TNA User Report

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Project title	Training in Chemical Analysis of SOA Constituents Using High-Resolution Mass Spectrometry
Name of the accessed chamber	OGTAC CC
Number of users in the project	1
Project objectives (max 100 words)	The aim of the visit to the calibration centre for organic tracer and particulate aerosol constituents (OGTAC CC) of the Atmospheric Chemistry Department (ACD) at TROPOS was to gain insight and training in the chemical analysis of SOA constituents with HR LC/MS
Description of work (max 100 words):	As part of the training, sample preparation and the separation technique LC/MS) were described and explained in great detail. Sample preparation (extraction) was completed under expert supervision. Quantification and data interpretation were done for a wide number of chamber-generated samples. Aside from quantification, non-target approaches were developed together with the participant and applied to the same samples.

Principal Investigator's and group's information	
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Gender	Male
User status[3]	Academic
New user	Yes

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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 EXP= Engineer; ACA= Academic; TEC= Technician.

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: Matthieu Riva
Chamber name and location: OGTAC CC at TROPOS ACD
Campaign name and period: Training in Chemical Analysis of SOA Constituents Using High-Resolution Mass Spectrometry
Text:

Introduction and Motivation

The OGTAC CC is a calibration centre for the analysis of atmospheric organic tracers and particle-phase constituents. This is the first of its kind worldwide, focusing on main constituents of and tracers for secondary organic aerosol (SOA) of biogenic and anthropogenic origin. This individual training course is dedicated to the application of high-resolution mass spectrometry (HRMS) in combination with ultra-high pressure liquid chromatography (UHPLC) to atmospherically relevant aerosol particles and gases. The training will mainly cover targeted as well as untargeted screening methods using UHPLC-ESI/Orbitrap MS and complementary techniques. A special focus of this training course is the analysis of sulphur-containing organic compounds, in particular organosulphates and nitrooxy organosulphates, which are an ubiquitous class of compounds in atmospheric aerosol particles. However, these compounds are rarely analysed on a routine basis because their measurement is typically hampered by a lack of authentic standards and the abundance of yet unidentified compounds.

Scientific objectives

Within the two weeks, the applicant attended lectures on chemical analysis of atmospheric particles using HRMS. In the practical part, filter samples were prepared, extracted and analysed by HRMS. In a first step, important biogenic marker compounds were identified and quantified. Subsequently, the filter samples underwent a comprehensive non-target screening (NTS) method using high-resolution Orbitrap mass spectrometry in combination with ultra-high performance liquid chromatography (UHPLC) to identify and determine sulphur-containing organic compounds in chamber-generated SOA.

Reason for choosing the simulation chamber/ calibration facility

The OGTAC CC was the ideal location to perform this offline chemical analysis as it has the required instrumentation and necessary protocols, as well as the expertise to train and guide visitors. Following training, sample preparation, analysis, and quantification was completed under expert guidance and supervision. In particular, a NTS approach developed at TROPOS allows a semi-automated detection and identification of functionalized organic compounds in SOA particles, and thus, the detection and quantification of organosulphates and nitrooxy organosulphates. The NTS approach combines optimized procedures for sample processing and analysis as well as subsequent software-assisted data analysis. The UHPLC-HRMS system in combination with the NTS approach enabled the applicant to achieve detailed and comprehensive insights into the chemical composition of organic compounds in aerosol samples. Moreover, in complementary targeted analyses, quantification of single compounds was carried out with high sensitivity and low detection limits.

Method and experimental set-up

The filter samples were generated in the aerosol chamber at TROPOS ACD (see Table 1 for details) by oxidizing a-pinene under various conditions, in the presence of NO_x and/or SO_2. For each experimental run, several filter samples were taken at 20 L/min with a sampling time of 30 min. All samples were directly stored at below –18 °C until extraction and analysis. During sample preparation, half of the filter was extracted by ACN/H_2O. Subsequently, the extract was analysed by UHPLC-HRMS according to Brüggemann et al. (Environ. Chem. 2019). Relative quantification of sulphur-containing monoterpene oxidation products was conducted using Xcalibur 4.1 (ThermoFisher Scientific, USA) from peak areas of the corresponding $[M–H]^-$ ion signals in full scan mode (*m/z* 50–750, R = 70k). In a NTS approach, all LC-HRMS data obtained in full scan and ddMS2 mode were analyzed using the open-source software package MZmine 2.51 (http://mzmine.github.io, Pluskal et al., 2010, 2012). The automated workflow comprised: signal detection in MS and MS/MS spectra, filtering of shoulder peaks in the mass spectra, chromatogram building, chromatogram deconvolution, grouping of isotopes / adducts / complexes, and retention time alignment. Additionally, MFs were assigned using the SIRIUS module, which considers isotopic patterns and MS/MS fragmentation spectra during formula prediction of detected compounds.

Table 1: Overview on the experimental conditions during the chamber runs.

experiment	type	seed	oxidant	α-pinene / ppb	NO / ppb	SO_2 / ppb
1	NPF; RH = 0-50%	-	H_2O_2 + hv -> OH	60	15	15
2	acidic seed; RH > 50%	$Na_2{}^{34}SO_4$ / H_2SO_4	H_2O_2 + hv -> OH	60	15	15
3	acidic seed; RH > 50%	$Na_2{}^{34}SO4$ / H_2SO_4	NO_2 + O_3 -> NO_3	60	0	15
4	acidic seed; RH > 50%	**seed 1** = $Na_2{}^{34}SO4$ / H_2SO_4; **seed 2** = Na_2SO_3 / H_2SO_4	O_3	60	15	15
5	acidic seed; RH > 50%	**seed 1** = $Na_2{}^{34}SO_4$ / H_2SO_4; **seed 2** = Na_2SO_3 / H_2SO_4	H_2O_2 + hv -> OH	60	15	15
6	neutral seed; RH > 50%	**seed 1** = $Na_2{}^{34}SO_4$; **seed 2** = Na_2SO_3	H_2O_2 + hv -> OH	60	15	15
7	neutral seed; RH > 50%	**seed 1** = $Na_2{}^{34}SO_4$; **seed 2** = Na_2SO_3	NO_2 + O_3 -> NO_3	60	0	15
8	neutral seed; RH > 50%	**seed 1** = $Na_2{}^{34}SO_4$; **seed 2** = Na_2SO_3	O_3	60	15	15
9	NPF; RH = 50-25%	-	H_2O_2 + hv -> OH	100	5	15

Preliminary results

From the untargeted screening of the LC-MS data of the filter samples and the assignment of molecular formulas, 147 potential organosulphates were detected. As shown in Figure 1, these compounds cover a wide range of molecular weights and retention times from *m/z* 150 to 620 Da and 1 to 15 min, respectively.

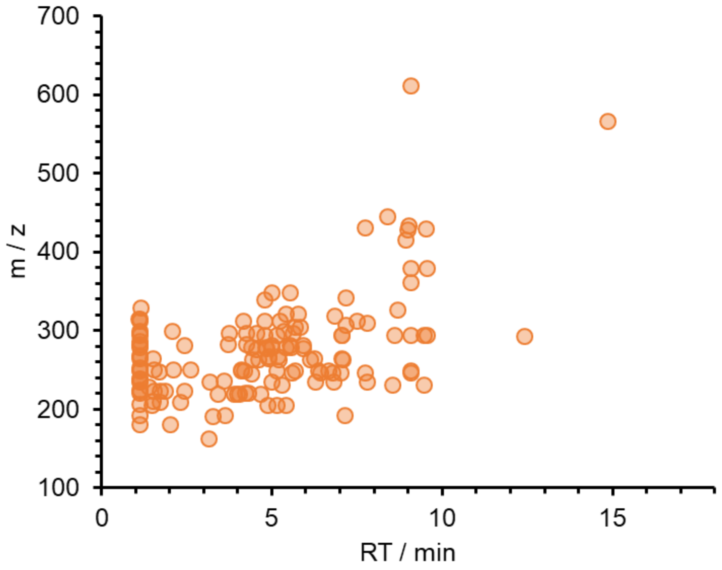

Figure 1: Mass to charge (*m/z* of $[M–H]^-$) and retention time (RT) of tentatively identified organosulphates from filter extracts of the chamber experiments.

Remarkably, merely four formulas for nitrooxy organosulphates were determined among the 147 organosulphates. In particular, a nitrooxy organosulphate at *m/z* 294.0653 ([M-H]-) with the molecular formula $C_{10}H_{17}NO_7S$ was observed in several filter extracts for different experiments with enhanced intensities, yielding up to 7 isomeric structures. Previously, this compound was observed in numerous laboratory and field studies. However, a detailed investigation of its formation pathway and conditions was not conducted so far.

As shown in Figure 2, enhanced concentrations of this species were particularly observed for chamber experiments with nitrate radicals (NO_3) as primary oxidant, in which night-time chemistry was simulated. Largest abundances were observed when neutral seed particles were injected into chamber. Nonetheless, also with acidic particles significant amounts of this compound were determined. Besides nitrate-induced oxidation of α-pinene, also the oxidation through ozonolysis yielded enhanced abundances for this analyte. Nonetheless, in this case the acidity effect was reversed, giving larger abundances for acidic seed particles. In contrast, for all OH radical-induced experiments merely weak signals were determined at *m/z* 294.0653, thus indicating daytime chemistry to be of minor importance in the formation of nitrooxy organosukphates. These preliminary results warrant further studies on the formation mechanism of organosulphates, and in particular nitrooxy organosulphates.

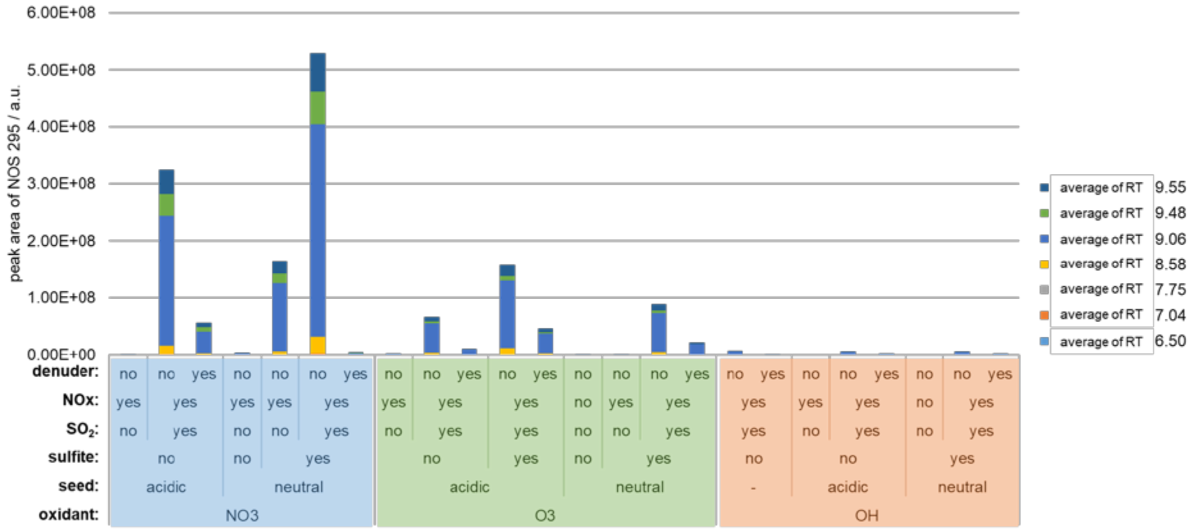

Figure 2: Abundance of the detected isomers of NOS 295 in filter extracts from the conducted chamber experiments.

Outcome and future studies

The main objectives of the proposed TNA activity were successfully completed. A high level of training was received and each of the samples were analysed, generating a reliable data set. The findings of this project will provide new insights into chemical composition. More efforts will be spend to evaluate and corroborate the findings of this project.