Nuclear ICP-MS Applications made possible by MS/MS mode

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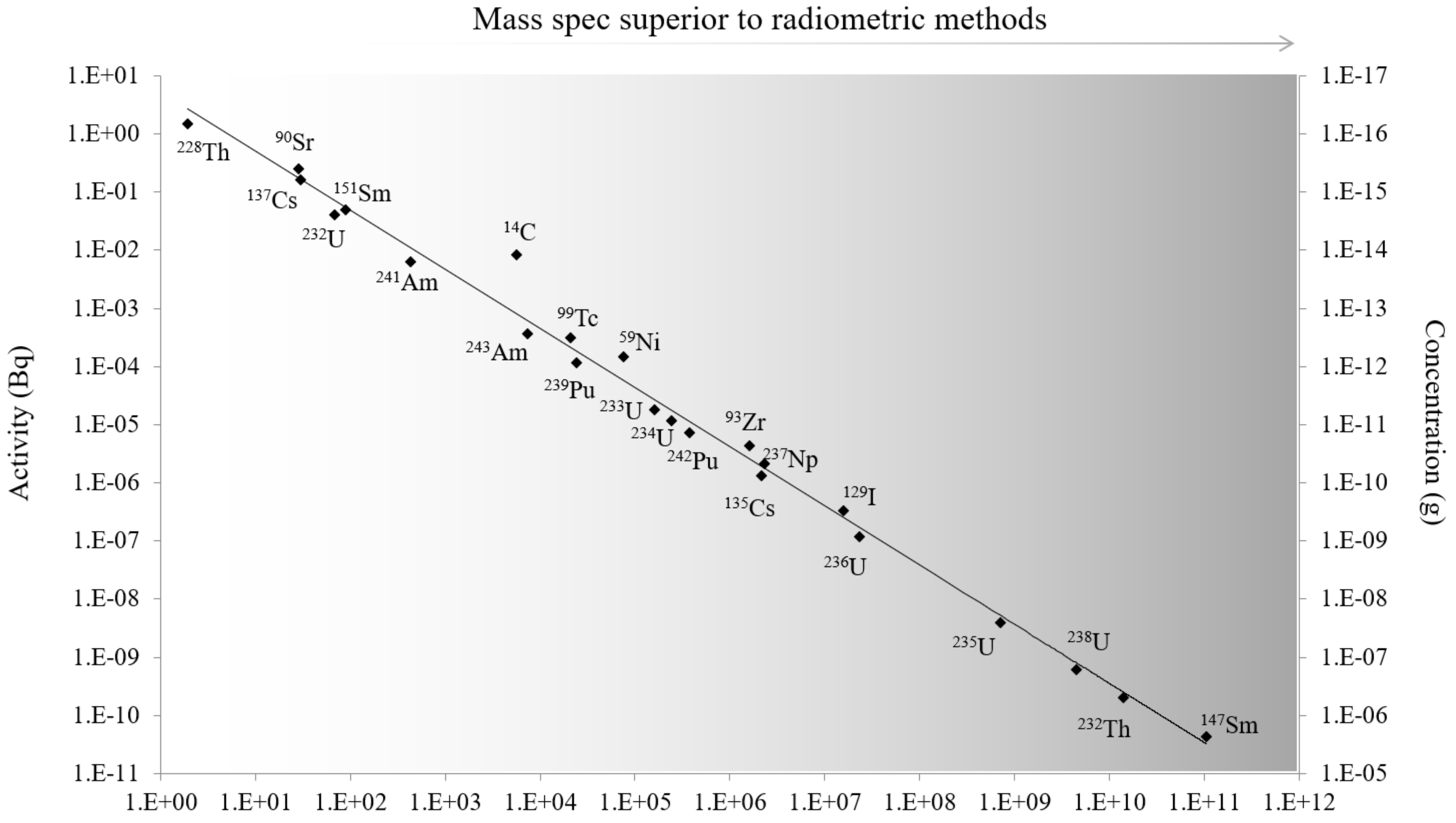
Radionuclide measurement by mass spectrometry- the longer-lived the better!



Radio-nuclide	$t_{1/2}$ (years)	1 Bq g^{-1} (pg g^{-1})
^{90}Sr	28.8	**0.2**
^{151}Sm	94.7	**1.1**
^{135}Cs	2.3×10^{6}	**2.4×10^{4}**
^{129}I	1.5×10^{7}	**1.5×10^{5}**
^{238}U	4.5×10^{9}	**8.0×10^{7}**

Applications

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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

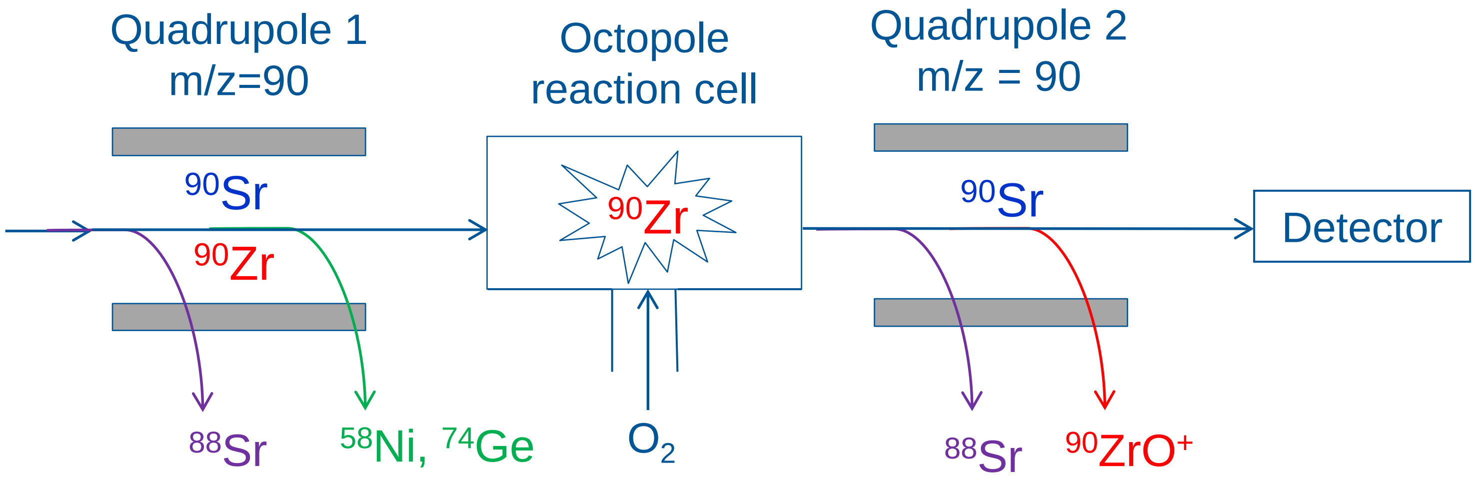
Interferences

- Effectiveness of mass spectrometry dependent on the **half-life** and **interference removal**
- No isobaric interferences resolvable using High Resolution ICP-MS

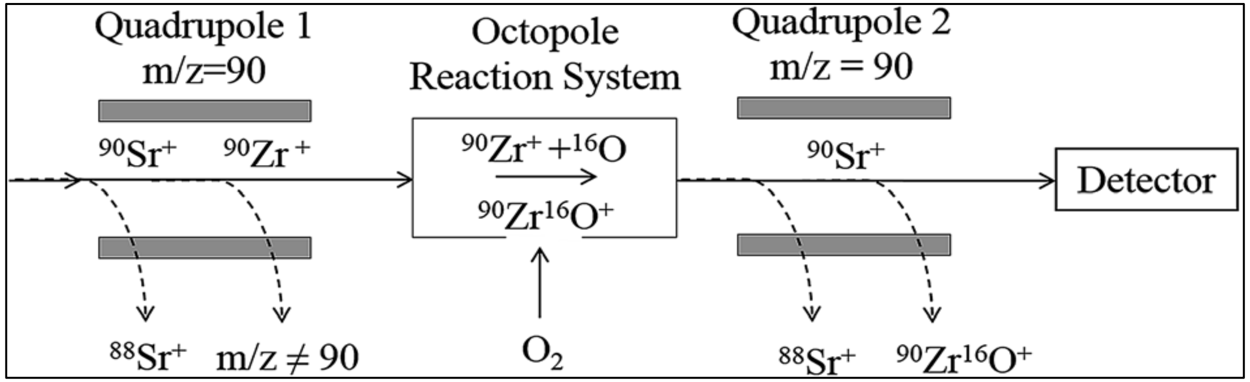
Isobaric	Polyatomic	Tailing
Isotope with similar mass to analyte	Reaction of elements with gases in the plasma	High concentration of stable isotope at a neighbouring mass
^{90}Zr	$^{52}Cr^{38}Ar$, $^{89}Y^{1}H$ $^{58}Ni^{16}O_2$	^{88}Sr

ICP-MS/MS Advantages

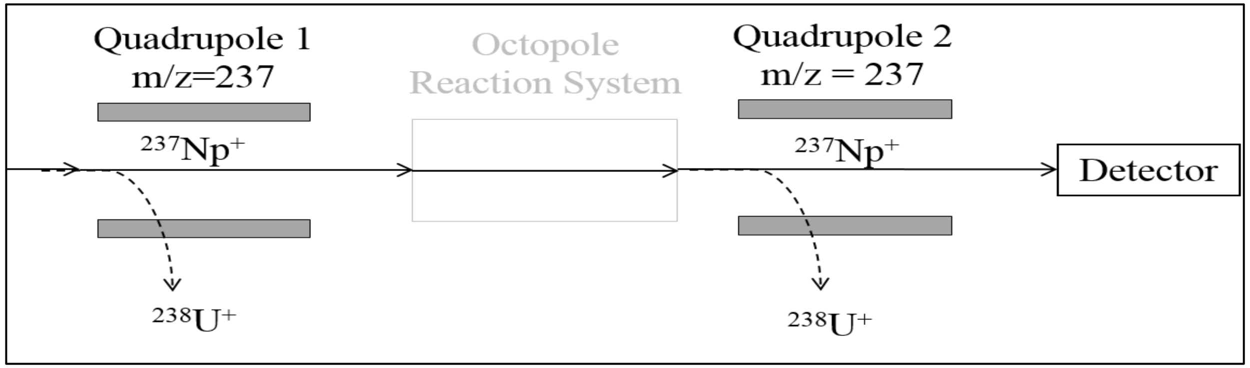
- **Isobaric** (^{90}Zr)- removal by cell-based separation
- **Polyatomic** ($^{58}Ni^{16}O_2$, $^{74}Ge^{16}O$)- cell-interferences removed by Q1
- **Peak tailing** (^{88}Sr)- removal by Q1+Q2
- Balancing act between interference removal and sensitivity, particularly for shorter-lived radionuclides



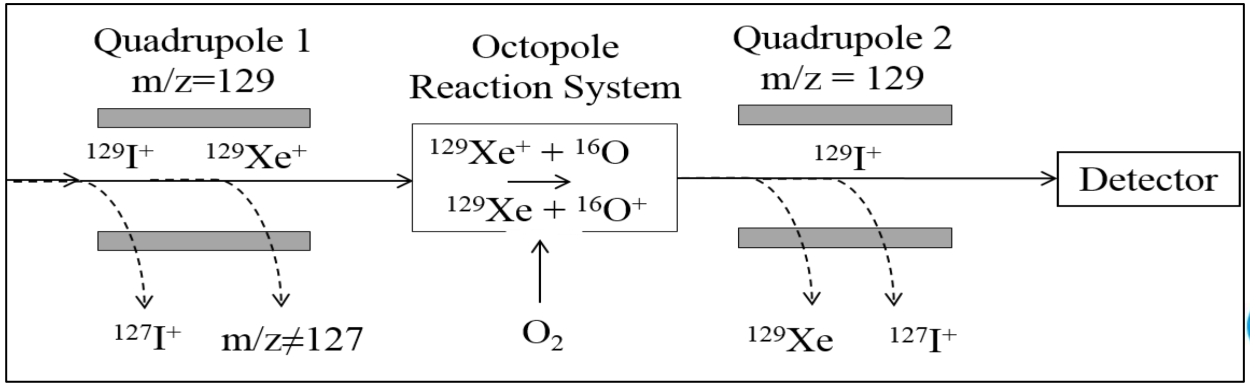
Example applications



Radionuclide	Sr-90
Major interference	Zr-90
Instrument setup	MS/MS O2
Sample matrix	Soil, sediment, water
LOD (pg g^{-1} / Bq g^{-1})	1.0 / 5.0

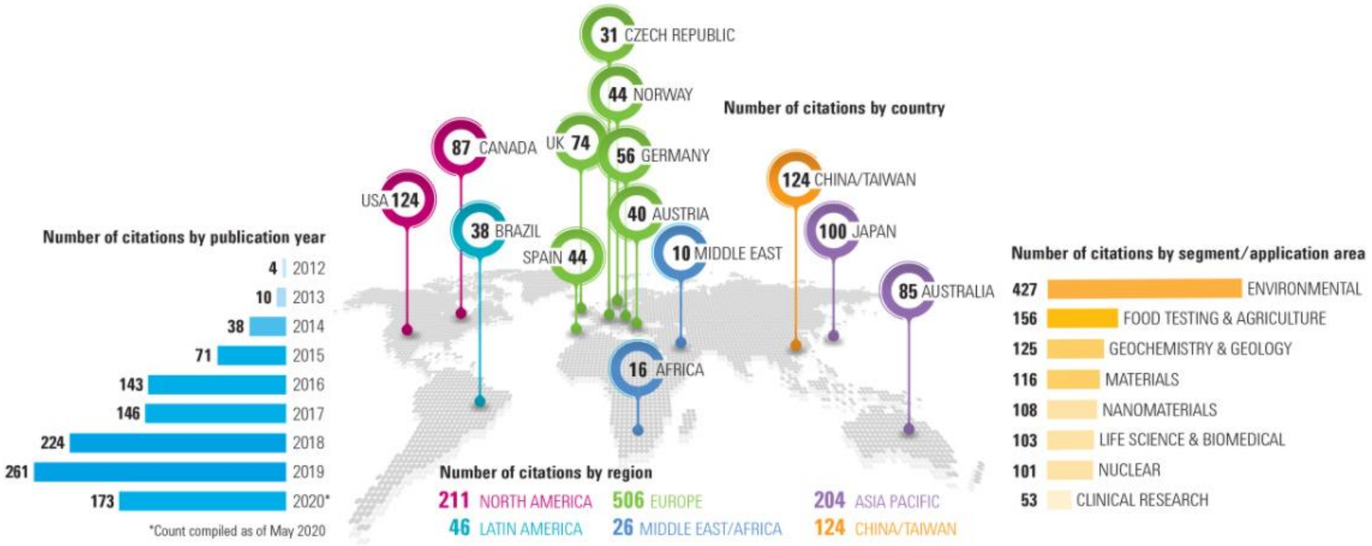


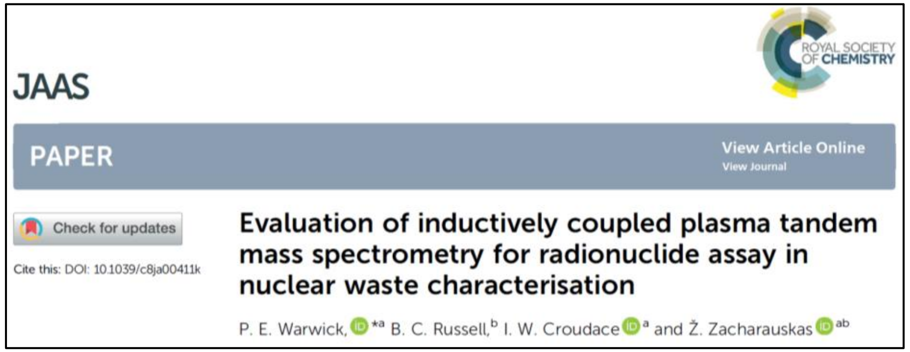
Radionuclide	Np-237
Major interference	U-238
Instrument setup	MS/MS no gas
Sample matrix	Aqueous waste
LOD (pg g^{-1} / Bq g^{-1})	4.2 / 1.1×10^{-4}



Radionuclide	I-129
Major interference	Xe-129
Instrument setup	MS/MS O_2
Sample matrix	Decommissioning samples
LOD (pg g^{-1} / Bq g^{-1})	5.1 / 8.6×10^{-5}

Radioactivity measurement using ICP-MS/MS

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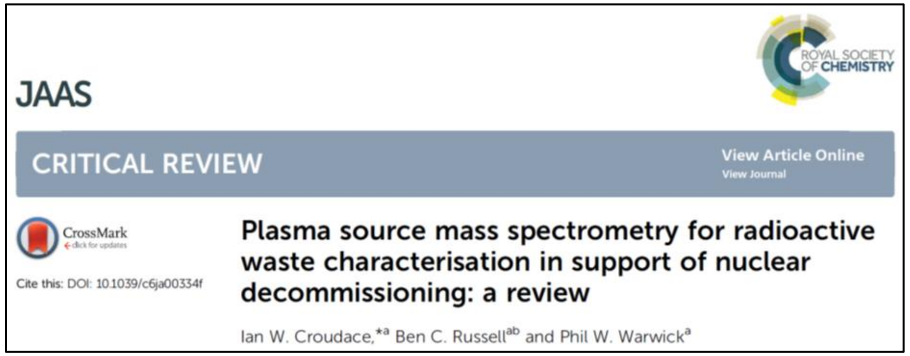
Cite this: DOI: 10.1039/c8ja00411k

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

P. E. Warwick,*[a] B. C. Russell,[b] I. W. Croudace[a] and Ž. Zacharauskas[ab]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CRITICAL REVIEW

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Cite this: DOI: 10.1039/c6ja00334f

Plasma source mass spectrometry for radioactive waste characterisation in support of nuclear decommissioning: a review

Ian W. Croudace,*[a] Ben C. Russell[ab] and Phil W. Warwick[a]

- Over 100 papers on Nuclear Applications
- NPL publications including:
  - First measurements of challenging radionuclides
  - Characterisation (resins, reference materials, nanoparticles)
  - Method validation combined with decay counting techniques
  - Invited reviews

Zirconium-93
Why measure it?

- High yield fission product (6.35 %)
- Activation of stable Zr in zircalloy fuel cladding
- Significant contributor to total waste inventory over longer timescales
- Half-life 1.64 x 10^6 years
- Beta-emitter (maximum decay energy 60 keV)
- Measurable by LSC and ICP-MS
- Interference separation required prior to measurement

Zirconium-93 interferences

NPL National Physical Laboratory

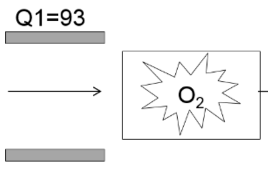
Isobaric	Polyatomic	Tailing
Isotope with similar mass to analyte	Reaction of elements with gases in the plasma	High concentration of stable isotope at a neighbouring mass
^{93}Nb ^{93}Mo	$^{92}Zr^{1}H$	^{92}Zr

Zirconium-93- can ICP-MS/MS help?

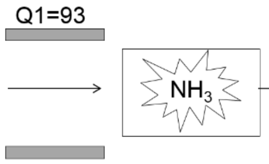
- Mass shift of 102 $(NH_3)_6$ optimal for Nb removal
- Low-level measurement of ^{93}Zr in standards, aqueous waste samples and dissolved steel
- Detection limit below the 10 Bq/g criteria
- Recent measurements on 8900 suggests other mass shifts are possible
- New standard in development for instrument calibration

Q1/Q2 (*m/z*)	90/155	90/159	90/175	90/176	90/177	90/192	90/206	90/207
Mass-shift	65	69	85	86	87	102	116	117
Zr/Nb Separation Factor (8800)	<1	<1	<1	1	4	6,200	<1	<1
Zr/Nb Separation Factor (8900)	2,300	470	715	155	400	10,200	2,800	4,300

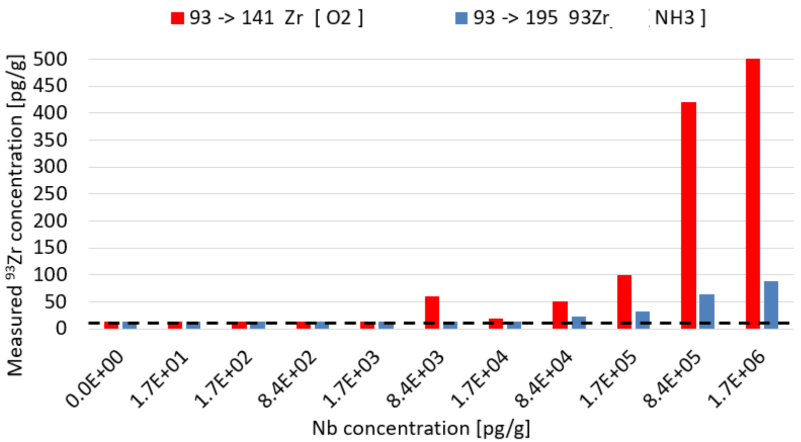
Parameter	8800 ICP-QQQ		8900 ICP-QQQ	
Q1/Q2 (*m/z*)	90/90	90/192	90/90	90/192
^{90}Zr sensitivity (cps, 10 ng/g)	1,800	2,000	53,000	166,000
*IDL (pg/g)	6.5		0.1	
*IDL (mBq/g)	0.6		8.8×10^{-3}	

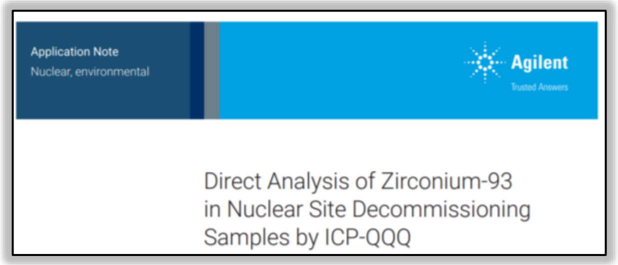


	141	144	159	162	188
Nb/Zr	6.8×10^{-5}	7.1×10^{-3}	2.7×10^{-3}	8.4×10^{-3}	1.0×10^{-1}
Mo/Zr	7.5×10^{-3}	9.8×10^{-2}	9.1×10^{-2}	3.0×10^{-2}	1.8×10^{-1}



	142	143	144	178	195
Nb/Zr	1.5×10^{-2}	3.6×10^{-3}	1.9×10^{-3}	2.1×10^{-3}	6.9×10^{-5}
Mo/Zr	3.7×10^{-4}	9.1×10^{-4}	2.9×10^{-2}	2.1×10^{-5}	2.7×10^{-5}

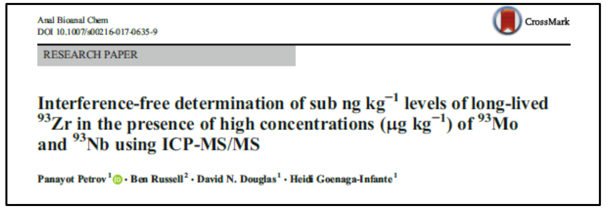




Application Note
Nuclear, environmental

Agilent
Trusted Answers

Direct Analysis of Zirconium-93 in Nuclear Site Decommissioning Samples by ICP-QQQ



Anal Bioanal Chem
DOI 10.1007/s00216-017-0635-9

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RESEARCH PAPER

Interference-free determination of sub ng kg^{-1} levels of long-lived ^{93}Zr in the presence of high concentrations ($\mu g\ kg^{-1}$) of ^{93}Mo and ^{93}Nb using ICP-MS/MS

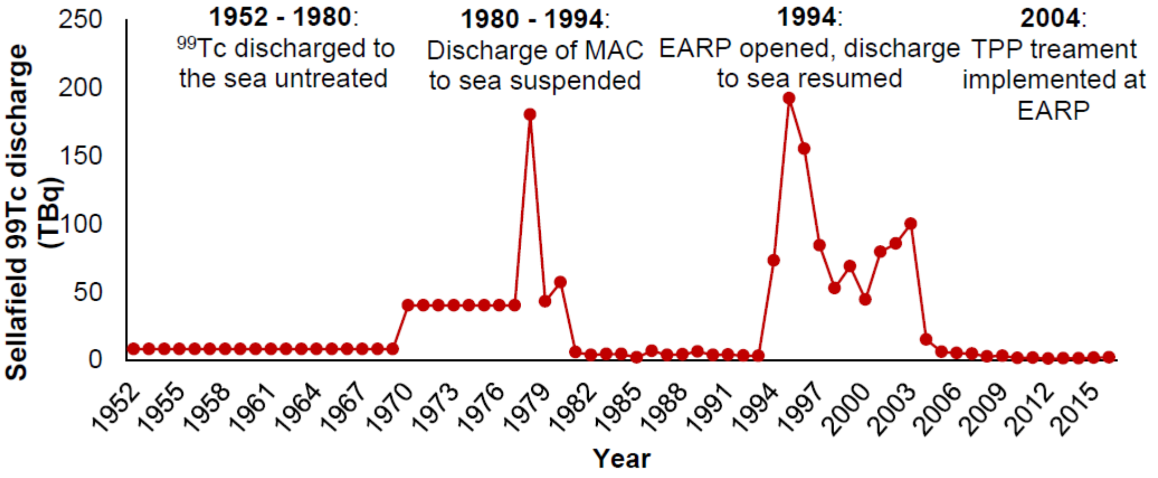
Panayot Petrov[1] · Ben Russell[2] · David N. Douglas[1] · Heidi Goenaga-Infante[1]

Technetium-99
Why measure it?

- High yield fission product
  - ^{235}U thermal yield: 6.132(92)%

- Long lived radionuclide
  - $T_{1/2}$: 2.111(12) x 10^5 y

- Environmental concern
  - Forms mobile ions: $Tc(VII)O_4^-$
  - Sellafield (UK) has discharged 1720 TBq over the period of 1952-2008



Reference	Source	^{99}Tc release (TBq)
Cefas, 2008	Sellafield reprocessing plant (1952-present)	1720
Shi *et al.*, 2012a	La Hague reprocessing plant (1966-present)	154
Aarkrog *et al.*, 1986	Atmospheric weapons testing (1940s-70s)*	140
Uchida *et al.*, 1999	Chernobyl nuclear accident	0.97
Bailly du Bois *et al.*, 2012	Fukushima-Daiichi nuclear accident⁺	220

* Calculated from Cs-137 fallout and fission yield of ^{99}Tc

⁺ Calculated from seawater Tc/Cs ratio of 0.01, with 22PBq estimated Cs release

Technetium-99 Interferences

National Physical Laboratory

Isobaric	Polyatomic	Tailing
Isotope with similar mass to analyte	Reaction of elements with gases in the plasma	High concentration of stable isotope at a neighbouring mass
^{99}Ru	$^{98}Mo^{1}H$	^{98}Mo

Technetium-99- Can ICP-MS/MS help?

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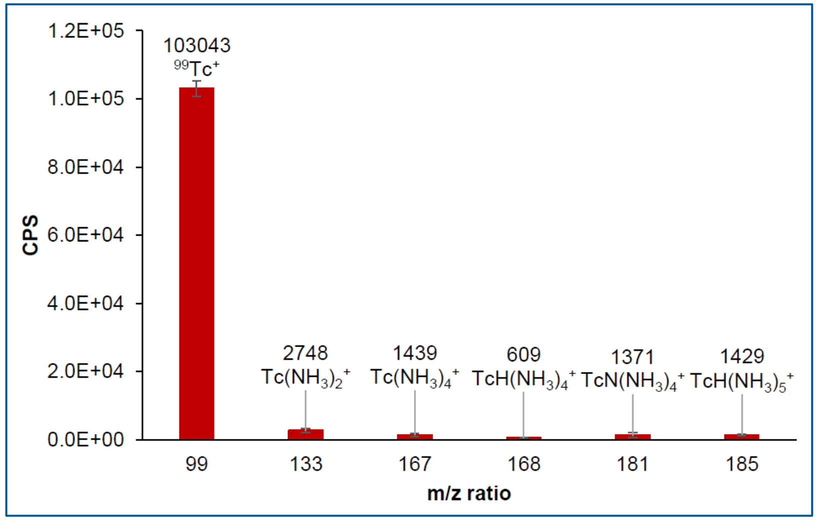
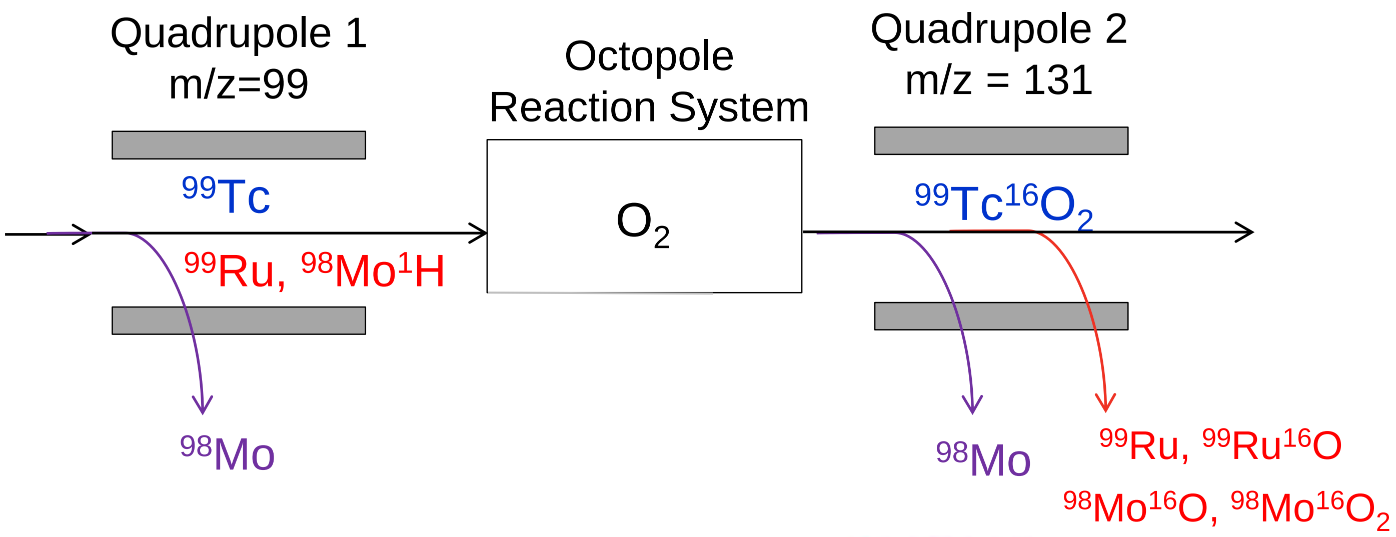
- NH_3 ineffective (multiple products, low sensitivity)
- O_2 promising:
  - Similar sensitivity for single and double oxide
  - Improved Ru and Mo removal with double oxide
- Tested on aqueous waste samples
- LOD 0.5 pg g^{-1} (0.3 mBq g^{-1})
- ^{97}Tc tracer standard in development





Mode	Q1	Q2	CPS per Bq g^{-1} Tc	10 ng g^{-1} Ru signal (CPS)	1 µg g^{-1} Mo signal (CPS)
O_2 (on mass)	99	99	126,500	111,000	200
O_2 (single oxide)	99	115	24,500	15,000	35
O_2 (double oxide)	**99**	**131**	**25,000**	**160**	**5**
NH_3	99	185	3,000	40	120

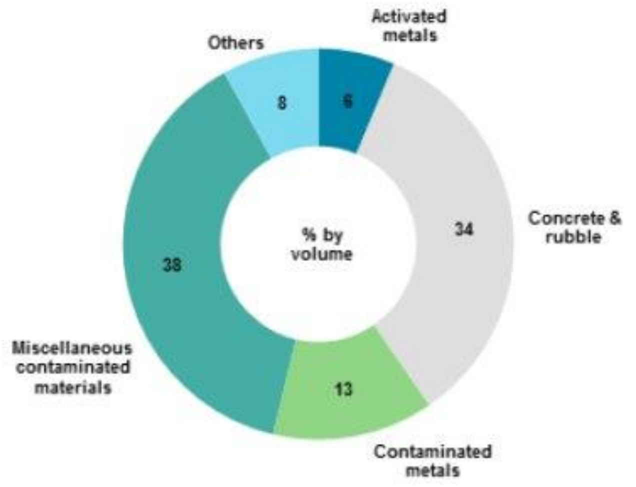
Calcium-41
Why measure it?

- Activation product
  - Stable ^{40}Ca in concrete

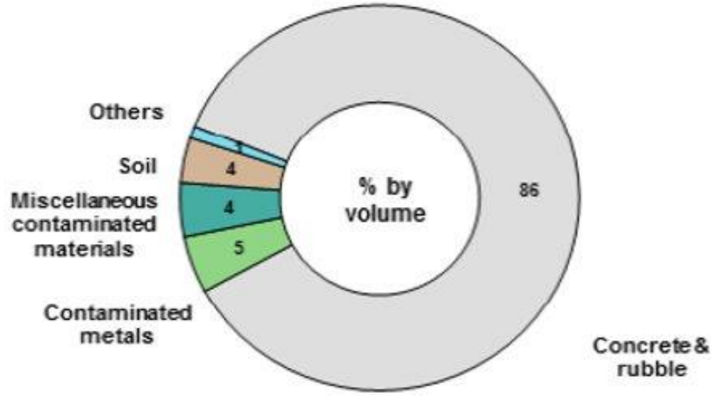
- Long half-life
  - $T_{1/2}$: $1.002(17) \times 10^5$ y

- Significant volume of concrete at reactor sites to be characterised
  - Activity levels ~0.03-30 Bq g^{-1} (~0.01-10 ng g^{-1})
  - $^{41}Ca/^{40}Ca$ as low as 10^{-12}

The different forms of waste that make up LLW



The different forms of waste that make up VLLW



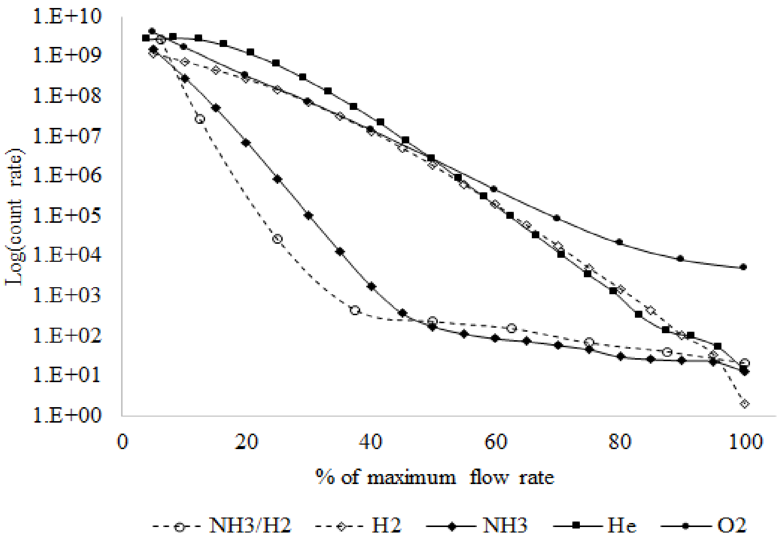
Calcium-41 Interferences

Significant- not previously considered measurable by ICP-MS

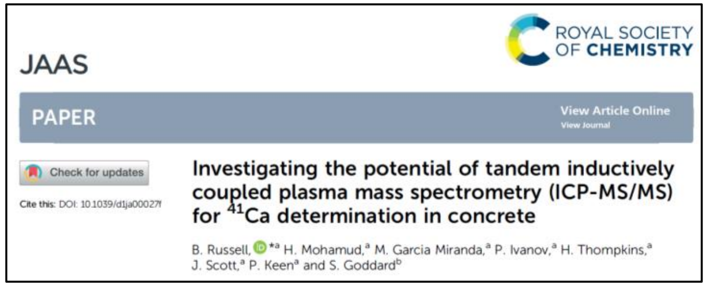
Isobaric	Polyatomic	Tailing
Isotope with similar mass to analyte	Reaction of elements with gases in the plasma	High concentration of stable isotope at a neighbouring mass
^{41}K	$^{40}Ca^{1}H$ $^{40}Ar^{1}H$	^{40}Ca ^{40}K

Calcium-41- Can ICP-MS/MS help?

- MS/MS improved tailing removal
- NH_3+H_2 for background reduction
- Tested on IRMM standards
- LOD 0.2 ng g^{-1} (0.6 Bq g^{-1})
- $^{41}Ca/^{41}Ca$ at 10^{-7} – 10^{-6} measurable
- First known ^{41}Ca measurement
- Publication in review (JAAS)
- Potential improvements (8900, N_2O reaction gas for Ca/K)



Instrument Parameter	Value
H_2 (mL min^{-1})	5.0
NH_3 (mL min^{-1})	7.5
LOD (ng g^{-1})	0.084
CPS per ng g^{-1} ^{40}Ca	1,300
Bgd CPS at m/z 41	7.3
Signal-to-noise	1.7×10^5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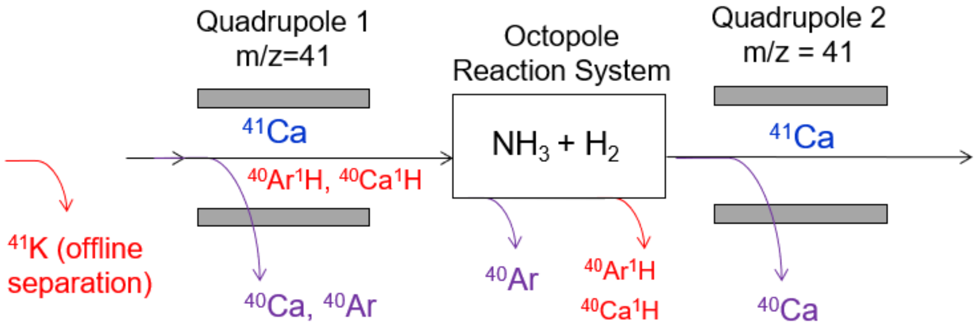
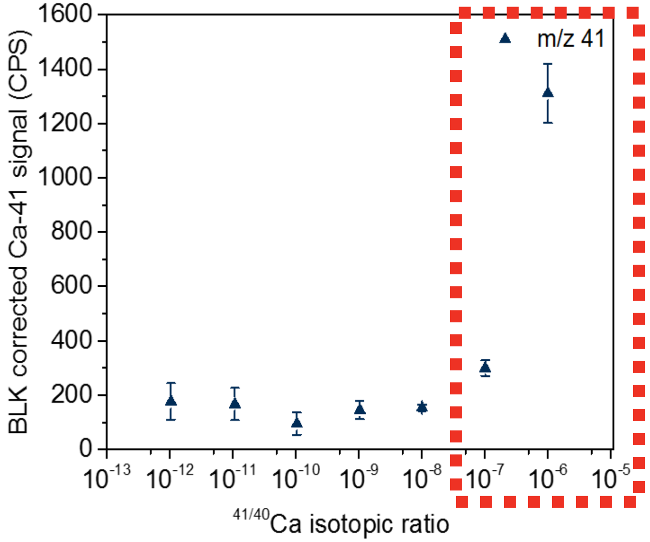
Investigating the potential of tandem inductively coupled plasma mass spectrometry (ICP-MS/MS) for ^{41}Ca determination in concrete

B. Russell,[*a] H. Mohamud,[a] M. Garcia Miranda,[a] P. Ivanov,[a] H. Thompkins,[a] J. Scott,[a] P. Keen[a] and S. Goddard[b]





What radionuclides are measurable?

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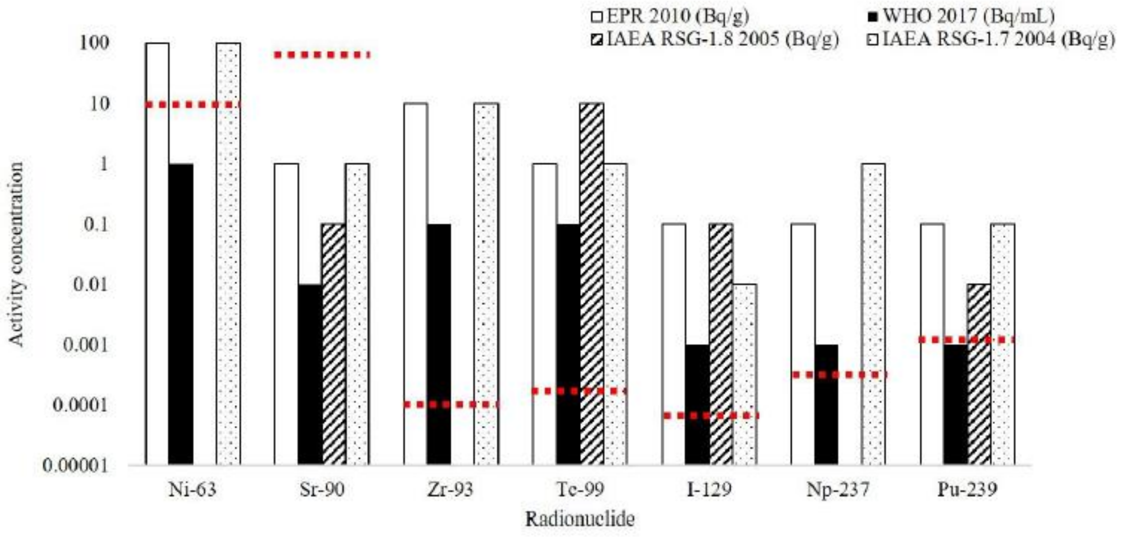
Origin	Nuclide	Half life (years)
Activation products	^{41}Ca	100,200
	^{59}Ni	76,000
	^{63}Ni	99
Fission products	^{79}Se	600,000
	^{90}Sr	28.64
	^{93}Zr	1,530,000
Act. Prod.	^{94}Nb	20,000
Fission products	^{99}Tc	211,300
	^{107}Pd	6,500,000
	^{126}Sn	100,000
	^{129}I	15,690,000
	^{135}Cs	2,400,000
	^{147}Pm	2.6
	^{151}Sm	90
NORM	^{210}Pb	22.2
	^{226}Ra	1,600
Actinides	^{235}U	703,800,000
	^{236}U	33,146,000
	^{237}Np	2,140,000
	^{238}U	4,468,000,000
	^{239}Pu	24,113
	^{240}Pu	6,563
	^{241}Pu	14.4
	^{241}Am	432.7

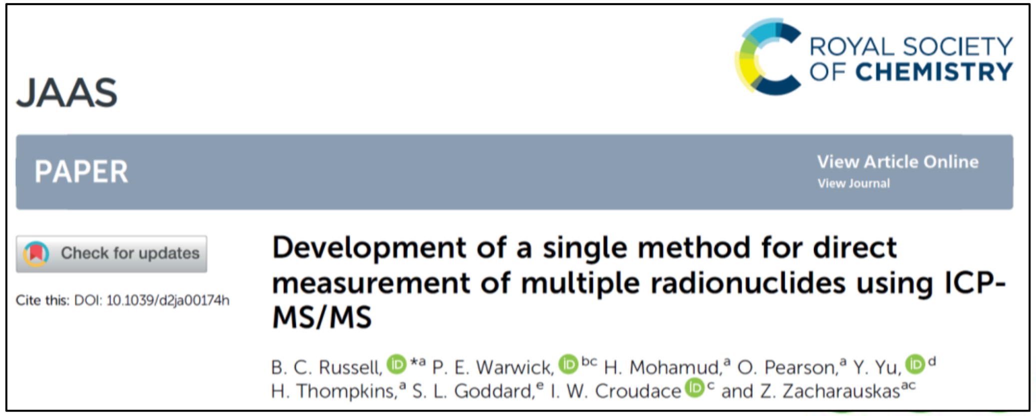
- Method in place
- Work in progress
- No method (yet)
- Radionuclides that benefit from ICP-MS/MS:
  - ^{41}Ca
  - ^{63}Ni
  - ^{90}Sr
  - ^{93}Zr
  - ^{99}Tc
  - ^{129}I
  - ^{135}Cs
  - ^{151}Sm
  - ^{237}Np
  - ^{239}Pu

Simultaneous radionuclide measurement

- ~20 radionuclides measurable by ICP-QQQ
- Aim for stable and radionuclide composition in a single run
- Measurement of groundwater, drinking water, soil, concrete and sediment digests without offline separation
- Approximately 7 minutes per sample, ~3.5 mL sample used
- Tested on aqueous waste samples
- Further testing planned- 8900, Apex sample introduction
- Shorter-lived nuclides require offline preparation before measurement (e.g. ^{90}Sr)

Parameter	Stable	^{63}Ni	^{90}Sr	^{93}Zr	^{99}Tc	^{129}I	^{237}Np	^{239}Pu
Mode	MS/MS							
Q1 – Q2	Various	63 - 114	90 - 90	93 - 195	99 - 131	129-129	237 - 237	239 - 255
RF (W)	1550							
Carrier gas (L/min)	0.99							
Extract 1 (V)	0							
Extract 2 (V)	-175							
H_2 (mL/min)		3.00		3.00				
He (mL/min)	4.00	1.00		2.00				
O_2 (mL/min)			0.40		0.30	0.55		0.40
NH_3 (mL/min)		1.00		0.15				
Energy discrimination (V)	5.0	-13.0	-18.0	-9.0	-7.0	-6.0		-7.0
Octopole bias (V)	-18.0	-4.5	0.0	-2.8	-5.0	-2.0		-5.0
Internal standard	^{115}In/^{209}Bi	^{115}In	^{115}In	^{115}In	^{115}In	^{130}Te	^{209}Bi	^{209}Bi

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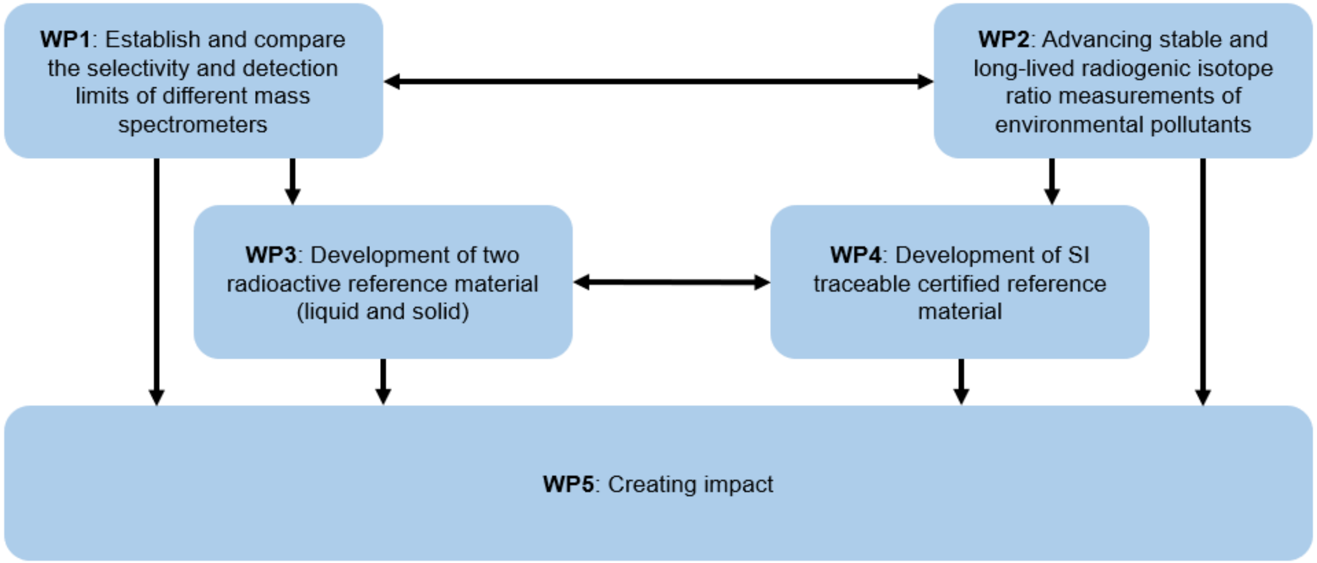
Development of a single method for direct measurement of multiple radionuclides using ICP-MS/MS

B. C. Russell,[*a] P. E. Warwick,[bc] H. Mohamud,[a] O. Pearson,[a] Y. Yu,[d] H. Thompkins,[a] S. L. Goddard,[e] I. W. Croudace[c] and Z. Zacharauskas[ac]

Detection limit compared to regulatory limits

Metro POEM- Metrology for the harmonisation of measurements of environmental pollutants in Europe

- October 2022-2025
- 22 partners, coordinated by PTB
- Poster introducing the project (Thursday)



EURAMET

- **Establish link** between radiometric techniques and mass spectrometry.
- Close the **traceability gap** for isotope ratio measurements.
- Report of different mass spectrometers **advantages and limitations.**
- Si-traceable **reference materials**
- Establish **calibration chain** for single collector ICP-MS.
- **Harmonized methods** for measurement of polluting elements.

Thank you

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