1 Methods

We use a sequential workflow outlined in figure 1.1. It consists of the following steps:

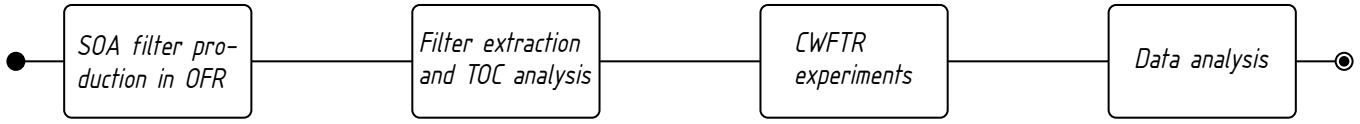


FIGURE 1.1: Overview over Workflow. The initial step consists of producing a filter containing volatile organic compound (VOC) in the oxidation flow reactor (OFR), which is subsequently extracted to produce a solution.

1. **Secondary organic aerosol (SOA) filter production in OFR**: Within the OFR, we produce SOA through the reaction of a VOC with ozone (O_3). The resulting SOA is collected on a filter. The detailed procedure is outlined in section 1.1.
2. **Filter extraction and total organic carbon (TOC) analysis**. The filters produced in the previous step are extracted into aqueous solution and TOC is measured as a proxy for sample content of organics. This is outlined in detail in section 1.2.
3. **CWFTR experiments**. In this step, the solutions from the extracted filters are mixed with iron and iodide (I^-). Using such solutions, flow tubes are coated and the products of the reaction of their film with ozone are measured in a BTOF CIMS (BTOF-CIMS). The exact methodology is described in section 1.3
4. **Data Analysis**. In this step, the data from the BTOF-CIMS are analysed using *IGOR Pro* and *Python*. Details are available in section 1.4.

1.1 SOA filter production in OFR

An overview over the setup for filter production is displayed in figure 1.2. Molecular oxygen (O_2) and molecular nitrogen (N_2) from the in-house gas connection at Paul-Scherrer Institute (PSI) are first mixed at controlled ratios and guided inton the flow tube of the OFR. Usually, $\overset{*}{V}_{N_2} = 3.95\,\mathrm{L\,min^{-1}}$ and $\overset{*}{V}^{(3)}_{O_2} = 1.05\,\mathrm{L\,min^{-1}}$ was set, giving a relative fraction of $N_2 : O_2 \approx 0.79 : 0.21$, which is close to atmospheric comoposition. This was achieved through the mass flow controllers (MFCs) 2 (for molecular nitrogen) and 3 (for molecular oxygen), respectively (see also figure 1.2). MFC 1 was used to control the flow of molecular nitrogen through a glass bottle containing VOC, with a value set at $\overset{*}{V}_{VOC} = 0.04\,\mathrm{L\,min^{-1}}$. In order to inhibit diffusion of VOC into the OFR, a plug valve (PV1) was installed on the VOC input line just before the OFR. Finally, MFC 4 was used to control the flow of molecular oxygen into the ozone generator, where molecular oxygen reacted with UV light to produce ozone, as in reaction below:

$$O_2 + h\nu \longrightarrow 2\,O(^1D)^{\bullet} \qquad \text{[R1.1.1]}$$

For this, MFC 4 was set to provide a flow of $\overset{*}{V}^{(4)}_{O_2} = 3\,\mathrm{L\,min^{-1}}$ to the ozone generator. Without any additional measures, this molecular oxygen flow is efficiently converted into ozone by the generator, such that concentrations in excess $\chi_{O_3} \approx 100\,\mathrm{ppm}$ are reached within the OFR. In order to decrease ozone levels within the OFR, a pump was installed that pumped a flow of $\overset{*}{V}_P \approx 2.2\,\mathrm{L\,min^{-1}}$ of generated ozone into exhaust 2, such that steady-state concentrations of ozone within the OFR were not usually in excess of $\approx 70\,\mathrm{ppm}$. The flow rate of the pump was adjusted using a needle valve (NV1). This was done once before the start of experiments, and the valve setting was not changed throughout experiments. Within the OFR, thus, the flows of VOC (on its N_2 carrier gas), "air" (with $N_2 : O_2 = 0.79 : 0.21$) and ozone (at $\overset{*}{V}_{O_3} \approx 0.8\,\mathrm{L\,min^{-1}}$) converge. Here, VOC is oxidised by ozone into oxygenated volatile organic compounds (OVOCs) and low-volatility organic compounds (LVOCs). These LVOCs condense into SOA.
Two lines exit the OFR: One that takes an air sample from within the middle of the flow tube, where the flow is nearly laminar, and another one consisting of four different outlets at the flow tubes' rear end that converge into a single outlet line. The latter line is connected to a filter holder through which a flow of product gases $\overset{*}{V}_F \approx 4.5\,\mathrm{L\,min^{-1}}$ is guided into exhaust 1 — it is here that SOA is collected: within the filter holder, a Nylon filter with pore size $0.45\,\mu\mathrm{m}$ is installed, on which SOA is collected. The other line is guided into the scanning mobility particle sizer (SMPS) and the ozone analyser.

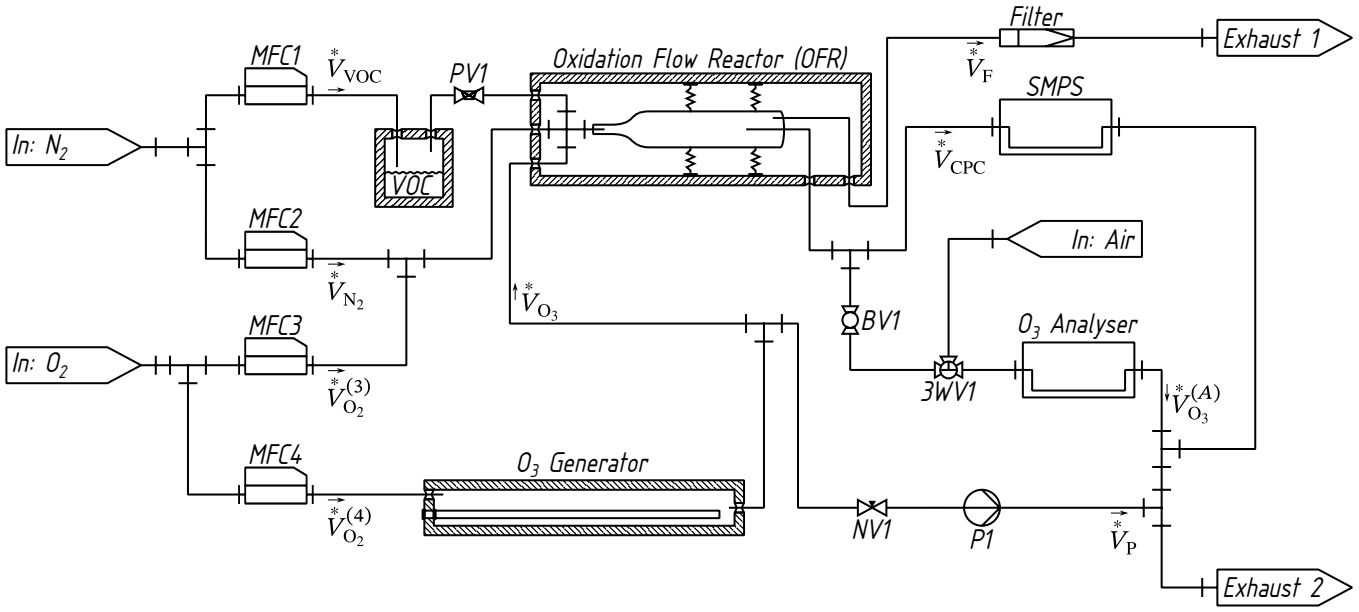


FIGURE 1.2: Overview over OFR Flowchart. Flow Chart displaying the functionality of the OFR Setup, including various flows, instruments, diverse valves and other things.

Downstream of those instruments, the flow through the former line is converging again, and sucked into exhaust 2 along with excess ozone from the pump. The SMPS allows for an online measurement of particle size, and is described in detail in section 1.1.3. Using a ball valve (BV1), the line can be opened or closed towards the ozone analyser: if BV1 is closing the OFR outlet flow towards the analyser, a three-way-valve (3WV1) allows for the ozone analyser to sample ambient air. In normal operation, BV1 is open and 3WV1 closes off the system towards the ambient. In this configuration, a flow of $\dot{V}^*_{CPC} \approx 0.3\,\mathrm{L\,min^{-1}}$ is guided into the SMPS and a flow of $\dot{V}^{*(A)}_{O_3} \approx 1\,\mathrm{L\,min^{-1}}$ flows through the ozone analyser.

1.1.1 Procedure

A detailed methodological procedure is available in appendix **??**. Throughout the experiments, SMPS data was collected within $\approx$ 60 (this number varied across experiments) samples, each of which constitutes of aggragating data for 180 s. Briefly, the following steps need to be undertaken:

1. All lines are checked and it is ensured that SMPS and ozone analyser are ready for data logging;
2. The ozone analyser and condensation particle counter (CPC) are switched on so that they can warm up.
3. Flows are set at $\dot{V}^*_{N_2} = 3.95\,\mathrm{L\,min^{-1}}$, $\dot{V}^{*(3)}_{O_2} = 1.05\,\mathrm{L\,min^{-1}}$ and $\dot{V}^{*(4)}_{O_2} = 1.05\,\mathrm{L\,min^{-1}}$. The ozone excess pump is switched on.
4. Ozone data logging is started, filter holder is loaded with filter and attached to the system.
5. Start logging SMPS data and turn on ozone generator. Let the system equilibrate for 45 min (for 15 samples)
6. Just before ($\approx$ 10 s) 15 samples have been recorded, open the VOC valve (PV1). At the onset of the next sample, set $\dot{V}^*_{VOC} = 0.04\,\mathrm{L\,min^{-1}}$. Let the system run for 1 h (for 20 samples).
7. When 1 h has passed, and at the onset of the sample subsequent to the ones recorded in the last step, reset $\dot{V}^*_{VOC} = 0\,\mathrm{L\,min^{-1}}$. Within $\approx$ 10 s, close the VOC valve (PV1). Let the system equilibrate for 30 min.

1.1.2 Oxidation Flow Reactor

1.1.3 Scanning Mobility Particle Sizer

The aerosol concentration is measured using a SMPS, which in turn consists of a neutraliser, a differential mobility analyser (DMA) and a CPC, arranged in series. The DMA is ramping a time-dependent voltage profile $U(t)$ between its two electrodes. This creates a time-varying electric field of the strength $E \approx U/(d_o - d_i)$ which in turn causes particles within the DMA to experience a drift in this field of velocity $v = Z_p E$, where Z_p denotes the electrical mobility.

$$m_{\mathrm{F}} = \int_{t_{\mathrm{in}}}^{t_{\mathrm{out}}} \overset{*}{m}\,\mathrm{d}t \approx \sum_{\mathrm{Samples}} \overset{*}{m}_i \Delta t_i \tag{1.1}$$

1.1.4 Ozone analyser and other instrumentation

TABLE 1.1: Overview over filters and flows

Date	$\overset{*}{V}_{\mathrm{VOC}}$	$\overset{*}{V}_{\mathrm{N_2}}$	$\overset{*}{V}^{(3)}_{\mathrm{O_2}}$	$\overset{*}{V}^{(4)}_{\mathrm{O_2}}$	$\overset{*}{V}_{\mathrm{P}}$	$\overset{*}{V}_{\mathrm{O_3}}$	$\overset{*}{V}_{\mathrm{F}}$	$\overset{*}{V}_{\mathrm{CPC}}$	$\overset{*}{V}^{(A)}_{\mathrm{O_3}}$
	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$	$\mathrm{m^3\,s^{-1}}$
a	a	a	a	a	a	a	a	a	a

1.2 Filter extraction and TOC-analysis

In order to quantify the exact (organic) carbon content used in coated wall flow tube reactor (CWFTR) samples, the organic carbon content on filters needs to be known. While an estimate is provided via the SMPS measurements, the exact quantity of organic carbon on the filters is determined using TOC analysis. For this, non-purgeable organic carbon (NPOC) and TOC of filter samples are measured. While the pertaining instrument, Shimazdu TOC Analyser 200, directly provides measurements of NPOC, the value of TOC has to be computed via measurements of total carbon (TC) and inorganic carbon (IC), respectively:

$$\mathrm{TOC} \coloneqq \mathrm{TC} - \mathrm{IC} \tag{1.2}$$

The values of TOC and NPOC are measured in $\mathrm{mgC\,L^{-1}}$.

1.2.1 Preparation

Preparation for TOC measurements essentially consists in cleaning glassware required for analysis and extraction. This is rather not straightforward, and two procedures need to be distinguished: a special procedure before the campaign to obtain a standard of cleanliness, and a procedure during the campaign to retain the obtained standard.

Intial Glassware Cleaning

During initial cleaning, NPOC of glassware is tested. Glassware is considered clean if $\mathrm{NPOC} < 0.1\,\mathrm{mg\,L^{-1}}$.

Subsequent Glassware cleaning

1.2.2 Extraction

1.2.3 Calibration

Calibration for TOC and NPOC measurements require that the instrument be calibrated prior to measurements. For this, stock solutions of known quantites are related to the instrument response, i.e. area under the voltage curve. For TOC measurements, two stock solutions are required, one containing a known quantity of TC, and one where the exact amount of IC is known. In practice, TC calibration can be performed using a TOC stock solution. This is possible because the used standard of TOC is practically free of any IC — for the used TOC standard, it therefore holds that $\mathrm{TC} \approx \mathrm{TOC}$.
A TOC solution of $1000\,\mathrm{mgC\,L^{-1}}$ is used to create a TOC calibrant stock solution of $4\,\mathrm{mgC\,L^{-1}}$. For this, exactly 1 mL of $1000\,\mathrm{mgC\,L^{-1}}$ solution is mixed with 244 mL MQ. Similarly, an IC stock solution of $1000\,\mathrm{mg\,L^{-1}}$ is used to mix an IC calibrant stock of $4\,\mathrm{mgC\,L^{-1}}$ by mixing 1 mL of stock solution with 244 mL MQ.

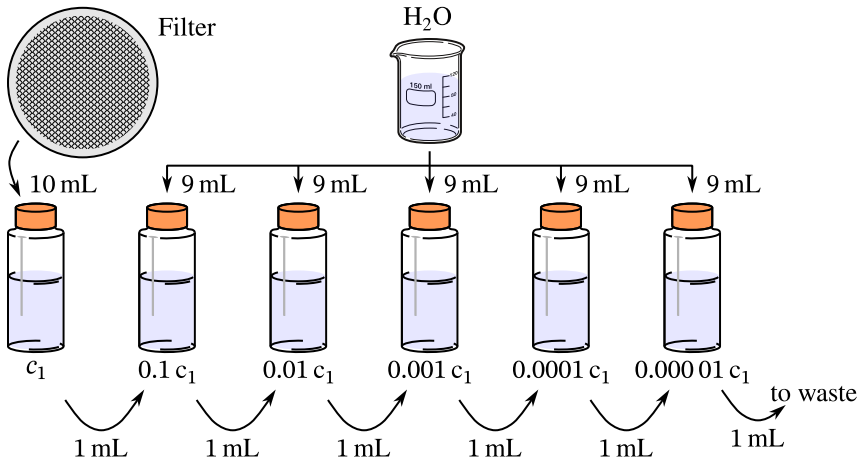


FIGURE 1.3: Procedure to create solutions. Beaker apapted from: Diogo Losch De Oliveira (2026). Beakers [Illustration]. CC-BY 4.0. SciDraw.io. https://scidraw.io/drawing/beakers-ba8583ed, accessed 10. August 16:16

1.2.4 Measurements

1.3 CWFTR experiments

1.3.1 Preparation

1.3.2 Coating solution Preparation

1.3.3 Procedure

1.4 Data analysis