State-of-the-Art
Real-Time, Low Level VOC Monitoring in Stationary and Mobile Platforms

Montrose Environmental

Emerging Technologies

Fence-line Monitoring and Remote Sensing

Presented by

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MONTROSE ENVIRONMENTAL

RJ Lee Group & Montrose Environmental

Montrose Environmental Group and RJ Lee Group have formed a strategic partnership to combine the most advanced, sensitive environmental monitoring technology to enhance Montrose Environmental's existing emissions testing services.

What is PTR-MS?

- Proton Transfer Reaction-Mass Spectrometry
- A chemical ionization-based technique developed in the late 1990s at the University of Innsbruck; became commercially available in 2000
- Capable of making near real-time measurements (between 1-10 Hertz) of whole air samples for a wide variety of organic compounds with detection limits in the PPT regime

What is PTR-MS?

- Common applications/industries
  - Environmental monitoring and research
  - Vapor intrusion studies and indoor air quality
  - Food and flavor science
  - Process monitoring
  - Medicine and biotechnology (breath based)
  - Industrial worker safety
  - Security and law enforcement

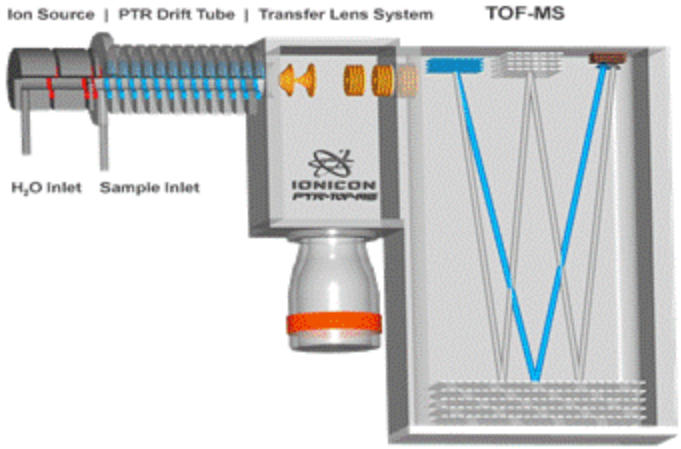
Advantages of PTR-MS

- Detects trace organic vapors (chemicals, drugs, explosives)
- In situ, real-time, continuous results
- Fully automated process – no operator needed
- No sample or reagent preparation
- Scalable and customizable
- Mobile or stationary setup
- Single unit can handle multiple sampling ports

Chemical and Explosive Detection Equipment

RJ Lee Group, Inc. Mobile Laboratory For Real Time Vapor Monitoring

- Proton Transfer Reaction Mass Spectrometry for Real Time VOCs
- Carbon Dioxide Monitor (NIR)
- Ammonia Monitor (CRDS)
- Gas Chromatography/Mass Spectrometry (TO-15, TO-17, Headspace)
- Alternative Sampling Media (TO-11a, TO-15, TO-17, NIOSH 2522, others)
- Weather Station & GPS
- Other Configurations Available

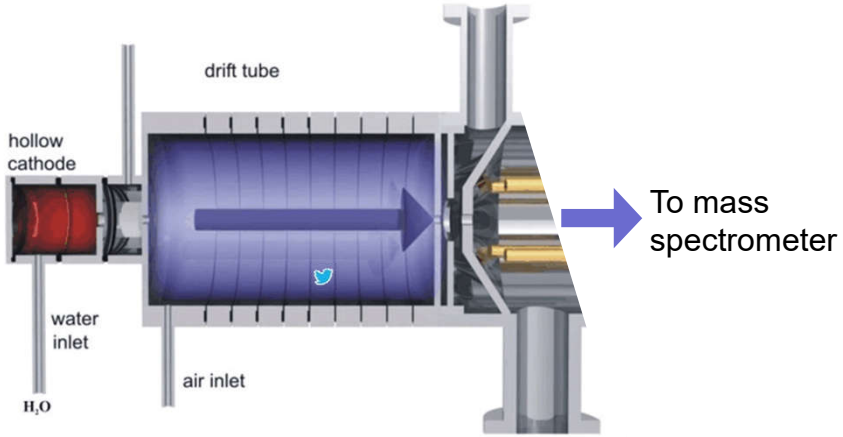


$H_3O^+ + R \rightarrow RH^+ + H_2O$

$O2+ + R \rightarrow R^+ + O_2$

PTR-MS

- In the ion source (red region), water vapor is ionized in the hollow cathode ion source to produce various ions.
- These ions are allowed to react with excess water vapor in the second region of the ion source to produce primarily hydronium ions, H_3O+.
- These hydronium ions are continuously drawn into the drift tube (blue region), where they interact with the whole air sample.

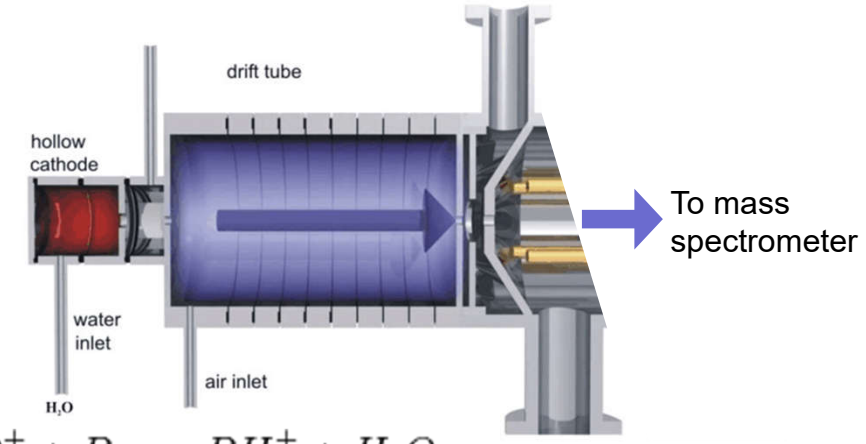


$$H_3O^+ + R \longrightarrow RH^+ + H_2O$$

PTR-MS

- The air sample is continuously drawn through the inlet at a flow rate of approximately 30 ml/min, with typical drift tube pressures between 2.0 and 2.4 mbar.
- Any compounds in the sample with a higher proton affinity than water will accept a proton from the hydronium ions at a collisional rate.

Type of Compound	Proton Affinity (kcal/mole)
Permanent gases (Ar, O_2, N_2, CO_2)	< 130
Small alkanes (up to octane)	< 167
Water	167
>C_2-olefins and aromatics	> 167
Alcohols, ethers, esters, organic acids	> 167
Aldehydes and ketones	> 167
Amines, amides, thiols	> 167



$$H_3O^+ + R \longrightarrow RH^+ + H_2O$$

PTR-MS

- Quadrupole spectrometers were standard until Time-of-Flight (TOF) options were introduced in 2007.
- Recent improvements include a modular system based on customer's needs for sensitivity and resolution; this includes specific inserts in the area of the Transfer Lens System – results are detection limits in parts per quadrillion.

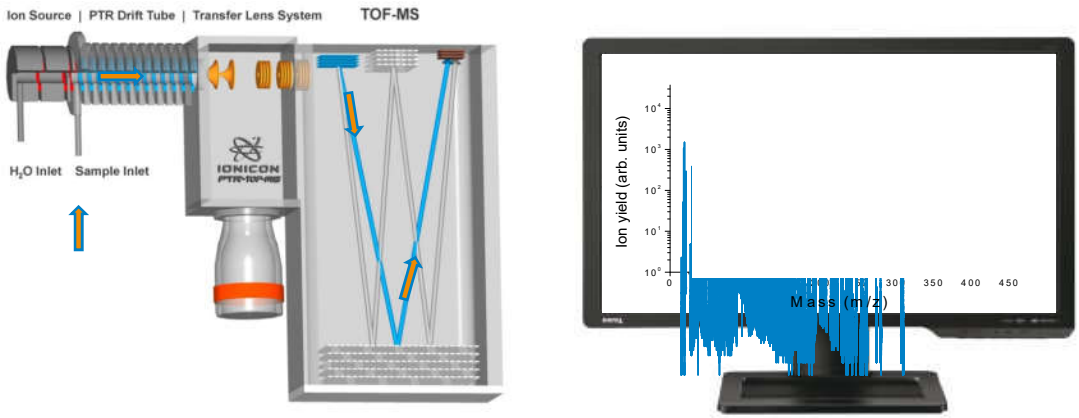
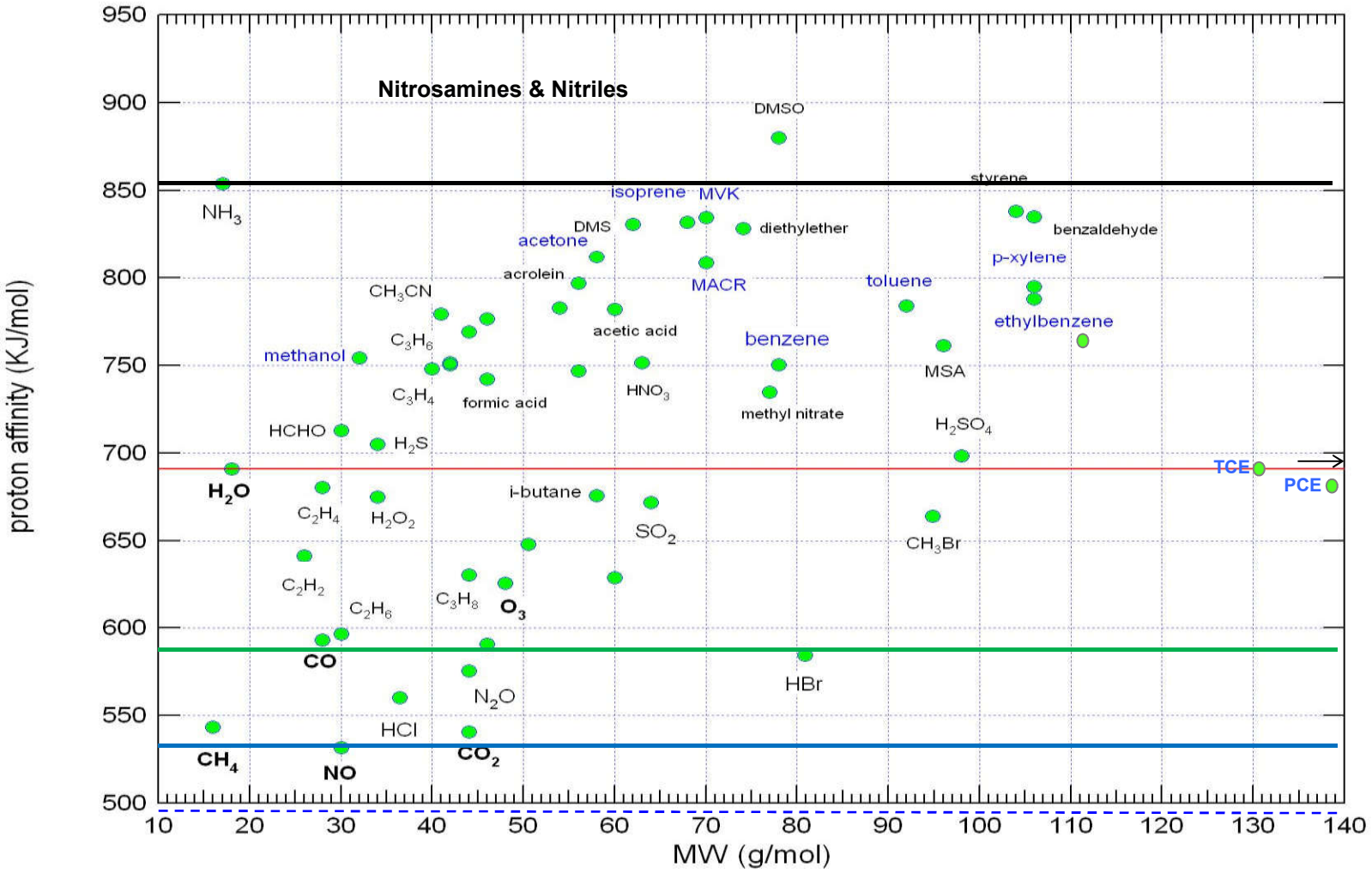


Figure 1. Animation courtesy of Ionicon Analytik

Speciation with Selective Ionization



Anything above the blue line with NO^+

Anything above the red line with H_3O^+

Anything above the green line with O_2^+

Anything above the black line with NH_3^+

Residential Sampling Site Map
South Franklin County, WA

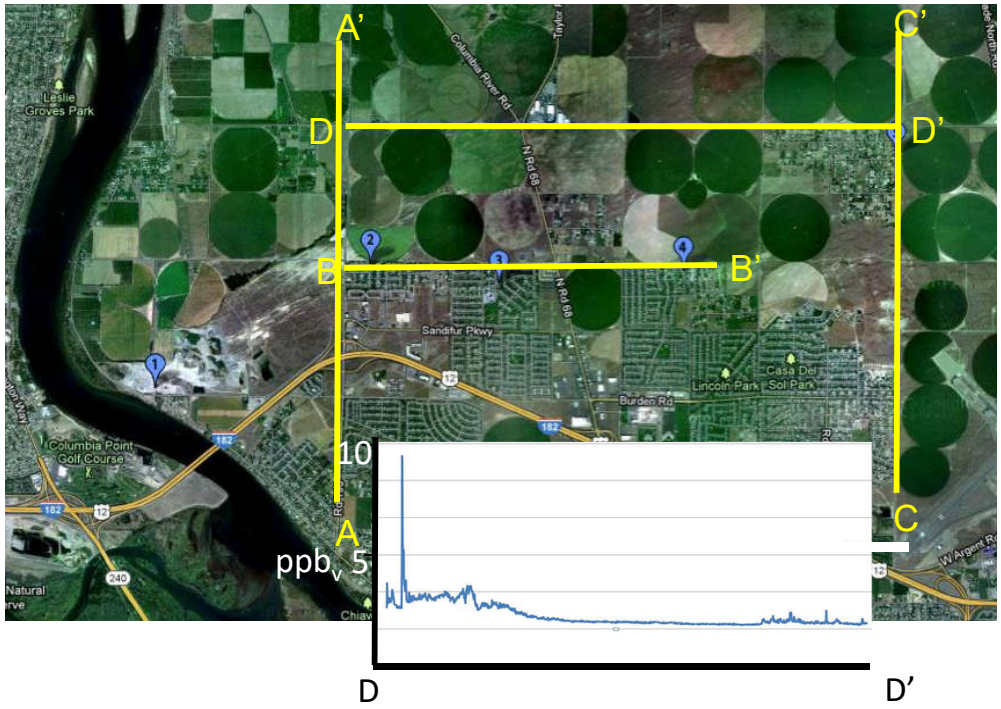
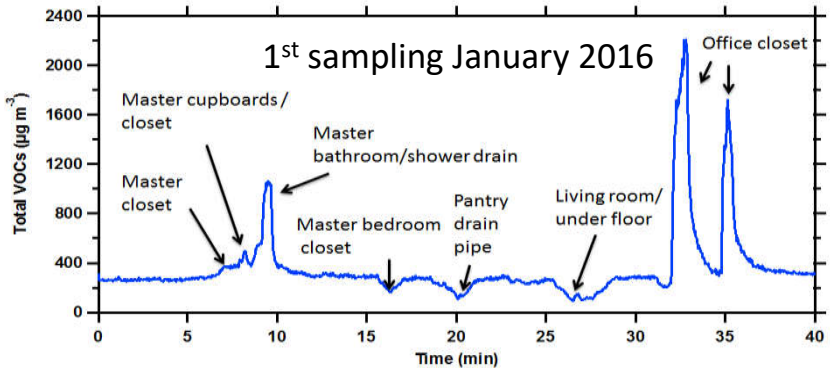
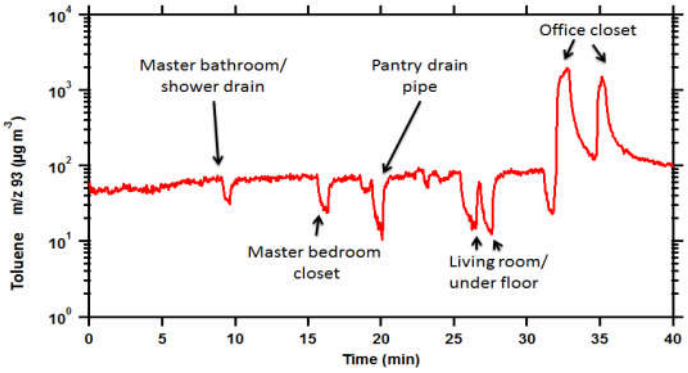


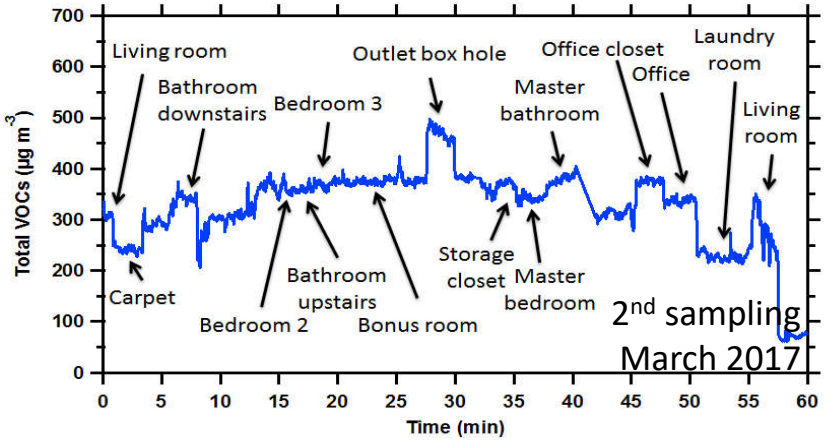
Figure 2. MITC concentrations in ambient air along PTR-MS mobile lab driving route D – D'

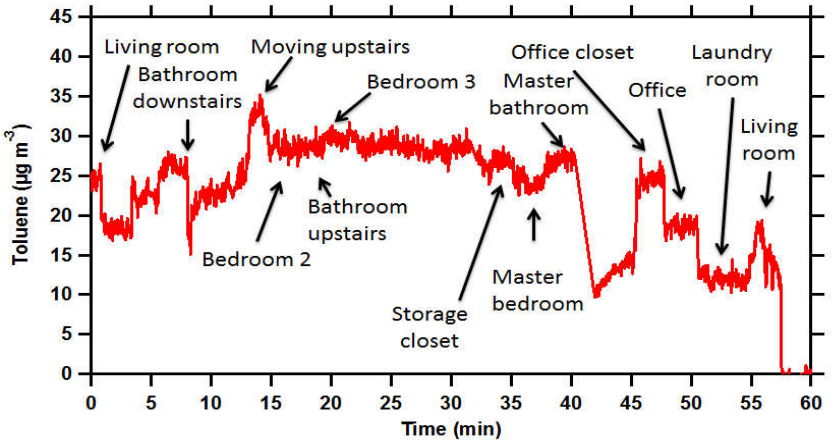
Sick Building Syndrome VOC Identification

Location: Single family home, built in 2015 in Kennewick, WA
Symptoms: Upon entry to the house, the person would encounter headaches, dizziness, extreme skin irritation (rashes), swelling of eyes and tightening of chest. Upon leaving the house and staying at different location for several days the symptoms improved.
Approach: RJLee Group performed two PTR-MS campaigns, in conjunction with TO-15 and TO-11a analyses.









Case Study

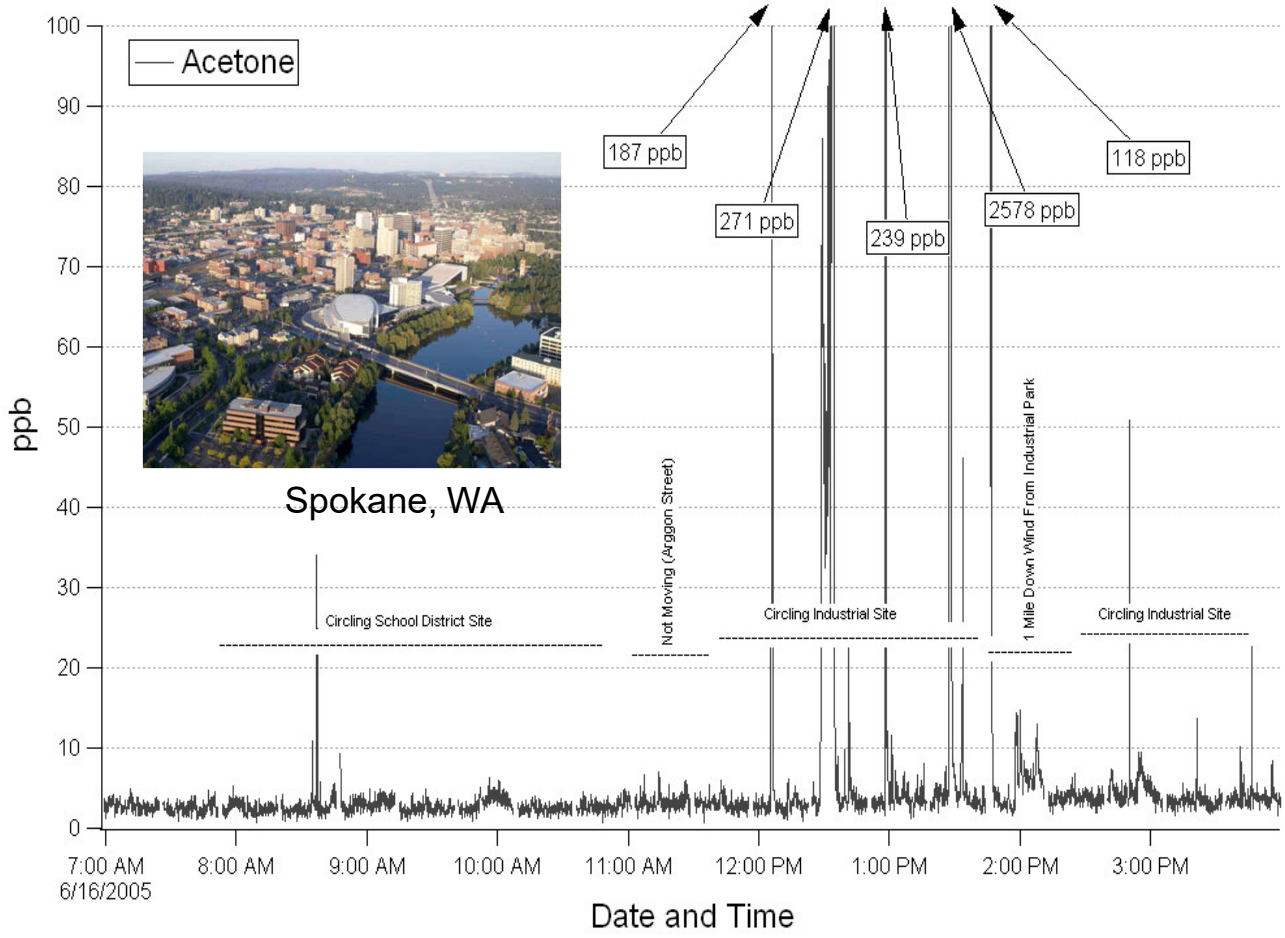
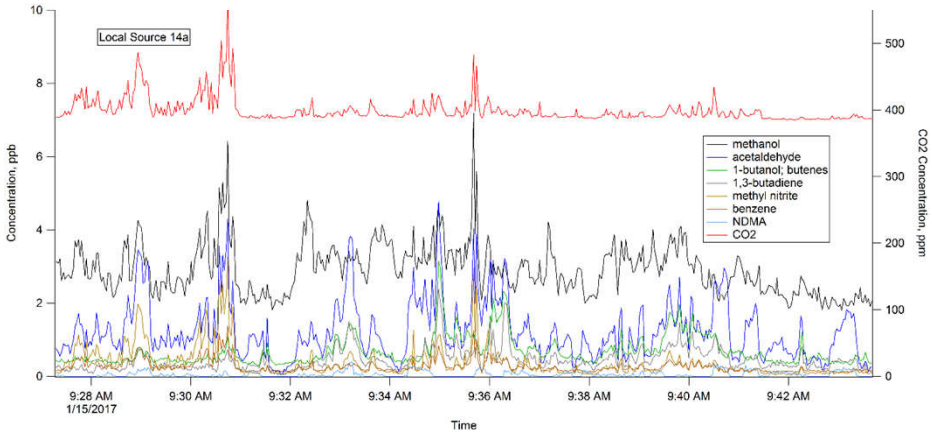


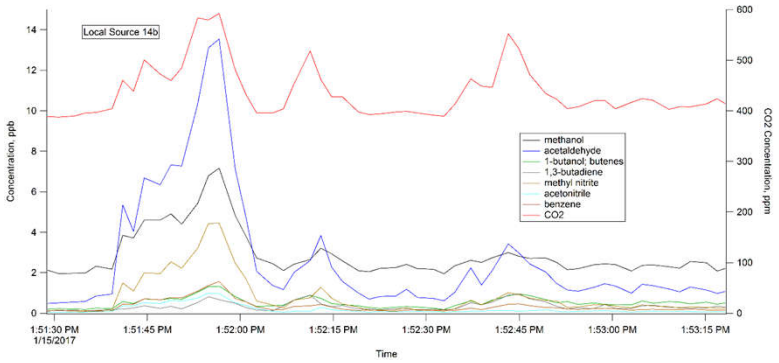
Figure 3. Organic vapor monitoring around schools and industrial parks during a working day.

Vapor Monitoring on the DOE Hanford Site

- Compounds of concern:
  - Nitrosamines
  - Furans
  - Nitriles
  - Aromatics
  - Carbonyls
  - Alcohols
  - Ketones
  - Amines

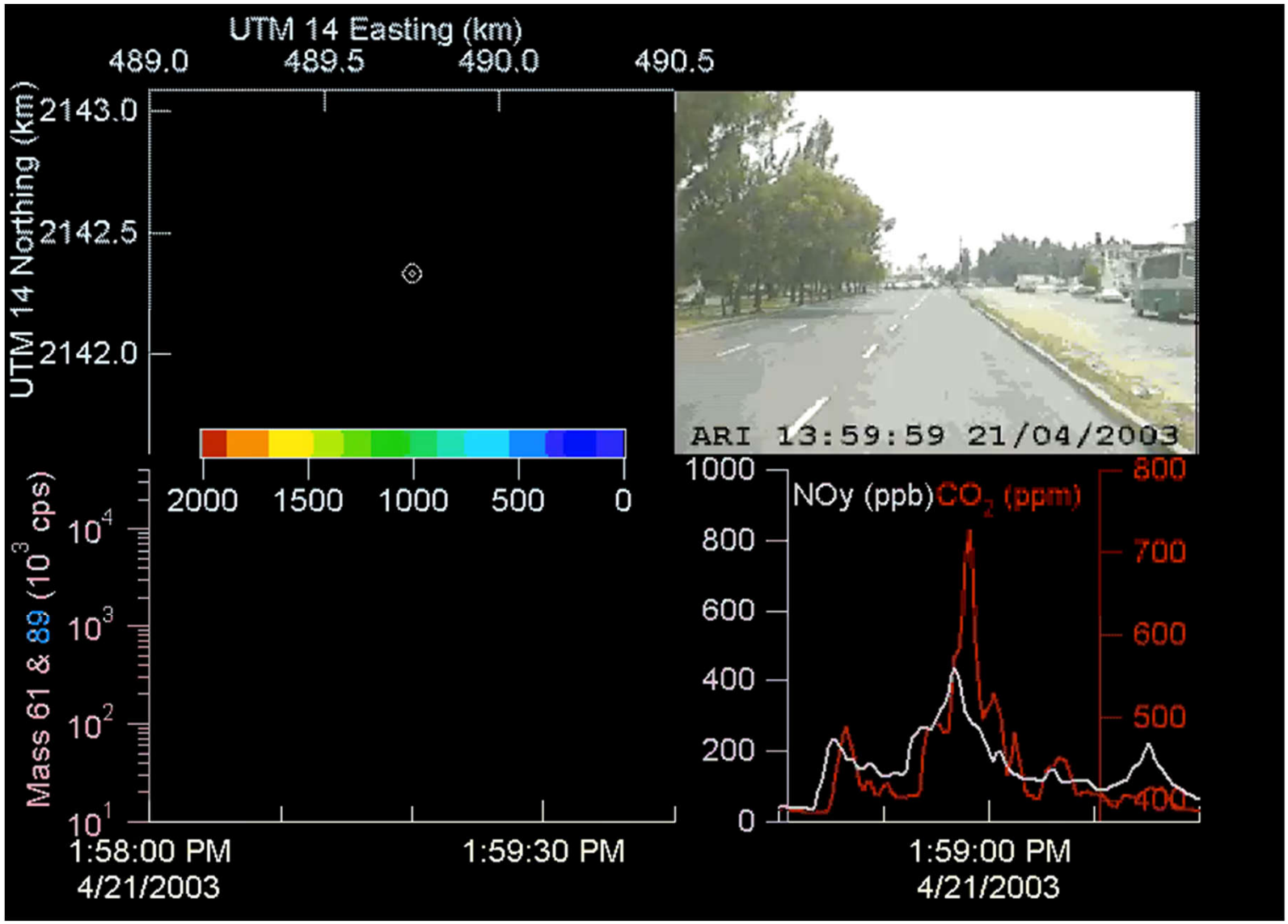
Vapor Monitoring on the DOE Hanford Site





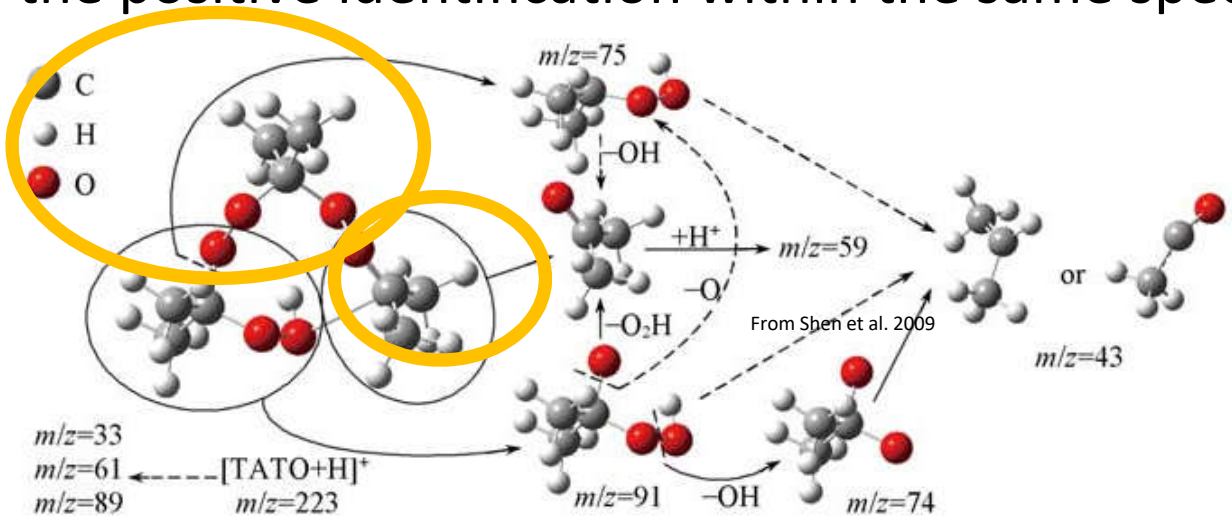
Retrieved from publically available online presentation of Hanford monitoring activities: https://hanfordvapors.com/

Mobile Laboratory



Explosive Monitoring

- TATP is the common home made explosive these days. Highly effective and easy to prepare.
- TATP is highly fragile, making it hard to detect. Fragmentation of TATP occurs whenever it is exposed to influx of energy. Be it to detonate or to slowly fragment.
- Soft ionization within a PTR-MS makes it possible to detect.
- RJLG uses the specific decay pattern of TATP to detect and validate the positive identification within the same spectrum.



Detection of TATP

- Optimized instrumentational settings for detection of TATP from a distance.

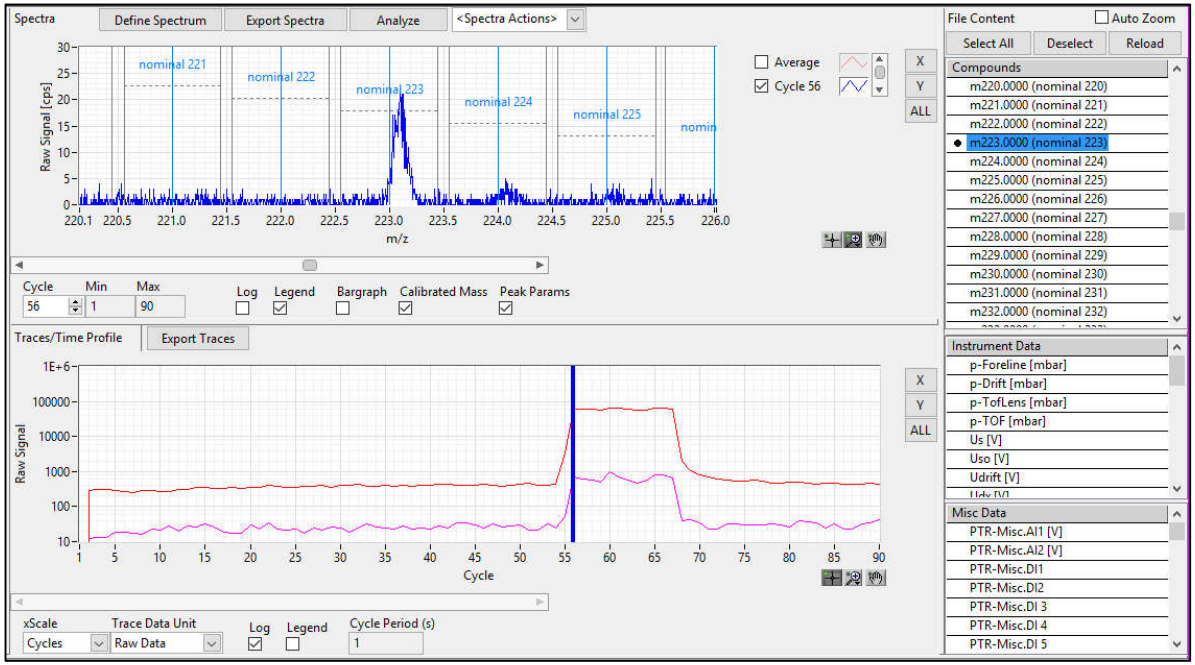
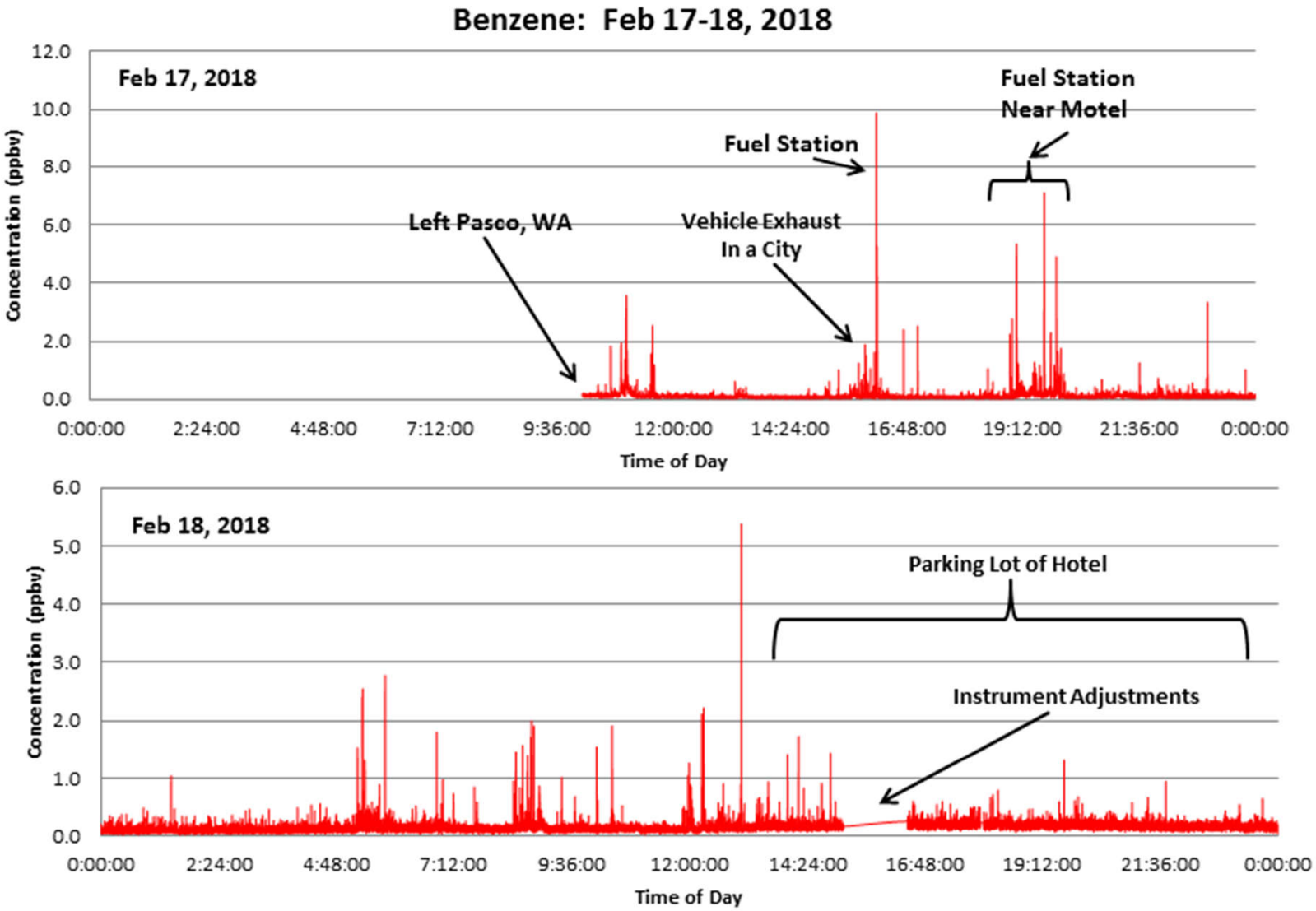
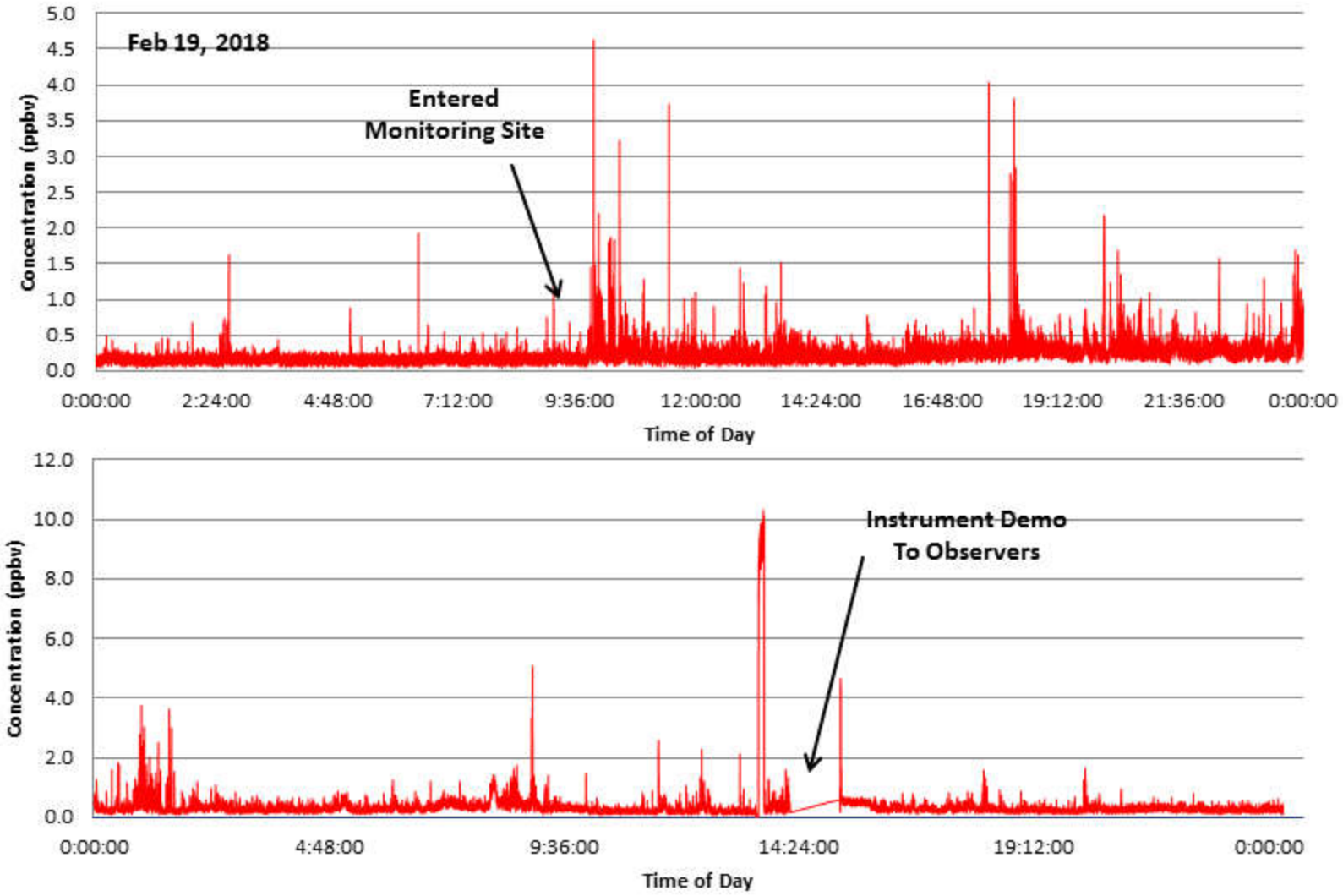


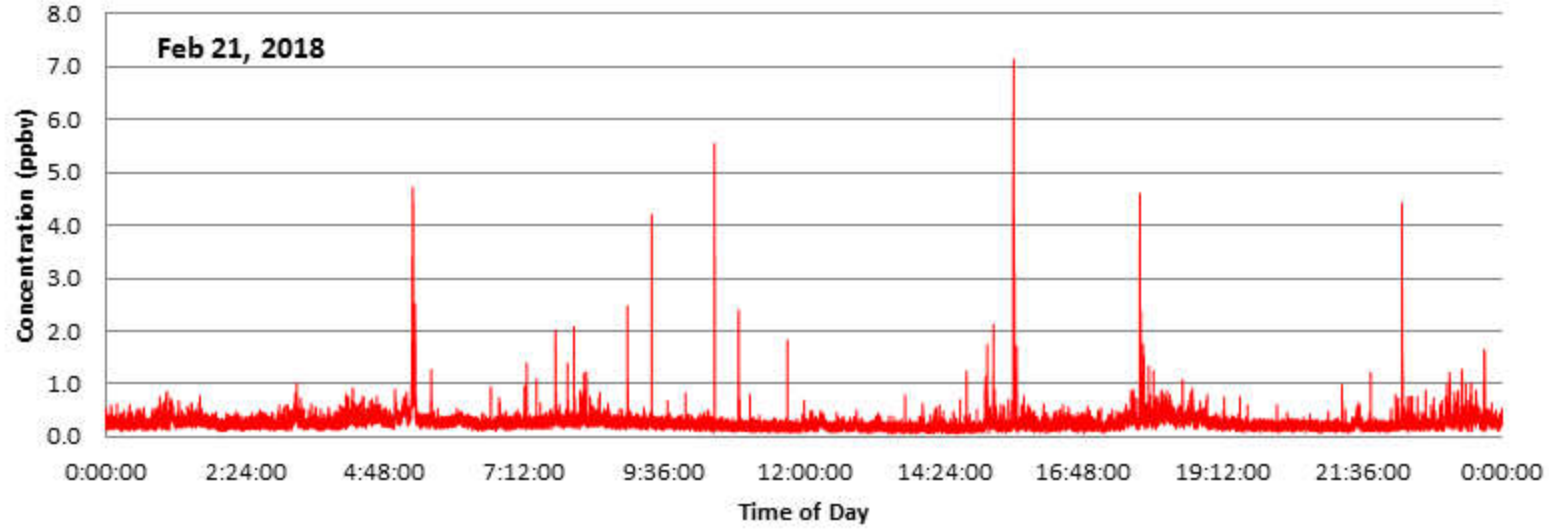
Figure 4. Example shows the spectrum of 0.5g of TATP at 6’ distance.

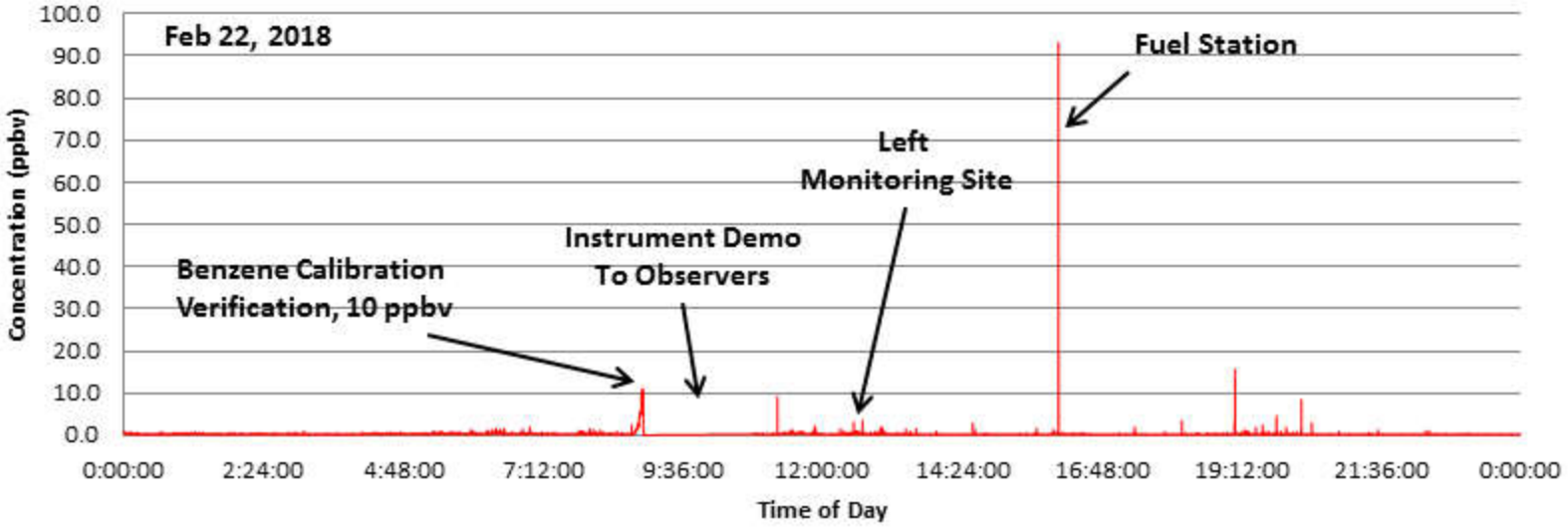

Benzene: Feb 17-18, 2018
Feb 17, 2018
Concentration (ppbv)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Left Pasco, WA
Vehicle Exhaust
In a City
Fuel Station
Fuel Station
Near Motel
0:00:00
2:24:00
4:48:00
7:12:00
9:36:00
12:00:00
14:24:00
16:48:00
19:12:00
21:36:00
0:00:00
Time of Day
Feb 18, 2018
Concentration (ppbv)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Parking Lot of Hotel
Instrument Adjustments
0:00:00
2:24:00
4:48:00
7:12:00
9:36:00
12:00:00
14:24:00
16:48:00
19:12:00
21:36:00
0:00:00
Time of Day

Benzene: Feb 19-20, 2018

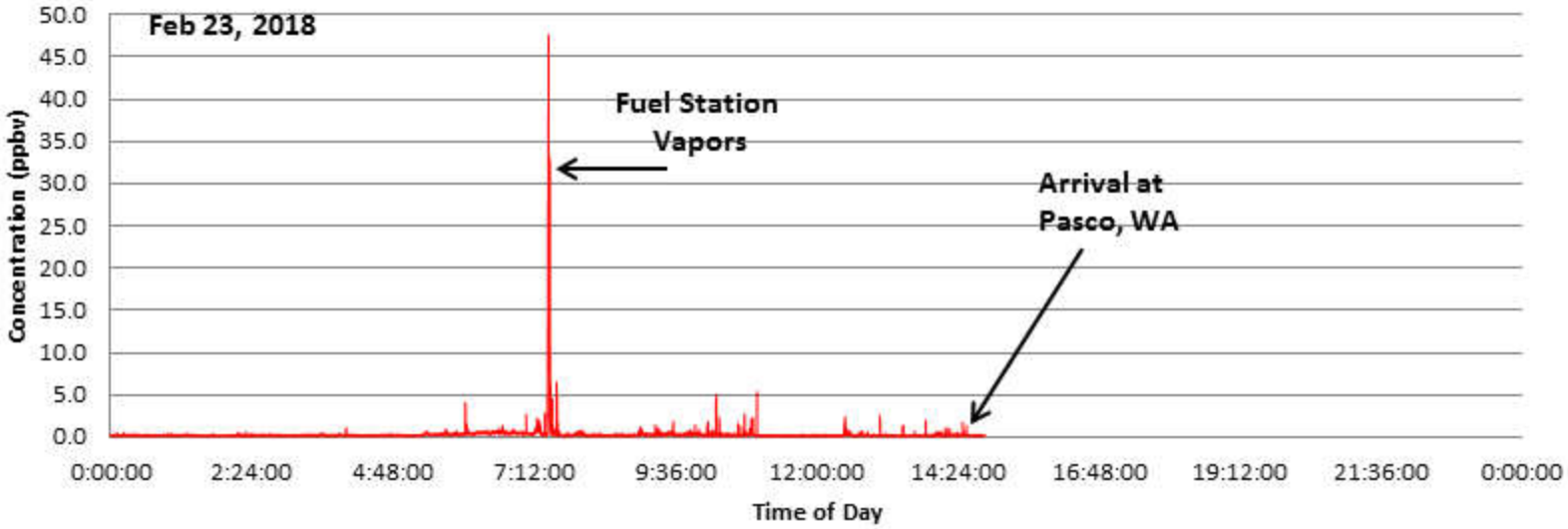


Benzene: Feb 21-22, 2018

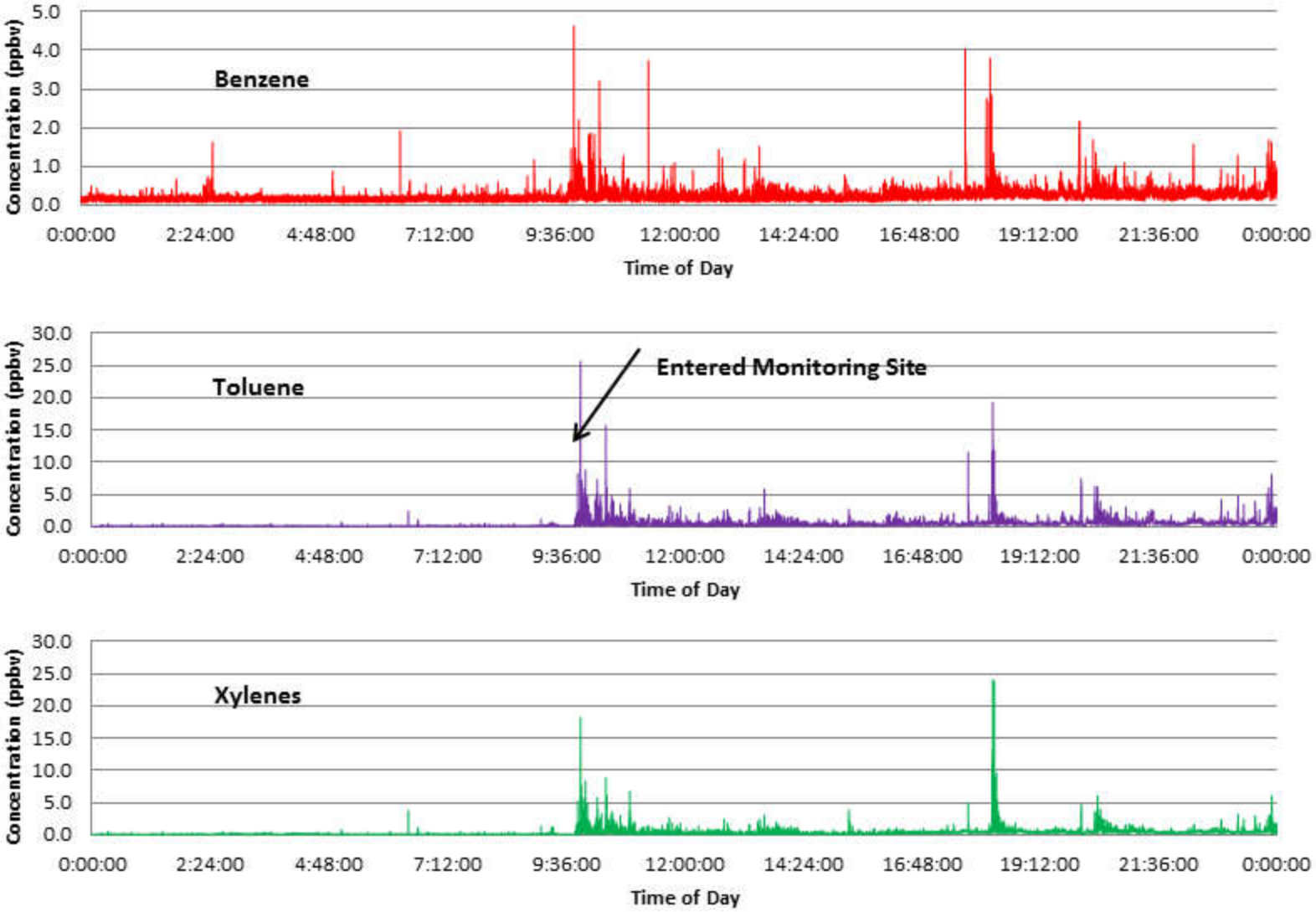




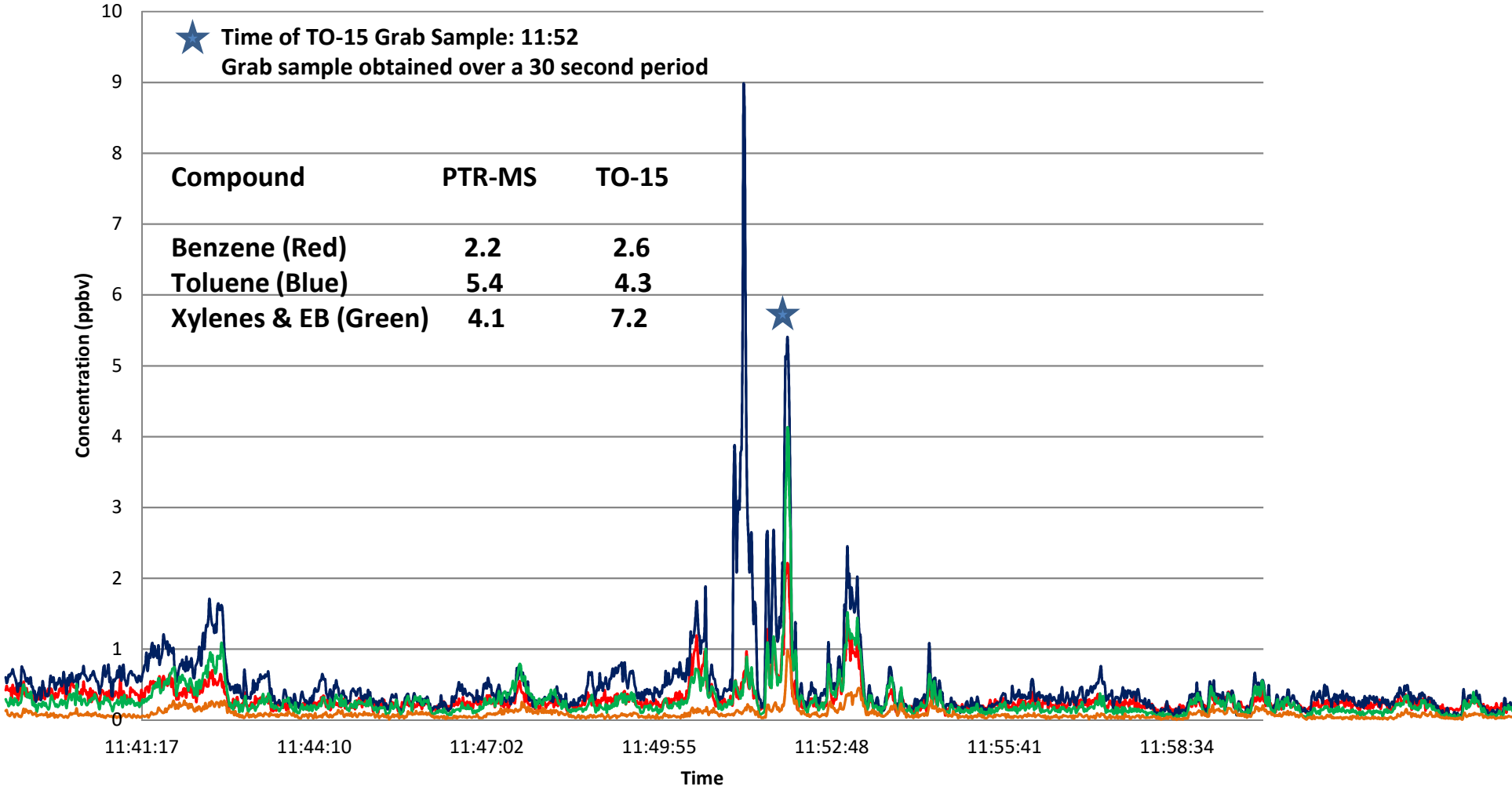
Benzene: Feb 23, 2018



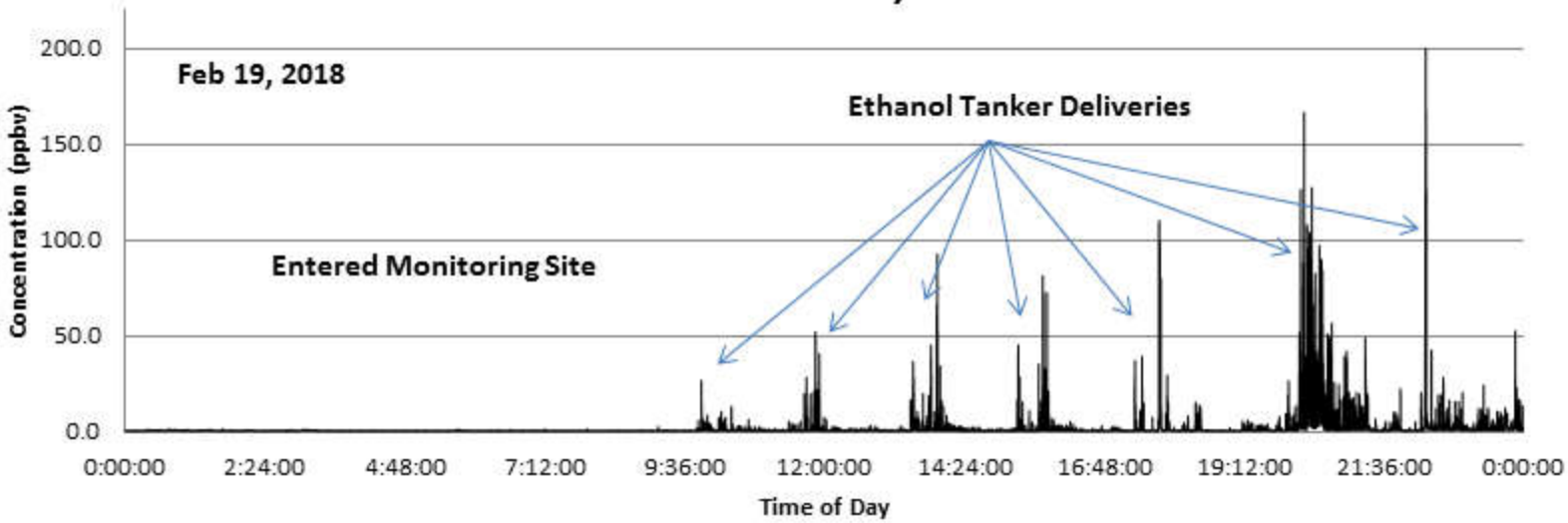
Benzene/Toluene/Xylenes: Feb 21, 2018

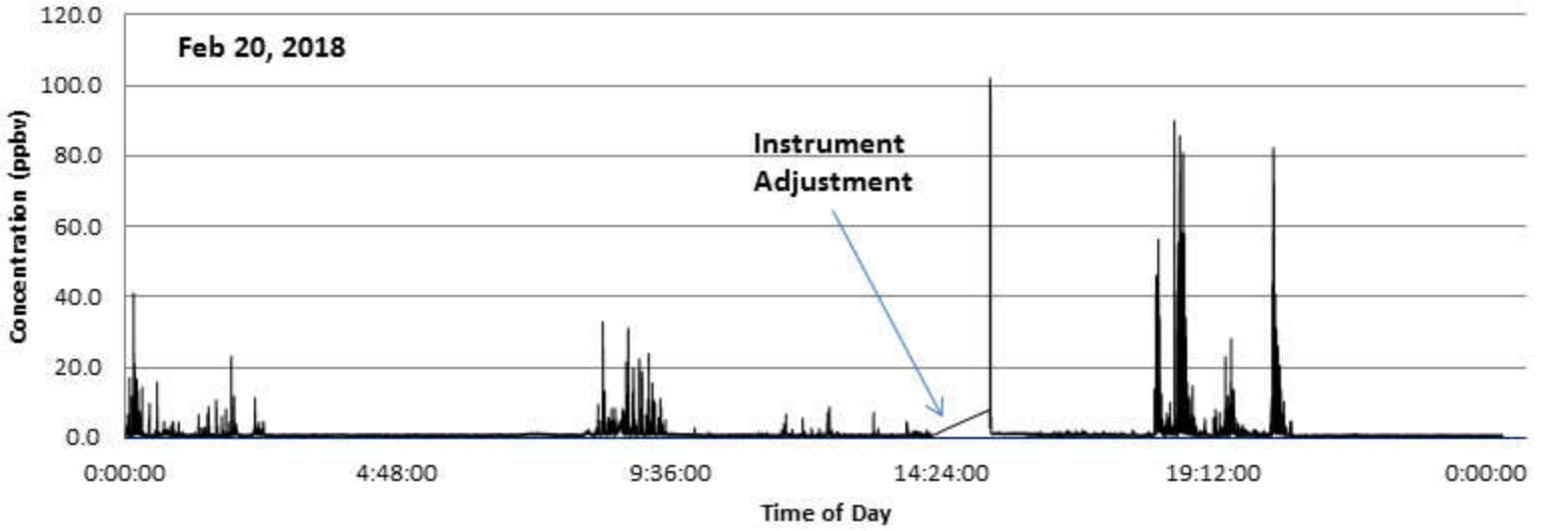


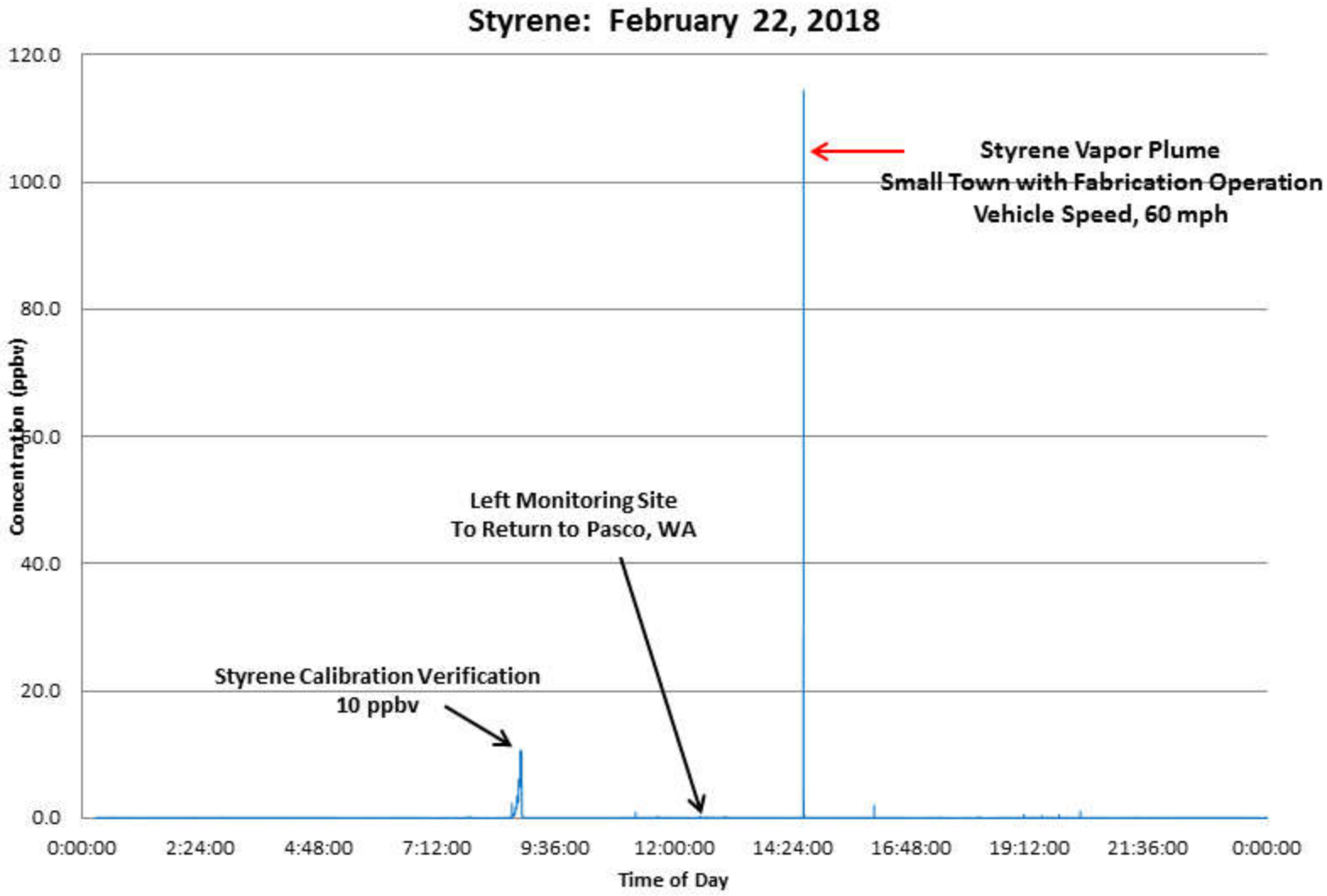
BTEX Feb 22, 2018; PTR-MS vs. TO-15



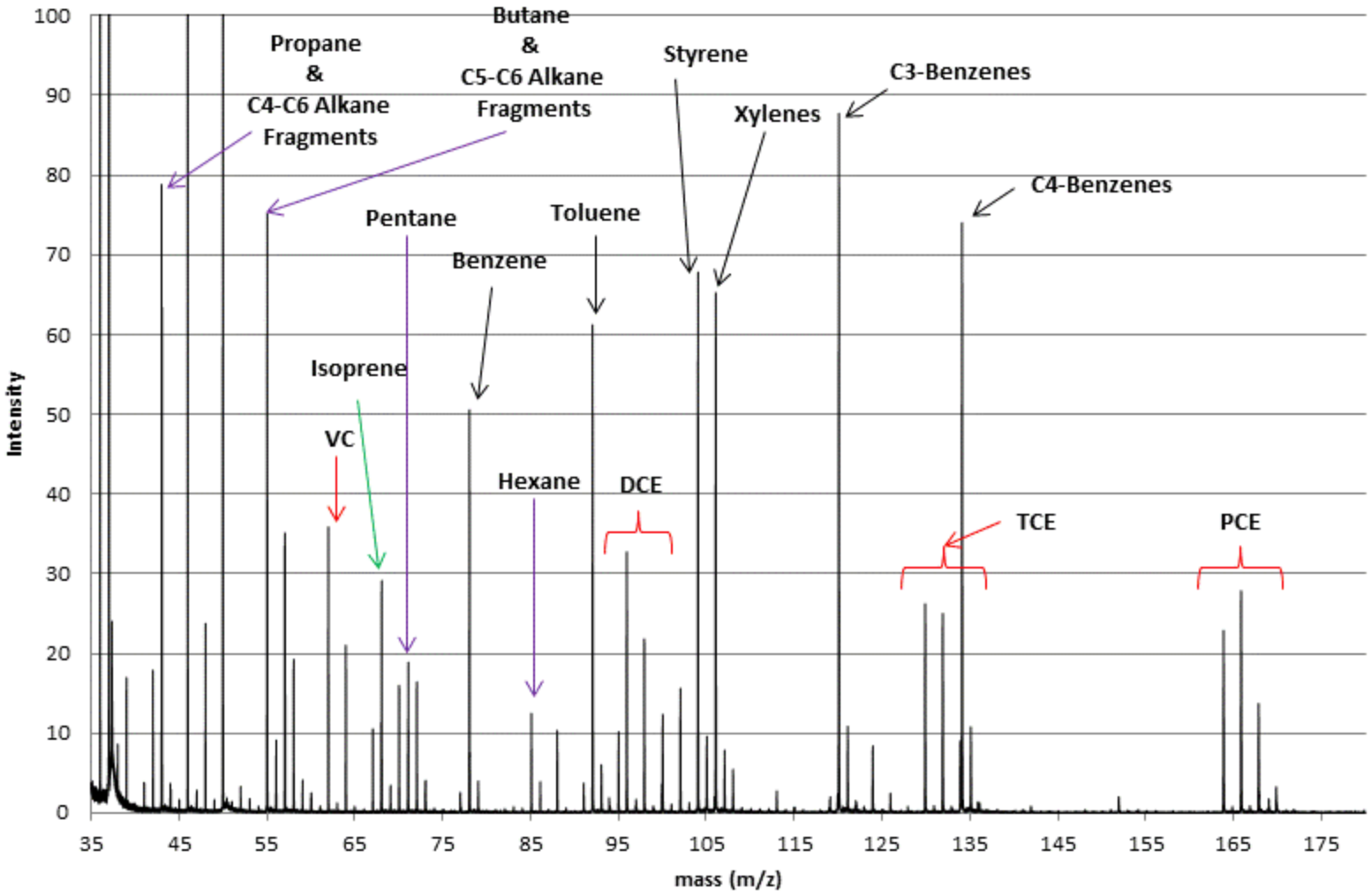
Ethanol: Feb 19-20, 2018



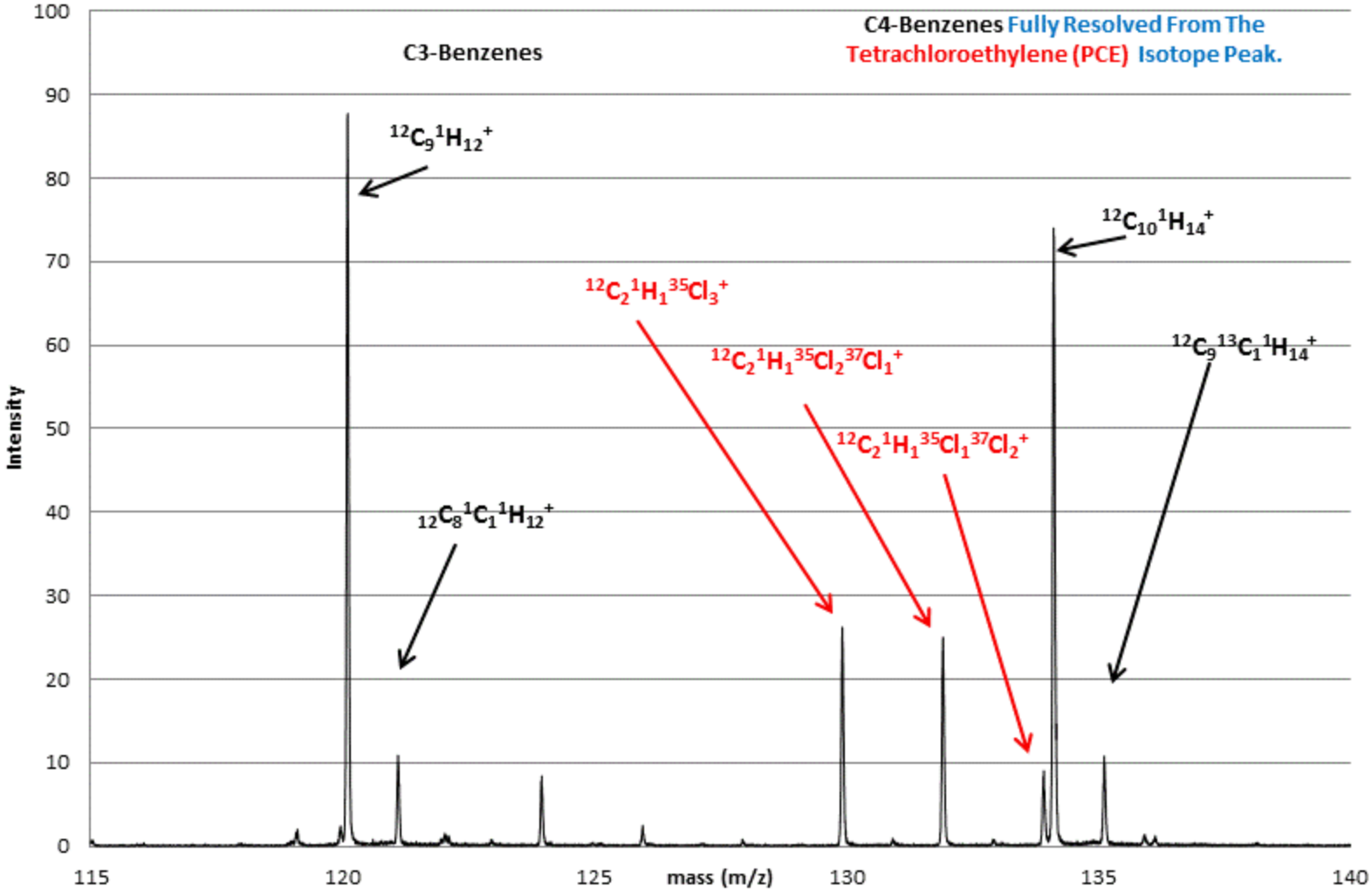


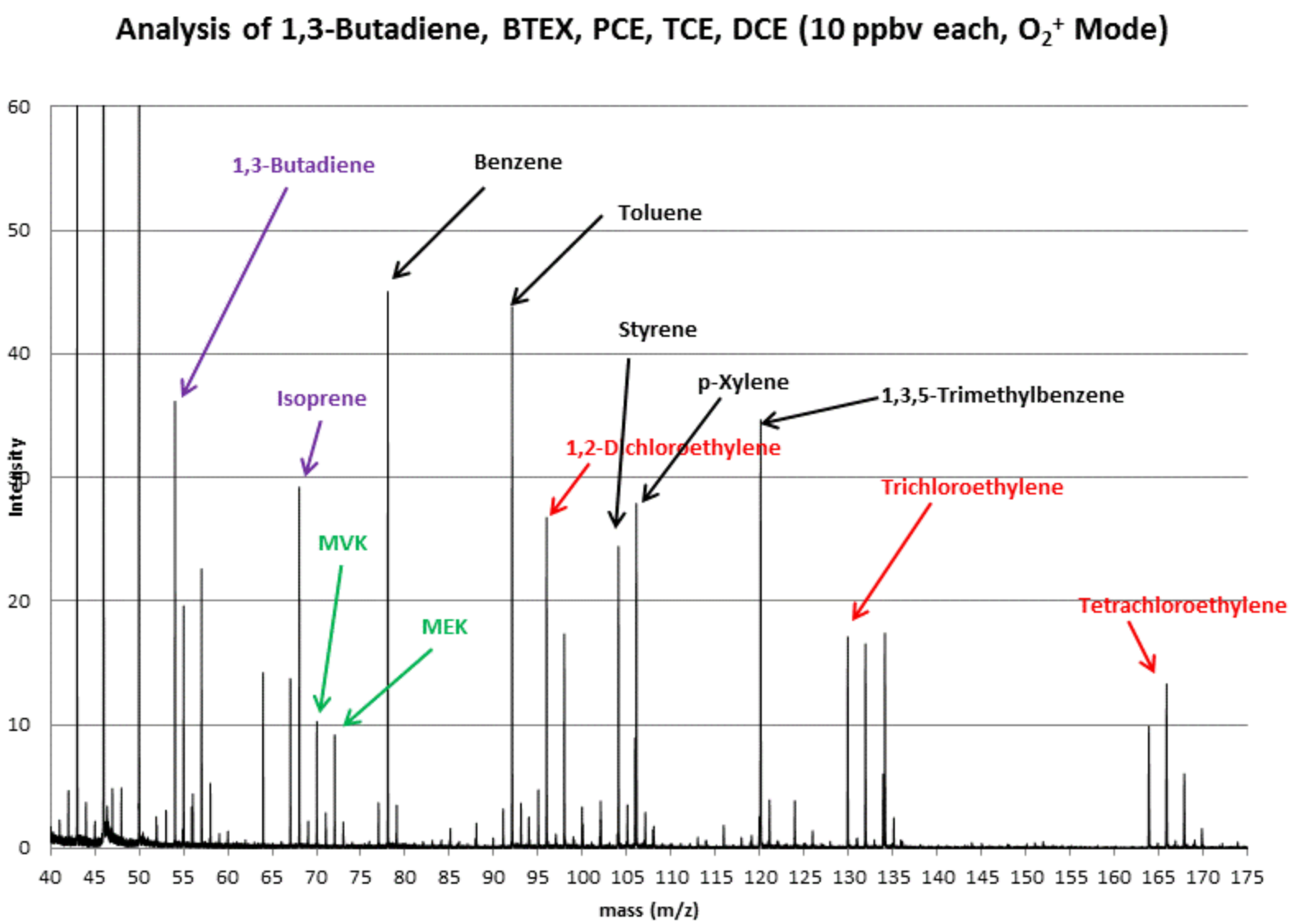

Styrene: February 22, 2018
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Concentration (ppbv)
Styrene Vapor Plume
Small Town with Fabrication Operation
Vehicle Speed, 60 mph
Left Monitoring Site
To Return to Pasco, WA
Styrene Calibration Verification
10 ppbv
0:00:00
2:24:00
4:48:00
7:12:00
9:36:00
12:00:00
14:24:00
16:48:00
19:12:00
21:36:00
0:00:00
Time of Day

Analysis of C3-C6 Alkanes, BTEX, PCE, TCE, DCE, & VC (10 ppbv each)



Expanded Mass Spectrum Showing Advantage of High Mass Resolution on the TOF
(Reduction of Isobaric Interferences Experienced Using Quadrupole MS)

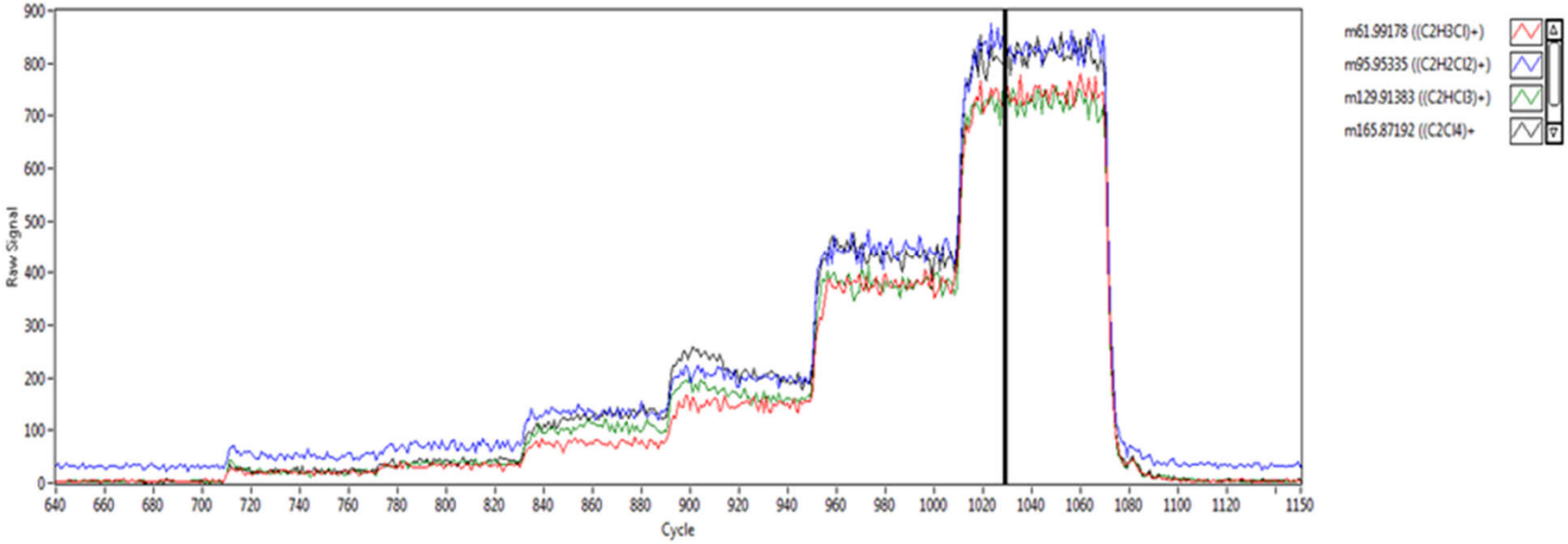



Analysis of 1,3-Butadiene, BTEX, PCE, TCE, DCE (10 ppbv each, O_2^+ Mode)
1,3-Butadiene
Benzene
Toluene
Styrene
p-Xylene
1,3,5-Trimethylbenzene
Isoprene
1,2-Dichloroethylene
Trichloroethylene
MVK
MEK
Tetrachloroethylene
Intensity
mass (m/z)
0
10
20
30
40
50
60
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175

Simultaneous Acquisition of PCE, TCE, DCE, & VC for Calibration

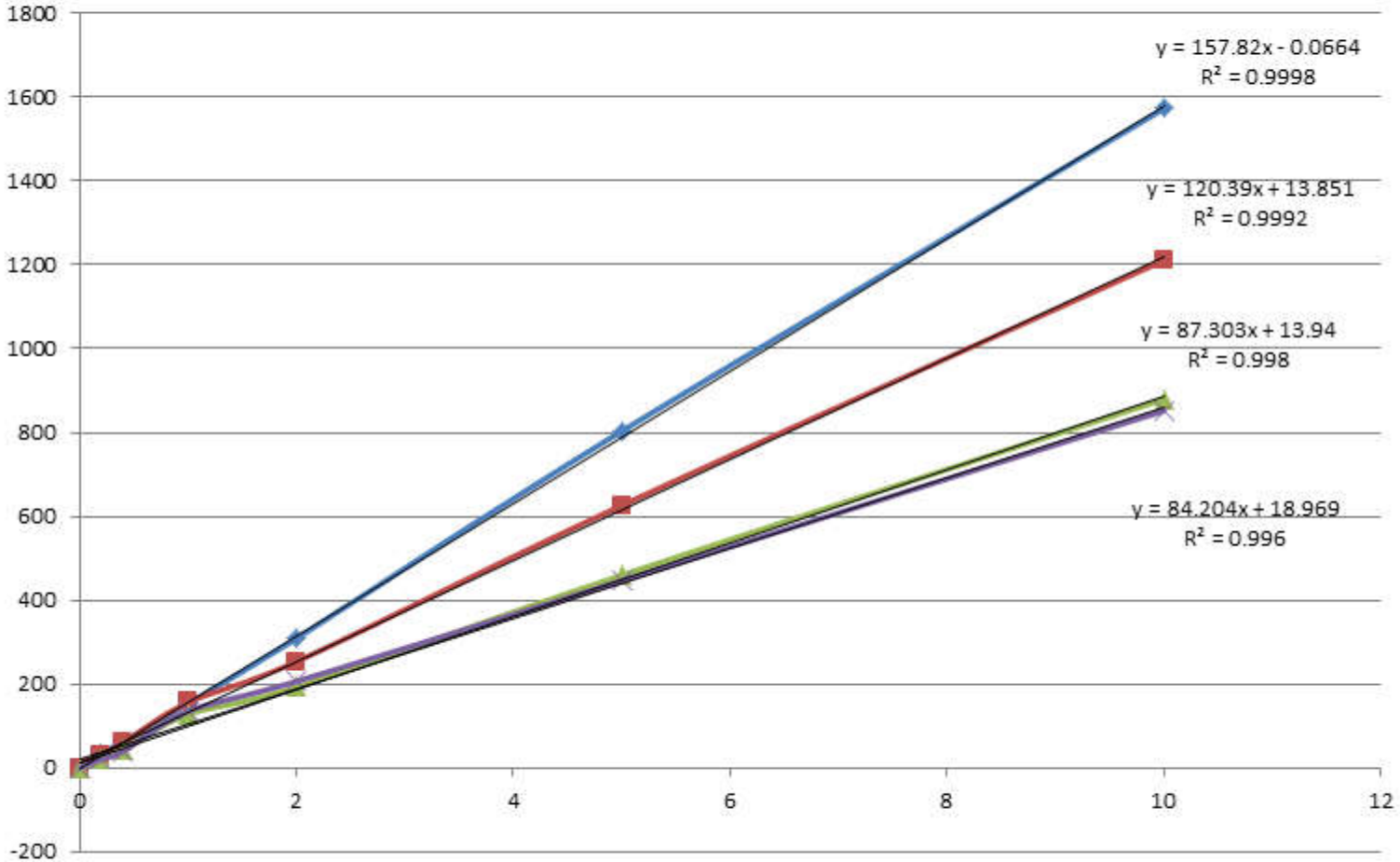
(O_2^+ Mode; 1 Second Acquisition @ 50kHz)

Concentration Range is 0.20 – 10 ppbv

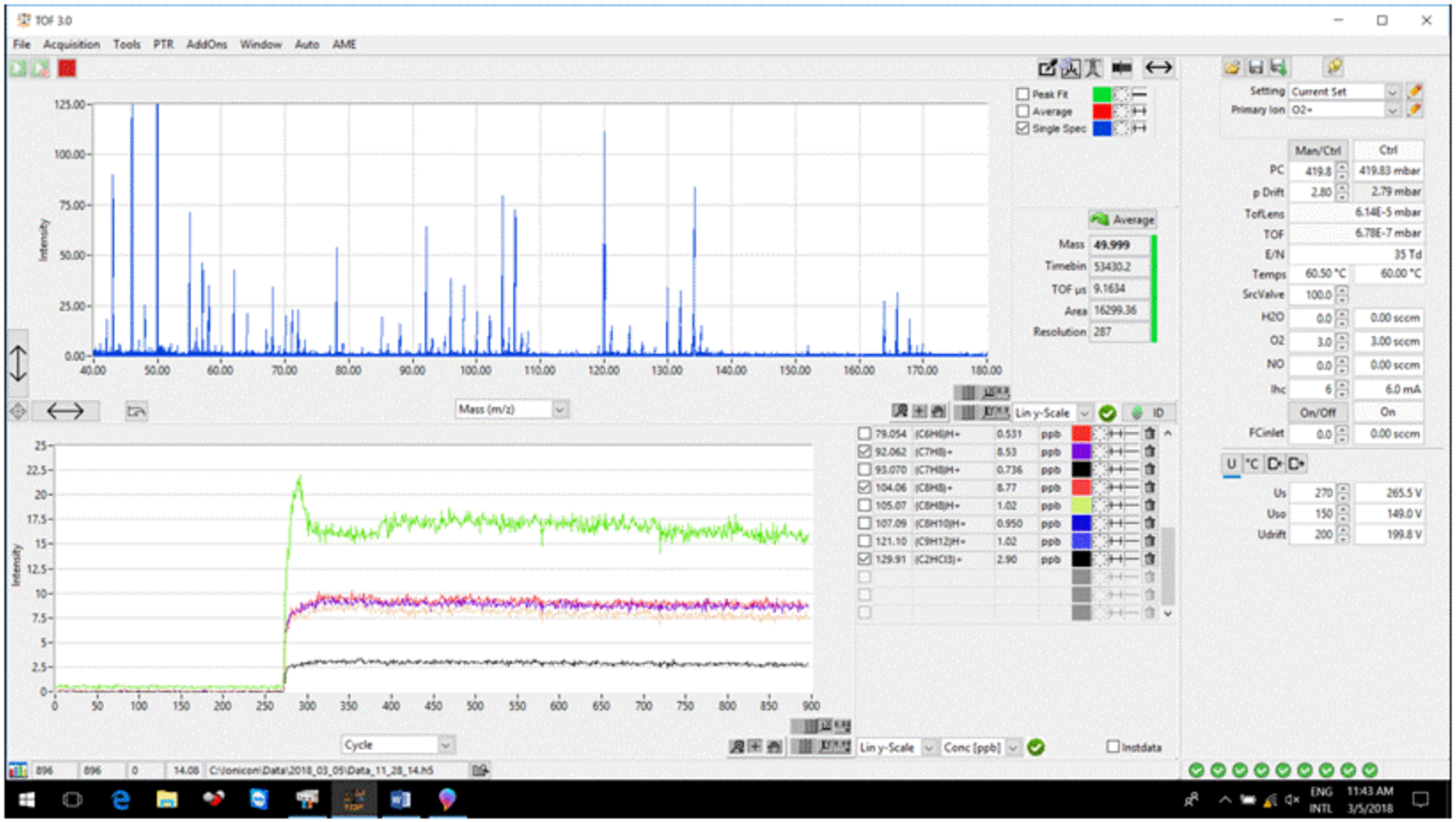


Calibration Curves for PCE, TCE, DCE, & VC

(O_2^+ Mode; 0.20 – 10 ppbv; 1 Second Acquisition Time; Average of 20 Seconds/data point.)

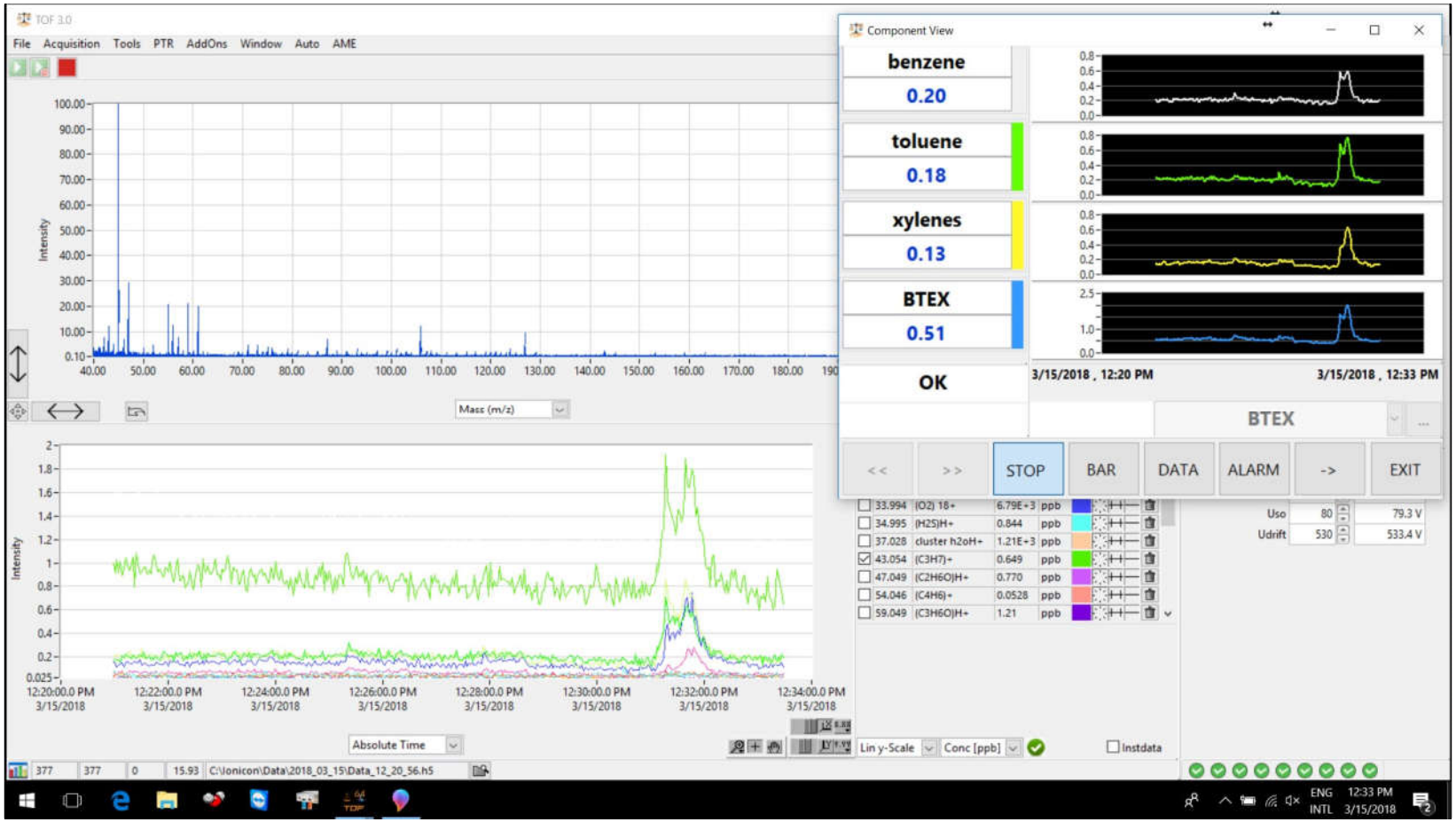


Screen Shot of the PTR-MS Graphical User Interface
Mass Spectrum on top: Temporal Ion Profiles on Bottom



RJ LEE GROUP

Screen Shot of the PTR-MS Graphical User Interface
Mass Spectrum on top: Temporal Ion Profiles on Bottom



Summary

- PTR-MS is a ***sensitive*** analytical tool for ***real-time*** monitoring of compounds of concern.
- PTR-MS is a ***mobile*** system capable of being moved from one location to another within any urban, rural or other boundaries.
- The system can be set up to monitor several locations within an area to allow for ***changes*** in emission drift due to fluctuations in wind direction, barometric pumping or burping characteristics.
- PTR-MS is a ***cost-effective*** compliment to current sampling and analysis protocols that require ***multiple*** sampling matrices and analytical methods by increasing their effectiveness.