Application of plasma mass spectrometry for half-life measurement of medium and long-lived radionuclides

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Outline

- Introduction to NPL
- ICP-MS background
- Uses of ICP-MS at NPL
- Application to half-life measurements
  - Motivation
  - Theory
  - Results to date
  - Conclusions and future work
National Physical Laboratory

The UK’s National Measurement Institute

- Founded in 1900
- Based in Teddington, South West London
- ~900 specialists in measurement science (~30 in Nuclear Metrology)
- Purpose built laboratory campus
- Operated and owned by the Department for Business, Energy and Industrial Strategy
- Strategic partners- University of Surrey and Strathclyde
Inductively coupled plasma mass spectrometry (ICP-MS)

Expand the number of radionuclides measurable compared to decay counting techniques alone

Aim: to develop innovative procedures for measurement of radionuclides using state-of-the-art mass spectrometry

June 2014

September 2015 onwards
Inductively coupled plasma mass spectrometry (ICP-MS)

- **Sample introduction** - aqueous sample, typically in dilute acid
- **Torch** - sample evaporated, atomised and ionised into beam of singly charged positive ions
- **Interface** - focusing of ion beam as it passes from atmospheric to vacuum conditions
- **Mass analyser** - focus ions by mass-to-charge ratio
- **Detector** - output in counts per second
- Measurement time of several minutes per sample
Radioactivity measurement by mass spectrometry

\[ m = A \times MM \times t_{1/2} \div \ln(2) \times N_A \]

- If \( t_{1/2} \) is in seconds, MM in g/mol, and A in Bq/g, m will be expressed as g/g

- What does this mean?
  - For an equivalent activity, the number of radioactive atoms is proportional to analyte molar mass and half-life
  - Mass spectrometry is more sensitive for measurement of long-lived radionuclides

Lariviere et al. 2006
Radioactivity measurement by mass spectrometry

Specific activity \( (\text{Bq/g}) = \frac{\ln(2) \times N_A}{m \times t_{1/2}} \)

Mass equivalent to 1 Bq (pg) = \( \frac{1}{\text{SpA}} \times 1 \times 10^{12} \)

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>( t_{1/2} ) (years)</th>
<th>Specific activity (Bq/g)</th>
<th>Mass equivalent to 1 Bq (pg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{90}\text{Sr})</td>
<td>28.8</td>
<td>(5.1\times10^{12})</td>
<td>0.2</td>
</tr>
<tr>
<td>(^{151}\text{Sm})</td>
<td>94.7</td>
<td>(9.3\times10^{11})</td>
<td>1.1</td>
</tr>
<tr>
<td>(^{135}\text{Cs})</td>
<td>(2.3\times10^6)</td>
<td>(4.1\times10^7)</td>
<td>(2.4\times10^4)</td>
</tr>
<tr>
<td>(^{129}\text{I})</td>
<td>(1.5\times10^7)</td>
<td>(6.5\times10^6)</td>
<td>(1.5\times10^5)</td>
</tr>
<tr>
<td>(^{238}\text{U})</td>
<td>(4.5\times10^9)</td>
<td>(1.2\times10^4)</td>
<td>(8.0\times10^7)</td>
</tr>
</tbody>
</table>

*1 pg = \(1\times10^{-12}\) g- typical ICP-MS limit of detection 0.001 – 1 pg/g
<table>
<thead>
<tr>
<th>Application</th>
<th>Radionuclides currently measurable</th>
<th>Industry need</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinides</td>
<td>$^{231}$Pa, $^{232}$Th, $^{237}$Np, $^{235}$U, $^{236}$U, $^{238}$U, $^{239}$Pu, $^{240}$Pu, $^{241}$Am, $^{243}$Am</td>
<td>Fuel reprocessing, decommissioning, NORM</td>
</tr>
<tr>
<td>Medium-lived radionuclides</td>
<td>$^{90}$Sr, $^{151}$Sm, $^{226}$Ra, $^{63}$Ni</td>
<td>Waste characterisation and decommissioning</td>
</tr>
<tr>
<td>Isotope ratios</td>
<td>$^{135}$Cs/$^{137}$Cs, $^{129}$I/$^{127}$I, $^{239}$Pu/$^{240}$Pu</td>
<td>Nuclear forensics</td>
</tr>
<tr>
<td>Long-lived, low abundance radionuclides</td>
<td>$^{129}$I, $^{93}$Zr, $^{99}$Tc</td>
<td>Decommissioning, long-term waste monitoring</td>
</tr>
<tr>
<td>Stable analogues of short-lived nuclides</td>
<td>Rare earth elements</td>
<td>Nuclear medicine- rapid development and validation of procedures</td>
</tr>
<tr>
<td>Material characterisation</td>
<td>Various (recent examples $^{226}$Ra and $^{99}$Tc)</td>
<td>Reference material characterisation, separation materials e.g. resins, graphene, nanomaterials</td>
</tr>
<tr>
<td>Radionuclide standards</td>
<td>Nuclides with half-life &gt;30 years</td>
<td>High purity mass spectrometry standards for validation</td>
</tr>
</tbody>
</table>
Radionuclide measurement by mass spectrometry

- Effectiveness of mass spectrometry dependent on the **half-life** and interference removal

**Isobaric**
- Isotope with similar mass to analyte
  - $^{90}$Zr

**Polyatomic**
- Reaction of elements with gases in the plasma
  - $^{52}$Cr$^{38}$Ar, $^{89}$Y$^1$H, $^{58}$Ni$^{16}$O$_2$

**Tailing**
- High concentration of stable isotope at a neighbouring mass
  - $^{88}$Sr
Removing interferences using ICP-MS/MS

- Collision/reaction cell and additional quadrupole mass filter
- Improvement in interference removal capability
- Reduces or removes need for offline separation, reducing procedural time
Example applications

**Zr-93** (aqueous waste, steel)

**Np-237**
(aqueous waste, soil, sediment)

**I-129** (aqueous waste, solid decommissioning samples)
How can ICP-MS contribute to decay data?

- Underpin methods developed for challenging nuclides
- ICP-MS increasingly used to contribute to half-life measurements
- In some cases, values have not been carried out for a long time
- Inconsistencies in the methodology used from a mass spectrometry perspective

Aim for a comprehensive assessment of different ICP-MS techniques for measurement and interference assessment
What has to be considered?

- **Mass bias**
  - For ICP-MS, lighter isotopes are more scattered than heavier isotopes
  - Correction using isotope dilution and sample/standard bracketing with a certified isotopic standard

- **Isobaric, polyatomic and tailing interferences**
  - Chemical and/or instrument separation

- **Detector response**
  - Calibration across pulse and analogue detector modes

- **Instrument response**
  - Monitoring of internal standard during run
General experimental approach

Isotope spike of known amount $m_z$

- Use activity and abundance ratios if decay constant is known
- Isotope ratio analysis $m_{A,Z}/m_z$
- Mass of source material $m_{tot}$

Molar mass of radioisotope $M_{A,Z}$

- Activity of source material $A_{tot}$
- Activity of radionuclide $A_{A,Z}$

Concentration of radionuclide $n_{A,Z}$

- Avogadro’s number $N_A$
- Number of atoms of isotope of interest $N_{A,Z}$

Decay constant $\lambda$

- $\ln(2)$
- Half-life $T_{1/2}$

Absolute measurement of activity concentration

$$\lambda_{A,Z} = \frac{A_{A,Z}}{N_{A,Z}} = \left( \frac{A_{tot}}{m_{tot}} \right) \left( \frac{N_A}{M_{A,Z}} \times \frac{m_{A,Z}}{m_z} \times \frac{m_z}{m_{tot}} \times \frac{m_{tot}}{m_{tot}} \right)$$

Weighing of the source material

Determination of isotopic composition

(where $A,Z$ is a specific radionuclide)
What approaches can be used?

Isotope dilution

- Measurement of relative abundance of the radionuclide of interest using another isotope of the same element

- Relies on:
  - Precise instrument calibration
  - Accurate correction for isotope fractionation and interferences
  - Well-known recovery after sample preparation
Isotope dilution

Single isotope dilution

- Add known amount of isotope of the element of interest, and measure the isotopic ratio
- Can calculate the concentration of the isotope of interest:

\[
iA = \frac{jA_S}{(R_{mix} - R_{master}) \times F}
\]

- \(R_{mix}\) = measured isotope ratio
- \(R_{master}\) = isotope ratio before spike
- \(F\) = mass discrimination factor
- \(A\) = abundance of the element of interest
- \(iA\) = target isotope and \(jA_s\) = spiked isotope
Isotope dilution

Calibration standard dilution

- A set of isotope dilution solutions can be prepared against a reference standard to generate a calibration curve. This can be compared to the spiked sample to determine composition.
Isotope dilution

Double dilution
- Used when composition and amount of spiked solution is unknown
- Reverse dilution - spike is diluted with a natural standard of known composition, followed by dilution with spike and sample of interest

Triple dilution
- $2 \times$ reverse isotope dilution
- Eliminates the need to determine sample composition
- Theoretically lower measurement uncertainty, longer procedural time
- Recommended for enriched spikes with challenging sample compositions, or memory effects between sample dilutions
Example: $^{238}\text{U}$ by $^{234}\text{U}$ dilution

$$ [U]_S = [U]_{Sp} \times \frac{m_{Sp}}{m_S} \times \frac{M_S}{M_{Sp}} \times (\frac{234}{234})_{Sp} \times \frac{(\frac{238}{234}U)_M}{(\frac{238}{234}U)_S - (\frac{238}{234}U)_M} $$

$M$, $S$ and $Sp$ = mixture, sample and spike, respectively

$m$ and $M$ = masses and atomic weights of sample and spike, respectively

$(234)$ is the atomic abundance of $^{234}\text{U}$ expressed in atoms

$(238)_S$ is the mass abundance of $^{238}\text{U}$

Half-life calculated from:

$$ t_{1/2} = \frac{\ln(2) \cdot N_0 \cdot m}{A \cdot M \cdot f} $$

$N_0$ = Avogadro’s number

$m$ = mass concentration of $^{238}\text{U}$

$A$ = activity of the solution per unit mass

$M$ = atomic mass of $^{238}\text{U}$

$f$ = number of seconds in a year

Cassette et al. 2010
What approaches can be used?

Separation and ingrowth

- Measurement of long-lived radionuclide with relatively short-lived daughter
- Chemical separation, followed by ingrowth measurement relative to the parent over several years
- Method does not assume secular equilibrium e.g. between $^{234}$U and $^{238}$U
- Alternative approach for when a stable isotope is not available for isotope dilution
- Assumes that there is no external input of either nuclide over time

Candidates for ingrowth-based half-life measurement

<table>
<thead>
<tr>
<th>Nuclide Pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U / $^{230}$Th</td>
</tr>
<tr>
<td>$^{233}$U / $^{229}$Th</td>
</tr>
<tr>
<td>$^{239}$Pu / $^{235}$U</td>
</tr>
<tr>
<td>$^{240}$Pu / $^{236}$U</td>
</tr>
<tr>
<td>$^{231}$Pa / $^{227}$Ac</td>
</tr>
</tbody>
</table>

Varga et al. 2016
Example: $^{234}\text{U}$ by $^{230}\text{Th}$ ingrowth

- $^{230}\text{Th}$ ingrowth after separation can be calculated by:

$$\frac{n(^{230}\text{Th})(t)}{n(^{234}\text{U})(t)} = \frac{\lambda_{\text{U}-234}}{\lambda_{\text{Th}-230} - \lambda_{\text{U}-234}} \left( e^{-\lambda_{\text{U}-234}t} - e^{-\lambda_{\text{Th}-230}t} \right) + \frac{n(^{230}\text{Th})^0}{n(^{234}\text{U})(t)} e^{-\lambda_{\text{Th}-230}t}$$

- $n(^{230}\text{Th})(t)$ and $n(^{234}\text{U})(t)$ = number of atoms as a function of time
- $\lambda_{\text{Th}-230}$ and $\lambda_{\text{U}-234}$ = decay constants
- $n(^{230}\text{Th})^0 = ^{230}\text{Th}$ after chemical separation ($t = 0$)
- $t =$ elapsed time since separation

- Low decay constant and short ingrowth time (3-4 years) means $\lambda t$ is close to 0
- Using approximations $e^x \approx 1+x$ and $(1 - \lambda_{\text{Th}-230}t) \approx 1$, and that decay of accumulated of $^{230}\text{Th}$ and $^{234}\text{U}$ decay is negligible:

$$\frac{n(^{230}\text{Th})(t)}{n(^{234}\text{U})(t)} \approx \lambda_{\text{U}-234}t + \frac{n(^{230}\text{Th})^0}{n(^{234}\text{U})^0}$$

- $n(^{234}\text{U})^0 = ^{234}\text{U}$ at the time of separation ($t=0$)
- $n(^{230}\text{Th})/n(^{234}\text{U})$ is linearly proportional to the time since chemical separation ($t$), where the regression coefficient is equal to the decay constant

Varga et al. 2016
Measurement of certified U isotopic standard by ICP-MS/MS

<table>
<thead>
<tr>
<th>Isotope</th>
<th>234</th>
<th>235</th>
<th>236</th>
<th>238</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom %</td>
<td>1.6653</td>
<td>97.6630</td>
<td>0.1491</td>
<td>0.5229</td>
</tr>
<tr>
<td>Interference</td>
<td>235U tailing</td>
<td>234U tailing</td>
<td>235U tailing</td>
<td>236U1H2</td>
</tr>
</tbody>
</table>

- Tailing removed by one or two quadrupole mass filters
- Hydride formation due to splitting of water in the plasma. Removal options:
  - Desolvating sample introduction (reduces water loading into the plasma)
  - ICP-MS/MS
Measurement of certified U isotopic standard by ICP-MS/MS

Single quadrupole measurement

- Most significant interference is bias towards $^{236}\text{U}$ due to $^{235}\text{U}^1\text{H}$
- No evidence of $^{235}\text{U}$ tailing onto $^{234}\text{U}$

- Change in bias with mass analysed
- Some mass bias correction laws are based solely on mass difference between isotopes, which would not be applicable here
- Wider range of masses needs investigating
Measurement of certified U isotopic standard by ICP-MS/MS

**MS/MS O₂ measurement**

- Two quadrupole mass filters removes tailing
- O₂ shifts $^{235}U^1H$ to $^{235}U^{16}O$, but not $^{235}U^{16}O^1H$
- Change in bias as lighter isotopes more readily form oxides
- Under cell conditions tested, lighter isotopes more readily form oxides, ‘hiding’ instrument bias
- Needs further investigation
Measurement of certified U isotopic standard by ICP-MS/MS

Instrument drift
- Due to variations in instrument performance, and matrix effects
- Different effect on different isotopes
- Internal standard with multiple isotopes must be considered

Pulse/analogue detector settings
- High abundance isotope (e.g. $^{235}$U) in analogue, lower abundance isotopes in pulse
- P/A correction with calibration standards for each isotope that cross the detector modes
Conclusions and next steps

- ICP-MS primarily used at NPL to expand radionuclides measurable compared to decay counting techniques alone
- This needs to be underpinned with contribution to nuclear decay data
- Aim for comparison of approaches to address inconsistencies between techniques
- A comparison with alternative instrument designs would be useful:
  - Multi-collector instrument- multiple detectors, improved isotope ratio precision, no need for peak ‘hopping’
  - RIMS/AMS- improved sensitivity, interference removal
Thank you

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