

AQRP Monthly Technical Report

PROJECT TITLE	Apportioning the Sources of Ozone Production during the San Antonio Field Study	PROJECT #	19-025
PROJECT PARTICIPANTS	Aerodyne Research, Inc.	DATE SUBMITTED	Oct 31, 2018
REPORTING PERIOD	From: Oct. 16, 2018 To: Oct 31, 2018	REPORT #	1

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

Task 1: High-Resolution (HR) Analysis

A HR analysis workshop has been completed and was attended by scientists in charge of HR fitting. This course focused on using ToFWare and associated software tools to inspect, mass-calibrate, quality-assure, and fit results from a variety of instruments with time of flight (ToF) spectrometers. The table of contents from notes taken during the course is reproduced as an appendix, showing the breadth of material covered.

Mass-calibrations are the first step in performing a high-quality HR fit. The full PTR-ToF mass-calibration has been accomplished. Partial progress has been made on the two remaining instruments remain: I-CIMS and GC-ToF.

A time-saving peak-identification technique (see “Identify Problems” section) has been developed and tested for the PTR-ToF dataset. It will be applied to the I-CIMS dataset as well, and shows promise for the GC-ToF dataset, which consists of a 3-dimensional dataset with variation in sample time, chromatographic elution time, and mass spectrum.

Pseudo-HR fits (where a set of automatically-identified peak positions are used in a full HR fit) have been done on the PTR-ToF dataset. Results showing the quality of this mass calibration are available in the “Preliminary Analysis” section.

Task 2: PMF Analysis

A training course on PMF analysis has been designed and planned by Manjula Canagaratna.

Task 3: 0D Box Model

0D box model software has been installed on a company server, and is ready for testing using the model-provided test case.

Task 4: Back-Trajectory Footprint Analysis

None yet.

Preliminary Analysis

Mass calibration of ToF datasets is the first and most important step in ensuring good data of the resulting fits. The figure below shows intermediate results of doing the mass calibration for the PTR-ToF dataset. The entire campaign period has been processed. The p1, p2 and p3 parameters are fit parameters to calibrant peaks in the mass spectrum: $p1 \cdot m^{p3} + p2$ where m is the mass. Factors p1 and p2 are seen to vary diurnally, as can be expected when the time of flight region expands and contracts with temperature.

The scale labeled “ppm” is the main data quality indicator for the mass calibration. This metric should not exceed ± 10 ppm, and should not contain glitches. In the figure shown here, the mass call looks adequate except for one or two glitches (e.g. see ppm traces at 5/21/2017). These glitches were fixed in the final step of the mass calibration.

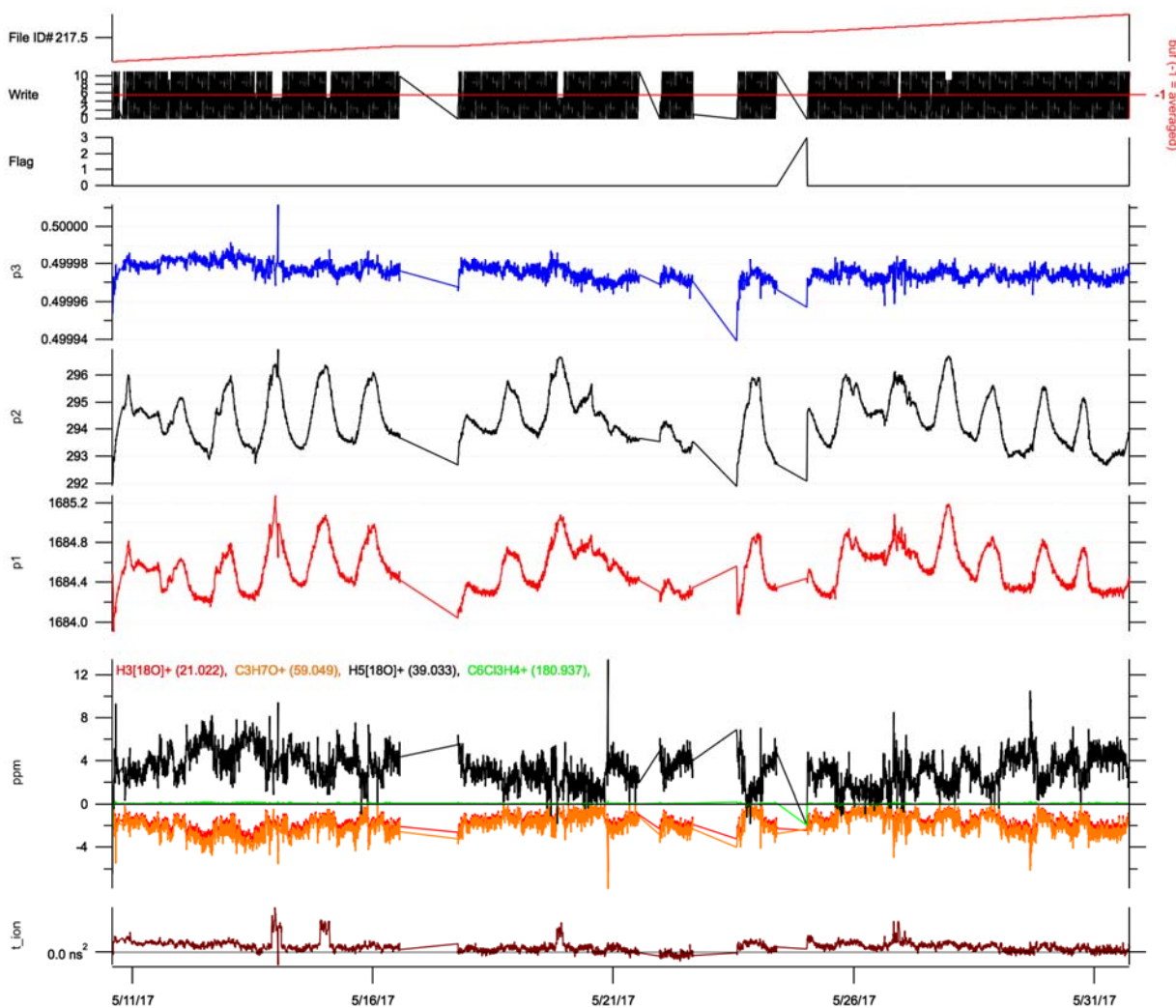


Figure 1. Intermediate mass calibration result for the PTR-ToF instrument, showing generally good mass calibration quality with the ppm scale not exceeding ± 10 ppm. A few glitches can be observed, and were fixed in the final result.

Data Collected

No data will be collected as part of this project. However, data will be generated after completion of Task 1, HR analysis.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

In the proposed research, we outlined a schedule that completed all high-resolution (HR) analysis before starting any positive matrix factorization (PMF) work. A full HR analysis involves both HR fitting and peak identification. While good progress is being made on the fitting, one challenge that has come up in this approach is in identifying the immense number HR peaks manually, only a subset of which are chemically relevant. For example, in the PTR-ToF dataset, many chloride-containing peaks are present and are attributed to the internal mass calibrant in the instrument (i.e. not relevant to San Antonio photochemistry).

The proposed solution is two-fold: 1) use automated peak-finding tools to exhaustively identify peaks in the mass spectra, producing something we are calling a “pseudo-HR fit” and 2) use PMF on this automatically-generated list to separate co-varying groups of compounds. Peaks that correlate to known instrumental artifacts can then be excluded from the labor-intensive peak identification process. Conversely, those groups of peaks that vary along with real chemical tracers like isoprene or aromatics are prioritized for identification. The grouping itself will also help in peak identification by suggesting different chemical classes of compounds.

This proposed solution will be an iterative process of PMF and peak identification. Ultimately, a final HR fit, with a finalized set of identified species, will need to be completed. While on paper this will extend Task 1 beyond the first few months of the project, the total effort expended on this task will still be less than the alternative, and the scientific benefit is large in terms of the number of chemical species identified in the final dataset.

Goals and Anticipated Issues for the Succeeding Reporting Period

In the next reporting period, there are several goals:

- Hold a project meeting to ensure that all researchers have clearly defined tasks to work on and know the broader goals of the project.
- Finish the mass calibration and initial pseudo-HR fitting of the I-CIMS dataset.
- Begin to use learn and use PMF techniques on datasets from the I-CIMS and the PTR-ToF instruments.
- Explore PMF analysis techniques for the GC-ToF dataset with its extra degree of complexity.

No issues are anticipated, besides the delay in project start date, discussed elsewhere.

Detailed Analysis of the Progress of the Task Order to Date

The major challenge in the project in this early stage has been a delay in project start date from July 2018 in the proposal to October 16 2018. This three-month delay means that we will need to compress the schedule of this project in order to accomplish all needed goals in a timely manner. In response to this time pressure, we will start on Task 2 (PMF analysis) ahead of schedule. This has the secondary benefit of revealing a time-saving solution to Task 1 (HR analysis, see “Proposed Solutions” above).

Do you have any publications related to this project currently under development? If so, please provide a working title, and the journals you plan to submit to.

Yes No

Do you have any publications related to this project currently under review by a journal? If so, what is the working title and the journal name? Have you sent a copy of the article to your AQRP Project Manager and your TCEQ Liaison?

Yes No

Do you have any bibliographic publications related to this project that have been published? If so, please list the reference information. List all items for the lifetime of the project.

Yes No

Do you have any presentations related to this project currently under development? If so, please provide working title, and the conference you plan to present it (this does not include presentations for the AQRP Workshop).

Yes No

Do you have any presentations related to this project that have been published? If so, please list reference information. List all items for the lifetime of the project.

Yes No

Submitted to AQRP by Dr. Tara Yacovitch
Principal Investigator

Appendix A: ToFWare Training Course Notes – Table of contents.

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