Tritium extraction from organic-rich sample matrices using the HBO_2

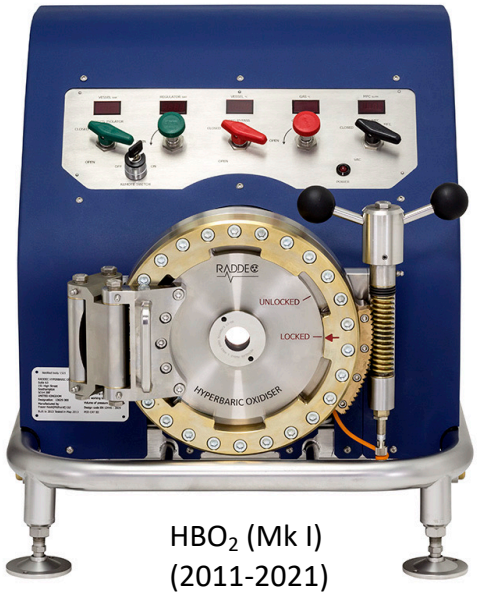
Ian Croudace, Rich Marsh, Phil Warwick, Dave Reading

Raddec International Ltd

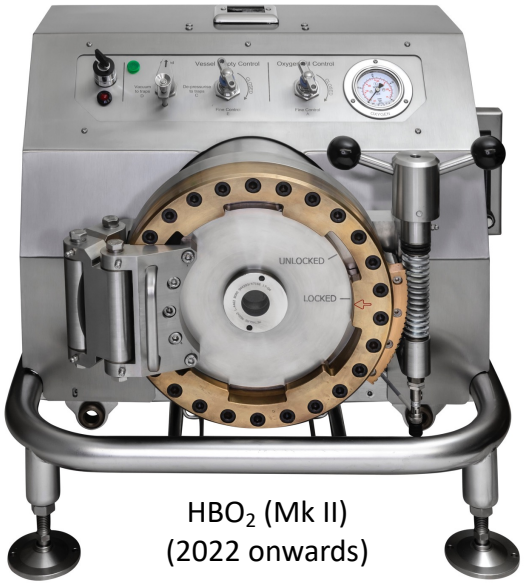
Raddec-Triskem International Technical Workshop April 2024

Outline

- ^{3}H extraction by bomb combustion
- Introduction to the HBO_2
- Combustion Procedure
- Safety Assessment
- HBO_2 (Mk II) developments
- User case study



HBO_2 (Mk I)
(2011-2021)



HBO_2 (Mk II)
(2022 onwards)

Analytical requirements?

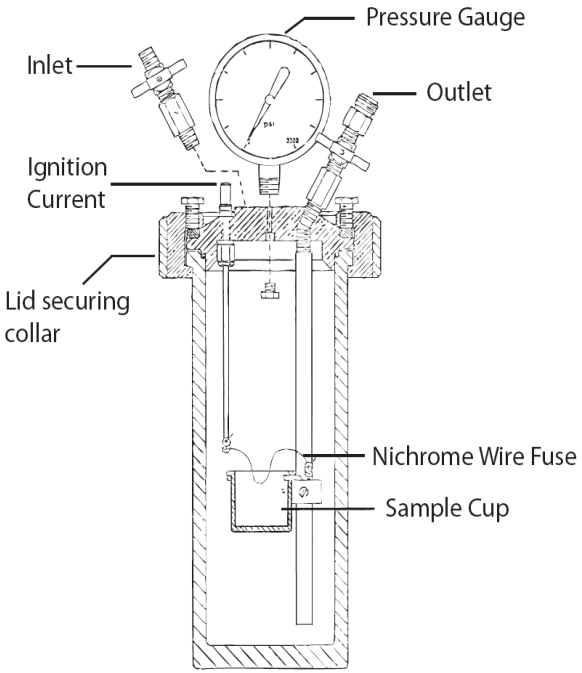
Instances where extraction of ^{3}H from organic-rich samples is beneficial:

- Environmental monitoring
  - ↪ **Often organic rich + low LOD requirements**
- Nuclear decommissioning
  - ↪ **Orphan wastes e.g. oils, rubbers, plastics**
- Fusion reactor operational support
  - ↪ **Heterogeneous soft wastes**

Bomb Combustion

- Enable ^{3}H extraction via complete oxidation in an excess oxygen environment.
- Few commercial systems available for ^{3}H extraction, typically a Parr 1121 used

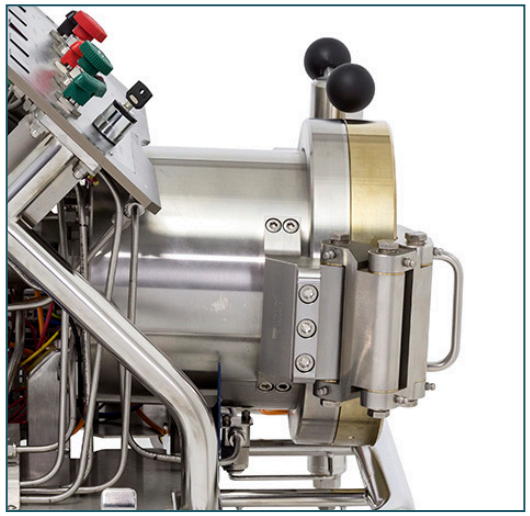
  e.g. Moghissi et al., (1974)



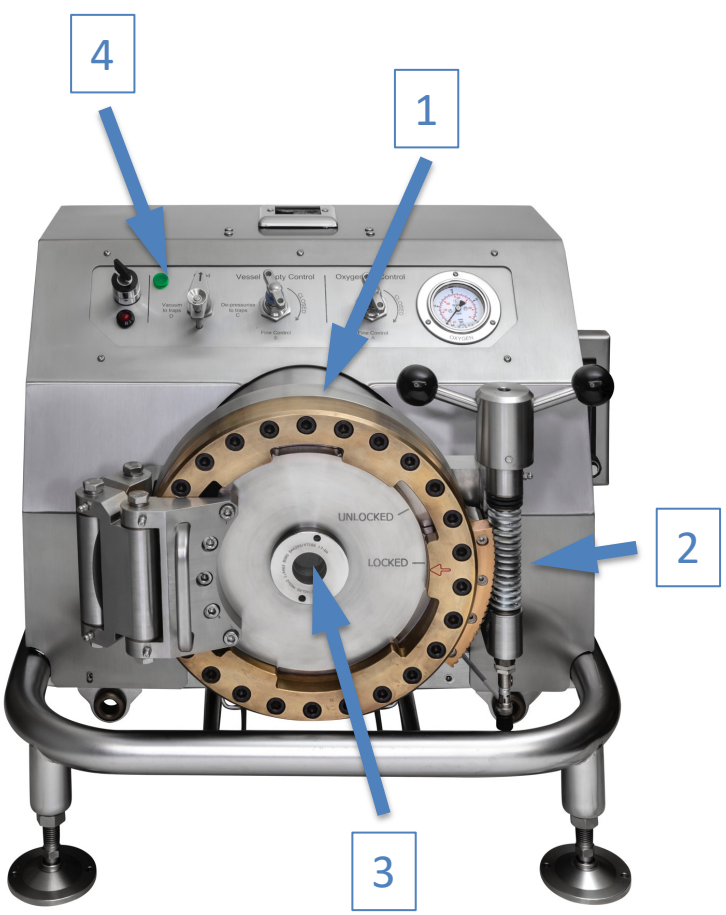
- Limited sample size (< 10 g)
- Manual operation
- Incomplete oxidation (quenching)

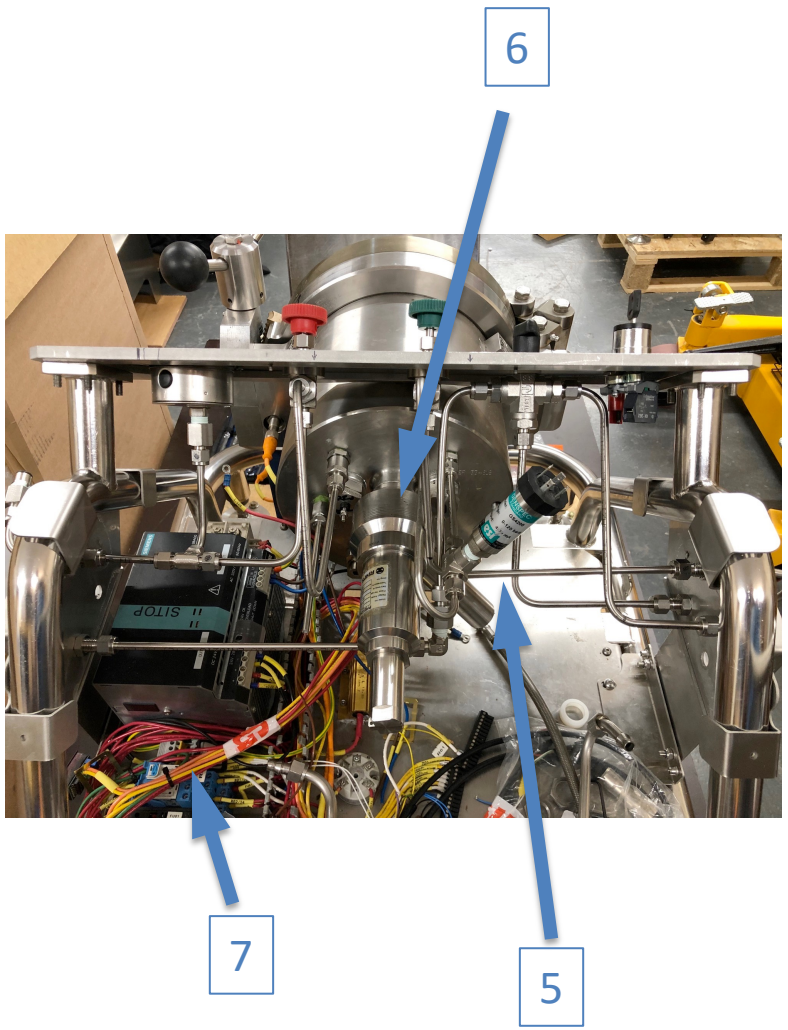
The Raddec Hyperbaric Oxidiser (HBO_2)

- Designed specifically for ^3H extraction
- High capacity combustion vessel
- Operates at pressures ≤ 100 bar
- Optimised for organic-rich matrices
- Large samples can be combusted (typically up to 30 g)



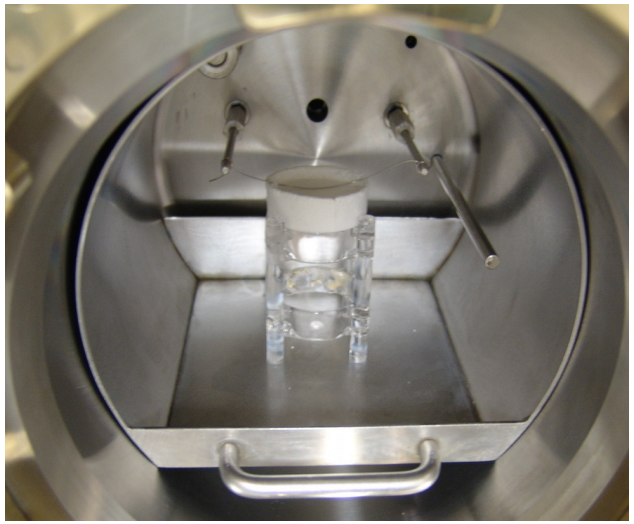
System components (I)





Combustion Procedure

Sample pelletised or cut to size



Sample loaded into disposable silica crucible

Measurement by LSC

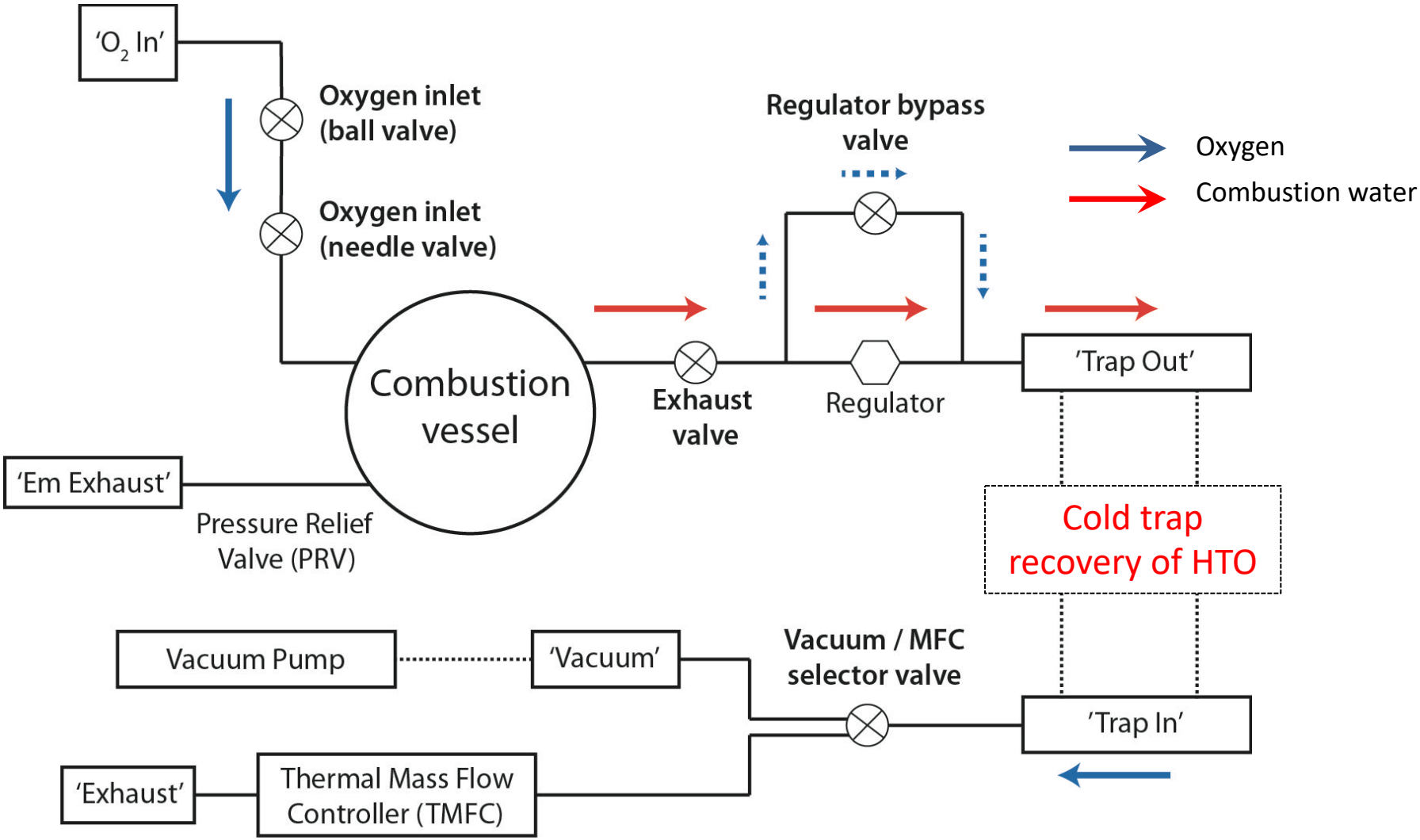
Combustion water recovered under vacuum

Sample combusted

Safety Systems & Verification

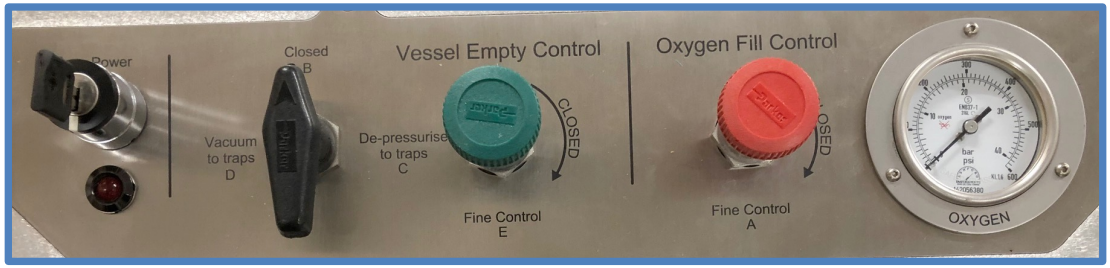
- Independently verified hydraulic pressure test (136 bar)
- Finite Element Analysis - pressure compatibility
- Meets Directive 2014/68/EU (III B Prod + C2)
- High-volume Swagelok PRV
- Dual vessel closure interlocks
- Dual ignition interlocks

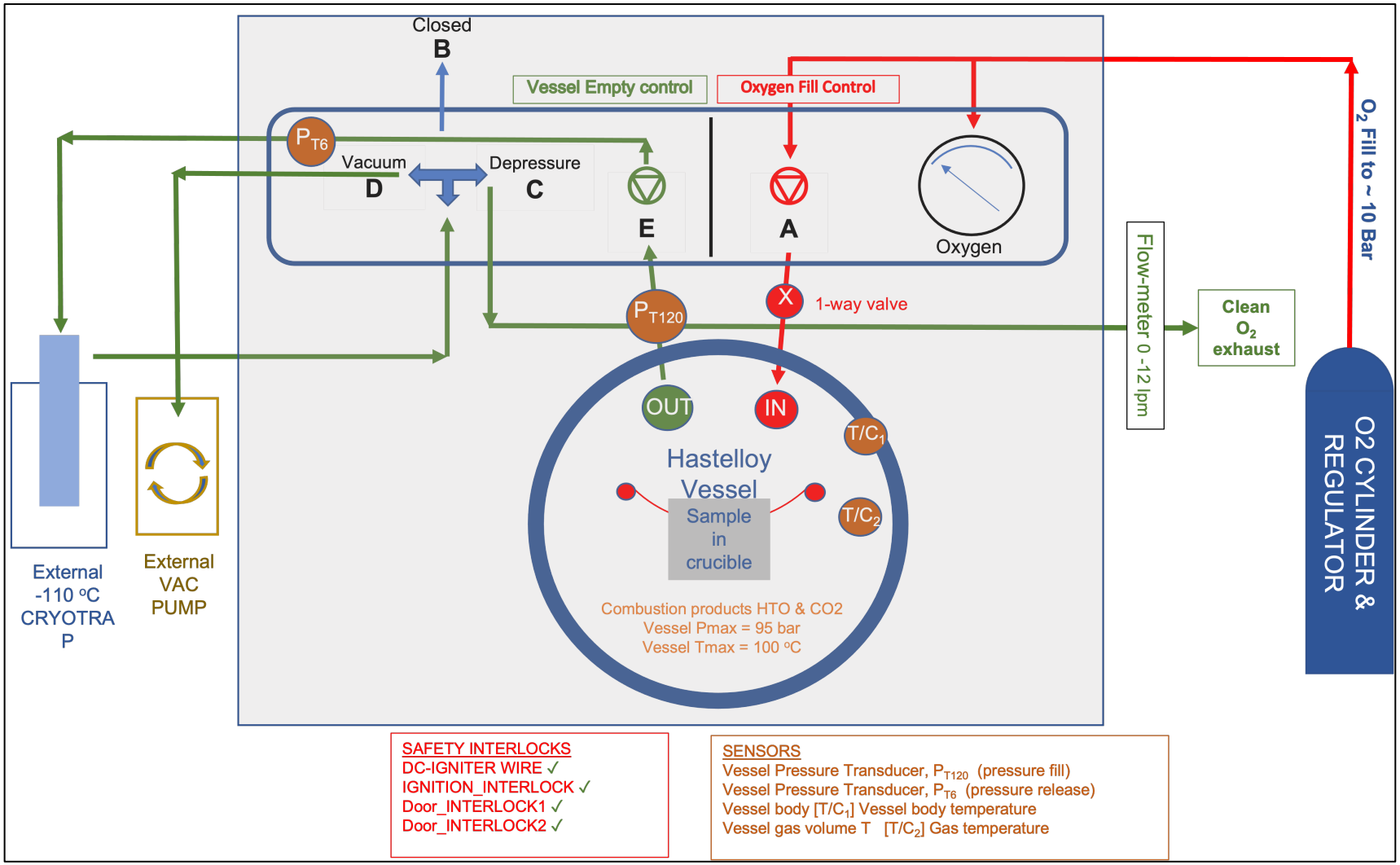
Flow schematic (HBO_2 Mk I)



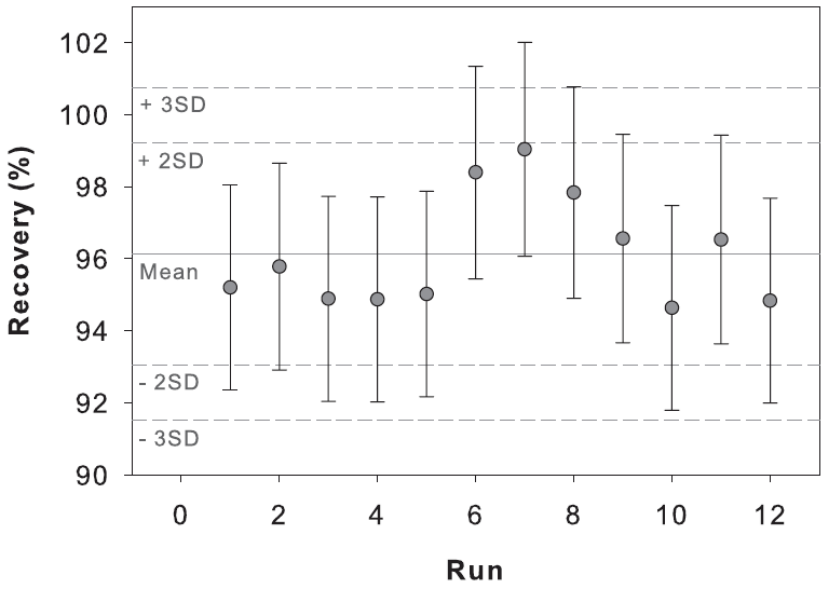
HBO_2 Mk II Developments

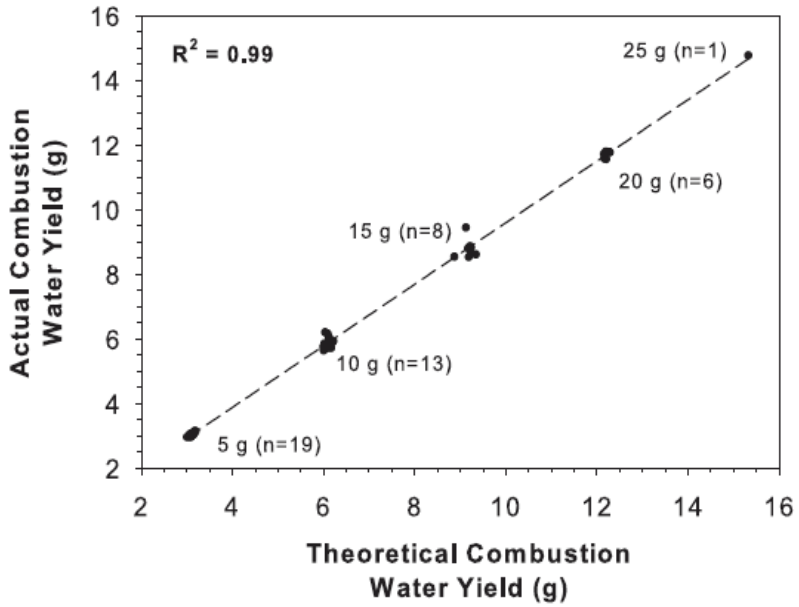
- Simplified gas handling system and flow control
- Optional Hastelloy C/276 vessel
- Upgraded software interface & tablet PC
- Integrated exhaust outlet tube heating
- Re-design of service connections (ergonomic)




Closed
B
Vessel Empty control
Oxygen Fill Control
P_{T6}
Vacuum
D
Depressure
C
E
A
Oxygen
O_2 Fill to ~ 10 Bar
Flow-meter 0 -12 lpm
Clean O_2 exhaust
P_{T120}
X
1-way valve
OUT
IN
T/C_1
Hastelloy Vessel
Sample in crucible
T/C_2
Combustion products HTO & CO2
Vessel Pmax = 95 bar
Vessel Tmax = 100 °C
External -110 °C CRYOTRAP
External VAC PUMP
O2 CYLINDER & REGULATOR
SAFETY INTERLOCKS
DC-IGNITER WIRE ✓
IGNITION_INTERLOCK ✓
Door_INTERLOCK1 ✓
Door_INTERLOCK2 ✓
SENSORS
Vessel Pressure Transducer, P_{T120} (pressure fill)
Vessel Pressure Transducer, P_{T6} (pressure release)
Vessel body [T/C_1] Vessel body temperature
Vessel gas volume T [T/C_2] Gas temperature

Validation (I)

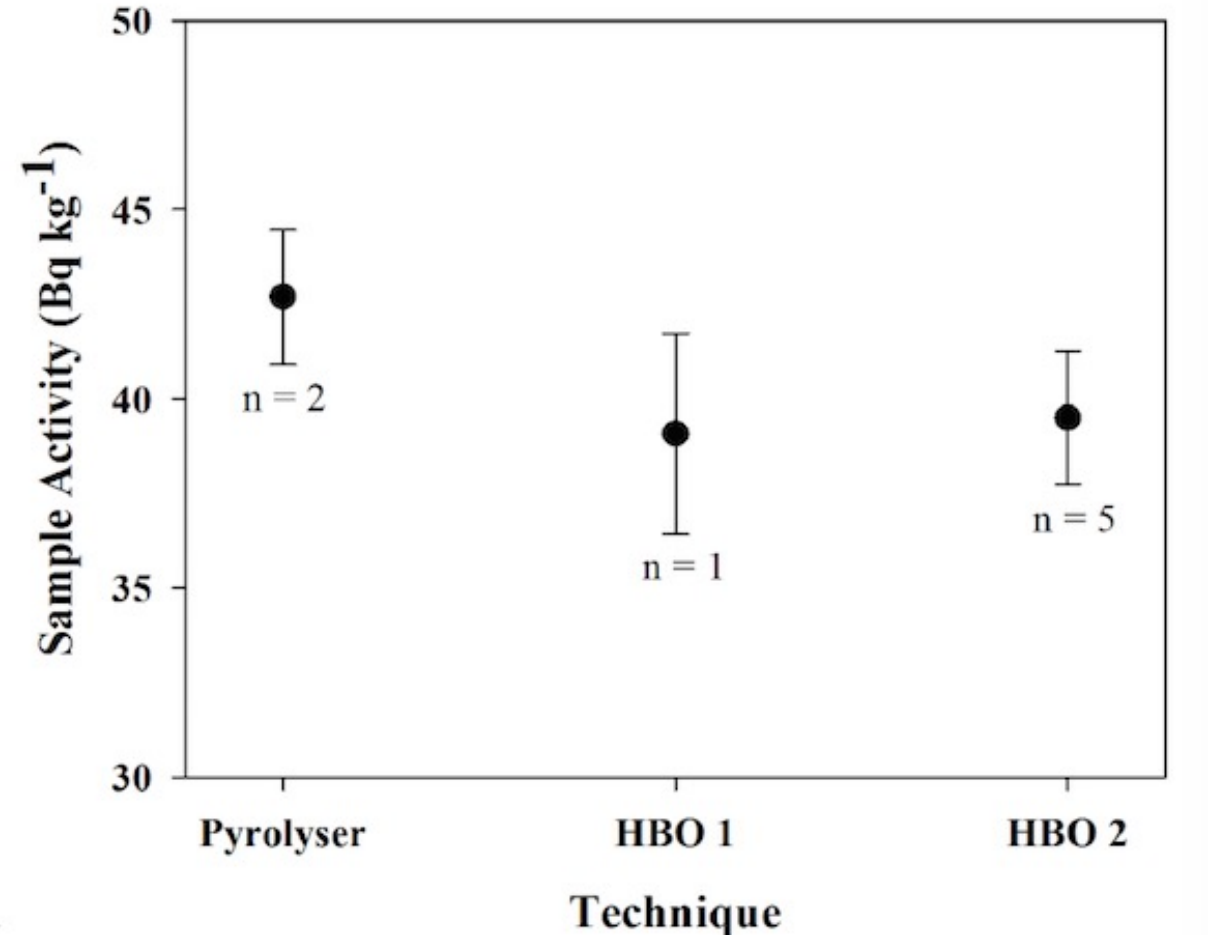




Gravimetric recovery testing based on cellulose pellet combustions - 20 g replicate pellets (left); incremental masses (right). Completed on HBO_2 (Mk I).

Validation (II)

OBT in Wheat Intercomparison sample



Case Study

Environmental ^{3}H Measurement

Canadian Nuclear Safety Commission (CNSC), Ottawa

All data & images courtesy of Nadereh St-Amant, CNSC, Ottawa. See also Marsh et al. (2017)

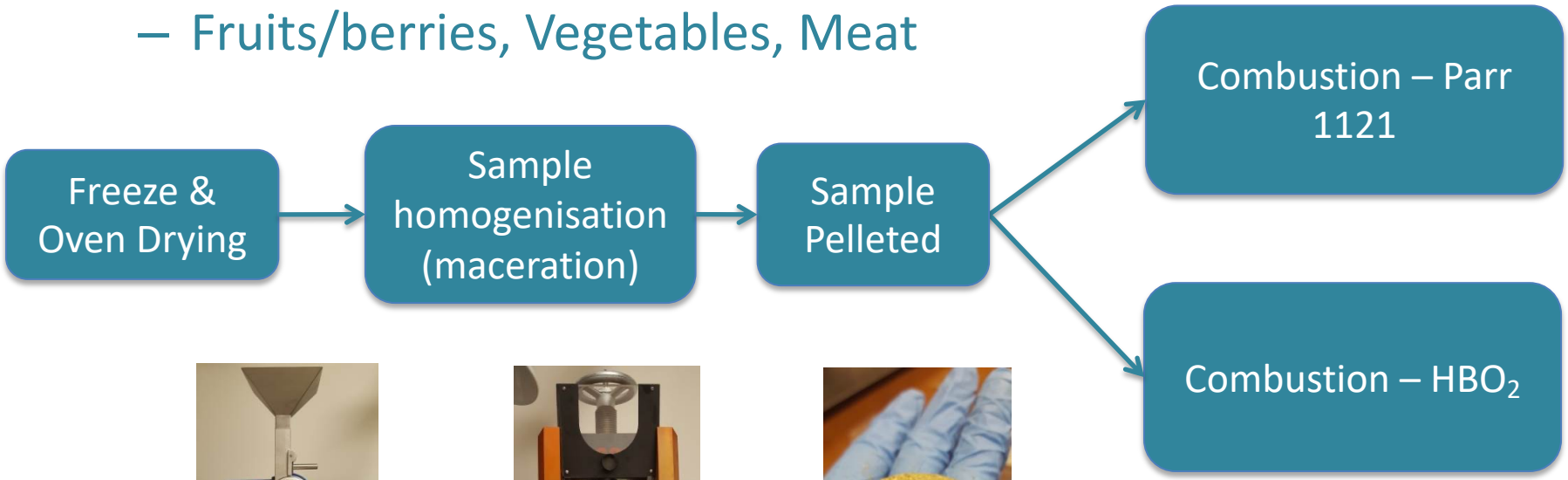
Background

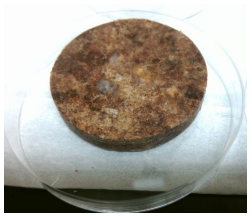
- Discharges from Canada's nuclear industry regulated by CNSC
- Principal releases from D_2O moderated CANDU reactors e.g. Bruce, Darlington etc.
- Also ^{3}H processing, removal and research facilities e.g. Chalk River, SRB Technologies etc.

Independent discharge and environmental monitoring – compliance and reassurance

^{3}H analysis

- HTO in water, HT/HTO in air and OBT in foodstuffs
  - Fruits/berries, Vegetables, Meat





System comparison (I)

Parr 1211

- Max sample size 10 g
- Combustion process not visible and maybe quenched
- Manual combustion water recovery
- Cloudy / coloured combustion water
- Requires purification prior to counting by LSC

HBO_2

- Max sample size 30+ g
- Combustion progress is visible
- Integrated vacuum collection of combustion water
- Direct measurement of combustion water is possible

System comparison (II)

Parr 1211

tSIE % difference typically 12-24%

HBO_2

tSIE % difference typically 0-1%

tSIE % difference values measured for wheat samples, relative to distilled water quench values.

OBT Environmental data

- 1.5 to 60 Bq/kg fresh weight

All results are Bq/kg fresh weight

System	HBO_2						Parr 1121	
Foodstuff	Fruits and Berries	Vegetables	Potatoes	Beef	Chicken	Pork	Milk	Fish
Typical LOD (10 g sample)	2 Bq/kg (0.5 - 1 for 20-30 g sample)						3 Bq/kg	
Tritium Processing Facility	11.8 - 17.5	1.5	1.5	N/A	N/A	N/A	1.5	N/A
NPP1	1.5 - 2	1.5 - 2	2	2 - 56.5	1.5	2 - 21	2	1.8 - 2
NPP2	1.5	1.5	1.6 - 2.1	N/A	1.5 - 10.5	N/A	1.5	N/A
NPP3	1.5 - 2.8	1.5 - 1.6	N/A	N/A	N/A	N/A	1.5	1.5 - 15.9

All data courtesy of Nadereh St-Amant, CNSC, (Marsh et al. 2017.

HBO_2 – Pyrolyser validation

Sample	HBO_2	Pyrolyser	HBO_2 memory (%)
Cardboard	11300 ± 3000	11000 ± 2000	0.6
Cardboard	6000 ± 1000	8000 ± 2000	0.5
"Housekeeping"	600 ± 100	3100 ± 600	0.3
"Housekeeping"	80 ± 20	2700 ± 500	1.3
PVC	3000 ± 600	2600 ± 500	N/A

All data courtesy of Natasha Gotts, CCFE (Marsh et al. 2017.

- Good agreement for Cardboard and PVC samples
- Minimal observed memory
- Discrepancy between "Housekeeping" data are associated with the highly heterogeneous nature of the samples

Conclusions

- The HBO_2 enables rapid and efficient recovery of ^3H from organic rich samples up to 30 g
- The system is applicable to a wide range of sample types including biota and soft-waste
- Also applicable to orphan wastes such as oils and sludge's
- Can offer improved LODs compared to thermal oxidisers.

Acknowledgments

- Thank you to CNSC Ottawa and CCFE for sharing their data and experiences with the HBO_2 and allowing us to present some of these in this talk.