

Q1. Defining the precise onset of RH stabilization is critical, as it directly fixes the time origin for calculating τ and the derived D_w . Currently, the choice of five characteristic times (5ω) for RH stabilization appears empirical. The authors should provide a clear physical mechanism or appropriate literature references to justify this criterion, or adopt a more rigorous mathematical definition for the stabilization point. Moreover, using the term "characteristic time" for both the experimental RH response parameter (ω) and the isotope diffusion timescale (τ) introduces unnecessary confusion.

We thank the reviewer for this important comment. We agree that the definition of the RH stabilisation point should be more clearly justified because it determines the time origin used in the subsequent calculation of D_w . In the revised manuscript, we have therefore clarified both the mathematical basis and the literature support for the criterion used to determine RH stabilisation.

The temporal evolution of RH during the transition toward the boundary condition is described by a first-order exponential function:

$$RH = \alpha e^{-\frac{t}{\omega}} + \beta, \quad (1.1)$$

where ω is the time constant of the exponential response, and α and β are fitting parameters. At $t = 5\omega$,

$$\frac{RH(5\omega) - \beta}{RH(0) - \beta} = e^{-5} \approx 0.0067. \quad (1.2)$$

Thus, approximately 99.3% of the fitted RH transition has been completed after $t = 5\omega$, with only about 0.67% of the initial deviation remaining. On this basis, 5ω is used as an operational criterion for the onset of RH stabilisation. This treatment is also consistent with established practice in transient sensor-response studies. Osorio-Arrieta et al. (2018), for example, described sensor transients using exponential functions and explicitly adopted five times the time constant as the criterion for attaining the steady-state response. We have therefore added this reference and the above quantitative explanation of the 5ω criterion to the revised manuscript.

We also agree with the reviewer that using the term "characteristic time" for both the RH response parameter ω and the diffusion timescale τ could lead to unnecessary ambiguity. In the revised manuscript, ω is referred to as the RH response time constant, following the terminology commonly adopted in previous studies, whereas characteristic time is used only for τ , which is employed here to retrieve D_w following the definition of Seinfeld and Pandis (1998). We have clearly distinguished these two quantities throughout the manuscript.

Q2. The authors should include, for at least a subset of the measured droplets, a side-by-side comparison of D_w values obtained via the new characteristic-time method and conventional fitting of the entire D₂O-fraction time series. Such comparison would provide a more direct and convincing validation of the proposed method, rather than relying solely on qualitative agreement with literature values obtained under different conditions and platforms.

We thank the reviewer for these detailed comments. We applied the characteristic-time (CT) method and the conventional full-curve fitting (FCF) method to the same experimental datasets and directly compared the resulting D_w values, including uncertainties from random fluctuations in the experimental data. The additional analyses are presented below and will be added to the Results and Discussion in the manuscript.

2.1 Comparison of retrievals and uncertainties between characteristic-time and full-curve fitting methods

We applied the characteristic-time (CT) method to nine experiments conducted at different relative humidities to determine the water diffusion coefficient, D_w , over 30%–45% RH. To further assess its performance relative to the conventional full-curve fitting (FCF) method, we also fitted the same nine experimental datasets using the FCF method and compared the resulting D_w values and retrieval uncertainties.

Both methods use the same D₂O fraction measurements. In the CT method, the experimental data are first smoothed, and the resulting curve is used to identify the characteristic time, from which D_w is calculated. We select the smoothing parameter objectively using blocked cross-validation. In the FCF method, the complete experimental curve, from the initial time to the end of the record, is fitted with the spherical diffusion model to obtain the optimal D_w . Thus, the two methods share the same physical model but differ in how they use the temporal information in the experimental data. The CT method primarily uses the time at which the experimental curve reaches the D₂O fraction corresponding to the characteristic time, whereas the FCF method uses the full temporal evolution of the D₂O fraction to retrieve D_w . Figures 2.1 and 2.2 show results from a representative experiment at 35% RH. Figure 2.1 presents the CT retrieval, with the smoothed curve shown in blue. Figure 2.2 presents the FCF retrieval, with the fitted curve shown in red.

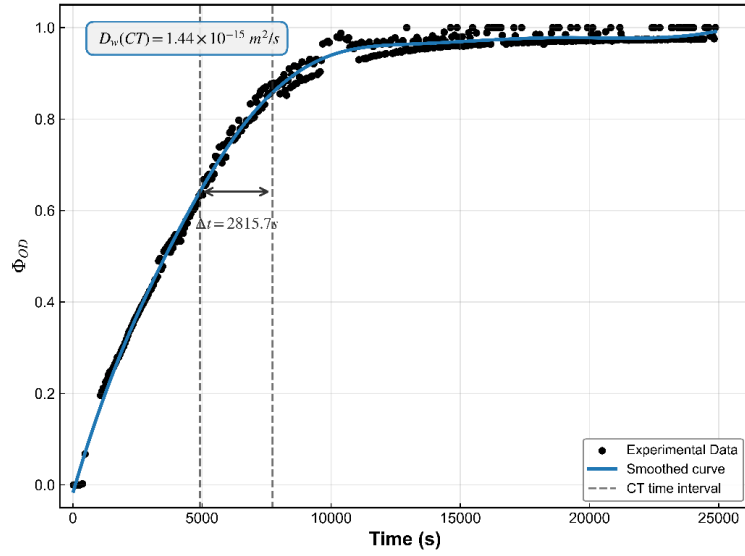


Figure 2.1: Smoothed curve, characteristic-time interval, and D_w retrieved using the CT method.

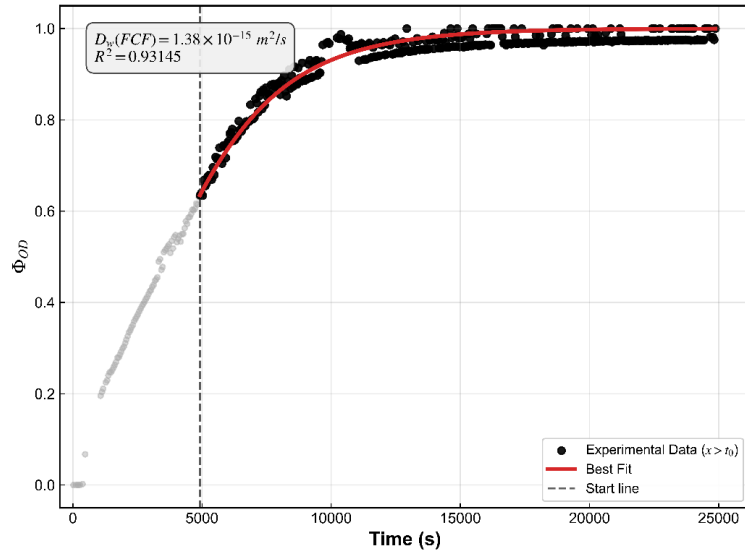


Figure 2.2: Fitted curve and D_w retrieved using the FCF method.

55 To compare the sensitivity of the two retrieval methods to fluctuations in the experimental data and assess the resulting uncertainty in D_w , we evaluated their robustness using residual bootstrap. First, we constructed a trend curve using the same smoothing procedure as in the CT method, and used the residuals relative to this curve to represent random fluctuations in the experimental data. The residuals were then resampled and added to the original trend curve to generate a new perturbed dataset for each bootstrap replicate. We applied both CT and FCF to the same perturbed dataset in each replicate. This

60 ensures that the uncertainties are compared under identical data perturbations and avoids introducing additional variability

from different random samples. For each experiment, 1000 bootstrap replicates were generated to obtain the bootstrap distributions of D_w for the CT and FCF methods. The 2.5th and 97.5th percentiles of each distribution were taken as the lower and upper bounds of the 95% confidence interval. Because D_w spans a wide range of orders of magnitude, we defined the equivalent half-width of the 95% confidence interval in $\log_{10}^{D_w}$ space to facilitate comparisons of uncertainty across experiments and between the two methods:

$$H_{95,\log} = \frac{1}{2} [\log_{10} D_{97.5} - \log_{10} D_{2.5}], \quad (2.1)$$

This half-width was then converted to a relative percentage:

$$H_{95,\%} = (10^{H_{95,\log}} - 1) \times 100\%. \quad (2.2)$$

Figure 2.3 compares the D_w retrieved using the CT and FCF methods for the nine experiments. The results generally follow the 1:1 relationship, with all data points lying within the $\pm 20\%$ deviation band or close to its boundaries. Although D_w spans a wide numerical range across the experimental conditions, the differences between the two methods show no clear systematic dependence on D_w . This indicates that the CT method yields absolute values of D_w similar to those obtained by FCF and captures the relative variation in D_w with RH across the experimental conditions, demonstrating broad consistency between the two methods.

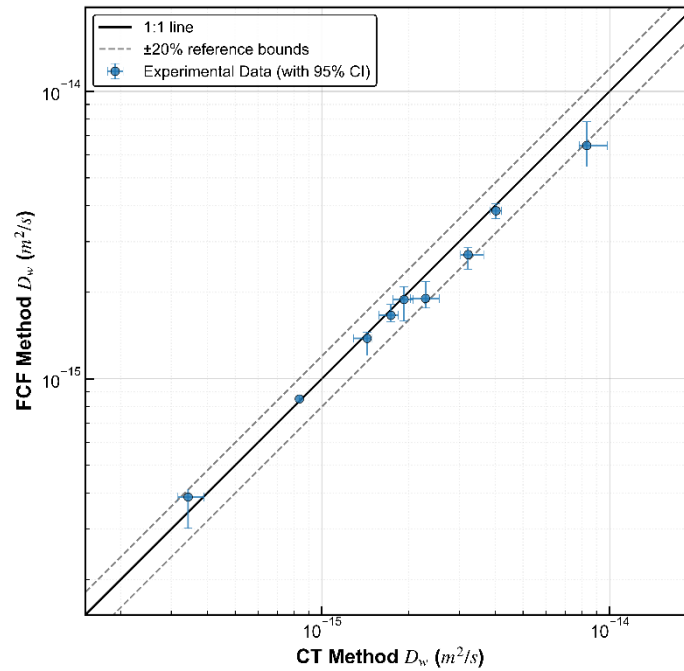


Figure 2.3: Comparison of D_w retrieved using the CT and FCF methods.

Figure 2.4 further compares the half-widths of the 95% confidence intervals on the logarithmic scale for the two methods across the nine experiments, expressed as relative percentages, $H_{95,\%}$, to provide a more intuitive measure of retrieval uncertainty. Overall, CT and FCF show comparable uncertainties. The CT method yields a smaller $H_{95,\%}$ than FCF in six of

the nine experiments. These results indicate that using only the characteristic-time information, rather than the full time-evolution curve as in FCF, does not reduce retrieval precision. Combined with the D_w comparison in Figure 2.3, these results indicate that the CT method can simplify data processing while yielding diffusion coefficients broadly consistent with those obtained by conventional FCF and comparable uncertainty levels.

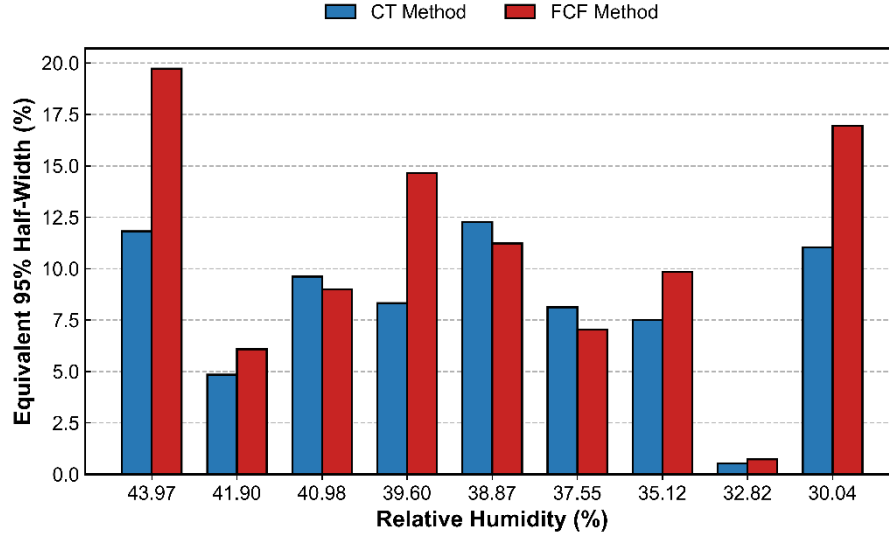


Figure 2.4: Comparison of retrieval uncertainties for the CT and FCF methods.

2.2 Comparison of the observation times required by CT and FCF

We further compared the observation durations required by the CT and FCF methods. For CT, the required duration follows directly from the definition of the characteristic time. The experimental record must extend from the initial time to the time at which the corresponding D_2O fraction is reached. The method therefore has a clearly defined time criterion. We denote the observation duration required by CT as Δt_{CT} . For FCF, however, no clear, unified criterion currently defines the required observation duration. Because FCF retrieves the diffusion coefficient by fitting the full diffusion process, the required observation time must be assessed from the convergence of the fitting results. We therefore fitted progressively longer portions of each experimental record and compared the resulting diffusion coefficients to determine the minimum observation time needed for stable, reliable FCF retrievals.

Specifically, starting from the initial fitting time, t_0 , we progressively advanced the end time of the fitted data, increasing the observation duration by 50 s at each step. For each truncated dataset, we repeated the FCF retrieval and the uncertainty analysis described above to obtain $D_w(t_i)$ and its uncertainty, where t_i denotes the endpoint of the i th truncated record. Taking the retrieval based on the complete record as the reference, we constrained the minimum observation time required by FCF using the stability of both $D_w(t_i)$ and its uncertainty.

100 For the diffusion coefficient, the 95% confidence interval of D_w obtained by fitting the complete experimental record was used as the reference range. We defined t_{D_w} as the earliest time at which $D_w(t_i)$ enters this range and remains within it for all subsequent observation durations.

For uncertainty, each fit to a truncated record was evaluated using the bootstrap resampling procedure described above:

$$H_{95,\log}(t_i) = \frac{1}{2} [\log_{10} D(t_i)_{97.5} - \log_{10} D(t_i)_{2.5}]. \quad (2.3)$$

105 Here, $D(t_i)_{2.5}$ and $D(t_i)_{97.5}$ are the 2.5th and 97.5th percentiles of the FCF bootstrap distribution for the current truncated record, respectively. The quantity $H_{95,\log}(t_i)$ represents the half-width of the 95% confidence interval on the logarithmic scale and quantifies uncertainty. The uncertainty of the fit to the complete record is denoted by $H_{95,\log}(t_{full})$, which is identical to $H_{95,\log}$ as defined above, with the record duration added to the notation. To establish an allowable upper limit for uncertainty, we generated 2000 resamples from the 1000 bootstrap diffusion coefficients obtained using the complete record.

110 Each resample contained 1000 values, from which the half-width of the 95% confidence interval on the logarithmic scale was calculated using the definition above. This procedure yielded a distribution of 2000 half-width estimates. Their standard deviation, denoted by $SE(H_{95,\log}(T_{full}))$, was used as the standard error of the uncertainty estimate. The allowable upper limit was then defined as the sum of the uncertainty for the complete record, $H_{95,\log}(T_{full})$, and its standard error, $SE(H_{95,\log}(T_{full}))$:

$$115 \quad H_{max} = H_{95,\log}(T_{full}) + SE(H_{95,\log}(T_{full})). \quad (2.4)$$

Here, H_{max} denotes the allowable upper limit for uncertainty. For the fits to records truncated at different times, we defined t_H as the earliest time at which $H_{95,\log}(t_i)$ does not exceed H_{max} and this condition remains satisfied for all subsequent observation durations.

Finally, the later of t_{D_w} and t_H was taken as the earliest observation endpoint satisfying both criteria:

$$120 \quad t_{FCF} = \max(t_{D_w}, t_H). \quad (2.5)$$

Thus, we considered an observation time sufficient for reliable FCF retrieval only when both the retrieved diffusion coefficient and its uncertainty had stabilised. The minimum observation duration required for the FCF method was denoted as Δt_{FCF} and calculated as the difference between t_{FCF} and the initial time.

Figure 1.5 compares the observation durations required by CT and FCF at different RH values. In our observations, CT consistently required substantially shorter records than FCF. To quantify this advantage, we defined the fractional reduction in observation duration achieved by CT as:

$$125 \quad \eta = \frac{\Delta t_{FCF} - \Delta t_{CT}}{\Delta t_{FCF}} \times 100\%. \quad (2.6)$$

Across the eight experiments where comparison was possible, CT reduced the required observation duration by 54.0%–73.8% relative to FCF, with a mean reduction of 65.7% and a median of 66.7%. Under the criteria adopted in this study, CT

130 therefore saves approximately two-thirds of the observation time on average, with a reduction achieved in every experiment included in the comparison. The absolute time savings are particularly substantial for experiments involving slow isotope

exchange. At 35.1% RH, FCF required 8200 s, whereas CT required only 2815.7 s, a reduction of 65.7%. At the lower RH of 32.8%, the required duration decreased from 235.0 min for FCF to 69.6 min for CT, a 70.4% reduction. Of the nine experiments conducted, the droplet at 30% RH escaped from the optical trap before isotope exchange was complete, terminating the observation prematurely. The subsequent record was therefore insufficient to establish the minimum sufficient observation duration for FCF using the criteria above, and this experiment was excluded from the time comparison. Nevertheless, the record acquired before escape from the optical trap covered the characteristic time required by CT and could still be used to retrieve the water diffusion coefficient. This example further illustrates that CT reduces the dependence of diffusion measurements on late-stage exchange data. As long as the record covers the characteristic time, CT can still extract diffusion information from an experiment that terminates prematurely.

Together with the consistent diffusion coefficients and comparable retrieval uncertainties reported above, this comparison shows that the CT method can substantially reduce the required record length while maintaining results broadly comparable to those obtained by FCF.

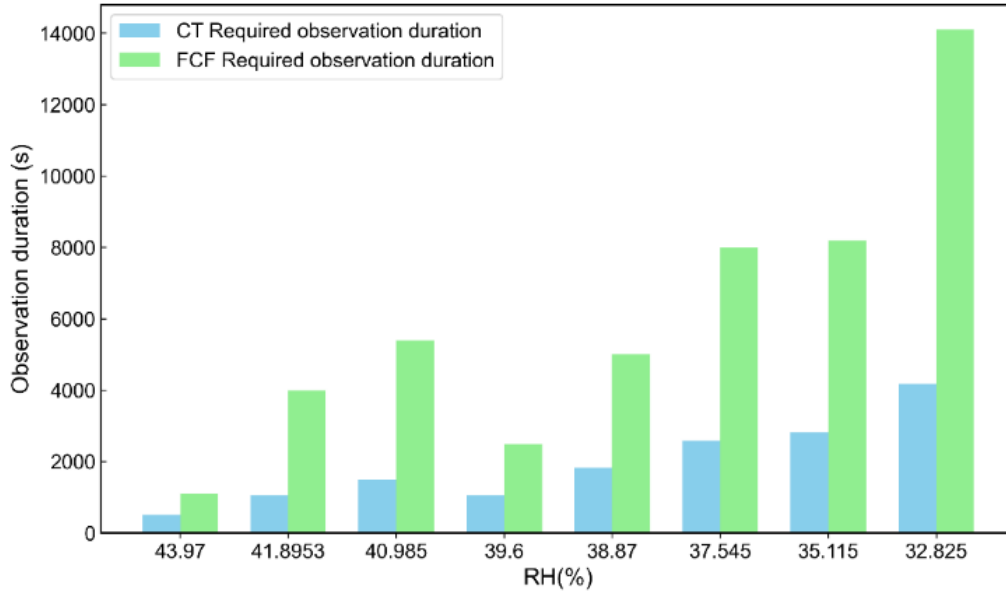


Figure 2.5: Comparison of the observation durations required by the CT and FCF methods.

It should be noted that, following the reviewer's minor suggestion that the RH record should be extended to include the period before the D₂O flow switch, we now present the complete RH response covering both the initial perturbation and the subsequent process toward the new steady level (Fig. 2.6). Accordingly, the fitting function for RH was modified to:

$$RH = \alpha e^{-\frac{t-\theta}{\omega}} + \beta, \quad (2.7)$$

where θ is the time of the fitting start point. We further specified the fitting start point as the earliest point after the RH minimum at which the smoothed RH trend maintained a positive slope thereafter, ensuring a sustained increase in RH.

Meanwhile, in this revision, we modified the procedure for selecting the smoothing parameter in the CT method. Consequently, the final D_w values differ slightly from those in the original submission.

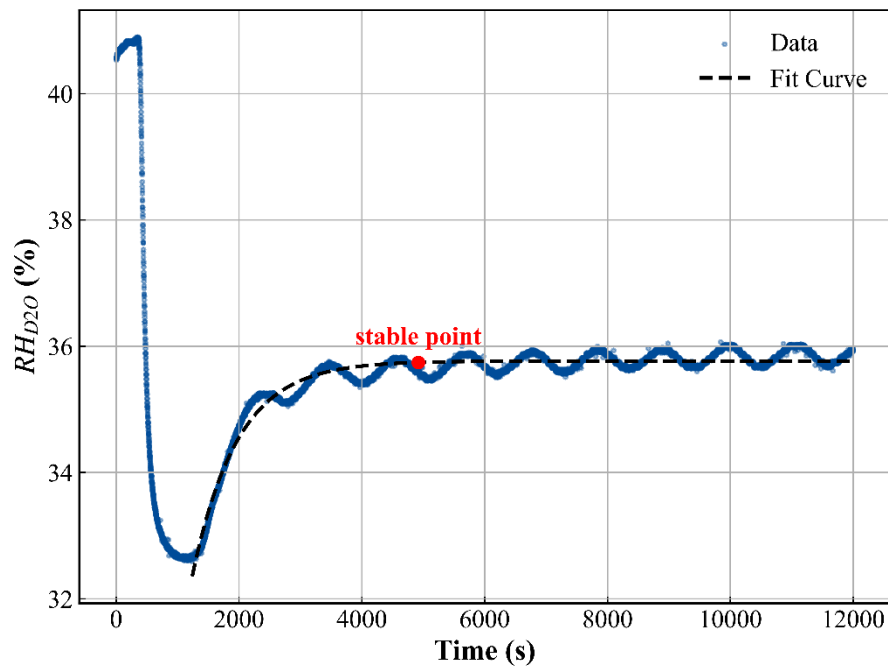


Figure 2.6: Temporal variation of RH and the corresponding exponential fit in a representative experiment.

165 **Q3. The Introduction and Discussion repeatedly emphasize that the method is particularly advantageous for slow-diffusion (low-RH, high-viscosity) systems where conventional isotope-tracer measurements become impractical. However, the RH range investigated here (30–45%) does not extend into this regime. I recommend that the authors extend the measurements to lower RH (or lower temperature) to directly demonstrate the method's capability under conditions where conventional approaches fail.**

170 We thank the reviewer for this suggestion. We acknowledge that extending the measurements to lower RH or lower temperatures would further demonstrate the method's advantages in systems with slow diffusion. In future work, we plan to apply the CT method at lower temperatures and lower RH, as well as to other highly viscous systems.

For the present study, our primary objective is to develop an accurate and more efficient method for measuring D_w . Based on the quantitative comparison added in our response to Q2, the available experimental results support this central conclusion:
175 under the conditions investigated, the CT method substantially reduces observation time while yielding water diffusion coefficients and associated uncertainties that are overall consistent with those obtained using FCF. We therefore consider the current experimental results sufficient to support the main conclusions of this study regarding the efficiency and reliability of the CT method.

At the same time, following the reviewer's suggestion, we have examined the statements in the manuscript concerning low-
180 RH, low-temperature, and slow-diffusion systems. We revised statements about low-RH, low-temperature, and slow-diffusion conditions that were not directly examined in the present experiments to avoid making overly definitive claims about the method under these conditions. The revised text now more clearly distinguishes between conclusions directly supported by the present experiments and the method's potential application to systems with slower diffusion. The specific revisions are described below. Further explanation is provided below.

185 (1) Across the eight comparable experiments within the 30%–45% RH range, CT reduced the observation time relative to FCF by 54.0%–73.8%, with a mean reduction of 65.7% and a median of 66.7%. At the two lowest comparable RH conditions (35.1% and 32.8% RH), the reductions were 65.7% and 70.4%, respectively. Together with the overall agreement between the D_w values obtained using the two methods and the comparable magnitudes of their 95% confidence interval half-widths, these results show that CT's advantage in reducing observation time holds across a range of RH conditions and
190 remains pronounced under conditions associated with slower diffusion within this range. This provides an experimental basis for expecting this advantage to extend to lower RH.

(2) The experiment at 30% RH further illustrates the practical significance of the shorter observation time required by CT. In this experiment, the droplet escaped from the optical trap before isotope exchange was complete, terminating the observation record prematurely. Nevertheless, the available data covered the characteristic time required by CT and could therefore still
195 be used to retrieve D_w . By comparison, the record was insufficient for a reliable FCF retrieval. This case demonstrates that CT can still determine the diffusion coefficient from the available data even when observations do not extend through the later stages of isotope exchange.

(3) We also recognise the need to distinguish the existing results from the anticipated applicability of the method at lower RH and lower temperatures. We have therefore revised overly definitive statements in the Introduction and Conclusions, restricting the relevant conclusions to the conditions directly supported by the existing experiments and describing extensions to lower RH or lower temperatures as potential applications. Based on the reductions in observation time and their consistency across different RH conditions, we consider that CT has the potential to reduce the required observation time under these additional conditions.

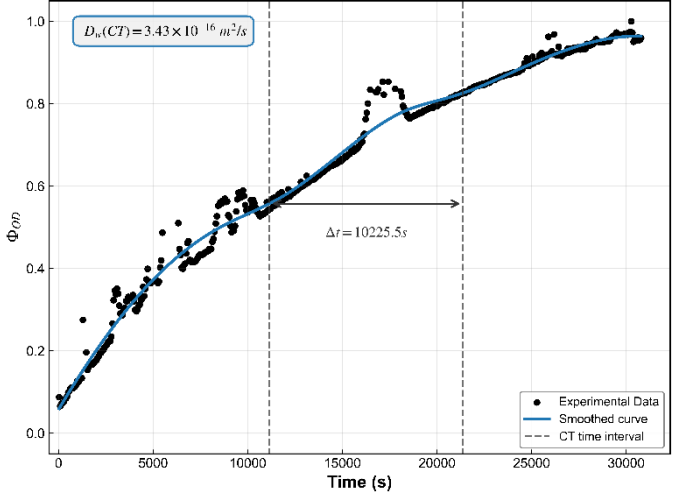


Figure 3.1: Smoothed curve, characteristic-time interval, and D_w retrieved using the CT method at 30% RH.

Reference

- 210 Osorio-Arrieta, D. L., Muñoz-Mata, J. L., Beltrán-Pérez, G., Castillo-Mixcóatl, J., Mendoza-Barrera, C. O., Altuzar-Aguilar, V., and Muñoz-Aguirre, S.: Reduction of the Measurement Time by the Prediction of the Steady-State Response for Quartz Crystal Microbalance Gas Sensors, *Sensors*, 18, 2475, <https://doi.org/10.3390/s18082475>, 2018.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics: from air pollution to climate change*, Wiley, New York, 1998.

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