TNA User Report

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Project title	EESI-Vocus Optimization, Kalibration, and Evaluation (EVOKE)
Name of the accessed chamber	PACS-C3
Number of users in the project	3
Project objectives (max 100 words)	The scientific objective was to evaluate the dual gas- and particle-phase EESI-TOF's quantification capabilities via comparisons with reference measurements obtained from a new Vocus-PTRMS. Vocus-PTRMS is ideal for use as a reference detection scheme because compared to most chemical ionization schemes, it has similar detection sensitivities for different chemicals. Moreover, the Vocus' inlet is significantly improved from older PTRMS instruments, allowing it to efficiently detect low volatility molecules that form aerosols and would be detected by the EESI-TOF. Experimental modulation of gas/particle partitioning allows the Vocus-PTRMS to serve as a calibration reference for both gas- and particle-phase EESI-TOF measurements.
Description of work (max 100 words):	The work here included generating oxygenated gas- and aerosol-phase products in the PSI environmental chamber and measuring them simultaneously with a dual-mode EESI-TOF and Vocus PTRMS. In many different experiments, we used secondary organic aerosol precursors that simulated rural (monoterpenes, sesquiterpenes), urban (aromatic hydrocarbons, alkanes), and marine (dimethyl sulfide) emission environments. After generating secondary compounds, we injected seed to alter the gas/particle partitioning states. The study used both the PSI atmospheric simulation chamber and a flow tube to assess the sensitivity of the suite of products produced via these oxidation reactions.

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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: Jordan Krechmer
Chamber name and location: PACS-C3, Paul Scherrer Institute, Switzerland
Campaign name and period: EESI-Vocus Optimization, Kalibration, and Evaluation (EVOKE)
Text:

Introduction and motivation

Atmospheric organic aerosols are a persistent cause of human disease and affect the climate by altering cloud formation. We still are largely unable to predict their concentration and composition, partially due to a lack of sensitive, real-time, and chemically-specific measurements of atmospheric aerosol constituents and aerosol-forming low-volatility gases. Recently, several new mass spectrometric techniques that utilize chemical ionization have been developed to address these needs. One of the most promising techniques within this context is the dual inlet Extractive Electrospray Ionization Time-of-Flight Mass Spectrometer (EESI-TOF) which allows for real-time, online chemical characterization of aerosol constituents in the gas and particle phases without thermal decomposition or ionization-induced fragmentation. Interpretation of the EESI-TOF measurements, however, are still limited by the need for careful evaluation of the technique's quantification capabilities over the wide range of different organic compounds present in

atmospheric aerosols. Furthermore, there is a great need for simultaneous measurements of aerosol partitioning in both the gas- and particle-phase.

Scientific objectives

The scientific objective of this project is to evaluate the dual gas- and particle-phase EESI-TOF's quantification capabilities via comparisons with reference measurements obtained from a new Vocus proton-transfer reaction mass spectrometer (Vocus-PTRMS). Vocus-PTRMS is ideal for use as a reference detection scheme because compared to most chemical ionization schemes, it does not have widely varying species-dependent detection sensitivities. Moreover, the Vocus' inlet is significantly improved from older PTRMS instruments, allowing it to efficiently detect low volatility molecules that form aerosols and would be detected by the EESI-TOF. Experimental modulation of gas/particle partitioning allows the Vocus-PTRMS to serve as a calibration reference for both the gas- and particle-phase EESI-TOF measurements.

Reason for choosing station/ infrastructure

The PACS-C3 chamber facility is an advanced chamber facility with the capabilities to conduct many experiments in succession with a full suite of auxiliary gas- and particle measurement instrumentation, including scanning mobility particle sizers (SMPS), ozone and NOx monitors, and mass spectrometers. It also offers an oxidation flow reactor that can be used in between chamber measurements during cleaning periods.

Method and experimental set-up

Ozonolysis and OH-aromatic oxidation of monoterpenes, xylenes, and trimethyl benzene precursors were performed in a flow tube reactor under dry conditions. Seed particles were introduced as condensation nuclei to promote gas-to-particle partitioning. Particle-phase compounds were measured with an EESI-TOF, which used a 1:1 water:acetonitrile solution containing 240 ppm sodium iodide as the working electrospray fluid. An AMS was used to quantify the inorganic seed and bulk organic concentrations. A Vocus proton-transfer mass spectrometer (Vocus-PTR) was used to quantify lightly-to-moderately oxygenated organic compounds in the gas-phase (Krechmer et al., 2018). As seed particle concentration increased, so did the condensation sink, driving gas-phase depletion and particle-phase growth. The EESI-TOF sensitivity can be derived from the relative changes in EESI-TOF and Vocus-PTR signals.

Preliminary results and conclusions

The EESI-TOF was able to measure O_1 to O_9 oxidation products in the particle phase in response to seed particle injections. Comparison with AMS (Fig. 1a) indicates that EESI-TOF responds quantitatively to the total mass concentration of inorganic seed particles. For OH-cresol oxidation products, for example, the EESI-TOF sensitivity relative to that of Vocus-PTR increases with the organic oxidation state (Fig. 1b). These results show the EESI-TOF's potential to quantify individual ions in complex samples without direct calibration with a chemical standard.

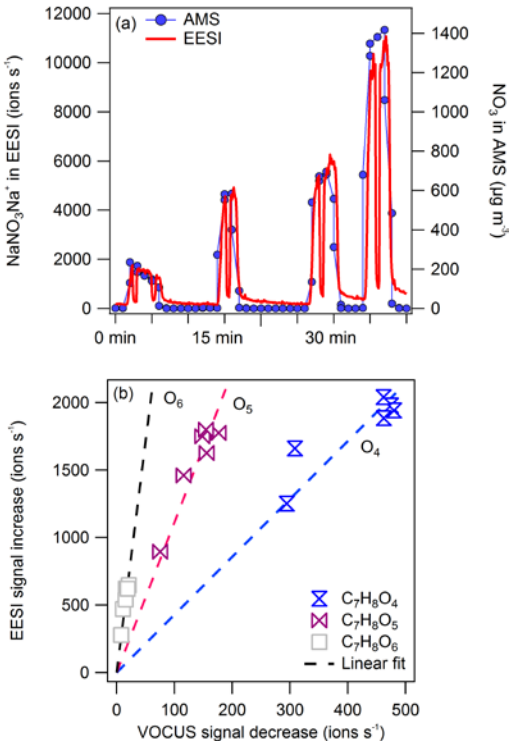

Figure 1. (a) Responses to ammonium nitrate seed particles by the AMS and EESI. The dips in EESI time-series correspond to filtered measurements. (b) increases in the EESI signal and decreased in VOCUS signal due to organic vapour condensation onto seed particles under different condensation sinks

Outcome and future studies

The EVOKE experiments resulted in a rich data set that will help us understand EESI calibration and

Analysis of EVOKE data is ongoing and will eventually be included in a peer-reviewed publication by a PSI postdoctoral scholar. Additional future results will also be presented at the meeting of the European Aerosol Conference (EAC) and AAAR.

References

Lopez-Hilfiker, F. D., Pospisilova, V., Huang, W., Kalberer, M., Mohr, C., Stefenelli, G., Thornton, J. A., Baltensperger, U., Prevot, A. S. H. and Slowik, J. G., *Atmos. Meas. Tech. Discuss.*, doi: 10.5194/amt-2019-45, *in review*, 2019.

Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoermer, C., Deming, B., Kimmel, J., Warneke, C., Holzinger, R., Jayne, J., Worsnop, D., Fuhrer, K., Gonin, M. and de Gouw, J, *Anal. Chem.*, 90, 12011-12018, doi: 10.1021/acs.analchem.8b02641, 2018.