

Triskem UGM – Bath Sept 2014

# Developments with the Pyrolyser and HBO systems

Phil Warwick



RADDEC  
INTERNATIONAL

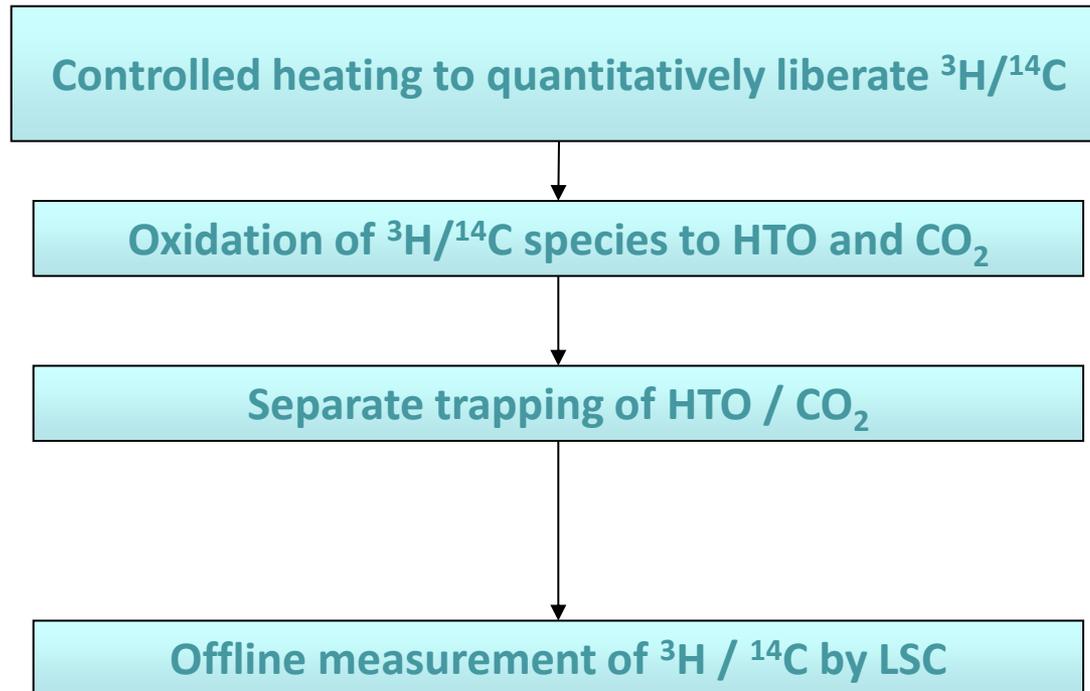
RADDEC  
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# The PYROLYSER series



- **Easy to use system designed by scientists / analysts.**
- **Simultaneous decomposition of up to 6 samples.**
- **Efficient oxidation of the liberated  $^3\text{H}$  and  $^{14}\text{C}$  species (and  $^{36}\text{Cl}$  and  $^{129}\text{I}$ ).**
- **The furnace design has been thoroughly tested and proven over many years. The system has been in use commercially since 2003.**
- **Continued R&D programme ensures that the system and procedures are based on the latest research and best available technologies.**

# Principle of $^3\text{H}/^{14}\text{C}$ extraction



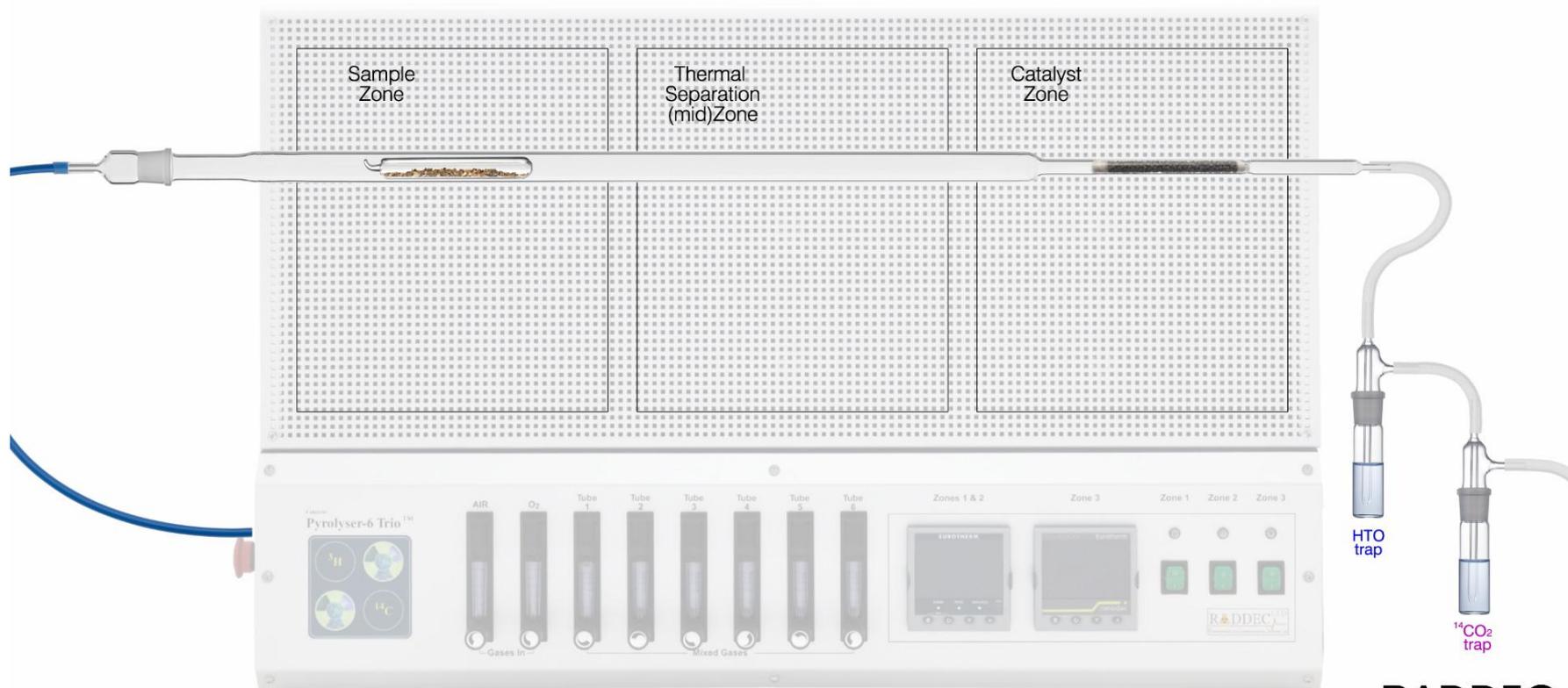
# Purpose-built tube furnace for $^3\text{H}/^{14}\text{C}$ analysis



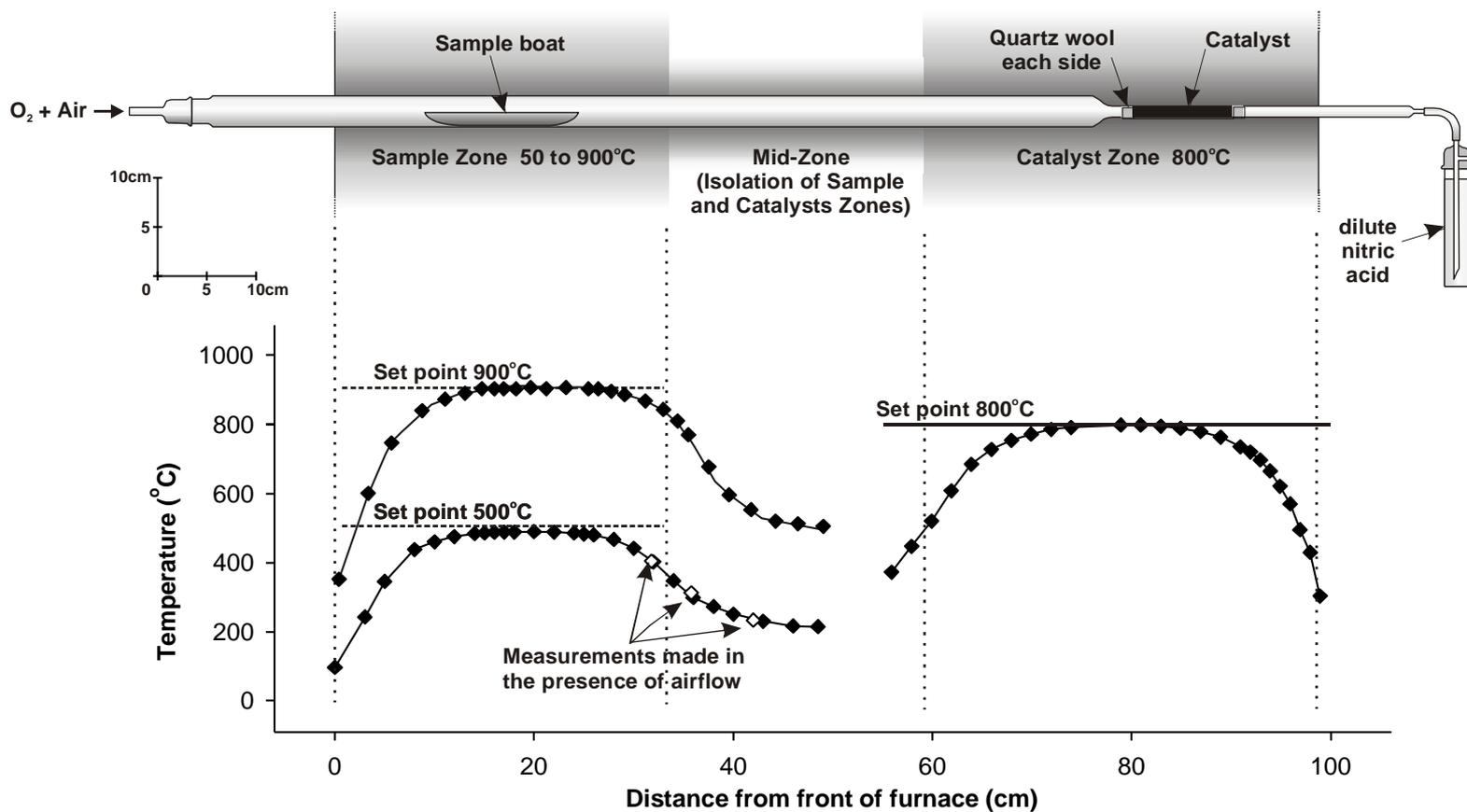
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Also available as Pyrolyser 2 and 4 variants

# Configuration of the system



# Furnace temperature profiles



# Features

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- 6 samples decomposed simultaneously within a single system in ~2-4 hours (depending on sample type) using a programmable thermal ramp.
- The multi-tube, small footprint design, permits high sample throughput without occupying significant laboratory space (unlike with multiple single-tube furnaces).
- 10g Pt-alumina catalyst per tube lasting 20+ determinations.
- Sample zone can operate up to 900°C permitting efficient  $^3\text{H}$  extraction from concrete and graphite

# Features

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- Rapid cool-down of sample zone enabling good cycle times between runs.
- Incorporation of a mid-zone furnace to prevent condensate problems whilst maintaining thermal separation of the sample and catalyst zones.
- Bubbler-traps (20mls) have >95% efficiency.
- The Pyrolysers have been in regular use for extraction of  $^3\text{H}$  and  $^{14}\text{C}$  from a wide range of materials (vegetation, fish, soil, sediment, concrete, metal etc).
- The design and proven effectiveness follows several years of testing of samples from intercomparison exercises, environmental studies and nuclear site decommissioning programmes.

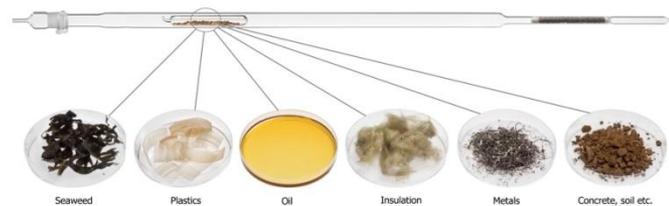
# Recent developments

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- Over-temperature protection on all furnaces
- Fan cooling of electronics compartment
- Automated Gas Control to activate air and oxygen flows (AGS system)
- Improved furnace control and data logging functionality using Eurotherm 3504 & Nanodac controllers
- Glassware development for  $^{36}\text{Cl}$  &  $^{129}\text{I}$  extraction

# Sample types routinely run

- Environmental samples
  - Soil/Sediment, Fruit, Water, Grass, Milk, Fish, Sludge etc.
- Decommissioning samples
  - Concrete, Brick, Asbestos, MMMF, Metal, Plastic, Desiccants, Paper, Electrical wire, Sewage sludge, Graphite, Paint, Oil etc.



# Sample sizes

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- **Samples with low organic contents**

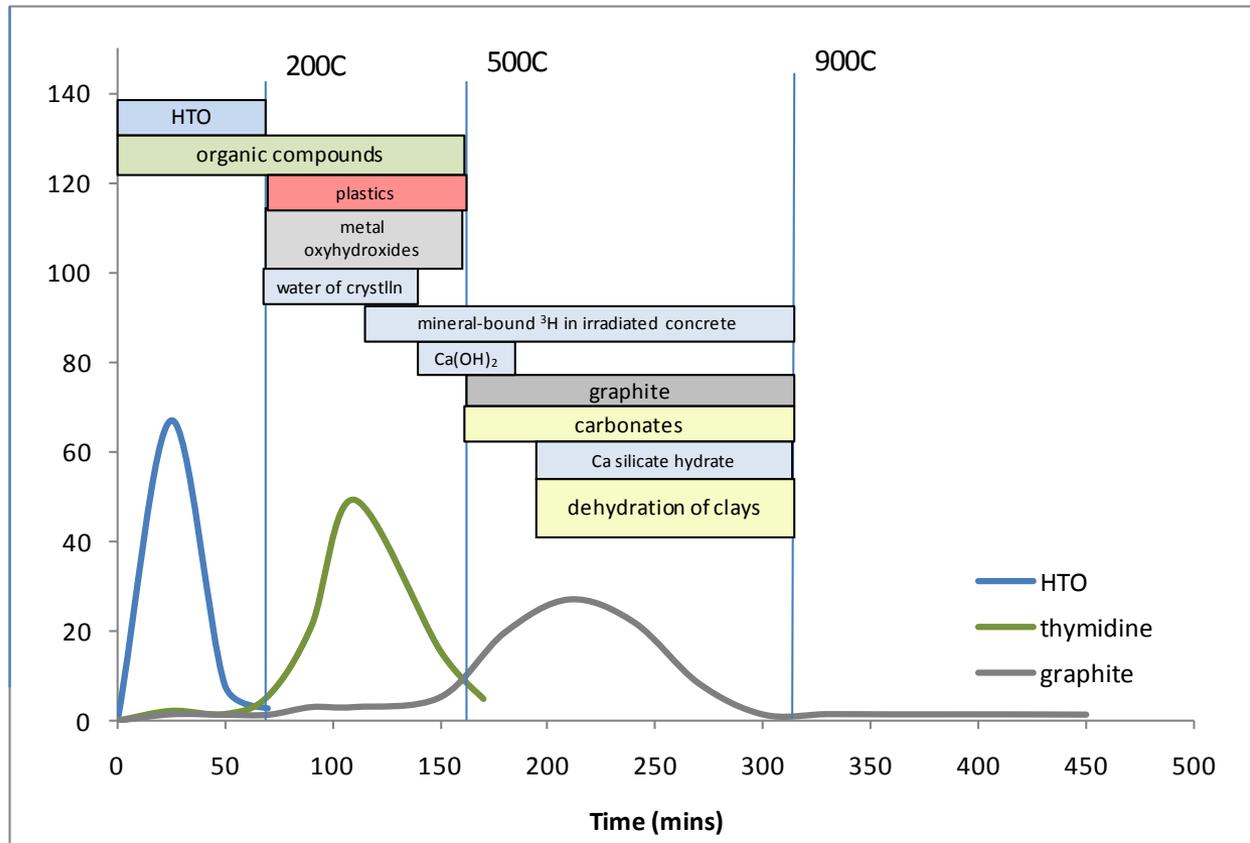
Soil/Sediment, concrete, brick, metal etc. (1 - 30g)

- **Samples with high organic contents**

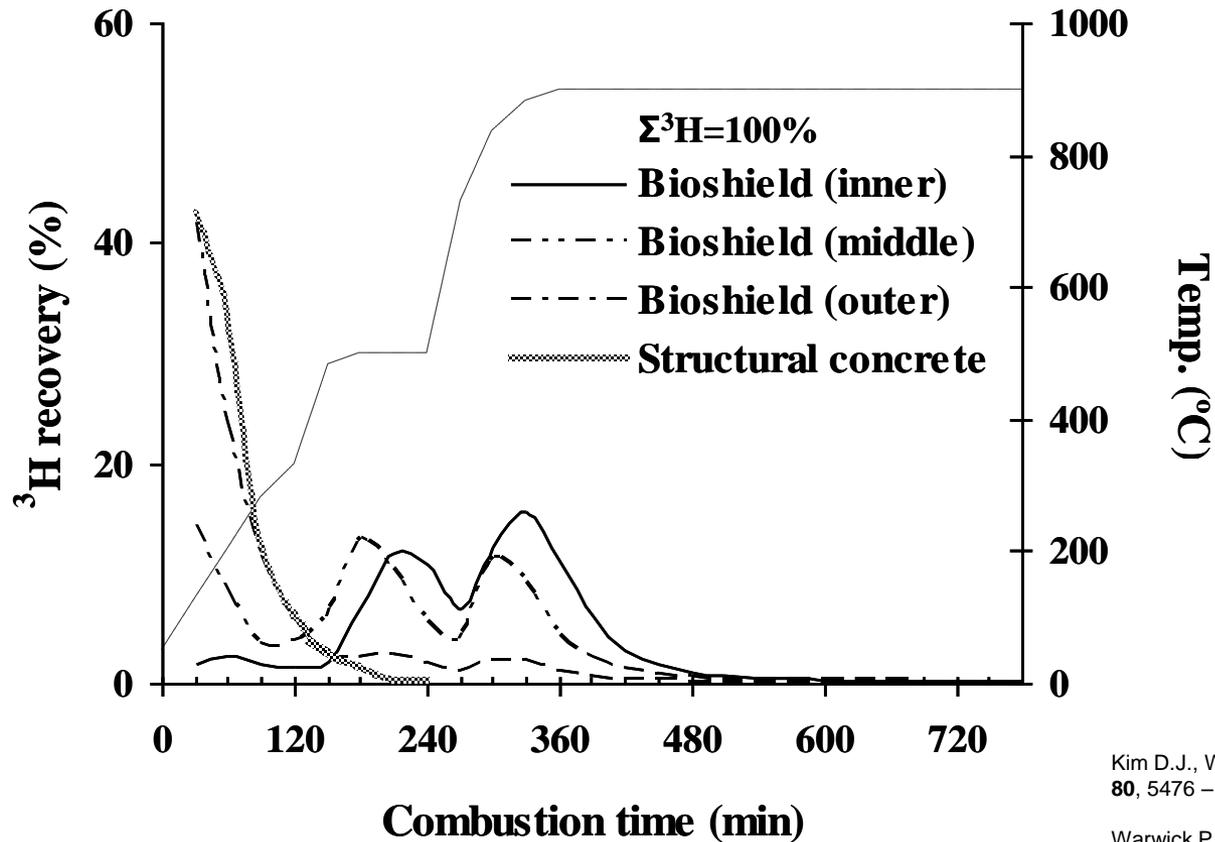
Biota, plastics, organic rich sediment/soil etc. (Normally 0.5 - 1g if  $^{14}\text{C}$  is being determined).

Samples up to 5g can be run if only tritium is being measured.

# $^3\text{H}$ desorption profiles



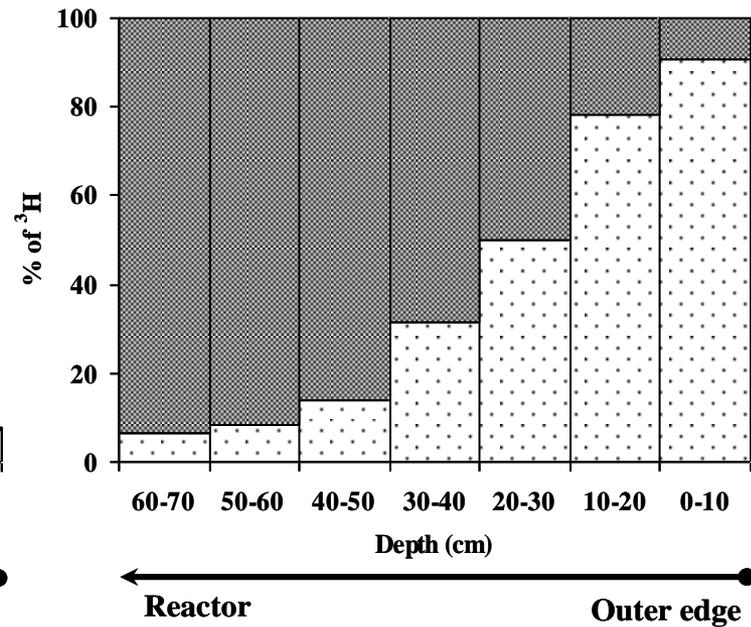
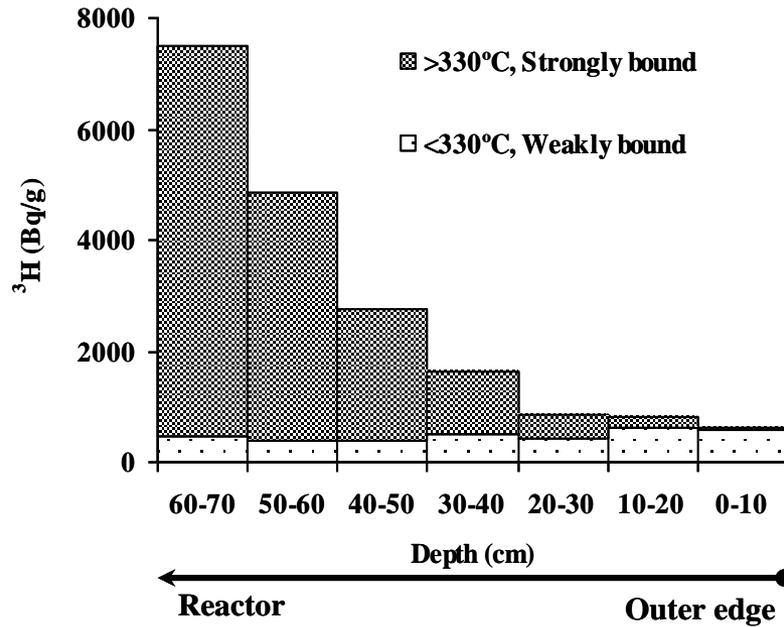
# Thermal Evolution profiles



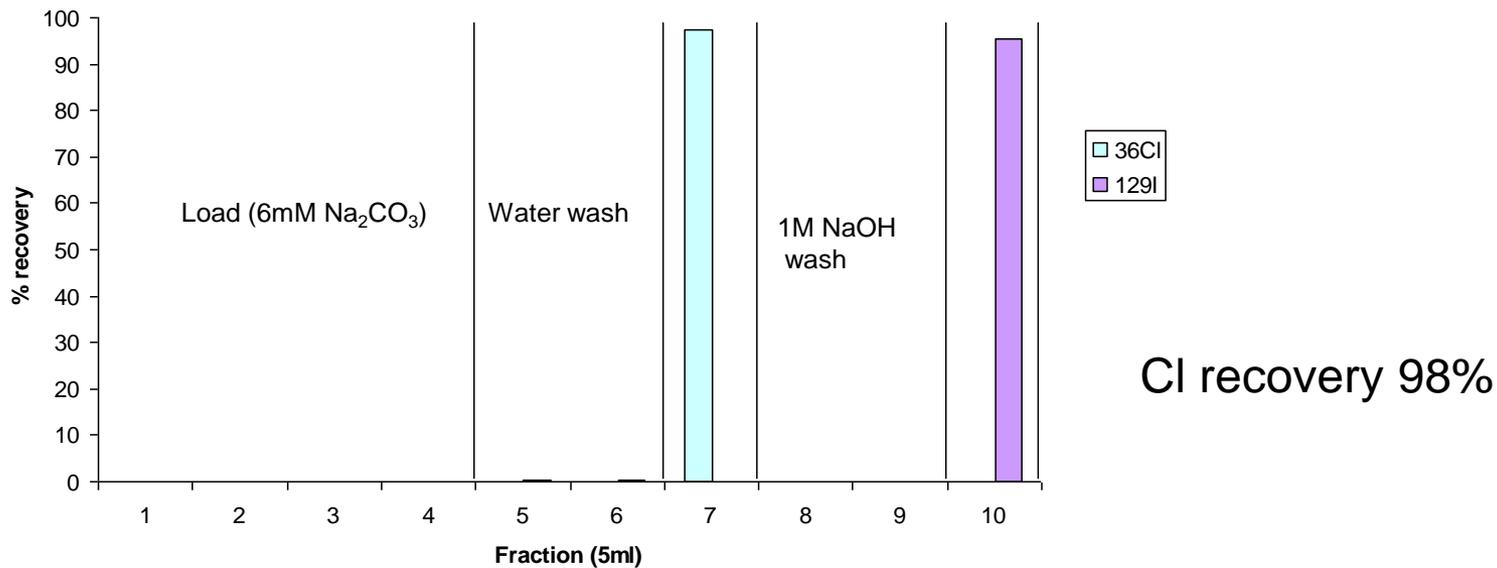
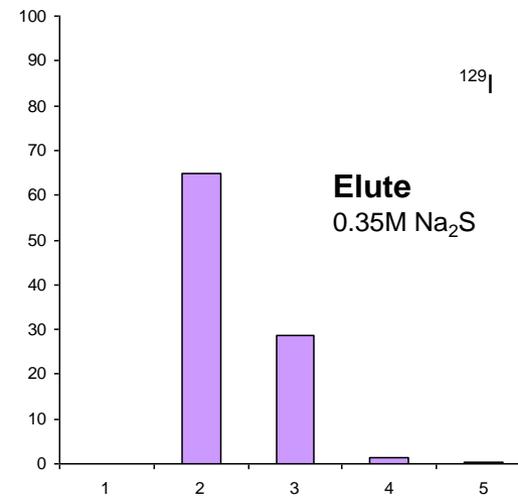
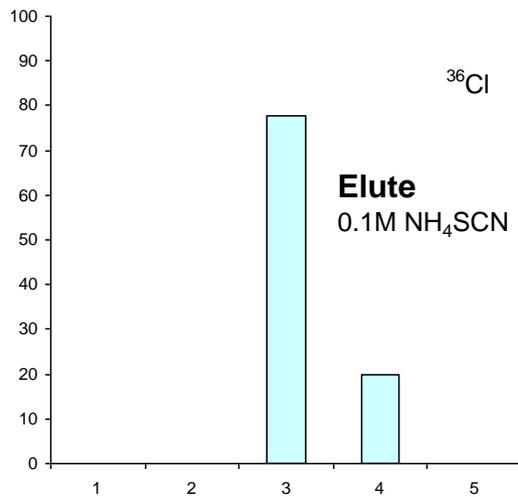
Kim D.J., Warwick P.E. & Croudace I.W. (2008). *Anal. Chem.*, **80**, 5476 – 5480.

Warwick P.E., Kim D.J., Croudace I.W. & Oh J-S. (2010). *Anal. Chim. Acta*, **676**, 93 – 102.

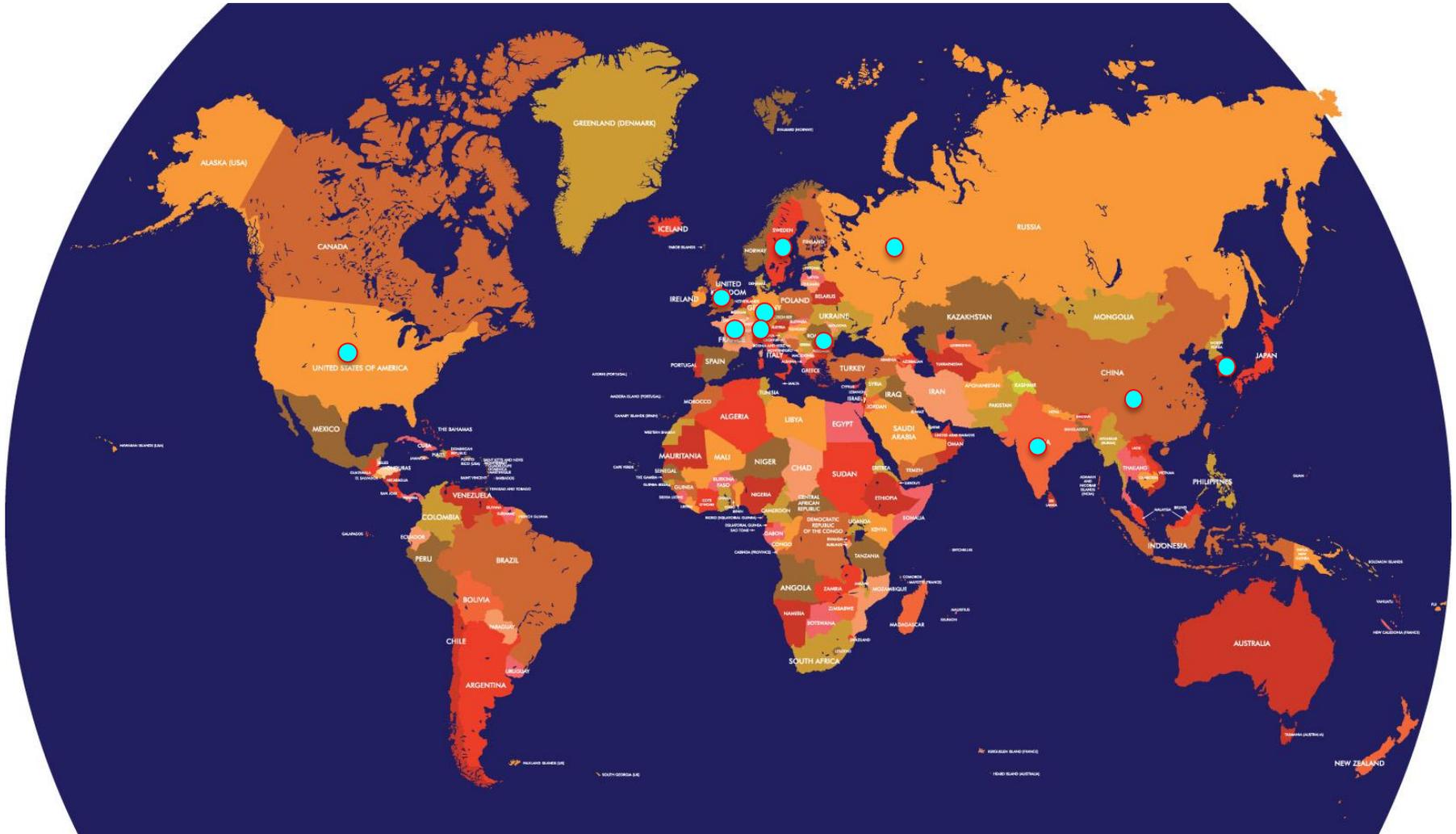
# Tritium evolution profile



# Separation using Triskem Cl resin



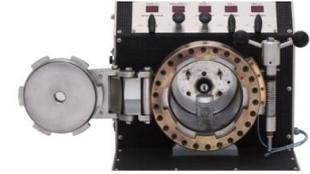
# 70 Pyrolysisers worldwide



# The new HBO<sub>2</sub> system



# Advantages of HBO



- A high capacity sample oxidiser (RADDEC Ltd)
- Quantitative combustion in an excess oxygen environment
- Operates at pressures  $\leq 100$  bar
- Large samples ( $\leq 30$  g) can be combusted
- Wide range of sample matrices maybe combusted:

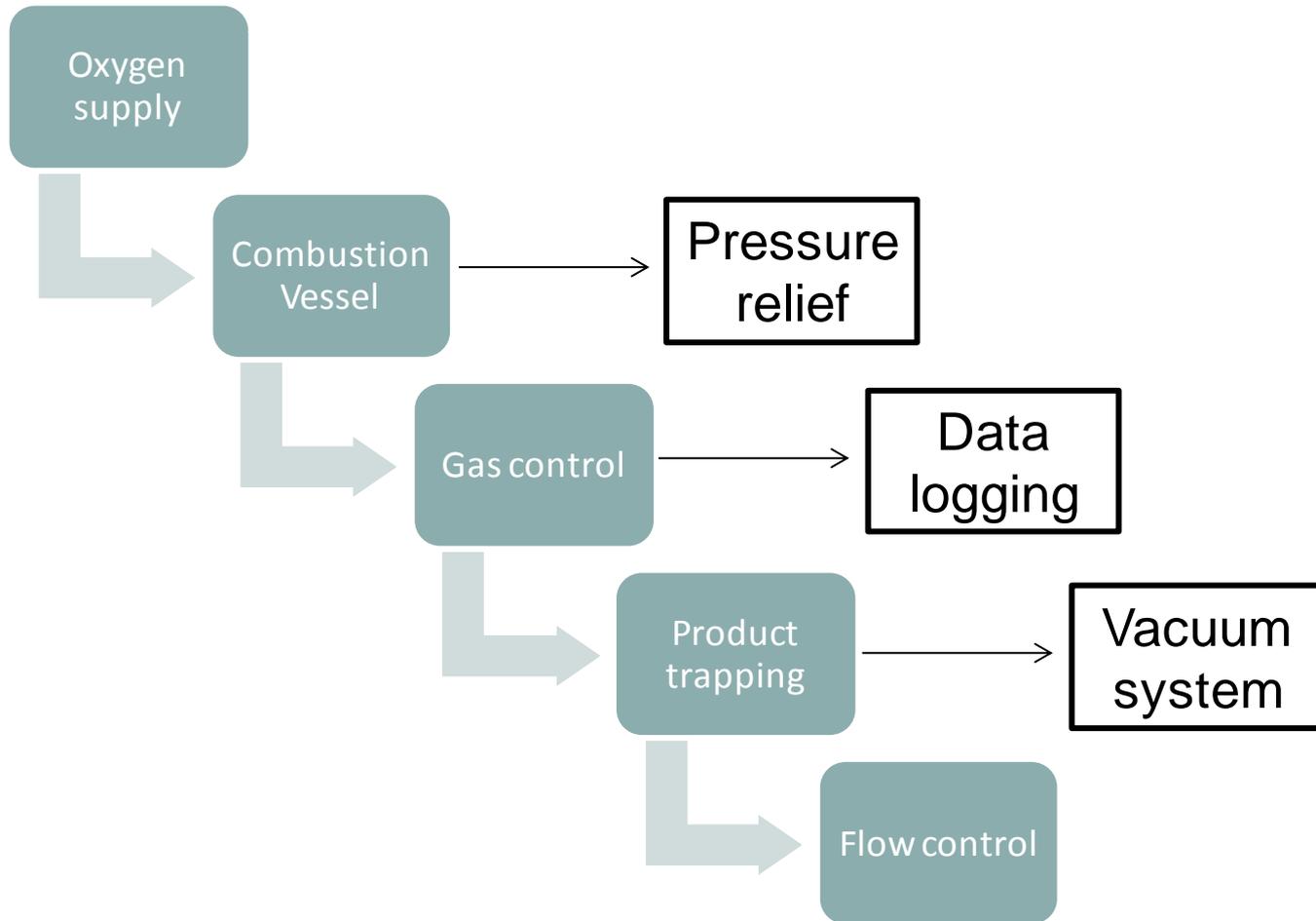
Cellulose (e.g. vegetation)

Environmental samples (biota / veg.)

Vacuum pump oil

Nitrile rubber (e.g. lab waste)

# Instrument schematic



# Combustion Procedure



Sample pelletised  
or cut to size



Sample loaded into  
disposable silica  
crucible

Chamber  
filled with either  
10, 20 or 30  
bar pure O<sub>2</sub>

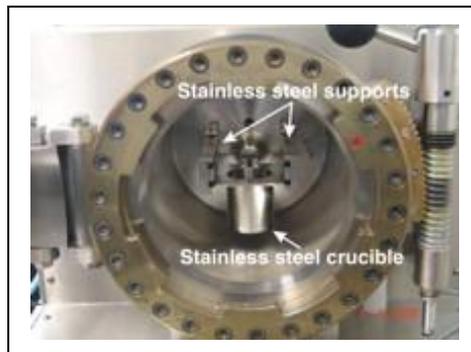


Sample combusted

Measurement  
by LSC



HTO / H<sub>2</sub>O  
trapped from  
exhaust gas

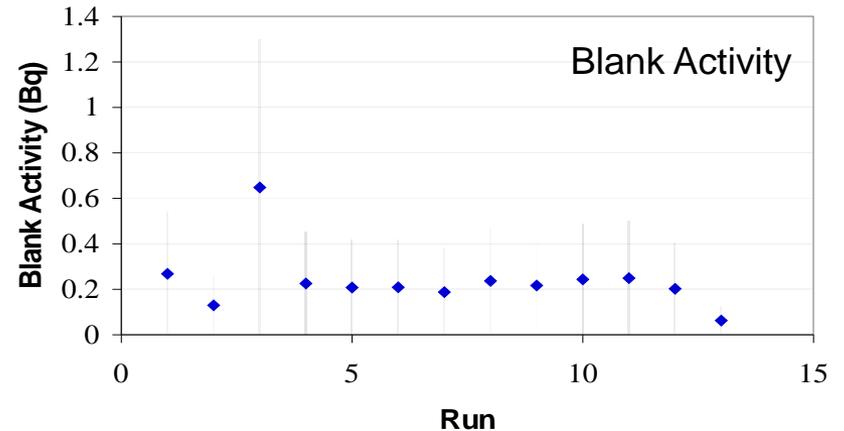
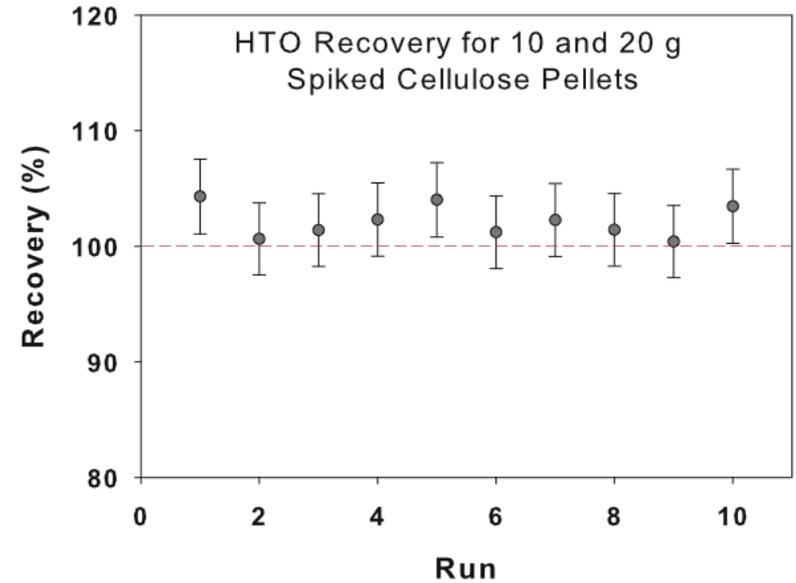


**Original steel  
sample cup  
abandoned due  
to combustion  
quench**

# Instrument Evaluation

## HTO activity recovery:

- Ability to recover HTO activity from within the HBO assessed
- Cellulose pellets spiked with HTO (~100 Bq)
- Recovered activity compared to spike activity
- Very small memory effect  $\leq 0.7\%$



# HBO<sub>2</sub> Mk2 developments

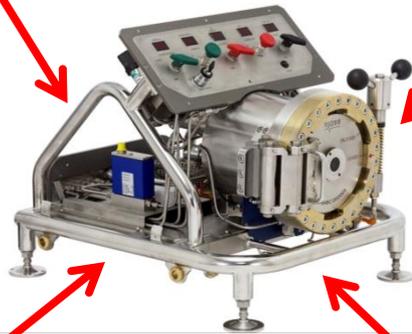


High volume pressure relief valve

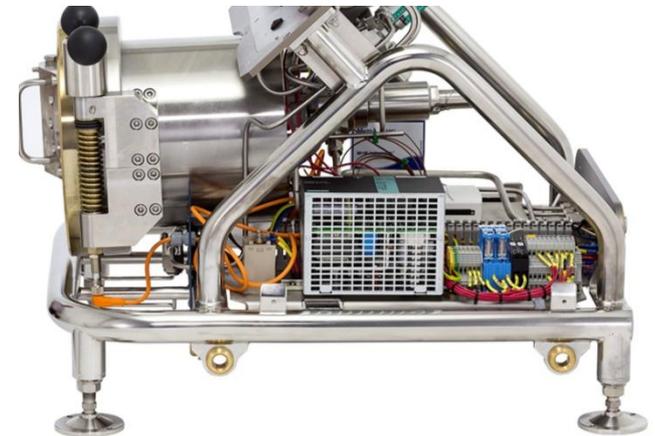
Improved pressure vessel with resistance wire ignition



Digital flow control and pressure regulation

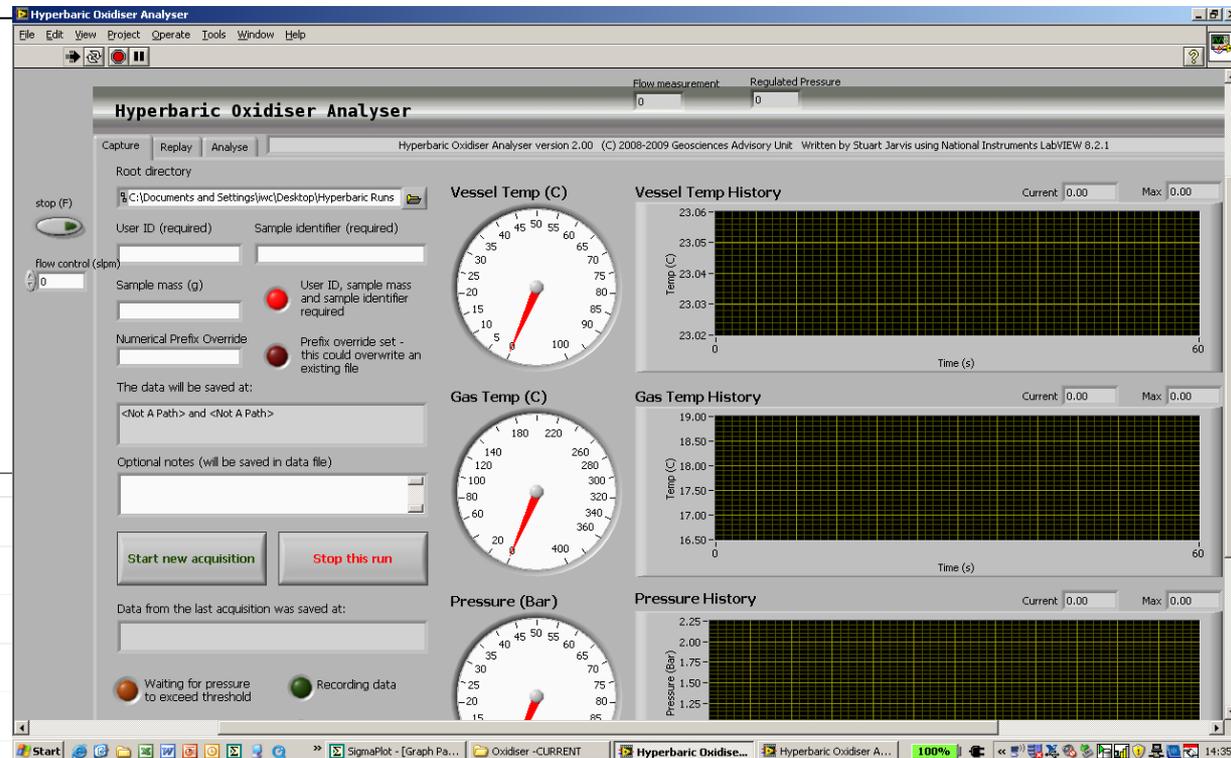
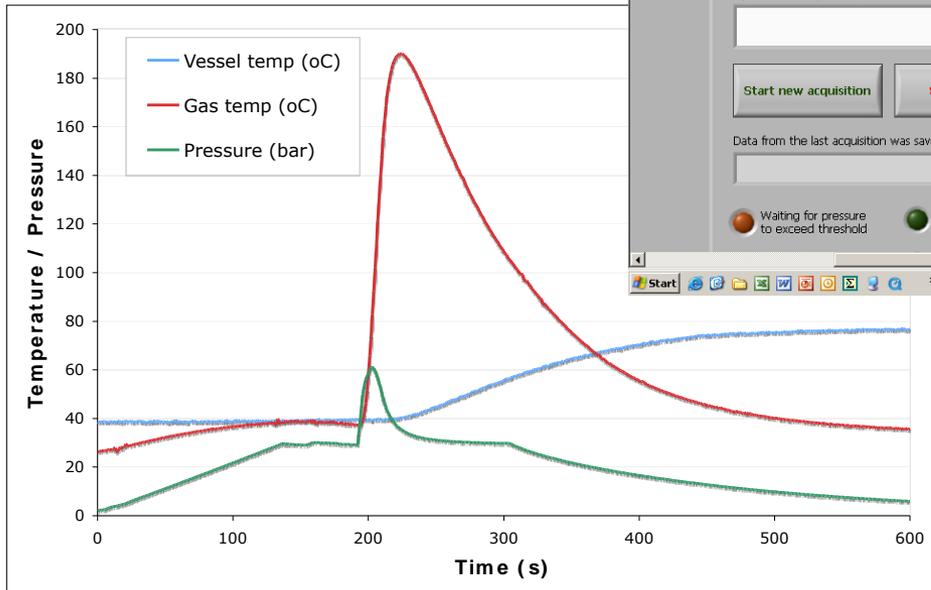


Lightweight yet robust SS frame and lifting system



# Real time data output

LabVIEW interface allows continuous data output and process control



# Software development

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## LSC+

Liquid scintillation data processing

## Raddec LIMS

Laboratory information management system

# LSC+ Data processing software

## Results for the H-3 in water (8ml + 12ml Gold Star™)

Report date : 7-Nov-2003

Customer : Raddec Ltd

Job reference : Raddec 372

Date samples received : 6-Nov-2003

Date of analysis : 7-Nov-2003

Working instruction number: - Raddec/RC/2022

Calibration report number: - Raddec/CAL/16

Counter S/N	Laboratory S/N	Reference date	H-3 Bq/ml	2 s.d.
1 INST STD		7-Nov-2003	23.224	2.548
2 6-169-1	372-1	7-Nov-2003	< 0.006	
3 6-169-2	372-2	7-Nov-2003	< 0.007	
4 6-169-3	372-3	7-Nov-2003	< 0.006	
5 6-169-4 STD		7-Nov-2003	0.115	0.014

All results are in Bq/ml and are decay corrected to the reference date (12.30 Years half life)

\* < values\* are limits of detection as defined by Currie, 1968

Uncertainties are at the 2 s.d. confidence level and are based on propagated method uncertainties

Analyst : A Other

- Calculates activities directly from counter files
- Eliminates transcription errors
- Calculates LODs (Currie)
- Quality Control Built-in
- Statistical analysis of results
- Full diagnostic report
- Range of input file formats for all LSC counters

