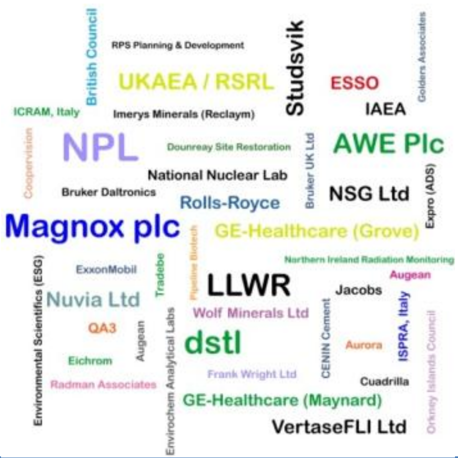
Rapid on-site screening of aqueous waste streams using dip stick technology and liquid scintillation counting

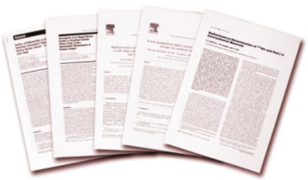
Phil Warwick
University of Southampton

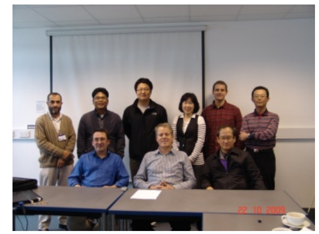
GAU-Radioanalytical

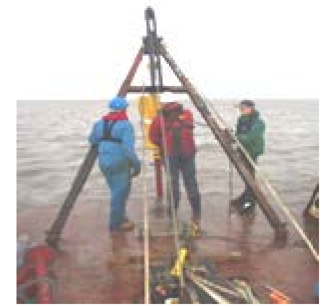
- Industry-focused laboratory formed in 1987 and employs 10 full time scientists
- Extensive radioanalytical and geochemical expertise
- Well equipped radioanalytical laboratories accredited to ISO17025:2005
- Undertakes approximately 300 commercial contracts (> 3000 samples) p.a.
- Comprehensive multi-nuclide radiometric and mass spectrometric capability



Role of the GAU







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

<u>Current research</u>:

Nuclear forensics

Lab automation

PRB technologies

Environmental geochem

Mass spectrometry

Bioassay

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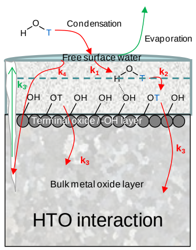
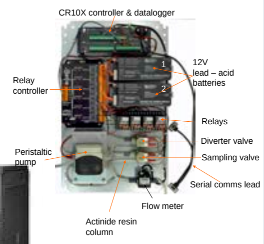
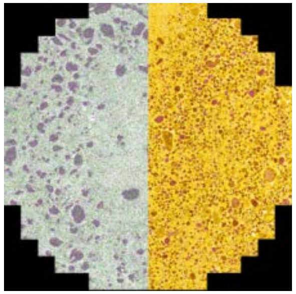
Research themes

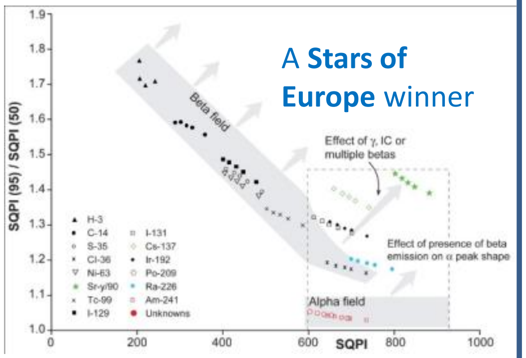
Waste characterisation / analysis





Nuclear Forensics / homeland security





A **Stars of Europe** winner

Remediation technologies

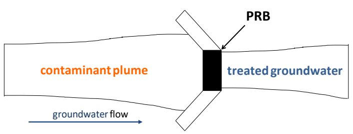
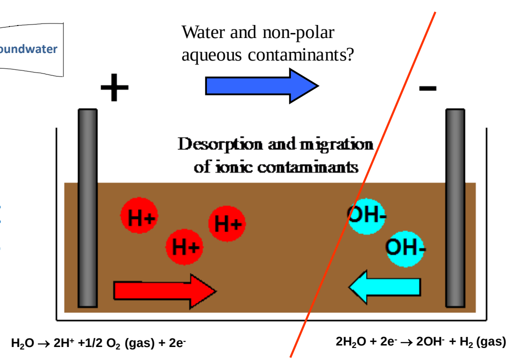


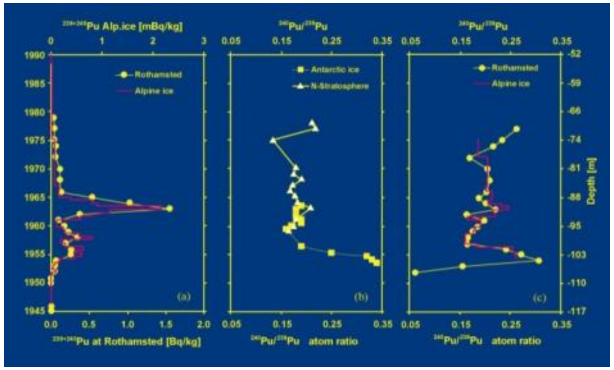
Fig. 2. Plan view of a Permeable Reactive Barrier.

FIRS project NERC KTP

1st prize to AWE



Environmental studies / isotopics



Need for screening techniques

Emergency

- Rapid screening to support / inform emergency response.

Routine

- Routine screening of DTM radionuclides to confirm absence in wastes.
- Confirmation of stability of radionuclide vector (fingerprint).
- Use in combination with more conventional characterisation methodologies.

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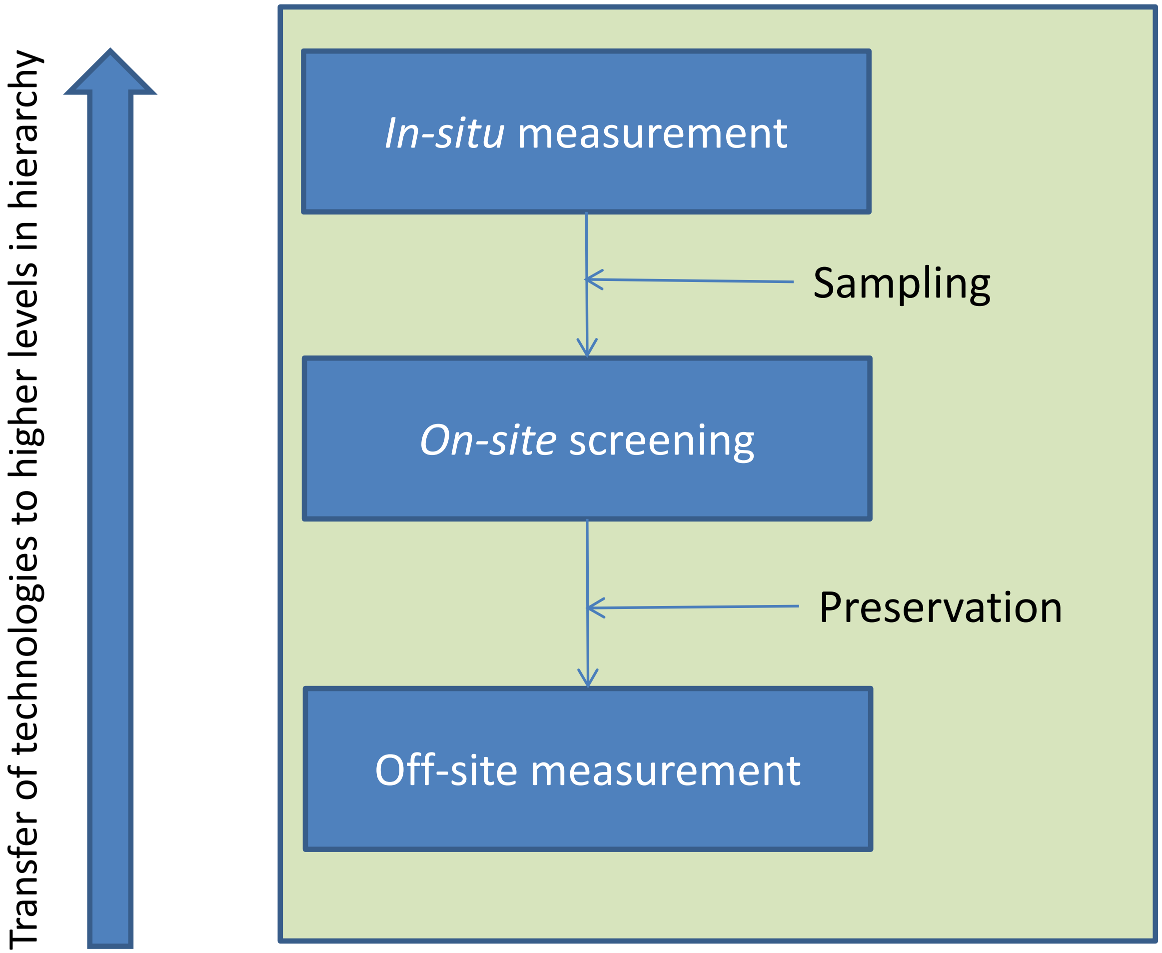
Strategy of research



Integration of characterisation approaches

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LSC 2017 COPENHAGEN

Aims

- To develop a rapid screening technique for radionuclides in aqueous wastes and acid digests.
- To develop supporting radionuclide detection hardware and identification / confirmation strategies.
- To demonstrate and validate these techniques for in-situ or on-site applications.

Target radionuclides (nuclear)

	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

Other target radionuclides

NORM

Natural radionuclides including ^{210}Pb and Ra isotopes

Why LSC?

- High beta efficiency – even for low energy beta.
- High alpha efficiency.
- Potential for alpha / beta discrimination.
- Spectral information.
- Well established and widely available technology.

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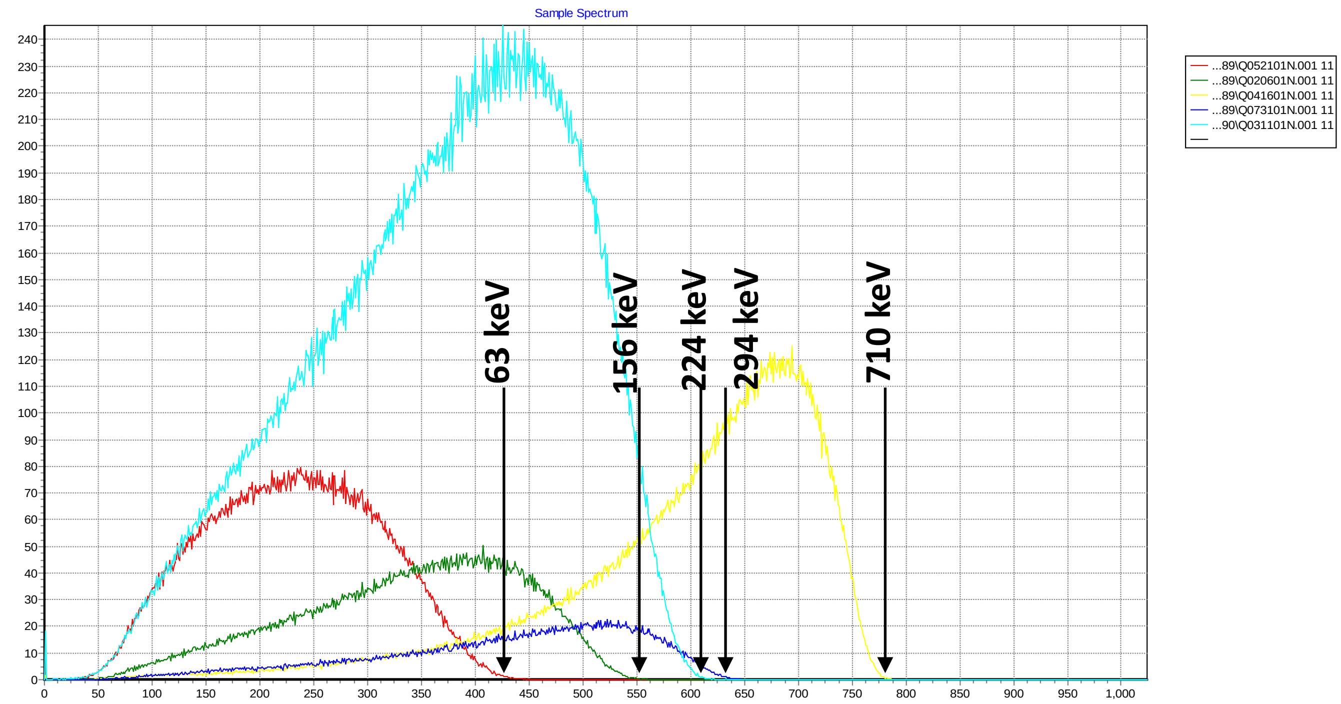
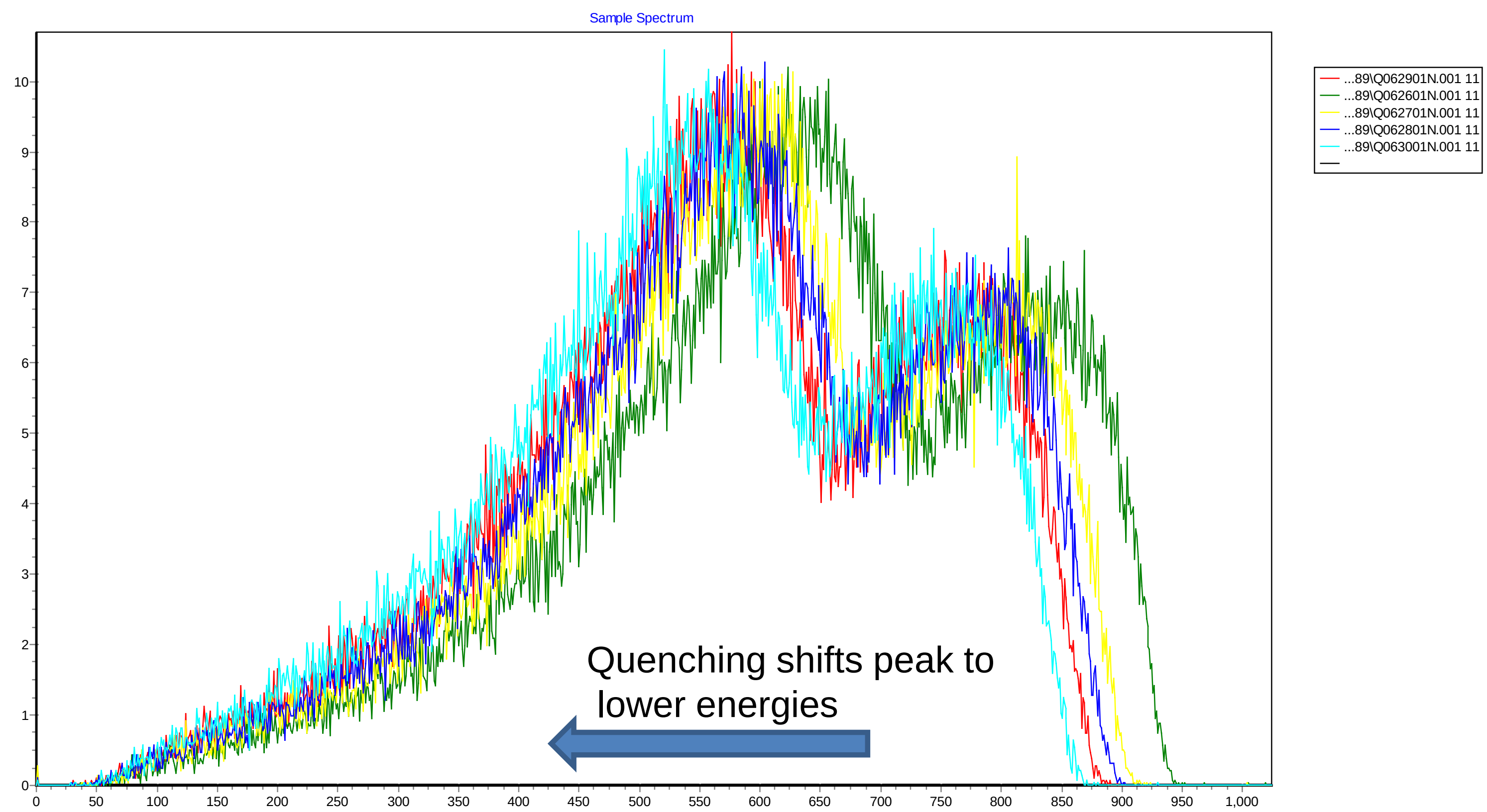
Radionuclide identification

Radionuclide identification by LSC



Liquid scintillation analysis provides spectral information that can be used to determine β energy.

Effect of quench on peak position



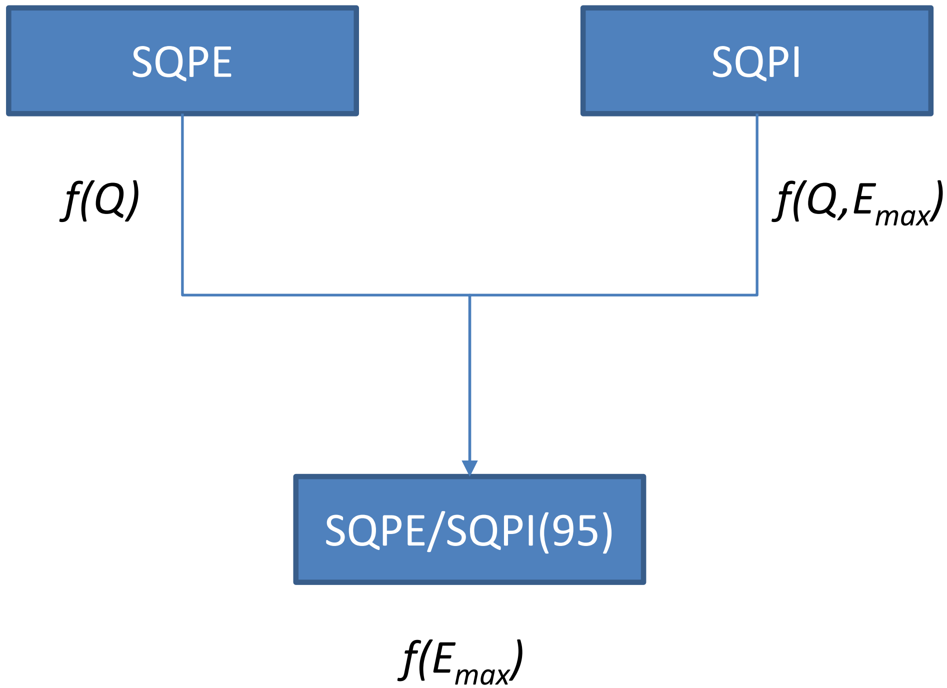
Problems with beta energy measurement

- **Peak position** is dependent on both the beta energy and quench level of the sample.

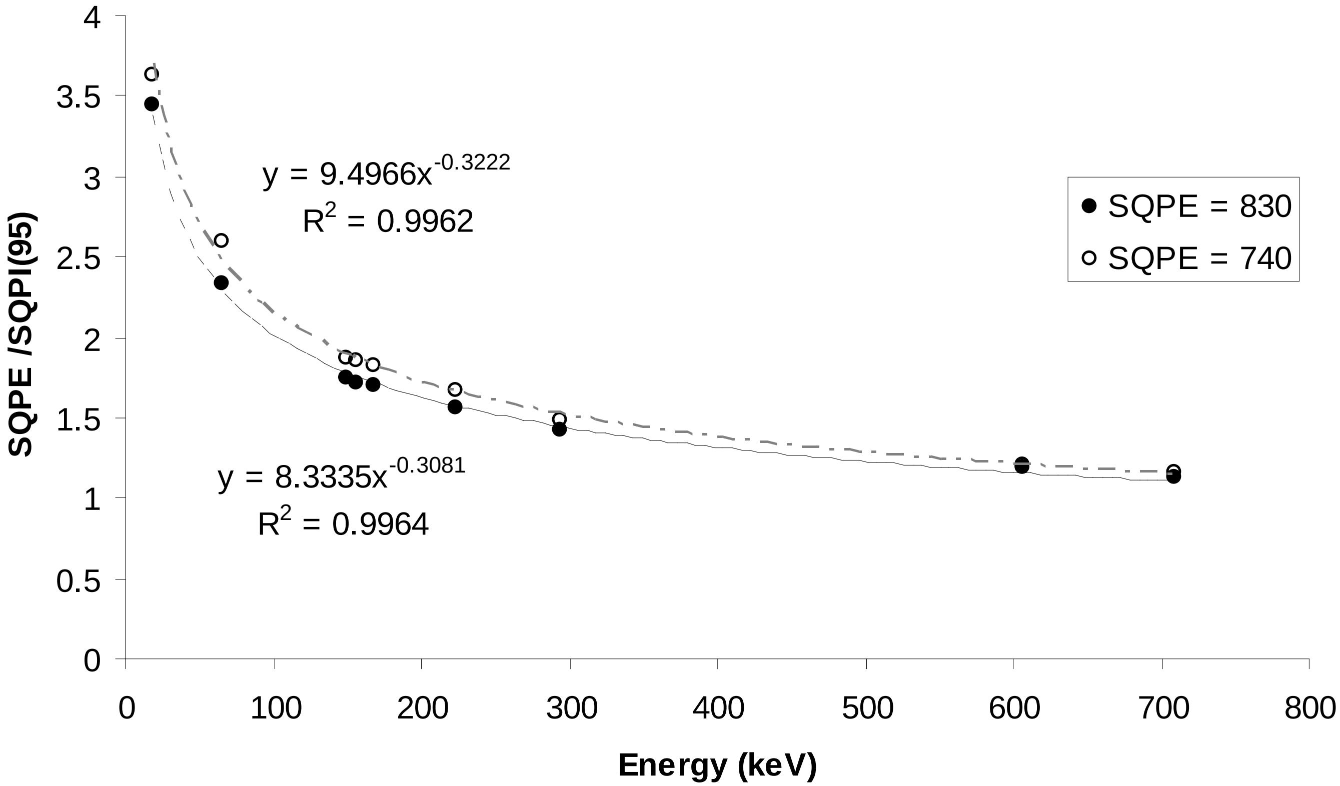
- Increases in quench will shift the beta spectrum to lower energies, reducing the apparent beta energy of the nuclide.

- To overcome this, the ratio of two quench parameters (SQPE & SQPI) are used to determine the beta energy.

Use of the dual quench parameter



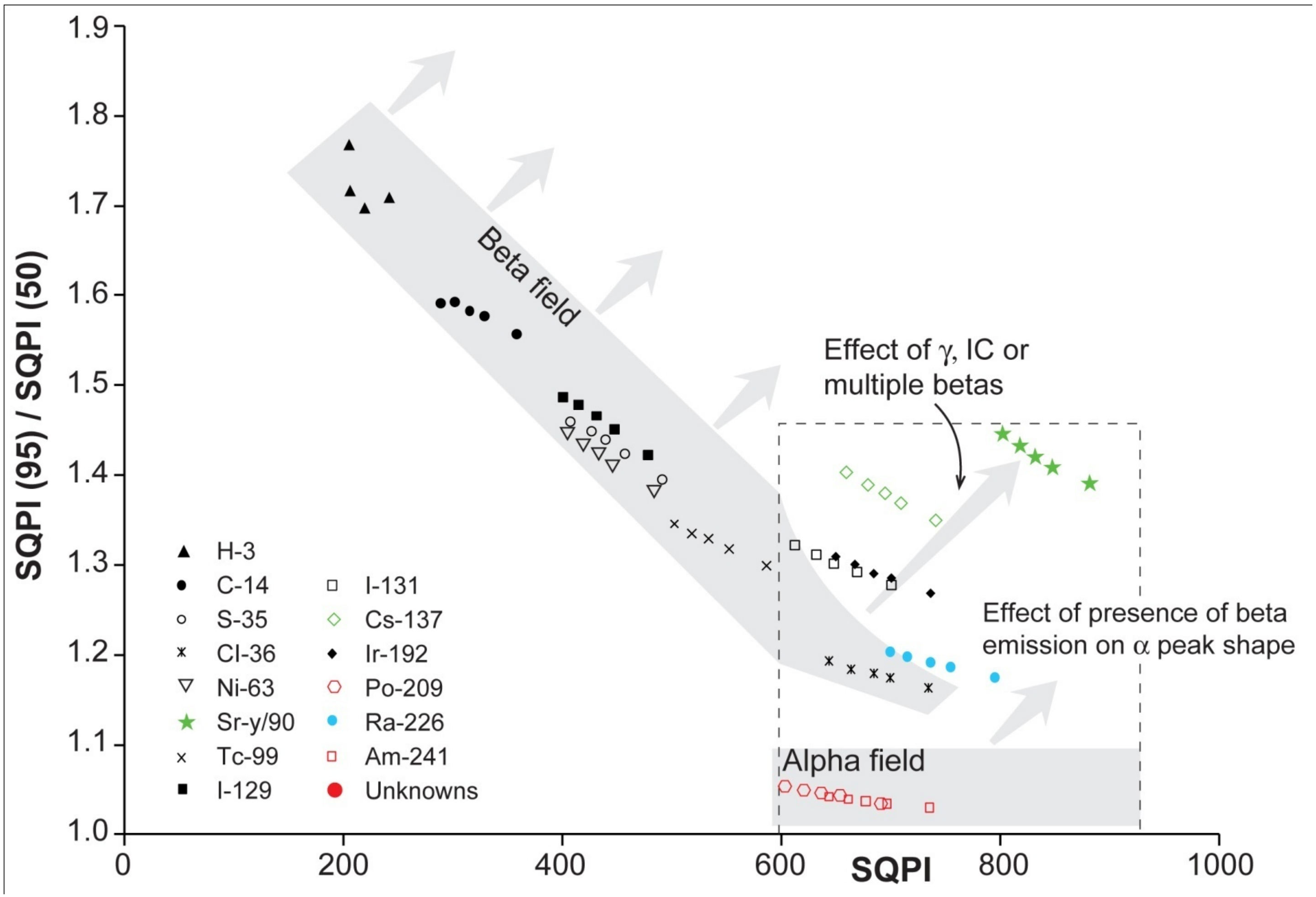
Dual quench parameter and energy



Peak shape analysis

- **LSC Quench Parameter models** works well for determining energies of pure beta emitting nuclides
- A refinement of the model for peak shape is needed to permit identification of alpha and beta/gamma emitting nuclides
- The peak shape is determined by adapting one of the quench parameters [SQPI(95)/SQPI(50)] to give a '**peak shape factor'**
- The **peak shape factor** is used in conjunction with a **quench parameters** to differentiate between alpha, low energy and high energy beta emitting radionuclides

Peak shape



SQPI (95) / SQPI (50)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0
200
400
600
800
1000
SQPI
Beta field
Effect of γ, IC or multiple betas
Effect of presence of beta emission on α peak shape
Alpha field
H-3
C-14
S-35
Cl-36
Ni-63
Sr-y/90
Tc-99
I-129
I-131
Cs-137
Ir-192
Po-209
Ra-226
Am-241
Unknowns

Testing the method

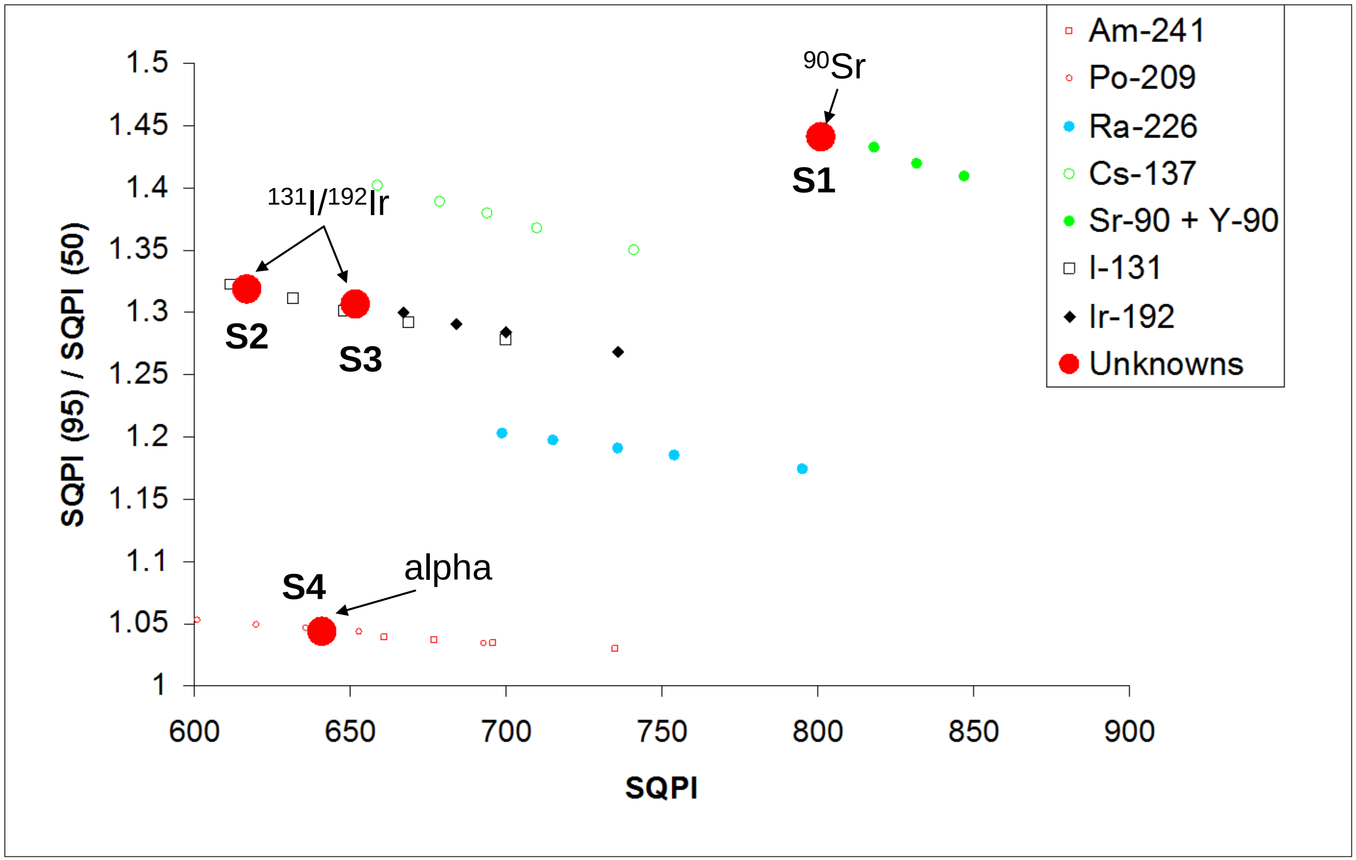
- Eight test water samples prepared using a mixture of alpha and beta emitting radionuclides.

- Four samples prepared at activity concentrations equivalent to the WHO drinking water action levels.

- Four samples prepared at activity concentrations equivalent to 10% of the action level.

- Samples for LSC prepared by mixing 8ml of test solution with 12ml Gold Star and counting for 60 minutes on a Quantulus liquid scintillation counter.

Radionuclide identification



SQPE/SQPI used to differentiate ^{131}I (β) and ^{192}Ir (β)

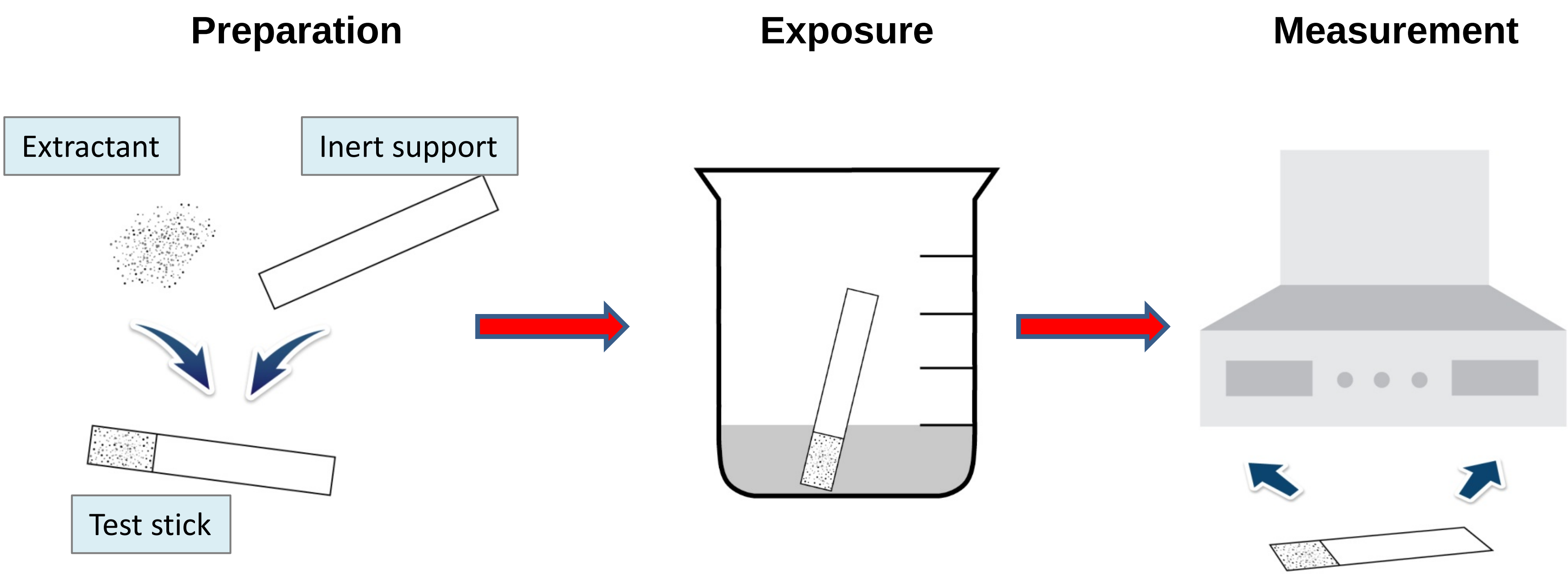
Sample 2 – 609 keV
- ^{131}I

Sample 3 - > 700 keV
- ^{192}Ir

**** Note correct position of S2, S3 & S4 due to a background correction ****

Development of test stick technologies

Concept



Quantitative extraction is not required

$$A_{stick} \propto A_{aq}$$

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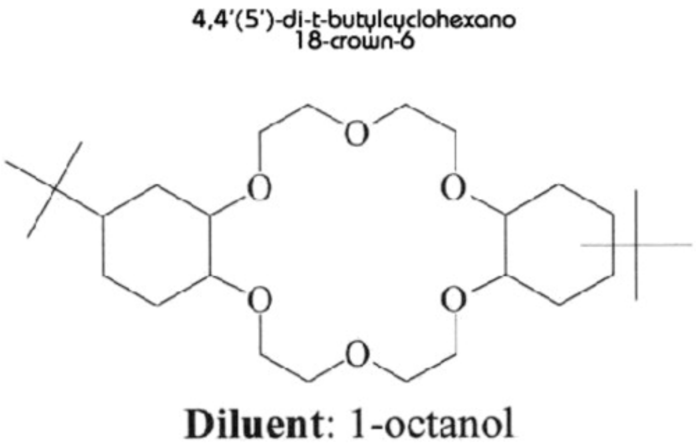
Extractant materials

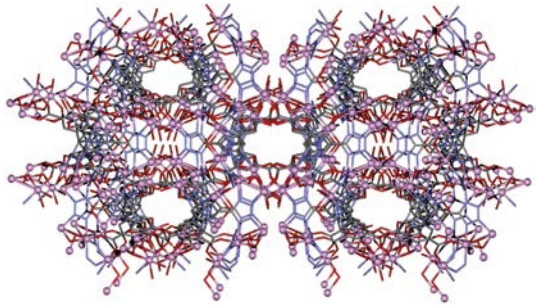
- **Commercially available**

  Sr-resin
  TRU-resin
  TEVA resin
  Actinide resin
  TK100 resins



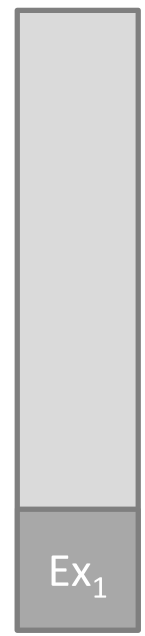
- **Designed**

  Metal organic frameworks (MOFs)
  Ion imprinted polymers (IIPs)
  Functionalised silicas
  Nano materials e.g.FeOOH, AuNP



Single extractant stick (SES)

- Test stick loaded with selective extractant.
- Extractant targets **<u>one</u>** radionuclide of interest.
- Total radionuclide activity measured on strip using either LSC or plate reader.
- Measured activity on stick is proportional to the activity of the target radionuclide in solution.

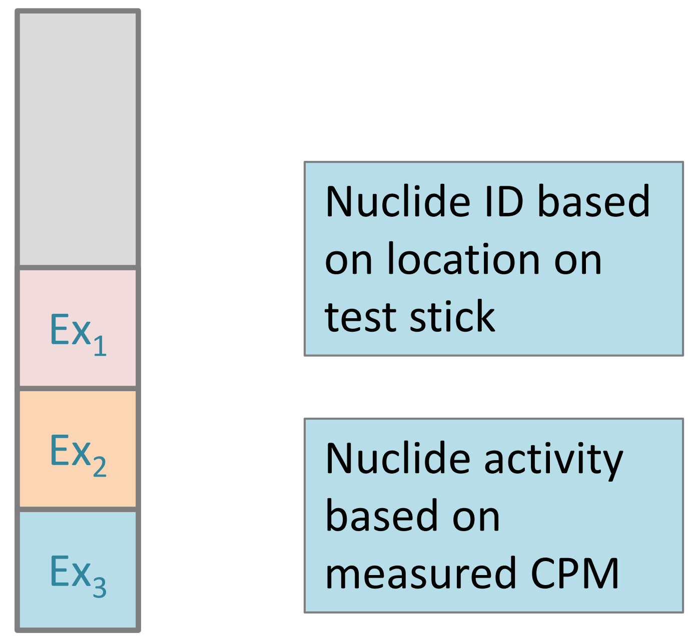


Nuclide ID based on extractant (EX_1) selectivity

Nuclide activity based on measured CPM

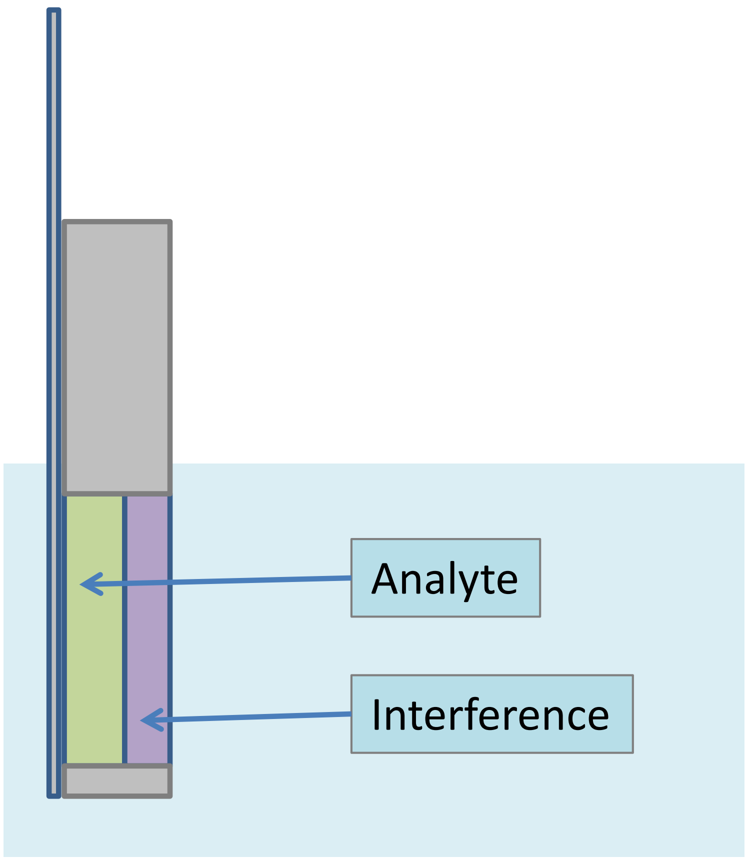
Multi-extractant stick (MES)

- Different extractants are distributed in regions of the test stick to detect **multiple** radionuclides.
- Each extractant targets a particular radionuclide.
- The activity on the stick is measured using a plate reader to provide activity and distribution information.
- The activity is proportional to the activity of each radionuclide in solution.
- The position of the activity on the test stick is diagnostic of the radionuclide.



Layered extractant stick (LES)

- The stick is layered with different extractant and designed so that the solution interacts separately with each extractant in turn as it diffuses through the multiple layers.
- The layers are then separated prior to measurement.
- This approach could be used to exclude a species from the final extractant to overcome potential interferences.



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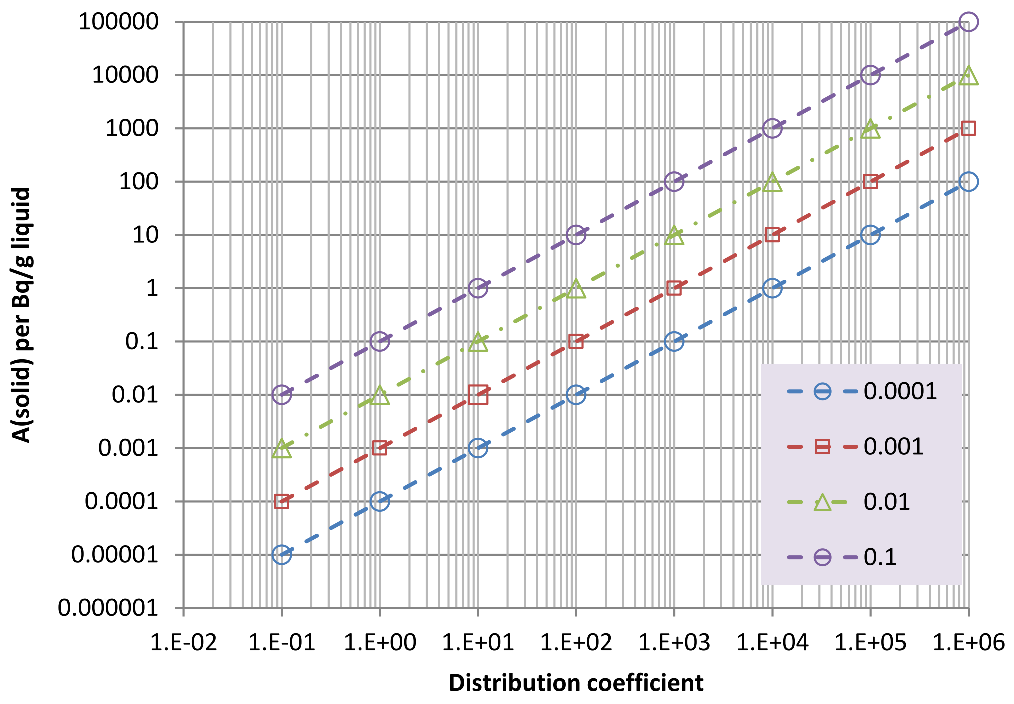
Uptake of radionuclide on test stick



Loading on stick (g)

Bq on strip per Bq/g in aqueous phase at equilibrium for a range of distribution coefficients

In practice

$$A_{stick} = f(A_{aq}, k_{D,} {}^{dk}/_{dt}, m_{s,} V_{eff}, t)$$

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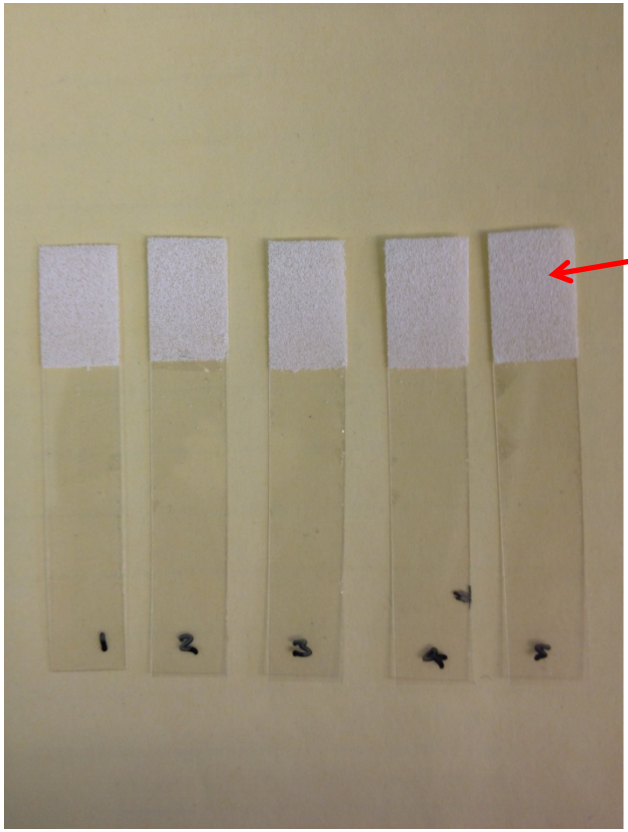
SES Sr-stick preparation



Sr resin – active area

Active area = 1 cm^2

Mass Sr resin + glue = 7 mg

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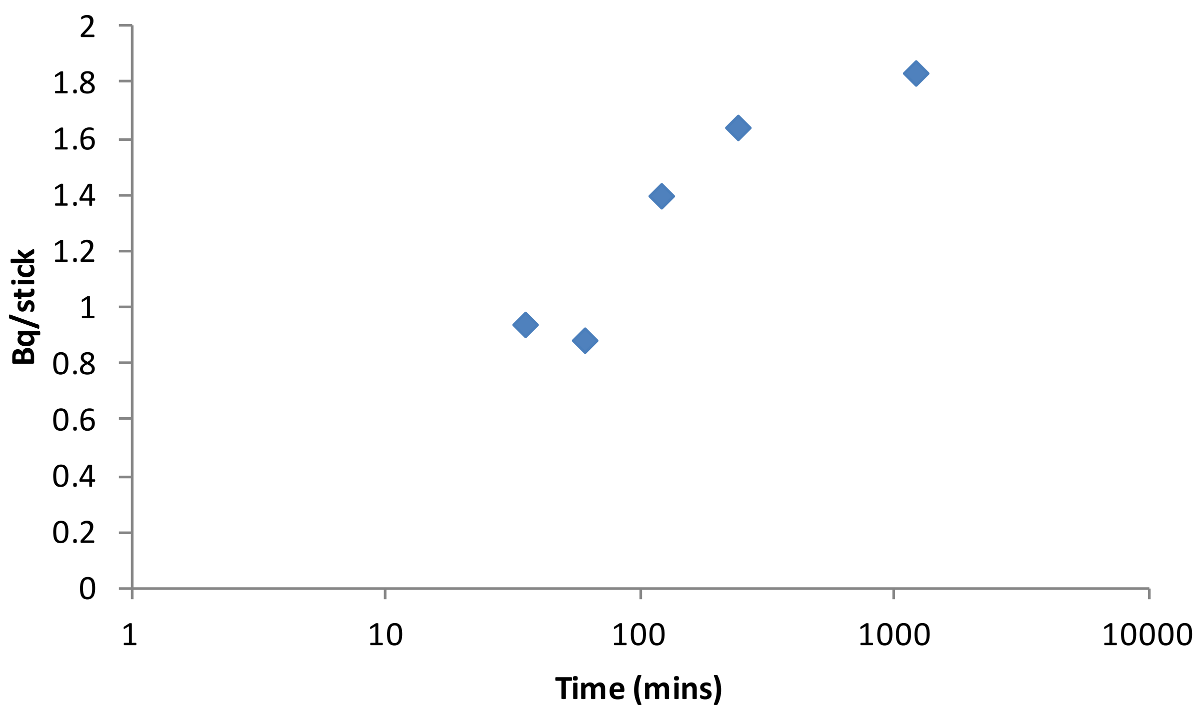
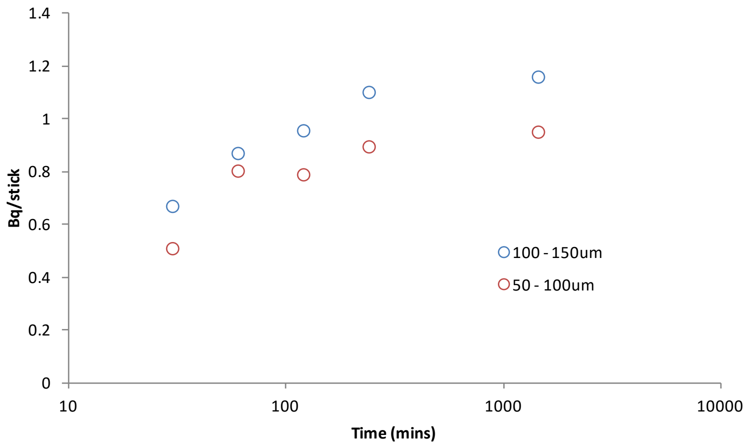
Rate of reaction

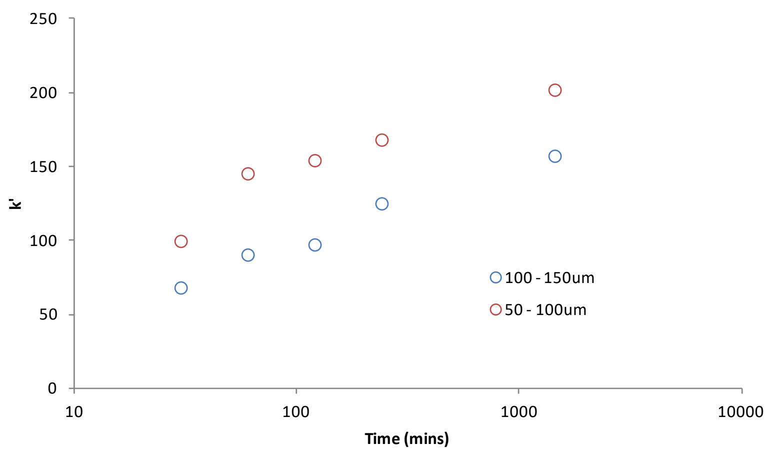


2.1 Bq/ml ^{90}Sr
5ml solution
Non-stirred

Effect of particle size



2.1 Bq/ml ^{90}Sr
5ml aqueous (8M HNO_3)
Non-stirred



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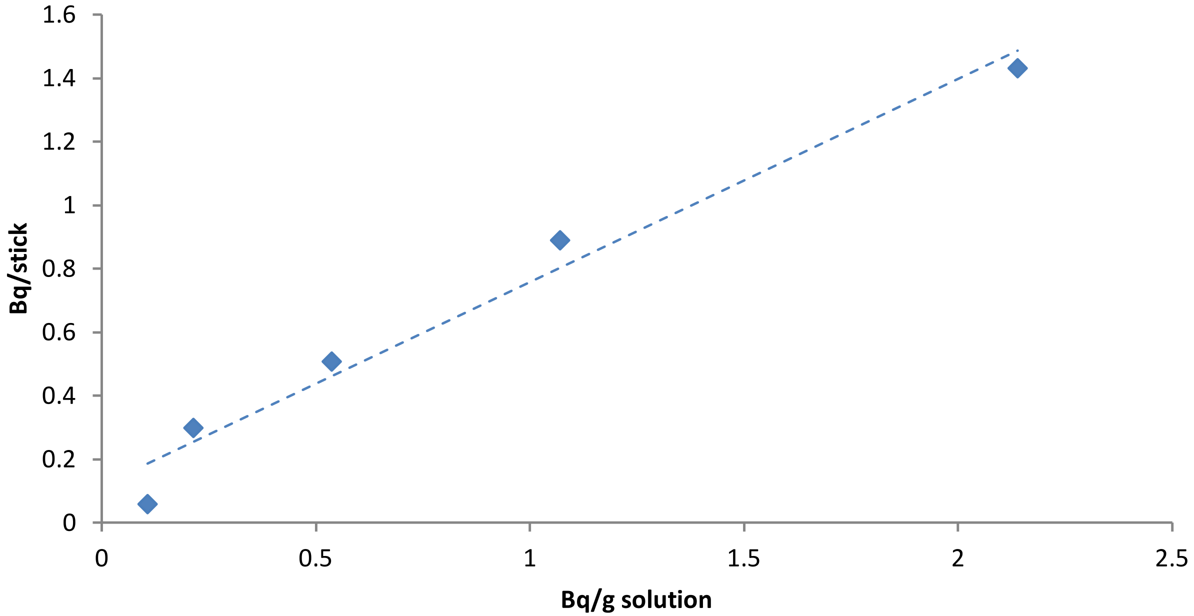
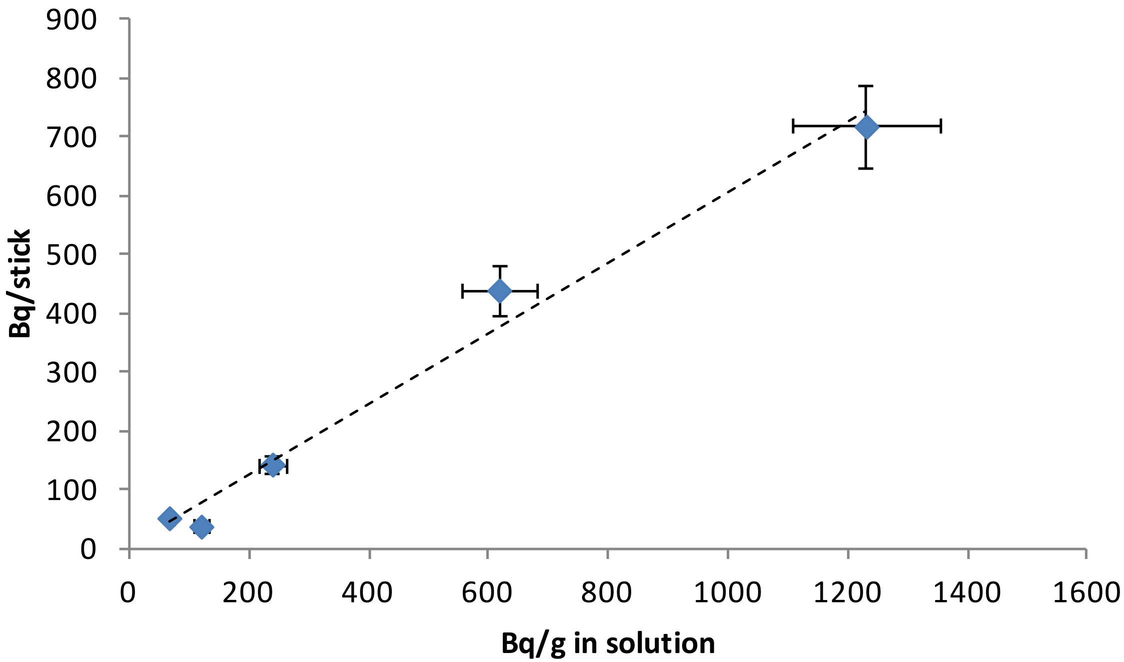
SES Sr-stick response



From 8M HNO_3

SES TEVA-stick response



Detection of ^{99}Tc from water @ pH 7

Equilibration time 300 mins

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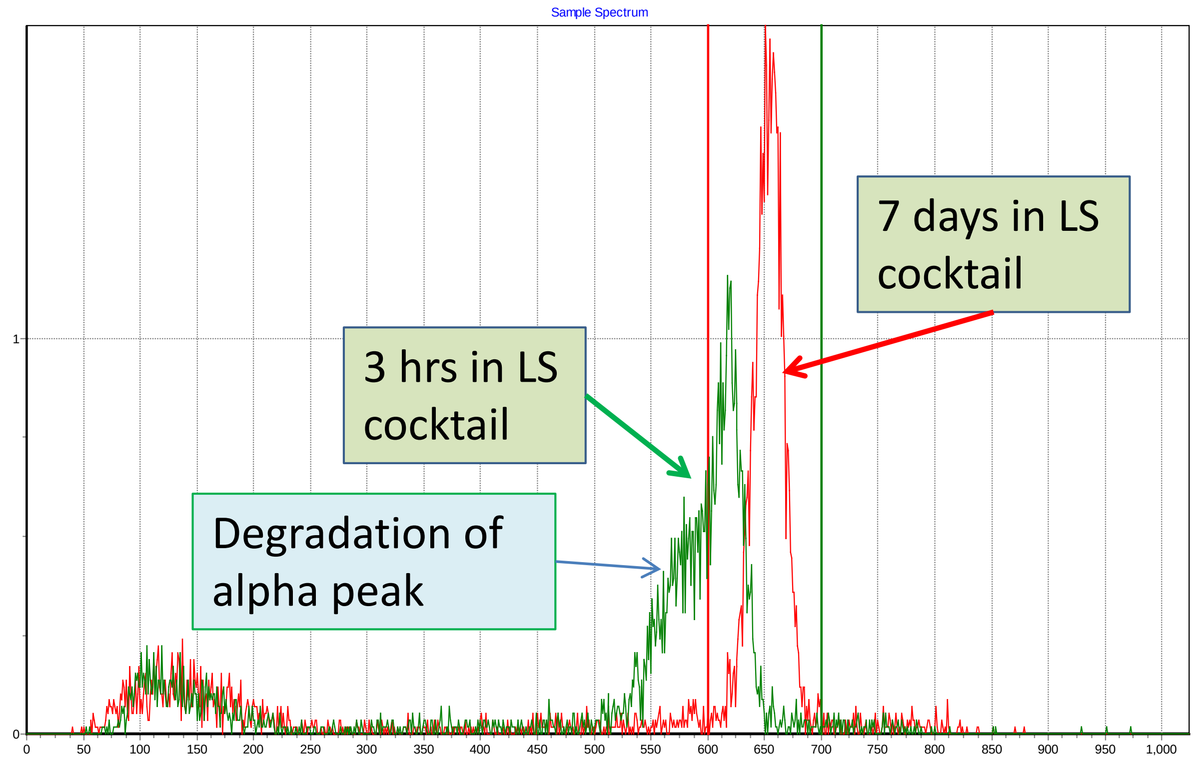
SES Ac-stick response

^{242}Pu solution activity = 2.5 Bq/g in 0.05M HNO_3



Degradation of alpha spectrum as ^{242}Pu is still entrained within resin.

After 7 days, the Pu+extractant has leached into the scintillation cocktail resulting in less alpha degradation

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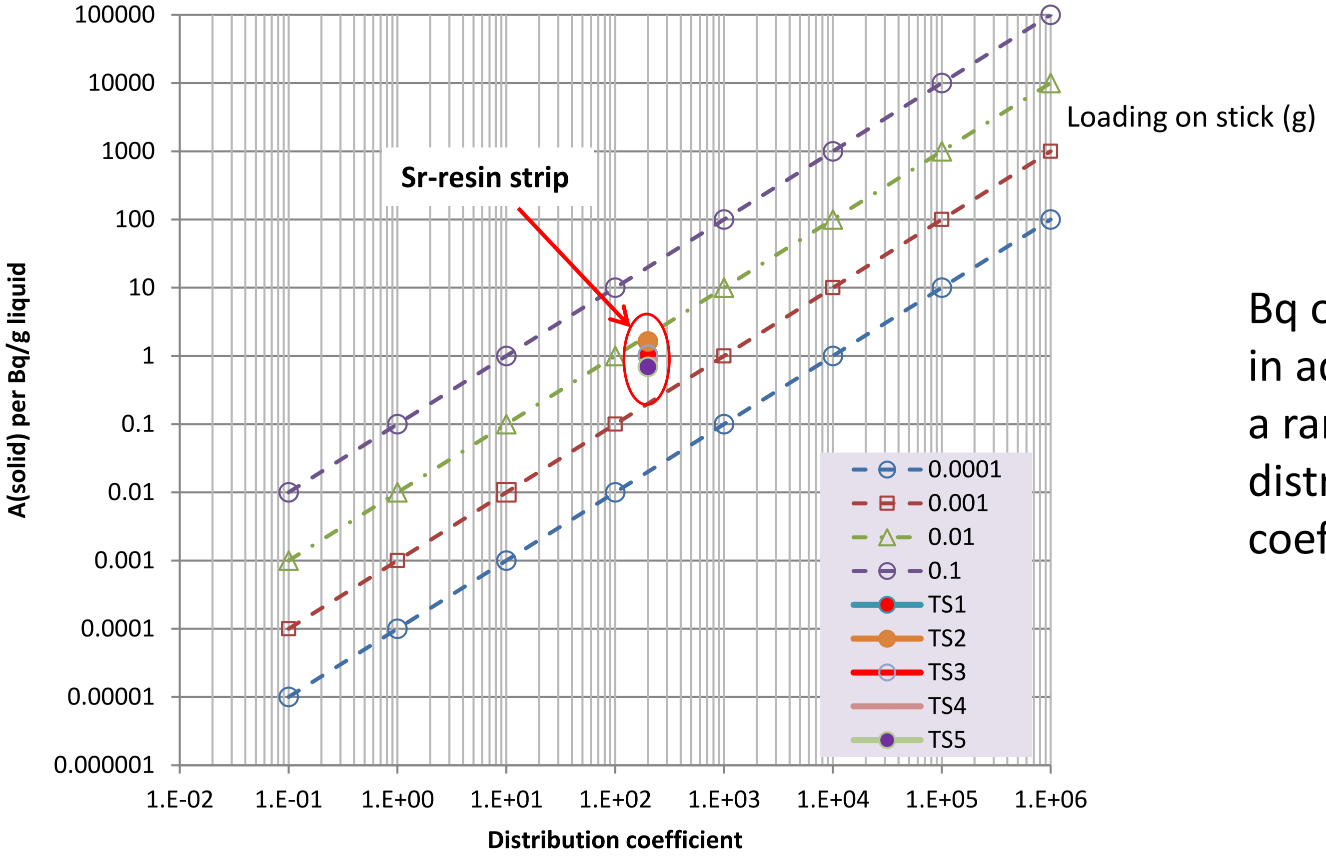
Uptake of radionuclide on test stick



Bq on strip per Bq/g in aqueous phase for a range of distribution coefficients

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Next stages

- Development of sample preparation procedures.
- Evaluation of extractant systems in terms of selectivity, sensitivity and uptake kinetics.
- Testing of multi extractant systems and spatial readers.
- Response over extended activity ranges.
- Modification of response by matrix elements.
- Development of integrated radionuclide identification.

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Acknowledgments

- NDA for funding a PhD relating to this work
- EU Framework 7 – ‘Secureau’.
- Triskem – for provision of many of the extractants being evaluated.
- LSC2017 committee for the invitation to present.

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DISCOVERY