WEEKLY REPORT FOR WEEK 19
(DECEMBER 10, 2018 – DECEMBER 14, 2018)

Report No. 53005-81-RPT-030
Revision 0

September 2019

Prepared for:

Washington River Protection Solutions, LLC
P.O. Box 850
Richland, WA 99352

Subcontract 53005, Release 81

Prepared by:

TerraGraphics Environmental Engineering, Inc.
2926 E. Ainsworth
Pasco, WA 99301

TerraGraphics
www.terragraphics.com

Approval Form

Prepared by:

Date: 09/10/2019

Tyler Williams

Reviewed by:

Date: 09/10/2019

Matthew Erickson, Ph.D.

Approved by:

Date: 09/10/2019

Rich Westberg

Record of Revision

Revision	Date	Pages/Sections Changed	Brief Description
0	09/2019	All	Original Issue.

Table of Contents

Figures

Acronyms

ML	Mobile Laboratory
NDMA	N-nitrosodimethylamine
PST	Pacific Standard Time
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
SME	Subject Matter Expert
SOW	Statement of Work
SRI	Selective Reagent Ionization
VOC	Volatile Organic Compound

1.0 DECEMBER 10, 2018 – MOBILE LABORATORY MAINTENANCE AND TESTING

All times reported in this document are recorded in Pacific Standard Time (PST).

1.1 Summary

On December 10, 2018, the Mobile Laboratory (ML) operators arrived at 09:30 and began working on assembling a rack for the interior of the ML. NO^+ mode testing on the Proton Transfer Reaction – Mass Spectrometer (PTR-MS) was initiated at 10:17. The PTR-MS began a zero-air and a multipoint calibration and the Volatile Organic Compound (VOC) mix standard was started 18 minutes later. At 11:39, Cylinder CC707561, which contained 5.22 ppm of 1,3-butadiene along with other constituents, was connected and two auto multipoint calibrations were performed. At 13:44, Cylinder CC496322, which contained only 1.06 ppm of N-nitrosodimethylamine (NDMA) and nitrogen, was connected and a new auto multipoint calibration began. At 14:35, 15:27, and 16:19, more multipoint calibrations were started on the PTR-MS for NDMA.

Figure 1-1 below shows the sequence of calibrations run on the PTR-MA, selecting for analytes of particular interest. The red trace shows the two multipoint calibration sequences performed for 1,3-butadiene, located at m/z 54 in NO^+ mode, in the early afternoon. The blue trace shows the four multipoint calibrations performed for NDMA, at m/z 74 in NO^+ mode, through the rest of the afternoon. The green and gray trace represent 2,4-dimethylpyridine (m/z 107 in NO^+), also present in Cylinder CC707561, and a 2,4-dimethylpyridine-NO cluster formed by the union of the analyte and the NO^+ reagent ion, 30 amu higher in the mass scale at m/z 137. Nothing else in the certified gas standard cylinder could account for a mass appearing at that m/z in the mass spectrum.

Despite not being the focus of the analysis in the multipoint calibration, it can be easily observed that 2,4-dimethylpyridine has some conditioning effects occurring, where no steady-state equilibrium was ever reached at any calibration level for a prolonged period of time. This is denoted by the tailing behavior and lack of plateaus present in the green trace. Additionally, after conditioning the calibration lines for several hours, it can be observed that the 2,4-dimethylpyridine off-gassed from the calibration lines throughout the NDMA calibrations, despite not being present in the NDMA standard cylinder. This issue is somewhat alleviated in the ML's actual sampling line, due to heated lengths of line preventing the worst of the line losses due to chemical adsorption to the walls of the inlet tubing. Also of note is that 2,4-dimethylpyridine seems to readily cluster with the NO^+ reagent ion, producing an unintended byproduct of the NO^+ reaction chemistry at m/z 137. It is possible this tends to appear in a specific, predictable ratio with the 2,4-dimethylpyridine peak under steady-state conditions.

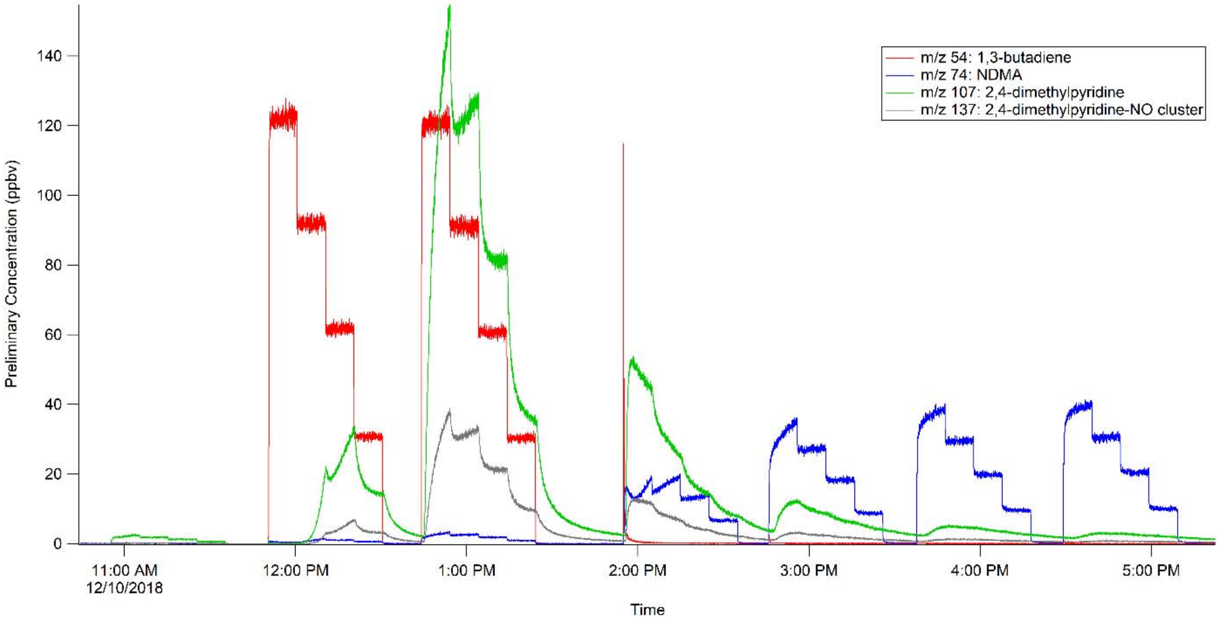

Figure 1-1. Time Series Plot of Analytes of Interest for Calibration Sequences Performed on December 10, 2018.

Figure 1-2 shows the average mass spectra at m/z 54 obtained during each level of the second multi-point 1,3-butadiene calibration, as well as for the zero air. No counts were apparently detected in the zero-air at m/z 54, meaning that the signal encountered during the calibration sequence can be solely attributed to the gas standard cylinder.

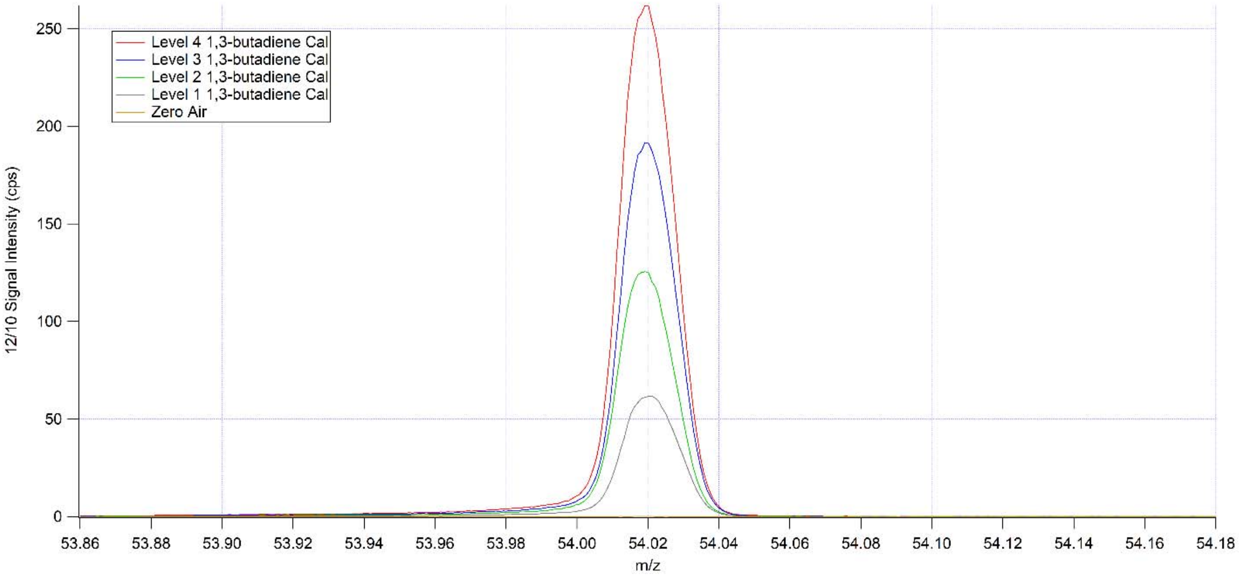

Figure 1-2. Average Mass Spectra at m/z 54 for 1,3-butadiene at Multiple Calibration Levels in NO$^+$ Mode.

Figure 1-3 shows a preliminary time-series plot of the second NO$^+$ multipoint calibration performed using Cylinder CC707561, focusing on 1,3-butadiene. The second calibration curve is the focus of this preliminary discussion due to the Subject Matter Expert's (SME's) opinion that the second multipoint calibration obtained was of higher quality. This plot serves as a visual aid for the varying calibration levels obtained during testing. Further testing will be done to empirically characterize the reaction kinetics of NO$^+$ and analytes of interest and is considered an important part of the conversion between the instrument's observed ion counts and actual ambient concentration.

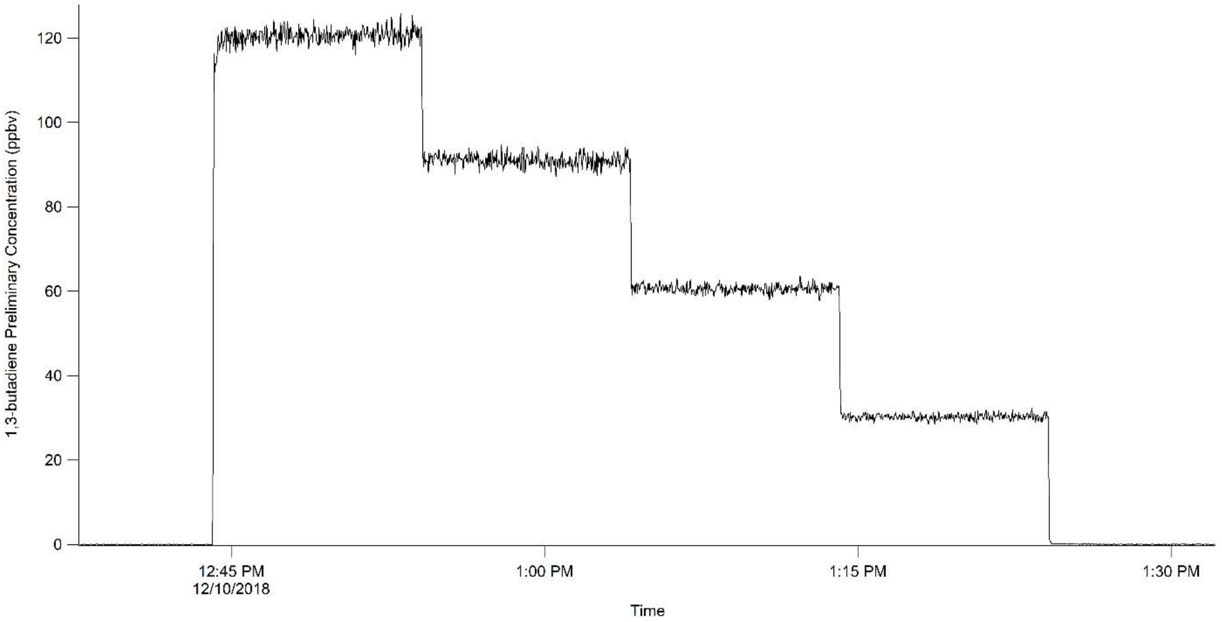

Figure 1-3. Preliminary Time Series Plot of 1,3-butadiene at Multiple Calibration Levels in NO$^+$ Mode.

Figure 1-4 shows the average mass spectra at m/z 74 obtained during each level of the fourth multipoint NDMA calibration, as well as for the zero-air. No counts were apparently detected in the zero-air at m/z 74, meaning that the signal encountered during the calibration sequence can be solely attributed to the gas standard cylinder.

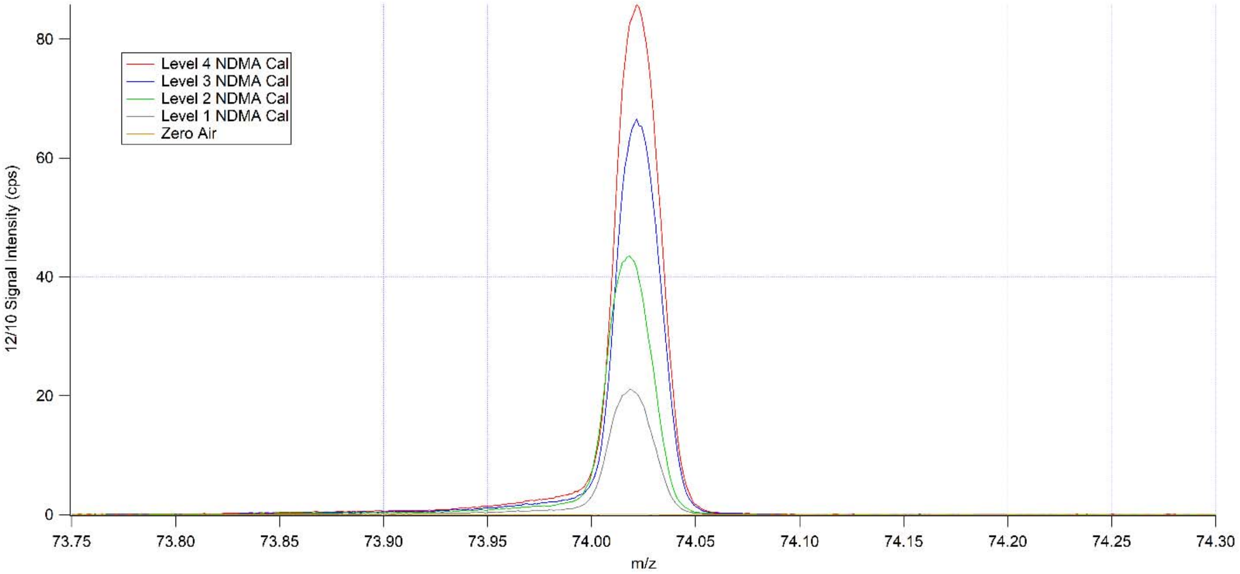

Figure 1-4. Average Mass Spectra at m/z 74 for NDMA at Multiple Calibration Levels in NO$^+$ Mode.

Figure 1-5 shows a preliminary time-series plot of the fourth NO$^+$ multipoint calibration performed using Cylinder CC496322, focusing on NDMA. The fourth calibration curve is the focus of this preliminary discussion due to the SME's opinion that the fourth multipoint calibration obtained was of highest quality. As can be observed in Figure 1-1, it took several multipoint calibration sequences to obtain a relatively consistent measurement, likely due to NDMA conditioning effects. These effects will be significantly less pronounced when sampling through the ML's main inlet line due to heating. This plot serves as a visual aid for the varying calibration levels obtained during testing. Further testing will be done to empirically characterize the reaction kinetics of NO$^+$ and analytes of interest and is considered an important part of the conversion between the instrument's observed ion counts and actual ambient concentration.

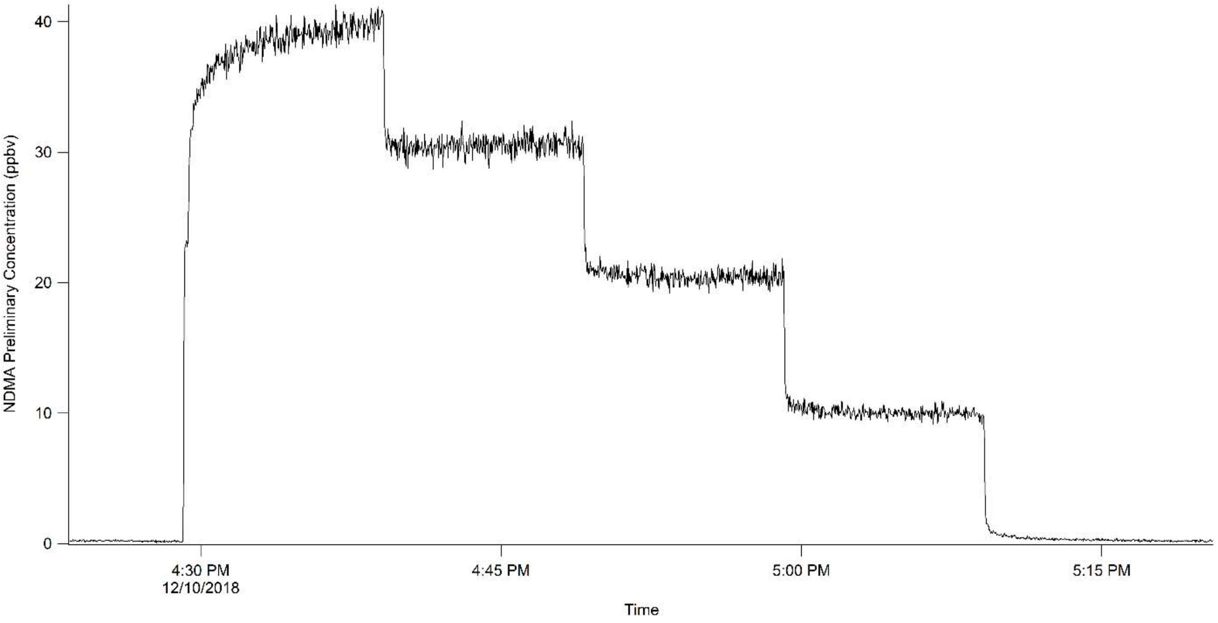

Figure 1-5. Preliminary Time Series Plot of NDMA at Multiple Calibration Levels in NO$^+$ Mode.

At this point, using the average observed concentrations at each level, the average flow rates recorded in the ML, and the expected concentration of known analytes in the gas standard Cylinders CC707581 and CC496322, a multipoint calibration curve that relates observed to expected concentration can be generated for both 1,3-butadiene and NDMA. It is expected to then apply the slope factors generated using this method to correct for the apparent difference between observed and actual concentrations. This correction factor will take into account the differing selectivity and reaction kinetics between these compounds. Another test (or tests) will then be performed, comparing the corrected concentration values to expected. If the values are in relative agreement, then the correction factor can be assumed to accurately capture the kinetics and can be applied to the reportable data. It is expected that this process will be performed for all analytes specified in the project's Statement of Work (SOW) for NO$^+$ mode, provided an accurate gas standard cylinder for those analytes can be sourced. As such, all concentrations shown in this report are taken to be preliminary values and subject to change upon further testing. The full results of this analysis are pending and expected to be completed as part of the Month 4 Report.

2.0 DECEMBER 11, 2018 – MOBILE LABORATORY MAINTENANCE AND TESTING

2.1 Summary

On December 11, 2018, the ML personnel arrived and continued assembling the rack for the interior of the ML. The new exhaust hose arrived in the mail and was assembled at 09:45. After testing was performed, it was confirmed that the new exhaust hose worked effectively. At 10:41, the PTR-MS was switched to sample zero-air and set to 1000 sccm. A multipoint calibration for the VOC mix standard was performed at 11:00. The calibration flow was set to 20 sccm at 11:58. The PTR-MS was switched to H_3O^+ mode at 12:10 and a new file was created. From 12:21 to 15:54, the PTR-MS was switched between H_3O^+ and NO^+ modes while various tuning changes occurred. Results from testing suggests that the H_3O^+ mode was not ran long enough to achieve equilibrium, thus further testing at a later date will be performed. Figure 2-1 shows a time series plot of the mode switching between H_3O^+ and NO^+ performed during the afternoon on December 11, 2018. The red trace represents counts of the NO^+ ^{15}N isotope present at m/z 31, one unit away from the actual NO^+ reagent ion, which saturates under typical operation. It is normally taken to be an analogue for reagent ion abundance, due to its existence in a precise isotopic abundance with ^{14}N NO^+. The black trace represents counts of the H_3O^+ ^{18}O isotope present at m/z 21, two units away from the actual H_3O^+ reagent ion, which saturates under typical operation. It is normally taken to be an analogue for reagent ion abundance, due to its existence in a precise isotopic abundance with ^{16}O H_3O^+. For both of these isotopes, their relative abundances are used to account and correct for changes in actual reagent ion counts during normal instrument operation.

The primary reagent ion at any given time is the trace with higher counts. Thus, while the red trace is higher, the instrument is in NO^+ mode and H_3O^+ ion generation is kept to a minimum. The reverse is true for the black trace. Various tuning parameters were adjusted throughout this time period, as part of an ongoing effort to further understand these parameters' effects on reagent ion abundance. This can be observed in some of the "stair-step" behavior present in both traces while they were the primary ion. This also produced a net doubling of the NO^+ reagent ion while in NO^+ mode over the course of tuning, as shown by the higher plateaus in the red trace towards the latter half of the dataset.

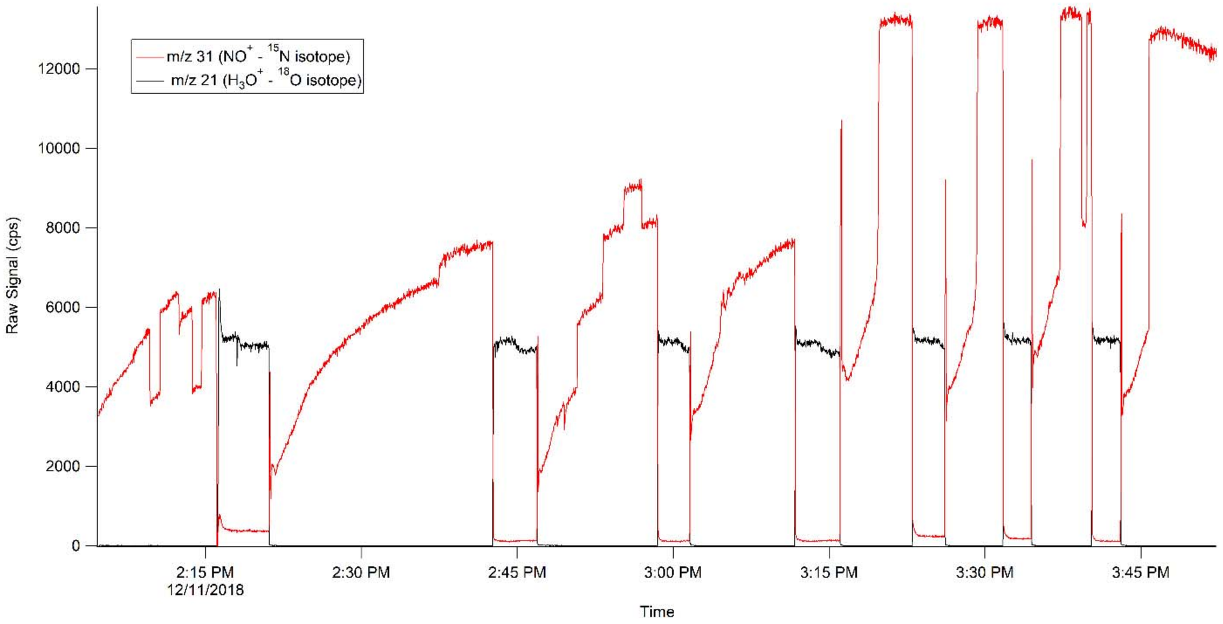

Figure 2-1. Time Series Plot of Raw Counts of Reagent Ion Isotopes While Switching Between NO$^+$ and H$_3$O$^+$ Modes.

Since the instrument was sampling a constant flow of VOC standard during this time period, benzene was used as an example to show the varying effects of the mode switching and tuning performed. This is shown in Figure 2-2, which shows a time series plot of the benzene trace, measured in raw ion counts, in both NO$^+$ and H$_3$O$^+$ mode. The first noteworthy observation is that sensitivity to benzene appears to be higher in H$_3$O$^+$ mode, due to a generally higher raw signal observed at m/z 79 while in this mode, as compared to m/z 78 in NO$^+$. The raw signal obtained while analyzing m/z 78 in NO$^+$ mode was improved upon further tuning and mode switching, as evidenced by the higher counts obtained in the red trace during the latter half of the dataset. More “stair-step” behavior can be observed in the red trace, further evidence of the ongoing tuning taking place during this time. Furthermore, it appears that, even under a constant VOC flow, some equilibration time is observed in the raw counts upon switching modes, even when switching to the more well-understood H$_3$O$^+$ mode. This can be observed in the downward slope of the black trace while H$_3$O$^+$ is the primary ion. Presumably, either a few minutes of equilibration time when mode-switching in the field or the correction factor provided by the observed reagent ion isotope counts (i.e., corrected counts) should account for this. It is also clear that some signal still appears at m/z 79 when the bulk of the observed benzene signal would be predicted to appear at m/z 78 while in NO$^+$ mode, and vice versa. While it would not be wholly expected for the signal to entirely disappear in this scenario, it is not currently fully understood whether this effect is caused by lingering unwanted reagent ion from the previous mode, or other effects.

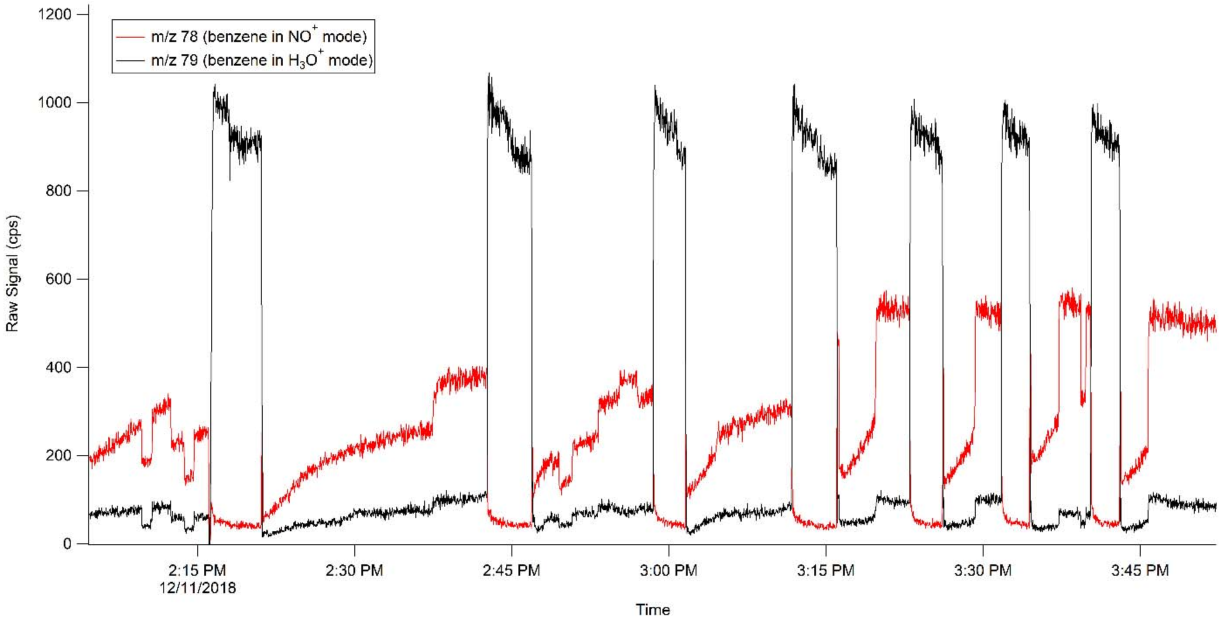

Figure 2-2. Benzene in Both NO$^+$ and H$_3$O$^+$ Mode While Mode-Switching.

3.0 DECEMBER 12, 2018 – MOBILE LABORATORY MAINTENANCE AND TESTING

3.1 Summary

On December 12, 2018, Selective Reagent Ionization (SRI) testing on the PTR-MS was performed. At 10:40, auto switching between H_3O^+ and NO^+ modes on the PTR-MS was tested. An error occurred at 11:19 and a new file was created. The results from the SRI testing completed on December 11, 2018 suggests that the H_3O^+ mode was not ran long enough to achieve equilibrium, thus todays testing will focus on expanding the intervals of each mode. At 11:21, the PTR-MS was set to run SRI testing with 5 minutes in each mode. At 13:12, the PTR-MS SRI testing was increased to 15 minutes in each mode. At 15:45, the PTR-MS duration spent in each mode was increased to an hour.

From 15:45 to 16:15, ML personnel tested the heated line with the use of a temperature controller. The heated line was observed to be getting too much power and rewiring was required. After the line was rewired though the Variac®[1], the power was set at 10%.

---

[1] Variac is a registered trademark of Instrument Service & Equipment, Inc., Cleveland, Ohio.

4.0 DECEMBER 13, 2018 – MOBILE LABORATORY MAINTENANCE

4.1 Summary

On December 13, 2018, ML personnel arrived at 09:00 and began installing the newly completed rack by 09:45. At 10:00, work began on connecting the PTR-MS instrument to the network in the ML. The rack installation was completed by 14:28. The heated line underwent testing at 15:00 and it was confirmed that the new line could maintain a stable temperature of 60 degrees.

5.0 DECEMBER 14, 2018 – MOBILE LABORATORY MAINTENANCE

5.1 Summary

On December 14, 2018, the ML Operators arrived at 08:00 and began programming the PTR-MS to communicate with DAQFactory®[2]. For this to occur, the PTR-MS must transmit information through MODBUS®[3], a communication protocol software. At 10:00, Operators continued the work of programming the Picarro software to communicate effectively with DAQFactory. Testing of the heated line continued from the previous day to ensure that the line could maintain a temperature of 60 degrees. A new box to house the temperature controllers was also constructed.

Review Comment Record removed - Pages 20 and 21.

---

[2] DAQFactory is a registered trademark of AzeoTech, Inc., Ashland, Oregon.
[3] MODBUS is a registered trademark of Schneider Electric USA, Inc., Palatine, Illinois.