

# Novel analytical applications using the Pyrolyser Trio furnace system – case studies

Raddec-Triskem International Technical Workshop – 18<sup>th</sup> April 2024.  
Portsmouth Historic Dockyard

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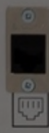


# Introduction

ZONE 1

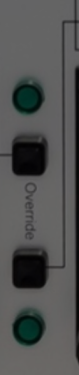
ZONE 2

ZONE 3



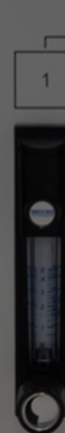
Gases In

AIR



O2

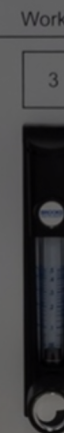
Override



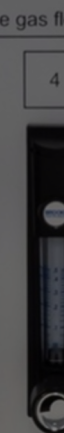
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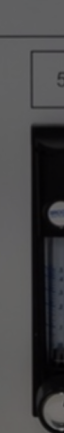
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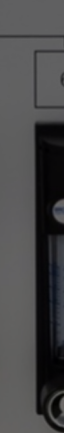
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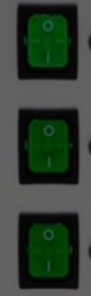
5



6

Work-tube gas flow

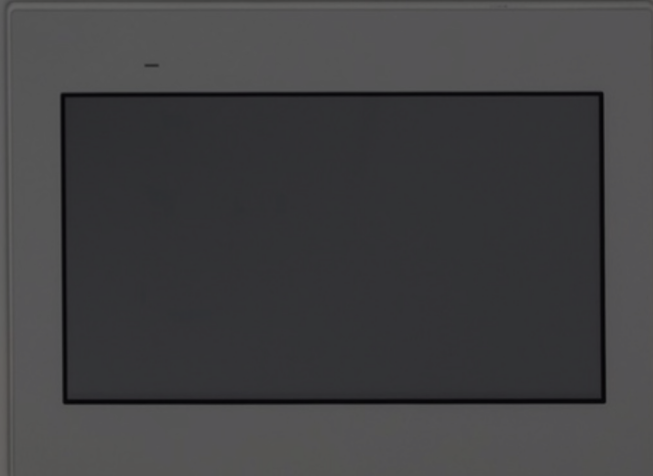
Power



Zone 1

Zone 2

Zone 3



# Commonly analysed materials

- Concrete
- Soil & sediment
- Metals
- Biota
- Fish
- Paint / plastics



# Challenging materials

- Mixed waste streams
- Asbestos
- Toxic / dangerous metals (Be, Cd, Hg, Na)
- Gaseous samples
- High organic component
- Oil / scintillant



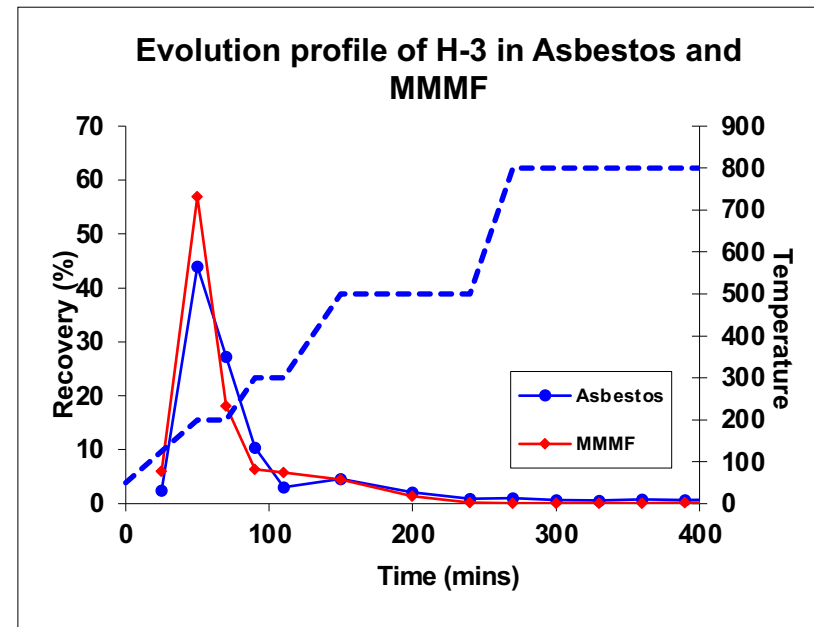
# Asbestos

- Common contaminant in site clearance.
- Use Raddec hazardous sample boats.
- Sample contained between quartz wool plugs.
- Can be prepared in suitably designated workspace and contained.
- Load to the Pyrolyser and combust according to sample type.



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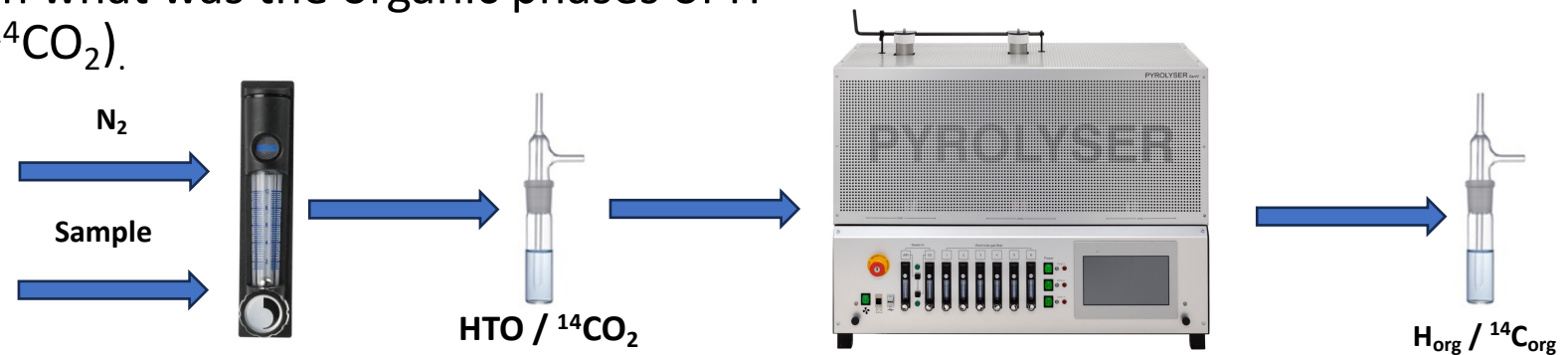


## **Additional uses for hazardous sample boats:**

- High activity samples.
- Static or light samples.
- Samples that may ignite / flash.

# Gas

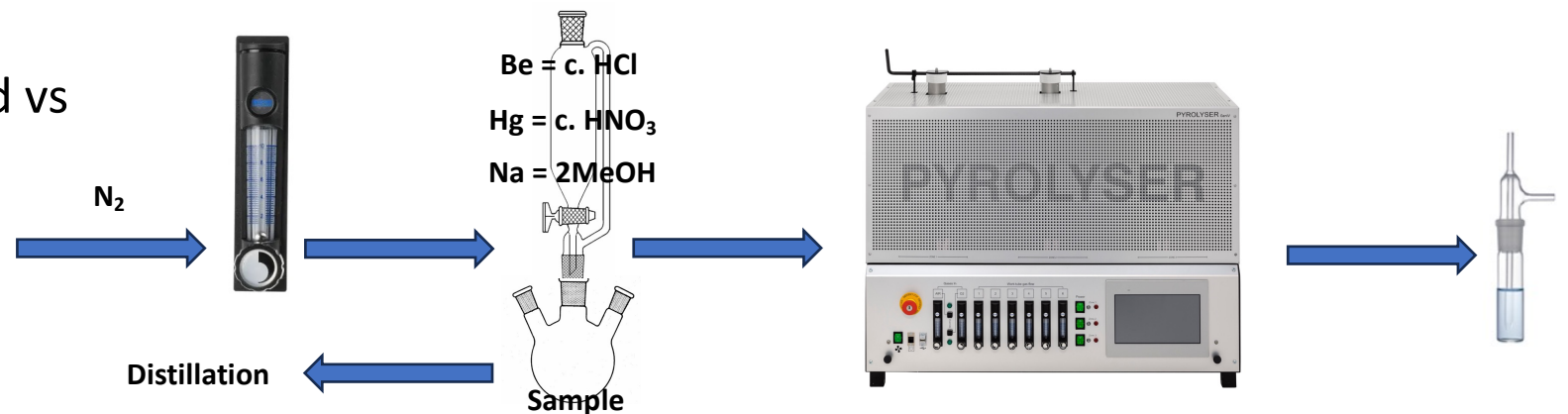
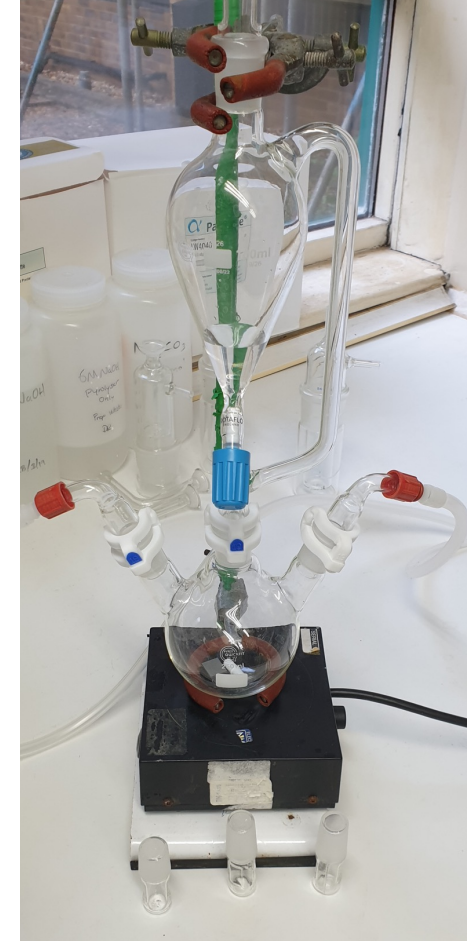
- Origins: flare stack, landfill, pipeline, borehole
- Sample zone at 600 °C. Mid zone at 500 °C. Cat zone at 800 °C.
- Cat zone uses CuO (oxidant).
  - $^3\text{H}_2 + \text{CuO} \rightarrow ^3\text{H}_2\text{O} + \text{Cu}$
  - $^{14}\text{C} + \text{CuO} \rightarrow ^{14}\text{CO}_2 + \text{Cu}$
- Sample extracted from containment bag (Tedlar) and pressurised into Gresham Tube.
- Sample slowly bled into  $\text{N}_2$  purge gas.
- Bubbler pre-Pyrolyser can be used to determine HTO or  $^{14}\text{CO}_2$  already in the sample.
- Bubbler post-Pyrolyser will contain what was the organic phases of H and C (now converted to HTO or  $^{14}\text{CO}_2$ ).





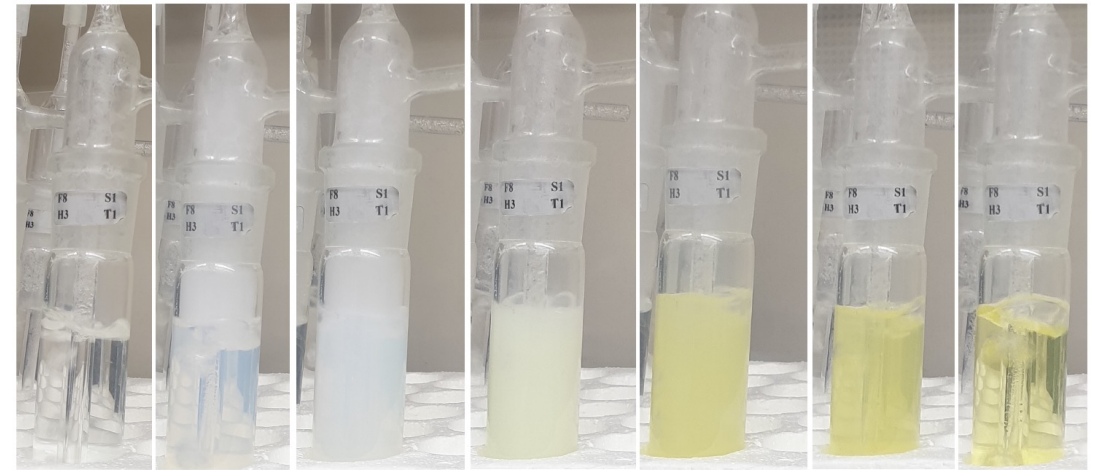
# Toxic / dangerous metals

- Reaction vessel for sample digestion.
- N<sub>2</sub> purge gas + CuO oxidant in Pyrolyser
- $\text{Be} + 2\text{HCl} \rightarrow \text{BeCl}_2 + \text{H}_2$
- $2\text{Hg} + \text{HNO}_3 \rightarrow \text{Hg}_2(\text{NO}_3)_2 + \text{H}_2$
- $2\text{Na} + 2\text{MeOH} \rightarrow 2\text{Na}(\text{MeO}) + \text{H}_2$
- Digest is then distilled prior to LSC.
- Bubbler and distillate activities combined.
- Ensure surplus CuO oxidant is used vs anticipated H<sub>2</sub> budget.



# High organic content – An example of method development

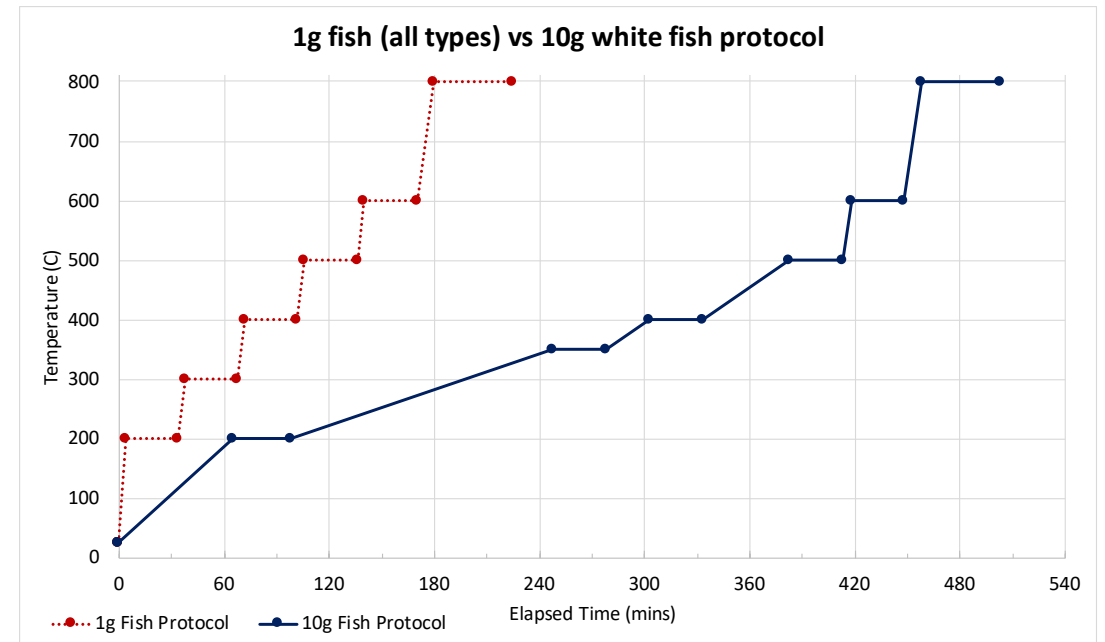
- Sample type: White fish (cod, haddock, pollock).
- Raddec “fish” protocol recommended mass = 1-2g.
- 1-2g can provide  $L_D \sim 10$  Bq/kg with 1hr count.
- A more demanding  $^3\text{H}$  LOD was required ( $<1$  Bq/kg) – Increase count time and sample mass.
- Cannot increase sample mass without modification to the default heating profile.
- Incomplete combustion / decomposition of the sample. Overwhelmed catalyst.
- Method development required.



Incomplete combustion  
280 > 300 C.  
5 minutes.

# High organic content – An example of method development

- Numerous experiments and failed attempts
  - Critical heating stages:
    - 200-350 °C
    - 350-500 °C
  - New heating profile allows complete combustion obtained.
  - No discolouration of bubbler solution.
  - Validated with 10g fish spiked with OBT.
  - 98% recovery.
  - Old run-time = 4 hrs
  - New run-time = 8 hrs
- 
- To further drive down  $L_D$  it is possible to collect combustion water only using cold traps / cryo cooler.
  - 10g fish = 6ml combustion water yield.
  - This is from one worktube only! Scale up to 60g.



# Oil / scintillant

- Concern with combusting oil / scintillant.
- Direct counting preferred by Client. What about other beta nuclides?
- Can be achieved with slow ignition up to 900 °C over 6 hours.
- Sample mass should not exceed ~1 g or ml.
- $^3\text{H}$  contaminated oil was measured directly by LSC and via combustion.
  - Direct LSC =  $80,300 \pm 600$  (counting stats only)
  - Combustion + LSC =  $76,000 \pm 9,000$  (inc 12% method uncertainty)
  - Combustion vs direct counting = 95%
- Direct LSC counting almost always results in an elevated LOD due to other low energy beta present. Example:

Direct LSC with other low energy beta contribution

$$^3\text{H} = <5 \text{ Bq/g} \quad ^{14}\text{C} = <1 \text{ Bq/g}$$

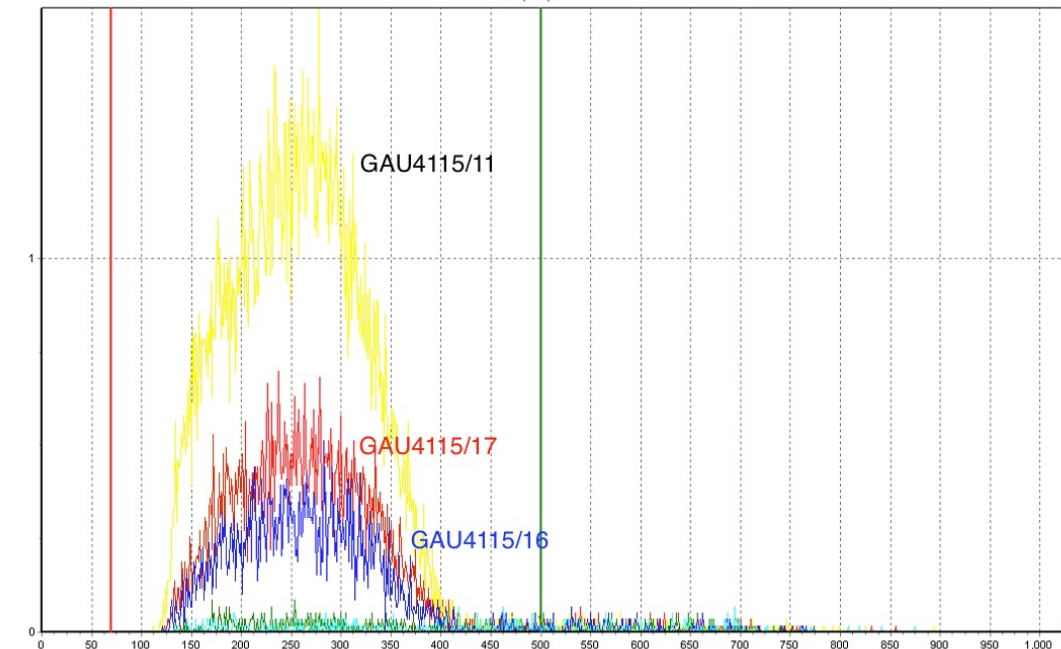
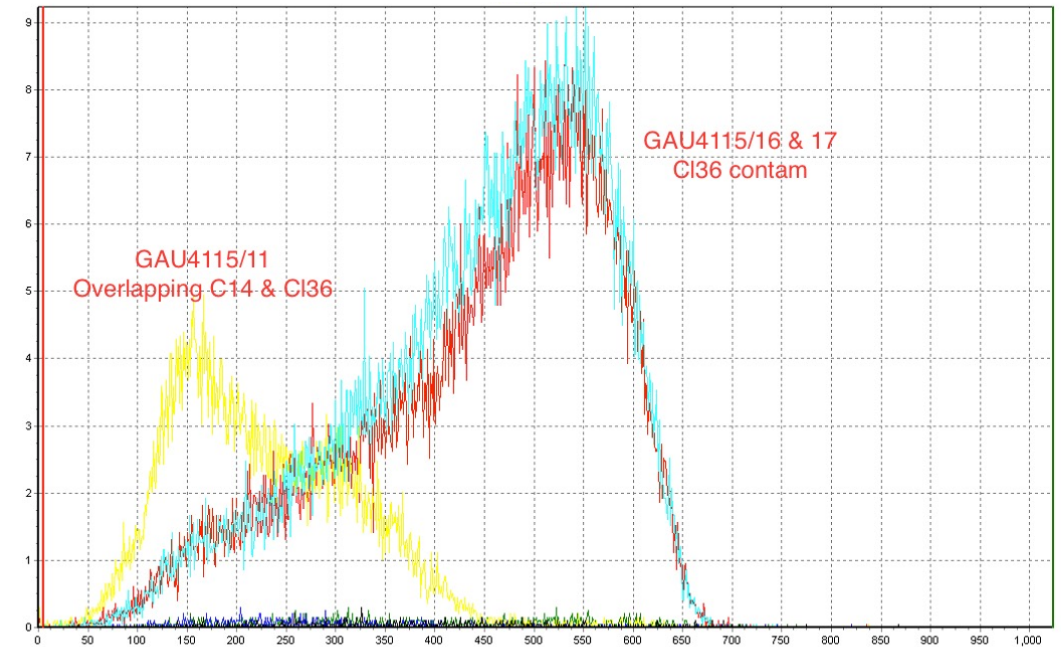
Achievable via combustion

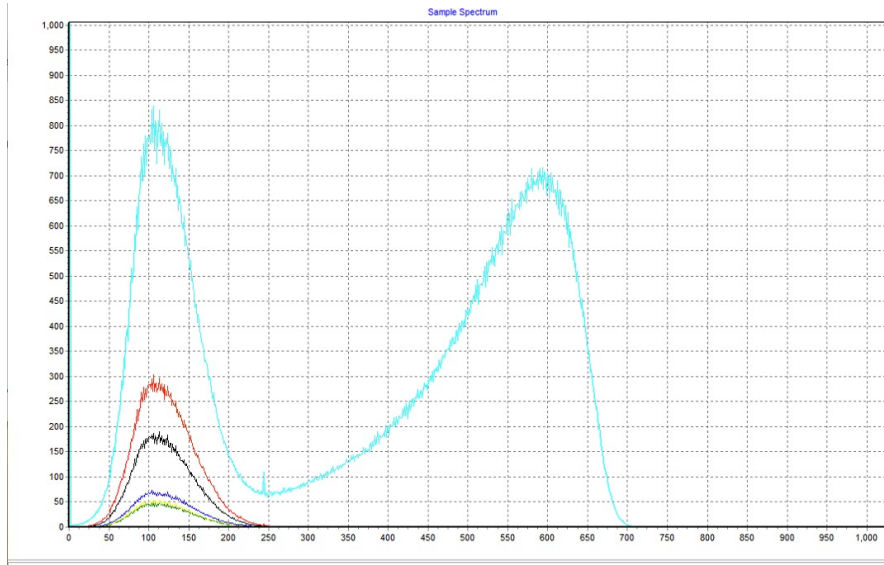
$$^3\text{H} = 0.4 \pm 0.1 \quad ^{14}\text{C} = 0.12 \pm 0.02$$



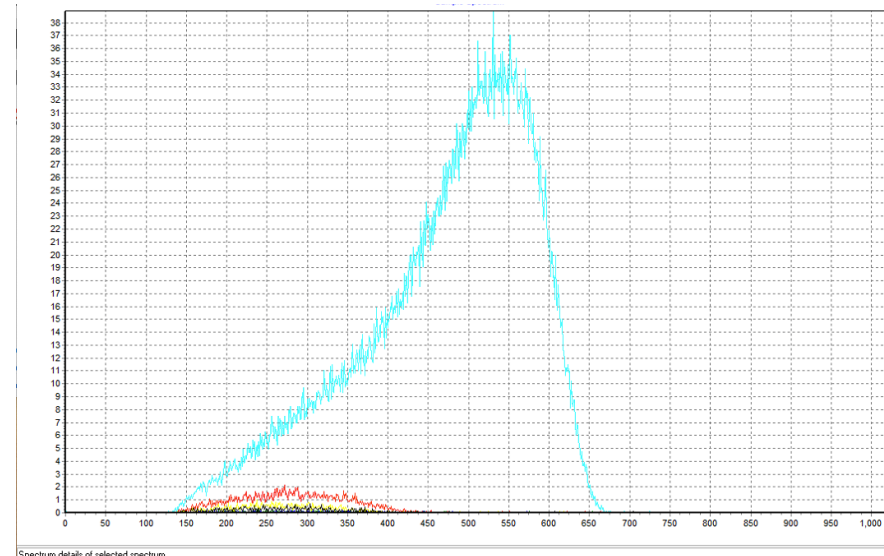
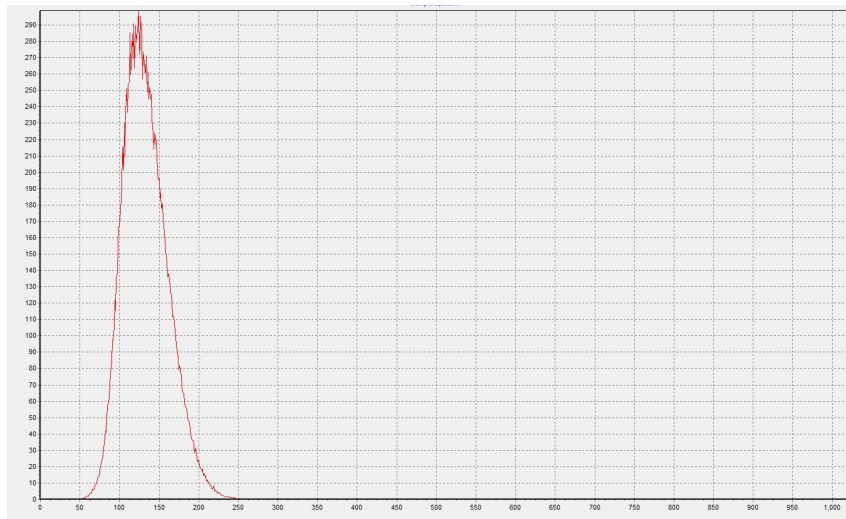
# Contamination by halogens

- $^{36}\text{Cl}$  and  $^{129}\text{I}$  can co-trap with  $^3\text{H}$  &  $^{14}\text{C}$
- Distil  $^3\text{H}$  bubbler.
- Acidify Carbontrap (remaining bubbler solution) and collect the off-gas.
  - (Not the LSC fraction mixed with cocktail)
- Use a reaction vessel and purge reaction gases with air. Re-trap in clean Carbontrap / carbosorb.
- Tested with certified  $^{14}\text{C}$ . Average recovery of 4 replicates = 91 +/- 10 %.

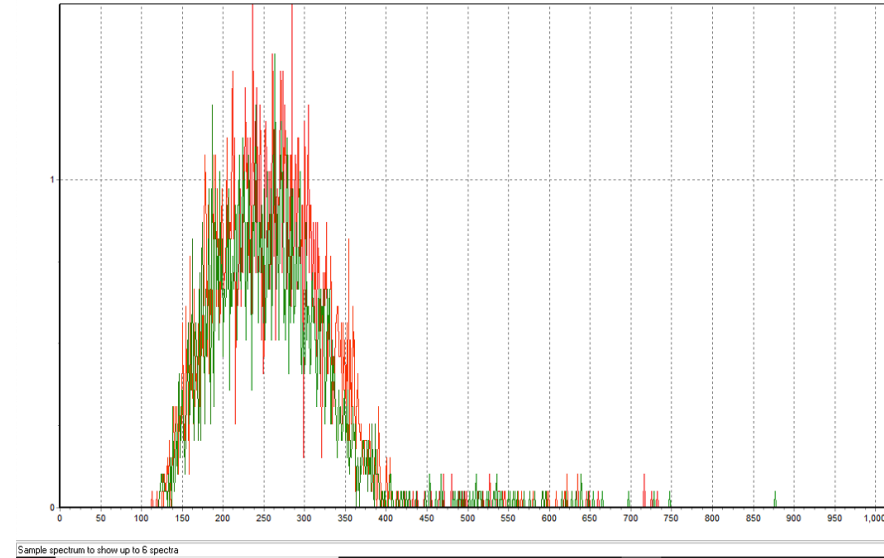




Distillation of  $^3\text{H}$



Acidification and re-trap of  $^{14}\text{C}$



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