Methodologies for determination of radionuclides in environmental or waste samples

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GAU-Radioanalytical
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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

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

GAU Radioanalytical Laboratories
National Oceanography Centre, Southampton
Why is radioanalytical science important?

- Actinide / heavy element chemistry
- Medical radionuclides
- Radiation metrology
- Radioecology
- Environmental process studies
- Radiotracer studies
- Nuclear fission
- Nuclear fusion
- Contaminated land clearance
- Environmental monitoring
- Waste characterisation
- Nuclear forensics
- Homeland security
The changing analytical landscape

**OPERATIONAL**
- Radiological protection
- Process control
- Environmental monitoring
- Routine waste sentencing

**DECOMMISSIONING**
- Waste exemption
- Waste stream fingerprinting
- Waste characterisation of unusual matrices
- Land remediation

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© Magnox sites
More challenging matrices

- Heterogeneous soft wastes
- Construction materials (metals / concretes)
- Ion exchange resins / desiccants
- ‘Sludges’ (highly variable composition)
- Oils
Changes in analytical requirements

- Historically, analytical schedules have focussed on activation and fission products which dominate the fingerprint in terms of activity and pose the greatest radiological risk e.g.:

$^{60}\text{Co}$

$^{90}\text{Sr, }^{137}\text{Cs}$

$^{239+240}\text{Pu, }^{241}\text{Am}$
Changes in analytical requirements

$^{41}\text{Ca}$ (1.03 x $10^5$ y – irradiation of bioshield concrete)

$^{79}\text{Se}$ (6 x $10^5$ y – fission product)

$^{93}\text{Zr}$ (1.5 x $10^6$ y – fission + activation product)

$^{113m}\text{Cd}$ (14 y – irradiation of Cd metal)

$^{151}\text{Sm}$ (90 y – fission product)
Factors impacting analytical quality

- Highly trained & experienced staff
- Use of validated procedures
- Robust QA / QC systems
- Suitably calibrated instrumentation
Key stages in analysis

- Sample collection / storage
  - Homogenisation / sub-sampling
  - Solubilisation / liberation of analyte
  - Separation / purification of analyte
  - Quantification of analyte
  - Clear / accurate reporting of data

Knowledge of analyte distribution & association with matrix
Knowledge of potential interferences
Suitable calibration standards
Method validation

Experienced / trained staff
Validated procedures

Use of validated procedures
Sample collection

Loss of $^3$H during sample collection / storage
Sampling

Use of validated procedures
Radionuclide association with matrix

Speciation of $^3$H in reactor bioshield concrete

Potentially impacts on sampling, storage and analysis procedures
Leaching of $^{241}$Am from ‘debris’

Use of validated procedures
Borate fusion

Fusion of soils / marine sediments

D.A.R. – Double aqua regia digest
F / Pyro – fluoride / pyrosulphate fusion
Fusion – borate fusion

Fusion of Actinide resin for actinide in water extraction

Proportion of U extracted with time
(0.1 g of Actinide resin in 100ml of 0.8M HNO₃ with stirring)
Instrument calibration

• Traceable standard solutions do not exist for some of the radionuclides now being requested.

• For liquid scintillation analysis, proxy radionuclides are often used which is not ideal.
Use of proxy radionuclides for LSC calibration
CN2003 calibration of $^{41}\text{Ca}$ & $^{45}\text{Ca}$

- $^{41}\text{Ca}$ (EC)
  - Measured
  - Predicted

- $^{45}\text{Ca}$ ($\beta^-, E_{\text{max}} 257\text{keV, allowed}$)
  - Measured
  - Predicted

Suitably calibrated instrumentation
$y = 0.0709x^2 - 0.6274x + 97.353$

$R^2 = 0.9999$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gamma spec.</th>
<th>LSC</th>
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<tbody>
<tr>
<td>Sample A</td>
<td>8.7 ± 1.6</td>
<td>12.0 ± 0.8</td>
</tr>
<tr>
<td>Sample B</td>
<td>8.6 ± 1.4</td>
<td>11.2 ± 0.8</td>
</tr>
</tbody>
</table>

**Gamma emission probabilities**
(collaboration with PTB)

- Published: 0.023
- Revised: 0.01839

Beta nuclide identification

Suitably calibrated instrumentation
Beta nuclide identification

Effect of γ, IC or multiple betas
Effect of presence of beta emission on α peak shape

GAU Radioanalytical Laboratories
National Oceanography Centre, Southampton
UNIVERSITY OF SOUTHAMPTON
Mass spectrometry – U isotopes

Warneke et al. (2002). EPSL, 203, 1047 - 1057
Mass spectrometry – $^{135}$Cs

<table>
<thead>
<tr>
<th>Instrumental setup</th>
<th>Counts per ng/L</th>
<th>LOD (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aridus II + X-skimmer cone + JET interface (turbo pump and sample cone)</td>
<td>21 000 ± 80</td>
<td>0.03</td>
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<tr>
<td>Aridus II + X-skimmer cone</td>
<td>5 000 ± 30</td>
<td>0.08</td>
</tr>
<tr>
<td>Aridus II</td>
<td>2 500 ± 2</td>
<td>0.15</td>
</tr>
<tr>
<td>Standard</td>
<td>700 ± 10</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Repeat measurement of $^{135}$Cs

Comparing gamma spec and ICP-MS measurement of $^{137}$Cs

- Final Ba concentration determines accuracy and LOD
- Applications for $^{135}$Cs/$^{137}$Cs include:
  - Arctic Ocean water samples
  - Salt marsh sediment core

Preliminary $^{137}$Cs results (Bq/m$^3$)
Other applications

$^{55}\text{Mn} (p,n) ^{55}\text{Fe}$

Comparison of iron uptake in surface waters in the hypothesised iron depleted “South” and iron replete (because of the Crozet Isles) “Central” sites

Zubkov et al (2007)
Deep Sea Res. II, 54, 2126 - 2137
Reference materials

• Reference materials are required for method validation and ongoing quality control purposes.

• Reference standards are required that more closely reflect the matrices and contaminant form encountered in decommissioning samples.

  ▪ Range of matrices
  ▪ Analyte present in form comparable with real samples
  ▪ Range of certified analytes to reflect nuclides encountered
  ▪ Presence of contaminants comparable to those found operationally.
Method validation

Sample type

Exposure history

Interfering radionuclides

Test sample

Accuracy

Precision

Decon. Factors

Robustness

Matrix interferences
Summary

• Decommissioning analysis has resulted in new challenges for the radiochemical laboratory.

• High quality analysis relies on a good understanding of the distribution and association of the analyte with the matrix.

• Careful consideration must be given to instrument calibration, particularly for less common radionuclides.

• There is a clear requirement for more representative matrix-matched standards for method validation and quality control. However, alternative approaches to method validation are also required.
Acknowledgements

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• Nicola Holland (CN2003 studies)
• Mike Zubkov \((^{55}\text{Fe} \text{ tracer studies})\)