NPL National Physical Laboratory

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CCRI Webinar Series
Mass spectrometry in Radionuclide Metrology

Developments in mass spectrometry relevant reference materials

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Mass spectrometry at NPL

- Tandem ICP-MS/MS
- Operating since September 2015
- Measurement of medium and long-lived radionuclides (>30 years) as a rapid alternative to decay counting techniques
- Expands number of radionuclides measurable compared to decay counting techniques alone
- Tandem mass spectrometry design and integrated reaction cell reduces or removes need for relatively time-consuming offline chemical separation
- New projects, services and standards

Expansion of measurement services

- Existing standards re-measured for ICP-MS related impurities
- Spiking of standards with known interferences e.g. ^{90}Sr spiked with ^{90}Zr isobaric interference
- Proficiency test exercises:
  - Dilution checks
  - Comparison with decay counting techniques
  - More participants reporting the use of mass spectrometry for long lived radionuclides

Applications of mass spectrometry

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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

Examples of radionuclides measurable by mass spectrometry at NPL

Origin	Nuclide	Half life (years)
Activation products	^{41}Ca	$99.4(15) \times 10^4$
	^{59}Ni	$7.6(5) \times 10^4$
	^{63}Ni	101.2 (15)
Fission products	^{79}Se	$3.27(28) \times 10^5$
	^{90}Sr	28.91 (3)
	^{93}Zr	$1.61(5) \times 10^6$
	^{99}Tc	$211.5(11) \times 10^3$
	^{126}Sn	$2.30 (14) \times 10^5$
	^{129}I	$1.57(4) \times 10^7$
	^{135}Cs	$2.3(3) \times 10^6$
	^{151}Sm	90(8)
NORM	^{210}Pb	22.20(22)
	^{226}Ra	1,600(7)
	^{231}Pa	$3.276(11) \times 10^4$
Actinides	^{235}U	$7.04(1) \times 10^8$
	^{236}U	$2.342(4) \times 10^7$
	^{237}Np	$2.144(7) \times 10^6$
	^{238}U	$4.468(6) \times 10^9$
	^{239}Pu	24,110(30)
	^{240}Pu	6,561(7)
	^{241}Pu	14.329(29)
	^{241}Am	432.6(6)

- Method in place
- Work in progress
- No method (yet)

Range of instrument designs

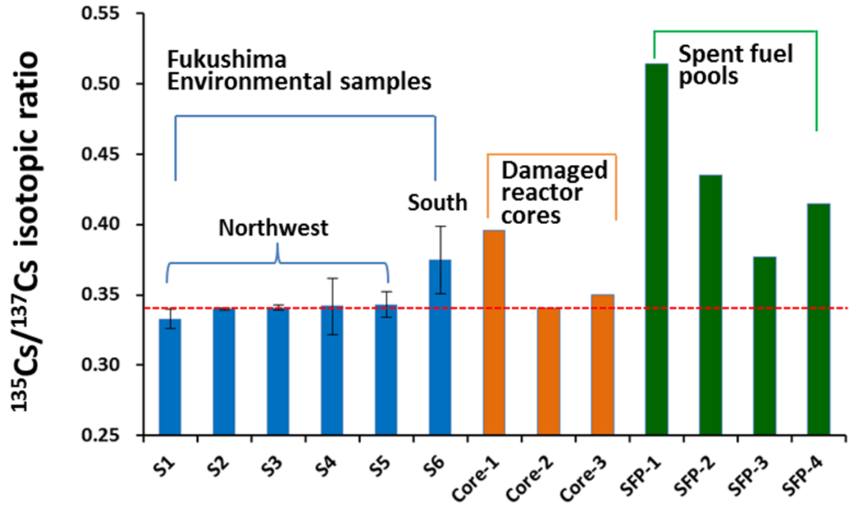
Sample introduction
Membrane desolvation
Online chemical separation (flow injection/sequential injection, capillary electrophoresis
Laser ablation
‘Cold’ plasma
Electrothermal vaporisation

Instrument design
Quadrupole ICP-MS
Tandem ICP-MS
Sector field ICP-MS
Multi-collector ICP-MS
Thermal ionisation MS
Secondary ionisation MS
Accelerator MS
Resonance ionisation MS
Time of flight MS

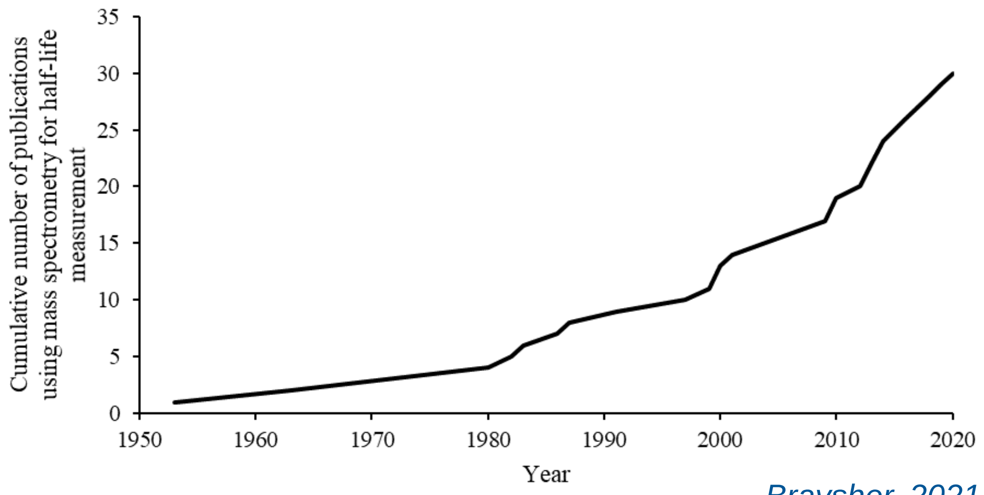
- Differences in sensitivity, isotope ratio precision, interference removal capability, mass bias…

The need for mass spectrometry reference materials

- Increasing application of mass spectrometry for radionuclide measurement
- Underpinning standards e.g. ISO TC147/SC3/WG14
- Expanded number of radionuclides measurable
- Opportunity for comparison with decay counting techniques and between mass spectrometer designs
- There is a need to develop and evolve standards and reference materials to reflect this



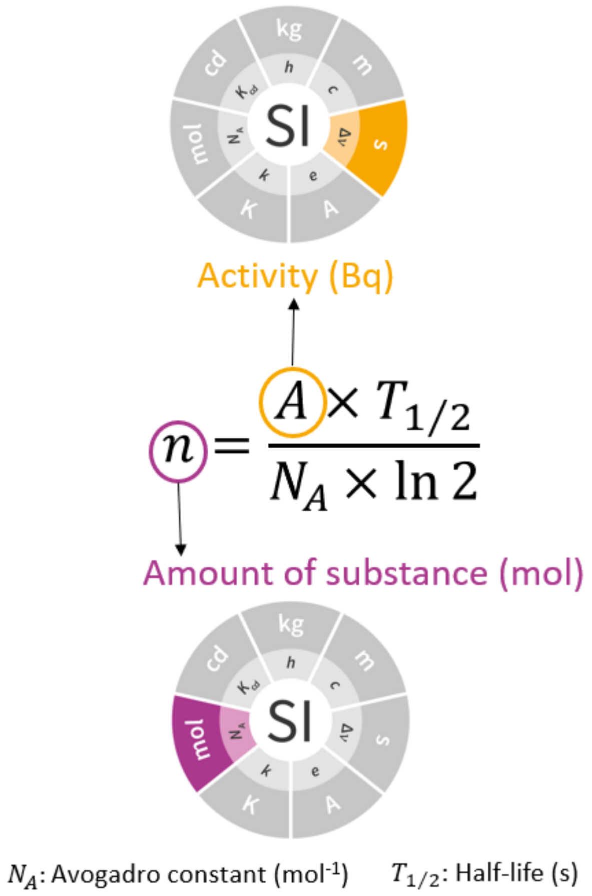
Zheng et al. 2015



Braysher, 2021

Mass spectrometry reference materials

- RM: '*material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process*'
- CRM: '*reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'
- There are mass spectrometry and radioactivity RM and CRM providers (CETAMA, JRC, NIST, PTB, NPL…)
- However, RMs for 'amount' and activity are rare



NMIs & Accredited CRM producers. Refs, *ISO 17034, ISO Guide 35*

Challenges for reference materials characterised for activity and mass

- What is being measured?
  - Activity concentration (Bq g^{-1})
  - Amount concentration
  - Isotopic ratios (e.g. $^{235}U/^{238}U$)
- Differences in interferences
  - Similar emission energies (e.g. $^{239}Pu+^{240}Pu$ by alpha spectrometry)
  - Isobaric, polyatomic and tailing
- Purity considerations
  - Contamination during preparation
  - Use of carriers and stable isotopes (may introduce interferences)
- Radionuclides of interest
  - Range in half-lives
  - Difference in activities and amount of material required
  - Current mass spec RM’s- stable elements, actinides

Next stages

- Existing materials

  Can these be measured to include mass spectrometry-relevant radionuclides?

- Resources available
  - Enriched and pure isotopes available
  - Can be measured for concentration and isotopic composition
- Future reference materials
  - Can be certified for decay counting and mass spectrometric
  - What radionuclides and materials are a priority?
  - Application area? Decommissioning, forensics, environmental…

Radionuclide	Characterisation
^{231}Pa (doi: 10.1007/s10967-019-06711-6)	Mass spectrometry (LLNL) Activity measurement (NIST, NRC, NPL)
^{233}U (https://doi.org/10.1016/j.talanta.2020.121638)	Titration (ORNL) Isotope dilution mass spectrometry (LLNL)
^{244}Pu (10.1007/s10967-020-07075-y)	Mass spectrometry (LLNL, LANL, CEA)

Summary

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- Mass spectrometry increasingly used for measurement of radionuclides
- Expands the number of radionuclides measurable compared to decay counting techniques alone
- Reference material development offers opportunities for:
  - Investigating links between decay counting and mass spectrometric techniques
  - Report on advantages and limitations of different instrument designs
  - Underpin methods that have demonstrated the increasing number of radionuclides measurable using mass spectrometry

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Thank you for your attention

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