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Characterization of the Catalytic Stripper for Aerosol Volatility
Measurements at the Aerosol Observatory in Vienna

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Abstract

Atmospheric aerosols are key participants in atmospheric processes, with significant consequences for climate and human health (Hinds, 2022). Characterising their behaviour is thus central to the understanding of the atmosphere. Among others, one of their defining characteristics is volatility. Volatility describes how readily certain components of atmospheric aerosols evaporate into the gas phase or, conversely, condense from the gas phase onto particles (Brooks et al., 2007). This partitioning is a key part of secondary aerosol formation, and because it shifts the size and mass distributions of the aerosol population, it also influences cloud formation and, in turn, the radiative effect of aerosols (Gao et al., 2024).

This thesis presents the characterization of a custom-modified device called the Catalytic Stripper (CS, CCS004, Catalytic Instruments GmbH & Co. KG), along with preliminary results of the device’s deployment at an urban station for aerosol in situ measurements, the Aerosol Observatory of the University of Vienna. These preliminary measurements focus on the quantification of volatile and non-volatile aerosol number fractions.

CS is designed to evaporate the semi-volatile fraction of an aerosol sample through thermal fractionation and to chemically remove these compounds from the sample via oxidation using a catalyst. Thus far, CSs have mainly been used in emission studies within the automotive industry (Giechaskiel et al., 2020). However, the literature has shown promising results suggesting that such a device might also be suitable for atmospheric aerosol sampling.

Although volatility is a complex aerosol property, several studies have defined volatility based on an operational definition tied to the chosen temperature of the device (such as a thermodenuder) rather than an absolute material property. For example, a species counts as non-volatile only insofar as it does not evaporate at that set device temperature. Sulfate, nitrate, ammonium and several organic compounds are commonly considered volatile, whereas sea salt, crustal material, carbonaceous compounds and other species can be classified as non-volatile (i.e. refractory) (Wehner et al., 2002). Subsequently, depending on the detector used downstream of the CS (and a reference detector if available) one could learn about the number fraction or size distribution of the volatile and/or non-volatile aerosol measured.

In this study two condensation particle counters (CPC, GRIMM 5410, cut off size of 10 nm in diameter) are first compared and used to characterize the particle losses in the CS operating at 350 °C. This is done using a sample aerosol of monodisperse silver particles (with diameters between 10 and 100 nm). The relative difference between the CPCs appears to be constant and within a few percent of each other, showing good comparability in this size range. Below 20 nm, the difference increases and ranges between 3 and 10 %.

Further, the CS is characterized to determine the particle losses due to diffusional deposition and thermophoresis. For this, the CS is included in one of two parallel sampling lines, each connected to a CPC. Characterization showed that particle losses through the CS were dominated by diffusion at small sizes and by thermophoresis across the size range, with the transmission efficiency ranging from 33 % at 10 nm to 83 % at 100 nm.

The device is then deployed at the Aerosol Observatory for a period of two weeks (April 20 – May 3, 2026) to gather the first in situ atmospheric data of urban air, using the same two-CPC setup at a PM_{2.5} sampling inlet. The CS is installed upstream of one of the CPCs to measure non-volatile number concentration of particles, while the other CPC provides the total number of particles. Comparing the data from the two CPCs yields the non-volatile number fraction - the fraction of particles that remain in the condensed phase below the operating temperature of the device (350 °C) - while the complementary volatile fraction corresponds to those particles that evaporate below this temperature. Over the two-week deployment period, the non-volatile number fraction of the urban aerosol ranged from 7 % to 77 %, indicating the presence of aerosol with various compositions.

These results suggest that CS is a promising alternative to commonly used devices (e.g. thermodenuders) for atmospheric volatility measurements. Further testing of the device and analysis of the data are proposed as next steps.

Zusammenfassung

Atmosphärische Aerosole sind zentrale Akteure in atmosphärischen Prozessen und haben erhebliche Auswirkungen auf das Klima und die menschliche Gesundheit (Hinds, 2022). Die Charakterisierung ihres Verhaltens ist daher von grundlegender Bedeutung für ein Verständnis der Atmosphäre. Eine wichtige Eigenschaft ist unter anderem die Volatilität (Flüchtigkeit) eines Aerosols. Volatilität beschreibt, wie leicht bestimmte Bestandteile atmosphärischer Aerosole in die Gasphase verdampfen oder umgekehrt aus der Gasphase re-kondensieren (Brooks et al., 2007). Der Übergang zwischen Gas- und Flüssigphase spielt eine wesentliche Rolle bei der Bildung sekundärer Aerosole. Die daraus resultierende Veränderung der Massen- und Größenverteilung beeinflusst die Wolkenbildung und den Strahlungseffekt der Aerosole (Gao et al., 2024).

Diese Arbeit präsentiert die Charakterisierung eines individuell konfigurierten Geräts, des Catalytic Stripper (CS, CCS004, Catalytic Instruments GmbH & Co. KG), sowie erste Ergebnisse des Einsatzes des Geräts an einer urbanen Messstation für in situ Aerosolmessungen, dem Aerosol-Observatorium der Universität Wien. Diese vorläufigen Messungen konzentrieren sich auf die Quantifizierung der Anteile flüchtiger und nichtflüchtiger Aerosole.

Der CS ist darauf ausgelegt, den semivolatilen Anteil einer Aerosolprobe durch thermische Fraktionierung zu verdampfen und die freigesetzten Komponenten anschließend durch Oxidation an einem Katalysator chemisch aus der Probe zu entfernen. Bislang wurden CS hauptsächlich in Emissionsstudien innerhalb der Automobilindustrie eingesetzt (Giechaskiel et al., 2020). Die Literatur hat jedoch vielversprechende Ergebnisse gezeigt, die darauf hindeuten, dass ein solches Gerät auch für das Sampling atmosphärischer Aerosole geeignet sein könnte.

Da die Flüchtigkeit eines Aerosols von verschiedenen Faktoren abhängt, wird sie in vielen Studien nicht als absolute Materialeigenschaft, sondern anhand der jeweiligen Messbedingungen definiert. Entscheidend ist dabei insbesondere die eingestellte Temperatur des verwendeten Geräts, beispielsweise eines Thermodenuders. Eine Substanz wird demnach als nichtflüchtig eingestuft, wenn sie bei dieser Temperatur nicht verdampft. Sulfat, Nitrat, Ammonium und verschiedene organische Verbindungen gelten üblicherweise als flüchtig, während Meersalz, mineralische Bestandteile und organische Verbindungen als nichtflüchtig beziehungsweise refraktär eingestuft werden können (Wehner et al., 2002). Mithilfe eines Detektors hinter dem CS (und gegebenenfalls eines zusätzlichen Referenzdetektors) können anschließend der Anteil sowie die Größenverteilung der flüchtigen und nichtflüchtigen Aerosolbestandteile bestimmt werden.

In dieser Studie werden zunächst zwei Kondensationspartikelzähler (CPC, GRIMM 5410, unterer Cutoff von 10 nm Durchmesser) verglichen und verwendet, um die Partikelverluste im (bei 350 °C betriebenen) CS zu charakterisieren. Das wird anhand von Proben aus monodispersen Silberpartikeln (mit Durchmessern zwischen 10 und 100 nm) gemacht. Der relative Unterschied zwischen den CPCs erweist sich als weitgehend konstant und liegt innerhalb weniger Prozent. Dies zeigt eine gute Vergleichbarkeit der CPCs in diesem Größenbereich. Unterhalb von 20 nm nimmt der Unterschied zu und liegt zwischen 3 und 10 %.

Weiterhin wird der CS charakterisiert, um die Partikelverluste durch Diffusion und Thermophorese zu bestimmen. Dazu wird der CS in eine von zwei parallelen Sampling-Lines eingebunden,

die jeweils mit einem CPC verbunden sind. Die Charakterisierung zeigt, dass die Partikelverluste durch den CS durch Diffusion bei kleinen Größen und Thermophorese über den gesamten Größenbereich beeinflusst wurden, wobei die gesamte Transmissionseffizienz von 33 % bei 10 nm bis 83 % bei 100 nm reicht.

Anschließend wird das Gerät für einen Zeitraum von zwei Wochen (20. April – 3. Mai 2026) am Aerosol-Observatorium eingesetzt, um mit demselben Messaufbau (zwei CPCs) erstmals in situ Daten urbanen Aerosols an einem PM_{2.5}-Inlet zu erfassen. Dabei ist der CS vor einem der beiden CPCs installiert, sodass dieser die Konzentration der nichtflüchtigen Partikel misst, während der zweite CPC die Gesamtpartikelkonzentration erfasst. Aus dem Vergleich beider Messungen lässt sich der nichtflüchtige Anteil bestimmen, also jener Anteil der Partikel, der bei der Betriebstemperatur des Geräts (350 °C) in der kondensierten Phase verbleibt. Der flüchtige Anteil entspricht dementsprechend den Partikeln, die bei dieser Temperatur verdampfen. Über den zweiwöchigen Messzeitraum lag der nichtflüchtige Anteil des urbanen Aerosols zwischen 7 % und 77 %. Diese Spannbreite deutet auf eine unterschiedliche Zusammensetzung des gemessenen Aerosols hin.

Diese Ergebnisse suggerieren, dass der CS eine vielversprechende Alternative zu häufig verwendeten Geräten (z. B. Thermodenudern) für atmosphärische Messungen von Volatilität darstellt. Weitere Tests des Geräts und weitere Analyse der Daten werden als nächste Schritte vorgeschlagen.

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1. Introduction

1.1. Atmospheric Aerosol and the Importance of Aerosol Volatility

Atmospheric aerosols play a central role in shaping both the Earth’s climate and the air we breathe, with far-reaching consequences for human health and quality of life. Through the scattering and absorption of solar radiation, they directly influence the Earth’s radiative balance, while their role in cloud formation gives rise to important indirect climate effects. At the same time, the inhalation of airborne particles illustrates how aerosols can directly impact respiratory health (Hinds, 2022).

By definition, an aerosol is a suspension of liquid or solid particles in a carrier gas - in the atmospheric case, air. These particles originate from both natural sources, such as sea spray and dust storms, and anthropogenic activities, including industrial emissions and vehicle exhaust. Variations in lifetime, heterogeneous composition, and continuous chemical transformation reflect the chemical and physical diversity of atmospheric aerosols, which in turn mirrors the breadth of their sources, evolution pathways, and impacts on the Earth system (Hinds, 2022).

Understanding this variability is essential for understanding the behavior and impacts aerosol particles have. Their impact depends not only on the particle number concentration and sizes but also on their chemical composition. An important compositional characteristic is volatility. The volatility of a particle refers to how readily material evaporates into the gas-phase when heated (Brooks et al., 2007). In low-volatility material more mass remains in the particle-phase, while in high-volatility material more mass is lost upon heating. In atmospheric chemistry, it is often used to describe whether aerosol components are effectively particle-bound, semi-volatile, or easily lost by evaporation. It depends on factors like temperature, chemical composition, and the substance’s saturation vapor pressure while existing in multiple mixing states. Volatile material might occur in a mixed state through condensation on surfaces of non-volatile material, whereas nucleation processes can also cause formation processes of separate volatile particles (Babar et al., 2020; Dickau et al., 2016). Unlike the non-volatile core of particles that remains stable even at elevated temperatures, the volatile fraction is highly responsive to atmospheric changes and plays a disproportionate role in aerosol growth, composition, and environmental impacts. Non-volatile particles, for instance, include soot directly from combustion, or mineral dust components, like Na, K, Ca; volatile particles on the other hand include organic compounds, like hydrocarbons and sulfur containing compounds or some inorganics, like ammonium salts (Engler et al., 2006; Swanson & Kittelson, 2010).

While chemical analysis of aerosol particles is usually complex and/or expensive, one can gain indirect information about the particle chemical characteristics and their potential sources, by measuring aerosol volatility (Engler et al., 2006). The volatile fraction of an aerosol can have impacts on air quality, human health as well as the climate impact of aerosols in ways that differ from the impacts of refractory, meaning non-volatile, components. Gao et al., 2024 shows that volatility for example governs the location of an aerosol, their lifetime and how they affect our climate. Semi-volatile components for instance, go through evaporation, oxidation and re-condensation processes that cause them to distribute further from their source and potentially

reach higher altitudes. Because of their altitude redistribution they are also removed differently from the atmosphere through wet and dry removal because they sit above the cloud layer - this is seen in a longer lifetime of the semi-volatile fraction. Going through constant evaporation and condensation processes also importantly shifts the size and mass distributions of an aerosol: partitioning, re-condensing, coating all moves an aerosol through different size and mixing schemes. In addition to the location and lifetime of an aerosol, cloud formation might also be affected by the change of cloud droplet number and properties since aerosol particles act as condensation nuclei for cloud formation. If cloud formation is influenced a subsequent result is a changed radiative effect and climate. As the pathway of volatile and semi-volatile parts of atmospheric aerosols remain a large uncertainty in microphysical processes and corresponding impacts the resolution of aerosol volatility in aerosol science is needed (Gao et al., 2024).

Some studies refer to volatile and non-volatile aerosol fraction as all particles that evaporate or remain stable in their condensed phase over the course of measurements conducted. For instance compounds such as sulfate, nitrate, ammonium and several organic compounds are expected to vaporize below 250 °C, so according to Wehner et al., 2002 they are considered volatile. Sea salt, crustal material, trace metals, fly ash, and carbonaceous compounds are only expected to be volatile above this temperature, so these would be considered non-volatile or refractory (Wehner et al., 2002). The threshold definition of volatile and refractory varies across literature, this work will consider particles that are thermostable at up to 350 °C to be refractory, the rest referred to as volatile. This temperature corresponds to the operating conditions of the device that is subject to this thesis.

Based on the above approach measurements of aerosol volatility typically rely on heating an aerosol sample to induce preferential evaporation of more volatile species. In standard devices like a thermodenuder (TD), a heated section is usually followed by a cooling section that contains adsorbing material to capture the evaporated components (Huffman et al., 2008). This way the volatile components are adsorbed and only non-volatile fraction reaches an aerosol detector. Whether the volatility removal will take place depends on residence time the particle spends in the heated section, particle size, its chemical composition and mass loading (Fierz et al., 2007). Thus there are many designs that vary in tubing length, diameter, flow rate etc. These devices are installed upstream of detectors such as Condensation Particle Counters (CPC) (e.g. Swanson and Kittelson, 2010), Optical Particle Counters (OPC) (e.g. Kupc et al., 2018), Scanning Mobility Particle Sizer (SMPS) (e.g. Fierz et al., 2007), or mass spectrometers such as an Aerosol Mass Spectrometer (AMS) (e.g. Huffman et al., 2008), that measure the number concentration of non-volatile particles, their size distribution, or chemical composition, respectively. The simultaneous measurement of for instance the total particle number concentration of an ambient aerosol and the non-volatile particle number concentration would provide its volatile number fraction (e.g. Kupc et al., 2018).

TD have been frequently used in atmospheric aerosol measurements (Huffman et al., 2008; Kupc et al., 2018; Weinzierl et al., 2009). It was installed upstream of one of the OPCs during the ATOM mission to measure volatile and non-volatile aerosol size distribution over the remote regions of the oceans to understand the shift in size distributions over oceanic regions (Kupc et al., 2018). During SAMUM (Weinzierl et al., 2009) it was used for similar measurements analyzing mineral dust in Saharan regions while being operated upstream of a CPC and OPC. Another example is described in Wehner et al., 2004, where number size distributions of traffic-emission dominated aerosol are measured in urban areas using a TD and SMPS. Based on these examples of TD application, the non-volatile fraction varied between 4 % and 6 % by number in the free troposphere and marine boundary layer (Kupc et al., 2018), 10 and 20 % by number for traffic-related particles near the highway (Wehner et al., 2004), and 70 and 78 % by volume for sub-2.5 µm particles over the Saharan source (Weinzierl et al., 2009).

An example of a potential issue with TD, as shown by Swanson and Kittelson, 2010 is the potential re-condensation of evaporated material. A TD is operated by a heating section that is followed by a cooling section before reaching any counting device. Material that is previously evaporated might re-condense when being cooled down and re-introduced as an individual particle before reaching the detecting device, which cannot be accounted for via number fraction alone (Swanson & Kittelson, 2010). An alternative device, a Catalytic Stripper (CS) could also be used to provide the non-volatile fraction of an aerosol load through thermal processing. However, compared to a thermodenuder, in a CS the volatile aerosol fraction undergoes catalytic transformation to carbon dioxide and water vapor, thus, preventing the potential recondensation of such back into particles. So far, however, CS was mainly used in automotive industry (Giechaskiel et al., 2020) and in the laboratory studies (Swanson & Kittelson, 2010), and thus requires detailed characterization before it could be used for ambient measurements.

This involves quantification of aerosol particle losses that might be introduced by the addition of the CS into a measurement setup. The inverse relationship can be applied to ambient measurements to correct for mass lost - without such a correction any measurement response would be biased (Huffman et al., 2008). The dominant causes of particle losses are diffusional losses as well as thermophoretic losses while the device is under use. Studies have shown these losses to be size dependent, with visibly higher losses in the small nanometer range, while the effective total particle losses are being setup-dependent (Giechaskiel et al., 2018). An example for these losses would be the values reported by Swanson and Kittelson (2010), where only about 10 % of 5 nm and 30 % of 10 nm particles penetrate the device, with penetration increasing to 70 and 75 % for particles between 50 nm and 100 nm.

Once characterized, the CS is intended to be used at the Aerosol Observatory of the University of Vienna which represents an urban background aerosol sampling station. However, as currently there are no measurements at the Aerosol Observatory that provide direct information on the aerosol chemical composition (apart from the organic and elemental carbon mass concentration), measurements using the CS upstream one of the CPCs would provide additional information on the aerosol volatile and non-volatile fraction and possibly on the potential sources of particles measured there, such as organic aerosol components that originate from biomass burning events or fossil-fuel combustion, as well as secondary components that have further developed.

1.2. Research Objectives

The overall goal of this thesis is to characterize the Catalytic Stripper for aerosol volatility measurements at the Aerosol Observatory in Vienna. This will allow CS to be used for ambient aerosol measurements and provide a first look into the urban volatility fraction at this measurement site. In this context, the following research questions will be addressed in this Master Thesis:

1. What are the particle losses in the CS, and how do these compare to literature data?
2. What is the number fraction of volatile and non-volatile particles in the air in Vienna during the first measurement using CS at the Aerosol Observatory?

2. Volatile and Non-volatile Aerosol

The following section focuses on volatile and non-volatile aerosol. First, it gives an overview on atmospheric aerosol, their sources and composition. This is followed by a more detailed description of aerosol volatility, based both on the thermodynamics, and on the operational definition used in various studies. Finally, examples of volatile and non-volatile aerosol found in urban environments are given.

2.1. Atmospheric Aerosol

2.1.1 Sources and Composition

Atmospheric aerosols comprise a wide variety of chemical components and particle types. The main chemical constituents of particulate matter (i.e. aerosol particles) include sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon (Pöschl, 2005).

The sources of aerosols can be broadly divided into primary emissions and secondary formation processes, spanning both natural and anthropogenic origins. Figure 2.1 shows a schematic of the formation and lifetime processes of aerosols in the atmosphere. Primary emissions can be of natural and anthropogenic sources and secondary formation occurs as a further reaction. Cloud processing, physical and chemical aging accompany an aerosol through its lifetime in the atmosphere until it is removed from the atmosphere by wet or dry deposition (Pöschl, 2005).

Pöschl (2005) summarizes that primary emissions include biomass burning, fossil-fuel combustion, volcanic eruptions, sea spray, biological materials such as pollen and microorganisms, and wind-driven or traffic-related suspension of soil, mineral, and road dust. Secondary particles form via nucleation and condensation of gaseous precursors such as the oxidation of biogenic and anthropogenic volatile organic compounds (VOCs). Anthropogenic sources, particularly fossil-fuel combustion and biomass burning, have massively increased since preindustrial times and make up a major fraction of fine particulate matter in urban and global environments (Pöschl, 2005).

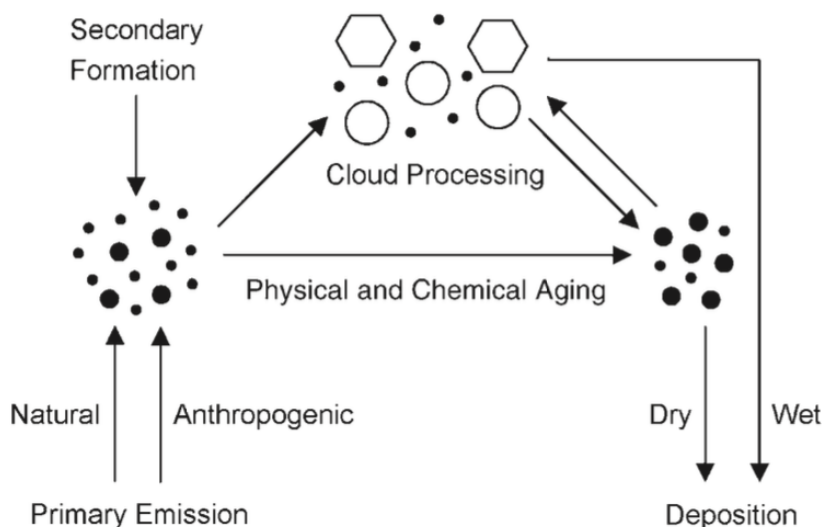


Figure 2.1. Atmospheric life cycle of aerosols. Reproduced from (Pöschl, 2005).

2.2. Organic Aerosol: Formation and Volatility

Organic aerosol (OA) comprises almost 50 % of the submicron particle mass in many environments (Kanakidou et al., 2005; Zhang et al., 2007). OA consists of solid or liquid particles suspended in the atmosphere that contain carbon-based organic compounds, and spans the entire range of organic particles in the atmosphere. It is not reduced to one species (Seinfeld & Pandis, 2016), but represents many various compounds with a wide range of properties such as volatilities (Sun et al., 2025).

As with atmospheric aerosols, organic aerosol components are further classified by origin into primary and secondary categories. Primary organic aerosol components are directly emitted in the condensed phase or as semivolatile vapors, whereas secondary organic aerosol (SOA) components form through chemical reactions and gas-to-particle conversion of VOCs in the atmosphere (Pöschl, 2005). Primary sources include biogenic emissions (from vegetation), anthropogenic emissions (industrial processes, motor vehicles, solvent use), and long-distance transport (Zheng et al., 2023).

While it was a long-term scientific consensus that the origin of atmospheric aerosols is primary, because the sources of organic compounds, like soot or smoke had been clearly visible, it has later been proposed, that processes of atmospheric chemistry might be responsible for further particle-phase products (Seinfeld & Pandis, 2016). Gas-phase organic precursors are oxidized to products with higher polarity and lower vapor pressure, and part of that material partitions into the aerosol phase as SOA (Seinfeld & Pandis, 2016).

Organic aerosols and volatile compounds are closely intertwined because VOCs and semivolatile organic compounds (SVOCs) act as the primary gaseous precursors for SOA formation. Through gas-to-particle conversion, condensation, and multiphase reactions, these volatile vapors partition into the condensed phase to form and grow atmospheric particulate matter (Pöschl, 2005). Whether a given organic compound acts as such a gaseous precursor or resides in the particle phase is governed by its volatility, which we therefore define next.

2.3. Thermodynamic Foundation of Volatility

Swanson and Kittelson (2010) states, that the volatile fraction of an aerosol commonly originates from the condensation of gas phase organic and inorganic species onto particles. A major source is combustion for example, especially engine exhaust, where hydrocarbons from incomplete combustion and sulfur-containing compounds appear in vapor phase or particulate phase. Sulfur dioxide can transition to form sulfuric acid droplets or sulfates contributing to volatile aerosol fractions (Swanson & Kittelson, 2010). Generally, atmospheric compounds span a large range of volatile properties, behaviours and sources - from highly volatile gases that remain airborne, to extremely low-volatility substances that almost immediately condense. This wide range necessitates a systematic classification scheme.

2.3.1 Definition

The term volatile in atmospheric science stems from the chemical property of a substance to leave its current state of matter. In chemistry it is defined as "the conversion of a solid or liquid to a gas or vapor by application of heat, by reducing pressure, by chemical reaction or by a combination of these processes" (Clarke et al., 1994). A substance is therefore considered volatile, when it readily undergoes this phase transition under given conditions.

In more precise terms, volatility tracks the saturation vapor pressure along with a substance's molecular structure. The saturation vapor pressure is the vapor pressure of a pure compound at a given temperature. The intermolecular forces that must be overcome for a molecule to reach gas phase are strongly determined by polarity and size of a compound, making the molecular structure the largest influence on the vapor pressure of a substance. Generally speaking, a substance is considered to be volatile, or to have higher volatility, the more readily it evaporates (Kroll & Seinfeld, 2008). Conversely, substances with low saturation vapor pressure are considered to be non-volatile, or refractory (Kreidenweis et al., 1998).

2.3.2 Gas-particle Partitioning

In atmospheric systems, chemical species partition between gas and particle phases according to thermodynamic equilibrium. Whether a compound remains predominantly in the gas phase, partitions between both phases, or condenses into the particle phase depends fundamentally on its saturation vapor pressure relative to the total available condensed mass. The driving force for phase partitioning is the tendency of vapor molecules to condense when the actual vapor concentration exceeds the saturation concentration. At equilibrium, the rate of evaporation from the condensed phase equals the rate of condensation from the gas phase, establishing a stable phase distribution.

For a given compound i , the equilibrium gas-particle partitioning can be described by a partitioning coefficient K_p (in $\text{m}^3 \mu\text{g}^{-1}$), which is inversely proportional to the saturation vapor pressure. The same relation is also often expressed through the effective saturation mass concentration C^* , which is the mass concentration at which 50% of compound i is in the condensed phase (Donahue et al., 2012; Kroll & Seinfeld, 2008; Pankow, 1994):

$$K_p \propto \frac{1}{p_{\text{sat}}} \quad \text{or} \quad K_p \propto \frac{1}{C^*} \quad (2.1)$$

A higher saturation vapor pressure (higher volatility) yields a smaller partitioning coefficient, meaning the compound preferentially remains in the gas phase. Conversely, a lower saturation vapor pressure (lower volatility) yields a larger partitioning coefficient, favoring partitioning into the particle phase (Kroll & Seinfeld, 2008), as illustrated in 2.2.

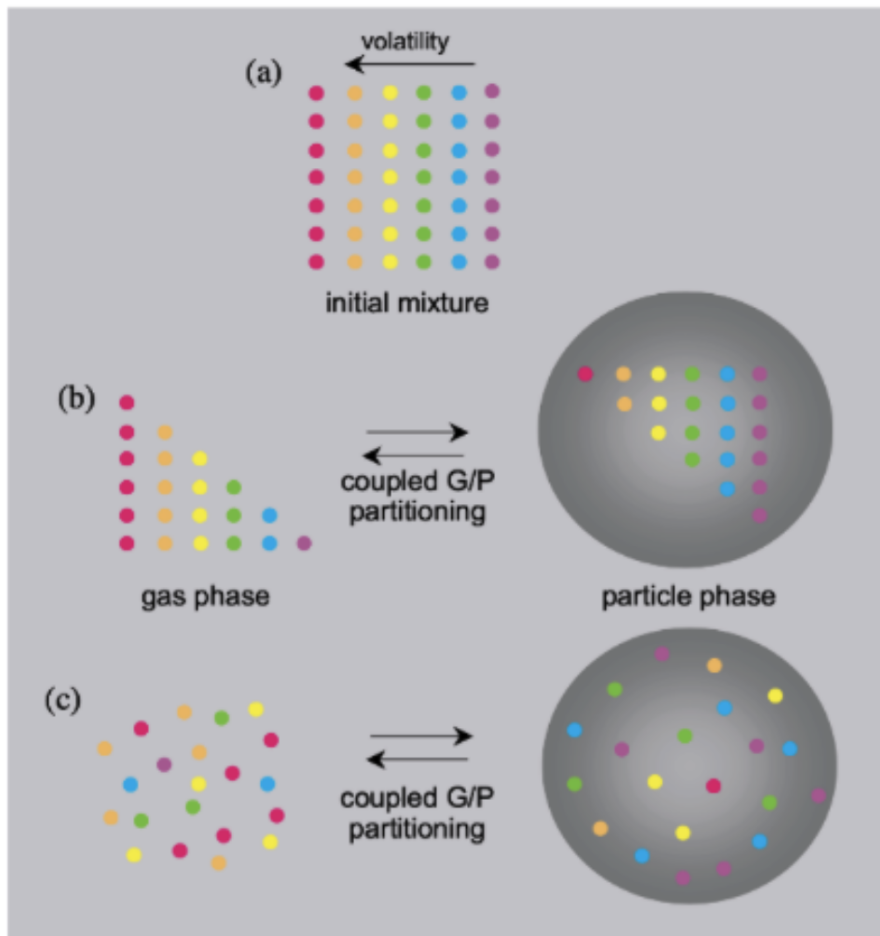


Figure 2.2. Gas-particle phase distribution of six compounds of differing volatility at thermodynamic equilibrium. (a + b) More volatile compounds (red) preferentially remain in the gas phase, while less volatile compounds (violet) prefer the particle phase. (c) Within each phase, compounds are homogeneously mixed. Reproduced from Pankow (2003).

This relationship indicates that volatility is not an absolute property of a substance, but rather controls the distribution between gas and particle phases under given atmospheric conditions.

2.3.3 Temperature Dependence

The saturation vapor pressure (and hence volatility) of any substance is strongly temperature-dependent. This temperature dependence is described by the Clausius-Clapeyron equation, which relates the change in saturation vapor pressure to temperature:

$$\ln p_{sat}(T) \approx \ln p_{sat}(T_{ref}) + \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \quad (2.2)$$

where:

- $p_{sat}(T)$ is the saturation vapor pressure at temperature T (Pa)
- $p_{sat}(T_{ref})$ is the saturation vapor pressure at reference temperature T_{ref} (Pa)
- ΔH_{vap} is the enthalpy of vaporization (J mol^{-1}), representing the energy required to convert a substance from liquid to gas phase

- R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- T is the absolute temperature (K)

This relationship demonstrates that the saturation vapor pressure increases exponentially with temperature. As temperature increases, more molecules possess sufficient kinetic energy to escape the condensed phase, leading to higher vapor pressures and greater volatility. Conversely, at lower temperatures, fewer molecules escape, and vapor pressures decrease, causing substances to preferentially condense (Donahue et al., 2012).

The previously discussed dependence of volatility on saturation vapor pressure and consequently temperature makes it a direct subject to atmospheric dynamics. The atmosphere’s kinetic processes lead to volatility being a dynamic partitioning process rather than a given chemical property. Emissions that might preferentially remain in condensed phase during cooler and/or more dense conditions might experience a shift of phase equilibrium towards evaporation when heated or diluted. E.g. organic compounds emitted by a diesel engine partition preferentially into the condensed phase at the high concentrations and low temperatures near the source, but dilution with cleaner air or heating drives the phase equilibrium back towards the gas phase, evaporating a large fraction of the condensed material (Huffman et al., 2009). The fate of an aerosol is thus dependent on their volatility and directly changes according to atmospheric conditions. As temperature changes volatile components evaporate or condense, continuously reshaping an aerosol.

2.3.4 Particle Mixing States and Internal Structure

To further understand this shift and how it can vary within an aerosol, the distribution of volatile vs. refractory components across an aerosol is another essential factor. The aerosol mixing state tells us the distribution of properties across an aerosol population. We are thus now moving on from how volatility is a property of a single particle in certain conditions, to how these properties are shared and spread on population-level. The first thing we need to understand is the basic principle that in the atmosphere there are two fundamental types of mixing as well as two mixing states in which particles exist: chemical mixing vs. physicochemical mixing and internal vs. external mixtures of particles (Riemer et al., 2019).

Chemical mixing is the distribution of chemical species across particles, whereas the physicochemical mixing state adds physical properties (morphology, phase) to any chemical descriptors. When talking about volatiles, both of these mixing states can be of relevance. Once the type of mixing in a substance is determined, the way the mixing occurs can be externally or internally (Riemer et al., 2019).

An externally mixed aerosol consists of particles that each contain only a single chemical species, with different particles being composed of different species. In other words, one particle might consist entirely of one substance and the next of an entirely different one. In contrast, an aerosol is internally mixed when all particles in the population contain the same species in the same mass fractions, so that each individual particle is itself a chemical mixture reflecting the bulk composition (Riemer et al., 2019).

However, these distinctions mark both ends of a spectrum between external and internal mixing - fully external and fully internal mixtures are not representative of atmospheric reality. The “same net composition of an aerosol can be caused by an infinite variety of different internal distributions of the various compounds” (P. Winkler, 1973). Even if an aerosol source generates an entirely externally mixed aerosol, atmospheric processes like condensation, cloud processing or coagulation can convert external mixtures to be internally mixed aerosols (Brooks et al., 2007). Fresh emissions, new particle formation and the closed transport of distinct air masses benefits

more external mixing by adding single species particles into the atmosphere. The atmospheric mixing interactions are displayed in Figure 2.3 (Riemer et al., 2019).

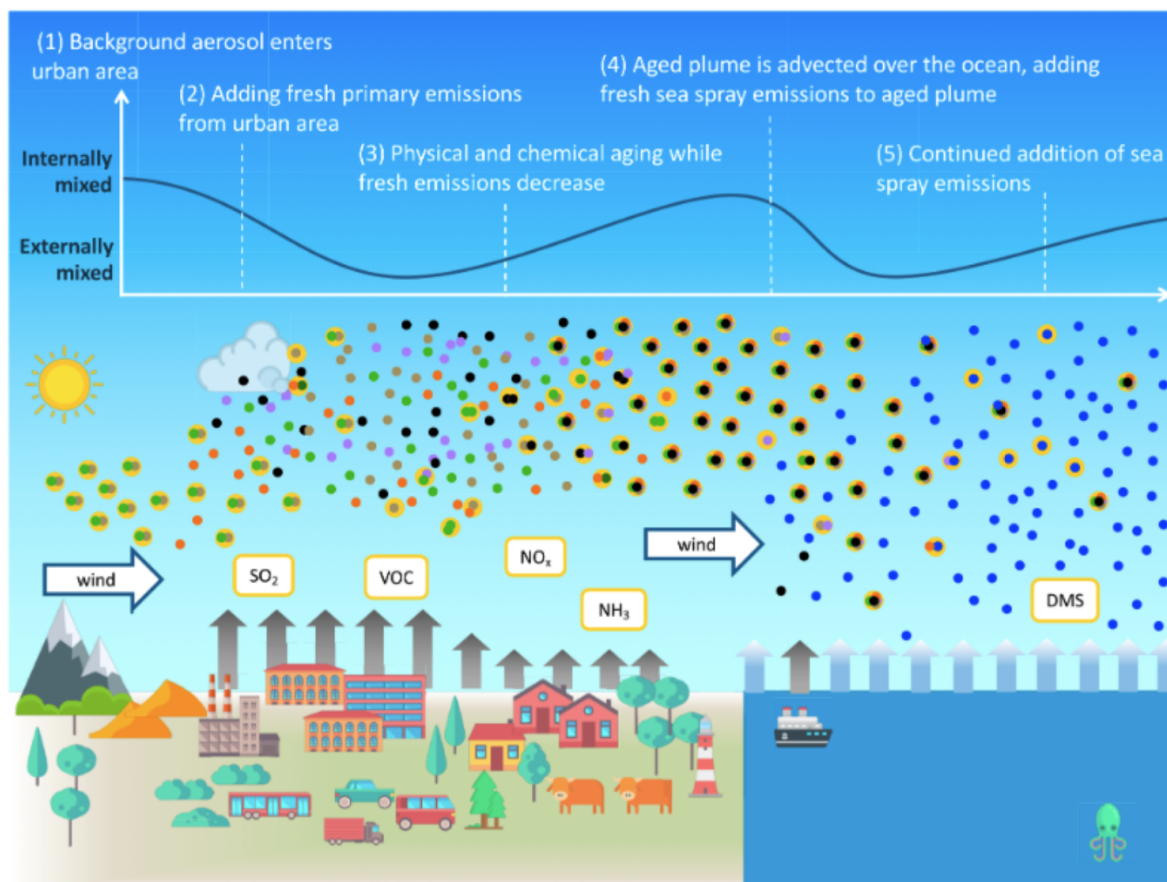


Figure 2.3. Competing processes between internal and external mixing in the atmosphere under the addition of fresh aerosol, while aging processes happen simultaneously. Reproduced from (Riemer et al., 2019).

So the mixing state is not just a descriptive property, it's dynamic and constantly governed by atmospheric action. By the definition established previously, the determining factor for an aerosol's mixing state has been the choice of species (Riemer et al., 2019). However one could group components just as well by a shared property - for instance, the distinction between volatile and refractory, enabling quantification of the volatile mixing state of an aerosol. Just as the concept was described in the previous section, one can distinguish aerosol material as being non-volatile particles, volatile material condensed on those particles, and separate volatile particles in the gas/aerosol phase. It directly applies the concept of external mixing, where components are mostly separate, and internal mixing, where volatile material is carried on or within non-volatile particles (Dickau et al., 2016).

Let us now bring together what we have stated about volatility so far. The property of a substance to be volatile is on one hand dependent on its chemical structure while at the same time dependent on atmospheric circumstances in relation to pressure and temperature. It describes an underlying willingness or aversion of a substance to undergo phase transition into the gas-phase, while the transition occurring is then related to thermodynamic properties of the surrounding airmass. So to find out how volatile a substance is in one moment, one needs to know:

1. How willing is a substance transitioning between particle-phase and gas-phase (under ref-

erence conditions)?

2. Are the thermodynamic conditions in the moment of interest sufficient for the particle to cross the threshold reaction into gas phase?

We will then know the volatility of a substance under certain conditions. This allows us to not only understand the volatility of one particle/one substance, but allows to gain a broader picture on how this is distributed over the entire aerosol, showing us what parts of the aerosol are more volatile than others.

2.4. Volatile Organic Aerosol Components

Because atmospheric temperature and pressure span only a limited, well-characterised range, the volatility of aerosol constituents can be assessed specifically for these conditions. More precisely, within our atmosphere, some substances will generally occur only as refractory, while some will not reach particle-phase and remain stable in the gas phase. However, very prominently so, for the group of organic aerosols this clear distinction cannot be made.

Historically OA has been classified as either POA or SOA - however, this confinement into two distinct formation categories has been under discussion, as it has been shown that a large fraction of organic compounds are considered to be in the semi-volatile range with the extensive reach of oxidation chemistry producing a number of states between volatile and not (between gas and particle phase) (Donahue et al., 2012; Seinfeld & Pandis, 2016). Primary compounds, once emitted directly in particle form most often do not remain in their particulate form, but evaporate. They mostly are volatile enough. From these evaporated POA the atmosphere gets enriched in semivolatile organic vapors that may go through processes of oxidation, making them recondense into particulate phase - lower volatility compounds primarily form through gas-phase oxidation of VOCs. In general there are two important pathways from oxidation, the primary oxidants in the atmosphere being hydroxyl radicals (OH), ozone (O₃), and nitrate radicals (NO₃) (Seinfeld & Pandis, 2016):

The so-called functionalization pathway: Oxidation of organics means adding functional groups to their carbon skeleton, creating functional groups like hydroxyl (-OH), carbonyl (-C=O), nitrooxy (-ONO₂), hydroperoxy (-OOH), carboxyl (-C(O)OH), and ester (-C(O)OR) groups. This process increases the polarity of a molecule and decreases its volatility. Oxidation products following this pathway are more likely to condense into particle phase (Seinfeld & Pandis, 2016).

The second main pathway is fragmentation. Increasing oxidation products might become susceptible to breakage of their carbon-carbon bond, which decreases their molar mass and leads to an increase in volatility (Seinfeld & Pandis, 2016).

Figure 2.4 shows the multiple evolution options for compounds through one or multiple oxidation processes and depicts how the evolution of an organic aerosol can span a range of volatilities.

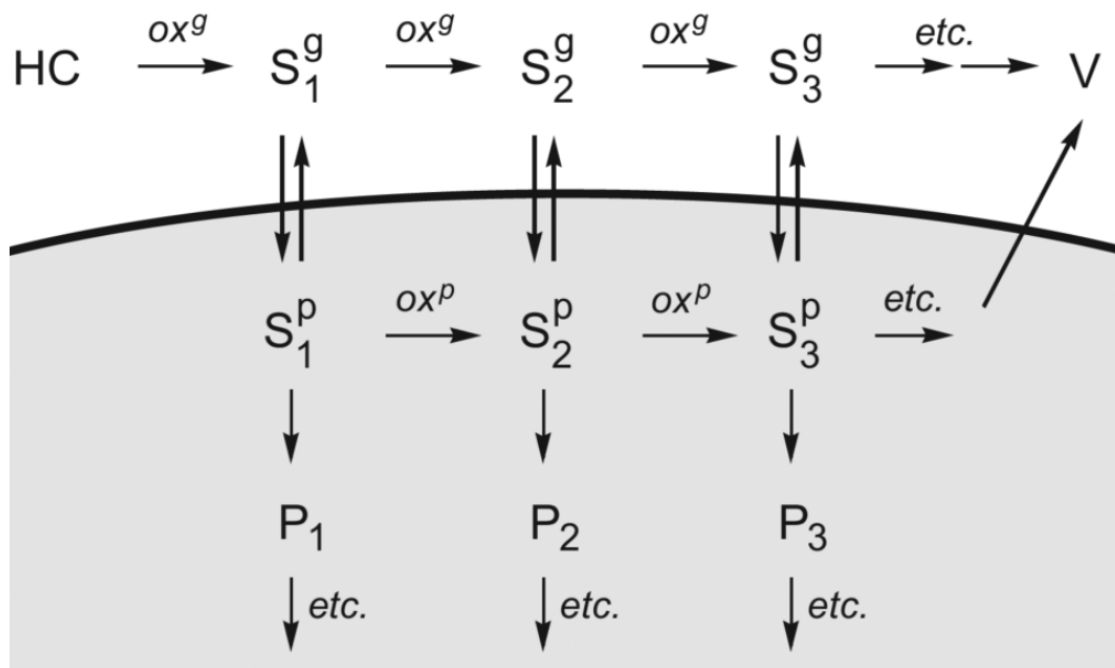


Figure 2.4. SOA Formation and evolution processes depicting semivolatile (S), particle-phase compounds (P) and fully volatile compounds (V). Reproduced from (Seinfeld & Pandis, 2016)

This shows one of the most important points when looking at scientific literature of atmospheric volatiles: while volatility is a general physical property of any substance, the need to organise atmospheric constituents into discrete volatility classes arises primarily from the organic fraction. Unlike the inorganic components, which are either clearly refractory (e.g., elemental carbon, mineral dust, sea salt) or can be treated as individual, well-defined species (e.g., ammonium nitrate), organic aerosol comprises hundreds to thousands of distinct compounds spanning a continuous range of volatilities (Burtcher et al., 2001; Huffman et al., 2008; Kreidenweis et al., 1998).

2.4.1 Classification Framework: Volatility Basis Set

The most widely adopted classification scheme is the Volatility Basis Set (VBS), which organizes organic compounds into bins based on their saturation mass concentration (C^*), measured in $\mu\text{g m}^{-3}$ (Donahue et al., 2012). This framework enables systematic treatment of gas-particle partitioning across the full range of atmospheric compounds. The conditions to which these categories are referenced are standard ambient conditions.

- **Extremely low volatility organic compounds (ELVOC):** $C^* < 3 \times 10^{-4} \mu\text{g m}^{-3}$; almost entirely in the particle phase in most ambient conditions
- **Low volatility organic compounds (LVOC):** $3 \times 10^{-4} < C^* < 0.3 \mu\text{g m}^{-3}$; predominantly in the particle phase in the atmosphere
- **Semi-volatile organic compounds (SVOC):** $0.3 < C^* < 300 \mu\text{g m}^{-3}$; phase strongly dependent on ambient conditions - usually have mass fractions in both
- **Intermediate volatility organic compounds (IVOC):** $300 < C^* < 3 \times 10^6 \mu\text{g m}^{-3}$; relatively low vapour pressure but still reside almost exclusively in the gas phase under

atmospheric conditions

- **Volatile organic compounds (VOC):** $C^* > 3 \times 10^6 \mu\text{g m}^{-3}$; always in gas-phase - important precursors for Secondary Organic Aerosols

Zheng et al. (2023) instead classify organic aerosol by boiling point, grouping compounds into volatility classes according to their volatilization temperature. This provides a more intuitive basis for compositional analysis than the volatility basis set (VBS), which bins organics by their effective saturation mass concentration and is less directly tied to a measurable evaporation temperature (Zheng et al., 2023).

- **Very Volatile Organic Compounds (VVOCs):** boiling point below 50°C
- **Volatile Organic Compounds (VOCs):** boiling point between 50 and 260°C
- **Semi-Volatile Organic Compounds (SVOCs):** boiling point between 260 and 400°C
- **Particulate Organic Matter (POMs):** boiling point $\geq 400^\circ\text{C}$

In general, depending on the temperature settings of a respective device, distinction of components can be achieved. Bartscher et al., 2001 has experimentally identified temperature ranges of 30 to 125°C for highly volatile organic carbon (OC) and sulphuric acid, 125 to 175°C for ammonium sulphate and bisulphate, 175 to 300°C for low volatile OC and $>300^\circ\text{C}$ for refractory aerosols such as elemental carbon, mineral dust and sodium chloride.

2.5. Urban Aerosol Composition and Volatility

Before introducing measurement methods for the volatile fractions of an aerosol, it is worth providing an overview of the estimated composition of aerosol species in urban areas together with their volatile properties. The following examples are meant to give an approximation of what an air sample in urban areas might contain.

Urban particulate matter is largely made up of constituents such as organic and elemental carbon, sulfate, nitrate, ammonium, silicates, alkali and alkaline earth metals, aluminum, iron, and lead, and fine particles contain most of the sulfates, ammonium compounds, hydrocarbons, elemental carbon, toxic metals, and water (Hinds, 2022). Figure 2.5 depicts this graphically - organics, elemental carbon (EC) and black carbon (BC), ammonium, sulfate and nitrate being the leading components of urban aerosol composition. The size distribution of this urban aerosol compositions peaks between 10 nm and 100 nm , indicating that it is dominated by fine and ultrafine particles.

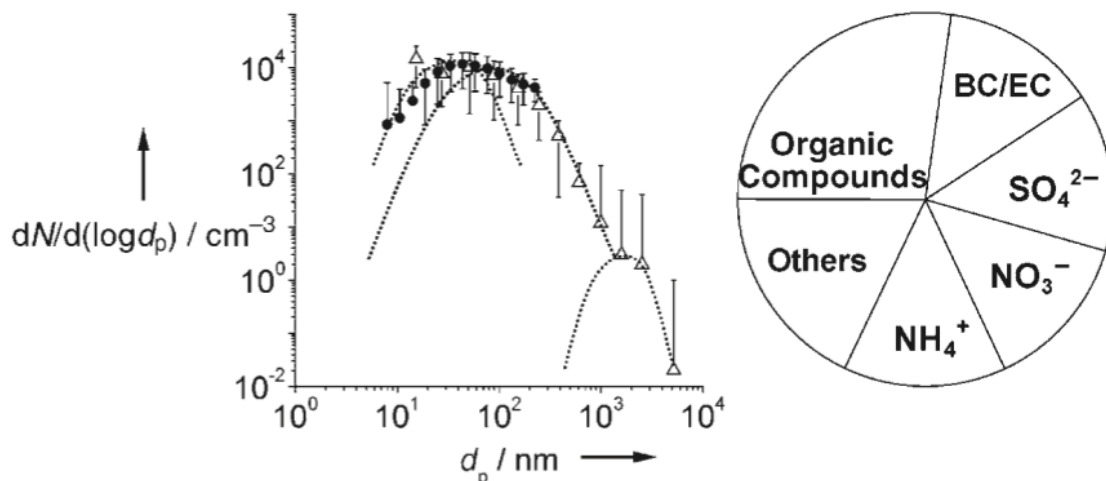


Figure 2.5. Examples of aerosol composition and particle size in urban air (Munich, 500 m). Reproduced from (Pöschl, 2005).

To relate this composition to volatility, it is useful to order these constituents from the organic fraction, whose volatility spans a continuous range, through the volatile inorganic compounds, to the clearly refractory, non-volatile species.

2.5.1 Volatile Aerosol

According to Jimenez et al. (2009) organic aerosol dominates the submicron mass at urban European sites. Figure 2.6 depicts the range of aerosol types at different measurement sites in the northern hemisphere, showing the composition of organic versus inorganic aerosol. It illustrates how variable the organic fraction is across sites, and that organic aerosol makes up a large part of the submicron mass. The organic aerosol itself is grouped by how volatile and how oxidized it is: hydrocarbon-like organic aerosol (HOA); oxygenated organic aerosol (OOA), divided into semi-volatile OOA (SV-OOA), representing fresh SOA of lower oxidation, and low-volatility OOA (LV-OOA), representing aged, regional SOA of high oxidation; alongside total OOA and other components. At these sites, LV-OOA accounts for the largest fraction, reflecting the aged, regional character of European air masses. Note that here exclusively non-refractory components are measured: refractory species such as BC/EC and mineral dust are not captured and would add to the total mass fractions shown (Jimenez et al., 2009).

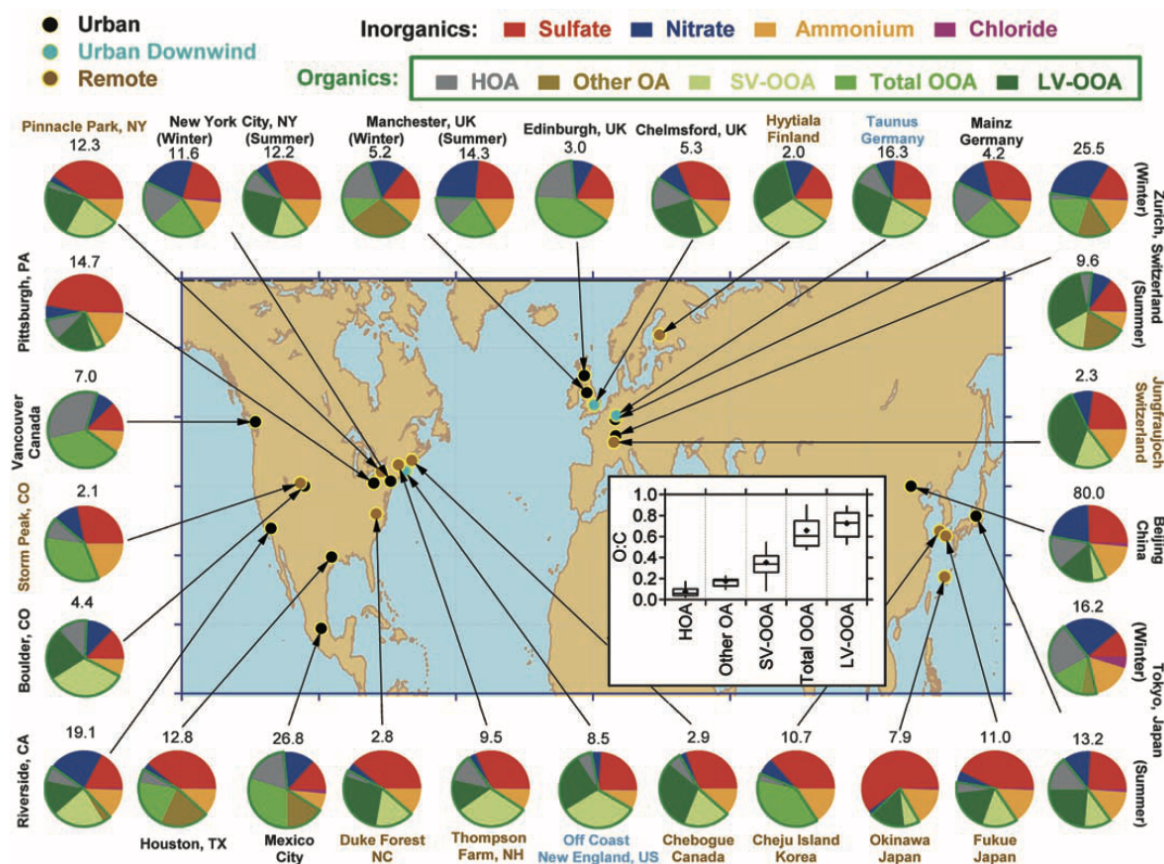


Figure 2.6. Mass concentration and relative contributions of non-refractory inorganic and organic aerosol components measured by AMS at various surface sites. Numbers shown are distributions of O:C. Reproduced from (Jimenez et al., 2009)

Unlike at the two ends of the spectrum, the simple split into volatile and non-volatile does not hold for the organic fraction, which spans a continuum of volatilities. The thousands of species that make up organic aerosol cover a wide range of polarity, volatility, and molecular mass, and direct speciation techniques can resolve only about 10 % of the ambient OA mass as individual compounds (Huffman et al., 2009).

Kupc et al. (2018) shows that not only organic, but also inorganic species can be semi-volatile. Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) was the most volatile of the materials tested, evaporating almost completely below 300°C , whereas secondary organic aerosol from limonene ozonolysis was less volatile, with its smaller particles volatilizing at lower temperatures than larger ones of the same composition.

So, within the inorganic fraction there is likewise a volatility gradient. Ammonium nitrate (NH_4NO_3) is the most volatile major inorganic component; it dissociates readily upon mild heating, for example in summertime. Ammonium chloride (NH_4Cl) shows a similar dissociation behavior and is likewise quite volatile, so that together they form the two major volatile inorganic compounds (Huffman et al., 2009; Seinfeld & Pandis, 2016). Ammonium sulfate, by contrast, is of markedly lower volatility and can be regarded as the low-volatility anchor of the inorganic fraction (Huffman et al., 2009; Seinfeld & Pandis, 2016).

2.5.2 Non-volatile Aerosol

Beyond the inorganic salts lies the clearly refractory end of the spectrum. Here the salts of ammonia differ from those of sodium, potassium, and calcium, which remain non-volatile at

300 °C, whereas the ammonia salts are entirely volatile at this temperature (Engler et al., 2006). The unambiguously refractory, non-volatile species are elemental or black carbon (EC/BC), mineral dust, and sea salt (Pöschl, 2005). For example, Kupc et al. (2018) found that sodium chloride showed no significant volatilization at temperatures up to 310 °C, consistent with the behaviour of other primary, refractory material such as soot, sea salt, and mineral dust. These are the components that the non-refractory measurement in Figure 2.6 does not capture and that would add to the mass fractions shown.

Now, the full chemical composition of an urban aerosol is difficult to measure directly, so data such as that shown are not readily available. What is more commonly obtained is the inference of chemical properties from physical volatility measurements (Pöschl, 2005). Because volatility is temperature-dependent, thermal methods allow an in situ determination of some of these fractions and, in particular, separate the volatile from the refractory components, which motivates the measurement methods introduced in the following chapter.

3. Measurement Methods for Volatile and Non-Volatile Aerosol Fractions

A common way to measure aerosol volatility is through a process called thermal fractionation. This entails for specific temperatures evaporation of a species due to their vapor pressures, boiling points and enthalpies of vaporization. Particles are heated and thus the more volatile species will evaporate while less-volatile or refractory species (depending on temperature) will be left behind (Huffman et al., 2008). If used at a single temperature, as in the context of this thesis, one separates the non-volatile fraction from the volatile fraction for a given sample at that fixed temperature. It is worth noting that "non-volatile" is here an operational definition tied to the chosen temperature rather than an absolute material property: a species counts as non-volatile only insofar as it does not fully evaporate at that temperature within the available residence time, i.e. the time the aerosol sample spends in the section of the respective device (Swanson & Kittelson, 2010).

Operational Definition of Volatility These devices, installed upstream of the detector (e.g. a CPC or mobility sizer), separate aerosol components by evaporation. Combining this with the composition-dependent evaporation temperatures discussed above, the aerosol can be partitioned into volatile and non-volatile fractions according to a chosen operational threshold temperature. In this study, that threshold is set to 350 °C: material that evaporates at or below 350 °C is assigned to the volatile fraction, while material that remains after heating is considered non-volatile, or refractory.

3.1. Devices

3.1.1 Thermodenuder

The standard operating device for such thermal fractionation processes is what is called a thermodenuder, as seen in Figure 3.1 - it is also the physical predecessor for the measurement device central to this thesis. They generally work by a two-stage principle: a sample stream of aerosol passes through heated tubing that is held at a constant temperature (e.g. 200 °C) making species whose evaporation temperature lies below, evaporate. In a second stage, the sample flow may enter a cooling section lined with carbon charcoal, where evaporated gases adsorb preventing recondensation onto the remaining particles (Huffman et al., 2008).

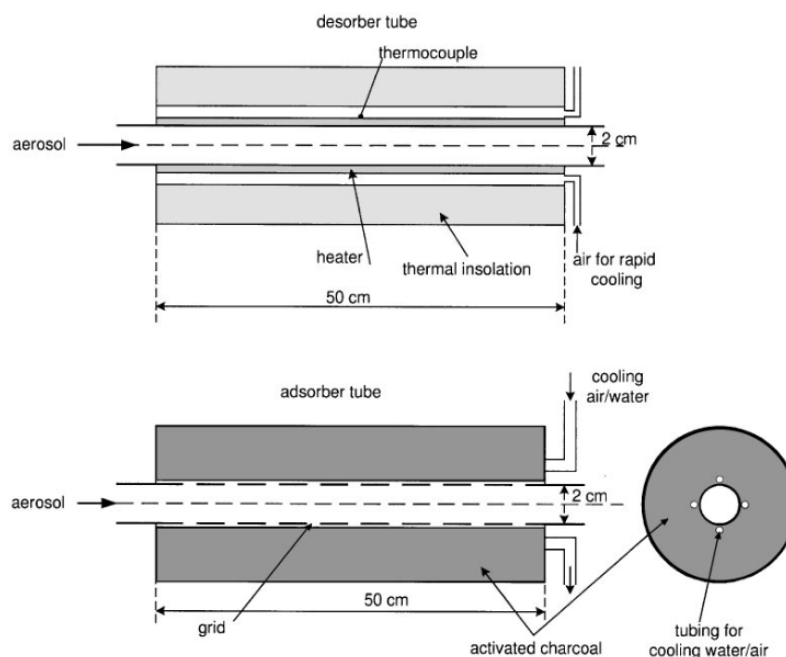


Figure 3.1. Schematic of a thermodesorber design by (Burtscher et al., 2001)

It is the conventional design of thermodenuders to consist of a heating section followed by an activated-carbon adsorption section that is actively or passively cooled. Fierz et al. (2007) shows however, that this arrangement introduces a temperature drop at the junction between the heated and cooled sections, which is undesirable. Firstly, it can induce turbulent flow and thereby high thermophoretic losses. Secondly, the cooling proceeds faster than the removal of the volatile species. As a consequence, recondensation might occur before the volatile material can be adsorbed, unless the gas has been heated well above the boiling point of the volatile species. Once recondensation has taken place, the remainder of the adsorption section no longer affects the aerosol and simply adds to the particle losses (Fierz et al., 2007). It is stated that in the Burtscher et al. (2001) design the gas temperature is reported to fall to near-ambient values after only 10 cm of the 50 cm adsorption section at flow rates below 21 min^{-1} . While on the one hand incomplete removal of volatiles is shown to be caused by insufficient residence time in heated sections (An et al. (2007) and Wehner et al. (2002)), this rapid cooling adds another issue (Fierz et al., 2007). Because of these limitations alternatives had to be developed that might prevent recondensation down the flow stream.

3.1.2 Catalytic Stripper

Another method using thermal fractionation and also the core measurement device for this thesis is the Catalytic Stripper (CS). This device, rather than heating followed by absorption, uses oxidation caused by a catalyst within a heating section, held at a single fixed temperature (e.g. between 300 and 400 °C, (Swanson & Kittelson, 2010; Swanson et al., 2011)).

In general, there are multiple types of catalytic strippers, as listed by Giechaskiel et al. (2020). There is devices that use an oxidation catalyst and a sulfur trap, some that reverse the order of said components and, finally, devices that contain solely the oxidation catalyst. Semi-volatile particulate matter is evaporated according to the temperature of the device and oxidized to end products of CO_2 and H_2O , while inorganic compounds, such as sulfate are absorbed onto the washcoat (Giechaskiel et al., 2020). Further it is explained in Giechaskiel et al. (2020) that, similar to thermodenuders, the CS stems from the automotive industry where it was developed from

a commercial diesel oxidation catalyst with the addition of a cooling tube to bring samples back to ambient temperature levels. It was then used in combination with particle number systems, replacing the previously frequently used evaporation tube (that works solely based on evaporation through heating; it deviates from thermal denuders via lack of charcoal adsorption). This system was followed by introducing the sulfur trap, which was originally introduced upstream of the oxidation catalyst, but found to have more sulfur storage capacity downstream of the catalyst. It is today commonly used as either catalyst followed by the sulfur trap or purely through catalytic oxidation (Giechaskiel et al., 2020). A device as such, combining thermal fractionation with catalytic removal of volatile species, composes the central subject of this thesis.

Figure 3.2 shows a visual comparison of two volatile particle remover (VPR) configurations, one based on an evaporation tube and one based on a catalytic stripper, as discussed above. In the configuration shown, the diluted exhaust aerosol typically consists of soot particles with some species condensed on them, volatile nucleation-mode particles, and volatile species in the gas phase, containing compounds such as organics and sulfuric acid. A primary hot diluter first evaporates part of the condensed material by heating and reducing the partial pressures of the volatile species through dilution. Then, in the evaporation tube and CS most volatile species and condensed material further evaporate at 350 °C and in the CS oxidation happens. The cooling section brings the sample back to appropriate temperature levels for further analysis. It is during this step that VPRs operating without catalytic conversion might be subject to re-condensation on the soot particles or re-nucleation of volatile species (Giechaskiel et al., 2020).

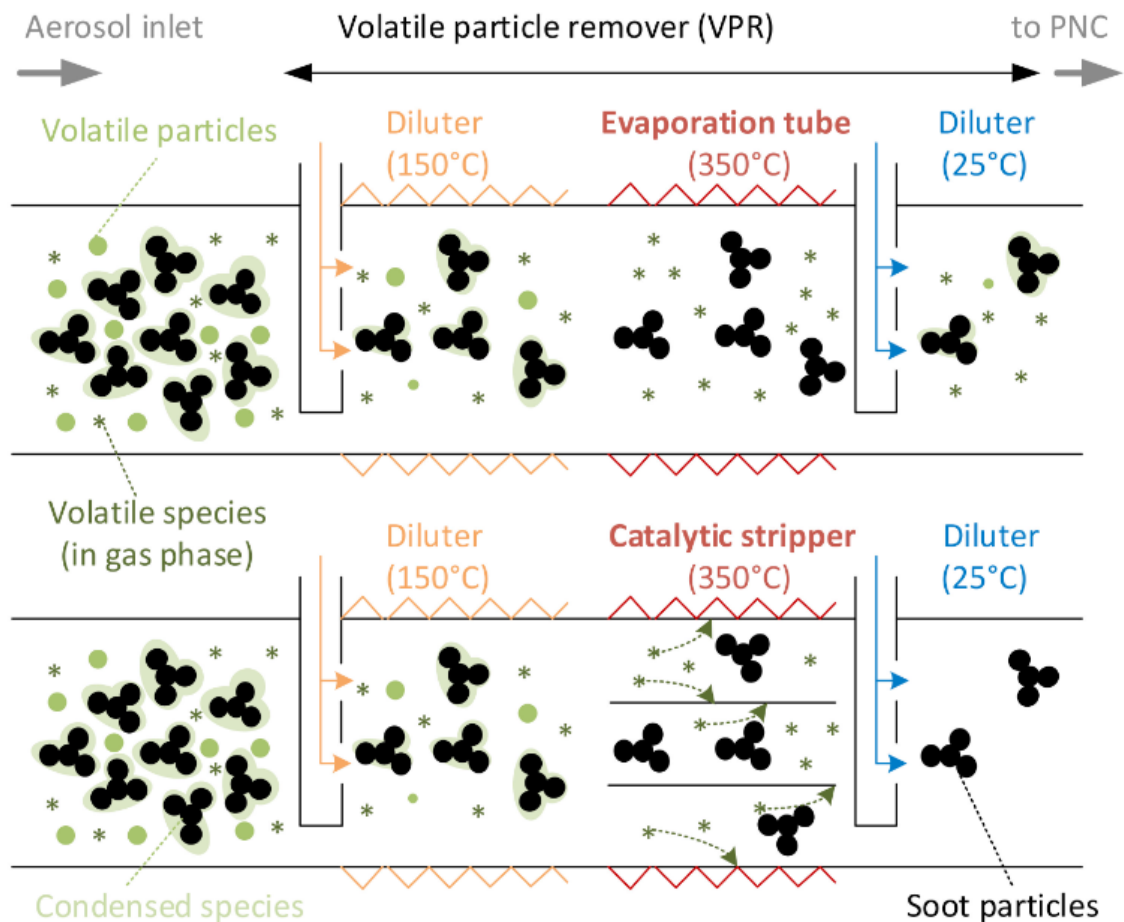


Figure 3.2. Drawing of the principle of measurement in volatile particle removers: Evaporation tube (upper) and Catalytic Stripper (lower). Reproduced from (Giechaskiel et al., 2020)

3.1.3 Comparison of Catalytic Stripper and Thermodenuder

In a comparison study by Swanson and Kittelson, 2010 an evaluation of two methods of thermal fractionation was done, a TD and a CS, as seen in Figure 3.3. This study compared the efficiency of both devices in the separation of non-volatile and volatile components using Diesel exhaust, as well as atmospheric aerosol.

Here a TD that is heated to 300 °C is used, with evaporation products being adsorbed by activated carbon in the absorption section. This is accompanied by a diffusion drier with water cooling at 25 °C. To compare, a CS was also used for the same sample - here 300 °C - at which the volatile fraction is oxidised away. It is used at 10 l min⁻¹. Additionally to the oxidation catalyst a washcoated ceramic substrate called an S-trap is inserted upstream of the catalyst. It is used to trap sulfur-containing compounds (Swanson & Kittelson, 2010).

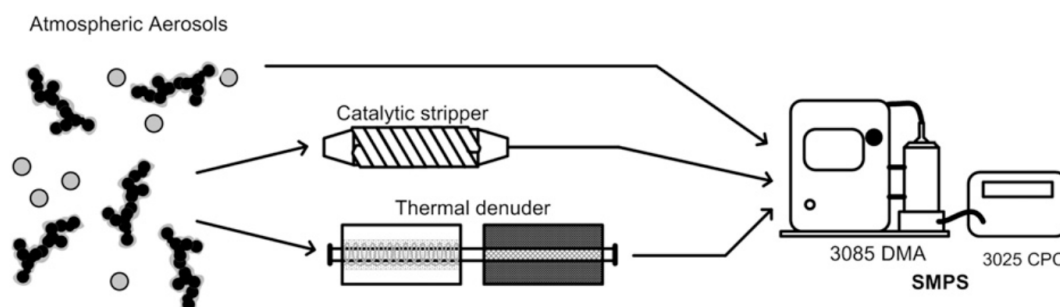


Figure 3.3. Schematic of the experimental setup using the TD and CS. Reproduced from (Swanson & Kittelson, 2010)

Figure 3.4 shows the results of this study. The reduction in number concentration after passing CS is clearly visible, whereas for the TD a minimized number concentration is only visible for particle sizes exceeding 10 nm. Further, (below 10 nm) there is a steep increase in number concentration, exceeding the original sample concentration. This suggests such re-nucleation processes and correspondingly the formation of smaller, new volatile particles in the TD (Giechaskiel et al., 2020; Swanson & Kittelson, 2010). Swanson and Kittelson (2010) concluded that the catalytic stripper is a more reliable alternative to the thermodenuder, as it removed the semi-volatile material almost completely without producing the artefacts they observed in the thermodenuder.

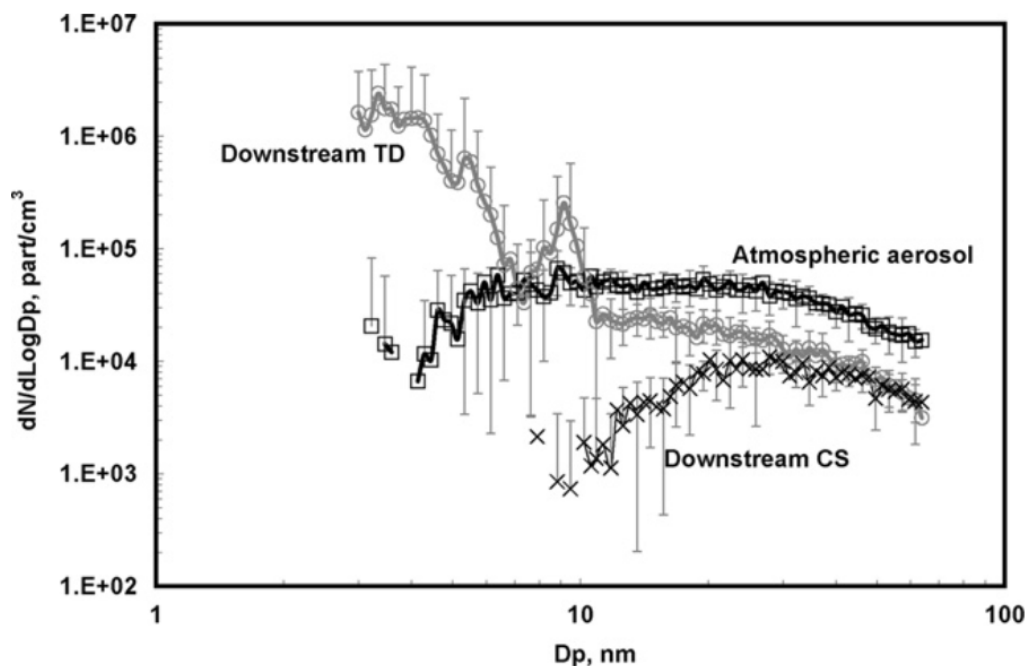


Figure 3.4. Particle size distribution downstream the TD and CS compared to atmospheric sample. Reproduced from (Swanson & Kittelson, 2010)

3.2. Applications

3.2.1 Automotive Industry

Devices based on thermal fractionation offer a range of applications over various fields. Very commonly they are used in the automotive industry to discard volatiles from solid particles in vehicle exhaust (Giechaskiel et al., 2020; Swanson & Kittelson, 2010) in order to quantify only the refractory particle number above the regulated size, without miscounting volatile particles that may nucleate downstream. Diesel exhaust consists of multiple species of particulate matter and gases. Particulate matter consists mostly of solid carbonaceous particles (such as EC and OC), and gaseous/semi-volatile compounds. The latter are mainly composed of hydrocarbons (HC) that form from incomplete combustion, and of sulfur containing compounds, mostly sulfur dioxide that can eventually form sulfuric acid droplets or sulfates (Swanson & Kittelson, 2010).

In Giechaskiel et al. (2018) a CS is used as part of a VPR, which removes volatile particles in the legislatively prescribed solid particle number (SPN) systems. In the context of evaluating whether the lower detection limit of the SPN measurement methodology should be reduced from 23 nm to 10 nm, systems using a catalytic stripper showed promising results, which is driving the discussion of whether it might become mandatory in future regulations (Giechaskiel et al., 2018). It serves as an alternative to an evaporation tube and is particularly effective for small particles. In the <23 nm range, its use is recommended to prevent re-nucleation and the growth of re-nucleated material (Giechaskiel et al., 2018). This is illustrated in Figure 3.5, which compiles vehicle-exhaust data from evaporation tubes and catalytic strippers. Evaporation-tube systems produced volatile artefacts extending into the 10 and 23 nm range, whereas catalytic strippers left no particles >10 nm in any tested case (Giechaskiel et al., 2020).

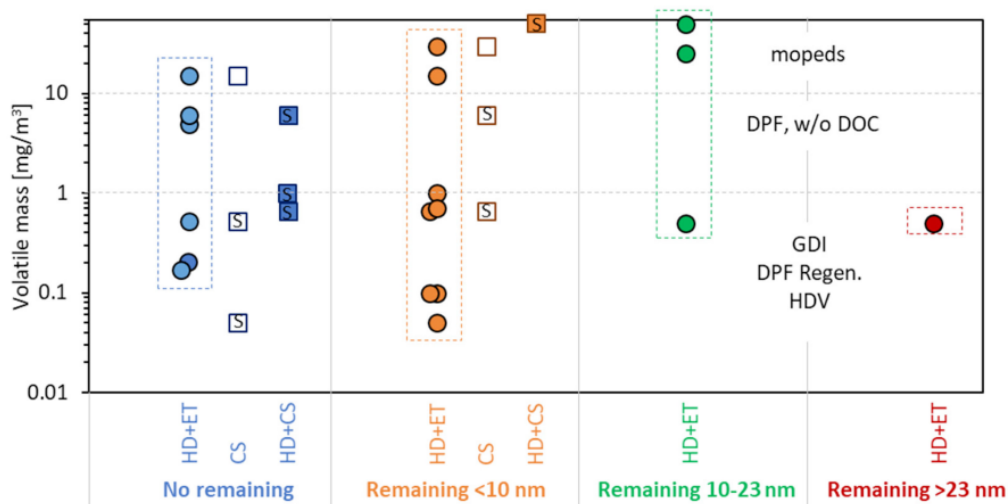


Figure 3.5. Volatile removal efficiency of different VPR systems for vehicle exhaust, sorted by whether particles remained downstream in the size ranges <10 nm, 10 and 23 nm, and >23 nm. Reproduced from (Giechaskiel et al., 2020).

3.2.2 Atmospheric Measurements

Another application for these devices is within aerosol science. Whereas exhaust measurements use thermal fractionation primarily to strip volatiles so that solid particles can be counted, in atmospheric science the aim is characterization. TD are the established tool for this and have been widely used in ambient aerosol measurements (Kupc et al., 2018; Wehner et al., 2004; Weinzierl et al., 2009). CS, by contrast, have so far seen little use in this context, despite offering a promising alternative that could equally be applied to ambient sampling.

Kupc et al. (2018) used a TD at 300°C to identify non-volatile particles (sea salt, dust) and the volatile, secondary fraction over the remote ocean atmosphere. TD was placed upstream of one of their Ultra-High Sensitivity Aerosol Spectrometer (UHSAS) so the size distribution of the total and the thermodenuded (non-volatile) aerosol could be compared. The fraction info could aid in deriving a distinction between primary sea-salt and dust particles and secondary particles. In their example case (Figure 3.6), only about 6 % of particles by number in the marine boundary layer and 4 % in the free troposphere were non-volatile.

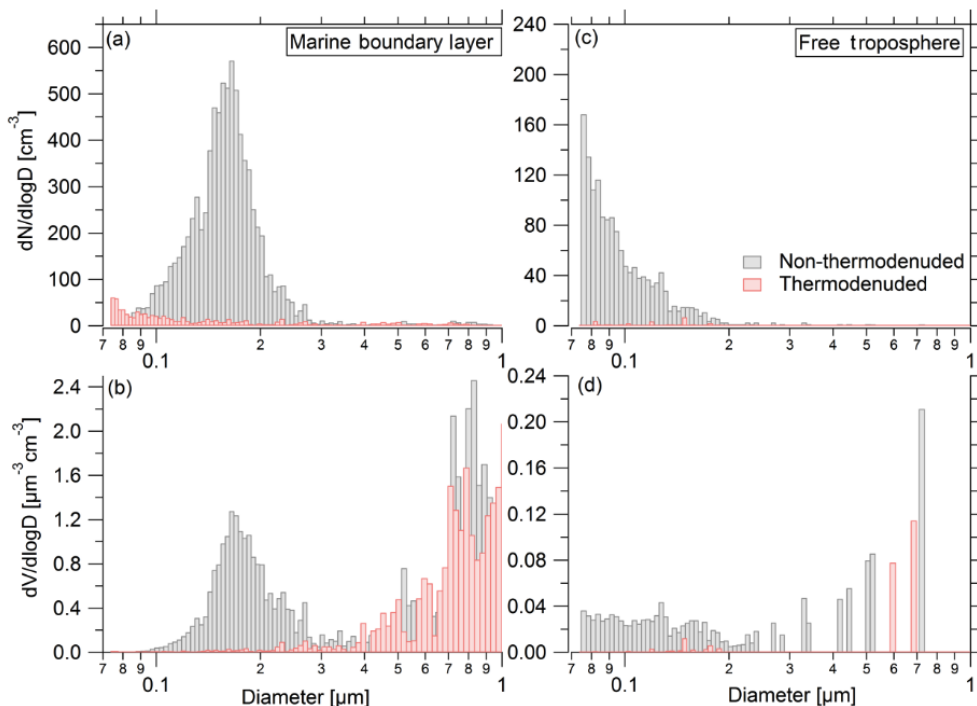


Figure 3.6. Thermodenuded and non-thermodenuded UHSAS size distributions during ATom. (a, b) show the number and volume distributions in the marine boundary layer and panels (c, d) in the free troposphere. Reproduced from (Kupc et al., 2018).

Another example of TD application is described in study by Weinzierl et al. (2009) during the airborne Saharan Mineral Dust Experiment (SAMUM). In order to gain size-resolved information about particle volatility using thermo-optical methods, TD (250 °C) was used in combination of a CPC and an OPC. By heating the sample, one can obtain the volatile material fraction. By using the optical methods measurement of size resolved distributions of total as well as non-volatile fraction is possible (see 3.7). Comparison of both allows the inference of the mixing state of the measured sample. The denuder was operated at 250 °C separating high to medium volatile organics, components of sulphuric acid-like and ammonium sulphated-like behaviour and non-volatile components, e.g. EC/BC, sea salt, dust and crustal material.

Figure 3.7 shows results of the SAMUM flight for two different days and locations. By reading the gap between the total and non-volatile distributions one can infer whether the aerosol was in a mixed state or not (coinciding lines). Above 0.5 μm the total and non-volatile curves coincide - nothing evaporates, indicating bare refractory mineral dust. At around 0.5 μm the coinciding lines at both locations start to separate, moving towards smaller diameters. This suggests that these particles have lost material on heating: the non-volatile distribution retains the same shape and a similar number concentration as the total, but is shifted towards smaller sizes. As the particles shrink rather than disappear, this indicates a refractory core with a volatile coating (identified by Weinzierl et al. (2009) as ammonium sulphate) that evaporates at 250 °C.

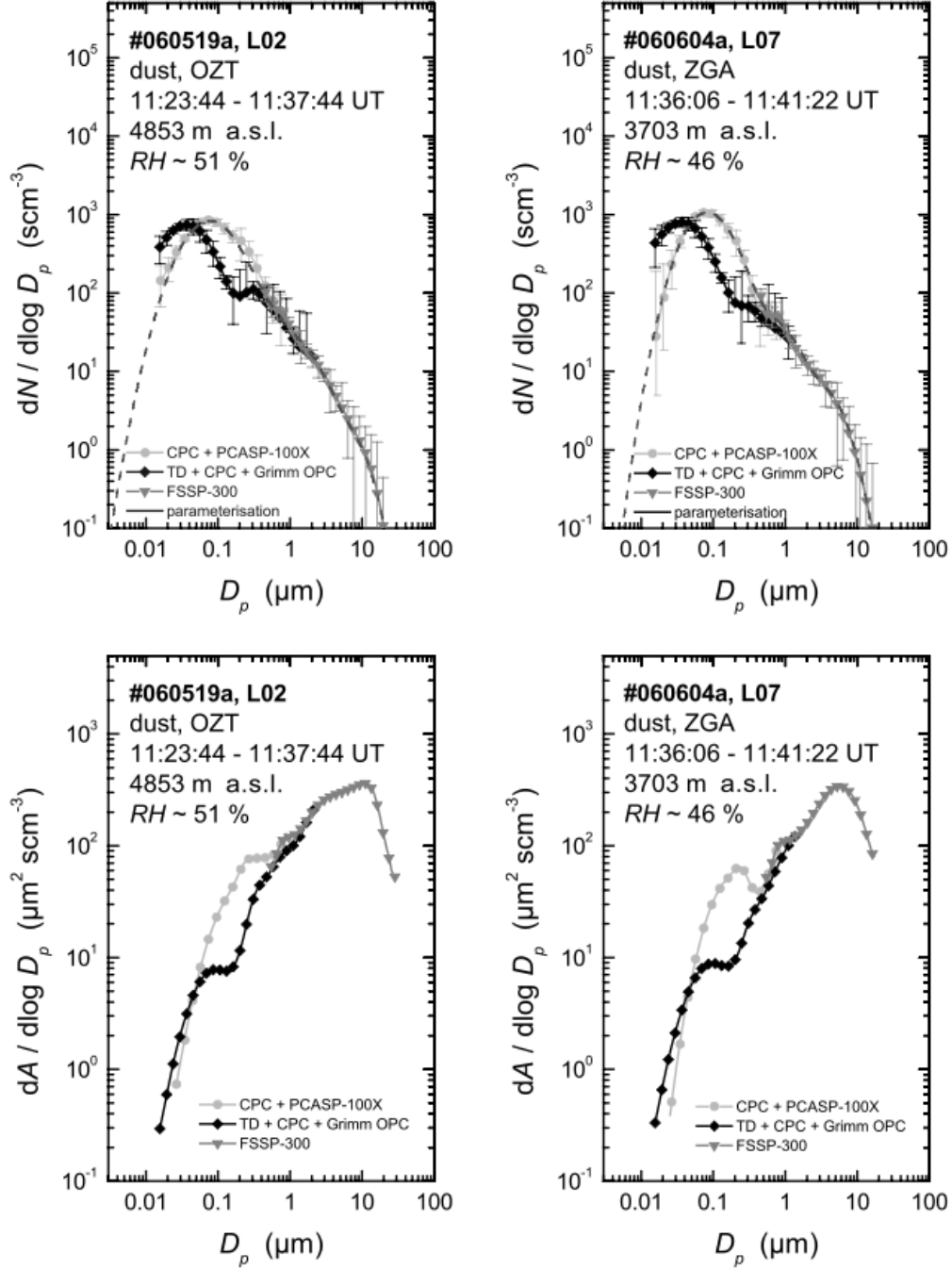


Figure 3.7. Number (top) and surface (bottom) size distributions of Saharan dust for two layers measured during SAMUM 2006. Black: non-volatile fraction after the thermal denuder (250 °C); light grey: total distribution; grey: extension to the coarse mode. Reproduced from (Weinzierl et al., 2009).

Thermal fractionation methods are used at different temperatures across various studies (Giechaskiel et al., 2020; Kupc et al., 2018; Swanson & Kittelson, 2010; Wehner et al., 2004; Weinzierl et al., 2009). These temperatures can vary between 250 and 400 °C, and are entirely dependent on the specific use of a device in its given context, e.g. whether one wants to remove all possible volatiles species or potentially is interested only in the removal of specific fractions. In fact, when extending the range of temperature used, even species that are not within atmospheric range of volatilities and may be considered refractory in that sense can be evaporated (O'Dowd et al.,

1992). This is made explicit by cycling the inlet temperature of an OPC and identifying species from their characteristic evaporation points. This can be seen in Figure 3.8.

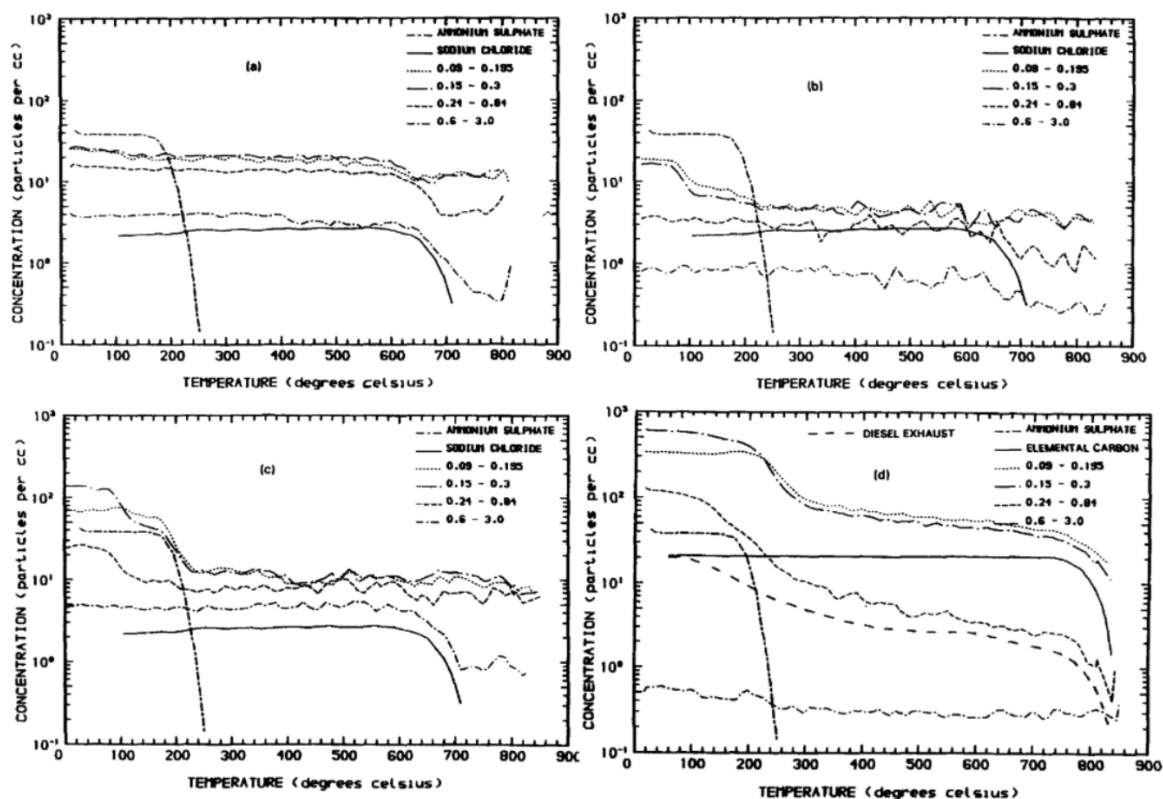


Figure 3.8. Temperature-dependent volatile fractions for (a) maritime aerosol at high wind speed, (b) Arctic aerosol, (c) modified Arctic aerosol, and (d) continental aerosol, determined using an optical particle counter downstream of a heated inlet. Reproduced from (O'Dowd et al., 1992).

They cycle the temperature from 20 °C to 870 °C effectively showing the decomposition of different species at 110 °C for H_2SO_4 , 220 °C for $(\text{NH}_4)_2\text{SO}_4$, 650 °C for NaCl and 820 °C for soot. Species that are effectively refractory at the temperatures used in atmospheric and automotive systems are therefore not refractory in any absolute sense - they simply lie above the chosen cut. This is an applied example of what the volatility basis set shows in numbers for the organic fraction. Volatility is a continuous value rather than binary, and the atmosphere equally presents a continuum of species, so any temperature chosen creates a cut within those species.

As far as atmospheric measurements are concerned, the primary device thus far has been a TD. However, for the removal of volatiles with minimal artifacts, catalytic processing, based on laboratory studies presented earlier, is expected to be a promising alternative and seems to be the most effective of the thermal fractionation methods discussed here. Since it avoids re-nucleation artefacts that are not unique to combustion aerosol (Section 3.1.2), the key question remains whether it could successfully be deployed for in situ atmospheric measurements. A remaining key limitation common to all of these methods is that the chemical identity of the evaporating material remains unknown (and so its evaporation temperature) without additional analysis. What is measured by a detector downstream of a TD or CS is the non-volatile mass or number fraction remaining after heating - that is, the fraction of aerosol that survives at a given temperature threshold set in the device - while the volatile fraction is lost to evaporation. The composition of neither fraction can be directly inferred from the measurement alone. Never-

theless, knowing the expected evaporation temperatures of the most commonly occurring urban aerosol components allows for a physically informed interpretation of the measured volatile and non-volatile fractions.

When including a device such as the CS into a measurement setup one needs to be aware of another thing before reading the data: instrumental artefacts, i.e. particle losses within the device that will bias the measurement product and must be accounted for. These losses arise from two main mechanisms: diffusion of small particles to the tube walls, and thermophoresis, which drives particles down the temperature gradient toward the cooler walls (Huffman et al., 2008). The following section will give theoretical insight to how these loss mechanisms work and will show the importance of characterizing a measurement device before gathering and interpreting results.

3.3. Relevant Aerosol Loss Mechanisms

When a new device (such as CS) is deployed in the field, it needs to be first characterized in the lab. As seen in the section above, particle losses both in the TD and CS are a critical quantity that needs to be accounted for. During the entry of any aerosol sample into an inlet system particles might be lost within the tubing. Equally when passing through any kind of measurement device before reaching the detection system losses are to be expected and should be accounted for. Generally, losses along sample tubing are caused by five different mechanisms: interception, inertial impaction, diffusion, gravitational settling and electrostatic attraction. They are responsible for the majority of aerosol deposition, whether this may be a sampling tube or deposition in the respiratory system. The first four are considered to be mechanical types of losses. Additionally one could face thermophoretic losses in devices governed by heating mechanisms (Hinds, 2022).

Studies of particle penetration within thermodenuders have shown that the main losses responsible in their case have been diffusional losses as well as thermophoretic losses. Sedimentation plays only a minor role in the submicron particle range (which is beyond the focus of this thesis), and thus is not discussed here.

3.3.1 Diffusional Deposition

Diffusional deposition occurs when small particles move due to Brownian motion, causing diffusion from high-concentration regions to low-concentration regions (Hinds, 2022). If the wall of any tubing is considered to be at zero concentration it effectively becomes a sink causing particle migration towards the wall. Thus, for small particles deposition at the wall becomes a prominent issue.

For laminar flow the transport efficiency depends on a single dimensionless deposition parameter

$$\xi = \frac{\pi DL}{Q}, \quad (3.1)$$

Brockmann, 2011, where L is the tube length and Q the volumetric flow rate. Notably, ξ does not depend on the tube diameter. The particle diffusion coefficient is given by

$$D = \frac{k_B T C_c}{3\pi\eta d}, \quad (3.2)$$

Hinds, 2022, with k_B the Boltzmann constant, T the absolute temperature, η the gas viscosity, d the mobility diameter and C_c the Cunningham slip correction factor. The transport efficiency is then a monotonically decreasing function of ξ alone (Brockmann, 2011).

While the general size range of diffusional losses cannot be defined, since it is dependent on geometric parameters of the measurement, Figure 3.9 shows that diffusional losses increase with decreasing particle size (Huffman et al., 2008). According to Burtcher et al. (2001), these losses amount to roughly 22 % at 10 nm, 10 % at 20 nm, and only about 1 % at 100 nm for their device - because these values depend on tube geometry, flow rate, and operating temperature, the actual losses vary between devices and configurations.

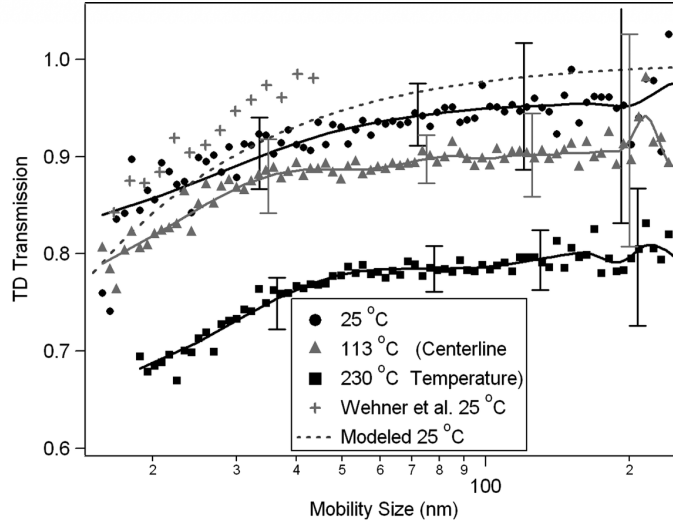


Figure 3.9. Particle number loss by size of a thermodenuder at three different temperatures. Reproduced from (Huffman et al., 2008).

It can be seen that particle losses in a TD increase both towards smaller particle sizes, consistent with diffusional deposition, and with increasing temperature. While the size dependence can be explained by the mechanism of diffusional deposition, the temperature dependence needs to be explained due to another loss mechanism, thermophoresis, which will be explained in the following section 3.3.2.

3.3.2 Thermophoretic Deposition

Once a gas is subject to a temperature gradient within sampling lines a suspended particle in that gas might be thermophoretically lost. Thermophoretic losses are caused by the particle moving down the gradient from higher to lower temperature; this movement is called thermophoresis. The balance between thermophoretic force and drag force is what gives the particle its thermophoretic velocity (Brockmann, 2011; Hinds, 2022), which can be written as

$$v_T = - \frac{2.8 \times 10^{-4} \text{ cm s}^{-1}}{\text{K cm}^{-1}} \frac{dT}{dx}, \quad (3.3)$$

This velocity is proportional to the temperature gradient and inversely proportional to the absolute temperature. It is not strongly dependent on particle size and becomes material-dependent for larger particles. Location is determined by the sign of the gradient: in the heated section the tube wall is hotter than the centre, causing particle drift away from the wall - in this case thermophoresis might compensate for some diffusional deposition. Most thermophoretic losses occur in cooling sections where warm aerosol meets a cold wall. Knowing temperature, drift velocity and residence time the drift distance can be calculated (Burtcher et al., 2001; Hinds, 2022):

$$s_T = v_T t, \quad (3.4)$$

All particles entering within that distance of the wall will be deposited (Burtscher et al., 2001). Thermophoresis is not strongly size-dependent, but it can move particles closer to the tube walls, where diffusion of small particles becomes more efficient (Huffman et al., 2008).

Figure 3.10 (Burtscher et al., 2001) shows that such losses can be reproduced by the theoretical mechanisms described above, as the modelled curves agree with the measured penetration.

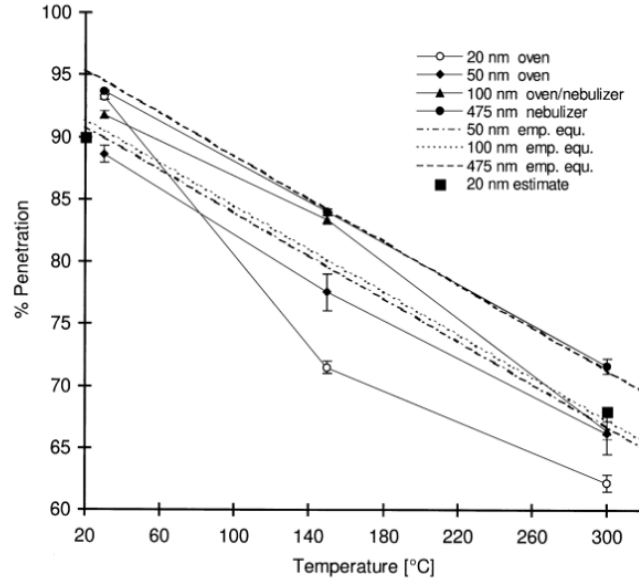


Figure 3.10. Losses in a thermodenuder as penetration in % versus temperature for multiple sizes; theoretical calculations are included. Reproduced from (Burtscher et al., 2001).

Once losses are characterized, the inverse relationship can be applied to ambient measurements to correct for mass lost as a function of temperature. Without this correction, the measured volatility response would be systematically biased (Huffman et al., 2008).

4. Experimental Methods

Before the catalytic stripper can be deployed for the first measurements at the Aerosol Observatory in Vienna, it must be characterized. This characterization constitutes the first research question of this thesis and is a prerequisite for addressing the second.

For the characterization, a series of in-lab experiments was designed. These experiments aimed to quantify the particle losses of the device. The following section describes the instruments used, the experimental setup, and their working principle. Section 4.2 further describes the setup of the Aerosol Observatory in Vienna and how the first ambient measurements with the catalytic stripper were conducted.

4.1. In-lab Characterization of the Catalytic Stripper

To address the first research question, an experimental plan consisting of three measurement stages was developed for the in-lab characterization of the catalytic stripper, and included:

- (1) Comparison of particle number concentrations measured by two condensation particle counters (CPCs; GRIMM 5410 with a cut-off size of 10 nm) to make sure both instruments are comparable and if not, quantify discrepancies. Details and the corresponding setup are presented in 4.1.2
- (2) Direct evaluation of particle losses in the catalytic stripper 4.1.2
- (3) Quantification of particle losses both in the CS and the sampling lines directly, in order to imitate the setup at the Aerosol Observatory 4.1.2

For the three stages of measurements a multitude of devices was used to build a functioning setup:

- A Silver Particle Generator (SPG) to generate the sample aerosol
- A soft X-ray charger
- A Differential Mobility Analyzer (DMA) for selection of a monodisperse aerosol of different sizes from the polydisperse sample generated
- A mixing section including dilution to ensure laminar, well mixed and sufficient flow
- A section of increased volume tubing to ensure additional mixing
- A flow splitting device that separates a singular sampling flow into equal separate lines of tubing
- The catalytic stripper
- Two Condensation Particle Counters (CPC) for counting of particle number concentration

The following section is going to give an insight of the working principle of each device and provides information on the instrument specification and their settings as used in the experimental

work described below. The corresponding experimental setup is presented in Section 4.1.2 below.

4.1.1 Devices

Silver Particle Generator (SPG)

The Silver Particle Generator (Catalytic Instruments GmbH & Co. KG, SPG-HT) serves as an aerosol source for any in-lab measurements performed in the context of this thesis. It produces silver nanoparticles with sizes between 2 and 300 nm in diameter, that are spherical below 20 nm, and in agglomerated shape above this size. They are refractory (non-volatile) entirely and chemically inert. A schematic of the SPG is presented in Figure 4.1.

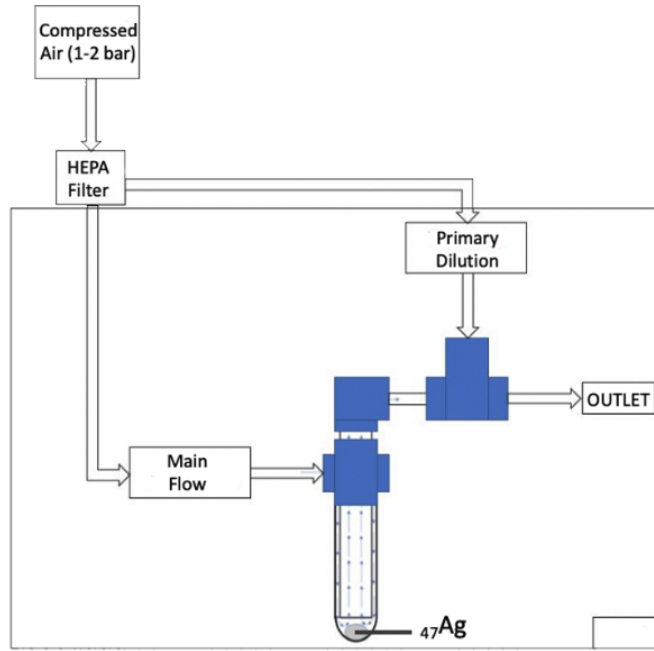


Figure 4.1. Schematic of the working principle of the SPG. Reproduced from (Catalytic Instruments GmbH & Co.KG, 2025)

Aerosol generation with the SPG follows the basic process of heating solid silver to its melting point of 961 °C, which vaporises the silver. Following vaporization, the silver atoms are brought into a cooling section, where condensation into nanoparticles can occur. Corresponding to figure 4.1, which shows compressed air (in this specific case N₂) entering the device and flowing into the thermal chamber where evaporated silver is suspended into the air stream. The main flow may be chosen between 0.1 and 5 l min⁻¹. The sampling line is then guided out of the instrument, where the cooling and subsequent particle formation occurs. Dilution may be added to increase the main flow up to 25 l min⁻¹.

Generation of silver particle size distribution between 2 and 300 nm in diameter is primarily dependent on the temperature setting of the SPG. The SPG reaches a temperature of 1250 °C, allowing for production of full size range as mentioned above. Adjustment of main flow and dilution flow rates may cause the size distributions at a given temperature to vary due to influence of aerosol residence time in the device and sampling system. For improved generation of larger particles, the instrument can be equipped with an integrated residence chamber or an external residence unit (P1000 PCRF Accessory Kit). These increase the aerosol residence time, promoting coagulation and agglomeration processes that result in further particle growth. If spherical particles >20 nm are required, an optional sintering unit (S8000 Particle Sintering Device) can be used to transform agglomerated particles into nearly spherical particles through thermal re-

structuring (Catalytic Instruments GmbH & Co.KG, 2025). Neither the residence chamber nor the sintering unit was employed in the experiments presented in this thesis.

For the experiments performed within the scope of this thesis the SPG was operated at a standard main flow rate of 2 l min^{-1} without additional dilution. This configuration provides the maximum particle size range achievable with the instrument under standard operation. The generated aerosol was transferred directly from the outlet of the SPG to the respective experimental setup without the use of a residence chamber. Under these conditions, the temperature settings used varied between 970 and 1110°C , providing silver particle sizes between approximately 10 and 100 nm .

Differential Mobility Analyzer

The sizes between 10 and 100 nm in diameter were further selected using a differential mobility analyzer (DMA). The size selection DMA is based on the separation of particles from a polydisperse aerosol according to their electrical mobility. Firstly, the particles need to be brought into charge equilibrium using a radioactive source or a soft X-ray upstream of the DMA. Then, in the DMA, charged particles are exposed to an electric field experience an electrostatic force, F_e , which causes them to move with a characteristic terminal velocity. This electrostatic terminal velocity is obtained by balancing the electrostatic force with the Stokes drag force (Hinds, 2022).

The motion of a particle in an electric field is described by its electrical mobility, Z , which is defined as the velocity of a particle carrying a charge of Ne in an electric field of unit strength. The electrical mobility is given by

$$Z = \frac{v_{TE}}{E} = \frac{NeC_c}{3\pi\eta d}, \quad \text{Re} < 1, \quad (4.1)$$

where v_{TE} is the electrostatic terminal velocity, E is the electric field strength, N is the number of elementary charges carried by the particle, e is the elementary charge, C_c is the Cunningham slip correction factor, η is the dynamic viscosity of air, and d is the particle diameter (Hinds, 2022).

A DMA then uses the electrical mobility of charged particles to select a nearly monodisperse aerosol fraction from a polydisperse aerosol source. The instrument typically consists of two coaxial cylindrical electrodes, as illustrated in Figure 4.2. The inner electrode is maintained at a high voltage, whereas the outer electrode is grounded (Flagan, 2011). The aerosol enters the classification region through a narrow inlet slit in the outer electrode. At the same time, a particle-free sheath flow is introduced into the DMA and transports the aerosol axially through the annular space between the inner and outer electrodes. The aerosol flow is therefore confined to a narrow region adjacent to the outer electrode at the entrance of the classification section (Flagan, 2011).

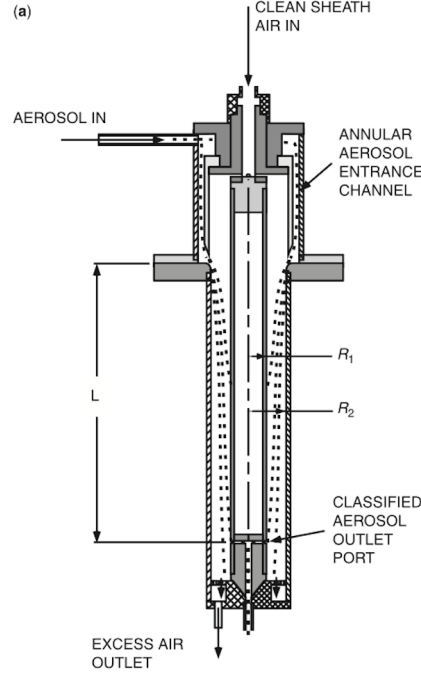


Figure 4.2. Schematic of the working principle of a cylindrical DMA, corresponding to the type of DMA used for this thesis . Reproduced from (Flagan, 2011)

The applied voltage generates a radial electric field between the two electrodes. Charged particles are consequently transported in two directions: they are advected downstream by the sheath flow, while simultaneously migrating radially towards the inner electrode according to their electrical mobility. Particles that travel the required radial distance between the aerosol inlet and the sample outlet during their residence time in the classification region are extracted through a narrow outlet slit in the inner electrode (Flagan, 2011).

Only particles within a narrow range of electrical mobilities reach the sample outlet. Particles with a higher electrical mobility migrate towards the inner electrode too rapidly and deposit on it upstream of the outlet slit. Particles with a lower electrical mobility do not migrate sufficiently far towards the inner electrode and are transported further downstream, where they leave the DMA with the excess flow. In this way, the DMA selects particles according to their electrical mobility and therefore, for a given particle charge, according to their particle size (Flagan, 2011).

By considering the geometric parameters of the DMA together with the operating flow rates, a characteristic electrical mobility can be determined for a given applied voltage. This characteristic mobility corresponds to the particle that enters the centre of the aerosol inlet flow and exits through the centre of the sample outlet (Flagan, 2011). It is given by

$$Z^* = \frac{(Q_{sh} + Q_e) \ln\left(\frac{r_2}{r_1}\right)}{4\pi V L}, \quad (4.2)$$

where Q_{sh} is the sheath flow rate, Q_e is the excess flow rate, V is the applied voltage, L is the classification length of the DMA, and r_1 and r_2 are the radii of the inner and outer electrodes, respectively. Since the electrical mobility is directly related to particle diameter, the selected particle size can be adjusted by varying the applied voltage or the operating flow rates (Flagan, 2011).

For the measurements performed in this thesis, a cylindrical Vienna-type DMA "RAX" was used. The DMA is denoted as RAX throughout this thesis. The abbreviation has no physical significance, but is retained for consistency with the measurement files and data evaluation.

A soft X-ray charger (TSI Advanced Aerosol Neutralizer) was used to charge the generated aerosol sample upstream of the DMA, allowing for size selection by electrical mobility.

This DMA is capable of classifying particles and producing a nearly monodisperse aerosol in a size range of approximately 5 to 800 nm. The DMA is operated by setting the voltage using a digital multimeter (DMM) controller. The voltage setting is adjusted manually according to the desired particle size, and is associated with an uncertainty of ± 0.0002 kV (± 0.2 V), which propagates to the uncertainty of the selected particle diameter through the calculation of particle diameter.

The particle diameter corresponding to a given DMA voltage was calculated using the spreadsheet supplied with the instrument. The calculation accounts for the DMA geometry, the operating conditions, and the Cunningham slip correction. Pressure and temperature were updated prior to each measurement according to the ambient conditions, while the fixed DMA parameters are summarized in Table 4.1. All particles were assumed to carry a single elementary charge ($N=1$).

Table 4.1. Operating parameters of the Vienna-type DMA "RAX" used in this work.

Parameter	Symbol	Value
Sheath flow rate	Q_{sh}	12.1 l min^{-1}
Inner electrode radius	r_1	4.8 cm
Outer electrode radius	r_2	5.6 cm
Classification length	L	39.4 cm

Condensation Particle Counter

To detect the number of monodisperse particles selected by the DMA, two Condensation Particle Counters (CPCs) GRIMM 5410, with a cut-off size of 10 nm were used. The cut off size is the size at which 50 % of incoming particles are counted by the CPC as compared to a reference instrument. CPC is a detection device for aerosol particles smaller than the optical detection limit in size ($\sim 0.1 \mu\text{m}$), by growing them in situ through controlled condensation of a working fluid onto their surfaces, until they reach several micrometers in diameter and can be counted optically. Vapor condenses onto pre-existing seed particles under supersaturated conditions in a process called heterogeneous nucleation, rather than forming new particles spontaneously (homogeneous nucleation) (Cheng, 2011).

This growth process is based on condensation theory, which describes the formation of a liquid phase from a supersaturated vapor. For small clusters re-evaporation is likely, whereas beyond a critical size further growth becomes energetically favourable and droplet growth by condensation occurs (P. M. Winkler & Wagner, 2022). The critical size is governed by the Kelvin equation. It relates the saturation ratio S to the smallest activable diameter D_p (Cheng, 2011).

$$\ln S = \ln \frac{p_v}{p_s(T)} = \frac{4 \cdot \nu \cdot \gamma}{R \cdot T \cdot D_p} \quad (4.3)$$

where

S	...	vapor saturation ratio
p_v	...	actual vapor pressure
$p_s(T)$	...	saturation vapor pressure as a function of temperature
ν	...	molar volume of the working fluid
γ	...	surface tension of the working fluid
R	...	universal gas constant
T	...	temperature
D_p	...	particle diameter

S is the ratio of the actual vapor pressure to the equilibrium vapor pressure over a flat surface. If $S = 1$, the liquid-vapor system is in equilibrium. For $S < 1$, evaporation is favourable in order to return to equilibrium conditions, and $S > 1$ corresponds to condensation as the dominating process. Thus, nucleation is favourable in supersaturated ($S > 1$) conditions (P. M. Winkler & Wagner, 2022). In a CPC a pre-existing seed particle enables heterogeneous nucleation which lowers the barrier so vapor can condense at lower supersaturation than during homogeneous nucleation (P. M. Winkler & Wagner, 2022). The Kelvin equation links the vapor saturation ratio to the smallest particle diameter that can be activated by heterogeneous nucleation, which in turn sets the smallest diameter a CPC can detect (GRIMM Aerosol Technik GmbH, 2025).

Figure 4.3 shows the working principle of a CPC as used in this work. The sample air is drawn in through the saturator. It contains a porous medium (wick) that is saturated with the working fluid of the device, n-butanol here. Heating of the saturator increases evaporation of the working fluid which leads to saturation of the sample flow (GRIMM Aerosol Technik GmbH, 2025).

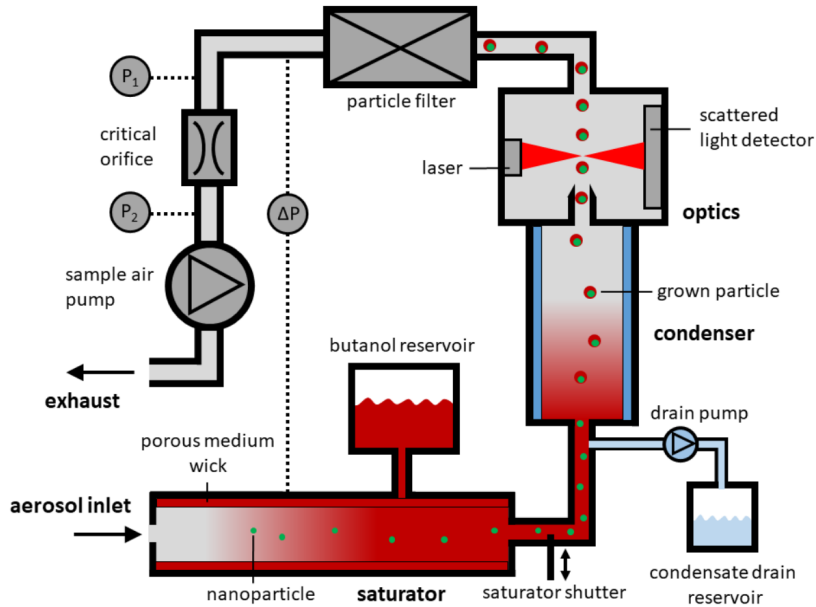


Figure 4.3. Schematics of the GRIMM CPC 5410 laminar flow, thermally diffusive condensation particle counter with the exception of the internal sample pump. The device in use uses an external pump. (GmbH, 2025)

The saturated sample flow is then lead into the condenser area where it is cooled, creating supersaturation of the butanol vapor. This corresponds exactly to heterogeneous condensation -

the particles act as condensation nuclei and grow into droplets several micrometers across, large enough to detect optically. The enlarged droplets are then counted via scattered light in an optical cell. A laser beam detects scattered light pulses in two counting modes: single-particle counting, which detects individual scattered-light pulses and is an absolute measurement, and photometric mode, which measures the total scattered light from an aerosol cloud (GRIMM Aerosol Technik GmbH, 2025).

Device specifications The Grimm CPC 5410 used for measurements is a thermally diffusive condensation particle counter operated at a flow rate of 0.6 l min^{-1} , controlled by a temperature-stabilized critical orifice at the inlet. It allows detection of up to $100\,000 \text{ cm}^{-3}$ in single-particle mode. At standard settings, the saturator is heated to 36°C and the condenser is cooled to 20°C , resulting in a lower cut-off diameter (D_{50}) of 10.0 nm , with 1 s data output and $\leq 95\%$ accuracy. Internal corrections of the CPCs account for coincidence effects.

The size-dependent counting efficiency of the CPCs used in this study (Grimm 3, CPC 5410, S/N 54102004 and Grimm 4, CPC 5410, S/N 54102005) was calibrated by the manufacturer at a volumetric flow rate of 0.6 l min^{-1} using silver particles (performed 19 December 2023). Figure 4.4 shows the manufacturer-specified efficiency curve, with a cut-off diameter $D_{50} = 9.69 \text{ nm}$ for Grimm 3 and $D_{50} = 9.95 \text{ nm}$ for Grimm 4.

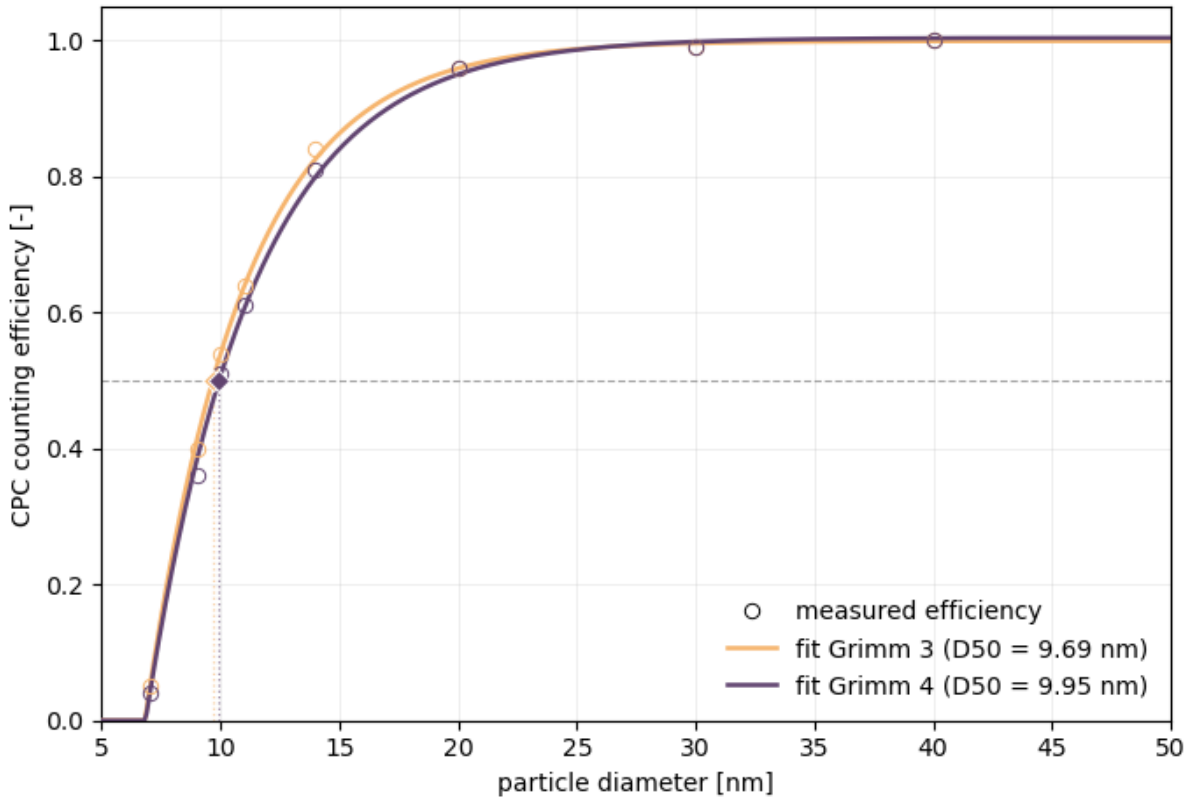


Figure 4.4. Measured counting efficiency of Grimm3 and Grimm 4, fit according to manufacturer with respective cutoff diameter for each device

To avoid coincidence, particle number concentrations were kept below approximately $10\,000 \text{ cm}^{-3}$ throughout this study.

Additionally, ambient aerosol measurements were recorded by two further Grimm CPCs operating at different cut-off diameters. The data from these two additional CPCs is not used in the core analysis of this thesis but is reported to document the full measurement setup and

provide context for the ambient conditions during sampling. Table 4.2 provides an overview on the specifications of all four models mentioned in this thesis.

Table 4.2. Operating parameters of the Condensation Particle Counters used in this study.

Device	Model	D_{50} (nm)	Saturation temp. (°C)	Condenser temp. (°C)	Inlet flow (L min ⁻¹)
Grimm 1	CPC 5410	4.55	36.0 ± 0.5	8.5 ± 0.5	0.599 ± 0.006
Grimm 2	CPC 5410	6.84	36.0 ± 0.5	17.0 ± 0.5	0.597 ± 0.006
Grimm 3	CPC 5410	9.69	36.0 ± 0.5	20.5 ± 0.5	0.588 ± 0.006
Grimm 4	CPC 5410	9.95	36.0 ± 0.5	20.5 ± 0.5	0.593 ± 0.006

Catalytic Stripper

The Compact Catalytic Stripper CCS004 characterized in this work (seen in Figure 4.5) is a custom-modified Catalytic Stripper by Catalytic Instruments GmbH & Co. KG. It is designed to minimize particle losses for the application with the GRIMM CPC 5410 used in this study and the system setup for in situ aerosol measurements at the University of Vienna. The working principle of CS is described earlier in section 3.1.2, and is only briefly mentioned here.



Figure 4.5. Catalytic Stripper CCS004 by Catalytic Instruments GmbH & Co. KG. (photo credit: Marlene Hotz)

The CCS004 is operated at a core temperature of 350 °C and a flow rate of 0.6 l min⁻¹ at atmospheric pressure. The operating principle of the CCS004 is to evaporate semi-volatile particles in a heated section. The resulting gas phase compounds are oxidized using a catalyst at the end of the heated section. A subsequent cooling section lowers the temperature of the aerosol sample to near ambient conditions before the sample exits at the outlet of the CCS004 (Catalytic Instruments GmbH & Co.KG., 2022).

4.1.2 Setup

Comparison of CPCs

A combination of the previously listed devices can now be used to explain the measurement setup for the characterisation of the catalytic stripper. The CPCs need to be compared and any differences in responses between these two devices need to be quantified. This is a critical starting point in order to evaluate the particle losses along sampling lines or within measurement

devices. There should not be any variability between the counting instruments themselves, or at the least, any offset needs to be previously determined so it can correctly be accounted for. This comparison was done for both monodisperse (silver particles) and polydisperse (indoor lab air) aerosol.

Comparison of CPCs using monodisperse silver particles

As shown in Figure 4.6, a SPG (at 21min^{-1}) was used to produce a silver aerosol, which was then brought into charge equilibrium using the soft X-ray charger. The sample was further passed through a DMA (Q_{sh} and Q_{ae} flow rates of 12.11min^{-1} and 21min^{-1} , respectively) to select a monodisperse size fraction. Discrete particle sizes between 10 and 100 nm were selected sequentially. The sample was then led from the DMA through a mixing section used to provide thorough mixing of the sample aerosol with dilution flow in order to meet the flow rates of the devices. It was then led through a section of tubing with increased diameter to "relax" the aerosol. The aerosol was distributed through a three-way flow splitter, with both CPCs (sampled at 0.61min^{-1}) connected to the outer paths at equal line lengths (23 cm) to ensure identical particle losses. To avoid the additional particle losses introduced by the branching angle, the central path was not used for sampling but was instead fitted with a critical orifice drawing 21min^{-1} . The additional flow required at the sampling end was supplied as a clean, particle-free dilution flow through an annular gap mixer (mixing section), establishing flow equilibrium between the generation and sampling ends of the setup. For each selected size, an interval of up to five minutes was recorded, from which a one-minute interval was extracted for the data analysis.

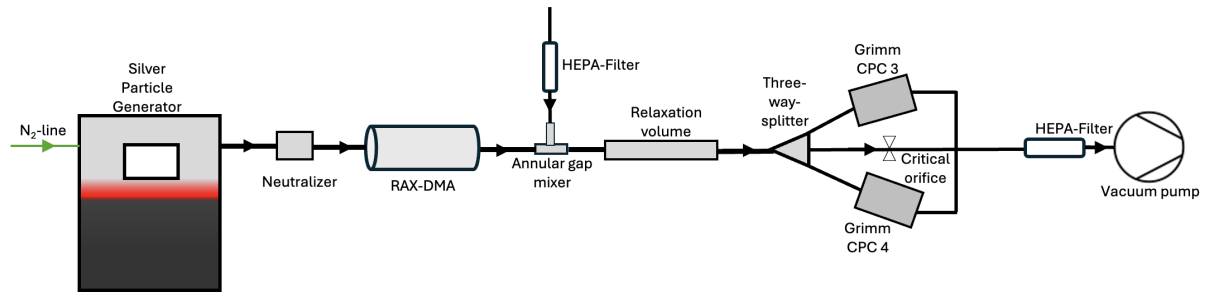


Figure 4.6. Setup used to determine comparability of the measured number concentrations of both Grimm CPCs . Adapted from work of Mickajel Jengojan, University of Vienna

The flow rates were verified with flowmeters (Gilibrator 2 - Gilian Sensidyne - Bubble Flowmeter/TSI Thermal mass flowmeter 4140) to confirm that the instruments operated at their nominal set-points, on which their internal calculations of particle number concentration rely. Measured flows agreed with the set-points within $\pm 0.005\%$, confirming that the instruments' calculations are applicable. SPG settings were chosen in a range of 990 and 1100°C to provide a maximum concentration of $10\,000\text{cm}^{-3}$ to avoid coincidence correction.

Comparison of CPCs using polydisperse indoor lab air

In addition, a short measurement of approximately 15 minutes was carried out in which the particle generator and DMA were bypassed and ambient (polydisperse) laboratory air was sampled. This allowed the CPC response to be compared not only for the size-selected monodisperse silver aerosol but also for polydisperse ambient air. To perform this measurement the setup described in the previous section 4.1.2 was disconnected after the DMA, so that laboratory air entered the setup through the mixing section. The setup downstream of the DMA remained unchanged.

Characterization of Catalytic Stripper

After making sure both CPCs were comparable, the next steps focused on the quantification of the losses in the CS for both CS settings, one at room temperature (referred to as “cold”) and at its operating temperature of 350 °C (referred to as “hot”). This was done using monodisperse silver particles. In addition, the response time of CS when changing temperature settings from room temperature to 350 °C was investigated using polydisperse particles present in laboratory air.

The approach of studying CS at cold and hot settings allows to distinguish between diffusional and both, diffusional and thermophoretic losses in the CS. Comparing the total number concentration measured by two CPCs between the two lines indicates the overall particle losses caused by the additional device (i.e. CS), while particle size selection provides information on the size dependency of these losses.

Determination of particle losses in CS at hot and cold CS settings

To determine the particle losses in CS the setup, as seen in Figure 4.7, was kept largely the same as in the previous section, with the difference being that now the catalytic stripper was included and placed directly in front of CPC 4, extending the distance between the flow splitter and the CPC by the length of the device only, without any additional tubing. The reference CPC 3 was connected to the flow splitter using 23 cm of conductive tubing, whereas the path to CPC 4 consisted of the same 23 cm of tubing followed by the catalytic stripper, which adds an external device length of 60 cm. This ensured that any decrease in particle number concentration could be attributed solely to losses occurring within the device.

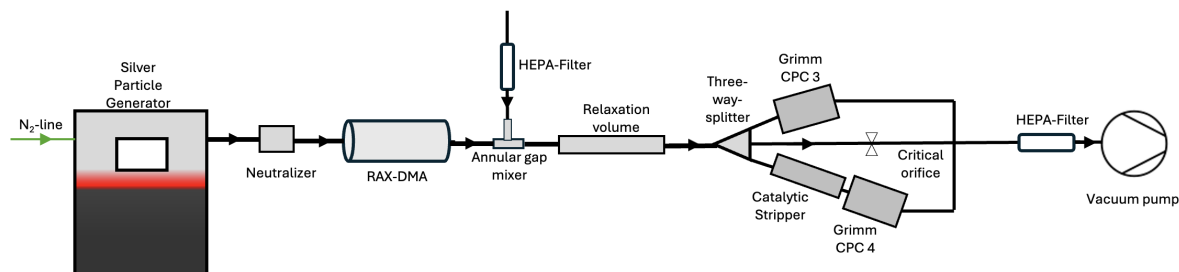


Figure 4.7. Setup to determine transmission efficiency due to absolute particle losses from sample stream passing through CS. Adapted from work of Mickajel Jengojan, University of Vienna

Silver particles were again the core component of the aerosol generation. Because silver is refractory, the particles were expected to remain essentially unaffected by the heat and the catalyst of the catalytic stripper. Any losses observed could therefore be attributed to diffusional and thermophoretic deposition within the device, rather than to evaporation of the particles themselves.

The measurement was carried out in two sessions. Since all flow-relevant devices were identical to those used previously, the flow configuration remained unchanged. In the first session, the catalytic stripper was kept cold (i.e. operated at room temperature), so that any losses observed were due to diffusional deposition. As before, particle sizes 5 and 100 nm were selected.

The measurement was then repeated at the hot CS setting, meaning with the catalytic stripper at 350 °C. Any additional losses observed in this case also included thermophoretic losses, again as a function of particle size.

Determination of particle losses in the CS under measurement configuration at the Aerosol Observatory

Following the determination of particle losses within the CS itself, the next step focused on the quantification of particle losses both in the CS and the sampling lines directly leading to it, in order to imitate the setup at the Aerosol Observatory.

For this purpose, the setup again remained largely the same, with one difference: the sampling line of the reference CPC was extended, as seen in 4.8. In the previous configuration, only the line containing the catalytic stripper was extended (by the device, 60 cm), while the reference CPC remained closer to the flow splitter. In this configuration, the reference line was extended by a length of stainless steel tubing equal to the total length of the catalytic stripper (60 cm). This tubing acted as a dummy in the parallel sampling line, matching the two paths in length. The flow distribution, the size range, and all remaining components of the setup were identical to those described previously.

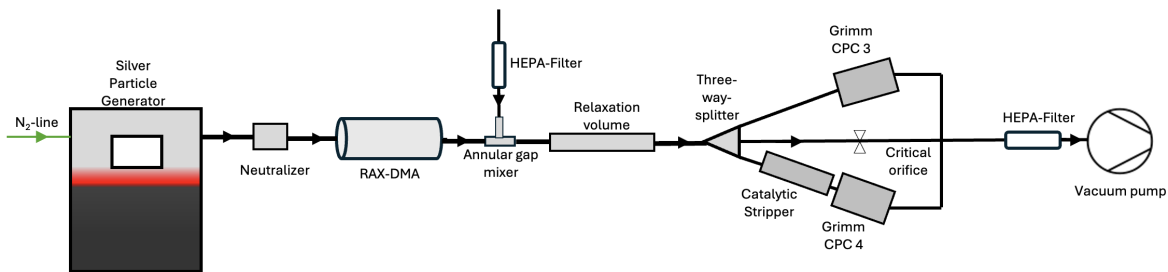


Figure 4.8. Setup to determine transmission efficiency due to particle losses when simulating conditions at the AerObs. Adapted from work of Mickajel Jengojan, University of Vienna

The purpose of this configuration was to reproduce the conditions encountered in actual aerosol measurements, where an inlet is followed by sampling lines of equal length to the counting instruments. This allowed the measurement efficiency to be determined under realistic conditions, in preparation for the ambient measurements at our observatory and providing a representative estimate of the efficiency expected there.

Determination of the CS response time to a change in CS temperature setting

Finally, an interval of polydisperse laboratory air was measured during the heating phase (transition from cold to hot CS setting) of the catalytic stripper. The setup displayed in Figure 4.7 was disconnected downstream of the DMA, sampling laboratory air, with all devices following this point of disconnect remaining unchanged. This measurement provided a time-resolved view of the device warming up: it indicated the time required to reach full operating temperature.

Preliminary Laboratory Work

Part of the preliminary laboratory measurements had already been carried out prior to the main measurement that used RAX DMA. Initial measurements relied on a different DMA i.e. nano-DMA. In this preliminary setup, neither the mixing section nor the mixing volume tube was installed. Apart from these different components, the arrangement was identical to the setup described in the previous sections. Since there were issues with the nano-DMA (i.e. configuration did not provide a stable, well-mixed laminar flow) the experimental setup was modified, and RAX DMA was used instead of nano-DMA resulting in the final configuration used for the main

measurements. However, a small number of reliable and reproducible datapoints obtained during these preliminary measurements is nevertheless included as additional reference points.

4.2. Measurement of Non-Volatile and Volatile Aerosol Fraction at the Aerosol Observatory

To address the second research question, which focuses on the number fraction of non-volatile material during measurements, the CS was deployed for a trial measurement period at the Aerosol Observatory to characterize the volatile and non-volatile fractions of ambient aerosol. These measurements were carried out over a two-week period, from 2026-04-20 to 2026-05-03.

The Aerosol Observatory of the University of Vienna is an aerosol measurement facility located at 32 m above ground level on the rooftop of the Faculty of Physics of the University of Vienna. The facility represents an urban background site for aerosol in situ measurements and is in the process of becoming an ACTRIS National Facility.

As shown in Figure 4.9, ambient air is sampled through a PM_{2.5} (i.e. particulate matter with an aerodynamic diameter of 2.5 μm or less) inlet head, then passes through Nafion dryers and reaches a setup in which the flow is split several times and distributed among a number of instruments. Of primary relevance to these measurements are again CPC 3 and CPC 4, connected to the side arms of the central pathway, with CPC 4 being the instrument initially equipped with the catalytic stripper in its sampling line. The lengths and shapes of the sampling lines shown in the figure do not correspond directly to reality, they were chosen for clarity of illustration.

During this period, all four CPCs sampled ambient air according to their respective cut-off diameters and the CS was continuously operated at 350 °C. CPC 3 and CPC 4, which share the same cut-off, were connected by sampling lines of equal length. Their setup followed the same dual sampling line configuration used for the laboratory characterization, with one line incorporating the CS and a parallel reference line equipped with stainless steel tubing of equivalent length to match the flow residence time and diffusional losses.

For the first 10 days, and in accordance with the laboratory measurements, CPC 4 was the instrument positioned behind the catalytic stripper, sampling polydisperse urban air. For the final 3 days of the measurement period, CPC 3 and CPC 4 were interchanged, so that CPC 3 was placed behind the catalytic stripper and CPC 4 on the parallel sampling line. This switch was carried out to test the reproducibility of the response and to confirm that it was independent of the specific instrument used.

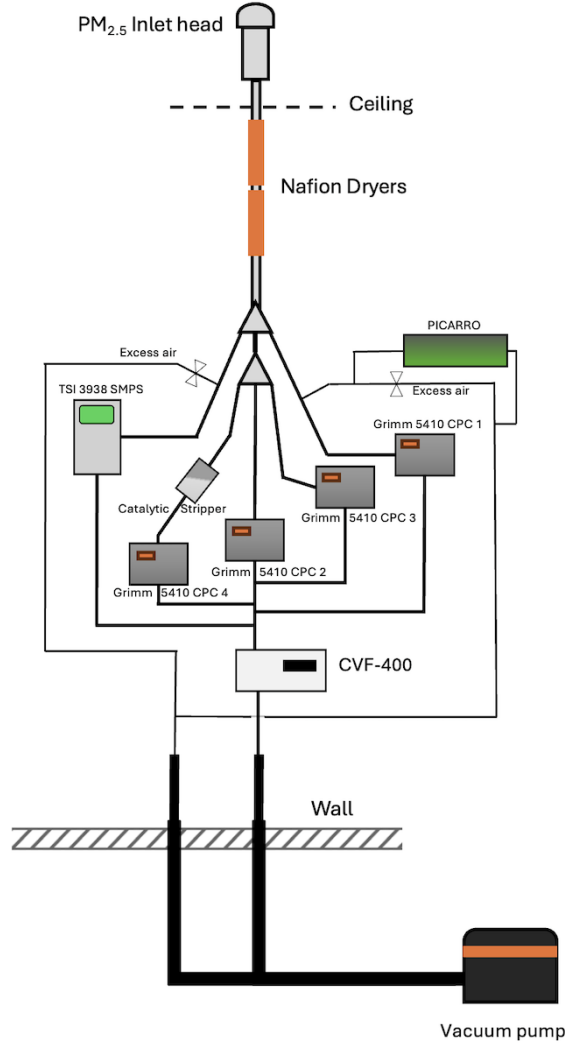


Figure 4.9. Setup used for preliminary measurements using CS at the Aerosol Observatory at the University of Vienna. Created by Mickajel Jengojan.

4.3. Data Analysis

Laboratory work

Particle number concentration used in analysis was taken from the CPC data files. The particle number concentration after the internal coincidence correction factor had been applied was used for all data analysis. During all measurements sample concentrations were kept below $10\,000\text{ cm}^{-3}$ to avoid coincidence. For all laboratory work aerosol was sampled at approximately two to five minute intervals, from which a constant one-minute interval was extracted for the data evaluation.

The difference between CPCs of each interval was calculated by

$$\text{diff}_{\text{rel}} = \frac{\bar{N}_4 - \bar{N}_3}{\bar{N}_3} \cdot 100\%, \quad (4.4)$$

where $\bar{N}$ is the concentration mean over an interval, with CPC3 being defined as the reference device. Boxplots that show the statistical behaviour within each measurement interval are provided in appendix figure B.1.

For the comparison of CPCs using polydisperse indoor lab air and determination of the CS response time to a change in CS temperature setting again, the same particle number concentration provided by the CPC data files was used and plotted as a time series of all raw data points. Figure 5.2 shows a relative difference calculated per data point by

$$\text{diff}_{\text{rel},i} = \frac{N_{4,i} - N_{3,i}}{N_{3,i}} \cdot 100 \%, \quad (4.5)$$

where N is the concentration. The relative difference shown in figure 5.2 was resampled to 10s for visual purposes only. All data provided was calculated from raw data.

For the characterisation of the catalytic stripper, the transmission efficiency η was determined for each measured size interval as the ratio of the mean concentrations of both instruments,

$$\eta = \frac{\bar{N}_4}{\bar{N}_3}, \quad (4.6)$$

with CPC3 serving as the reference instrument.

Each concentration mean carries a statistical standard error ($s/\sqrt{n}$) and a systematic CPC uncertainty (5 % per instrument, manufacturer specification), combined in quadrature. Uncertainties were propagated through the derived quantities using Gaussian error propagation.

Measurements at the Aerosol Observatory

Particle number concentrations downstream of each line were measured simultaneously using the same two CPCs operating at the same cut-off diameter, allowing direct comparison between the total and non-volatile aerosol populations. The non-volatile number fraction (NVNF) was derived as the difference between total particle number concentration and the non-volatile particle number concentration according to:

$$\text{NVNF} = \frac{\text{PNC}_{\text{non-vol}}}{\text{PNC}_{\text{total}}} \quad (4.7)$$

Any daily analysis was done using raw, unsmoothed data from CPC data files. Unexpected spikes (will be discussed at a later point) within the raw data were removed to provide better visual data display, as can be seen in the plots. The weekly overview plots show data that was resampled to 60s bins, the NVNF was calculated after re-sampling.

5. Results

5.1. Characterization of the Catalytic Stripper in the Laboratory

The following section will show the results of all conducted laboratory measurements, showing the comparability of CPCs used, as well as the particle losses that were determined for both configurations described.

5.1.1 Comparison of CPCs

Comparison of CPCs using monodisperse silver particles

Results of the CPC comparison are presented in Figure 5.1. It shows the relative difference between the concentrations measured by the two CPCs as a function of particle diameter. Below 20 nm, the relative difference increases with decreasing particle diameter. Above 20 nm, the difference levels off and reaches a plateau of approximately $(1.07 \pm 0.08) \%$, with a maximum deviation of 1.15 % across all points in this range. The preliminary measurement points lie below the zero reference line, but within the same range of relative difference as the main measurements. With the exception of the smallest size interval at 9.5 nm, all data points lie within 5 % deviation from the 0 % reference line.

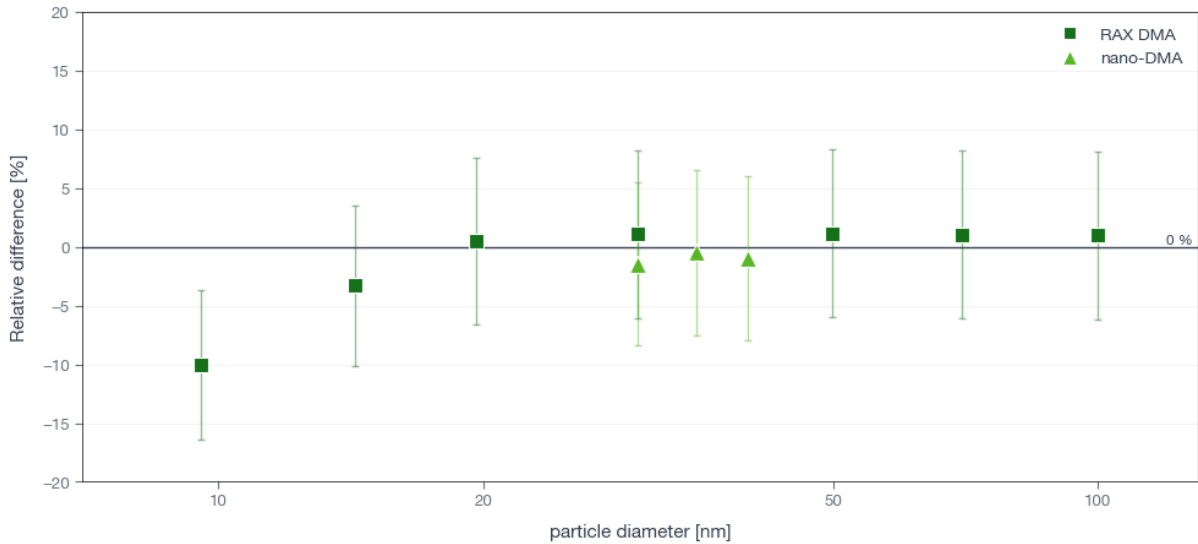


Figure 5.1. Relative difference between CPC3 and CPC4, referenced to CPC3, as a function of particle diameter. Each data point corresponds to one measured size interval. The symbols denote the DMA used: squares represent the main sequence of measurements performed with the RAX DMA, whereas triangles show reproducibility points measured during preliminary measurements using a nano-DMA.

Comparison of CPCs using polydisperse indoor lab air

An additional measurement was carried out to characterise the difference between the two instruments without size selection. In this case, no test aerosol was generated. Ambient laboratory air was sampled directly, so that the total number concentration was measured by both CPCs and varied between 275 and 400 cm⁻³. Figure 5.2 shows the resulting concentration time series. The number concentrations of both instruments overlap continuously throughout the measurement period, and the relative difference remains within 10 % over the entire period. The mean relative difference amounts to $(-0.80 \pm 0.04) \%$.

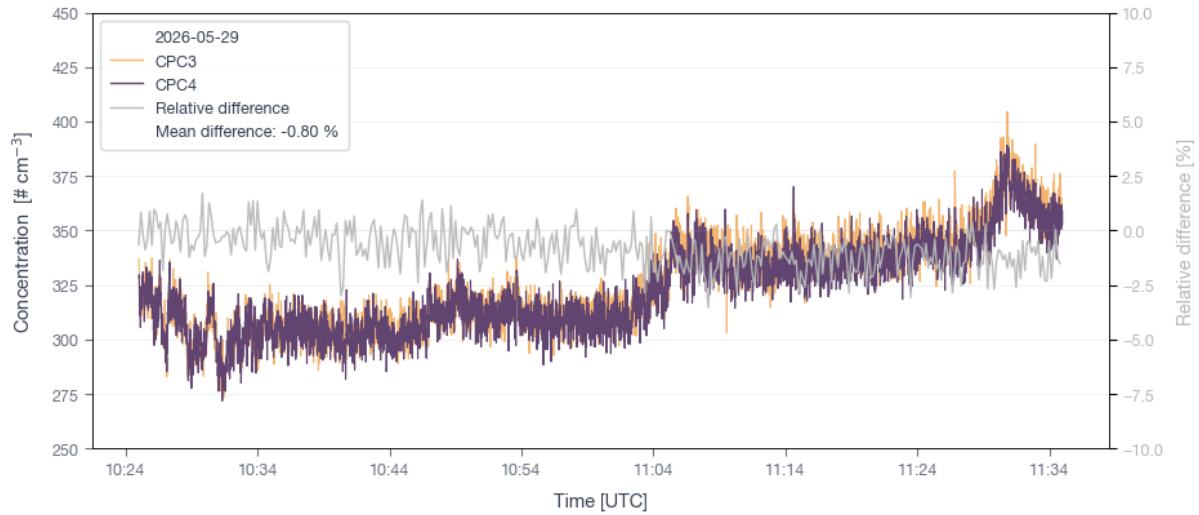
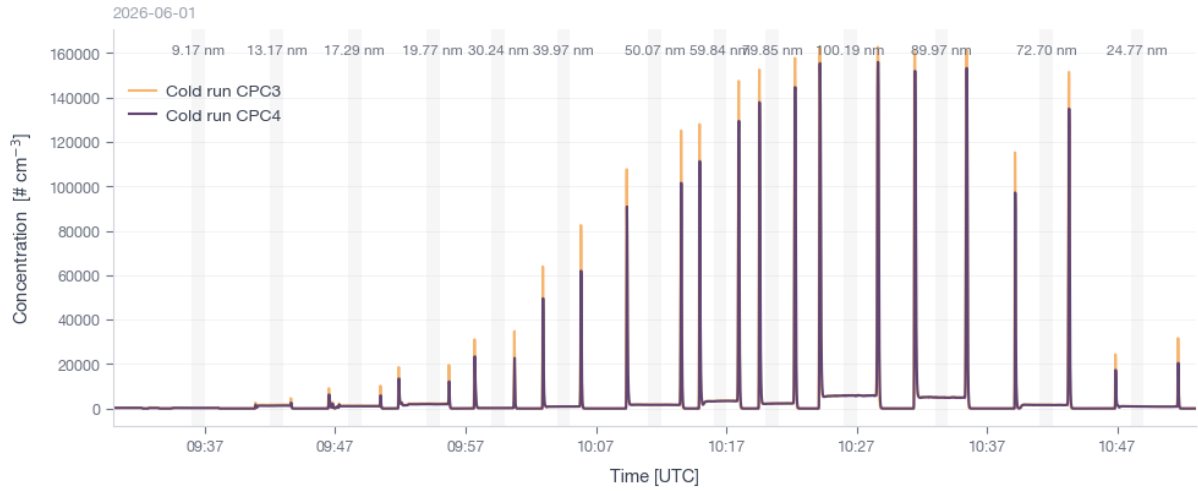


Figure 5.2. Number concentrations measured by both CPCs (left axis) and their relative difference referenced to CPC3 (right axis) for ambient laboratory air. The difference curve shown is smoothed over 10 s for better visibility. All reported values are based on the unsmoothed data. The dotted horizontal line marks zero difference.

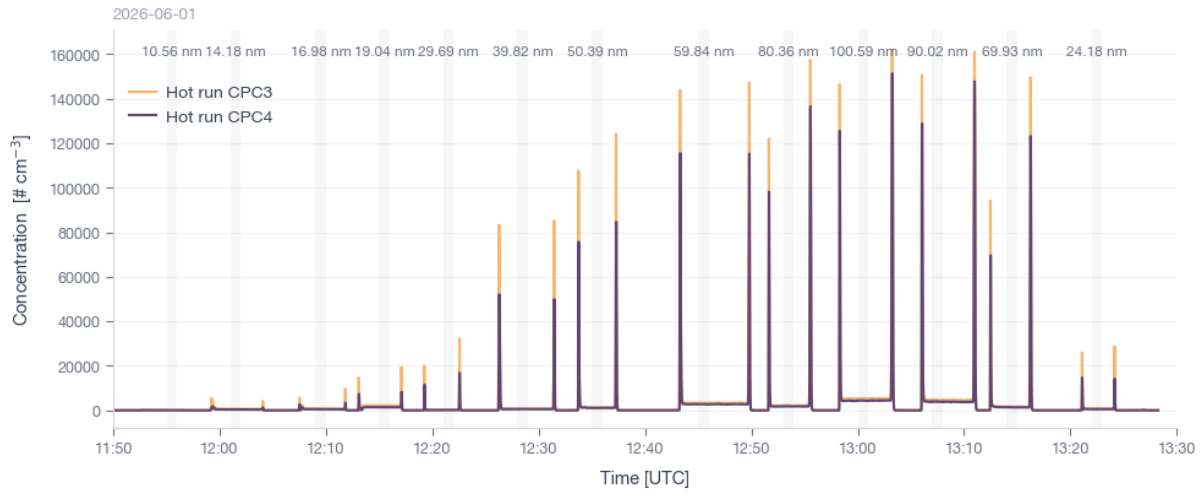
5.1.2 Determination of Particle Losses in the Catalytic Stripper

Time series

Time series of the recorded data are presented in Figure 5.3 (1 s data points). It shows the time series of the measurement intervals for both the cold run and the hot run of the catalytic stripper characterisation, corresponding to the setup described in Sect. 4.1.2. Intervals were recorded in a size range from 9 nm to 100 nm. The concentration levels varied depending on the output of the aerosol particle generator but only particle number concentrations below 10 000 cm⁻³ were used for data evaluation to avoid coincidence issues in the CPCs. The grey shaded areas indicate the measurement intervals selected for data analysis. High peaks are related to the adjustment of the DMA high voltage setting and are not used or relevant for data analysis.



(a) Measurement intervals during the cold run of the catalytic stripper.

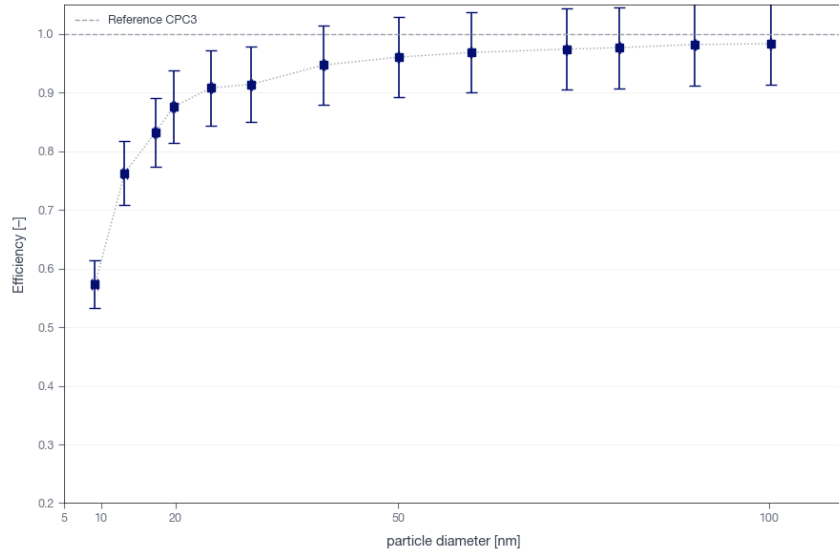


(b) Measurement intervals during the hot run of the catalytic stripper.

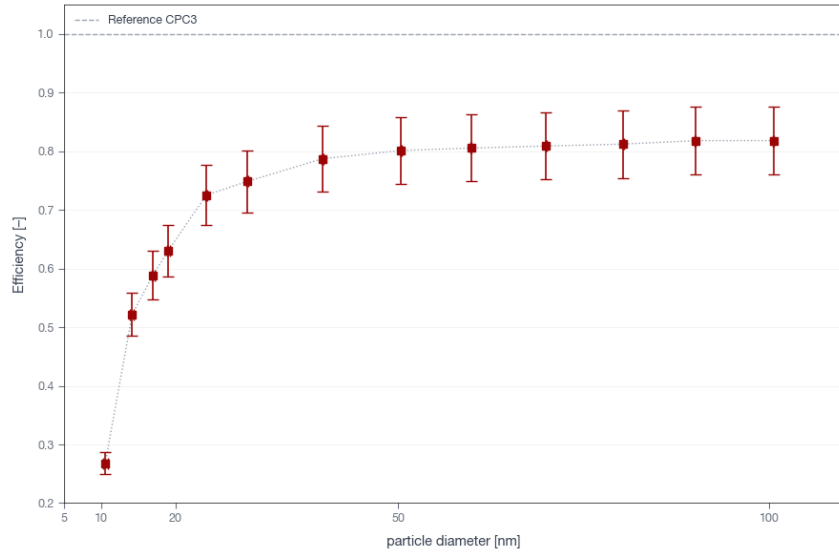
Figure 5.3. Concentration time series of both CPCs during the catalytic stripper characterisation. Grey shaded areas mark the intervals selected for data analysis; the labels give the selected particle size.

Transmission efficiency

Result of the determination of transmission efficiency is presented in Figure 5.4. It shows the measured transmission efficiency for the setup described in Sect. 4.1.2. During the cold run, the transmission efficiency increases with increasing particle size, with a minimum of 0.573 ± 0.041 at the smallest particle diameter of 9 nm and a maximum of 0.983 ± 0.070 at the largest diameter of 100 nm. The same behaviour is observed for the hot run, where the transmission efficiency also increases with increasing particle size. However, the overall transmission is considerably lower during hot operation of the catalytic stripper, with a minimum of 0.268 ± 0.019 at 10 nm and a maximum of 0.818 ± 0.058 at 100 nm.



(a) Cold run of the catalytic stripper.



(b) Hot run of the catalytic stripper.

Figure 5.4. Transmission efficiency as a function of particle diameter, determined as the ratio of the concentrations measured downstream and upstream of the catalytic stripper.

Figure 5.5 shows the transmission efficiencies of the cold and hot characterisation in a single plot, in which the downward shift in transmission efficiency during hot operation of the catalytic stripper is clearly visible. In addition, comparable data from the preliminary measurements using the nano-DMA are included. Although the data points do not fully coincide with those of the main measurements, these are within the uncertainties, and the same trend is observed. At comparable particle sizes, the data points of the preliminary measurements agree with the main measurements within their respective uncertainties.

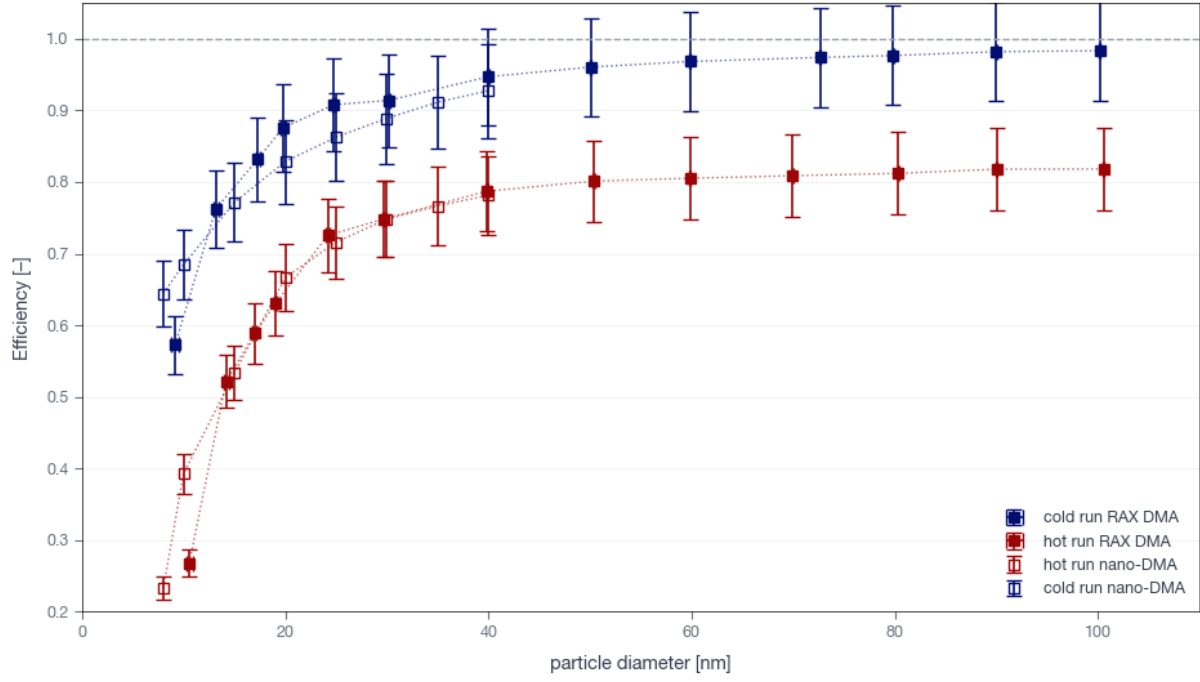
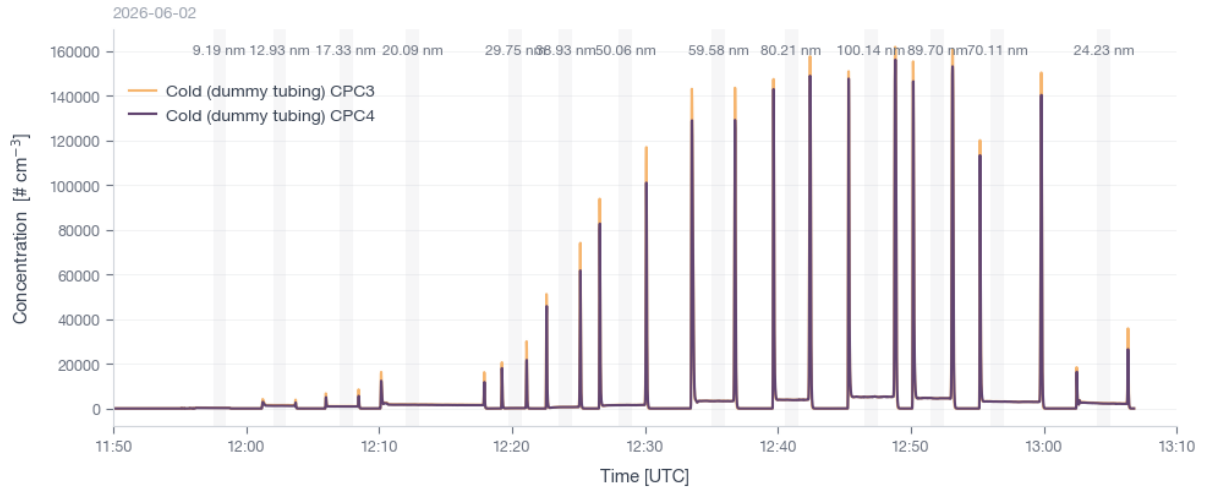


Figure 5.5. Transmission efficiency of the catalytic stripper for cold and hot operation as a function of particle diameter. Filled symbols denote the main measurements, open symbols the preliminary measurements performed with the nano-DMA.

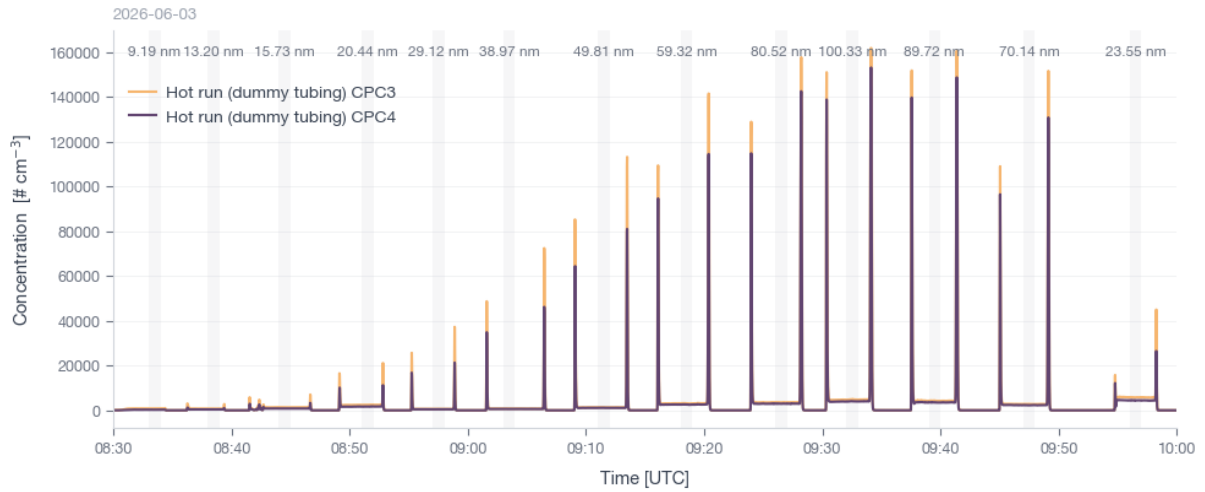
5.1.3 Determination of Particle Losses in the CS under Measurement Configuration at the Aerosol Observatory

Time series

Figure 5.6 shows the time series of the measurement intervals for both the cold run and the hot run of the measurement simulated catalytic stripper characterisation, corresponding to the setup described in Sect. 4.1.2. It provides an overview of how the experiment was conducted. Data was taken for sizes between 9 nm and 100 nm. The concentration levels varied depending on the output of the aerosol particle generator. The grey shaded areas indicate the measurement intervals selected for data analysis. High peaks are related to the adjustment of the DMA high voltage setting and are not used or relevant for data analysis.



(a) Measurement intervals during the measurement simulated cold run of the catalytic stripper.

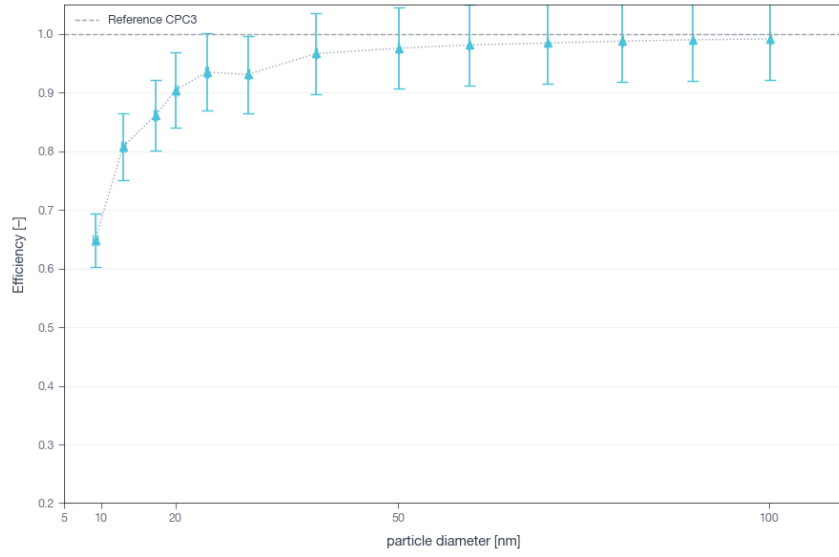


(b) Measurement intervals during the hot run of the catalytic stripper.

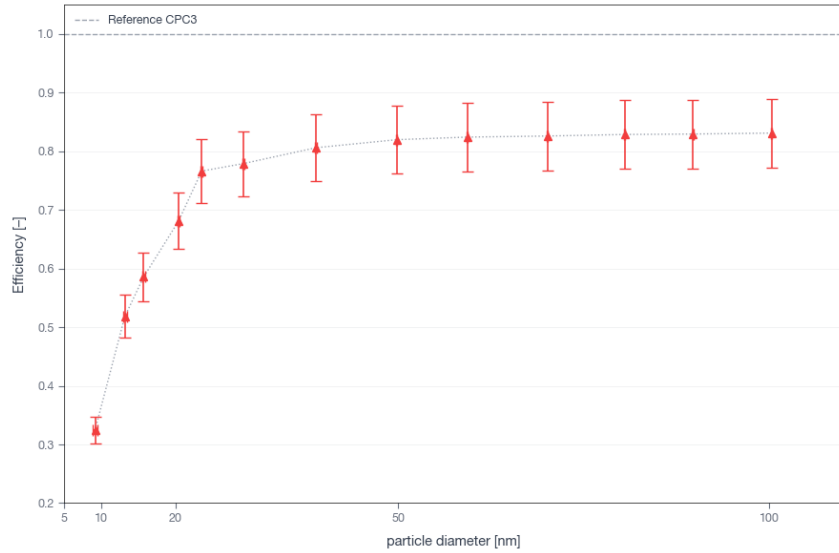
Figure 5.6. Concentration time series of both CPCs during the measurement simulated catalytic stripper characterisation. Grey shaded areas mark the intervals selected for data analysis; the labels give the selected particle size.

Transmission efficiency

Figure 5.7 shows the measured transmission efficiency for the setup described in Sect. 4.1.2. During the cold run, the transmission efficiency increases with increasing particle size, with a minimum of 0.648 ± 0.046 at the smallest particle diameter of 9 nm and a maximum of 0.992 ± 0.070 at the largest diameter of 100 nm. The same behaviour is observed for the hot run, where the transmission efficiency also increases with increasing particle size. However, the overall transmission is considerably lower during hot operation of the catalytic stripper, with a minimum of 0.325 ± 0.023 at 10 nm and a maximum of 0.831 ± 0.059 at 100 nm.



(a) Cold run of the measurement simulation with catalytic stripper.



(b) Hot run of the measurement simulation with catalytic stripper.

Figure 5.7. Transmission efficiency as a function of particle diameter, determined as the ratio of the concentrations measured downstream of the catalytic stripper and downstream of stainless steel tubing simulating the length of the catalytic stripper device.

The final plot of the laboratory characterisation, Fig. 5.8, combines the transmission efficiencies of all measurement runs: the cold and hot run of the characterisation of the catalytic stripper itself, for which the concentration was measured downstream and upstream of the device, as well as the cold and hot run of the corresponding reference configuration, in which the catalytic stripper was replaced by a piece of stainless steel tubing of equal length. The preliminary measurements performed with the separate DMA are excluded here for better visibility of the main measurements.

All curves follow the same trend of increasing transmission efficiency with increasing particle diameter. Between the cold and the hot runs, a gap of approximately 15 % is observed. For the cold run, the efficiency curve obtained with the dummy tubing lies continuously slightly above the curve measured directly upstream and downstream of the device. The same behaviour is found for the hot runs.

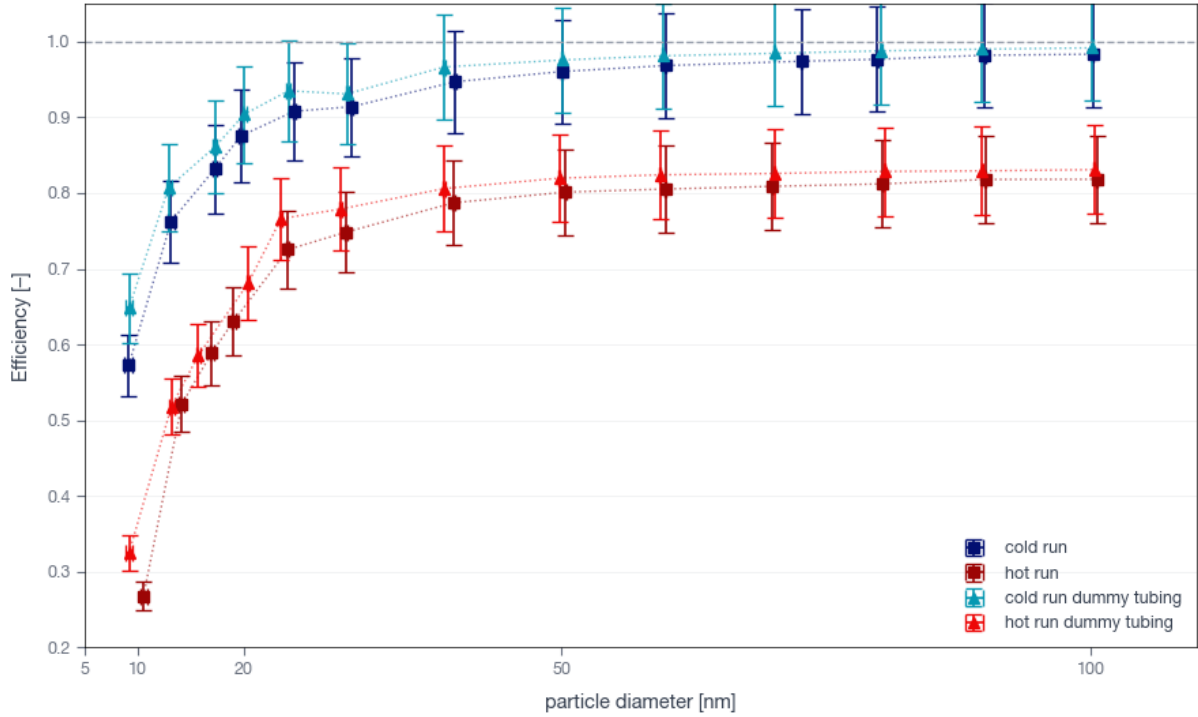
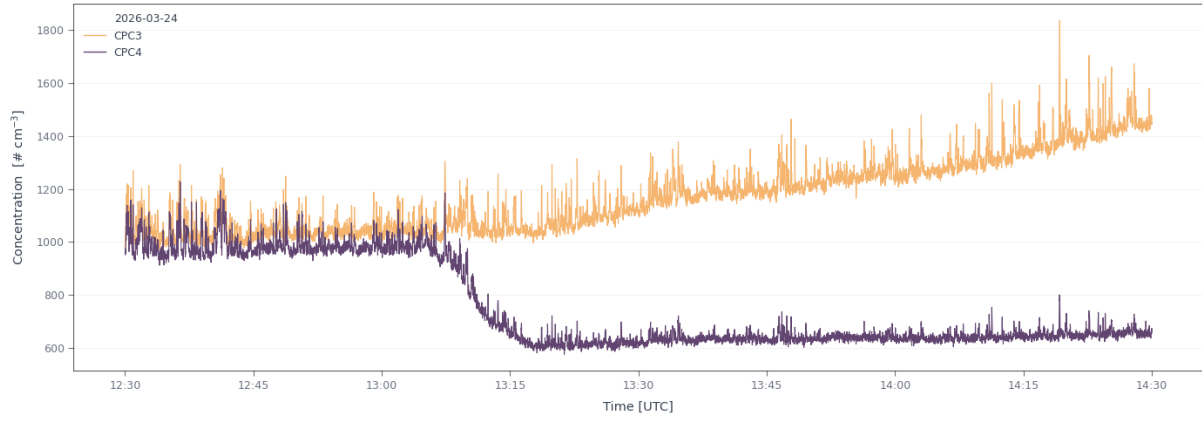


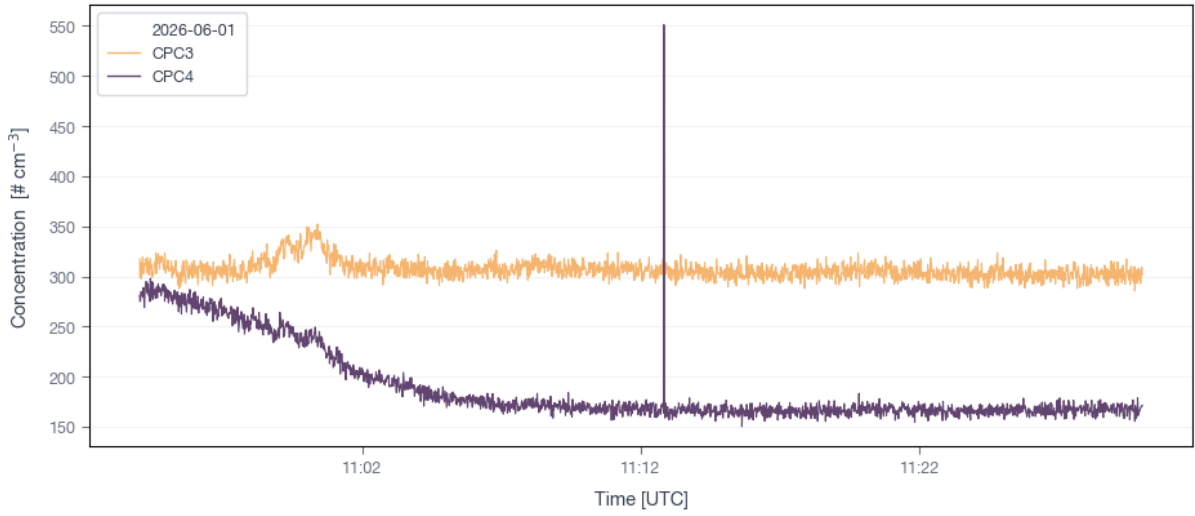
Figure 5.8. Transmission efficiency of the catalytic stripper for cold and hot operation as a function of particle diameter. Dark blue and red denote particle losses in the CS, light blue and red denote particle losses in the CS under measurement configurations.

5.1.4 Determination of the CS Response Time to a Change in CS Temperature Setting

The following two figures 5.9b and 5.9a show the response time to a change of T settings of CS between room T and the set T of 350°C , using polydisperse lab air. The catalytic stripper operated as presented in Fig. 4.7, while sampling polydisperse ambient laboratory air through a flow splitter. Figure 5.9a shows a period that starts with the catalytic stripper cold, followed by switching it on: the gradual heat-up is visible, which is roughly 15 minutes, after which the concentration remains at the reduced, fully heated level.



(a) Transition from cold to fully heated operation of the catalytic stripper, showing the gradual heat-up.



(b) Concentration decrease during heating of the catalytic stripper.

Figure 5.9. Total number concentration measured by both CPCs while sampling polydisperse ambient laboratory air through a flow splitter, with the catalytic stripper operated in line and no dummy extension.

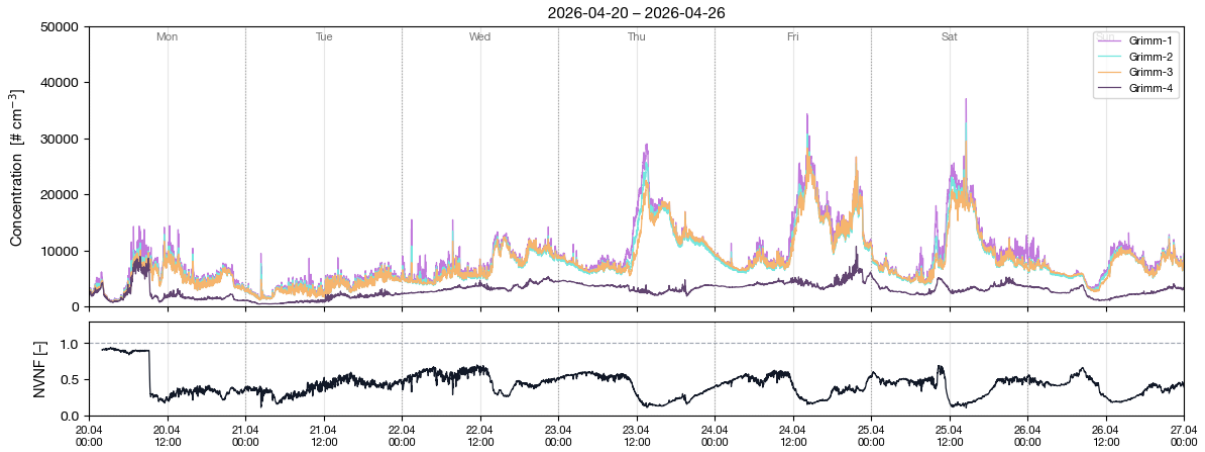
Figure 5.9a shows that during the initial period, while the catalytic stripper is still cold, the difference in concentration between the two CPCs is small, amounting to $(6.03 \pm 0.39) \%$. A subsequent steep decrease in concentration is observed in both cases, corresponding to the heating of the catalytic stripper. This decrease occurs over a period of approximately 15 min, after which the concentration stabilises again, indicating that the device has reached its fully heated state. In this state, the difference increases to $(54.93 \pm 0.16) \%$.

As an example of reproducibility, Figure 5.9b correspondingly also shows the decrease in particle concentration once the catalytic stripper is heated, within a similar time frame, with a starting concentration difference of $(7.91 \pm 0.55) \%$ and once temperature is reached $(44.55 \pm 0.33) \%$. The spike that can be seen will be described in more detail and discussed at a later point (Section 6.2.2).

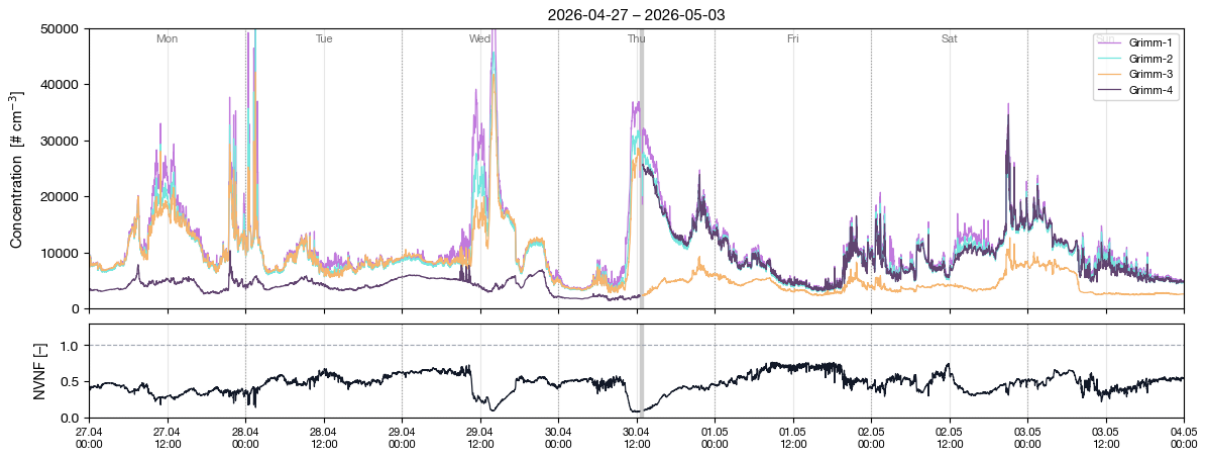
5.2. Measurement of Non-Volatile and Volatile Aerosol Fraction at the Aerosol Observatory

5.2.1 Overview

Figure 5.10 shows the time series of all four CPCs at the aerosol observatory over the two-week campaign, each subfigure covering one week from Monday to Sunday.



(a) First week (20-26 April 2026), before the instrument swap. Grimm 4 was operated downstream of the catalytic stripper, Grimm 3 served as the reference.



(b) Second week (27 April-3 May 2026), including the instrument swap on 30 April. After the swap, Grimm-3 was operated downstream of the catalytic stripper and Grimm 4 served as the reference; the gap marks the exchange.

Figure 5.10. Time series of the total number concentration measured by the four CPCs (upper panels) and the resulting non-volatile number fraction (NVNF, lower panels) over the two-week campaign at the aerosol observatory. Concentrations are shown as 60s averages in local time (CET). The NVNF is the ratio of the downstream (CS) concentration to the reference concentration.

During the first week, concentrations mostly remained below $10\,000\text{ cm}^{-3}$ from Monday to Wednesday. In the second half of the week (Thursday to Sunday), a pronounced rise was observed each afternoon, reaching up to $30\,000\text{ cm}^{-3}$. During each of these rises, the non-volatile number fraction dropped below 50 %: while the three upstream CPCs showed a clear increase, the non-volatile concentration downstream of the catalytic stripper remained almost constant, which appears in the lower panel as a marked decrease of the NVNF.

In the second week, several distinct concentration increases were recorded, with the highest reach-

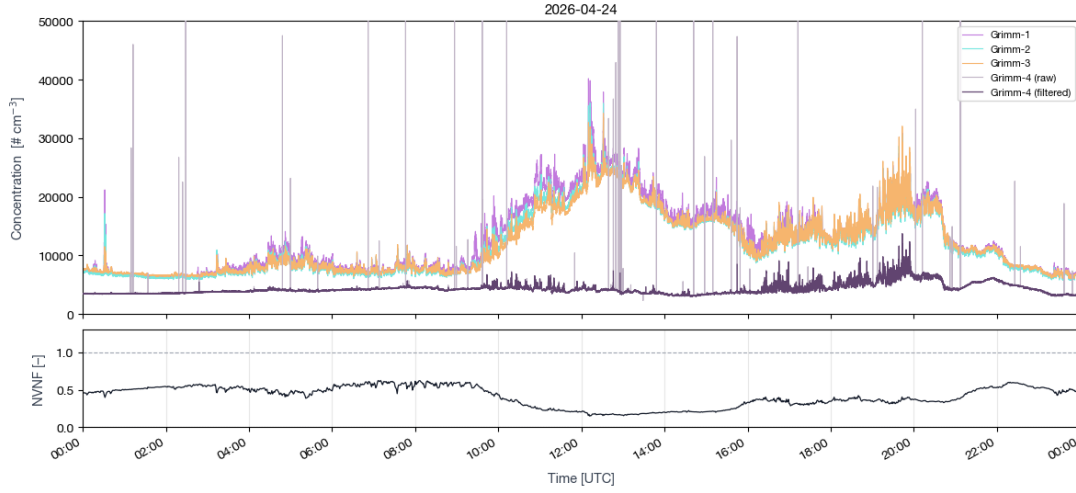
ing nearly $50\,000\text{ cm}^{-3}$ on Wednesday, 29 April. Further rises occurred on Monday, Wednesday and Thursday, as well as during the night from Saturday to Sunday, where concentrations reached about $20\,000\text{ cm}^{-3}$. Notably, during the night from 27 to 28 April, a sharp increase around midnight was observed, in which the two CPCs with the lowest cut-off diameters also approached $50\,000\text{ cm}^{-3}$.

The behaviour of the non-volatile fraction differed between these events. During the two pronounced rises on Wednesday and Thursday, the NVNF again dropped clearly, indicating a predominantly volatile contribution. In contrast, during the rise on Monday and the nighttime spikes around midnight on 29 April, the NVNF did not decrease significantly, implying that the non-volatile concentration increased together with the total concentration. On Friday, the NVNF approached a value of one. The relative uncertainty corresponding to the NVNF displayed is ca. 7%.

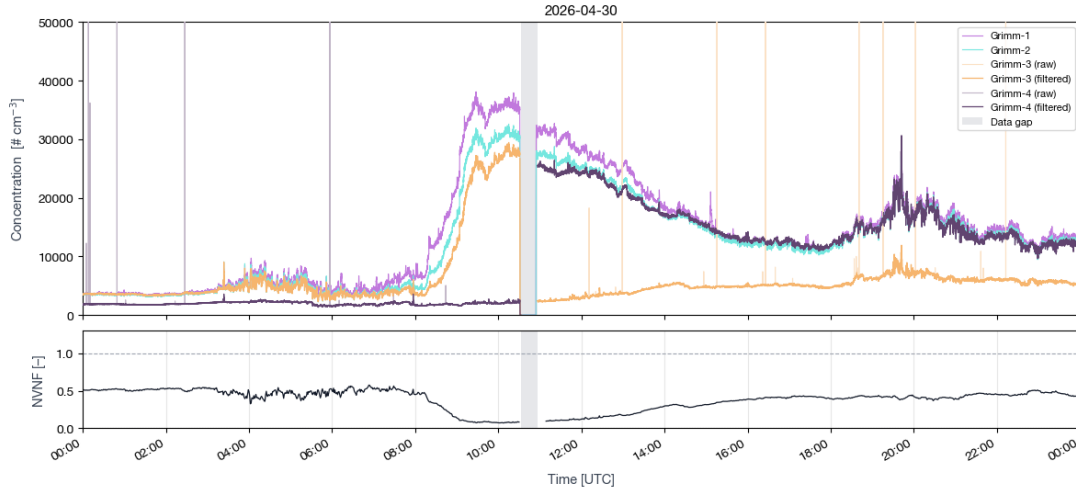
Ambient measurements revealed a recurring feature: regardless of which sampling line contained the catalytic stripper, the CPC downstream of it recorded irregular high spikes in particle number concentration. The origin of these spikes is examined further in the discussion. For the following plots, however, the spikes were filtered out to provide a clearer overview of the ambient particle number concentrations.

5.2.2 Daily measurements

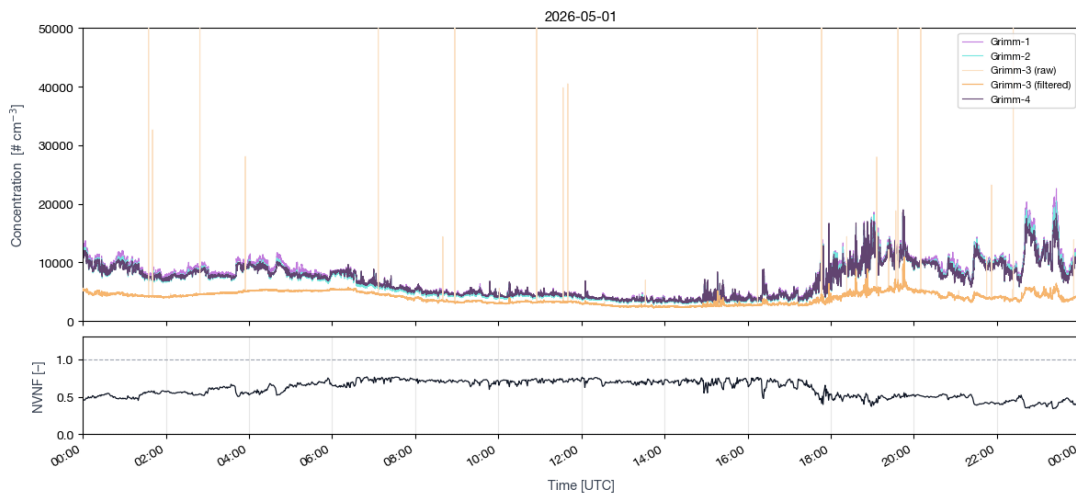
Figure 5.11 shows three example days from the two-week measurement series at the aerosol observatory, corresponding to the measurement conditions described in Sect. 4.2. The results additionally include number concentrations recorded by CPC 1 and CPC 2 during all measurement periods. These are not of primary relevance to the volatility measurements. On each day, four CPCs measured over a full 24-hour period according to their respective cut-off diameters (see Sect. 4.1.1). The concentration of the ambient atmospheric aerosol ranged from the low thousands up to nearly $40\,000\text{ cm}^{-3}$.



(a) First week of the campaign, with CPC4 downstream of the catalytic stripper. Pronounced spikes are visible in the raw signal. The filtered time series is shown for comparison.



(b) Day of the instrument swap: CPC4 was operated downstream of the catalytic stripper until the swap, CPC3 afterwards.



(c) End of the campaign, with CPC3 downstream of the catalytic stripper for the entire day.

Figure 5.11. Example days of the raw and spike-filtered concentration time series over the course of the campaign. Grey shaded areas indicate data gaps. Up to the instrument swap, CPC4 was operated downstream of the catalytic stripper; it was then replaced by CPC3 to verify that the observed spikes were not specific to a single instrument.

The three upstream CPCs show two distinct increases in particle concentration in Figures 5.11a and 5.11b, whereas the instrument downstream of the catalytic stripper does not follow this trend and remains at a comparatively constant level. During the evening hours in Figure 5.11a and the morning hours until about 6 a.m. in Figure 5.11c, however, the downstream CPC follows the same maxima and minima as the other instruments, including the reference CPC.

Clear spikes are visible in the CPC downstream of the catalytic stripper, partly exceeding the plotted concentration range. The instrument swap (Fig. 5.11b) shows that these spikes are independent of the specific CPC used, as they also appear on the last day (Fig. 5.11c), where the other CPC was operated downstream. The spike frequency varies over the campaign: spikes occur frequently throughout the day in Figure 5.11a, are noticeably less frequent in Figure 5.11b, and in Figure 5.11c are rare in the morning until about 6 a.m. but frequent for the remainder of the day.

6. Discussion

In this section the experimental results are discussed, in connection to the following research questions asked in this thesis: The following section is going to map out the previously shown results in connection to the research questions defined at the start of this thesis:

1. What are the particle losses in the CS, and how do these compare to literature data?
2. What is the number fraction of volatile particles in the air in Vienna during the first measurement using CS at the Aerosol Observatory?

The results are going to be discussed stepwise in correspondence to these questions and any issues and possible solutions will be analyzed along the way.

6.1. Characterization of the Catalytic Stripper in the Laboratory

6.1.1 Comparison of CPCs

To begin with, the CPC comparison presented in Figure 5.1 shows that for sizes above 20 nm in particle diameter the relative difference between the CPCs appears to be constant and within a few percent (below 2 %) of each other, showing good comparability in this size range. Below 20 nm, however, the two data points show a higher deviation in their relative difference (3 % at 15 nm and 10 % at 10 nm).

This difference might be related to the CPC calibration curve (i.e. counting efficiency, Figure 4.4), where CPC3 and CPC4 cut off sizes equal to 9.69 nm and 9.95 nm, respectively, and their d_{90} (the particle diameter at which the counting efficiency reaches 90 %) equal to 17.34 nm and 17.99 nm, respectively. CPC3 thus has a lower cut-off than CPC4. This will predominantly show for particle sizes that are still below the d_{90} of the calibration curve, because in that range the devices are not expected to measure an equal amount of particles (consistent with the diverging counting efficiencies of both instruments close to their lower detection limits). Unfortunately, the calibration of each CPC was not successfully performed in the laboratory due to issues with the nano-DMA (which provides particle sizes down to 2 nm in diameter), thus it relies on the manufacturer's calibration. However, a thorough direct comparison between these two CPCs was undertaken to ensure that the devices can validly be used for comparative measurements, since the relative differences are all within range.

The additional three data points from preliminary measurements using the nano-DMA show a similar difference but a reversed trend. Still, all three remain below 2 % deviation, which shows reproducible comparability of both CPCs.

The room-air measurement confirms the two counters are comparable for unknown, polydisperse aerosol (Figure 5.2): the mean relative difference was 0.80 %, consistent with the size-resolved comparison above. So, also for an unknown polydisperse aerosol sample, comparability is given.

To summarize, for monodisperse silver particles both CPCs are comparable (agreeing to within ± 2 % for sizes above 20 nm, and below 20 nm to within 4 % at 15 nm and 10 % at 10 nm). For

the polydisperse lab air aerosol they agree to within 0.80 % on average.

6.1.2 Determination of Particle Losses in the Catalytic Stripper

Before evaluating the preliminary aerosol in situ measurements at the observatory, it is important to understand particle losses in the catalytic stripper in order to evaluate the observatory measurements to their full correctness. For this, two central measurements are discussed next.

The first measurement focused on the determination of the particle losses that are caused by the device (Figure 5.5). A clear distinction can be seen between the catalytic stripper operating at the room temperature (i.e. cold, where the aerosol sample simply passes through the device) and at its operating temperature of 350 °C (i.e. hot; where heating induces evaporation and the catalyst is activated).

At cold setting of the CS, the particle losses clearly increase at small particle sizes (starting <50 nm; steep increase <20 nm). Since there is no elevated temperature in this setting, these losses can be attributed mainly to diffusional losses, which are described in Chapter 3.3.1. For particles larger than 20 nm, it is clearly visible that the transmission efficiency reaches a plateau (above 50 nm), stalling at almost full efficiency, which tells us that with increasing particle size diffusional losses are not as relevant or as predominant, which agrees with theory, where diffusional losses increase with decreasing particle size (Huffman et al., 2008). The thermodenuder in Burtscher et al., 2001 showed 22 % at 10 nm and 1 % at 100 nm. The results for the CS differed slightly, with 42 % at 10 nm and 2 % at 100 nm. This is however to be expected, since these values depend on tube geometry, flow rate, and operating temperature, the actual losses vary between devices and configurations (Burtscher et al., 2001).

At hot setting of the CS, a similar curve can be observed but is shifted now downwards overall. So the difference between cold and hot for large particles (16 % at 100 nm) is about the same as the difference for small particles (18 % at 20 nm), which indicates that the additional thermophoretic losses the sample experiences are mainly independent of particle diameter. Below 20 nm there is another increase under thermophoresis reaching 30 % difference at 10 nm. This is supported by theory as described in Section 3.3.2 on thermophoretic losses, where thermophoresis is not size-dependent itself, but can induce additional diffusional deposition (Huffman et al., 2008) - For the general trend (total losses), even with the thermophoretic losses added (since it is not only thermophoretic losses but also the diffusional losses that add to them), it can still be seen that the total losses in the device increase with decreasing particle size, because there is always an amount of thermophoretic losses, while the additional diffusional losses only apply to the smaller particle sizes.

Taken together, these results show that adding a device such as the CS to a sampling line introduces significant losses. To avoid biasing the resulting data, these losses must be corrected for. Since the measurement setup at the Aerosol Observatory corresponds to the configuration discussed in Section 4.2, the potential losses in the parallel sampling line must be taken into account. This was done according to Figure 4.8.

6.1.3 Determination of Particle Losses in the CS under Measurement Configuration at the Aerosol Observatory

Extending this discussion to the second measurement, the observatory simulation (reference line was extended by a length of stainless steel tubing equal to the total length of the catalytic stripper to reproduce the conditions encountered in actual aerosol measurements), the following can be observed. The simulated characterization of the measurement setup (see Figure 4.8) at the observatory shows a similar trend to the device characterization: again, the diffusional losses increase with decreasing particle size reaching a transmission efficiency of more than 99 %

at 100 nm (<1 % losses) and the additional thermophoretic losses again shift the same trending transmission curve to lower efficiencies, showing 83 % at 100 nm. At smaller sizes (10 nm), both diffusional (35 %) and total (67 %) losses again increase.

Comparing the losses in the device to the losses in the device including the sampling lines, it can be seen that both the cold curves that track diffusional losses and the hot curves that track total (diffusional plus thermophoretic) losses each lie close to their respective counterparts. The transmission efficiencies of the simulated setup measurements tend to be higher (within 1 and 8 %) than their respective counterparts. This tracks when one considers that in the additional tubing that simulates the setup there are also going to be particle losses along the line, which in total will increase the transmission efficiency, since this is calculated from the ratio of both lines.

This means, that determining the losses specific to a device, such as CS (discussed in 6.1.2), can provide the means to correct for the amount of particles that are being lost throughout a measurement. However, for valid determination of the non-volatile fraction (which is result of the comparison of two sampling lines) the parallel particle losses of the second sampling line need to be accounted for. The inverse relationship of these results can be applied to ambient measurements to correct for mass lost as a function of temperature to avoid systemic bias of the measured volatility response (Huffman et al., 2008). Application of these corrections are beyond the scope of this thesis, as size distributions would need to be considered also.

6.1.4 Determination of the CS Response Time to a Change in CS Temperature Setting

Finally, in the determination of the response time of the device (polydisperse laboratory air is measured during the heating phase), the plots show the heating periods of the catalytic stripper appear reproducible in time and the response of the CS to a change in temperature is clearly visible. Both figures (5.9a, 5.9b) show a response time of roughly 15 minutes from cold (room temp.) to hot (350 °C) settings. Figure 5.9a shows a minimal difference (6 %) in concentrations during the cold period - which can be attributed to diffusional losses. For 5.9b the measurement starts only when the heating period begins, so this cannot really be seen. Additional thermophoretic losses cannot be read from these plots, since laboratory air is of unknown composition and evaporation/oxidation processing is also occurring.

6.2. Preliminary measurements at the Aerosol Observatory

6.2.1 Volatile vs. Non-volatile Fraction

For the ambient measurements, there are two parts that should be discussed. The first concerns the seven-day overview plots that include the non-volatile fraction. During the 14 day long preliminary measurements using a CS upstream of the CPC 4 the non volatile fractions varied between 7 % and 77 % (Figure 5.10a, 5.10b). The CS operated continuously at 350 °C. Although on depth analysis and interpretation of this data is beyond the scope of this thesis, some aspects will be discussed here.

What can clearly be seen is how the non-volatile fraction changes throughout those two weeks. During the first week, for example, there are some clear peaks in total number concentration. However, the refractory concentration remains mostly constant, which indicates that the increase in concentration would stem mostly from volatile material. This is also indicated by the non-volatile fraction, where it can clearly be seen that this fraction decreases strongly on the 23rd, 24th, 25th, 29th and 30th of April, around midday (dropping as low as 7 % on April 30th).

On the 27th and 28th, increases in total particle concentration do not show behavioural differences to the refractory particle number concentration. The NVNF over those two days does not

show steep increases or decreases. And also, on 2nd and 3rd of May, there are peaks in total concentration, but the trend for the refractory core follows them, and the non-volatile fraction remains stable and does not drastically change - which indicates just an increase in overall aerosol number concentration, while the proportion between volatile and non-volatile does not change. Another thing that can be noticed is that on May 1st, for example, there seems to have been the least volatile material present (75 % refractory material at noon).

Connecting these results to literature of urban aerosol composition some clues to urban aerosol composition can be given. Wehner et al., 2002 defines that 250 °C evaporates most sulfates, nitrates, ammonium and volatile organic compounds - while non-volatile cores (mainly soot/elemental carbon) survive. The operational definition of the CS in this study at 350 °C would thus indicate that similarly sulfates, nitrates, ammonium and volatile organic compounds would be evaporated passing through the device. At this temperature it is suggested that even a large number of semi-volatile particles are also evaporated. The boiling point classification from Zheng et al., 2023 e.g. shows a range of 260 and 400 °C as the boiling point range of semi-volatiles, showing that raising the CS to 350 °C compared to other studies additionally extends into the semi-volatile range, leaving only particulate organic matter and non-volatile material (Zheng et al., 2023).

Summarizing the NVNF over the entirety of the two weeks of measurement, the range of the non-volatile fraction lies between 7 and 77 %. During periods of low NVNF it could be suggested that a bulk amount of the aerosol sample can be attributed to the more volatile species (sulfates, nitrates, ammonium, VOC, SVOC). Periods of high NVNF can be thought of as mainly refractory material, such as soot, mineral dust, POM. Wehner et al. (2004) report that at their urban site the non-volatile number fraction (the ratio of non-volatile to ambient particle number concentration after heating to 280 °C) fell in the range 40 and 80 %, considerably higher than the 10 and 20 % they observed near a highway (Wehner et al., 2004). More detailed information in chemical composition, even though beyond the scope of this thesis, could be gained from combining this information with further data, such as wind speed/direction, size distributions (using SMPS) or varying the operational temperature of the CS in further measurements.

6.2.2 Spikes in Particle Number Concentration

During the measurements of indoor polydisperse aerosol present in the laboratory (Figure 5.9b), as well as measurements at the Aerosol Observatory (Figures 5.11), there were instances where spikes (i.e. sudden short ($\sim 1-3$ s) increases in the particle number concentration up to $100\,000\text{ cm}^{-3}$) in CPC4 placed downstream of the CS occurred both during the day and at night. It is not clear where these come from however there are a couple of hypotheses on their origin that were investigated.

Spikes were not observed when using silver monodisperse aerosol sample with the size range between 10 and 100 nm in diameter. To check whether these spikes resulted from an accumulation of particles (within the CS) being released, filters were included in front of the catalytic stripper, after which no spikes were shown. The only occurrence observed was when an unknown, polydisperse, ambient aerosol is measured, whether it is outside air or the lab air. It was noticed that once people were around while the polydisperse lab air was sampled (present in the lab, working around the room) the frequency of spikes would increase. The hypothesis is that evaporation or sudden bursting of larger particles might induce such spiking.

During the preliminary measurements however, there are no people in the vicinity of the PM_{2.5} inlet head presenting the question which components of atmospheric samples could be responsible for such a response. Periods with an overwhelming number of spikes was recorded e.g. on the 24th of April (Figure 5.11a), or on the 29th (Figure C.10). However, what has to be considered for the ambient measurement is that it is taken under a PM_{2.5} inlet, so the size range is limited accordingly, which has not been reproduced accordingly in qualitative lab measurements. To

check whether this is not included by the detector (i.e. CPC4), CPC4 and 3 switched places to check whether this could solve the issue with the spikes (seen in Figure 5.11b). However, no change was observed.

The hypothesis is proposed that evaporation or sudden bursting of larger particles could induce such a spiking response and was tested by shaking our clothing (releasing particles from clothing such as polyester fibres), with which a spiking response could be induced in the lab almost immediately. A quick qualitative test was undertaken to check at which temperature setting the spikes disappear. To do so the core temperature was stepwise decreased until at approximately 230 °C, where no more spikes were observed. However, since it is also below the melting point of a lot of semi-volatile atmospheric components, a temperature of 230 °C would diminish the function of the device itself. Recommendations for further steps are suggested in the outlook section (7.2).

7. Conclusion and Outlook

The following, final section of the thesis is going to give a brief summary of the findings and further point out how this work adds to current research in aerosol science and give pointers as to further questions and work that might result from the findings of this thesis.

7.1. Conclusion

This work aimed to characterize the Compact Catalytic Stripper CCS004 (Catalytic Instruments GmbH & Co. KG) for particle losses in the laboratory, and subsequently use this device upstream of the GRIMM CPC 5410 to undertake preliminary measurements of the non-volatile aerosol fraction at the Aerosol Observatory in Vienna.

The experimental part consisted of comparison of two GRIMM 5410 CPCs to make sure both instruments are comparable and if not, quantify discrepancies. One of these CPCs was planned to serve as a reference instrument that measure total number concentration of particles, while the other CPC was intended to be placed downstream of the catalytic stripper to measure non-volatile fraction of particles above the temperature setting of the catalytic stripper (350 °C). This was done using both monodisperse silver particles in the size range between 10 and 100 nm, as well as polydisperse laboratory air. It was found, that the difference between the CPCs appears to be constant and within a few percent (below 2 %) of each other, showing good comparability in this size range. Two data points show a higher deviation in their relative difference (3 % at 15 nm and 10 % at 10 nm), consistent with the diverging counting efficiencies of both instruments close to their lower detection limits. The polydisperse measurement found an average difference of 0.8 % between devices across the measurement interval.

Further, particle transmission through the device was evaluated at room temperature (cold setting of the CS) and at operating temperature (350 °C, hot setting) to separate losses due to diffusion from those due to thermophoresis: the cold measurement captures diffusional losses alone, while the hot measurement captures the combined diffusional and thermophoretic losses. The transmission efficiency was found to plateau above 50 nm in both cases. For the cold (diffusion-only) setting it reached about 98 % at 100 nm, falling to 58 % at 10 nm; for the hot (total-loss) setting it plateaued at about 82 %, falling to 27 % at 10 nm.

Next, particle losses with additional tubing (that ensure the distance between the flow splitter and both CPCs is equal), were measured (at room T and at operating T) to simulate the setup used with CS at the Aerosol Observatory. It was found that for both the diffusional and the total losses the transmission efficiency comes out slightly higher, with the diffusional (cold) transmission efficiency reaching 99 % at 100 nm and the total efficiency reaching 83 % at 100 nm (65 % and 33 % at 10 nm). For all four measurements, it was seen that the losses increase with decreasing particle size, corresponding to the expected behavior of diffusional losses.

The preliminary measurements including catalytic stripper at the Aerosol Observatory to characterize the volatile and non-volatile fractions of ambient aerosol were undertaken over a period of 14 days. During these preliminary continuous measurements, the non-volatile fraction varied

between 7 and 77% with low values implying a volatile-dominated aerosol and high values a refractory-dominated one. Because a catalytic stripper at 350 °C evaporates sulfates, nitrates, ammonium and VOCs and (unlike more common 250 and 300 °C thermodenuder setups) much of the semi-volatile range too (SVOC boiling points span 260 and 400 °C), the surviving material can be estimated to be mainly refractory (soot, mineral dust, and particulate organic matter) (Wehner et al., 2002; Zheng et al., 2023).

One interesting observation were the spikes in a CPC downstream of the catalytic stripper. These were qualitatively investigated and a hypothesis (bursting/evaporation of larger, micron-range particles) was determined.

Overall the CS serves as a promising alternative to the TD for atmospheric applications. Further detailed investigations and characterizations are recommended and some of these are mentioned in the outlook section below.

7.2. Outlook

Although a thorough characterization of the particle losses in the catalytic stripper was undertaken it is recommended to further investigate the performance of the device that could focus on e.g. the influence of the temperature settings of the performance of the catalytic stripper, as well as particle material (i.e. chemical composition with focus on volatile and non-volatile particles) and size. For instance, sodium chloride could be used to investigate the response of the CS as an alternative refractory material. Ammonium sulfate, etc. might be used at various sizes to evaluate the response of the device to varying degrees of volatility (including organic and inorganic material).

To investigate the spikes, one could use larger particles (such as above 100 nm in diameter) in the laboratory setting to see whether such spikes also appear for particles generated in the lab, and at which sizes, compositions and temperatures of the catalytic stripper. What also needs to be considered is the restriction of the PM_{2.5} size range at the aerosol observatory in Vienna. The qualitative testing of clothing fibres that has been done is not directly comparable to the observatory's PM_{2.5} size-cut configuration, which limits their interpretability.

While the application of the characterization has gone beyond the scope of this thesis, using size-resolved data (such as SMPS) a correction of the measurements at the Aerosol Observatory can be developed.

To analyze the preliminary data (which was beyond the scope of this thesis) one could combine size-resolved aerosol measurements (such as using SMPS also available at the Observatory), meteorological data, such as wind speed and direction, etc. to see if when the spikes appeared the sizes of particles were on the large spectrum, of the size distribution or if weather data might show the spikes being traceable to air masses appearing from certain directions.

Further, back trajectories should be used to analyze if the Saharan dust (non-volatile) has reached Vienna and was detected by instrumentation used. Such events might correlate with the periods of high NVNF.

One could also combine the number concentrations from the observatory's CPCs (which operate at different lower cut-off diameters) with the SMPS size distributions to determine the changes driving the NVNF, and connect it to periods of volatile secondary particles formed after emission, as described by Wehner et al. (2004). Separately, regional new particle formation (NPF) would bring new volatile particles into the aerosol population. Such events might influence the ratios observed and NPF events might be suggested.

As demonstrated in the deployment of the SAMUM campaign and the results that were obtained

using the thermal denuder, using size-resolved data can also yield strong compositional insights (Weinzierl et al., 2009). Comparative size-distributions will not just show whether material is volatile, it allows to map that volatility onto particle size, revealing whether a particle population is internally or externally mixed, meaning that non-volatile material originates from chemically mixed particles or an entirely separate particle type (Engler et al., 2006). Using the catalytic stripper can allow similar interpretation with less risk of any additional re-condensation of volatile material.

7.3. Use of Artificial Intelligence

Artificial intelligence (AI) tools were used as an assistive resource during the preparation of this thesis, including support for writing, programming, and understanding scientific literature. All substantive scientific work, including the design of the analyses, interpretation of the results, and the conclusions presented, was carried out by the author. The author takes full responsibility for the content of this thesis.

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A. Manufacturer Calibrations

A.1. CPC Calibration

All four CPCs were calibrated by the manufacturer. For each instrument, the actual inlet flow rate was measured and compared against its nominal value. The number concentration linearity was determined and fitted to

$$N_{\text{CPC}} = k N_{\text{FCE}}, \quad (\text{A.1})$$

where an ideal instrument yields a slope of $k = 1$. The size-dependent counting efficiency was measured over a range of particle diameters, from which D_{50} and D_{90} were derived. Calibration was performed using monodisperse silver particles, size-selected by a DMA, with a Faraday cup electrometer (FCE) as the reference instrument (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b). The counting efficiency was fitted following (Wiedensohler et al., 2018) according to

$$\eta(d_p) = A \left(1 - \exp \left(\frac{B - d_p}{C - B} \ln 2 \right) \right), \quad (\text{A.2})$$

with A , B , and C as instrument-specific fit parameters. The measured counting efficiencies for all four instruments are listed in Table A.1. The corresponding efficiency curves, obtained by fitting Eq. A.2 to the data, are shown in Figure A.1. The two instruments used in the main analysis are highlighted, while the two additional CPCs are shown for completeness (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b).

The resulting fit parameters, the derived cut-off diameters D_{50} and D_{90} , and the number concentration linearity slopes k are summarised in Table A.2.

The calibration dates and operating conditions of the four CPCs are given in Table A.3

Table A.1. Size-dependent counting efficiency of the four CPCs (model 5410), as specified by the manufacturer. Empty cells indicate diameters not measured for the respective instrument (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b).

Diameter d_p (nm)	Counting efficiency η (-)			
	Grimm 1	Grimm 2	Grimm 3	Grimm 4
2	0.03	-	-	-
3	0.18	-	-	-
4	0.40	-	-	-
5	0.59	0.18	-	-
6	0.70	0.36	-	-
7	0.77	0.52	0.05	0.04
9	-	0.73	0.40	0.36
10	0.89	-	0.54	0.51
11	-	-	0.64	0.61
12	-	0.91	-	-
14	-	0.96	0.84	0.81
15	-	0.98	-	-
20	1.00	1.01	0.96	0.96
30	1.02	1.03	0.99	0.99
40	1.03	1.04	1.00	1.00

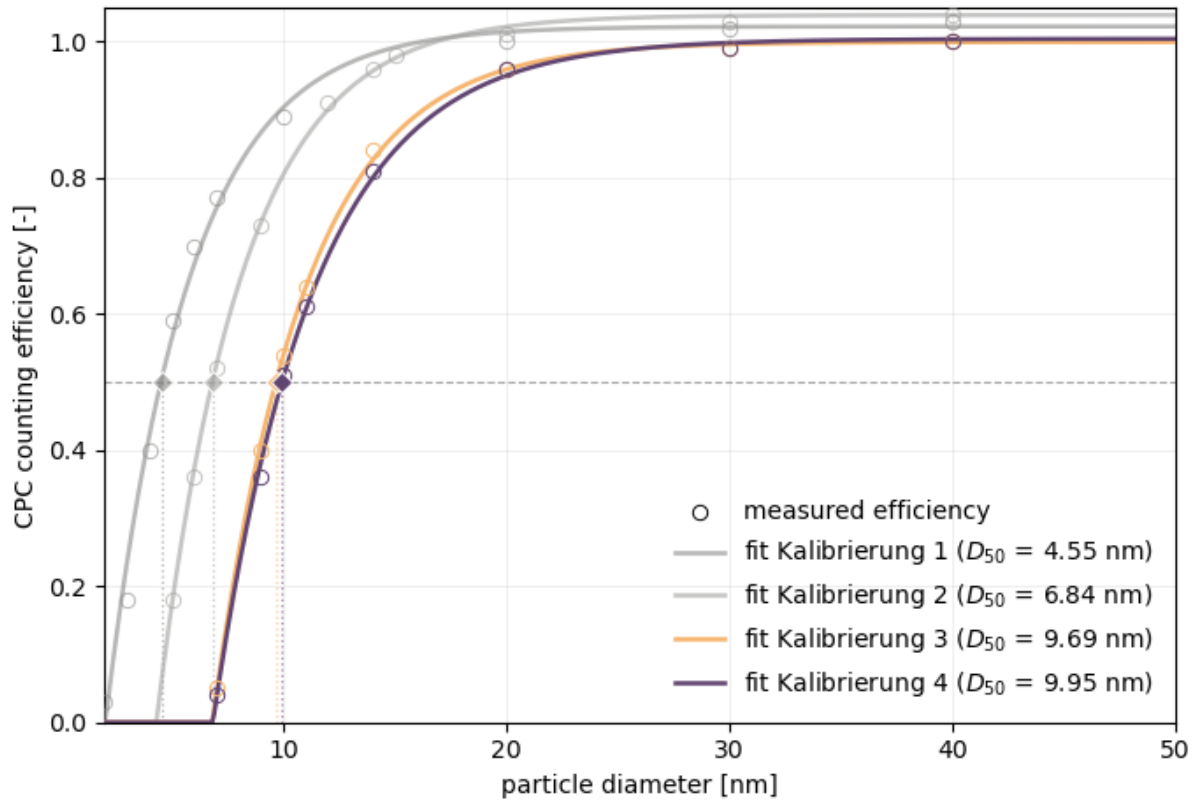


Figure A.1. Measured counting efficiency of Grimm 1-4, fit according to manufacturer with respective cutoff diameter for each device (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b)

Table A.2. Fit parameters of the counting efficiency curve (Eq. A.2), derived cut-off diameters, and number concentration linearity slope k (Eq. A.1) for the four CPCs (model 5410) (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b).

Instrument	Fit parameters			Cut-off		k
	A	B (nm)	C (nm)	D_{50} (nm)	D_{90} (nm)	
Grimm 1	1.0223	2.0246	4.5944	4.55	9.93	0.9432
Grimm 2	1.0390	4.3095	6.9582	6.84	11.99	0.9322
Grimm 3	0.9994	6.8235	9.6651	9.69	17.34	0.93517
Grimm 4	1.0041	6.8452	9.9614	9.95	17.99	0.92635

Table A.3. Calibration date and operating conditions of the four CPCs (model 5410), as reported in the manufacturer calibration certificates (GRIMM Aerosol Technik GmbH, 2023a, 2023b, 2024a, 2024b).

Instrument	Cal. date	Q_{nom} (l min ⁻¹)	Q_{act} (l min ⁻¹)	T_{sat} (°C)	T_{cond} (°C)
Grimm 1	2024-09-19	0.600	0.599 ± 0.006	36.0 ± 0.5	8.5 ± 0.5
Grimm 2	2024-10-08	0.600	0.597 ± 0.006	36.0 ± 0.5	17.0 ± 0.5
Grimm 3	2023-12-19	0.600	0.588 ± 0.006	36.0 ± 0.5	20.5 ± 0.5
Grimm 4	2023-12-19	0.600	0.593 ± 0.006	36.0 ± 0.5	20.5 ± 0.5

B. CPC Performance Comparison

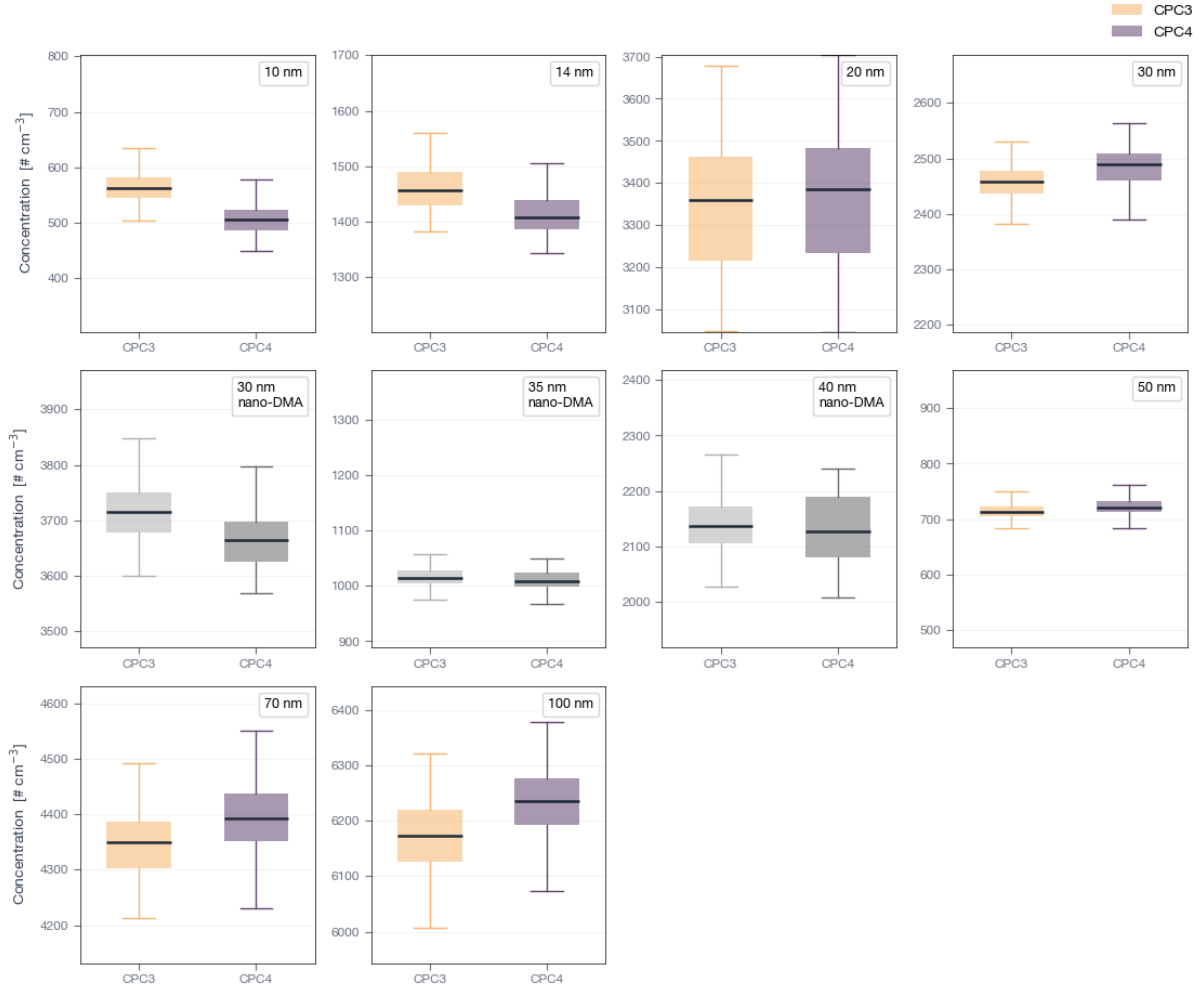


Figure B.1. Boxplots for each recorded measurement interval that show statistical comparison of CPC response for monodisperse silver sample. Colored: RAX-DMA; Grey: nano-DMA. The box spans the interquartile range (IQR) with the median marked by the central line, the whiskers extend to the most extreme values within $1.5 \times \text{IQR}$ of the quartiles.

C. Daily Time Series of the Full Deployment

This appendix presents the complete set of daily time series recorded over the two-week deployment of CS (20.04.2026 - 03.05.2026). Three representative days are discussed in the results (Section 5.2.2). The below figures show all days for completeness. Each panel follows the same layout of: Particle number concentration (cm^{-3}) versus time (UTC). Lower panel: non-volatile number fraction (NVNF).

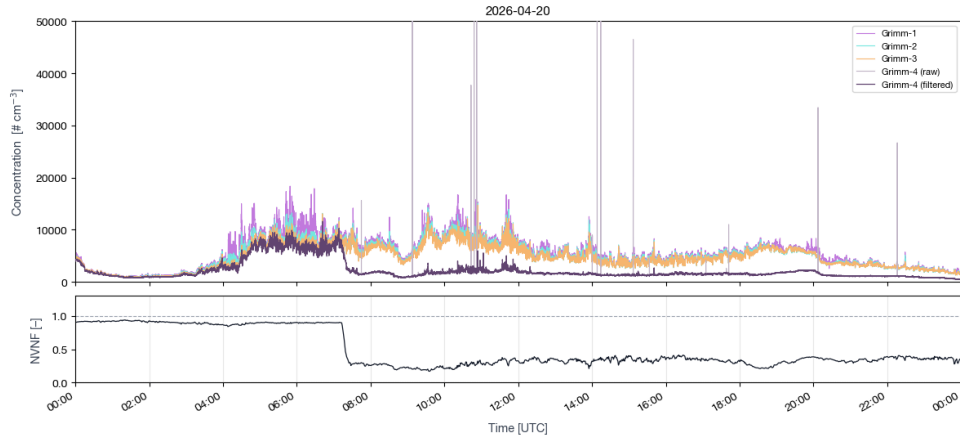


Figure C.1. 20.04.2026

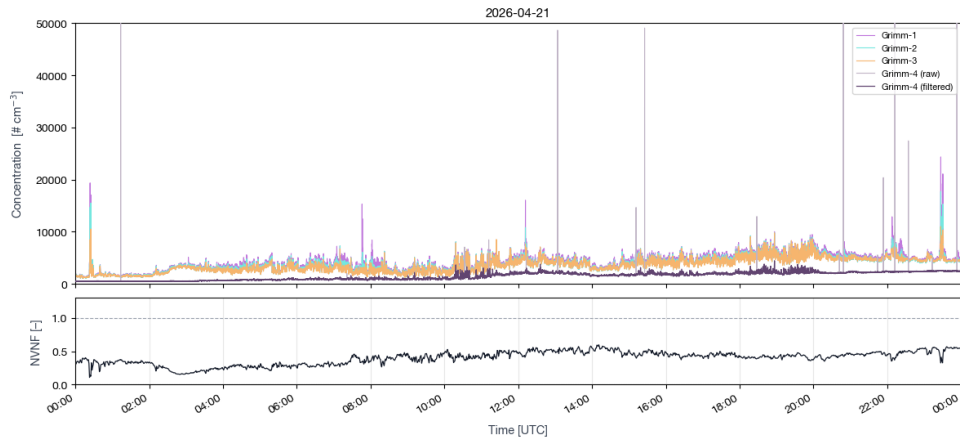


Figure C.2. 21.04.2026

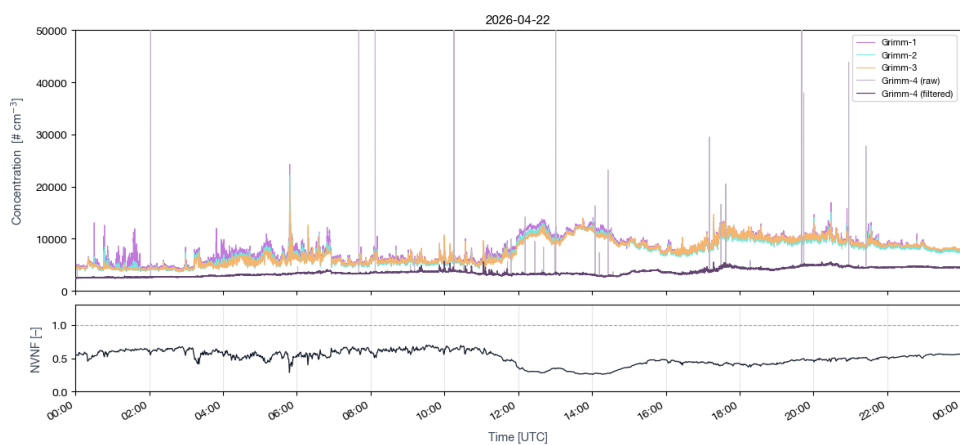


Figure C.3. 22.04.2026

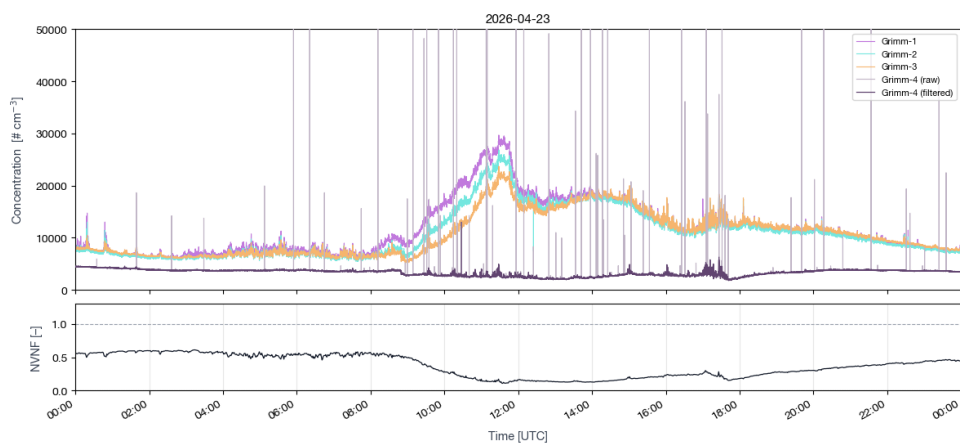


Figure C.4. 23.04.2026

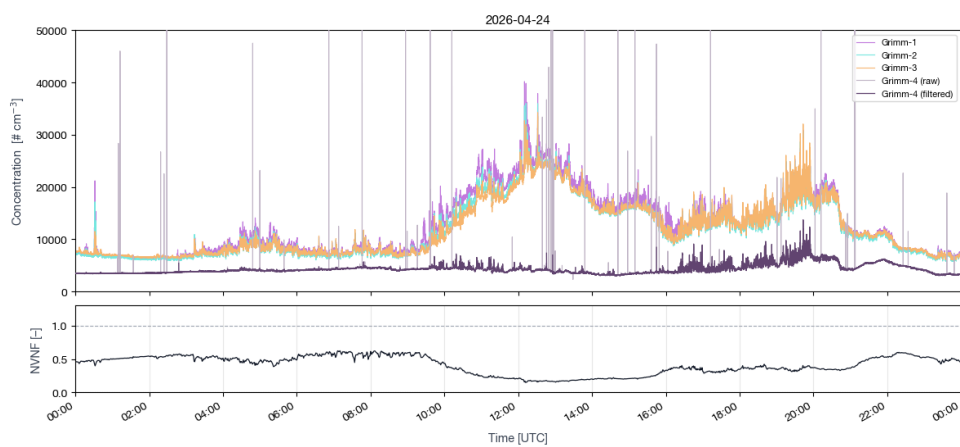


Figure C.5. 24.04.2026

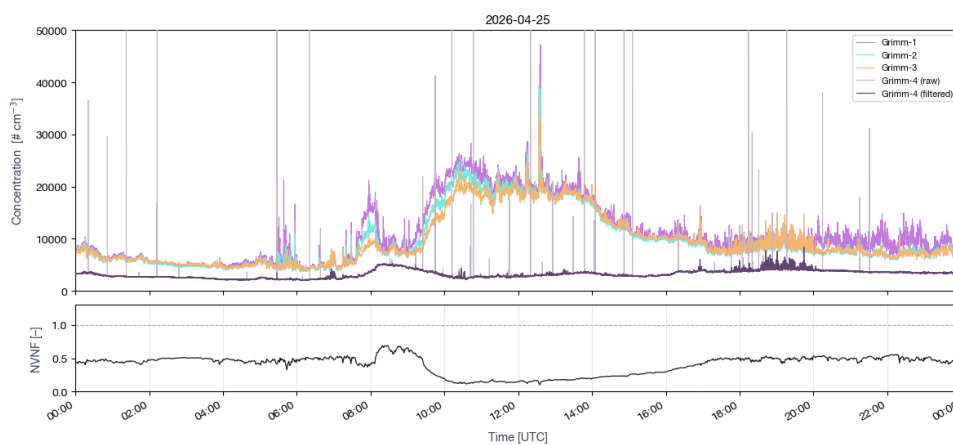


Figure C.6. 25.04.2026

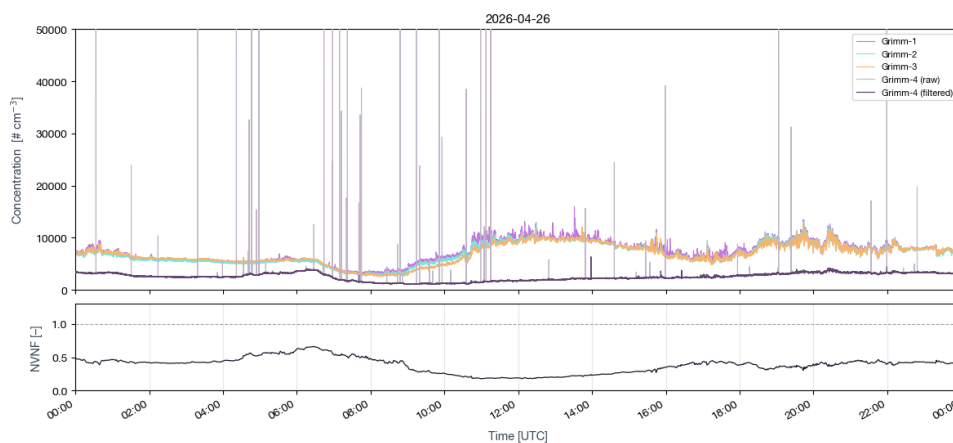


Figure C.7. 26.04.2026

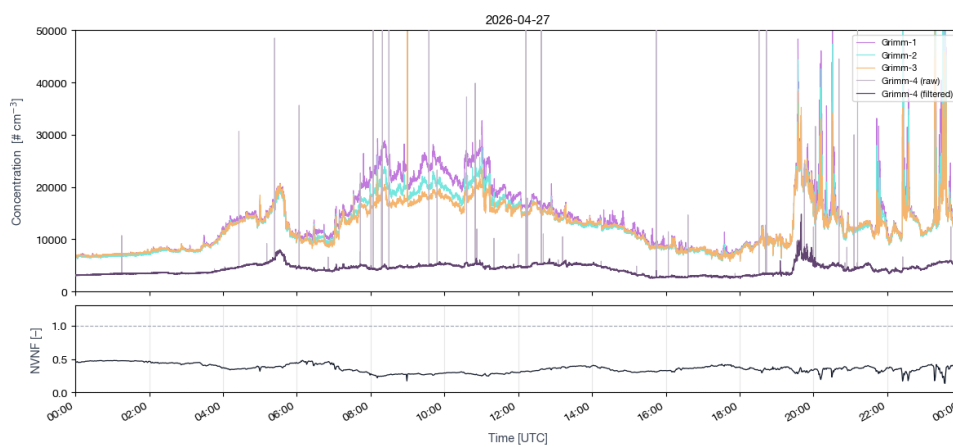


Figure C.8. 27.04.2026

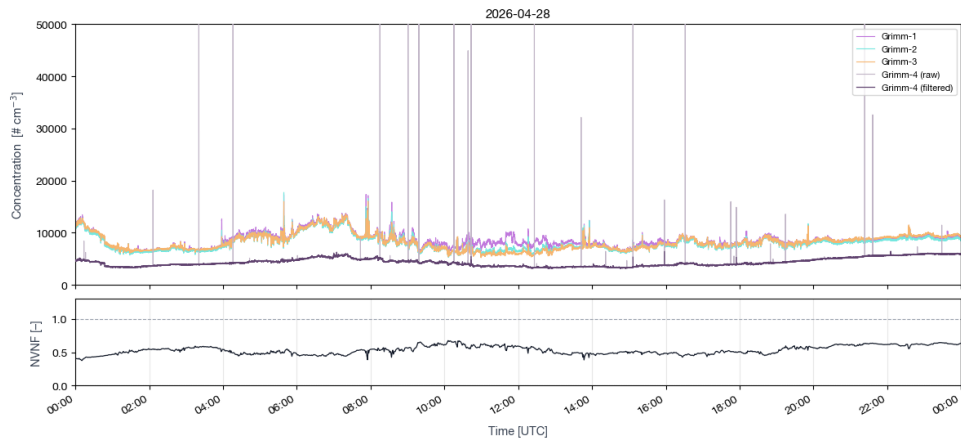


Figure C.9. 28.04.2026

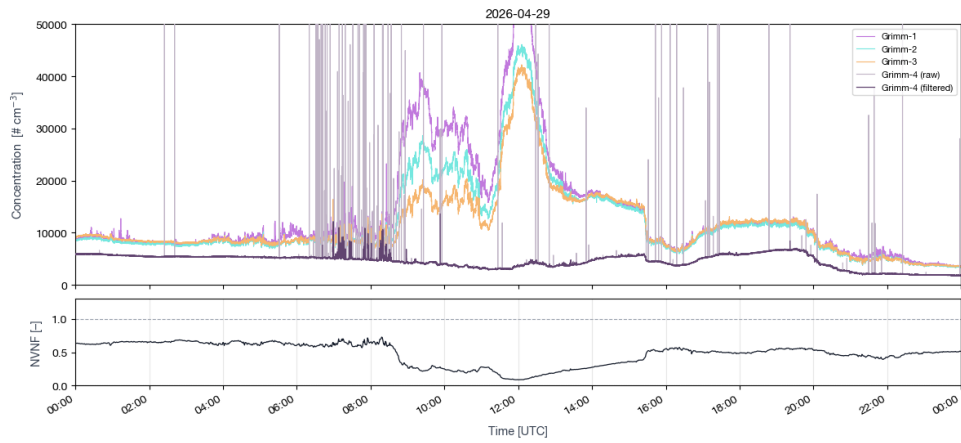


Figure C.10. 29.04.2026

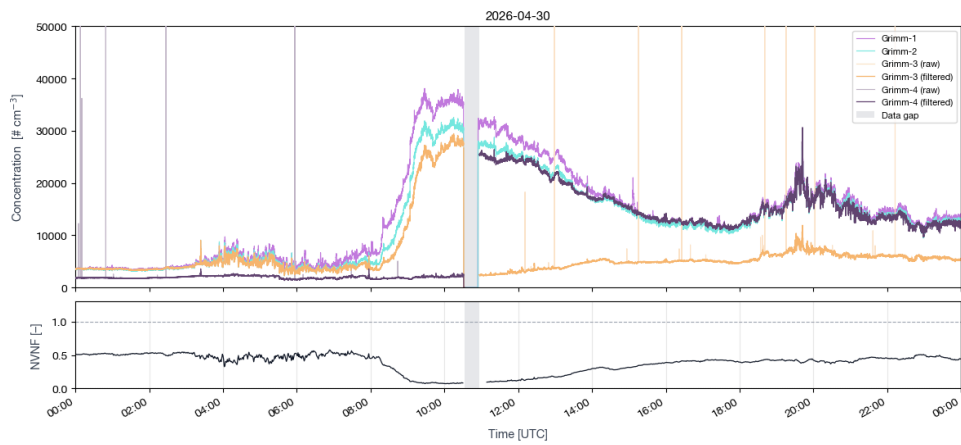


Figure C.11. 30.04.2026

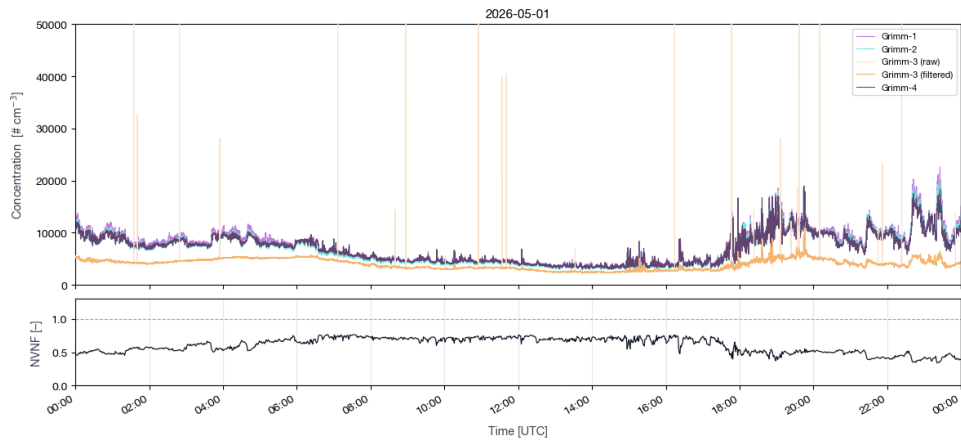


Figure C.12. 01.05.2026

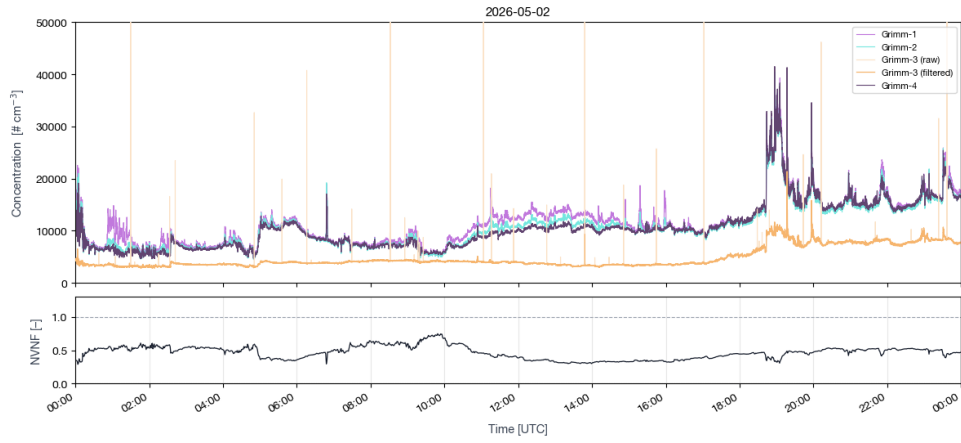


Figure C.13. 02.05.2026

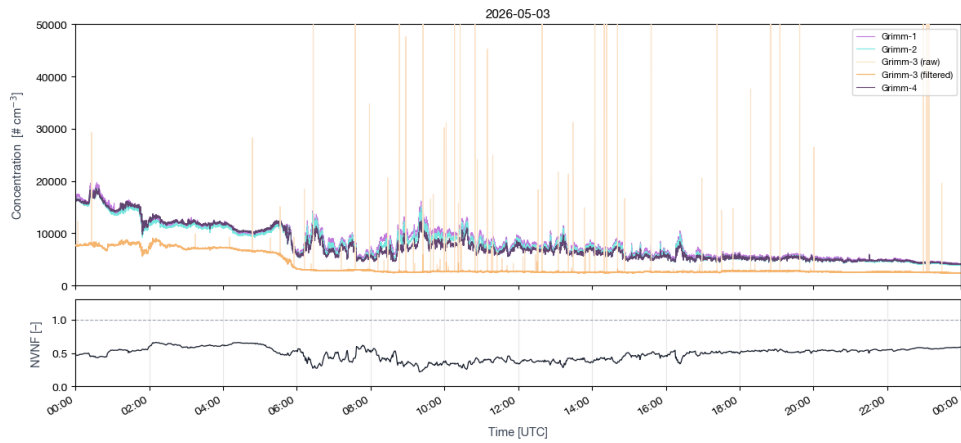


Figure C.14. 03.05.2026