

Triskem UGM – Bath Sept 2014

Developments with the Pyrolyser and HBO systems

Phil Warwick



RADDEC
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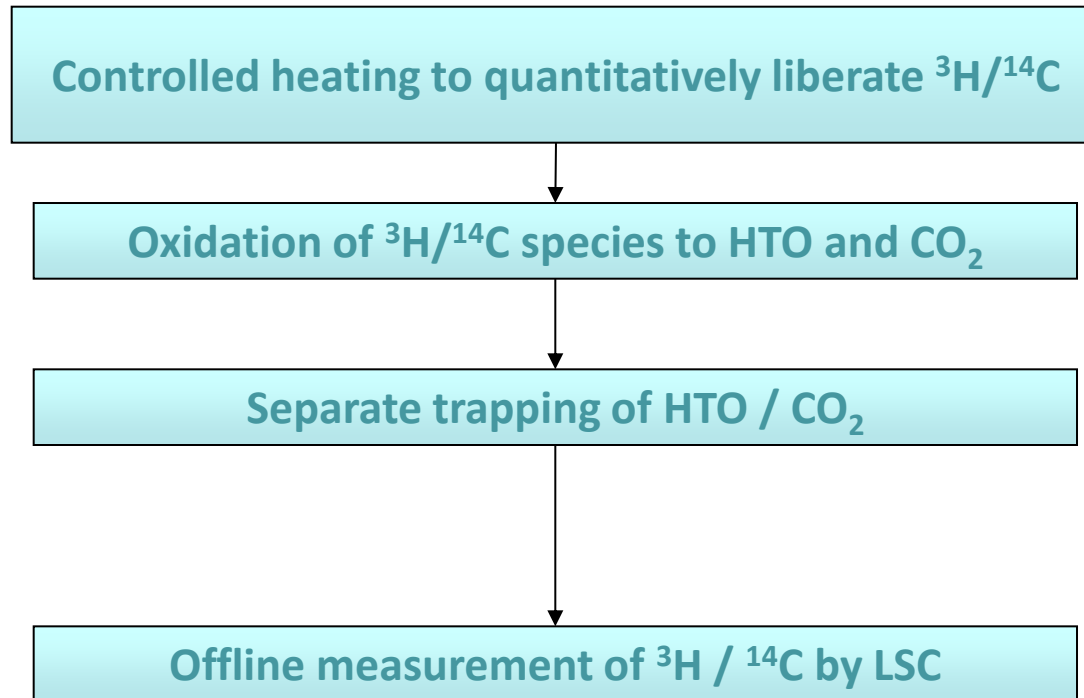
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The PYROLYSER series



- **Easy to use system designed by scientists / analysts.**
- **Simultaneous decomposition of up to 6 samples.**
- **Efficient oxidation of the liberated ^3H and ^{14}C species (and ^{36}Cl and ^{129}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



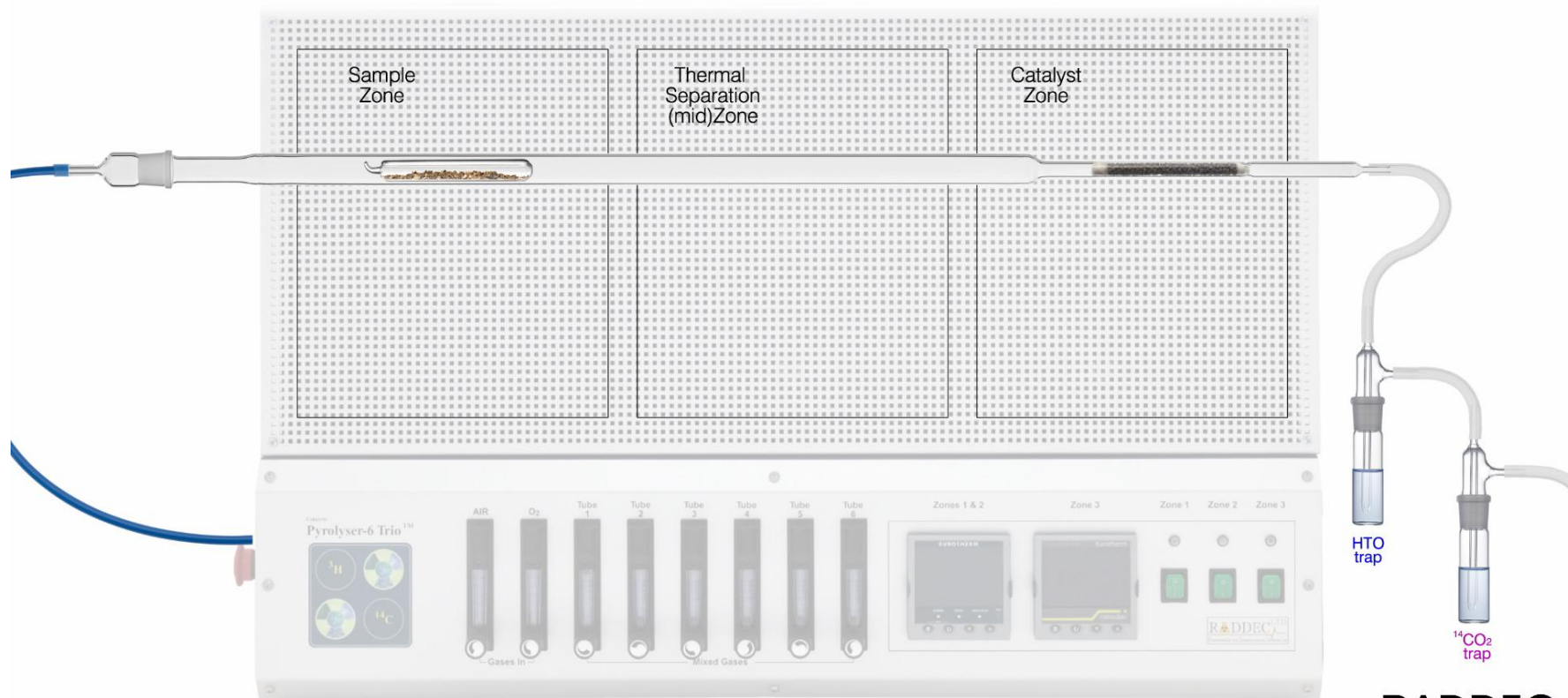
Purpose-built tube furnace for $^3\text{H}/^{14}\text{C}$ analysis



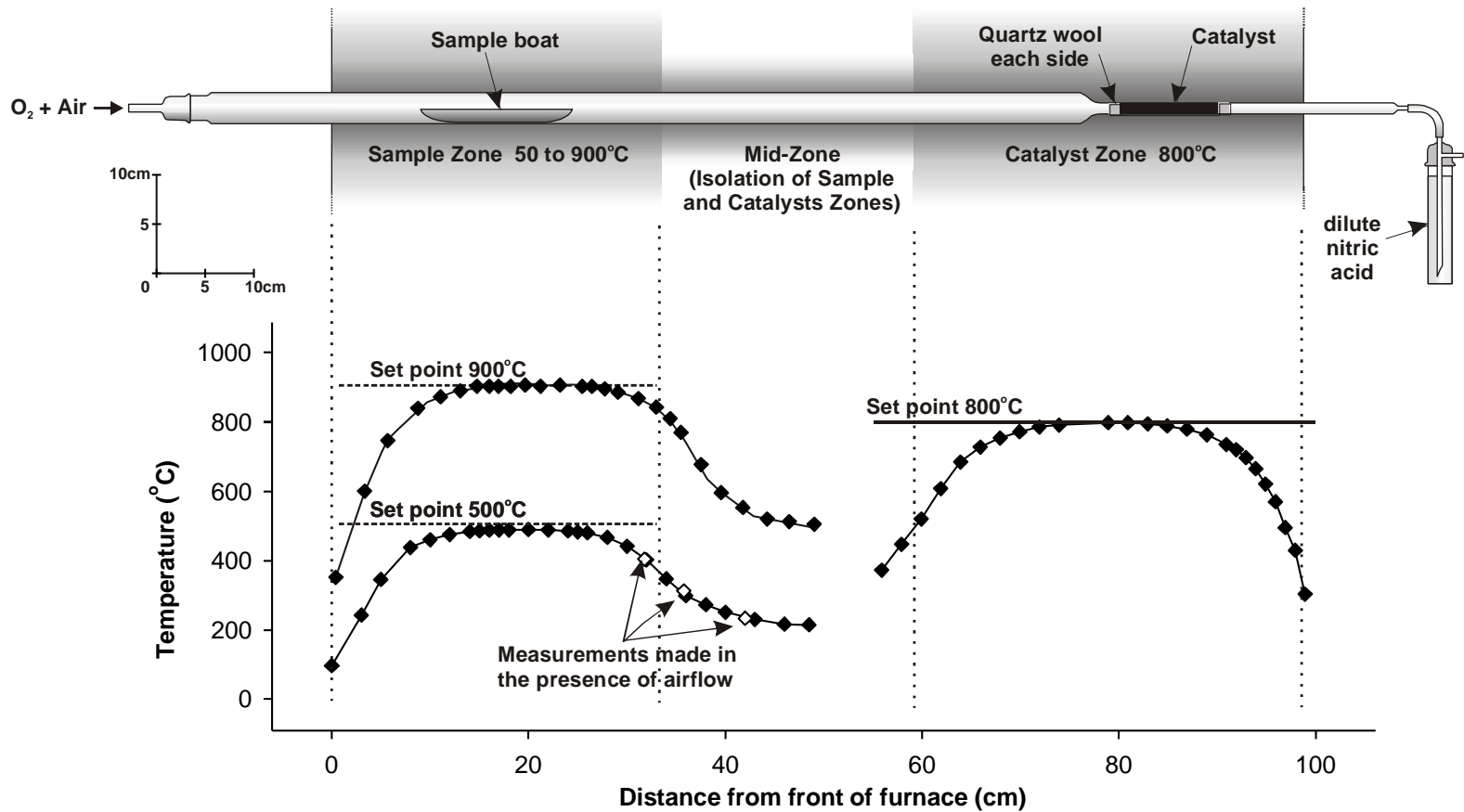
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Also available as Pyrolyser 2 and 4 variants

Configuration of the system



Furnace temperature profiles



Features

- 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 ^3H extraction from concrete and graphite

Features

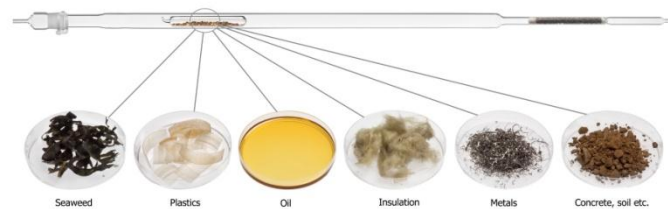
- Rapid cool-down of sample zone enabling good cycle times between runs.
- Incorporation of a mid-zone furnace to prevent condensate problems whilst maintaining thermal separation of the sample and catalyst zones.
- Bubbler-traps (20mls) have >95% efficiency.
- The Pyrolysers have been in regular use for extraction of ^3H and ^{14}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

- 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}Cl & ^{129}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

- **Samples with low organic contents**

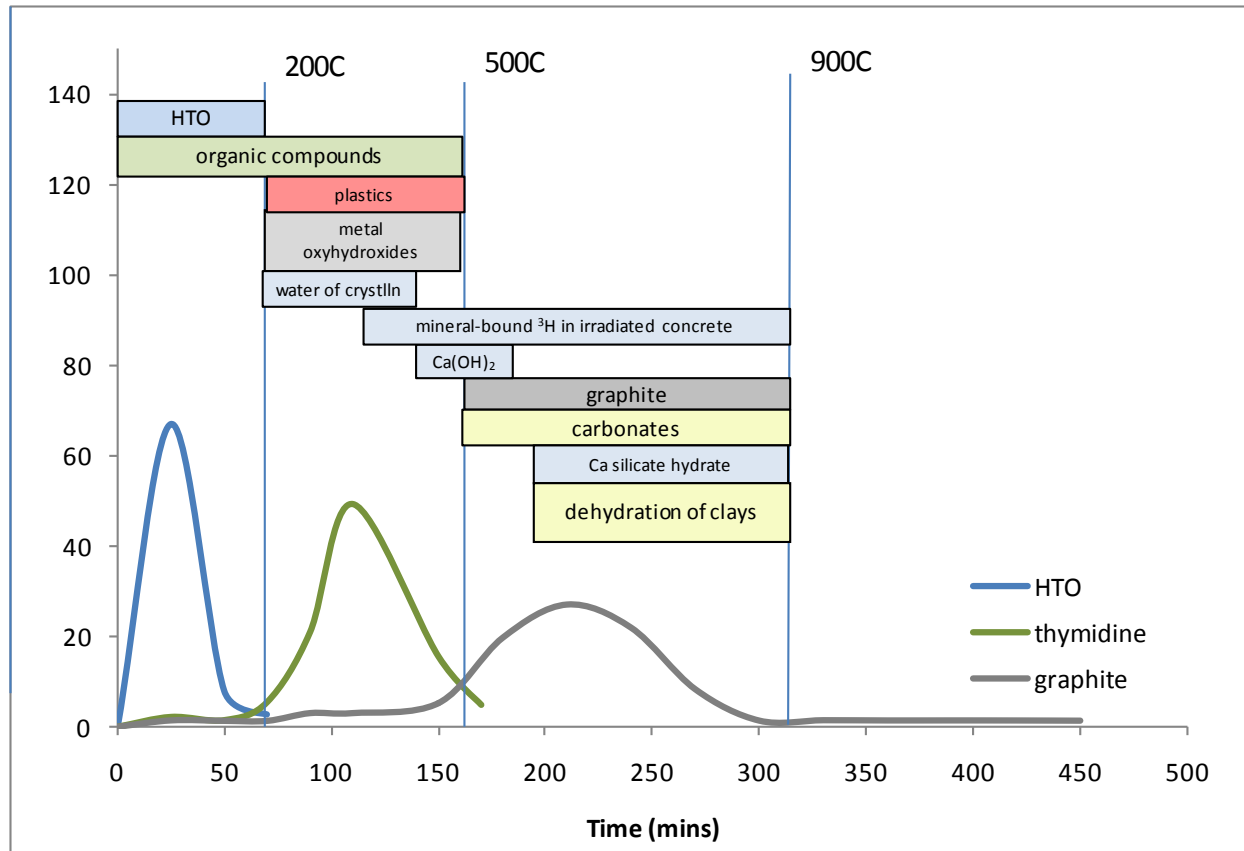
Soil/Sediment, concrete, brick, metal etc. (1 - 30g)

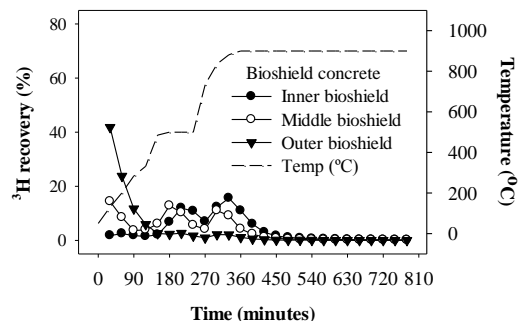
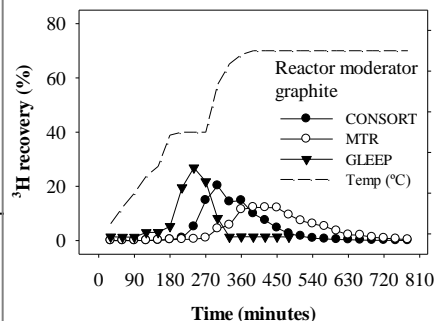
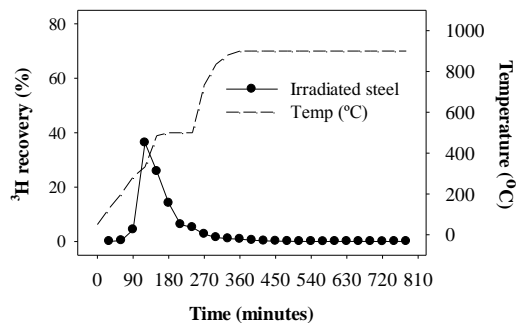
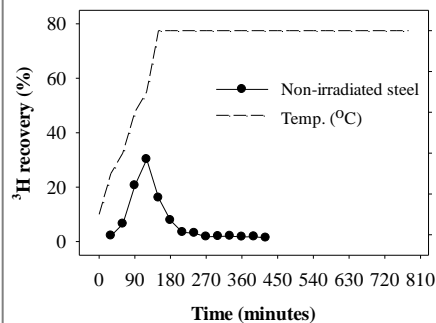
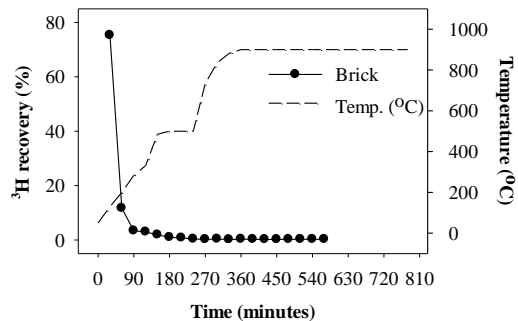
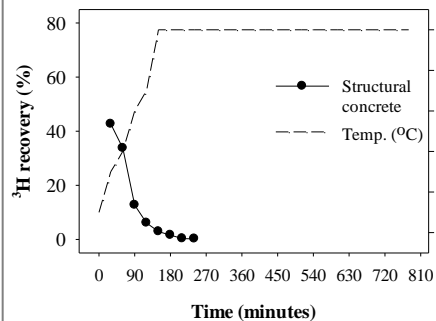
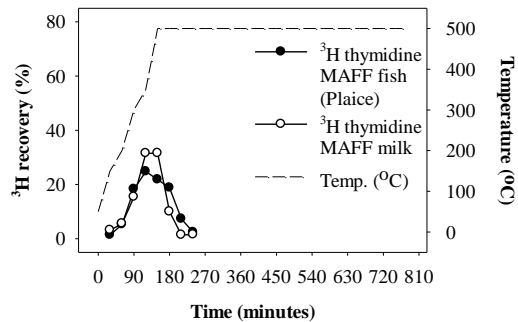
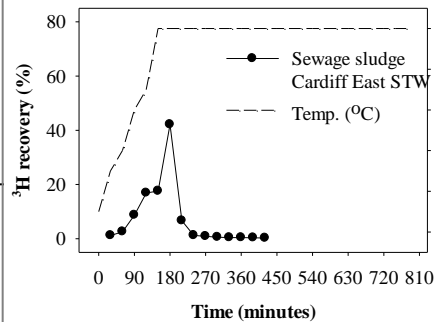
- **Samples with high organic contents**

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

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

^3H desorption profiles



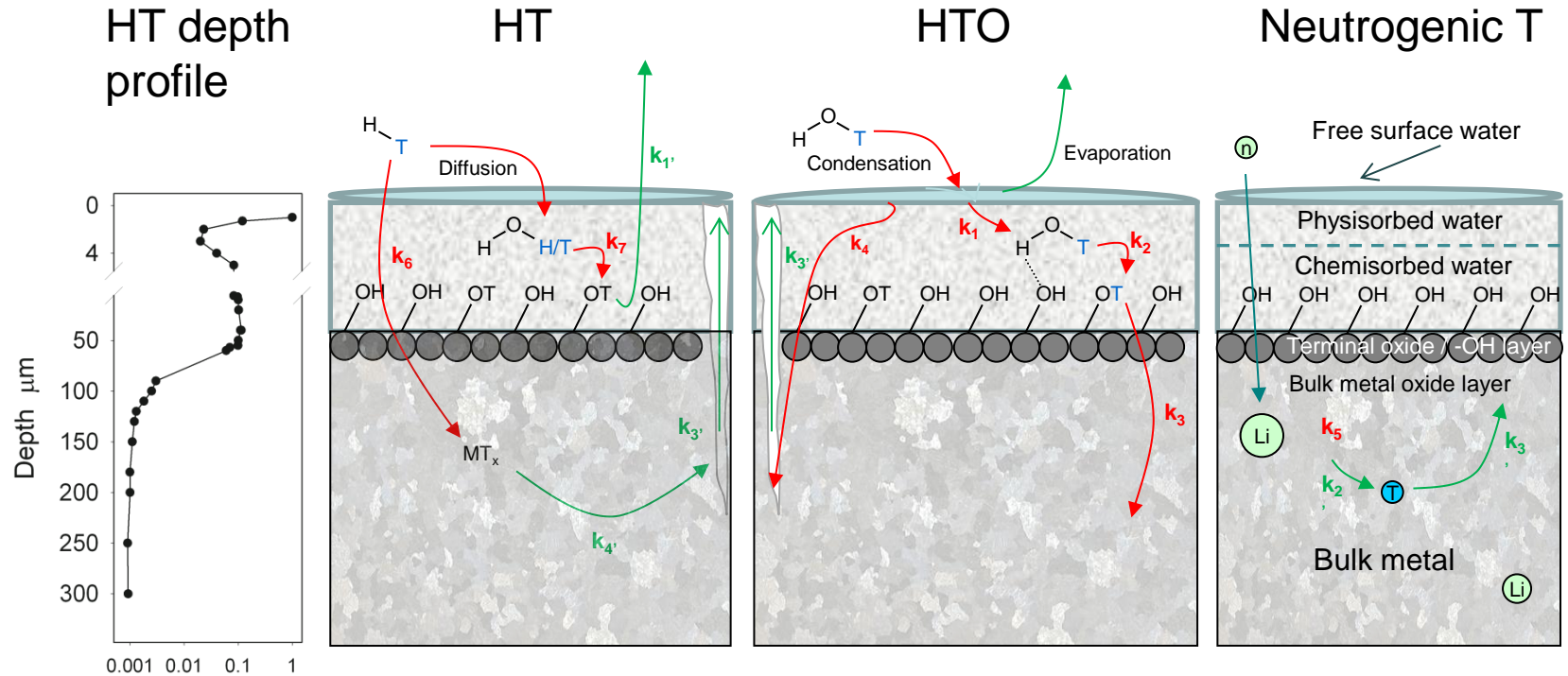


Thermal Evolution profiles

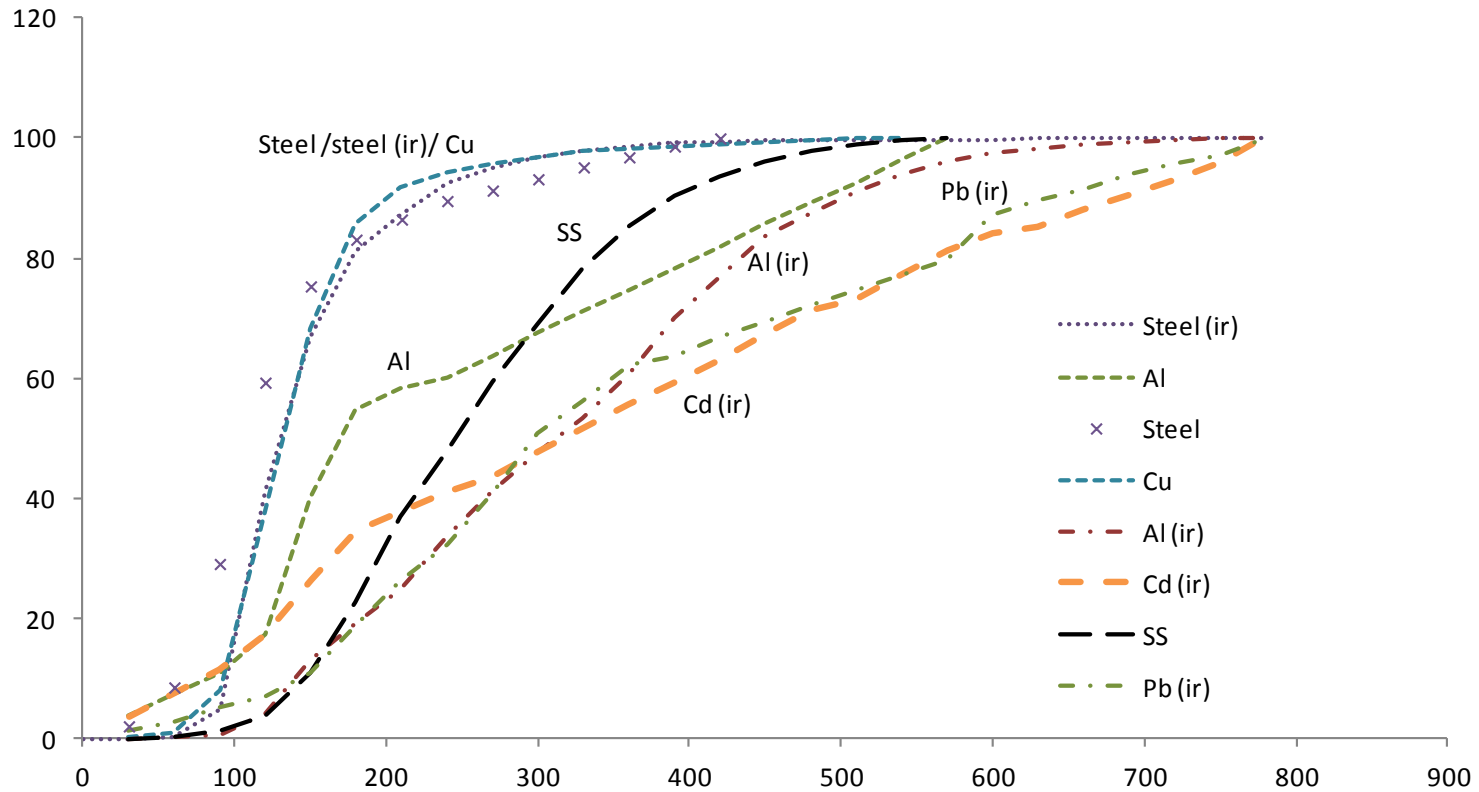
Kim D.J., Warwick P.E. & Croudace I.W. (2008). Anal. Chem., **80**, 5476 – 5480.

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

Tritium in metals

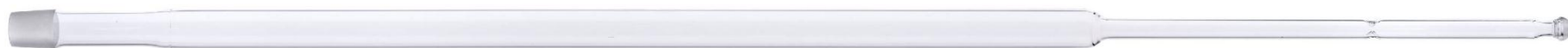


Tritium in metals profiles



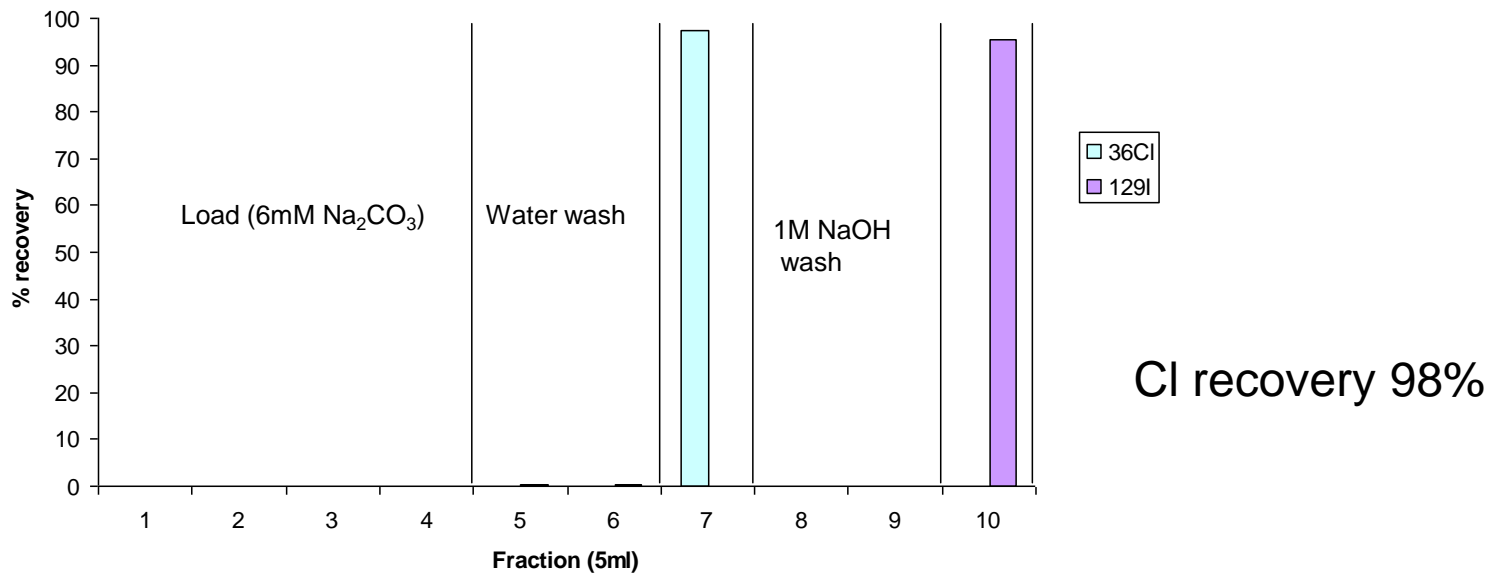
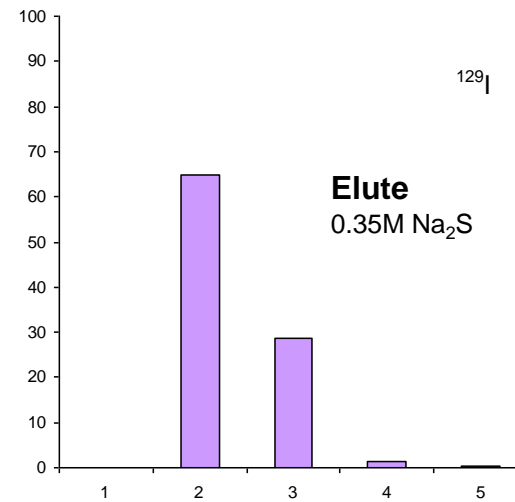
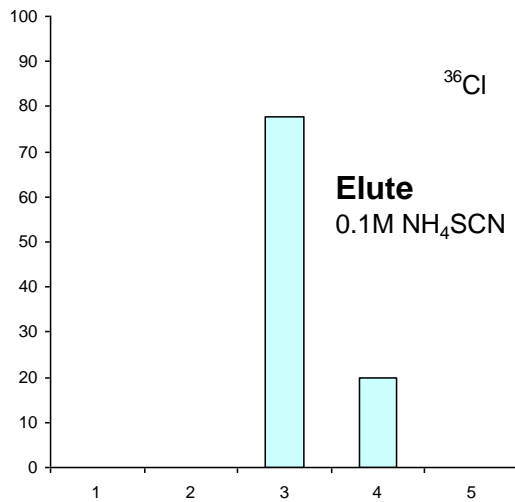
Croudace I.W., Warwick P.E. & Kim D.J. (2014). Anal. Chem., in press.

^{36}Cl / ^{129}I analysis set

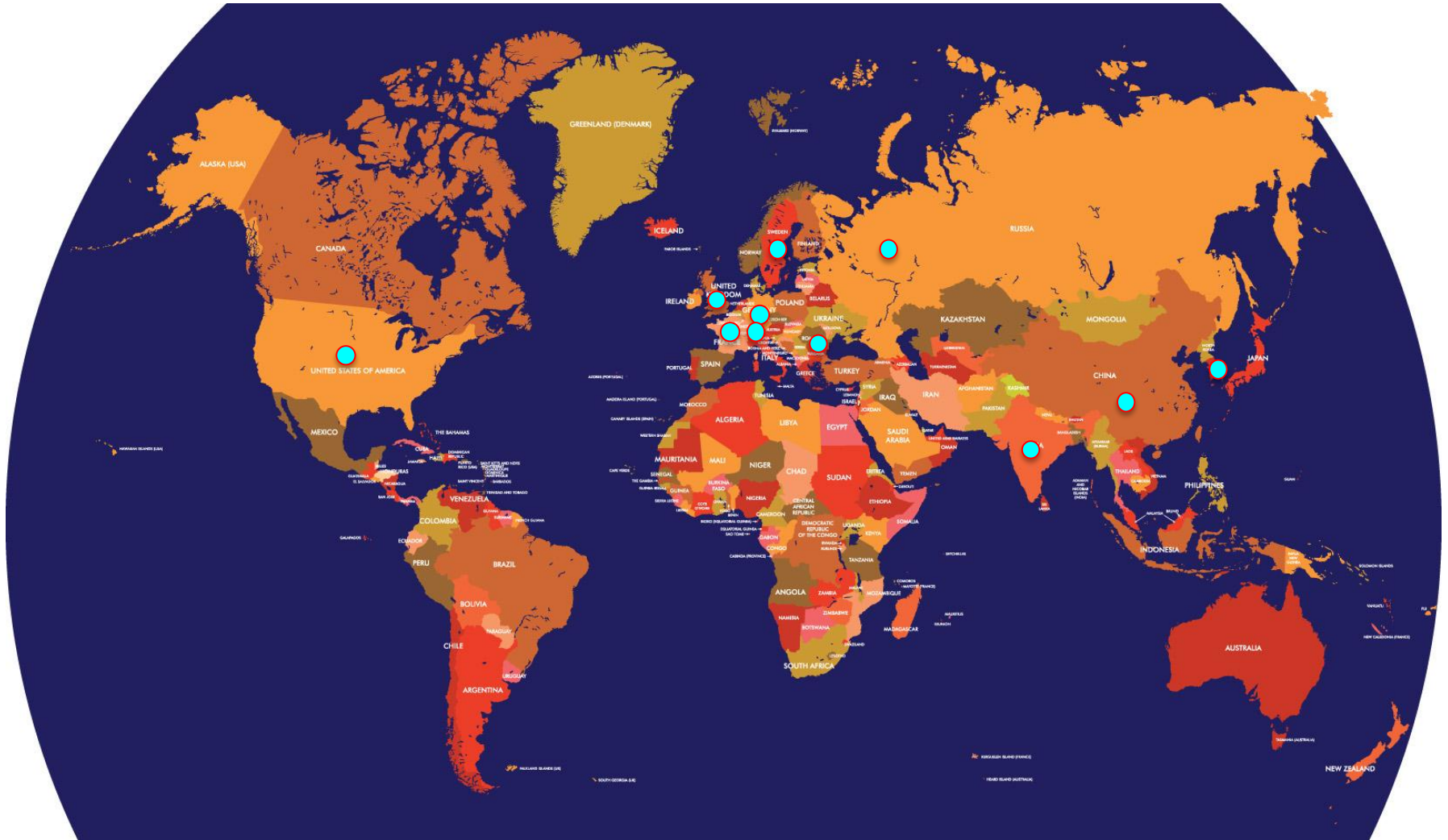


Bubbler solution 6 mM Na_2CO_3

Separation using Cl resin



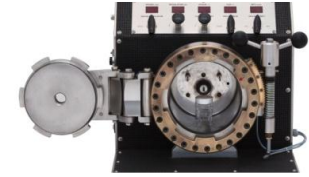
70 Pyrolyzers worldwide



The new HBO₂ system



Advantages of HBO



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

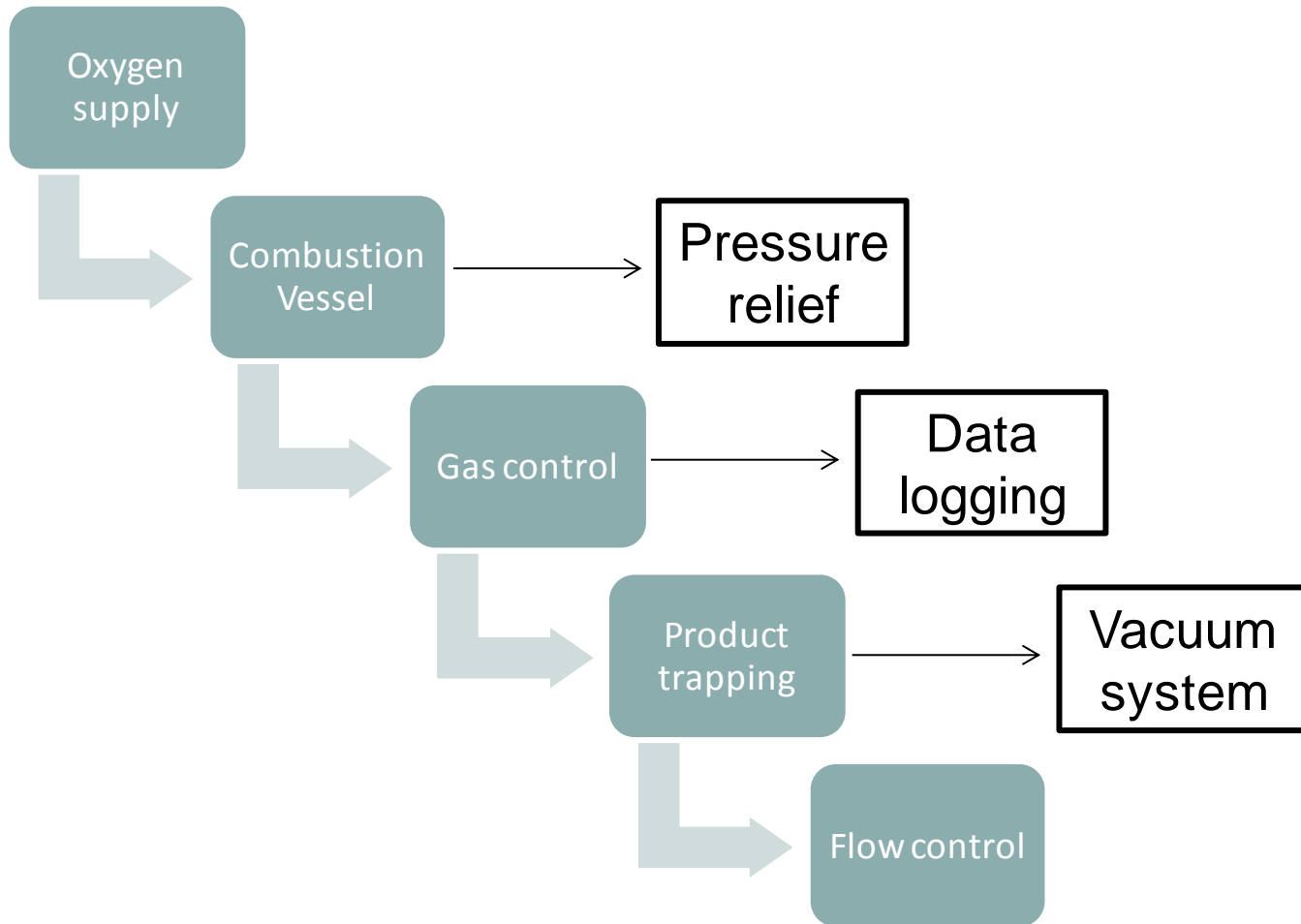
Cellulose (e.g. vegetation)

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 O₂

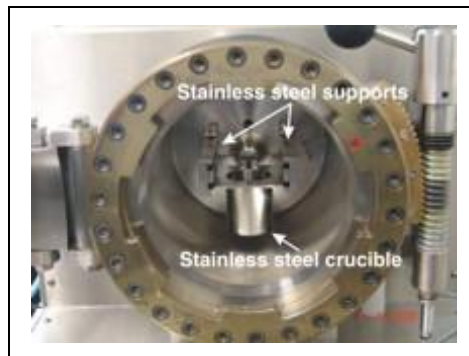


Sample combusted

Measurement
by LSC



HTO / H₂O
trapped from
exhaust gas

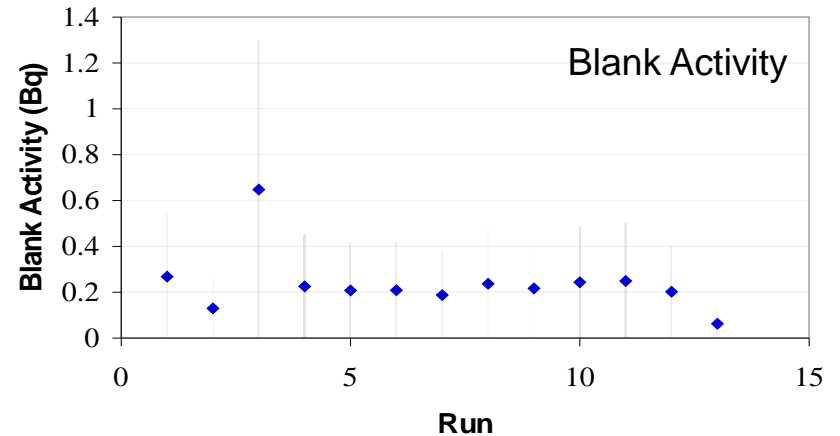
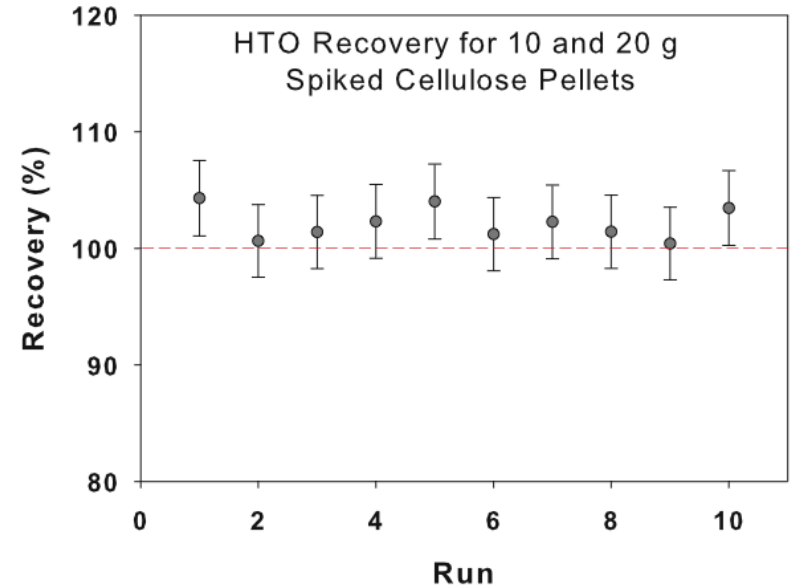


**Original steel
sample cup
abandoned due
to combustion
quench**

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 $\leq 0.7\%$



HBO₂ Mk2 developments

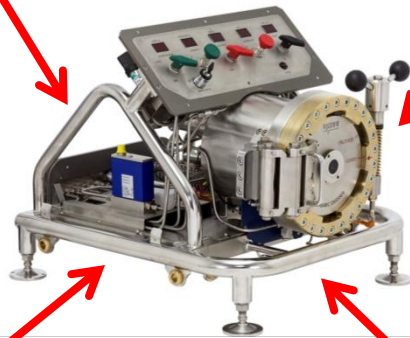


High volume pressure relief valve

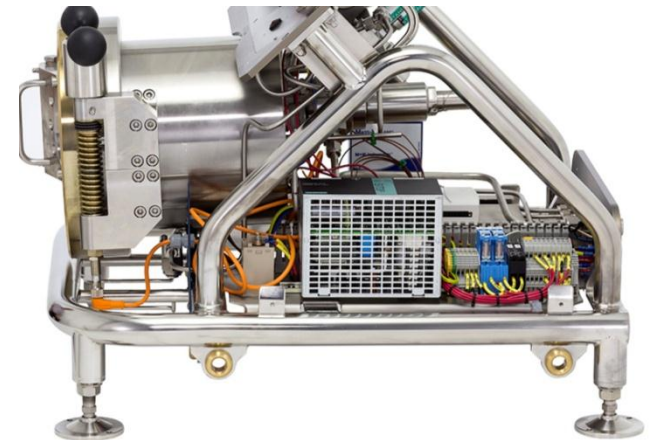
Improved pressure vessel with resistance wire ignition



Digital flow control and pressure regulation

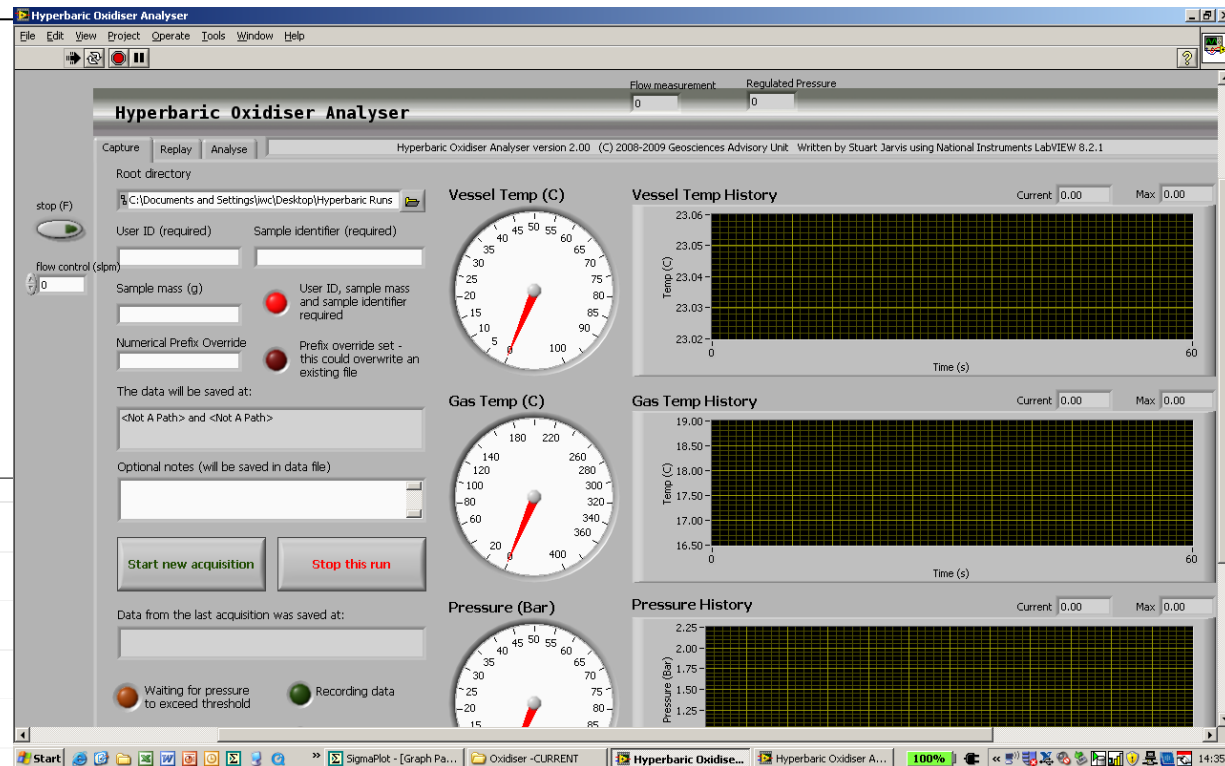
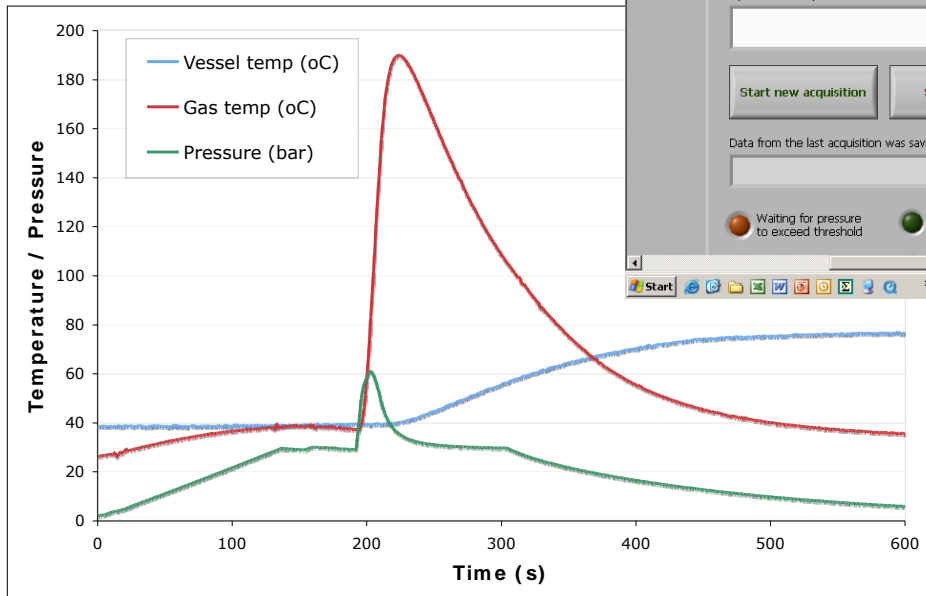


Lightweight yet robust SS frame and lifting system



Real time data output

LabVIEW interface allows continuous data output and process control



Software development

LSC+

Liquid scintillation data processing

Raddec LIMS

Laboratory information management system

Itrax plot

Data visualisation software for XRF core loggers

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

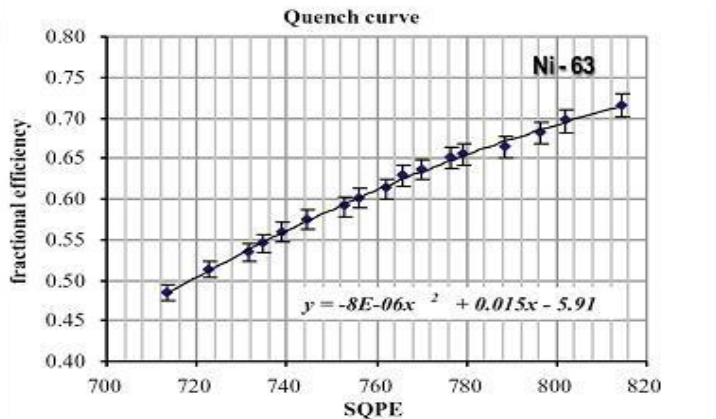
All results are in Bq/ml and are decay corrected to the reference date (12.30 Years half life)

* < 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



For more information

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