A compact, dual-zone vertical tube furnace for the determination of tritium and carbon-14 in decommissioning wastes

Phillip E Warwick\*, Ian W Croudace and Frances M Burrell

University of Southampton, National Oceanography Centre, European Way, Southampton SO14 3ZH, UK

\*Corresponding author [phil.warwick@noc.soton.ac.uk](mailto:phil.warwick@noc.soton.ac.uk)

# Abstract

A compact dual zone, two work-tube, vertical tube furnace system (Raddec Pyrolyser-Mini) has been designed for the determination of H-3 and C-14 in decommissioning wastes. An optimised methodology was developed following improvements to sample holder and bubbler trap design, sample loading and loading temperature, as well as length and style of heating programmes. A significant efficiency enhancement was obtained through ‘hot-loading’ of the sample into the furnace at 600 °C before finally ramping to 900 °C. Direct trapping of H-3 and C-14 in a scintillation vial located in a special anti-suck-back bubbler further improved operations, leading to a reduction in analysis time and measurement sensitivity. Co-trapping of the analytes and dual-label liquid scintillation counting were also proven effective. Overall, the developed methodology led to a reduced analyte extraction/trapping time of 150 minutes whilst achieving limits of detection of <1 Bq/g. Validation of the procedure was assessed using a range of spiked matrices relevant to nuclear site decommissioning, reference materials and operationally-exposed materials. The compact size of this thermal extraction system is such that it allows for deployment in fume cupboards, gloveboxes and a mobile laboratory.

# Keywords

Pyrolyser-Mini; H-3; C-14; Decommissioning; Rapid method; Bubbler design

# Introduction

Tritium (H-3) is present in a wide range of materials that arise from the decommissioning of nuclear facilities, being formed via neutron capture and ternary fission. The waste types that arise are diverse and include (but are not limited to) soft wastes, metals, plastics, cement/concrete, soils and oils. The highly mobile nature of H-3 species makes predictive modelling of H-3 activity in this diverse range of materials challenging and subject to considerable uncertainties. As a consequence, direct measurement of samples to determine H-3 activities is the preferred approach to underpin the development of waste inventories and environmental assessments. This has resulted in a high demand for the rapid characterisation of H-3 in a diverse range of matrices. The analytical techniques in use for H-3 analysis are also suitable for the determination of carbon-14 (C-14), which also derives from neutron capture reactions, and these two radionuclides are often extracted and measured together.

Currently the standard method for determining H-3 and C-14 content in solid decommissioning waste and environmental materials involves the high temperature baking or incineration (thermal desorption) of the sample to release H-3 and C-14 species (Warwick et al, 2010; Croudace et al, 2014 and 2017). Tritium is typically released as, or rapidly converted to, water (HTO) while C-14 is released through the production of 14CO2 from carbonaceous and/or carbonate materials in the samples. The liberated H-3 and C-14 gases are trapped in acidified aqueous or alkaline traps respectively. The trap solutions are then measured by liquid scintillation counting to quantify the H-3 and C-14. The established techniques are effective and through judicious choice of sample size and count-time can reach detection limits commensurate with current clearance and exemption requirements. However, the techniques can be slow due to the need for sometimes lengthy heating profiles. A further disadvantage of the current generation of instrumentation (e.g. the Pyrolyser-Trio series of furnaces; [www.raddec.com](http://www.raddec.com)) is that they are quite large and modifications are required if they are to be installed in standard laboratory fume cupboards or glove boxes.

The Pyrolyser-Mini was conceived as a smaller system to meet the needs of laboratories concerned with analysing the diverse range of decommissioning-relevant materials. Desirable features include,

* ability to measure down to Environmental Permitted Levels (EPRs)
* able to reach a detection limit of at least 1 Bq/g for tritium and 14C and ideally 0.1 Bq/g
* reduced analyte extraction time
* no need for an oxygen gas supply from a compressed gas cylinder
* reduced equipment size to allow deployment in fume cupboards / gloveboxes
* a separate control unit from the heating unit to simplify servicing
* ability to operate from a single phase ~220 V, 13 Amp supply.

The prototype Mini system developed is a two work-tube, dual-zone, vertical furnace. Many of the components and elements were derived or adapted from the Pyrolyser-Trio series (Warwick et al 2010). The efficient and controlled combustion of the samples was achieved through careful design of a safe sample loading system that permitted hot-loading (i.e. loading at elevated temperatures) that has led to reduced extraction times. The use of a CuO oxidant layer above the sample replaces the requirement for an external O2 gas supply; an O2 gas supply can however, still be used if desired. Trapping of oxidised forms of H-3 and C-14 by bubbling directly into scintillation vials held in purpose-designed anti-suck-back bubblers improved operational efficiency and safety and ensured quantitative recovery of the radionuclides. The potential for co-trapping and simultaneous dual-labelling measurement of H-3 and C-14 was also evaluated. The revised methodology was validated using spiked concrete, steel, plastic (polythene), soil and simulated Magnox spent fuel sludge as well as operationally-exposed concretes, metals and sediments.

# Methodology

## Reagents and instrumentation

Carbon-14 labelled EDTA and H-3 as HTO were supplied as traceable standards by PTB, Braunschweig, Germany. Tritium as glucose was supplied by Perkin Elmer, Beaconsfield, UK. Pt-alumina catalyst (0.5 % Pt on 3mm pellets) was supplied by Raddec International, Southampton, UK. Copper oxide (CuO) pellets (0.71 – 2mm) were supplied by Sigma Aldrich Chemicals, Gillingham, UK. Carbontrap™, Carboncount™ and Gold Star™ scintillation cocktails were supplied by Meridian Biosciences, Epsom, UK. All other reagents were supplied by Fisher Scientific Ltd, Loughborough, UK. Nichrome (Ni-Cr) wire was supplied by the Scientific Wire Company (Great Dunmow, UK)

All liquid scintillation measurements were performed using a Quantulus 1220 (Perkin Elmer, USA) liquid scintillation counter.

## Furnace system

## Sample combustion and analyte trapping were performed using a Pyrolyser-Mini system (Raddec International, Southampton, UK). The Pyrolyser-Mini is a prototype vertical furnace system (Figure 1) comprising an upper sample zone and a lower catalyst zone which are individually controlled and thermally isolated by a layer of insulation. Thermal control of the system is via a single Eurotherm 3504 dual-loop PID controller. End caps are connected to the top of the quartz work-tubes above the air inlet. The sample tubes were lowered into the work-tube using Ni-Cr wire until they met 3 supporting dimples. The lower section of the work-tube contained Pt-alumina catalyst pellets held in position by plugs of quartz wool. The lowermost part of the work-tube incorporates an S19 glass ball joint for connecting to an anti-suck-back bubbler (with an S19 socket) containing the analyte trapping solvent held in a 20 mL scintillation vial.

Diagram

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**Figure 1: Cut-through schematic of the Pyrolyser-Mini system showing the closed sample tube design (with CuO oxidant included) and the anti-suck-back bubblers incorporating scintillation vials.**

### Sample holder and loading configurations

Two sample holder designs suited to a vertical furnace were evaluated using four loading configurations (see Figure 2).

a). The first holder design comprised a 20 mm OD quartz glass tube that was open at both ends (referred to as an open sample tube). This was a flow through design where the sample with or without CuO oxidant is loaded into a silica glass tube fitted with a porous silica wool support plug at the bottom. Further quartz wool plugs were placed on top of the sample and between the sample and CuO (if present).

b). The second holder design was also a 20 mm OD quartz tube that was only open at its upper end (referred to as a closed sample tube; analogous to a test tube; Figure 1). This design could also be configured with or without a layer of CuO oxidant.

Insertion and later removal of the sample tube into the work-tube was achieved using a length of Ni-Cr wire attached to the top of each sample tube. The sample tube stops were two sets of internally protruding dimples located to ensure efficient vapour transport through the work-tube when the sample tube was in position.

The efficiency of HTO volatilisation from an inert (acid-washed) sand matrix (1 g) and subsequent delivery of the mobilised analyte to the trapping bubbler was tested for the four loading configurations. In some experiments, an additional volume of deionised water (0.5 mL) was added to the sample tube as this had been shown to act as a carrier for volatile species. Upon heating, the volatile species released were hypothesised to follow different flow paths depending on the sample holder type chosen. For the closed-end version, volatile species must first travel vertically upwards against the applied air flow before being carried downwards to the bubbler. For the open-ended sample tube, volatilised species may travel either up, out and down or straight down. The latter flow route was expected to involve a shorter residence time in the quartz tube. Different sample tube loading configurations were therefore adopted for tests involving the use of granular CuO oxidant depending on the different flow routes available. For the closed-end sample tube, the oxidant was loaded above the spiked acid-washed sand whereas for the open tube, the CuO was loaded both above and below the spiked sand.

HTO evolution profiles were obtained for all four configurations for sample holding-tube loaded at sub-operating temperatures (~150 °C) whilst only the two configurations containing the CuO oxidant (both with 0.5 mL deionised water added) were used in further (hot-loading) experiments. For the sub-operating temperature experiments, the sample zone was ramped to 300 °C over 30 minutes after the sample tube had been loaded.

The hot-loading experiments were conducted at 300 °C, 600 °C and 850 °C. For loading at 300 °C, two loading conditions were evaluated (i) sample zone temperature set to 300 °C one hour prior to loading and (ii) sample zone temperature set to 300 °C the previous evening permitting the temperature of the quartz work-tube to equilibrate overnight. For all experiments, the catalyst zone was maintained at 300 °C overnight and set to 800 °C less than one hour prior to loading. For the hot-loading experiments, the sample zone was maintained at 300 °C overnight and adjusted to the target temperature one hour prior to loading. The temperature of the sample zone was set at the loading temperature for the duration of the evolution profile collection i.e. the temperature profile was level. For the experiments run at 300 °C, a slight increase in temperature was observed due to heat transfer from the catalyst zone with the sample zone reaching ~350 °C after 6.5 hours.

Evolution profiles were also determined for tritium-labelled glucose and C-14 labelled carbonate and EDTA using the closed sample tube with CuO configuration. Samples were loaded into the furnace at 300°C. The sample zone was then heated to 900°C. The catalyst zone was maintained at 800°C. For all evolution profile experiments, the flow rate was set to 0.1 L/min.

### Bubbler design

An anti-suck-back bubbler incorporating a scintillation vial was developed (Figure 1). This trapping system permitted direct trapping of H-3 and C-14 in the replaceable scintillation vial, minimising cross contamination, avoiding the need for sub-sampling of the bubbler, reducing trapping solution volumes and increasing the measurement sensitivity.

The rate of evaporation from the novel trapping system, the analyte trapping efficiency and the condensation of analyte in other parts of the bubbler were investigated. The rate of evaporative loss from the new bubbler design was assessed by connecting a bubbler incorporating a scintillation vial loaded with either 8 mL of 0.1M HNO3 or 8 mL Carbontrap to the furnace for 6.5 hours. During this time, the sample zone was set to 600 °C and the catalyst zone to 800 °C, with an airflow rate of 0.1 L/min. The bubbler assembly was periodically weighed to determine mass loss.

The trapping efficiency and distribution of activity was assessed under a range of conditions. For all experiments, CuO oxidant was loaded into the sample tube along with a HTO spike. The tube type, airflow, collection time, loading temperature and addition of carrier water were varied. A secondary trap (Bubbler B) was placed after the main bubbler (Bubbler A) to determine the proportion of H-3 that was not retained in the first bubbler. On completion of the run, the activity of H-3 in each component of the bubbler, the end cap, the sample tube and the secondary trap was measured.

The CO2 capacity of Carbontrap was investigated by adding HCl dropwise to varying quantities of Na2CO3 solution spiked with Na214CO3 to produce a known quantity of CO2 at a controlled rate. This was bubbled through two vessels containing Carbontrap connected in series. The amount of CO2 trapped in each bubbler was determined via measurement of C-14. The experiment was repeated using increasing concentrations of Na2CO3.

The efficiency of H-3 trapping in Carbontrap was investigated as well as the mechanisms for loss of analyte from either 0.1 M HNO3 or Carbontrap. For the first set of tests, H-3 or C-14 solution (0.1 mL) was spiked onto sand and loaded into the furnace in the sample tube. Two bubblers in series (Bubbler A and Bubbler B) were attached for 360 minutes with the second bubbler being changed every 90 minutes. As the majority of activity was expected to reach Bubbler A within the first 90 minutes, any activity reaching Bubbler B between 90 – 360 minutes was considered to be due to either evaporation of the trapped analyte or aerosol formation. The second set of tests involved spiking the Bubbler A solution directly, then passing air through the bubbler and measuring the activity passing through to the Bubbler B in each 90-minute period.

## Extraction and analysis of H-3 and C-14 from spiked matrices

The efficiency of combustion of the material, the oxidation of the volatile species and the trapping of radionuclides were assessed using five spiked test matrices:

* Magnox sludge simulant – 35 % Mg(OH)2; 3.5 % cellulose; 62 % water (by mass)
* Steel – wire cut into short pieces
* Concrete – crushed and ignited (at 900 oC)
* Soil – topsoil from grassy area, garden compost or mixture of the two
* Plastic – cut up HDPE bottle

The test materials were spiked with 0.1 mL of H-3 labelled glucose in ~1:9 ethanol:deionised water (~1 pg glucose) or C-14 labelled EDTA (~0.2 μg EDTA) solutions (~10 Bq total spike activity for each nuclide) and introduced to the Pyrolyser-Mini at elevated operating temperatures. An additional 0.5 mL of deionised water was added to the sample tube to provide a carrier for the H-3. The initial test for each material was carried out by loading 0.5 g of sample at 300 °C before progressing to loading at a higher temperature (600 °C) and adjusting the sample mass loaded.

For all tests, the sample tube was loaded at an elevated operating temperature (either 300 °C or 600 °C). The sample zone was held at this temperature for 30 minutes before ramping at 10 °C/min to a maximum of 900 °C. This maximum temperature was based on previous research (Warwick et al 2010) to ensure complete combustion and release of H-3 from matrices such as reactor moderator graphite (DIDO) and bioshield concrete. After a total of 90 minutes, the sample tube was removed from the quartz work-tube and the anti-suck-back bubbler (Bubbler A; direct trapping in scintillation vial) and secondary bubbler (Bubbler B) disconnected. Another bubbler (Bubbler C; 20 mL anti-suck-back design) was then attached for the cool down period (90 – 300 mins) in order to collect any activity that had not been transferred to the bubbler during the 90-minute collection period. This allowed for a complete inventory of the activity added as well as giving an indication of activity carryover if multiple samples were run in a working day. The catalyst zone was held at 800 °C for the duration of the experiment (300 minutes) whilst the airflow was maintained at 0.1 L/min.

## Analysis of reference materials and operationally-exposed materials

Two reference samples, originally supplied by NPL (Teddington, UK) as part of their Proficiency Exercise, were analysed. One sample (2016 PTE B1) was a very dilute NaOH solution containing H-3, C-14 and Cl-36 which was originally circulated in 2016 (Dean et al, 2017). The other sample (2012 PTE S) was a heat-treated sewage sludge sample containing H-3, C-14, K-40, Pb-210 and Po-210 and was originally circulated in 2012 (Dean et al, 2013).

Validation of the technique involved comparison of results obtained from a sample archive of operationally-exposed and other relevant and challenging matrices that had been evaluated using a conventional Pyrolyser-6-Trio.

i). **Concrete samples** from a decommissioned nuclear site, previously analysed for tritium (Kim et al, 2008) and subsequently continuously stored in a freezer at -18 °C, were re-analysed. The **structural concrete** was a building material that had not been exposed to neutrons but which had been exposed to HTO vapour. The two irradiated concrete samples were from **bioshield concrete** surrounding a heavy water nuclear reactor. Irradiated concrete #1 had been sampled from a depth of 60-70 cm away from the reactor core whilst irradiated concrete #2 was sampled from the top 10 cm closest to the reactor core. Tritium in these two samples originated from exposure to HTO as well as activation of lithium within the sample matrix. Tritium produced via the latter pathway is more strongly bound than the adsorbed HTO. The amount of strongly bound tritium activity in irradiated concrete #2 was expected to be greater than that in irradiated concrete #1 as the concrete closest to the reactor was subject to a higher neutron flux (Kim et al, 2008).

ii). **Metal swarf samples** taken from multi-element bottles (MEB) previously used to store Light Water Reactor spent fuel underwater in storage ponds. The swarf (fine filings/drillings) had been stored in a freezer prior to sub-sampling. The contamination was expected to be present on the surface of the metal bottle making representative sub-sampling difficult.

iii). **OBT intercomparison sample** is a marine sediment that was blended with sewage sludge contaminated with H-3 organic compounds arising from authorised discharges from the former Cardiff radiopharmaceutical manufacturing site (Croudace et al 2012; Warwick et al, 2018). The material was dried, ground and homogenised and stored at room temperature prior to sub-sampling. Tests showed this material to contain strongly-bound tritium.

The reference materials, operationally-exposed materials and OBT intercomparison sample were combusted using the optimised heating programme (90-minute heating programme with sample loading at 600 °C and heating to 900 °C) with CuO oxidant (~4 g) and Pt-alumina catalyst. The bubbler neck washing technique was also applied. H-3 and C-14 were trapped in 0.1M HNO3 and Carbontrap respectively. In addition, replicate tests were performed whereby the H-3 and C-14 were co-trapped in Carbontrap and activities of each radionuclide determined using dual-label liquid scintillation counting.

# Results

## Sample loading temperature

The four sample tube configurations (all with 0.5 mL additional deionised water as water vapour carrier) produced similar evolution profiles for HTO with >85 % of the activity added reaching the bubblers in the first ~90 minutes when loading at sub-operating temperatures (Figure 2a). After ~6.5 hours, the sample tubes were removed and the remaining activity calculated. In all cases residual activity was <1 % of total activity for all sample tube configurations. The open-ended sample tube without oxidant showed the fastest rate of analyte release. It was observed that this could lead to discoloured bubbler solutions due to incomplete oxidation of volatilised organic species. This was prevented by adding a short bed of granular CuO oxidant above the sample to provide a reactive, oxygen-rich surface and a longer residence time to ensure complete oxidation of organic rich samples.

The rate of analyte release and transfer to the bubbler increased with increasing loading temperature (Figure 2b). Similar profiles were obtained for the open-end tube configuration (data not shown) with >90 % of the added activity collected within 90 minutes for both configurations when loading at 300 °C (maintained overnight) or at the higher temperatures tested.An evolution profile obtained for H-3 labelled glucose (spiked onto acid-washed sand), loaded at operating temperature (300 °C) showed no significant change in the release, oxidation and trapping efficiency compared to HTO with the majority of activity (>90 %) being recovered in 90 minutes. Additional evolution experiments showed that transfer of nuclide to the bubbler solution was faster for C-14 labelled compounds (EDTA and carbonate) than tritium.



**Figure 2: Comparison of the evolution of H-3 (as HTO) from a). different sample tube configurations whilst loading at sub-operating temperatures and b). the closed sample tube configuration (including CuO oxidant) whilst loading at a range of operating temperatures**

A test was carried out to assess the ability to load multiple samples in a working day whilst maintaining a constant sample zone temperature of 600 °C and a catalyst zone temperature of 800 °C (Table 1). No decline in recovery was observed for the third sample loaded and no significant memory effect was evident when a 0.5 mL H2O sample was introduced to liberate any trapped H-3 in the work-tube. There was also little difference in the activity collected from the samples loaded with different volumes of water present.

Table 1: Total activity collected (% or Bq) and memory effect using rapid loading

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Collection time** | **Work-tube 1** | | **Work-tube 2** | |
| **Analyte load** | **Activity collected** | **Analyte load** | **Activity collected** |
| 90 minutes | 0.1 mL HTO + 0.5 mL H2O | 79 % | 0.1 mL HTO | 85 % |
| 60 minutes | No sample tube \* | 0.08 ± 0.06 Bq | No tube \* | 0.5 ± 0.1 Bq |
| 90 minutes | 0.5 mL H2O \* | 0.02 ± 0.02 Bq | 0.5 mL H2O \* | 0.3 ± 0.3 Bq |
| 60 minutes | No sample tube \* | 0.06 ± 0.06 Bq | No sample tube \* | <0.1 Bq |
| 90 minutes | 0.1 mL HTO + 0.5 mL H2O | 95 % | 0.1 mL HTO + 0.5 mL H2O | 92 % |

All samples were loaded into closed-end tubes using inert sand as support. \*Memory evaluation test

## Bubbler trapping system

### HTO trapping efficiency of 0.1M HNO3

The rate of evaporation of 0.1M HNO3 from the bubblers was constant over the 6.5-hour test period with an average mass loss of 0.18 g/hr. This is comparable to the rate of evaporation measured from the conventional anti-suck-back bubblers loaded with 20 mL of 0.1 M HNO3, which exhibited an average mass loss of 0.2 g/hr but is lower than observed for a standard bubbler system on a Pyrolyser-Trio where loss rates are typically 0.3 g/hr. By comparison, when Carbontrap was used, its rate of evaporation was greater, showing a linear rate of evaporation with an average mass loss of 0.35 g/hr from a starting mass of ~7 g.Evaporation from bubblers, though low, could be suppressed using a small granulated ice bath.

The trapping efficiency with 8 mL 0.1M HNO3 in the first bubbler (Bubbler A) was >70 % (Table 2). For a longer run time (3 hours), a larger amount of analyte passed through into the second bubbler (Bubbler B), indicating that evaporation of trapping solution from bubbler A is the main mechanism of transfer from Bubbler A to Bubbler B. Evaporative loss can be reduced by shortening the run time or reducing the airflow rate. This, however, caused an increase in the amount of activity remaining in the bubbler neck and therefore not reaching the collection vial (Tests C and D; Table 2). Due to the shorter time taken for the activity to reach the trapping solution when loading at high temperatures (as observed in the evolution profile experiments), the activity distribution was also assessed for sample loading at 600 °C. Under these conditions, and with a short collection time (90 minutes), minimal activity was found in both the neck of Bubbler A and in Bubbler B. This illustrated that the transfer of H-3 was not compromised by adhesion to the bubbler neck.

### CO2 trapping efficiency with Carbontrap and saturation effects

As the volume of Carbontrap used in the new bubbler design (8 mL) is less than that used in conventional Pyrolyser-Trio applications (20 mL), there is a greater risk of the capacity being exceeded. The theoretical capacity of Carbontrap is 4.8 mmol (0.21 g) of CO2 per mL of solution. Experimentally measured CO2 capacity was compared with the theoretical value to evaluate if the trapping efficiency decreases as the maximum capacity is approached (Figure 3). Quantitative trapping of CO2 was observed up to the theoretical capacity with no carryover into the second bubbler despite evaporative loss from the first bubbler. It is notable that saturation of the Carbontrap and further trapping in the second bubbler was observed when the total CO2 released was greater than 4.8 mmol/mL (0.21 g/mL).

Chart, scatter chart

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**Figure 3: Amount of CO2 trapped in Bubbler A. The dotted line indicates 100 % uptake.**

For solutions of Carbontrap nearing, or at, CO2 capacity an exothermic reaction was noted along with an increase in the density and viscosity of the solution. Quantification of density revealed a linear relationship with an increase in CO2 measured in the bubbler from ~1 mmol/mL to ~5 mmol/mL corresponding to an increase in density from ~0.9 g/mL to ~1.1 g/mL. The increase in density also correlated with a decrease in quench (as indicated by an increase in the quench parameter, SQPE from ~620 to ~670). The change in counting efficiency for samples with a high carbon content (as indicated by the SQPE value) may reduce the validity of using a matrix matched instrument standard to assess efficiency, and an SQPE-based quench correction is recommended.

The co-trapping of H-3 and C-14 in Carbontrap and subsequent dual-label counting would permit the use of a single bubbler solution. Any water in the sample tube would be transferred and retained in the Carbontrap bubbler solution or condense inside the bubbler’s neck chamber. Increasing the water content of the Carbontrap solution could result in phase separation when mixing with Carboncount scintillant. To test this, deionised water was added to a mixture of Carbontrap and Carboncount (~8 mL : 12 mL) until phase separation occurred. For Carbontrap solutions containing >3 mmol/mL CO2, as little as 0.05 – 0.5 mL of water was sufficient to cause phase separation whereas for Carbontrap solutions containing <1 mmol/mL CO2, up to 1 mL of water could be added without phase separation occurring (Figure 9). Phase separation can be reversed by the addition of either methanol or fresh Carbontrap. In the current study 1 – 3 mL of Carbontrap was able to produce a single-phase solution in all the mixtures tested.

### Carry over of analyte from Bubbler A to Bubbler B

No C-14 activity was observed to transfer from the Carbontrap solution probably due to the formation of low volatility carbamate species. H-3 activity was observed to be released from a bubbler containing 0.1 M HNO3. This occurred when H-3 as glucose was spiked into the sample tube and when HTO was spiked into bubbler A but not when spiked as glucose directly into the bubbler solution indicating evaporation of HTO rather than aerosol formation was the dominant transfer mechanism. A slight increase in the rate of H-3 transfer could be due to the decrease in volume of solution in Bubbler A over time. Evaporation of H-3 from Carbontrap when spiked as glucose into the sample tube was also observed suggesting that it is not chemically incorporated into a complex but physically trapped as HTO.

Table 2: Activity distribution from different loading tests

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Test** | **Sample Tube type** | **Airflow** | **Loading temperature** | **Additional H2O added** | **Collection time** | **Bubbler-A** | | | | **Bubbler-B** | **Sample**  **end cap** | **Sample tube** |
| **Vial** | **Neck** | **After vial** | **Vial exterior** |  |
| A | Closed | 0.1 L/min | 300 °C | 0.5 mL | 3 hours | 89 ± 3 % | 0.6 ± 0.3 % | <0.5 % | <0.4 % | 5 ± 1 % | <0.5 % | <1 % |
| B | Open | 0.1 L/min | 300 °C | 0.5 mL | 3 hours | 90 ± 3 % | 0.4 ± 0.3 % | 0.5 ± 0.3 % | <0.4 % | 6 ± 1 % | <0.5 % | <1 % |
| C | Closed | 0.05 L/min | 300 °C | 0.5 mL | 3 hours | 73 ± 3 % | 15 ± 1 % | <0.5 % | <0.5 % | 0.8 ± 0.8 % | <0.5 % | <1 % |
| D | Closed | 0.1 L/min | 300 °C | 0.5 mL | 90 mins | 75 ± 3 % | 14 ± 1 % | <0.5 % | <0.5 % | 1.1 ± 0.8 % | <0.5 % | <1 % |
| E | Closed | 0.1 L/min | 600 °C | 0.5 mL | 90 mins | 72 ± 3 % | 5.0 ± 0.6 % | N/A | 0.2 ± 0.2 % | 1.9 ± 0.7 % | N/A | <0.9 % |
| F | Closed | 0.1 L/min | 600 °C | None | 90 mins | 82 ± 3 % | 0.6 ± 0.3 % | N/A | <0.4 % | 2.1 ± 0.8 % | N/A | <0.9 % |
| G | Closed | 0.1 L/min | 600 °C | 0.5 mL | 90 mins | 91 ± 3 % | 0.7 ± 0.3 % | N/A | <0.4 % | 3.3 ± 0.9 % | N/A | <1 % |
| H | Closed | 0.1 L/min | 600 °C | 0.5 mL | 90 mins | 89 ± 3 % | 0.4 ± 0.3 % | N/A | <0.4 % | 1.7 ± 0.8 % | N/A | <1 % |

## Efficiency of combustion

The efficiency of combustion of the spiked matrices was determined for the two heating programmes by calculating the mass change of the sample tube during ignition. Any visual changes were also noted. The change in mass was calculated by subtracting the known mass of aqueous solution added (tracer spike plus deionised water) from the difference in total sample tube mass before and after ignition. The resulting change in mass has been expressed as a percentage of the total sample taken (Figure 4). For comparison, a spiked sand matrix (comprising a high melting point inorganic material) had 100 % sample remaining after ignition implying no sample mass loss. Mass change will result from thermal degradation of the sample as well as reduction of the CuO oxidant (when present).

The steel matrix had >100 % mass remaining indicating that some oxidation of the sample had occurred. Only one sample mass (0.5 g) was tested for this material and there was negligible difference between the two heating programmes. After both heating programmes, the steel changed from silver to black in colour whilst there was no obvious change to the CuO oxidant.

The concrete matrix had between 92 – 95 % of the original sample mass remaining at the end of the 90-minute heating programme. Different sample masses were assessed for this material (0.5 – 1.5 g) but showed no significant difference in mass loss; no difference was observed between the two heating programmes. The samples lightened in colour in all experiments but no other visual changes were observed.

The sludge matrix had a larger percentage mass loss due to the high-water content, with 25 – 27 % of the sample (0.5 g only) remaining. As with the steel and concrete matrices, there was no difference between the two heating programmes. Some darkening of the small amount of sample deposited around the sample tube opening during preparation was observed but was not apparent in the bulk sample.

The soil matrices tested varied in composition with the low organic content topsoil showing less mass loss (87 % remaining), whilst the organic rich compost showed >100 % mass loss (-26 % remaining). This indicated that in addition to loss of sample mass, loss of oxygen from the CuO oxidant also occurred. The only colour change occurred in the topsoil, which changed in colour from dark brown to light reddish brown. The compost matrix showed a large reduction in volume and generated a clear reduction of CuO as evidenced by the presence of metallic copper. There was also a significant difference in density of these two materials prior to ignition with 1.5 g of topsoil taking up <10 % of the sample tube and 1.5 g of compost taking up ~50 %. There was no significant difference in mass loss between the range of sample masses (0.5 – 1.5 g) investigated for the mixed soil matrix or between the two heating programmes. The percentage of sample remaining ranged from 47 – 76 % with the lowest value being attributed to the sample containing a larger proportion of the organic rich compost. This was also confirmed visually by a greater reduction in volume seen for this sample in comparison to the other mixed soil samples as well as a dark brown product observed after ignition (reddish brown product observed for other mixed soil samples).

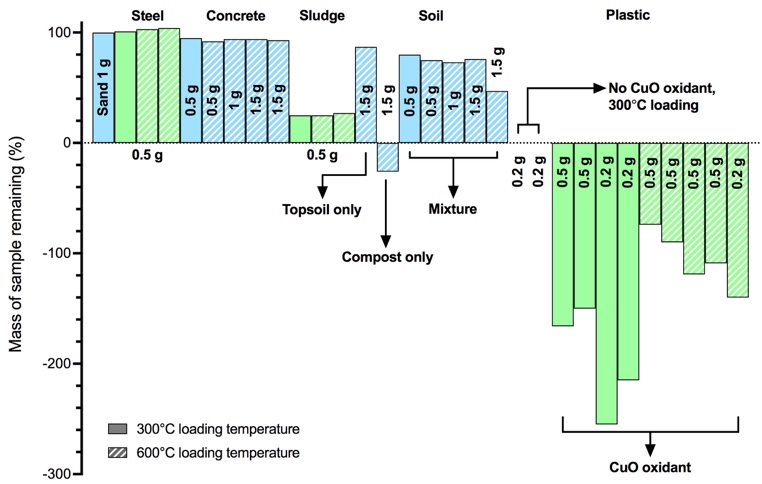


Figure 4: Percentage of spiked sample remaining after a 90-minute heating programme.

The plastic matrix showed complete combustion when ignited without the presence of CuO oxidant. This was evidenced by <0.3 % of the original sample mass remaining and no visible residue left in the sample tube. When ignited in the presence of CuO oxidant, combustion was accompanied by reduction of the oxidant to metallic copper. The extent of reduction varied with almost all the available oxygen used for 0.5 g samples loaded at 300 °C whilst only 50 – 60 % of the available oxygen was used for 0.2 g samples loaded at 300 °C. The percentage of available oxygen used was calculated simply based on the assumption that complete oxidation had occurred and no sample remained at the end of the 90-minute heating programme. However, this assumption may not be totally valid as the visual observation of the sample tube after ignition showed some black residue remaining. Reduction of CuO to metallic copper was also visible in the samples loaded at 300 °C. Black residue was not seen in the samples loaded at 600 °C with the exception of the 0.5 g sample with the lowest use of oxygen. The samples loaded at 600 °C used less oxygen than the samples loaded at 300 °C for the corresponding mass. This could be due to the faster rate of combustion making use of atmospheric oxygen in preference to solid phase oxygen from the CuO oxidant. Theoretically, the maximum mass of polythene that could be oxidised solely by 4 g of CuO was 0.23 g, although the reaction has been shown to make use of both solid phase oxygen and oxygen from the air supply. Suck-back was also observed (after ~1 hour) for samples loaded at 300 °C with or without CuO oxidant, whilst the trapping solution did not fill the anti-suck-back chamber, the flow of air stopped temporarily.

The aqueous NPL reference material (2016 PTE B1) was spiked on to sand (1 g) and no additional deionised water was added. The aqueous sample showed complete mass loss with <0.3 % of the aqueous sample remaining after the 90-minute heating programme. The sludge reference material (2012 PTE S) showed a similar result to the spiked samples containing a high organic content (plastic and compost), with the sample tube mass loss recorded as greater than the original sample mass indicating additional mass loss via reduction of CuO. This was calculated to correspond to 69 % and 76 % of the available oxygen being used for the two measurements made.

The efficiency of oxidation was also assessed for the plastic matrix. If incomplete oxidation occurs, the more complex volatile organic species can pass through the furnace and co-trap in the bubbler solution causing discolouration which reduces the liquid scintillation counting efficiency by increasing quench. Discolouration of either the trapping solution or the plastic scintillation vial was observed when 0.5 g of plastic sample was loaded at 600 °C in the absence of catalyst or oxidant. The discolouration was significantly reduced by decreasing the sample mass loaded to 0.2 g, also reducing the potential for Carbontrap saturation or phase separation upon addition of scintillant. Theoretically, the maximum mass of polythene that could be loaded without saturating 8 mL of Carbontrap is 0.54 g. The use of both CuO oxidant and 0.5 % Pt-alumina catalyst improved oxidation efficiency as evidenced through reduction of quench. Coloured residues were also observed inside the quartz work-tube and end cap after either a plastic or soil sample was loaded and ignited. The amount of activity, however, deposited within the end cap was measured to be <1 % of the total spiked activity.

## Transfer efficiency of HTO and 14CO2 through the system

The recovery of the analyte from spiked matrices within the trapping solution (8 mL) was assessed. There are a number of factors that can potentially affect the transfer of analyte into the trapping solution. Firstly, incomplete release of analyte from the sample tube could occur. However, measurement of the activity remaining in the sample tube via washing and counting, showed that negligible activity (<1 %) remained after a 90-minute heating programme for all experiments. Secondly, the volatilised species may deposit onto cooler areas within the quartz work-tube. As previously mentioned, <1 % of the total spiked activity was found when the end cap washings were counted. This measurement was not carried out for every sample type.

Once analytes are released from the sample tube and pass down the quartz work-tube, it is expected that they would trap in the scintillation vial (8 mL solution; Bubbler A). Alternative locations include deposition on the inside of the anti-suck-back chamber, deposition within the bubbler in the post trapping solution areas or passage through the bubbler and release to the atmosphere. The mechanism of atmospheric release could be through inefficient trapping, aerosol formation or evaporative loss. Evaporative loss was previously observed to occur for H-3 whereas no post-trapping loss was observed for C-14. The extent of evaporative loss was measured for both analytes by the attachment of a secondary bubbler (Bubbler B) in series. Deposition within the bubbler in the post trapping solution areas was also measured by taking a swab of the scintillation vial exterior and (for some tests) washing of the bubbler interior. Liquid scintillation counting showed that <1 % of the total spiked activity was found in this area. Deposition within the anti-suck-back chamber can be a significant factor reducing the recovery of activity in the bubbler solution as previously observed for the spiked sand samples (Table 2). A routine method to wash down the chamber is required in order to recover as much of this activity as possible.

Finally, recovery of analytes within the 90-minute heating programme may be reduced by slow release and/or transfer through the work-tube. This was assessed by replacing Bubbler A after 90 minutes with a standard anti-suck-back bubbler (20 mL solution; Bubbler C) and collecting for an additional 210 minutes. The sample tube was also removed after 90 minutes so any activity collected after this time would be due to delay within the work-tube rather than incomplete release. This measurement is also an indicator of cross-contamination if a second sample were to be loaded immediately after the first.

The distribution of activity and percentage recovery between these four key areas (Bubbler A, A neck, Bubbler B and Bubbler C) was compared for a sub-set of the spiked sample tests (Figure 5). The most suitable sample mass for each matrix and analyte (based on the results of combustion efficiency analysis) was chosen and only experiments using CuO oxidant (4 g) included. Only data obtained using a sample loading temperature of 600 °C are included in this comparison as, when loading at 300 °C, a higher percentage of the total H-3 activity added was found in both Bubbler A neck and Bubbler C. In addition, no decrease in the efficiency of combustion or pressure excursions were observed when loading at the higher operating temperature.

Under these optimised conditions, the results for C-14 as EDTA showed efficient trapping and no transfer of activity from Bubbler A. There was also no measurable deposition within the bubbler neck. The transfer of CO2 to the trapping solution (8 mL Carbontrap) was completed within the 90-minute heating programme. The average recovery in the Bubbler A vial was 100 ± 20 % (2sd) with no significant relationship to sample type.

For H-3 as glucose, the results showed that whilst efficient trapping and low transfer of activity from Bubbler A occurred (2 % - 3 % of the total activity added measured in Bubbler B), there can be significant deposition of activity within the anti-suck-back chamber as well as some delay in the transfer of H-3 from the work-tube. As with the C-14 data, there was no significant correlation between recovery and sample type with an average recovery in Bubbler A vial only of 80 ± 20 % (2sd). Between 4 % and 14 % of the total activity added was measured in the Bubbler A neck wash. Combining the activity recovered in both Bubbler A and the neck fraction, the average recovery could be increased to 90 ± 10 % (2sd). Activity measured in Bubbler C (2 % - 5 % of the total activity added) has been released from the sample tube in the 90-minute heating programme but delayed in the work-tube by reversible deposition on internal surfaces. The activity collected in Bubbler A (vial + neck) could be increased by extending the collection time beyond 90 minutes (during the furnace cool down and prior to loading of the next sample). Although this would not decrease turnaround, it could increase evaporative losses.

### Bubbler washing for enhanced recovery

Two washing techniques were investigated using fresh trapping solution to wash down the inside walls of the anti-suck-back chamber into the scintillation vial (collected separately for quantification of this method), and use of the solution already present in the vial to rinse the chamber. Whilst washing the bubbler neck with fresh trapping solution significantly reduced the amount of activity lost via deposition in the anti-suck-back chamber, the volume in the scintillation vial was increased, reducing measurement sensitivity.

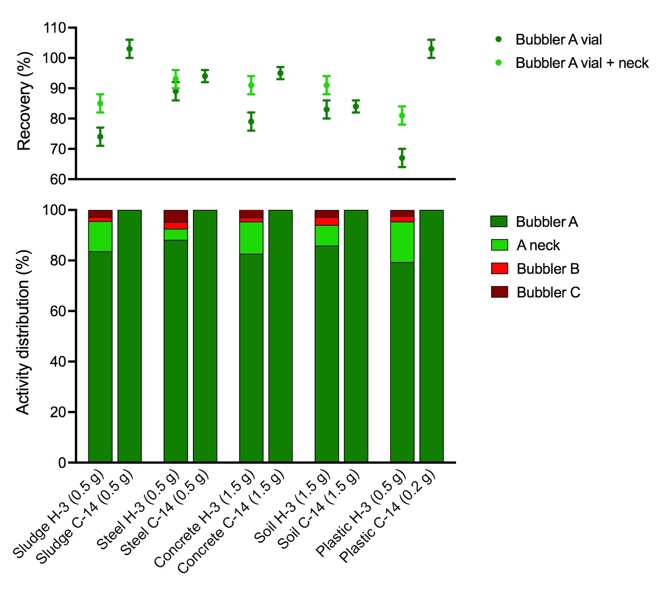


Figure 5: Distribution of H-3 and C-14 activity and percentage recovery between the four key areas for spiked samples. Recovery is the percentage of total spiked activity. Activity distribution is normalised to 100 % of the activity measured; values <LoD have been omitted.

Washing the anti-suck-back chamber with the trapping solution already present in the scintillation vial was achieved by connecting an empty dropping bottle to the bubbler outlet and gently applying positive pressure to push the solution up into the chamber. The bubbler was then tipped horizontally and rotated 360° and righted to allow the solution to drain back into the vial. This was repeated without the 360° rotation. This washing technique was able to recover a larger percentage of the total activity added and did not increase the volume of trapping solution in the scintillation vial. This technique did result in a small loss of C-14 via trapping solution remaining in the bubbler neck where previously none had been deposited. This loss is minimal however and should be reproducible so can be accounted for in the overall method yield. In addition, any C-14 activity deposited in the bubbler neck via suck-back mechanisms can be mostly recovered.

## Analysis of reference standards and operationally-exposed materials

The accuracy and precision of the method including the developed washing technique was assessed through the analysis of reference materials, comparing the total activity measured in the scintillation vial with the reference value (Table 3). Measured results were corrected assuming a 90 ± 10 % recovery for both H-3 and C-14. The recovery is based on average recoveries of 90 ± 10 % (2sd) for H-3 activity in Bubbler A vial and neck combined and 100 ± 20 % (2sd) for C-14 activity in Bubbler A vial for spiked samples loaded at 600 °C. The recovery for C-14 has been adjusted down to account for trapping solution remaining in the bubbler neck due to the washing stage. Recovery estimates could be refined through a replicate standard analyses and more data for spiked matrices using the developed washing technique. They are, however, similar to the recoveries applied to the conventional Pyrolyser; 90 ± 10 % for H-3 and 100 ± 5 % for C-14 which were used in the calculation of the working values for operational-exposed materials.

Table 3: Comparison between reference activity on day of measurement and that measured in Bubbler A

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **H-3 activity (Bq/g)** | | | **C-14 activity (Bq/g)** | |
| **NPL Reference Material** | **Reference value** | **Measured\* in 0.1M HNO3** | **Measured\* in Carbontrap** | **Reference value** | **Measured\*** |
| Sludge (0.5 g) | 57 ± 3 | 45 ± 5 | 50 ± 6 | 1.9 ± 0.1 | 1.6 ± 0.2 |
| Aqueous (1 g) | 0.87 ± 0.02 | 0.9 ± 0.1 | 0.9 ± 0.1 | 0.497 ± 0.007 | 0.56 ± 0.09 |

\*corrected for an estimated recovery of 90 ± 10%.

Radionuclide recovery from both of the reference materials was measured twice; once using 0.1 M HNO3 to trap and measure H-3 activity only and once using Carbontrap to trap and measure H-3 and C-14 activity simultaneously (dual measurement). For each of these measurements the developed internal flushing technique was applied. Comparing the reference activity and the total activity measured in Bubbler A, including an assumed recovery of 90 %, a good agreement was achieved for both materials for the two H-3 measurements as well as the C-14 measurement It is noted that no Cl-36 was detected in the bubbler solution even though the aqueous sample also contained Cl-36 at a concentration of 0.25 Bq/g.

For the operationally-exposed materials, the mass of material in the sample tube remaining after combustion was calculated using the method detailed for the spiked samples. The results show similar trends to the spiked materials. The mass of concrete remaining after the 90-minute heating programme was 91 ± 1 % (2 sd) and the only visual observation was a lightening of the residual solid. As with the spiked steel, >100 % of the swarf metal mass remained after combustion indicating oxidation of the material. This material, however, caused a blackening of the entire sample tube. Whilst it was possible to remove the majority of this deposited material with HCl, some sample had adhered to the sample tube in the region where it was loaded. The OBT sediment sample had 75 ± 1 % (2 sd) remaining after combustion and showed a similar colour change to the concrete and top-soil samples, with no change in volume.

After the 90-minute heating programme, the amount of H-3 and C-14 activity remaining in the sample was measured. The measured activity in this fraction as well as that measured by swabbing the exterior of the scintillation vial was negligible (either <LoD or <0.5 Bq respectively) except for the washing of the ignited swarf metal samples with 0.1 M HNO3 where inspection of the liquid scintillation spectra suggested the presence of a non-volatile radionuclide (possibly Ni-63).

Although both H-3 and C-14 were released from the sample matrices during the 90-minute heating programme, significant amounts of H-3 activity were retained in the quartz work-tube beyond 90 minutes for the irradiated concrete and swarf metal samples (Figure 6a). This resulted from the later onset of H-3 release from these samples due to the higher temperature required to liberate the more strongly bound H-3 present in these samples. It is noted that the total H-3 activity for swarf metal 1 is <0.5 Bq hence the 90-300 mins value is below the limit of detection.

The rate of H-3 release from the irradiated concrete and swarf metal samples was further investigated by conducting evolution profile experiments. The sample was loaded at 600 °C and the temperature in the sample zone ramped to 900 °C as in the previous recommended heating programme. The sample zone was, however, held at 900 °C for a total of 240 minutes and the sample tube left in the work-tube for this duration. For all 4 samples, an initial transfer of activity to the bubbler solution was observed during the 30 minutes that the sample zone was held at 600 °C (Figure 7). This transfer of activity coincided with water transfer to bubbler as evidenced by an increase in mass. After the initial 30 minutes, no further evidence of water transfer was observed. Unlike the previous data, where mass change of the bubbler was correlated to activity in the bubbler, further activity transfer was measured beyond the initial 30 minutes.

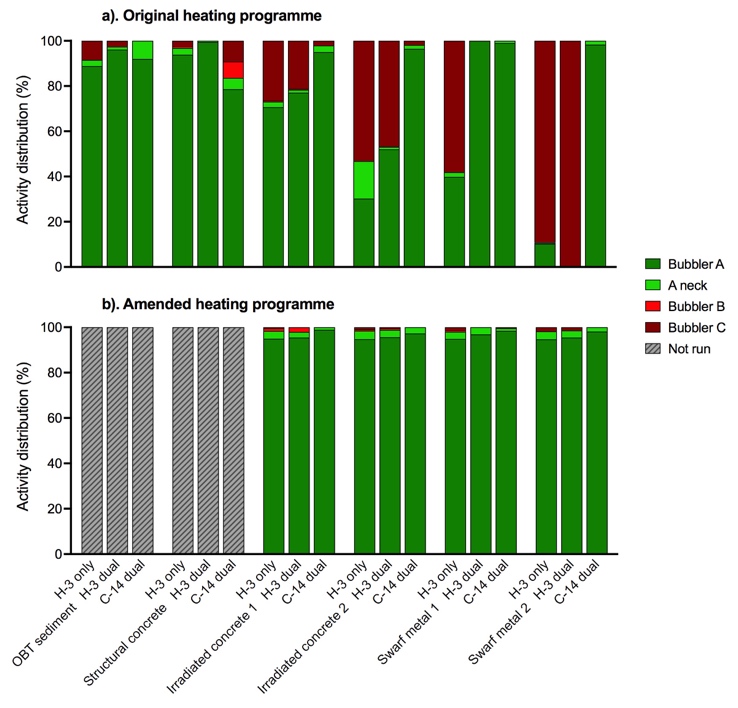


Figure 6: Distribution of H-3 and C-14 activity between the four key areas for operationally-exposed materials under a). the original heating programme and b). the amended heating programme. Activity distribution is normalised to 100 % of the activity measured; values <LoD have been omitted.

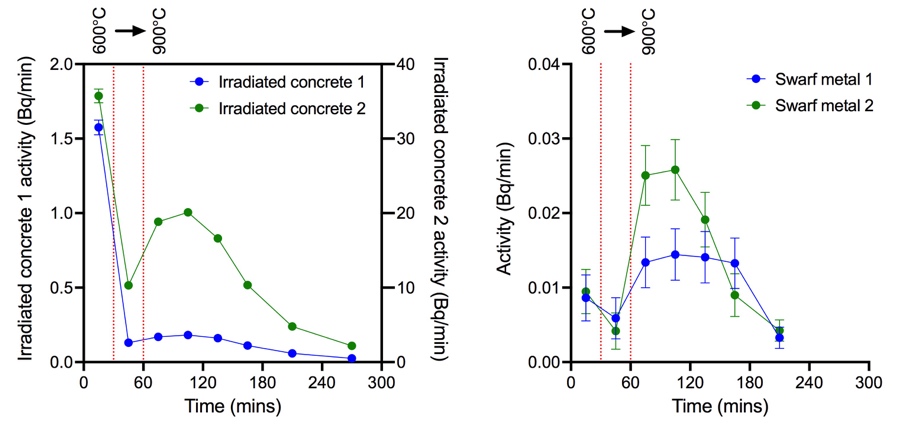


Figure 7: Comparison of the evolution of H-3 from operationally-exposed materials showing activity collected per minute.

For all 4 samples, the H-3 collected during the temperature ramping stage (600 °C – 900 °C), was low compared to that collected at 600 °C. Once the sample zone reached 900 °C, the H-3 activity recovered increased with protracted evolution of H-3 over a period of >180 minutes.

For the two irradiated concrete samples, the ratio of activity collected between 0-90 minutes and 90-300 minutes was similar to the values measured in the original heating programme (Figure 6a). The difference between the two samples is likely to be due to the different ratios of weakly-adsorbed to strongly-bound tritium. Irradiated concrete-2 has been sampled from closer to the reactor than irradiated concrete-1 and is therefore expected to contain more strongly bound tritium. All data for the total H-3 activity collected over the 5-hour period was in reasonable agreement with the reference activity determined using a conventional Pyrolyser-Trio (laboratory data from 2018).

Data from analysis using a conventional Pyrolyser-6-Trio has shown the swarf metal samples to be more heterogeneous and therefore have a larger uncertainty on the reference values. The results collected from the evolution profile experiments and 90-minute heating programme tests also showed a large degree of heterogeneity.

The similarity in total activity recovered, for experiments where the sample tube was removed and those where the evolution profiles was obtained by leaving the sample tube in, suggest that tritium was released from the matrix during the 90-minute heating programme but was retarded within the quartz work-tube. This observation was tested by conducting an evolution profile where the sample tube was removed after 90 minutes and the sample zone (and catalyst zone) allowed to cool down to 600 °C. After 150 minutes, the sample zone was heated back up to 900 °C (catalyst zone set to 800 °C). Finally, the sample tube was reintroduced for an hour to assess whether any additional tritium was liberated. The results of this test showed a similar evolution profile to that obtained when leaving the sample tube in with a total recovery of 131 ± 6 % over 5 hours. No increase in tritium transfer to the bubbler solution was observed when either increasing the furnace temperature or reintroducing the sample tube.

A method to increase the rate of transfer of the released H-3 to the bubbler was also tested. The sample tube was swapped after 90 minutes with a sample tube containing 0.5 mL of deionised water spiked onto vermiculite (~0.2 g). It was hypothesised that this additional water would act as a carrier and accelerate the desorption of tritium that was reversibly deposited within the quartz work-tube. This method was successful with a significant increase in activity being transferred to the bubbler in the 30 minutes after introduction of water to the system. In the following 30 minutes the activity collected was only 0.004 ± 0.002 % of the total activity collected. A slight increase in activity was observed when reintroducing the sample tube. The total recovery over 5 hours was 128 ± 8 %.

Based on the tritium evolution profile experiments, a modified method was developed. The sample is loaded at 600 °C and heated to 900 °C as before. After 90 minutes, however, the sample tube is left in the quartz work-tube for an additional 30 minutes during the cool down period. After 30 minutes, the sample tube is swapped for one containing 0.5 mL of deionised water spiked onto vermiculite (~0.2 g). This is left in the work-tube for 30 minutes. After 30 minutes, the bubbler is disconnected (total collection time = 150 minutes). The sample zone should have cooled down to 600 °C ready for immediate loading of the next samples.

The activity distribution between the four key areas has been compared for all the operationally-exposed materials using the original heating programme (Figure 6a) and for the irradiated concretes and swarf metal samples using the modified heating programme (Figure 6b). Under these conditions, >95 % of activity was recovered in the scintillation vial (Bubbler A). Discounting the C-14 measurements for the structural concrete and the OBT sediment sample, which had large uncertainties on the measurement (<1 Bq total activity measured), less than 4 % (0.5 – 3.7 %) of the total activity measured was deposited in the bubbler neck. This was transferred to the sample by washing. It is recommended that this simple washing method is used routinely to maximise recoveries.

Comparing the reference activity and the total activity recovered in Bubbler A and correcting for a furnace recovery of 90 ± 10 % (Table 4), a good agreement was achieved for all operational-exposed materials for the two H-3 measurements as well as the C-14 measurement with the exception of tritium activity in the highly heterogeneous swarf metal samples.

Table 4: Comparison between the working activity value on the day of measurement and that measured in Bubbler A using either the original heating programme (OBT sediment sample and structural concrete) or the modified heating programme (irradiated concrete and swarf metal) including an assumed recovery of 90 ± 10 %. A LSC counting time of 1 hour was used.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **H-3 activity (Bq/g)** | | | **C-14 activity (Bq/g)** | |
| **Working value** | **Measured in 0.1M HNO3** | **Measured in Carbontrap** | **Working value** | **Measured** |
| Structural concrete (1.5 g) | 4.8 ± 0.5 | 6.5 ± 0.8 | 6.9 ± 0.8 | 0.55 ± 0.07 | 0.59 ± 0.08 |
| Irradiated concrete 1 (1.5 g) | 37 ± 8 | 38 ± 4 | 46 ± 5 | 2.5 ± 0.3 | 2.8 ± 0.3 |
| Irradiated concrete 2 (1.5 g) | 1700 ± 200 | 1900 ± 200 | 2200 ± 300 | 7.7 ± 0.9 | 8 ± 1 |
| Swarf metal 1 (1.5 g) | 0.9 ± 0.6 | 7.6 ± 0.9 | 2.2 ± 0.3 | 7.0 ± 0.3 | 8 ± 1 |
| Swarf metal 2 (1.5 g) | 4 ± 7 | 3.4 ± 0.4 | 19 ± 2 | 7.9 ± 0.1 | 8 ± 1 |
| OBT sediment sample (0.5 g) | 11 ± 3 | 10 ± 1 | 10 ± 1 | 0.44 ± 0.04 | 0.6 ± 0.1 |

# Discussion

Initially developed methods have been tested on a range of spiked samples and reference materials with sample loading at either 300 °C or 600 °C. No evidence of incomplete decomposition, incomplete oxidation or reduction in analyte recovery was seen using either heating programme. Whilst a small change in pressure during the combustion of plastic samples caused the airflow to stop temporarily, complete bubbler solution suck-back was not observed. Nevertheless, the anti-suck-back design with the developed washing technique would be able to recover any activity deposited following suck-back. Due to the faster rate of analyte transfer to the trapping solution, it is therefore recommended that all sample matrices are loaded at 600 °C and heated to 900 °C. It is also recommended that a closed-end sample tube with CuO oxidant (~4 g) loaded on top of the sample is used. This is particularly important for organic rich sample types where incomplete oxidation of the decomposition products can lead to discolouration of the bubbler solution, increased quenching and corresponding decrease in liquid scintillation counting efficiency.

The major limiting factor in the mass of sample taken was its carbon content, as too much CO2 release can lead to saturation of the Carbontrap medium. A high H2O content in the sample can also lead to phase separation upon addition of the scintillant. A sample mass limit of 0.2 g is therefore recommended for sample matrices with high carbon content (e.g. organic-rich soils, graphite, plastics, biota). A limit of 1 g is suggested for sample matrices with a moderate to low carbon content but a high H2O content (e.g. wet organic-poor soils, sludge, desiccants). Finally, a limit of 1.5 g is recommended for sample matrices with a low carbon content and a low water content (e.g. concrete, brick, organic-poor soils, metals).

With the exception of the plastic matrix, the efficiency of combustion was shown to be unaffected by sample loading temperature with complete combustion occurring after a 90-minute heating programme ramping to a maximum temperature of 900 °C. Combustion of plastic matrix was more effective when loaded at 600 °C. The efficiency of oxidation of the plastic matrix was improved by the presence of CuO oxidant and Pt-alumina catalyst as well as the use of smaller sample masses (0.2 g). The rate of transfer from the sample tube to the bubbler solution was faster for C-14 than H-3 with minimal post-trapping loss and deposition within the anti-suck-back chamber. The deposition of H-3 within this chamber could be mitigated by adopting the developed washing technique and including the reproducible loss in the overall method recovery correction. Slow transfer of analyte from the work-tube to the bubbler can also lead to cross-contamination and memory effects. Therefore, the recommended sample loading temperature is 600 °C. The optimised method with an associated method recovery of 90 ± 10 % has been shown to have a good level of accuracy and precision for reference materials.

The 90-minute heating programme used for spiked matrices and reference materials was found to be unsuitable for certain operationally-exposed materials containing strongly-bound tritium. Although the majority of the activity was found to be released during the 90-minute heating programme, the transfer of H-3 to the bubbler was delayed due to reversible deposition within the quartz work-tube. The method was therefore modified to extend the bubbler collection time and to introduce water to the system to speed up the transfer of tritium from the work-tube to the bubbler solution. This modified method was successful in recovering the activity released from irradiated concrete and swarf metal samples in 150 minutes.

The achievable limit of detection (LoD) depends on the sample mass taken, the chemical recovery, the counting efficiency and the background counts for a matrix matched blank sample. The chemical recovery has been estimated to be 90 % The counting efficiency and background varied depending on the instrument used to make the measurements as well as the counting matrix, trapping solution to scintillant ratio and instrument settings such as windowing. For liquid scintillation counting, typical background count rates for H-3 in 0.1 M HNO3, H-3 in Carbontrap and C-14 in Carbontrap of 1, 7 and 5 cpm respectively have been used in the calculation of LoD values. Counting efficiencies have been measured as 20 % (H-3 in 0.1 M HNO3), 15 % (H-3 in Carbontrap) and 35 % (C-14 in Carbontrap) based on 8 mL of trapping solution mixed with 12 mL of scintillant. A limit of detection of 1 Bq/g for both H-3 and C-14 is achievable for sample sizes as low as 0.2 g with a 1 hour counting time. To achieve a LoD of 0.1 Bq/g with only 1 hour counting time, it is recommended that a sample size of 1 – 1.5 g is taken and that tritium is trapped in 0.1 M HNO3 rather than Carbontrap.

The overall performance of the method indicated that it could be applied to other sample types providing that the total carbon content did not exceed the capacity of the trapping solution. A limit of detection of 1 Bq/g can be achieved for the co-trapped analytes with a liquid scintillation counting time of 1 hour per sample. The robustness of the method was assessed with the key factors being the sample loading temperature, the carbon content of the sample matrix, the bubbler collection time and the use of CuO oxidant and Pt-alumina catalyst for organic-rich samples.

Table 5: Recommended operating parameters.

|  |  |  |
| --- | --- | --- |
| Parameter | Range tested | Optimised selection |
| Sample tube design | Open-end, closed-end | Closed-end |
| Sample mass to load | 0.2 – 1.5 g | Sample dependant |
| Use of oxidant | CuO (4 g) or none | CuO (4 g) |
| Use of catalyst | 0.5 % Pt-alumina (10 g) or none | 0.5 % Pt-alumina (10 g)\* |
| Sample zone loading temperature | Room temperature up to 600 °C | 600 °C |
| Sample zone maximum temperature | 300 °C – 900 °C | 900 °C |
| Catalyst zone temperature | 300 °C or 800 °C | 800 °C |
| Time held at 900 °C | 30 mins – 60 mins | 60 minutes |
| Analyte collection time | 10 mins – 6 hours | 150 minutes |
| Airflow | 0.05 L/min and 0.1 L/min | 0.1 L/min |
| Anti-suck-back bubbler | Yes | Yes |
| Bubbler volume | 8 mL or 20 mL | 8 mL in scintillation vial |

\* 0.3 % Pt-alumina catalyst is now used as it functions identically

An operational assessment was also carried out. The operator requirements totalled ~25 minutes per 2 samples with the time for analysis, including 150-minute furnace run time and a 60-minute counting time, totalling <5 hours for 2 samples. The sample throughput for the furnace would readily enable 6 samples per working day. The instrumental footprint and overall size have been minimised to allow the furnace to sit within a fume cupboard. This is an advantage over the conventional Pyrolyser design. The Pyrolyser-Mini should have lower **operational costs** due to lower power and reagent consumption. Based on the analytical characterisation, a set of optimised operating parameters are recommended (Table 5).

Several aspects of the operation of the Pyrolyser-Mini have the potential for automation, including robotic sample loading and on-line measurement of radionuclide activity concentrations using a flow-through scintillation system. The sample tube loading process can also incorporate a Ni-Cr rod assembly to hold and handle the tube securely during loading and unloading. Whilst the automation of operator tasks would reduce labour costs and dose to the operator (if working with highly active samples), the most significant limit on sample turnaround is the duration of the heating programme. For the current proposed application of the Pyrolyser-Mini, the benefits of automation therefore do not significantly outweigh the cost of installation and maintenance. Additionally, online radiation detection could have a lower counting efficiency and would reduce the ability to tailor the duration of count time depending on the expected activity, required limit of detection and required turnaround time.

The design of the Pyrolyser-Mini furnace system could also permit deployment within a mobile laboratory environment. The simple need for a single-phase electrical supply (~220 V 13 Amp) for the Mini and the smaller footprint means it can be installed in a mobile laboratory extraction hood or glove box. The separation of the furnace from the control instruments introduces resilience in the event of service replacement of components. Also, no additional working space is required for the Mini with regards to heat output from the instrument, or for loading and removing the samples, as the work-tube orientation is vertical and the furnace is mounted on a swivel joint. The locking pins on the swivel joint ensure the Mini remains stable during operation. There is limited storage in a mobile laboratory for chemical reagents and waste, and the waste will generally have to be stored in the laboratory until it returns to its host organisation. The lower volumes of Carboncount™ and Carbontrap™ for operating the Mini are therefore advantageous. Operating without an oxygen cylinder is a significant advantage, as it overcomes the potential concerns of risks associated with operating with compressed oxygen, as well as the regulations required for transport and operating pressurised cylinders on a nuclear or other industrial site.

# Conclusions

The capability of the Pyrolyser-Mini system designed for the extraction of volatile radionuclide from diverse sample types has been evaluated. Particular features investigated are the extraction yields, the effectiveness of ‘hot-loading’ of samples and the novel bubbler trapping system. Hot-loading of the sample tube at 600 °C followed by heating up to 900 °C appreciably shortens extraction times and shows no loss of activity for all sample types examined. A complete heating and cooling cycle lasts 150 minutes. The addition of 1 mL of water to the system during the later cooling step scavenges any residual or deposited activity, minimising memory effects and maximises recovery.

The novel bubbler traps incorporate scintillation vials and reliably trap all released sample activity whilst minimising reagent consumption, waste production and operator weighing operations. The reduction in the volume of trapping media allows for a smaller mass of sample to be used to reach limits of detection of 1 Bq/g for a range of operationally-relevant matrices using short count times (1 hour). The Pyrolyser-Mini performance was assessed using spiked samples, reference materials and operationally-exposed materials. The total recovery was estimated to be 90 ± 10 % for H-3 and C-14 based on results from spiked matrices loaded at 600 °C. Cross-comparison between the performance of the conventional Pyrolyser-Trio system and the Pyrolyser-Mini is shown to be favourable.

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# References

Croudace I.W., Warwick P.E. & Marsh R (2011) Advances in tritium extraction methods to aid efficient waste characterisation *Nuclear Future,* 7, 48-53.

Croudace IW Warwick PE, and Morris JE (2012) Evidence for the Preservation of Technogenic Tritiated Organic Compounds in an Estuarine Sedimentary Environment. *Environ. Sci. Technol*., 46, 5704–5712.

Croudace IW, Warwick PE & Kim D-J. (2014) Using thermal evolution profiles to infer tritium speciation in nuclear site metals: an aid to decommissioning. *Analyt. Chem*., 86, 9177–9185.

Croudace I.W., Warwick P.E. & Marsh R (2017) A Suite of Robust Radioanalytical Techniques for the Determination of Tritium and Other Volatile Radionuclides in Decommissioning Wastes and Environmental Matrices, *Fusion Science and Technology*, 71:3,290-295*.*

Dean J., Collins S. and Ham G. (2013) Acoustics and Ionising Radiation Division, NPL Report IR 28. Environmental Radioactivity Proficiency Test Exercise 2012. NPL, Teddington, UK.

Dean J., Aitken-Smith P., Collins S. and Woods S. (2017) Chemical, Medical and Environmental Science Division, NPL Report IR 43, Environmental Radioactivity Proficiency Test Exercise 2016. NPL, Teddington, UK.

Kim D-J., Warwick P.E. and Croudace I.W. (2008) Tritium speciation in nuclear reactor bioshield concrete and its impact on accurate analysis. *Analyt. Chem.,* 80, 5476 – 5480.

Kim D., Croudace IW and Warwick PE (2012) The requirement for proper storage of nuclear and related decommissioning samples to safeguard accuracy of tritium data. *J. Hazard. Mater*., 213-214, 292–298.

Oh J.S., Warwick P.E., Croudace I.W. (2014) Rapid determination of tritium and carbon-14 in urine samples using a combustion technique. *J. Radioanal. Nucl. Chem*, 299, 187-191.

Warwick P.E., Kim D. Croudace I.W. & Oh J. (2010) Effective desorption of tritium from diverse solid matrices and its application to routine analysis of decommissioning materials. *Analyt. Chim. Acta,* 676, 93-102.

Warwick P.E., Croudace I. W., Marsh R. M., Baglan N. and Kim S. B. (2018) A new reference material for tritium organic molecules in sediment: results of an international intercomparison exercise. *J. Geostand Geoanalytical Res.* 42, 253-262. doi:10.1111/ggr.12207