

MASTER'S THESIS

Determination of elemental carbon and mineral dust in snow and ice samples

Conducted at the Institute of Chemical Technologies and Analytics
at the Vienna University of Technology
in the working group Environmental Analytics

under the supervision of Ao.Univ.Prof. Dipl.-Ing. Dr.techn. Anne Kasper-Giebl

by Daniela Kau, BSc

Date

Signature (student)



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Abbreviations

Avg	Average
BC	Black carbon
CC	Carbonate carbon
DOC	Dissolved organic carbon
e.g.	Exempli gratia (for example)
EC	Elemental carbon
EU	EUSAAR2
EU1.5	EUSAAR2_x1.5
FID	Flame ionisation detector
i.e.	Id est (that is)
IC	Ion chromatography
IMPR	IMPROVE_A
LOD	Limit of detection
LOQ	Limit of quantification
MD	Mineral dust
MSA	Methanesulfonic acid
NA	Not analysed
NI	NIOSH870
NI1.5	NIOSH870_x1.5
OC	Organic carbon
PC	Pyrolytic carbon
Stddev	Standard deviation
t	Time
T	Temperature
TC	Total carbon = organic carbon + elemental carbon
TOA	Thermal-optical analysis

Abstract

Mineral dust (MD) and elemental carbon (EC) deposited on snow surfaces lead to a variety of consequences for the environment. Both compounds cause a reduction of albedo of the snow surface and thereby lead to an increase in annual melt. Additionally, MD increases the concentrations of ions (e.g. Ca^{2+} and Mg^{2+}) as well as the alkalinity of snow and is capable to function as a supplier of nutrients influencing the biogeochemistry in the area of deposition. Hence, the determination of both parameters, MD and EC, in snow is of great interest. Thermal-optical analysis (TOA) is routinely used for the determination of EC, while its use for the analysis of carbonate carbon (CC), as possible proxy for MD, is not common. Within this work the possibility to determine both CC and EC in snow samples within one analytical run is evaluated. Thereby the challenges of the optical properties of hematite are considered, as the small amount of hematite in MD affects TOA, which uses an optical correction for the quantification of organic carbon (OC) and EC.

Regarding sample preparation, i.e. the filtration of the liquid sample, a slight vacuum has to be applied to avoid leaks. The filter loadings were found to be homogeneous, but a slight enrichment on the outer rim of the filter was observed. Using isopropanol to rinse the glassware was found to be unfavourable as it did not desorb any EC from the glassware, but reduced the amount of OC collected on the filter. Cutting filters into halves and weighing of these aliquots was found to be the best procedure for partitioning of the filters. Adding $\text{NH}_4\text{H}_2\text{PO}_4$ as coagulant to increase the filter efficiency for EC when filtrating liquid samples led to problems regarding the determination of OC and EC from the thermograms, since the optical correction could not be performed, and is therefore not recommended. For the removal of CC both fumigation and rinsing of samples with HCl were suitable, but rinsing with HCl proved not to damage the oven of the Lab OC-EC Aerosol Analyzer since acidic residues can be removed sufficiently. Temperature steps attributed to CC were identified by reference substances (e.g. CaCO_3 and MgCO_3) and real samples containing MD after HCl treatment. They proved to be different for the thermal protocols used. IMPROVE_A showed carbon signals in the oxidising atmosphere when analysing carbonate standards, which might interfere with the quantification of EC. EUSAAR2 and NIOSH870 proved to be suitable for the analysis of CC and EC. An elongation of NIOSH870 showed improved results compared to its standard version. An elongation of EUSAAR2 showed negligible improvements for the samples analysed, as the original method is already sufficient. CC concentrations were quantified by comparing the respective temperature steps after analysis of original samples and samples treated with HCl. CC assessed from the thermograms correlated with the Ca^{2+} concentration in the eluate of snow sample filters, but CC from TOA was higher than CC estimated from Ca^{2+} . A comparison of the change in transmittance due to iron compounds was performed based on reference substances and samples containing defined amounts of MD. Possible approaches for the correction of transmittance for samples containing MD are presented but need to be further evaluated including an independent method for iron analysis. The comparison of TOA results from surface snow samples measured in different laboratories showed differences in the range of the reported errors for the single laboratories for half of the samples. In the other cases variability between the different laboratories was markedly higher and could not be explained. The small scale variability of concentrations within surface snow samples within 1 m^2 sampling surface were computed for inorganic ions based on the empirical coefficients of variation and ranged up to 25 %. To minimise errors sampling for different analyses should be conducted evenly distributed over the defined area and not only in a small part of it to achieve higher comparability of the results.

1. Introduction

1.1. Motivation

Organic carbon (OC) and elemental carbon (EC) are routinely determined via thermal-optical analysis (TOA) in snow and ice samples (e.g. Aamaas et al., 2011, Wang et al., 2012). It is well known that mineral dust (MD) events regularly occur at Sonnblick, the sampling region of this work (Greilinger et al., 2018). MD and EC deposited on snow surfaces have many effects on the environment, including changes in melt, albedo and other impacts on the ecosystem, which are described more detailed further down. Although carbonate carbon (CC) can be used as proxy for MD in ambient air samples and the procedure of analysis is described in literature (Ashley and O'Connor, 2017), literature regarding snow samples containing MD and its analysis via TOA is scarce. Only Wang et al. (2012) described the change in the laser signal for samples containing MD and proposed a correction to obtain proper values for OC and EC, which is only valid for the thermal protocol IMPROVE. A correction for the thermal protocol EUSAAR2, which is the commonly used protocol in Europe, as well as a detailed description of the effect of MD on TOA are still missing.

Since the late 1980's samples of depth profiles were collected at the glaciers surrounding Sonnblick Observatory annually. They were analysed for inorganic components, leading to a time series which enables the observation of changes in the concentrations of these components over decades (Greilinger et al., 2018). A similar time series describing the carbonaceous components in the depth profiles is planned for the future. These samples shall be analysed for OC and EC and the amount of MD in the samples shall be estimated using CC as proxy for MD. A suitable method is needed for sample preparation, analysis and data evaluation especially for samples containing MD.

1.2. Aim of this work

The aim of this work is to evaluate the determination of OC and EC in background snow samples using a thermal-optical method, i.e. EUSAAR2 or NIOSH870, and considering the possibility that elevated concentrations of MD are present. The simultaneous detection of OC, EC and CC as a proxy for MD, would be the ultimate goal. Until now, CC as an indicator of MD could only be determined using a two-stage method, where CC is removed from a sample aliquot by fumigation with HCl (Ashley and O'Connor, 2017). The treatment of snow samples with liquid HCl is evaluated by comparison to the fumigation with HCl. The relevant temperature steps for the determination of CC are assessed by the measurement of reference substances and the comparison of thermograms of samples before and after HCl treatment. A comparison between CC obtained by TOA and CC estimated from the amount of Ca^{2+} in the sample eluate measured via ion chromatography (IC) is conducted. By using the data obtained from these and further experiments, the possibility to estimate the amount of MD directly from the thermograms is studied. During the course of this work the following subtasks developed and were studied as well: The changes in the transmittance caused by hematite in MD were described and possible approaches for a correction of the transmittance if MD is present were proposed. The possibility to increase the retention of EC for quartz fibre filters by adding coagulant to the snow sample was studied, including the assessment to quantitatively remove CC with the coagulant and its additional effects on TOA.

1.3. Sample origin

The snow samples analysed in this work were collected at the surrounding glaciers of the Sonnblick Observatory located in the Austrian National Park Hohe Tauern in the Eastern Alps at more than 3000 m a.s.l., see Figure 1. Sonnblick is one station of the Global Atmosphere Watch Programme (GAW) network by the World Meteorological Organization (WMO, 2020).



Figure 1: Location of the Sonnblick Observatory (photo by ZAMG, map taken from Greilinger et al., 2018)

Depending on the research objective, surface samples, depth profiles and samples with or without MD contamination were collected and analysed. Sampling was conducted in cooperation with ZAMG (Zentralanstalt für Meteorologie und Geodynamik) by the staff of the observatory. The samples were collected in PE bags (WhirlPak) and stored in a deep freezer at the observatory. They were kept frozen during the transport to Vienna and were stored in a deep freezer until analysis.

Greilinger et al. (2018) state that online aerosol measurements at Sonnblick Observatory showed an influence of MD, transported mainly from the Sahara, in up to 30 days per year. The deposition of dust from the atmosphere can occur via wet or dry deposition.

1.4. Composition of mineral dust and identification in samples

The composition of MD varies depending on its origin. This can be used to relate airborne dust to its source (Kandler et al., 2007). Kandler et al. (2007) analysed Saharan dust aerosols sampled in Spain regarding its composition and found an average composition of 64 % silicates, 6 % quartz, 5 % calcium-rich particles, 14 % sulfates, 1 % hematite, 1 % soot and 9 % other carbonaceous material, see Figure 2.

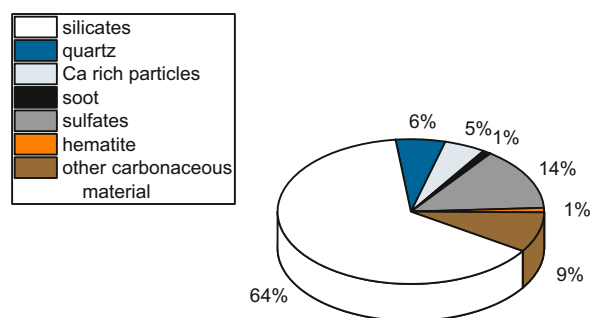


Figure 2: Composition of MD according to Kandler et al. (2007)

In this work the amount of Ca in the samples was determined using IC. Soot and other carbonaceous material were analysed using TOA. Hematite influenced the carbon measurements due to a change in its optical properties depending on the prevailing temperature, leading to a change in the transmittance and reflectance of the laser during TOA. The other compounds of MD were not analysed as the snow was filtrated on quartz fibre filters and only cation IC and TOA were used.

Snow samples containing MD can often be recognized visually due to the reddish colour originating from the iron containing compounds, as shown by Greilinger et al. (2018). Greilinger et al. (2018) defined a pH > 5.6 and a Ca²⁺ concentration > 10 µeq/l as thresholds for the identification of snow samples affected by Saharan dust. Especially calcium and magnesium carbonate lead to lower acidity of snow samples.

As carbonate contains carbon, TOA can be used to identify snow samples containing MD. Until now no threshold for CC from TOA was defined to identify samples containing MD and literature describing a definite procedure to prepare snow and ice samples for the analysis is not available. Furthermore, the influence of hematite on the transmittance and reflectance of the laser hinders the determination of the OC/EC split point and therefore makes a correct determination of OC and EC impossible if no correction of the transmittance is applied. The temperature dependence of reflectance spectra is described in literature (Yamanoi et al., 2009). The only attempt to correct the laser signal found in literature was made by Wang et al. (2012). They use a very general approach to obtain a proper OC/EC split by defining the reflectance at 250°C as the new initial reflectance for samples containing MD, as they observed a decrease in reflectance at this temperature when measuring Fe₂O₃. This approach is only applicable for the thermal protocol IMPROVE, which does not include a cooling step, and only little data is presented to support the evaluation.

1.5. Influence of black carbon and mineral dust on a glacier's environment

Literature regarding the influence of EC, which is also called black carbon (BC) depending on the analysis method, and MD, often particularly Saharan dust, is highly available. Here some aspects of the consequences of the deposition of MD and BC are highlighted.

Regional and global biogeochemical cycles are influenced by dust, which also leads to earlier and faster snowmelt (Field et al., 2010). Furthermore, pathogens can be distributed by dust and introduce nutrients to environments on a global scale (Field et al., 2010).

Schulz et al. (2012) state that MD is rich in iron, phosphorus and other potential micronutrients. MD acts as a major source of nutrients in the world oceans and can be found in ice cores (Schulz et al., 2012).

Microbial communities were shown to vary in different events of Saharan dust deposition on the Mont Blanc glacier (Chuvochina et al., 2011). Chuvochina et al. (2011) refer to many studies that showed that a correlation is given between the concentration of mineral particles from the atmosphere and bacterial biomass in surface snow layers and that microbial diversity correlates with the concentration of atmospheric dust.

The presence of Saharan dust and BC led to a reduction of the mean annual albedo by 0.04-0.06 and therefore to an increase in annual melt of 15-19 % in the Swiss Alps (Gabbi et al., 2015).

Doherty et al. (2013) showed that melting of the surface snow can lead to a 5-fold increase of the concentrations of BC (and other insoluble light-absorbing particulate impurities) on the surface and therefore lead to increased albedo reduction.

2. Methodology

2.1. Thermal-optical analysis

2.1.1. Instrument setup

TOA was performed with the Lab OC-EC Aerosol Analyzer by Sunset Laboratory Inc.. A schematic of an instrument for TOA is shown in Figure 3. The instrument is built up of a valve box, where the gas flows can be regulated, a box containing the main oven which consists of two sectors, the sample oven and the back oven, and a box containing the methanator and a flame ionisation detector (FID). The gas mixture flows through these parts in this order. The composition of the gas mixture varies during the measurement. There is either an inert He-atmosphere or an oxidising He/O₂-atmosphere.

The sample is introduced into the sample oven on a quartz glass spoon, which is positioned in a way that the sample is in the path of the laser ($\lambda=658$ nm) that runs through the main oven at right angle. The transmittance and the reflectance of the sample are detected by photodiodes and logged during the analysis. A thermocouple measures the temperature inside the sample oven. Depending on the thermal protocol used for the measurement the temperature of the sample oven rises, falls or is held constant for a certain amount of time depending on the temperature step. Depending on their chemical composition carbonaceous compounds contained within the sample desorb, volatilise or combust at different temperatures and atmospheres.

The back oven, which is filled with oxidising MnO₂, is heated and held at a constant temperature of 870°C. It oxidises evolving carbonaceous compounds to CO₂ which is then transported to the methanator in the gas flow. In the methanator, which is filled with a nickel catalyst heated to 500°C, CO₂ is reduced to CH₄ which is detected by the FID.

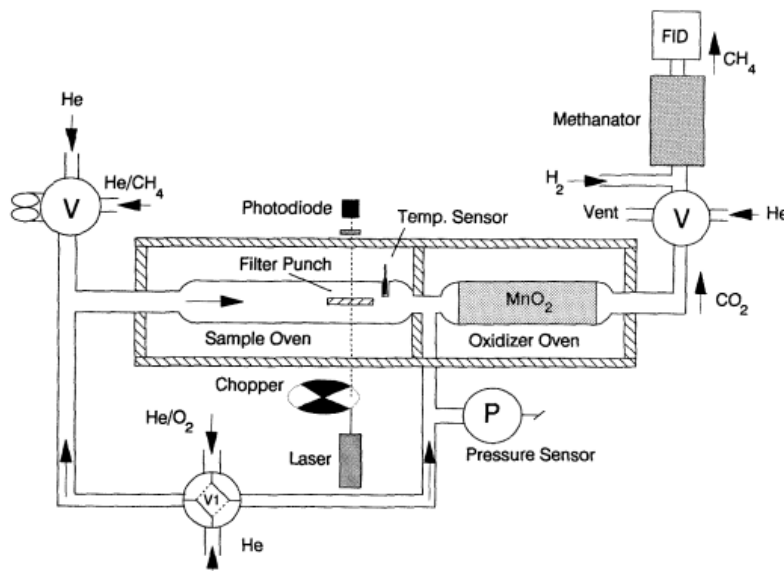


Figure 3: Schematic of an instrument for thermal-optical analysis (taken from Birch and Cary, 1996)

The Lab OC-EC Aerosol Analyzer uses H₂ and synthetic air for detection via FID, He as carrier gas for the inert atmosphere and a He/O₂-mixture (10 vol% O₂) for the oxidising atmosphere. Calibration is being carried out at the end of each measurement. In the thermograms shown in this work no normalisation by the area of the calibration peak was conducted, as the fluctuation of the area was low. The calibration gas is a mixture of He with 5 vol% CH₄ and is injected via an internal sample loop. The ranges of possible flow rates are shown in Table 1. He1, He2 and He3 have their own gas lines and are introduced at different positions of the instrument.

Table 1: Gases and flow rates used for the Lab OC-EC Aerosol Analyzer

Gas	Flow rate min (cc/min)	Flow rate max (cc/min)
Synthetic air	280	300
H ₂	50	54
He1	48	52
He2	7	9
He3	63	67
He/O ₂	7	9
Calibration gas	10	15

2.1.2. Thermal protocols and thermograms

Depending on the atmosphere and the temperature in the oven different carbon compounds are evolving. Therefore, various thermal protocols were developed varying in number, height and length of the temperature steps as well as the type of gas used. The most established thermal protocols are EUSAAR2, NIOSH5040 and IMPROVE_A.

EUSAAR2 is the standard thermal protocol for the analysis of ambient air filters in Europe. It was developed to standardise the measurement of carbonaceous fractions throughout Europe, since EC/TC ratio can vary up to a factor of five when different thermal protocols are used, hindering a comparison of different sites (Cavalli et al., 2010). In the inert phase (He-atmosphere) the temperature rises to 650°C in 4 steps. In the oxidising phase (He/O₂-atmosphere) the temperature rises from 500°C to 850°C in 4 steps. The total measurement time using EUSAAR2 is 1160 s.

When using NIOSH5040, temperatures higher than 850°C are reached in the inert atmosphere, desorbing both organic carbon and carbonate carbon, if present (Ashley and O'Connor, 2017). In the oxidising atmosphere pyrolytically generated carbon (char) is desorbed as well as elemental carbon (Ashley and O'Connor, 2017). In this work the maximum temperature in the inert atmosphere was 870°C, therefore the thermal protocol used is called NIOSH870. The overall measurement time is 850 s. NIOSH5040 was used for samples from urban sites in the US-EPA's Speciation Trends Network (Cavalli et al., 2010).

In IMPROVE_A (Chow et al., 2001) the temperature rises to 580°C in 4 steps, stays constant for 300 s while a change in the atmosphere from inert to oxidising occurs. The temperature then rises to 840°C in 2 steps. In contrast to EUSAAR2 and NIOSH5040 there is no cooling step between the inert and the oxidising atmosphere. Additionally, the reflectance signal is used for the determination of the OC/EC split point contrary to EUSAAR2 and NIOSH5040, where the transmittance is used. Equal to EUSAAR2, the total measurement time of IMPROVE_A is 1160 s. IMPROVE_A was used for samples from non-urban background sites in the US IMPROVE network. Since October 2009 IMPROVE_A replaced NIOSH5040 also for urban samples to get consistent results (Cavalli et al., 2010).

In this work elongated versions of EUSAAR2 and NIOSH870 were used additionally to these common thermal protocols. The time of the temperature steps was extended to the 1.5-fold length, excluding the calibration phase, leading to overall measurement times of 1685 and 1195 s for the elongated versions of EUSAAR2 and NIOSH870, respectively. The common thermal protocols in use were developed for ambient air samples. As particle sizes in snow samples may exceed the size typical for ambient air samples, extended periods at one temperature step might be needed (personal conversation with Sönke Szidat). Additionally, this should lead to a better separation of peaks in the thermogram and therefore make it easier to determine the different fractions of carbon in the sample.

Other thermal protocols used were another version of NIOSH5040 that was used to analyse samples for a comparison experiment in Kolm Saigurn (chapter 6) and variations of EUSAAR2, e.g. elongation of the highest temperature step in the oxidising atmosphere and logging of the cooling phase at the end of the analysis. As mentioned above the EC/TC ratio can vary strongly when using different thermal protocols, therefore it is important to register which protocol was used. The parameters of thermal protocols used are shown in Table 31 to Table 37 in the supplement.

The data obtained during TOA is shown in a thermogram. Usually the temperature, transmittance or reflectance and the FID signal are shown. Additionally, the change of inert to oxidising atmosphere is marked as well as the OC/EC split. An exemplary thermogram labelling the different carbon fractions that can be found in samples is shown in Figure 4. As this exemplary thermogram was taken from literature (Ashley and O'Connor, 2017) no changes were made, e.g. addition of labelling of the axes.

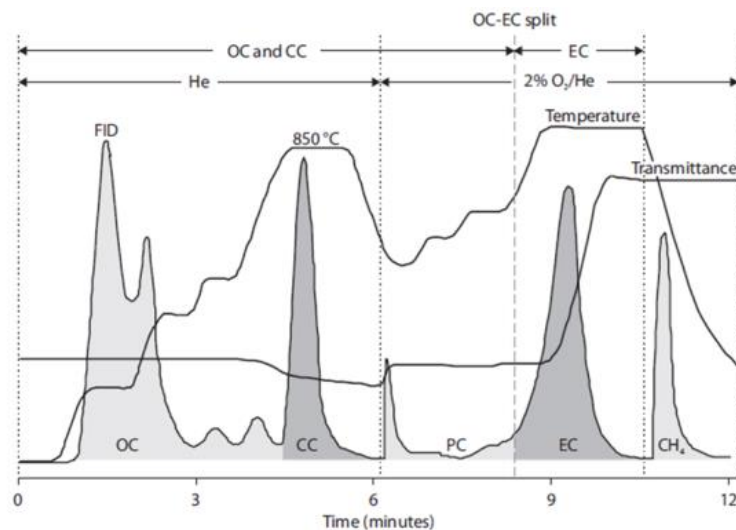


Figure 4: Exemplary thermogram (taken from Ashley and O'Connor, 2017)

Charring is a phenomenon that can occur at any thermal protocol, although the established thermal protocols are developed to reduce charring. Charring leads to reduced laser transmittance since pyrolytic carbon (PC) darkens the filter. PC is included in OC, but desorption takes place in the oxidising atmosphere. Oxidation of PC leads to a rise in transmittance, whereby the separation between OC and EC can be made when the

transmittance reaches the initial value (Ashley and O'Connor, 2017). For thermal protocols using reflectance the OC/EC split is determined when reaching the initial reflectance. The initial transmittance or reflectance is determined at the start of the measurement and is the maximum or minimum value, respectively, within a fixed amount of time, e.g. for EUSAAR2 the maximum value of the transmittance reached within the first 250 s of the measurement. The OC/EC split is determined automatically by the software of the Lab OC-EC Aerosol Analyzer but can be adjusted manually by the analyst.

Unfortunately, not all samples have such a clear split point and distinct fractions as the example in Figure 4, for example samples containing MD. This can already be the case for ambient air samples, but it becomes more obvious when samples contain elevated amounts of MD. A thermogram of a sample containing MD is shown in Figure 5. The transmittance does not reach the initial signal during the analysis, since iron containing compounds change their optical properties depending on the temperature, as described in chapter 4.4. The determination of EC is not possible without a correction of the laser signal. In this work, the transmittance signal is not shown in the thermograms for most samples, as certain compounds in the sample, e.g. Fe, preclude the determination of an OC/EC split point. The evaluation of these samples refers to the temperature steps of the measurements.

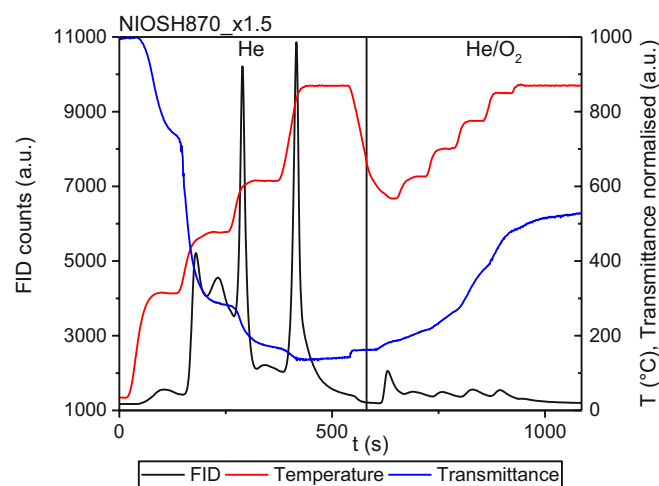


Figure 5: Thermogram of a sample containing MD

The thermograms in this work are usually presented as follows: The FID signal is coloured black and the respective scale is shown on the left side of the thermogram. For the thermogram shown in Figure 5, the transmittance, coloured blue, is normalised between 0 and 100 units by dividing the signal by the highest value and multiplying the signal by. This way, the transmittance can be shown on the secondary axis with the temperature on the right side of the thermogram, as the temperature ranges between 0 and 1000°C for all thermal protocols used. The change from inert to oxidising atmosphere is indicated by a vertical black line, the OC/EC split is not shown in this work, as the transmittance is influenced by iron containing compounds for most samples shown and an OC/EC split could not be determined. The calibration phase is usually not shown in the thermograms as the FID signal of the calibration peaks is much higher than the peaks of the sample. The thermal protocol used is recorded above the thermogram.

2.1.3. Quality assurance

To ensure that the instrument is performing as intended, sucrose solution was analysed at the start of every day before measuring the samples. The concentration of the sucrose solution used was 5 gC/l. First a clean run was performed to remove possible carbon residue from the filter left in the instrument after the last analysis of the day before. For the clean run a parameter file is available at the instrument. Then 10 µl sucrose solution were pipetted onto the filter. After drying the filter in the sample oven via a method defined in the instrument with a maximum temperature of 123°C, the measurement was started. Depending on the thermal protocol used at that day to analyse the samples, either EUSAAR2 or NIOSH870 was used for the sucrose measurement. The result of acceptable measurements had to be in the range of 50 ± 2 µgC.

The result of the sucrose measurement as well as the area of the peak from the calibration gas was added to a control chart to keep track of malfunction or changes in the system. Incidents observed during this work were a leak in the system due to a loose screw joint, a crack in the main oven and lower carbon contents due to the reaction of acid with the methanator filling.

2.1.4. Limit of detection and limit of quantification

The limit of detection (LOD) for the samples in this work was determined by blank measurements, that are described in chapter 3.6.1. in detail. Cleaned filters were rinsed with water, dried, cut and measured with the Lab OC-EC Aerosol Analyzer. The LOD is computed as the average of the blank measurements plus double the standard deviation of the blank measurements at a level of significance of 5 % (Lohninger, Fundamentals of Statistics: Detection Limit, 2012). The limit of quantification (LOQ) is the threefold LOD. The determination of the LOD for TOA differs from the determination of the LOD for IC, where the standard deviation of a standard with small concentrations is used instead of a blank. As the LOD of TOA includes the average of the blank measurements, LOD and LOQ cannot be converted to atmospheric concentrations. Additionally, after correction of the results from TOA with the blanks, the resulting values might be below the LOD, but are still valid.

The LOD is 2.49 µgC/cm² for TC or OC, as the blanks did not contain EC. The average of the blank measurements is for 1.69 µgC/cm² and the respective standard deviation is 0.40 µgC/cm². The corresponding LOQ is 7.47 µgC/cm².

To get an estimate of LOD and LOQ for EC, a lightly loaded ambient air filter was measured repeatedly and the standard deviation of EC on this filter was used for the computation. The standard deviation is 0.07 µgC/cm². Assuming an average of 0 µgC/cm² EC for the blank measurements, the LOD for EC is 0.14 µgC/cm². The respective LOQ for EC is 0.42 µgC/cm².

The detection limit of the instrument, according to Sunset Laboratory, is on the order of 0.2 µgC/cm² for OC as well as EC (Sunset Laboratory Inc., 2020).

2.2. Ion chromatography

In IC separation is achieved due to different affinities of the ions in the sample to the ion exchange material. Depending on the number, valence and location of the charges in the sample species, the strength of interaction with the exchange material varies. The exchange material is located in the separator column and is positively charged for the separation of anions and negatively charged for the separation of cations (Hein und Kunze, 2004). The eluent is pumped through the separator column and the suppressor and reaches the electrolytic conductivity detector. The sample is introduced in the column and the eluent affects the interaction of the ions from the sample with the exchange material. Depending on the strength of the ionic interaction, the ions exit the column in an order from weakest interactions to strongest interactions.

A sodium carbonate/bicarbonate solution was used as eluent for inorganic anion chromatography. It leads to a high background conductivity, which leads to a negative peak at the beginning of the chromatogram from the water contained in the sample. For the analysis of cations diluted methanesulfonic acid (MSA) was used as eluent. In the suppressor the counterions of the eluent are exchanged, which leads to a decreased background conductivity and therefore to increased sensitivity.

The parameters of the cation and anion chromatography system used are shown in Table 2. For the separations isocratic methods were used. The cations Na^+ , NH_4^+ , Mg^{2+} , K^+ and Ca^{2+} and the anions Cl^- , NO_2^- , NO_3^- and Cl^- were analysed.

Table 2: Parameters of ion chromatography

Parameter	Cations	Anions
Column	Dionex Ion Pac CS16A	Dionex Ion Pac AS22A
Guard column	Dionex Ion Pac CG16A	Dionex Ion Pac AG22A
Eluent	38 mM MSA	4.5 mM Na_2CO_3 /1.4 mM NaHCO_3
Flow	1 ml/min	1 ml/min
Suppressor	Dionex CSRS 500 - 4mm	Dionex ASRS 300 - 4mm
Sample loop	150 μl	100 μl
Detection	Conductivity	Conductivity

The calibration standards used were in the range of 0.01 to 12 mg/l, see Table 3. The standards (Std) contained a mixture of all cations and anions analysed, respectively. The standards Std1 and Std2 were only used for the analysis of surface snow samples in chapter 7, the standards Std3 to Std9 were used by default. For the calibration curve a quadratic function without offset was used.

Table 3: Calibration standards for ion chromatography

Standard	Std1	Std2	Std3	Std4	Std5	Std6	Std7	Std8	Std9
Na ⁺ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	2	5
NH ₄ ⁺ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	3	7
Mg ²⁺ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	2	5
K ⁺ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	2	5
Ca ⁺ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	3	7
Cl ⁻ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	2	4
NO ₂ ⁻ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	2	4
NO ₃ ⁻ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	1	4	12
SO ₄ ²⁻ (mg/l)	0.01	0.03	0.05	0.1	0.5	0.8	2	4	12

The results of each sample were evaluated using all standards. Samples that contained less than 1 mg/l of an ion were evaluated again using all standards except Std8 and Std9.

2.2.1. Quality assurance

In every measurement sequence not only standards for calibration and samples but also standards for external control were measured. These standards include F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻ for anions and Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ for cations. The concentrations of the ions of the standards for external control quantified by default are shown in Table 4. Only KStd2 and KStd4 were used for the quality assurance.

Table 4: Standards for external control used for quality assurance of ion chromatography

Standard	KStd1	KStd2	KStd3	KStd4
Na ⁺ (mg/l)	0.04	0.2	0.4	2
NH ₄ ⁺ (mg/l)	0.05	0.25	0.5	2.5
Mg ²⁺ (mg/l)	0.05	0.25	0.5	2.5
Ca ²⁺ (mg/l)	0.1	0.5	1	5
K ⁺ (mg/l)	0.1	0.5	1	5
Cl ⁻ (mg/l)	0.1	0.5	1	3
NO ₂ ⁻ (mg/l)	0.1	0.5	1	3
NO ₃ ⁻ (mg/l)	0.1	0.5	1	3
SO ₄ ²⁻ (mg/l)	0.1	0.5	1	3

After the measurement, the concentrations of the standards KStd2 and KStd4 were evaluated as described above and the results were registered in a control chart. Additionally, the curve and slope of the calibration function of each ion was recorded. Hence the stability of the system could be monitored and potential disturbances in the system could be detected in a fast way. The target value of the concentration of KStd2 and KStd4 was defined as the average μ of their concentrations obtained in the period between June 2017 to October 2018. The warning limit and action limit were defined as $\mu \pm 2s$ and $\mu \pm 3s$, respectively, s being the standard deviation of the data in the period mentioned before. If the concentrations of the standards for external control are not within the action limit, the results of the measurement sequence are discarded and the samples are measured again after checking the system for disturbances.

2.2.2. Limit of detection and limit of quantification

The LOD and LOQ of the analysis of ions via ion chromatography were determined prior to this work based on multiple analyses of standards close to the limit of detection. For the determination of the LOD the threefold standard deviation of these analyses was used. The currently effective LOD is 0.01 mg/l for all ions except Cl⁻, which has an LOD of 0.005 mg/l. The respective LOQ is 0.03 mg/l for all ions except Cl⁻, which has an LOQ of 0.015 mg/l.

2.3. Measurement of pH and conductivity

2.3.1. Conductivity measurement

The conductivity of a sample, which is its reciprocal specific resistance, is measured using a conductivity cell, i.e. a cell which has at least two electrodes. The area of the electrodes and the distance between them are essential for the conductivity measurement and define the cell constant. The determination of the cell constant is done by calibrating the measurement system using a standard with known conductivity. The cell constant in (cm⁻¹) is the ratio of the distance between the electrodes in (cm) and the area of the electrodes in (cm²). The conductivity, which is reported from the measurement in (μS/cm), is the product of the conductance (μS) and the cell constant (cm⁻¹) (GAW, 2018).

The conductivity of precipitation samples is within the range of 5 to 1000 μS/cm. The conductivity of samples is typically reported at 25°C, as the measurement itself takes place at room temperature, which is usually lower than 25°C, the measurement system corrects the measured conductivity to the conductivity at 25°C using an internal temperature correction function (GAW, 2018).

During this work a quality assurance system was introduced. KCl-solutions with concentrations of 1, 0.5 and 0.1 mM were prepared according to GAW Guidelines (GAW, 2018). The standard with the highest concentration, 1 mM, and a theoretical conductivity of 147 μS/cm was not used for the quality assurance, as the samples measured possessed much smaller conductivities. Instead, an additional standard with a concentration of 34 μM and a theoretical conductivity of 5 μS/cm was prepared. For the standard with a concentration of 0.5 mM and a theoretical conductivity of 73.9 μS/cm an error of 5 % was accepted and for the 0.1 mM standard with a theoretical conductivity of 14.9 μS/cm an error of 10 % was accepted, as recommended by GAW. For the additional standard with a low concentration of 34 μM an error of 10 % was accepted. The measurements of the 34 μM standard did not lead to the expected conductivity of 5 μS/cm. Therefore, the average conductivity of the standard determined from 15 measurements on different days, 6 μS/cm, was used as target value. Each standard was measured once at room temperature before measuring the samples. The results were recorded in a control chart and all results had to be within the error margins to allow measurement of the samples.

2.3.2. pH measurement

The pH of a sample, which describes its acidity or alkalinity, is determined using an electrode. The system has to be calibrated using pH buffers, which possess the ability to resist changes in pH. Two-point or three-point calibrations are most common, it is important that the calibration buffers used border the pH range expected in the samples to be measured. The pH is defined as the negative logarithm of the hydrogen activity, for ideal behaviour of dilute solutions the hydrogen concentration can be used (GAW, 2018).

A pH electrode consists of two electrodes, the indicating electrode and the reference electrode. The electrical potential of the indicating electrode is directly proportional to pH, whereas the electrical potential of the reference electrode is constant and independent of pH. The electrodes are connected by an ionic fill solution, which poses as an electrolytic bridge. When the electrode is introduced in a sample, a potential between the indicating and the reference electrode builds up, which is within the millivolt range. The potential, which is dependent not only on the pH of the sample but also on the temperature, is converted to a pH value. A correction for the temperature dependence of the signal is possible if a temperature sensor is included in the electrode (GAW, 2018).

The pH of precipitation samples is within the range of 3.0 to 7.5 pH units. It is important to select an electrode which can measure pH accurately in samples which possess low ionic strength (GAW, 2018).

In this work an MPC 227 pH/Conductivity Meter by Mettler Toledo was used. Before each measurement a two-point calibration of the conductivity and the pH system was done using air as 0 $\mu\text{S}/\text{cm}$ calibration point and a 84 $\mu\text{S}/\text{cm}$ standard at 25°C by Reagecon or buffer solutions with a pH of 4 (citric acid/sodium hydroxide/hydrogen chloride) and 7 (di-sodium hydrogen phosphate/potassium dihydrogen phosphate), both at a temperature of 20°C, by Certipur. The standards were kept in the fridge and after filling an aliquot in a vial the vial was left in the laboratory until the prevailing room temperature was reached. First the conductivity of the sample was determined, the pH of the same sample aliquot was measured subsequently.

2.4. Statistical tests

In this work statistical tests were carried out to compare datasets. For most comparisons, the averages of parameters were computed and compared using t-tests. The prerequisites for the application of t-tests are interval-scaled data, independent samples, normal distribution and homogeneity of variances. The tested parameters in chapter 7, concentration in mg/l, conductivity in $\mu\text{S}/\text{cm}^2$ and pH, are interval-scaled. The normal distribution was tested with the Shapiro-Wilk-test. The homogeneity of variances was tested with the F-test, which requires normal distribution of the samples.

If at least one of the samples is not normally distributed the t-test cannot be applied. If the two samples belong to the same distribution, they can be compared using the U-test. If the samples belong to different distributions, e.g. one sample is normally distributed while the other is not, the median test can be used. In case of unequal variances but normal distribution of the samples, the Welch test can be applied instead of the t-test. For the comparison of the averages of more than 2 datasets, ANOVA can be used.

All tests in this work were conducted using DataLab, Version 4.0, if not stated otherwise for a level of significance of 5 %. Information about the null hypothesis of the tests as well as when to reject it, are taken from DataLab.

2.4.1. Test for normal distribution – Shapiro-Wilk-test

The null hypothesis of the Shapiro-Wilk-test is that the sample belongs to a normal distribution. To test if the null hypothesis has to be rejected the test statistic W is calculated and compared with the tabulated critical threshold W_α , α being the level of significance. For the calculation of the test statistic W the data, including n samples, is sorted in ascending order (y_1 smallest value, y_n biggest value). The sum S^2 is computed (Shapiro and Wilk, 1965):

$$S^2 = \sum_{i=1}^n (y_i - \bar{y})^2$$

y_i ... value of sample i

\bar{y} ... average of data set

For an even number of samples, as in this case, the calculation of b is shown below. The value k is half of the number of samples n . The coefficients a_{n-i+1} are listed in the publication by Shapiro and Wilk (1965).

$$b = \sum_{i=1}^k a_{n-i+1} * (y_{n-i+1} - y_i)$$

The test statistic W is computed by dividing the square of b by S^2 . The test is suitable even for small samples with less than 20 objects. (Shapiro and Wilk, 1965). The null hypothesis, normal distribution, has to be rejected if the test statistic W is smaller than the critical threshold W_α .

2.4.2. Test for equality of variances – F-test

The null hypothesis of the F-test is that the variances of two datasets are equal and therefore the ratio of the variances is 1. The prerequisites for two-sample two-tailed F-tests is that the data is normally distributed and the samples are independent of each other (Lohninger, Fundamentals of Statistics: Two-Sample F-Test, 2012). The variances of the datasets that are to be compared are computed. The ratio of the variances is computed, whereby the bigger variance is the denominator, to obtain the test statistic F . The test statistic F is then compared to the tabulated critical value $F_{\alpha/2}$. The null hypothesis that the variances are equal has to be rejected if the test statistic F is bigger than the critical value $F_{\alpha/2}$.

2.4.3. Test for equality of averages – t-test

If the prerequisites for t-tests are fulfilled, two-sample t-tests can be conducted for the datasets. The null hypothesis of the t-test is that the averages of the data sets are equal. The null hypothesis of equal averages of the datasets has to be rejected if the absolute value of the test statistic t is bigger than the tabulated critical value $t_{\alpha/2}$. The computation of the pooled variance s_p^2 is the averaging of the variances of the datasets, since the datasets used in this work contain the same number of samples ($n_1=n_2$). The test statistic t is calculated as shown below (Lohninger, Fundamentals of Statistics: Two-Sample t-Test – Small Sample Sizes, 2012):

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{s_p^2 * \left(\frac{1}{n_1} - \frac{1}{n_2}\right)}}$$

\bar{x}_i ... average of data set i

n_i ... number of samples of data set i

2.4.4. Test for equality of averages – ANOVA

If the averages of more than two samples shall be compared, ANOVA (Analysis of Variances) can be performed. Using ANOVA instead of multiple t-tests prevents performing a high number of tests and an increase in the level of significance (Lohninger, Fundamentals of Statistics: ANOVA, 2012). The prerequisites for ANOVA are normal distribution of the data and equality of the variances for all samples. Normal distribution was tested with the Shapiro-Wilk-test for all samples. To test the equality of variances of the samples, DataLab offers to use the Levene test, which was used in this work. The null hypothesis, equality of the sample means, has to be rejected if the test statistic F is higher than the critical value $F_{k-1;n-k}$. The test statistic F is computed as the ratio of the variance of factors and the variance of errors (Lohninger, Fundamentals of Statistics: ANOVA – How to perform it, 2012).

2.4.5. Test for equality of medians – median test

The median test can be used even if the data sets do not belong to the same distribution and do not possess equal variances. The test statistic, X^2 , is computed and compared to a critical value. DataLab offers X^2 values with Yates' continuity correction, which were used in this work. The null hypothesis, equality of the expected values, has to be rejected if the test statistic X^2 is bigger than the critical value.

As nonparametric tests like the median test possess higher type II errors than parametric tests at a given level of significance, nonparametric tests should only be used if the prerequisites for parametric tests are not met (Lohninger, Fundamentals of Statistics: Parametric and Non-Parametric Tests, 2012).

3. Procedure of sample preparation and analysis

Within this chapter basic considerations about the sample preparation and analysis are discussed and the respective results presented.

3.1. Preparation of quartz fibre filters

Filters with a diameter of 27 mm were cut from quartz fibre filters (PALLFLEX Membrane Filters, 150 mm) with a circular punch. These discs were cleaned in a muffle furnace at about 500°C for 24 h. Afterwards, the punches were put in a desiccator, whose bottom was filled with water, for at least 24 h to saturate the highly reactive surface of the filter material with water. The filters were either used immediately or stored in a PS petri dish sealed with Parafilm until use. In chapter 5 the topics of the filter efficiency of quartz fibre filters for inorganic cations and sample preparation when adding a coagulant to a snow sample are discussed.

3.2. Filtration setup

The filtration setup is shown in Figure 6. It consists of a vacuum pump, a manometer, a T-piece and a side-arm flask which has a rubber cone, a frit and a funnel on top. The frit and the funnel are held together by a clamp. The vacuum pump and the manometer as well as the T-piece and the side-arm flask are connected with a vacuum hose.

To load filters, the cleaned quartz fibre filter is installed and fixed by the clamp. The sample is poured into the funnel and the sample flow is regulated by partially closing the T-piece to generate a slight vacuum to filtrate the sample slowly and constantly.

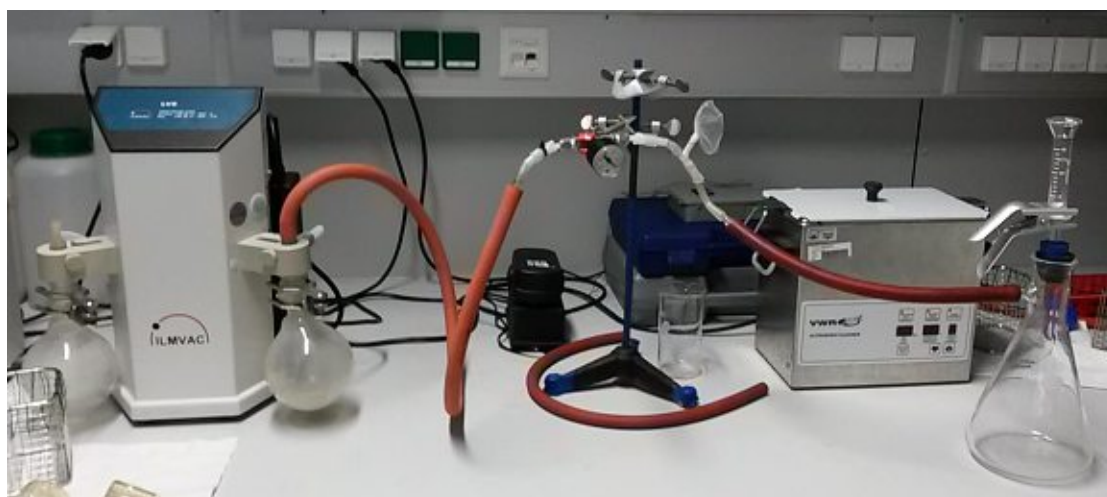


Figure 6: Setup for the loading of filters

3.3. Filtration test with rain samples

As rain samples were available in larger quantities than snow samples and are expected to have a similar matrix, the filtration procedure was tested and optimised using rain samples.

To examine the homogeneity of the loading of the filters, a large volume of a well-defined rain sample was needed. For this purpose several rain samples with visible pollution by particulates have been merged to enable a visual evaluation of the homogeneity. The resulting sample was filtered onto the quartz fibre filters.

For the filtration the filter was moistened with 5 ml Milli-Q water to prevent particles from unevenly distributing on the dry filter. Then 15 ml of the rain sample were put in the funnel and filtrated with or without applying low pressure. The addition of rainwater was repeated two times, leading to a sum of 45 ml rain sample used. The setup was washed with 15 ml Milli-Q water to remove residues of the sample from the glassware and the filter was dried at low pressure for about 10 s.

At the filtration of the first 15 ml sample without applying a vacuum it was noticed that the setup was leaking after some time, i.e. the sample leaked between the funnel and the frit. Hence a slight vacuum was applied for all future filtrations.

The following filtrations were performed at 0.1; 0.2; 0.3; 0.4; 0.5 bar below atmospheric pressure and the maximum reachable low pressure with this setup of about 0.7 bar. The loaded filters are shown in Figure 7. The filters are labelled from #1 to #7 with increasing low pressure, #1 being the filter loaded at normal pressure, #7 being the filter loaded with 0.7 bar negative pressure.

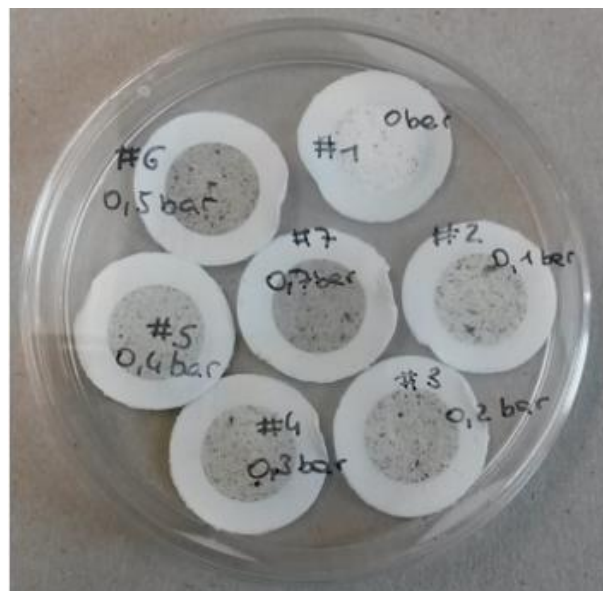


Figure 7: Filters loaded at different negative pressures

Filter #1, which was loaded at normal pressure, is much lighter than the other filters. The reason for this is that only one third of the sample volume of the other filters has been drawn. The filters #6 and #7 are darker, those have been loaded after the rain mix has been refilled with additional rain samples, that possessed a higher particle pollution than the previously merged samples.

Generally, all filters show a homogeneous loading across the filter area, as can be seen by the greyish colour of the filters. Still some larger particles appear as darker spots. Since the concentration of the large particles is low, a homogeneous distribution of these particles cannot be expected. Overall, the loading is rather homogeneous across the entire loaded area, although in previous experiments in the working group the filtration of snow samples led to darker areas at the edge of the loaded area. Still, subsequent filtrations with snow samples showed this effect again, especially when larger volumes of snow sample were filtrated.

The filtration setup leaked during the filtration at normal pressure. Additionally, the filtration took a lot of time which might lead to contamination of the sample. Therefore, the filtration should only be done applying a slight vacuum. No leaks were detected using negative pressures between 0.1 and 0.7 bar. The homogeneity of the loading at different negative pressures was not visually distinguishable. Thus, it appears that negative pressures between 0.1 and 0.7 bar are suitable for the loading of filters with rain samples.

3.4. Cutting of filters to obtain aliquots for analysis

Aliquots are required for TOA of the filter loaded as described above, since the loaded area is too big to fit on the sample spoon of the Lab OC-EC Aerosol Analyzer. Additionally, aliquots are useful for the comparison of different procedures. Various ways to get aliquots can be used, here three different types of partitioning are reviewed.

Loaded filters were dried overnight in a desiccator above silica gel. Prior to the analysis a punch with a diameter of 15 mm was made from the loaded area of 16 mm. The punch was divided in one of the three types: crescent, halves or punches. The crescent was obtained by making another punch with a diameter of 10 mm on the very side of the 15 mm punch. Both parts were used as samples. To obtain halves, the 15 mm punches were cut with a cutting device. The third type, the punches, was obtained by making two punches with a diameter of 8 mm next to each other without making a punch of 15 mm first. Schematics of the types of dividing are shown in Figure 8 and loaded filters after partitioning are shown in Figure 9.

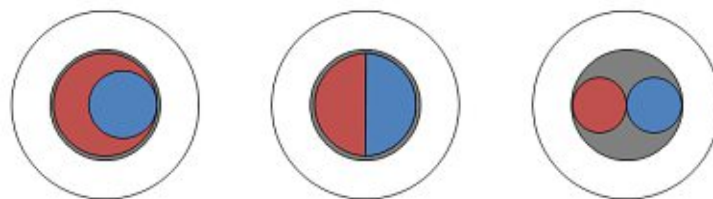


Figure 8: Schematics of the types of partitioning; left: crescent, middle: halves, right: punches; white: filter, grey: loaded area, red/blue: aliquots

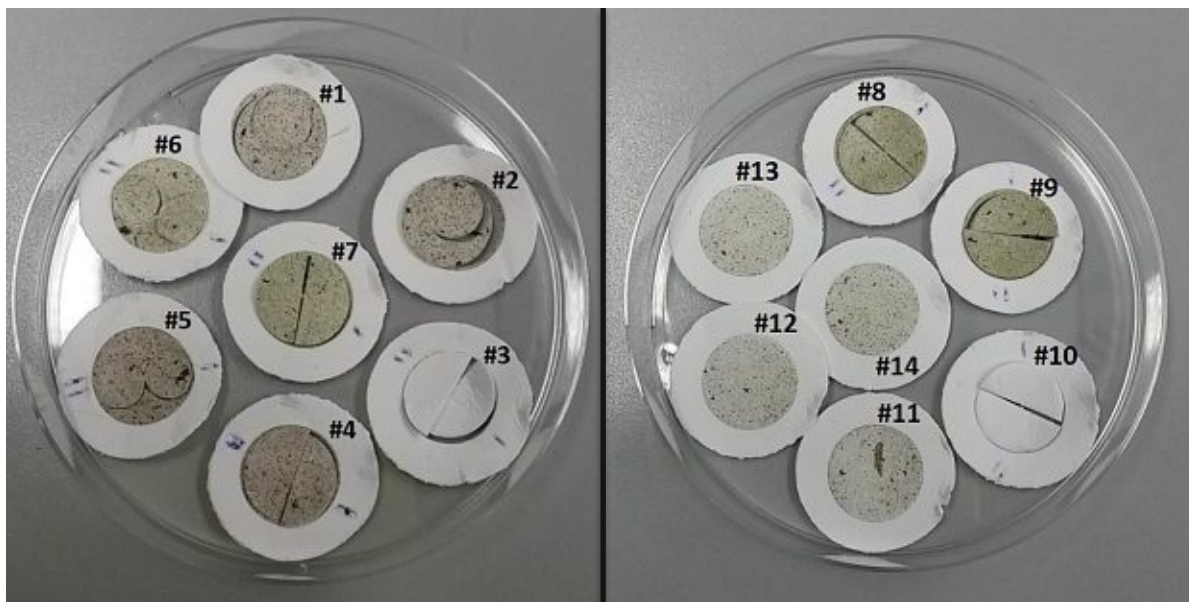


Figure 9: Filters loaded with rain samples after partitioning

The halves were weighed prior to TOA to enable corrections if the filter was not cut exactly in halves. This was necessary, since the cutting device is not optimized for this procedure and the halves obtained with this method may have some variation. At first each filter part, independent of the type of partitioning, was weighed three times to get reliable results for the correction of the halves. The results of 56 filter parts, halves, punches and crescents, was evaluated to decide if threefold weighing is necessary. The relative standard deviation (i.e., standard deviation divided by average) of the three measurements of one filter part was below 2 % for all 56 samples and below 1 % for 51 samples. Due to the small deviations future filter parts were only weighed once. The weighing step can be neglected for punches and the crescent, as the aliquots are obtained by cutting with punches. This leads to a much bigger reproducibility than cutting the filter in halves and the weighing of these samples was only conducted to collect more data to decide if threefold weighing of filter aliquots is necessary.

To estimate the error induced by the cutting or punching process 14 loaded filters were cut in halves and punches were made of 12 loaded filters. The filter parts were weighed and the sum of the weights was computed. The difference in percent of the filter parts to half of the total weight was calculated for each filter. The difference was less than 1 % for 7 out of 12 filters with punched-out aliquots, less than 2 % for 4 filters and slightly above 2 % for 1 filter. The difference using halves was below 5 % for 10 out of 14 filters and less than 10 % for the remaining 4 filters. Weighing is therefore not necessary for punches, which are approximately the same size, but is essential for halves, as the difference in area and, if the loading is homogeneous, carbon content can range up to 10 %.

In later experiments with snow samples it was discovered that a higher loading may occur at the edge of the loaded area. Separate analyses of halves of 9 samples excluding the outermost loaded area and the outermost loaded area from the comparison experiment in Kolm Saigurn (chapter 6) were conducted to estimate the error induced by not analysing the

rim. The results showed that the amount of TC is underestimated in average by 18 % with a standard deviation of 9 %, the maximum values ranging from 7 % to 32 %. As the loaded area had a diameter of 16 mm, a punch of 17 mm was used from there on. The bigger punch size allowed to analyse the entire loaded area, however it was important to cut the non-loaded area in half when cutting aliquots as the loaded area usually was not centred. The halves were weighed and corrected for their area as described above. A schematic as well as a filter loaded with a snow sample are shown in Figure 10. The area with higher loading at the edge can be seen on the filter.

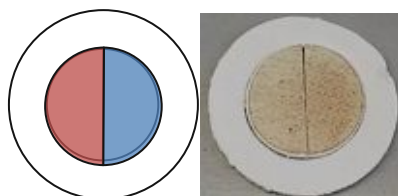


Figure 10: Schematic of halves using a punch of 17 mm diameter and filter loaded with snow sample after partitioning

3.5. Homogeneity of the loadings determined via TOA

With all types of partitioning two samples were obtained per filter, labelled I and II, which were analysed in two analytical runs. By analysing both, the carbon content of segment I and segment II, and after including a possible correction for the segments' sizes, the homogeneity of the loadings could be evaluated.

The filter area of the segments used TOA is shown in Table 5.

Table 5: Filter areas after different types of partitioning

Type of partitioning	Filter area (cm ²)
crescent	0.982 (crescent); 0.785 (punch)
halves	0.884 each
punches	0.503 each

Analyses were performed using the thermal protocols EUSAAR2 or NIOSH870, respectively. As only TC was considered for the determination of the homogeneity to get an overall estimate, the applied thermal protocol is not of importance. The filter parts were analysed separately and the deviation of TC was used to estimate the homogeneity. The halves were corrected for their weight to consider non-uniform cutting. The data is not shown here but provided in Table 38 in the supplement. Note that the results of both blanks, b, and samples, S, are considered and that the correction might lead to a small change in TC on the filter. The change was up to 1 % for 17 out of 18 samples and 3 % for the remaining sample.

For the evaluation of the homogeneity the sum of TC of the filter parts was computed. The deviation of the TC load of the single filter parts from the value calculated according to their size was determined. In a second step the correction of filter areas obtained by the weighing process was considered. This comparison showed that the correction of the filter areas improved the comparison for more than half of the analyses (10 out of 18 filters). The effect was especially pronounced for filters where the deviation before the correction was higher than 5 %, leading to an improvement by up to 10 %. For the remaining cases (8 filters) the correction led to slightly poorer results, ranging up to 1 % for half of the filters, up to 2 % for 7

out of 8 filters and up to 4 % for all filters, compared to the deviation before the correction. Therefore, the weight of halves should be determined when using this type of partitioning and the corrected values were used for the evaluation of the homogeneity of loading.

The homogeneity was only analysed using filters divided in halves and punches. The approach to evaluate the homogeneity was to compute the sum of TC of both filter parts and calculate the fraction of each part. Data of 18 filters that were cut in halves and of 12 filters with punches was analysed, whereby each data set contained one outlier that was removed prior to the subsequent assessment. The data for halves is shown in Table 38 in the supplement and the data for punches is shown in Table 39, both in the supplement. The outliers, which were not considered are marked in red. The average deviation of the loadings of TC from the desired value of 50 % for one half of the filter was 2 % for punches and 3 % for halves, the standard deviation was 2 % for punches and 3 % for halves. The datasets were tested for normal distribution using the Shapiro-Wilk-test. The null hypothesis, the sample is part of a normal distribution, cannot be rejected for both datasets at a level of significance of 1 % (test statistic $p(W)$ halves: 0.0386; punches: 0.2828; critical value (α): 0.01). The homogeneity of the variances was tested using the two-tailed two-sample F-test. The null hypothesis, homogeneity of the variances, must be rejected if the test statistic F is bigger than the critical value $F_{0.01/2}$. The test statistic is 1.9838 and the critical value is 5.4221. The averages were compared using the two-tailed two-sample t-test. The null hypothesis, the averages are equal, has to be rejected if the absolute value of the test statistic t is bigger than the critical value $t_{0.01/2}$. The test statistic is 0.9769, the critical value is 2.7787. There is no reason to assume that the variances or the averages of both data sets differ significantly at a level of significance of 1 %. The deviation of 9 of the 17 filters that were cut in halves was ranged up to 2 %, the deviation of 5 more filters ranged up to 5 % and for only 3 filters the deviation ranged up to 8 %. The deviation of 5 of the 11 filters where aliquots were punched out ranged up to 2 % and the deviation of the other 5 filters ranged up to 5 %. Although higher deviations may arise from using halves, the difference in deviations between halves and punches were not statistically significant at a level of significance of 1 %.

The crescent was discriminated from the assessment of the homogeneity as the crescent-shaped filter part was too big to fit on the spoon of the Lab OC-EC Aerosol Analyzer used to introduce the sample into the main oven. The tips had to be cut off and put on the rest of the crescent for analysis. This procedure might introduce a contamination of the sample. For a reliable split between OC and EC the path of the laser beam should run through one layer of filter only, which can hardly be checked as the heating coil blocks the view into the main oven. Two layers would lower the transmittance and make it harder to set the OC/EC split point in experiments that do not only consider TC but also OC and EC. Additionally, the filter parts of the crescent do not possess the same area, increasing the uncertainty of the comparison of the filter parts, mainly because the loading in the middle of the filter and the edge may not be equal and the partitioning using the crescent is asymmetrical. Furthermore, the punch of the circle must be made at the very side of the bigger punch. If it is put too far at the side, the area of the circle is too small. If it is not put at the very side, small parts of the filter will be lost and the area of the crescent is too small. Due to the difficult handling and the high error-proneness the idea of the crescent was neglected for future experiments.

The results of TOA of halves and punches were equivalent according to the statistical evaluation, therefore other reasons for favouring one of the types of partitioning can be considered. The halves are easy to prepare with suitable equipment, although some of the divided filters are even visually not halves. Weighing the filter parts and calculating the ratio of their masses and subsequently calculating the ratio of their carbon contents show that most of the ratio of the masses and the ratio of the carbon contents are in agreement. Furthermore, almost the entire loaded area of the filter is being measured and therefore even filters with small loading can be analysed without having an issue with the LOD. Additionally, inhomogeneity in loading, e.g. enrichment of particles on the outer rim, are not neglected if the entire loaded area is analysed. The punches are the safest way to get two parts of the filter with the same size. Weighing of the samples is not necessary. Since only small parts of the filter are used, there may be problems regarding the LOD. Filters with small loadings might show carbon contents below the LOD, especially if clean snow samples with low EC content are analysed. For the samples analysed in this work, halves are a suitable method of partitioning and were therefore used.

3.6. Choice of a proper solvent for sample preparation

Non-polar particles, e.g. EC, that are attached to the glass wall of beakers used for melting samples or the funnel of the filtration setup can be rinsed with solvents less polar than water. Here isopropanol was used due to its high volatility and therefore the little chance of having residues left on the filter interfering with the subsequent carbon measurements. Blank values were determined for the filtration with water only and both water and isopropanol. Samples containing a reference material or a snow mix, respectively, were filtrated several times, using either water or water and isopropanol to determine whether the desorption leads to higher carbon recovery.

3.6.1. Blanks

To determine blank values, clean quartz fibre filters were used. The filters were handled like sample filters: They were moistened with 5 ml Milli-Q water, then 75 ml Milli-Q water was used for the cleaning of the beaker and 15 ml Milli-Q water was used to clean the funnel, leading to a sum of 95 ml Milli-Q water that was drawn through the blank filter. Air was drawn through the filter to remove remaining liquid for about 10 s. The filters were dried above silica gel overnight, cut in halves, weighed and subsequently measured with the Lab OC-EC Aerosol Analyzer.

For blank filters with isopropanol the same procedure was used, but 75 ml isopropanol used for the cleaning of the beaker were drawn after drawing the sum of 95 ml Milli-Q water. 15 ml isopropanol were used to clean the funnel.

A sum of 24 filters was analysed. For the preparation of half of them only water was used, for the other half of them both water and isopropanol were used. One half of each filter was analysed with EUSAAR2, the other half with NIOSH870.

None of the measured blank filters contained EC. The results for TC are shown in Table 6.

Table 6: Results of blank measurements comparing water and water/isopropanol for sample preparation

Thermal protocol	EUSAAR2	EUSAAR2	NIOSH870	NIOSH870
Solvent	Water	Water/isopropanol	Water	Water/isopropanol
TC Avg ($\mu\text{gC}/\text{cm}^2$)	1.71	1.73	1.67	1.68
TC Stddev ($\mu\text{gC}/\text{cm}^2$)	0.43	0.33	0.38	0.44

The blanks with the lowest measured TC concentration contained $1.23 \mu\text{gC}/\text{cm}^2$ for water and $1.28 \mu\text{gC}/\text{cm}^2$ for isopropanol. The blanks with the highest results contained $2.76 \mu\text{gC}/\text{cm}^2$ for water and for isopropanol.

The two datasets water and water/isopropanol, independent of the thermal protocol used, were tested for normality using the Shapiro-Wilk-test. The null hypothesis, the samples are normally distributed, has to be rejected if the test statistic $p(W)$ is smaller than the chosen level of significance, 0.05. The test statistic for both datasets is 0.0008, therefore both datasets are not part of a normal distribution. As normality is a prerequisite for the F-test and the t-test, none of these tests can be applied to compare the datasets.

Hence, the two datasets were compared using the two-sample median test. The null hypothesis, the expected values of the two datasets are equal, has to be rejected if the test statistic X^2 is bigger than the critical value $X^2_{0.05,1}$. The exact value of X^2 is 0.7732, the critical value is 3.8415. There is no reason to assume that there is a difference in the blank values of blanks prepared with water or water and isopropanol.

A comparison of the data of EUSAAR2 using water or water and isopropanol as well as a comparison of NIOSH870 showed that the null hypothesis cannot be rejected (exact value for X^2 EUSAAR2: 1.0000; NIOSH870: 0.4136; critical value: 3.8415). The results of the blank measurements suggest that the use of isopropanol for sample preparation does not lead to significantly higher blank values at a level of significance of 5 %. The TC values for cleaned filters that were stored in plastic petri dishes and sealed with Parafilm until use were equal or above the blank values obtained when using water and isopropanol. Therefore, it is assumed that there are no residues of isopropanol left on the filter disturbing the measurement of carbon.

3.6.2. Reference material and snow samples

The reference material San Joaquin soil (NIST SRM 2709, 2003), containing 1.2 w% carbon, was weighed in and suspended in water. The sample was filtrated as described above, filtering the sample after moistening the filter. The beaker and the funnel were rinsed either with water or both water and isopropanol. Three filters were loaded for each preparation method. The filter halves were thermal-optically analysed, using EUSAAR2 for one half and NIOSH870 for the other. After adding the results of both halves and correcting the results with the weight of the amount of San Joaquin soil used, about 9 g, the results, shown in Table 7, were compared using statistical tests and a level of significance of 0.05. For the statistical evaluation only the TC values of the samples were used as the initial transmittance of the laser was not reached during the measurement and a split between OC and EC was therefore not possible.

Table 7: TC of filters loaded with San Joaquin soil using water or water/isopropanol for sample preparation

Sample	TC ($\mu\text{gC}/\text{filter}$)	Sample	TC ($\mu\text{gC}/\text{filter}$)
SJW1	56.47	SJP1	51.95
SJW2	60.47	SJP2	54.37
SJW3	56.24	SJP3	47.37

The two datasets SJW (San Joaquin soil water) and SJP (San Joaquin soil isopropanol) were tested for normal distribution using the Shapiro-Wilk-test. The null hypothesis, the sample is part of a normal distribution, has to be rejected if the test statistic $p(W)$ is smaller than the level of significance, 0.05. The test statistic is 0.9076 for SJW and 0.3367 for SJP. Hence, there is no reason to assume that the datasets are not normally distributed. The variances of the two datasets were compared using the two-sample F-test. The null hypothesis, the variances of the two datasets are equal, has to be rejected if the test statistic F is small than the critical value $F_{0.05/2}$. The test statistic is 2.2339 and the critical value is 39.0000. Therefore, there is no reason to reject the null hypothesis. The means of the two datasets were compared using the two-sample t-test. The null hypothesis, the means of the datasets are equal, has to be rejected if the absolute value of the test statistic t is bigger than the critical value $t_{0.05/2}$. The test statistic is 2.6307 and the absolute value is 2.7764. Hence, there is no reason to assume that the means of the samples prepared with water or water and isopropanol are different.

It has to be kept in mind that three samples per dataset is a small number for statistical evaluation. But since the reference material might not be representative for the snow samples processed and analysed in this work, just this small number of samples was analysed for a first test.

The same experiment was conducted with a sample of mixed snow samples. Snow samples were melted at room temperature and united in a flask. After homogenisation portions of the sample, about 500 g, were weighed into a beaker and filtrated as described above. Four filters were loaded for each preparation method, i.e. rinsing with water or water and isopropanol. The filters were dried, cut in halves and weighed. One half of the sample was measured using EUSAAR2, the other half was measured using NIOSH870. The results of TOA were corrected by the weight of the sample and the weight of the filter aliquots. For the statistical evaluation the sum of results of the two filter halves was computed and used. The thermal-optical measurements provided results for TC as well as OC and EC. The datasets SW (snow water) and SP (snow isopropanol) were compared regarding their TC, OC and EC results using statistical tests and a level of significance of 5 %. The averages and standard deviations of TC, OC and EC are shown in Table 8.

Table 8: Average and standard deviation of TC, OC and EC when using water or water/isopropanol as solvent for the preparation of a snow sample

Solvent	Water	Water/isopropanol
Avg \pm Stddev TC ($\mu\text{gC}/\text{filter}$)	275 \pm 40	182 \pm 29
Avg \pm Stddev OC ($\mu\text{gC}/\text{filter}$)	274 \pm 40	181 \pm 28
Avg \pm Stddev EC ($\mu\text{gC}/\text{filter}$)	0.99 \pm 0.21	1.21 \pm 0.26

The Shapiro-Wilk-test was used to test for normal distribution. The test statistic $p(W)$ for TC is 0.2751 for SW and 0.2021 for SP; for OC 0.7383 and 0.8680; for EC 0.4379 and 0.5144. The critical value is the level of significance, 0.05. There is no reason to assume that TC, OC or EC are not normally distributed for SW or SP at the chosen level of significance. The two-sample F-test was used to check if the variances of the datasets are equal. The test statistic F is 1.9433 for TC, 1.9660 for OC and 1.5800 for EC. The critical value $F_{0.05/2}$ is 15.4392. There is no reason to reject the null hypothesis, equality of variances, for TC, OC or EC. The two-sample t-test was used to compare the averages of the two datasets regarding TC, OC and EC. The absolute value of the test statistic is 3.7991 for TC, 3.8165 for OC and 1.3194 for EC. The critical value $t_{0.05/2}$ is 2.4469. The null hypothesis, equality of the averages, must be rejected if the test statistic is bigger than the critical value. Hence, the null hypothesis must be rejected for TC and OC, but there is no reason to assume a difference in the averages of the two datasets for EC at the chosen level of significance of 5 %.

The statistical evaluation of snow samples showed that the amount of TC and OC decreased when isopropanol is used for sample preparation. On the contrary the amount of EC is not altered, i.e. not increased, when isopropanol is used. The expected effect of rinsing with isopropanol, the desorption of non-polar EC particles from the glassware, could not be observed. In contrast isopropanol reduced the amount of OC on the filters, which may be due to either dissolving particular components present in snow or due to its smaller surface tension compared to water (surface-tension.de, 2017). This might permit small particles to pass through the filter pores. Therefore, isopropanol is not a suitable solvent for the sample preparation conducted in this work due to incomplete retention of water insoluble particles on the filter and water should be used only for the preparation of snow samples.

3.7. Relative standard uncertainty

The relative standard uncertainty for the process of filtration and obtaining aliquots was calculated from multiple filters loaded with the same snow sample. The amount of TC obtained by TOA was corrected by the amount of snow mix filtered. Halves of a punch with a diameter of 17 mm were used for the measurement and the sum of TC measured on both halves of the filter was used to calculate the relative standard uncertainty.

The average and the standard deviation of the amount of TC were calculated. The relative standard uncertainty was obtained by multiplying the square root of the standard deviation divided by the number of samples with the inverse value of the average (Zilli, 2013). The relative standard uncertainty includes the error of all weighing steps, the error of dividing the filter and correction by the weight of the filter halves and the instrument error.

$$u_{rep}(x) = \sqrt{\frac{s_{rep}(x)}{n}} * \frac{1}{\bar{x}}$$

$u_{rep}(x)$... relative standard uncertainty of repeatability

$s_{rep}(x)$... repeatability standard deviation

n ... number of samples

\bar{x} ... average

For the computation of the relative standard uncertainty a test for outliers has to be conducted. Additionally, the data used for the computation must be normally distributed (Zilli, 2013). A data set of 12 samples was used.

The data set was tested for normal distribution using the Shapiro-Wilk-test, as normal distribution is a prerequisite for the subsequently conducted test for outliers. The null hypothesis, normal distribution, has to be rejected if the test statistic $p(W)$ is smaller than the level of significance used, here 0.05. The test statistic is 0.9599, therefore there is no reason to reject the null hypothesis.

The data set was tested for outliers using the Dean-Dixon-Test. This test is suitable for small data sets. The data was sorted in ascending or descending order to test the smallest or the biggest value, respectively. The test statistic Q was computed as follows (Lohninger, Fundamentals of Statistics: Outlier Test – Dean and Dixon):

$$Q = \frac{x_2 - x_1}{x_n - x_1}$$

The value tested is x_1 (smallest value for ascending order, biggest value for descending order), the number of samples, n , was 12. The null hypothesis, the tested value x_1 belongs to the sample, must be rejected if the test statistic Q is bigger than the critical value $Q_{0.05}$. According to the result of the test in DataLab no outliers were found.

Since none of the samples were eliminated, the data set is normally distributed, as testing with the Shapiro-Wilk-test showed above. The average of the sample is $2.28 \mu\text{gC}/\text{cm}^2$ and the standard deviation is $0.43 \mu\text{gC}/\text{cm}^2$. All prerequisites for the computation of the relative standard uncertainty are met and the relative standard uncertainty proved to be 8 %. Therefore, presuming an error of 10 % for the samples is legitimate.

3.8. Summary of chapter 3

A slight vacuum should be applied when loading filters to prevent the system from leaking. Filters loaded using negative pressures between 0.1 and 0.7 bar did not show visible differences in homogeneity and these negative pressures are therefore suitable for the loading of filters with liquid samples.

Three types of partitioning of filters were tested for their applicability: the crescent, the halves and the punches. The crescents should not be used due to problems with the handling of filters and possible loss of filter material when punching out the smaller circle. The halves and punches were shown to be equally suitable regarding the difference in TC loading on filter aliquots. However, a correction of the filter weight and therefore a weighing step is necessary for the filter halves. Still, using punches might lead to problems with the LOD for samples which are lightly loaded. Due to the enrichment of particles at the outer rim of the loaded area, which was observed when filtrating higher volumes of liquid snow samples, halves should be favoured for these samples, as only small parts of the outer rim can be analysed when using punches. It was shown that neglecting the analysis of the outer rim leads to an underestimation of TC by 18 % in average.

The blanks for rinsing filters with water or water and isopropanol did not differ significantly and were $1.72 \mu\text{gC}/\text{cm}^2$ in average when rinsing with water. Analyses of the reference material San Joaquin Soil prepared with these two methods did not differ significantly. However, rinsing filters loaded with liquid snow samples led to a significant decrease in TC and OC but no significant change in EC.

The relative standard uncertainty for the process of filtration and obtaining aliquots calculated from multiple filters loaded with the same snow sample was determined to be 8 %.

4. Application of thermal-optical analysis for the analysis of snow samples

This chapter includes considerations of TOA regarding thermal protocols, temperature steps attributed to CC and the usage of HCl vapour or liquid HCl and addresses the challenges introduced into TOA by iron containing compounds found in MD.

4.1. Comparison of thermal protocols

The following diagrams present raw data of TOA measurements. The transmittance and reflectance are logged during the measurement and the respective software of the Lab OC-EC Aerosol Analyzer, Calc415, performs corrections, which are not included in the raw data. Plotting the thermograms in a software other than the Calc software led to unsatisfactory results. In spite of multiple requests sent to Sunset Laboratory Inc. to offer a solution for this problem, it was not possible to solve this during this work. Hence, the course of transmittance was checked in the mentioned software and the transmittance signal is not plotted for most samples in this work.

All thermal protocols used for TOA should completely remove carbonaceous compounds on the filter. To ensure that carbon is completely removed during the measurement of the filter independent of the thermal protocol used, aliquots of filters loaded with snow samples were analysed again after using different thermal protocols of this work with the clean parameter file. The clean parameter file includes a rise in temperature to 870°C and a hold of the temperature after reaching 870°C in oxidising atmosphere. This takes 3 min and is followed by a drop of temperature and a calibration phase taking 2 min. Carbon residues from the measurement with the thermal protocol should be completely removed after the clean run. No carbon could be determined with the subsequent clean run for the thermal protocols mainly used in this work, EUSAAR2, NIOSH870 and their elongated versions as well as IMPROVE_A. Therefore, all of these thermal protocols can be used and are used for TOA.

4.1.1. Comparison of the thermograms obtained by measurements of ambient air filters with various thermal protocols

Two ambient air filters from Sonnblick Observatory (PM10) with light and medium loadings (178 and 184) and a highly loaded ambient air filter from Leibnitz (PM10) were measured with the thermal protocols NIOSH870, NIOSH870_x1.5, NIOSH5040_Kolm, EUSAAR2, EUSAAR2_x1.5 and IMPROVE_A. For each measurement, an aliquot with a diameter of 10 mm was used. Filter 178 was lightly loaded, coloured light grey, Filter 184 was more heavily loaded, coloured dark grey, and Filter Leibnitz was highly loaded, coloured black. Ambient air filters were used to compare the different thermal protocols due to their high availability and homogeneous loading. A comparison of the thermal protocols should provide an insight into the suitability of the protocols to analyse certain carbon fractions, e.g. CC, and the effect of elongation of thermal protocols on the thermograms.

Ambient Air Filter 178 from Sonnblick

The thermograms of the lightly loaded ambient air filter 178 from Sonnblick obtained by using NIOSH-like temperature protocols are shown in Figure 11. The elongation of the temperature steps of NIOSH870 leads to a better separation of the carbon fractions combusting in each temperature step. Both NIOSH870 and NIOSH870_x1.5 lead to 4 peaks in the inert atmosphere. Using the temperature protocol NIOSH5040_Kolm, where the atmosphere is changed to oxidising already after 300 s reaching the same maximum temperature of 870°C in the inert atmosphere, only 3 peaks which are not separated well are visible. Additionally, the temperature, which shall be reached at each temperature step, is not held constant for a sufficient amount of time to completely combust each carbonaceous fraction.

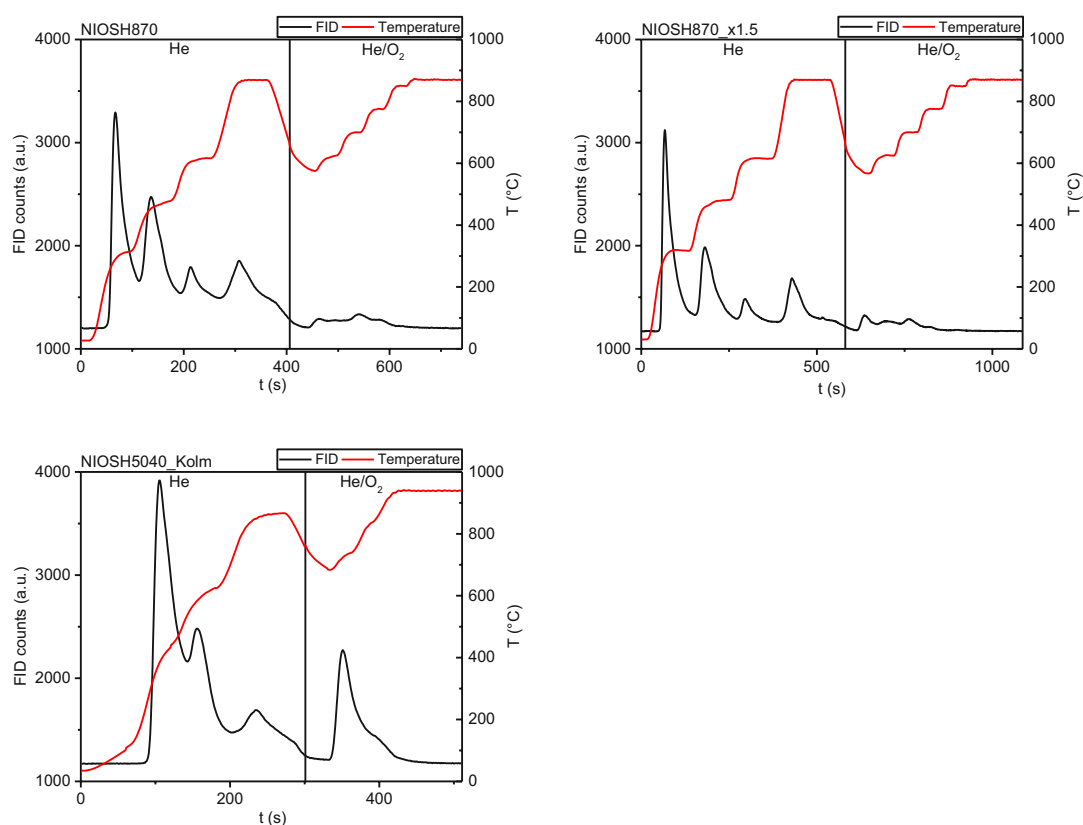


Figure 11: Thermograms of the measurements of ambient air filter 178 using NIOSH870, NIOSH870_x1.5 and NIOSH5040_Kolm

The thermograms of the same filter obtained by using EUSAAR2 and its elongated version, EUSAAR2_x1.5, are shown in Figure 12. Due to the adequate length of the EUSAAR2 protocol all peaks are separated, the elongation of the temperature steps does not enable the analyst to observe a higher number of peaks and does not lead to better separation of peaks in this sample. The elongation of the cooling step makes it possible to reach the temperature in the first step in the oxidising atmosphere, 500°C, before switching to oxidising conditions.

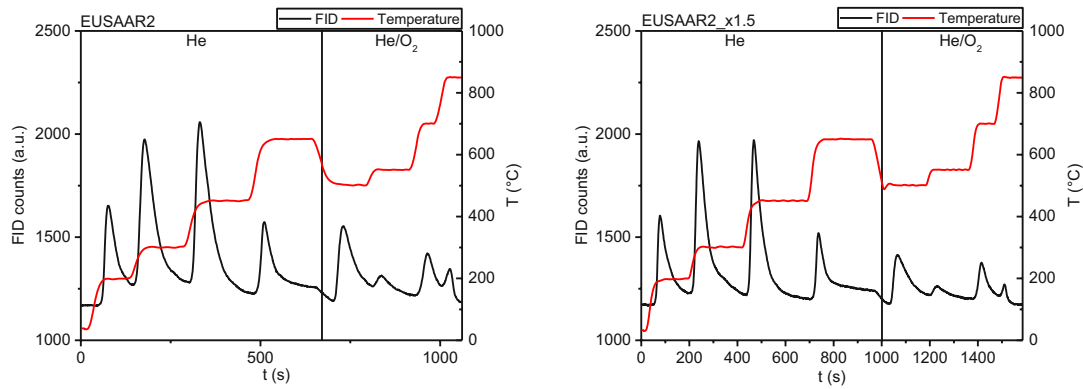


Figure 12: Thermograms of the measurements of ambient air filter 178 using EUSAAR2 and EUSAAR2_x1.5

In contrast to EUSAAR2, which leads to 8 peaks, the thermogram of ambient air filter 178 obtained by the measurement with IMPROVE_A only shows 5 peaks, see Figure 13. Depending on the temperature and atmosphere at which particular carbon fractions that are of interest combust, it may be more difficult to analyse them precisely when only a low number of peaks is available. The temperature in the inert atmosphere only reaches 580°C in IMPROVE_A and it does not contain a cooling step, which leads to a peak with high intensity at the start of the oxidising phase.

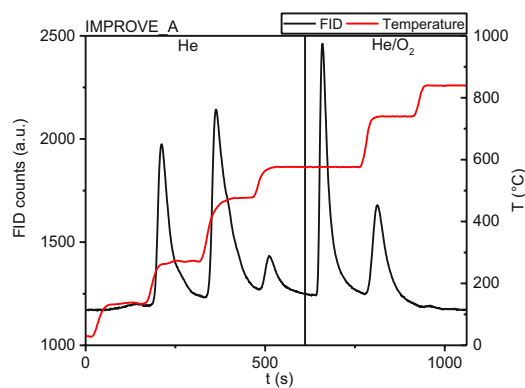


Figure 13: Thermogram of the measurement of ambient air filter 178 using IMPROVE_A

Ambient Air Filter 184 from Sonnblick

The ambient air filter 184 from Sonnblick shows a higher number of peaks in the oxidising atmosphere than filter 178 did when measured with a NIOSH-like temperature protocol, see Figure 14. Both the regular as well as the elongated NIOSH870 thermal protocol show 4 peaks in the inert and 4 peaks in the oxidising atmosphere. The peak in step OC2 is better separated from the peak of high intensity in OC1 when using the elongated protocol. The peaks in the oxidising atmosphere are slightly better separated as well when using the elongated protocol. When measuring the sample using NIOSH5040_Kolm only 3 peaks can be seen in the inert atmosphere and only 2 peaks can be seen in the oxidising atmosphere, which are not well separated.

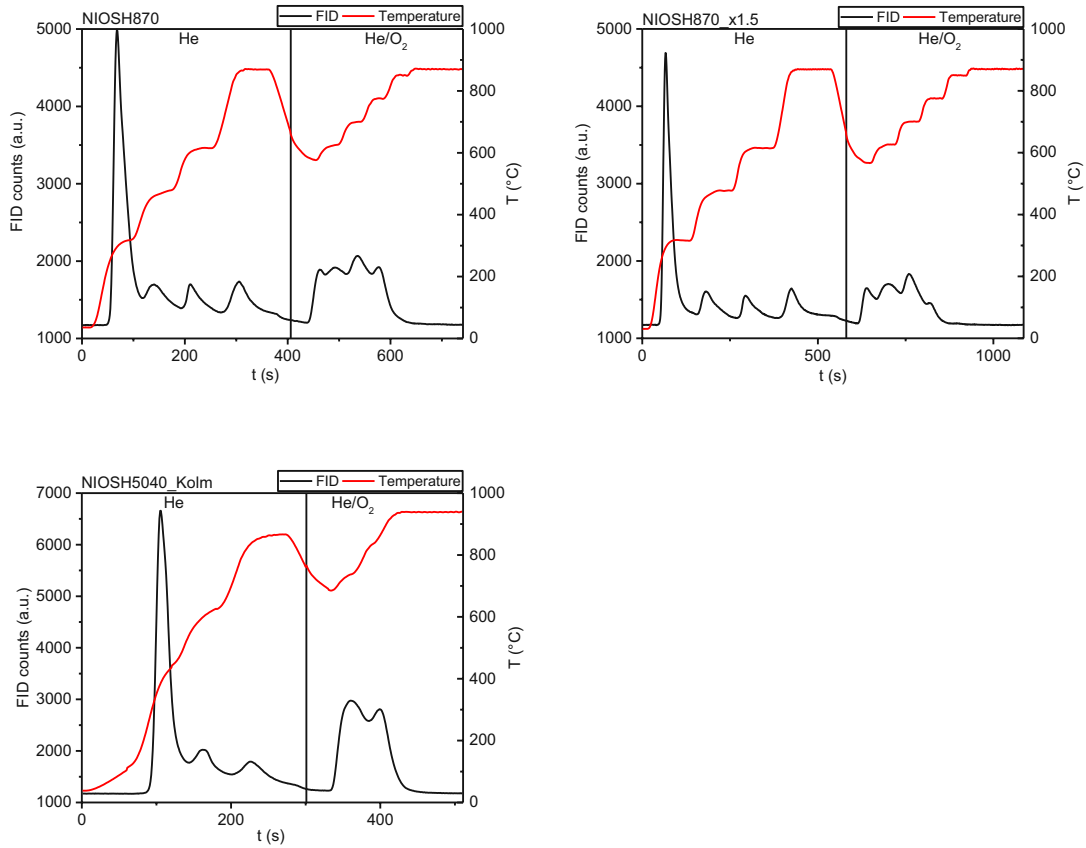


Figure 14: Thermograms of the measurements of ambient air filter 184 using NIOSH870, NIOSH870_x1.5 and NIOSH5040_Kolm

The eight peaks obtained by using the elongated version of EUSAAR2 are slightly better separated than when using the standard EUSAAR2 protocol, which is especially distinctive in the EC4 temperature step, see Figure 15.

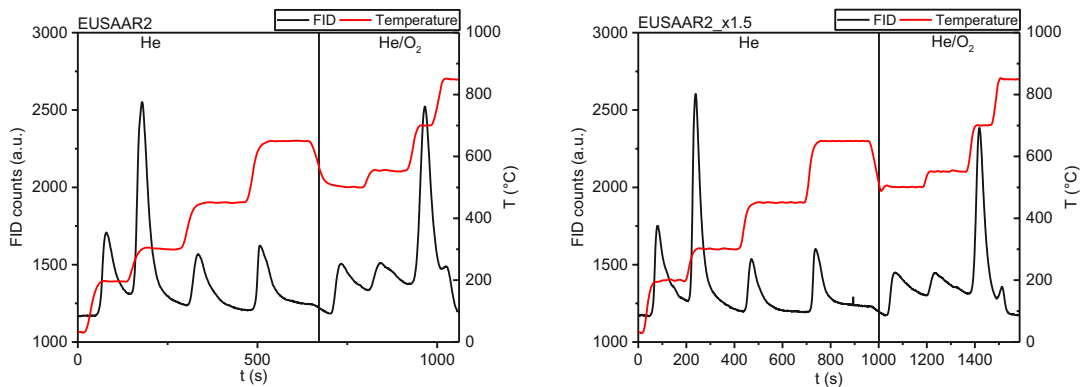


Figure 15: Thermograms of the measurements of ambient air filter 184 using EUSAAR2 and EUSAAR2_x1.5

When analysing ambient air filter 184 using IMPROVE_A, only 3 peaks are visible in the inert atmosphere and 2 peaks are visible in the oxidising atmosphere, see Figure 16. The issue with analysing particular carbon fractions observed at ambient air filter 178 occurs here as well, as only a smaller number of peaks can be observed and a better separation of the peaks in the oxidising atmosphere would be desirable.

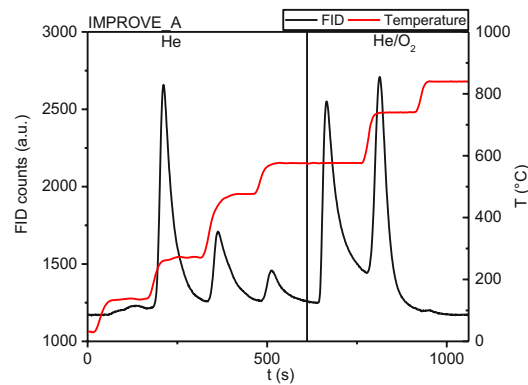


Figure 16: Thermogram of the measurement of ambient air filter 184 using IMPROVE_A

Ambient Air Filter from Leibnitz

The comparison between the thermogram of the standard NIOSH870 protocol and the elongated version shows that the peaks in the inert atmosphere are better separated when using the elongated version, see Figure 17. The signal in the oxidising atmosphere measured with NIOSH870 shows a mixture of peaks, but it is not possible to identify the number of peaks or to integrate the peaks separately. Measured with NIOSH870_x1.5 3 peaks can be identified and integration with deconvolution techniques could be conducted if necessary. The thermogram obtained by measurement with NIOSH5040_Kolm shows vaguely 2 overlapping peaks and one short but broad peak in the inert atmosphere and only one peak in the oxidising atmosphere. The analysis of particular carbon fractions is hardly possible with his thermal protocol and highly loaded filters.

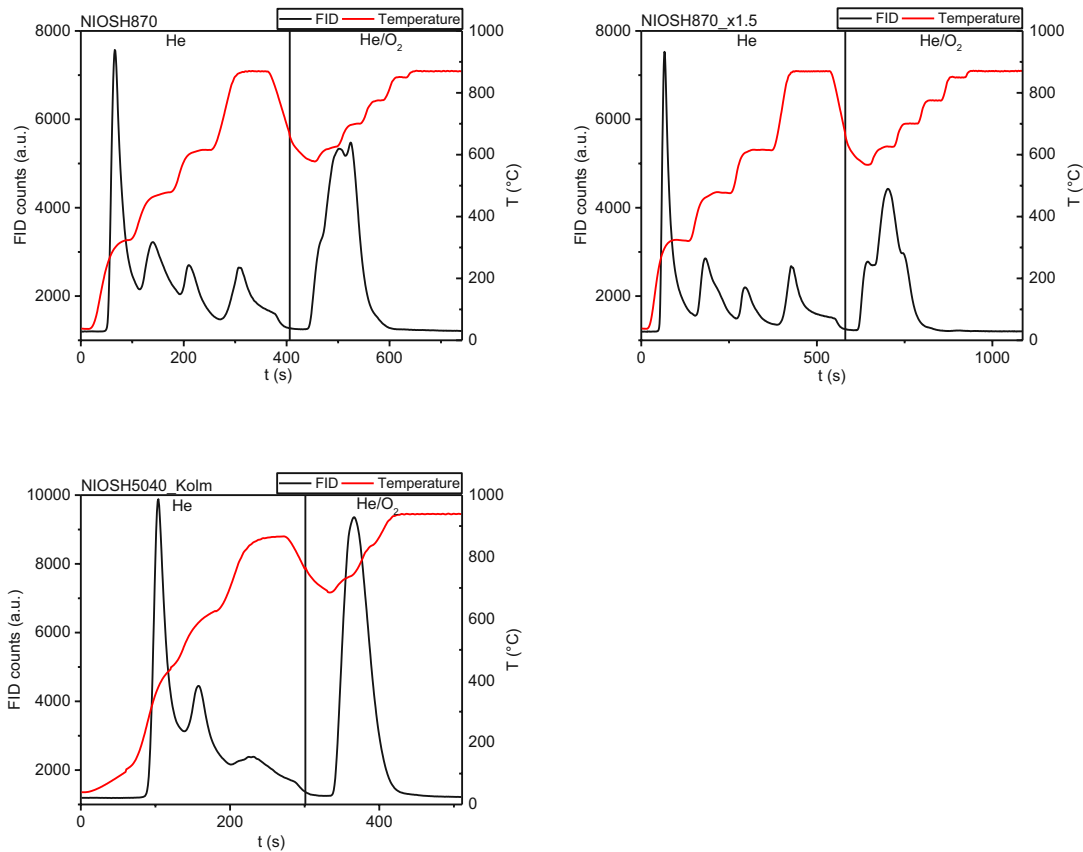


Figure 17: Thermograms of the measurements of ambient air filter Leibnitz using NIOSH870, NIOSH870_x1.5 and NIOSH5040_Kolm

The measurements of the sample with the standard EUSAAR2 temperature protocol and the elongated version are shown in Figure 18 and show 4 peaks in the inert and 3 peaks in the oxidising atmosphere each. The separation of the peaks is only marginally improved when elongating the temperature steps. Premature combustion of pyrolytic OC or EC, i.e. a rise in the transmittance towards the end of a temperature step, cannot be observed in spite of the elongation for this sample or the other ambient air samples, respectively. The height of the peaks in this sample are smaller for EUSAAR2_x1.5. For highly loaded filters containing a high amount of carbon combusted in one particular temperature step, this elongation might make it possible to stay within the range of the FID. No negative effects when elongating the thermal protocol, e.g. premature combustion of EC, visible in the transmittance logged during the measurement, were observed in the thermograms of the ambient air filters measured. As the transmittance could not be shown in the thermograms presented here, the thermograms of two samples, filter 178 and the filter from Leibnitz, taken from the Calc software are shown in Figure 76 and Figure 77 in the supplement. The thermogram of each sample measured with the standard EUSAAR2 thermal protocol and its elongated version are shown.

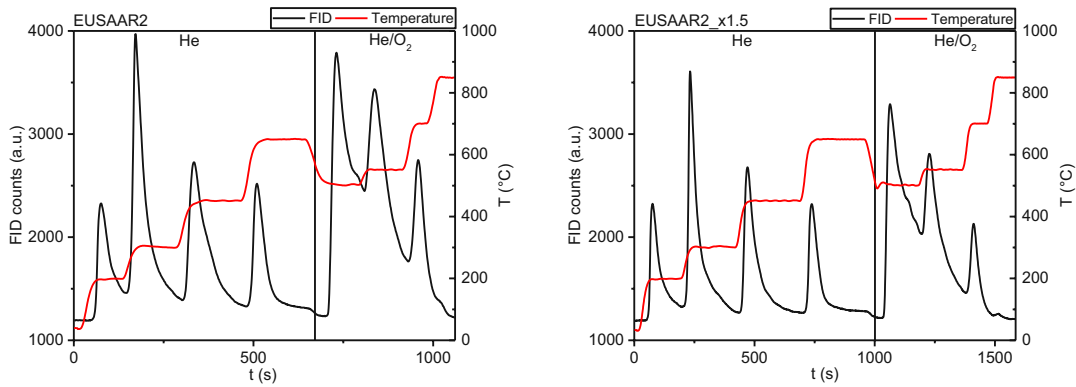


Figure 18: Thermograms of the measurements of ambient air filter Leibnitz using EUSAAR2 and EUSAAR2_x1.5

The thermogram of the measurement of the filter from Leibnitz using IMPROVE_A is shown in Figure 19. 3 peaks can be observed in the inert and 2 peaks can be observed in the oxidising atmosphere. A high fraction of TC in this sample combusts in the first temperature step in the oxidising atmosphere, EC1. If the transmittance slightly varies around the OC/EC split a high variability of the two fractions OC and EC in repeated measurements can be the consequence.

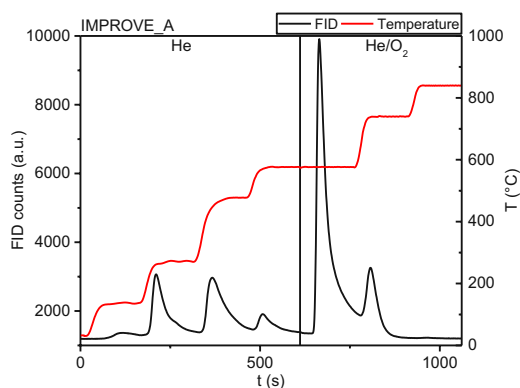


Figure 19: Thermogram of the measurement of ambient air filter Leibnitz using IMPROVE_A

4.1.2. Comparison of the measurement time

The standard thermal protocols NIOSH870, EUSAAR2 and IMPROVE_A last 850, 1160 and 1160 s, respectively. The elongated thermal protocols NIOSH870_x1.5 and EUSAAR2_x1.5 last 1195 and 1685 s, respectively. The thermal protocol NIOSH5040_Kolm lasts 698 s.

NIOSH870 is timesaving and still leads to good results. A 1.5-fold increase in the measurement time leads to better separation of the peaks and the measurement takes only 35 s longer than when using the standard EUSAAR2 and IMPROVE_A protocols. EUSAAR2 lasts as long as IMPROVE_A, but IMPROVE_A does not include a cooling step between the inert and the oxidising atmosphere. This can lead to high peaks when oxygen is introduced in the sample oven and makes it harder to analyse particular carbon fractions, since the number of peaks observed is highly reduced. NIOSH5040_Kolm is the shortest of all

protocols used, but led to non-satisfying results. Hence, it was only used for the comparison experiment (chapter 6) but not for any experiments regarding other research objectives in this work.

The carbonaceous particles collected on the sample filters were removed quantitatively with all thermal protocols used. NIOSH5040_Kolm showed a lower number of peaks for all samples analysed here compared to NIOSH870. An improvement in the separation of peaks in the thermogram by elongation of the temperature steps was especially pronounced for NIOSH870. The effect was less distinct for EUSAAR2, which holds the temperature constant for a longer time in each step compared to NIOSH870, apart from the last temperature step in the oxidising atmosphere. The use of the elongated version of EUSAAR2 might be reasonable for samples where only one aliquot is available and the particles sizes are bigger, e.g. snow samples. If the sample is highly loaded and the peaks are not separated sufficiently, using the elongated version leads to smaller peaks, which might help to stay in the measurement range of the FID. Also, with the instrument used the cooling between inert and oxidising atmosphere was not sufficient with the standard EUSAAR2 protocol, so a small elongation of the cooling step is advisable. It is possible to use the elongated version because no negative effects were observed, i.e. no premature combustion of pyrolytically generated OC or EC. Therefore, the elongated versions should be used for critical measurements, however, for most samples it was observed that using the standard EUSAAR2 protocol is adequate. IMPROVE_A led to a small number of peaks compared to EUSAAR2 and NIOSH870. Smaller numbers of peaks and badly separated peaks might lead to problems in the analysis of particular carbon fractions, e.g. CC. As the determination of CC is an important aspect of this work, the elongated versions of EUSAAR2 and NIOSH870 were mainly used here.

4.2. Identification of CC within the thermograms

4.2.1. Identification of CC signals with carbonate standards

For the identification of the CC peak in the thermogram carbonate standards were analysed. Solutions or suspensions of CaCO_3 , K_2CO_3 and MgCO_3 in Milli-Q water as well as a mixture of the carbonates were prepared. The concentrations of the standards were $5 \mu\text{gC}/10 \mu\text{l}$ or $15 \mu\text{gC}/10 \mu\text{l}$ for the individual standards and $5 \mu\text{gC}/10 \mu\text{l}$ or $37.5 \mu\text{gC}/10 \mu\text{l}$ for the mixture standards.

CaCO_3 and MgCO_3 were chosen due to the elevated concentrations of Ca^{2+} and Mg^{2+} in snow samples containing MD described by Greilinger et al. (2018). Since these substances could not be dissolved but suspensions were obtained, a solution of well soluble K_2CO_3 was prepared to ascertain that the amount of CC pipetted onto the filter agrees with the theoretical amount regardless of the standard being a suspension or a solution. Both the solution and the suspensions led to the expected amount of carbon on the filters.

Variable volumes of the standards were applied to clean filters to identify the CC peak. Subsequently, filters loaded with snow samples were doped with carbonate mixture standard. All filters were dried in the OC-EC Aerosol Analyzer prior to analysis with the implemented option.

The CC standards were analysed using IMPROVE_A and the elongated versions of EUSAAR2 and NIOSH870. The thermograms of the mixture standards showed the sum of the peaks in the thermograms of the CC standards as expected and are not shown here. The signals of the CC standards with a concentration of 5 µgC/10 µl are lower than the signals of the standards with higher concentration. Since the peak assignment is easier with higher signals compared to the blank readings of the filters, only the thermograms of CaCO₃, K₂CO₃ and MgCO₃ with a concentration of 15 µgC/10 µl are shown below.

EUSAAR2_x1.5

The thermograms of the CC standards using an elongated version of EUSAAR2 are shown in Figure 20. CaCO₃ shows one peak in the 4th temperature step in the inert atmosphere. MgCO₃ shows two peaks in the 3rd and 4th temperature steps in the inert atmosphere. K₂CO₃ shows three peaks in the 1st, 3rd and 4th temperature steps.

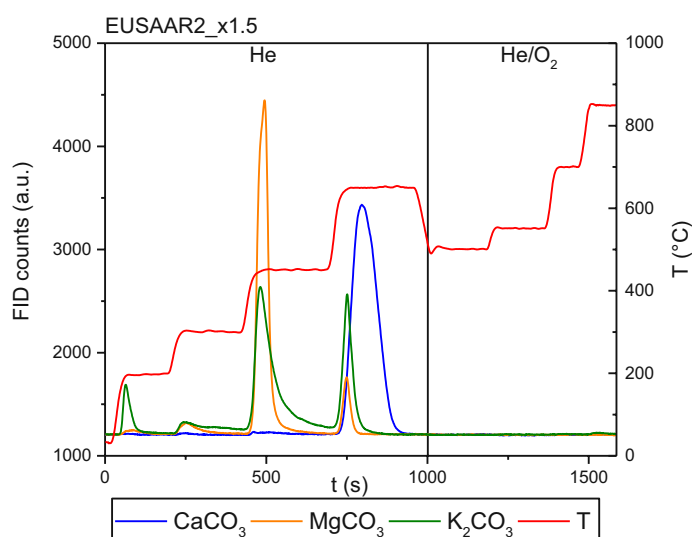


Figure 20: Thermograms of CaCO₃, MgCO₃ and K₂CO₃ with a concentration of 15 µgC/10 µl measured with EUSAAR2_x1.5

NIOSH870_x1.5

The thermograms of the CC standards using an elongated version of NIOSH870 are shown in Figure 21. The peak of CaCO₃ is spread over the 3rd and 4th temperature step in the inert atmosphere. MgCO₃ shows one peak in the 2nd temperature step in the inert atmosphere. The signal of K₂CO₃ is spread over all four temperature steps in the inert atmosphere. Even the elongation of the temperature steps did not allow the separation of the CC peaks.

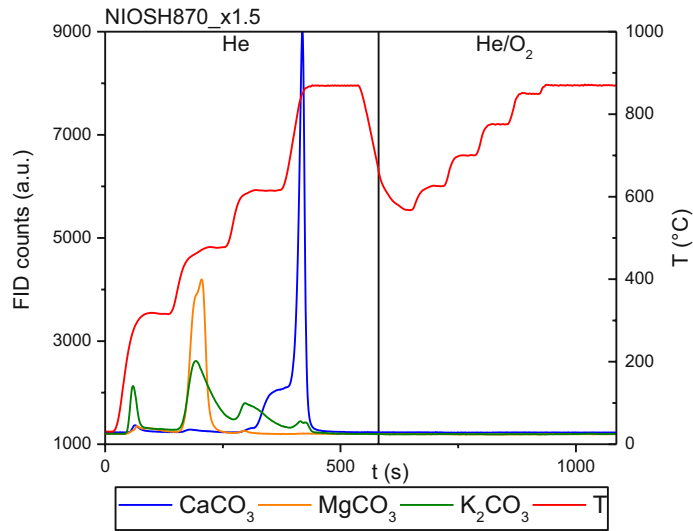


Figure 21: Thermograms of CaCO_3 , MgCO_3 and K_2CO_3 with a concentration of $15 \mu\text{gC}/10 \mu\text{l}$ measured with NIOSH870_x1.5

IMPROVE_A

The thermograms of the CC standards using IMPROVE_A are shown in Figure 22. The signal of CaCO_3 is spread over the 4th temperature step in the inert atmosphere and the 1st temperature step in the oxidising atmosphere and there is a sharp peak in the 2nd temperature step in the oxidising atmosphere. The signal of both MgCO_3 and K_2CO_3 is spread over the 3rd and 4th temperature step in the inert atmosphere as well as the 1st step in the oxidising atmosphere and there is a small peak in the 2nd temperature step in the oxidising atmosphere for both compounds.

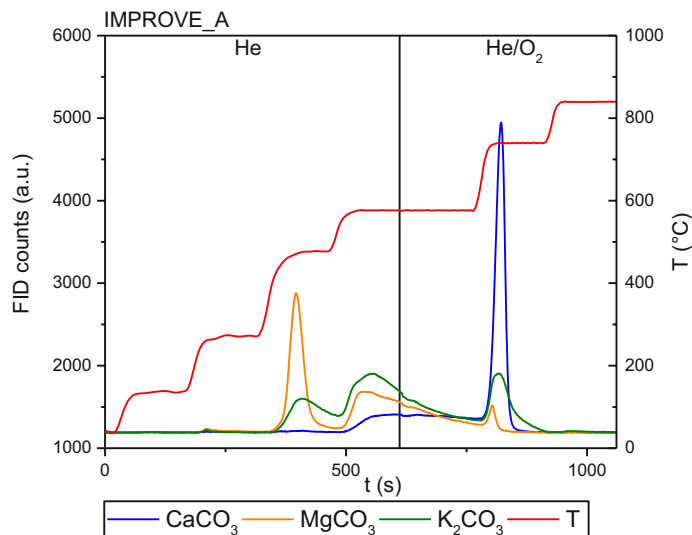


Figure 22: Thermograms of CaCO_3 , MgCO_3 and K_2CO_3 with a concentration of $15 \mu\text{gC}/10 \mu\text{l}$ measured with IMPROVE_A

For an easier comparison of the thermal protocols regarding the combustion of CC standards, the temperature steps relevant for each standard are summarized in Table 9. Temperature steps in brackets mean that only small peaks were visible, which might be neglected for the estimation of CC due to their small relative intensity.

Table 9: Relevant temperature steps for CaCO₃, MgCO₃ and K₂CO₃ when using EUSAAR2_x1.5, NIOSH870_x1.5 and IMPROVE_A

EUSAAR2_x1.5		NIOSH870_x1.5		IMPROVE_A	
Carbonate	Steps	Carbonate	Steps	Carbonate	Steps
CaCO ₃	OC4	CaCO ₃	OC3, OC4	CaCO ₃	OC4, EC1, EC2
MgCO ₃	(OC2), OC3, OC4	MgCO ₃	OC2	MgCO ₃	OC3, OC4, EC1, EC2
K ₂ CO ₃	OC1, (OC2), OC3, OC4	K ₂ CO ₃	OC1, OC2, OC3, (OC4)	K ₂ CO ₃	OC3, OC4, EC1, EC2

The standard substances evolve during different temperature steps. If all analysed carbonates were present in snow it would be complex to determine if MD is present in the sample using CC as proxy. Due to the elevated concentrations of Ca²⁺ and Mg²⁺ in snow samples containing MD this short comparison focuses on the thermograms of CaCO₃ and MgCO₃. IMPROVE_A showed multiple peaks for all analysed carbonates. An estimation of CC is therefore expected to be difficult, especially because it was shown in chapter 4.4. that IMPROVE_A leads to a small number of peaks which complicates the analysis of a particular carbon fraction. Note that these are measurements of carbonate standards and CC from snow samples might not combust in the same temperature steps. Using EUSAAR2_x1.5, CaCO₃ combusted only in OC4 as a broad peak, whereas MgCO₃ combusted in 2 temperature steps, OC3 and OC4. When using NIOSH870_x1.5, MgCO₃ combusted only in OC3, whereas CaCO₃ combusted in OC3 and OC4. Considering only these standard measurements, analyses of CC in samples should be carried out using either EUSAAR2 or NIOSH870.

The main differences between the thermal protocols are the number and location of the peaks of the standard substances in the thermograms. IMPROVE_A is the only thermal protocol where the reference substances evolve in the oxidising atmosphere. Since the amount of EC in atmospheric samples, e.g. ambient air samples and snow samples, is usually much lower than the amount of OC the combustion of CC in the inert atmosphere is to be favoured (Karanasiou et al., 2011). Therefore, IMPROVE_A is the least suitable of the examined thermal protocol for the analysis of CC.

Measurement of a snow sample doped with carbonate standard

A sample, which consisted of merged retained snow samples, was filtrated on quartz fibre filters. After preparing the filters for TOA, two filters were doped with the carbonate mixture standard with a concentration of 37.5 µgC/10 µl. The filters with and without doping were measured using NIOSH870 and the overlaid thermograms after correction by the sample weight and weight of the halves is shown in Figure 23. Additionally, the baseline was subtracted from the FID signal to enable visual comparison of the curves. The first 50 s of each measurement were used to compute the average baseline signal and was subtracted from the FID signal of the entire measurement.

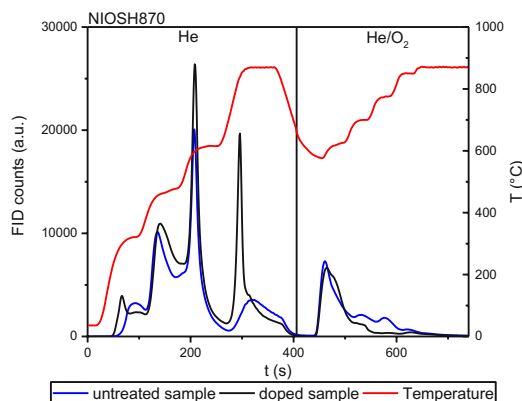


Figure 23: Snow sample measured directly and after doping with 37.5 µgC/10 µl carbonate mixture standard

The signal increased in all temperature steps in the inert atmosphere, OC1 to OC4, as expected for the carbonate mix measured with NIOSH870. For the changes observed in the oxidising atmosphere no explanation can be given, but it is assumed that the pyrolysis slightly changed.

4.2.2. Removal of CC with HCl vapours

Storing a sample above concentrated HCl for a sufficient amount of time leads to the complete removal of CC (Ashley and O'Connor, 2017). To ensure the complete removal clean filters doped with carbonate standards were stored in a desiccator whose bottom was filled with HCl (1:1 diluted with water) for 2 h 45 min and then left to ventilate in a fume hood for at least 1 h.

Treatment of an ambient air filter influenced by MD with HCl vapour

According to literature (e.g. Ashley and O'Connor, 2017), the CC peak occurs at the highest temperature step in the inert atmosphere for ambient air filters. To compare the changes in the thermogram occurring at ambient air filters and liquid samples containing MD after treatment with HCl, measurements of an ambient air filter with visible MD contamination were conducted with different thermal protocols.

12 Filter punches with a diameter of 10 mm were made, half of them were stored over 1:1 diluted HCl (v/v) for 2 h 45 min and left to ventilate for 1 h in a fume hood prior to TOA to remove HCl residues. One filter was measured directly and one filter was measured after HCl treatment with each thermal protocol. The thermal protocols used were EUSAAR2, EUSAAR2_x1.5, NIOSH870, NIOSH870_x1.5 and IMPROVE_A. The thermograms are shown in Figure 24 to Figure 26. The FID counts of two different measurements are super-imposed in the diagrams. The data of the sample temperature was taken from the direct measurements, the data of the sample temperature from the measurements after HCl treatment were comparable.

The thermograms of the measurements using EUSAAR2 and its elongated version are shown in Figure 24. The main change due to HCl treatment can be seen in the highest temperature step in the inert atmosphere, OC4, using EUSAAR2 and its elongated version. The shape of the peak in OC4 is noticeable, since it is askew due to an overlap of the OC peak that is left after HCl treatment and the, in this case, prominent CC peak. Small changes can be observed in the first temperature steps in both the inert and oxidising atmosphere, OC1 and EC1, where the signal after HCl treatment is slightly higher than the signal from the direct measurement. The inverse effect can be observed at the second temperature step in the inert atmosphere, OC2, and the third temperature step in the oxidising atmosphere, EC3. Since these are only slight differences and may be due to small inhomogeneity in the loading of the filter, it cannot be decided from these few measurements if this due to the HCl treatment.

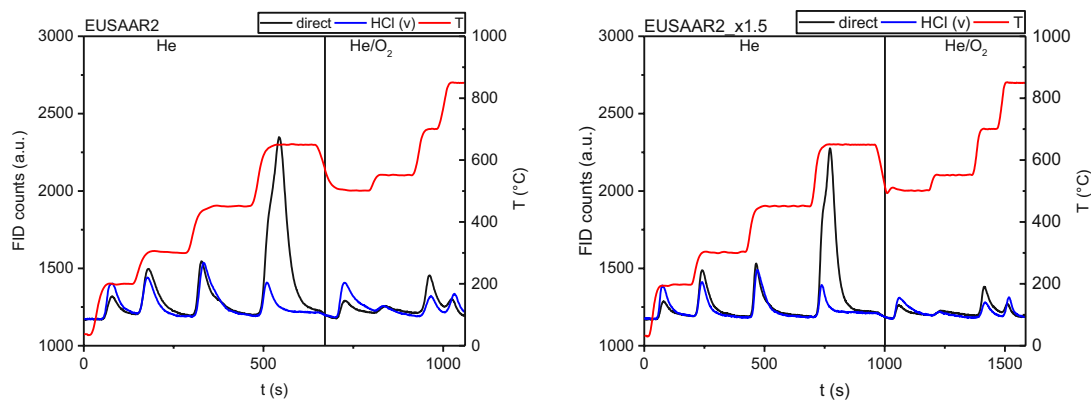


Figure 24: Thermograms of an ambient air filter influenced by MD using EUSAAR2 and EUSAAR2_x1.5

Comparing the changes in the inert atmosphere of this ambient air filter with the reduction after HCl treatment of a snow sample described above, the marked change in the temperature step OC4 has to be considered when using EUSAAR2 or its elongated version, as described in literature. Compared to the measurement of snow samples, which are shown later on, where big changes occur not only in OC4 but also in OC3 and the carbonate appears as a shoulder of the sharp peak in OC4, for the ambient air sample the carbonate peak dominates in OC4. An estimation based merely on the change or even the peak in OC4 seems therefore possible for heavily polluted ambient air samples, but questionable for snow samples with high amounts of MD.

In both measurements with NIOSH870 and its elongated version the CC peak is split in the third and fourth temperature step in the inert atmosphere, OC3 and OC4, see Figure 25. This might complicate the determination of CC since two temperature steps have to be considered. It is obvious in these diagrams that the elongation of NIOSH870 leads to a better separation of the carbonaceous fractions in the inert atmosphere.

However, many NIOSH-like protocols are available. It might be possible to burn CC mainly in one temperature step when slightly changing the temperature protocol, so that the OC peak left in OC4 burns in the highest temperature step and the OC peak in OC3 burns in OC2

already. Then CC would mainly combust in OC3 and the quantification of CC might be easier. This method development might require a big amount of time.

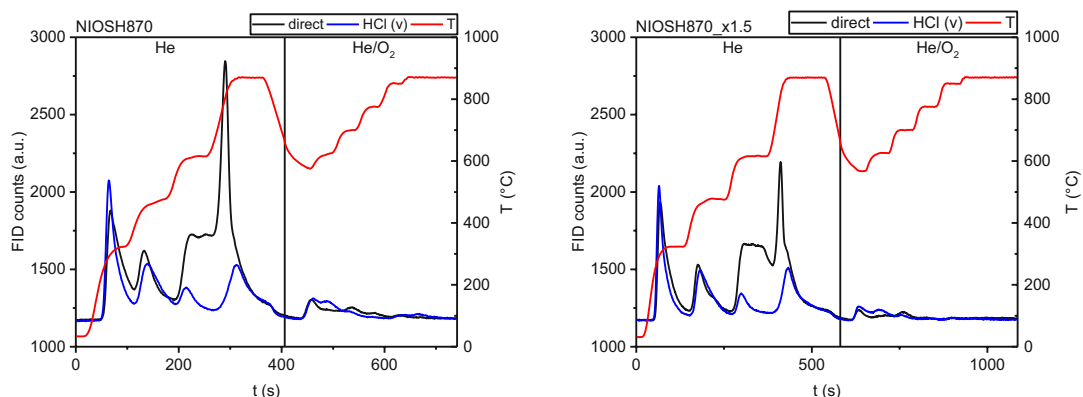


Figure 25: Thermograms of an ambient air filter influenced by MD using NIOSH870 and NIOSH870_x1.5

Compared to the measurements of snow samples treated with HCl, no reduction of the signal in OC2 can be observed. The decrease in OC3 after HCl treatment is much more pronounced at the ambient air filter.

The measurements of the ambient air filter with MD contamination using IMPROVE_A show that CC can be found in the highest temperature step in the inert atmosphere, OC4 and in the second temperature step in the oxidising atmosphere, EC2, see Figure 26. Since the aim of this work is to determine both CC as a proxy for MD and EC, the occurrence of CC in the oxidising atmosphere is a strong drawback of IMPROVE_A. Therefore, IMPROVE_A was neglected for most subsequent experiments.

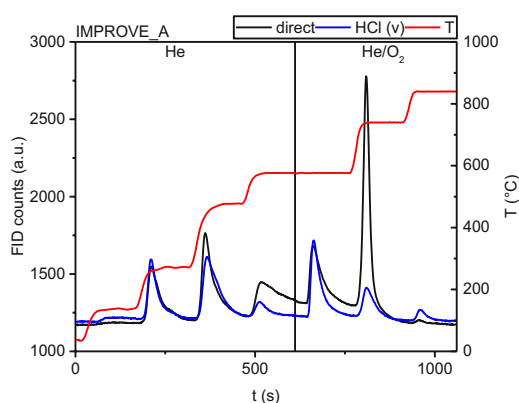


Figure 26: Thermogram of an ambient air filter influenced by MD using IMPROVE_A

The relevant temperature steps for the determination of CC which were found using an ambient air filter with visible MD contamination correspond to the temperature steps found when measuring carbonaceous reference materials. The reduction of signal occurred in the temperature steps, where CaCO_3 evolved for all thermal protocols. Therefore, for comparisons of CC with results from IC only Ca^{2+} was used.

For a direct determination of CC from the thermogram without HCl treatment the temperature steps outlined above have to be integrated. However, it was shown that in these temperature steps also various amounts of OC or EC can be found. An estimation of CC using these temperature steps without subtracting other carbonaceous compounds found after HCl treatment would lead to an overestimation of CC, especially for samples containing low amounts of MD. Furthermore, the amount of OC would be underestimated if CC is subtracted from OC.

Since the peaks have a strong overlap it is not possible to use only part of the temperature step for the determination of CC. Therefore, it is not possible to estimate the amount of MD straightforward from just one analytical run, the analysis of another aliquot of the sample after HCl treatment is essential.

Karanasiou et al. (2011) studied the possibility to obtain the concentration of CC on ambient air filters by integration of temperature steps in the thermogram. They observed changes in the volatility properties of OC after fumigation with HCl and state that it leads to loss of volatile organic compounds. Furthermore, they observed that about 14 % of the area of the peak that contributes to CC for the thermal protocol they used, RT-QUARTZ-840, a NIOSH-like protocol, remains after treatment with HCl vapour. Using the loss of TC for the quantification to avoid overestimation of CC proved to be permissible only in 1 out of 2 ambient air samples. Additional loss of organic compounds led to an overestimation of CC when using the difference in TC.

One eye-catching phenomenon was observed at the analysis of the ambient air filter: The colour of the filter prior to TOA differs from the colour after analysis. The filters are shown in Figure 27. EUSAAR2 (EU), EUSAAR_x1.5 (EU1.5) and IMPROVE_A (IMPR) are coloured darker after the analysis than before, compared to NA (not analysed). The colour of the filter after the analysis with NIOSH870 (NI) and NIOSH870_x1.5 (NI1.5) cannot be distinguished from the colour of the sample that was not analysed. The change of colour can be observed both for samples that were measured directly and for samples that underwent treatment with HCl, although the change of colour is less apparent after HCl treatment. At present no reasonable explanation for the change in colour based on the maximum temperature reached in the oxidising and inert atmosphere can be given.

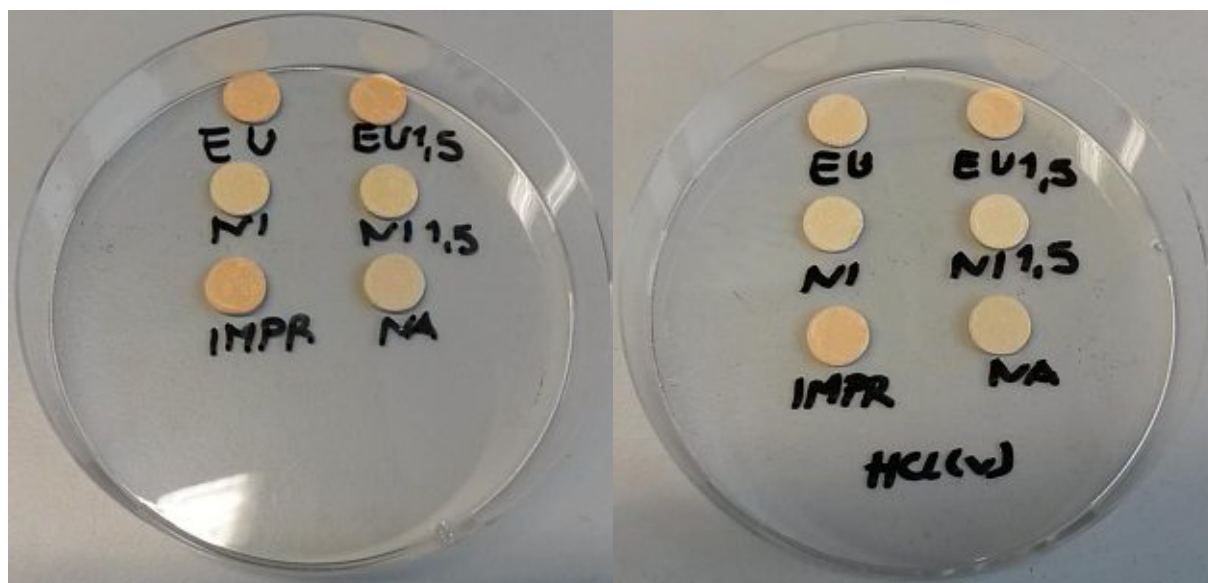


Figure 27: Filter aliquots of an ambient air filter influenced by MD after direct analysis (left) and after analysis with HCl treatment prior to analysis (right); filter marked with NA represents a filter punch prior to analysis

According to Köhler and Kischkewitz (2014) hematite, $\alpha\text{-Fe}_2\text{O}_3$, is coloured red, while goethite, $\alpha\text{-FeOOH}$, is coloured yellow and lepidocrocite, $\gamma\text{-FeOOH}$, is coloured orange. In the sample oven CO , CO_2 , H_2 and O_2 are available for reaction during the measurement and different temperatures prevail depending on the thermal protocol used. It is possible that this leads to different mixtures of iron compounds appearing coloured differently. An accurate explanation cannot be given from TOA alone. Additional measurements which reveal the oxidation state of Fe or the crystal lattice of the compounds are needed for further insight.

Thermal-optical measurements of Fe compounds and the corresponding evaluation of the transmittance are presented in chapter 4.4.

Treatment of snow samples with HCl vapour

Four filters were doped with a carbonate mix of a concentration of $5\ \mu\text{gC}/10\ \mu\text{l}$. Two of those filters were measured directly, one was measured using EUSAAR, the other using NIOSH870. The remaining two filters were treated with HCl vapours prior to analysis and one filter was measured using EUSAAR2, the other using NIOSH870. The thermograms of the directly analysed filter and the filter treated with HCl, which are shown in Figure 28, were then compared. The expected pattern obtained by the mixture of carbonates can be observed. The filters that were directly measured using EUSAAR2 and NIOSH870 possessed 5.9 and $5.6\ \mu\text{gC}$, respectively, and the filters treated with HCl possessed 1.5 and $2.0\ \mu\text{gC}$, which is within the range of the blanks. Comparing the analyses with and without HCl treatment, about 30 % of TC was left on the filter after the treatment. Still this value is below the average blank value. Thus, quantitative removal can be assumed.

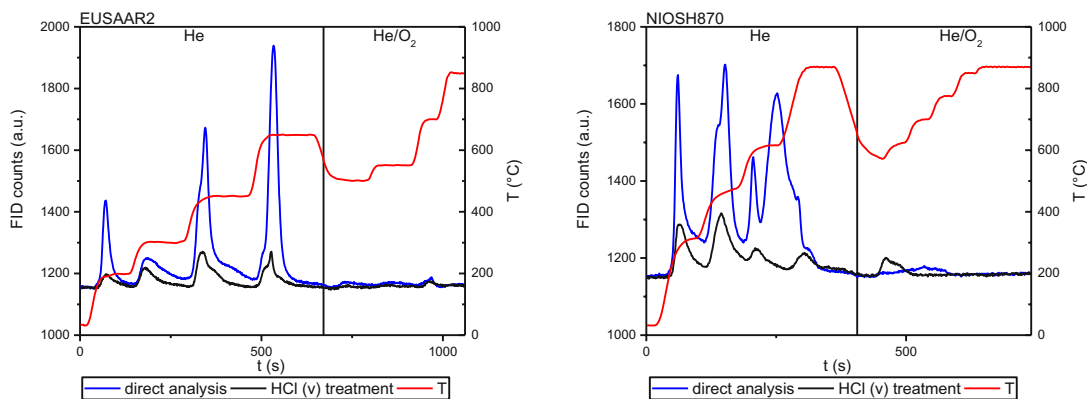


Figure 28: Thermograms of direct analysis of carbonate mixture and analysis after fumigation with HCl

The experiment described above was repeated using the 37.5 µgC/10 µl carbonate mixture standard. Three samples were measured directly and three samples were fumigated with HCl prior to TOA. All samples were analysed using the standard NIOSH870 thermal protocol. The average and standard deviation for TC of the directly analysed samples were 36.85 ± 1.48 µgC and 2.55 ± 1.03 µgC for the filters treated with HCl vapour. Hence, the amount of TC after HCl treatment was in the range of the blank values. Only 7 % of TC was left on the filter after removing the carbonates with this treatment.

A snow sample was prepared by merging different retained snow samples. Some of the snow samples were visibly polluted by MD, which contains CC. Therefore, an effect on the sample should be visible after treatment with HCl vapour. Clean quartz fibre filters were loaded with the snow sample. After drying and cutting, one half of each filter was stored above HCl, while the other half was analysed directly using the standard versions of EUSAAR2 or NIOSH870. The thermograms of one filter were overlaid and are shown in Figure 29.

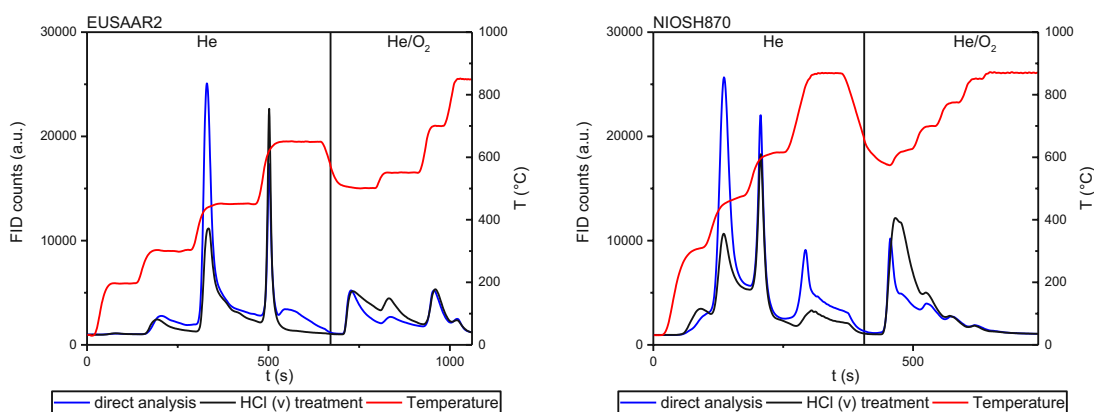


Figure 29: Thermograms of snow samples which were directly analysed and treated with HCl vapour using EUSAAR2 and NIOSH870

The sample measured with EUSAAR2 showed a decrease after HCl treatment in OC3 and OC4, whereas the signal increased in EC1 and EC2. When comparing a sample directly measured and one treated with HCl analysed using NIOSH870 a decrease in OC2, OC3 and OC4 is visible and an increase in signal can be seen in EC1 and EC2. An additional increase in EC3 is visible, however, the peaks in the inert atmosphere are not separated and the increase observed may be due to incomplete combustion of the carbon fraction in EC2. Although the transmittance might give information about shifts in carbon fraction, e.g. due to increased pyrolysis, the transmittance signal is not shown here, as the influence of Fe in samples on the transmittance is high. This will be discussed in chapter 4.4.

The sharp CC peak observed in OC4 for ambient air samples was not observed for snow samples containing elevated concentrations of CC. Changes occur in additional temperature steps. The straightforward application of approaches for the determination of CC described in literature for ambient air samples is therefore not possible for snow samples. A detailed evaluation of the temperature steps attributed to CC is necessary and discussed in chapter 4.2.

Measuring filters that were fumigated with HCl proved to damage the oven of the Lab OC-EC Aerosol Analyzer reversibly, temporarily leading to lower carbon amounts. The effect wears off after approximately 2 days of measurement.

4.2.3. Removal of CC with liquid HCl

To prevent damaging the oven of the Lab OC-EC Aerosol Analyzer, filters were loaded with snow equally to the previous approach, where sample halves were treated with HCl vapour, but were treated with 1:1 diluted HCl (v/v) after washing the beaker with 15 ml Milli-Q water. 5, 10 and 15 ml diluted HCl were put on the filter and the HCl was filtered slowly at ambient pressure to provide enough time to react with the sample. Afterwards HCl residues were washed out with 45 ml Milli-Q water, which proved to be sufficient to obtain pH neutral washing water, and the funnel was washed with 15 ml Milli-Q water at low pressure. No differences could be observed in the thermograms of the samples treated with 5, 10 or 15 ml diluted HCl. Therefore, for future samples 5 ml diluted HCl were used for the treatment with liquid HCl.

After the measurement of filters treated with liquid HCl the effect of lower carbon amounts at subsequently measured filters could not be observed leading to the assumption that only small amounts of HCl residue are left on the filter. Additionally, this treatment is timesaving compared to the treatment with HCl vapour, as it can be done during the filtration process and it is not necessary to remove HCl residues for at least 1 h in the fume hood. One drawback of this approach is that two filters have to be loaded, one for direct analysis and one which is treated with HCl, as cutting one filter and treating an aliquot with HCl is not possible. Hence, the treatment is unsuitable for samples with small volumes, which cannot be divided in two subsamples for filtration. This treatment should be preferred if possible, to prevent dealing damage to the system of the Lab OC-EC Aerosol Analyzer.

In the course of the experiment described above, where filters were loaded with 37.5 µgC from a carbonate mixture standard and 3 filters were analysed directly while 3 filters were stored above HCl, 3 filters were loaded and treated with 10 ml 1:1 diluted HCl (v/v). The average amount of TC and the respective standard deviation found after analysis was 2.44 ± 1.38 µgC and therefore within the blank values. The amount of TC left on the filter after treatment with liquid HCl was 7 %, equal to the treatment with HCl vapour.

The thermograms of snow samples which were directly measured or rinsed with liquid HCl are overlaid in Figure 30. Measurements using the elongated versions of EUSAAR2 and NIOSH870 are shown.

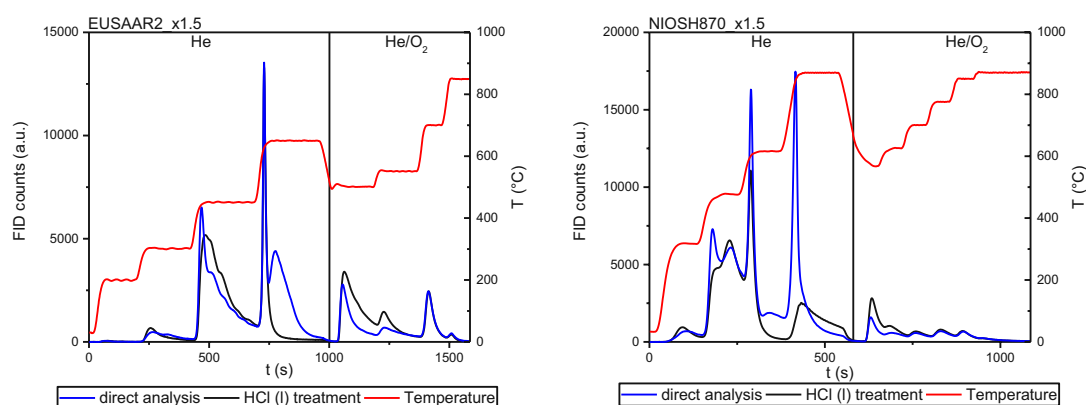


Figure 30: Thermograms of snow samples which were directly analysed and treated with liquid HCl using EUSAAR2_x1.5 and NIOSH870_x1.5

The main changes due to the interaction with HCl are in OC3, OC4, EC1 and EC2 for EUSAAR2_x1.5. For NIOSH870_x1.5 changes are visible in OC2, OC3, OC4, EC1 and EC2. For both the elongated versions of EUSAAR2 and NIOSH870 the signal is reduced after HCl treatment in the inert atmosphere and increased in the oxidising atmosphere. The changes that occurred when treating a sample with liquid HCl are in agreement with the measurements of samples treated with HCl vapour.

4.2.4. Changes in the thermogram according to the treatment with HCl

According to Ashley and O'Connor (2017) CC desorbs as one sharp signal at the maximum temperature of the He-phase for ambient air filters using NIOSH5040. This could only be proven for EUSAAR2 when analysing an ambient air filter influenced by MD. As this work focuses on snow samples, the temperature steps which correspond to the combustion of CC when analysing snow samples have to be determined.

An alternative approach to identify the CC peak in the thermograms was to compare the areas of the peaks of the respective temperature steps (OC1 to OC4 and EC1 to EC4 for EUSAAR2; OC1 to OC4 and EC1 to EC6 for NIOSH870) of a directly analysed sample and a sample treated with HCl. One sample with MD contamination was prepared by merging snow samples visibly polluted with MD. Another sample was equally prepared by merging snow samples which visibly did not contain MD. The samples were loaded on 8 filters each and

were cut in halves. One half was treated with HCl vapour. Half of the filters were measured with the EUSAAR2 thermal protocol, the other half using the NIOSH870 thermal protocol. The peak areas of the different temperature steps of the half that was treated with HCl and the half that was measured directly were plotted. For samples containing little to no MD the data points are expected to scatter along the 1:1-line as the treatment with HCl should have almost no effect. The plots for the samples not containing MD are shown in Figure 31 for EUSAAR2 and Figure 32 for NIOSH870.

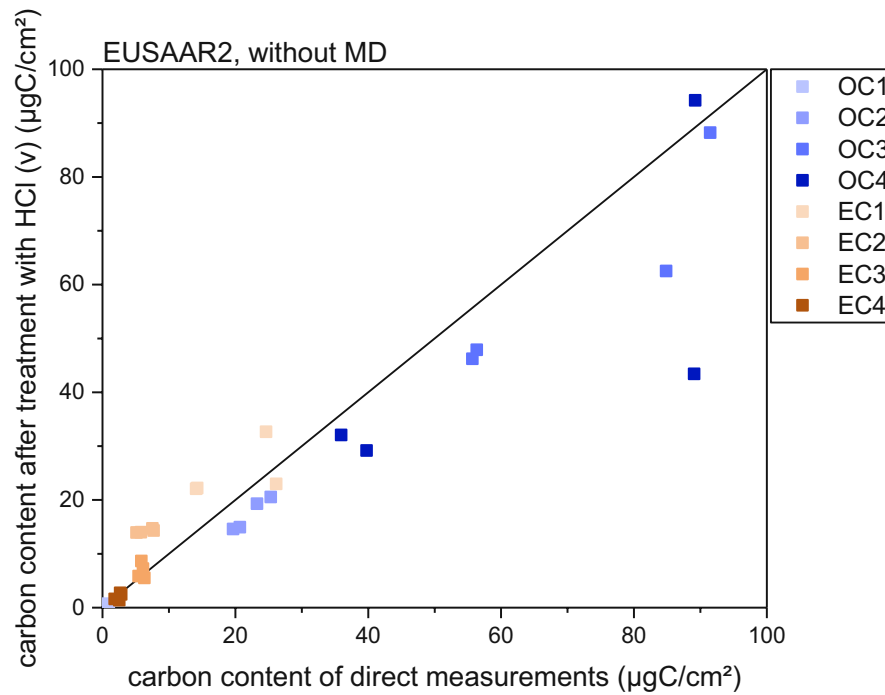


Figure 31: Comparison of the carbonaceous fractions of a snow sample without visible MD contamination measured directly and after HCl treatment using EUSAAR2

The data points scatter along the 1:1-line for the sample not visibly contaminated with MD as expected when using EUSAAR2. Two data points, one of OC3 and one of OC4, are deviating from the 1:1-line. Both data points belong to one sample and it is assumed that the marked deviation is due to contamination of the directly measured filter half.

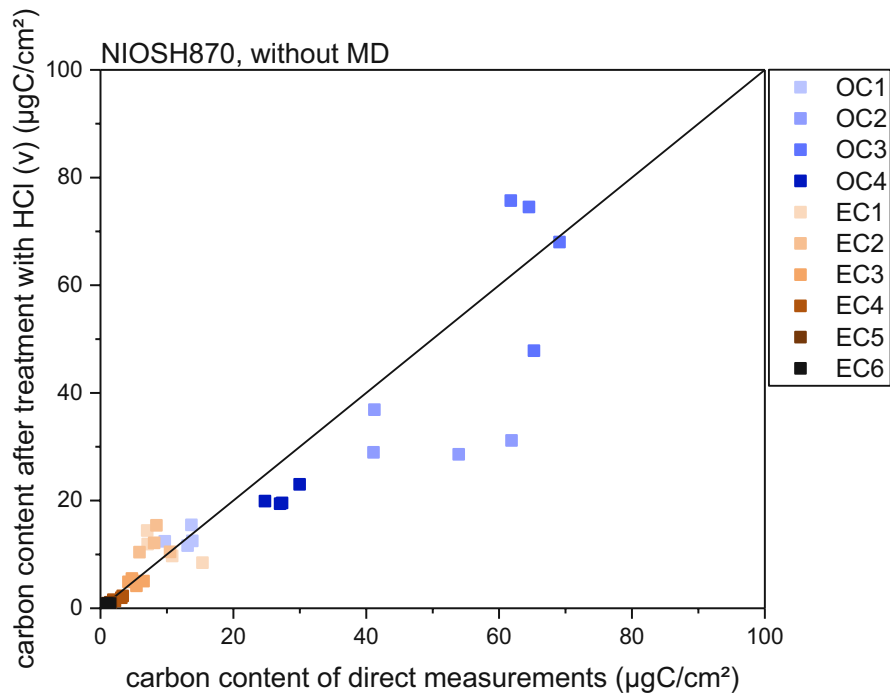


Figure 32: Comparison of the carbonaceous fractions of a snow sample without visible MD contamination measured directly and after HCl treatment using NIOSH870

The same behaviour can be observed when measuring the sample not visibly contaminated with MD using NIOSH870. Two out of four samples show a marked deviation from the 1:1-line for OC2, although they do not show distinct deviations in other temperature steps. The treatment with HCl vapour did not have a visible influence on these samples for both EUSAAR2 and NIOSH870.

The respective diagrams of the measurement of a sample visibly contaminated with MD are shown in Figure 33 for EUSAAR2 and in Figure 34 for NIOSH870.

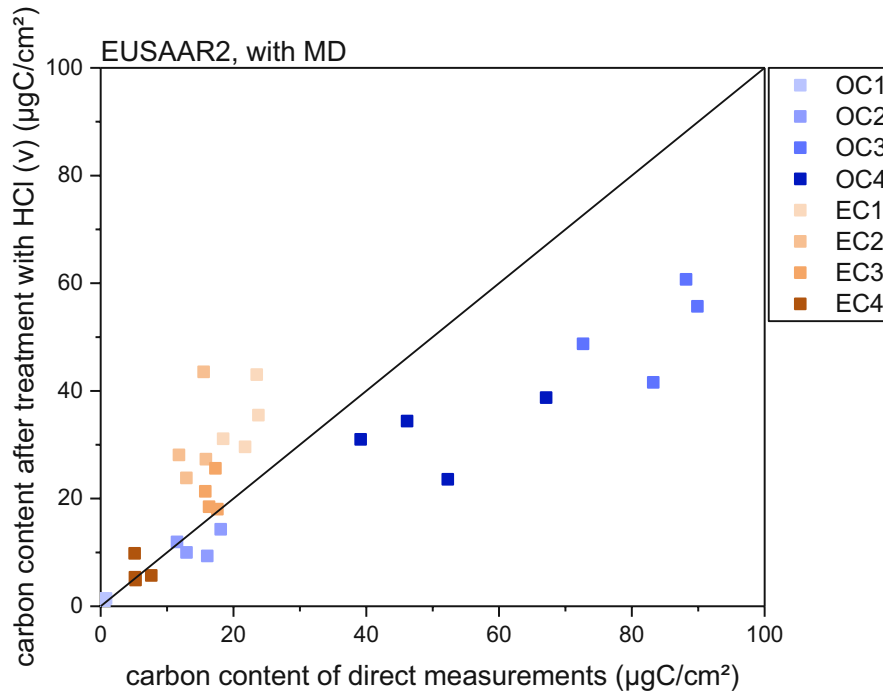


Figure 33: Comparison of the carbonaceous fractions of a snow sample with visible MD contamination measured directly and after HCl treatment using EUSAAR2

The carbon content of filters directly analysed and of filters treated with HCl varies in 4 temperature steps when using EUSAAR2: OC3, OC4, EC1 and EC2. The carbon contents in the inert atmosphere are shifted to lower values after HCl treatment, in contrast carbon contents in the oxidising atmosphere are shifted to higher values after HCl treatment.

Comparing the temperature steps in which changes occurred due to the acid treatment with the carbonate standard measurements shows that CaCO_3 completely combusts in OC4 when using EUSAAR2. However, MgCO_3 combusts both in OC3 and OC4.

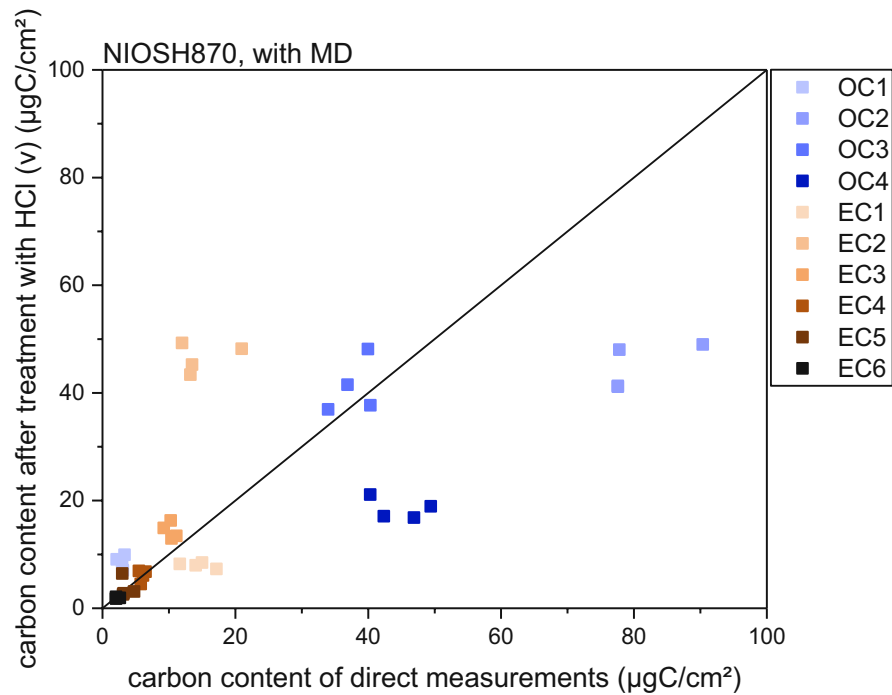


Figure 34: Comparison of the carbonaceous fractions of a snow sample with visible MD contamination measured directly and after HCl treatment using NIOSH870

When using NIOSH870 the carbon content in 3 temperature steps differs: OC2, OC4 and EC2. The carbon contents in the inert atmosphere are shifted to lower contents after HCl treatment while they are shifted to higher contents in the oxidising atmosphere.

The CaCO_3 standard combusted both in OC3 and OC4. Surprisingly, the analysis of the snow sample did not show changes in the OC3 temperature step. However, a change in OC2 was visible, which corresponds to the combustion behaviour of MgCO_3 .

The reduction of carbonaceous compounds matches the combustion of CaCO_3 and MgCO_3 for both EUSAAR2 and NIOSH870. Therefore, the comparison of CC from TOA and calculated from the ion concentrations in the eluted sample might agree better if Mg^{2+} is considered as well. The increase in carbon in the oxidising atmosphere cannot be explained by the measurements of carbonate standards, compare Figure 28. Still, the treatment with HCl might have changed OC compounds leading to increased pyrolysis and thus higher EC1 and EC2 fractions. Since this could not be observed at the sample not visibly contaminated with MD, it is possible that compounds in MD, e.g. Fe compounds, act as a catalyst and therefore lead to a change in the combustion behaviour of some compounds.

4.3. Comparison of CC from TOA with Ca^{2+} concentrations determined via IC

Two groups of snow samples, one group containing MD and one group without visible MD contamination, were filtrated and thermal-optically analysed using EUSAAR2 and NIOSH870. One half of each sample filter was treated with HCl vapour prior to TOA. The filters were subsequently eluted with 38 mM MSA and analysed via IC. Assuming that the entire Ca^{2+} in the eluate was present as CaCO_3 , the amount of CC was calculated from the results of IC for each sample. A comparison of the amount of CC estimated from Ca^{2+} and the amount of CC from TOA shows a clear differentiation of the two groups, as can be seen in Figure 35. This diagram includes the data of measurements with both thermal protocols, EUSAAR2 and NIOSH870. Although the amount of CC clearly differed for the two methods, TOA and IC, the groups can still be distinguished.

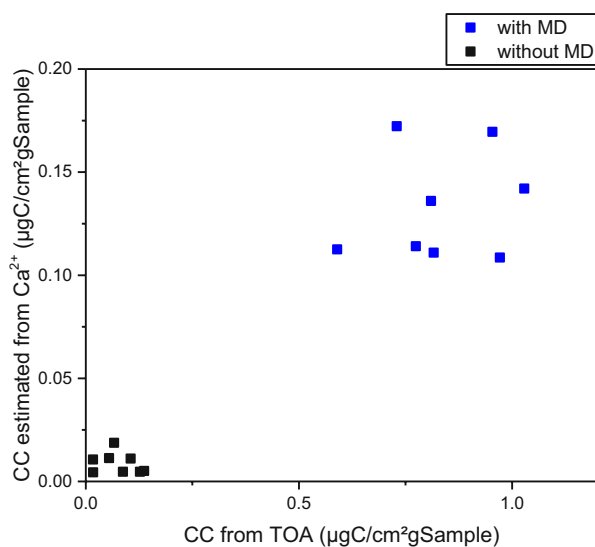


Figure 35: Comparison of CC estimated by Ca^{2+} and CC from TOA in a sample not visibly contaminated with MD and a sample with visible MD contamination

4.3.1. Comparison of CC from TOA with Ca^{2+} concentrations determined via IC for samples with lower mineral dust concentrations

Further analyses were conducted to study the relationship of CC estimated from Ca^{2+} , analysed via IC, and CC from TOA. A sample was prepared from melted snow samples that were not visually contaminated by MD and was divided into 6 flasks. A snow sample which visibly contained MD was melted and different amounts of the contaminated sample were used to dope the samples leading to 5 samples with different compositions, called levels in the following passage. The percentage of MD-containing sample ranged from 0 to 11 wt%. Five filters were loaded with sample of each level. Prior evaluations showed that the relative standard uncertainty for the process of filtration and obtaining aliquots calculated from multiple filters loaded with the same snow sample is below 10 %, see chapter 3.7. Hence, the difference between the 5 filters loaded for each level can be expected to be relatively small and treatment with liquid HCl of 2 filters of each level (rinsing with 5 ml of 1:1 diluted (v/v) HCl) was conducted. The filters rinsed with HCl were washed thoroughly with Milli-Q water until the pH of the filtrate was neutral. Washing the filters 4 times with 10 ml Milli-Q water proved to be sufficient to remove acidic residues. After drying, cutting in halves and

weighing the filters TOA was conducted. Both elongated EUSAAR2 and NIOSH870 thermal protocols were used.

After TOA, the filters were eluted with 2.5 ml of diluted MSA, used as eluent in cation chromatography, in an ultrasonic bath for 20 min. The concentration of the eluent was either 30 or 38 mM, as the routine method for cation analysis was slightly changed during the course of this work. The samples were centrifuged with 3000 rpm for 10 min and an aliquot of 1.5 ml was taken. The aliquot was centrifuged again with 13 400 rpm for 5 min and the supernatant was filled in a vial and analysed via ion chromatography for Ca^{2+} and Mg^{2+} .

To determine CC the amount of carbon evolving in the temperature steps associated with the decarboxylation of CaCO_3 (see chapter 4.2.1) were considered, i.e. the results of the sample that was rinsed with HCl were subtracted from the directly measured sample.

The amount of CC deduced from ion chromatography was calculated based on Ca^{2+} in the eluate, assuming that all Ca^{2+} originates from CaCO_3 . Additionally, Mg^{2+} was quantified. It was expected that plotting the amount of CC from TOA and CC from IC will lead to a linear relationship.

IC measurements

Before the comparison of CC estimated from Ca^{2+} and CC from TOA is discussed, measurements of the liquid samples and the eluates depending on the amount of MD-containing sample added are shown. The measurements of the liquid samples, which were taken prior to filtration over a quartz fibre filter for TOA, were centrifuged to prevent the IC system from taking damage. The samples showed good correlation between the Ca^{2+} concentrations and the weight percentage of MD polluted sample. There is also a correlation between the Mg^{2+} concentrations and the percentage of MD polluted sample, although the concentration of Mg^{2+} in the sample with the highest amount of MD is much lower than expected from a linear correlation, see Figure 36. The concentration of Ca^{2+} is more than one order of magnitude higher than the concentration of Mg^{2+} in these samples.

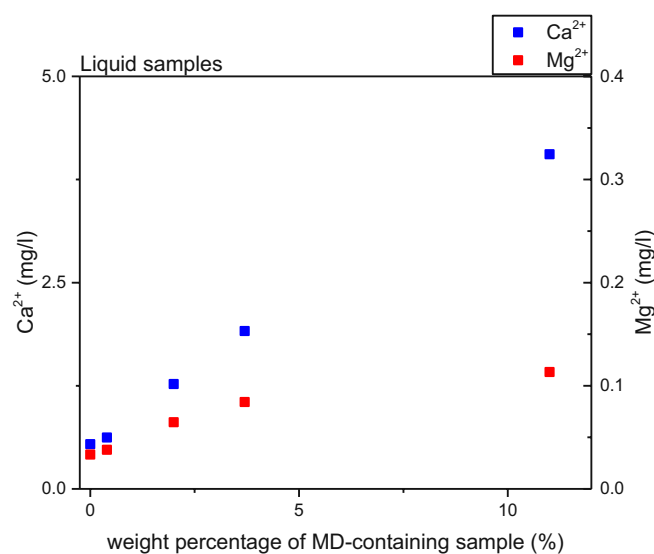


Figure 36: Concentrations of Ca^{2+} and Mg^{2+} in liquid samples containing variable amounts of MD

Greilinger et al. (2018) used a pH > 5.6 and a Ca²⁺ concentration > 10 µeq/l as thresholds for the determination of snow samples containing MD. Since some of the snow samples used in this experiment were already melted once and frozen again, volatile compounds, e.g. organic acids, may not be present in the sample anymore. Furthermore, gases present in the laboratory atmosphere may have been dissolved in the sample. Therefore, the pH of the original sample might have been altered and the pH of these samples was not measured. The criteria for the identification could not be used. Cross-checking with snow samples analysed and evaluated following these criteria showed that the pH criterion is essential and using the Ca²⁺ concentration threshold alone is not sufficient.

Table 10: Ca²⁺ concentrations in liquid samples containing variable amounts of MD

Sample	Ca ²⁺ in liquid sample (mg/l)
S0	0.54
S1	0.62
S2	1.27
S3	1.91
S4	4.06

The Ca²⁺ concentration of the liquid samples of this experiment are shown in Table 10. The threshold of 10 µeq/l equals 0.4 mg/l Ca. The Ca²⁺ concentration in the master sample, S0, exceeds the threshold already. Still, the presence of MD in this sample cannot be confirmed, as the pH value is unknown and no contamination with MD was visible. In any case the addition of the MD-containing sample leads to Ca²⁺ concentrations markedly above the threshold.

The automatic split point of TOA could only be set for S0 and S1, the split point for the other samples was set at the end of the measurement during the calibration phase. This confirms that the determination of EC is disturbed when a certain amount of MD is present on the filter.

The measurements of the eluate of the filter after TOA showed high scatter for Ca²⁺ and Mg²⁺. The results for Ca²⁺ are shown in Figure 37, the plot for Mg²⁺ is very similar and therefore not shown. Only samples which were not treated with HCl are shown. Since the amount of CC estimated from the ion concentration on the filter half is of interest for further evaluations, the concentrations of Ca²⁺ and Mg²⁺ were converted to µgC/gSample.

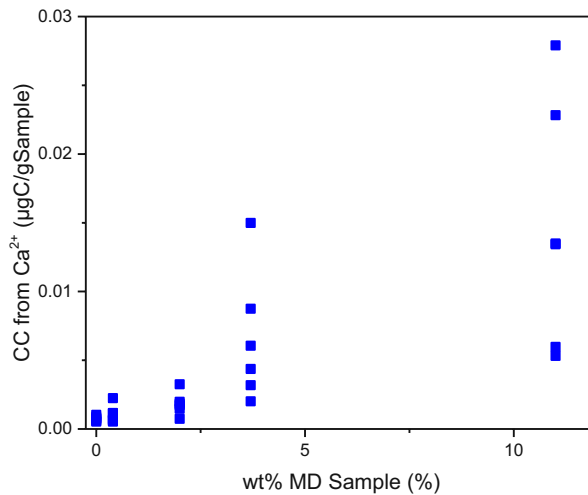


Figure 37: Concentrations of Ca²⁺ in samples containing variable amounts of MD eluted after TOA

The ratio of solid Ca²⁺ compounds removed by filtration and of Ca²⁺ in the liquid sample was computed. The result of the eluate of the filters was corrected by the volume of eluent, filter area and volume of the filtrated sample. The ratio was found to be between 0.4 and 1 % for S0, 0.2 to 1.4 % for S1, 0.3 to 1.2 % for S2, 0.3 to 1.6 % for S3 and 0.4 to 3.2 % for S4. No fixed ratio could be determined due to the high scatter of Ca²⁺ concentrations in the filter eluate and no trend regarding the weight percentage of MD-contaminated sample was observed. In any case, most of the Ca²⁺ ions were determined in the soluble fraction.

The average and the standard deviation of the concentrations of Ca²⁺ and Mg²⁺ were calculated for samples measured using EUSAAR2 and NIOSH870 and the average was computed for all samples measured independent of the thermal protocol used. The standard deviations are shown as error bars. The standard deviation of the entire data set is not shown to provide a clearer diagram. While the standard deviations of the Ca²⁺ concentrations are too big to see a difference between the samples measured using EUSAAR2 and NIOSH870 considering the standard deviation, see Figure 38, the concentration of Mg²⁺ was lower when using NIOSH870, see Figure 39.

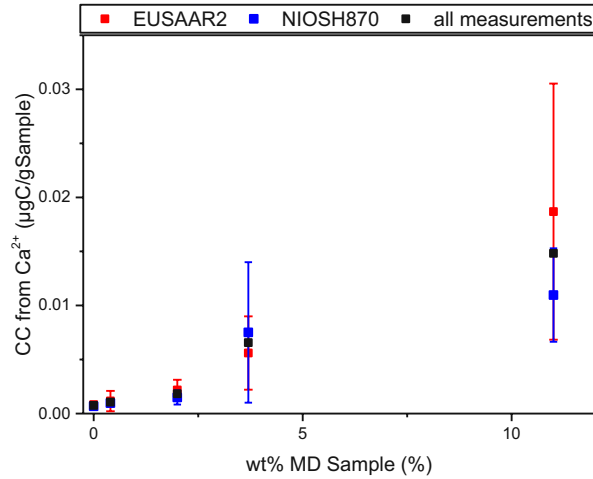


Figure 38: Concentrations of Ca²⁺ in samples containing variable amounts of MD eluted after TOA, divided into samples measured using EUSAAR2 and NIOSH870

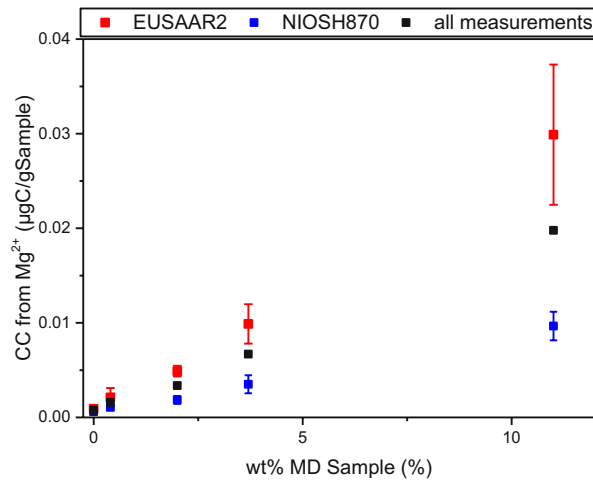


Figure 39: Concentrations of Mg²⁺ in samples containing variable amounts of MD eluted after TOA, divided into samples measured using EUSAAR2 and NIOSH870

Groups 3 and 4 measured with NIOSH870 (4 and 11 wt% MD) were eluted with 30 mM MSA due to a temporary change in the chromatography system, whereas the rest of the samples was eluted with 38 mM MSA. The difference in the averages might be a result of the differing concentrations of the eluent, but the trend of smaller concentrations for Mg²⁺ is already visible in the groups with lower concentrations of MD that were eluted with 38 mM MSA. Furthermore, the trend is not visible for Ca²⁺, which leads to the assumption that due to the higher temperatures in He-atmosphere at the NIOSH870 protocol Mg²⁺ ions are less accessible via elution with 38 mM MSA.

The high scatter of the results might either be due to inhomogeneous loading or incomplete elution of the analyte. CaCO₃ reacts with decarboxylation when heated up. Although CO₂ is lost and analysed during thermal optical analysis, CaO should stay on the filter and not be desorbed. CaO reacts with water to Ca(OH)₂, which might absorb CO₂ and form CaCO₃. All those compounds possess a higher solubility in water than the Ca concentrations measured.

Since the eluent was acidic, the solubility of the compounds should be further increased compared to water.

The relative standard uncertainty was found to be less than 10 % for carbon measurements when repeatedly loading filters with the same sample. The relative standard uncertainty for the Ca^{2+} concentrations ranged between 260 % for the highest concentration and 970 % for the second lowest concentration. It cannot be excluded that the loading of the ions is less homogeneous than the loading of the carbon compounds and that this is the reason for the high scattering. For this evaluation it is assumed that Ca^{2+} is only existent as CaCO_3 and therefore the loading of Ca^{2+} should be as homogeneous as the loading of the carbon contents.

TOA

Based on the assumption that the entire Ca in the sample is present as CaCO_3 , the amount of CC was calculated from the eluates of the filters as described above. Additionally, the amount of CC was computed from the thermograms, considering only the relevant temperature steps for CaCO_3 using EUSAAR2 and NIOSH870, as described in chapter 4.2.1. A comparison between the results of filters directly measured and the filters rinsed with HCl was used to determine the amount of CC by TOA. A linear relationship is expected from plotting the two values for CC of each sample. The plot includes data of EUSAAR2 and NIOSH870 and is shown in Figure 40.

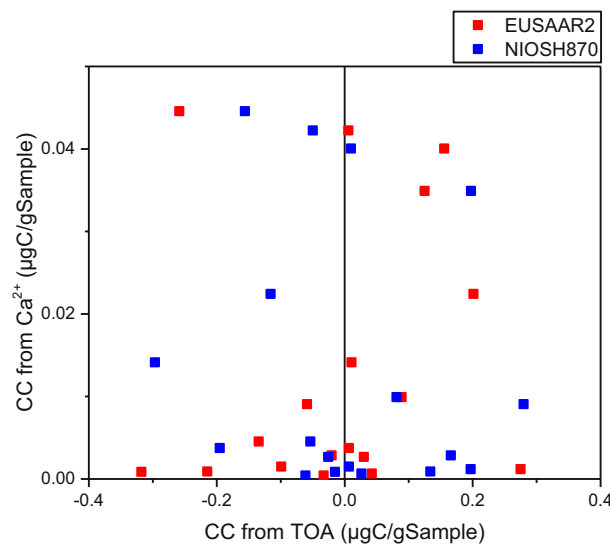


Figure 40: Comparison of CC estimated by Ca^{2+} and CC from TOA in samples containing variable amounts of MD

As can be seen in the plot, the amount of CC estimated from the thermograms scatters around $0 \mu\text{gC/gSample}$. The linear relationship that was expected could not be obtained not only due to the high difference in Ca^{2+} concentration per level but also due to the high difference and also negative values in the results of CC determined from the thermograms.

A possible explanation for the scatter around 0 of CC from TOA is the low amount of MD in the samples. Real snow samples containing MD were used to dope snow samples without visible MD contamination. The amount of MD in the sample used for doping is unknown. The maximum percentage of the sample containing MD was about 11 wt%, the real sample being 100 wt%. Therefore, the amount of MD in the prepared samples was much lower than the amount in actual snow samples containing MD and might therefore be too low in this experiment to obtain the desired results. Additionally to the low concentrations of CC, the relative standard uncertainty of 10 % for filtrating and measuring the same sample several times adds to the difficulty of obtaining the expected results in this experiment, as CC from TOA was obtained by comparison of 2 different filters.

4.3.2. Comparison of CC from TOA with Ca^{2+} concentrations determined via IC for samples with higher mineral dust concentrations

To overcome the problem of too low concentrations of MD a new series of samples containing different amounts of MD was made. The first sample, S0, contained only melted clean snow. The sample with the highest concentration of MD, S5, contained a mixture of melted snow samples, which were visibly contaminated with MD. The samples in between, S1, S2, S3 and S4, contained the sample S0 and 10, 26, 47 and 72 wt% of S5, respectively. The snow samples were melted at room temperature.

The samples were filtrated on clean quartz fibre filters. The filter was moistened with 5 ml Milli-Q water, the sample was filtrated, the beaker which contained the sample was washed with 75 ml Milli-Q water and the funnel of the filtration setup was washed with 15 ml Milli-Q water.

The amount of sample varied depending on the level of the sample itself, since a moderate loading was sought. About 50 g sample were used to load filters with S0, about 15 g for S1, S2 and S3, about 12 g for S4 and about 10 g for S5. The first 3 filters of each sample were loaded as described above, the 3 following filters were treated with 5 ml liquid 1:1 diluted HCl (v/v) after washing the beaker, resulting in 6 filters per level. The filter was then rinsed 4 times with 15 ml Milli Q water to remove HCl residues. At the end, the funnel was washed with 15 ml Milli Q water.

The filters were dried above silica gel, a punch with a diameter of 17 mm was made and cut in half and the halves were weighed. The samples were thermal-optically analysed and afterwards eluted and measured via IC.

Analysis via IC

The liquid samples were analysed via IC after centrifugation with 13 400 rpm for 5 min to prevent particles from entering the IC system. The concentrations of Ca^{2+} are shown in Figure 41 and the threshold of the Ca^{2+} concentration of Greilinger et al. (2018) is shown as a horizontal line. The concentration of Ca^{2+} in the liquid samples is approximately twice as high as in the previous experiment, where no relationship between CC estimated from Ca^{2+} concentrations in the eluate and CC from TOA could be found.

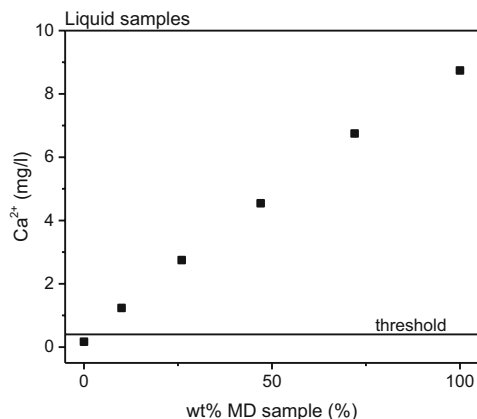


Figure 41: Ca²⁺ concentration in liquid samples with higher amounts of MD sample

The clean snow sample S0 was stored in the freezer until the experiment and the snow was melted at room temperature. Since the volatile compounds should still be present in the sample it was possible to determine the pH of the sample. The pH was 5.50 and therefore under the threshold of 5.6 for samples containing MD. S0 contained 4.2 µeq/l Ca²⁺ which is under the threshold of 10 µeq/l for samples containing MD. Therefore, S0 does not contain MD as defined by Greilinger et al. (2018).

Since S5 is a mixture of samples containing MD, which were refrozen and melted for the experiment. As mentioned before, it is generally not useful to determine the pH value of samples which have undergone one or more thawing and freezing processes already. Therefore, no pH measurement was conducted. In retrospect this is unfortunate, as the respective pH values, although no longer representative for the original snow sample, would have given an idea about the solubility of carbonates.

After TOA the filter halves were eluted with 2.5 ml 76 mM MSA for the analysis via IC. The concentration of MSA was increased to ensure the complete solubility of the respective CaCO₃ loads.

The filter was sonicated for 20 min at room temperature after addition of eluent. The vessel was shaken and centrifuged at 3000 rpm for 10 min. The supernatant was transferred in another vessel and the sample was centrifuged at 13 400 rpm for 5 min. The supernatant was transferred into a vial and measured via IC. The results were corrected by the weight of the sample used to load the filter and by the weight of the sample halves.

The analysis of Ca²⁺ and Mg²⁺ in the eluates showed two different trends for filters that were directly measured and filters that were treated with liquid HCl, see Figure 42. The concentrations of Ca²⁺ and Mg²⁺ on the filters treated with liquid HCl were much lower than the concentrations of the filters that did not receive treatment. HCl can dissolve compounds of water insoluble particles collected on the filter during filtration, leading to a reduction of Ca and Mg on the filter. Hence, the estimate of CC by using Ca or Mg should be done from filters not treated with HCl. The relative standard deviations of the Ca²⁺ concentrations are

much lower than at the previous experiment, where the concentrations on filters within one level showed a high variation.

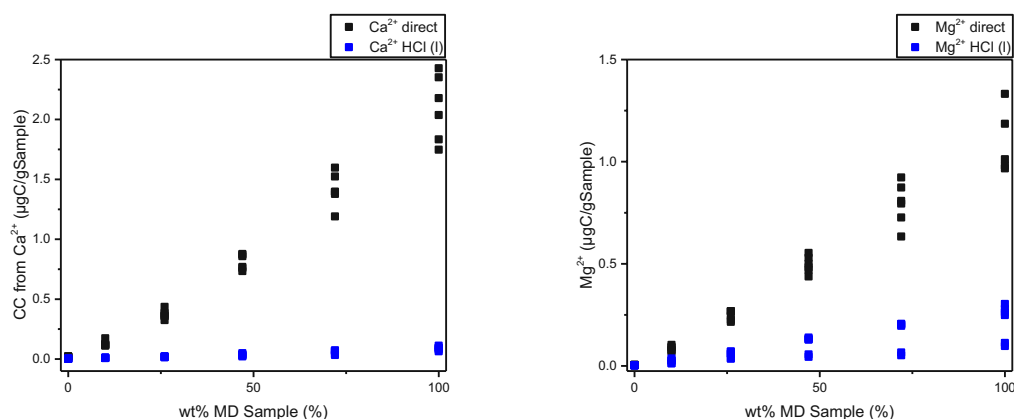


Figure 42: Ca^{2+} and Mg^{2+} concentration in eluates of samples with different higher of MD sample, directly analysed and treated with HCl

Additionally, a trend within the data of the filters treated with liquid HCl was visible regarding the Mg^{2+} concentration of their eluates. The concentration of Mg^{2+} on filters analysed with NIOSH870_x1.5 was lower than the concentration on filters analysed with EUSAAR2_x1.5 or IMPROVE_A, as shown in Figure 43. This trend could not be observed at the Ca^{2+} concentrations. The trend for Mg^{2+} was already addressed previously at the filters loaded with smaller CC concentrations and was confirmed with these additional samples.

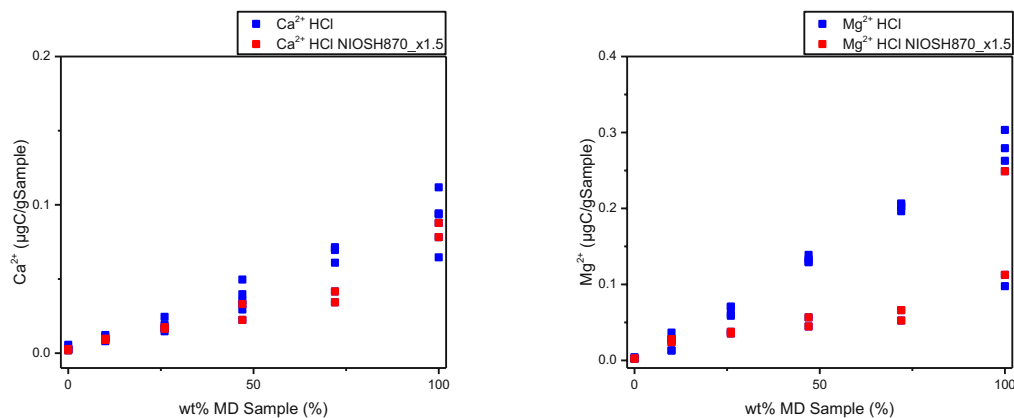


Figure 43: Ca^{2+} and Mg^{2+} concentration in eluates of samples with higher amounts of MD sample treated with liquid HCl

Analysis with thermal-optical method and comparison with results from IC

For TOA of the filters three different thermal protocols were used: EUSAAR2_x1.5, NIOSH870_x1.5 and IMPROVE_A. This way the different protocols can be compared and the applicability of the protocols regarding the analysis of samples containing MD can be evaluated. Two halves of different filters were analysed with each protocol to get more representative results since it cannot be excluded that individual filters are contaminated during the sample preparation.

The results for the carbon content in the different temperature steps were corrected by the weight of sample used to load the filter and by the weight of the filter halves. The data of samples treated with liquid HCl and the directly analysed filters were plotted and are shown in Figure 44.

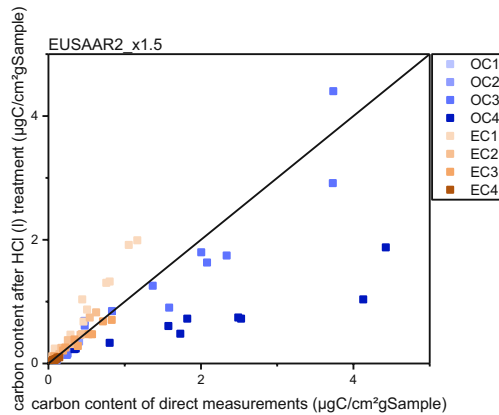


Figure 44: Comparison of the carbonaceous fractions measured directly and after HCl treatment using EUSAAR2_x1.5

The plot shows that for samples which contain higher concentrations of carbon, the amount of carbon in OC4 decreases, while the amount of carbon increases in EC1 after HCl treatment. Samples with higher carbon concentrations equal samples with higher amounts of MD-containing sample. The concentration in OC3, which is attributed to $MgCO_3$ according to the measurements of the reference substance, does not differ distinctly between the directly measured samples and the samples treated with HCl. Hence, for the comparison of CC from TOA and the assessed amount of CC from IC only OC4 was used for TOA and Ca^{2+} for IC. Both concentrations of CC were plotted, see Figure 45, and the trend line was computed for the data and is shown as a continuous line. The 1:1-line is shown as a dashed line to assess the deviation of the trend line.

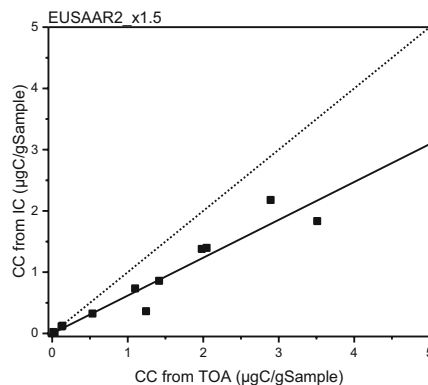


Figure 45: Relationship of CC from IC and CC from TOA for EUSAAR2_x1.5

The slope of the trend line is 0.6181 for the measurements using EUSAAR2_x1.5. The intercept is 0.0046 and therefore negligible. The CC content from TOA is higher for all samples than the amount of CC estimated from the Ca^{2+} concentration.

An equal evaluation of the data was conducted for samples measured with NIOSH870_x1.5 and IMPROVE_A. The plots for NIOSH870_x1.5 are shown in Figure 46. The concentration of carbon is lower for measurements with HCl treatment for OC3 and OC4, corresponding to CaCO_3 , whereas it is increased for EC1. OC3 and OC4 were used to compute CC from TOA.

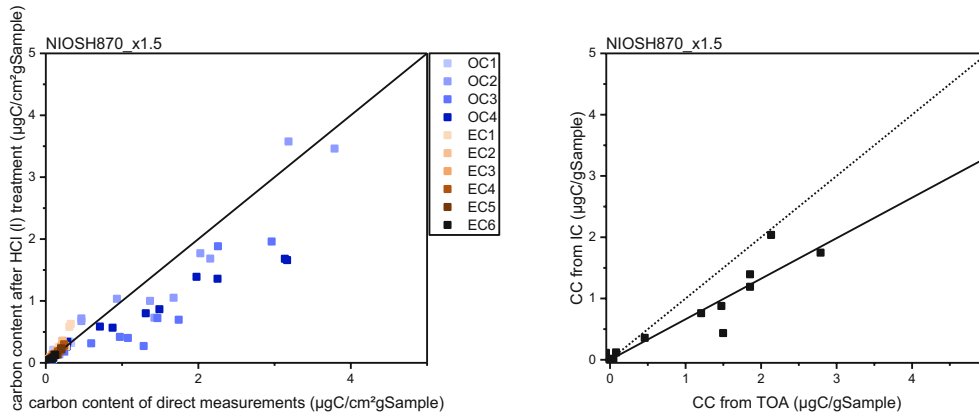


Figure 46: Comparison of the carbonaceous fractions measured directly and after HCl treatment (left) and relationship of CC from IC and CC from TOA for NIOSH870_x1.5 (right)

The slope of the trend line between CC from IC and CC from TOA is 0.6615 and the intercept is 0.0233. 2 samples, one from level 0 and one from level 1, exhibit negative values for CC from TOA.

The plots for samples measured with IMPROVE_A are shown in Figure 47. A decrease in carbon concentrations for OC3 and EC2 after HCl treatment is visible. These fractions were used to compute CC from TOA.

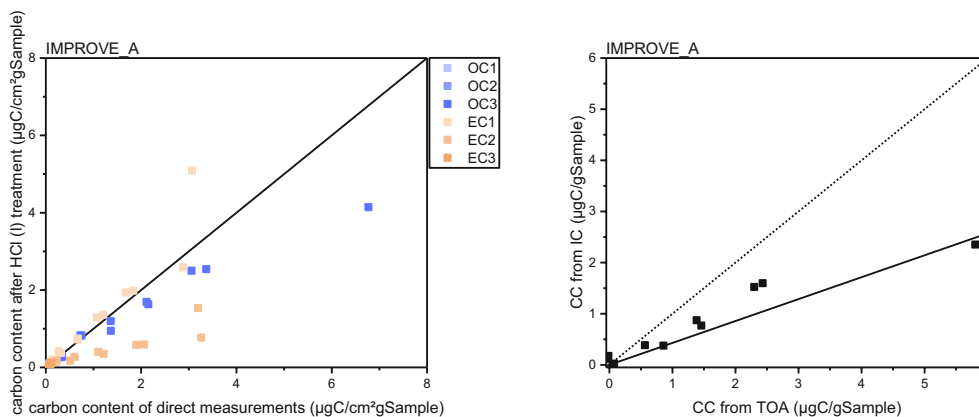


Figure 47: Comparison of the carbonaceous fractions measured directly and after HCl treatment (left) and relationship of CC from IC and CC from TOA for IMPROVE_A (right)

The slope of the trend line is 0.4285 and the intercept is 1.1669. CC from TOA was below 3.5 $\mu\text{gC/gSample}$ for level 5 samples measured with EUSAAR2 and NIOSH870. Measuring these samples with IMPROVE_A led to a concentration of CC of almost 6 $\mu\text{gC/gSample}$ for one sample and to one negative value of about -6 $\mu\text{gC/gSample}$ for the other sample. This is due to very high carbon concentrations in OC3 and EC2 for the sample treated with HCl, which was used to compute CC. Therefore, only one data point is available for the samples of the highest level and due to its elevated CC value from TOA the slope of the trend line differs from the ones obtained by samples measured with EUSAAR2_x1.5 and NIOSH870_x1.5. Neglecting level 5 samples for IMPROVE_A leads to a trend line with a slope of 0.6161 and an intercept of 0.0306, similar to the trend lines of EUSAAR2_x1.5 and NIOSH870_x1.5. However, two samples led to negative values for CC from TOA, both of level 1.

Karanasiou et al. (2011) used ICP-AES to determine the concentration of Ca^{2+} on ambient air filters. Computing the corresponding maximum CC concentrations of Ca^{2+} , assuming that all Ca^{2+} is present as CaCO_3 , and comparing this to the CC concentrations obtained by integration of one temperature step in the thermogram obtained by measurement with the thermal protocol RT-QUARTZ-840, a NIOSH-like protocol. They found that CC concentrations from TOA were always lower than CC from Ca^{2+} . CC from TOA was $55 \pm 11\%$ of CC from Ca^{2+} (99 % confidence level). Roughly half of the Ca^{2+} that was found on the filter was associated to carbonate. Here, CC from TOA was higher for all thermal protocols than CC estimated from Ca^{2+} measured via IC. After the elution of the filters, particles of MD were still visible in the eluate. Although a distinct relationship between CC from IC and CC from TOA was obtained here, it is possible that the concentration of Ca^{2+} would be higher if the filters were digested and not eluted. However, the difference in the thermal protocols and the different samples used might contribute to the difference between the results reported by Karanasiou et al. (2011) for ambient air filters and the data presented here for snow samples.

4.4. Measurement of Fe-containing compounds

MD contains hematite (Kandler et al., 2007). Filters, which are loaded with snow that contains MD, are therefore not white after TOA, but remain coloured orange. The transmittance of the sample can be monitored during TOA. Samples, which contained high amounts of MD, did not reach the initial laser signal during the analysis, which is required for the determination of the automatic split point. Therefore, it was not possible to determine the amount of EC in the sample if MD contamination was visible.

Wang et al. (2012) described the drop of the transmittance signal for the thermal protocol IMPROVE in ice samples. The decrease was found to occur at 250°C in He-atmosphere and was confirmed by comparing the transmittance signal of the samples containing MD with the transmittance signal of Fe_2O_3 . The determination of EC was conducted by correcting the split point manually including the decrease in transmittance due to iron compounds. Although the transmittance signal of Fe_2O_3 showed 2 drops in transmittance, only the first drop was used for the correction.

Bladt et al. (2012) described extensive research on the impact of iron compounds in soot aerosol on the composition, structure and thermo-chemical properties. For these analyses they used SEM/EDX combined with cluster analysis, ICP-MS, Raman microscopy and temperature-programmed oxidation amongst others. According to their research, iron is mainly present as amorphous Fe_2O_3 in soot which crystallizes to $\alpha\text{-Fe}_2\text{O}_3$ upon thermal treatment. Additionally, the temperature necessary to oxidise carbon in the sample decreased with increasing iron content. Fe_2O_3 acts as a supplier for oxygen and therefore it is possible that EC is combusted in He-atmosphere already. Fe_2O_3 is later on reoxidised by external oxygen.

4.4.1. Changes in transmittance of snow samples containing mineral dust

The presence of MD in snow samples led to problems regarding the OC/EC split point, i.e. no automatic split point could be determined. Here the changes in transmittance that were observed during TOA are discussed for snow samples, which were previously used to evaluate the relationship between CC from IC and CC from TOA in chapter 4.3. These samples were analysed using the elongated versions of NIOSH870 and EUSAAR2.

For the first set of samples, which contained lower amounts of MD, an automatic split point could only be set for the samples that contained no MD (S0) and the least amount of MD (S1) using EUSAAR2_x1.5, an automatic split point could not be set for any of the samples using NIOSH870_x1.5. EUSAAR2 and NIOSH870 are well known to result in different amounts of EC (Cavalli et al., 2010).

The transmittance signals of the samples were normalised by dividing the signal through the transmittance at the split point assigned by the software. For most samples, the split point was located in the calibration phase and therefore, as described above, the determination of OC and EC was impossible. Normalised transmittances that start above 1 indicate that the initial transmittance was not reached during the analysis. The 5 samples of each group were averaged and the average transmittance during the analysis was plotted for each thermal protocol, see Figure 48.

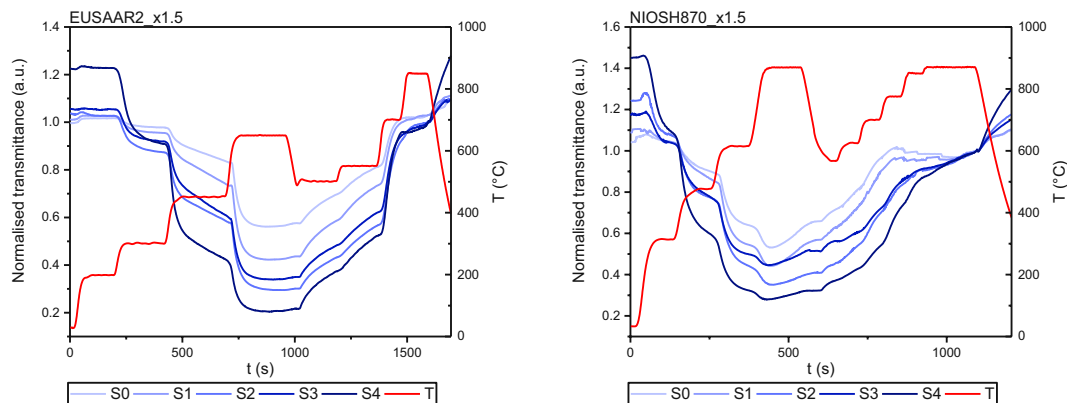


Figure 48: Course of transmittance for samples with variable amount of MD

The plots show not only one but two marked drops in the transmittance signal that vary depending on the amount of MD in the samples for both temperature protocols.

For EUSAAR2_x1.5, the transmittance is constant within the first temperature step at 200°C. The first drop is within the second temperature step at 300°C, located at the heating period. The second drop is within the third temperature step at 450°C.

For NIOSH870_x1.5, the first drop is within the first temperature step at 310°C and the second drop is subsequent within the second temperature step at 475°C. After these two drops the course of the transmittance of all samples is rather similar, leading to approximately parallel curves in the following temperature steps for both temperature protocols. Hence, no clear interference of MD is visible for these temperature steps. Filters measured with NIOSH870_x1.5 were always coloured darker after analysis than filters measured with EUSAAR2_x1.5.

When aiming at a correction for the transmittance not only the first but the first two temperature steps should be considered for EUSAAR2_x1.5 and NIOSH870_x1.5. The split point would then be in EC2 or EC3 for the samples measured with EUSAAR2_x1.5 and NIOSH87_x1.5. Another eye-catching aspect in the thermograms is the increase in transmittance during the calibration phase, when cooling down the sample oven.

For a first try at a correction of the transmittance the times between which the drops occur were determined from the thermograms. The first drop occurred approximately between 205 s and 285 s and the second drop between 430 s and 495 s for EUSAAR2_x1.5. For NIOSH870_x1.5, the first drop can be observed between about 50 s and 110 s and the second drop between 152 s and 200 s. The difference in transmittance at these points in time was computed from the averaged thermograms shown above after normalisation by the initial transmittance used to set the automatic split point. As the concentrations of CC were too low to be reasonably plotted vs. the change in transmittance, the amount of MD-containing sample in wt% was plotted on the abscissa, see Figure 49.

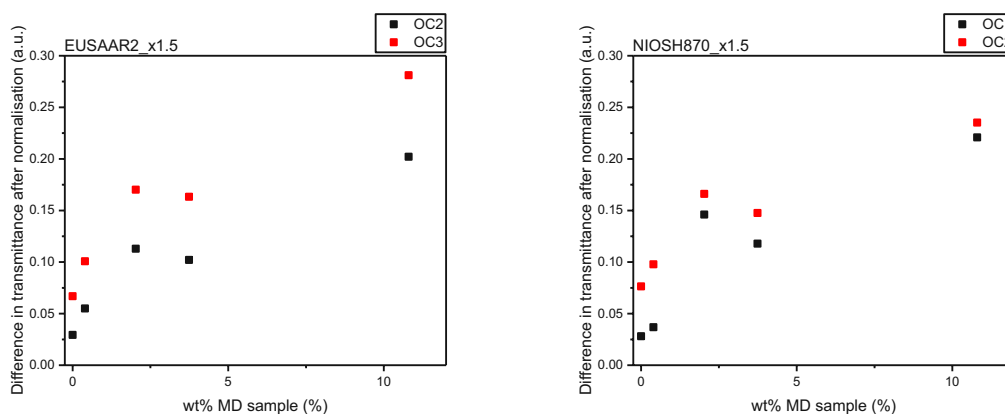


Figure 49: Differences in transmittance in OC2 and OC3 for EUSAAR2_x1.5 and OC1 and OC2 for NIOSH870_x1.5 for samples containing variable amounts of MD

A trend can be observed for the differences in transmittance and the amount of MD-containing sample. The differences in transmittance are rising with increasing percentage of MD-containing sample. As the amount of sample used for loading the filter differed for S0 to S2 (about 50 g) and S3 to S4 (about 25 g), the difference in transmittance was corrected by the weight of sample used to load the filter. The respective diagrams for EUSAAR2_x1.5 and NIOSH870_x1.5 are shown in Figure 50.

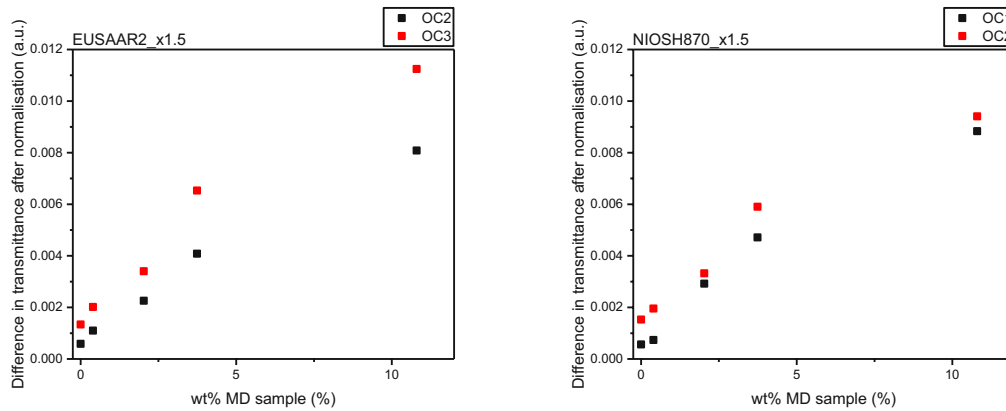


Figure 50: Differences in transmittance in OC2 and OC3 for EUSAAR2_x1.5 and OC1 and OC2 for NIOSH870_x1.5 for samples containing variable amounts of MD after correction by sample weight

After the correction by sample weight the relationship between the difference in transmittance and the amount of MD sample improved if all samples are considered. Although the amount of MD-containing sample was too low to obtain results for CC, the change in transmittance conditioned by the change in optical properties of Fe depending on the prevailing temperature seems to be more sensitive. However, it is possible that these changes are due to the addition of MD-containing sample, which altered the composition of the sample. Increased pyrolysis of OC might occur for samples with higher amounts of MD-containing samples analysed here.

The approach presented above was applied to the second set of samples, which contained higher amounts of MD. Due to the high number of samples and the three different thermal protocols used for TOA, this evaluation is limited to data of samples measured with EUSAAR2_x1.5. It can be seen in Figure 51 that the relationship of the difference in OC2 and OC3 and the amount of MD-containing sample is similar to the first set of samples: Instead of a linear relationship the difference in transmittance rises for the samples with lower amounts of MD-containing sample but flattens for samples with higher amounts of MD-containing sample. The data presented in the left plot was computed from the raw data, without correction by the weight of the sample used to load the filter. After correction by the weight of the sample and the weight of the filter halves the data was plotted again and is shown on the right.

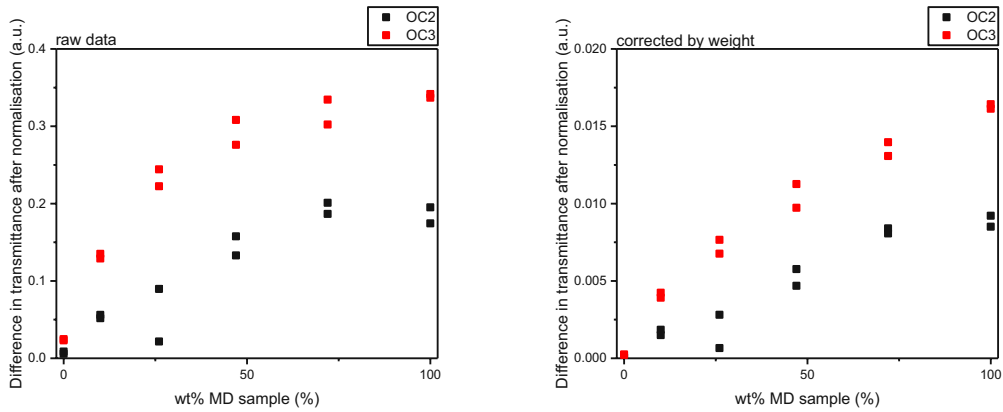


Figure 51: Differences in transmittance in OC2 and OC3 for EUSAAR2_x1.5 for samples with higher MD concentration; data from raw data and after correction

The correction by the weight of the sample used to load the filter and by the weight of the filter halves led to a more linear relationship especially for OC3. As pyrolysis of OC contributes to the decrease of transmittance, deviations may be due to a different degree of pyrolysis within one group of samples. This relationship has yet to be confirmed by the quantification of Fe in the samples, which was not possible during this work.

Assuming that a relationship between the amount of Fe on the sample filters and the transmittance recorded during TOA exists, the influence of pyrolysis can be neglected if the transmittance after the measurement is used. As mentioned above, a rise in transmittance can be observed, when the sample oven is cooled down during the calibration phase. During this phase, the data is still recorded until a sample temperature of approximately 400°C is reached at the end of the calibration phase. Hence, it was possible to compute the rise in transmittance for these samples. The data for the laser signal in transmittance was normalised by division by the initial transmittance, i.e. the maximum laser signal within the first 250 s of measurement, and multiplied by the factor 1000. The period from 1648 to 1723 s was used for EUSAAR2_x1.5. The result was plotted against the sample temperature and the rise of the trendline was plotted against the amount of MD-containing sample in wt% for each sample. The plots without correction and correction by weight are shown in Figure 52.

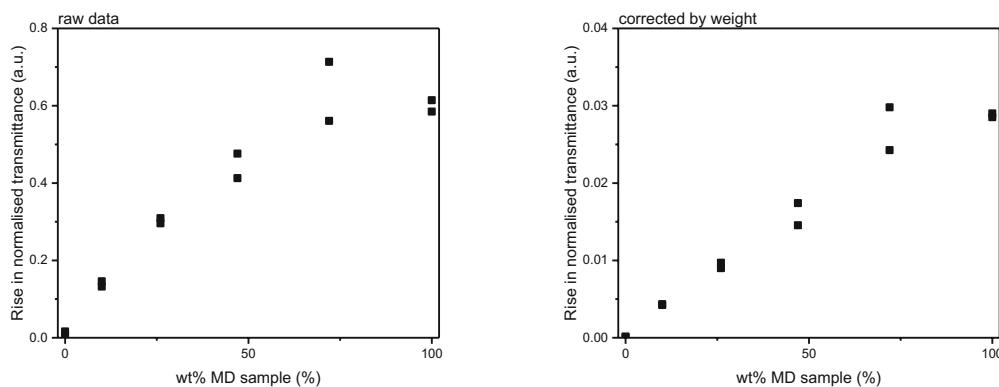


Figure 52: Rise in transmittance in the calibration phase for EUSAAR2_x1.5 for samples with higher MD concentration; data from raw data and after correction

The correction by the sample weight used to load the filter and the weight of the filter halves led to a more linear relationship, equal to the approach above. This data can be assumed to be independent of any pyrolysis phenomena, as no carbon should remain on the filter at this stage of measurement. As the samples of this experiment were eluted for analysis via IC it was necessary to filtrate the eluate again to prepare the samples for the quantification of Fe in the future. The rise in transmittance is expected to correlate well with the amount of Fe on the filter. A correction by weight is not necessary for this relationship, as Fe should directly lead to this effect. For the quantification of Fe and an assessment of MD in the snow sample the sample weight used to load the filter is naturally important.

As these are just preliminary results and more research is needed to confirm the relationships, the evaluation was only done for EUSAAR2_1.5, but could be done for NIOSH870_x1.5 and IMPROVE_A as well. Furthermore, plotting the rise in transmittance in the calibration phase against the amount of CC showed good correlation within one experiment, but the results of different experiments did not match. The data is not shown in this work. However, it is possible that MD in the samples of different experiments has different origins and therefore the ratio of the amount of Fe, estimated by the rise in transmittance, and the amount of CC is not constant. Measurements of the Fe content of the samples are therefore inevitable to research if an assessment can be done by evaluating the transmittance in the calibration phase of TOA. If the concentration of Fe and CC are different for the experiments that were compared, it might even be possible to distinguish different sources of MD in the samples.

4.4.2. Measurements of Fe-containing reference substances

The effect of iron containing compounds on the transmittance during TOA was tested using reference substances. Three iron containing compounds, $\text{Fe}(\text{OH})_3$, FeO and Fe_2O_3 , were suspended in water, filtrated on clean quartz fibre filters and dried in a desiccator above silica gel. For each compound two filters were loaded with different amounts of the compound. Two aliquots, i.e. circular punches with a diameter of 8 mm, were made of each filter, one aliquot was measured with EUSAAR2_x1.5 and the other with NIOSH870_x1.5.

All compounds were insoluble in water. The compounds possess different colours. $\text{Fe}(\text{OH})_3$ has an orange colour, FeO is black and Fe_2O_3 is coloured red prior to analysis. The appearance of FeO is similar to carbon black and it could not be suspended well in water. The loading of FeO was therefore inhomogeneous, see Figure 53.

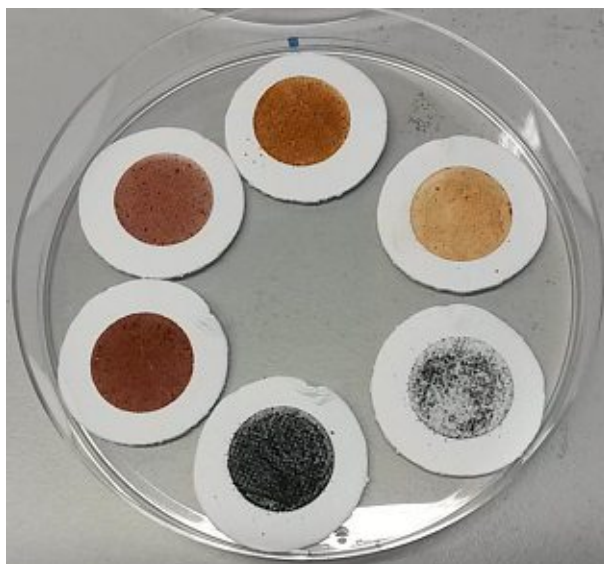


Figure 53: Filters loaded with $\text{Fe}(\text{OH})_3$ (top and top right), FeO (bottom and bottom right) and Fe_2O_3 (left)

The filter punches after TOA are shown in Figure 54. The residual filter material of the respective filter surrounds the analysed punches. The punches on the left were analysed with EUSAAR2_x1.5, the punches on the right were analysed with NIOSH870_x1.5. The colour of the loading has changed for $\text{Fe}(\text{OH})_3$ and slightly for Fe_2O_3 , independent of the thermal protocol used. After the analysis the colour of the $\text{Fe}(\text{OH})_3$ punches was similar to the colour of the Fe_2O_3 punches, which confirms the assumption that $\text{Fe}(\text{OH})_3$ is transformed to Fe_2O_3 during the analysis. TC values of the measurements of $\text{Fe}(\text{OH})_3$ and Fe_2O_3 were within the blank values. FeO showed higher TC concentrations, ranging from 4.5 to 16 $\mu\text{gC}/\text{cm}^2$.

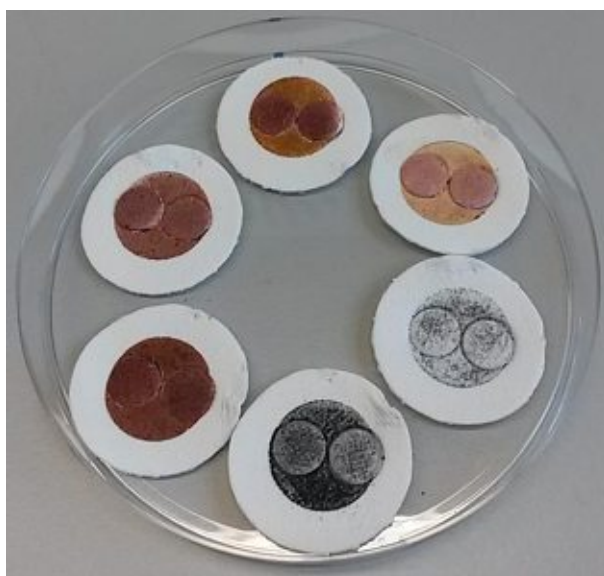


Figure 54: Filters loaded with $\text{Fe}(\text{OH})_3$ (top and top right), FeO (bottom and bottom right) and Fe_2O_3 (left) after TOA

The change in transmittance during measurements of these Fe-compounds using the EUSAAR2_x1.5 thermal protocol is shown in Figure 55. The same plot for measurements using NIOSH870_x1.5 is shown in Figure 56. The transmittances were normalised to the initial transmittance that the software uses to determine the automatic split point, as was done previously for the evaluation of the rise in transmittance during the calibration phase for snow samples.

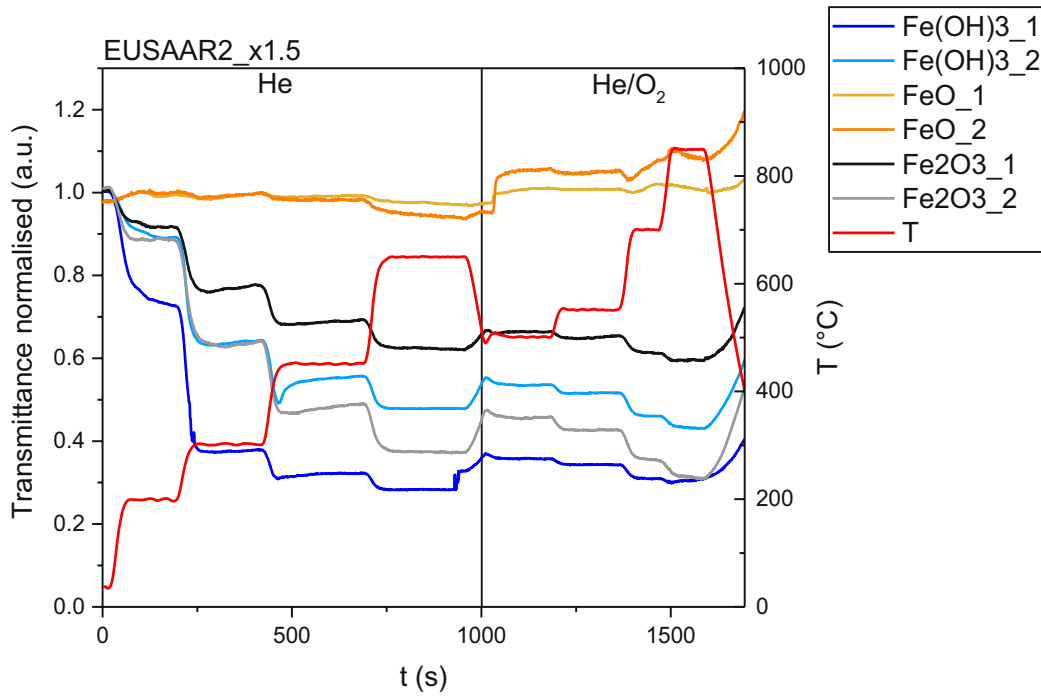


Figure 55: Change in the transmittance of iron compounds using EUSAAR2_x1.5

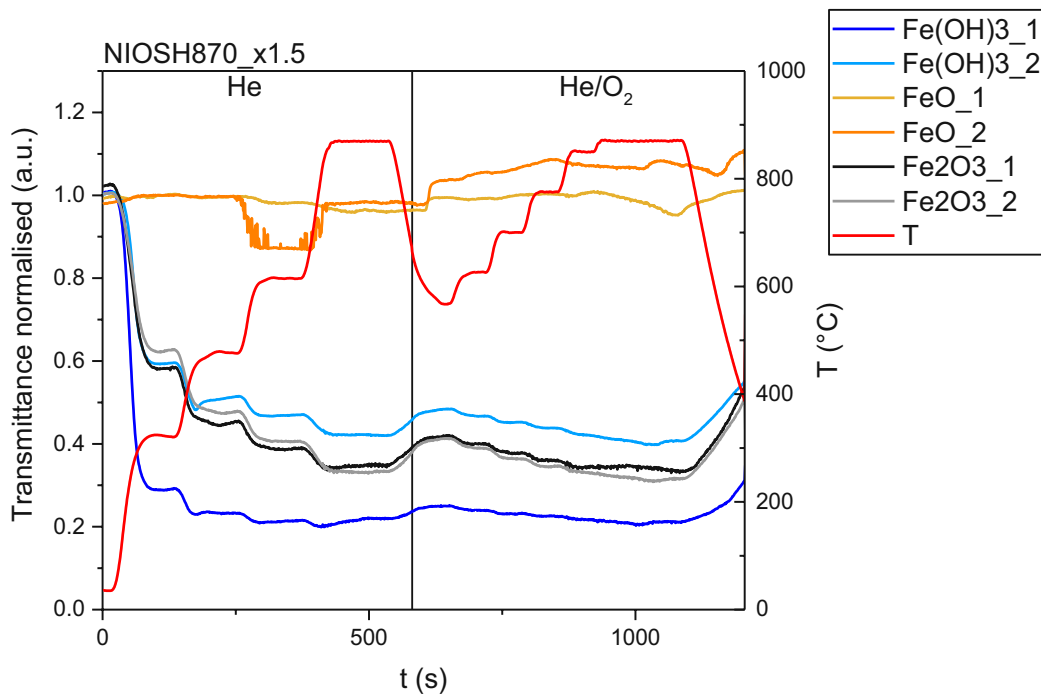


Figure 56: Change in the transmittance of iron compounds using NIOSH870_x1.5

FeO showed almost no change in transmittance during the analysis, except for a sharp bend shortly after the atmosphere was changed from inert to oxidising. FeO_2 shows a negative peak in the OC3 area when measured with NIOSH870_x1.5, which might be due to contamination on the filter or movement of the filter in the sample oven.

The transmittance curves are very similar for Fe(OH)₃ and Fe₂O₃. The filters did not reach the initial transmittance during the analysis independent of the thermal protocol used. The transmittance decreases when heating up the sample and increases when cooling the sample.

For the correction of the split point and a best possible assessment of EC, all changes of the transmittance signal should be considered. Not only decreases the transmittance when heating up the sample, but it also increases when cooling the sample. The strongest decrease in transmittance takes place in the inert phase when heating up to about 300°C. This happens in the first temperature step for NIOSH870 but is split on temperature step 1 and 2 for EUSAAR2. Most samples analysed in this work showed hardly any pyrolysis effects in OC1 and only slight pyrolysis in OC2 when using EUSAAR2. The drop in transmittance due to iron containing compounds happens during the heating-up, the transmittance stays constant during the temperature step.

The decrease in transmittance is much higher in the inert phase than in the oxidising phase. Before the oxidising phase starts, the oven is cooled and the transmittance of the iron compounds rises. This is especially a problem for samples which contain EC that combusts during the first temperature steps in the oxidising phase and leads to a higher rise in transmittance than the drop in transmittance due to the iron containing compounds. This might lead to an overestimation of EC if only the first drops in transmittance are considered for the correction.

The rise in transmittance occurring from the cooling step can only be neglected if the split point is in the EC5 or EC6 area for NIOSH870, since the transmittance of the iron compounds is approximately as big as before the rise before the change to oxidising atmosphere. For EUSAAR2, it can only be neglected if the split point is in the EC3 phase, since the transmittance drops more in the EC4 phase due to the higher temperature by comparison to the inert phase. Since the decrease in transmittance due to iron containing compounds is very high, the initial transmittance was not reached during the measurement for any of the samples analysed in this work containing MD. Therefore, a correction of the transmittance for samples containing iron has to be researched if the quantification of EC in samples containing MD shall be carried out. The measurement of iron was not possible during this work and since the ratio of CC to Fe can vary depending on the origin of MD, a correction using the amount of CC found in the sample was not undertaken.

To check if an estimate of EC is possible when only considering the first drops in transmittance, one point in time was chosen in the middle of each temperature step, where the transmittance reaches a plateau. This was possible for the measurement of Fe-containing compounds, as almost no carbon was found on the filters and pyrolysis did not occur. For samples containing noticeable amounts of carbon where pyrolysis can be expected, the points in time should be chosen at the end and the start of a temperature step so that the effect of pyrolysis on the transmittance is not wrongly attributed to Fe. For EUSAAR2_x1.5 128, 340, 583, 861, 1124, 1289, 1439 and 1544 s were chosen and the

normalised transmittance at these points of time was used to compute the fall in transmittance in relation to the initial transmittance, see Table 11. Due to the advantages of using EUSAAR2 described above, e.g. CC only evolves in one temperature step, and its wide use in Europe for ambient air samples, the following evaluation of the data was only performed for EUSAAR2_x1.5.

Table 11: Reduction in normalised transmittance for Fe-containing compounds using EUSAAR2_x1.5

t (s)	Reduction in normalised transmittance (%)					
	Fe(OH) _{3_1}	Fe(OH) _{3_2}	Fe ₂ O _{3_1}	Fe ₂ O _{3_2}	FeO_1	FeO_2
128 (OC1)	26	11	9	13	0.4	0.7
340 (OC2)	63	37	24	38	1.0	1.4
583 (OC3)	68	45	32	53	1.0	2.3
861 (OC4)	72	52	38	63	2.6	6.2
1124 (EC1)	64	47	34	55	-0.7	-4.7
1289 (EC2)	66	49	36	58	-0.6	-3.9
1439 (EC3)	69	54	39	65	-1.1	-5.4
1544 (EC4)	70	57	41	69	-1.1	-8.5

The measurements of samples containing MD described above led to the assumption the main decrease in transmittance attributed to Fe occurs when heating from OC1 to OC2 and from OC2 to OC3. For the iron compounds measured here, a marked drop in transmittance can already be observed when heating up from to OC1 (11 and 26 % for Fe(OH)₃ and 9 and 13 % for Fe₂O₃ in relation to the initial transmittance). For Fe(OH)_{3_1} the reduction in transmittance from OC1 to OC3 is 42 %, a maximum reduction of 72 % can be observed in OC4. Hence, additional 30 % reduction occur outside the temperature steps previously determined from the snow samples. For Fe(OH)_{3_2} the reduction from OC1 to OC3 is 34 %, the maximum reduction is reached in EC4, 57 %. Therefore, a reduction of 23 % occurs not between OC1 and OC3. For Fe₂O_{3_1} the reduction between OC1 and OC3 is 23 %, the maximum reduction is reached in EC4 and is 41 %. A reduction of 18 % occurs additionally to the reduction between OC1 and OC3. For Fe₂O_{3_2} the transmittance was reduced by 40 % between OC1 and OC3, the maximum reduction is reached in EC4 and is 69 %. Therefore, a reduction of 29 % occurs additionally to the reduction between OC1 and OC3. For FeO_1 and FeO_2 the transmittance is reduced in the inert atmosphere by a maximum of 7 %, while it is increased in the oxidising atmosphere by a maximum of 9 %.

The reduction of transmittance is not constant independent of the concentration of Fe on the filter. By using only the first temperature steps for the correction of the transmittance, it might be possible to set an OC/EC split point, but the accuracy of the determination of OC and EC is questionable. The amount of Fe in samples with low and high MD contamination has to be determined and suitable Fe filters thermal-optically analysed, as was done here. It is possible, that the amount of Fe on these filters is much higher than the amount of Fe would be in snow samples. Furthermore, iron compounds were analysed here that were available, it cannot be excluded that the difference in the reduction of transmittance between these compounds and the reduction observed in snow samples is due to a difference in the iron compound itself. Therefore, this might give an idea of the impact of iron in the samples, but the results cannot be used directly for snow samples.

However, one more evaluation was done for Fe_2O_3 , the compound of interest. The relative reductions were computed, i.e. the reductions described above were divided by the maximum reduction of this sample and the ratios are shown in Table 12.

Table 12: Relative reductions in normalised transmittance for Fe_2O_3 using EUSAAR2_x1.5

t (s)	Relative reductions in normalised transmittance ()	
	Fe2O3_1	Fe2O3_2
128 (OC1)	0.22	0.19
340 (OC2)	0.57	0.55
583 (OC3)	0.77	0.76
861 (OC4)	0.92	0.91
1124 (EC1)	0.83	0.80
1289 (EC2)	0.87	0.84
1439 (EC3)	0.95	0.94
1544 (EC4)	1	1

The two measurements of Fe_2O_3 are in good agreement regarding the relative reductions in normalised transmittance in each temperature step. This suggests that these ratios are comparable independent on the concentration of Fe_2O_3 on the filter. As in the middle of EC4 most of the carbon compounds should be removed from the filter and only little EC may be left in real samples, using the transmittance at the end of EC4 might lead to a possible correction. For this approach the initial transmittance is used, which depends not only on the amount of iron on the filter of a real sample but on the entire loading. However, the influence of components other than MD might be negligible for samples featuring high amounts of Fe. Further research is needed to confirm this assumption and the quantification of Fe in the samples would be helpful to assign which percentage of the drop in transmittance is due to Fe and which is due to pyrolysis during the measurement.

4.5. Summary of chapter 4

The comparison of the thermal protocols EUSAAR2, NIOSH870, their elongated versions and IMPROVE_A showed that the length of the protocol has an effect on the separation of carbon signals and can therefore influence the quantification of certain carbon fractions. The standard EUSAAR2 protocol proved to be sufficiently long for most samples. The elongation of NIOSH870 led to improved results. IMPROVE_A led to a lower number of peaks for the analysed ambient air filters, which might be disadvantageous if certain carbon fractions shall be analysed. The measurements of carbonate standards, e.g. CaCO_3 , showed carbon signals in different temperature steps for the thermal protocols used. IMPROVE_A led to signals in the oxidising atmosphere, which might result in problems regarding the determination of EC.

The removal of CC of an ambient air filter influenced by MD by fumigation with HCl and a comparison with snow samples containing MD treated equally showed that CC signals in ambient air filters and filters loaded with snow samples differ. Hence, approaches presented in literature regarding CC or MD cannot be applied to snow samples without further evaluation. The removal of CC with liquid HCl and HCl vapour proved to be equal for snow samples. Using liquid HCl, acidic residues can be removed by rinsing and damage of the oven of the Lab OC-EC Aerosol Analyzer can be prevented.

A comparison of carbon fractions in snow samples containing MD with and without HCl treatment showed differences in OC3 and OC4 as well as EC1 and EC2 for EUSAAR2 and in OC2, OC3 and EC2 for NIOSH870. The analysis of CaCO_3 showed signals in OC4 for EUSAAR2 and in OC2 and OC3 for NIOSH870. A shift of carbon from OC3 to EC1 and EC2 was observed when treating snow samples containing MD with HCl. Hence, for the comparison of CC from TOA and CC estimated from IC the temperature steps associated with CaCO_3 and the concentration of Ca^{2+} in the filter eluate were used. This comparison showed a linear relationship between CC from TOA and CC from Ca^{2+} for all thermal protocols used, if sufficient amounts of MD were contained in the samples. The slopes of the trend lines were similar for the different thermal protocols, about 0.6, and TOA led to higher CC concentrations than IC.

In the presence of MD, no OC/EC split point could be determined. A correction of the transmittance for the presence of iron compounds is necessary to determine EC and OC in these samples. Different approaches for a correction were presented, including the drop in transmittance in OC2 and OC3 for EUSAAR2 and in OC1 and OC2 for NIOSH870, where an increased reduction in transmittance occurred for samples with increasing amount of MD. Another approach uses the rise in transmittance during the calibration phase, where the transmittance is not influenced by pyrolysis of carbon. Both approaches seem promising but have to be confirmed via the quantification of Fe in the samples.

The measurement of iron containing reference substances, e.g. Fe_2O_3 , showed changes in transmittance in every temperature step, i.e. decreased transmittance when heating and increased transmittance when cooling. For reference substances, including only the first temperature step for a correction is not sufficient, as the additional decrease in normalised transmittance during the measurement is noticeable. However, the relative reductions of two measurements of Fe_2O_3 with different concentrations were similar and a correction of the transmittance by the relative reductions may be possible. To confirm these preliminary results, more data is needed.

5. Use of quartz fibre filters for filtration of snow samples

In this chapter the usage of quartz fibre filters for the filtration of melted snow samples is discussed, including an evaluation of the filter efficiency for inorganic cations and the effects on TOA when treating the snow sample with a coagulant. Quartz fibre filters are used whenever sample material collected on filters shall be analysed via TOA, as the filter material withstands high temperatures and does not change its optical properties depending on the prevailing temperature. The filters used in this work (Pallflex® Filter Tissuquartz™) possess an aerosol retention of 99.9 % according to the specification sheet (VWR: Pallflex® Filter, 2020). The retention of particles in fluids, e.g. rain or snow samples, is not specified. For the analysis of particles in these fluid samples a high retention is important, as insufficient retention leads to underestimation of the compounds of interest. In this work the compounds of interest are water-insoluble OC, EC and CC contained in snow samples.

5.1. Filter efficiency for inorganic ions

The applicability of quartz fibre filters for liquid filtration was tested to ensure that the quartz fibre filter used is sufficient to hold back the insoluble components of the snow sample. In literature doubts are being expressed that EC is not sufficiently held back by quartz fibre filters (e.g. Torres et al., 2014). Used for ambient air sampling, the filters ensure the collection efficiency of ambient particulate matter, but regarding liquid filtration this may not be the case.

DIN EN 1484 defines dissolved organic carbon (DOC) as the fraction of organics passing a membrane filter with a pore width of 0.45 µm (DIN, E 1484, 1997). No such standard specification for the separation of EC is available, as EC is insoluble, i.e. will be present in particulate form. Still, EC particles can be rather small and may pass quartz fibre filters. Therefore, the standard specification defined for DOC was used. Since the filter material used for TOA must withstand high temperatures up to almost 900°C, syringe filters cannot be analysed for carbon compounds and a direct comparison of material collected on the two filter types is not possible. Hence, it was decided to base a first comparison on the analysis of inorganic cations remaining in the filtrate after the filtration with a quartz fibre filter or a syringe filter. The analysis of TC remaining in the liquid would have been favoured, but no suitable method for this analysis was available. Still, a certain relationship between the occurrence of carbon fractions and insoluble ions can be expected and Ca²⁺ could be regarded as a marker for CC and therefore MD, the other compound of main interest within this work. The setup for a possible experiment addressing carbonaceous particles will be discussed at the end of chapter 5.1.

A snow mix was prepared and samples were taken directly from the snow mix, after filtration through a clean quartz fibre filter and after filtration through a clean quartz fibre filter and additional filtration through a PTFE syringe filter with a mesh width of 0.45 µm. The samples were measured via IC, the concentrations of the cations Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ were analysed. The samples taken directly from the snow mix were centrifuged (13 400 rpm, 5 min) prior to analysis to remove large particles and therefore to protect the IC system from taking damage. Other particles (especially carbonates connected to MD) are expected to dissolve within the acidic eluent of IC.

To observe possible contamination during the filtration process, Milli-Q water was analysed directly, after filtration through a clean quartz fibre filter and after additional filtration through a PTFE syringe filter with a mesh width of 0.45 μm .

The concentrations of the ions in Milli-Q water or the filtrate of the blank measurements are shown in Figure 57 and the results of the measurements with snow samples are shown in Figure 58. The LOD, 0.01 mg/l for all analysed ions, is shown as a red horizontal line in the diagrams. Each sample is represented by a number in the diagrams, 1 to 3 for blanks and 1 to 4 for snow samples. The particular step at which a liquid sample was taken for analysis via IC is indicated by the abbreviations nf, f and sf (nf: no filtration, sample directly analysed; f: filtration through a clean quartz fibre filter; sf: additional filtration through a syringe filter). The concentration of Mg^{2+} was below the LOD for all blank samples and all filtration steps. Therefore, no plot is shown for Mg^{2+} in Figure 57.

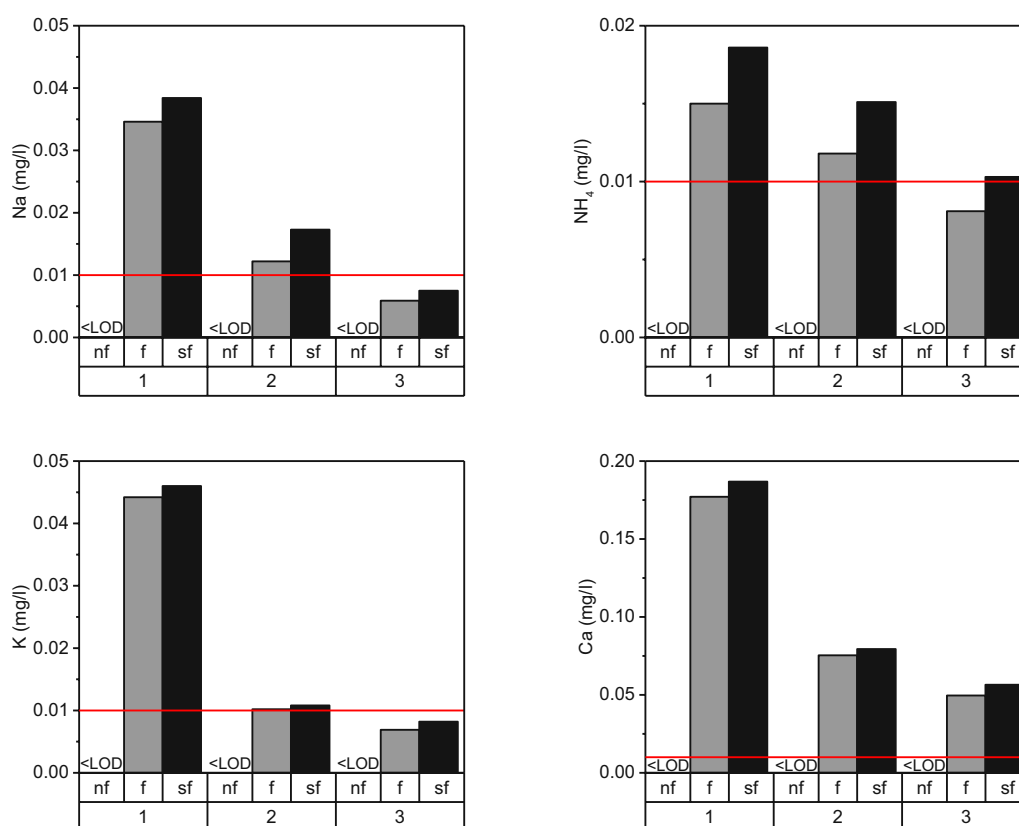


Figure 57: Results of the blank measurements of filter efficiency

The concentrations of all analysed ions increase with each step of the filtration procedure, as the contaminations are summed up. Concentrations were below the LOD for all ions for the blank samples, which were not filtrated, and are marked as <LOD in the diagrams. For Na^+ and K^+ the concentrations of the filtrated and syringe filtrated sample of sample 3 were below the LOD, for NH_4^+ only the filtrated sample of sample 3 was below the LOD. Still, these values are shown as they are just slightly lower than the LOD. The main contamination derives from the filtration through the quartz fibre filter. During the filtration, the sample is in contact with the glass funnel, the quartz fibre filter, the frit and the side-arm flask. The liquid sample for IC was taken out of the side-arm flask. For additional filtration through a syringe

filter the sample is also in contact with a PP/PE syringe and the syringe filter, but this leads to small additional contaminations only. However, contaminations remain below 0.2 mg/l for Ca^{2+} , below 0.05 mg/l for Na^+ and K^+ and below 0.02 mg/l for NH_4^+ . Compared to the subsequent measurements of snow samples, which showed concentrations of approximately 0.8 mg/l for Ca^{2+} , 0.08 mg/l for Na^+ and NH_4^+ and 0.025 mg/l for K^+ after subtraction of the respective blank value, the blanks cannot be neglected. However, the concentrations of these ions in the snow sample are well above the blank value except for K^+ , which showed lower concentrations.

Another noticeable observation is that the contaminations in sample 1 are higher than in the following two samples. The glassware was washed thoroughly with Milli-Q water prior to the first filtration, but contaminations may have remained in the filtration setup which might have been washed out at the subsequent filtrations. It is also possible that the contamination of the quartz fibre filters used was different, as they are cleaned in a muffle furnace to remove carbon residues, but ionic components are not removed during this process. A definite reason for this cannot be given.

Samples were taken at the three steps nf, f and sf from a snow sample as done for the blank values. Four aliquots of the sample were filtrated, displayed as sample 1 to sample 4 in the diagrams. The ion concentrations obtained from the snow sample were corrected by the average blank values. Concentrations of ions below the LOD of blank samples were replaced by half of the LOD for the calculation of the average value. The average of the blank value in one particular work step, i.e. nf, f or sf, was subtracted from the sample value in this step for sample 1 to sample 4.

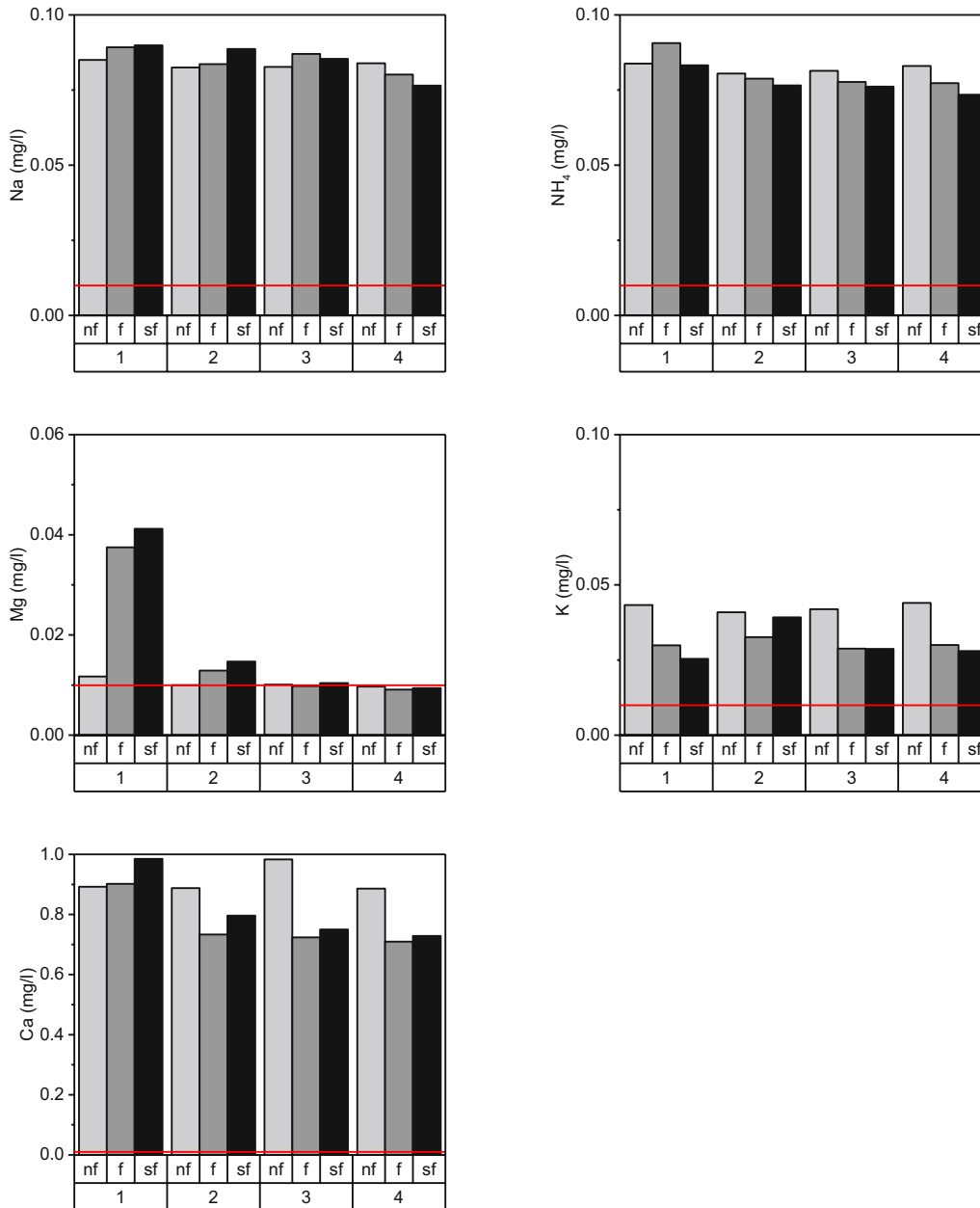


Figure 58: Results of the test of filter efficiency using a snow sample

The differences between the concentrations of the different work steps of one sample were calculated. As the blank values contained some variance, the standard deviations of the blank values of each step were computed for each ion. The difference between two steps of one sample is only meaningful if it is bigger than the standard deviation of the blank values, as the difference might be due to variations of the filter material or contamination of the filtration setup otherwise. Based on these assumptions, no obvious differences could be determined for filtration with the quartz fibre filter or the syringe filter. One might argue that this is likely as the analytes (inorganic ions) are rather water soluble and thus not a lot of insoluble material is present, which could be removed by filtration. This is definitely the case for ammonium, which consequently shows well comparable concentrations for all steps. The compound of interest was Ca, as this element is linked to MD and thus to insoluble particles.

In this case three out of four samples showed lower concentrations after filtration with either quartz fibre filters or syringe filters.

Since there is no trend visible in the samples that the ion concentrations are lower after additional filtration with a syringe filter with a mesh width of 0.45 μm , it can be assumed that the filter efficiency of quartz fibre filters is sufficient for the separation of MD particles. Still, it could not be proven for carbon parameters.

To assess the filter efficiency of quartz fibre filters for carbonaceous particles, samples prepared as described above could be analysed with a TC analyser. Water insoluble OC and in this case also insoluble EC should be held back by the syringe filter with a mesh width of 0.45 μm , while its soluble counterparts should pass the filter. Hence, if the amount of carbon in the liquid samples after filtration only and after additional syringe filtration differ significantly, it can be assumed that water insoluble carbonaceous particles (containing OC and EC) are not quantitatively held back by the quartz fibre filter. It has to be taken care that the TC analyser accounts for OC and EC.

As another possibility for the determination of the filter efficiency for EC, a suspension of soot in water could be made, filtrated, boiled down and the mass of the residues could be determined. However, sufficient soot has to be used to obtain masses for EC residues and the amounts necessary are likely to exceed the amount of EC in snow samples. As filters have to be heat-resisting for TOA, this is an alternative to TOA, giving the freedom to use filters with suitable mesh widths independent of the filter material. The difference of the weight before and after the filtration may allow to estimate the filter efficiency. As there is no standard specification which filter to use to quantitatively remove EC from a liquid sample the reliability of the filter used for this estimation is questionable. Additionally, the soot used might not be representative for aged EC in snow samples and soot is difficult to handle, as it adsorbs easily to walls of glassware, especially when suspended in water. Therefore, further investigation was abandoned and it was taken account of the fact that the filtration of EC with quartz fibre filters may not be quantitative without altering the sample.

5.2. Advantages and disadvantages after adding a coagulant

According to Torres et al. (2014) quartz fibre filters hold back less than 10 % of EC. They reported that the collection efficiency could be improved by adding various compounds, the most promising being $\text{NH}_4\text{H}_2\text{PO}_4$, which increased the collection efficiency to 95 % by increasing ionic strength of the sample. They state that the addition of $\text{NH}_4\text{H}_2\text{PO}_4$ (1.5 g in 100 ml precipitation sample) does not only lead to a high retention of EC but also does not damage the Lab OC-EC Aerosol Analyzer's oven, contrary to other substances which led to higher filter efficiencies. Torres et al. (2014) emphasized that the determination of the filter efficiency for EC must not be conducted by filtrating over more than one quartz fibre filters, as the filters possess the same mesh width and the filter efficiency is overestimated by this procedure due to a systematic error.

As the coagulant leads to a low pH in solution (5 %: 3.8 - 4.4) it can be expected that CC in snow samples will be removed by decarboxylation. The pK_a values of the dissociation of carbonic acid are 6.35 and 10.33 (Riedel and Janiak, 2011). At the prevailing pH caused by the addition of $NH_4H_2PO_4$ CC should mainly be existent as carbonic acid and therefore be removed from the sample as CO_2 . Although this might seem like a disadvantage because samples containing CC would be markedly altered, it might actually be a big benefit, as the determination of CC includes the treatment with acid, anyways. For analysis of CC via TOA two aliquots of each sample are needed. One of the aliquots is treated with HCl to remove CC, both aliquots are analysed and the amount of CC is subsequently computed by a comparison of the thermograms. If each sample is divided in two subsamples filtrated separately, one subsample can be filtrated directly and the other subsample can be filtrated after treatment with $NH_4H_2PO_4$. This way OC could be determined from the directly filtrated sample, as volatile organic compounds might be removed by the acidic pH in the sample treated with coagulant; EC, which should be quantitatively held back by the filter if coagulant is added, could be determined from the treated sample; CC could be determined from the difference of both thermograms in the temperature steps associated with CC in the inert atmosphere for EUSAAR2 and NIOSH870, if it is removed quantitatively due to the change in pH caused by the addition of coagulant. Hence, the removal of CC may be helpful in the determination of CC and render the treatment with HCl unnecessary. This will be evaluated here.

5.2.1. Removal of CC – Equality of HCl and $NH_4H_2PO_4$?

First the possibility of removing CC with the coagulant has to be assessed. Since the coagulant is mixed in the sample, sonicated and left for 24 h prior to filtration, working with carbonate standards is hindered. The standards would be added to a solution of coagulant and the solution would be filtrated. The used carbonate standards, which are partly or completely soluble in water, could not be held back by the filter, regardless of the pH value in the solution leading to erroneous assumptions.

Hence, the efficiency of the removal of CC was tested by using a snow sample containing high levels of CC, i.e. a sample visibly contaminated with MD, and treating one aliquot with the coagulant and one aliquot with HCl. For the sample treated with HCl the sample was filtrated directly and rinsed with 5 ml of 1:1 (v/v) diluted HCl, as done in previous experiments. HCl was shown to remove CC quantitatively, so equal thermograms in the highest temperature step in the inert atmosphere (OC4) for measurements using EUSAAR2 would lead to the assumption that CC is quantitatively removed by the addition of the coagulant.

As described by Torres et al. (2014) 1.5 g $NH_4H_2PO_4$ was used for 100 ml precipitation. The pH of the sample was measured before and after the addition of the coagulant using a pH electrode and changed from 8.23 to 4.61 due to the addition of coagulant. This pH should be sufficiently low to remove CC from the sample, compare Figure 59.

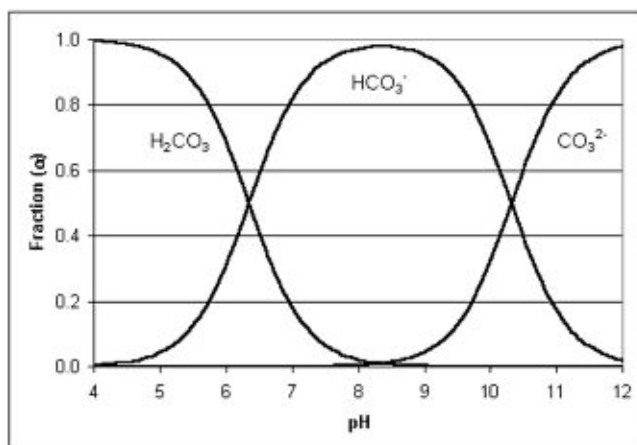


Figure 59: Carbonate equilibrium (taken from Utah State University: Carbon Dioxide and Carbonic Acid, 2006)

Additionally to the sample aliquots treated with HCl and $\text{NH}_4\text{H}_2\text{PO}_4$, respectively, an untreated sample aliquot was filtrated. This was done to determine the amount of CC in the sample (i.e. by comparison with the thermogram of the sample treated with HCl) and to observe possible changes in other temperature steps caused by the addition of coagulant. Possible CC residues can be assessed by comparison of all three thermograms.

Since rinsing the beaker and funnel with water after filtrating the sample might wash coagulant out and subsequently destroy agglomerates of EC, two groups of samples were prepared: In group 1, the beaker and the funnel were rinsed with Milli-Q water as done in previous experiments, in group 2, the sample was filtrated and the glassware was not rinsed. A comparison of the amount of carbon on the filter should give insight into a suitable approach.

For the filtration the clean filter was moistened with 5 ml Milli-Q water. The sample was drawn through the filter, the beaker which contained the sample was rinsed with 50 ml Milli-Q water and the funnel was rinsed with 20 ml Milli-Q water. At the end the filter was predried by sucking air through the filter for 10 s. For samples treated with HCl 5 ml 1:1 diluted HCl (v/v) passed through the filter before rinsing the beaker. For samples treated with coagulant without rinsing the rinsing steps of the beaker and the funnel were skipped.

Three types of blanks were prepared, using approximately 25 g of liquid for each filter: For type 1 (H_2O), representing the untreated samples and the samples treated with HCl, Milli-Q water was used instead of the sample for the filtration process. For type 2 ($\text{H}_2\text{ON}_{\text{mn}}$) and type 3 ($\text{H}_2\text{ON}_{\text{on}}$), representing samples treated with coagulant, a solution of 1.5 g $\text{NH}_4\text{H}_2\text{PO}_4/100$ ml Milli-Q water was prepared. Half of the blanks representing samples treated with coagulant were rinsed after filtration to obtain type 2 blanks, half of them were directly predried to obtain type 3 blanks. 5 filters were prepared for each type, giving a sum of 15 blank filters.

For the sample filters 5 filters were loaded for each group (untreated sample (S), sample treated with HCl (SHCl), sample treated with $\text{NH}_4\text{H}_2\text{PO}_4$ (with (SN_mn) and without (SN_on) rinsing), a sum of 20 filters. Each clean filter was loaded with approximately 25 g of sample and had a loaded area of 16 mm in diameter. The filters were dried overnight above silica gel, the filters treated with HCl were left in a fume hood to ventilate for 1 h prior to the drying step. Punches with a diameter of 17 mm were made and cut in halves, whereat not exact halves were obtained. For the evaluation of the data the sum of the halves of each sample was computed, therefore the exact area of each half was not of importance and weighing of the sample aliquots was not necessary. However, the cutting step was necessary, as the area of the entire filter exceeded the space on the sample spoon of the Lab OC-EC Aerosol Analyzer.

The samples were analysed using the standard EUSAAR2 thermal protocol. After the analysis in the Lab OC-EC Aerosol Analyzer both halves were eluted with 76 mM MSA, put in an ultrasonic bath for 20 min and centrifuged at 3000 rpm for 10 min. The supernatant was transferred in a smaller container and centrifuged at 13 400 rpm for 5 min. The centrifuged eluate was transferred to a vial and analysed for cations via ion chromatography. The data of Ca^{2+} and Mg^{2+} additionally to the carbon fractions were prepared for further evaluations and are not used in this work.

Blanks

The thermograms of all five samples from one group (H₂O, H₂ON_mn, H₂ON_on) were comparable, apart from one sample of the group H₂O, which showed much higher signals and was therefore excluded from the evaluation. The FID signals of the two halves of one filter were summed up and corrected by the weight of sample used, i.e. the amount of liquid filtrated. A baseline correction was performed by computing the average of the FID signal in the first 50 s of measurement and subtracting the average signal from the FID signal of the entire measurement. To compare the groups, the average signal within one group and the standard deviation at each point were computed and are plotted in Figure 60. The continuous line in the thermogram is the average FID signal of the group. The area around the average signal in the same colour represents the respective standard deviation. The thermograms of the individual blanks in each group are shown in Figure 78 in the supplement.

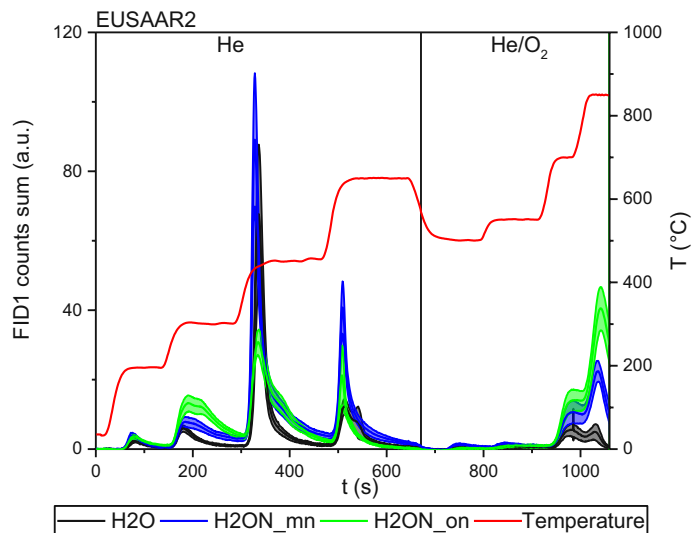


Figure 60: Average FID signal and standard deviation for each group of blanks prepared from Milli-Q water with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$

The blanks which contained coagulant, H2ON_mn and H2ON_on, show higher signals in EC3 and EC4 as well as OC2 and OC4. The signal of H2ON_mn is comparable to the signal of H2O in OC3 in height when considering the standard deviations, whereas the signal of H2ON_on is lower and the peaks of both blanks treated with coagulant are broader in OC3 than the signal of group H2O. For the blanks that were treated with coagulant it is visible in the thermogram that the signal does not reach the baseline at the end of the measurement. Therefore, future measurements should be conducted using a temperature protocol with an extended last temperature step (EC4).

The amount of EC was below the LOD of $0.2 \mu\text{gC}/\text{cm}^2$ for all blanks measured. The automatic split point was set at the start of the calibration phase for all sample groups, i.e. no EC was detected since the carbon evolving in the oxidising phase was attributed to OC. No signals of the laser transmittance are given in Figure 60, but the respective data is shown in Figure 61. The averages and standard deviations of the amount of TC (equal to OC) are shown in Table 13. One sample from the group H2O was removed, since the amount of TC and OC, respectively, was roughly three times higher than the amount of the other samples in this group and it was regarded to be an outlier.

Table 13: Average and standard deviation of TC of blank samples with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$

Group	Average \pm Stddev TC ($\mu\text{gC}/\text{cm}^2\text{gSample}$)
H2O	0.10 ± 0.02
H2ON_mn	0.19 ± 0.03
H2ON_on	0.19 ± 0.02

The average of the blank values regarding the TC and OC concentrations when adding $\text{NH}_4\text{H}_2\text{PO}_4$ was almost twice as high as the average blank value of Milli-Q water without coagulant. The standard deviations of all three groups are comparable. For completeness

and comparability it is useful to list the blank values based on the filter area as well. Quartz fibre filters, which were cleaned in a muffle furnace as described in chapter 3.1., showed TC values around $2 \mu\text{gC}/\text{cm}^2$ in previous experiments. Group H2O showed TC values of $2.5 \mu\text{gC}/\text{cm}^2$ in average, group H2ON_mn and H2ON_on $4.8 \mu\text{gC}/\text{cm}^2$.

The transmittance signal logged during the measurement was evaluated. The transmittance signal was normalised in a way that the initial transmittance, which is the highest signal in the first 250 s of measurement when using EUSAAR2, shows a value of 1. A correction using the weight of the sample was not conducted and the transmittance data of each measurement, i.e. of each half of a filter, was evaluated separately. The average and the standard deviation of the signal was computed for each group as done above for the FID signal and the resulting plot is shown in Figure 61.

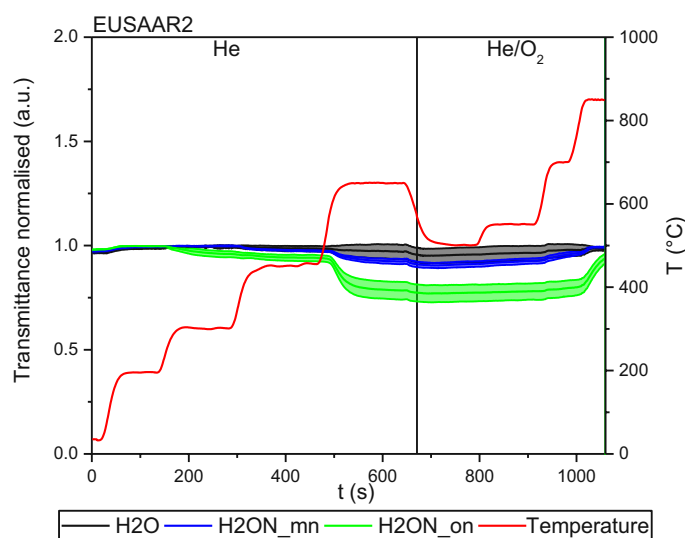


Figure 61: Average transmittance signal and standard deviation for each group of blanks prepared from Milli-Q water with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$

The transmittance signal of group H2O and group H2ON_mn are roughly constant during the measurement and show a similar course of transmittance. The transmittance signal of group H2ON_on decreases slightly at the start and during OC2 and decreases markedly at the start of OC4. An increase in transmittance can be observed at the end of the measurement, during EC4. This already shows an influence of the coagulant on TOA, which will be discussed further below.

Samples

The FID signal of the thermograms of both halves were added and corrected by the weight of sample used to load the filter to give results per g of liquid sample. Again, the procedure of subtracting the baseline, i.e. the average of the signal in the first 50 s of measurement, was applied. Additionally, a correction by the blank measurements was conducted and the average FID signal and its standard deviation were computed for each group. The resulting thermograms are shown in Figure 62. It is obvious that the addition of coagulant led to a

quantitative removal of CC as can be seen in OC4. Additional changes in OC2 and OC3 are discussed further below. Since not only the broad CC peak was altered in OC4 but also the defined signal at the beginning of this temperature step, which was not altered when treating the sample with HCl, the determination of CC is not as straightforward as when using HCl. Due to the change in optical properties depending on the prevailing temperature of hematite that is found in MD, no automatic split point could be determined for this set of samples. The thermograms of the individual samples of each group are provided in Figure 79 in the supplement.

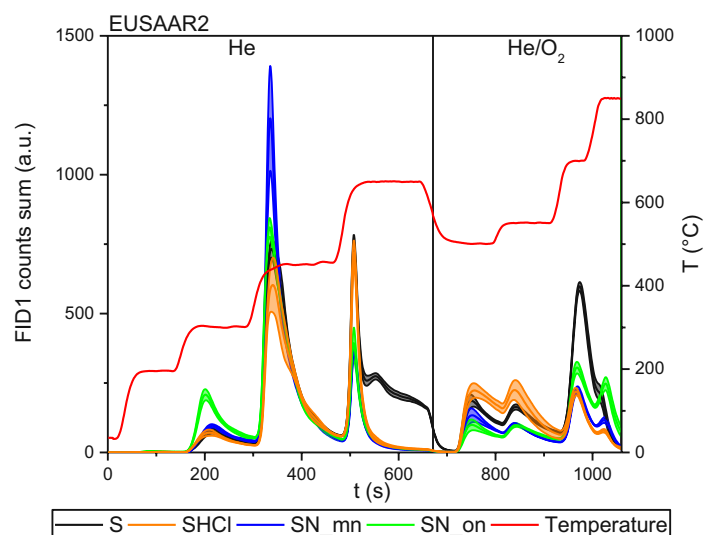


Figure 62: Average FID signal and standard deviation for each group of sample containing MD prepared with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

As observed in earlier experiments, the signal of the sample treated with HCl decreased in OC3 in average whereas the signal in EC1 and EC2 increased. These temperature steps show higher standard deviations than the rest of the thermogram, leading to the assumption that the combustion behaviour of carbon fractions evolving in OC3 in the untreated sample is changed and these fractions partly combust in EC1 and EC2 when treating the sample with HCl.

The addition of coagulant led to differences in the oxidising atmosphere: In EC1 and EC2 both sample groups treated with the coagulant show decreased signal compared to the untreated sample; in EC3 the untreated sample shows the highest signal of all groups, the sample treated with coagulant without rinsing shows the 2nd highest signal and the sample that was rinsed and the sample treated with HCl show comparable lower signals. The high signal in EC3 of the untreated sample cannot be explained. It is possible that more pyrolysis occurred in this sample, but since no split point could be set this cannot be confirmed. In EC4 the untreated sample has only little signal visible as a shoulder in the peak of EC3, the sample treated with coagulant which was not rinsed shows the highest signal in EC4, the sample rinsed shows a reduced signal and the sample treated with HCl shows an even lower signal.

The transmittance signal was evaluated as described for the blank values and the plot for the samples is shown in Figure 63.

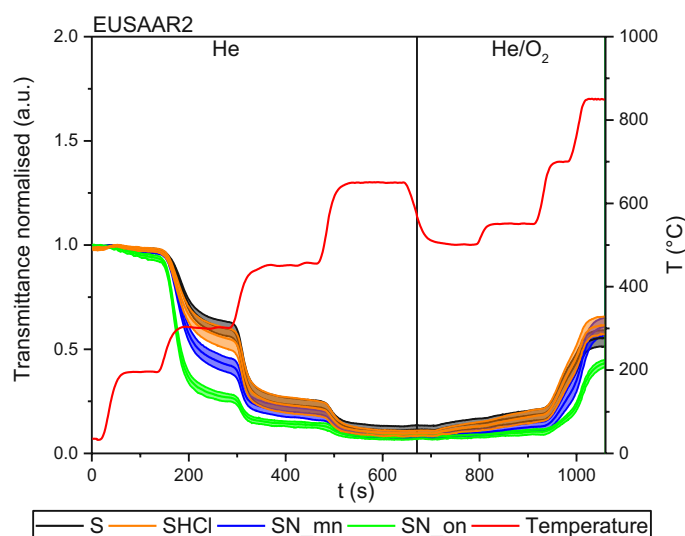


Figure 63: Average transmittance signal and standard deviation for each group of sample containing MD prepared with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

For all measurements the transmittance does not reach the initial transmittance during the analysis, which can be contributed to the Fe compounds in the sample. The transmittance signal of groups S and SHCl can be considered equal, if the standard deviations of the groups are included. The transmittance signal of groups SN_mn and SN_on shows a marked decrease at the start of OC2. The signal of group SN_on is below the signal of the other groups except for OC4, where the signals of all groups can be considered equal if the standard deviations are included. At the end of the measurement, group SN_on shows a lower signal than the other groups.

The results for TC after correction by the weight of the sample and correction by the blank values are shown in Table 14.

Table 14: Average and standard deviation of a sample containing MD with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

Group	Average \pm Stddev TC ($\mu\text{gC}/\text{cm}^2\text{gSample}$)
S	4.56 ± 0.08
SHCl	3.23 ± 0.08
SN_mn	2.95 ± 0.17
SN_on	3.22 ± 0.07

The amount of TC was not increased but clearly decreased by the addition of coagulant. Therefore, it can be assumed that the amount of CC in the sample, which was removed, is much higher than the amount of EC, which was additionally coagulated. In comparison to the samples which were treated with HCl, where CC was removed but no additional coagulation of EC was expected, the amount of TC was not increased if the standard deviations of the

groups are considered. However, it is possible that this randomly chosen snow sample, which was visually contaminated with MD, contained only low amounts of EC. Thus, the increase in EC caused by the addition of coagulant cannot be observed in TC with this sample. The evaluation of CC from S and SHCl from TOA measurements resulted in an average of $0.79 \mu\text{gC}/\text{cm}^2\text{gSample}$ and an error of $0.04 \mu\text{gC}/\text{cm}^2\text{gSample}$. The error was computed by error propagation after Gauss, using the standard deviations of the carbon concentration of groups S and SHCl in OC4. The decrease in TC due to rinsing with HCl was $1.33 \mu\text{gC}/\text{cm}^2\text{gSample}$, while only $0.79 \mu\text{gC}/\text{cm}^2\text{gSample}$ can be clearly attributed to CC. In this sample, group S shows a much higher signal in EC3 than all other groups and a higher signal in EC4 than all other groups except group SN_on. The sum of all temperature steps except EC3 and EC4 (OC1-OC4, EC1-EC2) led to a difference in carbon concentration between S and SHCl of $0.80 \mu\text{gC}/\text{cm}^2\text{gSample}$, matching the amount of CC determined in the sample. The additional difference between S and SHCl seems to be due to the high amount of carbon evolving at the end of the oxidising atmosphere in group S, which cannot be further specified. A marked difference in EC3 or EC4 between samples directly analysed and samples rinsed with HCl was not observed previously in this work. Assuming that this anomaly occurs only in this randomly chosen sample, the decrease in carbon caused by HCl is attributed to CC. The reduction of TC observed in sample group SN_on can be considered equal to the reduction in group SHCl when including the standard deviations.

A comparison of SN_on and SN_mn regarding their results for TC shows lower TC concentrations for SN_mn, even if the standard deviations are considered. Rinsing the filter with water after filtration of a liquid sample treated with coagulant might destroy agglomerates of EC formed due to the addition of coagulant.

Figure 62 shows that the FID signal of samples treated with coagulant, which were not rinsed, is increased in OC2 compared to the untreated sample. This can hardly be observed if the sample is rinsed with Milli-Q water. The signal of the sample that was not rinsed is similar to the signal of the untreated sample in OC3, whereas the sample that was rinsed shows increased signal in OC3. Both samples that were treated with coagulant show a similar signal in OC4, independent of the rinsing procedure. However, there is a marked difference to the sample treated with HCl. CC was quantitatively removed when adding coagulant, but not only the broad signal, which is attributed to CC, changed. The sharp signal at the start of OC4 was reduced by the addition of coagulant. For the quantitative determination of CC when using $\text{NH}_4\text{H}_2\text{PO}_4$ the lower signal in OC4, obviously caused not solely by the loss of CC, has to be discussed. Therefore, carbon contents found in each temperature step were compared to identify possible shifts of the evolving carbon signals. As the defined signal at the beginning of OC4 changes additionally to the removal of CC, S cannot be used for the comparison. SHCl did not show a change of the defined signal at the beginning of OC4 compared to S, but CC was removed in these samples. Therefore, the difference between SN_on or SN_mn, respectively, and SHCl was used to compute the difference in the defined signal at the beginning of OC4 for the samples treated with coagulant. This way, the loss of CC does not influence the comparison. The results are shown in Table 15, the error was computed from the standard deviations of the samples within each group in the temperature step using error propagation after Gauss. These errors include all deviations from sample preparation and TOA. Note that OC in different samples in one group might pyrolyse slightly different. The difference of the signals in the temperature steps is expected to be higher than the possible difference in pyrolysis and differences in pyrolysis are contained in the standard deviation of a temperature step within each group.

It is possible that $\text{NH}_4\text{H}_2\text{PO}_4$ acts as a donor of oxygen when heating up. The concentration of coagulant on the filter is possibly higher if the filter is not rinsed after filtration. The high supply of oxygen might lead to early combustion of OC4 carbon in OC2. If the sample is rinsed, the oxygen supply is reduced. Therefore, only little more carbon desorbs in OC2, whereas more carbon desorbs in OC3, as sufficient oxygen is available to desorb carbon at higher temperatures.

Table 15: Changes of carbon evolving in temperature step OC2, OC3 and OC4 when using $\text{NH}_4\text{H}_2\text{PO}_4$ compared to the analysis of a sample without coagulant

Group	Avg \pm error OC2; SN-S ($\mu\text{gC}/\text{cm}^2\text{gSample}$)	Avg \pm error OC3; SN-S ($\mu\text{gC}/\text{cm}^2\text{gSample}$)	Avg \pm error OC4; SN-SHCl ($\mu\text{gC}/\text{cm}^2\text{gSample}$)
SN_mn	0.041 ± 0.018	0.12 ± 0.12	-0.23 ± 0.04
SN_on	0.21 ± 0.03	-0.037 ± 0.054	-0.21 ± 0.04

The decrease in OC4 when using coagulant is comparable independent of the rinsing procedure, see Table 15. When rinsing the sample, the carbon signal evolving in OC2 is only slightly higher than in the untreated sample, but a marked effect is visible in OC3. The overall amount (OC2 and OC3) is on average lower than the amount of carbon lost in OC4, but considering the rather large errors in OC3 the comparison with OC4 leads to a reasonable agreement. As the error in OC3 is quite high, a straightforward and reproducible determination of CC is not possible if the sample is rinsed. If the sample is not rinsed after filtration then only slight changes in OC3 with rather high errors can be observed when comparing the carbon content of all samples in the groups SN_on and S in this temperature step. The amount of carbon lost in OC4 matches the amount of carbon additionally evolving in OC2. Contrary to group SN_mn only one temperature step has to be considered for the correction of carbon lost in OC4. This suggests that samples treated with coagulant should not be rinsed if CC shall be determined.

The slight reduction of carbon in OC3, if the sample is not rinsed, and the high error in OC3, if the sample is rinsed, might be caused by MgCO_3 in the sample. As shown in chapter 4.5.1., MgCO_3 desorbs in OC3 and OC4. The determination of CC via the addition of coagulant, and the related estimation of MD, may not represent a contribution of MgCO_3 correctly.

To sum up, although CC was quantitatively removed as shown in the thermograms, a change in the defined signal at the beginning of OC4 was visible after treatment with $\text{NH}_4\text{H}_2\text{PO}_4$. Due to the less pronounced changes in OC2 and the high error in OC3, both occurring when rinsing the sample, the determination of CC is not possible. If no rinsing step is performed, the changes in the thermogram in OC2 and the additional change in OC4 are considered equal for this sample. Hence, if coagulant shall be used to increase the amount of EC on the sample filter and CC shall be determined, one aliquot of the sample is directly filtrated and one aliquot is treated with coagulant. If the sample treated with coagulant is not rinsed, CC can be determined when considering changes in OC4 and OC2. The difference in carbon in OC4 of the directly filtrated sample and the sample treated with coagulant has to

be computed and the difference in carbon in OC2 has to be subtracted from the difference in OC4. Still, more experiments should be conducted before setting this procedure as a general method for the determination of CC. It has to be taken into account that the error of the CC determination may increase if two temperature steps, OC2 and OC4, have to be considered, especially if only one sample of the direct filtration and the treatment with coagulant are available.

5.2.2. Treatment of a snow sample not visibly contaminated by mineral dust

As the results of the sample containing MD were promising but an increase in EC could not be observed due to the optical properties of hematite contained in MD, the experiment was repeated using a sample not visibly contaminated by MD. It was expected that there would be almost no changes in the highest temperature step in the inert atmosphere due to the absence of CC and that the amount of EC accumulated on the filter was higher since 100 g of snow were filtrated instead of 25 g. Additionally, it should be possible to set an OC/EC split point for these samples, as no compounds that change their optical properties depending on the temperature were expected. The thermal protocol EUSAAR2_EC4 was used, where the last temperature step in the oxidising atmosphere was elongated from 80 s to 160 s to ensure complete combustion of EC when using $\text{NH}_4\text{H}_2\text{PO}_4$. The FID signal for samples directly analysed and samples treated with HCl returned to the baseline after analysis when using the standard EUSAAR2 thermal protocol. This was not the case for samples of the first set of samples treated with coagulant, making it necessary to elongate the last temperature step. This effect was especially pronounced for both blanks and samples treated with coagulant, when the rinsing step after filtration was skipped.

Blanks

The blank filters were prepared as described for the previous set of samples, but a larger amount of Milli-Q water (about 100 g) was used. Scaling the results of blank measurements with the amount of liquid drawn through the filter is not valid, as most of the contaminants are due to the handling and not the amount of water itself. The correction of samples from this set of samples with blanks of the previous set of samples scaled to larger volumes (all results in $\mu\text{gC}/\text{cm}^2\text{gSample}$) led to negative values in roughly half of the temperature steps in all groups. Hence, suitable blank filters should be prepared for each set of samples. Furthermore, an additional blank representing the treatment with HCl was prepared. As higher amounts of liquid were needed for these blanks, a 1-l-flask was used to prepare the Milli-Q water with coagulant addition. The flask was too big to stand in the ultrasonic bath by itself, therefore it was rotated by hand in the ultrasonic bath for about 6 min.

For each group 5 blank filters were prepared. The loaded area (diameter: 16 mm) of all filters was punched out with a diameter of 17 mm. The samples were subsequently cut in halves. Only 4 of 5 filters per group were thermal-optically analysed, one filter was left to be analysed directly via IC to quantify the amount of NH_4^+ , Cl^- and PO_4^{3-} on the filters. The other filters were analysed using the EUSAAR2_EC4 thermal protocol. The average and standard deviations of the respective thermograms are shown in Figure 64. The thermograms of the individual blanks of each group are shown in Figure 80 in the supplement.

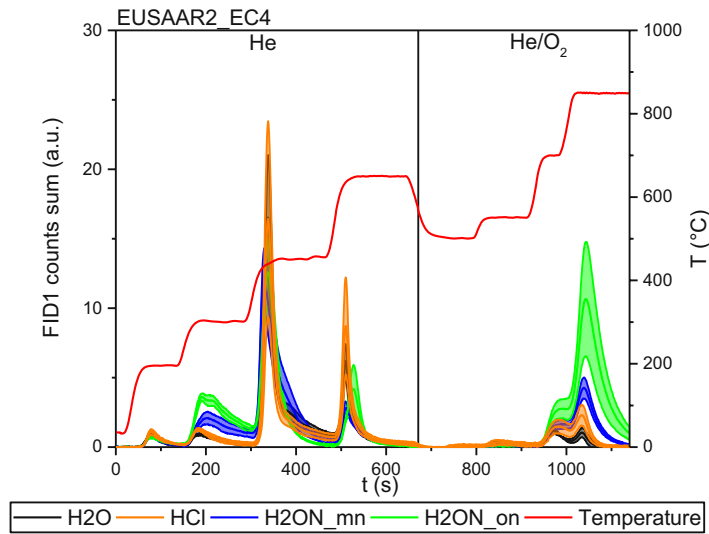


Figure 64: Average FID signal and standard deviation for each group of new blanks prepared from Milli-Q water with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

The thermograms of the groups H₂O, H₂ON_mn and H₂ON_on are similar to the thermograms of the respective groups in chapter 5.1.1.: increased signal in OC2 if coagulant is added, decreased signal in OC4 and increased signal in EC3 and EC4. The signal of H₂ON_on in OC3 is more narrow and higher than the signal of H₂ON_mn, which is smaller and broader. The sample from group HCl shows comparable signals in OC2 and OC3, while the signal is increased in OC4, EC2 and EC3, compared to an untreated blank.

The transmittance signal was evaluated as described above and the resulting plot is shown in Figure 65.

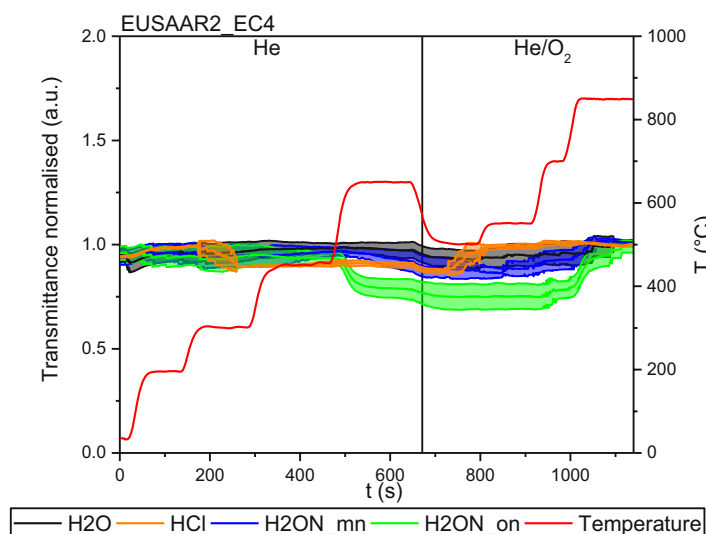


Figure 65: Average transmittance signal and standard deviation for each group of new blanks prepared from Milli-Q water with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

The course of transmittance of groups H2O, H2ON_mn and H2ON_on are similar to the course of transmittance of the respective groups of blanks discussed above. Again, the transmittance decreases at the start of OC4 for group H2ON_on and the transmittance of group H2O and group H2ON_mn are comparable if the standard deviations are considered. The new group of blanks, HCl, shows a decrease in OC2 and an increase in EC1, which cannot be observed for the other groups. The standard deviation at these changes in transmittance are much higher than in the rest of the thermogram, leading to the assumption that the decrease and increase in transmittance does not happen as reproducible as the changes in transmittance in the rest of the thermogram.

EC was below the LOD of the instrument of $0.2 \mu\text{gC}/\text{cm}^2$, as no split point could be set before the calibration phase (for 5 out of 8 halves for group H2O; 8 out of 8 halves for HCl, although with negligible differences; 3 out of 8 halves for H2ON_mn; 5 out of 8 halves for H2ON_on) or, as in 5 of 11 cases of all groups, an automatic OC/EC split could be determined but the resulting amount of EC was lower than the LOD. For the remaining 6 halves of all groups, an OC/EC split was determined and the resulting EC was higher than the LOD. For halves with EC concentrations below the LOD, the EC concentration was replaced with half of the LOD, $0.1 \mu\text{gC}/\text{cm}^2$. After adding the amount of TC found on each half of one filter and correcting for the amount of liquid used, the TC concentrations within each group were averaged and the standard deviation of each group was computed, see Table 16. The results were normalised by their weight to enable comparisons with the previous experiment. The concentration of TC on the blank filters is lower than in the previous experiment, when normalising the results by the weight of liquid used.

Table 16: Average and standard deviation of TC, OC and EC for new blanks with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

Group	TC average \pm Stddev ($\mu\text{gC}/\text{cm}^2\text{gSample}$)
H2O	0.029 ± 0.003
HCl	0.031 ± 0.007
H2ON_mn	0.035 ± 0.006
H2ON_on	0.052 ± 0.009

The group H2O shows the lowest average TC concentration as well as the smallest standard deviation. The highest average TC concentration was found within the group of blanks treated with coagulant without rinsing.

The blank filters, which were thermal-optically analysed, as well as the filters preserved for direct analysis via IC were eluted with 5 ml Milli-Q water. Water was used as eluent since PO_4^{3-} should be quantified to estimate the amount of coagulant on the filter before and after analysis with the Lab OC-EC Aerosol Analyzer. These analyses were conducted to estimate the amount of coagulant and HCl present on the filters before and after TOA. The differences observed in the thermograms of the different groups can only be explained if elevated concentrations of the respective ions can be found on the filters. Furthermore, the amount of $\text{NH}_4\text{H}_2\text{PO}_4$ removed by rinsing with water can be assessed.

The average of the amount of PO_4^{3-} measured via IC in the eluate of the filters previously measured with the Lab OC-EC Aerosol Analyzer (TOA) as well as the standard deviation are shown in Table 17 for each group. Four filters per group were eluted and analysed. Additionally, the amount measured in the eluate of the filters directly eluted is shown. Only one filter per group, which was directly eluted, was available. Hence, no standard deviation can be given for the directly eluted samples. The concentration of PO_4^{3-} of the directly measured H2ON_on filter was outside of the calibrated area and due to the COVID measures in 2020 it was not possible to repeat the measurement after a respective dilution of the samples. The value stated below can therefore only be seen as an estimate of the PO_4^{3-} content.

Table 17: Concentration of PO_4^{3-} in the eluates of blank filters with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

Group	PO_4^{3-} Average \pm Stddev TOA samples (mg/l)	PO_4^{3-} Directly eluted (mg/l)
H2O	1.82 \pm 0.41	0.84
HCl	1.22 \pm 0.04	0.74
H2ON_mn	2.37 \pm 0.10	4.76
H2ON_on	5.02 \pm 0.42	37.8

The amount of PO_4^{3-} left on the filters after TOA was highest for the group H2ON_on. The directly measured filters of the two groups where coagulant was added, H2ON_on and H2ON_mn, showed much higher concentrations of phosphate than the filters that were thermal-optically analysed and than the filters where no coagulant was added. Although no PO_4^{3-} can be found in Milli-Q water itself, the samples of group H2O, which were prepared using Milli-Q water only, shows noticeable amounts of PO_4^{3-} . This might be due to contamination of the filters. Although the results can be considered reliable to read out trends in the PO_4^{3-} concentrations on the filters, the surprisingly high concentrations of PO_4^{3-} on the filters of groups H2O and HCl relativise the results.

The concentration of Cl^- in the eluates of the thermal-optically analysed filters as well as the directly eluted filters is shown in Table 18. The concentration of Cl^- was below the LOD of 0.005 mg/l for many filters after TOA (H2O: 3 of 4; H2ON_on: 2 of 4; H2ON_mn: 3 of 4). For all groups except group HCl no standard deviation can be computed. Hence, only the average of samples above the LOD is shown. Note that the actual average is lower as the samples below the LOD were not considered for the averaging. The concentration of Cl^- in the directly eluted sample of group H2ON_on was below the LOD. The only group where all Cl^- concentrations were above the LOD is group HCl. The comparison of the average and standard deviation of the thermal-optically analysed filters with the directly eluted filter shows that most of the Cl^- on the filter is not present after TOA. Cl^- , PO_4^{3-} and NH_4^+ , which is described below, are removed during TOA due to their volatility or decomposition by heat. Although the filter that was treated with HCl was rinsed with Milli-Q water and was left in a fume hood to ventilate for 1 h, the concentration of Cl^- on the filter is about one order of magnitude higher prior to TOA. As no negative effects on the TOA system could be observed during this work, treating the filter with liquid HCl is a mild alternative to treating the sample with HCl vapour.

Table 18: Concentration of Cl⁻ in the eluates of blank filters with and without addition of NH₄H₂PO₄ or treatment with liquid HCl

Group	Cl ⁻ Average ± Stddev TOA samples (mg/l)	Cl ⁻ Directly eluted (mg/l)
H2O	0.007	0.020
HCl	0.012 ± 0.003	0.134
H2ON_mn	0.010	0.092
H2ON_on	0.043	<0.005

Due to problems with the IC system the eluate of the filters had to be stored at 6°C for several weeks before the analysis of NH₄⁺ was performed. The averages and standard deviations of the NH₄⁺ concentrations of the filters eluted after TOA as well as the NH₄⁺ concentration of the directly eluted filters are shown in Table 19. The groups treated with coagulant show higher concentrations at the directly eluted filter. Computing the molar concentrations of PO₄³⁻ and NH₄⁺ in the directly eluted sample of H2ON_on, the molar concentration of PO₄³⁻ is a bit higher (PO₄³⁻: 0.40 mmol/l; NH₄⁺: 0.38 mmol/l). The discrepancy might be caused by the high value for PO₄³⁻ outside the calibrated concentration range and the respective increased uncertainty. The ratio of the molar concentration of PO₄³⁻ and NH₄⁺ for the groups H2O, HCl, H2ON_mn and H2ON_on in the directly eluted samples is 5.3, 1.0, 1.2 and 1.1, respectively. Group H2O shows a ratio deviating from 1, leading to the assumption that the contamination does not derive from the coagulant but was introduced otherwise. For the samples eluted after TOA the ratios are 3.5, 2.6, 3.0 and 5.0, respectively. After TOA the amount of PO₄³⁻ is higher than the amount of NH₄⁺ for all samples.

Table 19: Concentration of NH₄⁺ in the eluates of blank filters with and without addition of NH₄H₂PO₄ or treatment with liquid HCl

Group	NH ₄ ⁺ Average ± Stddev TOA samples (mg/l)	NH ₄ ⁺ Directly eluted (mg/l)
H2O	0.10 ± 0.03	0.03
HCl	0.09 ± 0.01	0.14
H2ON_mn	0.15 ± 0.0019	0.75
H2ON_on	0.19 ± 0.05	6.77

Samples

Although the differentiation between OC and EC should not be a problem when measuring snow samples without visible MD contamination, it was not possible to set an OC/EC split point for all samples. However, it was possible to determine an automatic OC/EC split point for all untreated samples. A correctly set OC/EC split is the prerequisite for the determination of increased EC amounts and therefore decides if the coagulant is applicable. For the used thermal protocol, EUSAAR2_EC4, the latest acceptable split point is at 1140 s, before the calibration phase starts. All samples with split points later than 1140 s cannot be used for the determination of EC. This applies to all samples treated with coagulant that were not rinsed (SN_on), while for HCl and SN_mn only one half of one filter could not be evaluated. The reason why no automatic split point could be determined for one half of group HCl and one half of SN_mn might be that the sample was placed incorrectly inside the sample oven. For the determination of EC by an automatic split point, rinsing of the sample filter is essential if coagulant was used. Further evaluations regarding the split point are described below. First, the course of the FID signals in the thermograms will be discussed as was done for the previous samples and blanks.

Plotting the average FID signal and the respective standard deviation of the groups as done before, see Figure 66, it is obvious that the untreated sample and the sample treated with HCl combust comparably. The samples treated with coagulant show higher signals in OC2 and EC4, the effect being especially pronounced if the sample is not rinsed after filtration, and lower signals in OC3. The sample that was not rinsed after filtration shows lower signal in OC4. Due to the elongation of the last temperature step the EC4 peak is recorded completely. The thermograms of the individual samples of each group are displayed in Figure 81 in the supplement.

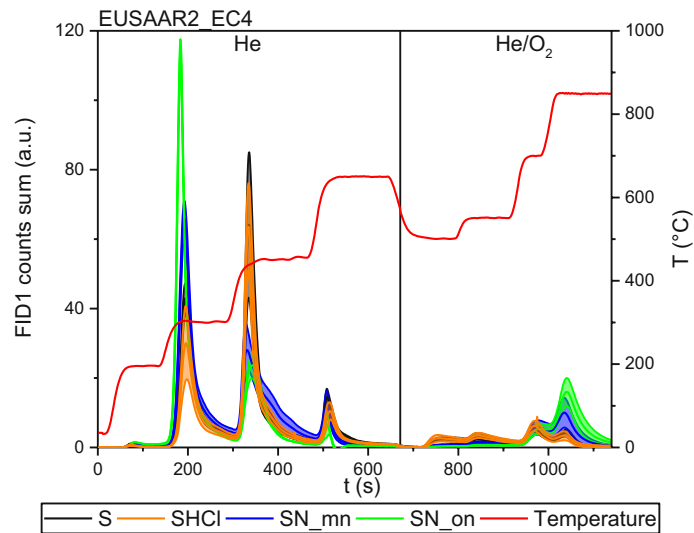


Figure 66: Average FID signal and standard deviation for each group of sample not visibly containing MD prepared with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

The evaluation of the transmittance was done as described above and the plot is shown in Figure 67.

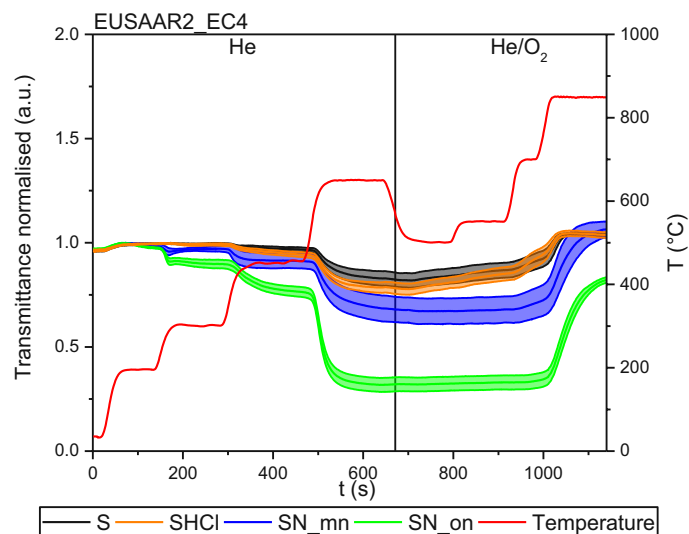


Figure 67: Average transmittance signal and standard deviation for each group of sample not visibly containing MD prepared with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl

The initial transmittance was reached in average for groups S, SHCl and SN_{mn} during the measurement. It was not reached in average for group SN_{on}, even when the standard deviation is considered, which agrees with the determination of the automatic OC/EC split point, which was not possible for any sample of group SN_{on}. The transmittance signal of group SN_{on} is below the transmittance signal of the other groups, starting at the beginning of OC2, where a decrease in transmittance occurs for this group. A marked drop in transmittance occurred at the start of OC4. While the transmittance of groups S and SHCl slowly increase in the inert atmosphere, the transmittance of groups SN_{mn} and SN_{on} is roughly constant until the start of EC4, where a marked increase in transmittance occurs.

The decrease in transmittance in OC2 for group SN_{on} might be explained by the high signal occurring in OC2. If the pyrolysis for group S and group SN_{on} is similar but the signal is much higher for group SN_{on}, then the decrease in transmittance must be bigger for SN_{on}. The decrease in transmittance of group SN_{on} in OC3 and OC4 cannot be explained equally, as the FID signal for group SN_{on} is smaller in these temperature steps than the FID signal of group S. Another peculiarity only observed when the sample was treated with coagulant is the roughly constant transmittance signal between the end of OC4 and the start of EC4. Usually, the transmittance increases in this time frame, as oxygen is introduced into the sample oven and EC or pyrolytic carbon can combust, both leading to an increase in transmittance. This behaviour was observed for group S and group SHCl. The coagulant may lead to delayed combustion of both EC and pyrolytic carbon. The possible oxygen donor effects of the coagulant seem to apply only to OC. Premature combustion of certain fractions of EC, which might explain the constant signal during OC4 and EC4, should be visible in the transmittance. Premature combustion of EC would lead to a higher transmittance in the inert atmosphere, however, the contrary can be observed.

The course of transmittance is especially changed when adding coagulant and not rinsing the filter with water during sample preparation. The results of the samples and blanks measured are in agreement. To determine if the coagulant itself changes its optical properties during the measurement, leading to the observed changes in transmittance, a NH₄H₂PO₄ standard, 0.5 g in 10 ml, was prepared. 10 µl of the standard were applied to a clean filter and the filter was dried in the Lab OC-EC Aerosol Analyzer prior to analysis using the thermal protocol EUSAAR2. Using 10 µl standard equals 0.004 mmol NH₄H₂PO₄ on the filter. The blank filter of group H2ON_{on}, which was directly eluted, showed 0.002 mmol PO₄³⁻. To ensure that bigger amounts of coagulant do not lead to changes in transmittance, another measurement was conducted, using 100 µl of the same standard. 10 µl of the standard were applied to a clean filter which was subsequently dried in the instrument. These steps were repeated until 100 µl of the standard were present on the filter. The transmittance of both measurements did not show changes as observed for the measurements of blanks with coagulant or samples treated with coagulant, see Figure 68. It can therefore be assumed that the changes in transmittance are not due to a change in optical properties of the coagulant but are caused by the combination of coagulant and carbonaceous compounds. Although the amount of carbon in the samples is about 4 times higher than in the blanks, similar effects on the transmittance can be observed. However, the normalised transmittance is decreased by approximately 25 % for H2ON_{on} and by approximately 75 % for SN_{on}, which confirms the assumption that the decrease in transmittance is connected with the amount of carbon on the filter.

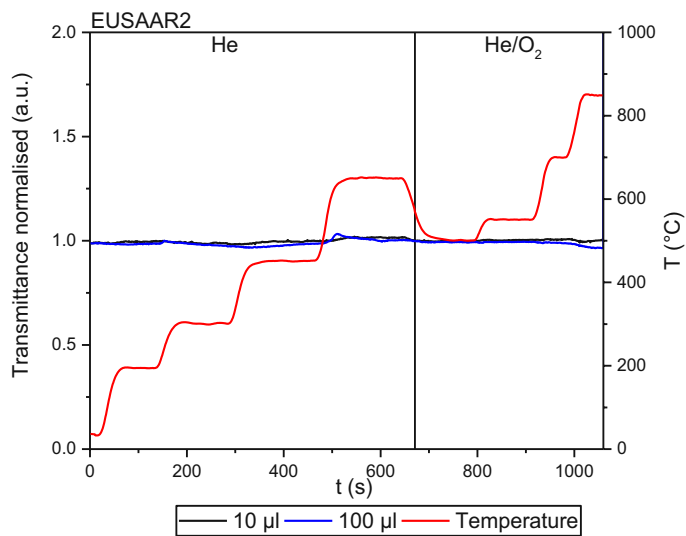


Figure 68: Transmittance of measurements of a $\text{NH}_4\text{H}_2\text{PO}_4$ standard

The samples were evaluated using the automatic split point obtained by the respective software of the Lab OC-EC Aerosol Analyzer. The averages and standard deviations of TC, OC and EC in $\mu\text{gC}/\text{cm}^2\text{gSample}$ after correction by the weight of the sample and by the blank values for each group are shown in Table 20. The EC values for group SN_on are negative since no automatic OC/EC split point could be set for this group and the blanks for group SN_on contained EC. Hence, no standard deviation for this group is available.

Table 20: Average and standard deviation of TC, OC and EC for samples without MD with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl; corrected by new blanks

Group	Average \pm Stddev TC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev OC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev EC ($\mu\text{g}/\text{cm}^2\text{gSample}$)
S	0.17 ± 0.03	0.17 ± 0.03	0.0017 ± 0.0006
SHCl	0.15 ± 0.02	0.15 ± 0.02	0.0023 ± 0.0011
SN_mn	0.18 ± 0.03	0.18 ± 0.03	0.00089 ± 0.00097
SN_on	0.19 ± 0.02	0.19 ± 0.02	-0.0017

Generally, the split points were not set exactly at the same time for two halves of the same filter, as pyrolysis might vary for different analyses. This does not necessarily mean that the results for EC are not in agreement. This can be checked by computing the EC/TC ratio. The ratio should be constant for aliquots of a highly homogeneous sample, but small variations can be expected for filters loaded with snow samples. A comparison of the split time might still give information about the reliability of the split since a high difference cannot be explained by little inhomogeneity in loading or slightly different pyrolysis. The two samples of SHCl and SN_mn where no split point could be set for one half are excluded from this assessment. The difference in split time of the two halves of one filter was between 1 and 12 s for the untreated sample (median: 3 s). For the sample treated with HCl the difference was between 0 and 16 s (median: 11 s). For the sample treated with coagulant and subsequent rinsing the difference was between 4 and 54 s (median: 32 s). This data shows that the median of the difference in split time of the two halves was smallest if the sample was untreated, about 3.5-times bigger if the sample was treated with HCl and about 10.5-

times bigger if the sample was treated with coagulant and rinsed with water. The sample treated with coagulant which was not rinsed with water could not be compared as no split point could be set for any of the samples within this group, although the sample did not contain iron compounds. The average EC/TC ratios as well as the respective standard deviations were computed for each group. The results are 0.010 ± 0.003 for group S, 0.018 ± 0.003 for SHCl and 0.007 ± 0.005 for group SN_mn.

The increasing variability of the time when the automatic split point is set is reflected by the increasing standard deviation of EC, which is 35 % for the untreated sample, 47 % for the sample treated with HCl and 110 % for the sample treated with coagulant and rinsing with water. An increase in EC could not be observed when using the automatic split point, since no split point could be set for samples of group SN_on and the amount of EC was not increased for group SN_mn compared to group S, the untreated samples. Hence, a more detailed evaluation of the data is necessary.

The amount of TC found in the groups was compared using ANOVA, as this evaluation is also possible for group SN_on, where no automatic split point could be determined. Firstly, all groups were tested for normality using the Shapiro-Wilk-test (test statistic $p(W)$ for S: 0.5924; SHCl: 0.0680; SN_mn: 0.1128; SN_on: 0.1234; critical value: 0.05). There is no reason to assume that any of the groups do not belong to a normal distribution at a level of significance of 5 %. Secondly, the equality of variances was tested using the Levene test at a level of significance of 20 %. The F-value is 1.028, the critical value is 1.75. Therefore, the null hypothesis, equality of variances, cannot be rejected. Finally, the ANOVA was conducted at a level of significance of 5 %. The F-Value is 1.668, the critical F value is 3.29. Therefore, the null hypothesis, all sample means are equal, cannot be rejected. A statistically significant increase in TC cannot be observed at a level of significance of 5 %. Hence, the straightforward evaluation of an increase in EC by using the amount of TC for samples not containing MD cannot be conducted. The amount of EC in the samples is small compared to the amount of TC on the filters, EC accounting for 0.5 to 1.5 % of TC, and therefore much smaller than the standard deviation of TC, which is between 13 and 18 % of TC. Observing an increase in EC by using the difference in TC is therefore not possible.

Since it was not possible to set an automatic split point for samples within the group SN_on, the data was evaluated again using the average split point of S (i.e. the average time the split point was set) for all groups. The blanks were evaluated again using this split point to enable a suitable correction by the blank values, see Table 21. Using this split point, the EC concentrations of all blanks of group H₂O and HCl were below the LOD of $0.2 \mu\text{gC}/\text{cm}^2$ and were replaced by half of the LOD. The averages and standard deviations of TC, OC and EC of the samples using the average split point of group S are shown in Table 22. This approach might show an increase in EC when treating the sample with coagulant but assumes similar pyrolysis for all groups.

Table 21: Average and standard deviation of TC, OC and EC for new blanks with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl; using the average split point of group S

Group	Average \pm Stddev TC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev OC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev EC ($\mu\text{g}/\text{cm}^2\text{gSample}$)
H ₂ O	0.029 \pm 0.003	0.029 \pm 0.003	<0.001
HCl	0.031 \pm 0.007	0.030 \pm 0.007	<0.001
SN_mn	0.035 \pm 0.006	0.032 \pm 0.006	0.0034 \pm 0.0005
SN_on	0.052 \pm 0.009	0.039 \pm 0.004	0.013 \pm 0.005

Table 22: Average and standard deviation of TC, OC and EC for samples without MD with and without addition of $\text{NH}_4\text{H}_2\text{PO}_4$ or treatment with liquid HCl; corrected by new blanks; using the average split point of group S

Group	Average \pm Stddev TC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev OC ($\mu\text{g}/\text{cm}^2\text{gSample}$)	Average \pm Stddev EC ($\mu\text{g}/\text{cm}^2\text{gSample}$)
S	0.17 \pm 0.03	0.17 \pm 0.03	0.0021 \pm 0.0013
SHCl	0.15 \pm 0.02	0.15 \pm 0.02	0.0022 \pm 0.0012
SN_mn	0.18 \pm 0.03	0.17 \pm 0.02	0.0083 \pm 0.0035
SN_on	0.19 \pm 0.02	0.17 \pm 0.01	0.019 \pm 0.009

The average of EC as well as the respective standard deviation of group S changed slightly, since the average of the automatic split point of that group was applied also to the samples of this group. The change in OC is too small for this group to be noticeable at the given number of significant digits. The amount of EC in samples treated with HCl decreased slightly in average when applying the split point of the directly filtrated samples (S) instead of the automatic split point of the measurements. The OC concentrations of the groups S, SN_mn and SN_on can be considered equal, leading to the assumption that pyrolysis was not considerably different for the sample analysed here. However, marked changes in the concentration of EC can be observed when adding coagulant during sample preparation and using the split point of an untreated sample, the effect being especially pronounced when the filter is not rinsed. Although the results presented using this evaluation seem reasonable, the comparison of the transmittance of the different groups during TOA showed that the transmittance signals may differ strongly for the untreated sample and the sample treated with coagulant. Hence, it is questionable if using the split point of samples without coagulant treatment for samples treated with coagulant is justified.

The increase in EC when treating the sample with coagulant without rinsing and using the split point of the untreated sample is obvious, even when considering the respective standard deviations. To see if rinsing has a statistically significant effect on the amount of EC on the filter when the sample was treated with coagulant, i.e. significant reduction of EC can be observed if the filter is rinsed after filtration, statistical evaluation was performed as the situation regarding the average amount of EC with errors considered is not as clear. Hence, the amount of EC from group SN_mn and SN_on was compared. First, the samples were tested for normality using the Shapiro-Wilk-test (test statistic $p(W)$ for group SN_mn: 2.011; SN_on: 0.0114; critical value: 0.05). The null hypothesis, normal distribution of the samples, has to be rejected for SN_on at a level of significance of 5 %. However, there is no reason to assume that any of the samples is not normally distributed at a level of significance of 1 % (critical value: 0.01). Second, the samples were tested for homogeneity of the variances using the two-tailed F-test (F-statistic: 7.2418; critical value: 24.2591). There is no reason to assume that the variances differ at a level of significance of 1 %. As the prerequisites for the

t-test are met a two-tailed 2-sample t-test was conducted (absolute value of test statistic t: 2.4642; critical value: 3.4995). There is no reason to assume that the averages of the two samples differ significantly at a level of significance of 1 %. Although the average of EC when rinsing is less than half of EC when not rinsing, the standard deviations of both groups are too high to get significantly different results. As the automatic split point of SN_mn could not be used for the processing of the data, because the amount of EC was lower than the amount of EC of the directly filtrated sample, rinsing is not recommended. It was shown in chapter 5.1.2. that for the determination of CC the sample should not be rinsed. Additionally, it cannot be excluded that rinsing destroys EC agglomerates rendering the addition of coagulant useless. The number of samples per group analysed here is definitely quite small. Still, the results can be regarded as a first evaluation of the problem.

As the increase in EC is based on the split point of the directly filtrated sample and the change in transmittance when using coagulant raises questions if this approach is justifiable, it is still possible that treatment of snow samples does not lead to significantly higher EC concentrations. Snow contains aged EC, which might form agglomerates big enough for filtration with quartz fibre filters leading to a higher yield than described by Torres et al. (2014), who used rain samples for their experiments. Therefore, the addition of coagulant might not be necessary for snow samples. Furthermore, the errors introduced by this procedure have to be considered. Often only a limited amount of snow sample is available, which has to be divided to load two filters separately, increasing both the analysis time and the error induced by inhomogeneous partitioning of the sample and loading of the filters. In addition, the error of the measurements of the directly filtrated sample and the sample treated with coagulant are inaccessible and if marked differences in the pyrolysis of the samples occur, the evaluation of EC is erroneous. This also applies to the determination of CC, which presumes that the amount of pyrolytic carbon produced in OC2 and OC4 is similar for the directly filtrated sample and the sample treated with coagulant. Hence, more data has to be collected before this procedure can be used for the determination of CC and EC by default.

5.3. Summary of chapter 5

The filter efficiency of quartz fibre filters was sufficient for Ca, used as a marker for MD. This assessment could also be conducted for DOC with the suitable equipment (TC analyser).

Although $\text{NH}_4\text{H}_2\text{PO}_4$ quantitatively removes CC a straightforward determination of CC is not possible since additional changes in the signal at the highest temperature step in the inert atmosphere occur. A simple subtraction of the carbon content in OC4, as done for samples treated with HCl, is not sufficient. Two temperature steps, OC2 and OC4, have to be considered if the filter is not rinsed with water. When rinsing the filter with water, three temperature steps, OC2, OC3 and OC4, have to be considered. A high error of the carbon fraction in OC3 was observed when rinsing the sample and thus MgCO_3 possibly contained in MD might not be included in the estimation of CC.

Evaluating an increase in EC when using coagulant for sample preparation posed a challenge. The elongation of the last temperature step in the oxidising atmosphere of the thermal protocol EUSAAR2 was necessary to completely record the thermogram if coagulant was added to the sample. If the filter of a sample treated with coagulant is not rinsed with water, it is not possible to set an automatic OC/EC split point even for samples not contaminated with MD. Therefore, the amount of EC in the sample cannot be determined. As the standard deviation of TC is much higher than the EC fraction, the quantification of additionally held back EC by the TC values of a sample not contaminated with MD was not successful. An estimate of EC in these samples was only possible using the average split point of directly filtrated sample, leading to EC values roughly seven times bigger than EC from the untreated sample. However, the transmittance of the sample was altered when using coagulant and the justified applicability of this approach is questionable. Rinsing the filter loaded with sample treated with coagulant enables the determination of an automatic split point. Using the automatic split point for the evaluation, less EC was held back by filtration compared to the direct filtration of the sample.

Utilizing the same blanks for filters loaded with different amounts of sample did not work, especially if a normalisation by the weight of the sample is carried out. Therefore, blanks should be prepared for each experiment with constant sample weights. This is demanding for snow samples from depth profiles, where each layer has a different density and therefore each sample has a different weight. Measuring only for example 100 g of each layer might lead to incorrect results, as layers containing bigger particles, e.g. MD particles, might not be homogeneously distributed in the main sample and the aliquot. If the deviations of density in the layers are small, the preparation of universal blanks for the entire set of samples might be acceptable.

The use of $\text{NH}_4\text{H}_2\text{PO}_4$ as coagulant might lead to higher collection efficiencies for EC, but introduces new challenges into TOA like a high error in the quantification of carbon fractions in snow due to many small uncertainties, e.g. more complicated quantification of CC since at least 2 temperature steps have to be considered. Furthermore, the split point of the directly filtrated sample is needed to get an OC/EC split for samples that are not rinsed. The applicability of the latter could not be confirmed and analysing only one aliquot of the sample directly and one treated with coagulant renders estimating the error impossible.

6. Field measurement

In this chapter the results of the analyses of snow samples collected during two sampling campaigns are discussed, including the analysis in different laboratories and the assessment of the variability of surface snow.

6.1. Comparison experiment Kolm Saigurn

A surface snow sampling campaign has been conducted at Kolm Saigurn in the national park Hohe Tauern on 28.02.2018 in 1600 m altitude. Surface snow samples have been taken at a location near the Naturfreundehaus, where the surface was visually undisturbed. The samples were distributed to three different laboratories located in Finland, Italy and Austria, where they have been analysed. For the sampling area S1 one bag, for the sampling areas S2 and S3 two bags and for the sampling area S4 four bags were available for analysis in Austria.

6.1.1. Sampling and sample preparation

Four sampling areas were defined with a folding rule. The top 3 cm of snow were collected, using a spoon for sampling, see Figure 69. Small portions of snow were put into three Whirlpak bags alternately to get representative samples, which were distributed to the different laboratories. Preliminary results of the partner laboratories were made available by Meinander (2018) and Becagli (2018).



Figure 69: Sampling for the comparison experiment Kolm Saigurn (photo by Anne Kasper-Giebl)

The samples of the laboratories in Finland and Italy were melted and filtrated on the same day as the sampling. Depending on the laboratory routine different filter areas were loaded. The samples of the laboratory in Austria were carried to Vienna and kept frozen until filtration on 11.10.2018 (first bag of S1 to S4) and 12.07.2019 (remaining bags of S2 to S4).

Different numbers and shapes of aliquots of the filters were taken by the different laboratories. The laboratory in Finland used filters with a diameter of 55 mm, although the loaded area was 35 mm. Punches of 1.5 cm² or 1 cm² were made for analysis. The samples were analysed with the EUSAAR2 thermal protocol.

The laboratory in Italy loaded a filter area with a diameter of 25 mm and analysed the entire filter since the loading was inhomogeneous. The NIOSH5040_Kolm thermal protocol was used for analysis and the sum of all filter parts were used to obtain results.

The laboratory in Austria loaded a filter area with a diameter of 16 mm, cut a punch with a diameter of 15 mm in halves and analysed one half with the EUSAAR2 and the other half with the NIOSH5040_Kolm thermal protocol. Since the rim of the sampled area showed a darker colour than the punched and analysed middle part of the filter, a bigger punch including the rim was made and analysed for the second set of samples, analysed on 12.07.2019, and the only sample available from S1, analysed on 11.10.2018. The results showed that the amount of TC is underestimated by 18 % if the rim is not analysed. The deviation of EC and OC could not be estimated as it was not possible to place the slim sample in a way that the laser pierces the loaded area, but assuming an even distribution of OC and EC, both are underestimated by 18 %. Thus, the results of the measurements were corrected by 18 %.

Blank values were determined by every laboratory and subtracted from the TC, OC and EC value, but EC blanks were hardly determined.

Errors were reported to be 10 % from the laboratories in Italy and Austria, based on an independent assessment of samples. The entire sample was filtrated on one filter, therefore it was not possible to compute a standard deviation for this one analysis. The laboratory in Finland measured one sample repeatedly and therefore the errors were reported as the standard deviations of these measurements.

6.1.2. Results

The average concentrations of TC, OC and EC of the samples S1 to S4 reported by the 3 laboratories and the respective errors are shown in Figure 70 to Figure 72. The results reported by the laboratory in Austria represent the average concentrations of all samples, analysed on 11.10.2018 and 12.07.2019.

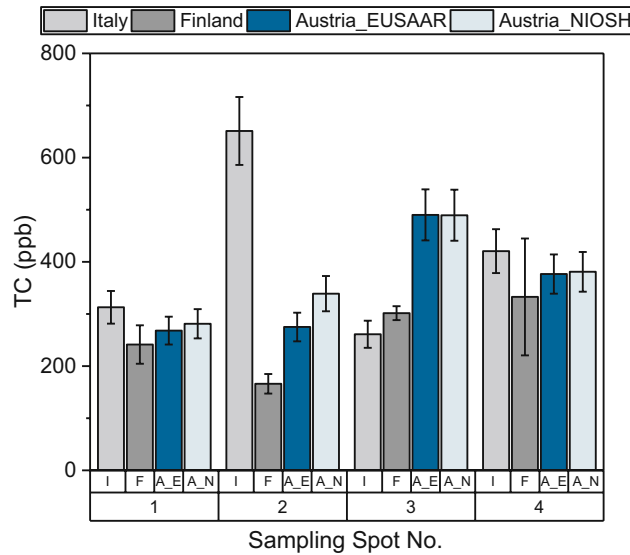


Figure 70: Concentrations of TC in the snow samples collected in Kolm Saigurn

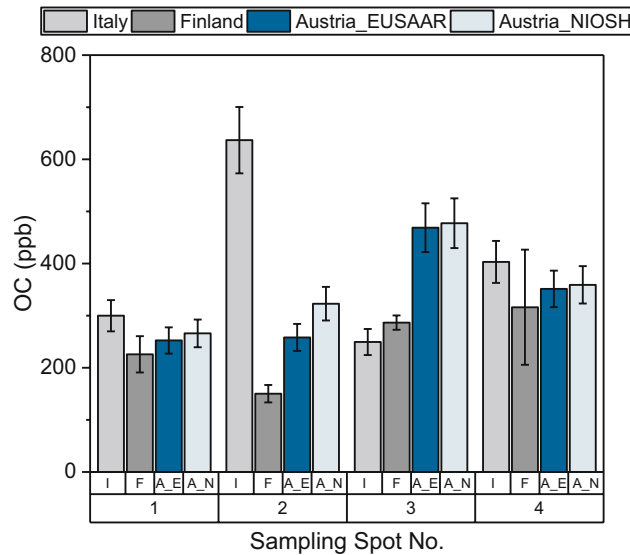


Figure 71: Concentrations of OC in the snow samples collected in Kolm Saigurn

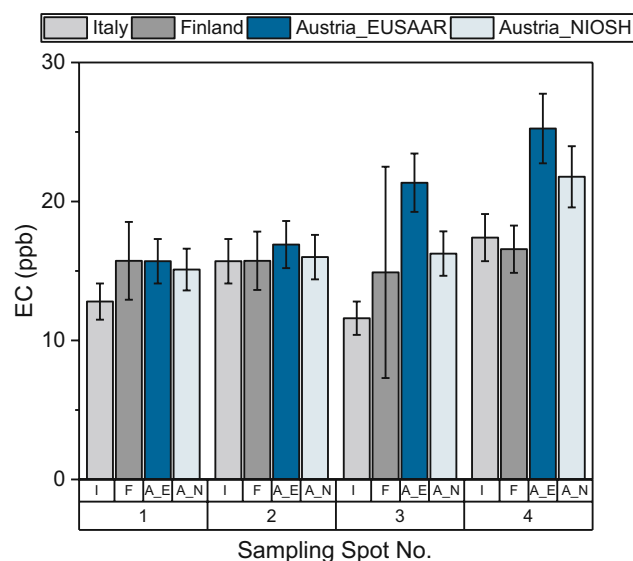


Figure 72: Concentrations of EC in the snow samples collected in Kolm Saigurn

The reported concentrations of TC from the different laboratories are similar for the samples S1 and S4. The concentration of TC reported by the laboratory in Italy for S2 is much higher than those reported by the laboratories in Finland and Austria. The laboratory in Austria reported higher concentrations of TC in S3 than the other laboratories.

The amount of OC was similar for all samples. Samples with higher concentrations of TC also showed higher concentrations of OC. If the higher reported values are due to contamination, it can be assumed that these contaminations are of organic nature.

The concentration of EC was similar for the samples S1 and S2, although the amount of TC was reported to be higher for S2 by the laboratory in Italy. For the sample S3 measured with EUSAAR2, the concentration of EC was reported higher by the laboratory in Austria, although the concentration of EC for the same sample measured with NIOSH5040_Kolm was comparable to the results of the other laboratories. EC was reported higher by the laboratory in Austria for S4 for the measurements with both thermal protocols.

Although the samples were stored for months in plastic bags until they were analysed in Vienna, no trend regarding the concentrations of TC, EC and OC is visible. Therefore, it is assumed that transporting snow samples to the laboratory in a sealed plastic bag and storing them in a freezer until analysis is unproblematic as long as they are kept frozen at all times.

6.1.3. Considerations about the reported errors

The errors reported by the laboratory in Austria were based on an independent assessment of samples. However, it was possible to calculate the standard deviation for the four samples of S4. Only one sample of S1 and two samples for S2 and S3 were available. Therefore, no standard deviation was computed for these sampling areas. The relative standard deviation, i.e. the standard deviation divided by the average, multiplied by the factor 100 to obtain a percentage value, of sample halves of S4 measured with EUSAAR2 was 11 % for OC and

TC, while it was 21 % for EC. For sample halves measured with NIOSH5040_Kolm, the relative standard deviation was 15 % for OC, 16 % for TC and 33 % for EC.

One of the sample halves measured with NIOSH5040_Kolm showed elevated carbon concentrations, TC was about one third higher than obtained by the other samples of S4. If this sample is not considered for the evaluation, the relative standard deviations are 4 % for OC, 2 % for TC and 30 % for EC. Although the relative standard deviations for OC and TC are reduced when neglecting this sample, the standard deviation for EC is still high. Hence, a contamination of organic nature is assumed in this sample.

The reported errors of 10 % were appropriate for samples measured with EUSAAR2 regarding OC and TC. For NIOSH5040_Kolm, the errors were only appropriate if the sample, which showed elevated carbon concentrations, was excluded from the evaluation. The relative standard deviation of EC was found to be above 20 %, exceeding the reported error. However, this evaluation could only be conducted for one sampling spot. Additional data of surface samples is required to determine if the relative standard deviation of EC is higher in general than the relative standard deviation of OC and TC.

6.1.4. EC/TC ratios

To compare the analyses conducted by the different laboratories, the EC/TC ratio was computed and is displayed in Figure 73. Although the amount of TC reported by the laboratory in Austria was much higher for sample 3, the EC/TC ratio is similar to the ones reported by the other laboratories. The EC/TC ratios of sample 2 exhibit a wide range between 0.024 (Italy) and 0.095 (Finland).

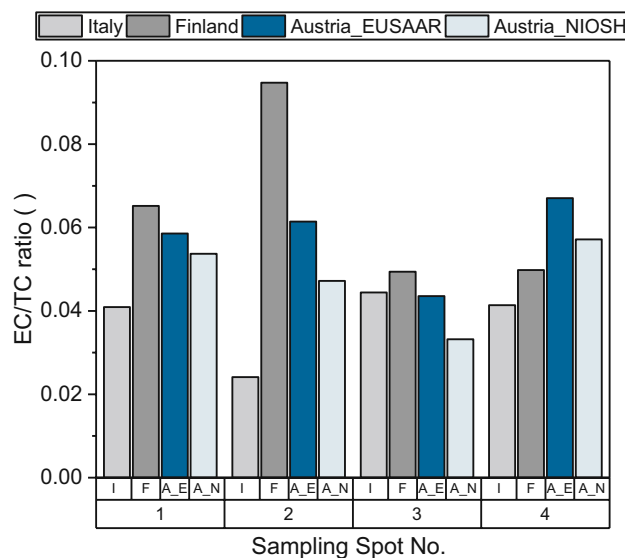


Figure 73: EC/TC ratios for the samples analysed at the comparison experiment Kolm Saigurn

Cavalli et al. (2010) state that the EC/TC ratio depends on the thermal protocol used. Here samples analysed with NIOSH5040_Kolm showed lower EC/TC ratios than samples analysed with EUSAAR2. However, the EC concentrations did not differ for any of the analysed samples considering the reported errors. The only sample where the TC concentrations reported by the laboratory in Finland, who used EUSAAR2, and Italy, who used NIOSH5040_Kolm, differ even if the errors are considered, is S2. Therefore, the difference in the EC/TC ratios cannot be considered significant for these samples.

The automatic split point set by the instrument was reasonable for all of the samples. To get an idea about the sensitivity of the analysis it was evaluated how far the split point would need to be shifted to reach similar EC/TC ratios as reported by the other laboratories. Sample 2 and sample 4 were evaluated more detailed. These samples were chosen since the reported concentrations of TC and OC showed big differences for sample 2, while for sample 4 the reported TC and OC values agree well but there are differences in the EC concentrations. The split point of the samples measured in Austria was moved until an EC/TC ratio similar to the ones obtained by the laboratory in Italy or Finland was received.

The samples S2/1 and S4/3 were chosen for the evaluation, because their individual EC/TC ratios were approximately like the EC/TC ratio of the average of the S2 or S4 samples, respectively. The split point was moved for these samples to match the EC/TC ratio reported by the laboratory in Finland for EUSAAR2 and Italy for NIOSH5040_Kolm. The split times are summarised in Table 23.

Table 23: Automatically and manually set split times for S2/1 and S4/3 of the comparison experiment Kolm Saigurn

Protocol	Old split (s)		New split (s)	
	EUSAAR2	NIOSH5040_Kolm	EUSAAR2	NIOSH5040_Kolm
S2/1	954	375	875	394
S4/3	951	383	963	394

The split point was moved forward by 79 s for S2/1 and backward by 12 s for S4/3 measured with EUSAAR2. For the measurements where NIOSH5040_Kolm was used, the split point was moved backward to 394 s for both samples, 19 s for S2/1 and 11 s for S4/3. To check if the manual adjustment of the split point is justifiable, the thermogram with the automatically set split point and the manually moved split point are compared. If the change of the transmittance signal is rather flat between the two split points, a small change in the initial transmittance, e.g. by slight movements of the filter in the sample oven, might justify a rather long time delay between the automatically and manually set split point. If the change of the transmittance signal between the two split points is steep, then the manual adjustment of the split point cannot be justified and the difference of the measurements has to be accepted. Reasons for actual differences in the measurements might be different composition of the sample, contamination during sampling, transport or sample preparation and differences in the systems used for TOA, i.e. overdue maintenance or unknown troubles with a part of the system.

As mentioned before, the raw data of the transmittance signal logged during the measurement and the transmittance output by the Calc software differ. Therefore, the thermograms and the respective automatically and manually set split points are shown as screenshots from the Calc software in the supplement. For the sample S2/1 measured with EUSAAR2, the transmittance between the automatically and manually set split points is rather flat. In spite of that the transmittance at the manually adjusted split point equals the transmittance in the middle of OC3, where pyrolysis has already occurred. Still, a change of the split point does not seem justified based on the thermogram. The shift of the split point led to an increase of 33 % for EC and a reduction in OC of 3 %.

For S2/1 measured with NIOSH5040_Kolm the transmittance between the split points is steep. Again, it cannot be justified to manually adjust the split point as it was done, since no evidence can be found in the thermogram of this sample why the split point should be moved to the new position. Additionally, the shift leads to a decrease in EC of 49 % and OC is increased by 2 %.

For the sample S4/3 measured with EUSAAR2, the transmittance between the split points is very steep. Although the split point was only shifted back by 12 s for this sample, a high difference between the transmittance at the manually set split point and the initial transmittance is evident. This high difference in transmittance cannot be traced back to slight movement of the filter in the sample oven. Hence, using the manually set split point is not justified. The shift led to a reduction of EC of 22 % and an increase in OC of 2 %.

The transmittance between the automatically and manually set split point is steep for the sample S4/3 measured with NIOSH5040_Kolm. The transmittance at the manually adjusted split point is much higher than the initial transmittance for sample. Due to the shift of the split point EC decreased by 35 % while OC increased by 2 %.

Manually adjusting the split point led to small changes in the results for OC of 2 or 3 % for these samples. The concentration of OC was one order of magnitude higher than the concentration of EC. The new split point led to a change in the EC concentration between 22 and 49 % for these samples. The effect of shifting the split point was similar for these two cases: Large shift regarding the time, when the transmittance between the automatically and manually set split points is flat, and small shift of a few seconds, when the transmittance between the split points is steep.

6.2. Variability of surface snow

The variability of surface snow is of great interest as surface snow samples are collected and analysed for many studies. For projects which require a huge amount of snow samples to be analysed with different methods, large areas of surface snow are being sampled. Only if the variability of surface snow is small, the results of the different methods can be compared. Therefore, an area of realistic dimensions for the sampling of surface snow was analysed via ion chromatography and both pH and conductivity of the samples were measured. The results were compared by calculating the empirical coefficient of determination for the different parameters and statistical evaluation of the data.

6.2.1. Sampling

Sampling has been performed at the end of April 2019 on the roof of Sonnblick Observatory. For the sampling, two areas of 1 m² each were marked with a folding rule and 10 paths per area were sampled using a plastic scoop, leading to a sum of 20 samples. The samples have been collected in plastic bags, which have been closed tightly after the sampling to avoid loss or contamination of the samples. The width of each path was about 7 cm, the depth was determined after the sampling and was about 5 cm. The two sampling areas are shown in Figure 74 and Figure 75. The snow that can be seen in the paths was carried there after the sampling by gusts since harsh conditions prevailed during sampling.



Figure 74: Sampling area 1 for the analysis of the variability of surface snow (photo by Marion Greilinger)



Figure 75: Sampling area 2 for the analysis of the variability of surface snow (photo by Marion Greilinger)

The samples have been stored and transported to Vienna in a cooling box filled with snow to ensure that the samples were frozen at all times. Until processing, the samples have been stored in a deep freezer.

6.2.2. Analysis

For the processing, the samples were melted at room temperature. The liquid samples have been homogenised by shaking the bags and were filled in different vials for the analysis of cations (Na^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , K^+) and anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-}), the pH and the conductivity. Details on the methods used are given in chapter 2.

NO_2^- was not present in detectable concentrations in any sample and is therefore excluded from the evaluation. The blanks used to check any contaminations during the processing of the samples (Milli-Q water) did not contain any of the measured ions in detectable concentrations and were therefore not subtracted from the results.

6.2.3. Results

Empirical coefficient of variation

The average and the standard deviation of each ion concentration, pH and conductivity were calculated for the sum of 20 samples as well as each area (10 samples). Additionally, the empirical coefficient of variation was calculated for all samples and each sampling area, see Table 24 to Table 26.

$$cv = \frac{s}{\bar{x}} * 100$$

cv... empirical coefficient of variation (%)

s ... standard deviation of data set

\bar{x} ... average of data set

Table 24: Average, standard deviation and empirical coefficient of variation of Cl⁻, NO₃⁻ and SO₄²⁻ of the analysis of the variability of surface snow

Area	Variable	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
area1	\bar{x} (mg/l)	0.1658	0.9736	0.7953
	s (mg/l)	0.0153	0.0734	0.0547
	cv (%)	9	8	7
area2	\bar{x} (mg/l)	0.1540	0.8725	0.7524
	s (mg/l)	0.0176	0.0585	0.0534
	cv (%)	11	7	7
area1+area2	\bar{x} (mg/l)	0.1599	0.9230	0.7738
	s (mg/l)	0.0172	0.0828	0.0570
	cv (%)	11	9	7

Table 25: Average, standard deviation and empirical coefficient of variation of pH and conductivity of the analysis of the variability of surface snow

Area	Variable	pH	Variable	Conductivity
area1	\bar{x} ()	6.10	\bar{x} (μS/cm)	8.91
	s ()	0.07	s (μS/cm)	0.51
	cv (%)	1	cv (%)	6
area2	\bar{x} ()	6.19	\bar{x} (μS/cm)	8.37
	s ()	0.06	s (μS/cm)	0.58
	cv (%)	1	cv (%)	7
area1+area2	\bar{x} ()	6.15	\bar{x} (μS/cm)	8.64
	s ()	0.08	s (μS/cm)	0.60
	cv (%)	1	cv (%)	7

Table 26: Average, standard deviation and empirical coefficient of variation of Na⁺, NH₄⁺, Mg²⁺, K⁺ and Ca²⁺ of the analysis of the variability of surface snow

Area	Variable	Na ⁺	NH ₄ ⁺	Mg ²⁺	K ⁺	Ca ²⁺
area1	\bar{x} (mg/l)	0.1144	0.3604	0.0136	0.0407	0.7407
	s (mg/l)	0.0109	0.0295	0.0019	0.0101	0.0513
	cv (%)	10	8	14	25	7
area2	\bar{x} (mg/l)	0.1192	0.3114	0.0144	0.0359	0.7324
	s (mg/l)	0.0195	0.0185	0.0022	0.0090	0.0592
	cv (%)	16	6	15	25	8
area1+area2	\bar{x} (mg/l)	0.1168	0.3359	0.0140	0.0383	0.7365
	s (mg/l)	0.0156	0.0348	0.0020	0.0096	0.0541
	cv (%)	13	10	14	25	7

The coefficient of variation is below or equal to 10 % for all ions as well as pH and conductivity except for Cl⁻, Na⁺, Mg²⁺ and K⁺. The concentrations of these ions were the lowest of all analysed ions and were below 0.2 mg/l. Therefore, even small contaminations during the sampling or processing lead to high deviations.

6.2.4. Statistical evaluation

A comparison of area 1 and area 2 was carried out using statistical tests. Basic information on the tests used is given in chapter 2.4.

The prerequisites for the application of two-sided two-sample t-tests for the comparison of averages of two data sets are interval-scaled data, normal distribution and homogeneity of variances. The analysed parameters, concentration in mg/l, conductivity in $\mu\text{S}/\text{cm}^2$ and pH are interval-scaled. The normal distribution was tested using the Shapiro-Wilk-test. The homogeneity of variances was tested using a two-sided two-sample F-test. All tests were conducted for both areas 1 and 2 (10 samples each).

Shapiro-Wilk-test

The null hypothesis of the Shapiro-Wilk-test is that the sample belongs to a normal distribution. The null hypothesis has to be rejected if the test statistic W is smaller than the tabulated critical threshold W_α , or, as implied in DataLab, $p(W)$ is smaller than the level of significance, which was chosen to be 5 %. As DataLab was used for the statistical test, $p(W)$ for the various parameters in area 1 and area 2 is shown in Table 27 and Table 28. Values of $p(W)$ smaller than the level of significance chosen are marked red.

Table 27: $p(W)$ of the Shapiro-Wilk-test for all variables in area 1 of the analysis of the variability of surface snow

Variable	Cl^-	NO_3^-	SO_4^{2-}	pH	Conductivity
$p(W)$	0.767	0.685	0.983	0.135	0.387
Variable	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
$p(W)$	0.280	0.981	0.138	0.850	0.128

Table 28: $p(W)$ of the Shapiro-Wilk-test for all variables in area 2 of the analysis of the variability of surface snow

Variable	Cl^-	NO_3^-	SO_4^{2-}	pH	Conductivity
$p(W)$	0.959	0.389	0.682	0.153	0.990
Variable	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
$p(W)$	0.030	0.394	0.878	0.004	0.906

The Shapiro-Wilk-test for a confidence interval of 95 % showed that there is no reason to assume that the pH, the conductivity as well as the concentrations of all anions and cations are not normally distributed in area 1. In area 2 Na^+ and K^+ are not normally distributed for a level of significance of 5 %. While K^+ is not normally distributed at a level of significance of 1 %, there is no reason to assume that Na^+ is not normally distributed at a level of significance of 1 % in area 1 and area 2.

F-test

The two-sample two-tailed F-test was used for all variables that are normally distributed. The null hypothesis for F-tests is that the variances of two datasets are equal and the ratio of the variances is 1. The ratio of the variance of the variables in area 1 and the variance of the respective variables in area 2 was computed to obtain the test statistic F . F was then

compared to the tabulated critical value $F_{\alpha/2}$. The level of significance chosen for the F-test was 5 %, except for Na^+ , which is not normally distributed at a level of significance of 5 %. For Na^+ the F-test was conducted for a confidence interval of 99 %. The test was not conducted for K^+ as the prerequisite normal distribution was not met in area 2. The test statistic F for all parameters is shown in Table 29.

Table 29: Test statistic F of the F-test for all variables except Na^+ and K^+ of area 1 and area 2 of the analysis of the variability of surface snow

Variable	Cl^-	NO_3^-	SO_4^{2-}	pH	Conductivity
F	1.320	1.573	1.047	1.743	1.308
Variable	Na^+ (99 %)	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
F	3.170	2.553	1.335	-	1.327

The critical value for a confidence interval of 95 %, $F_{0.025}$, is 4.026 and for a confidence interval of 99 %, $F_{0.005}$, it is 6.541. The null hypothesis has to be rejected if the test statistic F is bigger than the critical value $F_{\alpha/2}$. The F-tests showed that there is no reason to assume that the variances of any of the tested variables in area 1 and area 2 are significantly different at the chosen level of significance.

t-test

Since the prerequisites for t-tests are fulfilled, two-sided two-sample t-tests with a confidence interval of 95 % were conducted for all variables except Na^+ and K^+ to compare the averages of the variables of area 1 and area 2. Since the normal distribution and the homogeneity of the variances could not be rejected at a level of significance of 1 % for Na^+ , it is possible to conduct the t-test for Na^+ at this level of significance.

The null hypothesis of the t-test is that the averages of the data sets are equal. The null hypothesis has to be rejected if the absolute value of the test statistic t is bigger than the tabulated critical value $t_{\alpha/2}$. The absolute value of the test statistic t is shown in Table 30, values bigger than the critical value are marked red.

Table 30: Absolute values of the test statistic t of the t-test for all variables except K^+ of area 1 and area 2 of the analysis of the variability of surface snow

Variable	Cl^-	NO_3^-	SO_4^{2-}	pH	Conductivity
t	1.607	3.406	1.774	2.898	2.208
Variable	Na^+ (99 %)	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
t	0.683	4.449	0.839	-	0.334

The critical value $t_{\alpha/2}$ at a level of significance of 5 %, $t_{0.025}$, is 2.101 and at a level of significance of 1 %, $t_{0.005}$, is 2.878. There is no reason to assume that the average concentrations of Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} differ at a level of significance of 5 % and that the averages of the concentrations of Na^+ differ at a level of significance of 1 % in area 1 and area 2. The averages of the concentrations of NH_4^+ , NO_3^- , the pH and the conductivity are significantly different at a level of significance of 5 % as well as 1 %, except for the conductivity, where there is no reason to assume a difference in the averages at a level of significance of 1 %.

Alternatives for the t-test for K^+

As one of the prerequisites, normal distribution of the two samples to be compared, is not fulfilled for K^+ , the t-test could not be conducted. A possible alternative to the t-test is the U-test, which does not require normal distribution but has the prerequisite that both samples belong to the same distribution. Since one of the samples of K^+ is normally distributed while the other one is not, this prerequisite is not met and the U-test could not be conducted.

Another possibility to compare two samples is the median test. The two-sample median test was used for the comparison of the concentrations of K^+ in the two areas. The null hypothesis, the expected values of the median of area 1 and area 2 are equal, has to be rejected if the X^2 -statistic is bigger than the critical value at the chosen level of significance. The level of significance for this test was 5 %. The X^2 -statistic for K^+ using Yates' continuity correction was 1.8000, the critical value is 3.8415. Therefore, there is no reason to assume that the medians of the concentration of K^+ in area 1 and area 2 are different. The exact p-value after Fisher is 0.1789.

6.3. Summary of chapter 6

The sampling at the comparison experiment was performed in a way to minimize deviations between the samples distributed to the different laboratories. However, the concentrations of TC as well as OC differed for two out of four samples between the laboratories considering the reported errors. For the concentration of EC, which was one order of magnitude lower than the concentration of TC and OC, also two out of four samples differed considering the errors, only for one of these samples the concentrations of TC and OC differed. No difference in EC concentrations could be observed for measurements using EUSAAR2 or NIOSH5040 for these samples.

The laboratory in Austria observed that the outer rim of the loaded area should always be analysed for samples with small loaded areas, as the outer rim showed a higher loading leading to an underestimation of TC of 18 % in average. Furthermore, storing the samples in sealed plastic bags for months did not affect the concentrations of OC and EC as the samples were kept frozen at all times. The relative standard deviation of EC, calculated from the data of the four samples of one sampling spot, was above 20 %, exceeding the reported error of 10 %. The relative standard deviations for OC and TC matched the reported error for the samples measured with EUSAAR2. For the measurements with NIOSH5040_Kolm, the error was exceeded by 5 % when considering all samples. Eliminating a sample with possible organic contaminations, the relative standard deviations of OC and TC were below 5 %.

Adjusting the OC/EC split point to approximate the EC/TC ratio of the results the other laboratories reported did not lead to satisfactory results. No evidence could be found in the thermograms to adjust the split point accordingly and a difference in the EC concentration between 22 and 49 % was observed. The effect on the OC concentration was comparatively small, between 2 and 3 %, as the concentration of OC was one order of magnitude higher than the concentration of EC. Therefore, differences in the sample's composition, the sample preparation or the analysis have to be accepted and cannot be corrected by adjusting the split point as was tried here.

Sampling in an area of 1 m² led to empirical coefficients of variation of less than 10 % for Ca²⁺, NH₄⁺, SO₄²⁻ and NO₃⁻ as well as pH and conductivity. Na⁺ and K⁺ were not normally distributed in two sampling areas of 1 m² each at a level of significance of 5 %. For a level of significance of 1 % the normal distribution of Na⁺ could not be rejected in both areas. The variances of all tested variables were not significantly different for both sampling areas, whereas the average concentrations of NH₄⁺ and NO₃⁻ as well as the average of the conductivity and the pH differed significantly at a level of significance of 5 %. The average concentrations of Cl⁻, SO₄²⁻, Mg²⁺ and Ca²⁺ did not differ significantly at the same level of significance and the average concentrations of Na⁺ did not differ significantly at a level of significance of 1 %. The medians of the concentrations of K⁺ did not differ significantly at a level of significance of 5 %.

Therefore, it is recommended to sample in an area as big as needed for all analyses but also as small as possible to get comparable data. Taking samples not from one side of the sampling area but from various spots of the sampling area might help to get comparable results, as was done for the comparison experiment in Kolm Saigurn.

An alternative would be to take one big sample that is homogenised after melting and divided for the various analyses. This procedure bears the disadvantage that the melted sample has to be transported to other laboratories, which might lead to a change in the composition of the sample, e.g. the loss of volatile compounds. Furthermore, the sample would have to be refrozen to be sent to other countries for analysis which might as well lead to a change in its composition.

7. Summary of research conducted within this thesis

When preparing snow samples for TOA, loading of filters should be done by applying a slight vacuum to prevent the system from leakage. From the different types of partitioning necessary to obtain sample aliquots, crescent, halves and punches, the crescent was least suitable due to the difficult handling, whereas the halves and punches were equally suitable. For samples with low loadings the halves should be favoured to avoid problems with the LOD. Halves of loaded filters should be weighed, as no exact halves were obtained with the used partitioning method. TC deviated on two aliquots of the filters for both halves and punches by 2 % in average. The entire loaded area should be analysed, as the outer rim might be loaded more heavily and TC was shown to be underestimated by 18 % in average, if the outer rim is excluded from the measurement.

Sample preparation included the rinsing of beakers and funnel with water or water and isopropanol. The blank values of the two preparation methods did not differ significantly. TC on filters loaded with the SRM San Joaquin soil did not differ significantly. Still, TC and OC differed significantly for filters loaded with snow sample when water or water and isopropanol were used for sample preparation. TC and OC were lower for water and isopropanol, most likely due to dissolution of organics collected on the filter. A significant increase in EC could not be observed. Hence, only water should be used for sample preparation.

The relative standard uncertainty of repeatability of the overall process of sample preparation, determined by filtering and analysing a snow sample several times, was found to be below 10 %. All thermal protocols used in this work completely desorbed carbon from the sample filters. Improved separation of peaks in the thermogram by elongation of the temperature steps are especially pronounced for NIOSH870. The elongation of EUSAAR2 does not have any negative effects, however, the length of the temperature steps in the standard EUSAAR2 protocol are sufficient to achieve adequate separation of signals for most samples. When using IMPROVE_A a smaller number of peaks was obtained, which may lead to problems when analysing particular carbon fractions.

Carbonate reference materials, CaCO_3 , MgCO_3 and K_2CO_3 , were analysed with different thermal protocols and the temperature steps in which the carbonates decarboxylate were determined. IMPROVE_A is the only temperature protocol used where carbonates combust in the oxidising atmosphere. Due to a possible interference with the amount of EC when using IMPROVE_A, the protocols EUSAAR2 and NIOSH870 should be favoured for the determination of CC. Doping a snow sample with carbonate mix did not show an influence of the snow matrix on the combustion behaviour of the reference substances. Fumigation with HCl and treatment with liquid diluted HCl of filters doped with carbonate mixture standard led to carbon concentrations within the range of the blanks, i.e. CC can be removed quantitatively. Treatment of snow samples containing MD led to equal changes in the thermograms when using HCl vapour and liquid HCl. Washing the filters with 45 ml Milli-Q water proved to be sufficient to remove residues from the treatment with liquid HCl and filters treated with liquid HCl did not damage the system of the Lab OC-EC Aerosol Analyzer. A comparison of the temperature steps where CC is removed in snow samples and an ambient air sample polluted with MD showed differences in the thermograms and HCl treatment led to changes in more temperature steps for snow samples. Due to carbonaceous fractions combusting together with CC, the determination of CC by integrating one temperature step was not possible and would lead to an overestimation of CC while underestimating OC. Two analytical runs are needed to determine the amount of CC in the sample in a reliable way.

The ambient air filter showed a darker colour after analysis with EUSAAR2 and IMPROVE_A, while the filter analysed with NIOSH870 could not be visually distinguished from the filter that was not analysed. Change of colour after TOA was also observed for snow samples depending on the temperature protocol used. Further measurements to reveal the oxidation state of Fe and its crystal lattice would be necessary to explain the change in optical properties depending on the thermal protocol used.

Measuring a snow sample directly via TOA and after HCl treatment showed no distinct change in any of the temperature steps for samples not containing visible amounts of MD. HCl treatment of samples containing visible amounts of MD led to a decrease of carbon in OC3 and OC4 while it led to an increase in EC1 and EC2 for EUSAAR2. The temperature steps in the inert atmosphere match the combustion of CaCO_3 (OC4) and MgCO_3 (OC3 and OC4). For NIOSH870, samples with MD showed a decrease of carbon in OC2 and OC3 as well as an increase in EC2. The CaCO_3 standard decarboxylated in both OC3 and OC4, but no change in OC3 was observed at the snow sample. The reduction of carbon in OC2 corresponds to the combustion behaviour of MgCO_3 . Hence, the correlation of CC from TOA and CC from IC may be improved if both Ca^{2+} and Mg^{2+} are considered according to these measurements. However, measurements conducted later with samples with high amounts of MD showed a decrease of carbon only in OC4 for EUSAAR2_x1.5 and OC3 and OC4 for NIOSH870_x1.5, which corresponds to CaCO_3 . Eluates of these samples showed that the concentration of Ca^{2+} is double to three times as high as the concentration of Mg^{2+} . Hence, the temperature steps corresponding to CaCO_3 should be used for the determination of CC via TOA, but the temperature steps corresponding to MgCO_3 may be used to get a more accurate result if elevated concentrations of MgCO_3 are present.

The concentration of Ca^{2+} in the eluates of filters, which were thermal-optically analysed prior to elution, was found to be independent of the thermal protocol used, whereas the analysis with NIOSH870 led to lower Mg^{2+} concentrations in the eluate compared to EUSAAR2. The eluates of filters treated with HCl showed lower concentrations for both Ca^{2+} and Mg^{2+} than the filters that were directly analysed.

Using the temperature steps which are corresponding to CaCO_3 and the Ca^{2+} concentrations in the filter eluates, the slope of the trend line of CC from IC and CC from TOA is between 0.6 and 0.7 for EUSAAR2_x1.5, NIOSH870_x1.5 and IMPROVE_A. The amount of CC from TOA was higher than the amount of CC estimated from the Ca^{2+} concentration in the eluate.

Measurements of iron compounds showed a marked drop in transmittance already in the first temperature step for EUSAAR2_x1.5. It was shown that the reduction in transmittance is not constant for one iron compound, e.g. Fe_2O_3 , if the concentration of iron varies. However, the relative reductions of transmittance, i.e. the transmittance normalised by the initial transmittance divided by the maximum reduction in transmittance, were fairly constant for both concentrations analysed. Since the reduction in transmittance for the iron containing compounds did not match the drops in transmittance observed with snow samples, it is possible that the iron compounds used do not match the iron compound found in snow samples. Hence, a direct use of the data collected when measuring the iron compound for the snow samples is not possible.

For snow samples with varying amounts of MD, the drops in transmittance, which can be attributed to Fe, are marked in OC2 and OC3 for EUSAAR2_x1.5 and in OC1 and OC2 for NIOSH870_x1.5. The course of transmittance for the following temperature steps is rather

parallel for samples with different amounts of MD, leading to the assumption that considering the two drops in transmittance is appropriate if a correction of the transmittance for samples containing elevated amounts of Fe is sought. This could not be confirmed with the measurement of Fe_2O_3 , yet. Preliminary data suggests that a correlation between the amount of MD-contaminated sample and the drops in transmittance in these temperature steps exists also for samples with low amounts of MD, where the determination of CC from TOA was not successful. Still it always has to be considered, that pyrolysis during these temperature steps can occur as well and will be different when different amounts and types of OC are present.

Two approaches to estimate the amount of Fe in the samples and enable a correction of the transmittance and therefore the possibility to set an OC/EC split point were presented. One of them considers the two marked drops in transmittance in the inert atmosphere attributed to Fe, which might be influenced by loading of the filter as well as pyrolysis during the analysis. For the other approach the rise in transmittance when cooling the sample during the calibration phase is evaluated. At that time an influence of pyrolysis can be excluded. Preliminary data suggests a correlation between the rise in transmittance and the amount of MD. However, the results of two different experiments do not match, which might be due to different sources of the MD and thus the iron content present in the sample. More research, including an independent method to determine the iron concentration, is needed.

The collection efficiency of quartz fibre filters during liquid filtration was determined for inorganic cations only, as no method was available to check for carbon parameters. Samples and blanks were analysed directly, after filtration through a quartz fibre filter and after additional filtration through a syringe filter with a mesh width of $0.45\ \mu\text{m}$, which should remove insoluble compounds quantitatively. Regarding the concentrations of Na^+ , NH_4^+ , K^+ or Ca^{2+} filtration with the quartz fibre filter was sufficient. Still respective tests were made using $\text{NH}_4\text{H}_2\text{PO}_4$ as a coagulant to increase the collection efficiency of the quartz fibre filters as suggested in literature. For the determination of CC two temperature steps, OC2 and OC4, have to be considered, as the combustion behaviour of carbon fractions is altered by the coagulant. Furthermore, the altered combustion behaviour necessitates the elongation of the last temperature step in the oxidising atmosphere to completely record the thermogram. It was not possible to determine an OC/EC split point for snow samples treated with coagulant, even if the sample did not contain MD. The quantification of EC, which should be increased by adding coagulant, via the change in TC was not possible, as the standard deviation of TC was higher than the fraction of EC. Utilizing the split time of an untreated sample for the assessment of EC in the sample treated with coagulant, the EC concentration was roughly seven times higher than in the untreated sample. Differences in the transmittance of untreated sample and sample treated with coagulant were observed, putting in question if this approach is justified. The challenges introduced by the addition of coagulant, i.e. precluding the determination of an OC/EC split point, can be reduced when rinsing the filter after filtration. However, new challenges including high errors in the determination of CC are introduced. Hence, the sample filter should not be rinsed with water after filtration.

Furthermore, samples of a field intercomparison were analysed. The sampling for the comparison experiment in Kolm Saigurn was performed in a way to minimize the deviation of the samples distributed to the laboratories. While good agreement was reached for OC and TC for two out of four samples, deviations markedly higher than the errors reported by the single laboratories were found for the other samples. The concentration of EC was one order of magnitude lower than the concentration of TC and OC and for EC also two out of four

samples differed. Here the differences reached up to 184 %. Only for one of these two samples TC and OC differed as well. A difference in EC depending on the thermal protocol used, i.e. EUSAAR2 or NIOSH5040_Kolm, could not be observed for these samples. Storing the samples frozen in sealed plastic bags for months did not affect the concentrations of OC and EC. A possible manual adjustment of the OC/EC split point to match the EC/TC ratio that other laboratories reported could not explain the observed differences.

To prepare for future sampling campaigns, the variability of surface snow was assessed using cation and anion IC as well as the measurement of pH and conductivity. The empirical coefficients of variations were below 10 % for NO_3^- , SO_4^- , pH, conductivity, NH_4^+ , Ca^{2+} in both sampling areas of 1 m² each. The coefficients of variations were below 15 % for Cl^- and Mg^{2+} , up to 16 % for Na^+ and 25 % for K^+ .

8. Outlook

The determination of CC was not possible from the thermogram of one analytical run using the software provided by Sunset Laboratory Inc. for snow samples. Throughout this work a lot of data has been accumulated and the position and shape of the CC signals for snow samples from Sonnblick containing MD were identified. The signal evolving in OC4 when using the thermal protocol EUSAAR2 is of special interest. Here, the combined occurrence of OC and CC leads to an overlap of two peaks and quite pronounced tailing of the OC signal was observed if CC is removed. Thus, the possibility of assigning the peaks in the temperature steps relevant for the determination of CC by using deconvolution techniques should be investigated, starting with the peaks in OC4 for EUSAAR2.

The change in optical properties when MD, and consequently Fe, is contained in the sample did not allow to set an OC/EC split point. A definite correction for the transmittance could not be presented. However, different approaches were proposed and some preliminary results could be shown, e.g. the consideration of the drop in transmittance between OC1 and OC2 and OC2 and OC3 for EUSAAR2 or the rise in transmittance in the calibration phase. The correlation of the changes in transmittance and the amount of Fe in the sample has yet to be proven. Most samples analysed during this work were stored and prepared for future analysis of Fe via ICP-OES. The data of this method and TOA can then be compared and the development of a correction for the transmittance during TOA might be possible, leading to proper results for OC and EC even if MD is contained in the sample.

Using $\text{NH}_4\text{H}_2\text{PO}_4$ to achieve quantitative separation of EC on a quartz fibre filter led to unexpected challenges. To evaluate the possibility to determine the concentration of OC and EC in snow samples treated with coagulant when utilizing the split point of an untreated sample, more snow samples with different properties, i.e. collected during varying meteorological conditions, must be analysed. The relationship between the increase in carbon in OC2 and the decrease of the sharp signal at the start of OC4 when analysing a sample contaminated with MD must be proven with additional samples.

The understanding of proper sample preparation and data evaluation obtained in this work will be used for the analysis of depth profiles collected on the glaciers surrounding Sonnblick Observatory since 2016. This will be the start of a time series comparable to the one described by Greilinger et al. (2018). The amount of OC and EC in the depth profiles shall be monitored over a period of many years to observe trends in the deposition of carbon containing compounds at a background site.

9. References

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10. Supplement

Table 31: Parameters of the thermal protocol NIOSH870

NIOSH870			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	80	310
2	He	80	475
3	He	80	615
4	He	110	870
5	He	45	550
6	He/O ₂	45	550
7	He/O ₂	45	625
8	He/O ₂	45	700
9	He/O ₂	45	775
10	He/O ₂	45	850
11	He/O ₂	110	870
12	CalibrationOx	120	1

Table 32: Parameters of the thermal protocol NIOSH870_x1.5

NIOSH870_x1.5			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	120	310
2	He	120	475
3	He	120	615
4	He	165	870
5	He	45	550
6	He/O ₂	68	550
7	He/O ₂	68	625
8	He/O ₂	68	700
9	He/O ₂	68	775
10	He/O ₂	68	850
11	He/O ₂	165	870
12	CalibrationOx	120	1

Table 33: Parameters of the thermal protocol NIOSH5040_Kolm

NIOSH5040_Kolm			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	60	250
2	He	60	500
3	He	60	650
4	He	90	870
5	He	30	650
6	He/O ₂	30	650
7	He/O ₂	30	750
8	He/O ₂	30	850
9	He/O ₂	120	940
10	He/O ₂	68	850
11	CalibrationOx	120	1

Table 34: Parameters of the thermal protocol EUSAAR2

EUSAAR2			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	120	200
2	He	150	300
3	He	180	450
4	He	180	650
5	He	30	1
6	He/O ₂	120	500
7	He/O ₂	120	550
8	He/O ₂	70	700
9	He/O ₂	80	850
10	CalibrationOx	110	1

Table 35: Parameters of the thermal protocol EUSAAR2_x1.5

EUSAAR2_x1.5			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	180	200
2	He	225	300
3	He	270	450
4	He	270	650
5	He	45	1
6	He/O ₂	180	500
7	He/O ₂	180	550
8	He/O ₂	105	700
9	He/O ₂	120	850
10	CalibrationOx	110	1

Table 36: Parameters of the thermal protocol EUSAAR2_EC4

EUSAAR2_EC4			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	120	200
2	He	150	300
3	He	180	450
4	He	180	650
5	He	30	1
6	He/O ₂	120	500
7	He/O ₂	120	550
8	He/O ₂	70	700
9	He/O ₂	160	850
10	CalibrationOx	110	1

Table 37: Parameters of the thermal protocol IMPROVE_A

IMPROVE_A			
Stepno.	Atmosphere	Time (s)	Temperature (°C)
1	He	150	140
2	He	150	280
3	He	150	480
4	He	150	580
5	He/O ₂	150	580
6	He/O ₂	150	740
7	He/O ₂	150	840
8	CalibrationOx	110	1

Table 38: Data before and after correction by the weight of filter halves, used for the evaluation of the homogeneity of filter loading

Before correction by weight of filter halves				After correction by weight of filter halves			
Sample	TC _{Half} (µg)	Sum TC (µg)	Percentage (%)	Ratio of masses (m _{Half} /m _{SumHalves})	TC _{Half} (µg)	Sum TC (µg)	Percentage (%)
S1_I	66.1	134.0	49	0.44	74.9	135.7	55
S1_II	68.0		51	0.56	60.8		45
S2_I	68.9	147.1	47	0.51	68.2	147.2	46
S2_II	78.2		53	0.49	79.1		54
S3_I	82.3	157.3	52	0.49	84.6	157.6	54
S3_II	75.1		48	0.51	73.1		46
S4_I	88.2	182.0	48	0.50	87.6	182.1	48
S4_II	93.8		52	0.50	94.5		52
b1_I	2.1	4.0	51	0.50	2.1	4.0	51
b1_II	2.0		49	0.50	2.0		49
b2_I	0.7	2.0	33	0.48	0.7	1.9	35
b2_II	1.3		67	0.52	1.3		65
S5_I	44.6	80.2	56	0.55	40.4	80.2	50
S5_II	35.7		44	0.45	39.8		50
S6_I	40.5	88.9	46	0.44	46.1	89.3	52
S6_II	48.5		54	0.56	43.2		48
S7_I	46.7	91.3	51	0.49	47.5	91.3	52
S7_II	44.6		49	0.51	43.9		48
S8_I	37.8	74.9	50	0.48	39.0	75.0	52
S8_II	37.2		50	0.52	36.0		48
S9_I	34.7	75.1	46	0.47	36.6	75.0	49
S9_II	40.4		54	0.53	38.4		51
S10_I	27.1	83.6	32	0.40	33.6	80.9	42
S10_II	56.5		68	0.60	47.3		58
S11_I	43.5	79.5	55	0.53	41.0	79.4	52
S11_II	36.1		45	0.47	38.4		48
b3_I	1.3	3.1	43	0.52	1.3	3.1	42
b3_II	1.8		57	0.48	1.8		58
S12_I	21.7	43.2	50	0.51	21.2	43.3	49
S12_II	21.5		50	0.49	22.1		51
S13_I	19.7	43.8	45	0.49	20.0	43.7	46

S13_II	24.1		55	0.51	23.8		54
S14_I	23.3	57.5	41	0.48	24.5	57.1	43
S14_II	34.2		59	0.52	32.6		57
S15_I	20.6	41.8	49	0.52	19.7	42.0	47
S15_II	21.3		51	0.48	22.2		53

Table 39: Data of punches used for the evaluation of homogeneity of filter loading

Sample	TC _{Half} (µg)	Sum TC (µg)	Percentage (%)
S1_I	88.8	126.0	70
S1_II	37.2		30
S2_I	40.8	75.8	54
S2_II	35.1		46
S3_I	15.4	30.6	50
S3_II	15.3		50
S4_I	18.0	33.7	53
S4_II	15.7		47
S5_I	15.1	29.8	51
S5_II	14.6		49
S6_I	18.3	39.4	46
S6_II	21.1		54
S7_I	17.4	32.5	54
S7_II	15.1		46
S8_I	17.0	32.0	53
S8_II	15.0		47
S9_I	16.8	33.9	50
S9_II	17.1		50
S10_I	14.4	29.8	48
S10_II	15.4		52
S11_I	16.9	33.2	51
S11_II	16.3		49
b1_I	0.9	2.1	45
b1_II	1.1		55

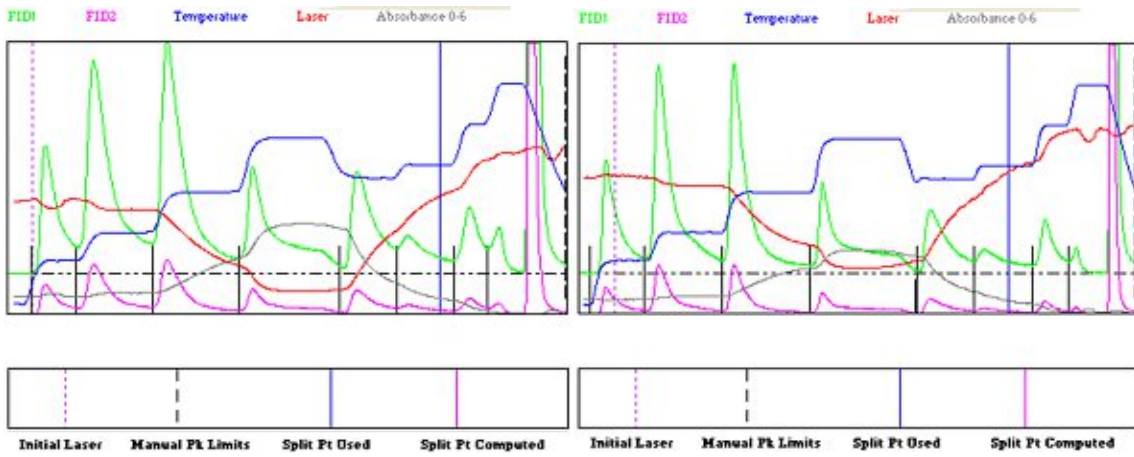


Figure 76: Ambient air filter 178 measured with the standard thermal protocol EUSAAR2 (left) and its elongated version EUSAAR2_x1.5 (right)

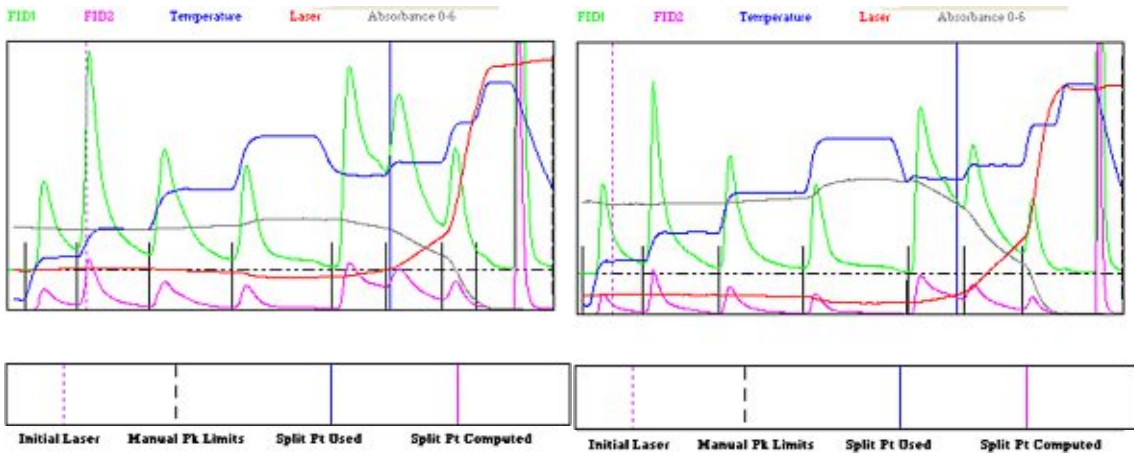


Figure 77: Ambient air filter Leibnitz measured with the standard thermal protocol EUSAAR2 (left) and its elongated version EUSAAR2_x1.5 (right)

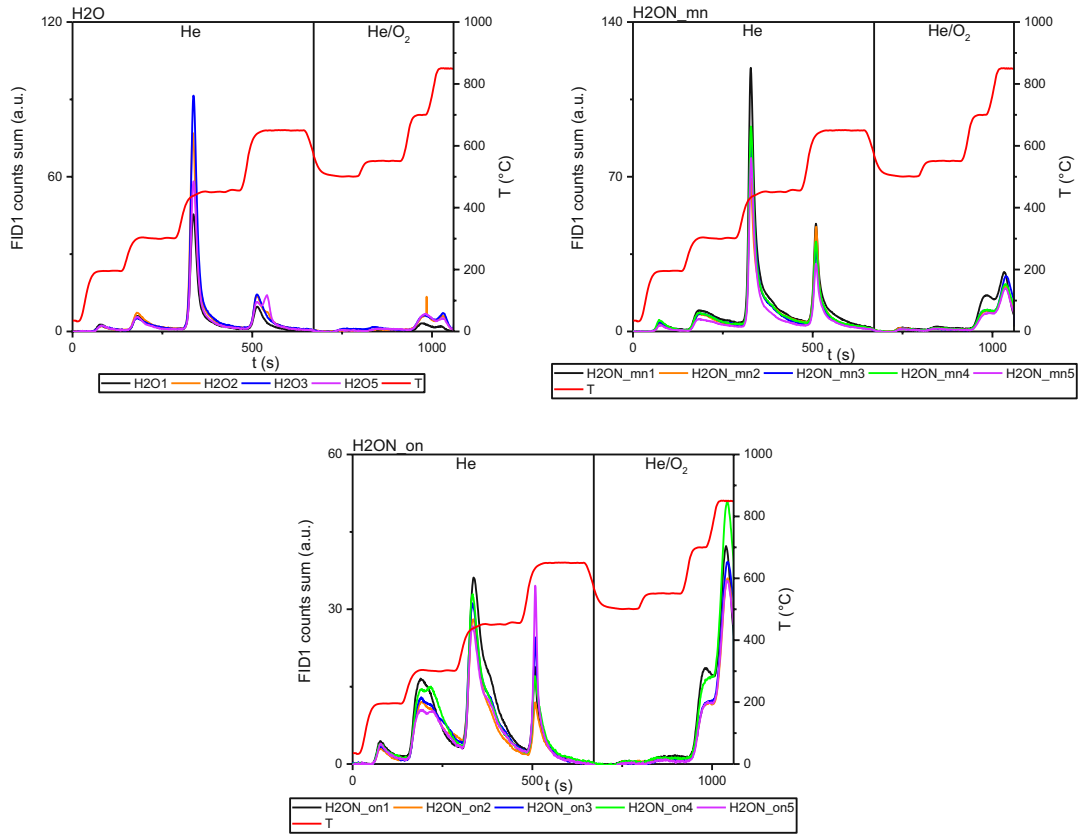


Figure 78: Thermograms of the individual blanks of groups H₂O, H₂ON_mn and H₂ON_on from the experiment using NH₄H₂PO₄

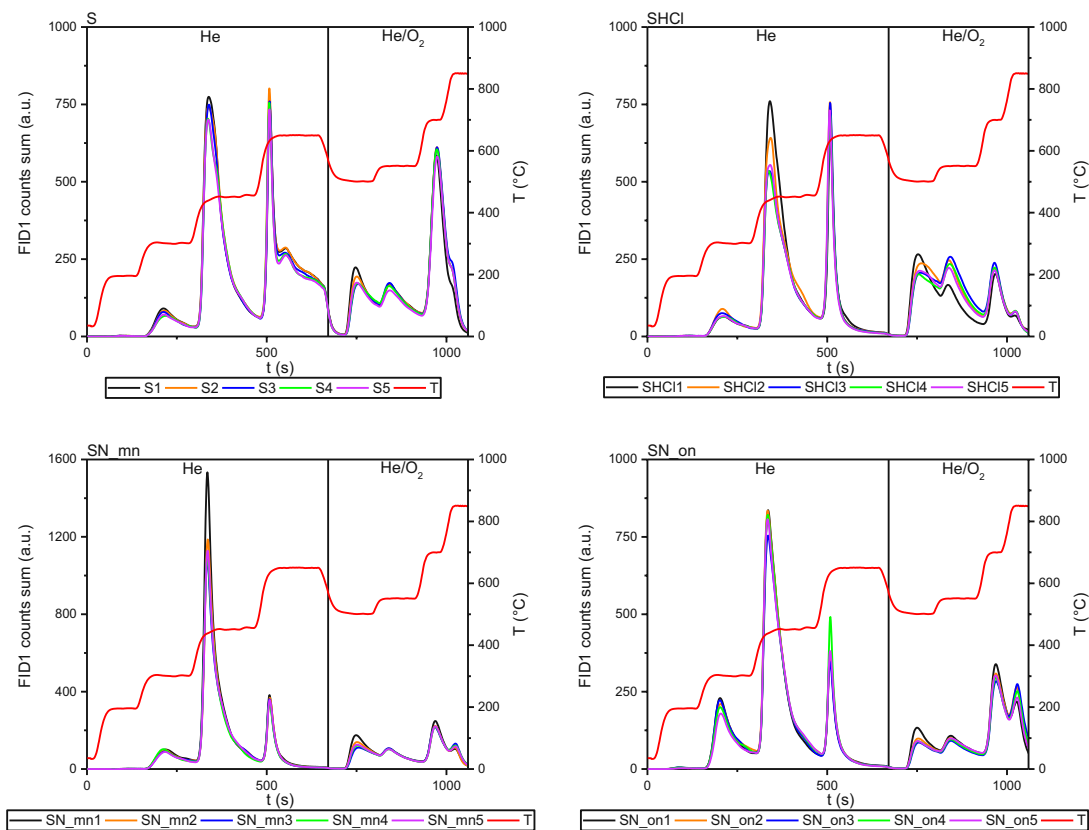


Figure 79: Thermograms of the individual samples contaminated with MD of groups S, SHCl, SN_mn and SN_on from the experiment using $\text{NH}_4\text{H}_2\text{PO}_4$

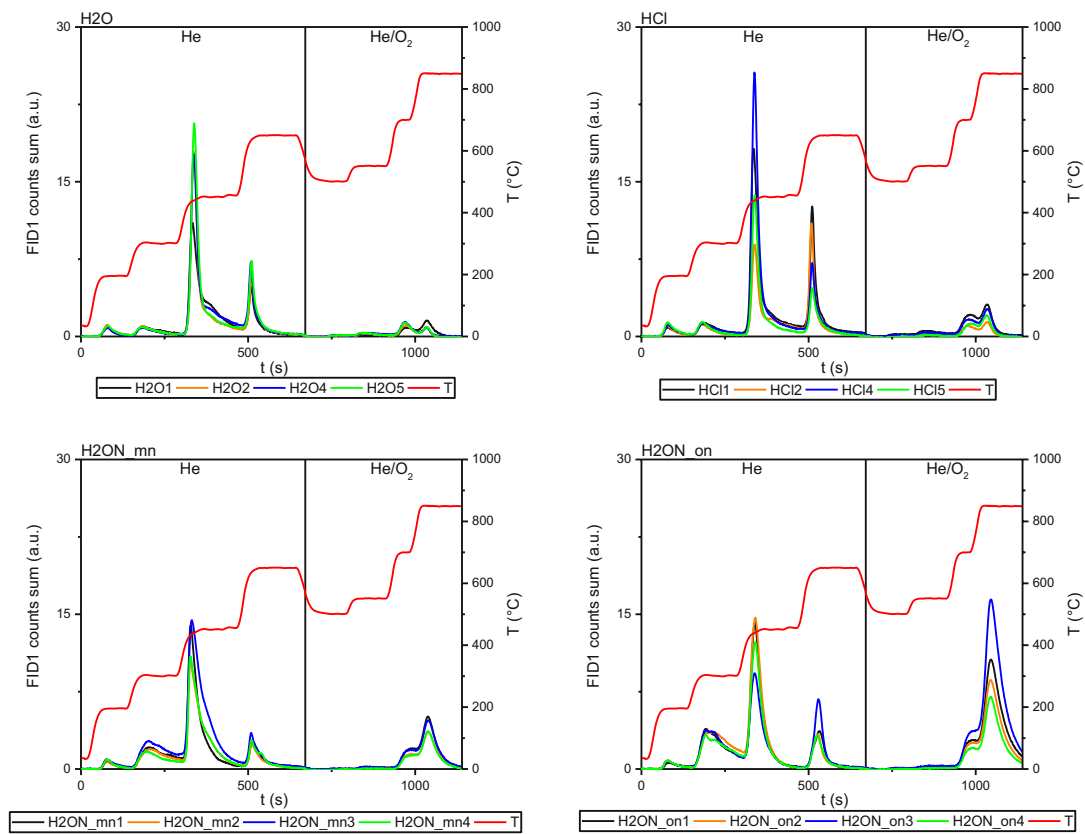


Figure 80: Thermograms of the individual new blanks of groups H2O, HCl, H2ON_mn and H2ON_on from the experiment using $\text{NH}_4\text{H}_2\text{PO}_4$

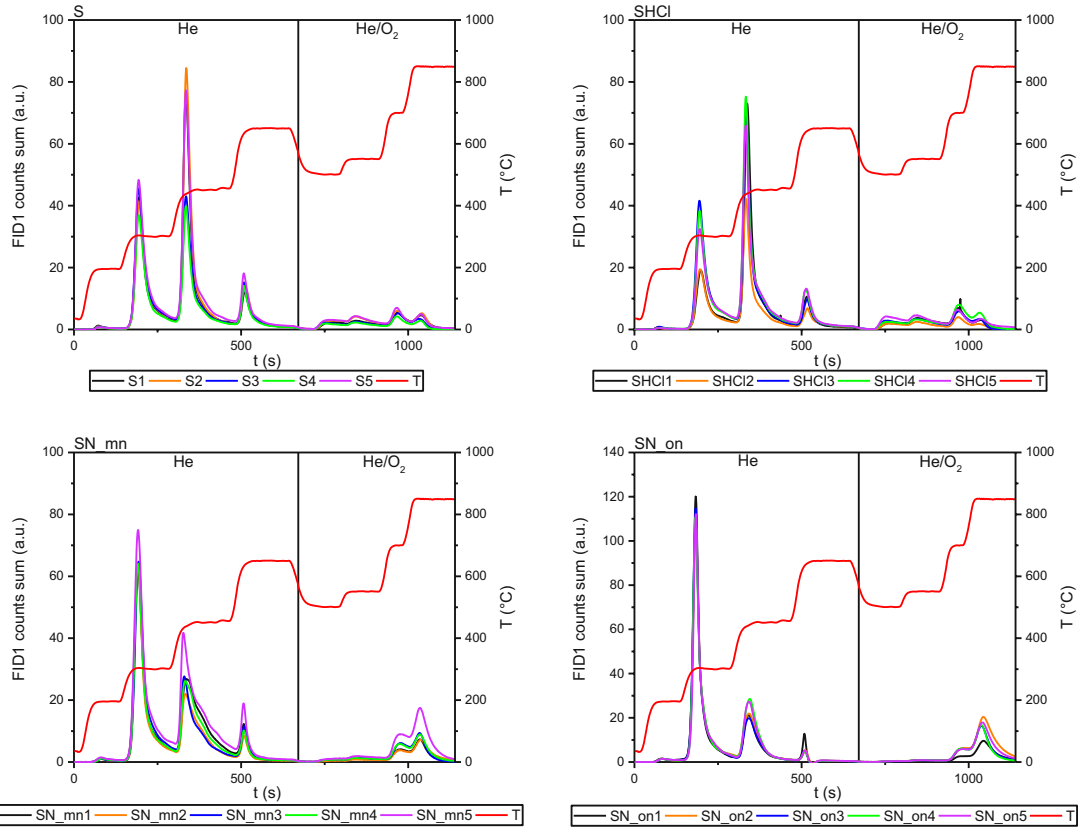


Figure 81: Thermograms of the individual samples without visible MD contamination of groups S, SHCl, SN_mn and SN_on from the experiment using $\text{NH}_4\text{H}_2\text{PO}_4$

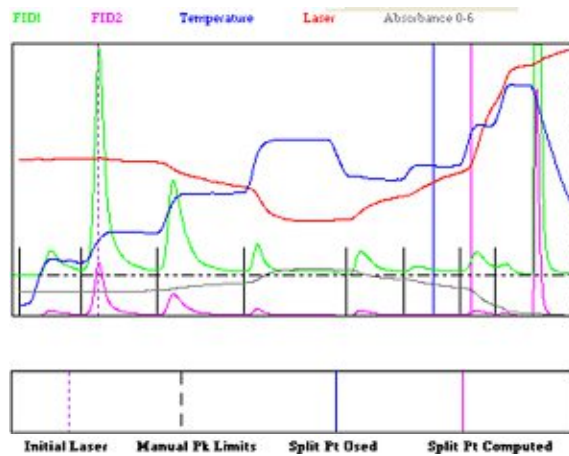


Figure 82: Thermogram of S2/1 from the comparison experiment Kolm Saigurn measured with EUSAAR2; automatic and manual split point are shown

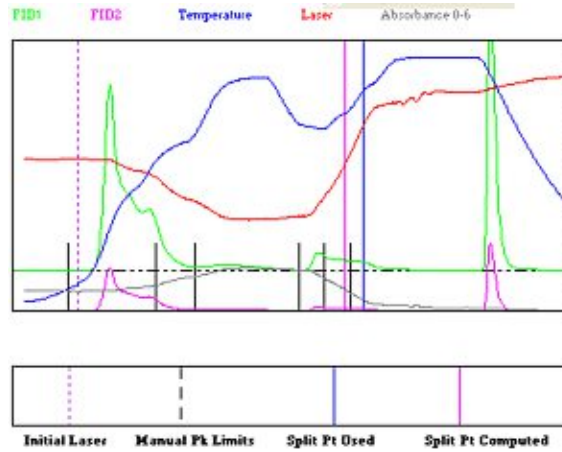


Figure 83: Thermogram of S2/1 from the comparison experiment Kolm Saigurn measured with NIOSH5040_Kolm; automatic and manual split point are shown

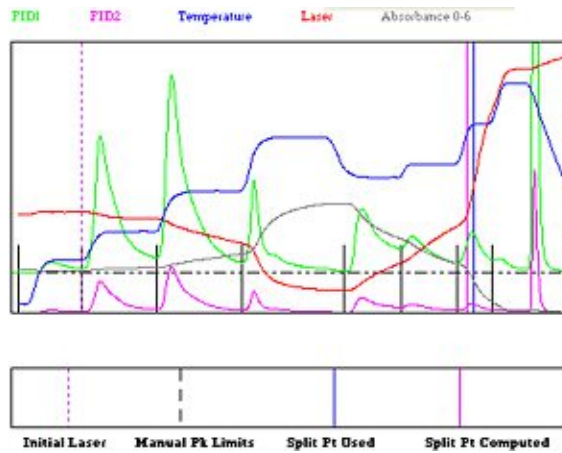


Figure 84: Thermogram of S4/3 from the comparison experiment Kolm Saigurn measured with EUSAAR2; automatic and manual split point are shown

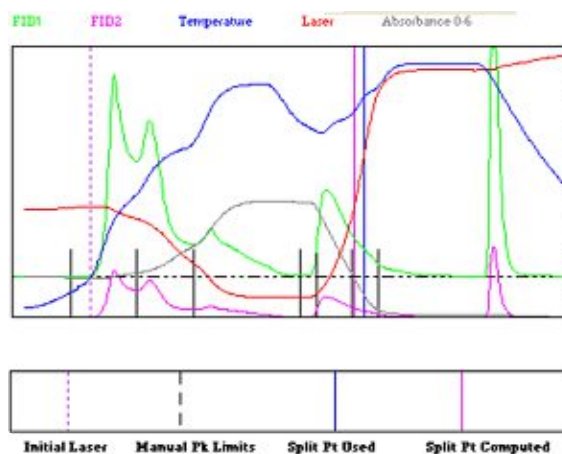


Figure 85: Thermogram of S4/3 from the comparison experiment Kolm Saigurn measured with NIOSH5040_Kolm; automatic and manual split point are shown