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

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Abstract. When combined with established primary counting techniques, atom counting using inductively coupled plasma mass spectrometry (ICP-MS) can be a powerful metrological tool for providing updated, precise half-life values for medium and long-lived radionuclides, giving end-users increased confidence in measurement for a range of nuclear applications. ICP-MS is increasingly being used for this application, and this study outlines the methods for atom counting using the latest generation tandem ICP-MS/MS. The aim is to provide a consistent methodology that is currently lacking, and attention is paid to the importance of interference removal and minimising uncertainties, with preliminary results given for uranium isotopes.

1. Background and motivation
Inductively coupled plasma mass spectrometry (ICP-MS) is a robust, flexible and high throughput analytical technique which has been increasingly applied to radionuclide quantification over the past 30 years[1]. Applications include measurement of one or multiple radionuclides in relation to decommissioning, environmental monitoring, nuclear forensics, nuclear medicine, and measurement of the half-life of medium and long-lived radionuclides (Table 1).
Table 1. Applications of ICP-MS for measurement of radionuclides.

| Application | Examples of radionuclides measurable | Industry need |
|-------------|-------------------------------------|---------------|
| Actinides[2] | $^{231}$Pa, $^{232}$Th, $^{233}$Np, $^{235}$U, $^{236}$U, $^{238}$U, $^{239}$Pu, $^{240}$Pu, $^{241}$Am, $^{243}$Am | Fuel reprocessing, decommissioning |
| Medium-lived radionuclides[3,4] | $^{90}$Sr, $^{151}$Sm, $^{226}$Ra, $^{65}$Ni | Decommissioning, waste characterisation, NORM |
| Isotope ratios[5] | $^{135}$Cs/$^{137}$Cs, $^{129}$I/$^{127}$I, $^{239}$Pu/$^{240}$Pu | Nuclear forensics, discharges |
| Long-lived, low abundance radionuclides[2] | $^{129}$I, $^{93}$Zr, $^{99}$Tc | Decommissioning, discharges, long-term waste monitoring |
| Stable analogues of short-lived nuclides[6] | Various (recent examples $^{226}$Ra and $^{99}$Tc) | Nuclear medicine - rapid development and validation of procedures, impurity testing |
| Material characterisation[7–9] | Various (recent examples $^{226}$Ra and $^{99}$Tc) | Reference material characterisation, separation materials e.g. resins, graphene nanomaterials |
| Radionuclide standards[10] | Various radionuclides | Nuclides with half-life $\geq$30 years | Reference material characterisation, separation materials e.g. resins, graphene. nanomaterials |

The effective use of mass spectrometry for accurate and low uncertainty radionuclide measurement is dependent on the half-life, as well as the effectiveness of interference removal using either chemical and/or instrument-based separation. For the same activity concentration, mass spectrometry is more sensitive for longer-lived radionuclides, as this corresponds to a higher number of atoms, contrary to decay counting which favors a higher decay rate[1].

Accurate measurement is dependent on the effective removal of interferences. The key interferences to consider are: isobaric (stable or radioactive isotopes with a similar mass to the analyte that cannot be resolved by the detector e.g. $^{238}$Pu and $^{238}$U); polyatomic (e.g. $^{235}$U$^1$H on $^{236}$U, formed by reactions of elements with gases in the plasma including Ar, O and H); and tailing (caused by a high concentration of an isotope one or two mass units either side of the analyte mass e.g. $^{235}$U on $^{236}$U). The instrument used in this study is a tandem ICP-MS/MS with two quadrupole mass analyzers, separated by a collision/reaction cell. The first quadrupole improves removal of tailing interferences compared to single quadrupole designs (Figure 1) and filters the ion beam prior to the collision/reaction cell, improving removal of cell-based polyatomics. A reaction gas e.g. O$_2$ or NH$_3$ can be introduced into the collision/reaction cell to selectively react with either the interference or the analyte (e.g. use of O$_2$ to shift $^{235}$U$^1$H to $^{235}$U$^{16}$O, which does not overlap with $^{236}$U$^{16}$O). Alternatively, a collision gas such as H$_2$ or He can be used to collide with and reduce the energy of polyatomic interferences, which then cannot overcome an energy filter at the cell exit prior to the detector. These interference removal capabilities have been applied to measurement of multiple radionuclides in complex sample matrices with minimal offline sample preparation, improving sample throughput[4,8,11].
In recent years, mass spectrometric techniques (primarily ICP-MS) have been used increasingly to contribute to half-life measurements for radionuclides including $^{90}$Zr, $^{151}$Sm and $^{176}$Lu\[10,12–16\]. Atom counting by ICP-MS can be combined with absolute activity measurement using established primary counting techniques (e.g. triple to double coincidence ratio and digital coincidence counting) and controlled sample preparation for accurate assessment of the half-life\[17\]. Despite the increase in publications, there is a lack of consistency in the methodology used and comparison between approaches. It is important to critically compare different methodologies, especially as a number of medium and long-lived radionuclides have not been measured for many years and would benefit from updated values (Table 2)\[18\]. The aim of this work is to develop and compare procedures for atom counting of radionuclides using state-of-the-art ICP-MS/MS, focusing on online interference removal capability, and optimising the instrument setup to minimise the measurement uncertainty. The aim is for the methodology developed to be transferable to atom counting of radionuclides where the half-life value currently suffers from outdated measurement and/or high uncertainty.

**Table 2.** Half-lives of selected long-lived natural and anthropogenic radionuclides with associated uncertainty.

| Origin       | Isotope | Half-life (a)       | ± %  | Latest measurement |
|--------------|---------|---------------------|------|--------------------|
| $^{238}$U chain | $^{238}$U | 4.468 (5) × 10$^{9}$ | 0.11 | 1971\[19\], 2017\[10\] |
|              | $^{234}$U | 2.4525 (49) × 10$^{3}$ | 0.20 | 2000\[20\]         |
|              | $^{230}$Th | 7.569 (23) × 10$^{5}$ | 0.30 | 2000\[20\]         |
|              | $^{235}$U | 7.04 (1) × 10$^{8}$ | 0.14 | 1993\[21\]         |
|              | $^{231}$Pa | 32765 (110) | 0.38 | 1969\[22\], 2019 \[23\] |
| $^{232}$Th chain | $^{232}$Th | 1.401 (7) × 10$^{10}$ | 0.50 | 1963\[24\]         |
| Anthropogenic | $^{229}$Th | 7917 (48) | 0.10 | 2014\[25\]         |
|              | $^{233}$U | 1.5903 (130) × 10$^{5}$ | 0.08 | 2009\[26\]         |
|              | $^{238}$U | 2.3415 (14) × 10$^{7}$ | 0.06 | 1972\[27\]         |

2. **Theory and experimental considerations**

2.1. **Atom counting**

For an equivalent activity, the number of radioactive atoms is proportional to analyte molar mass and half-life. This can be shown using equation (1):

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

(1)
Where \( m \) is the number of radioactive atoms in g/g; \( A \) is activity in Bq/g; \( MM \) is molar mass in g/mol; \( t_{1/2} \) is the half-life in s; and \( N_A \) is Avogadro’s number. This means that by using atom counting and a measurement of specific activity, we can find a value for the half-life. This is beneficial for medium to long half-lives, as usual decay curves over time will take too long to create and will come with high measurement uncertainties.

Mass spectrometry is more sensitive for measurement of long-lived radionuclides. The lower the specific activity of a radionuclide, the higher its mass equivalent. This can be shown using equations (2) and (3).

\[
SpA = \frac{\ln(2) \times N_A}{m \times t_{1/2}}
\]

\[
\text{Mass equivalent to 1 Bq (g) } = \frac{1}{SpA}
\]

Where \( SpA \) is the specific activity (Bq/g). It is well established that the uncertainty in the activity measurement will be relatively low (<1 \%) [23], therefore attention must be paid to minimizing the uncertainty associated with atom counting and hence, the overall uncertainty of the half-life measurement. Optimizing the instrument setup for interference removal and analyte sensitivity are key to achieving this.

There are two main approaches to atom counting using ICP-MS; isotope dilution, and chemical separation of the target radionuclide followed by measuring ingrowth of the decay product.

### 2.1.1. Isotope dilution

The radionuclide of interest can be measured in relative abundance of another isotope of the same element. This approach is ideal in the case where the radioisotope of interest has other stable or long-lived isotopes. However, it relies on precise instrument calibration, accurate correction for isotope fractionation and interferences and well-known recovery after sample preparation.

A single stage isotope dilution involves adding a known amount of an isotope of the element of interest to the sample, and then calculating the concentration of the isotope of interest relative to the known isotope. A set of isotope dilution solutions can be prepared against a reference standard to generate a calibration curve. This can be used to determine accurate isotopic concentration in the sample, or can be compared to an unknown sample to determine isotopic composition[28,29]. Figure 2 demonstrates an isotope dilution with \(^{234}\text{U}\) and \(^{238}\text{U}\) pure isotope solutions. Each solution can then be measured to find the concentration of each isotope per solution.

The isotope dilution approach has been applied to the half-life measurement of a range of radionuclides including \(^{176}\text{Lu}\) \((t_{1/2} = 3.640 \times 10^{10}\) years\), \(^{90}\text{Zr}\) \((t_{1/2} = 1.647 \times 10^7\) years\), \(^{93}\text{Zr}\) \((t_{1/2}=1.13 \times 10^6\) years\) and \(^{151}\text{Sm}\) \((t_{1/2} = 96.6\) years\)[12–15].

![Figure 2. Schematic of isotope dilution solutions with \(^{238}\text{U}\) and \(^{234}\text{U}\).](image)
2.1.2. Ingrowth. An alternative technique to measuring the half-life of a long-lived radionuclide is to measure the ingrowth of its daughter. Following separation from its daughters, the sample can be measured over a long period (several years) and the daughter ingrowth monitored and measured as a ratio of the parent. This will allow for the change in decay rate to be quantified and a decay curve to be generated. This technique works well for the measurement of long-lived radionuclides with a relatively short-lived daughter, as it allows for considerable simplifications to be made to the calculations. The activity of the decay products reach secular equilibrium with the parent. The activity of the long-lived parent can be assumed to be constant over the measurement time[16].

The ingrowth approach is useful for radionuclides with no stable isotopes (e.g. U), as the uncertainty in the decay data of the radioisotope used for isotope dilution is avoided. However, several years of ingrowth measurements are required, and it is applicable to only a limited number of radionuclides that have relatively short-lived daughters. The ingrowth approach has been applied in the literature for the half-life measurement of $^{234}$U ($t_{1/2} = 75.38 \times 10^3$ years) via ingrowth of $^{230}$Th, and $^{238}$U ($t_{1/2} = 4.456 \times 10^9$ years) via ingrowth of $^{234}$Th[10,16]. Other potentially suitable radionuclide pairs for this technique include $^{233}$U/$^{229}$Th, $^{239}$Pu/$^{235}$U and $^{240}$Pu/$^{236}$U for the measurement of the $^{229}$Th, $^{239}$Pu and $^{240}$Pu half-lives, respectively[16].

2.2. Consideration of interferences and instrument setup

For ICP-MS, lighter isotopes are located on the outer parts of the ion beam, whilst heavier isotopes are closer to the centre. As a result, when measuring isotopic ratios, lighter isotopes are more scattered, resulting in the instrument generally being biased towards the heavier isotope. This bias can be corrected for using isotope dilution and sample-standard bracketing with a certified isotopic standard. By running the standard, the difference between the observed and expected isotopic ratio can be used to correct for the instrument mass bias, and this correction can then be applied to unknown samples. Several different models can be used in to correct for mass bias (linear, power or exponential model)[30]. For half-life measurements, there has not been a comparison between mass bias models, with comparisons in non-nuclear applications suggesting that the choice of model should be carefully considered. Variations in the performance of different bias models between instruments should also be assessed[30,31].

Isobaric, polyatomic and tailing interferences can, for the most part, be removed using chemical and/or instrument separation. In cases where the interference is from an isotope of the same element, such as $^{235}$U tailing on $^{234}$U and $^{236}$U, the interference removal is dependent on the abundance sensitivity of the instrument. For ICP-MS/MS, an abundance sensitivity of $\sim 10^{-11}$ is achievable, compared to $\sim 10^{-7}$ for single quadrupole instruments.

Instrument drift must be monitored by measuring an internal standard throughout a run, using an element that is close in mass and ionisation energy to the radionuclide of interest, but does not interfere with the measurement, such as $^{209}$Bi for $^{235}$U. Finally, most single collector instruments have a dual-mode detector that operates in pulse or analogue mode depending on the count rate, which must be calibrated using standards at a range of concentrations.

3. Materials and instrumentation

An Agilent 8800 ICP-MS/MS was used throughout. The instrument was fitted with a quartz double-pass spray chamber, MicroMist nebuliser (Glass Expansion) and nickel sample and skimmer cones (Crawford Scientific). The nebulizer, spray chamber, torch and cones were all cleaned prior to use to reduce the U background at all isotopes to <5 CPS. The instrument was initially tuned using a mixed element standard to assess instrument performance over a range of masses, followed by a custom tune using a natural uranium standard prior to measurement. A range of cell gases (He, O$_2$ and NH$_3$) were tested to assess the impact on interference removal and mass bias.

Uranium was measured from CRM U970 (New Brunswick Laboratory, U.S. Department of Energy) U$_3$O$_8$ powder with 1.7 % $^{234}$U, 97.7 % $^{235}$U, 0.1 % $^{236}$U and 0.5 % $^{238}$U (w/w). The high concentration of $^{235}$U in the CRM can potentially interfere with the measurement of $^{234}$U due to tailing
and $^{236}\text{U}$ due to tailing and polyatomic $^{235}\text{U}^1\text{H}$, which must be considered. The powder was dissolved in concentrated nitric acid (trace analysis grade, Fisher Scientific) and diluted in 2% (v/v) nitric acid and deionised water to appropriate dilution. All masses were recorded using a 6-figure balance (Mettler Toledo XP20).

4. Results
The initial focus has been on measurement of the $^{238}\text{U}$ half-life using the isotope dilution method. Isotope ratios between $^{238}\text{U}$ and a $^{234}\text{U}$ spike (both standardized for activity) are being measured in a series of solutions of different spike quantities.

Assessment of the uranium measurements were done using different parameters with the aim of minimizing the uncertainty. Preliminary measurements were made to quantify interferences in uranium isotope ratio measurements using the CRM. Different instrument modes were assessed; single quadrupole (SQ) mode (with only the second quadrupole operating) and MS/MS mode (both quadrupoles operating) were assessed for the reduction in tailing effects from $^{235}\text{U}$ to m/z = 234 and 236. The addition of helium as a collision gas was assessed for reducing polyatomic interference (primarily from $^{235}\text{U}^1\text{H}$), whilst introducing oxygen as a reaction gas can be used to measure all uranium isotopes as an oxide, converting $^{235}\text{U}^1\text{H}$ to non-interfering $^{235}\text{U}^{16}\text{O}$, with no evidence of $^{235}\text{U}^1\text{H}^{16}\text{O}$ formation.

In SQ mode, a detection limit on the order of 0.1 pg/g was calculated for all uranium isotopes, which is equivalent to between $2 \times 10^{-5}$ ($^{234}\text{U}$) and $8 \times 10^{-9}$ Bq/g ($^{235}\text{U}$). Operating in MS/MS mode with cell gases reduces the sensitivity, and a balance between interference removal and sensitivity must be considered, particularly when focusing on low uncertainty measurement.

Figure 3 shows the difference between the measured and certified isotopic ratios in SQ mode without any correction or removal of interferences and mass bias. There is generally good agreement with certified values and limited evidence of mass bias for ratios of $^{234}\text{U}$, $^{235}\text{U}$ and $^{236}\text{U}$, with a bias observed towards $^{236}\text{U}$ and higher measurement uncertainty. This bias could be due to $^{235}\text{U}$ tailing and/or $^{235}\text{U}^1\text{H}$ but is unlikely to be tailing as there is no evidence for this affecting $^{234}\text{U}$.

![Figure 3. Percentage difference between certified and measured isotope ratios in SQ mode.](image-url)
A range of uranium solution concentrations were measured to determine the impact on measurement uncertainty (Figure 4). After increasing the uranium concentration above approximately 1 ng/g, no further reduction in relative standard deviation (RSD) was observed, with a value of ~1%. Instrument parameters including the number of replicates and number of sweeps per replicate were investigated but were found to yield limited improvement in uncertainty.

The difference between the measured and certified isotopic ratio was investigated as a function of the average isotopic mass; e.g. $^{234}$U/$^{238}$U would give a value of 236 (Figure 5). The results in SQ mode did not consider the $^{235}$UH interference on $^{238}$U, but across the mass range measured there was a positive correlation between isotopic mass and measured/certified ratios. Whilst the results only consider a limited mass range, the correlation is significant as it suggests that the mass bias is related to the mass of the isotopes being analyzed, which is contradictory to some models that only consider the mass difference between isotopes. This is in agreement with the results from Ingle et al.[31], and further demonstrates the importance of critically comparing all mass bias models.

![Figure 4. Average RSD response with varying concentrations of $^{238}$U in MS/MS mode. Error bars represent 1 standard deviation of RSD values over 10 repeat measurements.](image)

![Figure 5. Measured/certified value for uranium isotope ratios against their average m/z.](image)
5. Conclusions and future work

ICP-MS is increasingly being applied to atom counting to contribute to improving the half-life values of medium and long-lived radionuclides through updated and/or low uncertainty measurements. A project is underway to critically compare the different approaches that have been used to date, to develop a robust and reproducible procedure that is applicable to other radionuclides to improve end-user confidence.

Preliminary results are shown for measurement of uranium isotopes. Optimal instrument settings have been found for the measurement of $^{238}\text{U}$ by ICP-MS/MS to re-evaluate the half-life of $^{238}\text{U}$ using the isotope dilution method, with $^{234}\text{U}$ as a spike. Standardized $^{234}\text{U}$ and $^{238}\text{U}$ solutions are being used for the $^{234}\text{U}/^{238}\text{U}$ measurement, using the interference corrections and instrument parameters determined from the preliminary measurements. A uranium isotopic CRM will be used for sample-standard bracketing to correct for instrument mass bias using the most suitable model. Atom counting will be combined with absolute activity measurements to determine the $^{238}\text{U}$ half-life, aiming for an uncertainty of $<1\%$ in line with previous evaluations.

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