UNCERTAINTIES IN PYROLYSER ANALYSIS

Phil Warwick, Ian Croudace, Richard Marsh and Dave Reading

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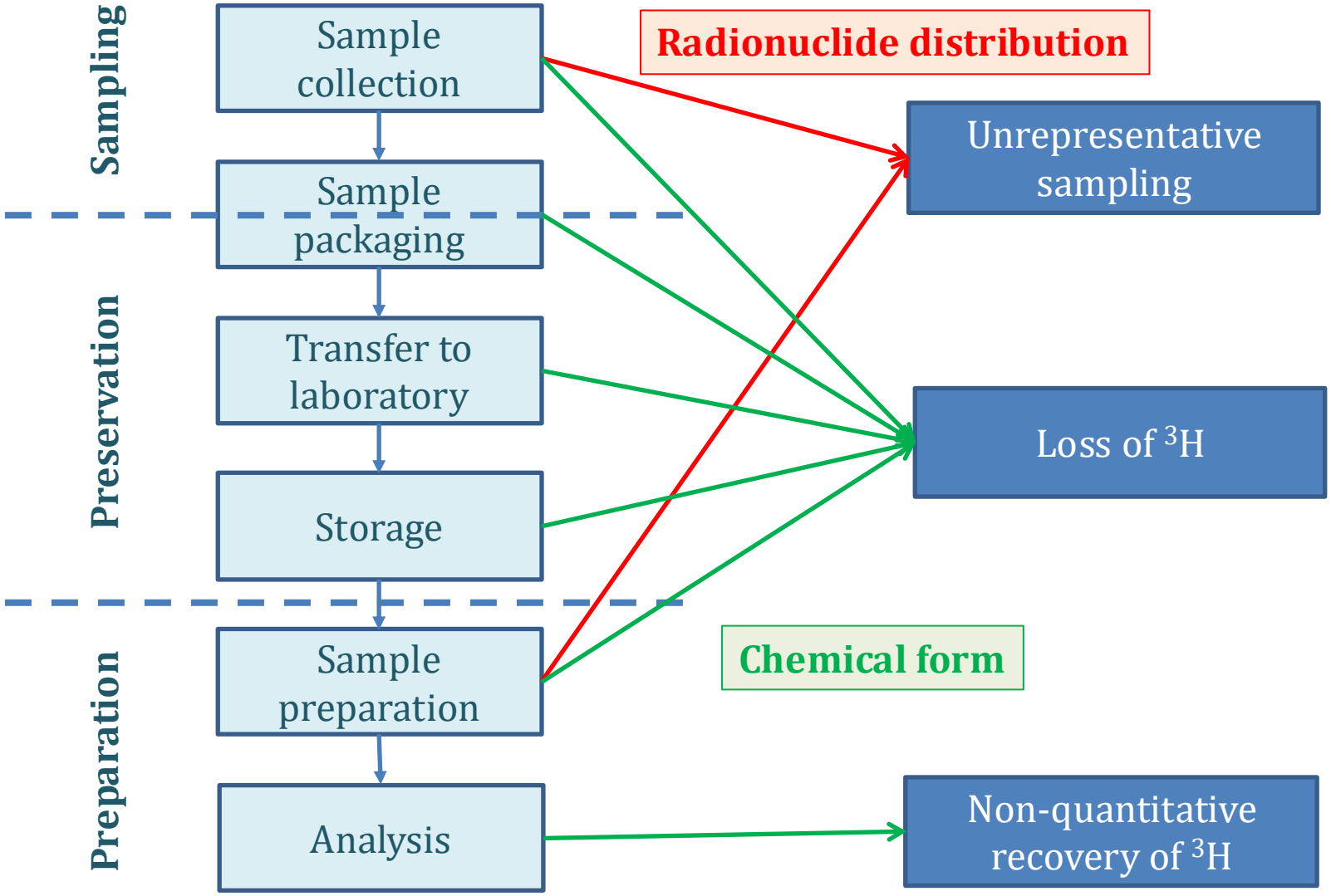
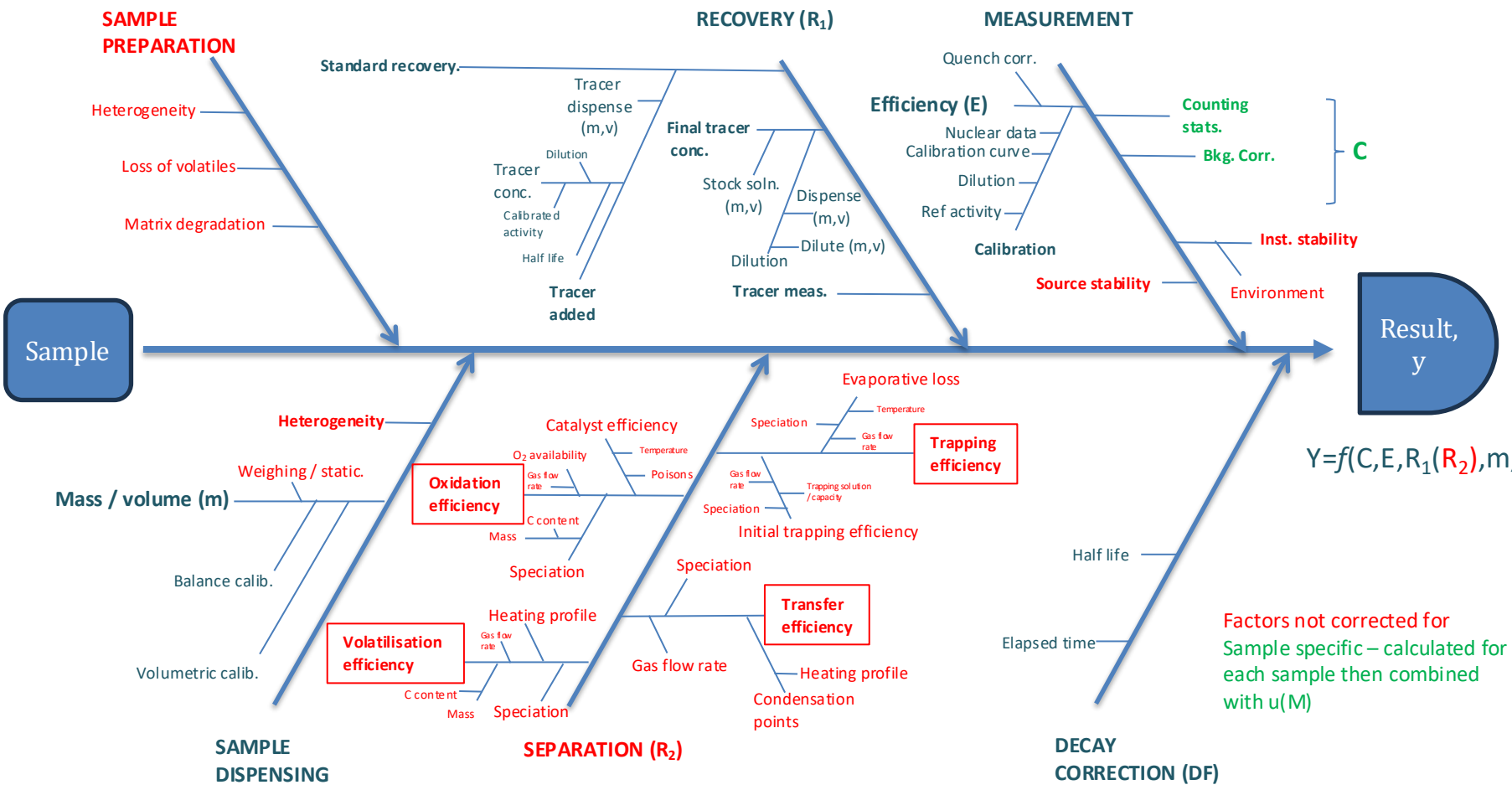
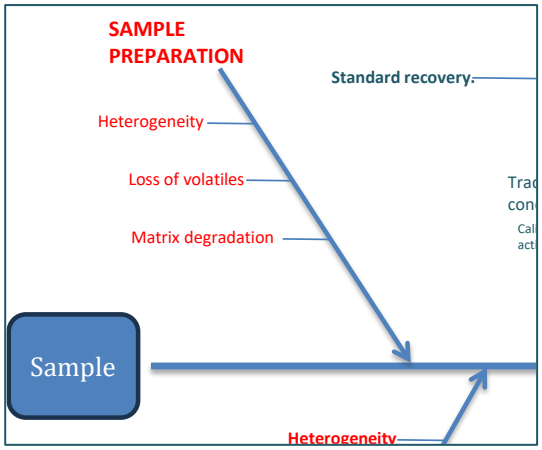
Sources of error

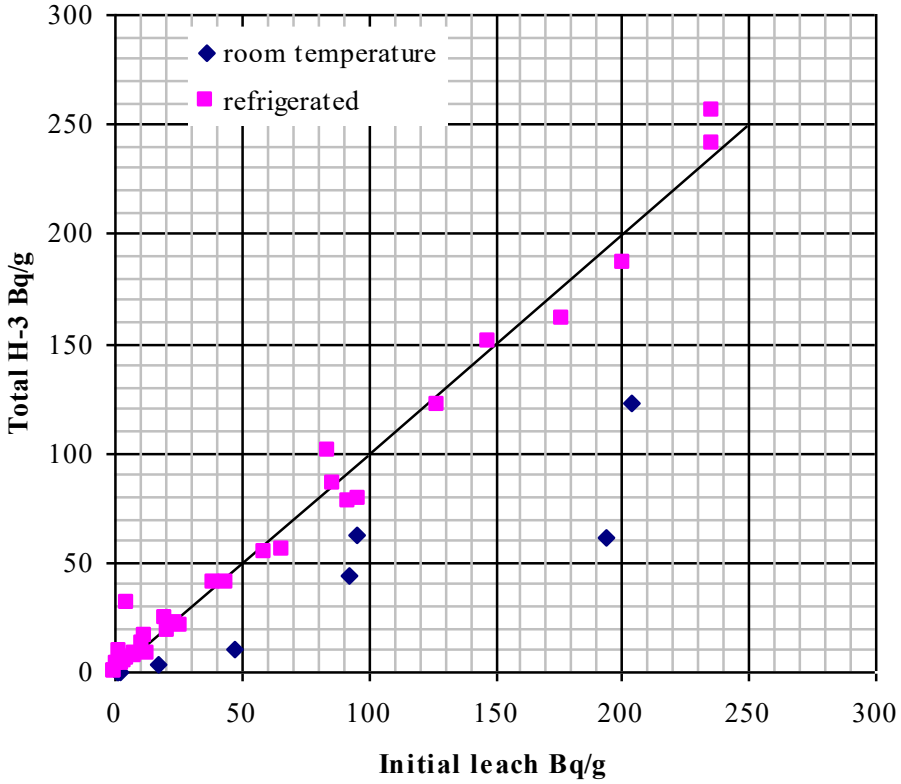


Volatile nuclide uncertainties



Sample preparation





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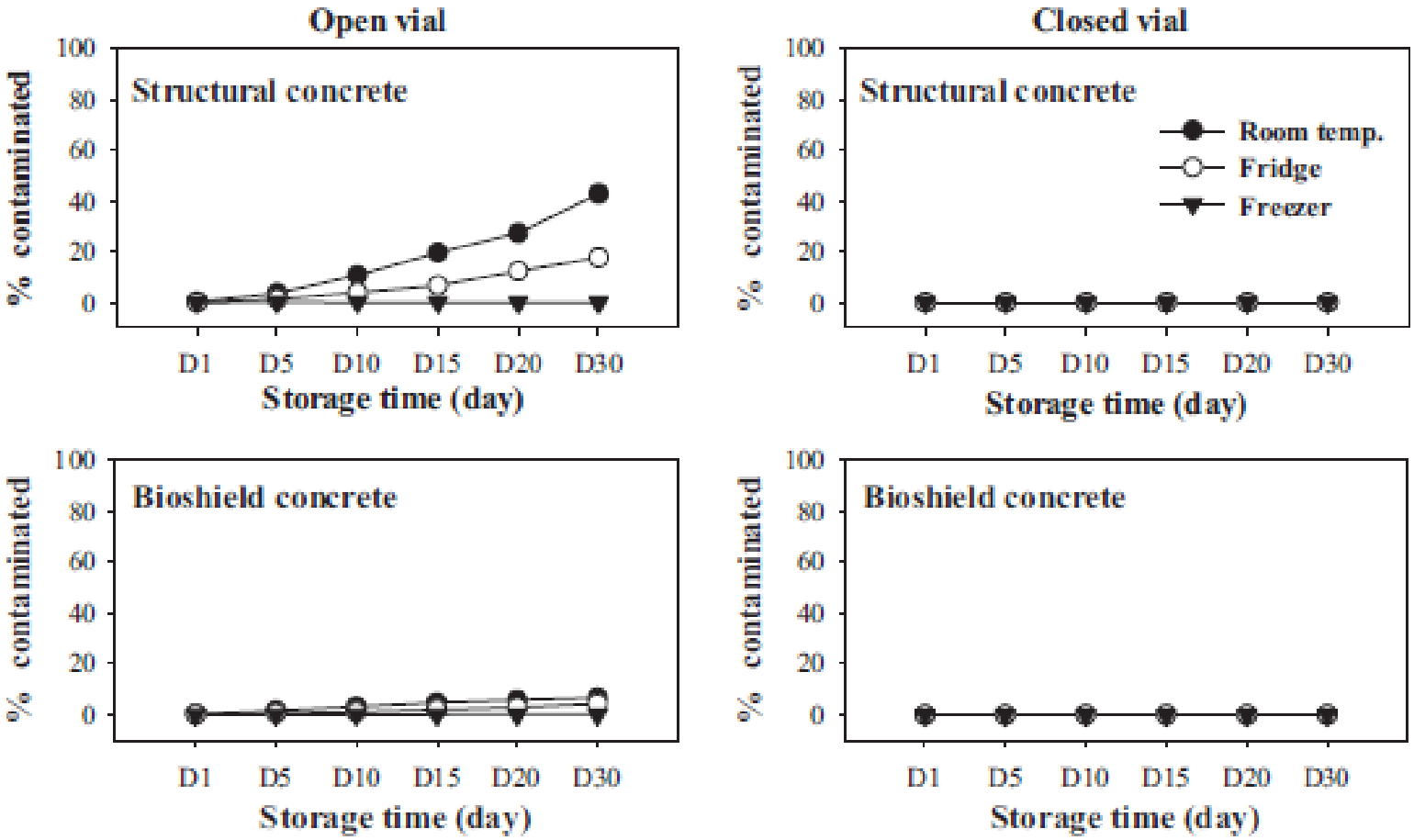
Effect of storage condition on ^{3}H loss

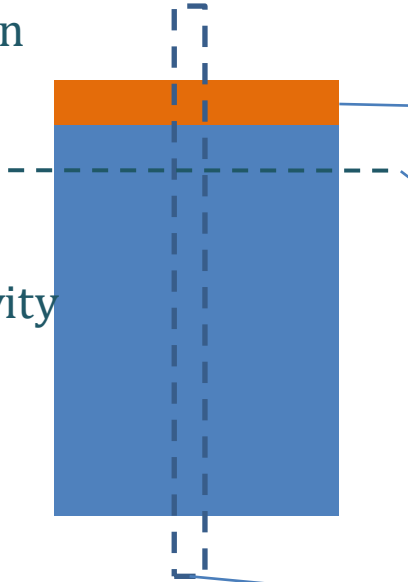


Kim D-J., Croudace I.W. & **Warwick P.E.** (2012). The requirement for proper storage of nuclear and related decommissioning samples to safeguard accuracy of tritium data. *J. Haz. Mat*, ***213 – 214***, *292-298*

Surface contamination & sub-sampling

Surface contamination
2 g/cm^3
100 Bq/g to 50µm

Bulk metal – no activity
20mm thick
Density = 8g/cm^3



Surface 50µm removed by filing

100 Bq/g

Surface 100µm removed by filing

20 Bq/g

Sample drilled through entire depth

0.06 Bq/g

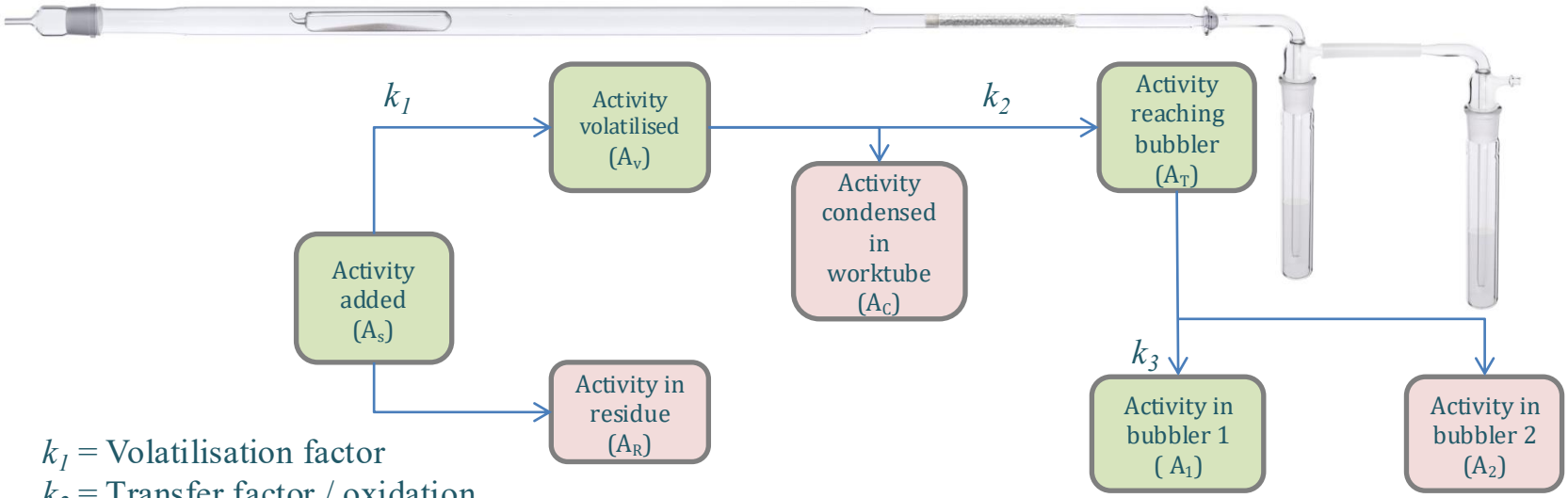
Key stages in process

Sample decomposition / analyte volatilisation

Analyte transfer

Oxidation of volatile species

Analyte trapping



k_1 = Volatilisation factor
k_2 = Transfer factor / oxidation
k_3 = Trapping factor

Overall recovery = k_1 x k_2 x k_3

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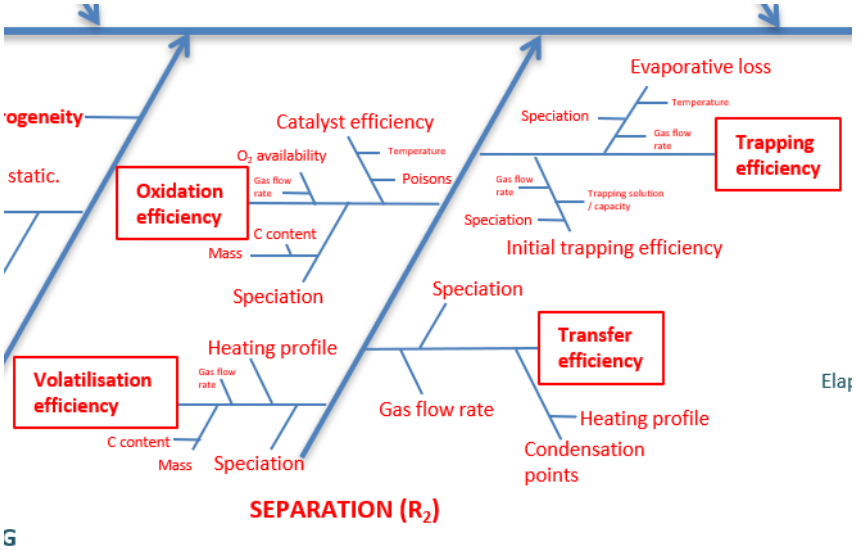
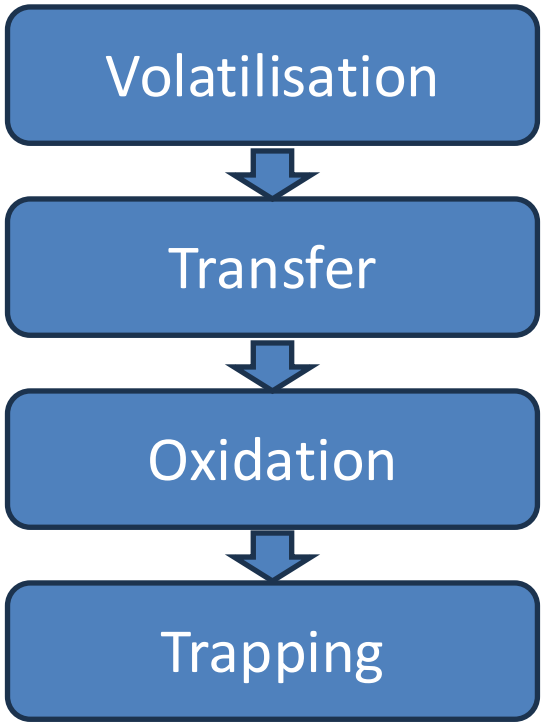
Separation


ogeneity
static.
Oxidation efficiency
Catalyst efficiency
O_2 availability
Temperature
Poisons
Gas flow rate
C content
Mass
Speciation
Volatilisation efficiency
Heating profile
Gas flow rate
C content
Mass
Speciation
Evaporative loss
Speciation
Temperature
Gas flow rate
Trapping efficiency
Gas flow rate
Trapping solution / capacity
Speciation
Initial trapping efficiency
Speciation
Transfer efficiency
Gas flow rate
Heating profile
Condensation points
SEPARATION (R_2)


Volatilisation
Transfer
Oxidation
Trapping

Key factors impacting separation

Parameter	Impact	Mechanism
Sample mass	Volatilisation efficiency	Mass impacts on heat transfer and rate of thermal decomposition / volatiles release.
Sample composition	Volatilisation efficiency Oxidation efficiency	Rate of volatilisation dependent on composition. Oxidation efficiency dependent on speciation of volatiles Catalyst efficiency impacted by poisons Rate of oxidation dependent on C content
Analyte speciation	Volatilisation efficiency Transfer efficiency Trapping efficiency	Rate of volatilisation dependent on analyte speciation. Magnitude of condensation dependent on speciation of volatiles. Trapping efficiency impacted by chemical form of analyte.
Gas flow rate	Volatilisation efficiency Transfer efficiency Oxidation efficiency Trapping efficiency	Oxidative volatilisation limited by O_2 inventory in carrier gas Rate of transfer controlled by gas flow rate. Rate of oxidation limited by O_2 inventory in carrier gas / oxidant. Trapping efficiency impacted by bubble size / rate Bubbler evaporative loss rate function of gas flow rate
Heating profile	Volatilisation efficiency Transfer efficiency Oxidation efficency	Rate of thermal decomposition / volatilisation controlled by heating profile Heating profile impacts on work tube temperature profile and condensation. Catalyst efficiency linked to catalyst temperature.
Catalyst / oxidant efficiency	Oxidation efficiency	Performance impacting by catalyst / oxidant type, condition and temperature
Bubbler evaporative loss	Trapping efficiency	Rate of evaporative loss relating to temperature of bubbler and gas flow rate.

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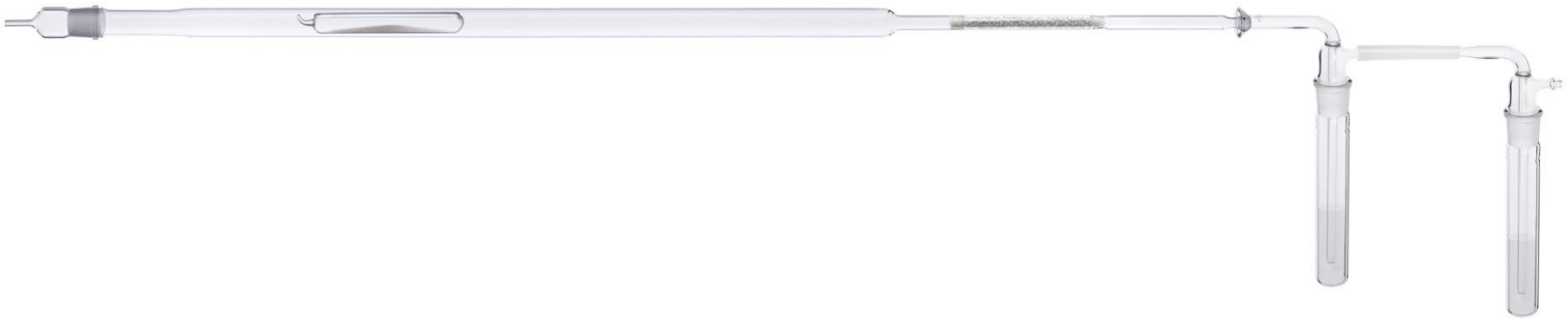
Volatilisation efficiency

Sample decomposition / analyte volatilisation

Analyte transfer

Oxidation of volatile species

Analyte trapping



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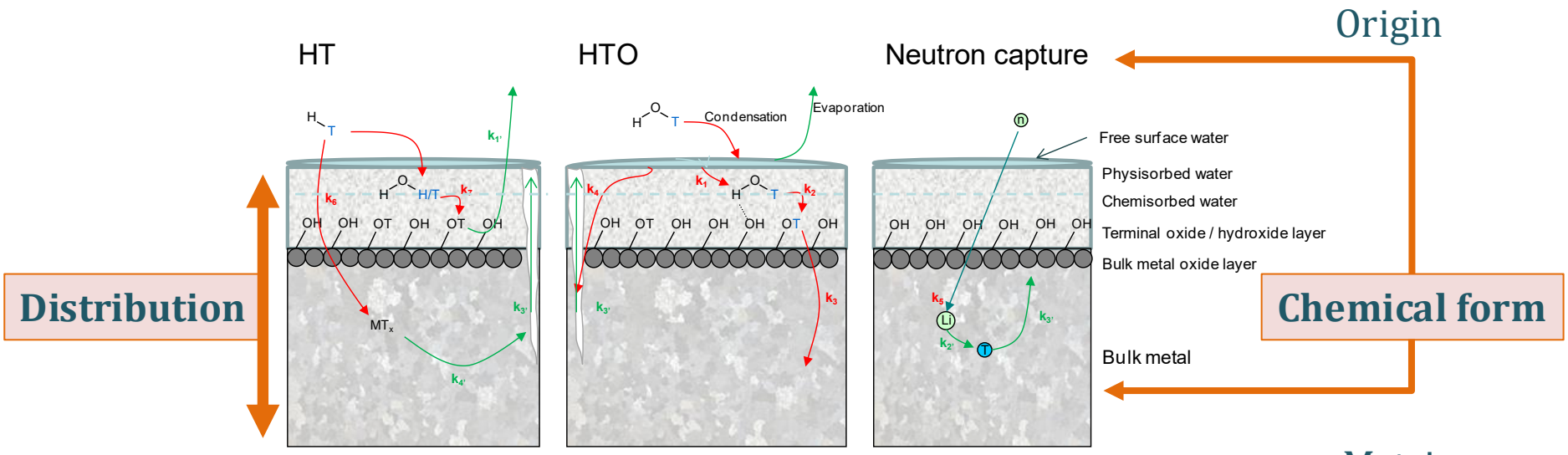
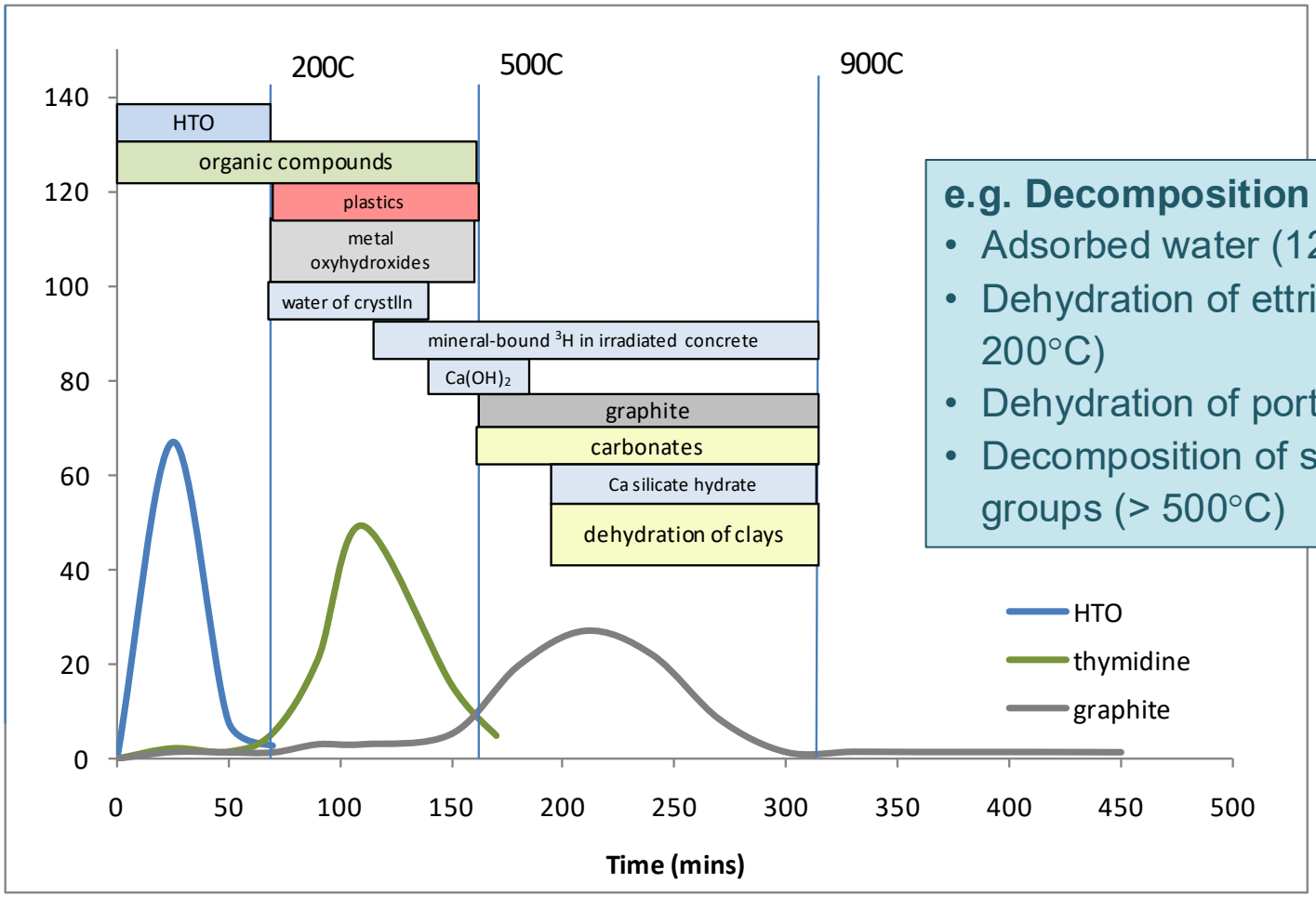
Factors impacting volatilisation



k_1	surface interaction between water molecule and surface oxyhydroxide layer via hydrogen bonding
k_2	tritium exchange between water and surface hydroxide / water
k_3	diffusion of surface tritium into bulk via grain boundaries
k_4	penetration of HTO into the bulk metal via defects
k_5	*in-situ* production of tritium via neutron capture by trace Li or B impurities
k_6	tritium gas diffusion into bulk metal via atomic hydrogen diffusion or along defects / grain boundaries
k_7	H/T exchange between tritium gas and adsorbed water / surface hydroxide
$k_{1'}$	decomposition of surface hydroxide and liberation of tritium
$k_{2'}$	diffusion of tritium produced *in situ* from impurity mineral lattice
$k_{3'}$	diffusion of bulk tritium to surface via grain boundaries / defects
$k_{4'}$	decomposition of metal tritide

Speciation



e.g. Decomposition of concrete

- Adsorbed water (120°C)
- Dehydration of ettringite (100 - 200°C)
- Dehydration of portlandite (> 450°)
- Decomposition of structural OH groups (> 500°C)

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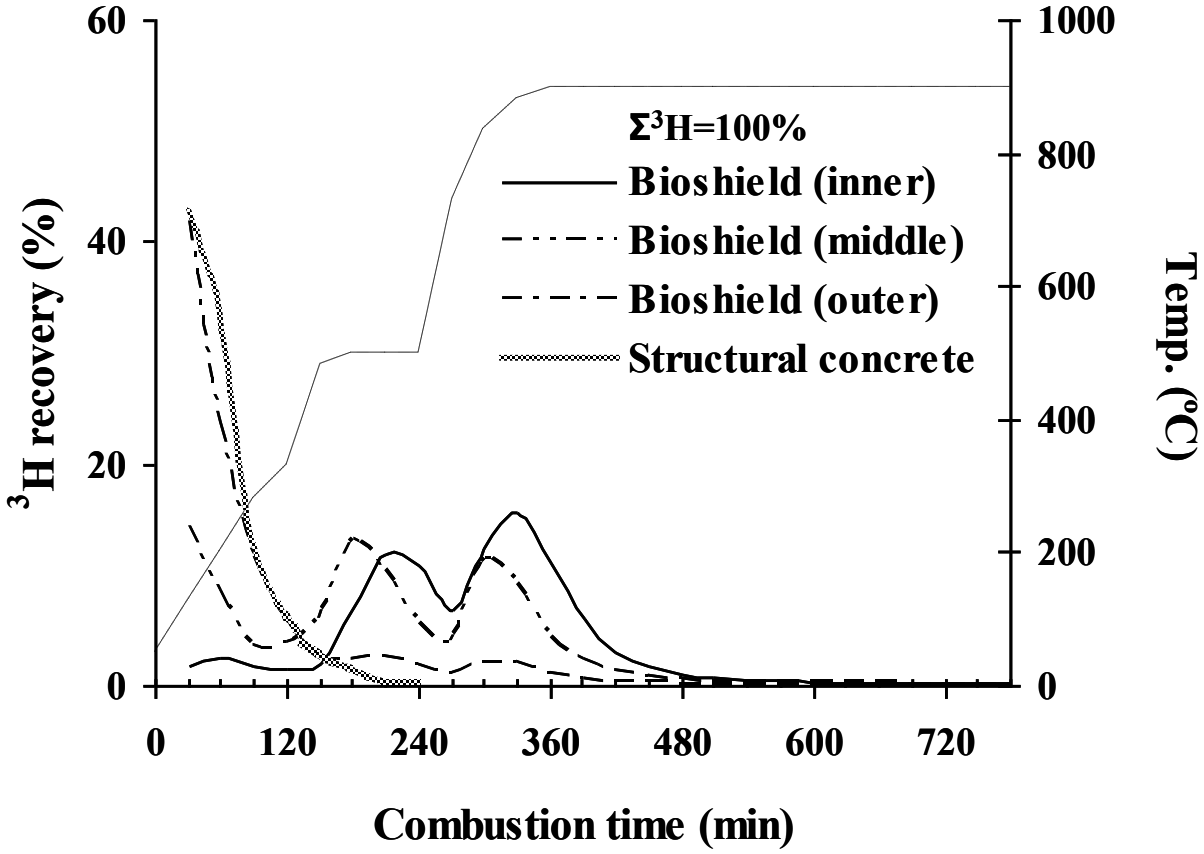
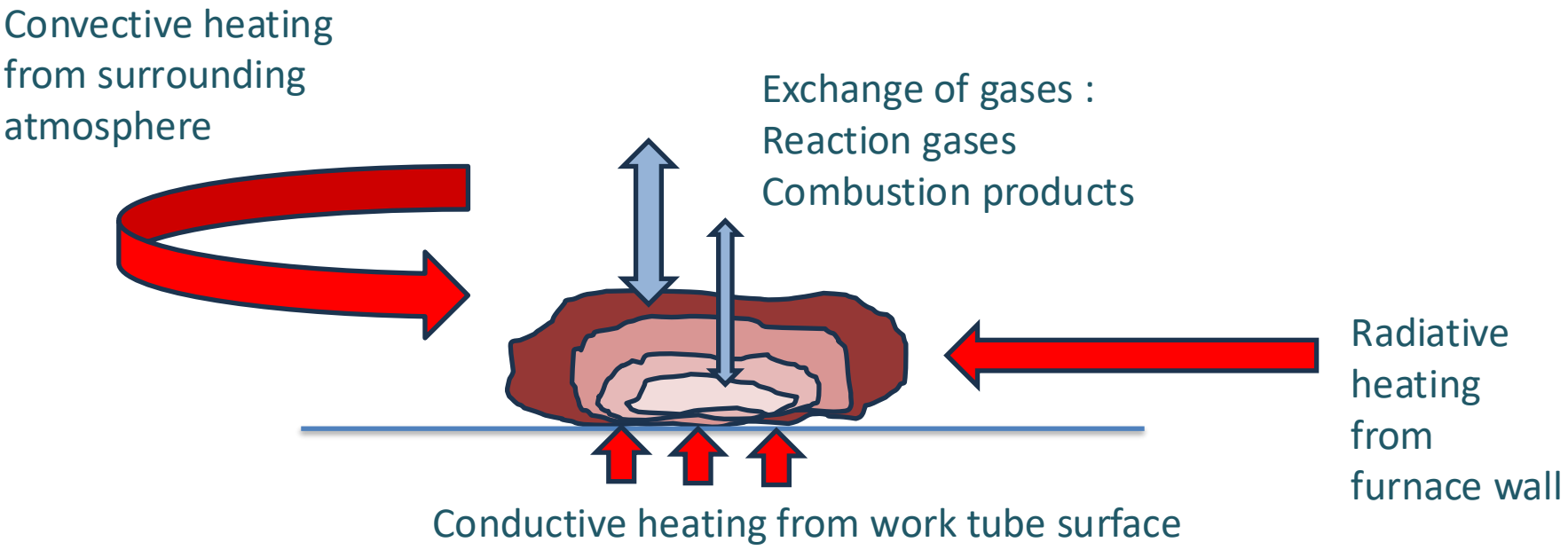
^{3}H in structural and bioshield concrete



Sample mass and heat transfer

- Increasing sample mass results in a shift in transitions to higher temperatures



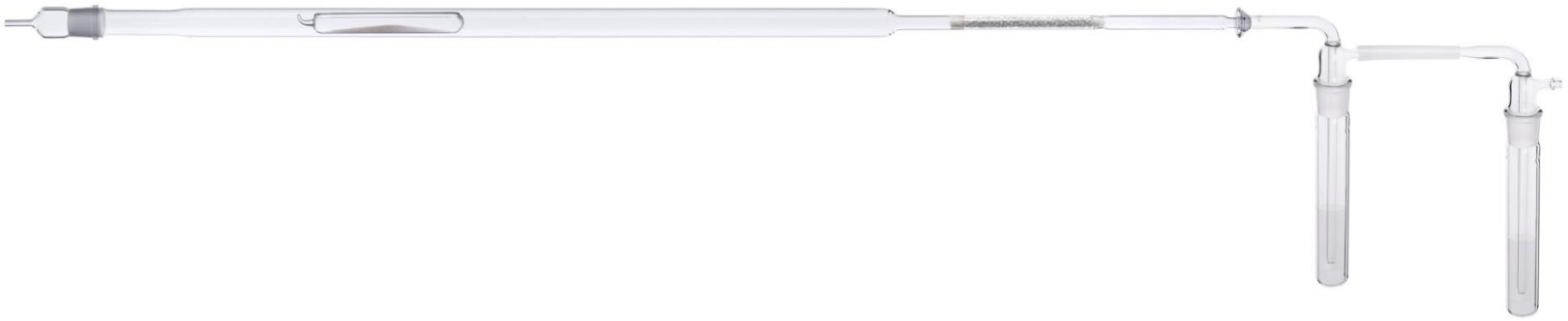
Transfer efficiency

Sample decomposition / analyte volatilisation

Analyte transfer

Oxidation of volatile species

Analyte trapping



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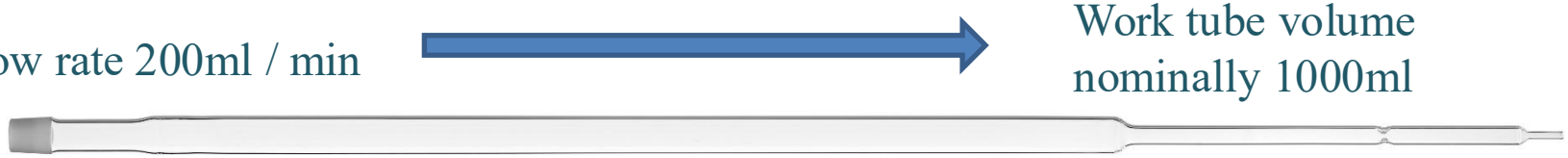
Transfer times

Air flow rate 200ml / min



Work tube volume
nominally 1000ml

Time to flush =
5 mins

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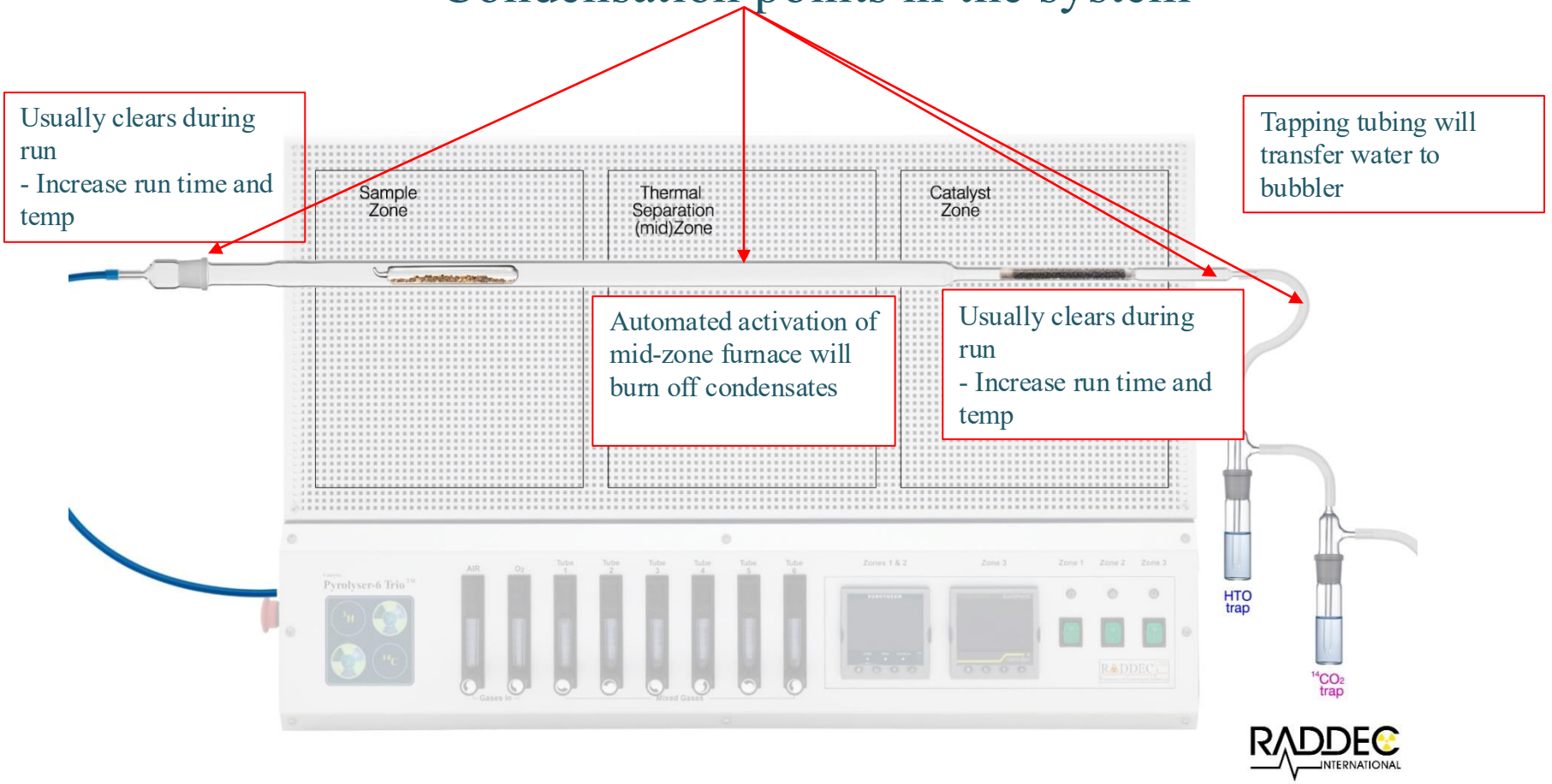
Condensation points

Condensation points in the system



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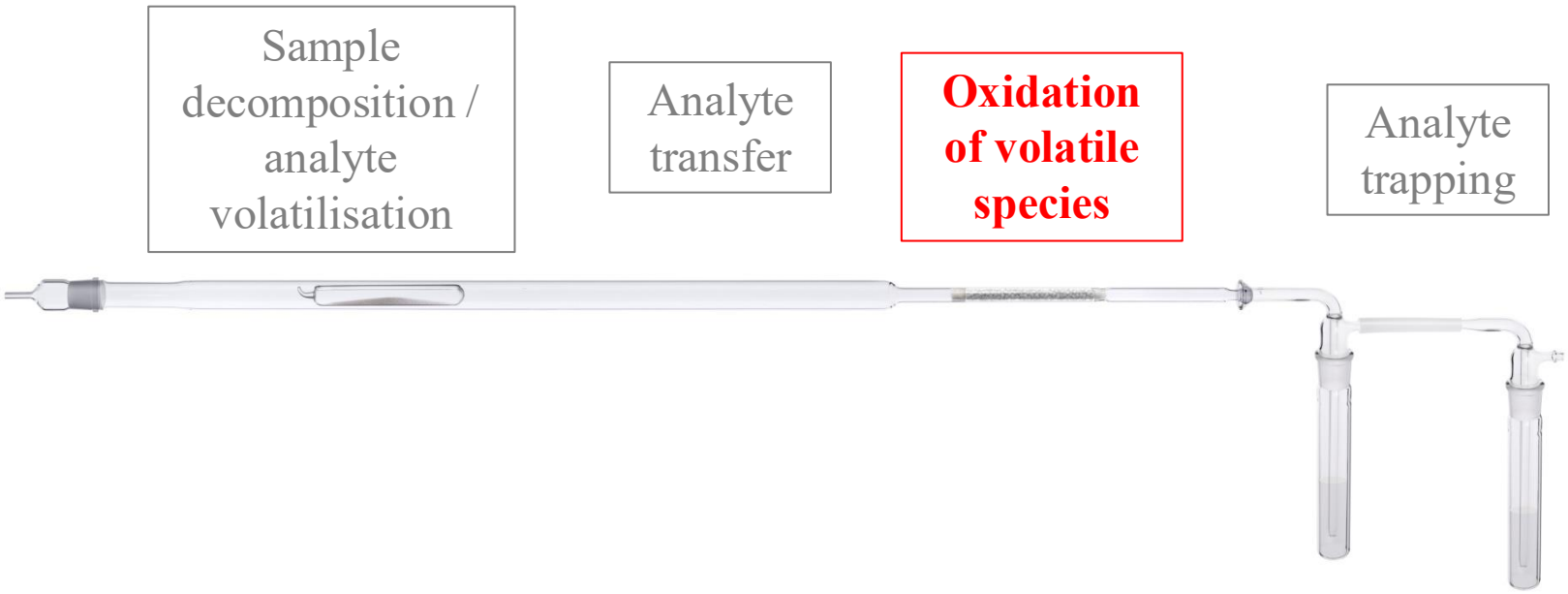
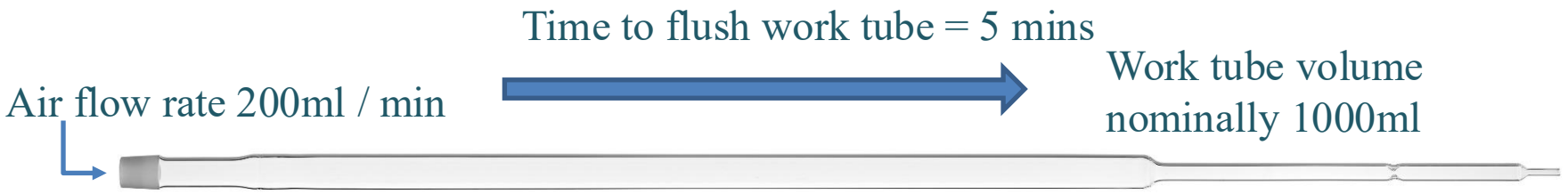
Oxidation efficiency



Maximum C oxidation rate



Percentage O_2 in air = 21% v/v

Rate of O_2 introduction = 42ml / min (STP)

Moles O_2 per min = 1.75×10^{-3} moles

Max C oxidation rate = 1.75×10^{-3} moles / min

Max C oxidation rate =
0.02 gC / min

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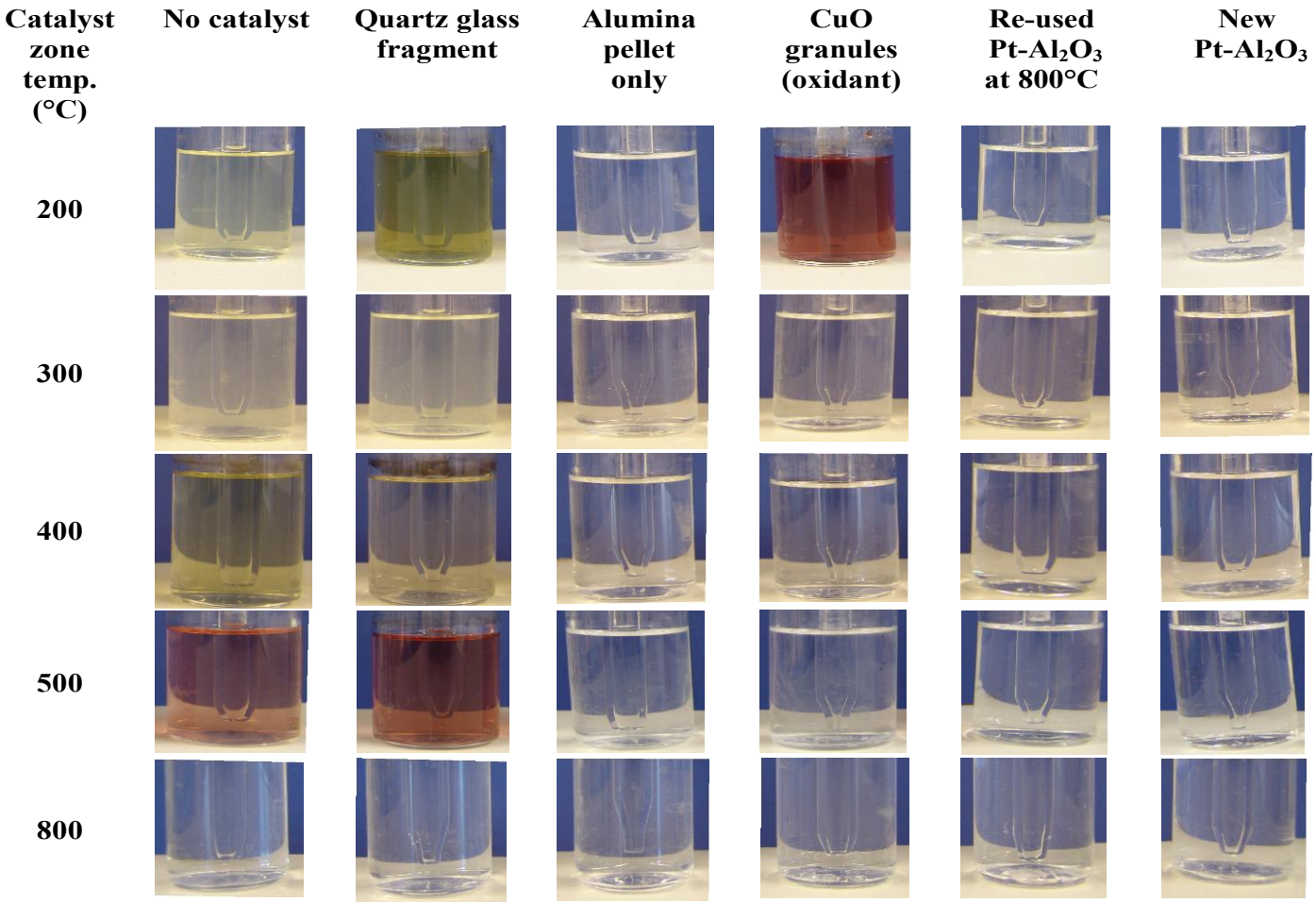
Effect of catalyst



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Catalyst performance test

Test using used catalyst at 400°C

Testing of catalyst performance using methanol.

Unoxidised MeOH reacts with cerium ammonium nitrate (yellow) to produce a red adduct

Visible indication of catalyst failure

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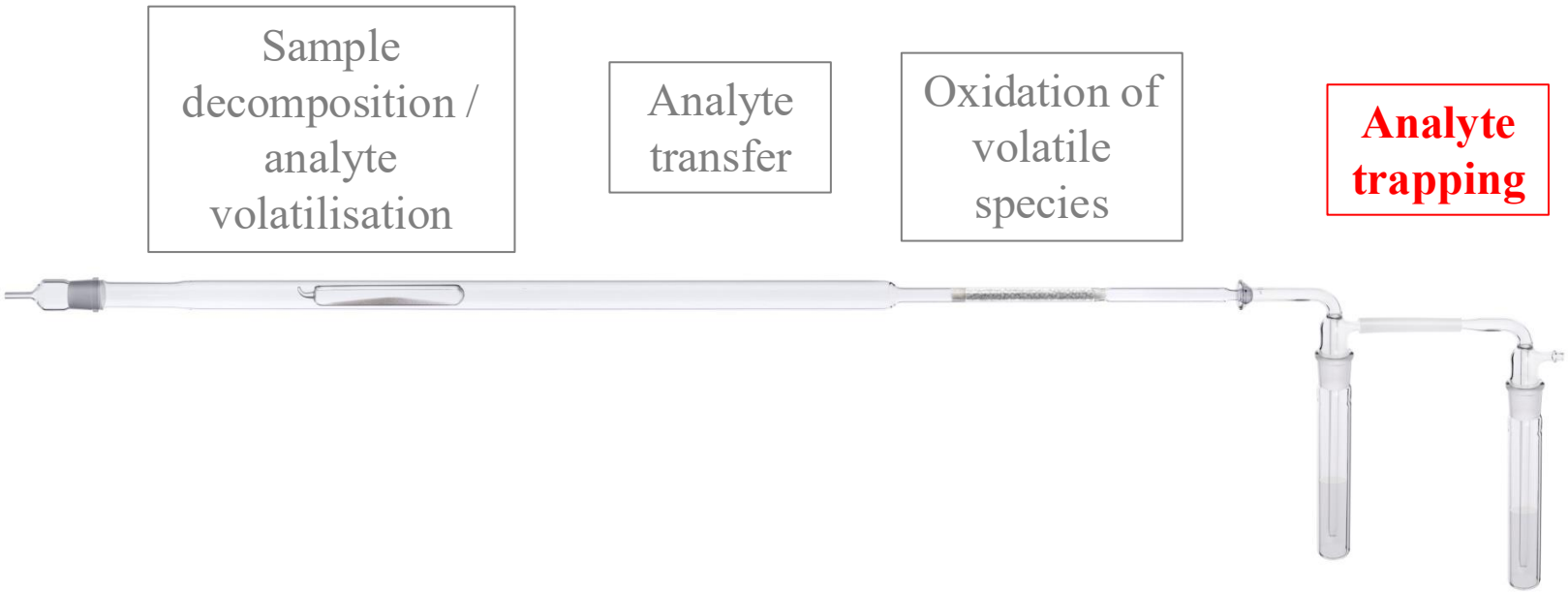
Trapping efficiency



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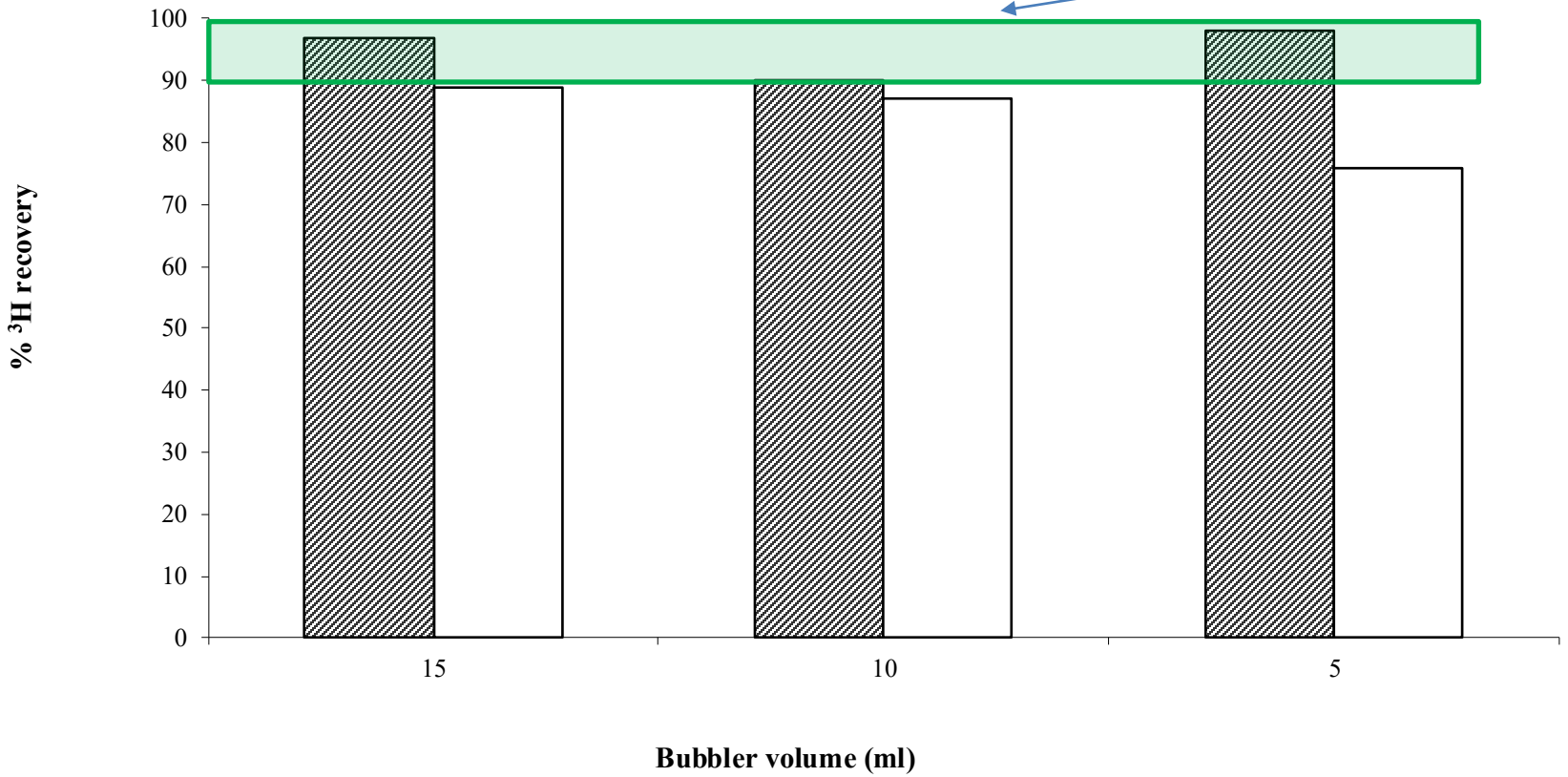
^{3}H trapping efficiency & bubbler volume

Accepted range for a 20ml bubbler



Typically 1 – 2 % transfer to a second bubbler if used

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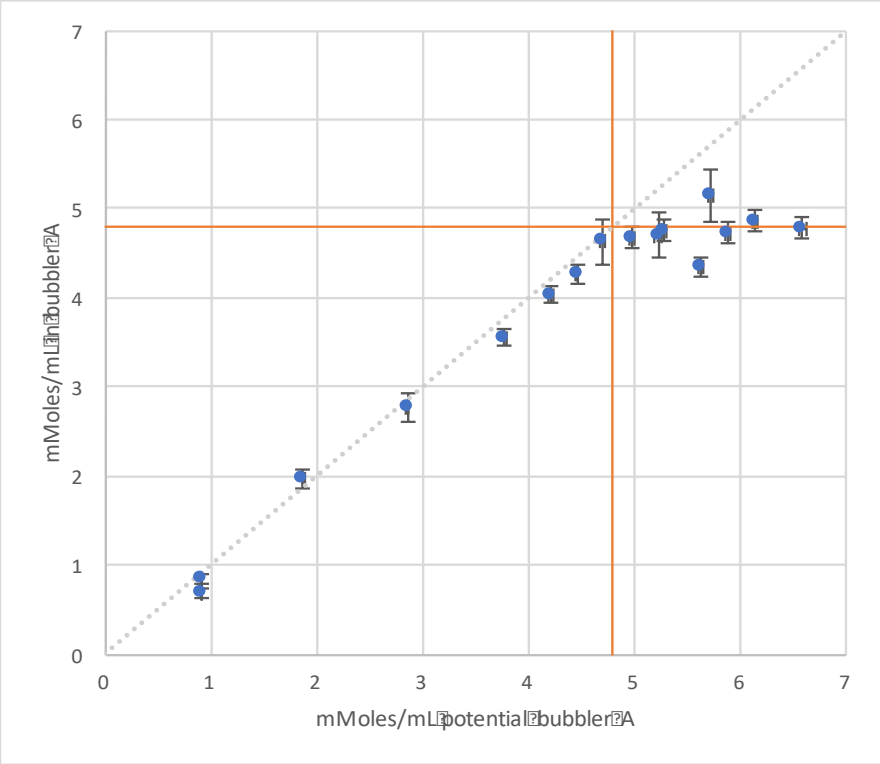
^{14}C trapping efficiency



- Typically achieved using Carbontrap (an amine).
- Trapping capacity is 4.8 mmol / ml.
- For a 20ml trap, this is equivalent to 1.1g of C.
- Bubblers containing Carbontrap should be extracted.
- White fumes are often observed emerging from the bubbler – this is normal

$$2\,[\,CH_3O(CH_2)_3NH_2\,] + CO_2 \longrightarrow CH_3O(CH_2)_3\text{-}NH\text{-}(CO)\text{-}NH\text{-}(CH_2)_3OCH_3 + H_2O$$

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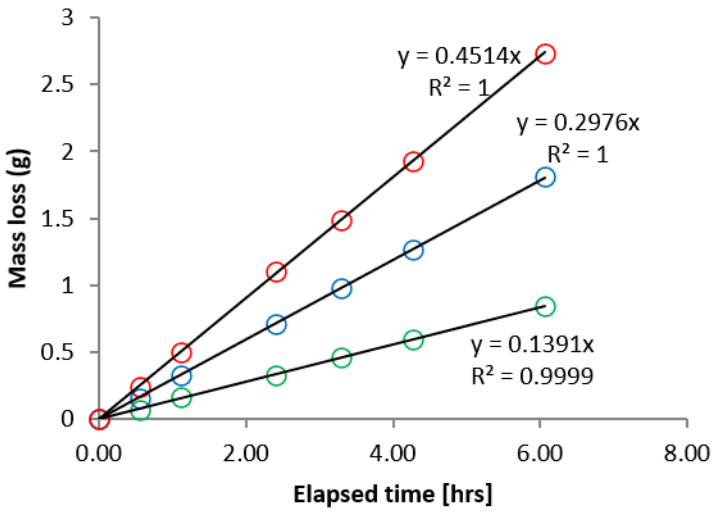
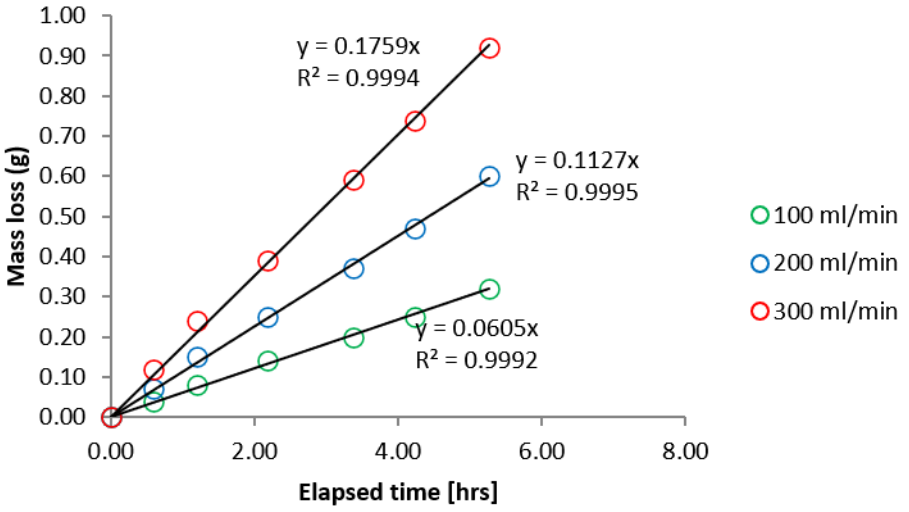
Rate of loss from water bubblers





23°C
0.3 g/hr

@ 200 ml/min

7°C
0.1 g/hr

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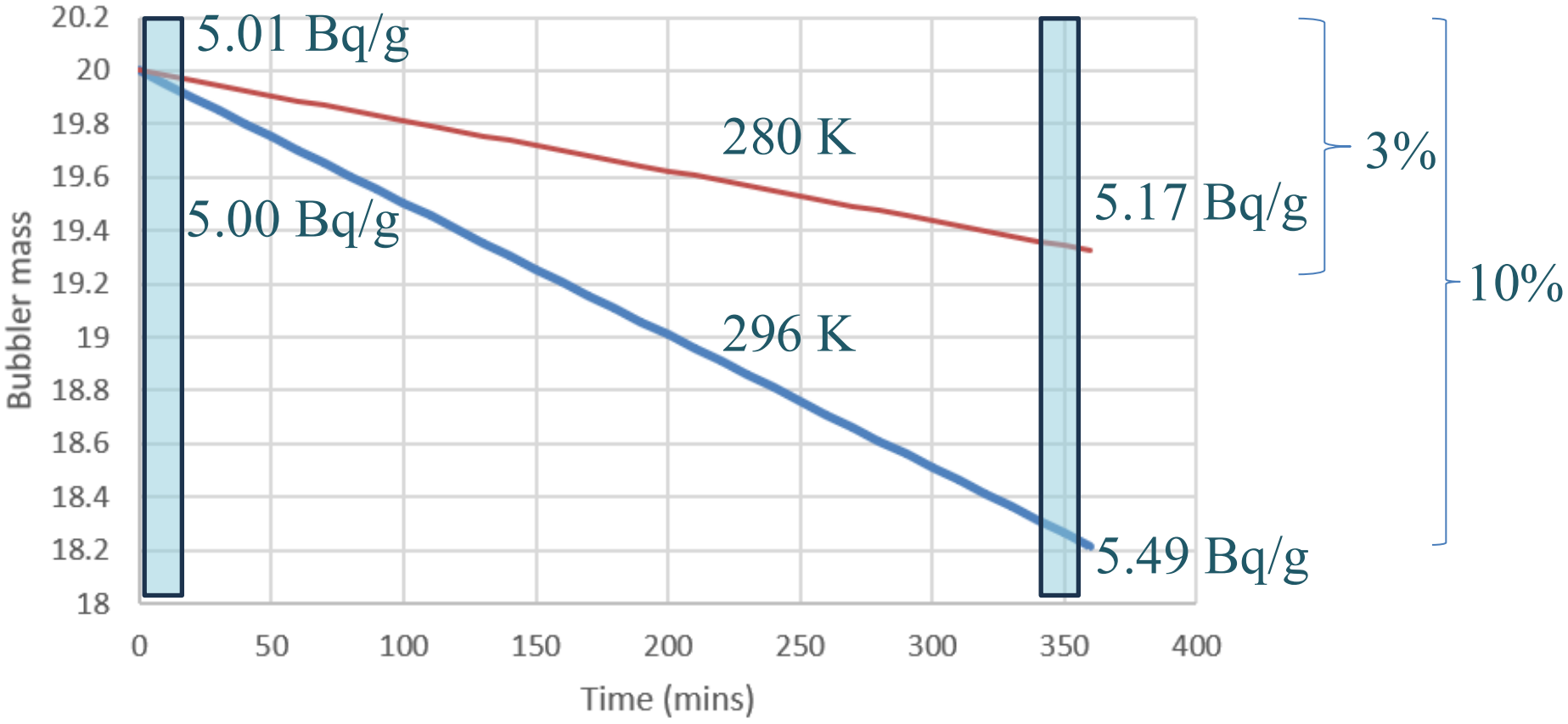
^{3}H desorption and bubbler loss



100 Bq released into bubbler. Gas flow 200ml/min

Managing uncertainties

- Many uncertainties can be quantified through analysis of standards. However, a significant number are sample-specific and need to be considered separately.

- Minimise sampling uncertainties where practicable through robust control of sample preservation and preparation.

- Minimise separation uncertainties through development of robust heating protocols that are not sensitive to sample composition / analyte speciation.

- Quantify remaining sources of uncertainty and combine into uncertainty budget

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Any questions?

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