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Interim report on the state of the art. Completion of design of experimental study

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Summary

A review of current tritium measurement techniques for soft waste together with a overview of the current state of knowledge about different forms of tritium likely to be present. An experiment to evaluate the effectiveness of the measurement techniques is described and planned which will constitute the remainder of the activities on this task.

Approval

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Abbreviations

CCFE	Culham Centre for Fusion Energy
UKAEA	United Kingdom Atomic Energy Authority
NPL	National Physical Laboratory
OBT	Organically Bound Tritium
PPE	Personal Protective Equipment
EPDM	Ethylene propylene diene monomer
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PP	Polypropylene
PU	Polyurethane
PE	Polyethylene

Summary

A state of the art of current measurement techniques for tritium in soft waste is given together with an overview of relevant experimental findings. The design of an experiment in collaboration with the National Physical Laboratory (NPL) which reviews the separate techniques is proposed and developed.



1 Introduction

Fusion and fission industries generate soft operational wastes which are contaminated with tritium from different processes. Regulators require appropriate characterisation of these wastes to identify and quantify the levels of tritium (and other radionuclides), which may be present, to reduce the opportunity for release into the environment. Where tritium is a small component of the radionuclide fingerprint, it may be acceptable to assay a waste container and calculate (estimate) the amount of tritium present from a dominant gamma emitting radionuclide present.

However, frequently the tritium source term is of a different origin to the activation components and therefore an alternative method of characterisation is required. Calorimetry is a technique currently in use to assay waste packages however, as well as being time consuming, it has relatively high levels for limit of detection (>10 TBq per drum) (Gilardi & Godot, 2009) and it is therefore less relevant for the majority of soft waste currently produced. Other methods such as the helium ingrowth method are only applicable to wastes with an activity range from 1TBq-10TBq per drum (Demange, Grivet, Pialot, & Chambaudet, 2002).

This proposal will consider the suitability for three alternative characterisation techniques on lower activity soft waste (<1MBq/g H-3):

1. Taking of small mass solid samples for tritium analysis
2. Monitoring of off gas within a package
3. Taking of larger mass solid samples for soaking and analysis of the soak liquid.

Each technique has significant uncertainties either in the sampling, measurement or methods by which the tritium is released. For example, the taking of small mass solid samples for tritium analysis is an expensive and time consuming process which involves opening waste drums and employing destructive techniques. If the tritium activity is not homogeneously spread within the drum then there is a risk that any sampling of individual items is unrepresentative of the total tritium content.

1.1 CCFE Operational Integrated Waste Strategy.

Solid waste is generated on site at UKAEA at an approximate rate of 42 tonnes per year. The current strategy for soft waste segregates waste such as items of furniture, housekeeping waste (e.g. coveralls, face masks, overshoes), filters, redundant plant and equipment into waste suitable for incineration and waste not suitable for incineration.

Currently, the site has no manned access to the vacuum vessel which in the past had created a lot of housekeeping waste. Entries are now carried out through remote handling. The majority of tritiated housekeeping waste produced on site is now created through support activities such as cleaning or maintaining components which occurs at radiologically controlled facilities. This waste consists primarily of personal protective equipment (PPE). For the purposes of this study the main forms of waste that are to be examined are representative of items such as gloves, overshoes, coveralls, masks and tent materials.

A dedicated Waste Handling Facility on site receives, stores, processes, compacts and packages radioactive waste. Bagged waste is opened in a fume cupboard allowing the contents to be segregated into separate waste types and sampled. The bags are then usually compacted using a low force as a standard pre-treatment. After this stage the wastes are stored in appropriate facilities on site before consignment to a suitable treatment route such as incineration.

Solid wastes that have been segregated according to similar activities over a similar period of time are subjected to a random sampling strategy whereby at least 1 sample is taken from each drum of

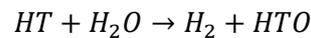
waste. These samples are then subject to a leach test followed by combustion to determine tritium content. A process known on site as TM3 or tritium method three.

2 Species of tritium in soft wastes

There are three main species of tritium that have the potential to be present within soft housekeeping waste. These are HT present as a volatile gas, HTO which can be found as condensate within the waste and organically bound tritium (OBT) which forms chemical bonds with the polymer material.

2.1 HT

HT is generally thought to have been removed from soft waste due to the volatile nature of the molecule or transformed into HTO. Tritium gas can be transformed into tritiated water via the exchange reaction



The equilibrium constant of which is approximately 6.25 at 298K and 3.4 at 398K (Lasser, 1989).

2.2 HTO

Tritium can exist as water vapour in the atmosphere or be present in liquid form. This water vapour is readily absorbed by polymeric materials as has been demonstrated experimentally (Iwai, Kobaysahi, & Yamanishi, 2011) both from water moisture and immersion in HTO containing water. Figure 2 shows their findings for EPDM exposed to an atmosphere of 740-1110 Bq/cm³ HTO moisture in gas form at 1kPa. For the purposes of the planned experiment this level of atmospheric tritium equates to a drum containing approximately 200 GBq of HTO.

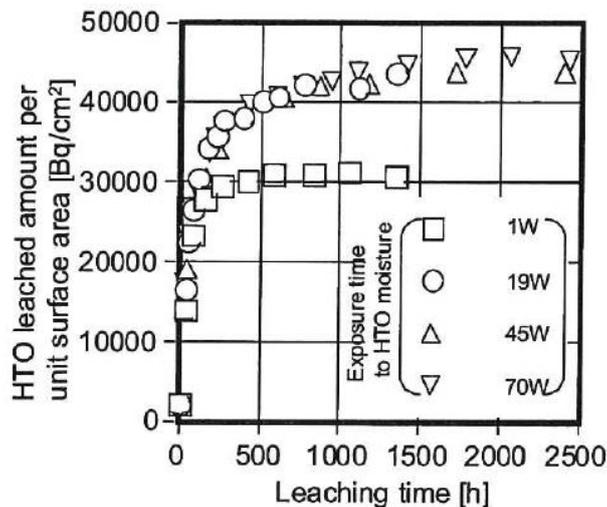


Figure 1: HTO present in EPDM exposed to HTO moisture from (Iwai, Kobaysahi, & Yamanishi, 2011)

2.3 OBT

The exact nature of OBT is often unclear in research on tritium in soft wastes and varying explanations of what it actually is exist (Kim, Baglan, & Davis, 2013), but it is generally described as tritium that has formed a chemical bond with the molecules that make up the polymer. This is often further divided into two categories of OBT, exchangeable and non-exchangeable. This classification primarily occurs in environmental assessment of the impact of tritium on organic matter, flora or fauna. (Diabate & Strack, 1993) defined OBT as arising either from exchange reactions or in enzymatically catalysed reactions replacing hydrogen in organic matter.

Exchangeable tritium occurs where hydrogen bonds can be easily dissociated in organic molecules (or in our case polymers) with a tritium-hydrogen exchange reaction occurring. The tritium in these positions is a function of the tritium concentration in cellular water for living organisms or HTO absorbed by the polymer or in the drum atmosphere for soft waste. This suggests that there will be a certain amount of time required for an equilibrium to be formed with a particular concentration of HTO in the water and that the exchangeable tritium could be eventually removed by washing with tritium free water. (Kim, Baglan, & Davis, 2013) mention that in this case the tritium is bonded to sulphur, nitrogen or oxygen atoms. Soft waste such as PVC which contain chlorine could foreseeably have exchangeable OBT linked to the chlorine atoms.

Non-exchangeable tritium is defined as only being incorporated into stable bonds to carbon atoms via enzymatically catalysed reactions such as photosynthesis. Initially there appears to be a lack of a suitable catalyst for soft waste with the absence of enzymes which could facilitate these reactions and therefore presumably an absence of non-exchangeable tritium according to this definition. However, there is reason to believe that the ionizing radiation of tritium can act as a suitable catalyst breaking down molecules to free radicals which could combine with tritium to form tritiated organic molecules. This is a phenomenon that has been reported for steel surfaces where methane or organic impurities are broken down with outgassing from the samples recorded having tritiated organic contents of 24-59% of the total tritium (Belot, Camus, Marini, & Raviart, 1993). The surface content of tritium is much higher in steels (see figure 1) than polymers due to the water layer that is bonded to the surface so the magnitude of this effect could be expected to be smaller in polymers.

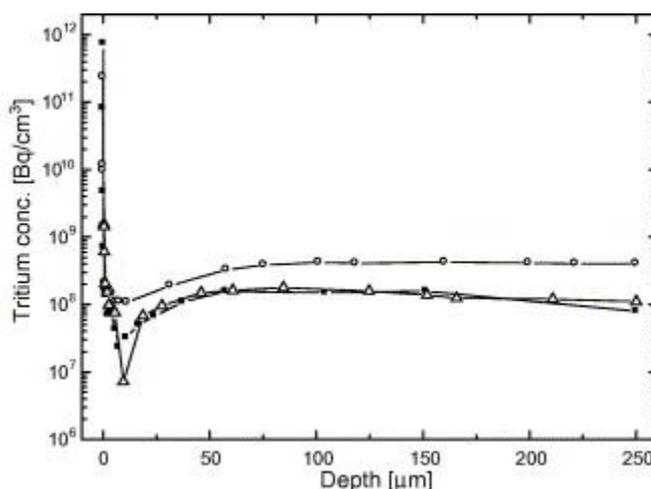


Figure 2: The depth profile of tritium in 3 different stainless steel samples from (Torikai, Penzhorn, Matsuyama, & Watanabe, 2004)

There is also a definition of buried tritium whereby tritium is not carbon bound but folded into macromolecules by a biochemical mechanism. This will not be considered further again due to the absence of a suitable biochemical mechanism in polymers which could facilitate the creation of buried tritium.

3 Comparison of existing methods of measuring tritium species content in polymer materials

3.1 Water Leeching

The current UKAEA waste sampling strategy (TM3) leaches polymer samples to establish HTO content in a volume of water approximately 1-2 litres. This soak is left for a month for the HTO to be fully released from the material. This assumption of a full release of water soluble tritium will be tested by the proposed experiments. Based on the results of (Iwai, Kobayashi, & Yamanishi, 2011)



who exposed polymer materials to HTO in liquid form it is likely that the whole amount of HTO present in the material is not removed by the process of soaking in purified water. The HTO present will rather be diluted by the water and a relationship between the concentration of HTO in the water and that in the material will develop as can be seen in figure 3.

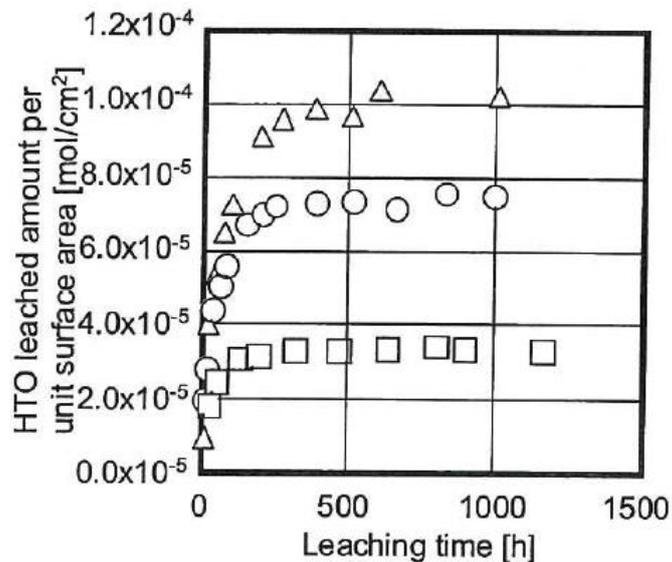


Figure 3: HTO present in Viton immersed in 70,000 Bq/cm³ liquid HTO (□ 1 week, ○ 26 weeks, △ 52 weeks) from (Iwai, Kobaysahi, & Yamanishi, 2011)

The process adopted by Iwai et al for measuring the HTO per unit surface area after exposure to liquid HTO was to leach the sample in 100 cm³ of purified water and after the value of HTO content had stabilised to immerse it in another 100 cm³ volume of purified water, using summation of the two values to determine HTO content. This in itself shows the dilutive properties of a leach measurement although the research doesn't give specific values for the difference between the two measurements.

A comparison of common polymeric materials with respect to the relationship between levels of tritium exposure and the amount of HTO found in an initial water leach followed by subsequent water leaches with the HTO value recorded will enable an experimental investigation of this property of polymer materials. The process that Iwai et al followed with purified water leaches being used to measure the total amount of HTO present in the material after it has been exposed should be avoided as this would potentially suffer from the same effects that we are trying to quantify. It is suggested that water leaches are used to evaluate how much tritium is being washed out of the material before a further step such as vacuum drying is used to remove any remaining tritiated water from the material.

Research conducted at CCFE in the past has assumed that any tritium still left in the material after this soak is OBT (Bernstein, et al., 2009). This has led to results such as table 2 which are likely to have overestimated the amount of OBT present. This research followed current waste practices at CCFE with a month long soak followed by combustion of the sample with a collection of released gaseous tritium in a sequence of water bubblers.



Material	Average Tritium Concentration (MBq/g)			Fraction of Inventory (%) ^{d)}	
	Combustion	Leaching and combustion	RLG	Water- soluble	Water non-soluble
Cellulose	25.9	3373	1155	99.97	0.03
PVC	59.7	360	373	89.4	10.6
PE	114	103	313	68	32
PP ^{b)}	18	24	146	45	55
Rubber ^{c)}	70.8	455	417	97.7	2.3
PU	23.5	579	223	99.6	0.4

- a) PVC is polyvinylchloride; PE, polyethylene; PU, polyurethane
- b) Polypropylene (PP) is a plastic of PE group.
- c) Rubber is of Nitrile group
- d) Was estimated from results of leaching followed by combustion

Table 1: levels of OBT and HTO in polymer wastes from (Bernstein, et al., 2009)

The ability to better define the actual level of HTO and OBT present within the soft waste would improve the accuracy of the characterisation. For example, according to the information in table 1 if the water leach was conducted on mainly cellulose materials and then an item of PP was combusted to give a correction for OBT then according to table 2 the error could be as large as +/- 55%.

Other results looking at the amount of OBT present within polymer waste suggest that the actual levels of OBT are much lower if they are present at all (Antoniazzi & Shmayda, 1995).

3.2 Headspace Method

At UKAEA the understanding of the headspace method is based on a Winfrith report (Weatherill, 1985). This technique does not provide an estimation of the products of exchange reactions between the polymers and the diffusing gas. Therefore, much like the water leaching method the OBT content is neglected. An equation relating to Fick's law is used to assess what the tritium content in the drum atmosphere implies for the levels of tritium in the material.

$$\text{Equation 1: } Hg = \frac{1}{2} \times Co \times l \times A$$

$$\text{Equation 2: } Co = S \times P$$

Where

Hg = Gas hold up (std mls)

Co = Concentration in the solid (std ml cm⁻³)

l = thickness (cm)

A = Area (cm²)

S = Solubility Constant (std ml cm⁻³ atm⁻¹)

P = Pressure (atm)



The polymers have different solubility constants for HTO and HT so often an assumption is made that all the tritium inside the drum is in the HTO form (as sniff measurements are often unable to distinguish between the two types). The effect of this can be determined for the case of neoprene which has a solubility constant of 3×10^{-2} std ml cm^{-3} for hydrogen and 3420 std ml cm^{-3} for water (Brandup & Immerman, 1975). A further error would be introduced by the isotope effect between H_2 and HT and H_2O and HTO on the solubility constant. For instance, with the case of PTFE the solubility constant of T_2 (1.2) is greater than that of H_2 (0.5) (Miyake, Matsuyama, Ashida, & Watanabe, 1983). Because different materials have varying levels of solubility constants for HTO this makes it important to know the exact makeup of the waste drum in terms of material types. The other methods which use direct sampling have the same issue which is addressed by a representative sample containing a mixture of materials being taken from the drum before water leeching or pyrolysis. How representative this sample is is determined by the skill of the operator in selecting what material to analyse.

For the method to work the assumption is made that the material is diffusionally 'thin'. The definition of thin is arbitrary and concerns how long the material takes to reach a certain percentage of the long term steady rate in the time of exposure. This is given by a time lag value defined by

$$\text{Equation 3: } Dt/l^2$$

Where

D = diffusion coefficient

l = thickness of the material

For the purposes of waste inside a drum the time of exposure is given by how long the waste has been present with an approximately constant atmosphere of tritium within the drum. The Weatherill report considers the definition of thin to mean that $Dt/l^2 > 0.14$.

A demonstration of this effect of reaching steady state can be seen from the work done by Antoniazzi and Shmayda on outgassing measurements relation to tritium inventory for soft wastes (Antoniazzi & Shmayda, 1995). Figure 5 demonstrates this where some clean paper products were sealed in a waste bag with contaminated vinyl gloves and progressively measured for contamination.

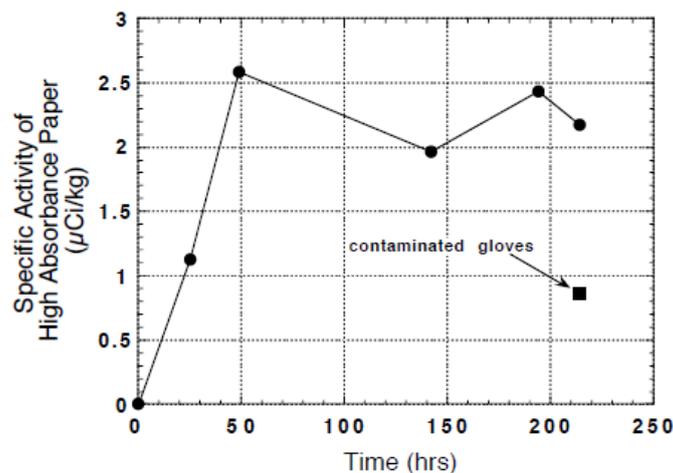


Figure 4: Tritium inventory in initially clean paper products sealed in with contaminated vinyl gloves from (Antoniazzi & Shmayda, 1995)

The results shown in figure 5 show a lag of about 50 hours before the tritium inventory in the paper reaches a peak. This makes sense considering the high diffusion coefficient that would be present in high absorbance paper (with other polymer materials having a much lower diffusion coefficient), and the relation of this to the calculated value for time from equation 3. Other materials can be

expected to have much lower diffusion coefficients and this shows the importance of leaving a suitable amount of time for the drum of waste to settle before measuring the tritium content via this technique.

3.3 Pyrolysis Technique

Pyrolysis of samples is the most effective technique for measuring the tritium content but it can be expensive and operator intensive and suffers from localised effects. Samples are heated in a furnace and as the tritium is liberated it is converted to HTO via a catalyst which can be platinum or copper oxide. The HTO is then trapped in a bubbler of purified water (or an alternative appropriate medium). This water is then measured via liquid scintillation counting.

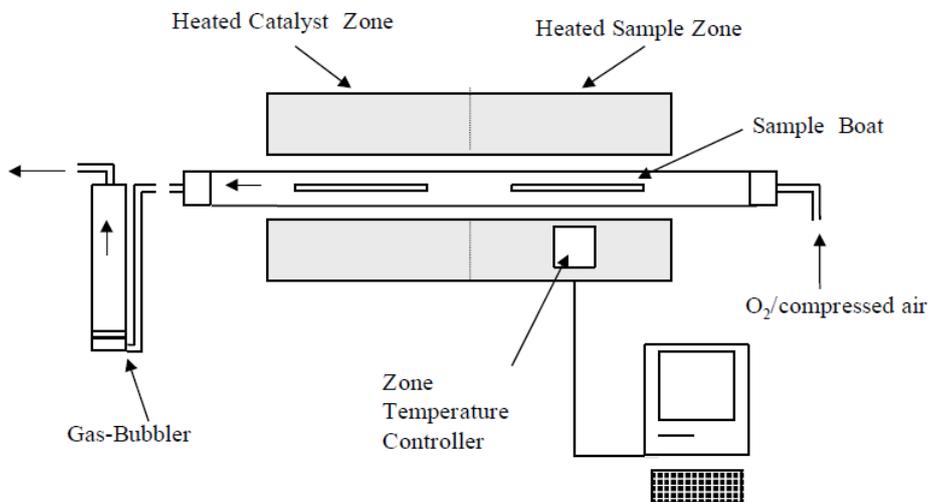


Figure 5: Carbolite MTT-Carbon14 – Tritium Furnace setup from (Wickenden, 2014)

Typical protocols for combustion involve measuring a 5g sample and the sample is combusted over a period of time to ensure that the catalyst is not overwhelmed which would result in an incomplete conversion of HT to HTO. This can involve ramping the temperature up and then holding it at a level where the sample is being carbonised rather than fully combusted before raising the temperature to a point where it is being combusted. The gas used can often be compressed air below a temperature before the combustion proceeds in a compressed air atmosphere above temperatures of 600 °C (Wickenden, 2014). An example protocol from a furnace manufacturer for plastics combustion is given in table 2.

Plastics (Polyethylene, Polyester, Polypropylene, Plasticised Polyvinyl Chloride).

Sample size of 5g.

Stage One	Raise sample temperature to 350°C from room temperature over thirty minutes.
Stage Two	Dwell at this temperature sixty minutes.
Stage Three	Raise temperature to 700°C over thirty minutes. Change the compressed air over to pure oxygen at 600°C.
Stage Four	Dwell at 700°C for sixty minutes.
Stage Five	Cease heating the sample zone and allow to cool.

Table 2: combustion protocol for plastics from (Wickenden, 2014)

The necessity for a cooling period after the pyrolysis can often mean that only one sample can be analysed per day by a trained operator. The solubility of tritium in polymer materials varies so an analysis of a drum of waste solely by combustion would have to take a sample from each material type present which would often result in long delays before consignment.

4 Experimental Design

4.1 Sample Selection

An initial review of material types present at Culham suggests that the following common plastics would be a good starting point for sample types.

Material	Use at UKAEA
PVC	Stretch vinyl polyco gloves
PP	Microgard plus suits
PU	PPE suits
PE	Waste bags
Cellulose	Tissues/paper towels

Table 3: Suggested materials for experimental tests

Due to the problems reported in associated experiments with ascertaining the exact makeup of some items it was decided to purchase base materials from plastic manufacturers with the exact composition known before exposing these samples to a tritiated atmosphere in a waste drum. Correspondence with the manufacturer of vinyl gloves determined for instance that the PVC gloves also contained a mixture of ingredients including

- Di-isononyl Phthalate
- Di-(2-ethylhexyl) adipate
- 2,2,4-Trimethyl-1, 3-Pentanediol Diisobutyrate
- Stabiliser Calcium Zinc

Which would make it difficult to ascribe any tritium effects in the gloves to a particular additive which contain additional hydrogen carbon chains and oxygen atoms for non-exchangeable and exchangeable OBT respectively (see figure 6).

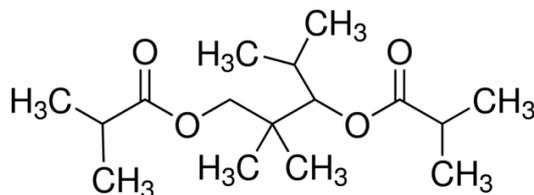


Figure 6: The chemical formula for 2,2,4- Trimethyl-1, 3-pentanediol diisobutyrate

However, the possibility of comparing PVC with the vinyl polyco gloves will be explored as part of the research.

The thickness of the samples will be a uniform 1.5mm and the area of the surface will be the same to eliminate any surface area to bulk ratio effects from affecting the results.

4.2 Sample Preparation

The samples will comprise of the following material types purchased from plastics manufacturers together with items (nitrile and PVC gloves) containing additives for the purposes of comparison and finally paper towels.

- Polyvinyl chloride
- Polypropylene
- HDPE
- Polyurethane
- Nitrile rubber CQ grade
- Cellulose paper towels
- Nitrile gloves
- PVC gloves

These will be of a uniform thickness of 1.5mm and will be cut prior to exposure into equally sized (area) samples.

Once the samples have been prepared 3 drums on site have been identified with varying activities (tested using the UKAEA process of water leaching and combustion). These activities are 474 GBq, 4 GBq and 158 MBq respectively. The samples will be placed within these drums for a period of approximately 6 months before the experiment commences. At this point the samples will be removed and stored in a freezer ready for the experiment.

The drum atmosphere represents a faithful recreation of the environment that the materials will be stored in prior to consignment. Unlike other studies which exposed the materials to gaseous hydrogen containing tritium the drum will contain tritium in HTO form as well as HT. This will be quantified using the equipment from the National Physical Laboratory (NPL).

4.3 Tritium Measurement in Samples

Vacuum drying is an industry standard method of drying polymers and therefore suitable for removing the HTO from the polymer samples. In order for the water vapor to be captured a cold trap will be installed in the foreline before the pump. A roughing pump will be utilised to reduce the pressure in the working tube to a level where the sublimation point of HTO is easily reached at temperatures close to ambient (figure 7). A period of 4-6 hours will be initially tested for efficiency of

HTO removal. This will be evaluated by running initial samples past this time period and seeing if further HTO is present in the cold trap.

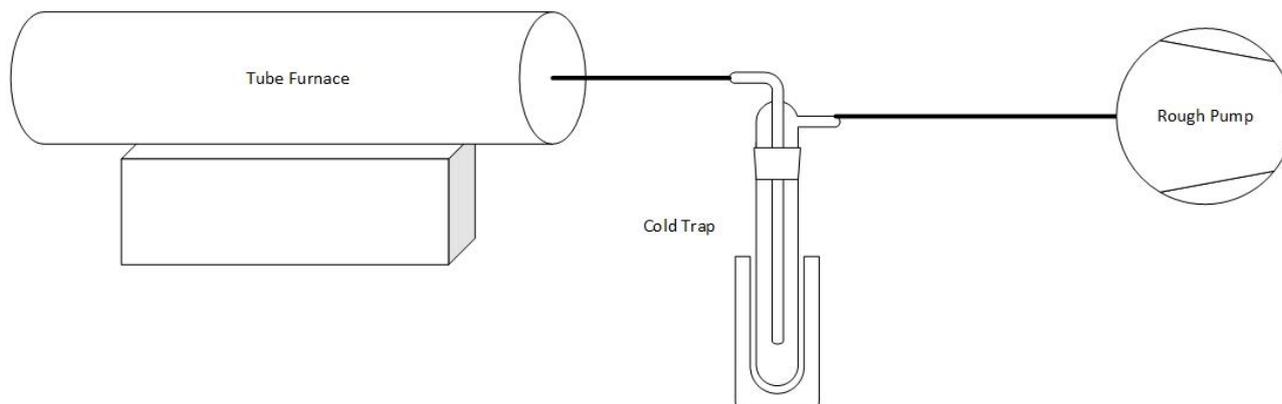


Figure 7: The setup intended for removing the HTO water vapour from the sample using vacuum drying.

The temperature being near to ambient will mean that there is no likelihood that the polymers will thermally degrade which could release other forms of tritium. The near vacuum in the working tube will also mean that exchangeable OBT will remain in its current form rather than being converted.

Subsequent to this the polymers will be washed in water overnight to remove/check for any exchangeable OBT following the process outlined by (Kim & Korolevych, 2013). Once this has occurred the sample will be pyrolysed in a combustion furnace with a copper oxide or platinum catalyst. It is expected that this final step will remove any non exchangeable OBT that is present within the samples.

4.3.1 Water Leaching

To evaluate the efficiency of water leaching in extracting the HTO from the samples some of the prepared samples will be evaluated via water leaching before they are processed through the technique outlined above. This will allow an accurate figure for how much HTO is removed from the sample using this technique of analysis.

4.3.2 Drum Sampling

Drum sampling will take place measuring the HT and HTO in the drum atmosphere before the samples are removed for analysis. This will allow for a comparison of the levels of tritium found in the samples and the concentration of tritium in the drum atmosphere. This will take place as part of a collaboration with the NPL who will sample the drum using an online tritium monitor (figure 8)



Figure 8: The WILMA online tritium monitor intended for use in drum sampling

4.4 Sampling Programme

Material Type	Water Leaching LS	Vacuum Drying	HTO LS	Pyrolysis Runs	Exchangeable OBT LS	Non - Exchangeable OBT LS
PVC	6	15	15	15	15	15
PP	6	15	15	15	15	15
PU	6	15	15	15	15	15
PE	6	15	15	15	15	15
Nitrile Rubber	6	15	15	15	15	15
Cellulose	6	15	15	15	15	15
PVC Gloves	6	15	15	15	15	15
Nitrile Gloves	6	15	15	15	15	15
Total Vacuum Drying		120				
Total Pyrolysis				120		
Total LS Counting						408

Table 4: Sampling requirements from experimental plan. LS (liquid scintillation counting)

5 Conclusions

UKAEA operate a sampling strategy for tritiated soft wastes that combines water leaching and a pyrolysis correction factor to assign an overall level of activity to soft waste before consignment. There are other characterisation methods available such as the head space method, however this method is unable to measure non-exchangeable OBT tritium and because it is not a direct sampling method mixtures of different materials of soft wastes could lead to complications.



There are potential issues with each of these methods. Water leaching for HTO removal will likely result in the leachate diluting the levels of HTO in the sample rather than completely removing it. The head space method could also give an underappreciation of the amount of tritium within the samples if sufficient time is not given for the tritium off-gassing to reach a steady state. Finally, pyrolysis is thought to suffer from an unequal distribution of tritium in different materials and also from hot spots on individual items.

A programme of research using equipment that has been designed to differentiate between HTO and OBT in a variety of soft wastes representative of the different materials has been planned for use on site at UKAEA. There will also be a comparison of the standard method of water leaching on the samples and measuring the residual HTO to assess the efficiency of the water leach measurement.

A further drum will be measured over a period of time from initial packing to determine the effects of tritium build up within the drum atmosphere on the accuracy of the headspace method. For each of these tests a relationship between polymer type and the amount of HTO retained as water within the sample will be explored. If possible this will be linked back to the level of tritium measured in the drum atmosphere (with the varying species of tritium in the atmosphere taken into account). Finally, the levels of non exchangeable and exchangeable OBT within the samples will be measured to verify whether there is an appreciable amount of tritium retained as non-exchangeable OBT. The results of this analysis will be used to inform the appropriateness of current tritium measurement strategies such as the TM3 method.



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