition of the spike and the sample (extra analyses)
Isotope Dilution

\[ R_m = \frac{Ab_{Asamp}N_{samp} + Ab_{Aspike}N_{spike}}{Ab_{Bsamp}N_{samp} + Ab_{Bspike}N_{spike}} \]

\[ N_{samp} = N_{spike} \times \left( \frac{Ab_{Aspike} - R_m Ab_{Bspike}}{R_m Ab_{Bsamp} - Ab_{Asamp}} \right) \]

\[ N = \text{number of atoms in the sample or spike} \]
\[ Ab = \text{abundance of isotope A or B in sample or spike} \]
\[ R_m = \text{measured ratio (ex. } ^{233}\text{U/}^{238}\text{U)} \]

\[ N_{(Usamp)} = N_{(Uspike)} \times \left( \frac{Ab_{233spike} - \frac{233}{238} Ab_{238spike}}{\frac{233}{238} Ab_{238samp} - Ab_{233samp}} \right) \]
Some Corrections/Sources of Uncertainty in Mass Spectrometry Measurement
Detector Corrections/Calibrations

Faraday cup

• Gain
  – The ratio between the amplifier input and output
  – Mass spectrometer programmed to put constant voltage on Faraday cup amplifier
  – Usually correction is stable
  – One of the ways Faraday cups are calibrated to each other

• Baseline
  – The signal recorded by the Faraday cup amplifier when no signal is applied
  – Reasonably stable in most cases
Detector Corrections/Calibrations

Secondary Electron Multiplier (SEM)

- **Darknoise**
  - Similar to baseline, it is the measured signal on the SEM when there is no ion beam
  - Darknoise will increase as the SEM ages
  - It will also increase if you are measuring very short-lived isotopes

- **SEM-Faraday Yield**
  - A correction factor that calibrates the SEM to the Faraday cups
  - Low voltage [e.g., 4 mV (Faraday) = ~250,000 cps] signal is alternately measured on the Faraday cup and the SEM
Detector Corrections/Calibrations

Electron Multiplier (SEM)

- Deadtime
  - Recovery time needed by SEM between pulses
  - Usually set by the instrument manufacturer (e.g., ~20 ns)
  - Affects measurements with high ion counts (not noticeable for lower ion counts)
Mass Calibration

- Magnet or quadrupole need to be set so that mass of interest is directed into the detectors
- Stable, but can change slightly over the course of an analysis

Multiple cup alignment with peak center marked. The peak center is used in the mass calibration. The factors by 234U and 236U are to scale the peaks to the major peaks\(^3\).
Mass Calibration

This figure shows the mass calibration curve (green) that was calculated by the software. The points used to extrapolate the curve are marked by vertical lines and are listed in the table to the right. The x-axis represents the mass (amu) of the ion and the y-axis represents the magnet setting (MDAC value) at which the ion beam is detected in the center detector.  

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Calibration mass</th>
<th>MDAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}\text{Na}$</td>
<td>22.99</td>
<td>34879</td>
</tr>
<tr>
<td>$^{39}\text{K}$</td>
<td>38.964</td>
<td>60630</td>
</tr>
<tr>
<td>$^{185}\text{Re}$</td>
<td>184.953</td>
<td>198138</td>
</tr>
<tr>
<td>$^{187}\text{Re}$</td>
<td>186.956</td>
<td>199373</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>235.044</td>
<td>226616</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>238.051</td>
<td>228163</td>
</tr>
<tr>
<td>$^{235}\text{U}^{16}\text{O}$</td>
<td>250.61</td>
<td>234377</td>
</tr>
</tbody>
</table>
Abundance Sensitivity

Top figure: Effects of peak tailing from $^{232}\text{Th}$ on the measurement of $^{230}\text{Th}$.

Bottom figure: Significantly reduced effects of peak tailing (improved abundance sensitivity) with a reducing potential quadrupole (RPQ) energy filter.$^{32}$
Abundance Sensitivity/Peak Tailing

Dashed line represents the correction for the peak tailing from $^{238}$U

Measurement of $^{236}$U on SEM with and without RPQ energy filter. The dashed line in the 236 peak represents the model used to correct for the peak tail. The solid line is an extrapolation of the peak tail.
Interferences

• **Isobaric Interferences:** Isotopes of different elements that have the same atomic mass
  - $^{87}\text{Sr}^+$ and $^{87}\text{Rb}^+$
  - $^{40}\text{K}^+$ and $^{40}\text{Ar}^+$
  - $^{238}\text{U}^+$ and $^{238}\text{Pu}^+$

• **Polyatomic Interferences:**
  - $^{56}\text{Fe}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$
  - $^{239}\text{Pu}^+$ and $^{238}\text{UH}^+$

• **Matrix Interferences:**
  - Suppression of the signal because of acid concentration or level of dissolved solids
  - When sample affects the ionization conditions in the plasma, suppression varies, based on matrix components
# Interferences

Some common polyatomic interferences for the analysis of uranium and plutonium

<table>
<thead>
<tr>
<th>233U</th>
<th>234U</th>
<th>235U</th>
<th>236U</th>
<th>238U</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO₃</td>
<td>ReO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReC₄</td>
<td>ReC₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbAl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbSi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga₃C₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>238Pu</th>
<th>239Pu</th>
<th>240Pu</th>
<th>241Pu</th>
<th>241Pu</th>
<th>244Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>238U</td>
<td>Ga₃O₂</td>
<td></td>
<td>24¹Am</td>
<td></td>
<td>24⁴Cm</td>
</tr>
<tr>
<td>ReFe</td>
<td></td>
<td>ReFe</td>
<td>ReFe</td>
<td>ReFe</td>
<td></td>
</tr>
<tr>
<td>23⁸UH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Interferences

Some examples of common polyatomic interferences and resolution required to distinguish them:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Matrix</th>
<th>Interference</th>
<th>Resolution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{Ca}^+$</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{40}\text{Ar}^+$</td>
<td>199,800</td>
</tr>
<tr>
<td>$^{44}\text{Ca}^+$</td>
<td>$\text{HNO}_3$</td>
<td>$^{14}\text{N}^{14}\text{N}^{16}\text{O}^+$</td>
<td>970</td>
</tr>
<tr>
<td>$^{56}\text{Fe}^+$</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{40}\text{Ar}^{16}\text{O}^+$</td>
<td>2,504</td>
</tr>
<tr>
<td>$^{75}\text{As}^+$</td>
<td>$\text{HCl}$</td>
<td>$^{40}\text{Ar}^{35}\text{Cl}^+$</td>
<td>7,725</td>
</tr>
<tr>
<td>$^{55}\text{Mn}^+$</td>
<td>$\text{HNO}_3$</td>
<td>$^{40}\text{Ar}^{15}\text{N}^+$</td>
<td>2,300</td>
</tr>
</tbody>
</table>

*Highest Resolution = 10,000

Thomas, Robert (2004)
Interferences

Some solutions:

• **Matrix interferences:**
  – Dilution
  – Chemical purification
  – Use of internal standardization, especially for multi-element analysis

• **Isobaric Interferences:**
  – Mathematical corrections

• **Polyatomic and Molecular Interferences:**
  – Quadrupole: collision/reaction cells
  – Magnetic sector: high resolution capabilities
Resolution

Comparison of resolution in (a) Quadrupole ICPMS and (b) ICPMS with a Magnetic Sector and ESA. In this case, it is possible to resolve the $^{56}$Fe $^{40}$Ar$^{16}$O interference (1 large peak to 2 individual peaks), but it will be at the expense of ion transmission.
Resolution

Schematic drawing of the use of slits that control resolution in magnetic sector ICPMS. The final graphs illustrate the results as the magnetic field is scanned over the slits.\textsuperscript{35}

A 100 ng/L solution of 115In at Low (R=300; \(\sim\) 350,000 cps), Medium (R=4000; \(\sim\)35,000 cps), and High (R=10,000; \(\sim\)6,000 cps) resolution\textsuperscript{36}
Mass Fractionation/Bias

- Mass fractionation or mass bias is observed in all types of mass spectrometry
- Can vary from instrument to instrument
- **Thermal Source**
  - Mass fractionation/bias due to different evaporation temperatures/rates of different isotopes
- **ICP Source**
  - Mass bias is observed, but source is less well characterized
  - May have to do with the flow of sample at the interface (sampling and skimmer cones)
- Corrected using standards/certified reference materials
Mass Fractionation/Bias

Change in the 235U/238U ratio with time in a single sample on a thermal source (TIMS) mass spectrometer\textsuperscript{37}
Mass Fractionation/Bias

<table>
<thead>
<tr>
<th>%RD from Certified Value</th>
<th>Overall %RD: -0.0025%</th>
<th>Triton %RD: -0.0062%</th>
<th>MAT 261 %RD: 0.0020%</th>
</tr>
</thead>
</table>

The region between the dashed lines represents the certificate value and the uncertainty on that value. All data fall within the certificate value; no correction is necessary (an ideal case). \(^{38}\)
In this figure, the measured values fall well above the certificate value. A correction factor must be applied to the data in order to report a true value.
Mass Fractionation/Bias

• To test and correct for mass fractionation/bias:
  – Need to use standards/certified reference materials
  – **External:** Certified/Standard reference materials are run as standards on the same turret, along with the unknown sample.
  – **Internal:** A sample is “spiked” with a two isotope standard material (e.g., using a $^{233}$U/$^{236}$U double spike
$^{233}$U-$^{236}$U double spike for natural uranium samples
$^{242}$Pu-$^{244}$Pu spike for plutonium samples

• Correction factor is calculated from the measurement of the standards, and applied to the samples

*This use of standards/CRMS also provides traceability for the measurements.*

*Traceability = a link to the base SI units.*
Three empirical corrections that are used to correct for mass fractionation.\textsuperscript{40}

- The exponential law provides the best fit for all masses
- At high mass numbers (e.g., $^{238}\text{U}$), the results of the three models are indistinguishable.
Mass Fractionation

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Internal Standard</strong></td>
<td>• U sample must have no $^{236}$U or the $^{236}$U must be well characterized</td>
</tr>
<tr>
<td></td>
<td>• Will have to correct the final sample ratios for any isotopes that were introduced by the spike</td>
</tr>
</tbody>
</table>
| **External Standard** | •外部标准。
|                       | • Do not need to know the isotopic composition of the sample                   |
|                       | • Will not contaminate the sample with the spike                               |
|                       | •外部标准。
|                       | • Must assume that the standards, which run on different filaments, have the same fractionation history as the samples |
Blanks

An analysis of “background” signatures that may come from the ion source, chemistry process, instrument

- **Instrument Blank**: The instrument is run under normal operating conditions, but no sample is analyzed (this is a background measurement)

- **Chemical Blank**: Blank in the chemicals used to process the sample

- **Process Blank**: Isotopic/elemental background that is created during the chemical processing of the sample (dissolution, ion exchange, loading)

- **Environment Blank**: Isotopic/elemental background contributed by the environment in which the sample is processed
Blanks

To measure blanks:

- **Instrument**
  - Thermal source: use a new filament, scan over mass range of interest
  - Plasma source: run plasma with only wash or matrix solution (no sample) scan over mass range of interest

- **Chemical**
  - Collect a sample of the chemical, spike it, measure element/isotope of interest

- **Process**
  - Use an empty beaker (usually Teflon for environmental work) through the same dissolution, purification, loading processes along with the samples (as if the empty beaker contained a sample)
  - Spike at the end for concentration of added isotopes

- **Environment**
  - Fill an empty beaker/Teflon jar with dilute acid
  - Leave it open in fume hood, near where samples are loaded, on benchtop, etc. Spike can be added before or after collection.
Blanks

Thermal instruments: Prior to loading, filaments are “degassed” (pre-heated under vacuum) to remove impurities.

A mass scan (from mass 230 to mass 245) of a filament that has not been degassed (light blue) and one that has been degassed.\textsuperscript{41}
Blanks

All filaments do have a background and may contain uranium. This background needs to be quantified and the measurement needs to be corrected for it.

Filament blank scans for three different filaments$^{42}$

![Graph showing filament blank scans for three different filaments](image-url)
SEM Linearity

Linearity tests on three different electron multipliers. At high count rates (>60,000 cps for ETP and SJUTS, >80,000 cps for Mascom), the electron multiplier loses detection efficiency. This can be corrected, but is a source of uncertainty in the measurement.  

*Note:* Current discrete dynode multiplies are linear up to about 500,000 cps.
Counting Statistics

- For very small samples, good quick estimate of uncertainty
- Final calculated uncertainty should not be better than the counting statistics
- Counting statistics are base on a Poisson distribution.
- Effectively, the more counts that are measured, the better the measured result is known.
- Not the only source of uncertainty in the measurement.
- Counting statistics = $\sqrt{n}$ where $n =$ number of counts
  - For 1,000,000 counts, the uncertainty is ±1,000 counts
- Relative uncertainty (counting stats) = $\frac{\sqrt{n}}{n} = \frac{1}{\sqrt{n}}$ (x 100 for %)
  - At ~95% level of confidence (~k=2) = $\frac{2}{\sqrt{n}}$
    - 40,000 counts = ~ 1% relative uncertainty
    - 4,000,000 counts = ~0.1% relative uncertainty
Uncertainty Calculations

The calculated uncertainty of the measurements will depend on the method used and corrections that are made

- Samples that have been corrected using an external standard will be limited by the uncertainty of that standard

- For environmental samples (and other measurements with low signals), the corrections related to peak-tailing, SEM-Faraday yield, background, and darknoise may become significant components of uncertainty
Uncertainty Calculations

- An example of the effect of the comparator on a series of measurements by Total Evaporation on TIMS (Mathew et al., 2013).

\[
\frac{^{235}\text{corrected}}{^{238}\text{measured}} = \frac{^{235}}{^{238}} \div CF; \quad CF = \frac{^{235}}{^{238}\text{ comparator, measured}} / \frac{^{235}}{^{238}\text{ comparator, certified value}}
\]

<table>
<thead>
<tr>
<th>Relative uncertainty on the measured value (235/238)</th>
<th>Relative uncertainty of the corrected value (k=2)</th>
<th>% contribution from the sample measurements (column 1)</th>
<th>% contribution from the uncertainty of the comparator (0.053%)</th>
<th>% contribution from the uncertainty of the comparator measurement (0.024%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.063</td>
<td>10</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>0.02</td>
<td>0.072</td>
<td>31</td>
<td>54</td>
<td>15</td>
</tr>
<tr>
<td>0.05</td>
<td>0.12</td>
<td>73</td>
<td>21</td>
<td>6</td>
</tr>
</tbody>
</table>

For the first two lines, though the uncertainty of the measurement is low, the combined uncertainty for the measurement after correction increases more than 2 times the uncertainty of the measurement due to both the uncertainty on the certified value of the comparator, and the uncertainty of the measurement of the comparator.
Summary/Conclusion:
Choosing a mass spectrometry method

Things to consider when choosing a method:

• What is the question that you are trying to answer?
• What is the information that you need?
• What method will best provide you with that information?
• What are the available funds?
• Are there any time constraints?
• How well do you need to know the answer? What kind of uncertainties are required?
Mass Spectrometers - A Comparison

**Q-ICPMS (Quadrupole) - $$**
- Trace element analysis, major isotopic analysis
- Fast sample throughput
- Fast scanning across many masses
- Lower resolution than sector field mass spectrometers

**Single Collector SF-ICPMS (Magnet-ESA) - $$$$$**
- Trace element analysis, isotopic analysis
- Reasonably fast sample throughput
- Reasonably fast scanning over masses
- Slower isotopic analysis due to single collector
Mass Spectrometers - A Comparison

• **TIMS (Magnet) - $$ $$ $$ $$**
  – Isotopics
  – Sample batch limited to turret size, can run up to ~21 samples a day (automatically)
  – High resolution
  – Few interferences for measurement of actinides

• **Multiple Collector SF-ICPMS (ESA-Magnet) - $$ $$ $$ $$**
  – Isotopic analysis
  – Could measure trace elements but it would be slow ... but optimized for isotopic analysis of one, or two elements at a time
  – High resolution
  – Faster isotopic analysis than single collector
References

General Textbooks on Mass Spectrometry


TIMS papers

- Buerger, S; Balsley, S. D; Baumann, S; Berger, J; Boulyga, S. F; Cunningham, J. A; Kappel, S; Koepf, A; Poths, J. Uranium and plutonium analysis of nuclear material samples by multi-collector thermal ionisation mass spectrometry: Quality control, measurement, and metrological traceability. *Int. J. Mass Spectrom.* **2012** 311, 40-50.

- Jakopic, R; Richter, S; Kuehn, H; Benedik, L; Pihlar, B; Aregbe, Y. Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with “multiple ion counting” and filament carburization. *Int. J. Mass Spectrom.* **2009** 279, 87-92.


References

General ICPMS papers


Magnetic Sector ICPMS papers

• Hoffmann, D. L; Prytulak, J; Richards D. A; Elliott, T; Coath, C. D; Smart, P. L; Scholz, D. Procedures for accurate U and Th isotope measurements by high precision MC-ICPMS. *Int. J. Mass Spectrom.* **2007** *264*, 97-109.

• Shen, C-C; Edwards, R. L; Cheng, H; Dorale, J. A; Thomas, R. B; Moran, S. B; Weinstein, S. E; Edmonds, H. N. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. *Chem. Geol.* **2002** *185*, 165-178.

• Shi, Y; Collins, R; Broome C. Determination of uranium, thorium and plutonium isotopes by ICP-MS. *J. Radioanal. Nucl. Chem.* **2013** *196*, 509-515.

Quadrupole ICPMS papers


• Greis, C; Karlsson, A; Dueker, A; Pettersson, H; Allard B. Determination of plutonium in environmental samples with quadrupole ICP-MS. *J. Radioanal. Nucl. Chem.* **2008** *275*, 55-70.

• Godoy, M. L. D. P; Godoy, J. M; Roldao, L. A; Tauhata, L. Determination of total content and isotopic compositions of plutonium and uranium in environmental samples for safeguards purposes by ICP-QMS. *J. Environ. Radioact.* **100**:613-625.

Uncertainty Calculations

References for Figures

2. https://www.physics.umn.edu/about/history/Nierweb.jpg
3. U.S. DOE – New Brunswick Laboratory
7. U.S. DOE – New Brunswick Laboratory
11. U.S. DOE – New Brunswick Laboratory
12. U.S. DOE – New Brunswick Laboratory
13. U.S. DOE – New Brunswick Laboratory
14. U.S. DOE – New Brunswick Laboratory
15. http://upload.wikimedia.org/wikipedia/commons/thumb/7/75/Quadrupole_mass_analyzer.svg/600px-Quadrupole_mass_analyzer.svg.png
17. http://www.chromedia.org/chromedia?waxtrapp=kwbgcDsHqnOxmOlIECpBgFlFyB&subNav=oibelDsHqnOxmOlIECvBG
18. http://www.shimadzu.com/an/hplc/support/qn5042000000by82-img/qn5042000000c196.gif
19. http://1.bp.blogspot.com/-XiWYMeLgdQU/TaOuwS_kf6I/AAAAAAAAAs/7GWH0Th05E/s1600/magnetic%2Bsector%2Banalyser.JPG
21. Thermo Scientific Neptune Brochure (this version out of print)
22. Thermo Scientific Element 2 Brochure (this version out of print)
23. U.S. DOE – New Brunswick Laboratory
References for Figures (cont)

28. U.S. DOE – New Brunswick Laboratory
29. U.S. DOE – New Brunswick Laboratory
30. U.S. DOE – New Brunswick Laboratory
31. U.S. DOE – New Brunswick Laboratory
33. U.S. DOE – New Brunswick Laboratory
37. U.S. DOE – New Brunswick Laboratory
38. U.S. DOE – New Brunswick Laboratory
39. U.S. DOE – New Brunswick Laboratory
40. U.S. DOE – New Brunswick Laboratory
41. U.S. DOE – New Brunswick Laboratory
42. U.S. DOE – New Brunswick Laboratory
Upcoming NAMP Radiochemistry Webinars

- Alpha Spectrometry – March 27, 2014
- Applications of Liquid Scintillation Counting – April 24, 2014
- Unconventional Drilling/Hydraulic Fracturing and Natural Radioactivity – May 22, 2014

Visit the NAMP website at www.wipp.energy.gov/namp