Application of Thermal Desorption Techniques to the Characterisation of Nuclear Decommissioning Wastes

Ian Croudace
Phil Warwick
GAU-Radioanalytical Laboratories
University of Southampton
National Oceanography Centre
In the beginning ....... why an efficient thermal desorption instrument was needed?

1998-2002 GAU conducted a research study funded by the FOOD STANDARDS AGENCY in 1998 to investigate the fate of OBT discharges from the Maynard Centre

1999 An efficient thermal desorption instrument was needed to allow the work to proceed

1999 The multi-sample PYROLYSER-Trio was invented and commercialised

Development of a novel thermal desorption instrument

1999 An efficient thermal desorption instrument was needed for the research work

2010 GE Healthcare commissions GAU to set up an on-site lab for 3H and 14C and also to provide analytical support during characterisation stage.

Approx. 6000 samples analysed for 3H and 14C OBT discharged into estuary from 1980-2009
The first main application of the Pyrolyser system

*OBT Tritium in Severn Estuary sediment*

Environmental Science & Technology

![Graph showing tritium profiles for Peterstone and Newport Deep](image)

*Figure 3. Tritium profiles for two Peterstone saltmarsh cores (PET 1 and PET2) and Newport Deep NPD10. NPD10 was collected by gravity coring at a water depth of ~6 m below the lowest astronomical tide, HAT. The OBT discharge data and the relative proportion of OBT to total tritium (bars) were supplied by J. Williams of Amersham (later GE-Healthcare) and are decay corrected to 2000 to provide a clearer comparison with the sediment core profiles.*

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**Development of a novel thermal desorption instrument**

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tr>
<td>1999</td>
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<td>2006-now</td>
<td>PYROLYSERS adopted worldwide</td>
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Pyrolysers worldwide (57)

<table>
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<tr>
<th>Country</th>
<th>Count</th>
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<td>S. Korea</td>
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<td>France</td>
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1998-2003 GAU conducted a research study funded by the FSA in 1998 to investigate the fate of OBT discharges from the Maynard Centre (Cardiff)

1999 An efficient thermal desorption instrument was needed to allow the work to proceed. "Necessity is the mother of invention"

1999 The PYROLYSER-Trio was invented

2000-now PYROLYSER widely adopted in the UK Magnox decommissioning programme >100,000 samples analysed in 10 years from Magnox sites

2006-now PYROLYSERS adopted worldwide

2010-now GE-Healthcare withdraws from radiopharmaceutical business and need to decommission their old manufacturing site

2010 GE-Healthcare commissions GAU to set up an on-site lab for $^3$H and $^{14}$C and also to provide analytical support during characterisation stage. Approx. 6000 samples analysed for $^3$H and $^{14}$C
GE Healthcare  The Maynard Centre Decommissioning Project
The UKs largest private sector decommissioning programme

The facility was built on a 15 Ha site east of Cardiff, S. Wales
1980-2009 - Manufactured \(^{14}\)C & \(^{3}\)H labelled products
2010 – now - Decommissioning involved radioanalytical characterisation of over 10,000 samples (so far)

Applications to decommissioning
Accumulating the evidence  PhD student ideal

- \(^{3}\)H origin
- Thermal Desorption profiles
- Sample Composition effects
  Concrete
  Asbestos
  Metals
  Graphite
  Plastic
Origin of $^3$H contamination

- Exposure to tritiated water (HTO) either as a liquid or vapour
  (Nuclear sites – particularly heavy-water reactors)
- In-situ production via neutron capture / ternary fission
  Nuclear sites
- HT gas - fusion and nuclear weapon fabrication sites
- Non-aqueous $^3$H (‘organically-bound $^3$H’)
  e.g. radiopharmaceutical manufacture and use

Measurement of $^3$H in solids

1. Thermal desorption followed by LSC on bubbler soln.
2. Simple leaching (equilibration) with $^3$H-free water and
   measurement of $^3$H in aqueous phase / LSC
3. Sample digestion / distillation / LSC
4. He-3 mass spectrometry (specialised)
**3H Thermal Desorption Profiles**

Single Total 3H thermal extraction or
Multiple incremental 3H extractions

The T °C at which 3H desorbs from samples varies and depends on

- origin of the 3H (HT, HTO, OBT, *in-situ* formation)
- chemical association of 3H in the sample (hydroxide etc)
- the sample composition (concrete, metal, graphite etc)

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**3H desorption profiles from concrete exposed to HTO**

![Graph showing 3H desorption profiles](image)
Desorption profiles for structural and bioshield concrete (heavy-water reactor site)

Relative proportion of ‘strongly bound’ and ‘loosely bound’ $^3$H in bioshield concrete
**³H extraction by leaching & thermal decomposition**

- A — difficult to leach quantitatively
- B — Comparable data
- C — difficult to leach quantitatively

**³H evolution profiles from asbestos insulation from a Magnox reactor site**

Asbestos exposed to HTO and no neutrons
**3H desorption profiles from metals (I)**

![Graphs showing desorption profiles from metals](image1)


**3H desorption profiles from metal (II)**

![Graphs showing desorption profiles from metals](image2)

Non-irradiated metals

**3H desorption profile from irradiated graphite**

Graphite moderator (irradiated)


**3H in plastics**

Polythene exposed to HTO
Determination of thermal desorption profiles & cumulative tdp’s provide an insight into the association of the $^{3}$H in metals.

- $^{3}$H lost at temperatures around 100°C is indicative of free $^{3}$H-water
- $^{3}$H lost around 300°C indicates breakdown of hydroxide or oxyhydroxide phases
- $^{3}$H lost at 800-900°C indicates a strongly bound form of $^{3}$H (e.g. n capture by Li)

\[ \text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{HCl} \]

$^{36}$Cl & $^{129}$I extractions using the Pyrolyser

$^{36}$Cl is present in nuclear graphite, concretes, ion exchange resins & desiccants
Bubbler solution \((\text{Na}_2\text{CO}_3)\) passed through a Triskem silver loaded Cl-resin

- Quantitative uptake of both isotopes by silver loaded Cl-resin
  - \(^{36}\text{Cl}\) is eluted quantitatively at any KSCN concentration
  - \(^{129}\text{I}\) remains on the resin at any KSCN concentration
  - \(^{129}\text{I}\) is eluted at elevated \(\text{Na}_2\text{S}\) concentrations

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**Pyrolyser capability**

Already proven \(^{3}\text{H}, \ ^{14}\text{C}, \ ^{35}\text{S}, \ ^{36}\text{Cl}, \text{ and } ^{129}\text{I}\)


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**PRELIMINARY STUDY OF RADIOISOTOPE \(^{14}\text{C}\) APPLICATION IN CHINA USING XI’AN ACCELERATOR MASS SPECTROMETER**

INCS News, 25th Issue, Volume VII, Number 1, January 2010

P E Warwick, A Zulauf, S Strippel, I W Croudace: TRISKEM SUPPORTED

**DETERMINATION OF \(^{36}\text{Cl}\) IN DECOMMISSIONING SAMPLES USING A PYROLYSER FURNACE AND EXTRACTION CHROMATOGRAPHIC SEPARATIONS**

Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK)
Conclusions

- Tritium may be present in a number of different forms depending on the source of $^3$H and sample composition and Thermal desorption instruments like the Pyrolyser efficiently provide $^3$H ‘speciation’ and total activity information.

- Tritium desorption profiles provide insights into the kind of tritium in a sample and can guide the practical approach to use for specific materials.

- Temperatures in excess of 800°C are required to liberate $^3$H from graphite, metals and irradiated materials. For all other sample types tested, 600°C is generally sufficient.

- The thermal desorption process is successful for $^3$H, $^{14}$C, $^{35}$S, $^{36}$Cl, and $^{129}$I.

- It is expected that it could be extended to include $^{99}$Tc and $^{210}$Po.

NEW FROM RADDEC

HBO$_2$ Hyperbaric Oxidiser
designed to collect tritium from large masses of soft wastes and environmental samples
Thank you

3H sources in concretes

- Adsorbed HTO > 105°C
- Dehydration of ettringite (CaO)₆(Al₂O₃)(SO₄)₃·32H₂O 100 - 200°C
- Dehydration of portlandite Ca(OH)₂ > 450°C
- Decomposition of structural OH groups > 500°C

Form of ³H present will depend on source of ³H
adsorption of HTO or
in situ production from neutron reactions with D, Li or B
Partitioning of $^3$H in concrete
(exposure source HTO)

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Desorption temperature (°C)</th>
<th>% of total $^3$H</th>
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<tbody>
<tr>
<td>Capillary / porewater</td>
<td>&lt; 200°C</td>
<td>77%</td>
</tr>
<tr>
<td>Water of crystallisation</td>
<td>200 – 450°C</td>
<td>15%</td>
</tr>
<tr>
<td>Calcium hydroxide (Portlandite)</td>
<td>450 – 550°C</td>
<td>7%</td>
</tr>
<tr>
<td>Calcium silicate hydrate</td>
<td>600 – 850°C</td>
<td>1%</td>
</tr>
</tbody>
</table>

$^3$H in metals – inferred from HT studies

- Surface oxyhydroxides (200 - 300°C)
- H diffused into metal lattice
- The form of $^3$H present depends on source of $^3$H (adsorption of HTO or in situ production via neutron activation of D or Li)

Generalised trend of $^3$H gas distribution in steel exposed to HT (after Perevezentsev et al, 2008)
Thermal decomposition temperatures for Fe(OH)$_3$ and Cu(OH)$_2$ are comparable at ca 275°C.

The similarity in profiles for non-irradiated and irradiated steels would suggest that the $^3$H retention mechanism is similar in both cases and probably associated with structural oxyhydroxide formation.

$^3$H in steel is likely trapped in hydroxyl groups that will thermally decompose to yield tritiated water.

The first stage occurs at temperatures comparable to those required for the decomposition of Fe(OH)$_3$ or Cu(OH)$_2$ and the first $^3$H evolution stage for Al is comparable with steel and Cu metal. The second stage occurs at much higher temperatures (above 425°C) giving rise to the observed step change in the cumulative evolution profile.

For non-irradiated stainless steels, the thermal desorption of $^3$H required temperatures in excess of 500°C. This is most likely due to the penetration of $^3$H into the bulk metal requiring high temperatures to facilitate the liberation of the $^3$H along metal grain boundaries.

The temperature of $^3$H desorption will depend on whether it is present in the metals as free water, water of crystallization, surface oxyhydroxides layer, structural OH groups or trapped along grain boundaries $^3$H.