Recent Challenges in Processing Legacy Tritiated Materials

Dr Rachel Wilson
Rachel.Wilson@AWE.co.uk

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Our Team – Scope

Tritium Technology
Dario Castiglione – Team Leader Tritium Technology

Gemma Allen (Sci)
Tom Holmes (FLW)
Josh Mancey (Tech)
Tony Provenzano (Sci)
Victoria Stanbridge (FLW)

Chris Farmer (FLW)
Chris Knott (Sci)
Malcolm Pizey (Tech)
Damaris Roffey (Sci)
Rachel Wilson (Sci)

Tritium Accountancy
- Material management
- Regulatory compliance
- Capability demonstration
- Capability maintenance
- CASD

Legacy Management
- Material management
- Regulatory compliance
- Tritium Recovery
- Tritium assay
- Waste sentencing
- New process development

Tritium Analysis
- Regulatory compliance
- HP support
- Tritium assay
- Waste sentencing
- New process development
Tritium at AWE

- Purpose built facility
- Undertakes work on tritium programmes in support of Continuous At Sea Deterrence (CASD)

- Key Design Features
  - Distributed Control System to monitor plant condition
  - Tritium monitoring of workspace, containments and discharges
  - Computer controlled process lines
  - HVAC system
  - Inert gas gloveboxes
  - Gas Clean Up Plant

Also houses legacy tritium items from other facilities
Tritiated Molecular Sieve
Various containers holding gram to kg quantities:

- 5 x Stainless steel tubes containing samples. 20 TBq (540 Ci) estimated based on maximum theoretical capacity.

- Detached vessel from a process line to dry process gas. 298 TBq (8 kCi) estimated based on maximum theoretical capacity.

- 4 x Driers for argon gloveboxes (1 nominally empty). Samples of sieve measured in 2008 on old calorimeters: < 11 TBq (297 Ci) each.
Removal from glovebox

- Glovebox has a history of particulate contamination.
- Area and items cleaned down with tack-rags.
- Items brought out via transfer tunnel into integral fume cupboard onto sticky mat.
- Initial off-gassing rate checked using installed monitor.
Fume Cupboard Activity

\[ \approx 10 \text{ MBq/m}^3 \]
(270 \text{ µCi/m}^3)

Argon plant driers

Tubes & detached vessel

Graph showing activity levels from 11:00 AM to 6:00 PM on 5/9/2018 and 5/9/2019.
Off-gassing Assessment

- Items placed into containers & sealed for 24 hours.
- Atmosphere measured using portable tritium monitor.
- Wrapped in PVC and transferred to calorimeter for assay.
  - Unable to transfer in blue cans due to size of some items.
- Tubes and detached vessel batch assayed, then split and re-assayed to determine activity distribution.
Tritium Assay

- Twin-cell heat flow calorimeters (Antech)
- Measurement range 0.5 mW – 5 W
  (~0.55 TBq – 5500 TBq = 15 Ci – 150 kCi)
Issues Encountered

- Unopened container within glovebox:
  - Had been X-rayed in the past – contained two molecular sieve tubes.
  - Did not open easily, released several GBq (~0.05 Ci) into glovebox when opened.
  - Revealed glovebox activity alarm system was configured differently.
  - Issue was quickly rectified & prompted checks on other gloveboxes.
  - Friable packing material remains which still contains a significant tritium hold-up & will be difficult to handle.
Issues Encountered

- Some items required calorimetry ‘bare’.
  - Wrapped in PVC to contain surface contamination.

- Continual off-gassing caused build-up in calorimeter chamber.
  - Released into room when opened & sounded room activity alarm.

- Health Physics advice note was issued and permission granted for operators to open lid, then vacate room until levels dropped before continuing.

- Once work complete, lids left open for several days to clear chambers.
  - Inside surfaces did not require decontamination.
Calorimeter Room Activity

Argon plant drier removed (HF2) & placed onto trolley in room.

Calorimeter lid (HF1) opened

Argon plant drier removed

Activity 'alert' level (0.12 MBq/m³ = 3.24 µCi)
## Assay Results

<table>
<thead>
<tr>
<th>Item Description</th>
<th>S/N</th>
<th>Activity</th>
<th>$^3$H mass</th>
<th>Off-gassing after 24 + hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MBq/m$^3$</td>
</tr>
<tr>
<td>Argon plant drier F(i)</td>
<td>F(i)</td>
<td>&lt; 550 GBq (&lt; 14.8 Ci)</td>
<td>&lt; 0.0015 g</td>
<td>11</td>
</tr>
<tr>
<td>Argon plant drier F(ii)</td>
<td>F(ii)</td>
<td>&lt; 550 GBq (&lt; 14.8 Ci)</td>
<td>&lt; 0.0015 g</td>
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<tr>
<td>Argon plant drier F(iii)</td>
<td>F(iii)</td>
<td>&lt; 550 GBq (&lt; 14.8 Ci)</td>
<td>&lt; 0.0015 g</td>
<td>9</td>
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<tr>
<td>Argon plant drier F(iv)</td>
<td>F(iv)</td>
<td>&lt; 550 GBq (&lt; 14.8 Ci)</td>
<td>&lt; 0.0015 g</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Mol. Sieve tubes A(1)</td>
<td>A(1)</td>
<td>0.36 TBq (9.7 Ci)</td>
<td>0.0008 g</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Mol. Sieve tubes A(2)</td>
<td>A(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Sieve tubes A(3)</td>
<td>A(3)</td>
<td>0.56 TBq (15.1 Ci)</td>
<td>0.0016 g</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Mol. Sieve tubes E(1)</td>
<td>E(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Sieve tubes E(2)</td>
<td>E(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detached vessel</td>
<td>-</td>
<td>0.92 TBq (24.8 Ci)</td>
<td>0.0026 g</td>
<td>&lt; 50</td>
</tr>
</tbody>
</table>

- All items below accountable levels.
- 99% reduction from estimated inventory.
Lithium deutero tritide (LiDT)
LiDT Material

- Origin unclear, may have been prepared for trials in 1980s but not used.
- Contained within glass Kilner jars, which were subsequently transferred into ASC032 containers at a later date.
- Transferred to current facility for long term glovebox storage.
- Reports suggest the LiDT is in the form of pressed pellets.
- Material not been inspected visually for a number of years.
- Estimated 0.25g tritium remaining.
Removal from glovebox

- Containers brought out via transfer tunnel into integral fume cupboard.
- Initial off-gassing rate checked using installed monitor.
Off-gassing Assessment

- Containers placed into secondary containers & sealed for 24 hours.
- Atmosphere measured using portable tritium monitor.
- Varying levels of off-gassing found:
  - \(< 5 \text{ MBq/m}^3 (< 0.13 \text{ mCi})\): transferred to calorimeter ‘bare’.
  - Between 5 \& 50 \text{ MBq/m}^3 (0.1 – 1.4 mCi): transferred to calorimeter in secondary container.
  - 3 x containers were 2 - 300 \text{ MBq/m}^3 (0.05 mCi – 8.1 mCi): not transferred & returned to glovebox for further investigation.
High off-gassing Investigation

- Survey with portable monitor showed higher activity levels around lid face and bolts.
  - Believed to be damaged or leaking O-ring seals.
- Containers opened inside glovebox.
  - \(~16 \text{ GBq/m}^3 (0.4 \text{ Ci})\) released from one container (exceeded glovebox ‘alert’ level).
  - O-rings found to be brittle and damaged. New O-rings fitted.
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<tr>
<td></td>
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<td>MBq/m$^3$</td>
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<tr>
<td>13324</td>
<td>$&lt; 550$ GBq (&lt;14.8 Ci)</td>
<td>$&lt; 0.0015$ g</td>
<td>$&lt; 1$</td>
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<tr>
<td>13323</td>
<td>$&lt; 550$ GBq (&lt;14.8 Ci)</td>
<td>$&lt; 0.0015$ g</td>
<td>$&lt; 1$</td>
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<tr>
<td>13327</td>
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<tr>
<td>13325</td>
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<td>$&lt; 0.0015$ g</td>
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</tr>
<tr>
<td>13329</td>
<td>$&lt; 550$ GBq (&lt;14.8 Ci)</td>
<td>$&lt; 0.0015$ g</td>
<td>9</td>
</tr>
<tr>
<td>13321</td>
<td>6.39 TBq (173 Ci)</td>
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<td>$&lt; 1$</td>
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<tr>
<td>13322</td>
<td>0.91 TBq (25 Ci)</td>
<td>0.003 g</td>
<td>$&lt; 1$</td>
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<tr>
<td>13328</td>
<td>4.94 TBq (134 Ci)</td>
<td>0.014 g</td>
<td>$&lt; 1$</td>
</tr>
</tbody>
</table>

- **2 items** above accountable levels.
Recovery of Tritium from LiDT material

- May be required to recover tritium from LiDT to be captured for disposal.
- Previous recovery methods have been considered (wet/dry chemistry processes and thermal processes).
  - May be unsuitable due to safety/hazards and disposal issues.

**Metal Fusion Technique**

- A method based on thermal desorption, using vacuum fusion or inert gas fusion technique was previously recommended for recovery of tritium from LiDT.
Metal Fusion Technique

- Used to determine quantities of gases in metals and inorganic compounds.

- Involves heating LiDT in a ‘bath’ of molten metal in a vacuum or inert gas, forming an alloy & evolution of gases contained within the metal/inorganic compound.

- CuO catalyst converts evolved tritium to water, which is collected & weighed.

- Inert gas fusion is similar, except that it is carried out at ambient pressure using an inert carrier gas flow.

\[
\text{LiDT}_{(l)} \xrightarrow{850 \text{ °C}} \text{Li}_{(s)} + D_{(g)} + T_{(g)}
\]

\[
\text{LiDT}_{(l)} + \text{Sn}_{(l)} \xrightarrow{300 - 500 \text{ °C}} \text{Li/Sn}_{(s)} + D_{(g)} + T_{(g)}
\]

Gases can be collected on a uranium bed or oxidised to water.

Questions?
Potential Experimental Set-up

1. Glass vessel containing LiDT/Sn mix inserted into heating furnace

2. Connected to flowing argon supply – pre-heated & scrubbed

3. Hydrogen isotopes are evolved and enter drying column containing Mg(ClO₄)₂

4. Isotopes pass through catalyst. Evolved tritium oxidised to tritiated water

5. Tritiated water vapour passes into vessel with moisture absorber

6. Vessel containing water is closed and weighed to calculate mass of water produced