



TNA User Report

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Project title	Direct aerosol chemistry investigations with advanced mass spectrometric methods
Name of the accessed chamber	PACS-C3
Number of users in the project	1
Project objectives (max 100 words)	To further understand the physico-chemical properties of SOA, good knowledge on the chemical composition is inevitable. Nevertheless, scientific progress in SOA chemistry is still hampered by the lack of analytical methods that comprehensively and quantitatively characterize the organic composition of particulate matter in the atmosphere. Therefore we deployed advanced mass spectrometric methods to analyze the chemical composition of SOA in unprecedented detail.
Description of work (max 100 words):	In this project, ten chamber studies of SOA formed from α -pinene, toluene, cresol and a mixture of α -pinene and toluene were performed at the PACS-C3 chamber. In addition to the current state-of-the-art high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS), the Paul Scherrer Institute has deployed their very recently developed extractive electro-spray ionization TOF-MS (EESI-TOF). These two instruments were complemented by Ionicon's modular "Chemical Analysis of Aerosol Online" (CHARON) particle inlet coupled to a new-generation proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF 6000 X2).

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¹ Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Markus Müller

Chamber name and location: PACS-C3, Paul Scherrer Institut, Villigen, CH

Campaign name and period: 16.04.2017 – 30.04.2017

Text:

Introduction and motivation

Secondary organic aerosol (SOA) directly impacts air quality and affects climate change¹⁻⁴. To further understand the physico-chemical properties of SOA, good knowledge on the chemical composition is inevitable. Nevertheless, scientific progress in SOA chemistry is still hampered by the lack of analytical methods that comprehensively and quantitatively characterize the organic composition of particulate matter in the atmosphere.⁵

The use of advanced mass spectrometry techniques has recently been evaluated to fully characterize atmospheric organic carbon and to assess current capabilities and remaining gaps.⁶ For this study, two next generation emerging analytical techniques for characterizing particulate organic carbon were deployed. In addition to the current state-of-the-art high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS⁷), the Paul Scherrer Institute deployed their very recently developed extractive electro-spray ionization TOF-MS (EESI-TOF⁸) operated in Na⁺ mode. These two instruments were complemented by Ionicon's modular "Chemical Analysis of Aerosol Online" (CHARON⁹) particle inlet coupled to a new-generation proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF 6000 X2).

Scientific objectives

This very unique set of advanced direct instrumentation allows us to further reduce the gaps of knowledge on the chemical composition and photochemical transformation of complex systems. Therefore a set of SOA experiments with α -pinene (O₃ and HONO as oxidants) as well as toluene and cresol (with HONO) were conducted using PSI's PACS-C3 facility.

In addition, evaporation studies based on isothermal dilution were conducted to give clear feedback on the saturation mass concentrations of the bulk SOA (by TOF-AMS) and of individual SOA compounds (by EESI-TOF and CHARON PTR-TOFMS). So far there are limited studies addressing the volatility of individual components that make up SOA during iso-thermal evaporation and these studies will further our understanding of this process for the scientific community.

After analysis of the full set of experiments, we anticipate a unique set of data that allows for an unprecedented comparison of current and future state-of-the-art instruments for the direct analysis of the chemical composition of organic aerosol. The direct comparison will help us to understand their advantages and limitations, which ultimately will make it possible to improve our understanding of each instrument and further our ability to develop new technologies.

Reason for choosing the simulation chamber

The PACS-C3 chamber is an ideal location for the planned and successfully conducted experiments. The instrumental capabilities present include a full set of state-of-the-art instrumentation (PTR-TOF-MS,

TOF-AMS, SMPS, monitors for NO_x and O₃ and others). In addition, PACS-C3 successfully deploys an emerging new-generation analytical method based on extractive electro-spray ionization (EESI-TOF) for a real-time chemical characterization of organic aerosol. This comprehensive analytical setup combined with the support of a well experienced staff of PSI allows for chamber experiments and studying of the production and composition of SOA at a world leading level.

Therefore the PACS-C3 facility at PSI is the perfect location to compare the performance of our new-generation CHARON PTR-TOF 6000 particle analyzer to existing and other newly emerging advanced mass spectrometric methods and to gain new insights in SOA chemistry and properties.

Method and experimental set-up

Experiments were conducted in PSI's 9 m³ temperature stabilized cool chamber facility. Details on the chamber, the injection system and attached analytical instrumentation are discussed elsewhere¹⁰. During this study, 10 SOA studies and one blank experiment were conducted. SOA precursor compounds ranged from the aromatic species of toluene and cresol, a major first order reaction product of gas-phase toluene oxidation, to the biogenic terpenoid α -pinene. Oxidants of choice were HONO for the aromatic compounds and HONO or ozone for α -pinene. A basic experimental overview is summarized in Table 1.

Table 1. Overview on the 11 conducted experiments.

#	date	SOA precursor	oxidant	seed	Comments
1	16.04.18	toluene	OH	ammonium sulfate (60 $\mu\text{g m}^{-3}$)	
2	17.04.18	toluene + α -pinene	OH	no seed	lights off after 6h
3	18.04.18	toluene	OH	ammonium sulfate (37 $\mu\text{g m}^{-3}$)	lights off after 4h
4	19.04.18	α -pinene	OH	no seed	
5	20.04.18	α -pinene	OH	no seed	lights off after 2h
6	22.04.18	α -pinene	O ₃	no seed	lights on after 4h
7	23.04.18	α -pinene	O ₃	no seed	
8	24.04.18	cresol	OH	no seed	
9	25.04.18	cresol	OH	ammonium sulfate (38 $\mu\text{g m}^{-3}$)	
10	26.04.18	α -pinene	OH	ammonium sulfate (36 $\mu\text{g m}^{-3}$)	low loading
11	27.04.18	chamber blank	OH	ammonium sulfate (21 $\mu\text{g m}^{-3}$)	

In addition to the standard analytical instrumentation, a TOF-AMS⁷, an EESI-MS⁸ (operated in Na⁺ ionization mode; both operated by PSI) and Ionicon's CHARON PTR-TOFMS⁹ were attached to a 12 mm stainless steel unheated particle sampling line. Sampling flows for the individual instruments were around 1000, 80 and 600 ml/min, respectively.

Ionicon's CHARON PTR-TOFMS detects sub- μm particulate organic matter on-line and in real-time down to 200 pg m^{-3} mass concentrations.¹¹ Soft proton transfer from hydronium ions quantitatively ionizes almost the full range of organic analytes in the intermediate to low volatility range. The high

mass resolution ($R > 6000$) and mass accuracy (< 10 ppm) of the Ionicon PTR-TOF 6000 X2 allows assigning elemental compositions to organic analyte ions over a large mass range.

Preliminary results and conclusions

Data analysis and interpretation is still in progress. Nevertheless, in the following we want to highlight preliminary results of CHARON PTR-TOFMS data by having a detailed look at one α -pinene experiment: experiment 5 (α -pinene + OH).

Figure 1 displays the time series as measured during experiment 5. Lights were turned on at 07:51, lights were turned off at 09:57 and dilution with fresh zero air at 150 lpm started at 13:35 and lasted until 14:03. As no initial seed was in the system, the particle size had to grow to around 170 nm to reach a near-constant particle enrichment factor of the CHARON particle inlet. Therefore, the CHARON PTR-TOFMS significantly underestimates the total mass concentration at the beginning of the experiment but shows near perfect agreement to SMPS mass concentrations after a proper particle size was reached. This result illustrates the good quantitative response of CHARON PTR-TOFMS.

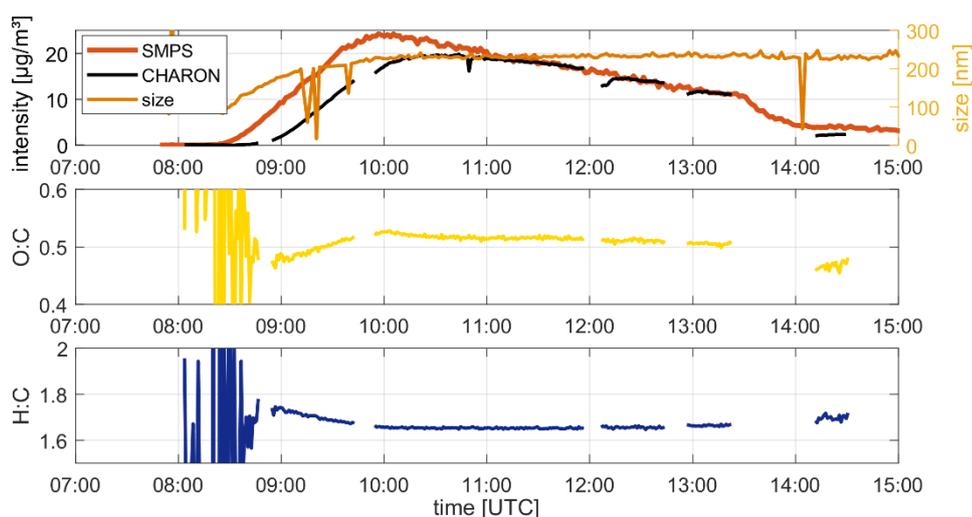


Figure 1. Time-series of the total mass concentration measured by SMPS and CHARON PTR-TOFMS and the evolution of the geometric mean size of the particles' volume distribution (top panel) as measured during experiment 5 (α -pinene + OH). Molecular O:C and H:C ratios as measured by CHARON PTR-TOFMS (middle and bottom panels, respectively).

In addition, Figure 1 illustrates the time evolution of molecular O:C and H:C ratios, two values that clearly reflect the oxidation state of the SOA. During the lights on period, oxidation increases and slightly drops again during lights off. This might be reflected by the importance of O_3 chemistry during the dark period that led to the formation and condensation of less oxidized species to the existing SOA. To illustrate the complexity of the analyzed α -pinene + OH condensed particulate products, Figure 2 displays two mass spectra as measured by CHARON during experiment 5. The high amount of conserved chemical information led to a mass spectrum containing more than 1300 ions. The highest

signal is measured for $C_8H_{11}O_5^+$ (m/z 187.061). Volatility measurements of CHARON PTR-TOFMS data indicate that signals $m/z < 140$ are predominantly formed by ionic fragmentation ($C_{<8}$, $140 < m/z < 230$ are monomers ($C_8 - C_{10}$) and signals of $m/z > 270$ are dimers ($C_{16}-C_{20}$; data not shown).

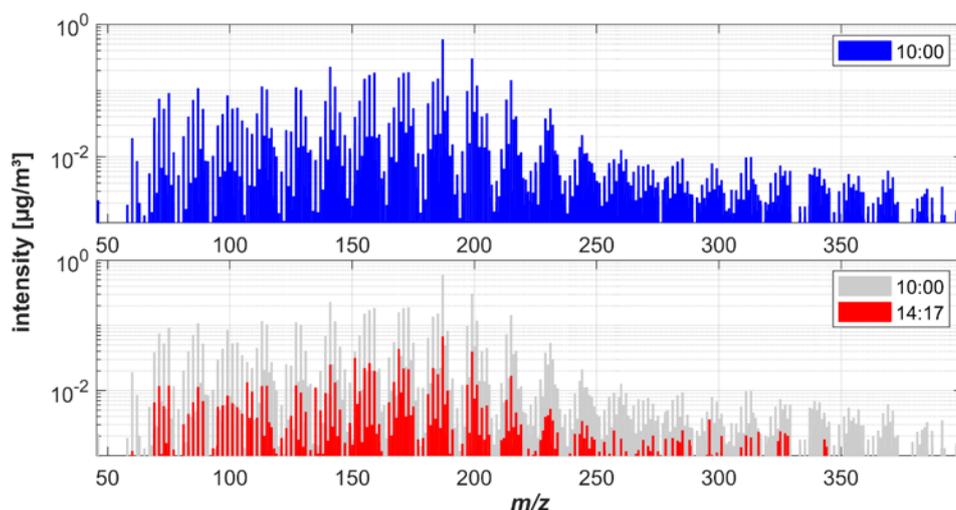


Figure 2. Two CHARON PTR-TOFMS mass spectra as recorded at around 10:00 (maximum concentration; top panel) and 14:17 (after dilution; bottom panel) as measured during experiment 5 (α -pinene + OH).

Outcome and future studies

A very successful set of 11 experiments was conducted during a two week period. During four experiments, CHARON PTR-TOFMS additionally sampled SOA, collected in isothermal evaporation chambers, to assess volatility information. The PACS-C3 facility allowed for flawless experiments with no significant loss of data for all deployed instruments, in particular the CHARON PTR-TOFMS.

Currently, data analysis and interpretation is still work in progress. About one month after finalizing the experiments a merge of results of relevant instruments is just starting. Therefore monthly data meetings are scheduled. The results from this work will be presented at the upcoming annual review meeting of EUROCHAMP, and the evaporation results will be incorporated into a presentation at the international aerosol conference in September 2018. The aim from this work will be to produce a methodological manuscript to be submitted before the end of the year, and drafts of further scientific papers in the same time period.

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