**Evaluation of inductively coupled plasma tandem mass spectrometry for radionuclide assay in nuclear waste characterisation**

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# Abstract

Decommissioning and monitoring around nuclear sites presents challenges with regards to the range of sample matrices and radionuclides that must be accurately characterised. Over the last few decades, inductively coupled plasma mass spectrometry (ICP-MS) has been increasingly used in the nuclear sector as a rapid alternative to decay counting techniques for long-lived radionuclides, as well as an expanding range of shorter-lived radionuclides. The presence of various interferences still presents a major challenge in achieving accurate measurements, often necessitating extensive chemical clean-up prior to measurement. This study evaluates the potential application of tandem ICP-MS/MS for the measurement of a range of radionuclides of interest to nuclear decommissioning and waste management. The flexibility of the instrumental setup is shown in achieving improved interference removal compared to alternative instrument designs, improving sample throughput by reducing reliance on offline separation, and increasing the potential application of ICP-MS/MS for routine measurement of difficult-to-measure radionuclides.

# Introduction

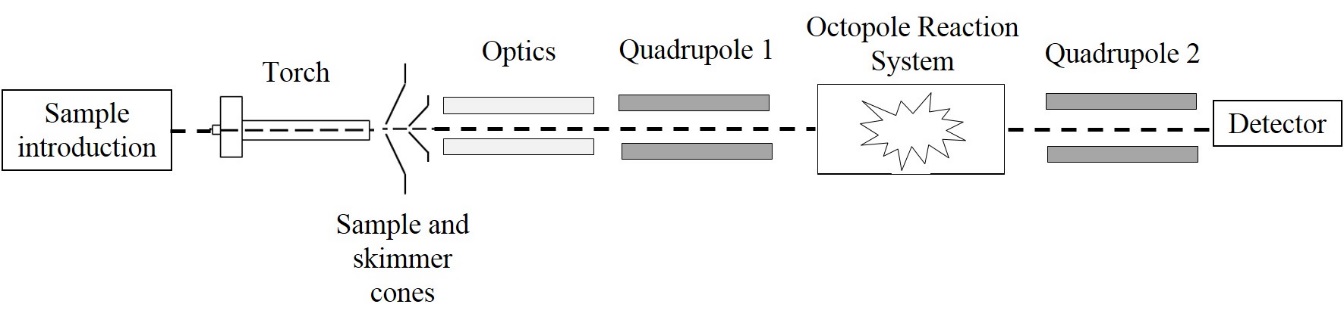
Effective radioactive waste management is critically dependent on robust, focussed and efficient waste characterisation in order to reliably inform all waste management steps and the safety of the operators, the general public and the environment. Nuclear waste characterisation represents a major challenge for nuclear sites, with a requirement to accurately measure a diverse range of activation products, fission products and naturally occurring radionuclides in various matrices. In particular, characterisation of Difficult-To-Measure (DTM) radionuclides (including pure alpha and beta emitting and long-lived, low abundance radionuclides) often involves complex separation chemistry to remove interferences and separate / concentrate the analyte from the matrix prior to radiometric or mass-spectrometric measurement. Of the available measurement techniques, mass spectrometry (most commonly inductively coupled plasma mass spectrometry, ICP-MS) has expanded the number of radionuclides measurable compared to decay counting techniques alone, as well as offering reduced measurement time and resulting improvements to the sample throughput. The most common early applications of ICP-MS with regards to radionuclide measurement were in the detection of long-lived radionuclides, most commonly in the actinide series1-3 where low specific activities favour atom counting-based techniques. However, developments in instrumentation have extended the range of radionuclides measurable. Extensive reviews of the role of ICP-MS for radionuclide analysis with regards to nuclear decommissioning and following nuclear accidents have recently been published.4,5

The accurate measurement of radionuclides by ICP-MS is impacted by multiple interferences, namely:

1. Stable or radioactive isobars
2. Polyatomic species formed by reactions with gases in the plasma and/or reaction cell
3. Peak tailing from an abundant isotope (mass m) to a neighbouring mass (m±1 or m±2; expressed as the abundance sensitivity).

The removal of interferences can be achieved by offline chemical separation (such as ion exchange and extraction chromatography) and/or instrumental separation through the use of a collision or reaction cell6-10, high resolution instruments11-13 and/or sample introduction-based separation such as membrane desolvation, electro thermal vaporisation and glow discharge14-18. The impact of the sample matrix in decommissioning samples must also be considered, as this can result in signal suppression, and reduced ion transmission through gradual blocking of the interface cones. The impact of the sample matrix can be reduced using the techniques listed above, but there are additional considerations. These include running matrix-matched rather than ‘clean’ calibration standards, and use of an internal standard to monitor drift and reduction in ion transmission. A number of newer ICP-MS designs also offer online aerosol dilution as a rapid alternative to offline dilution, enabling samples with up to 25 % total dissolved solid (TDS) content to be measured19, compared to ~0.25 % without aerosol dilution.

The recent commercial availability of tandem mass spectrometers (ICP-MS/MS) offers a potential improvement in interference removal capabilities over alternative instrument designs with regards to radionuclide measurement. Such instruments are equipped with a quadrupole mass filter positioned in front of a collision-reaction cell, followed by a second quadrupole mass filter (Figure 1). The use of two mass filters improves the abundance sensitivity compared to single quadrupole instruments. Additionally, filtering the ion beam entering the collision/reaction cell improves efficiency of the cell chemistry, and prevents the formation of secondary polyatomic interferences through interactions of ions with the reaction gas. ICP-MS/MS may reduce the extent of chemical separation required prior to sample introduction, further reducing the total procedural time and improving the sample throughput, as well as reducing the number of reagents used and analyst working time.

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**Figure 1. ICP-MS/MS layout (Agilent 8800/8900)**

ICP-MS/MS has been applied to measurement of radionuclides including 90Sr, 135Cs/137Cs, 129I, 226Ra, 236U/238U and 239Pu20-26. This paper reviews these applications and considers how the technique can be extended to include a broader range of radionuclides of interest in nuclear waste characterisation, considering the interferences that affect accurate measurement of these radionuclides and the capabilities of ICP-MS/MS for removal of these interferences. Given the diverse range of matrices that may be encountered in nuclear waste characterisation, specific matrix effects on instrument sensitivity and stability were not considered in this study although such effects would be significant when developing techniques for routine application.

# Methodology

## Selection of radionuclides

Radionuclides to be considered in the study were selected based on the following criteria -

* The radionuclide is a fission product, activation product or actinide that is typically associated with nuclear waste (based on IAEA, 2009a27) or NORM-contaminated wastes.
* The radionuclide is classified as Difficult-To-Measure (DTM) i.e. the radionuclide cannot be readily quantified in a waste package using non-destructive techniques such as gamma spectrometry (as detailed in IAEA, 2009b28).
* There are benefits of ICP-MS measurement of the radionuclide relating to good sensitivity, interference handling and speed of determination.

A total of 24 radionuclides relevant to nuclear waste decommissioning were identified (Table 1) where ICP-MS/MS could offer potential benefits for their determination.

**Table 1. Radionuclides of nuclear sector interest that can be measured by mass spectrometry**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Origin** | **Nuclide** | **Principle mode of decay** | **Half-life (years) (uncertainties in parenthesis)** | **SpA (Bq g-1)** | **Mass equivalent to 1 Bq g-1 (pg g-1)** |
| Activation products | 36Cl | β | 30.2(4)×104 | 1.2×109 | 821.8 |
| 41Ca | Electron capture | 100.2(17)×103 | 2.5×109 | 402.9 |
| 59Ni | X-ray | 76(5)×103 | 3.0×109 | 339.0 |
| 63Ni | β | 98.7(24) | 2.1×1012 | 0.5 |
| 94Nb | β | 20.0(24) ×103 | 7.0×109 | 1.4×102 |
| Fission products | 79Se | β | 356(40) ×103 | 2.8×108 | 3583.0 |
| 90Sr | β | 28.8(7) | 5.1×1012 | 0.2 |
| 93Zr | β | 1.61(6) ×106 | 9.3×107 | 1.1×104 |
| 99Tc | β | 211.5(11) ×103 | 6.3×108 | 1.6×103 |
| 107Pd | β | 6.5(3) ×106 | 1.9×107 | 5.3 ×104 |
| 126Sn | β | 2.3(14) ×105 | 1.0×109 | 952.4 |
| 129I | β | 16.1(7) ×106 | 6.5×106 | 1.5×105 |
| 135Cs  137Cs | β  γ | 2.3(3) ×106  30.1(8) | 4.1×107  3.2×1012 | 2.4×104  0.3 |
| 151Sm | β | 94.7(6) | 9.7×1011 | 1.1 |
| Naturally occurring radioactive material (NORM) | 226Ra | α | 1.6(7) ×103 | 3.7×1010 | 27.3 |
| Actinides | 235U | α | 704(1) ×106 | 8.0×104 | 1.3×107 |
| 236U | α | 23.4(6) ×106 | 1.7×106 | 4.2×105 |
| 237Np | α | 2.1(7) ×106 | 2.6×107 | 3.8×104 |
| 238U | α | 4.5(5) ×109 | 1.2×104 | 8.0×107 |
| 239Pu | α | 24.1×103 | 2.3×109 | 4.4×102 |
| 240Pu | α | 6.6(7) ×103 | 8.4×109 | 1.2×102 |
| 241Pu | β | 14.3 | 3.8×1012 | 0.3 |
| 241Am | α | 432.6(6) | 1.3×1011 | 7.9 |

## Instrumentation

All experimental work was carried out using two separate Agilent 8800 instruments operated by GAU-Radioanalytical Laboratories (based at the National Oceanography Centre, Southampton) and the Nuclear Metrology Group at the National Physical Laboratory, Teddington. As standard, the instruments were fitted with a collision-reaction cell (Octopole Reaction System, ORS3) positioned between two quadrupole mass filters (termed Q1 and Q2) (Figure 1). The instruments also incorporated a Scott double pass spray chamber, Micromist nebuliser (uptake rate 0.368 mL min-1, nebulisation efficiency 8.0 %) quartz torch, and nickel sample and skimmer cones. Both instruments were fitted with four cell gas lines- Lines 1 and 2 are dedicated to hydrogen and helium, respectively, Line 3 is for corrosive gases (in this study NH3) and Line 4 is for non-corrosive gases (in this study O2) (Table 2). The corrosive gas is balanced with at least 90% He to protect the ORS. When operating cell Line 3, the helium line automatically runs at a flow rate of 1 mL/min. All gases were provided by BOC with a purity of 99.9999% (N6.0). The major operational modes are termed ‘Single Quad’ (with only Q2 operating as a mass filter) and ‘MS/MS’ (with both Q1 and Q2 operating as mass filters).

**Table 2. General operating conditions of the Agilent 8800 for different setups**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Instrument parameter** | **MS/MS** | **H2** | **He** | **O2** | **NH3** |
| **RF power (W)** | **1550** | | | | |
| **Plasma gas (L/min)** | **15** | | | | |
| **Carrier gas (L/min)** | **1.05** | | | | |
| **Extraction lens 1 (V)** | **0** | | | | |
| **Extraction lens 2 (V)** | **-200 to -140** | | | | |
| **Omega Bias (V)** | **-120 to -70** | | | | |
| **Omega lens (V)** | **5-18** | | | | |
| **Octopole bias (V)** | **-8** | **-18** | **-18** | **-5** | |
| **Energy Discrimination (V)** | **5** | **5** | **0** | **-7** | |
| **Cell gas flow rate range (mL min-1)** | **-** | **0-10** | **0-12** | **0-1** | **0-10** |

## Characterisation of ICP-MS/MS performance

Experimental work was carried out using a combination of stable and radioactive tracers. Iodine-129 and 237Np were supplied by Amersham QSA (Amersham, UK), 93Zr from Kinetrics Inc. (Toronto, Canada), and 90Sr and 239Pu from NPL (Teddington, UK). All solutions were prepared in 0.3 M Trace Metal Grade HNO3 (Fisher Scientific, Loughborough, UK) with the exception of 129I, which was prepared in 0.5% tetramethylammonium hydroxide (TMAH; >97%, Sigma Aldrich, UK). Stable element standards were supplied by Fisher Scientific (Loughborough, UK).

Background scans were measured at the masses of the radionuclides of interest (Table 1) using 0.3 M HNO3 as a blank solution. Scans were performed in Single Quad and MS/MS mode with no reaction gas and with He as a collision gas.

For sensitivity determination, single element standards (1 – 10 ng mL-1) were measured in Single Quad and MS/MS mode, without specifically tuning at each mass. Where possible, stable element analogues of the radionuclide were used for sensitivity determinations. The normalised response in counts per second (cps)/ng g-1 was determined for each element, correcting for the isotopic abundance of the measured isotope. Matrix suppression was assessed through the measurement of a series of 5 ng mL-1 In, Re and/or Bi solutions with total dissolved solids (TDS) contents ranging from 0 to 0.1%. Dissolved solids comprised either CaCl2 or FeCl3 to represent either concrete or ferrous metal digests.

To determine the abundance sensitivity and degree of hydride formation, solutions of the interferent nuclide were prepared with concentrations ranging from 10 to 100,000 ng mL-1. The solutions were introduced and the signals at m/z+1 and m/z-1 were measured in Single Quad and MS/MS mode. The abundance sensitivity was determined from the m/z-1 signal and the MH+ formation was determined using the m/z+1 signal and correcting for the abundance sensitivity, assuming equal peak tailing on the low and high mass side. For radionuclides potentially affected by tailing from two mass units away e.g. 88Sr on 90Sr and 127I on 129I, the signals at m/z+2 and m/z-2 were also measured, permitting an assessment of the magnitude of MH2+ formation.

Assessment and potential for removal of isobaric interferences was achievedby reviewing the literature for potentially effective reaction gases that could overcome identified overlaps (either by reaction with the interferent or the analyte and subsequent mass shift). The potential for polyatomic interferences was similarly assessed and an evaluation was made of the effectiveness of collision gases for polyatomic suppression.

Data on the background and sensitivity were used to determine an effective instrument detection limit for each of the selected radionuclides. Detection limits were calculated based on 3 s.d. of the background count and assuming 1 g of sample was taken for analysis, a 100 % chemical recovery and a final purified solution volume of 10 mL. The potential for application of ICP-MS/MS for radionuclide measurement was then evaluated based on a comparison of the predicted limits of detection with specific radionuclide exemption limits for radioactive wastes, assessment of the impact of abundance sensitivity, hydride formation and potential for isobaric interference formation and removal.

## Case studies

The application of ICP-MS/MS to radionuclide measurement was further assessed using five case studies; 90Sr, 93Zr, 129I, 237Np and 239Pu. Measurement of each of these radionuclides is impacted to a greater or lesser extent by isobaric, polyatomic and/or abundance sensitivity interferences. Consideration of the way tandem mass spectrometry helps overcome these interferences and identification of other factors impacting on their measurement provides an insight into how ICP-MS/MS could be further developed for application to other radionuclides. The impact of customised tuning for achieving optimal radionuclide sensitivity and interference removal is a key consideration, with particular attention paid to the impact of varying the cell gas flow rate(s), the residence times of ions in the cell (energy discrimination), and the cell energy (octopole bias).

# Results & discussion

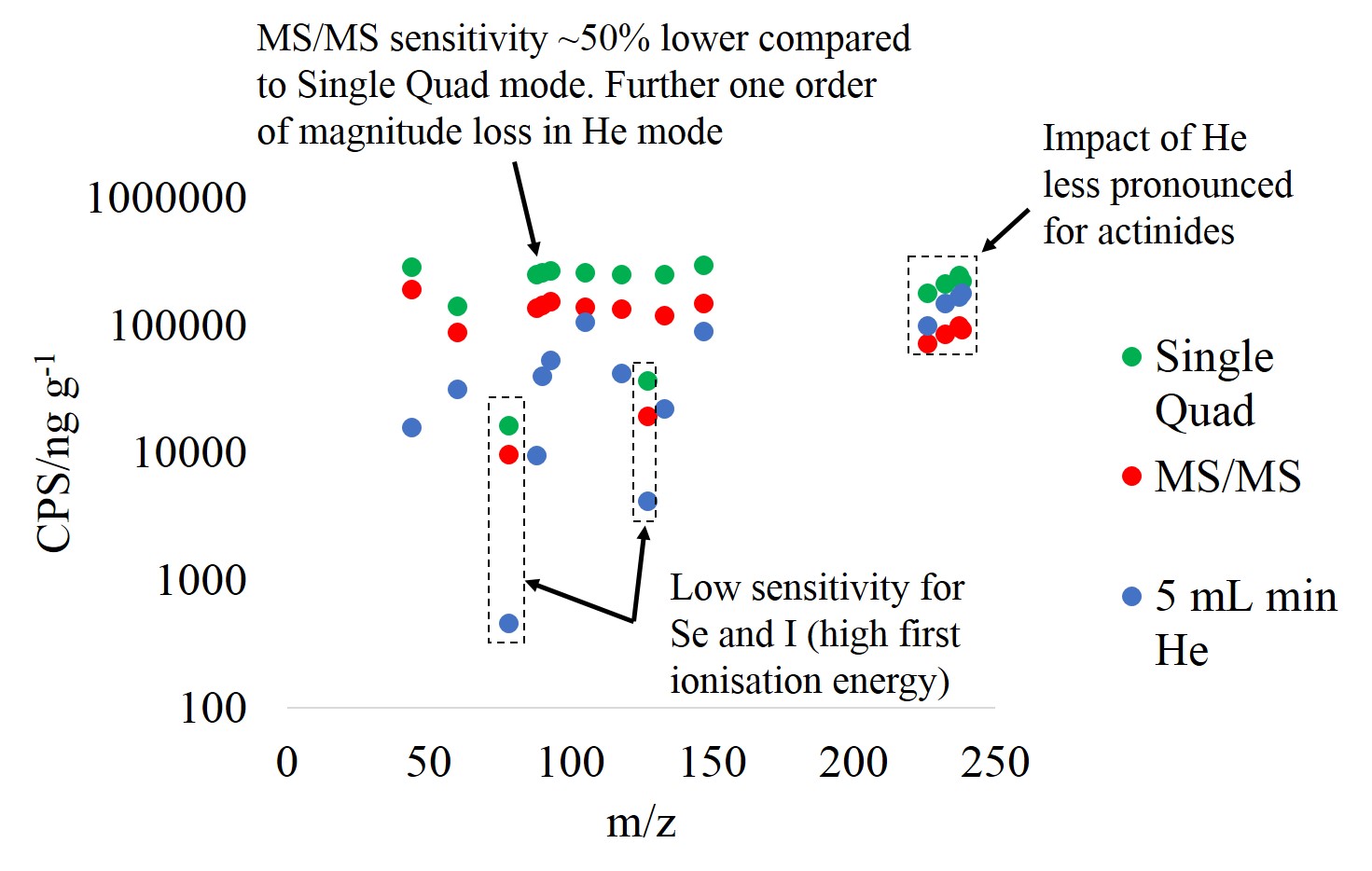
## Instrument background

Background scans of relevant masses measured during blank reagent runs showed significant peaks at m/z = 36 (36Ar, 0.3 % abundance) and m/z = 41 (tailing from 40Ar, 99.6 % abundance, and 40Ar1H). At m/z=36, the background reduced from 1.0×108 cps in MS/MS no-gas mode, to 1.6×106 cps with the introduction of 5 mL min-1 He. The instruments used in this study do not allow measurement of background at m/z=41 without the use of collision gas, but background signals reduced from 4.3×109 cps at 1 mL min-1 to 3.4×107 cps at 5 mL min-1 He. High collision gas flow rates are needed to significantly reduce the background, and this will impact the sensitivity for 36Cl and 41Ca, with a reduction of ~1 order of magnitude at 5 mL/min He compared to no-gas mode. The impact of isobaric, polyatomic and tailing interferences must also be considered for these nuclides, which may require the use of both collision and reaction gases in the cell.

Several other background peaks were also detected in MS/MS mode with no cell gas, the magnitude of which is likely to vary depending on the laboratory conditions, instrumental setup and composition of the samples being measured. In this study, a peak at m/z = 63 (~500 cps) was a result of 63Cu, potentially from copper in the interface cones. If measuring 63Ni, this contribution could be reduced by operating with Pt cones. The elevated background at m/z = 79 (~700 cps) was considered to be a combination of isobaric 79Br, polyatomic interferences and 40Ar40Ar tailing, whilst Ba contamination was responsible for the elevated background at m/z = 135 and 137 (~260 and 500 cps, respectively). Finally, the high background at m/z = 129 (~3,000 cps) was associated with 129Xe present as an impurity in the Ar plasma gas. In cases where polyatomic interferences are the cause of elevated background, the introduction of H2 or He into the cell at any flow rates reduced the background signal. In the case of isobaric interferences, the background increased at collision gas flow rates up to ~3 mL min-1 as a result of collisional focussing, before decreasing at higher flow rates (see discussion of sensitivity). In some cases, a reaction gas can also be used to reduce the background signal (e.g. using O2 to reduce the Xe interference at m/z = 129 – see later case study). Alternatively, reaction gases can be used to shift the target nuclide or interference to a different mass (e.g. using O2 to convert 239Pu and 238U1H to 239Pu16O and 238U16O, respectively, converting to a U polyatomic that no longer overlaps with the analyte). Background count-rates in MS/MS mode were 0 cps for actinides (<5 cps for 232Th and 238U), and for all other masses of interest ranged from 5-40 cps, with typical uncertainties of +/- 5-15% cps (1σ).

## Sensitivity

For the majority of nuclides, a sensitivity of approximately 1-2×105 cps/ ng mL-1 was achievable when operating in MS/MS mode with no reaction / collision gas (Figure 2). The sensitivity was lower for radionuclides with higher first ionisation potentials, specifically 129I (10.45 eV) and 79Se (9.75 eV). The sensitivity in MS/MS mode was approximately 40 % lower than for Single Quad mode, although this value varied depending on the radioanalyte, and any decrease was off-set by improved abundance sensitivity and control over cell chemistry. Introduction of dissolved solids resulted in a small reduction in sensitivity, with up to 14% reduction observed for both In and Re with a TDS of 0.1% CaCl2 or FeCl3.



**Figure 2: ICP-MS/MS instrument response versus mass number: Data for Single Quad and MS/MS in no gas and He modes. All analytes were measured in 0.3 M HNO3, other than iodine (0.5 % TMAH)**

Instrument sensitivity decreased by approximately a factor of 10 when He was introduced as a collision gas at a flow rate of 5 mL min-1. The decrease was less pronounced for the actinides, which may be a result of the heavier ions being more closely confined to the centre of the ion beam, resulting in less scattering at higher cell gas flow rates compared to lighter ions29. Operating with a collision gas (H2 or He) can reduce or eliminate polyatomic interferences, and at low flow rates (up to ~3 mL/min) can increase sensitivity compared to no-gas mode through collisional focusing. A similar effect was observed for reaction gases (NH3 or O2), for elements that did not react to form a cell product (e.g. Sr and I in O2 mode, see case studies). A reduction in radioanalyte sensitivity at higher flow rates may be necessary in order to achieve isobaric interference separation. It is also possible to use a mixture of a reaction and collision gas to simultaneously remove isobaric and polyatomic interferences, respectively, such as O2 and H2 for removal of 90Zr and 88Sr1H2, respectively, for measurement of 90Sr 30.

## Abundance sensitivity & hydride formation

Comparison of the response at m/z-1 and m/z+1 can be used to evaluate the magnitude of tailing and hydride formation, assuming symmetrical peak shape and hence equal tailing on the low mass and high mass side. A similar approach can be applied to assessing peak tailing over 2 mass units and di-hydride formation by measuring at m/z-2 and m/z+2, respectively, for example 127I and 127I1H2 affecting 129I. Examples of identified tailing interferences and measured hydride formation rates are summarised in Table 3.

Operating with two quadrupole mass filters (MS/MS mode) offers an improvement in abundance sensitivity compared to single quadrupole instruments, with values quoted by the instrument manufacturer of <10-10 for MS/MS mode compared with ~10-6 for single quad mode. For all radionuclides of interest affected by a tailing interference, the abundance sensitivity at m/z-1 in MS/MS mode was 10-9 or better, in good agreement with previous studies20,21. The improved abundance sensitivities facilitate the measurement of low abundance radionuclides in the presence of high abundance nuclides (e.g. 237Np in the presence of high concentrations of 238U) reducing or eliminating the need for chemical separation. Peak tailing from a high abundance isotope into a low abundance isotope of the same element is more problematic, as separation prior to detection is not practical. This is a particular issue for neutron activation products formed via the (n,γ) reaction which will typically be associated with significantly higher concentrations of their stable precursor and are one mass unit higher than the precursor due to the mode of their formation. For example, in irradiated bioshield concretes, the ratio of 41Ca to stable 40Ca has been measured as 10-7 – 10-8 (based on data from Warwick et al 31). For 59Ni measurement, it is estimated that 59Ni/58Ni ratios in irradiated Ni metal would be in the order of 10-8 for a 59Ni activity concentration of 100 Bq g-1. Measurement of 59Ni in the presence of 58Ni would be challenging for a single quadrupole ICP-MS, but theoretically achievable for ICP-MS/MS. However, although abundance sensitivities were low, hydride formation at m/z+1 was still significant (Table 3) with values of MH+/M+ ranged from 1×10-4 to 6×10-6. For Ni, the measured 59/58 ratios of 1×10-5 is sufficiently high to prevent the analysis of 59Ni without suppression of the hydride. Addition of a collision gas did not significantly improve the 59/58 ratio. Likewise, for 94Nb, the 94/93 ratio of 1×10-5 would limit the measurement of 94Nb to activity concentrations *ca* 2×105 Bq/g Nb. In such instances sample desolvation would be required to minimise hydride formation.

**Table 3. Tailing and hydride interferences for radionuclides. Those highlighted in bold represent tailing from an isotope of the radioanalyte. \*The hydride formation rate could not be reliably measured because of the high instrument background in no-gas MS/MS mode**

|  |  |  |  |
| --- | --- | --- | --- |
| Nuclide | Tailing interference | Isotopic abundance (%) | Hydride formation  (MH+/M+) unless otherwise stated |
| 36Cl | **35Cl** | 75.76 | -\* |
| 41Ca | **40Ca**, 40Ar | 96.94, 99.60 | -\* |
| 59Ni | **58Ni** | 68.08 | 1×10-5 |
| 79Se | **78Se** | 23.77 | -\* |
| 90Sr | **88Sr** | 82.58 | 1.7×10-5 (88Sr1H2) |
| 93Zr | 92Mo, **92Zr** | 14.77, 17.15 | 1.1×10-5 |
| 94Nb | **93Nb** | 100 | 1×10-5 |
| 99Tc | 98Mo | 24.19 | 5.6×10-6 |
| 107Pd | **106Pd** | 26.46 | 1.2×10-5 |
| 126Sn | 125Te | 7.07 | 2.5×10-4 |
| 129I | **127I**, 128Xe, 128Te, 131Te | 100, 1.91, 31.74, 34.08 | 9.0×10-6 (127I1H2) |
| 135Cs | **133Cs**, 134Ba, 134Xe | 100, 2.42, 10.44 | 2.4×10-4 (133Cs1H2) |
| 151Sm | **150Sm**, 150Nd | 7.38, 5.60 | 8.3×10-6 |
| 235U | **236U** | - | 4.6×10-4 |
| 236U | 238U | 99.27 |  |
| 237Np | 238U | 99.27 |  |
| 239Pu | 238U | 99.27 | 3.8×10-5 |

## Polyatomic suppression

Polyatomic interferences such as argides, hydrides and oxides can arise from the plasma gas / reagents (background peaks), via interactions with the sample matrix (sample-specific polyatomics interferences), or through interactions with a reaction gas in the cell. The introduction of a collision gas (H or He) can reduce or remove polyatomic interferences formed during sample introduction, however, the resulting impact on analyte sensitivity must be considered.

When only concerned with polyatomic interferences and not isobars (e.g. 226Ra), it is beneficial to operate in Single Quad rather than MS/MS mode, because the interferences are formed in the plasma (e.g. 88Sr138Ba) and will therefore not be removed by the additional quadrupole mass filter25. On the other hand, MS/MS mode is beneficial when using the reaction cell to remove isobaric interferences, as filtering the ion beam prior to the cell entrance can prevent the formation of polyatomics generated through reactions of elements with the reaction gas (e.g. oxide-based polyatomics affecting 90Sr- see later discussion). It is also possible to use a combination of a reaction and collision gas in the cell at the same time to remove isobaric and polyatomic interferences, respectively.

During method development, operating in MS/MS mode enables assessment of potential polyatomic interferences and cell products using pre-cursor and product ion scans, respectively. An early indication of the nature of polyatomic interferences can be established using a precursor ion scan. The second quadrupole (Q2) is set to a single mass value, and Q1 scans over a predefined m/z range. This can be used to identify the nature of the polyatomic interference e.g. argide, hydride etc. and to determine the optimal instrumental setup (e.g. which cell gas to be used). A product ion scan sets Q1 to a single mass, and Q2 scans the entire mass range. Product ion scans are used to establish the potential of a cell gas to intentionally generate polyatomic species that could be utilised to separate the analyte and isobaric interference

## Isobaric interference suppression

The separation of the analyte from stable or radioactive isobars using a reaction gas offers a rapid support, or in some cases replacement, for offline chemical separation. Additionally, MS/MS mode gives an improved understanding of the cell chemistry, by mass filtering the ion beam prior to entering the cell. This prevents formation of secondary polyatomic interferences that can potentially form in the cell and is also beneficial for understanding cell reactions with more complex reaction gases such as ammonia or methyl fluoride. The isobaric interferences affecting the radionuclides of interest are shown in Table 4, along with the examples where reaction gases have successfully been used for analyte/isobar separation. A number of decommissioning-relevant radionuclides have not been investigated for reaction cell-based separation capability.

**Table 4. The application of reaction gases for separation of isobaric interferences from decommissioning radionuclides**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Nuclide | Interference | Reaction gas | Reaction | Reference |
| 36Cl | 36Ar, 36S | C2H2 |  | Bandura (2005) 32 |
| 41Ca | 41K | N2O |  | Bandura (2005) 32 |
| 59Ni | 59Co | No known cell reaction | | |
| 63Ni | 63Cu | No known cell reaction | | |
| 79Se | 79Br | O2 |  | Bandura (2005) 32 |
| 90Sr | 90Zr | O2 |  | Russell et al. (2017)20, Amr et al. (2016)23 |
| 93Zr | 93Nb | NH3+H2 |  | Petrov et al. (2018)33 |
| 94Nb | 94Zr, 94Mo | NH3+H2 |  | Bandura (2005) 32 |
| 99Tc | 99Ru | No known cell reaction | | |
| 107Pd | 107Ag | C3H8 |  | Bandura (2005) 32 |
| 126Sn | 126Te | CH4 |  | Bandura (2005) 32 |
| 129I | 129Xe | O2 |  | Shikamori et al. (2012)32 |
| 135Cs  137Cs | 135Ba  137Ba | N2O |  | Zheng et al. (2014, 2015)21,22, Ohno et al. (2013)34 |
| 147Pm | 147Sm | No known cell reaction | | |
| 151Sm | 151Eu | O2 |  | Garcia-Miranda et al. (2018)35 |
| 239Pu | 238U1H | O2 |  | Tanimizu et al. (2013)26, This study |
| 241Am | 241Pu | No known cell reaction | | |

## Evaluation of ICP-MS/MS for DTM radionuclide measurement

A number of DTM radionuclides have been successfully measured by ICP-MS/MS in a range of instrument modes (see section 4.7). Where no data exist, the predicted detection limits based on the instrument background and sensitivity for interference-free standards in MS/MS mode with no cell gas have been calculated (Table 5).

The results highlight the impact of a high instrument background on the detection limits achievable for 36Cl (2.8×103 pg g-1) and 41Ca (7.3×104 pg g-1), compared to a maximum detection limit of 3.3 pg g-1 for other target radionuclides in Table 3.

**Table 5. Estimated limit of detection for radionuclides not yet measured by ICP-MS/MS. \*LOD based on no-gas MS/MS mode with interference-free standard solutions, assuming 5 g of a 1 Bq/g sample diluted in 5 g. \*\*0.5 mL/min He flow rate was required, as m/z = 41 cannot be measured in no gas mode. (E.L. – Exemption limit are as defined in IAEA/RS-G 1.7 27)**

|  |  |  |
| --- | --- | --- |
| Radionuclide | LOD, pg g-1 (Bq g-1)\* | E.L.  (Bq g-1) |
| 36Cl | 2.8×103 (34) | 1 |
| 41Ca\*\* | 7.3×104 (180) | - |
| 59Ni  63Ni | 0.3 (9×10-4)  3.3 (7) | 100  100 |
| 79Se | 2.4×102 (0.07) | - |
| 94Nb | 0.2 (1.×10-3) | 0.1 |
| 99Tc | 0.03 (2×10-5) | 1 |
| 107Pd | 1.1 (2×10-5) | - |
| 126Sn | 0.2 (2×10-4) | - |
| 147Pm | 0.1 (5) | 1000 |
| 239Pu | 0.1 (2×10-4) | 0.1 |
| 241Am | 0.1 (1×10-2) | 0.1 |

## Case studies

A number of difficult-to-measure radionuclides have been successfully measured using ICP-MS/MS (Table 6). This section considers several of these radionuclides in greater detail.

**Table 6. Measurement of radionuclides by ICP-MS/MS. (E.L. – Exemption limit as defined in IAEA/RS-G 1.7)**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Radionuclide | Sample matrix | Chemical separation | Instrument setup | Collision / reaction gas | LOD, pg g-1 (Bq g-1) | E.L.  (Bq g-1) | Reference |
| 90Sr | Soil, sediment, cement  Soil | 2-stage bulk matrix precipitation, extraction chromatography  None | MS/MS  MS/MS | O2 | 0.8-1.0 (4.0-5.0)  0.6  (3.1) | 1 | Russell et al. (2017)20  Amr et al. (2016)23 |
| 93Zr | Spiked standard solution | TBP extraction | MS/MS | H2, NH3 | 0.1 (1.3×10-5) | 10 | Petrov et al. (2018)33 |
| 129I | Standard solutions  Soils | None | MS/MS | O2 | 0.07 (1.10×10-6) | 0.01 | Shikamori et al. (2012)24  Ohno et al. (2013)34 |
| 151Sm | Spiked graphite | Bulk matrix separation, extraction chromatography | MS/MS | O2 | 1.1 (1.0) (instrument LOD) | 1000 | Garcia Miranda et al. (2018)35 |
| 135Cs/137Cs | Environmental samples | Ammonium molybdo-phosphate (AMP),  Anion exchange and  Cation exchange chromatography | MS/MS | N2O | 10/6 (4.1×10-4/19.2) | 100 / 0.1 | Zheng et al. (2014)22 |
| 226Ra | Water | Extraction or cation exchange chromatography | Single Quad | He | 0.1 (0.0035) | n/a | Van Es et al. (2017)25, Russell et al. (2017)36 |
| 236U/238U | Seawater | Chelating disk | MS/MS | O2 | 0.001  (4.1×10-10 / 1.2×10-10) | 10 / 1 | Tanimizu et al. (2013)26 |
| 237Np | Sediment | Bulk matrix separation, ion exchange chromatography | MS/MS | None | 25.0 (6.5×10-4) | 1 | Caborn (2017)37 |

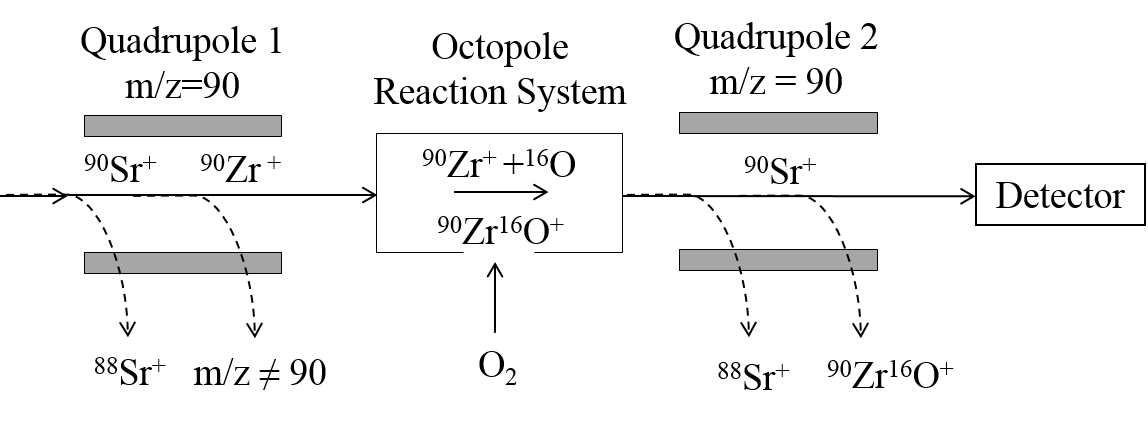
**Strontium-90**

Strontium-90 is a beta-emitting high yield fission product (5.84 %) with a half-life of 28.8 years, and is of major importance with regards to decommissioning, environmental monitoring and environmental protection. The capabilities of ICP-MS for 90Sr determination have been established using sector field ICP-MS 11,38, and more commonly using reaction cell instruments 7,39,40. Accurate measurement is affected by isobaric 90Zr (51.45% abundance), peak tailing from stable 88Sr (82.58 % abundance), and multiple polyatomic interferences including 89Y1H, 58Ni16O2 and 50Ti40Ar. The relatively short half-life of 90Sr also presents a challenge for ICP-MS, with an activity concentration of 1 Bq mL-1 equivalent to 0.19 pg mL-1.

Isobaric 90Zr can be shifted to 90Zr16O using O2 as a reactive gas 6,7,40, providing effective support to chemical separation prior to sample introduction. Significant formation of SrO (>5 % of the total signal) does not occur unless higher O2 flow rates (> ~0.3 mL min-1), or a stronger oxidant gas, such as N2O are used. The formation of secondary polyatomic oxide interferences in the cell, such as 58Ni16O2 and 74Ge16O are removed by the first mass filter in MS/MS mode, whilst this instrument mode also improved abundance sensitivity (<10-10) and tailing removal of 88Sr 19.

Strontium-90 has been measured by ICP-MS/MS using O2 as a reactive gas (Figure 3), with optimal flow rates ranging from 0.3-1.0 mL/min 20,23,41. In one study using stable element standards, H2 collision gas was also introduced into the cell to remove polyatomic 88Sr1H2 41. The extent of sample preparation prior to measurement varies between studies, with successful detection of soil samples after acid leaching and chemical separation20, and in a separate study following acid leaching and no further treatment 23. The latter achieved a detection limit of 3.1 Bq g-1 (0.6 pg g-1). Strontium-90 has also been directly measured in atmospheric particulate matter following gas-exchange introduction, which is beneficial for environmental monitoring following nuclear accidents42. A combination of O2, H2 and NH3 was used for removal of 90Zr and 89Y1H, achieving a detection limit of 1.8×10-6 Bq cm-3 (3.6×10-4 ng m-3).

For shorter-lived radionuclides such as 90Sr, the reduction in instrument sensitivity when operating in MS/MS mode with the reaction cell must be considered. The sensitivity dropped by approximately 50% when operating in MS/MS mode compared to Single Quad mode, and at an O2 flow rate of 0.3 mL min-1, ~5% of Sr was detected as SrO. Following offline chemical separation prior to measurement, the Zr concentration in the procedural blank (~10 pg mL-1) contributes significantly more to the signal at m/z=90 than 90Sr when measured at the Bq mL-1 level, necessitating the use of the reaction cell.

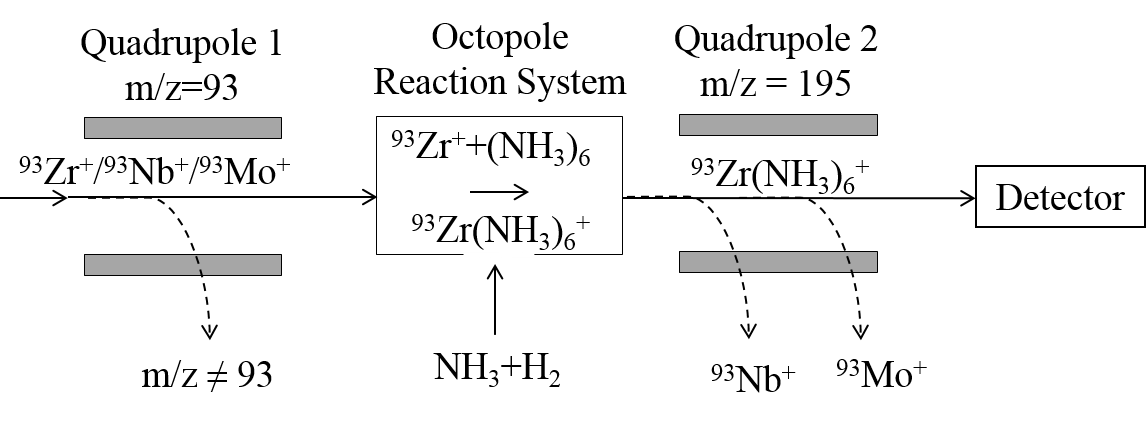


**Figure 3. Instrument layout for measurement of 90Sr in the presence of isobaric 90Zr and peak tailing from 88Sr**

**Zirconium-93**

Zirconium-93 is a high yield fission product (6.35 % yield) that is also produced from activation of stable 92Zr from the zircaloy fuel cladding in certain reactor designs. Routine radiometric measurement is challenging given the low beta energy (Emax = 56 keV), lack of gamma emission, and interference from 95Zr in irradiated materials. The long half-life (1.53 million years) is well suited to mass spectrometric determination, however, ICP-MS measurement of 93Zr is affected by isobaric interferences arising from stable 93Nb (100 % abundance) and activation product 93Mo (half-life 4.0×103 a), as well as polyatomic 92Mo1H. Of these, 93Nb is considered the primary challenge, given that it is monoisotopic, and the similarity in Zr/Nb chemistry that makes wet chemical separation challenging. Previous studies have used isotope dilution with a certified reference standard solution for Zr, followed by measurement by multi-collector ICP-MS 43,44. With regards to reaction cell separation, Bandura et al. concluded that a suitable reaction gas could not be found 32.

Operating in MS/MS mode using a combination of NH3 and H2 can separate 93Zr from isobaric interferences by shifting 93Zr to m/z=195 as 93Zr(NH3)6, whilst 93Nb and 93Mo do not react (Figure 4) 33. Multiple other potential cell products were formed in NH3+H2 mode and O2+H2 mode, however, the optimal decontamination factor for Nb was measured with a mass shift of 93Zr from m/z=93 to m/z=195. This highlights an advantage of the tandem mass spectrometry setup, as mass filtering the sample prior to the reaction cell gives greater understanding of the cell chemistry, which is particularly advantageous for more complex reaction gases like NH3 where multiple potential cell products can form. A further advantage of this application is that it facilitates Zr/Nb separation, which is challenging using offline separation techniques. The optimised instrument setup was effectively tested on a high salinity 93Zr standard solution, following liquid extraction to remove the sample matrix. A 93Nb separation factor of up to 105 was achievable in NH3+H2 mode, with a 93Zr detection limit of 1.3×10-5 Bq g-1 (0.1 pg g-1), which is significantly below the 10 Bq g-1 out of scope limit.



**Figure 4. Instrument layout for measurement of 93Zr in the presence of isobaric 93Nb and 93Mo 29**

**Iodine-129**

Iodine-129 (half-life 1.57×107 years) is a weak beta-gamma emitting fission product (0.6 % yield), with a beta Emax of 151.2 keV (99.5 %) and gamma energy of 39.6 keV (7.42 %). As well as quantification in nuclear wastes, variation in the 129I/127I ratio is of interest in identifying the source of contamination, with values ranging from 10-3 in reprocessing sites to <10-13 in uncontaminated samples 45-47. Mass spectrometric measurement is impacted by multiple interferences, as well as the high first ionization energy (10.45 eV) and corresponding reduction in sensitivity. Additionally, the volatile nature of iodine under acidic conditions requires sample introduction in alkali media, such as dilute ammonia, or tetramethylammonium hydroxide (TMAH) 24,34,48,49. These limitations also present a challenge in finding a suitable internal standard, with previous example including Te, Re, Cs and Rh 8,48.

Routine measurement of 129I by ICP-MS has been prevented by peak tailing from stable 127I (100 % abundance), an isobaric interference from 129Xe (26.40 % abundance) present as an impurity in the plasma gas, and polyatomic interferences, primarily 127I1H2, and others including 97Mo16O2 and 113Cd16O. These interferences led to the majority of previous procedures measuring isotope ratios by combining ICP-MS detection of 127I with accelerator mass spectrometry (AMS) measurement of 129I/127I ratios 50-52.

Improved removal of 127I tailing is achievable using ICP-MS/MS, with a measured abundance sensitivity of <10-10. In the presence of 88.9 mg L-1 127I, no signal was detected at m/z = 129 in MS/MS mode 24. Two papers measured 129I/127I in Fukushima-contaminated soil samples following digestion, one using ICP-MS/MS and the other using ICP-MS 34,53. Both used O2 to suppress 129Xe through conversion of Xe+ to Xe via a thermodynamically favourable charge transfer reaction (Equation 1) (Figure 5)51, whilst the reaction with iodine is not thermodynamically favourable and does not proceed (Equation 2)24.

Xe+ + O2 🡪 Xe + O2+ (∆Hr = -0.07 eV) [Equation 1]

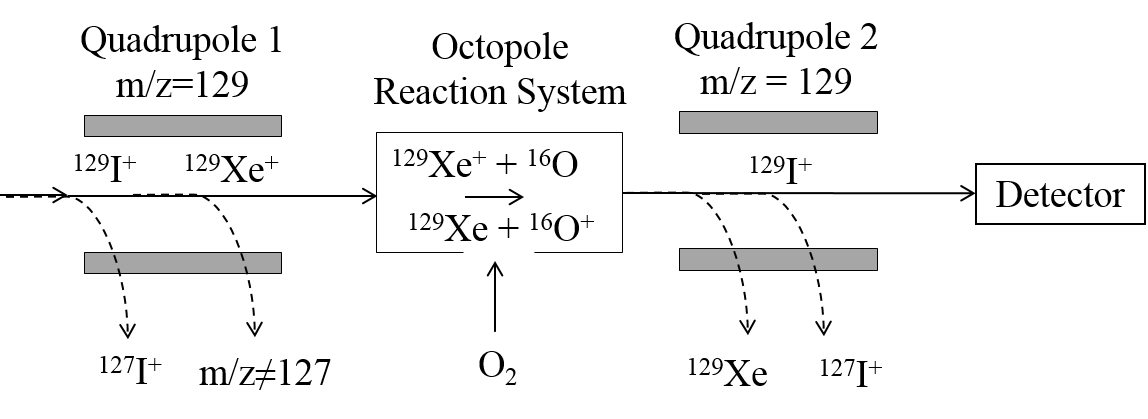
I+ + O2 🡪 I + O2+ (∆Hr = +2.08 eV) [Equation 2]

The study using ICP-MS/MS was able to operate with a negative voltage gap (energy discrimination) between the cell and the quadrupole for ICP-MS/MS, which enables Xe+ suppression without significantly impacting on 129I sensitivity compared to the single quadrupole instrument. The optimum flow rate using ICP-MS/MS was determined to be 0.9 mL min-1, which yielded a background equivalent concentration 100 times lower than achieved by ICP-MS.

Filtering of the ion beam by setting Q1 to m/z = 129 prevents 97Mo and 113Cd from entering the cell and potentially forming 97Mo16O2 and 113Cd16O when operating with O2 reaction gas. This instrument setup also removes 127I, so only 127I1H2 formed in the plasma passed through to Q2. The 127I1H2 / 127I ratio was an order of magnitude lower for ICP-MS/MS compared to ICP-MS, as the single quadrupole instrument allowed 127I to pass into the cell and react with hydride impurities. The use of collision gas has also been successfully used for removal of 127I1H2 (Equation 3)24.

[Equation 3]

ICP-MS/MS has measured 129I/127I isotope ratios in the 10-6 – 10-8 range, with the results showing good agreement with those measured by AMS 34. A recent study applied ICP-MS/MS to measurement of 129I in various decommissioning samples (including graphite, sludge and ion exchange resin) following combustion-based extraction of 129I in a tube furnace, with the results showing good agreement with LSC 55. The achieved detection limit of 1.05×10-4 Bq g-1 (0.016 ng g-1) was significantly lower than the out-of-scope waste criteria value of 0.1 Bq g-1 (1.53 ng g-1). The low iodine sensitivity as a result of high first ionisation energy was overcome through matrix modification, by increasing the TMAH concentration from 0.5 – 3 %, with the addition of methanol or glycerine at the same concentration being similarly effective. Tellurium-130 was determined to be the most effective internal standard.



**Figure 5. Instrument layout for measurement of 129I in the presence of isobaric 129Xe and peak tailing from 127I**

**Neptunium-237**

Neptunium-237 is an alpha emitting actinide with a half-life of 2.1×106 years. The radionuclide is produced via a series of neutron activation and decay steps within the reactor fuel. The long half-life and corresponding low specific activity means that 237Np is well suited to mass spectrometric measurement, and low-level detection in the fg g-1 region is achievable by sector field ICP-MS 56-58. Prior to measurement, removal of peak tailing from 238U usually necessitates chemical separation prior to sample introduction 59-61, increasing procedural time and the analytical expense through the number of resins and reagents required, as well as risking loss of 237Np through the procedure.

In MS/MS mode, a significantly higher uranium concentration can be tolerated without tailing into the 237 signal, reducing the extent of chemical separation required prior to measurement (Figure 6). In Single Quad mode, abundance sensitivities of ~10-6 were measured for 238U/237Np, with 238U concentrations of 100 ng g-1 resulting in increased background at m/z = 237. In MS/MS mode abundance sensitivities were reduced to < 10-9 with no observable tailing in the m/z=237 region in the presence of 50 μg g-1 U. This enabled direct measurement of 237Np in aqueous waste samples containing 0.1 - 1 μg g-1 U without sample pre-treatment62. The high salinity of the samples necessitated the use of matrix-matched calibration standards and High Matrix Introduction (HMI) aerosol dilution, with 209Bi used as an internal standard. Samples were measured at activities ranging from 1.7×10-3 – 95.5 Bq g-1 (65.2 – 3.64×106). ICP-MS/MS has also been successfully utilised for the measurement of 237Np in intertidal sediment samples with 237Np activity concentrations in the 0.5 – 10 Bq kg-1 range following digestion and chemical separation 37.

Reaction cell chemistry of other actinides has been well documented through the use of O2, NH3 as well as other reaction gases 32,63. A recent ICP-MS/MS application note used O2 reaction gas, which converted 99% of Np to NpO2, achieving a detection limit of 0.56 fg g-1, compared to 1.9 fg g-1 when measured in no-gas mode 64.



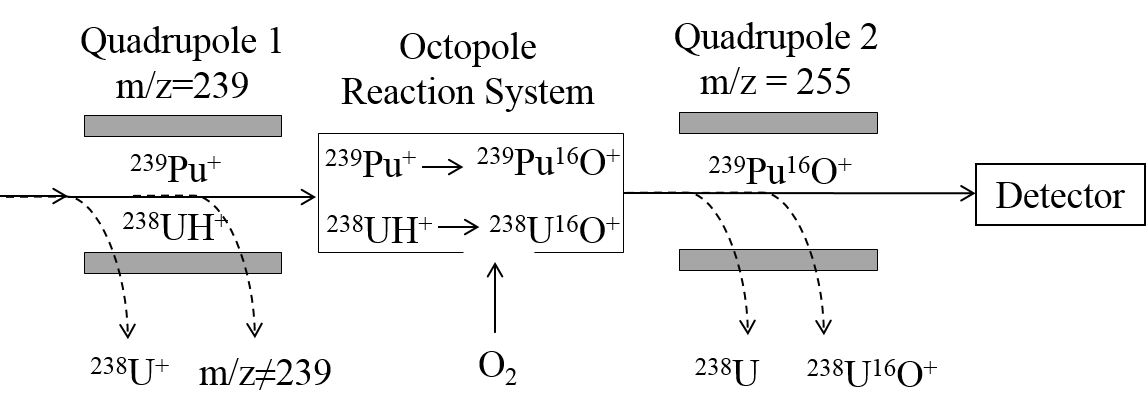
**Figure 6. Instrument layout for measurement of 237Np in the presence of peak tailing from 238U**

**Plutonium-239**

Plutonium-239 is an alpha emitting actinide with a half-life of 24,110 years, which is formed via neutron capture within the reactor fuel. Detection is achievable by ICP-MS, most commonly represented as 239Pu/240Pu isotopic ratios to determine the source of the Pu 65-66. This represents an advantage over alpha spectrometry, which cannot resolve the similar alpha energies of the two isotopes, and can therefore only measure a combined 239+240Pu activity. Detection limits in the fg g-1 (10-6 Bq g-1) are achievable by sector field ICP-MS65-68, with accurate measurement dependent on the removal of 238U, which interferes both as tailing and as polyatomic 238U1H, the latter of which forms during sample introduction.

Uranium can be removed by offline chemical separation, whilst 238U1H formation from residual U can be reduced using a desolvating sample introduction system 69,70. More rapid 238U separation is achievable using ICP-MS/MS, with improved peak tailing removal operating in MS/MS mode (<10-9). Additionally, polyatomic 238U1H can be removed by using O2 reaction gas, following a procedure developed for 236U/238U isotope ratio measurements 26. A 238U solution was introduced, and Q1 set to m/z=239 to monitor 238U1H. When operating with O2 reaction gas, the majority of the U signal (70 %) was detected as 238U16O, compared to 1 % measured as 238U16O1H, with the remainder measured as either 238U or 238U1H. This enabled measurement of 236U/238U as 236U16O/238U16O, with polyatomic 235U1H converted to 235U16O.

The same approach can be applied to separation of 239Pu from 238U1H. By setting Q1 to m/z=239, both 238U1H and 239Pu pass into the cell. Plutonium is detected by setting Q2 to m/z=255 (239Pu16O), whilst 238U1H is largely converted to non-interfering 238U16O at m/z=254 (Figure 7). Carbon dioxide has also been demonstrated as an effective reaction gas using a multi-collector ICP-MS, but this has not been applied to an ICP-MS/MS procedure 71. Using this gas, 238U was shifted to 238U16O or 238U16O2, whilst ~40 % of the 239Pu signal remained on mass.



**Figure 7. Instrument layout for measurement of 239Pu in the presence of polyatomic 238UH and tailing from 238U**

# Conclusions

ICP-MS is an increasingly used technique for radionuclide detection with regards to nuclear waste characterisation, expanding the range of radionuclides routinely measurable at nuclear sites, whilst offering an improvement in sample throughput as a result of reduced measurement time compared to decay counting techniques. The removal of isobaric, polyatomic and tailing interferences prior to detection remains the major factor preventing accurate measurement using this technique. The commercial availability of ICP-MS/MS offers improved interference removal over alternative instrument designs, which can be used to support or even replace relatively time-consuming and labour-intensive offline chemical separation techniques, further improving the sample throughput. ICP-MS/MS has been successfully applied to measurement of multiple radionuclides of interest to nuclear sites in a range of sample matrices, including 90Sr, 93Zr, 129I, 135Cs, 151Sm, 236U and 237Np, as well as NORM-relevant 226Ra. The flexibility of the instrument allows the setup to be varied depending on the analytical requirements e.g. sensitivity, tailing removal, or target decontamination factors for interferences. ICP-MS/MS is potentially applicable to detection of a number of other difficult-to-measure radionuclides relevant to nuclear waste clean-up, but for which no routine measurement technique currently exists. Reactive gases can be used to remove isobaric / polyatomic interferences and permit effective measurement of 126Sn and 239Pu. Reactive gases may also benefit 99Tc measurement although no suitable reactive gases have been identified to separate 99Tc from 99Ru. The significant improvement in abundance sensitivity achieved by ICP-MS/MS is beneficial to the measurement of 59Ni, 79Se, 94Nb and 107Pd in the presence of stable isotopes of the element. However, hydride formation is still a dominant contributor to m/z+1 signal and does not appear to be significantly affected (reduced) by the introduction of a collision gas. For fission products 79Se and 107Pd it is likely that the stable isotopes will not be present in significant concentrations to result in problematic levels of hydride generation. However, for activation products 59Ni and 94Nb, the stable analogues will always be associated with the nuclide of interest and desolvation is required to suppress hydride formation to acceptable levels. For 36Cl and 41Ca, sufficiently sensitive ICP-MS/MS measurement is considered unviable given the high background signals observed.

# Conflicts of interest

There are no known conflicts of interest

# Acknowledgements

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