N_2O Actinometry Experiment

1. Theoretical Background

The sulphuric acid calibration method described by Kürten et al. (2012) calculates the theoretical sulphuric acid concentration introduced into the CIMS, $[H_2SO_4]_{calc}$, based on the theoretical hydroxyl radical concentration generated in the Hg-lamp box, $[OH]_{calc}$, whose general equation is

$$[OH]_{calc} = I \cdot t \cdot \sigma_{H_2O} \cdot \Phi_{H_2O} \cdot [H_2O]\,, \qquad \text{(eq. 1)}$$

where I represents the photon intensity, t is the illuminating time, σ_{H_2O} and Φ_{H_2O} are, respectively, the absorption cross section of H_2O vapor at 184.9 nm and the quantum yield of H_2O photodissociation, which are tabulated.

As regards I and t, their combined product – hereafter referred to as It-product – is derived through chemical actinometry, i.e., by using another chemical reaction with known rates and accurately measurable products to conduct a separate experiment under the same conditions as during the sulphuric acid calibration experiment. The reaction chosen in the present case is the conversion of nitrous oxide (N_2O) to nitrogen oxides (NO_x):

$$\mathrm{N_2O} + h\nu\ (\lambda = 184.9\ \mathrm{nm}) \rightarrow \mathrm{N_2} + \mathrm{O}^*, \qquad \text{(R1)}$$

$$\mathrm{O}^* + \mathrm{N_2} \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{N_2}, \qquad \text{(R2)}$$

$$\mathrm{O}^* + \mathrm{N_2O} \rightarrow 2\mathrm{NO}, \qquad \text{(R3)}$$

$$\mathrm{O}^* + \mathrm{N_2O} \rightarrow \mathrm{N_2} + \mathrm{O_2}, \qquad \text{(R4)}$$

$$\mathrm{O}^* + \mathrm{N_2O} \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{N_2O}. \qquad \text{(R5)}$$

The relationship between the It-product and the concentrations of NO_x, N_2O, and N_2 is given by eq. 2:

$$It_{N_2O} = \frac{k_2 \cdot [N_2] + (k_3 + k_4 + k_5) \cdot [N_2O]}{2k_3 \cdot \sigma_{N_2O} \cdot \varphi_{N_2O} \cdot [N_2O]^2} \cdot [NO_x]\,. \qquad \text{(eq. 2)}$$

Table 1 *Absorption cross section, photochemical yield, and reaction rates used to calculate the It-product for the conversion of N_2O to NO_x.*

reaction and parameter	value or expression
R1, σ_{N2O} (cm^2)	1.43×10^{-19}
R1, Φ_{N2O} (cm^2)	1
R2, k_2 ($cm^3\ mol^{-1}\ s^{-1}$)	$2.0 \times 10^{-11}\ \exp(130/T(K))$
R3, k_3 ($cm^3\ mol^{-1}\ s^{-1}$)	7.6×10^{-11}
R4, k_4 ($cm^3\ mol^{-1}\ s^{-1}$)	4.3×10^{-11}
R5, k_5 ($cm^3\ mol^{-1}\ s^{-1}$)	6.0×10^{-12}

As detailed in Appendix A of Kürten et al. (2012), the absorption of UV light along its path through the quartz tube is non-negligible even at the low N_2O/N_2 mixing ratios used in the actinometry experiment. Therefore, a geometry-dependent correction factor should be calculated. According to the authors, the geometry factor K, which varies depending on the N_2O concentration and tube dimensions, should be computed as

$$K = \frac{2\int_{r=0}^{R}\int_{\varphi=0}^{\pi}\exp\left(-\sigma_{N_2O}\cdot[N_2O]\cdot\left(\sqrt{R^2-(r\cdot\sin\varphi)^2}+r\cdot\cos\varphi\right)\right)\cdot r\cdot d\varphi\cdot dr}{\pi\cdot R^2}\,, \qquad \text{(eq. 3)}$$

where $R\ (cm)$ is the radius of the quartz tube and $\left(\sqrt{R^2-(r\cdot\sin\varphi)^2}+r\cdot\cos\varphi\right)$ is the absorption path length. The first term represents the distance the light travels from the point of entry to the point at radius r, while the econd term accounts for the additional length due to the radial position.

The geometry factor K should be taken into account when calculating It_{N_2O}:

$$It_{N_2O\_corrected} = \frac{k_2\cdot[N_2]+(k_3+k_4+k_5)\cdot[N_2O]}{2k_3\cdot\sigma_{N_2O}\cdot\varphi_{N_2O}\cdot[N_2O]^2}\cdot\frac{[NO_x]}{K}\,. \qquad \text{(eq. 4)}$$

Finally, Kürten et al. (2012) demonstrated that it is possible to use different flow rates during the actinometry and the calibration experiments ($Q_{total,\,N_2O}$ and Q_{CIMS}, respectively) and then scale the derived It-product with the flow rate ratio, according to eq 5:

$$It = \frac{Q_{total,\,N_2O}}{Q_{CIMS}}\cdot It_{N_2O\_corrected}\,. \qquad \text{(eq. 5)}$$

2. Experimental Setup

Figure 1 shows the setup used for the N_2O actinometry experiment, which consists of two mass flow controllers (Alicat Scientific, MC Series) to regulate the flows of N_2O and N_2 introduced into the system, the Hg-lamp box used in the sulphuric acid calibration experiment, and a NO_x monitor (Teledyne Monitor Labs, Model T200 $NO/NO_2/NO_x$). Similarly to the calibration setup, N_2 is also required to flush the Hg-lamp box. An exhaust line is placed downstream of the Hg-lamp box. The tubing primarily consists of 1/4"-diameter Teflon tubes, except for a 3/4"-diameter stainless steel tube that passes through the box. All T-pieces and connections are Swagelok fittings.

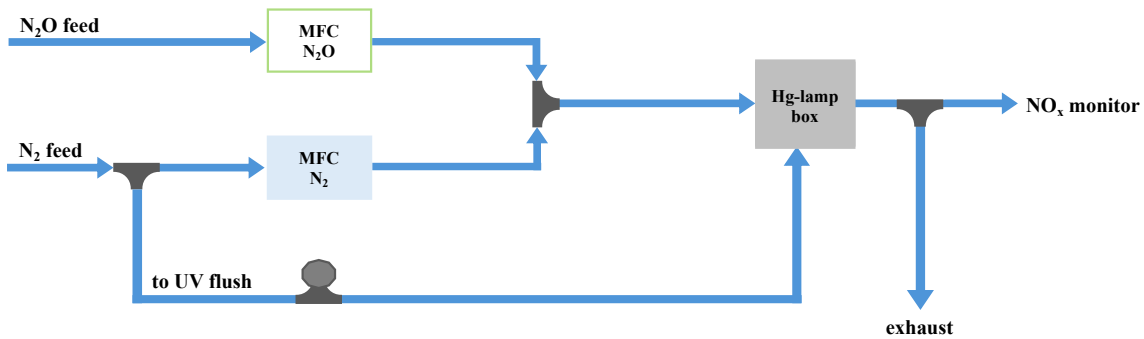

Figure 1 *Setup used for the N_2O actinometry experiment.*

3. General Guidelines

1. The NO_x monitor used for the experiment must be powered up at least two days in advance to ensure stability before the actinometry experiment begins. During this time, let it sample room air (if the setup is already connected, it will sample from the exhaust line).
2. Perform the experiment
    - Connect the setup to the NO_x monitor.
    - Open the program rslog.exe to start recording NO and NO_2 measurements.
    - Set the N_2 flush to the same flow rate as during the calibration experiment (1.5 lpm).
    - Turn on the Hg-lamp and let it to warm up for the same time as during the calibration experiment (~1.5 hours for calibrators 1, 3, and 4; ~2 hours for calibrator 2).
    - Once the Hg-lamp is fully warmed up, start the experiment by setting the desired N_2O and N_2 flow rates on the mass flow controllers. This can be done manually or by running the dedicated Python script (folder 'H2SO4_calibration_Alicat'). A minimum of 10 steps of 10 min each is recommended.
    - Optional (recommended): repeat the experiment with Hg-lamp off
3. Calculate the It-product
    - **A)** Using the Experiment_sheets.xlsx file and It_factor_correction.ipynb
        - **a.** Duplicate the most recent sheet and adapt the following sections (in green in the template):
            - General info (date, operator, and email).
            - Start and end time of each step of the actinometry experiment.
            - Average temperature of the N_2O and N_2 flows, as displayed on the mass flow controllers.
            - Desired N_2O/N_2 mixing ratio. The required flow rates (to set on the mass flow controllers) will be calculated automatically for a total flow of 7.5 lpm.
            - NO_x readings.

            The spreadsheet will automatically compute the non-corrected It-product values (before geometric correction).
        - **b.** Calculate the correction factor K for each step using the Python script It_factor_correction.ipynb.
        - **c.** Enter the K values into the designated section of the spreadsheet. The corrected It-product for each step will then be available for the total flow used during the actinometry experiment.
        - **d.** If needed, adapt the It-product for the flow used in the sulfuric acid calibration experiment using eq. 5 or the "Adapt_It" sheet.
    - **B)** Using the Python script It_factor.ipynb or the Matlab script It_factor.m

      In this approach, you need to manually adapt the following parameters
        - N_2O_flow: flow rate of N_2O (sccm)
        - N_2_flow: flow rate of N_2 (sccm)
        - NOx_ppb: NO_x concentration detected by the NO_x monitor (ppb)
        - T: average of N_2O flow and N_2 flow temperatures (°C)
        - QtotNOx: inlet flow rate used in the actinometry experiment (lpm)
        - Qinstrument: inlet flow rate used in the sulfuric acid calibration experiment (lpm)

- R: inner radius of quartz tube (cm)
- monitor_bg: background NO_x concentration (ppb) detected by the NO_x monitor when N_2O flow = 0 and Hg-lamp is on
- bottle_bg: NO_x concentration (ppb) detected by the NO_x monitor repeating the experiment with Hg-lamp off

The script will automatically compute the It-product corrected for the sulfuric acid calibration experiment.

C) Using the Matlab script It_product_calc_template.m
In this approach, you need to manually adapt the following parameters

- Temp: flow temperature (°C)
- N_2O_flow: flow rate of N_2O (sccm)
- N_2_flow: flow rate of N_2 (sccm)
- NOx_ppb: NO_x concentration detected by the NO_x monitor (ppb)
- NOx_bg: background NOx level (ppb)
- pres: pressure (Pa)
- R: inner radius of quartz tube (cm)
- NOx_moni_detec_limit: detection limit of the NOx monitor (ppb)
- flow_inlet_Cl_inlet: inlet flow rate used in the sulfuric acid calibration experiment (lpm)

The script will automatically compute the It-product corrected for the sulfuric acid calibration experiment.

4. Notes: Computation of the geometric correction factor (K)

The values of K computed using any of the four scripts are generally equivalent, with only negligible differences. These minor discrepancies result from the use of different coordinate systems.

It_factor_correction.ipynb and It_factor.m use cylindrical (polar) coordinates (r and φ), where the optical path length, $L(r,\varphi)$ is expressed as:

$$L(r,\varphi) = \sqrt{R^2 - (r \cdot \sin\varphi)^2} + r \cdot \cos\varphi \ . \qquad \text{(eq. 6)}$$

The integral used to calculate K follows the same formulation as eq. 3.

It_factor.ipynb and It_product_calc_template.m, on the other hand, use cartesian coordinates (x and y), where the optical path length, $L(x,y)$ is written as:

$$L(x,y) = \sqrt{R^2 - y^2} + x \ . \qquad \text{(eq. 7)}$$

This leads to an alternative integral formulation:

$$K = \frac{2\int_{-R}^{R}\int_{-\sqrt{R^2-x^2}}^{\sqrt{R^2-x^2}} \exp\left(-\sigma_{N_2O}\cdot[N_2O]\cdot\left(\sqrt{R^2-y^2}+x\right)\right)\cdot dy\cdot dx}{\pi\cdot R^2} \ . \qquad \text{(eq. 8)}$$

[1] Kürten *et al.* (2012), https://doi.org/10.1021/jp212123n