Tritium 2016 FST-16-226R1

A suite of robust radioanalytical techniques for the determination of tritium and other volatile radionuclides in decommissioning wastes and environmental matrices

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Robust radioanalytical instruments and techniques for the determination of ^{3}H and other volatile radionuclides in decommissioning wastes and environmental matrices

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Abstract

Tritium is ubiquitous in and around nuclear plants, being formed via neutron capture by ^{2}H, ^{6}Li, ^{10}B and ^{14}N and via ternary fission. The highly mobile nature of ^{3}H species results in widespread distribution of the radionuclide. Predictive modelling of ^{3}H activity concentrations is challenging and direct measurement of ^{3}H activities in materials is the preferred approach to underpin waste and environmental assessments. For well over a decade, the UK nuclear industry has engaged in a significant programme of site decommissioning of its first generation reactors. This has resulted in a high demand for the rapid characterisation of ^{3}H in a diverse range of matrices, including concretes, metals, plastics, sludges, resins, soils and biota. To support such assessments, it has been necessary to develop dedicated instrumentation in parallel with robust radioanalytical methodologies; namely a multi-tube furnace and a high-capacity, closed (pressurised) oxygen combustion system. Data are presented on the development and validation of these instruments, designed specifically to enable the quantitative extraction of ^{3}H (and other volatile radionuclides) from diverse sample types. Furthermore the furnace system has been employed as a tool to gain insights into the ^{3}H association in decommissioning and environmental matrices exposed to ^{3}H arising from nuclear power plant operations through tritium evolution with temperature profiling. The impact of the chemical speciation of ^3H on analytical strategy is discussed. A major benefit of the multi-sample furnace is its ease of use and applicability to ^3H determination in virtually any sample type. The complementary HBO_2 oxygen combustion system has been developed for the quantitative oxidation of organic-rich samples (e.g. wood, plastic, oil, biota) and analytical data prove its effectiveness.

Key words: TRITIUM DETERMINATION, WASTE CHARACTERISATION ANALYSIS, FISSION AND FUSION SECTOR NUCLEAR DECOMMISSIONING

I. Introduction

The development of first and second generation nuclear power within the UK (Magnox and AGR) in 1950s-1970s has left a legacy of sites in the UK that have entered various stages of decommissioning over the past 10 years. The dismantling of nuclear sites results in a significant volume of waste comprising of a diverse range of matrices that require robust characterisation to underpin appropriate disposal. Quantification of the tritium activity in such a broad range of materials represents a significant challenge as the low-energy pure beta emission of ^{3}H makes direct measurement of bulk activity impractical/infeasible, [1]. In addition, regulatory and reassurance monitoring of the environment around operational facilities has added a further challenge of quantifying tritium in biota. The limits of detection required for such monitoring are typically in the (Bq/kg) range necessitating the analysis of large sample masses. Another recent focus of interest in parts of Europe, Canada, S. Korea and elsewhere has been the assessment of organically bound tritium (OBT) due to its higher effective dose coefficient compared with tritiated water (HTO), [2,3,4,5]. Detailed definitions of the various forms of tritium are given in Ref 1 and 4.

In response to these challenges a UK company (Raddec International Ltd, Southampton UK) has spearheaded the development of innovative multi-sample devices for the extraction of total tritium and other volatile radionuclides from almost any sample type. These instruments are now distributed worldwide and have become the industry standard approach to total tritium extraction (including tritiated water, HTO and organically Bound Tritium, OBT), [1, 4] prior to analysis. The instrumental success is underpinned by their systematic scientific evaluation (see References). Following the quantitative extraction of the radionuclides, their measurement is made using liquid scintillation counting or helium-ingrowth counting. This paper is concerned with reviewing the characteristics and capability of these devices (Table I).

TABLE I: Essential characteristics of Raddec tritium extraction technology

Device	Principle	Time to extract	Max Temp ^{o}C	Sample types	Sample size	Trapping Approach	Extractable volatile radionuclide *	Application areas
Pyrolyser-2 **Pyrolyser-4** **Pyrolyser-6**	Controlled thermal desorption	1 - 5 hours	950	Virtually any material	0.5 - 20g	Bubbler Cryotrap	^{3}H, ^{14}C, ^{35}S, ^{36}Cl, ^{129}I	ENV ND FR
Pyrolyser - Mini	Controlled thermal desorption	1 - 5 hours	950	Virtually any material	0.5 - 20g	Bubbler Cryotrap	^{3}H, ^{14}C, ^{35}S, ^{36}Cl, ^{129}I	ENV ND FR
HBO$_2$	Instantaneous oxidation to HTO using 20 Bar oxygen	30 sec to decompose 1 hour to collect sample	2000+ in the gas	Combustible materials Oil, rubber, plastics, wood, biota	Up to 30 g	Bubbler Cryotrap	^{3}H, ^{14}C (^{35}S, ^{36}Cl, ^{129}I)	ENV ND FR

ENV – Environmental; ND – Nuclear decommissioning related; FR – Fusion Research Facilities

* These radionuclides are extractable or collectable in the HBO2 system but will require specific isolation procedures following combustion (these details are not covered in this paper)

II. The Pyrolyser series of combustion furnaces

IIa. The Pyrolyser multi-tube furnace system (multi-sample) was purpose-designed for the rapid and efficient extraction of volatile radionuclides from diverse matrices. The Pyrolyser-Trio™ systems comprise 2, 4 or 6 silica tubes that pass through three contiguous furnaces. The earliest Pyrolysers produced incorporated two independent furnaces (isolated by an insulated air gap) allowing the sample and catalyst to be heated separately. The more recent and advanced Pyrolyser Trio™ includes a third mid-zone furnace, added in place of the insulated air gap, that heats up after the sample zone ramp has reached 500 ^{o}C. This remobilises any condensed combustion products that may have accumulated in the cooler region between the two main furnaces and transfers the volatile products through the catalyst zone for oxidation.

Samples (contained in a quartz-glass boat) are progressively heated, first in a flow of air to inhibit the likelihood of rapid oxidation and pressure excursions, up to about 500 ^{o}C before changing to oxygen. The heating follows a selected ramping profile chosen to be suited to the sample matrix. Typically, a final target temperature of 500-600 °C is selected although higher temperatures may be more appropriate for certain sample types (up to a maximum of 950 °C). Towards the end of the run (normally when the heating cycle has reached 500 ^{o}C), oxygen is introduced to ensure complete oxidation of the sample. The combustion products from the sample are passed over a 0.5% Pt-alumina catalyst heated to 800°C in the catalyst-zone furnace. All tritiated species are converted to tritiated water and are trapped in 20 mL HNO_3 bubblers with a trapping efficiency of 95 +/- 5%. The ^{3}H activity of the bubblers is normally determined by taking 8 mL of the 20 mL bubbler using liquid scintillation counting. Alternatively the total tritium can be cryo-trapped, avoiding the effect of bubbler dilution, using a -110 ^{o}C cryoelectrical trapping system adapted by Raddec International Ltd.

The Pyrolyser systems are widely used in radioanalytical laboratories worldwide and have been validated for the determination of ^{3}H and ^{14}C in a wide range of environmental, biological and decommissioning matrices including biota, urine, soils / sediments, concretes, plastics, oils and metals. The systems have also be adapted for the analysis of ^{3}H and ^{14}C in gases and has been routinely used to monitor these in landfill off-gases. The use of thermal desorption profiles can also provide valuable insights into the speciation of ^{3}H and can be used to distinguish between HTO and organically-bound ^{3}H. With suitable modifications to catalyst and glassware, the Pyrolyser systems can also be used for the extraction of ^{35}S, ^{36}Cl and ^{129}I. Since Pt-alumina catalyst will trap sulphur and halogens if these are required then the catalysts must be replaced with either CuO (for ^{35}S) or glass beads (for ^{36}Cl and ^{129}I). Halogens are also adsorbed onto the silicone tubing that usually connects the work tube to the bubbler. The standard silica worktube is therefore replaced with a silica worktube incorporating ground glass joints for connection directly to a modified bubbler when extracting ^{36}Cl or ^{129}I. If ^{35}S, ^{36}Cl and ^{129}I are the analytical focus then additional chemical treatments of the bubbler solution are required.

IIb. Pyrolyser-Mini System

Recently, the Pyrolyser-Mini™, a compact, two-tube variant of the Pyrolyser system, has been developed that is suited for use in fume cupboards, glove boxes, mobile laboratories and also conventional laboratories (Fig. 1). Unlike the larger Pyrolyser-Trio™ systems, the Pyrolyser-Mini™ does not incorporate a furnace mid-zone to isolate the sample and catalyst zones, reducing the size and power rating of the system. A unique feature allows the furnace system to be pivoted allowing operation in a vertical or horizontal orientation. Electrical and gas supply controls are contained in a separate control box connected to the furnace via an umbilical cable, allowing controls to be located outside of any enclosures. Complete thermal oxidation of volatile combustion products is ensured using two separate beds. These comprise 2 gram CuO (oxidant) placed above the sample in the silica sample combustion tube (Fig. 1) and 10 gram Pt-alumina (catalyst) held in the silica work-tube.

During set-up, samples are loaded into the silica sample tubes that are then inserted into the work-tube. Liquid samples are prepared by loading onto a layer of inert quartz sand. A thin layer of copper oxide oxidant is loaded above the sample to enhance oxidation of combustion products. At the start of a combustion cycle, the catalyst zone is heated to 600°C . As the two zones are not completely thermally isolated, the sample zone also begins to heat up, liberating tritiated water vapour. Once the catalyst zone has reached the target temperature, the sample zone is heated using a defined heating protocol. The liberated combustion products are partially oxidised by the copper oxide in the sample tube. Combustion gases are carried down the work tube and through the platinum catalyst to ensure complete oxidation of combustion products to CO_2 and water. Volatile radionuclides are swept into the bubbler trapping system by the carrier gas. The vertical orientation of the silica work-tube and direct glass connection of the work-tubes and bubblers minimises water condensation and avoids the use of silicone tubing which can trap halogens if they are of interest.

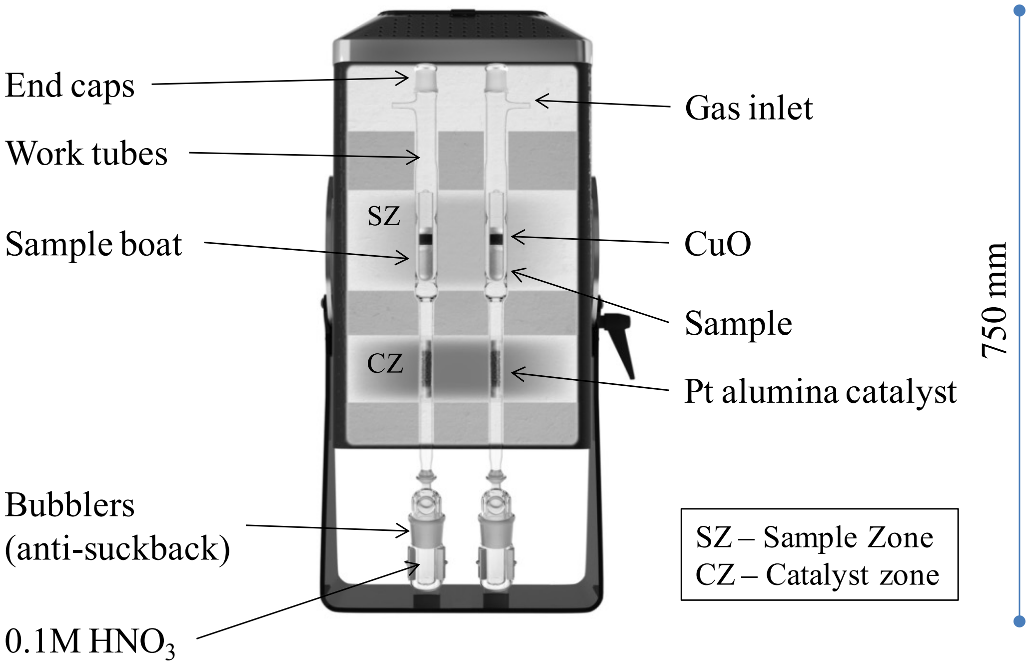

Fig 1: Pyrolyser-Mini revealing all main components (controller unit omitted)

III. The Hyperbaric oxidiser

The Hyperbaric Oxidiser (HBO_2™) is a purpose built ‘oxygen combustion bomb’ designed for the extraction of tritium from organic-rich sample matrices (e.g. fresh or dry fish, fresh or dry meat, plastics, oils, dry vegetation, dry seaweed etc). Other analytes will also be effectively extractable (e.g. ^{14}C, ^{36}Cl ^{129}I) although modified trapping approaches and additional chemical separation would be required to differentiate these radionuclides. High-pressure oxygen combustion has been established as a proven technique for tritium extraction, [6,7], however previous systems have required adaption on the part of the user to enable tritium recovery. With the HBO_2, tritium recovery has been considered from the outset, providing an integrated system for tritium extraction. The system utilises a high-performance 5-litre pressure vessel that safely contains the sample safely during combustion which is initiated using a glowing Ni-Cr wire. Sample ^{3}H is quantitatively oxidised to HTO and efficiently recovered through an integrated gas handling system and electro-mechanically cooled trap. Gravimetric and active validation indicates recoveries of >95% are routinely achieved for sample masses from 5-30g, [8, 9].

The HBO_2 is ideally suited to the extraction of ^{3}H from biota samples for environmental monitoring of total ^{3}H and organically bound ^{3}H (OBT) in the vicinity of nuclear sites. The large sample capacity results in significant volumes of combustion water which can be analysed directly by Liquid Scintillation Counting (LSC) or by enrichment followed by LSC to achieve low limits of detection. A range of biota samples originating from the Cotentin peninsula region (Brittany, France), close to the AREVA La Hague reprocessing facility, were combusted and data compared with equivalent analyses conducted using a high-capacity tube-furnace (Fig. 2a). Data show good agreement between the two techniques. The small positive bias exhibited by the HBO_2 data are due to the higher extraction efficiency (complete combustion) of this technique for large sample masses. Analysis of a low activity wheat (OBT intercomparison) sample has also been conducted using the HBO_2 as part of an international OBT inter-comparison exercise organised by CEA, France. The data for two independently operated HBO_2 systems exhibit close agreement with data obtained using a Pyrolyser-Trio™ and all data are in good agreement with the initially assigned value (Fig. 2b).

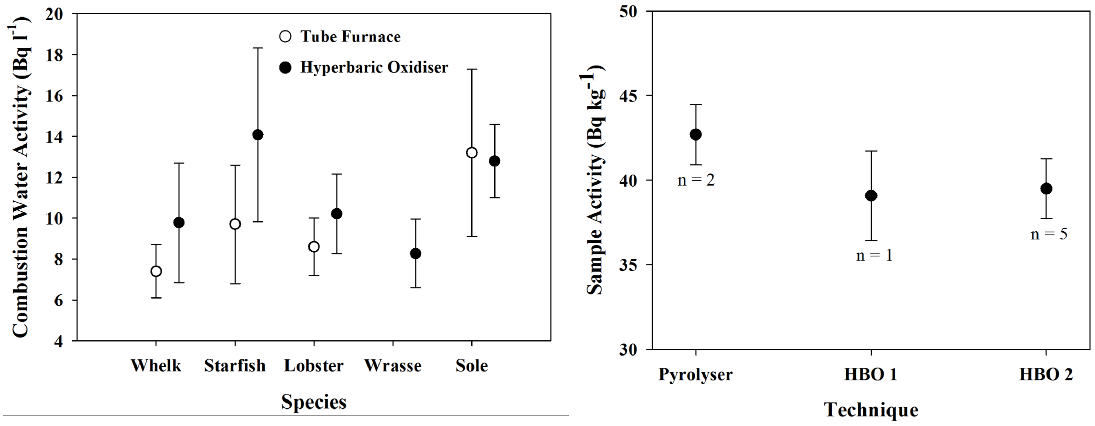

Fig. 2 a (left): Comparison of ^3H in marine biota extracted using a high capacity tube furnace (hollow circles) and using the HBO_2 (filled circles); b. (right): Comparison of ^3H analysis of an international OBT inter-comparison wheat sample by Pyrolyser-Trio and HBO_2. For biota, the HBO_2 system has an apparently higher efficiency than a tube furnace although all data agree within uncertainty. For wheat, the HBO_2 data are slightly lower but within uncertainty of the Pyrolyser data. The deviation may reflect an underestimate in ^3H recovery on the Pyrolyser systems.

IV.Applications

IV-A. Environmental research and monitoring

The Pyrolyser system was originally developed to provide the highly efficient extraction of tritium from sediment contaminated by technogenic organically bound tritium (OBT). This OBT entered the Severn Estuary (UK) under Regulator Approval from the Maynard Centre near Cardiff from 1982– 2009. The discharges arose from waste generated following the preparation of labelled radiopharmaceuticals. Around 1997, the UK Environment Agency reconsidered the discharge authorizations and demanded greater understanding of the environmental impact of the OBT, [10]. The research showed that a portion of the OBT compounds, rather than biodegrading as expected, became strongly bound to the clay/silt fraction of sediment and that the down-core OBT profiles in intertidal and subtidal sediments were broadly similar to the OBT discharge record.

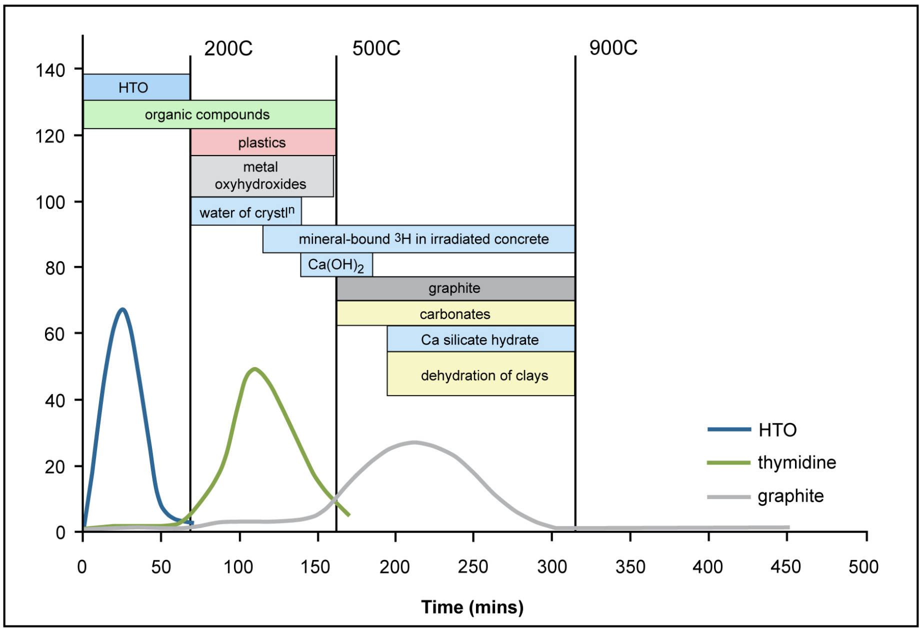

Fig. 3: Tritium evolution profiles obtained using the Pyrolyser for OBT contaminated sediment, [10].

Additional interest in environmental OBT arose from international researchers in Canada, France, Romania, UK and elsewhere. This related to assessments of tritium transfer to OBT that arose from nuclear production routes, particularly from PWR reactor discharges. Scientific groups from these countries established an International OBT Working Group, [4,5] to develop robust analytical procedures and a range of reference materials (e.g. potato, sediment and wheat; Fig. 2, 3 and 4). The Pyrolyser and HBO_2 (bomb) instruments performed well in intercomparisons facilitated using these materials.

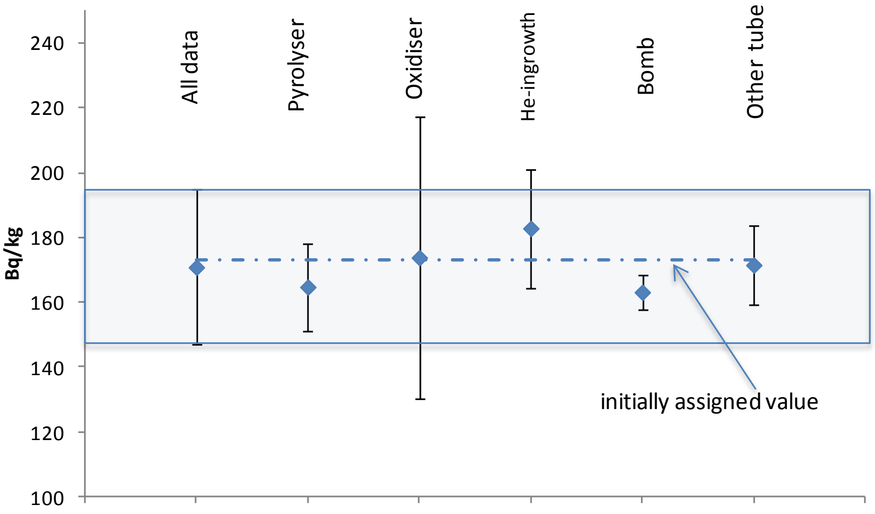

Fig. 4: Intercomparison exercise on OBT in a sediment reference sample (170 Bq/kg) using different extraction and measurement approaches, [11]. Bomb refers to the HBO_2 device.

IV-B. Nuclear decommissioning waste characterisation and fusion reactor operational support

Based on a combination of rigorous testing, development and publication in the international literature the Pyrolyser-Trio furnaces have become widely distributed with approximately 80 systems existing in radioanalytical laboratories worldwide. Most systems are used for waste characterisation in support of nuclear decommissioning programmes and the versatile design of the Pyrolyser systems enable total tritium determination as well as providing insights into tritium desorption with temperature in sediment, [10], concrete, [12], graphite, [13], soft wastes, plastics, [13, 14, 15], metals, [16,17].

IV-C. Other applications

The Pyrolyser series has also been used for the quantitative extraction of ^{129}I from marine biota and other samples, [18,19] where high sensitivity measurements are made using accelerator mass spectrometry, AMS.

V. Conclusions

- The escalation in nuclear facility decommissioning has resulted in significant challenges in ^{3}H analysis.
- Increased monitoring of ^{3}H in foodstuffs and the environment (particularly focussing on OBT) has also placed additional requirements for effective ^{3}H extraction from diverse environmental matrices.
- The Pyrolyser and HBO_2 systems have been developed and rigorously tested as robust extraction devices for volatile radionuclides.
- The Pyrolyser system permits high sample throughput whilst achieving quantitative ^{3}H extraction and is applicable to virtually all sample types encountered during decommissioning operations.
- In addition, the Pyrolyser system can provide valuable insights into ^{3}H through the measurement of ^{3}H evolution profiles.
- The Pyrolyser-Mini variant can be operated in fume cupboard / glovebox environments providing additional capability for handling of hazardous and significantly radioactive sample types.
- The HBO_2 system has been purpose-designed for safe and efficient extraction of ^{3}H from organic rich samples. The high sample capacity enables low-level ^{3}H analysis and is ideal for environmental monitoring applications.

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