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

Mass Spectrometry in the Nuclear Metrology Group

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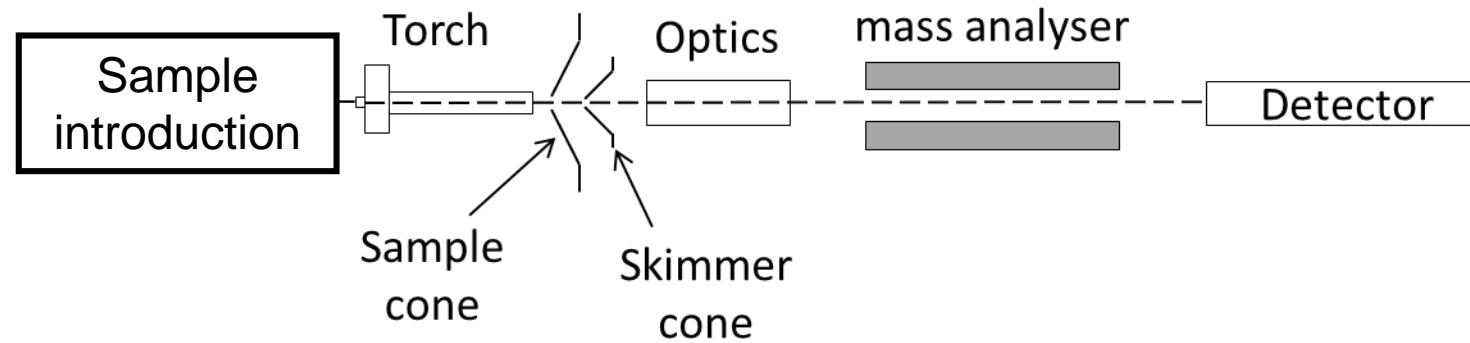

June 2014

September 2015 onwards

- Inductively coupled plasma mass spectrometry (ICP-MS)
- Expand the number of radionuclides measurable compared to decay counting techniques alone

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

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

- 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 (Bq/g) = (ln(2) × N_A)/ (m × $t_{1/2}$)

Mass equivalent to 1 Bq (pg) = (1/SpA) × 1×10^{12}

Radionuclide	$t_{1/2}$ (years)	Specific activity (Bq/g)	Mass equivalent to 1 Bq (pg)*
^{90}Sr	28.8	5.1×10^{12}	0.2
^{151}Sm	94.7	9.3×10^{11}	1.1
^{135}Cs	2.3×10^{6}	4.1×10^{7}	2.4×10^{4}
^{129}I	1.5×10^{7}	6.5×10^{6}	1.5×10^{5}
^{238}U	4.5×10^{9}	1.2×10^{4}	8.0×10^{7}

*1 pg = 1×10^{-12} g- typical ICP-MS limit of detection 0.001 – 1 pg/g

Applications

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

Radionuclide measurement by mass spectrometry

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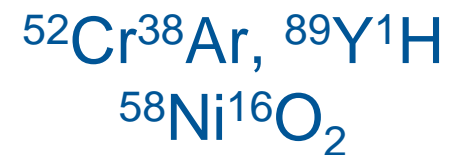
Isobaric

Isotope with similar mass to analyte

^{90}Zr

Polyatomic
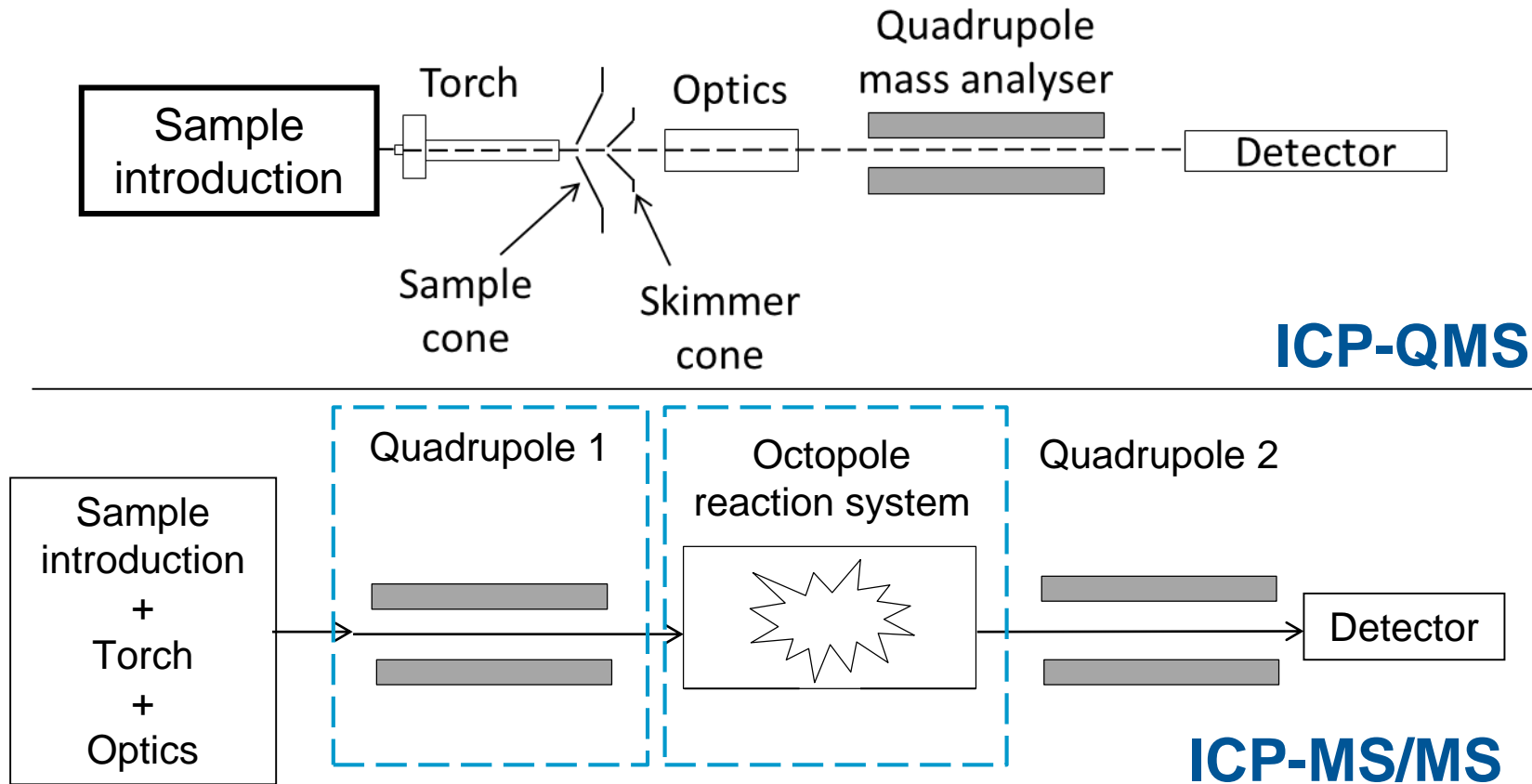
Reaction of elements with gases in the plasma

^{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
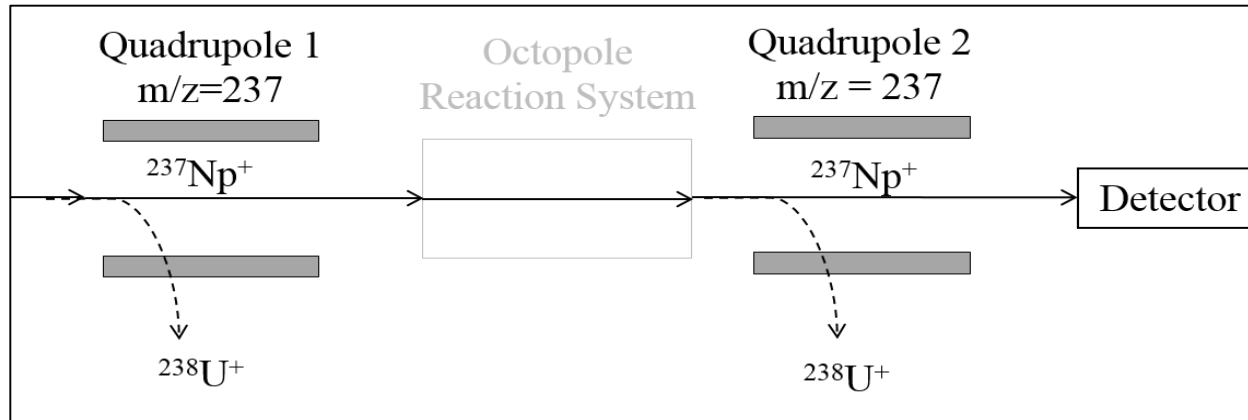

ICP-QMS

ICP-MS/MS

- Collision/reaction cell and additional quadrupole mass filter

- Improvement in interference removal capability

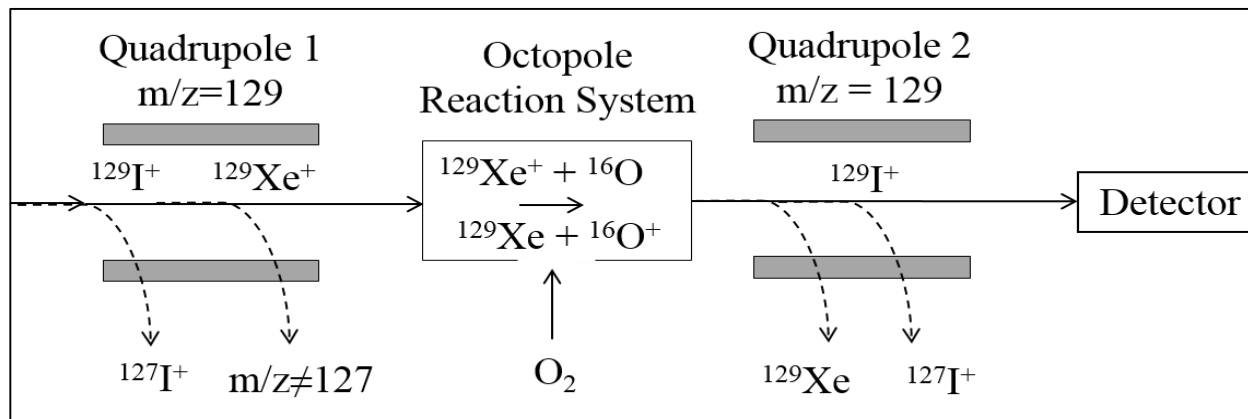- Reduces or removes need for offline separation, reducing procedural time

Example applications
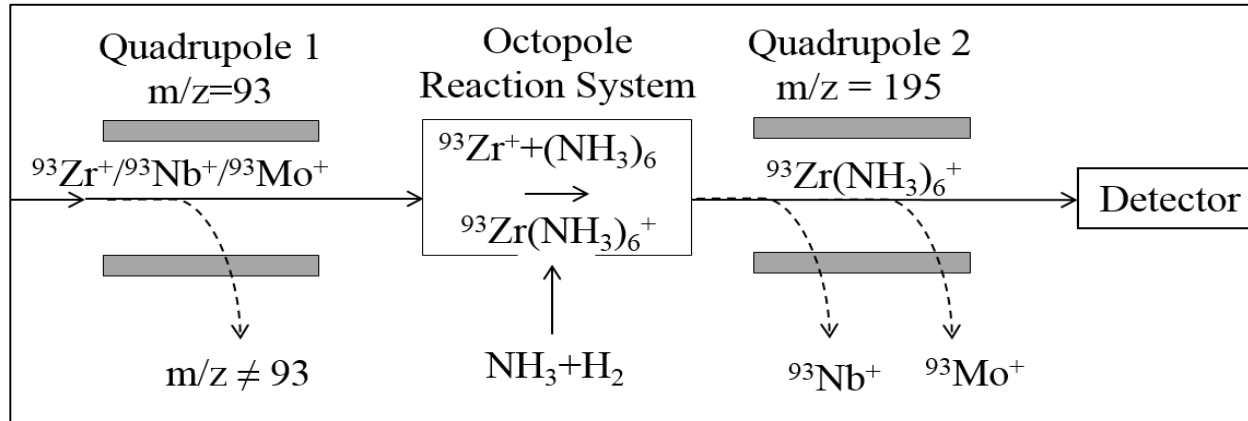
Zr-93 (aqueous waste, steel)

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
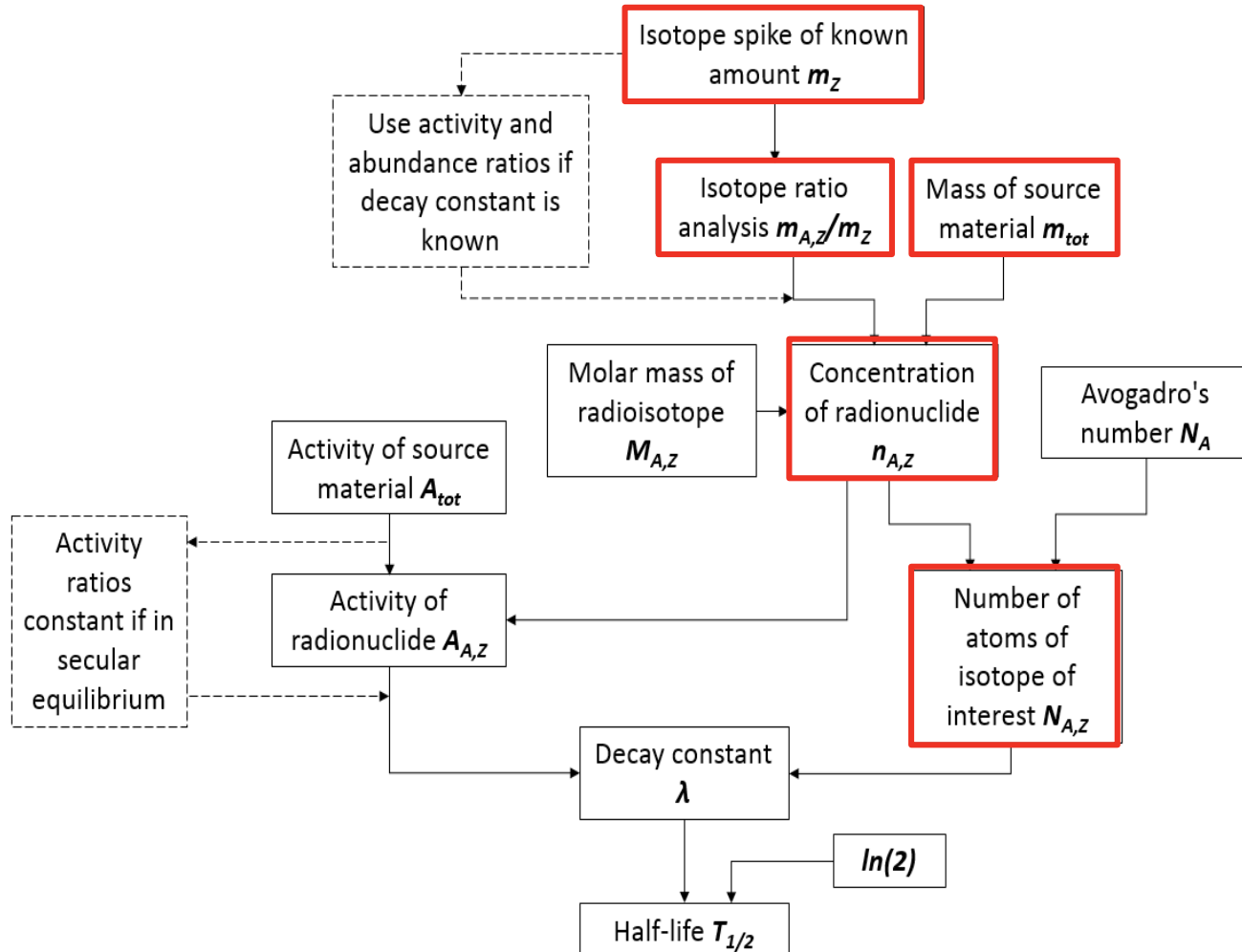
What approaches can be used?

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:

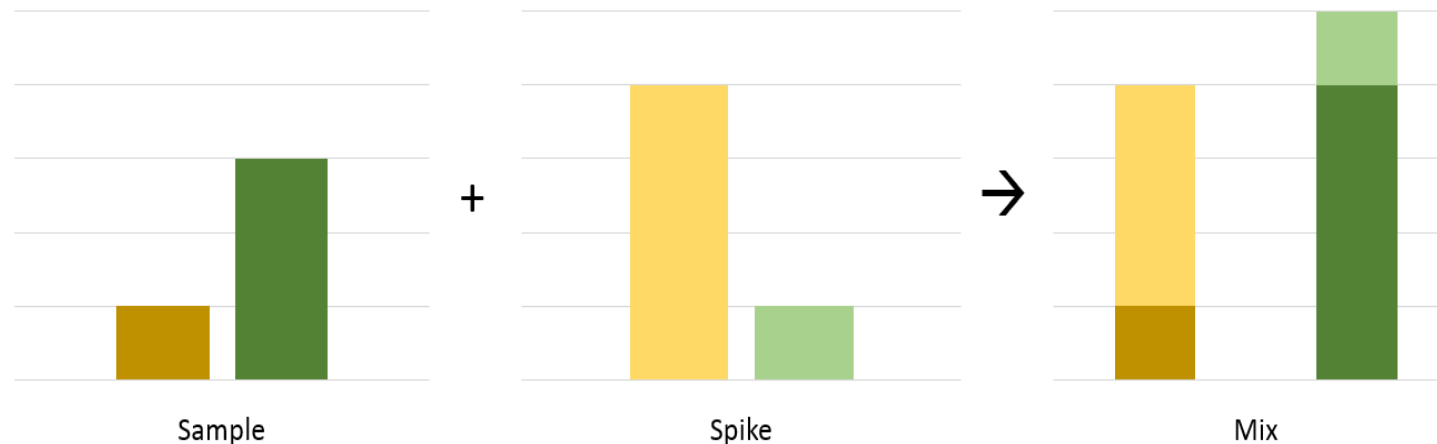$$^iA = \frac{^jA_S}{(R_{mix} - R_{master}) \times F}$$

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
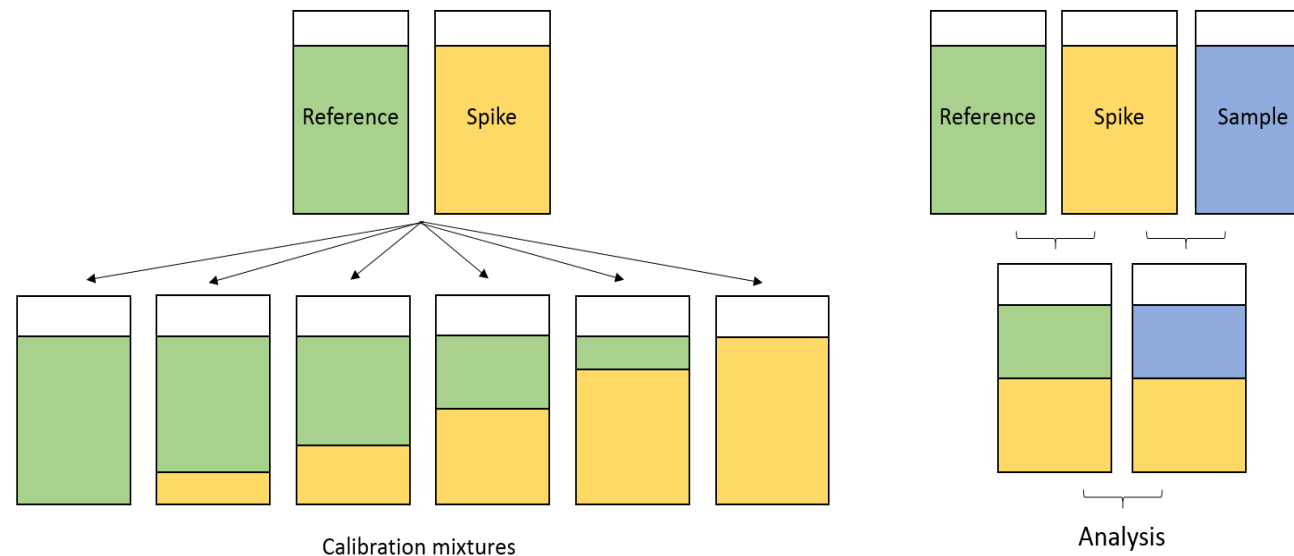

Sample   Spike   Mix

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

Calibration mixtures

Analysis

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× 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}U by ^{234}U dilution

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

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}U expressed in atoms

$(238)_s$ is the mass abundance of ^{238}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}U

A = activity of the solution per unit mass

M = atomic mass of ^{238}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
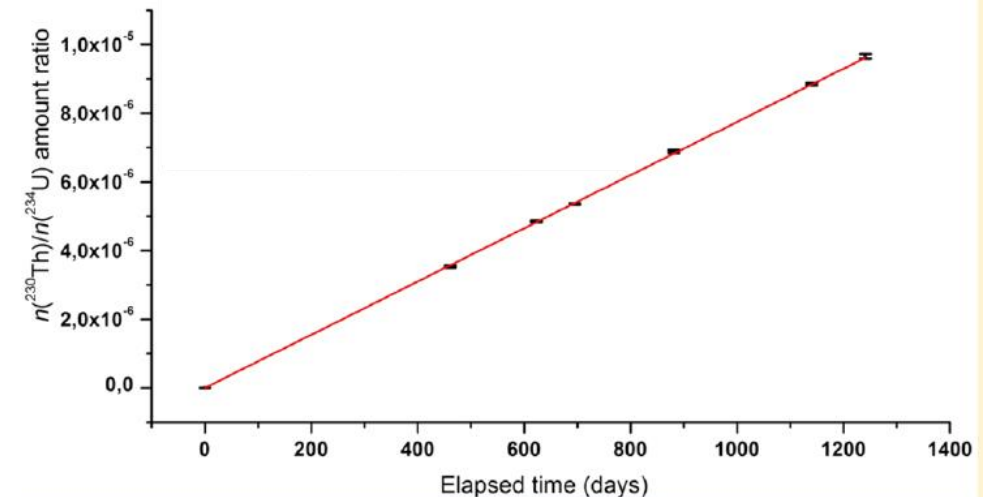
Candidates for ingrowth-based half-life measurement

^{234}U / ^{230}Th
^{233}U / ^{229}Th
^{239}Pu / ^{235}U
^{240}Pu / ^{236}U
^{231}Pa / ^{227}Ac

Varga et al. 2016

Example: ^{234}U by ^{230}Th ingrowth

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

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

- $n(^{230}\text{Th})(t)$ 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
- $n(^{230}\text{Th})^0 = {}^{230}$Th after chemical separation (t = 0)
- t = elapsed time since separation

- Low decay constant and short ingrowth time (3-4 years) means λt 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}Th and ^{234}U decay is negligible:

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

- $n(^{234}\text{U})^0 = {}^{234}$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

Isotope	234	235	236	238
Atom %	1.6653	97.6630	0.1491	0.5229
Interference	^{235}U tailing	^{234}U tailing ^{234}U^{1}H	^{235}U tailing ^{235}U^{1}H	^{236}U^{1}H$_2$

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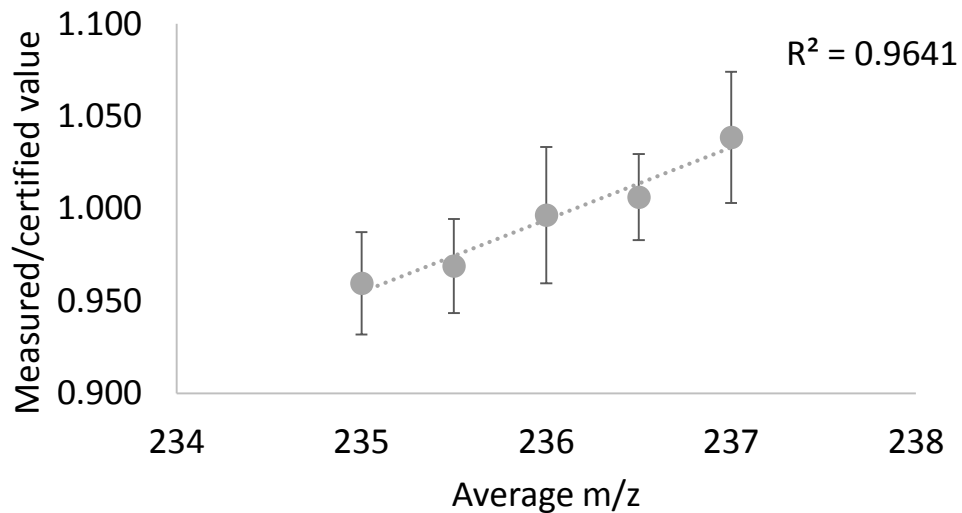 - Desolvating sample introduction (reduces water loading into the plasma)
  - ICP-MS/MS
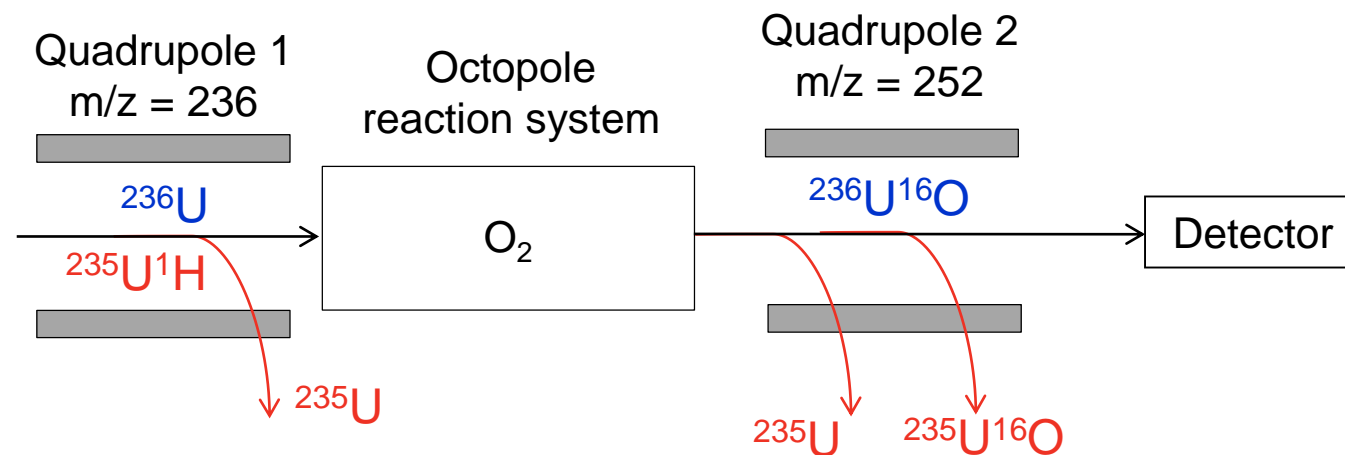
# Measurement of certified U isotopic standard by ICP-MS/MS
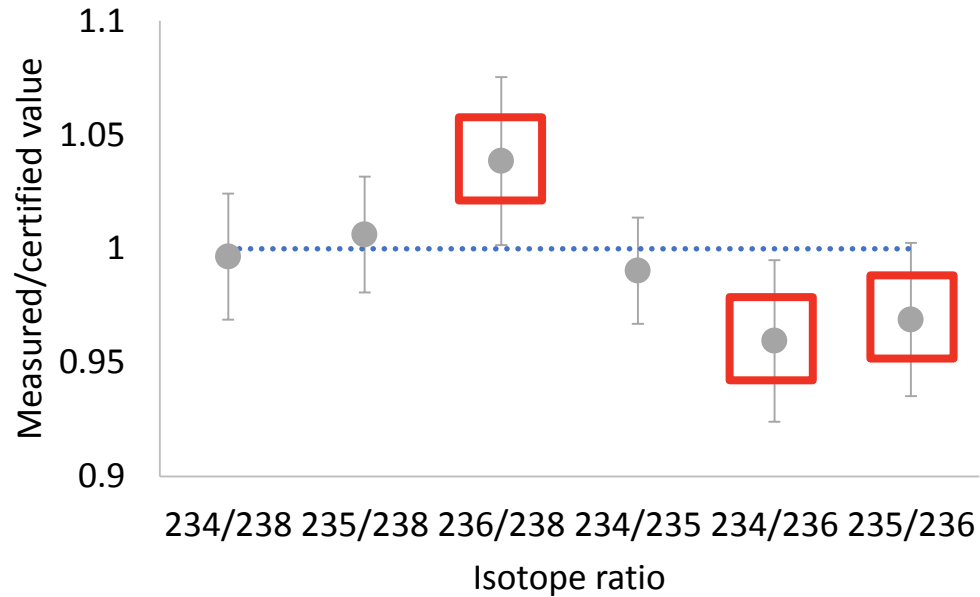
Single quadrupole measurement

- Most significant interference is bias towards ^{236}U due to $^{235}U^1H$

- No evidence of ^{235}U tailing onto ^{234}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
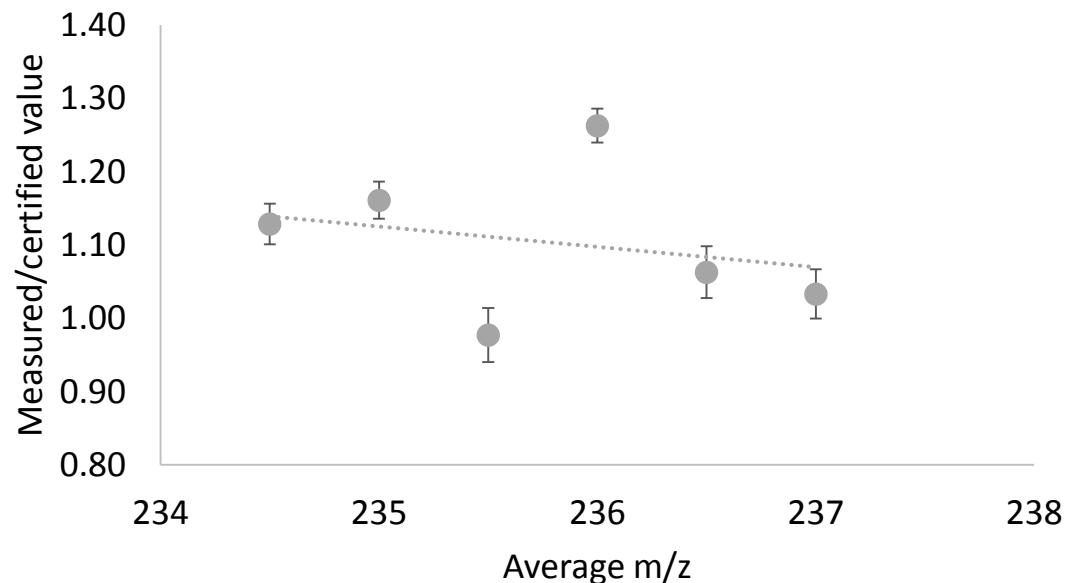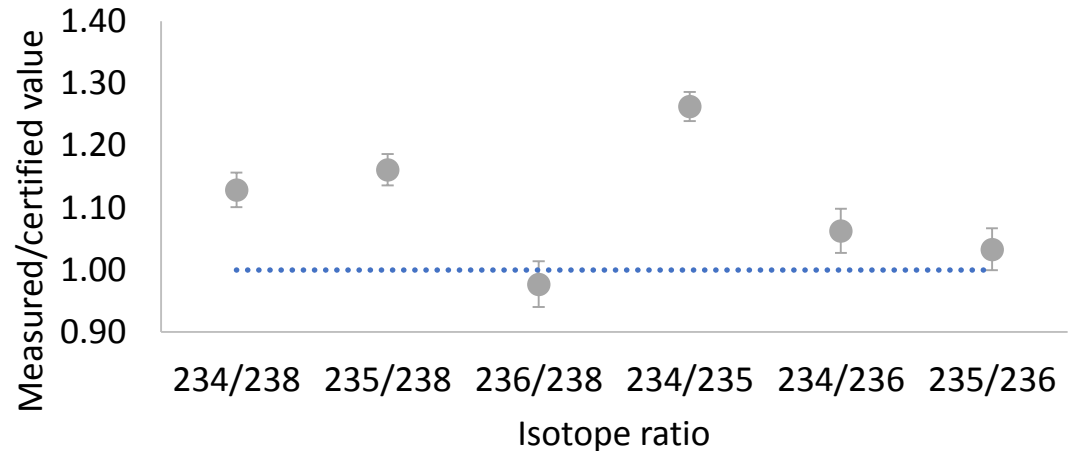
MS/MS O$_2$ measurement

- Two quadrupole mass filters removes tailing

- O$_2$ 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
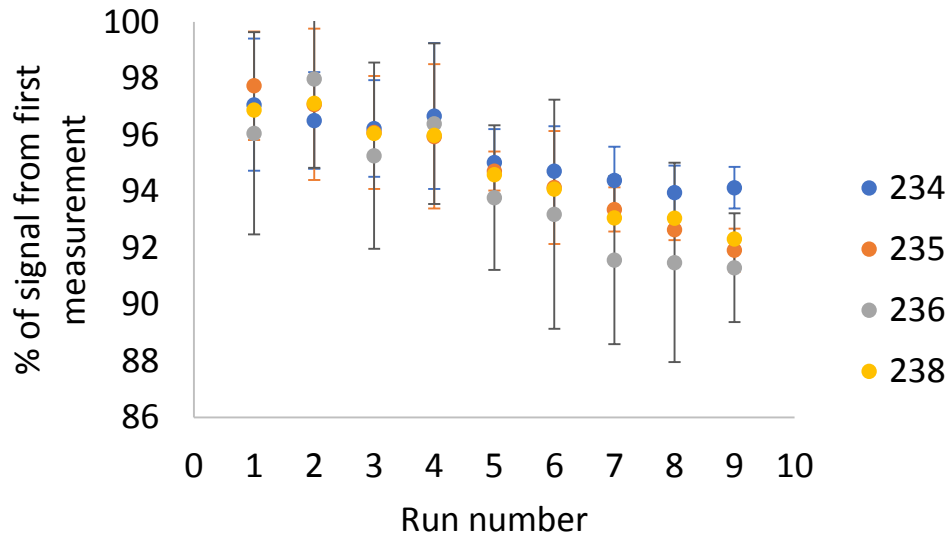
Conclusions and next steps

- 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