TRANSAT

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Final Report

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Summary

The results from an experimental study by UKAEA and the NPL looking at the effectiveness of current techniques for tritiated soft waste management are presented. Links between the levels and forms of tritium within tritiated atmospheres and tritium within representative soft waste items are investigated. The forms of tritium within the soft waste items were also explored with a pyrolysis programme designed to measure easily removable tritium with intransigent tritium that required a full combustion to be measured. The results from this work were used to comment on the effectiveness of current soft waste measurement techniques such as head space method, pyrolysis and water leeching.

Approval

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Abbreviations

CCFE	Culham Centre for Fusion Energy
UKAEA	United Kingdom Atomic Energy Authority
NPL	National Physical Laboratory
PPE	Personal Protective Equipment
PVC	Polyvinyl chloride
PP	Polypropylene
PU	Polyurethane
PE	Polyethylene

Summary

The results from an experimental study by UKAEA and the NPL looking at the effectiveness of current techniques for tritiated soft waste management are presented. Links between the levels and forms of tritium within tritiated atmospheres and tritium within representative soft waste items are investigated. The forms of tritium within the soft waste items were also explored with a pyrolysis programme designed to measure easily removable tritium with intransigent tritium that required a full combustion to be measured. The results from this work were used to comment on the effectiveness of current soft waste measurement techniques such as head space method, pyrolysis and water leeching.

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. Other commonly used methods involve a mixture of the following

1. Taking of small mass solid samples for tritium analysis via pyrolysis
2. Monitoring of off gas within the headspace of a waste drum
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.

2 Experimental Details

2.1 Sample Types

Representative waste samples were selected based on current PPE used at nuclear sites. The samples comprised 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 were of a thickness of between 1-2mm and will be cut prior to exposure into equally sized (area) samples. The sheet plastic supplied by the manufacturers was cut into wafer samples of 150x40mm whilst the other items (gloves and paper towels) were installed as supplied. 3 separate 200 litre waste drums containing tritiated soft waste from operations on site were selected opened and the fresh samples were added to each drum before they were resealed. After the samples were retrieved and analysed the HDPE and PP sheet plastic material types were found to have been contaminated with only trace levels of tritium. Due to this they were not used further in the analysis.

2.2 Standard UKAEA Analysis and further Water Leach Analysis

Data was also collected from the tritium analysis on the drum contents that had been undertaken by the waste management group prior to loading the drums with fresh samples. This consisted of a water leach of approximately 1kg of the drum contents after being left to stand in a 2 litre bottle filled with demineralised water for a period of at least a month. The drum C contents were not subjected to a water leach measurement as this is not used on the UKAEA site for PVC materials. 10g sub samples were also taken from the drums for pyrolysis.

Separate from this PPE used in operations at the waste management facility on site was collected and sent for a more detailed analysis which consisted of multiple measurements from the water leachate on a weekly basis to determine how quickly an equilibrium tritium value might be reached. This analysis included nitrile rubber gloves, PVC polyco gloves and LDPE sheeting.

2.3 Headspace Gas Sampling

After the samples had been stored for a period of six months the atmosphere of the drums were sampled by UKAEA and NPL staff for tritium using the WILMA device developed by a collaboration between the National Physical Laboratory and Lablogic (figure 1).

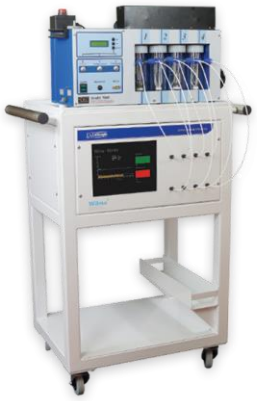


Figure 1: The WILMA online tritium monitor used for measuring tritium content within the atmosphere of the waste drums.

The drums were sampled for 20 litres of gas using a contained loop setup with the WILMA gas sampler attached to the two valves on the drum lids using rubber hosing. The gas flow was controlled using the WILMA unit pump and flowmeter.

Figure 2: An example of the double valved lids used on the waste drums for the experimental drums

Due to the WILMA unit incorporating a Marc 7000 tritium sampler the analysis was able to differentiate between HT and HTO in the gas from the drum. For drum B only 5.2 litre of gas was possible to be sampled, a situation potentially caused by a denser packing fraction within the container.

The samples were then removed from the drum and stored in airtight foil bags within a freezer in the waste management building.

2.4 Main Experiment Sample Analysis

The sample analysis consisted of a stepped pyrolysis programme targeting different species of tritium within the sample.

- Step 1 – Sample was heated to 100°C and held at this temperature for 4 hours. Aliquots were taken from the bubblers for liquid scintillation counting
- Step 2 - Fresh bubblers were used and the sample was heated to 400°C. Aliquots were taken from the bubblers for liquid scintillation counting
- Step 3 – Fresh bubblers were used and the sample was heated to combustion (850°C) and held at this temperature for 4 hours. Aliquots were taken from the bubblers for liquid scintillation counting

All liquid scintillation counting for the experimental samples was carried out using an UKAS accredited method.

3 Results

3.1 Standard UKAEA Analysis and further Water Leach Analysis

Table 1 gives the results of pyrolysis of sub samples of items within the drums prior to the loading of the experimental samples.

Drum	Material Type	Sample Mass (g)	Analytical Result (Bq/g)
A	Housekeeping	10	35070 ± 7014
B	Housekeeping	10	1231 ± 246
C	PVC	10	4050943 ± 810189

Table 1: Analysis of 10g samples taken of the items already present in the waste drums before the experimental samples were loaded.

Table 2 shows the results of water leaching of the larger initial sample from the waste drums. As mentioned earlier drum C is not shown because of the issues surrounding water leach of PVC based materials.

Drum	Sample Activity Bq/L
A	4323909
B	201179

Table 2: Water leach analysis of samples taken from drums used for experimental programme. Samples left to sit in demineralised water for a period of a month.

Further analysis was done on two separate waste batches that arose from PPE worn/used by operators at the waste management facilities. These materials were not subject to an interim storage period in a waste drum container.

	Nitrile Rubber	PVC	LDPE
Initial water leachate volume/l	1.456	1.588	1.434
Waste sample mass/g	746	556	548

Table 3: The experimental conditions for the first waste leach analysis

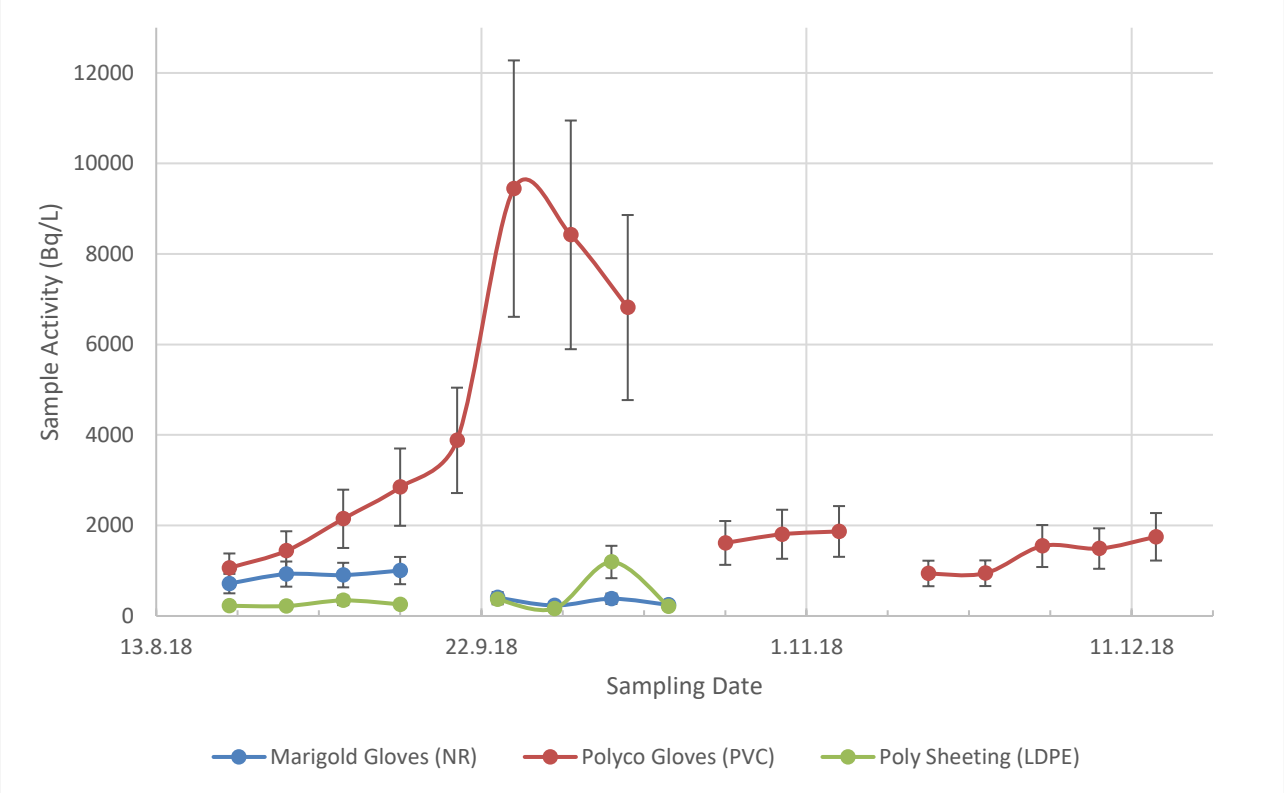


Figure 3: Results from the first water leach trial. Waste types were stored separately in 2 litre bottles with demineralised water. Samples were taken of water and analysed using liquid scintillation counting on a weekly basis. PVC trials extended to 3 separate water leaches due to first leach not reaching steady value.

Table 4 shows the conditions for the second water leach analysis with figure 4 giving the results.

	Nitrile Rubber	PVC	LDPE
Initial water leachate volume/l	1.636	1.828	1.879
Waste sample mass/g	524	316	248

Table 4: The experimental conditions for the second water leach analysis

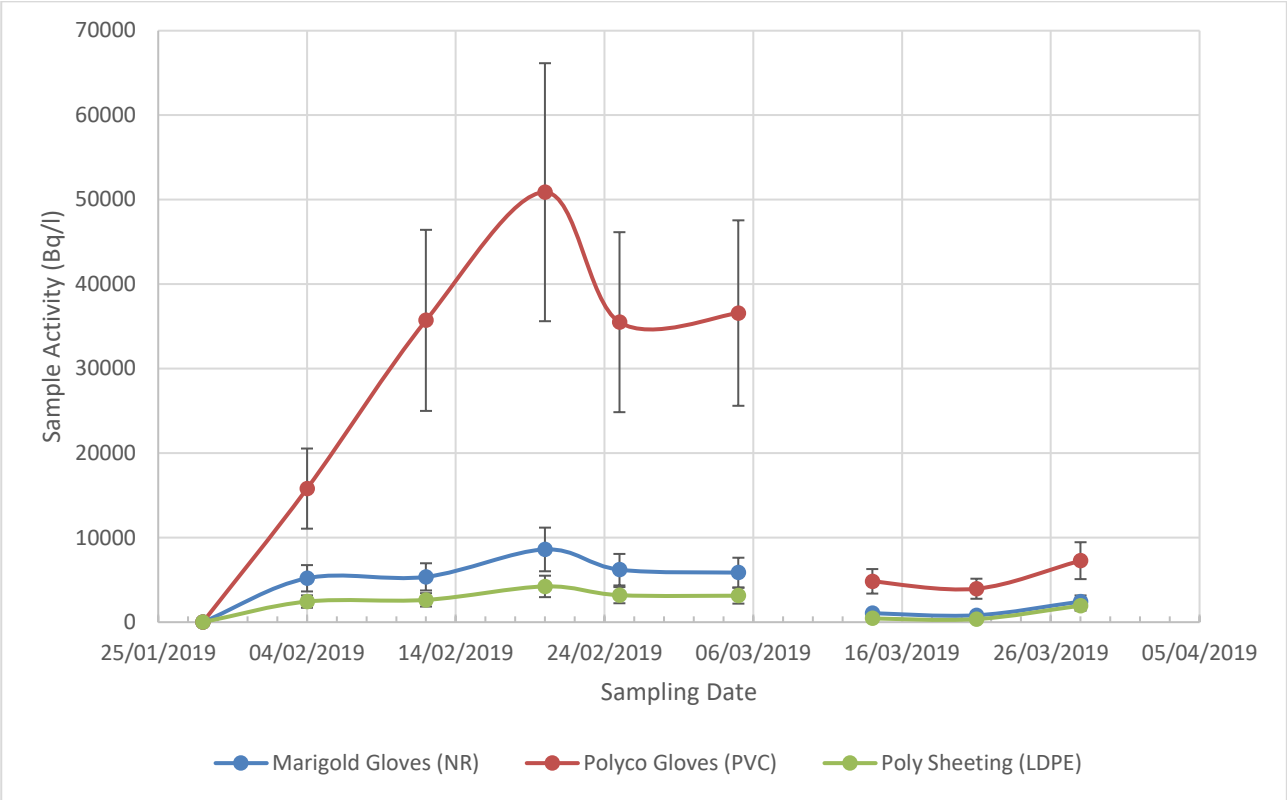


Figure 4: Results from the second water leach analysis subject to the same conditions as the first except that only two separate water leaches were used for the analysis.

3.2 Drum Atmosphere Monitoring

The results of the measurement of tritium in the gas present inside the experimental drums are given in figure 3. The HT fraction in the gas was consistent across all three measurements with an average value of 20.6% HT (SD 0.75). Drum A and B contained soft waste from general operations such as PPE and paper towels and wipes. Drum C contained PVC sheeting from tent material.

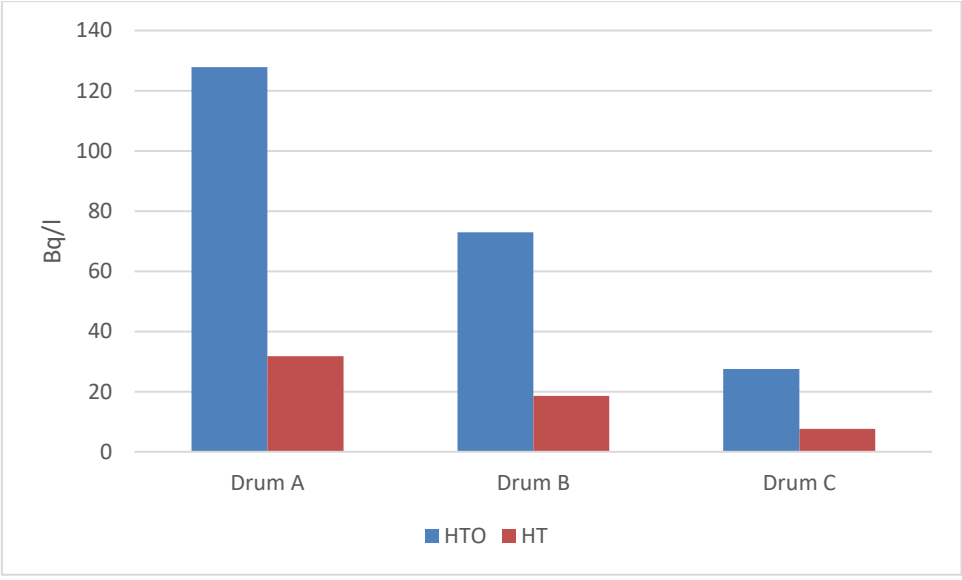
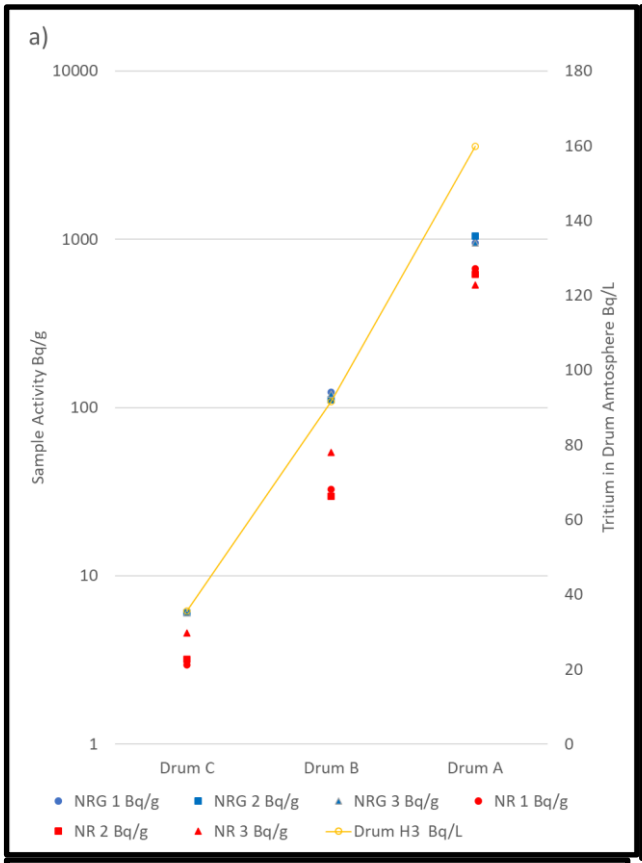
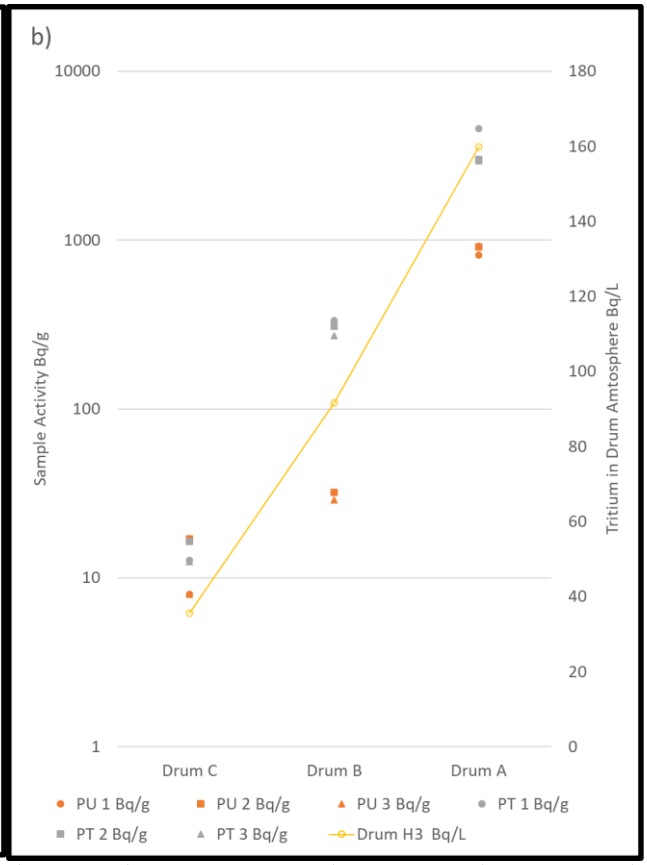


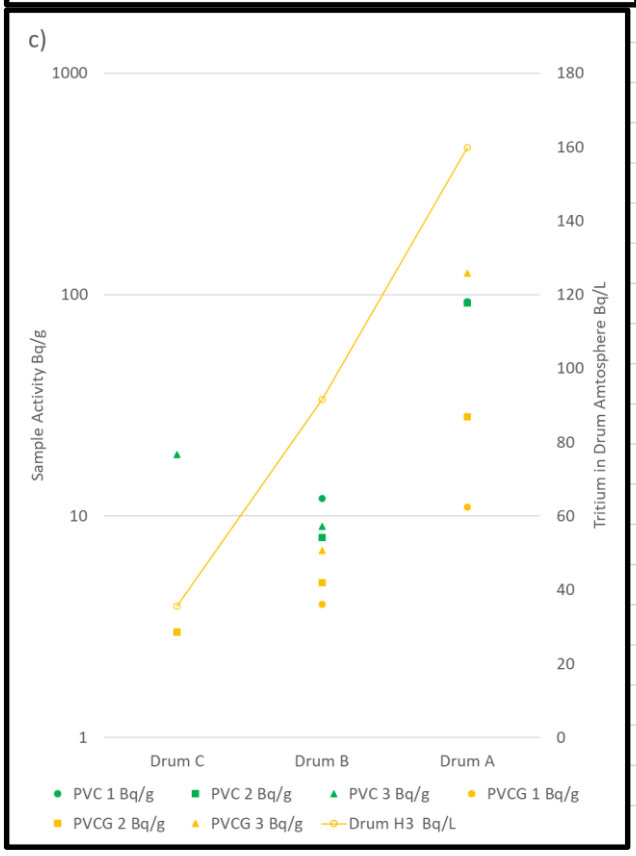
Figure 5: Results of measurements of tritium concentration in experimental drums. Activity given in Bq per litre of gas pumped from the drum.

3.3 Headspace Gas plotted against Total Inventory

In order to comment on the potential effectiveness of the headspace method the results from figure 5 were compared with the tritium activity in the samples measured through the experimental programme. The HT and HTO per drum were summed for a overall activity per litre pumped and compared with the total activity in Bq/g of the samples from the three experimental stages in figure 6,7 and 8. The different steps of the experimental programme included pyrolysis so therefore it represents the total amount of tritium present within the samples.







Sample	Drum C Bq/g	Drum B Bq/g	Drum A Bq/g
PVCG 1	3 ± <LOD	4 ± <LOD	11 ± 2
PVCG 2	3 ± <LOD	5 ± <LOD	28 ± 3.5
PVCG 3	3 ± <LOD	7 ± <LOD	125 ± 8.7
PVC 1	3 ± <LOD	12 ± 2	93 ± 7
PVC 2	3 ± <LOD	8 ± 2	92 ± 7
PVC 3	19 ± 3.3	9 ± 1	92 ± 7
PT 1	13 ± 1.3	332.8 ± 34	4560 ± 501
PT 2	16 ± 1.9	309 ± 34	3010 ± 330
PT 3	13 ± 1.3	271 ± 30	2946 ± 323
NR 1	3 ± 0.5	32.72 ± 3.4	669 ± 73
NR 2	3 ± 0.6	30 ± 1.2	618 ± 66
NR 3	5 ± 0.9	54 ± 3.4	536 ± 59
NRG 1	6 ± 0.8	123 ± 7.6	954 ± 39
NRG 2	6 ± 0.9	111 ± 6.7	1048 ± 43
NRG 3	6 ± 0.8	120 ± 7	951 ± 39
PU 1	8 ± 1.7	32 ± 4.2	816 ± 35
PU 2	17 ± 2.4	32 ± 4.1	911 ± 39
PU 3	8 ± 1.5	29 ± 4.2	924 ± 39

Figure 6: Tritium inventory for selected soft waste samples as a function of tritium in sealed environment of waste drum for a) nitrile rubber gloves and nitrile rubber, b) polyurethane sheet plastic and paper towels, c) PVC gloves and PVC sheet plastic. Original data plus uncertainties on table next to graphs. Sample activity scale logarithmic.

3.4 Experimental Programme

The experimental programme was used to compare the bakeout tritium (1st stage – sample heated to 100ºC and held there for 4 hours) with the overall tritium present within the sample. The overall tritium present in the samples is shown in figure 6. Drum C was not used due to the overall lower level of activity of samples in this drum.

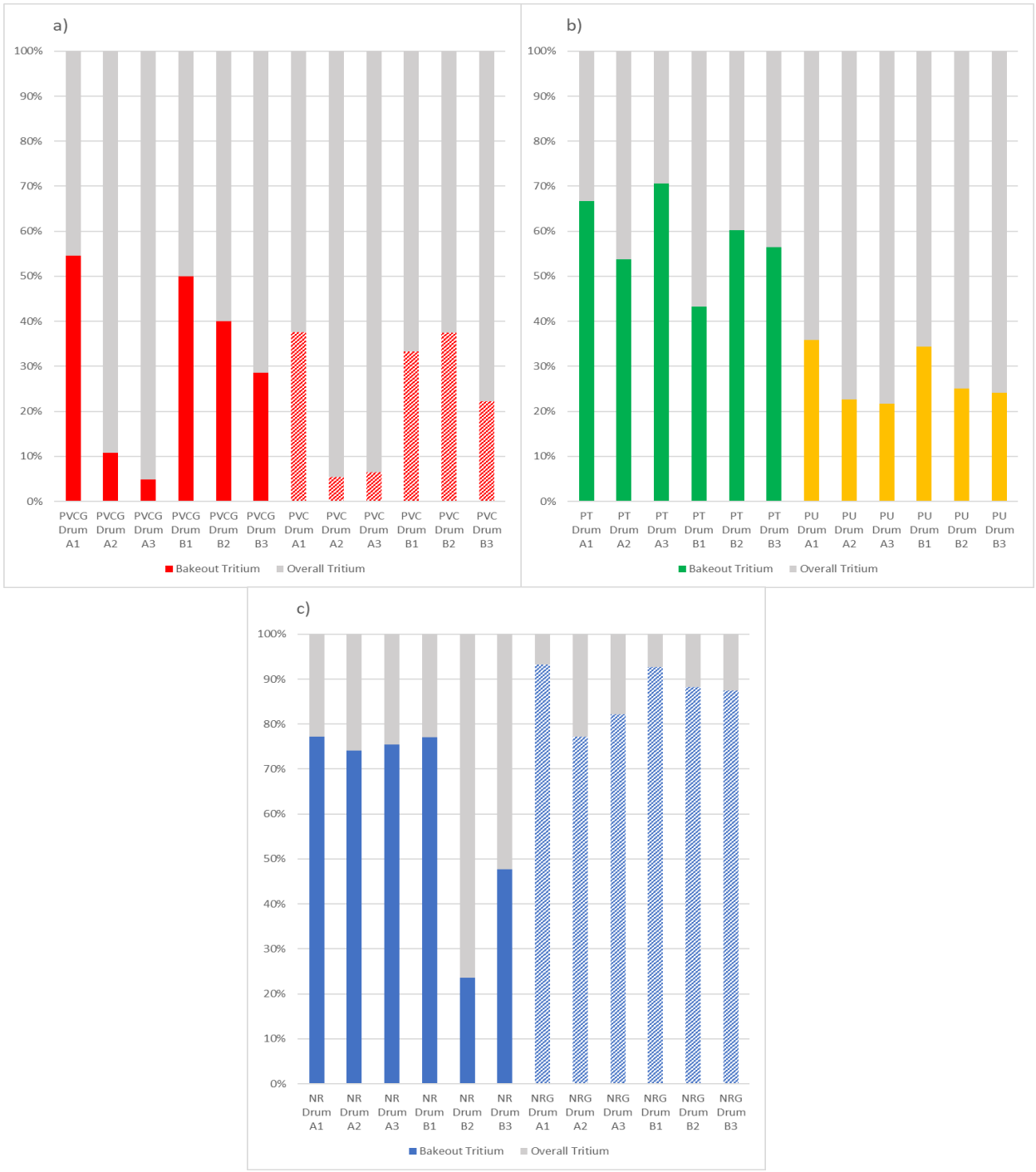


Figure 7: Tritium inventory released in bakeout stage as a function of overall tritium in the soft waste samples.

4 Discussion

A consideration for all the following measurement techniques is the nature of the exposure of the samples to tritium. For this experiment this consisted of exposure to tritium in the gas atmosphere surrounding the samples. The samples themselves were stored within plastic bags in the drums to protect them from tritiated oils or dust. Therefore, the following analysis of the experimental samples does not include these sources of contamination. The standard UKAEA analysis might contain hot spots due to oil or dust as it was carried out on items that were from operations on site.

4.1 Standard UKAEA Analysis and further Water Leach Analysis

The original pyrolysis results on drum A and B are in good agreement with later analysis using water leaching (table 5). The pyrolysis results from Drum A are approximately 28 times greater than Drum B whilst the water leach results are 21 times higher for drum A than drum B. These two drums contained general waste items from PPE with a mixture of material types (gloves, overshoes, masks etc).

Method	Ratio of A/B	Ratio of A/C	Ratio of B/C
Pyrolysis	28	9 E-03	3 E-04
Water Leach	21	N/A	N/A
Drum Atmosphere	2	5	3

Table 5: Comparison of tritium values derived from various measurement techniques

Drum C is a different case due to it being comprised of PVC tent material. The different in ratio measurements for drum A/C and B/C between pyrolysis and drum atmosphere measurements highlight concerns with respect to a pyrolysis sub sample being a hot spot. According to pyrolysis measurements drum C has the highest level of activity whilst drum atmosphere measurements suggest it has the lowest level of activity of the three drums. Although this doesn't confirm that the 10g sample from pyrolysis was a hot spot it would be a possible explanation.

In general, the difficulties in measuring PVC contaminated waste via a water leach method are demonstrated by figures 3 and 4. The weekly analysis of the water leachate using liquid scintillation counting show a activity level that fails to reach a steady state in the water. Both tests show the water leachate reaching a peak in activity before subsequent measure show lower levels of tritium activity. This may be due to chemical interactions between the tritium in the water and the PVC material which leads to tritium being re-incorporated within the PVC after it has been released into the water. Although it appears that if the PVC is then taken out from the water wash and placed in a subsequent wash the results are much more stable. This demonstrates why PVC is not a suitable material for water leaching measurements.

4.2 Drum Atmosphere

The results of the drum monitoring are interesting because they show the ratio of HT to HTO within the drum atmosphere. Drum monitoring on nuclear sites can involve attaching water bubblers and a pump to the drum to measure how much HTO is present within the drum atmosphere. If this was used on the three drums selected for this experimental programme then 20% of the tritium would have been missed. It's also interesting that all three drums had this very similar levels of HT to HTO in their atmosphere.

The headspace measurements plotted against total inventory for the samples shows a good correlation between tritium in the atmosphere and in the samples for material types NR, NRG, PU, PT. The results for PVC are less clear although they seem to still show a general agreement between drum atmosphere tritium and tritium within the samples. These measurements were taken

approximately 6 months after the samples had been stored within the drums. It is unclear how quickly an equilibrium would be reached after the waste had been stored in the drums between the tritium inventory in the atmosphere and that in the waste. This should be explored in future testing.

4.3 Experimental Programme

The results from the experimental programme show a link between tritium recovered in the bakeout stage and overall tritium present within the material for most types. The coefficient of variation shows low variance for all sample types measured (table 6)

Sample Type	Number of Samples	Average Percentage Released During Bakeout	Standard Deviation	Coefficient of Variation
PU	6	27	5.6	0.2
NRG	6	86.9	5.7	0.07
PT	6	58.5	8.9	0.2
NR	6	62.5	20.3	0.3
PVCG	6	31.4	18.7	0.6
PVC	6	23.8	13.6	0.6

Table 6: Average tritium released during bakeout stage for material types across drum A and drum B

4.4 Potential Benefit to Tritium Analysis Techniques

If the ratios shown in table 6 continue to be demonstrated for future tests then a bakeout step could be used to analyse tritium within the waste. An analysis technique based on a bakeout at 100°C would make it relatively easy to measure a whole drum of waste at the same time if the material makeup of the drum is well known. Together with analysing the tritium within the waste it also would act to detritiate the waste (especially the material types such as nitrile rubber) lowering the environmental impact of disposal/incineration. Tritium from the tritiated water used to capture the offgass activity can then be recovered using a water detritiation system. The following potential benefits in analysis have been identified

- Lower costs of disposal via incineration which is priced according to activity of waste
- Save on characterisation costs – waste would not need to be characterised again after bakeout
- Avoid sampling uncertainties due to sample size, the whole of the drum would effectively be the sample
- Act to detritiate the waste and recover the tritium for reuse whilst also measuring the tritium activity

5 Conclusions

Current tritium measurement techniques were compared using experimental samples and prior analysis that had already been carried out on the drums. The results from pyrolysis were found to correlate to drum atmosphere measurements for all of the experimental samples. The link between

activity in the PVC samples and the drum atmosphere were the least clear in this relationship. For the prior analysis carried out the drum containing the PVC tent material showed the potential dangers associated with tritium hot spots. The pyrolysis result being much higher than that suggested by drum atmosphere monitoring.

Water leaching was found to reach a steady value for all material types tested except for PVC which needed a second water leach before consistent activity measurements were given on a week to week basis.

An alternative approach based on a bakeout at 100^{o}C for 4 hours was found to give good consistency between samples of the sample material across two of the experimental drums. Future work in this area could be aimed at waste from general operations to see if this relationship between the bakeout recovery and total tritium remains consistent in waste that potentially has tritiated oil/dust contamination. This technique if proven to be successful could combine the whole drum analysis that comes from methods such as the headspace technique with a detritiation step that would be delivered by heating the waste to 100^{o}C.

The following benefits were then identified for a process based on the bakeout technique

- Cheaper disposal which is often costed according to the overall activity of waste
- If future tests continued demonstrating a steady ratio of tritium recovered via bakeout to the overall activity, waste would not need to be characterised again after bakeout
- Hot spots of higher activity or other sampling effects due to small sample sizes would be avoided, the whole of the drum would effectively be the sample
- Would achieve two different outcomes of detritiating the waste and measuring the residual tritium content.