

**WEEKLY REPORT FOR WEEK 18
(DECEMBER 3, 2018 – DECEMBER 7, 2018)**

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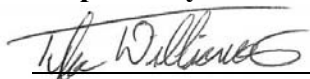
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Record of Revision

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Acronyms

DEF	Diesel Exhaust Fluid
ML	Mobile Laboratory
PST	Pacific Standard Time
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
SME	Subject Matter Expert
VOC	Volatile Organic Compound

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1.0 DECEMBER 3, 2018 – MOBILE LABORATORY MAINTENANCE

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

1.1 Summary

On December 3, 2018, the Mobile Laboratory (ML) was taken to McCurley^{®1} Integrity Dealership to undergo 5,000-mile vehicle maintenance from 09:30 to 15:58. The maintenance performed by the dealership included an oil change, air filter replacement, and replenishing of all fluids [wipe, coolant, diesel exhaust fluid (DEF)]. The ion-source on the Proton Transfer Reaction – Mass Spectrometer (PTR-MS) was cleaned by the Subject Matter Expert (SME), Matt Erickson, at 16:19.

¹ McCurley is a registered trademark of McCurley Integrity Dealerships, LLC, Tri-Cities, Washington.

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2.0 DECEMBER 4, 2018 – MOBILE LABORATORY MAINTENANCE

2.1 Summary

On December 4, 2018, ML Operators arrived at the ML at 08:39. The PTR was reassembled after the previous day's work of cleaning the ion source. The ML Operators received training on the internal components of the PTR-MS. The PTR-MS began pumping down at 09:19. The ML Operators received continuous training on temperature controlling. This training included testing of the temperature controllers with a thermocouple and programming the controllers to maintain a stable temperature on the heated lines in the ML. The remainder of the day was spent on coding the DAQFactory^{®2} software to communicate with the Picarro ammonia analyzer.

² DAQFactory is a registered trademark of AzeoTech, Inc., Ashland, Oregon.

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3.0 DECEMBER 5, 2018 – MOBILE LABORATORY MAINTENANCE AND TESTING

3.1 Summary

On December 5, 2018, the ML Operators continued work on the communication configurations between the DAQFactory and Picarro software. This has required contacting both DAQFactory and Picarro support teams and applying software code for the communication systems to correlate. The PTR-MS H_3O^+ and NO^+ modes were tested from 10:25 to 11:00. While operating in H_3O^+ mode, the water level for the PTR-MS was verified, source conditioning was performed, and stabilization of data was observed. The ML Operators continued training on temperature controllers from 14:00 to 15:00. The ML Operators have been learning how to program the temperature controller-related software Omega^{TM3} Platinum, to maintain 60 degrees, plus or minus 1 degree. At 15:00, a connector was replaced in the ML rear taillight and the bulb in the light was confirmed to be in working order.

³ Omega is a trademark of Omega Engineering, Inc., Norwalk, Connecticut.

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4.0 DECEMBER 6, 2018 – MOBILE LABORATORY TESTING

4.1 Summary

On December 6, 2018, testing of the NO^+ and H_3O^+ modes on the PTR was performed. At 10:15, the PTR was set to operate on H_3O^+ mode. The plumbing used for NO^+ testing required a reconfiguration. At 11:35, the Volatile Organic Compound (VOC) gas flow was initiated and set to 80 sccm by the SME. At 11:52, a leak was identified, and immediately fixed, in the recently reconfigured plumbing. The leak does not affect normal ML operations, since the plumbing is specifically used for testing purposes. The VOC flow was decreased to 60 sccm at 11:55. Three minutes later, the VOC flow was decreased again to 40 sccm. Within the next 7 minutes, the flow was incrementally decreased to zero. At 12:09, the PTR was switched to NO^+ mode and a new file was created.

The previous process was repeated in NO^+ mode, starting with sampling zero-air and then mixing in VOC calibration standard gas by setting the VOC cylinder's mass flow controller (MFC) 80 sccm, then incrementally decreasing the VOC flow by 20 sccm every few minutes. This was performed twice. The goal of this method was to obtain multi-point calibration curves using a multicomponent gas standard. This will provide a rudimentary basis for understanding analytes of interest in the NO^+ mass spectrum at a variety of mixing ratios. The preliminary results discussed below are the results of only analyzing the NO^+ data file, "Cal_181206_D."

One important goal of using this VOC standard cylinder is to understand the relation between furan and isoprene at m/z 68, using NO^+ as the primary reagent ion. Running a mixture containing roughly equal amounts of both of these compounds at multiple mixing ratios helps to boost confidence in the ability of the PTR and associated peak separation algorithm to resolve these compounds in NO^+ mode.

Figure 4-1 shows the average mass spectra at m/z 68 obtained during each level of the multi-point VOC calibration, as well as for the zero-air. It is evident that even at the highest level of VOC flow, there is still sufficient separation between the two peaks. This allows for easy peak separation by Fourier transform, removing the influence of one adjacent peak from the other. Furthermore, based on raw counts observed for the two compounds, it would appear that even with furan and isoprene present at equal concentrations, NO^+ is still over two times more selective towards furan than isoprene. It should also be noted that no counts were apparently detected in the zero-air at m/z 68, meaning that the signal encountered during the VOC calibration can be solely attributed to the VOC standard gas cylinder.

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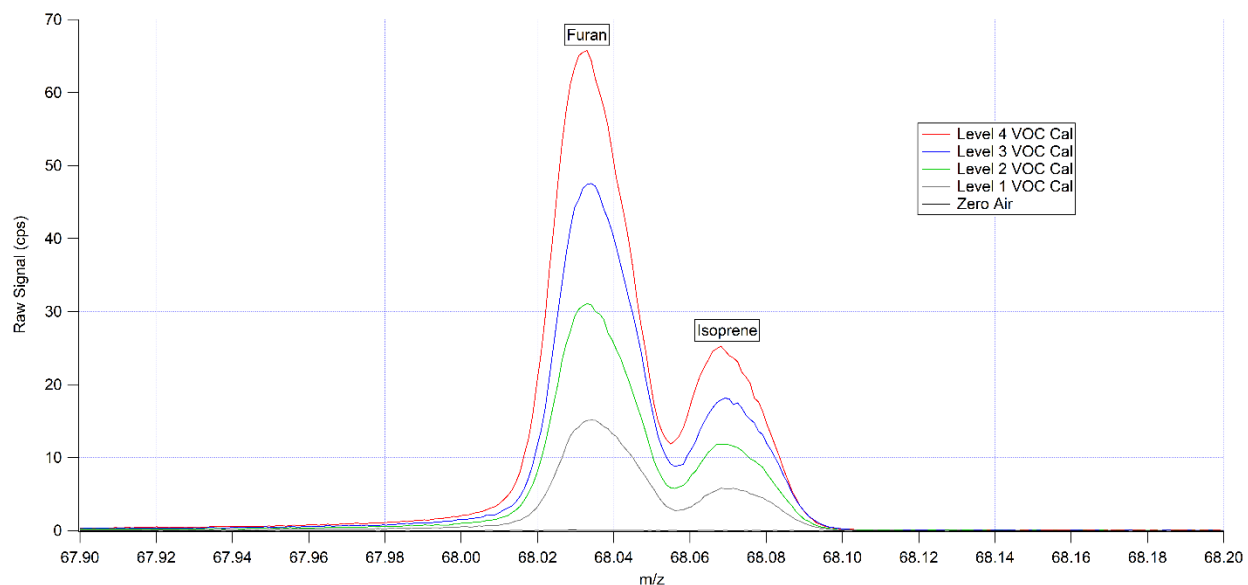


Figure 4-1. Average Mass Spectra at m/z 68 for an Equal Furan-Isoprene Mixture at Multiple Calibration Levels in NO⁺ Mode.

Figure 4-2 shows a preliminary time-series plot of the second NO⁺ multipoint calibration performed in the “Cal_181206_D” file, focusing on furan and isoprene. The second calibration curve is the focus of this preliminary discussion due to the fact that the SME, while performing the tests, was altering instrument parameters in order to achieve an ideal instrument tuning during the first half of the dataset. This plot serves as a visual aid for the varying calibration levels obtained during testing. The apparent difference in signal between the two compounds shown in Figure 4-1 is once again reflected here, as both furan and isoprene should be present in equal concentrations in the VOC standard cylinder. However, Figure 4-2 clearly shows concentrations for isoprene at a quarter or less of the concentration of furan. This is a direct effect of the selectivity of the NO⁺ reagent ion favoring furan over isoprene at this m/z, and the fact that the reaction kinetics of the two species are not yet being factored in. 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.

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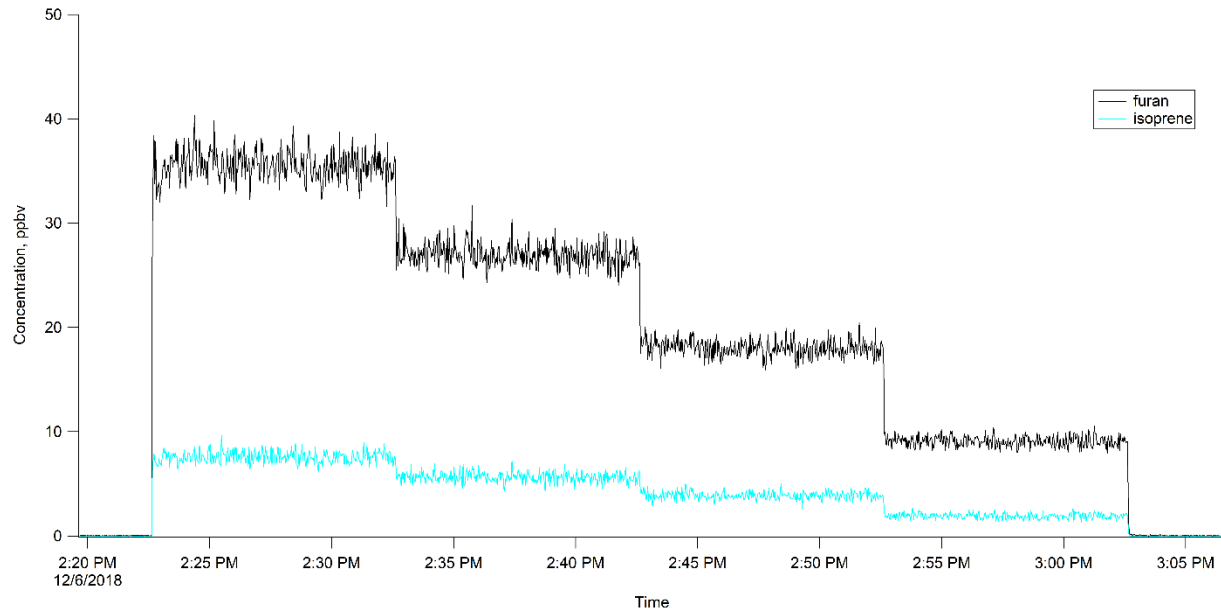


Figure 4-2. Preliminary Time Series Plot of Furan and Isoprene at Multiple Calibration Levels in NO⁺ Mode (Equal Furan/Isoprene Mix).

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 VOC cylinder, a multi-point calibration curve that relates observed to expected concentration can be generated. 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) 306312, "Mobile Laboratory Services and Lease," 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 53005-81-RPT-039, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 4*.

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5.0 DECEMBER 7, 2018 – MOBILE LABORATORY MAINTENANCE AND TESTING

5.1 Summary

On December 7, 2018, the ML operators continued work on the communication configurations between the DAQFactory and Picarro software. Picarro support helped establish what the correct output for the AEDS2077 system should be and the command interface was updated to reflect this. At 10:00, the operators began assembling new racks for the interior of the ML. The PTR underwent further NO^+ mode testing beginning at 11:30. A new auto multi-point calibration sequence was initiated at 11:49. The calibration was restarted at 11:51. The 1 ppmv furan standard was connected, and the auto multi-point calibration was started at 12:51. At 13:42, a second multi-point calibration with furan was initiated. For the purposes of this analysis, and as a contrast/comparison to the furan/isoprene mix data collected on December 6, 2018, only the NO^+ data file, "Cal_181207_B_part_001," was analyzed.

Using one of the multi-point furan calibrations obtained from this data file, a composite of five mass spectra (one for each calibration level and one for zero air) was created. This is shown below in Figure 5-1. The most notable observation is the disappearance of the smaller peak to the right of the furan peak that is observed when sampling the multi-component VOC standard. This is due to the absence of isoprene in the furan standard cylinder, providing valuable validation of the previous peak assignments. Higher counts were observed using the furan standard cylinder due to the cylinder having approximately twice the furan concentration as the VOC multi-mix cylinder. This roughly corresponds to a doubling of observed signal at each calibration level, compared to the December 6, 2018, data. As was the case with the December 6, 2018, data, virtually no signal is detected in the zero air at or near m/z 68.

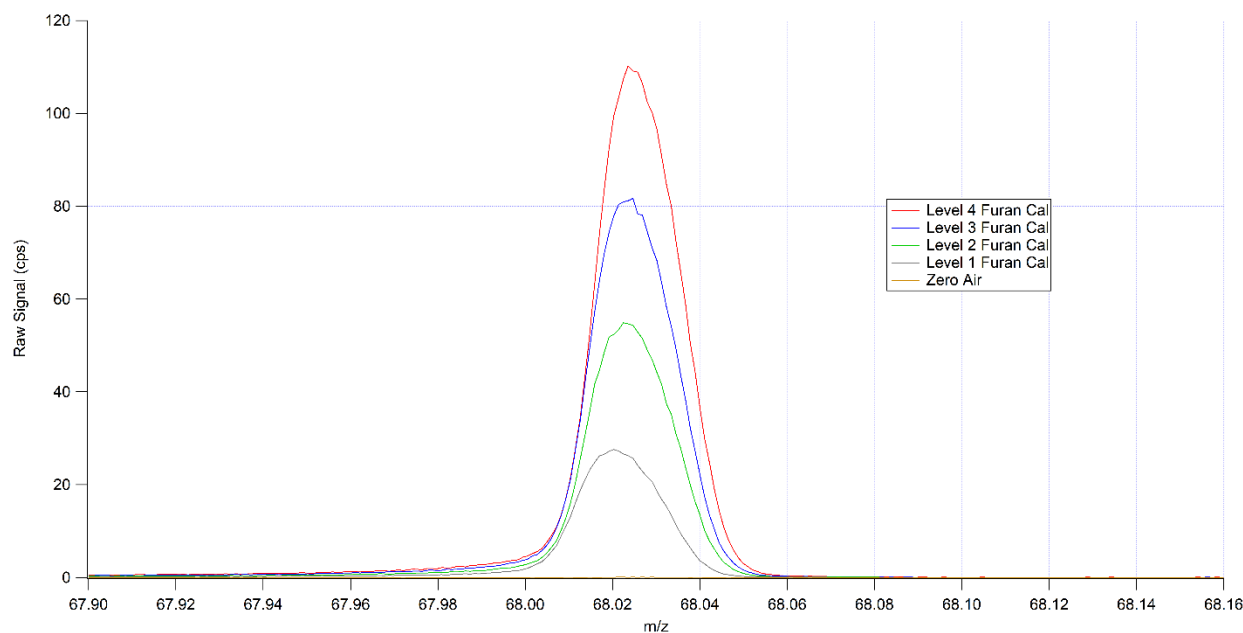


Figure 5-1. Average Mass Spectra at m/z 68 for a Furan Gas Standard at Multiple Calibration Levels in NO^+ Mode.

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Figure 5-2 shows a preliminary time-series plot of one of the NO^+ multi-point furan calibrations performed in the “Cal_181207_B_part_001” file, focusing on furan and isoprene. This plot serves as a visual aid for the varying calibration levels obtained during testing. The lack of isoprene signal observed during this time further validates that no furan signal is being inappropriately misattributed to isoprene, even at relatively high concentrations of only furan. Further testing will be done to improve actual concentration conversions once multi-point calibration curves are obtained for all mixing ratios observed in these datasets. As such, all concentrations shown in this report are taken to be preliminary values and subject to change upon further testing.

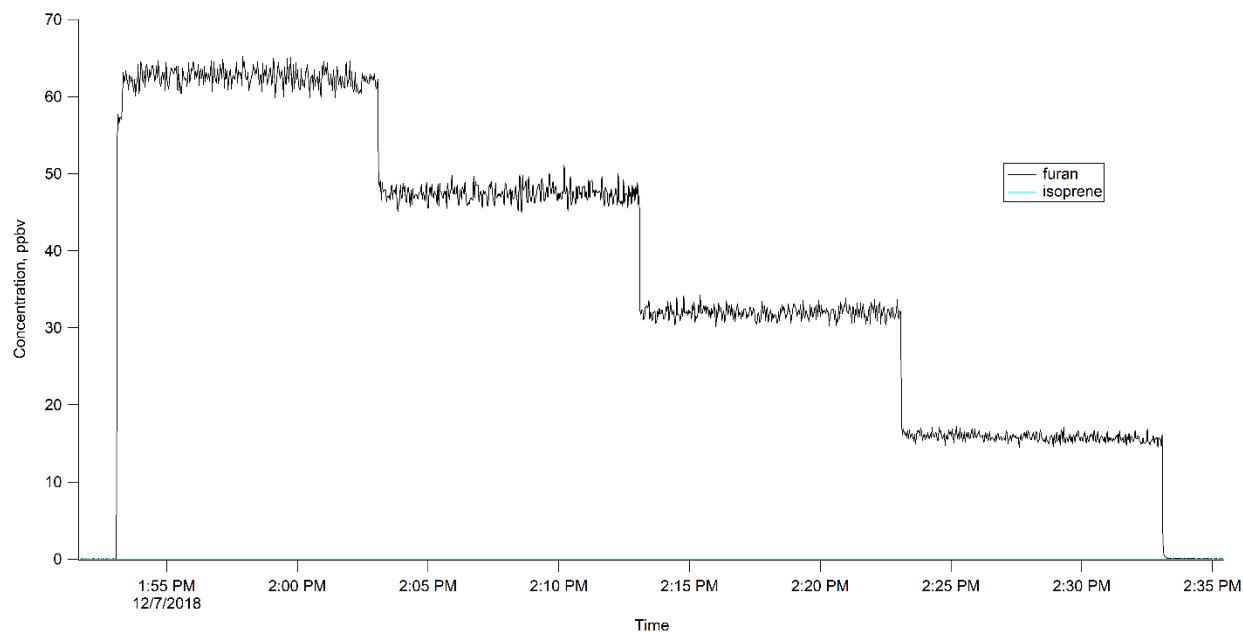


Figure 5-2. Preliminary Time Series Plot of Furan and Isoprene at Multiple Calibration Levels in NO^+ Mode (Furan Only).

In order to further investigate the relation between furan and isoprene at m/z 68 in NO^+ mode, a plot showing comparable levels of gas calibration mixing ratios from both days of testing was created. Figure 5-3 shows an overlay of the level 4 VOC calibration from December 6, 2018, and the level 2 furan calibration from December 7, 2018. The concentration of furan in the multi-component VOC standard is approximately half of the furan only standard, so the level 4 calibration on Dec 6, 2018 is equivalent to the level 2 calibration on Dec 7, 2018. The result was a plot with two overlapping peaks at the same m/z , which provides further evidence of a strong NO^+ mass calibration producing parity between datasets collected on differing days. Furthermore, both peaks seem to maintain the same general shape and width at the base, meaning resolution was comparable between testing a furan/isoprene mix and testing furan alone. However, the signal magnitudes differ at the center of mass for both calibrations as observed in the different y-axis scales.

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This difference was investigated further. Using the certificates for the furan concentrations present in both tanks and the certificates for the MFCs regulating both calibration gas and zero air flow, actual mixing ratios were calculated for both calibration levels investigated in Figure 5-3. The mixing ratio can be calculated as follows:

$$\text{Mixing Ratio} = \frac{\text{Cal gas flow}}{\text{Total gas flow}} * \text{Furan Concentration}$$

The total gas flow is the sum of the calibration gas flow and the zero-air flow. Using this information, the actual mixing ratios for both levels were calculated, and are tabulated below. These values were then compared to the average values observed by PTR during those calibration windows, and a percent difference was calculated.

Table 5-1. Comparison of Furan Calibration Levels.

Calibration Gas + Level	Certified Furan Concentration in Standard (ppbv)	Analytical Uncertainty	Furan Mixing Ratio in Calibration Level (ppbv)	Avg. Furan Concentration as Detected by PTR	Percent Difference (Expected - Observed)
Level 4 12/06, furan/isoprene mix	529	±20%	39.2	35.6	9.16%
Level 2 12/07, furan only	1003	±5%	38.57	31.98	17.1%

The percent difference calculated (expected minus observed) is for the purpose of understanding the error associated specifically with the conversion from ion signal intensity (cps) to parts-per-billion (ppbv). Generating correction factors by comparing the observed concentrations to the expected concentrations will be a focus of upcoming studies and monthly reporting. These correction factors will produce an empirical estimation of the reaction kinetics and allow for adjusting the observed values to align with expected values.

Since the ion signals observed on both days underwent the same process for conversion, a direct comparison between the two calibration levels is valid as well. The percent difference between the two levels as detected by PTR, relative to the level 4 VOC calibration from December 7, 2018, was calculated to be 10.2%. This is within the analytical uncertainty for the VOC gas standard cylinder. Thus, the difference in observed signals in Figure 5-3 can be adequately explained by the uncertainty in the gas cylinder furan concentration. Further sources of error could include unknown fragmentation species appearing at m/z 68 in the VOC mix, artificially raising observed ion counts on December 6, 2018. This will be investigated further in upcoming weekly and monthly reports.

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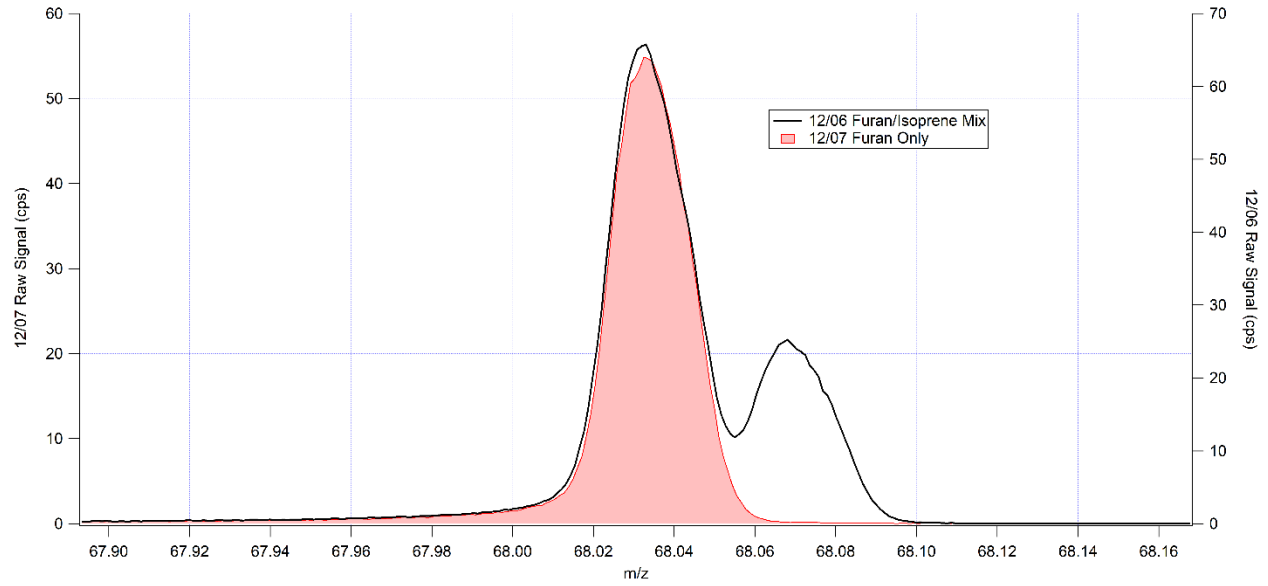


Figure 5-3. Mass Spectra Comparison of 12/06 Furan/Isoprene Mix to 12/07 Furan Only Calibrations.

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6.0 REFERENCES

53005-81-RPT-039, 2019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 4*, TerraGraphics Environmental Engineering, Inc., Richland, Washington.

SOW 306312, 2018, “Mobile Laboratory Services and Lease,” Revision 2, Washington River Protection Solutions, LLC, Richland, Washington.

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