Effective desorption of tritium from diverse solid matrices and its application to routine analysis of decommissioning materials

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1. Introduction

The requirement for ^3H measurement in a wide range of materials has increased in recent years mainly as a result of accelerated decommissioning programmes and the associated waste sentencing requirements. However, as ^3H is a low-energy beta emitter (E_{max} = 18.6 keV) with no associated gamma emissions, direct measurement of the nuclide is not feasible and quantification of ^3H typically requires the extraction of the nuclide from the sample matrix and separation from other nuclides that would potentially interfere. A number of techniques are routinely used for isolation of ^3H. The most widely applied technique is ambient pressure decomposition where the sample is thermally oxidised in air or O_2-enriched air within a tube furnace assembly [1-3]. The effective performance of thermal desorption / oxidation for ^3H recovery depends on the efficient performance of four key stages

1. Quantitative liberation of ^3H from the sample matrix
2. Quantitative conversion of all ^3H species to HTO
3. Efficient trapping of the ^3H as HTO
4. The effective separation of ^3H from other nuclides that may interfere with the final quantification of ^3H.

In this study, the temperature dependence of ^3H release from a range of tritiated materials commonly encountered during decommissioning and environmental surveys, the effectiveness of catalysts / oxidants under different conditions and the efficiency of the bubbler trap were investigated.

2. Methodology

Total tritium ($^3H_{total}$) is extracted using a Raddec Pyrolyser Trio™ System (Raddec Ltd, Southampton, UK) that was designed to simultaneously extract ^3H and ^{14}C from six samples at a time from nuclear and environmental samples (Fig. 1). Each sample is placed in a silica glass work tube within the sample zone of the furnace and heated using a preset heating cycle based on experimentally optimised studies. The liberated gases pass through a catalyst zone. The catalyst zone is normally filled with 10g of Pt-alumina catalyst pellets to oxidise any organic combustion products to CO_2 and H_2O (HTO). Any water vapour, including HTO, is trapped in a bubbler containing 20 mL of 0.1M HNO_3 which effectively prevents co-trapping of CO_2.

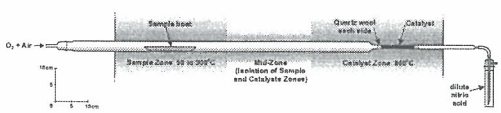

Fig. 1. Schematic diagram of the Pyrolyser triple zone furnace

Tritium evolution profiles were determined for a range of materials which were either artificially spiked with tritiated compounds or which had become contaminated as a result of exposure to tritiated organic compounds or HTO or via direct neutron activation. Evolution profiles were also determined for ^3H-labelled organic compounds and HTO.

All tritium measurements were performed using a 1220 liquid scintillation counter (Wallac Quantulus™). Eight milliliters of bubbler solution were mixed with 12mL Gold Star™ (Meridian) scintillation cocktail in a 22mL polythene vial. The vial was dark adapted for 8 hours to eliminate chemiluminescence and then counted for 1 hour (3×20 minutes). The counter was calibrated for ^3H using a traceable tritiated water standard (TRY-44, Nycomed Amersham PLC, Bucks, UK). For all samples, the measured quench levels (SQPE) ranged from 700 to 850 which correspond to ^3H counting efficiencies of 17 - 31%. All uncertainties are quoted at the 95% confidence level and refer to propagated method uncertainties

3. Results and discussion

Tritium thermal desorption profiles were measured for a range of pure ^3H-labelled compounds and samples contaminated with ^3H (Fig. 2). For concretes and brick exposed to HTO, release of ^3H occurred at around 100°C and complete recovery of ^3H occurring below < 300°C. For all other sample types studied, the release of ^3H was delayed with quantitative recovery only being achieved at temperatures in excess of 500°C. The most delayed release of ^3H was observed for graphite where quantitative recovery of ^3H was only achieved following the complete decomposition of the graphite at temperatures exceeding 850°C (Fig.3).

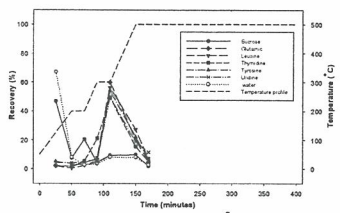

Fig. 2. Tritium evolution profiles for ^3H-labelled organics and water

For tritiated water and ^3H-sucrose, rapid liberation of ^3H occurred at low temperature (<100°C) whilst for all other tritiated compounds, the release of ^3H was delayed and occurred at furnace temperatures of 300-500°C. Solutions of ^3H-thymidine are often used as a ^3H standard to assess furnace recoveries. However, it has been noted that during storage, ^3H-thymidine appears to

decompose resulting in a portion of the ^{3}H being liberated at low temperatures comparable with tritiated water. For fish or milk spiked with ^{3}H thymidine no rapid release of ^{3}H was observed at low temperatures as any HTO arising from decomposition of thymidine had been removed during freeze-drying of the sample. Storage of the freeze-dried material at -20°C did not seem to result in significant degradation of the ^{3}H-thymidine.

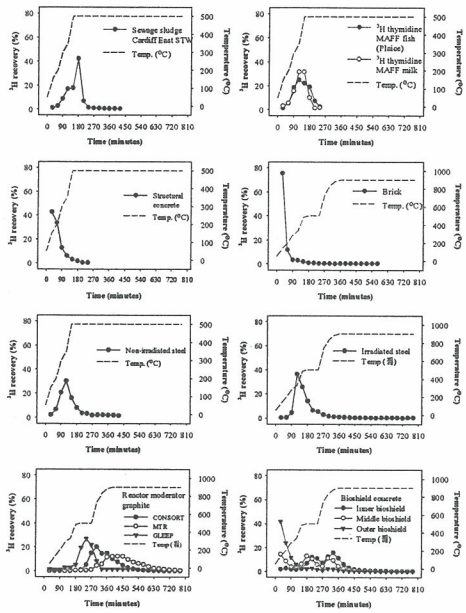

Fig. 3. ^{3}H thermal desorption profiles

For sewage sludges contaminated with organic ^{3}H, ^{3}H evolution was at a maximum at 500°C with over 97% of tritium was recovered within 4 hours. There was no rapid ^{3}H release in the early stages of combustion cycle or at temperatures in excess of 500 °C. This implies that there is no significant quantity of tritiated water in this sewage sludge. The sewage sludge originated from the Cardiff East Sewer Treatment Waste where liquid wastes containing variable tritiated organic compounds from radiopharmaceutical manufacture at Amersham plc Cardiff (now GE Healthcare) were treated.

Concretes, along with many other structural materials become contaminated with ^{3}H during routine operation as a result of the wide spread presence of tritiated water vapour in reactor buildings coupled with its rapid diffusion into relatively porous materials [4]. Rapid evolution of ^{3}H was observed from both structural concrete and brick at low temperatures with >95% of total tritium extraction at temperatures < 350°C. Such release of ^{3}H at low temperatures is consistent with the ^{3}H being present as adsorbed HTO. Both concrete and brick contain hydrous minerals that might exchange with tritiated water vapour, resulting in more strongly bound ^{3}H. The lack of ^{3}H evolution at temperatures > 400°C confirms that no significant proportion of ^{3}H is associated with such minerals.

Thermal desorption profiles for irradiated concrete were significantly different from those determined for structural concrete. For concrete sampled proximal to the reactor core, ^{3}H release occurred only at temperature in excess of 350°C, with no low temperature component apparent. For samples collected further from the reactor core, a low temperature component to the desorption profile was apparent. The proportion of ^{3}H released at low temperature increased with increasing distance from the reactor core and was most likely associated with adsorbed tritiated water. The ^{3}H liberated at higher temperatures originated from neutron activation of trace Li via the $^{6}Li(n,\alpha)^{3}H$ reaction (σ_{th} = 940 b) and was bound within the mineral lattice.

For mild steel samples exposed to HTO, ^{3}H evolution commenced at *ca* 200°C and reached a maximum at 300-500°C. A similar profile was observed for an irradiated steel sample. Kikuchi et al. [5] carried out similar experiment with stainless steel whereby a sample was heated up to 1000°C (constant ramp rate of 10°C/min) in a stream of nitrogen / hydrogen (<2% volume) as a carrier gas. Tritium release commenced at 250°C and reached a maximum at about 400°C, comparable with the thermal desorption profiles observed in this study. There was no additional tritium release observed from stainless steel at >400°C.

4. Conclusion

For the majority of materials investigated in this study, the ^{3}H evolution temperatures were dictated by the initial form of ^{3}H contamination and the mechanism of adsorption of these tritiated species to the sample substrate. For materials such as concrete and brick, there was no evidence for ^{3}H isotopic exchange involving structural hydrogen. However, for irradiated concrete and graphite, where ^{3}H was produced *in-situ* via neutron capture, the thermal desorption of ^{3}H was delayed to higher temperatures. These findings provide valuable information that can be used in assessing the ^{3}H evolution temperatures of other materials during combustion and help in developing heating profiles. In addition, the measurement of ^{3}H evolution profiles helps in assessing the potential for ^{3}H loss during sampling.

5. References

1. Lockyer, J.F. and A.E. Lally, *The Determination of Tritium, C-14 and S-35 in Milk and Crop Samples Using a Combustion Technique.* Science of the Total Environment, 1993. **130**: p. 337-344.
2. Payne, P.R., I.G. Campbell, and D.F. White, *The combustion of tritium-labeled organic compounds.* Biochem. J., 1952. **50**(4): p. 500-502.
3. Kim, D.J., P.E. Warwick, and I.W. Croudace, *Tritium speciation in nuclear reactor bioshield concrete and its impact on accurate analysis.* Anal. Chem., 2008. **80**(14): p. 5476-5480.
4. Furuichi, K., et al., *Study on behavior of tritium in concrete wall.* Journal of Nuclear Materials, 2006. **350**(3): p. 246-253.
5. Kikuchi, K., et al., *Evaluation of residual tritium in stainless steel irradiated at SINQ target 3.* Journal of Nuclear Materials, 2006. **356**(1-3): p. 157-161.