Review of TDS round robin experiments

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Plasma-Wall Interaction for Irradiated Tungsten and Tungsten Alloys in Fusion Devices
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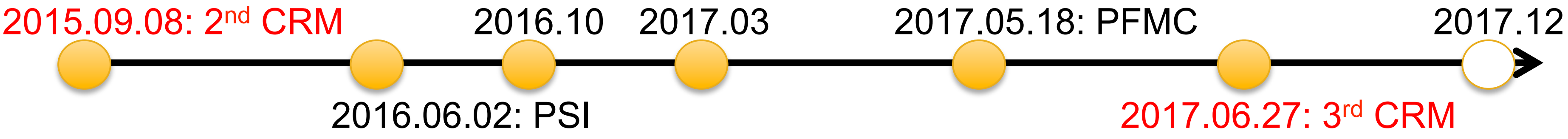
Summary of discussion on common protocol for TPD/TDS experiments

Background: TPD/TDS experiments are useful in that they have the ability to determine kinetic parameters of hydrogen trapping (e.g. binding energies) and the experiments are relatively simple to implement. However, in practice, the interpretation of the data is not straightforward due to system dependent parameters or several assumptions used in fitting or modeling.

Need: An easy way to compare results and discuss their interpretations from various labs.

Proposal/Consensus: Reference experiments needed to establish a common measure for various devices.

Timeline and key events



2015.09.08: 2nd CRM

2016.06.02: PSI

2016.10

2017.03

2017.05.18: PFMC

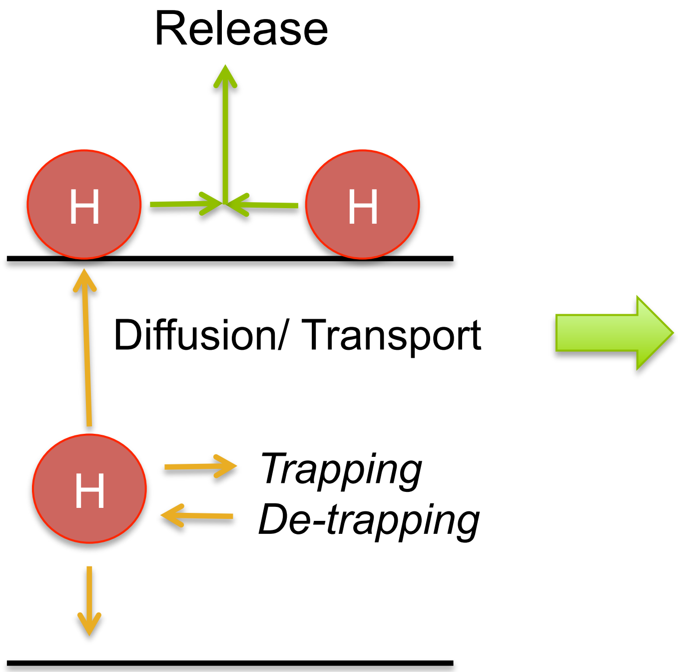
2017.06.27: 3rd CRM

2017.12

- 2015.09 – IAEA TDS RRE initiated
  - *System parameter survey/ Calibration sample preparation*
- 2016.06 – PSI mini meeting
  - *Confirm the experimental parameters and agreement on calibration samples to be produced by IPP*
  - *Perform experiments according to each group's standard procedure; Preferred ramping rate of 0.1 or 1 K/s*
- 2016.10 – Samples start shipping
- 2017.03 – Deadline for data submission
- 2017.05 – PFMC mini meeting
  - *Brief update on the progress*
- 2017.06 – NRA data released
- 2017.06.27 – 3rd CRM
  - *Release full TDS data (desorption data)*

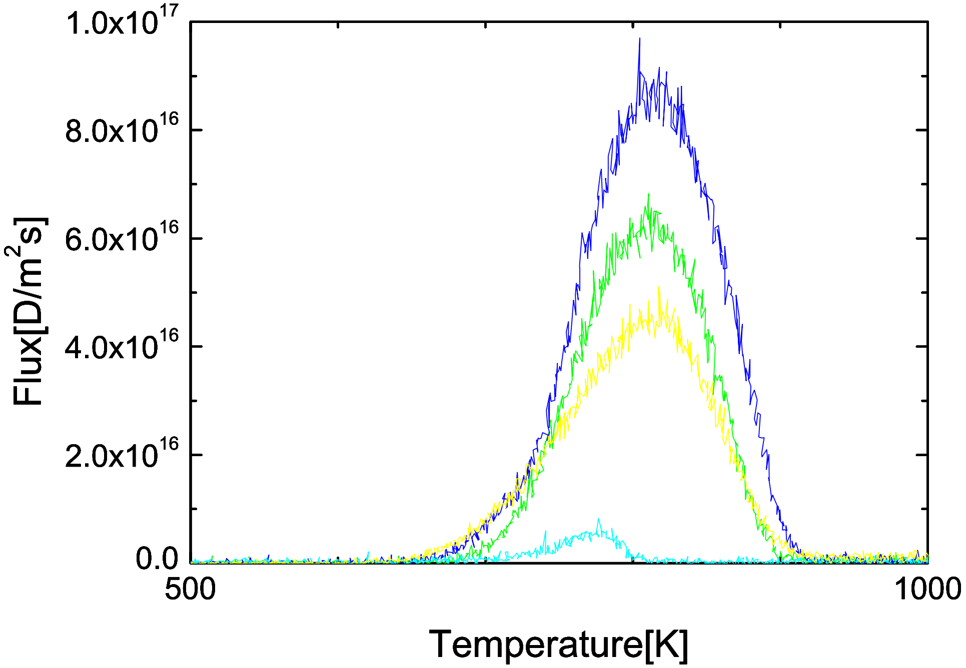
Typical assumption in interpreting TDS experiments

Idealized physical picture



- Generally interested in kinetic parameters of trapping.
- Typically assume surface release not rate limiting despite having zero information about the state of the sample surface.

TDS release spectra

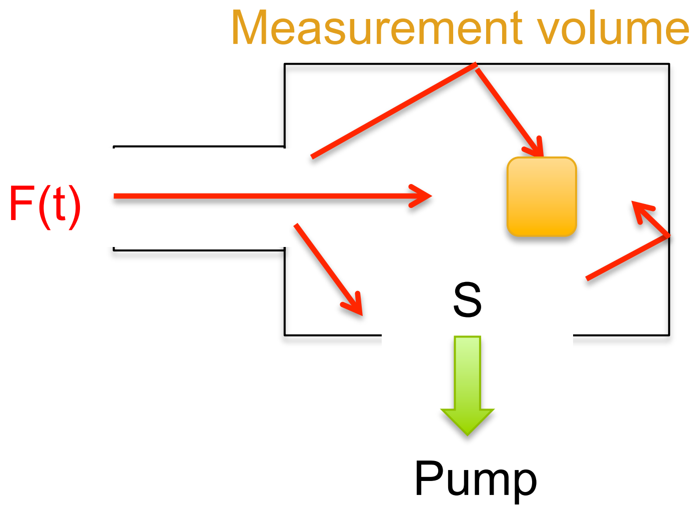


Generally, the desorption process is considered independently from the measurement vacuum system.

But in reality…

We are measuring pressure changes in a fixed volume in most TDS systems.

Idealized vacuum system



B. McCaroll, J. of App. Phys. (1969)

where N(t) is the # of gas particles at a given time t, F(t) is the rate of entry into the vacuum system, and S is the total pumping speed for this particular species

$$\dot{N}(t) = F(t) - SN(t)$$

The source term is distorted by convolution

Attenuation, phase shift

$$N(t) = \underline{N(0)\exp(-St)} + \int_0^t \exp[-S(t-p)]\,\underline{F(p)}dp$$

0 for steady state

Generalized source term

$$N(t) = \int_0^t \exp[-S(t-p)]\,\dot{n}(p)dp\,, S \geq 0$$

$$I(E,v,S,\alpha;t) = \dot{n}(t) + \alpha N(t), \alpha \geq 0$$

LOS Scattered component

Kinetics of desorption

System parameters

By using calibration samples, we “fix” the kinetics of desorption parameters.

This allows us to study the system dependent parameters and allows us to evaluate the magnitude of such effects and their distortion to TDS release curves.

Overview of goals of exercise

→ Distribute standard calibration samples to all participants (IPP)

✓ **Absolute calibration for retention**
  - Identification of systematic errors → service to the community/practitioner

☐ **Provide input for the modeling efforts**
  - Benchmark data, inform the modeler of unsaid experimental artifacts

☐ **Further our understanding underpinning TDS desorption curve analysis**
  - Service to a wider community than participants
  - Recommend guideline for curve fitting process

☐ **Consequences for analysis for neutrons irradiated samples**
  - Interpreting high temperature release peaks where additional experimental artifacts exist – more system outgassing, water signals, etc.

☐ **Distillation of the understanding of the knowledge gained**
  - IAEA mid term/ final reports
  - Publication (TBD)

Data submission request / respond

Excel file distributed requesting the following data

1. *Base pressure*
2. *Heating schedule as function of time*
3. *Best estimate of sample temperature as function of time*
4. *Raw Q-mass data for masses 2,3,4,18,19,20 as function of time*
5. *Calibrated Q-mass data for masses 2,3,4 as function of time*
6. *Calibration factor used for mass 4*
7. *Best estimate of temperature vs calibrated release*
8. *Best estimate of retention from masses 3,4 and their sum*

Outstanding participation by 17 groups in total. (including groups outside CRP)

- 14 groups responded with submission of data for standard samples
- 3 groups with non-standard samples

Submitted values for D retention (Mass 3, Mass 4, Sum)

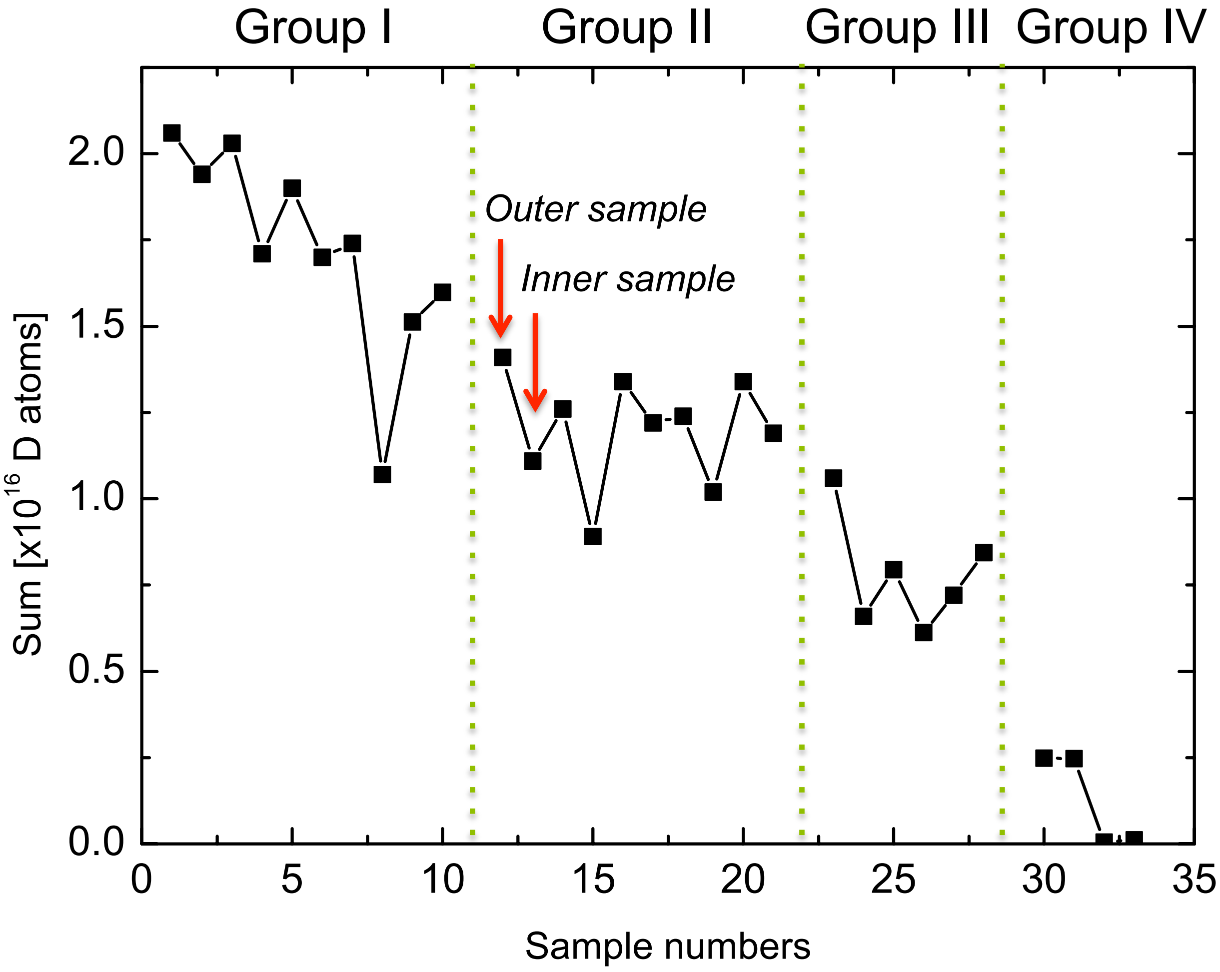
Data evaluation criteria

System parameters of interest

1. **Accuracy**
   - Need an absolute measure for comparison
   - Used NRA data for such comparison
   - Doesn’t mean that NRA data is absolute

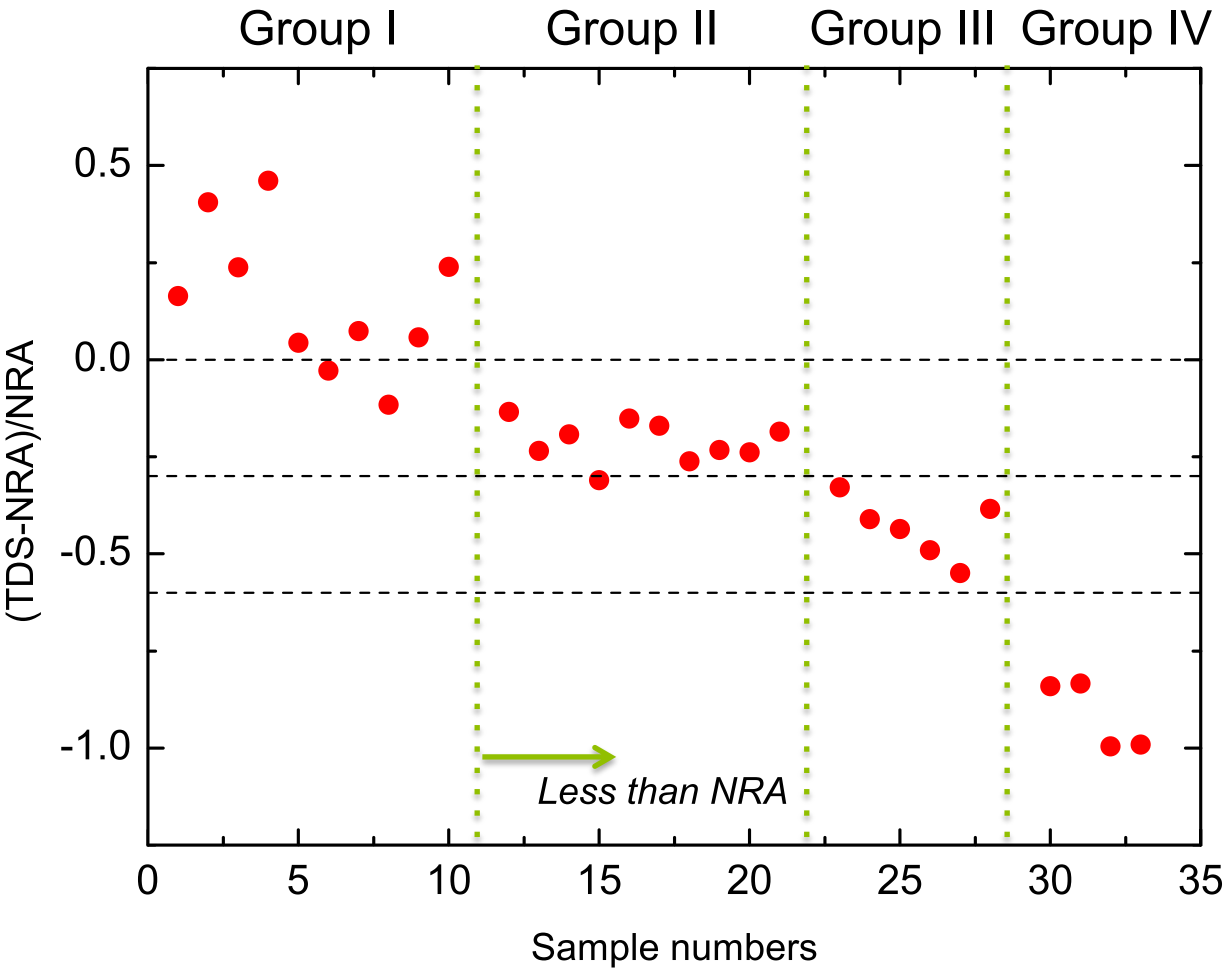
2. **Consistency (or reproducibility)**
   - Compare two samples (outer- vs. inner- ring samples)
   - Outer- ring samples contain more D (check if groups can measure small differences)

Classification of submitted data



- 10 by 10 mm standard samples.
- Sum = Mass 3 and Mass 4
- Data is organized by decreasing values of retention starting with outer ring sample. (arbitrary classification scheme)
- Outer-ring samples contain more D than inner-ring samples

Accuracy: Comparison with NRA data



- Data plotted is: (TDS-NRA)/NRA

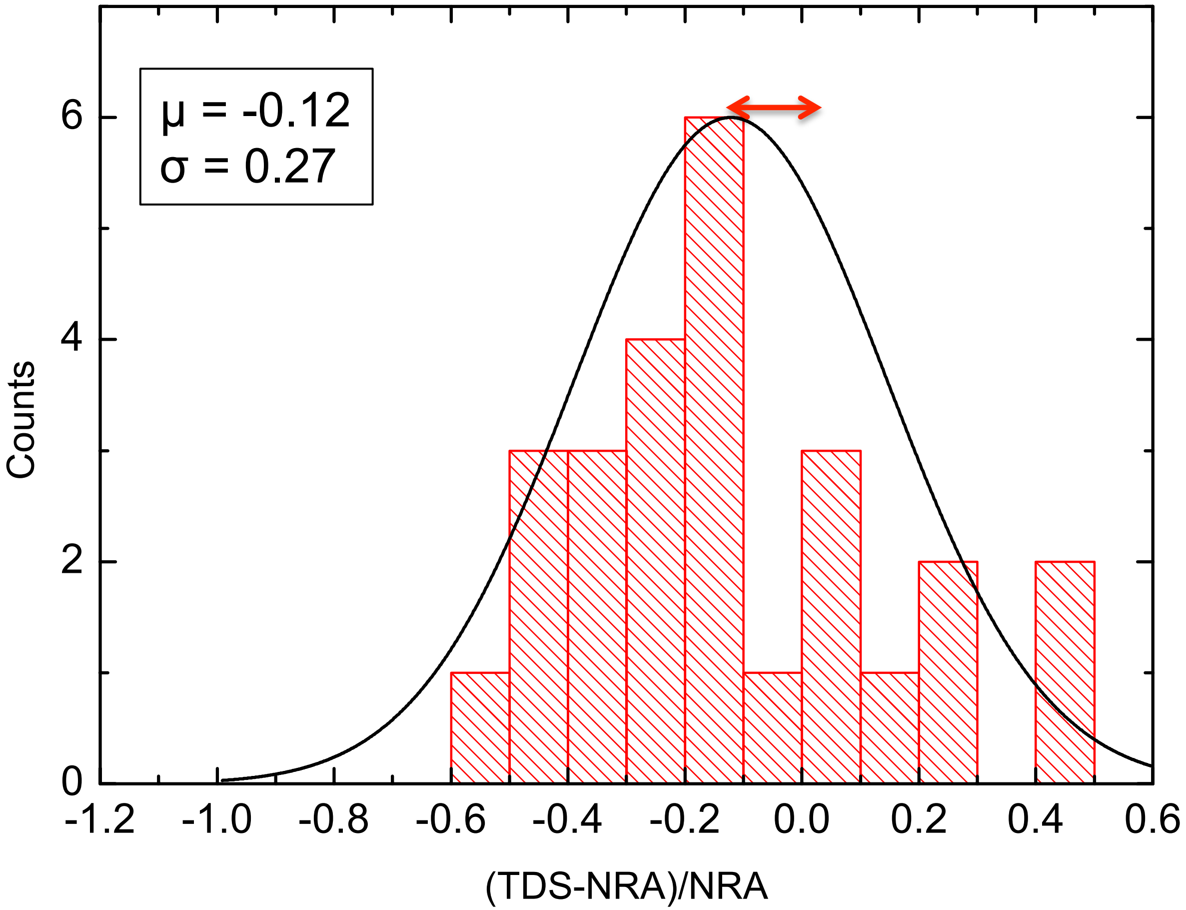
- Assume D release area to be 10 by 10 mm (i.e. ignore any edge effects)

- Consider only mass 3 and mass 4 release signals. (i.e. HD and D_2)

  Group I: x ≥0 (for outer)
  Group II: -0.3< x <0.1
  Group III: -0.6< x <-0.3
  Group IV: x < -0.6

- Negative values: Most groups report values lower than NRA data.

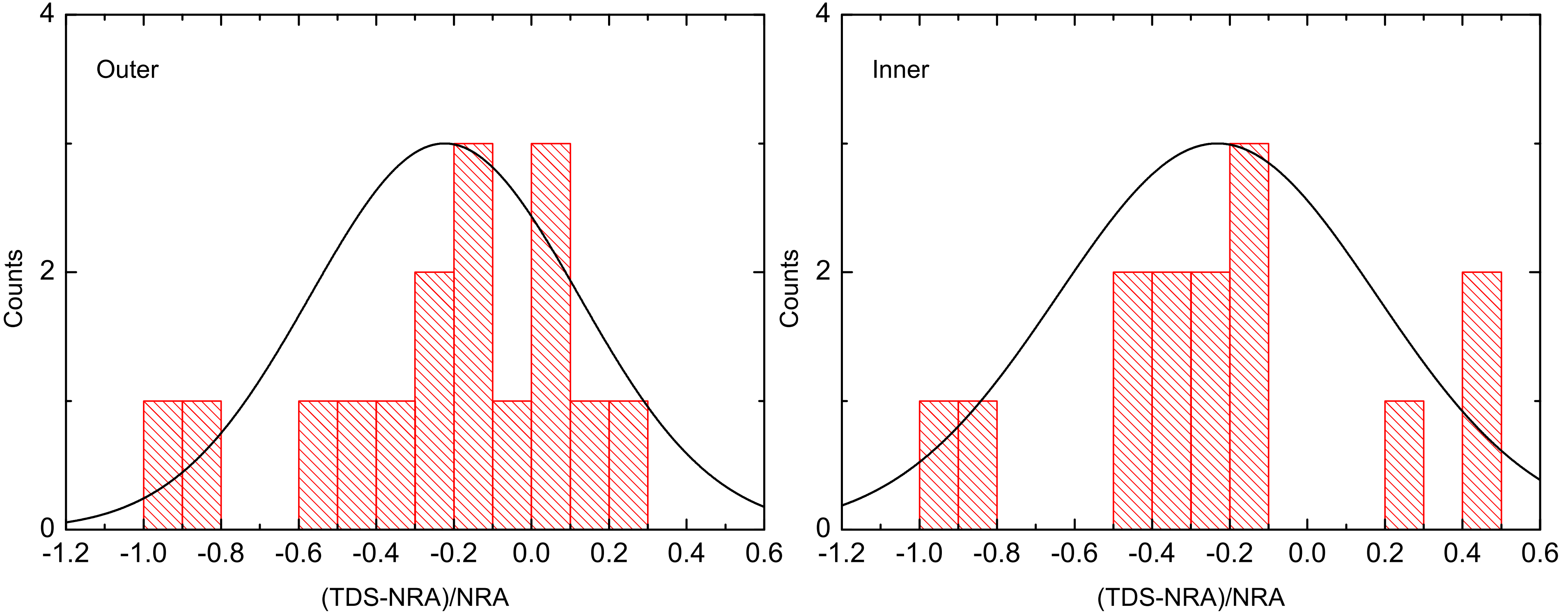
Distribution for all samples



- Mean values are 12% lower than NRA values.
- Standard deviation is ~30%
- Two considerations:
  - NRA overestimate
  - TDS underestimate
    - Other signals like mass 19, 20
    - Considering release from side walls of samples will shift the curve to lower values

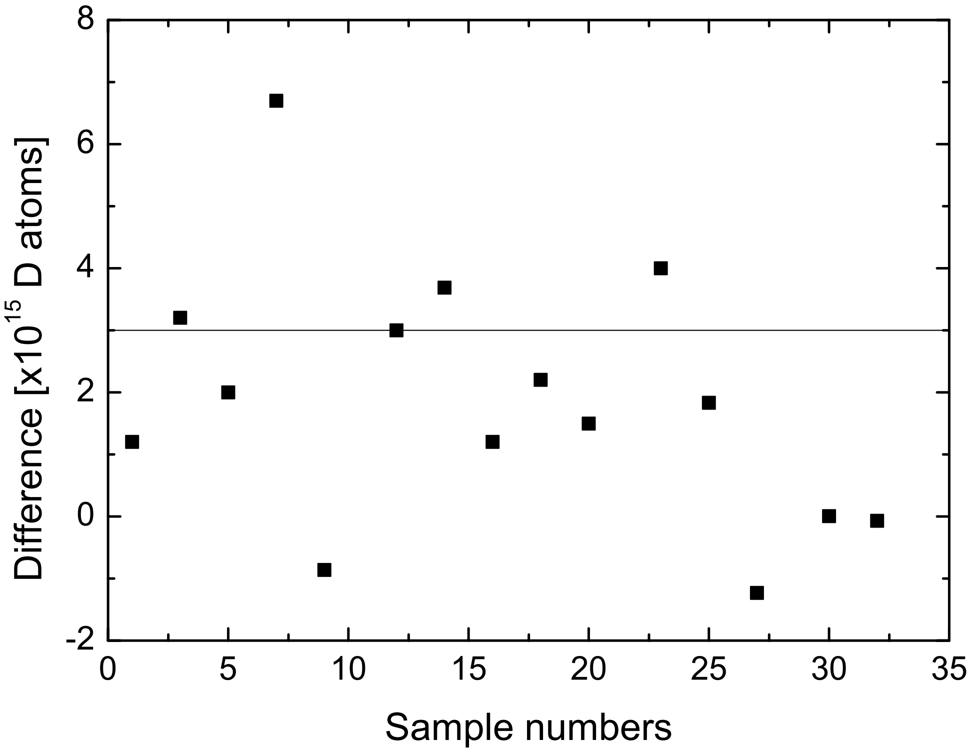
Discussion (1): Lower mean TDS values in comparison to NRA

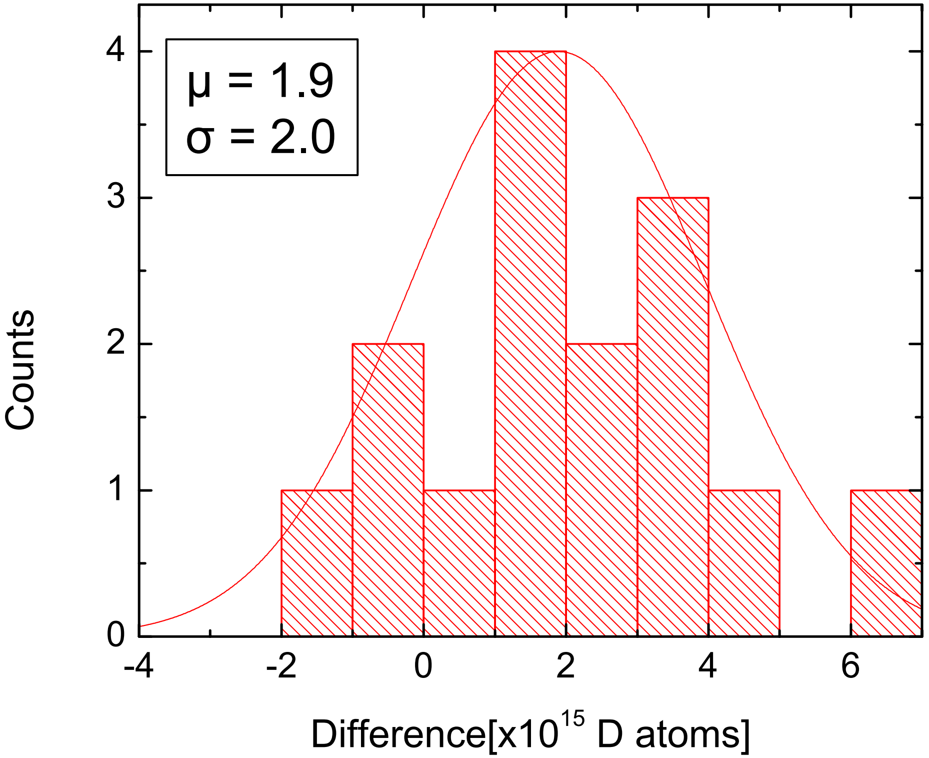
Distribution for outer- and inner- ring samples



- Qualitatively no significant difference between the two samples
- Not enough data to make firm conclusions

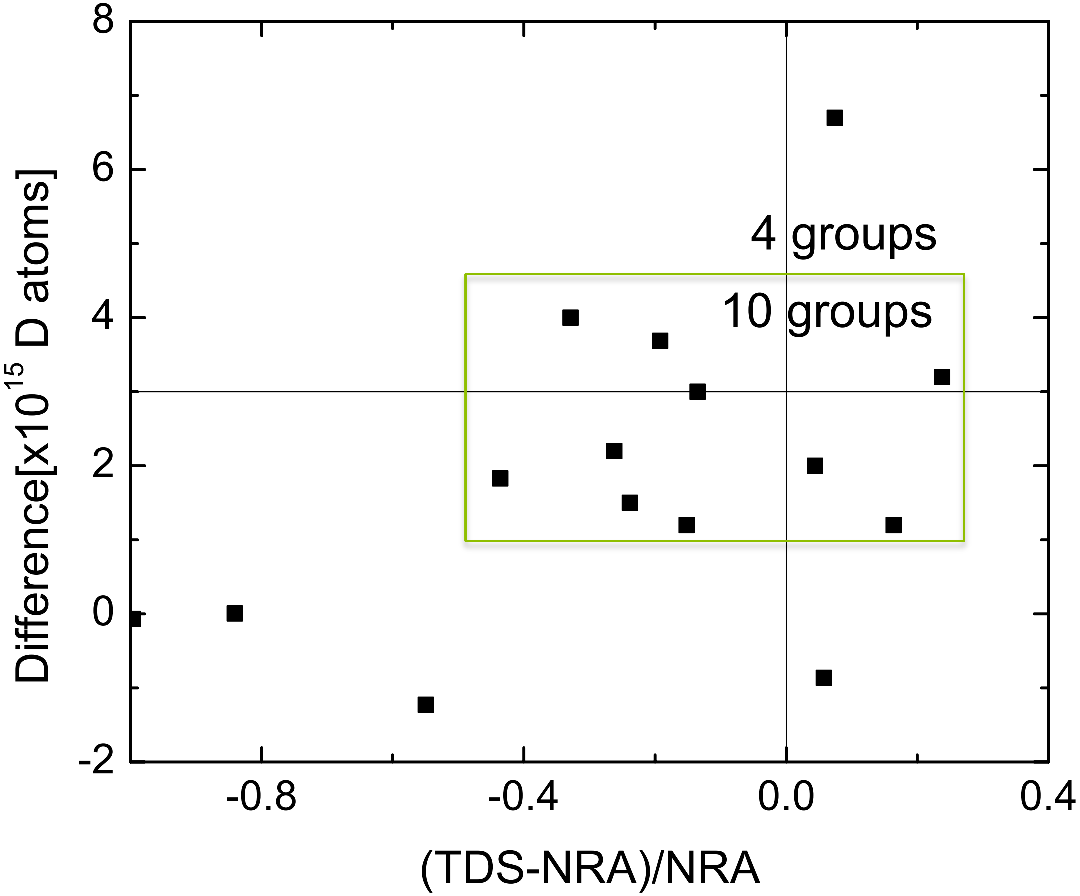
Consistency: Difference in outer and inner ring samples





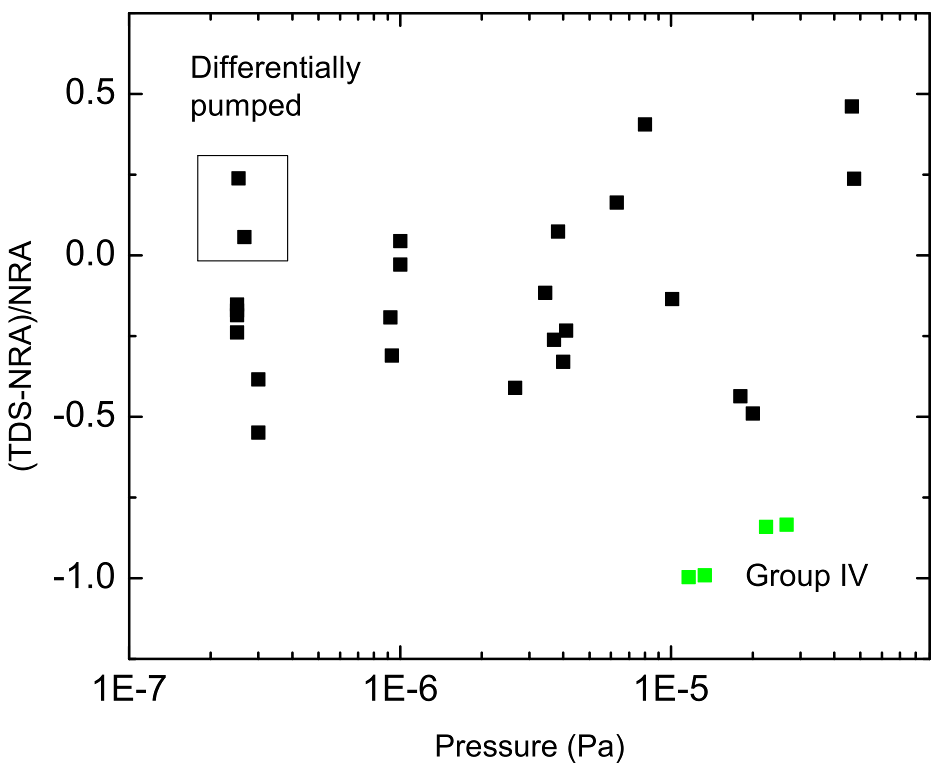
- Outer and inner ring sample difference from NRA: (2-3)×10^{15} D atoms/cm^2
- Negative values for two groups
- Both mean and standard deviation values are ~2×10^{15} D atoms/cm^2

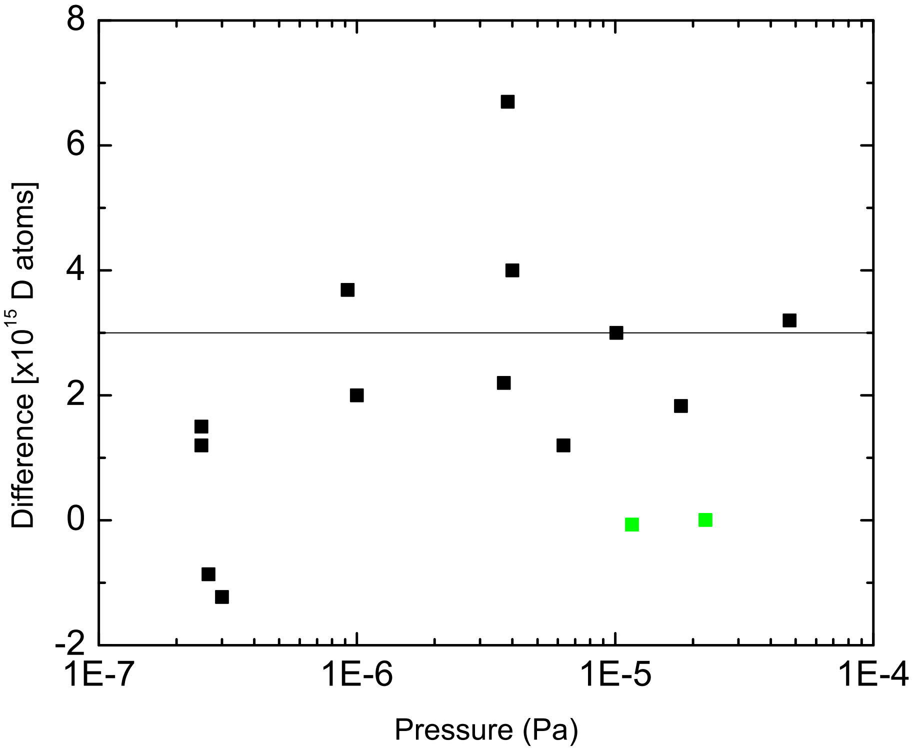
Quality factor: grading the performance



- What is the reason for the poor performance of the 2 groups?
- To be clarified and participating groups' feedback requested.

Dependence on system base pressure

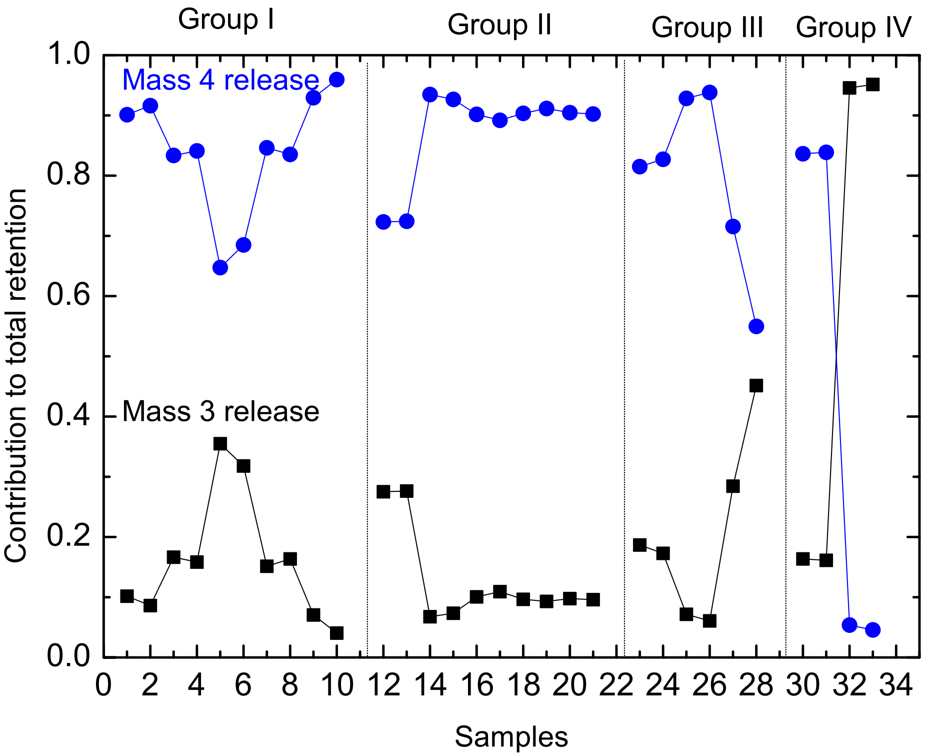


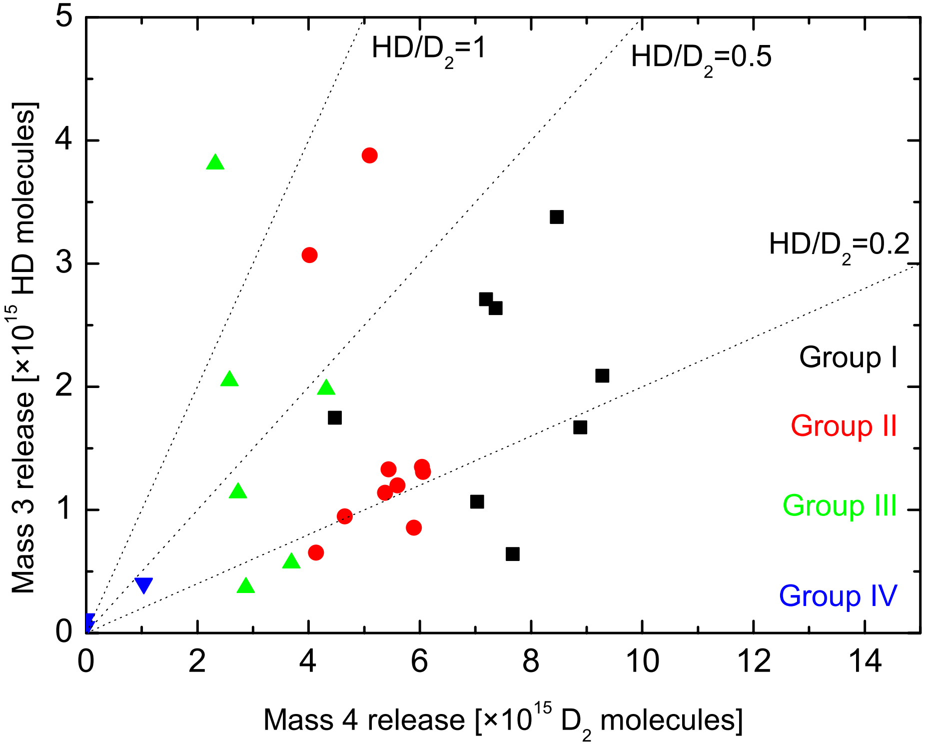


- Possible positive correlation
- No obvious dependence

Base pressure itself is not a sufficiently discriminatory parameter to evaluate the quality of the system

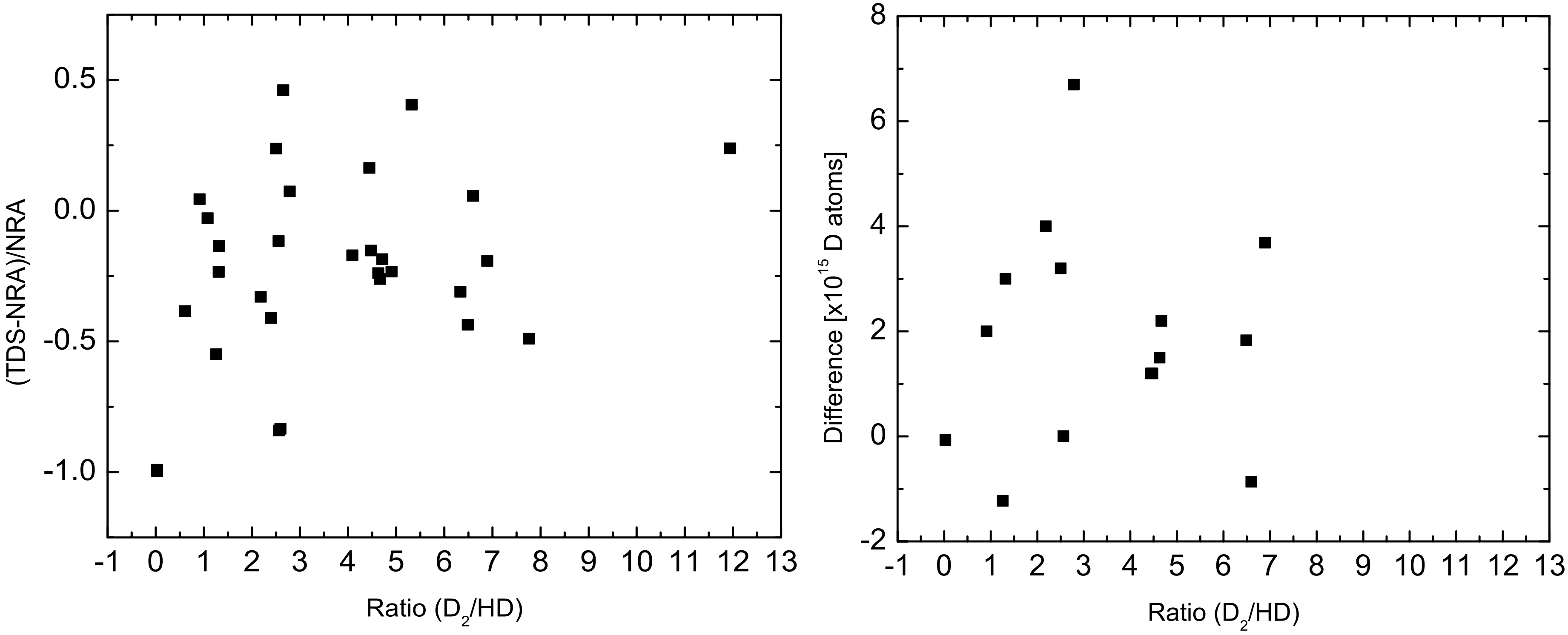
Dependence on Mass 4/ Mass 3





- All groups cover similar range of Mass 4 to Mass 3 ratio

Dependence on mass 4/mass 3 ratio



- Possible positive correlation

Mass 4/Mass 3 ratio itself is not a sufficiently discriminatory parameter to evaluate the quality of the system

Summary I

- Measure of accuracy determined by comparison to NRA data.
  - Mean is ~12% lower than NRA
  - Standard deviation is ~30%

- Measure of consistency determined by ability to differentiate D amount between outer- and inner- ring samples (2-3)×10^{15} D atoms/cm^2.
  - Both mean and standard deviation values are ~2×10^{15} D atoms/cm^2

- System base pressure or ratio of mass 3 and 4 are insufficient parameters to evaluate the quality of the system.

TDS desorption curves

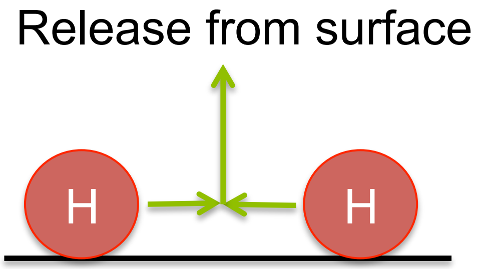
Data evaluation criteria

1. **Quality of shape**
   - To extract kinetic parameters only the release shape is of interest (absolute values are not important)
   - Identify distortions and their sources
     - Shifts in maximum peak temperature
     - Leading edge / trailing edge

2. **Consistency (or reproducibility)**
   - Release curves between outer- and inner- ring samples

3. **Others**
   - Effect of ramping rate (0.1 vs 1 K/s)
   - Contribution from other signals (Mass 3, 19, 20)

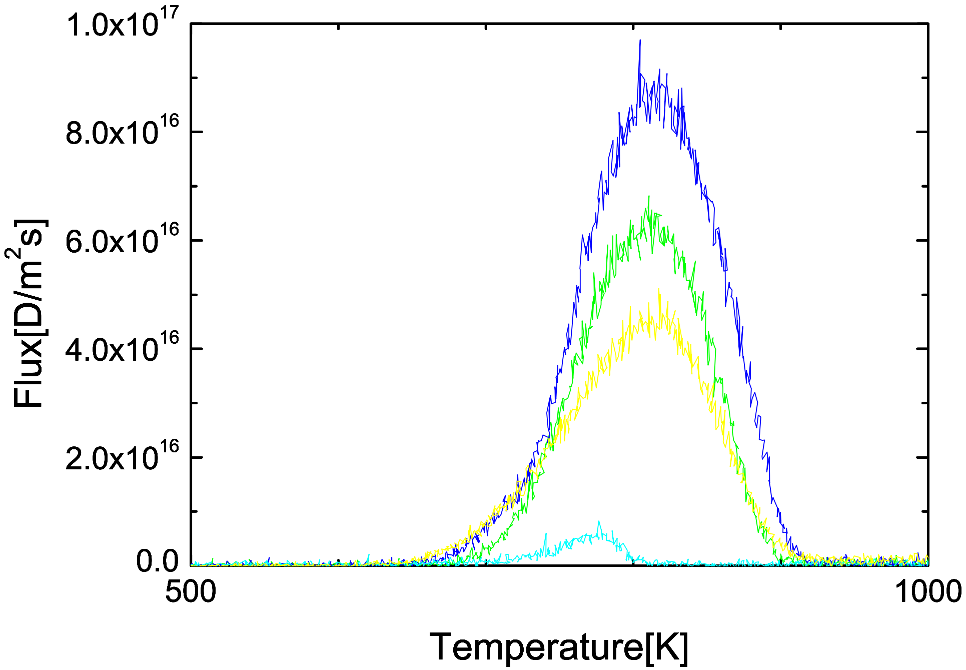
General question posed



Simple model of H release from surface

$$\dot{n}(t) = -v_b n(t)^b \exp\left[-\frac{E}{kT(t)}\right], b = 1{,}2$$

where b = 1,2 correspond to first, second order release



Q: Does a unique set of kinetic parameters describe a unique desorption curve?

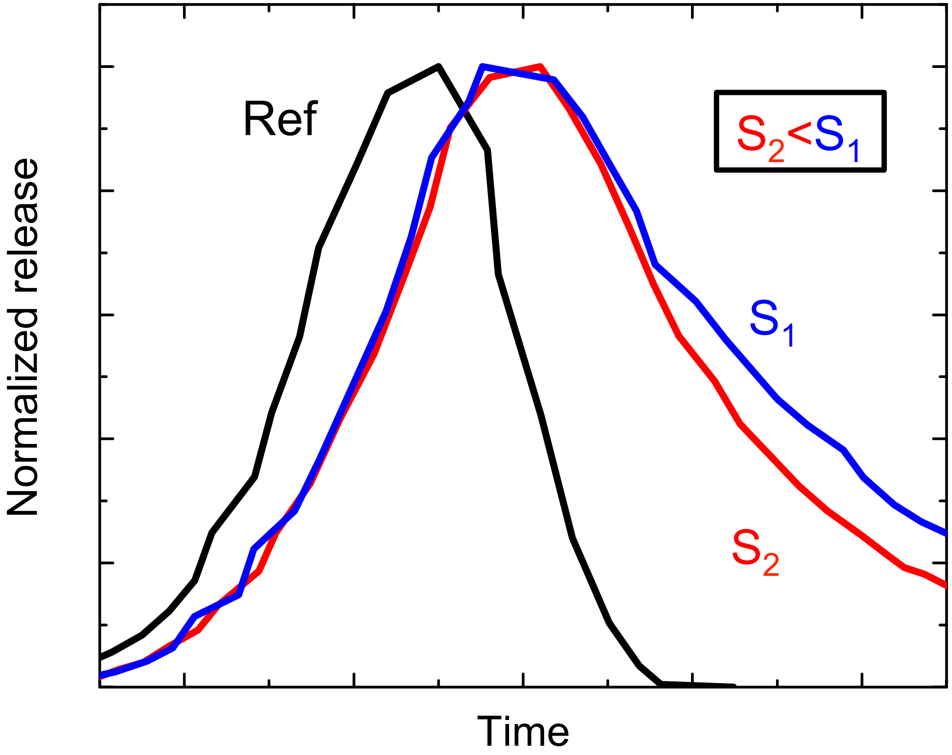
- *Order of the process*
- *Activation energy*
- *Pre-exponential factor*

A: Mathematically, yes.

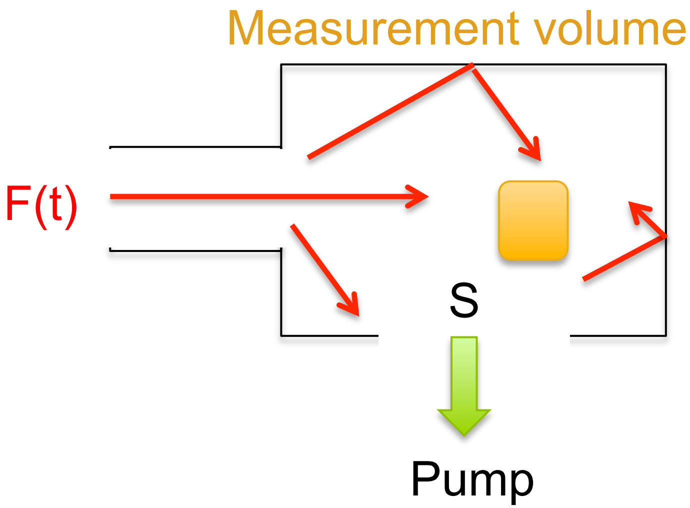
A: Practically, for curve-fitting experimental data, ambiguities do arise.

Effect of finite pumping speed on distortion of TDS curves

Qualitative comparison



- Finite pumping speed results in distortion of the signal resulting in shift in peak maximum and trailing edge distortion



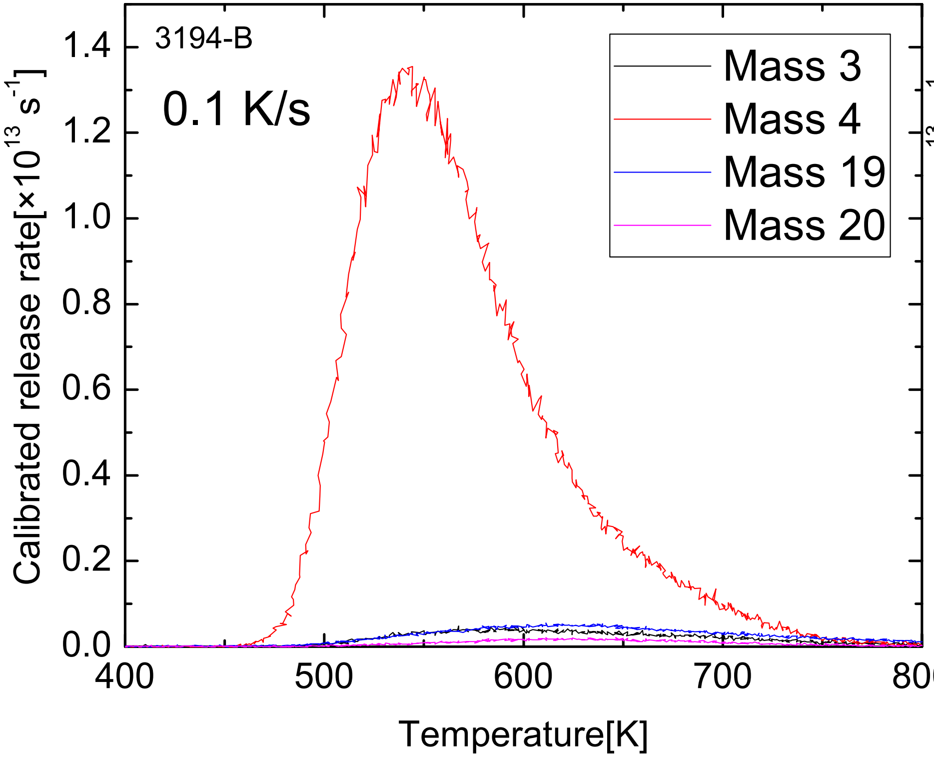
$$\dot{n}(t) = -v_1 n(t) \quad \exp\left[-\frac{E}{kT(t)}\right], b = 1$$

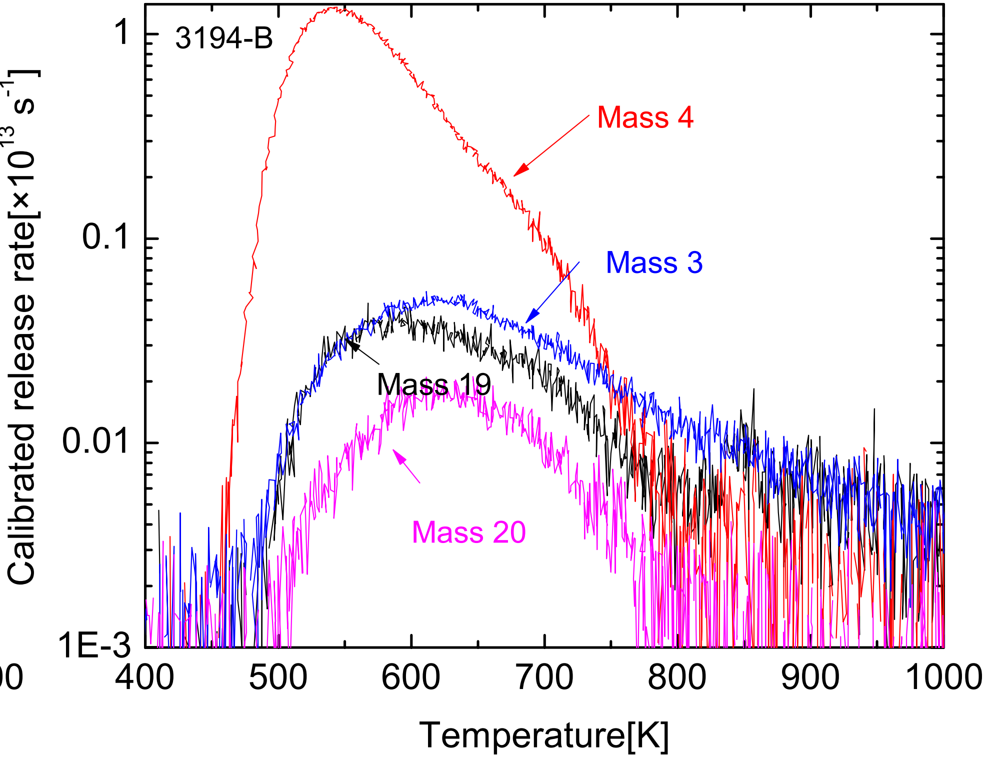
$$N(t) = \int_0^t \exp[-S(t-p)]\,\dot{n}(p)dp\,, S \geq 0$$

$$I(E, v, S, \alpha; t) = \dot{n}(t) + \alpha N(t), \alpha \geq 0$$

Example of desorption spectra I

Osaka Data

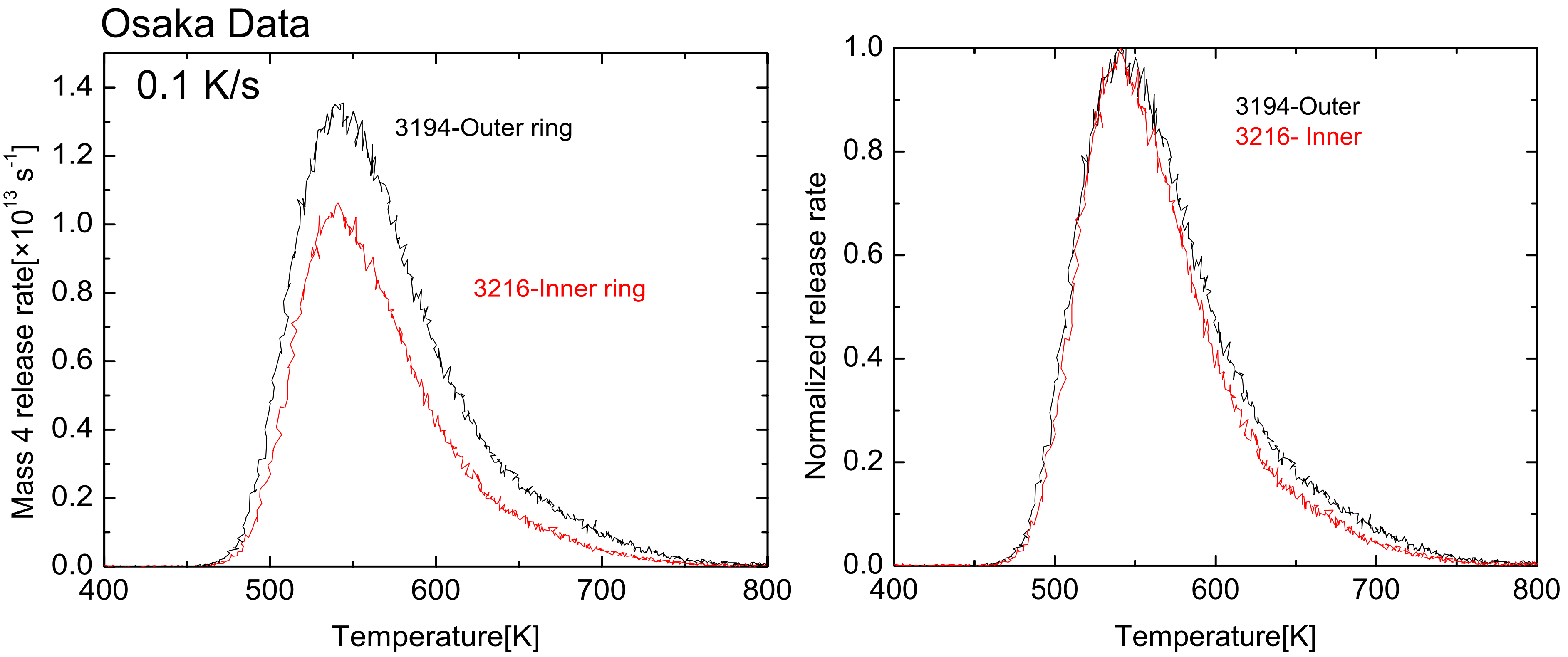




- Qualitatively, the release peak is not characteristic of single or second order

- Mass 4 signal dominates with other signals one to two order of magnitude lower.

Example of desorption spectra II



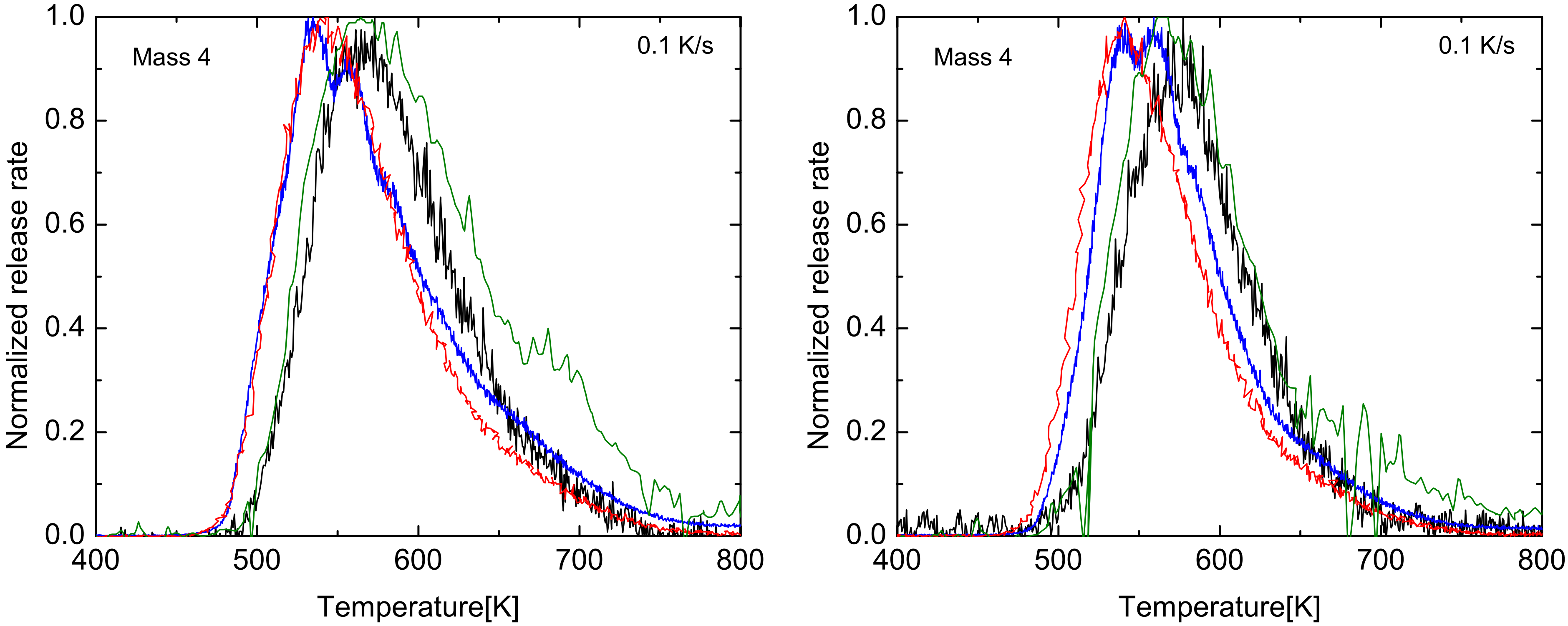
- Difference in absolute amounts between the outer- and inner- ring samples.

- Data normalized to peak maximum.
- The shapes are in good agreement
- No difference in TDS shape between two samples

Normalized desorption curves (0.1 K/s)

Outer ring samples (3190, 3191, 3192, 3194)

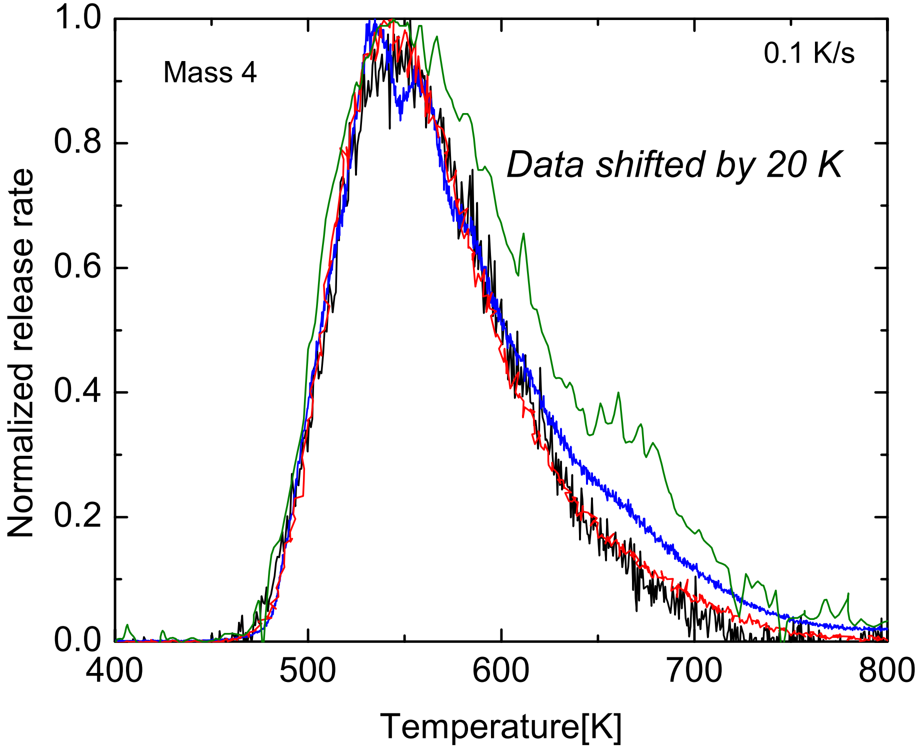
Inner ring samples (3212, 3213, 3214, 3216)



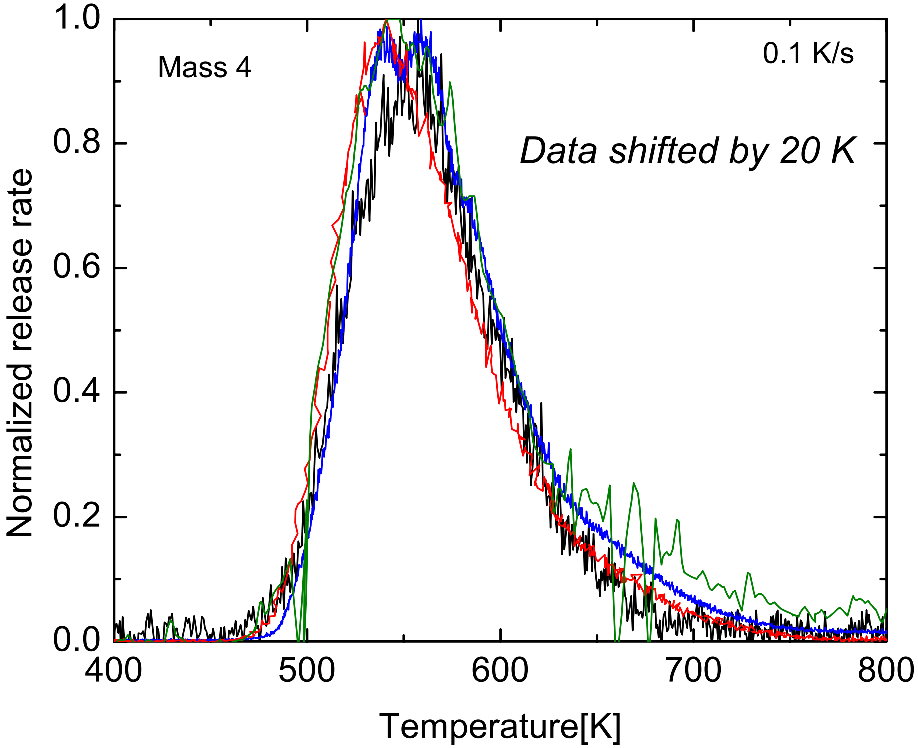
- Data from 4 groups (1 omitted)
- Difference in peak locations ~20 K

Normalized desorption curves (0.1 K/s)

Outer ring samples



Inner ring samples

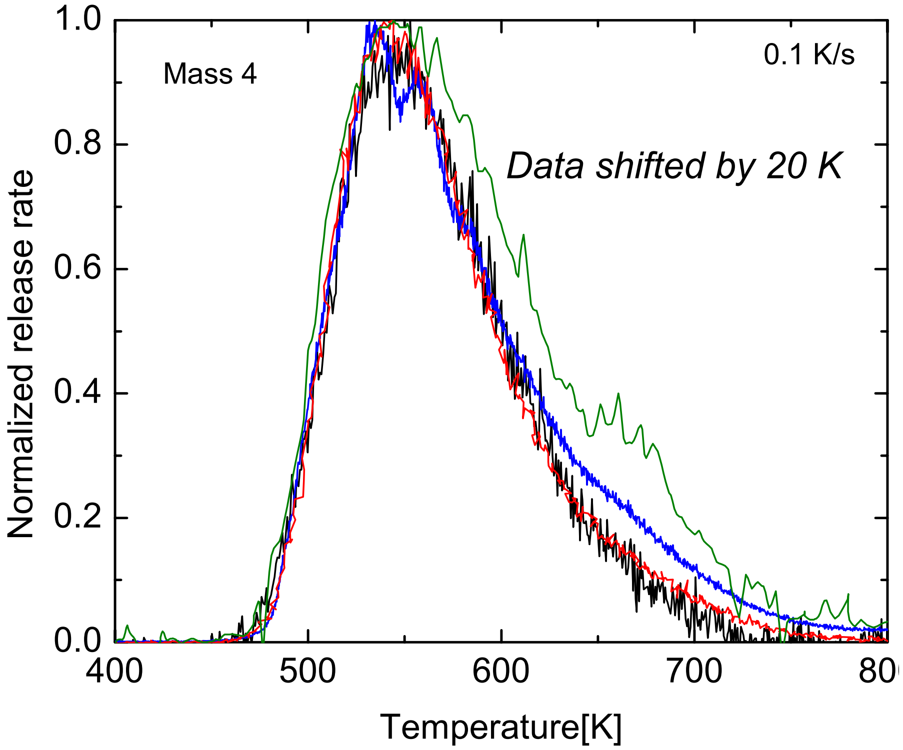


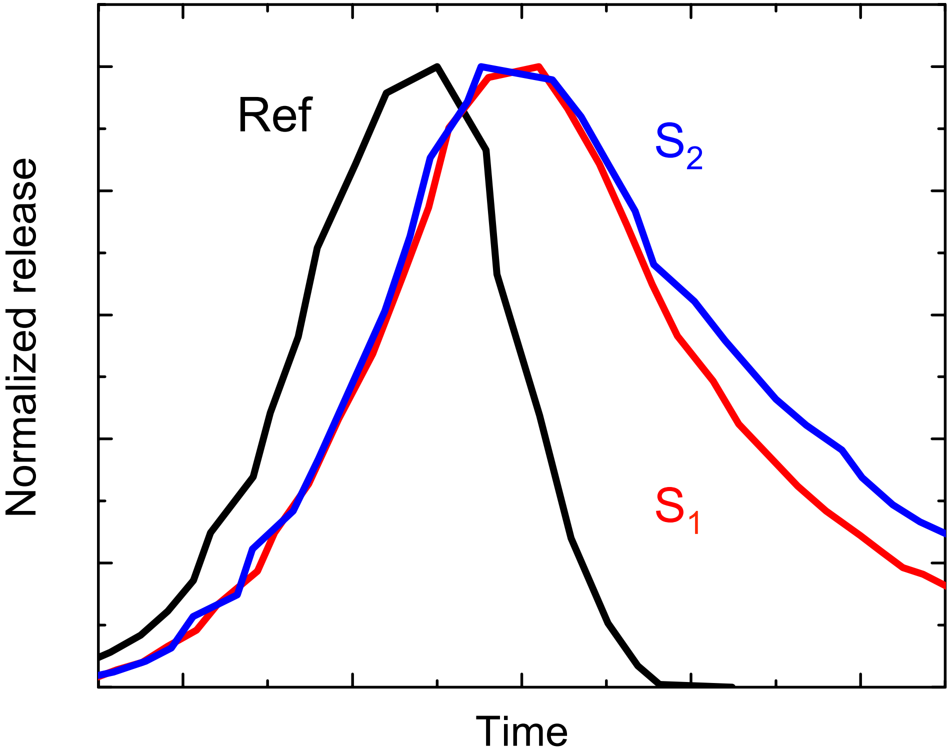
Discussion (2): Why the 20 K variation in peak shift?

- Systematic temperature errors.
- Phase shift from the finite pumping speed.
- For arbitrary signal like a pressure burst caused by thermal desorption of gas, the incremental time delay is not equal for all parts of the input signal because of the distribution in the frequencies and amplitudes that comprises the pulse.

Normalized desorption curves (0.1 K/s)

Outer ring samples

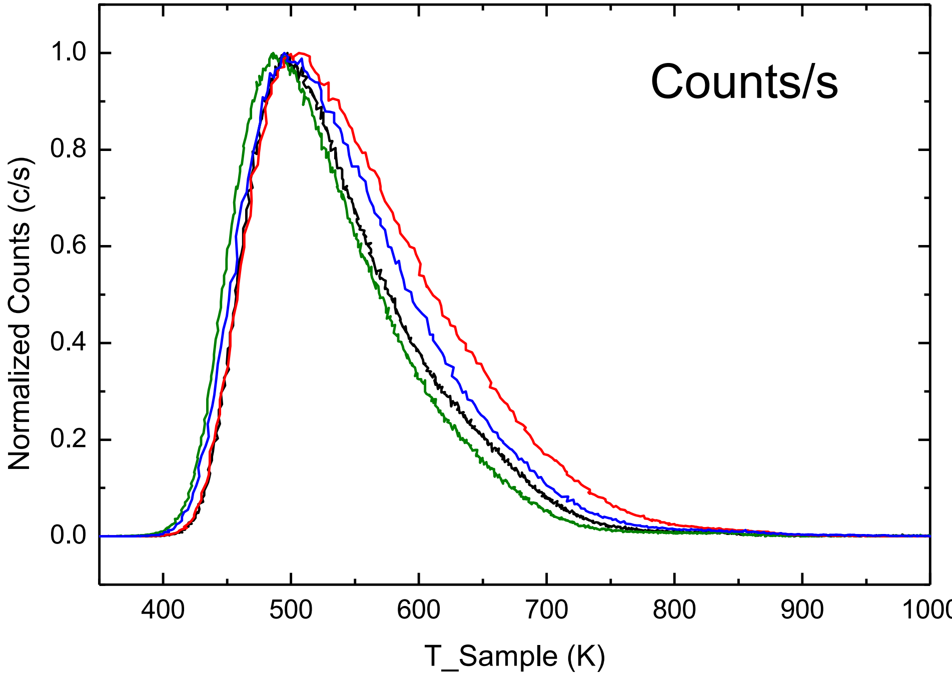


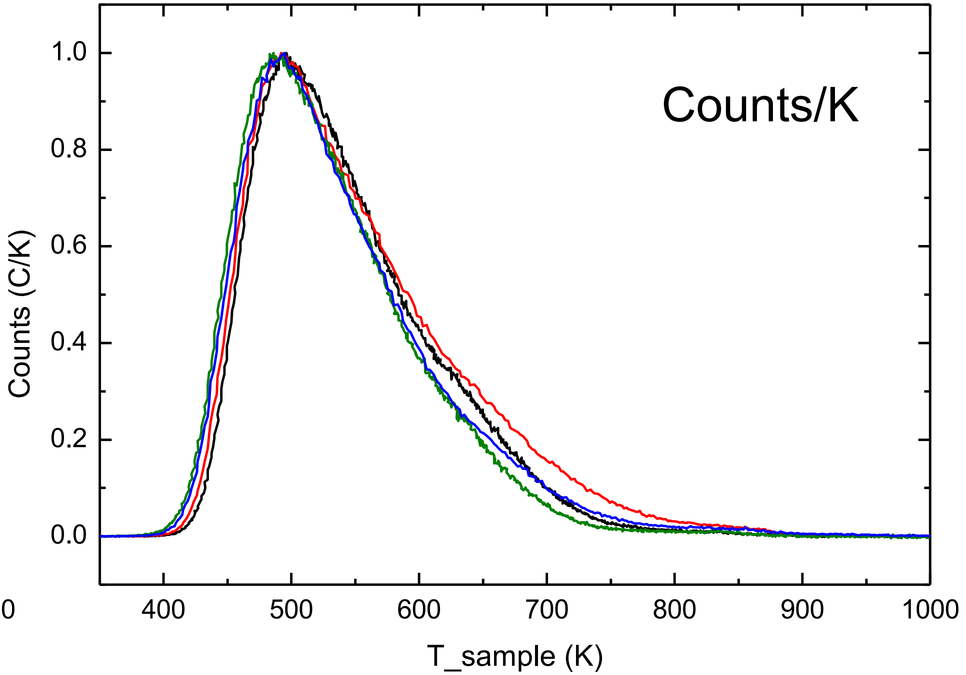


Discussion (3): Reason for the trailing edge distortion?

- Distortion from finite pumping speed.
- Nonlinear temperature ramp
- Background subtraction

Distortion from non-linear ramping





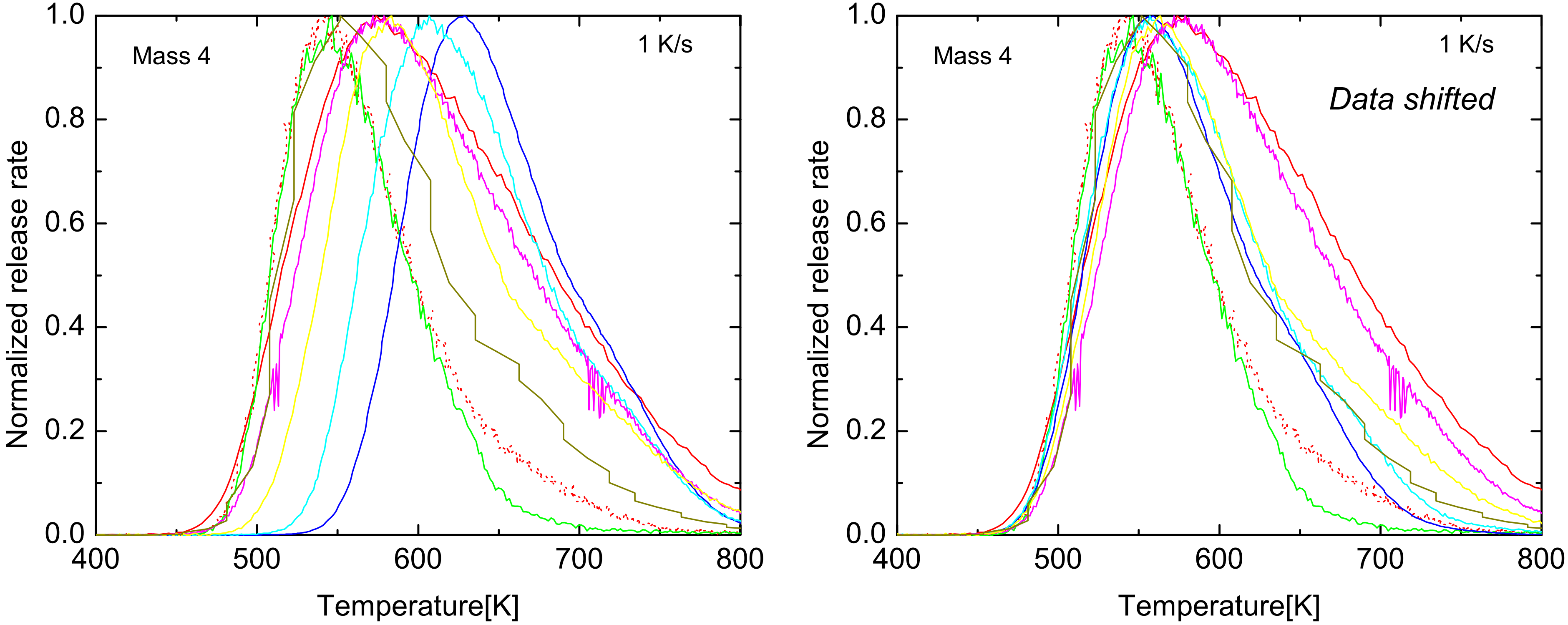
Normalized TDS spectra of Mass 4 for the measured 2 sets of samples:

in the left the normalization is done for the counting rate in **counts/sec** without local ramp determination, which is obviously broadened!!!

The right normalization is done for **counts/K** after the taking into account the local ramping rate)

Normalized desorption curves (1 K/s)

Outer ring samples (3188,3193,3195,3196,3200,3201; 3194 (0.1 K/s))

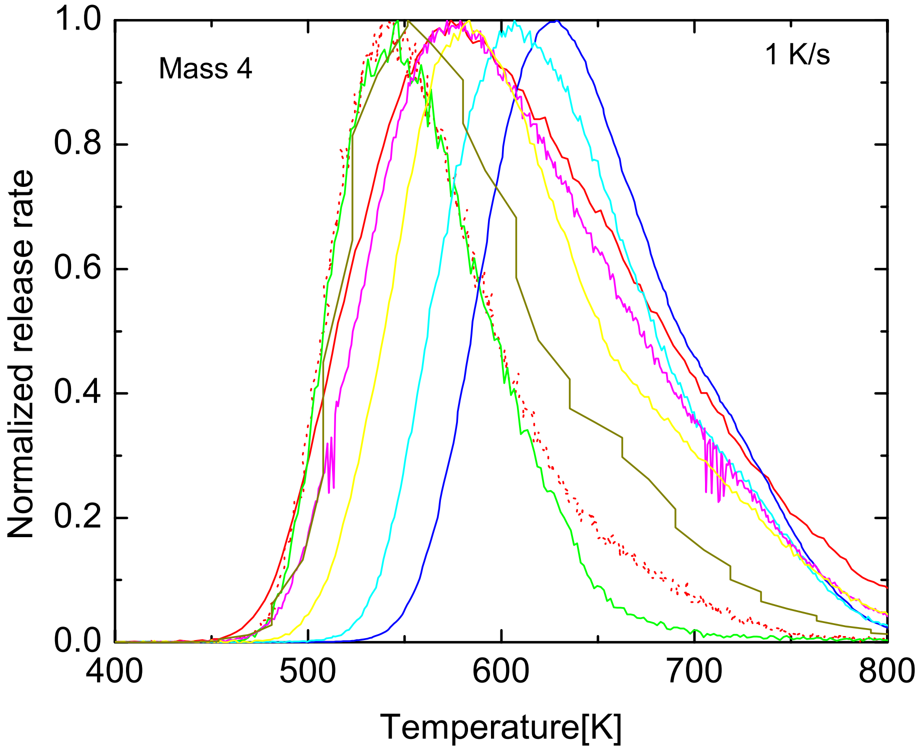


- Shown in red dotted is the Osaka data for 0.1 K/s
- Data from 7 groups
- Difference in peak locations ~80 K

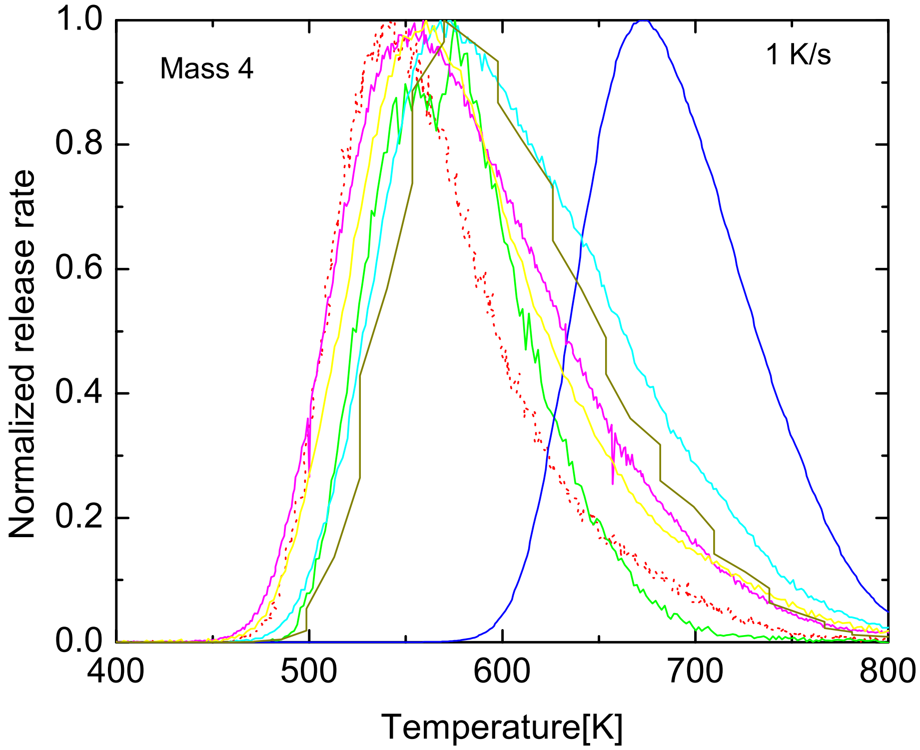
- Data shifted to match rising edge but one can now see distortion in both leading and trailing edges.

Normalized desorption curves (1 K/s)

Outer ring samples



Inner ring samples



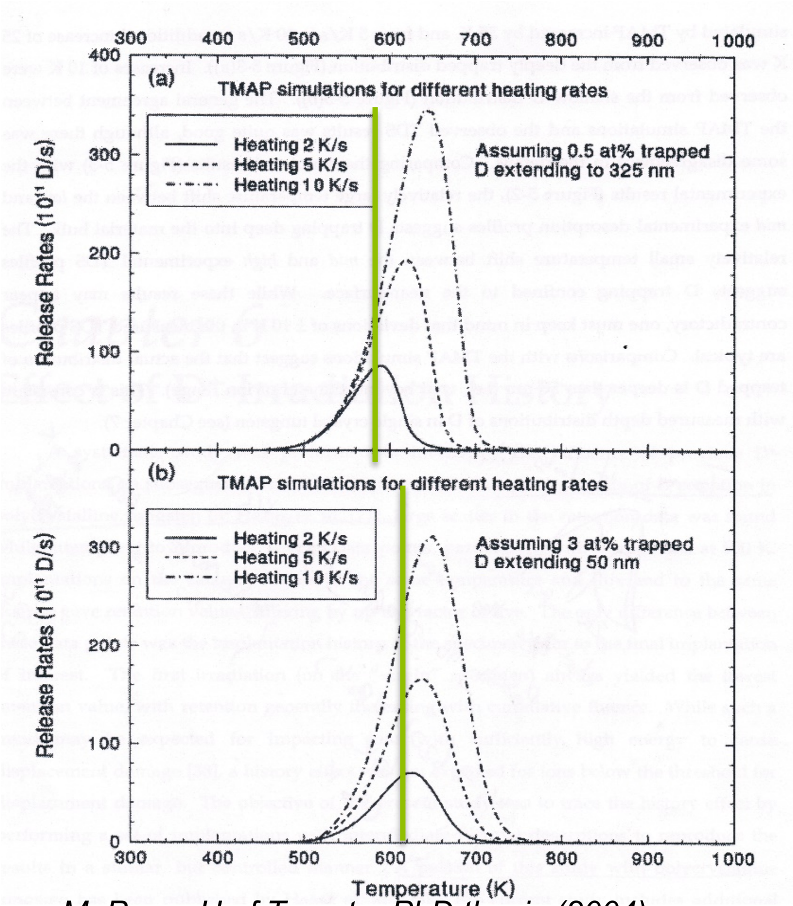
- Data from 7 groups
- Difference in peak locations ~80 K

- Difference in peak locations~30K

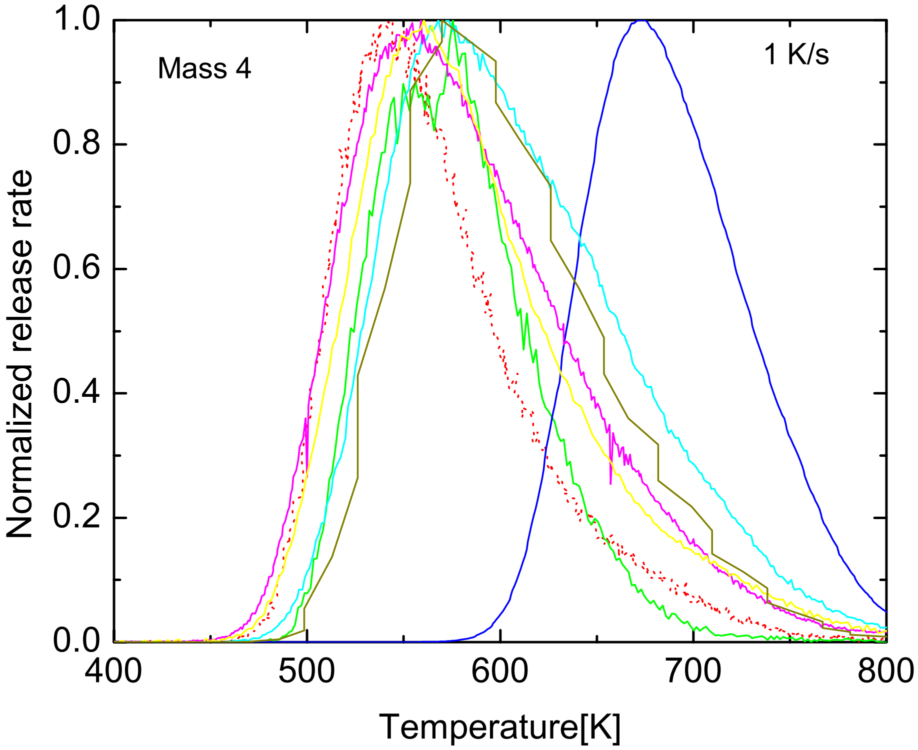
First order release and linear heating rate, β

$$I(E,v;t) = v n_o \exp\left[-\frac{E}{kT(t)}\right] \exp\left[\left(-\frac{v}{\beta}\right)\int_{T_o}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]$$

Direct release from sample



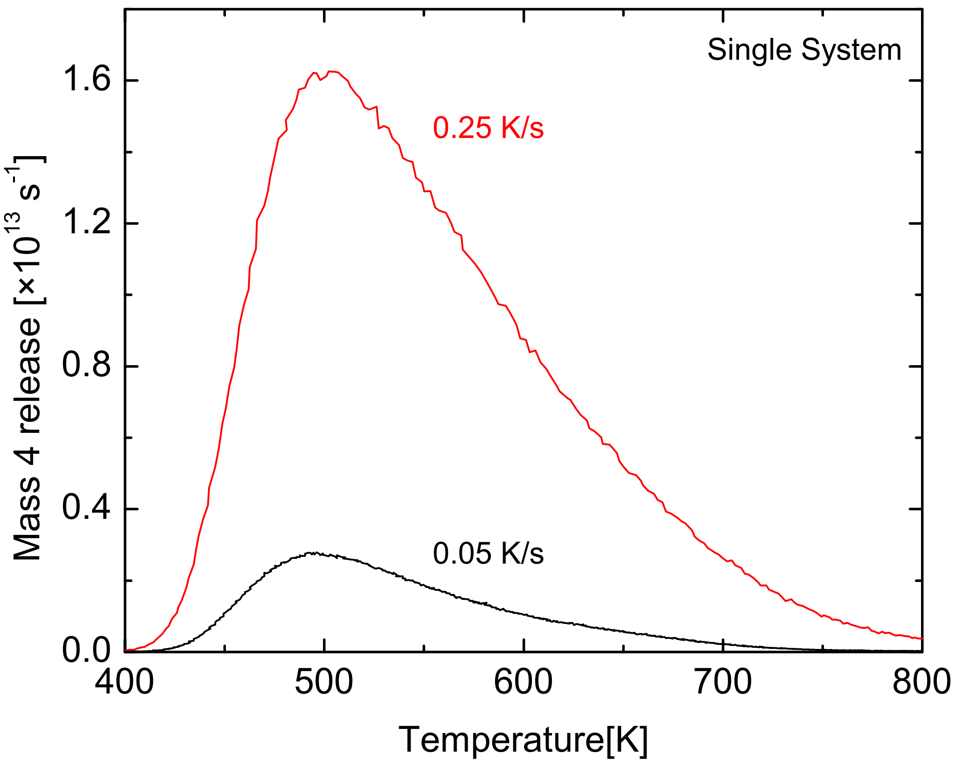
M. Poon, U of Toronto, PhD thesis (2004)

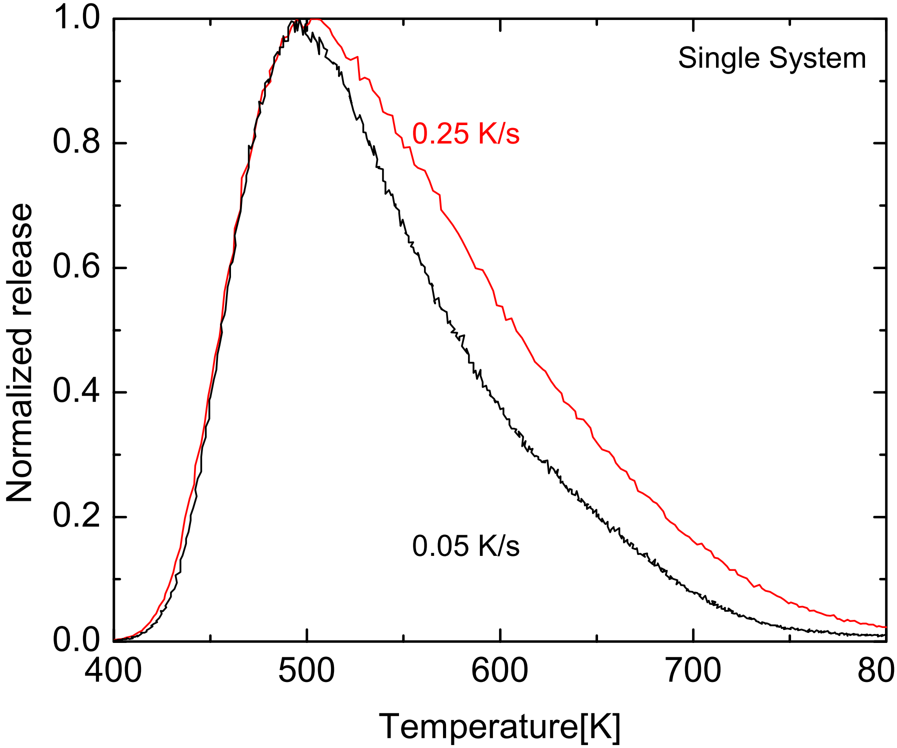


J.J Randall and M.H.F. Wilkins, Proc. Roy. Soc. A 184(1945)366

- The submitted data is convoluted and the effect of ramping rate on kinetic desorption parameters is not clear

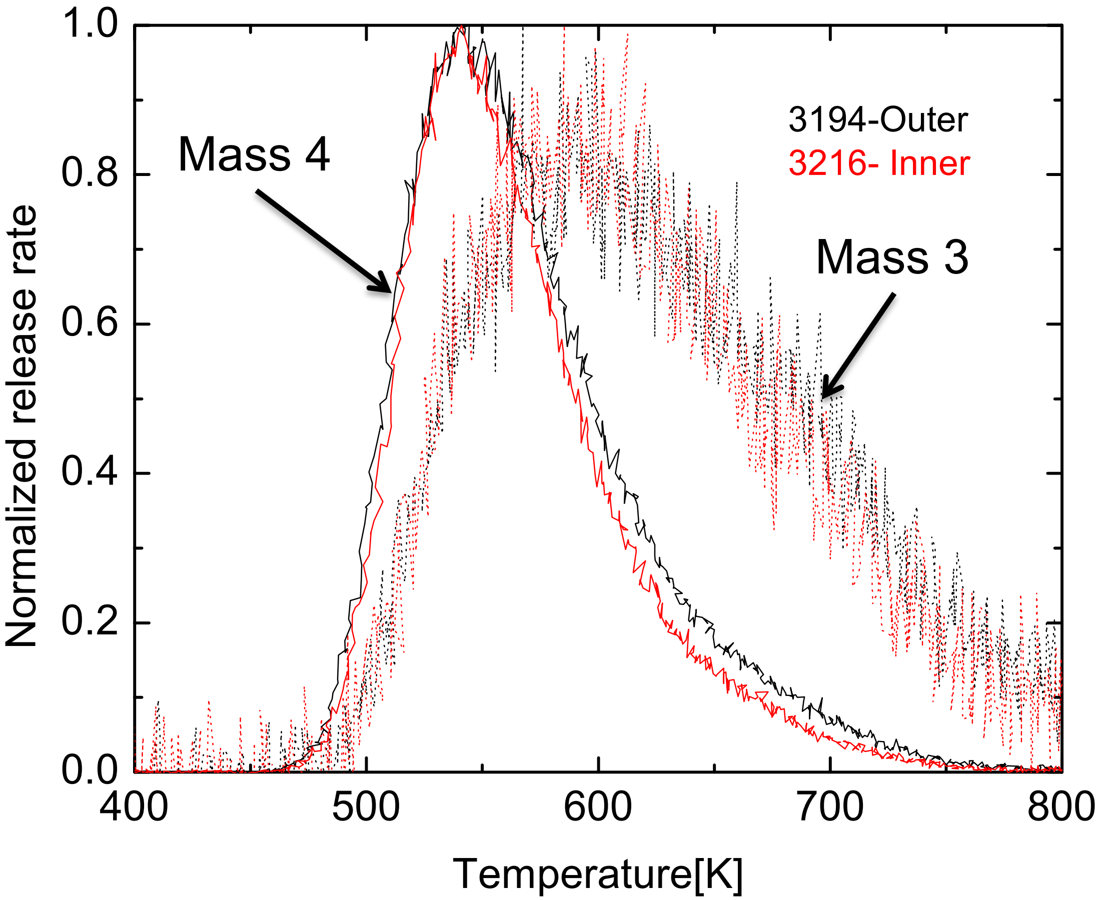
Lack of peak shift supported by experiments of two different ramping rates performed in a single system





- Trailing edge distortion due to nonlinear ramping rate.

Under progress : comparison of Mass 3/Mass 4 release



- Mass 3 signals show qualitatively different shapes.
- Likely the mass 3 signals are distorted by pumping effects.
- One needs to take into account the relative velocity distribution and the pumping speed difference.

Summary II

- Inner ring samples show better agreement between groups vs. outer ring

- Peak shifts and distortion of the leading and trailing edge of the profiles observed – effect of system parameters.

    - The peak shifts could occur due to systematic error in temperature or phase differences arising from finite pumping speed
    - Distortion of the peak shapes can arise from finite pumping speeds or nonlinear temperature ramping
    - The observed distortions are more significant at 1 K/s vs. 0.1 K/s

- The shift in desorption spectra with varying ramping rates arising from kinetic parameters could not be determined

    - Likely due to the fact that the system dependent parameters and their convolution dominate the release spectra over any kinetic parameters

- More analysis underway examining the Mass 3, 19, 20 signals

Considerations for TDS on neutron irradiated materials

- For neutron damage W studies, often the peaks are at higher release temperatures, therefore higher probability of vacuum system dependent distortions affecting the interpretations. (due to the convolution integral)

- One should be careful to assign “long tails” to actual desorption from samples (due to increased sources at the higher temperatures and effects of pumping speed)

- “Long tails” could also arise due to actual release from the backside of the sample

- At higher temperatures, the surrounding chamber heats up which changes the velocity distribution of the scattered molecular gas and affects its detection in the Q-mass

Outlook

- Release full TDS desorption data to participants
- Seek feedback/suggestions for analysis
- Seek feedback in identification of systematic errors
- Quantitative modeling of pumping speeds on the distortion of TDS spectra → will provide only system dependent information. Valuable for the practitioner of each system but not very useful for the general public.
- It may be useful, if we can distill it down to a procedure to determine such distortions and recommended guidelines for treatment of experimental data– but it is not self evident at this stage that this is possible.
- If this can be accomplished then a publication of paper is likely possible.

Discussion

Discussion (1): Lower mean TDS values in comparison to NRA (~12%)

Discussion (2): The reasons for variation in peak shift.

- Systematic temperature errors.
- Phase shift from the finite pumping speed.
- For arbitrary signal like a pressure burst caused by thermal desorption of gas, the incremental time delay is not equal for all parts of the input signal because of the distribution in the frequencies and amplitudes that comprises the pulse.

Discussion (3): Reason for the trailing edge distortion?

- Distortion from finite pumping speed.
- Nonlinear temperature ramp