NKS-B ICPM Users seminar, 2017

Advantages of ICP-QQQ for nuclear waste characterisation

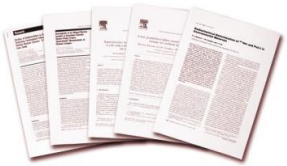
Phil Warwick
University of Southampton

GAU Radioanalytical Laboratories

UNIVERSITY OF Southampton

GAU-Radioanalytical Laboratories

A major provider of radioanalytical expertise to the nuclear sector



Research & Development

Research on :

Novel separation chemistries

Radioanalytical techniques

Instrument development

Validation

Consultancy services

Advice on sampling strategy & analytical programmes to :

Government Agencies

Nuclear industry

Decommissioning services

Waste disposal operators

Analytical services

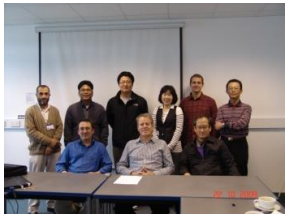
Commercial service to industry

Radionuclide analysis

Elemental/ complexant analysis

Opinions & Interpretations

UKAS TESTING 2758



Industry training

Specialist training programmes

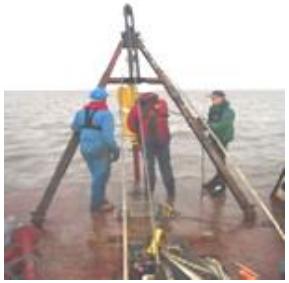
CPD training

Specialist analytical training

End user awareness

Guidance manuals

KTS schemes

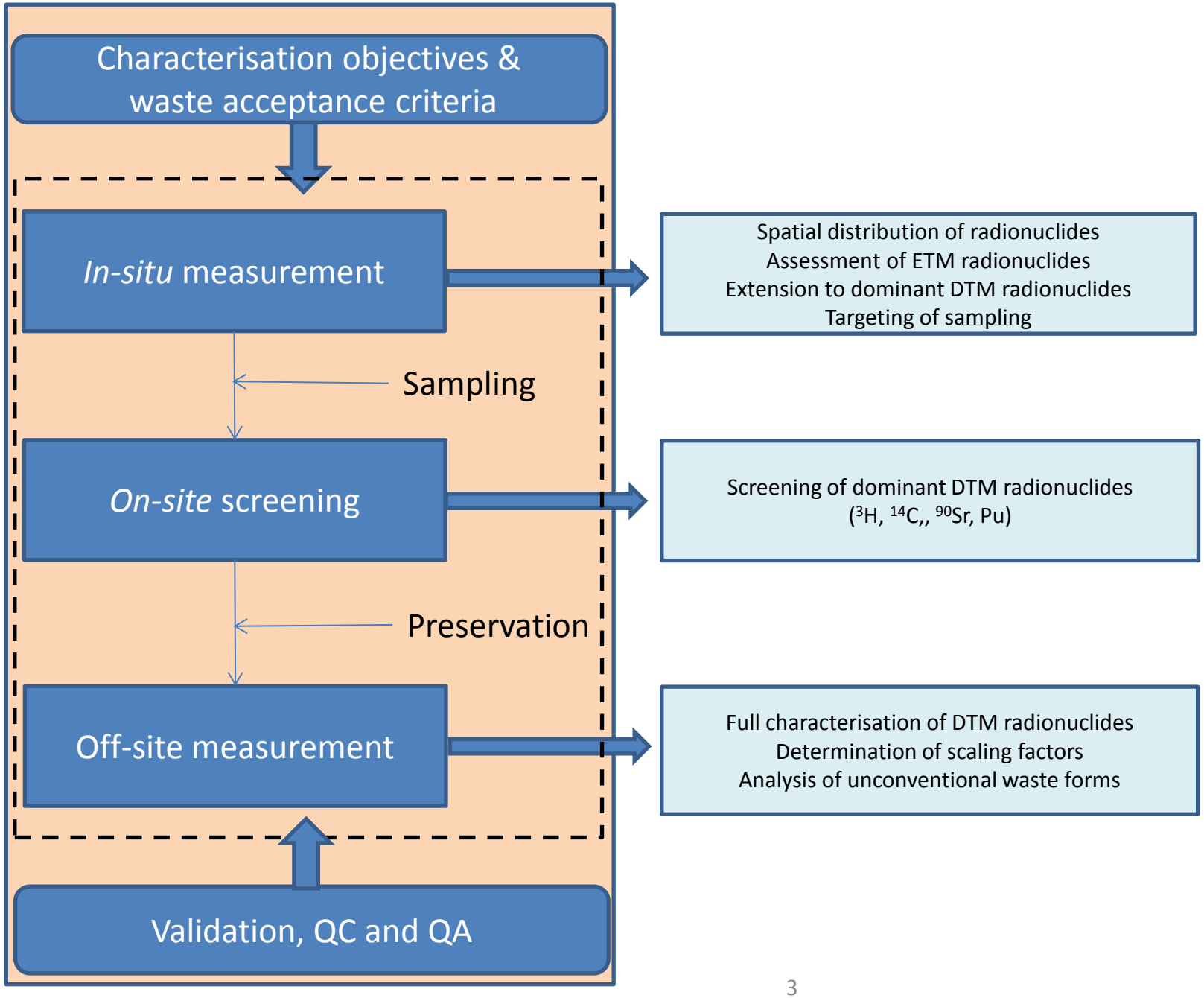


PhD training

NDA & industry funded studentships

Current research:

Nuclear forensics
Lab automation
PRB technologies
Environmental geochem
Mass spectrometry
Bioassay


Characterisation objectives & waste acceptance criteria
In-situ measurement
Spatial distribution of radionuclides
Assessment of ETM radionuclides
Extension to dominant DTM radionuclides
Targeting of sampling
Sampling
On-site screening
Screening of dominant DTM radionuclides
(^{3}H, ^{14}C,, ^{90}Sr, Pu)
Preservation
Off-site measurement
Full characterisation of DTM radionuclides
Determination of scaling factors
Analysis of unconventional waste forms
Validation, QC and QA

Waste characterisation challenges

Diverse sample types / Heterogeneity

Measurement of long-lived low abundance radionuclides

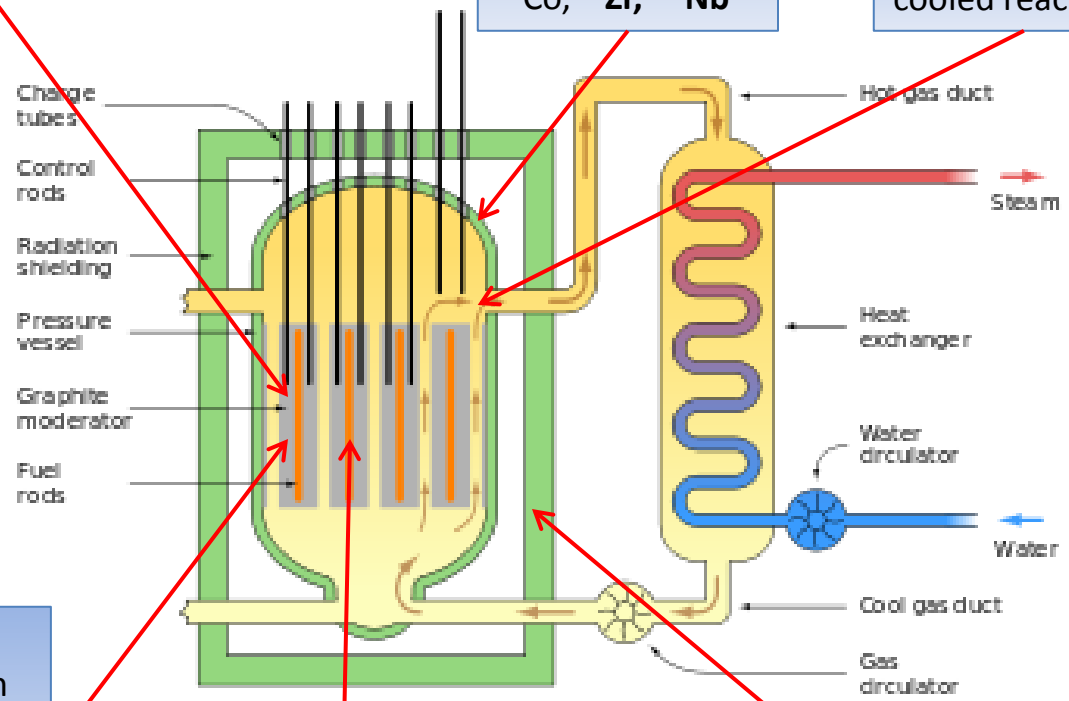
Requirement for rapid turn round times

Origin of artificial radionuclides

Activation of graphite
^{14}C and ^{36}Cl (from trace Cl impurities)

Activation of steel
^{55}Fe, **^{59}Ni, ^{63}Ni**, ^{60}Co, **^{93}Zr, ^{94}Nb**

Activation of CO_2
^{14}C (^{3}H in water-cooled reactors)



Fission products in fuel from ^{235}U fission e.g. **^{79}Se, ^{90}Sr, ^{93}Zr**, ^{95}Zr, **^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs**, ^{137}Cs, **^{147}Pm, ^{151}Sm**

Actinides in fuel from neutron capture by U e.g. **^{236}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am**

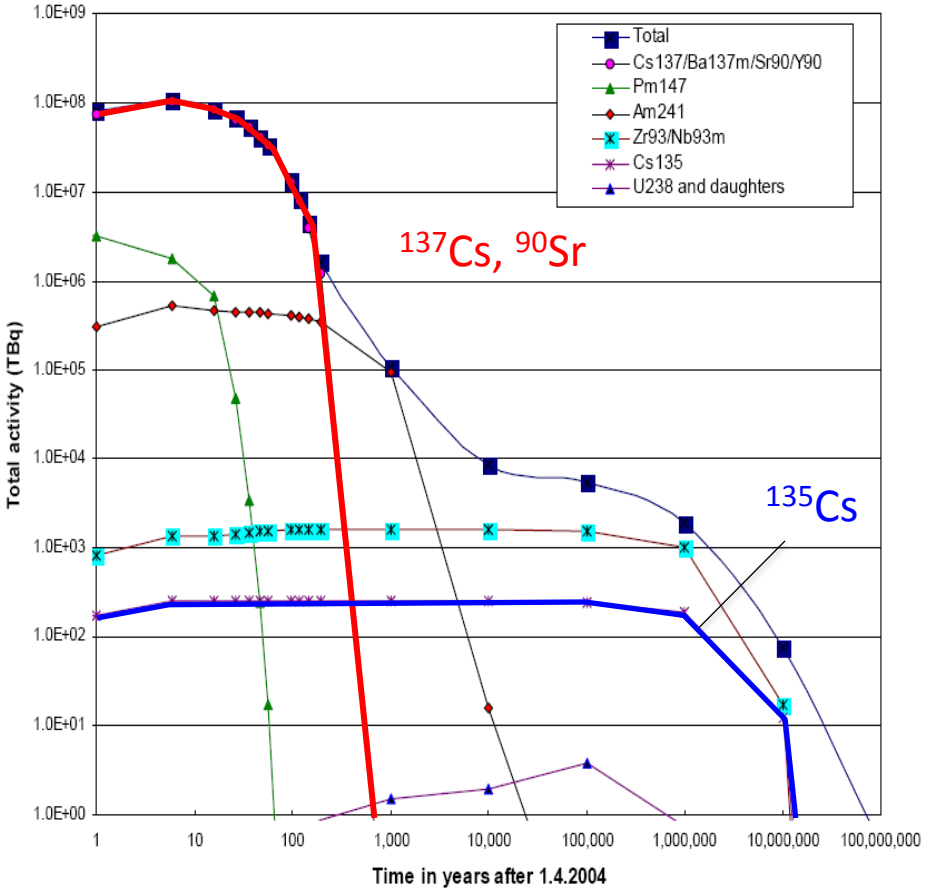
Activation of concrete bioshield
^{3}H, ^{152}Eu, ^{41}Ca

Radionuclide groups

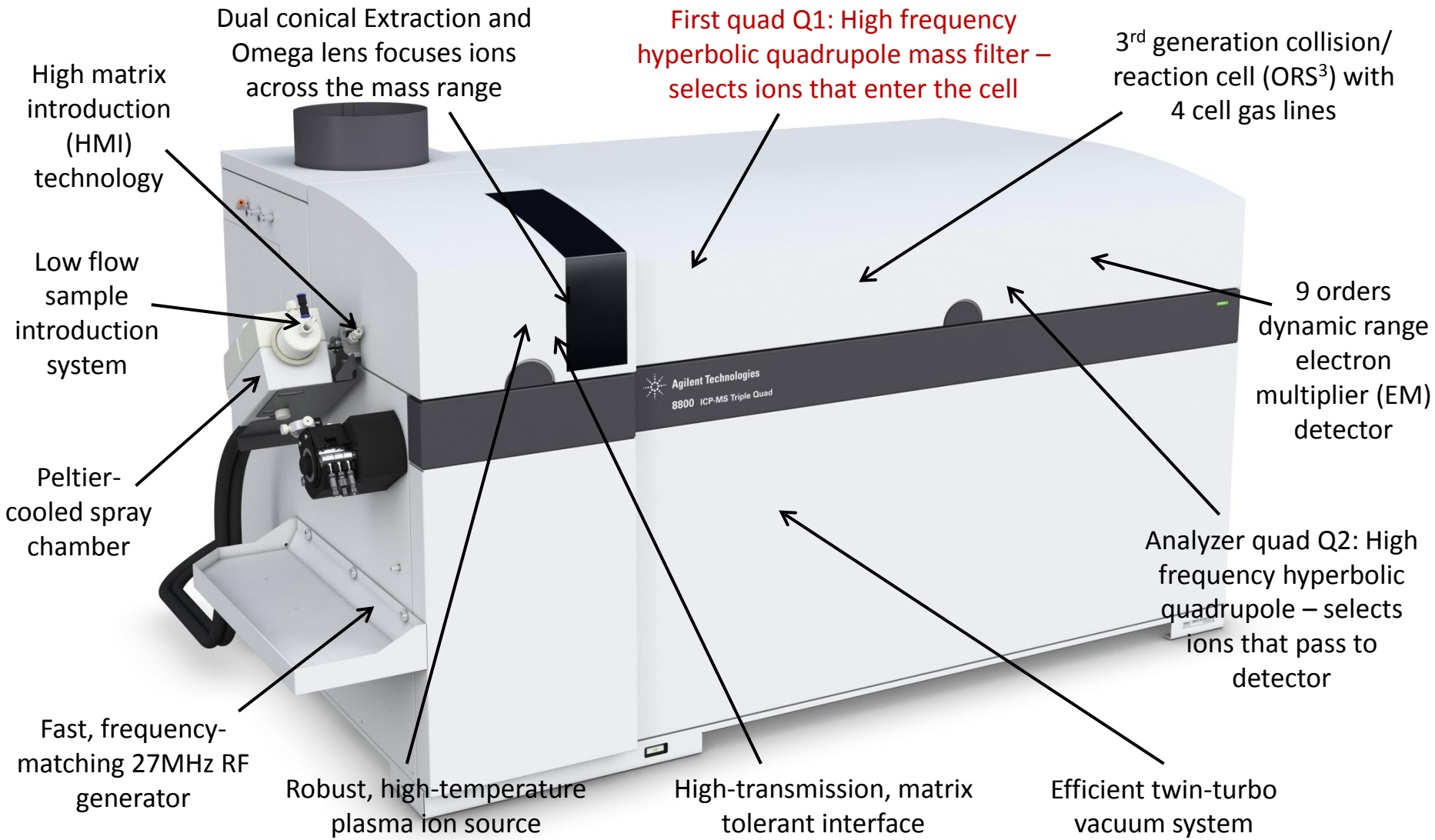
	Gamma (ETM)	Beta / EC (DTM)	Alpha (DTM)
Fission products	^{95}Zr/^{95}Nb, ^{106}Ru, ^{137}Cs, ^{144}Ce	^{90}Sr, ^{79}Se, ^{93}Zr, ^{99}Tc, ^{103}Ru, ^{107}Pd, ^{121m}Sn, ^{126}Sn, ^{129}I, ^{135}Cs, ^{147}Pm, ^{151}Sm	
Activation products	^{22}Na, ^{39}Ar, ^{54}Mn, ^{60}Co, ^{65}Zn, ^{93}Mo, ^{93m}Nb, ^{94}Nb, ^{108m}Ag, ^{110m}Ag, ^{125}Sb, ^{133}Ba, ^{134}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{166m}Ho.	^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{93}Zr	
Actinides	^{241}Am	^{241}Pu	^{228}Th, ^{230}Th, ^{232}Th, ^{234}Th, ^{231}Pa, ^{233}Pa, ^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{242}Am, ^{243}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm

Importance of mass spec in waste characterisation

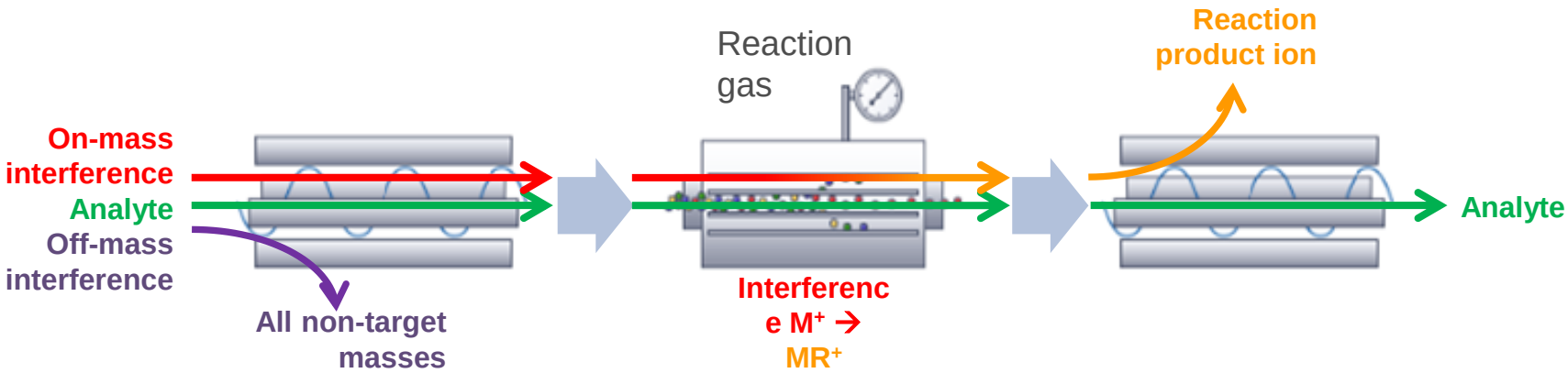
- Measurement of long-lived low abundance radionuclides ^{59}Ni, ^{93}Zr, ^{99}Tc, **^{135}Cs**
- Increase in sensitivity permits rapid measurement of shorter lived radionuclides ^{90}Sr, **^{137}Cs**
- High precision isotopic ratios for source apportionment



Source: Nirex


High matrix introduction (HMI) technology
Dual conical Extraction and Omega lens focuses ions across the mass range
First quad Q1: High frequency hyperbolic quadrupole mass filter – selects ions that enter the cell
3rd generation collision/ reaction cell (ORS3) with 4 cell gas lines
Low flow sample introduction system
9 orders dynamic range electron multiplier (EM) detector
Peltier-cooled spray chamber
Analyzer quad Q2: High frequency hyperbolic quadrupole – selects ions that pass to detector
Fast, frequency-matching 27MHz RF generator
Robust, high-temperature plasma ion source
High-transmission, matrix tolerant interface
Efficient twin-turbo vacuum system
Agilent Technologies
8800 ICP-MS Triple Quad

ICP-QQQ



Q1 set to analyte mass – rejects all non-target masses

Interference reacts to form product ion

Q2 set to original analyte mass – rejects any off-mass product ion(s)

Radionuclides of interest

Origin	Nuclide	Half life (years)	SpA [Bq/g]	Bq/ml of 1 ppb soln
Activation products	^{59}Ni	76000	3.0E+09	3.0E+00
	^{63}Ni	99	2.1E+12	2.1E+03
Fission products	^{79}Se	600000	2.8E+08	2.8E-01
	^{90}Sr	28.64	5.1E+12	5.1E+03
	^{93}Zr	1530000	9.3E+07	9.3E-02
Act. Prod.	^{94}Nb	20000	7.0E+09	7.0E+00
Fission products	^{99}Tc	211300	6.3E+08	6.3E-01
	^{107}Pd	6500000	1.9E+07	1.9E-02
	^{126}Sn	100000	1.0E+09	1.0E+00
	^{129}I	15690000	6.5E+06	6.5E-03
	^{135}Cs	2400000	4.1E+07	4.1E-02
	^{147}Pm	2.622	3.4E+13	3.4E+04
	^{151}Sm	90	9.7E+11	9.7E+02
NORM	^{226}Ra	1600	3.7E+10	3.7E+01
Actinides	^{235}U	703800000	8.0E+04	8.0E-05
	^{236}U	33146000	1.7E+06	1.7E-03
	^{237}Np	2140000	2.6E+07	2.6E-02
	^{238}U	4468000000	1.2E+04	1.2E-05
	^{239}Pu	24113	2.3E+09	2.3E+00
	^{240}Pu	6563	8.4E+09	8.4E+00
	^{241}Pu	14.4	3.8E+12	3.8E+03
	^{241}Am	432.7	1.3E+11	1.3E+02

Factors affecting limit of detection

Factor	Controlled by
Specific activity	Related to the nuclide half life. Short lived radionuclides have fewer atoms per Bq to measure.
Sensitivity	Related to the instrument mass response curve and ionisation energy of the analyte.
Background	Species arising from instrument.
Abundance sensitivity	Ratio of radionuclide to stable analogue.
Isobaric interference	Radionuclide mass and other species present.
Polyatomic interferences	Radionuclide mass and other species present.

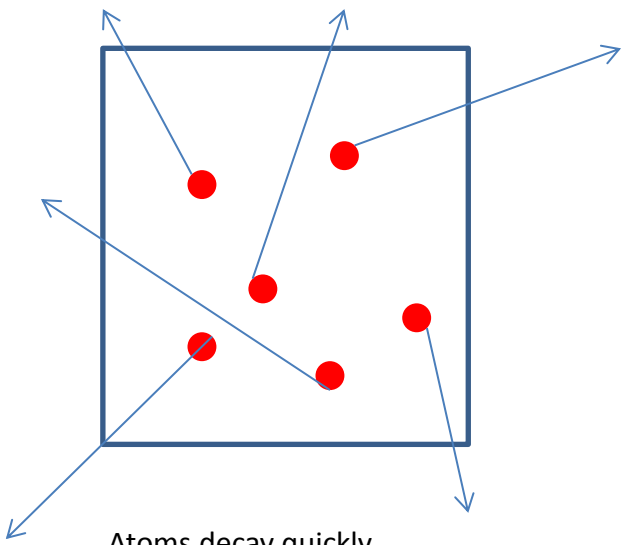
Potential improvements associated with use of ICP-QQQ

Specific activity

$$\frac{Bq}{g} = \frac{\ln(2) \times N_A}{t_{1/2} \times m_a}$$

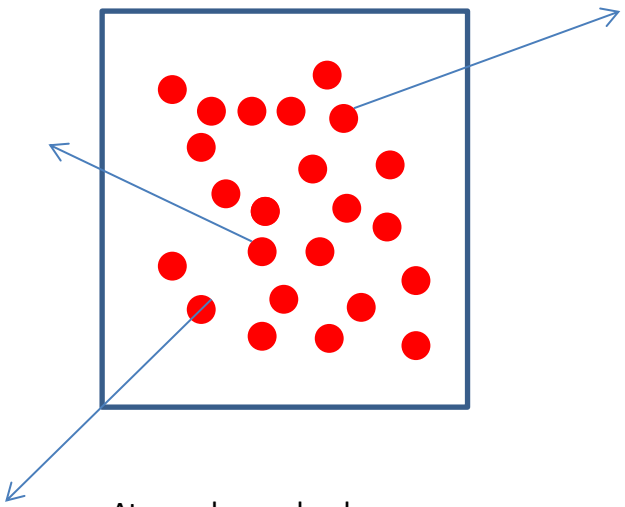
- The specific activity is the relationship between the activity (Bq) and mass (g) of a radionuclide and is dependent on the half life.

Short half life



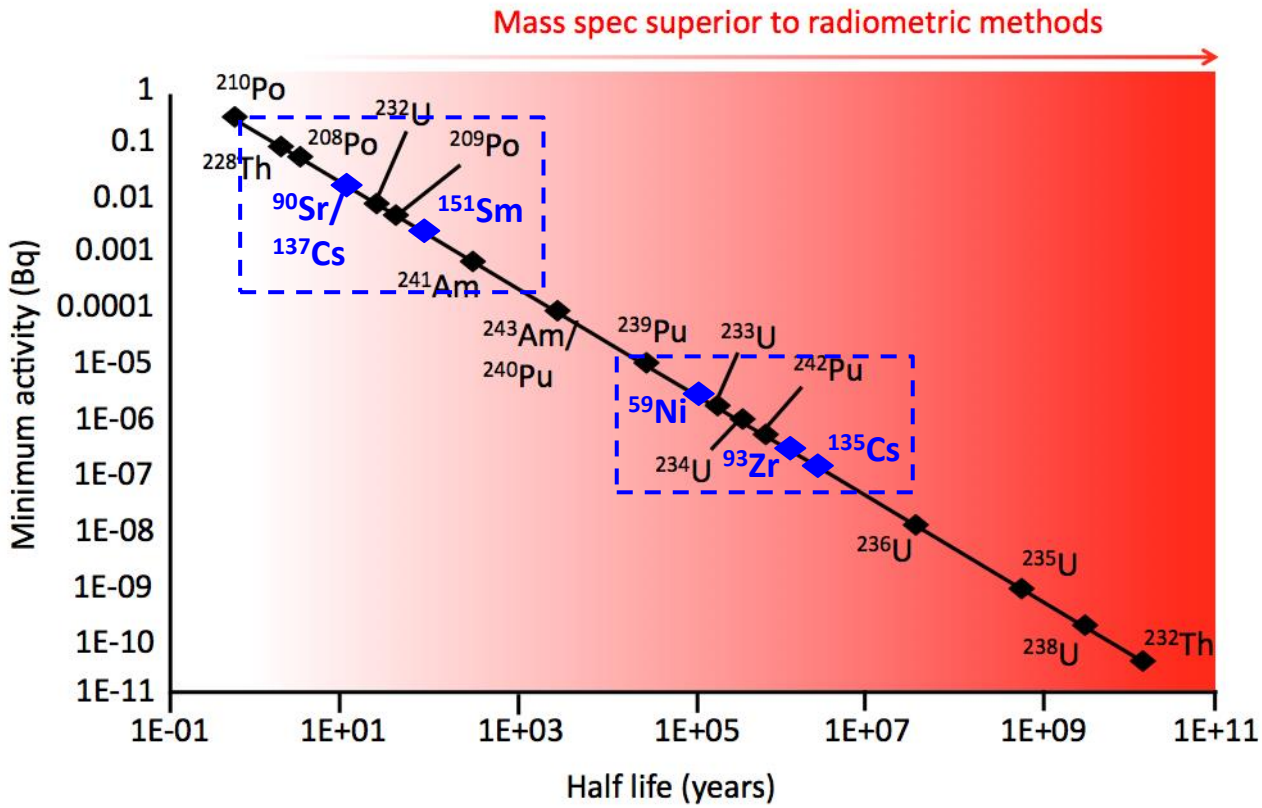
Atoms decay quickly
Large number of emissions for a given number of atoms

Long half life

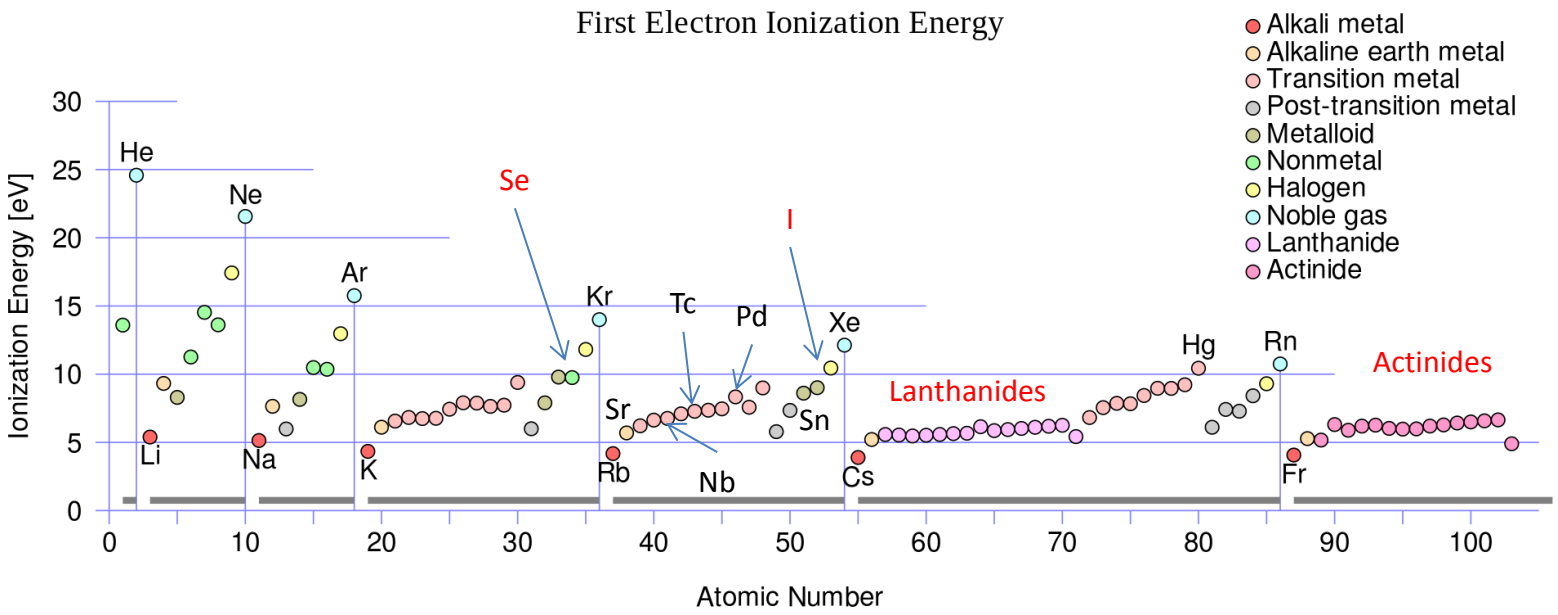


Atoms decay slowly
Small number of emissions for a given number of atoms

Radionuclides of interest

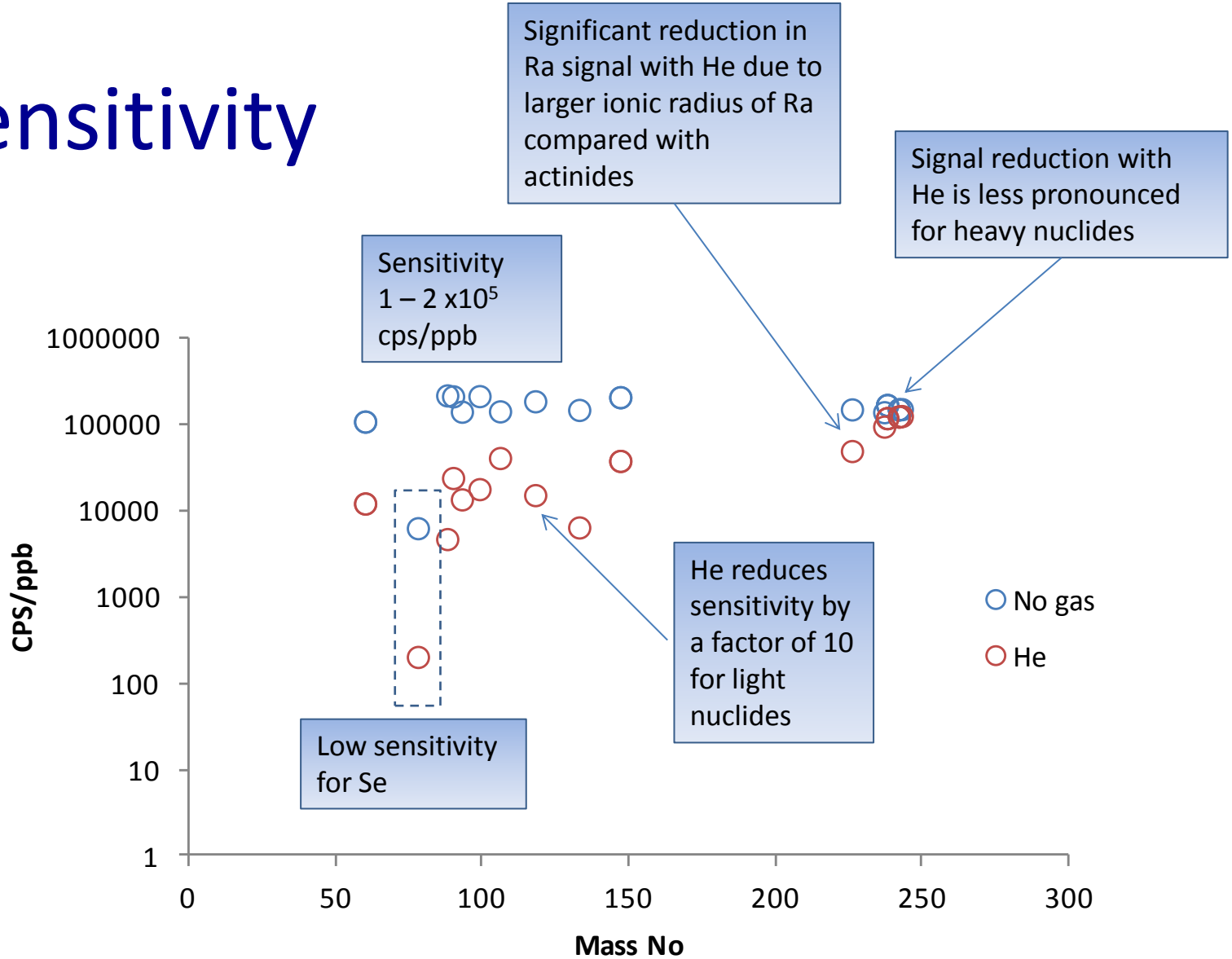


Ionisation energies



Wikipedia

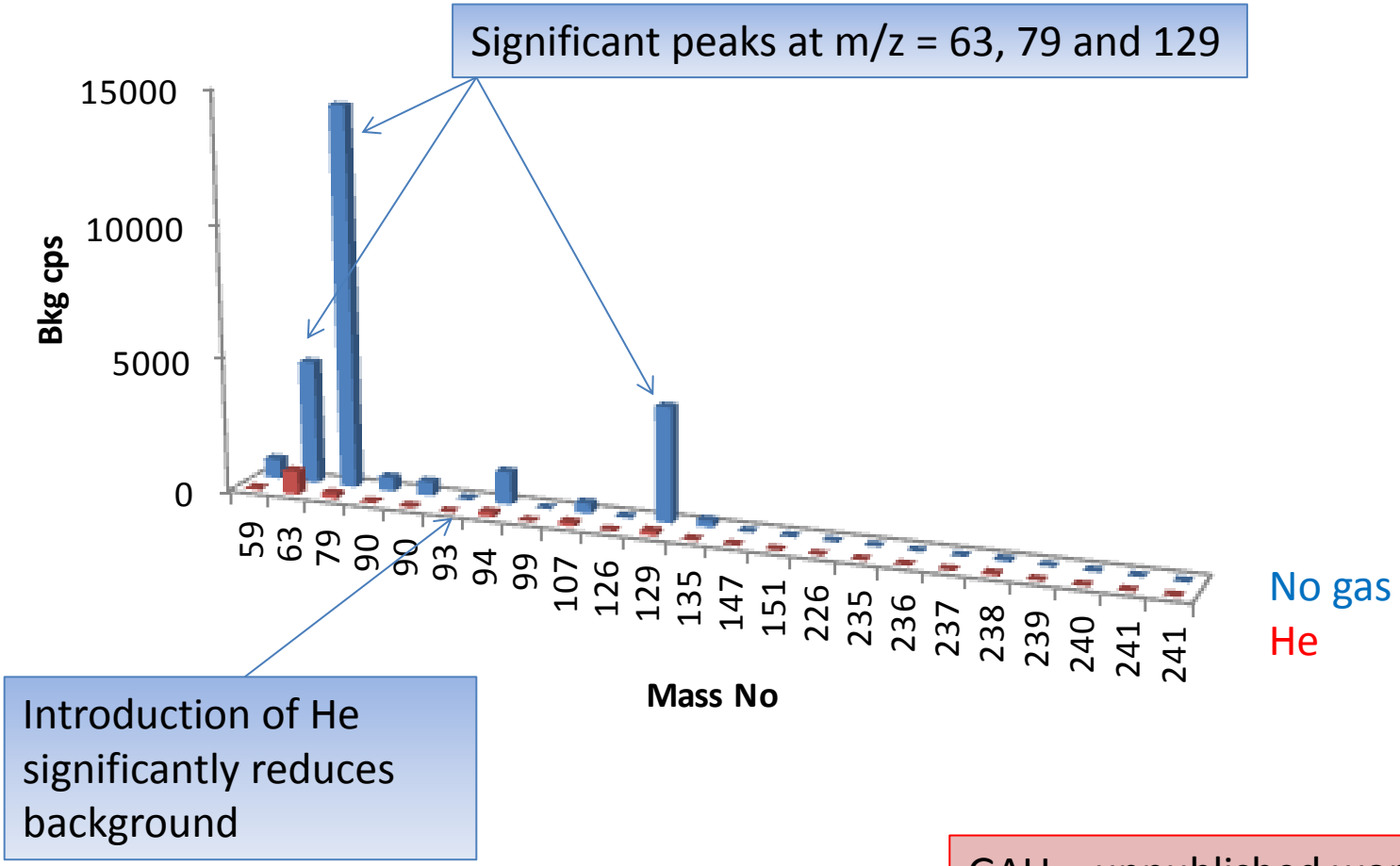
Sensitivity



[Iodine not measured]

GAU – unpublished work

Backgrounds at key masses

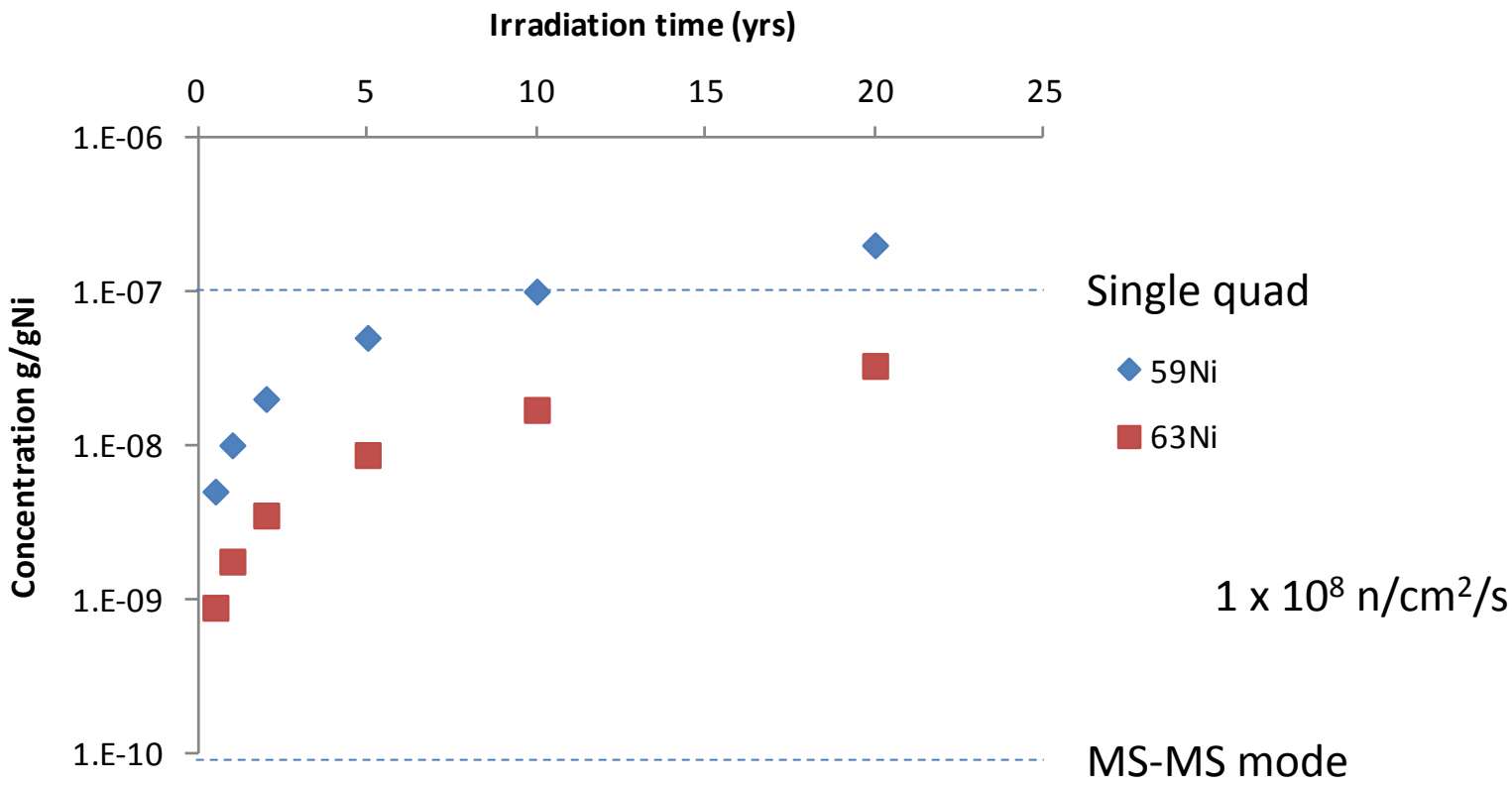


GAU – unpublished work

Abundance sensitivity

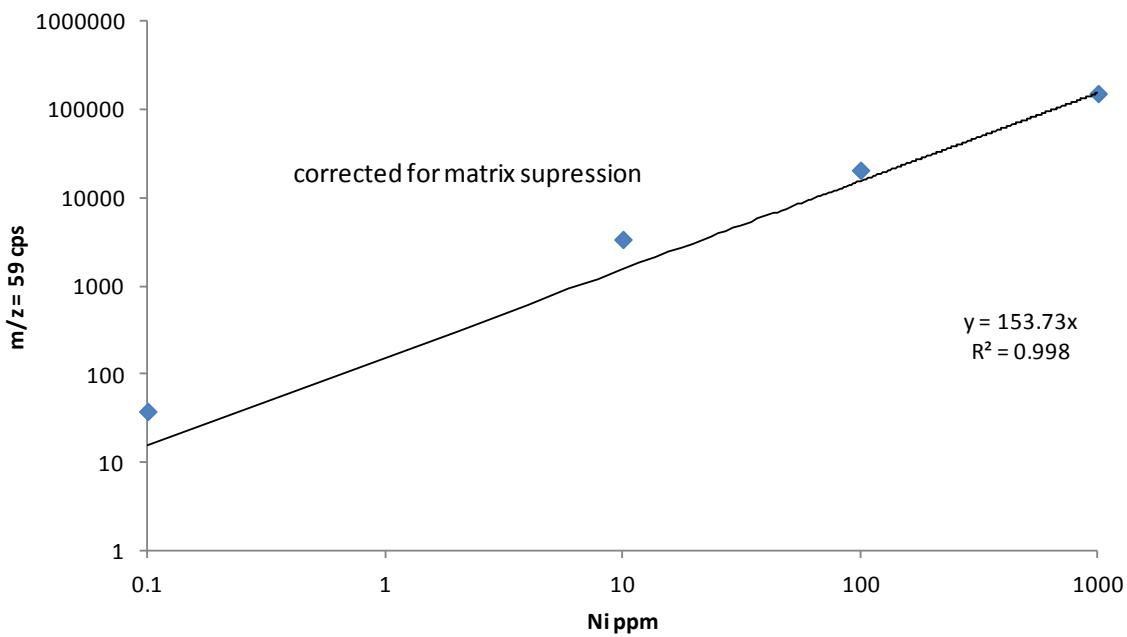
- The signal arising from a nuclide with mass = m at m ± 1.
- Particularly problematic for activation products (e.g. Ni) and fission products associated with commonly occurring elements (e.g. Sr).
- Limits measurement of ^{41}Ca due to abundance sensitivity of ^{40}Ar at m/z = 41.
- Theoretically, abundance sensitivities of 10^{-7} per MS are achievable. For MS-MS mode, abundance sensitivities of $<10^{-10}$ are reported.

Expected ^{59}Ni / ^{63}Ni concentration in irradiated Ni



GAU – unpublished work

Abundance sensitivity



Apparent abundance sensitivity = 2×10^{-6}
No improvement on introducing He
Signal is probably related to Co contamination in the Ni standard & $^{58}NiH^{+}$

GAU – unpublished work

Contributions to m/z = 59

Source	Contribution (cps)	% contribution
Background	1000	22.0%
Spillover from ^{58}Ni & ^{60}Ni	3400	74.8%
^{59}Ni	148	3.3%
TOTAL	**4548**	

Note RSD on ^{59}Ni cps for 10ppm Ni is ± 3.6% - comparable with the expected ^{59}Ni signal

Calculated assuming a 10ppm Ni solution
Ni irradiated for 20 years at 1 x10^8 n/cm^2/s
Assumes 74000 cps/ppb
^{59}Ni:Ni ratio of 2 x 10^{-7}

GAU – unpublished work

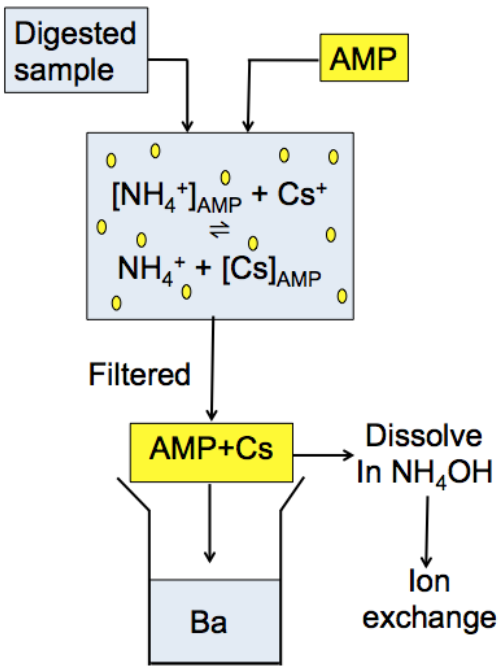
Isobaric interferences

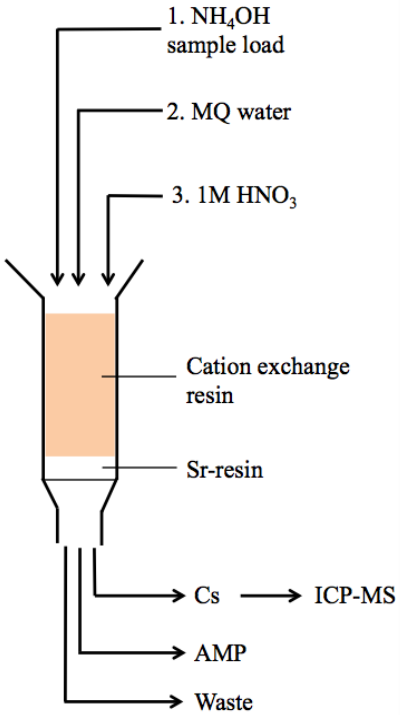
Nuclide	Isobaric interference (abundance)
^{59}Ni	^{59}Co (100%)
^{63}Ni	^{63}Cu (69.1%)
^{79}Se	^{79}Br (50.6%)
^{90}Sr	^{90}Zr (51.5%), ^{90}Y (daughter)
^{93}Zr	^{93}Nb (100%)
^{94}Nb	^{94}Zr (17.4%)
^{99}Tc	^{99}Ru (12.8%)
^{107}Pd	^{107}Ag (51%)
^{126}Sn	^{126}Te (18.7%), ^{126}Xe (0.09%)
^{129}I	^{129}Xe (26.4%)
^{135}Cs	^{135}Ba (6.6%)
^{147}Pm	^{147}Sm (15.1%)
^{151}Sm	^{151}Eu (47.8%)
^{226}Ra	None
^{235}U	None
^{236}U	None
^{237}Np	None
^{238}U	^{238}Pu
^{239}Pu	None
^{240}Pu	None
^{241}Pu	^{241}Am
^{241}Am	^{241}Pu

For fission products there may also be an isobaric interference from other nuclides in the isobar

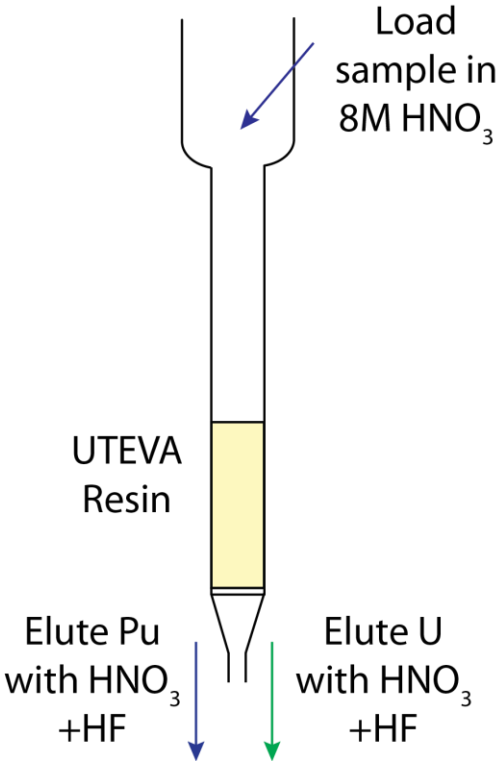
Chemical separation

Cs/Ba separation using ammonium molybdophosphate (AMP) and cation exchange/extraction chromatography

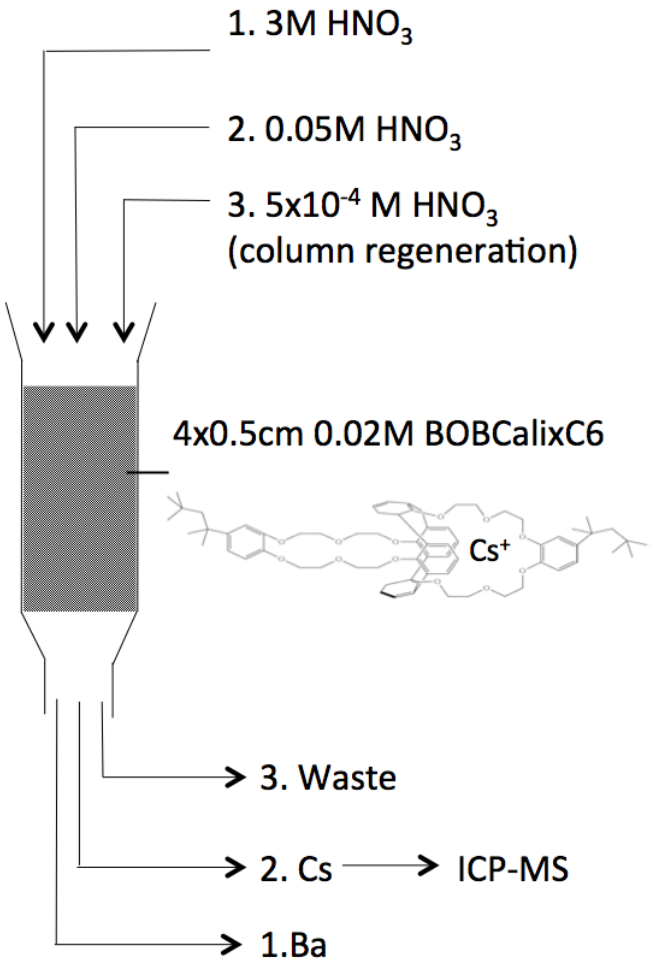




U/Pu separation using extraction chromatography



Novel separation materials



Cs/Ba separation by extraction chromatography using calixarene

Extraction chromatography using **calixarenes**
High selectivity, and potential back-extraction and re-use of material

Russell B.C., Warwick P.E. & Croudace I.W. (2014). Calixarene-based extraction chromatographic separation of ^{135}Cs and ^{137}Cs in environmental and waste samples prior to sector field ICP-MS analysis. *Anal. Chem, **86**, 11890 – 11896*

On-line separation of isobaric interferences

- Correction of contribution from isobaric interference using a different isotope of the element.

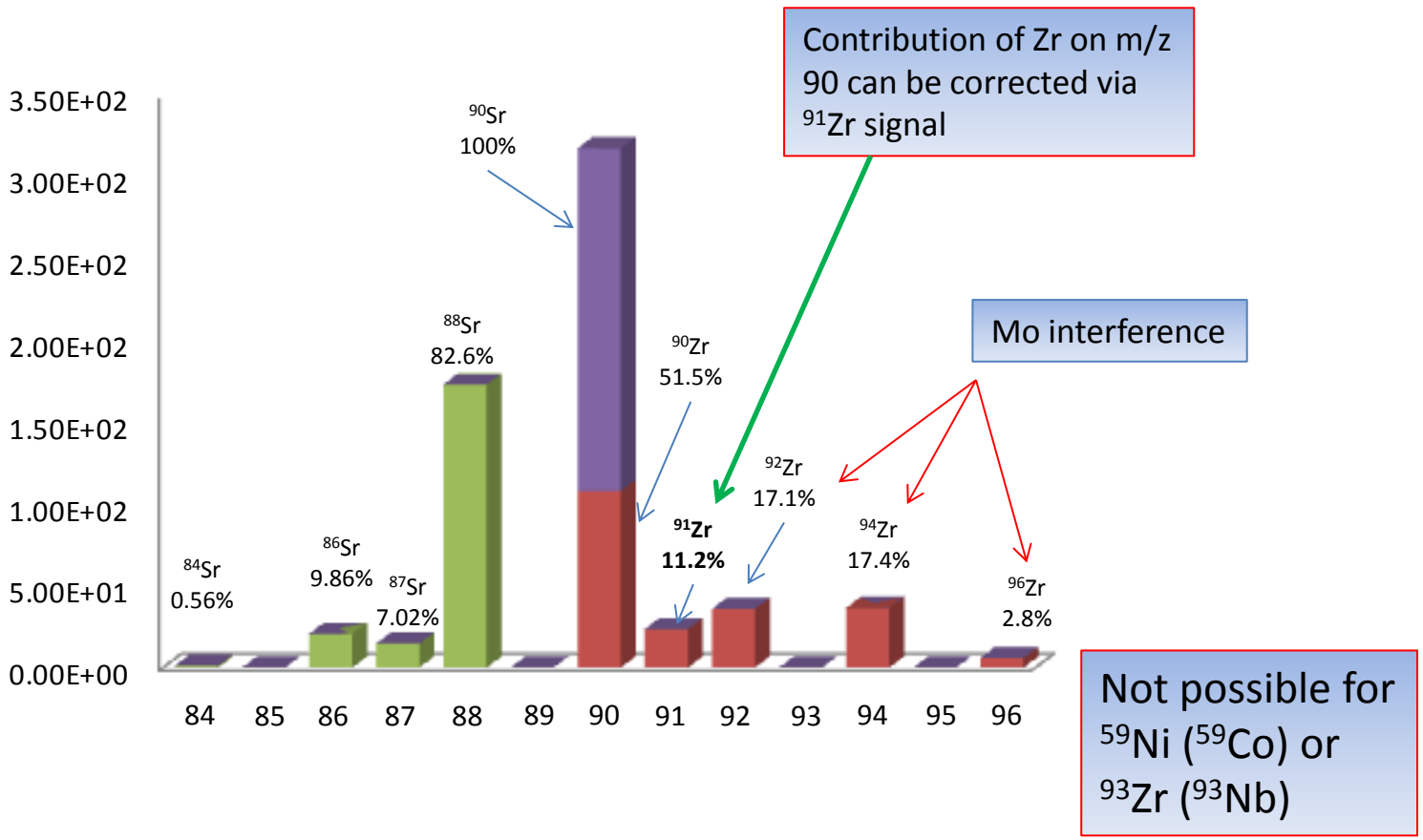
- Reaction of the analyte with a reactive gas to shift the mass of the analyte.

- Reaction of the isobaric interference with a reactive gas to shift the mass of the interference.

- Charge transfer from the interference to the reactive gas to suppress the signal of the interference.

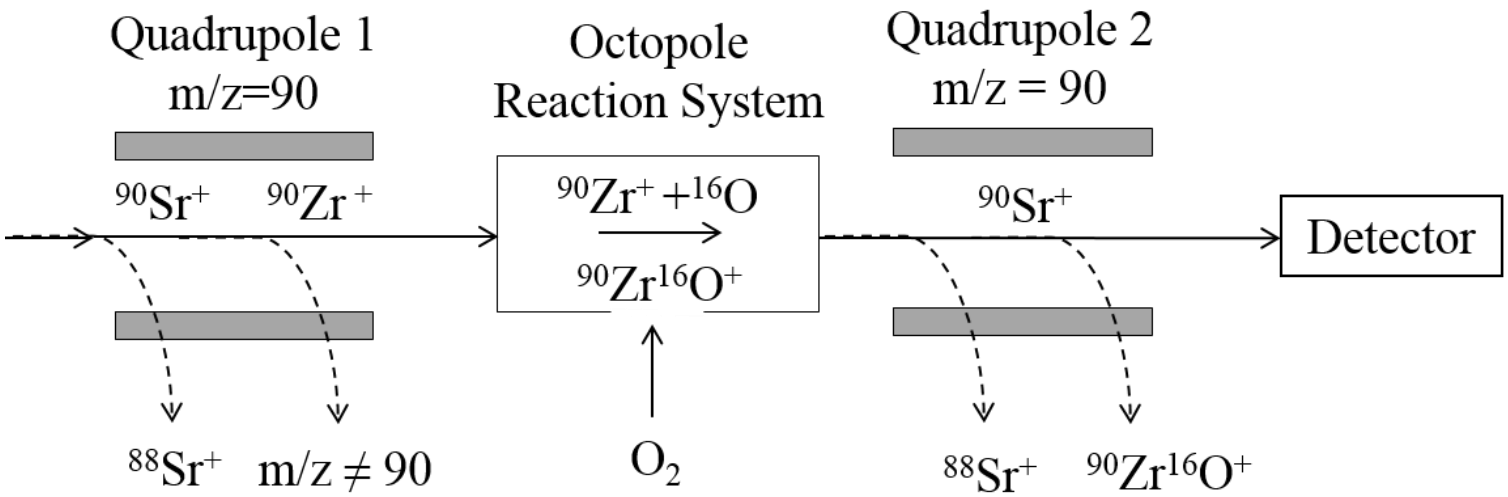
$$X^+ + O_2 \rightarrow X + O_2^+$$

Correction using other isotopes

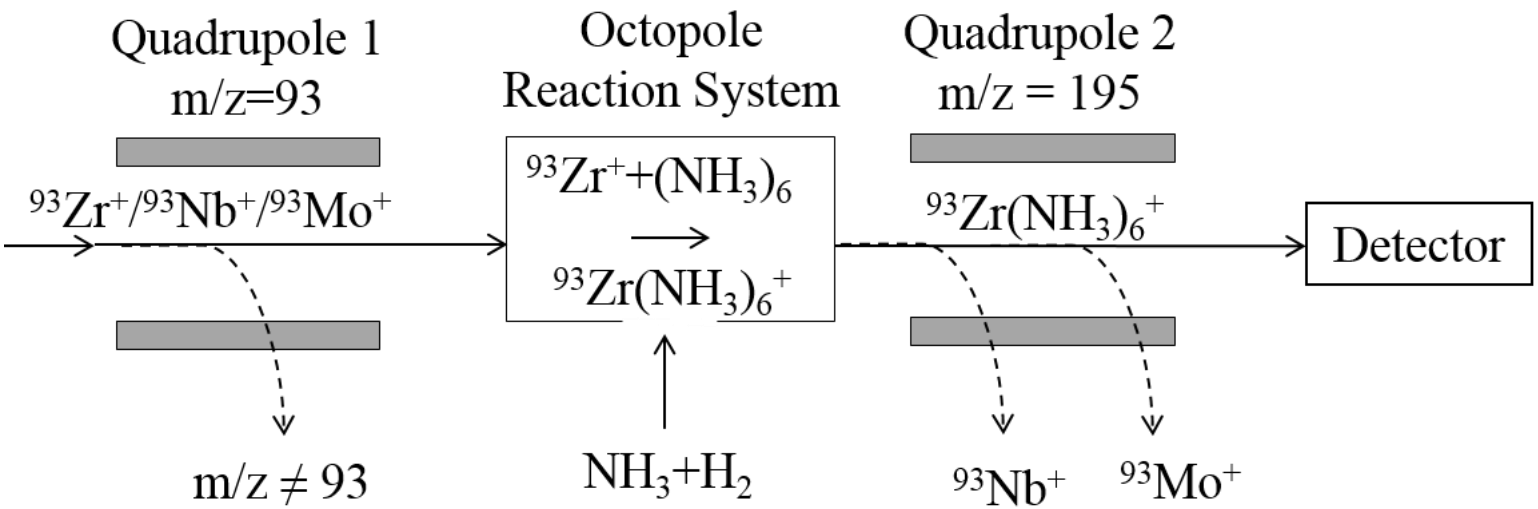


Signals from a 1 ppt Sr, Zr and ^{90}Sr solution (background subtracted)

Isobaric separation using MS/MS mode and reactive gas



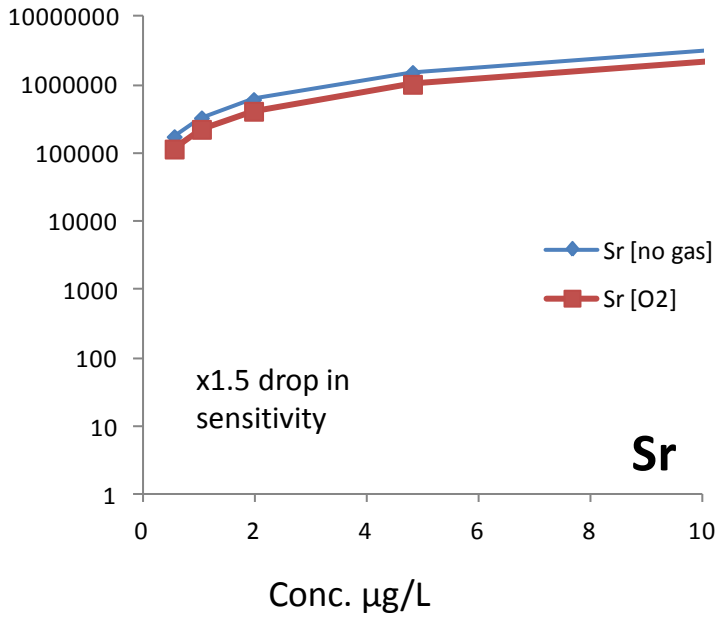
Isobaric separation using MS/MS mode and reactive gas

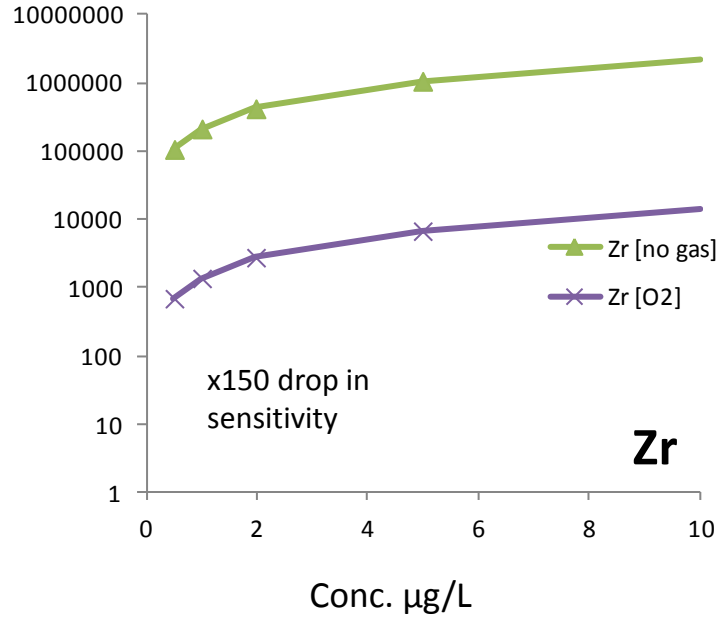


Instrument layout for measurement of ^{93}Zr in the presence of isobaric ^{93}Nb and ^{93}Mo (Petrov, 2017)

Nuclide	Interference	Reaction gas	Reaction	Reference
^{36}Cl	^{36}Ar, ^{36}S	C_2H_2	$S^+ + C_2H_2 \rightarrow CHCS^+ + H$ $Cl^+ + C_2H_2 \rightarrow$ No reaction	Bandura (05)
^{41}Ca	^{41}K	N_2O	$Ca^+ + N_2O \rightarrow CaO^+ + N_2$ $K^+ + N_2O \rightarrow$ No reaction	Bandura (05)
^{59}Ni	^{59}Co	No known cell reaction		
^{63}Ni	^{63}Cu	No known cell reaction		
^{79}Se	^{79}Br	O_2	$Br^+ + O_2 \rightarrow Br + O_2^+$ $Se^+ + O_2 \rightarrow$ No reaction	Bandura (2005)
^{90}Sr	^{90}Zr	O_2	$Zr^+ + O_2 \rightarrow ZrO^+ + O$ $Sr^+ + O_2 \rightarrow$ No reaction	Russell (17), Amr (16)
^{93}Zr	^{93}Nb	NH_3+H_2	$Zr^+ + NH_3 + H_2 \rightarrow Zr(NH_3)_6^+$ $Nb^+ + NH_3 + H_2 \rightarrow$ No reaction	Petrov (17)
^{94}Nb	^{94}Zr, ^{94}Mo	NH_3+H_2	$Zr^+ + C_6F_6 \rightarrow ZrF_2^+, ZrF_3^+$ $Mo^+ + C_6F_6 \rightarrow Mo^+C_6F_6$ $Nb^+ + C_6F_6 \rightarrow NbF_4^+, Nb^+C_6F_6$	Bandura (2005)
^{99}Tc	^{99}Ru	No known cell reaction		
^{107}Pd	^{107}Ag	C_3H_8	$Ag^+ + C_3H_8 \rightarrow$ No reaction $Pd^+ + C_3H_8 \rightarrow PdC_2H_4^+, PdC_3H_6^+$	Bandura (2005)
^{126}Sn	^{126}Te	CH_4	$Te^+ + CH_4 \rightarrow TeCH_2^+, TeCH_4^+$ $Sn^+ + CH_4 \rightarrow$ No reaction	Bandura (2005)
^{129}I	^{129}Xe	O_2	$Xe^+ + O_2 \rightarrow Xe + O_2^+$ $I^+ + O_2 \rightarrow$ No reaction	Shikamori (12)
^{135}Cs ^{137}Cs	^{135}Ba ^{137}Ba	N_2O	$Ba^+ + N_2O \rightarrow BaO^+ + N_2$ $Cs^+ + N_2O \rightarrow$ No reaction	Zheng (2014, 2015), Ohno (2013)
^{147}Pm	^{147}Sm	No known cell reaction		
^{151}Sm	^{151}Eu	O_2	$Eu^+ + O_2 \rightarrow$ No reaction $Sm^+ + O_2 \rightarrow SmO^+ + O$	Garcia-Miranda (2017)
^{239}Pu	$^{238}U^1H$	O_2	$Pu^+ + O_2 \rightarrow PuO^+ + O$ $UH^+ + O_2 \rightarrow UO^+ + H + O$	Tanimizu (2013), This study
^{241}Am	^{241}Pu	No known cell reaction		

Sr and Zr

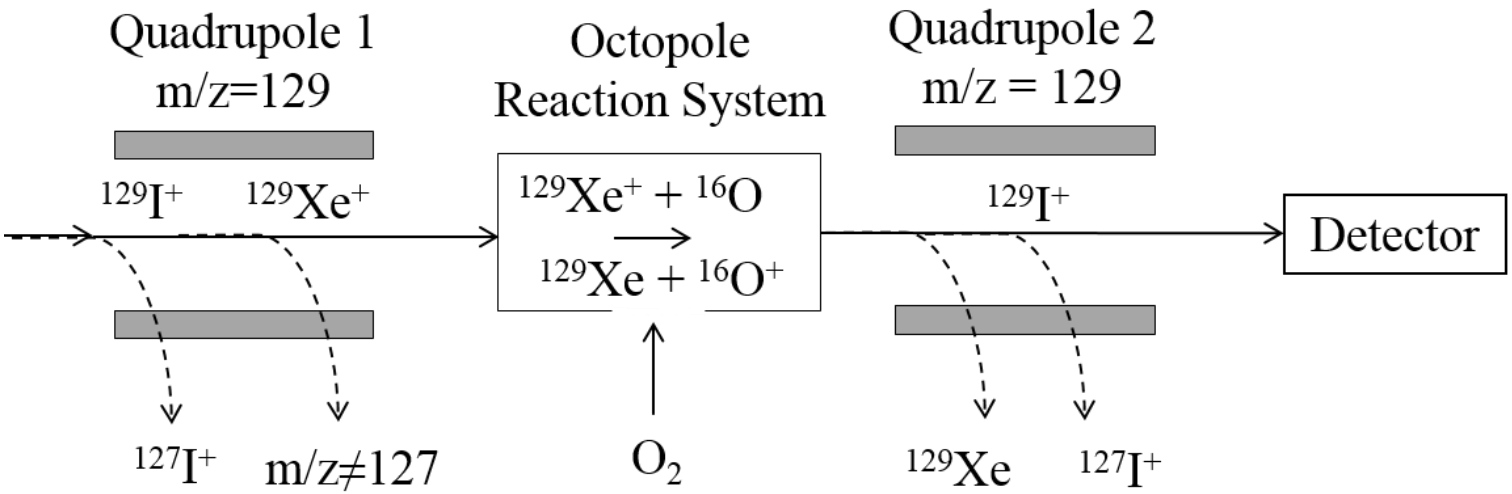




[Cps corrected for relative abundance of each nuclide]

GAU – unpublished work

Charge transfer



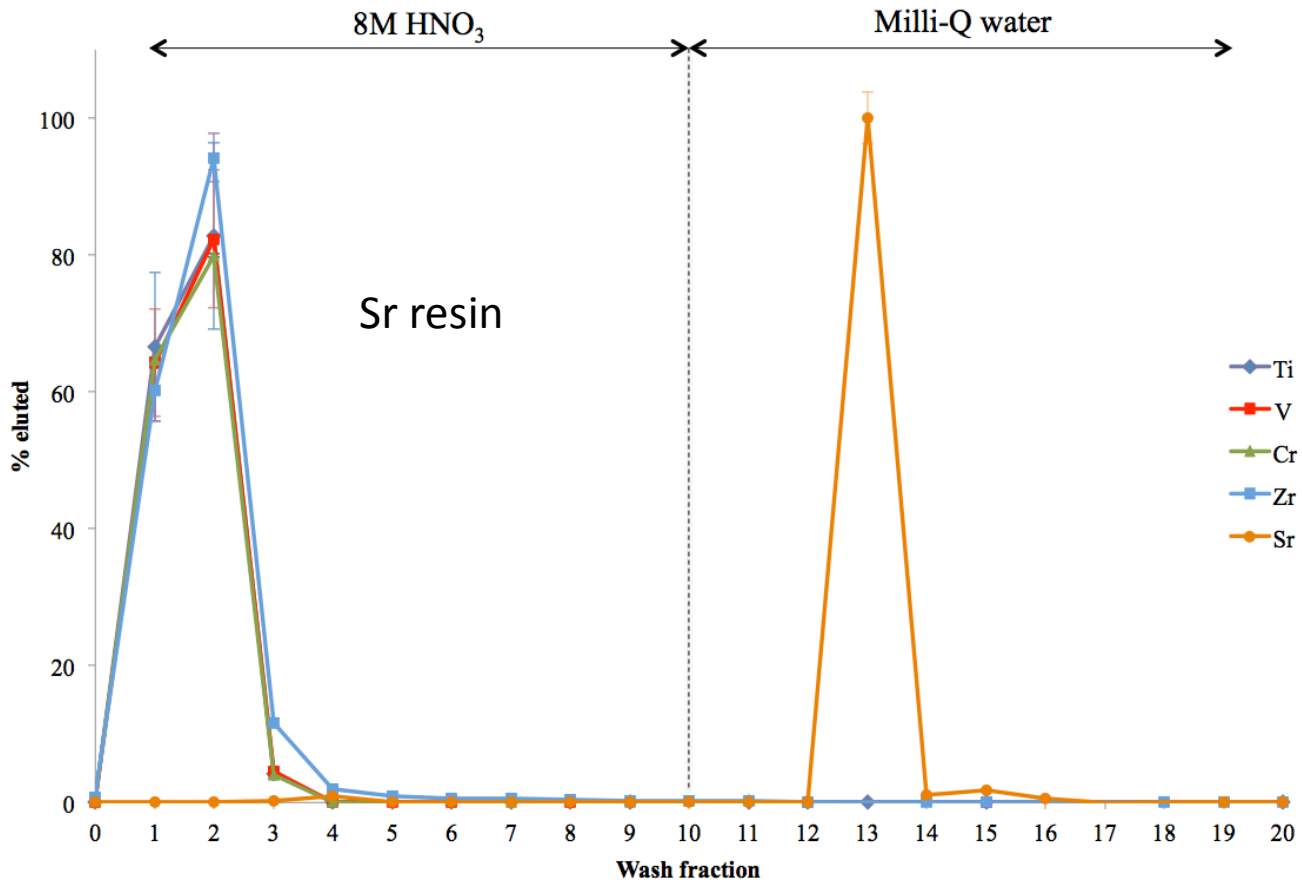
Polyatomic interferences

- Polyatomic species with masses identical to the analyte of interest.
- Precursors are introduced from the sample matrix, the plasma gas or the surrounding atmosphere.
- Typically hydrides, oxides, nitrides or argides.

Examples of polyatomic interferences

^{90}Sr	$^{89}Y\ ^{1}H$
	$^{78}Se\ ^{12}C$
	$^{78}Kr^{12}C$
	$^{76}Ge\ ^{14}N$
	$^{76}Se\ ^{14}N$
	$^{74}Ge\ ^{16}O$
	$^{74}Se\ ^{16}O$
	$^{55}Mn\ ^{35}Cl$
	$^{53}Cr\ ^{37}Cl$
	$^{50}Ti\ ^{40}Ar$
	$^{50}V\ ^{40}Ar$
	$^{50}Cr\ ^{40}Ar$
	$^{52}Cr\ ^{38}Ar$
	$^{54}Fe\ ^{36}Ar$
	$^{58}Ni\ ^{16}O_2$

Off-line separation of polyatomic precursors



On-line removal of polyatomic interferences

- Polyatomic interferences can be minimised on-line by screening out precursor species on quadrupole 1 and via the introduction of He or H_2 into the reaction cell.

- Introduction of He reduces analyte signal at low masses. Less of an effect at high masses

The challenges

Nuclide	SpA ($t_{½}$< 10^4 y)	Isobaric interference	Polyatomic interference	Background	Sensitivity	Abundance sensitivity
^{59}Ni		XX	X			X
^{63}Ni	X	X	X	X		X
^{79}Se		X	X	X	X	X
^{90}Sr	X	X	X			X
^{93}Zr		XX	X			X
^{94}Nb		X	X			X
^{99}Tc		X	X			
^{107}Pd		X	X			X
^{126}Sn		X	X			X
^{129}I		X	X	X	X	X
^{135}Cs		X	X			X
^{147}Pm	X	X	X			
^{151}Sm	X	X	X			X
^{226}Ra	X		X			
^{235}U			X			
^{236}U			X			
^{237}Np			X			
^{238}U		X	X			
^{239}Pu		X	X			
^{240}Pu			X			
^{241}Pu	X	X	X			
^{241}Am	X	X	X			

Agilent 8800 - LoDs

LoD Bq/ml	Nuclide
$< 1 \times 10^{-5}$	^{235}U, ^{236}U, ^{238}U, ^{237}Np
$1 \times 10^{-5} – 1 \times 10^{-4}$	^{93}Zr, ^{99}Tc, ^{107}Pd
$1 \times 10^{-4} – 1 \times 10^{-3}$	^{126}Sn, ^{135}Cs, ^{226}Ra, ^{239}Pu
$1 \times 10^{-3} – 1 \times 10^{-2}$	^{240}Pu
1×10^{-2} – 0.1	^{59}Ni, ^{94}Nb, ^{241}Am
0.1 - 1	^{79}Se, ^{151}Sm, ^{241}Pu
1 – 10	^{147}Pm
10 – 100	^{90}Sr
> 100	^{63}Ni

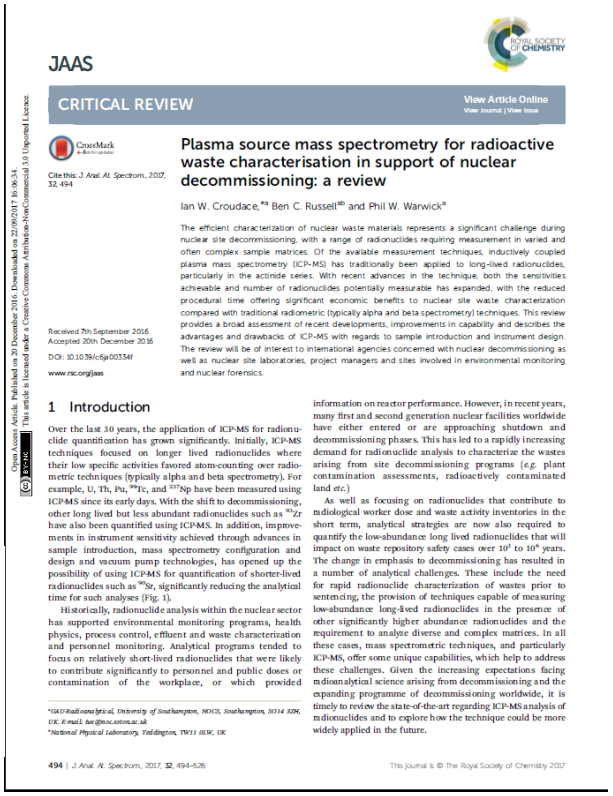
No gas option
Based on measured blank + 3σ and measured cps / ppb
Improvements expected through nuclide-specific optimisation

GAU – unpublished work

Conclusions

- ICP-QQQ offers potential advantages in terms of interference reduction and ultra low level measurement.

- The advantages of ICP-QQQ can be exploited for ultra low level measurement of radionuclides, extending the range of radionuclides that can be measured by ICPMS.



JAAS

CRITICAL REVIEW

View Article Online
View Journal | View Issue

Open Access Article. Published on 20 December 2016. Downloaded on 20/06/2017 16:06:34.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Cite this: J. Anal. At. Spectrom., 2017, 32, 494

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]

The efficient characterization of nuclear waste materials represents a significant challenge during nuclear site decommissioning, with a range of radionuclides requiring measurement in varied and often complex sample matrices. Of the available measurement techniques, inductively coupled plasma mass spectrometry (ICP-MS) has traditionally been applied to long-lived radionuclides, particularly in the actinide series. With recent advances in the technique, both the sensitivities achieveable and number of radionuclides potentially measurable has expanded, with the reduced procedural time offering significant economic benefits to nuclear site waste characterization compared with traditional radiometric (typically alpha and beta spectrometry) techniques. This review provides a broad assessment of recent developments, improvements in capability and describes the advantages and drawbacks of ICP-MS with regards to sample introduction and instrument design. The review will be of interest to international agencies concerned with nuclear decommissioning as well as nuclear site laboratories, project managers and sites involved in environmental monitoring and nuclear forensics.

Received 7th September 2016
Accepted 20th December 2016

DOI: 10.1039/c6ja00334f

www.rsc.org/jaas

1 Introduction

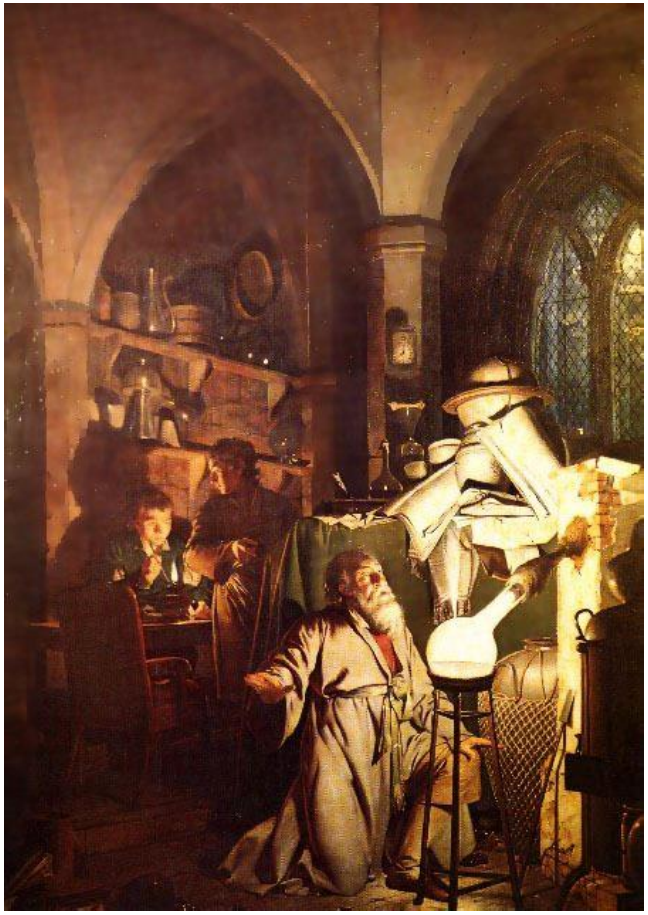
Over the last 30 years, the application of ICP-MS for radionuclide quantification has grown significantly. Initially, ICP-MS techniques focused on longer lived radionuclides where their low specific activities favored atom-counting over radiometric techniques (typically alpha and beta spectrometry). For example, U, Th, Pu, ^{99}Tc, and ^{237}Np have been measured using ICP-MS since its early days. With the shift to decommissioning, other long lived but less abundant radionuclides such as ^{93}Zr have also been quantified using ICP-MS. In addition, improvements in instrument sensitivity achieved through advances in sample introduction, mass spectrometry configuration and design and vacuum pump technologies, has opened up the possibility of using ICP-MS for quantification of shorter-lived radionuclides such as ^{90}Sr, significantly reducing the analytical time for such analyses (Fig. 1).

Historically, radionuclide analysis within the nuclear sector has supported environmental monitoring programs, health physics, process control, effluent and waste characterization and personnel monitoring. Analytical programs tended to focus on relatively short-lived radionuclides that were likely to contribute significantly to personnel and public doses or contamination of the workplace, or which provided information on reactor performance. However, in recent years, many first and second generation nuclear facilities worldwide have either entered or are approaching shutdown and decommissioning phases. This has led to a rapidly increasing demand for radionuclide analysis to characterize the wastes arising from site decommissioning programs (*e.g.* plant contamination assessments, radioactively contaminated land etc.)

As well as focusing on radionuclides that contribute to radiological worker dose and waste activity inventories in the short term, analytical strategies are now also required to quantify the low-abundance long lived radionuclides that will impact on waste repository safety cases over 10^3 to 10^6 years. The change in emphasis to decommissioning has resulted in a number of analytical challenges. These include the need for rapid radionuclide characterization of wastes prior to sentencing, the provision of techniques capable of measuring low-abundance long-lived radionuclides in the presence of other significantly higher abundance radionuclides and the requirement to analyze diverse and complex matrices. In all these cases, mass spectrometric techniques, and particularly ICP-MS, offer some unique capabilities, which help to address these challenges. Given the increasing expectations facing radioanalytical science arising from decommissioning and the expanding programme of decommissioning worldwide, it is timely to review the state-of-the-art regarding ICP-MS analysis of radionuclides and to explore how the technique could be more widely applied in the future.

[a]GAU-Radioanalytical, University of Southampton, NOCS, Southampton, SO14 3ZH, UK. E-mail: iwc@noc.soton.ac.uk
[b]National Physical Laboratory, Teddington, TW11 0LW, UK

This journal is © The Royal Society of Chemistry 2017

Croudace I.W., Russell B.C. & Warwick P.E. (2017). Plasma source mass spectrometry for radioactive waste characterisation in support of nuclear decommissioning: a review. *J. Anal. At. Spectrom.*, ***32***, *494-526.*

Any questions ?