

## N<sub>2</sub>O Actinometry Experiment

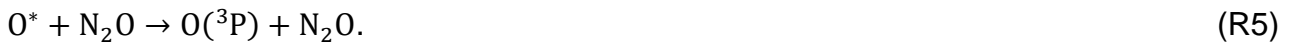
### 1. Theoretical Background

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

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

where  $I$  represents the photon intensity,  $t$  is the illuminating time,  $\sigma_{H_2O}$  and  $\Phi_{H_2O}$  are, respectively, the absorption cross section of H<sub>2</sub>O vapor at 184.9 nm and the quantum yield of H<sub>2</sub>O 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<sub>2</sub>O) to nitrogen oxides (NO<sub>x</sub>):



The relationship between the  $It$ -product and the concentrations of NO<sub>x</sub>, N<sub>2</sub>O, and N<sub>2</sub> is given by eq. 2:

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

**Table 1** Absorption cross section, photochemical yield, and reaction rates used to calculate the  $It$ -product for the conversion of N<sub>2</sub>O to NO<sub>x</sub>.

reaction and parameter	value or expression
R1, $\sigma_{N_2O}$ (cm <sup>2</sup> )	1.43 x 10 <sup>-19</sup>
R1, $\Phi_{N_2O}$ (cm <sup>2</sup> )	1
R2, $k_2$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	2.0 x 10 <sup>-11</sup> exp(130/T(K))
R3, $k_3$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	7.6 x 10 <sup>-11</sup>
R4, $k_4$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	4.3 x 10 <sup>-11</sup>
R5, $k_5$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	6.0 x 10 <sup>-12</sup>

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

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

where  $R$  (cm) is the radius of the quartz tube and  $(\sqrt{R^2 - (r \cdot \sin \varphi)^2} + r \cdot \cos \varphi)$  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 second term accounts for the additional length due to the radial position.

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

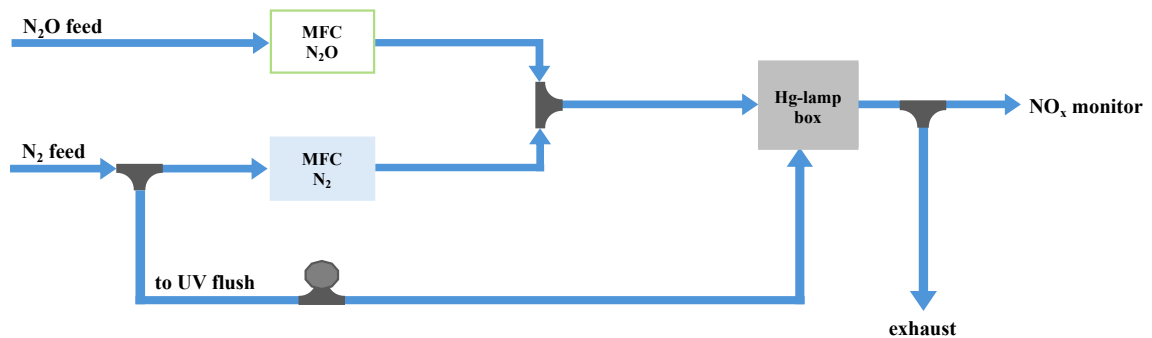
$$It_{N_2O\_corrected} = \frac{k_2 \cdot [N_2] + (k_3 + k_4 + k_5) \cdot [N_2O]}{2k_3 \cdot \sigma_{N_2O} \cdot \varphi_{N_2O} \cdot [N_2O]^2} \cdot \frac{[NO_x]}{K}. \quad (\text{eq. 4})$$

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:

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

## 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<sub>x</sub> 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<sub>x</sub> monitor.
  - Open the program rslog.exe to start recording NO and NO<sub>2</sub> measurements.
  - Set the N<sub>2</sub> 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<sub>2</sub>O and N<sub>2</sub> 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.
3. Calculate the It-product
  - A) Using the Experiment\_sheets.xlsx file and It\_factor\_correction.ipynb
    - a. Create a new sheet in the Excel file (copy the most recent sheet and modify it).
    - b. Update the following sections (in green in the template, **figure 2**):
      - General info (date, operator, and email).
      - N<sub>2</sub>O/N<sub>2</sub> 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.
      - Temperature (average temperature of the N<sub>2</sub>O and N<sub>2</sub> flows, as displayed on the mass flow controllers).
      - Step start and end times.
      - NO<sub>x</sub> readings. The spreadsheet will automatically compute the initial It-product values (before geometric correction).
    - c. Calculate the correction factor K for each step using the Python script It\_factor\_correction.ipynb.
    - d. Enter the K values into the designated section of the spreadsheet. The corrected It-product for each step (and its average) will then be available for the total flow used during the actinometry experiment.
    - e. 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 Code by Xu-Cheng He (It\_factor\_XCH.ipynb)

In this approach, you need to manually adapt the following parameters

    - N<sub>2</sub>\_flow: flow rate of N<sub>2</sub> (sccm)
    - N<sub>2</sub>O\_flow: flow rate of N<sub>2</sub>O (sccm)
    - NO\_conc: NO<sub>x</sub> concentration detected by the NO<sub>x</sub> monitor (ppb)
    - T: flow temperature (°C), averaged from mass flow controllers
    - flow\_inlet: inlet flow rate used in the sulfuric acid calibration experiment (sccm)

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

**C) Using the Matlab script It\_factor.m**

In this approach, you need to manually adapt the following parameters

- T: flow temperature (°C), averaged from mass flow controllers
- N<sub>2</sub>O\_flow: flow rate of N<sub>2</sub>O (sccm)
- N<sub>2</sub>\_flow: flow rate of N<sub>2</sub> (sccm)
- NO<sub>x</sub>\_ppb: NO<sub>x</sub> concentration detected by the NO<sub>x</sub> monitor (ppb)
- QtotNO<sub>x</sub>: inlet flow rate used in the sulfuric acid calibration experiment (lpm)
- Qinstrument: 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.

**A B C D E F G H I J K L M N O P Q R S T**

**Info:**  
Date: 1/1/2025  
Calibrator: #  
Operator: Name Surname  
Email address: name.surname@helsinki.fi

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**It-product calculation:**

parameter	value or expression
R1, $\Phi_{\text{exp}}$ ( $\text{cm}^2$ )	1.43E-19
R1, $\Phi_{\text{exp}}$ ( $\text{cm}^2$ )	1.00E+00
R2, $k_1$ ( $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$ )	3.09E-11
R3, $k_1$ ( $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$ )	7.60E-11
R4, $k_1$ ( $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$ )	4.30E-11
R5, $k_1$ ( $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$ )	6.00E-12
T (K)	298.15

**Actinometry experiment:**

step	time (UTC+2)	volume mixing ratio $\text{N}_2/\text{O}_2$	standard $\text{N}_2$ flow (sccm)	standard $\text{N}_2$ flow (sccm)	[ $\text{N}_2\text{O}$ ] (ppbv)	[ $\text{N}_2$ ] (ppbv)	[ $\text{NO}_x$ ] (ppbv)	It-product (photons $\text{cm}^{-2}$ )	corrected It-product (photons $\text{cm}^{-2}$ )
1	10:02-10:12	0.12	804	6696	1.07E+08	8.93E+08	4.325	7.11E+11	9.00E+11
2	10:12-10:22	0.16	1034	6486	1.38E+08	8.62E+08	5.650	6.00E+11	8.11E+11
3	10:22-10:32	0.20	1250	6250	1.67E+08	8.33E+08	6.749	5.21E+11	7.44E+11
4	10:32-10:42	0.24	1452	6048	1.94E+08	8.05E+08	7.642	4.61E+11	6.99E+11
5	10:42-10:52	0.28	1641	5859	2.19E+08	7.81E+08	8.609	4.26E+11	6.77E+11
6	10:52-11:02	0.32	1818	5682	2.42E+08	7.58E+08	9.410	3.96E+11	6.60E+11
7	11:02-11:12	0.36	1985	5515	2.65E+08	7.35E+08	10.060	3.69E+11	6.36E+11
8	11:12-11:22	0.40	2143	5357	2.86E+08	7.14E+08	10.657	3.47E+11	6.20E+11
9	11:22-11:32	0.44	2292	5208	3.06E+08	6.94E+08	11.241	3.31E+11	6.12E+11
10	11:32-11:42	0.48	2432	5068	3.24E+08	6.76E+08	11.581	3.11E+11	5.99E+11

Mean It-product (@ 7.5 lpm)	non-corrected	corrected
	4.47E+11	6.96E+11

**UV-light attenuation correction:**

step	volume mixing ratio $\text{N}_2/\text{O}_2$	geometry correction factor K
1	0.12	0.79
2	0.16	0.74
3	0.20	0.70
4	0.24	0.66
5	0.28	0.63
6	0.32	0.60
7	0.36	0.58
8	0.40	0.56
9	0.44	0.54
10	0.48	0.52

**Figure 2** Example of the Excel sheet for actinometry calculations.

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

The values of  $K$  computed using `It_factor_correction.ipynb`, `It_factor_XCH.ipynb` or `It_factor.m` are generally equivalent, with only negligible differences. These minor discrepancies result from the use of different coordinate systems in the three scripts.

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

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

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

`It_factor_XCH.ipynb`, on the other hand, uses cartesian coordinates ( $x$  and  $y$ ), where the optical path length,  $L(x, y)$  is written as:

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

This leads to an alternative integral formulation:

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

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<sup>1</sup> Kürten *et al.* (2012), <https://doi.org/10.1021/jp212123n>