SSSAAP (SES) 2019
Grand Hotel Marriott Resort
Point Clear, Alabama

MONTROSE ENVIRONMENTAL

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A Leading Provider of Environmental Solutions

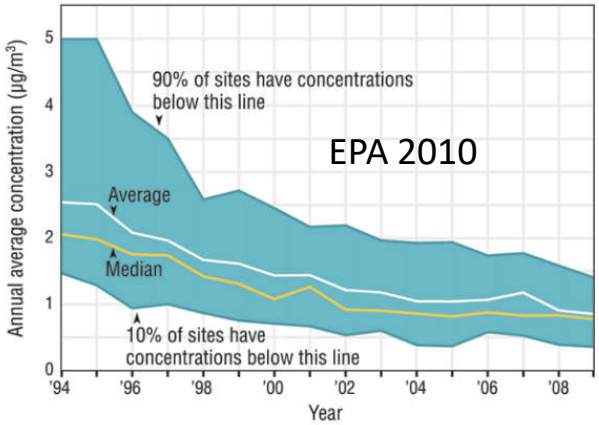
Emerging Technology

April 17, 2019

Difficult to Measure Compounds at Low Levels (ppb/ppt) Near/Real Time

- Real Need to Measure low levels in ambient air (low ppb) Compliance/Reference Method
- Need to measure low levels in Ambient and Sources (PSD, Expansion, Major Out, Non-Attain., RA and TITLE V MAJOR SOURCES - OUT
  - **Formaldehyde in Turbines (single digit ppb)**
  - **Ethylene Oxide (Stacks/Ducts, Ambient Air) Discuss Interferences**
    - **FTIR or GC-FID - Ducts - <10 ppb**
    - **Ambient – Need <150 ppt typically found**
  - **HRVOCs (1,3 Butadiene)**
  - **OHAPs**
  - **BTEX (ambient air geographical – Avg Benzene <0.3 ppb)**
  - **PFAS/Gen-X (particulate attachment or liquid injection vaporizer**

Ambient Benzene



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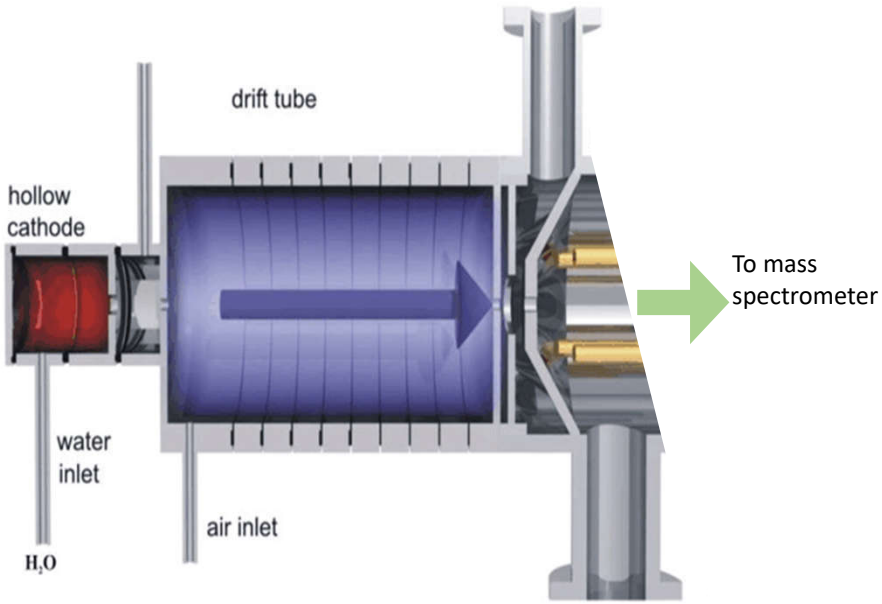
Proton Transfer Time of Flight Mass Spectrometry PTR-TOF-MS

- **Proton Transfer Reaction Mass Spectrometry for Real Time VOCs**
- **Part Per Trillion (PPT) LOD Virtually any C compound**
- **No Compressed Gases while in Real Time Mode**
- **EPA Reference Method 18 Compatibility with GC**
- **Weather Station & GPS**
- **Mobile GPS and Real Time Capability (1 data point per second)**



Typical but not limited

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

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

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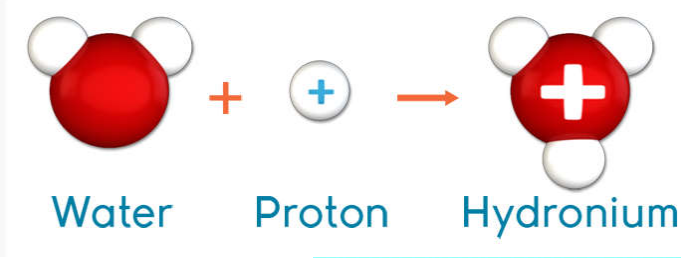
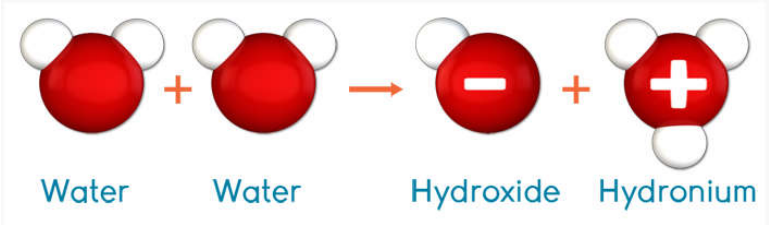
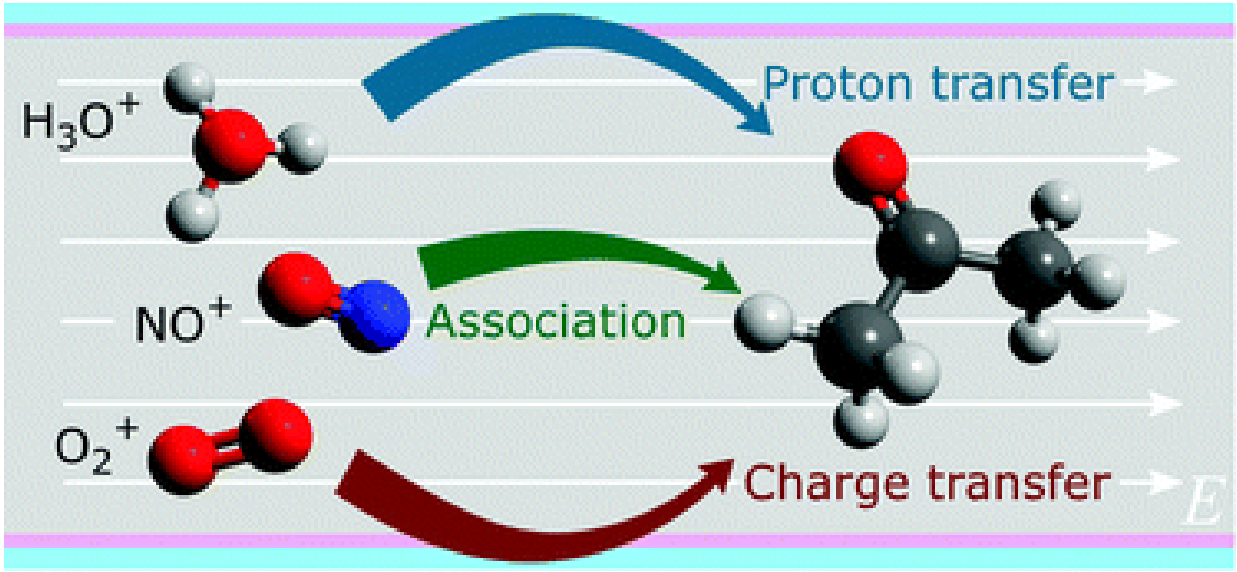
Reagents and Molecular Interactions





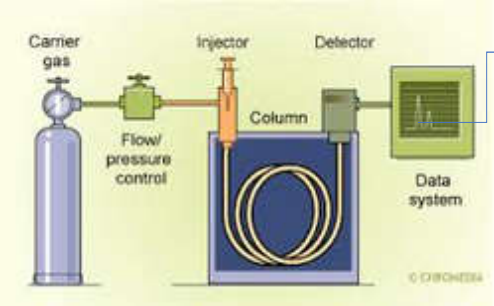


Anatolii Spesyvyi,a David Smitha and Patrik Španěl*

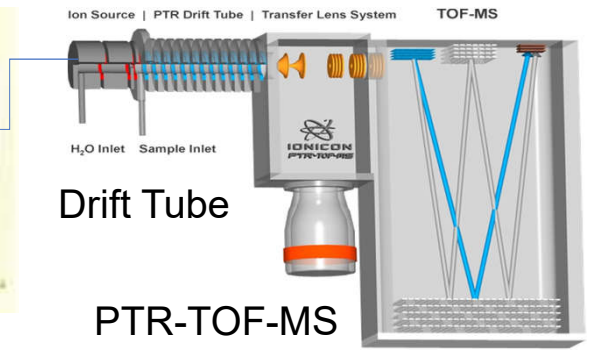
Mobile PTR-TOF-MS Platform

Advantages of PTR-MS

- Mobile Real Time
- Couple to GC for Compliance EPA M18
- Absolute Time and Space
- Real-time, continuous results (1/sec)
- No sample or reagent preparation
- New Reagents all the time
- Single unit can handle multiple sampling ports
- Team with RJ Lee Group for Multiple Mobile Platforms and PTR sensitivities (4000 RJ Lee and 6000 Series Montrose)



Gas Chromatograph



Drift Tube

PTR-TOF-MS

RJ LEE GROUP

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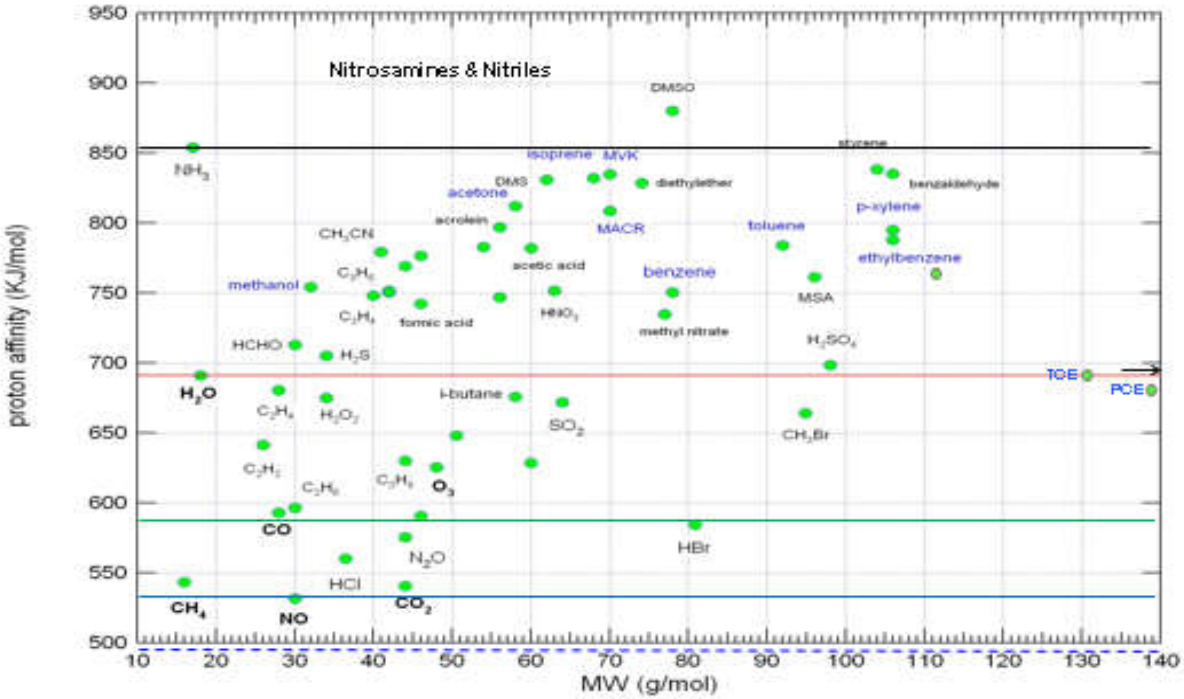
Selective Reagent Chemistry for Interferences with Selective Ionization



Anything above the blue line with NO+
Anything above the green line with O2+
Anything above the red line with H3O+
Anything above the black line with NH3+

- **Reagent Change in 10 seconds on the fly**
- **New Reagents being developed**
- **H2O+ (Hydronium)**
  O2+
  NO+
  NH3+ (Nitronium)
  Etc.

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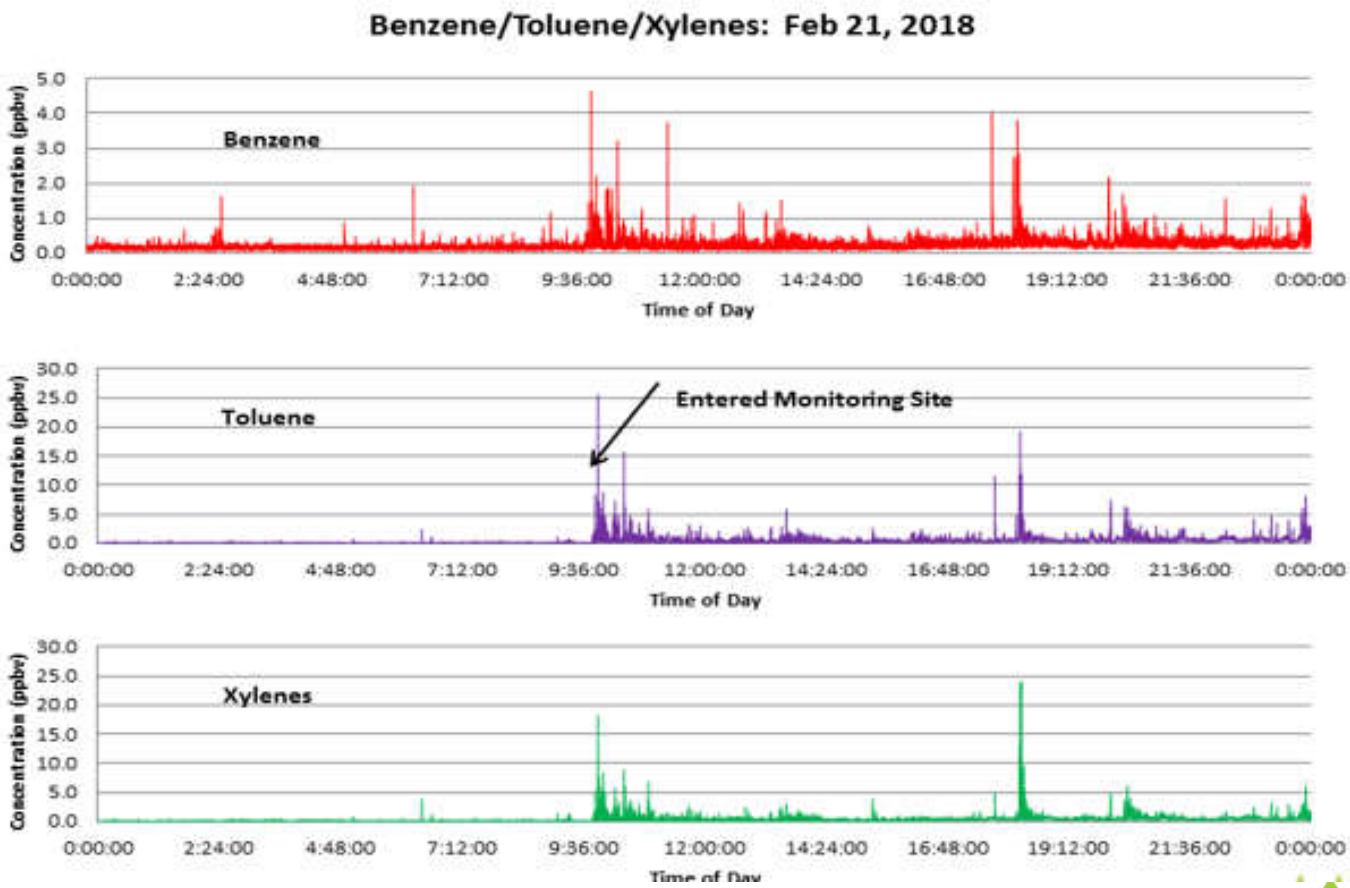
GC-PTR-TOF-MS Compliance Methods EPA Method 18 Direct Interface

- METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY
- "1.2.1 …gaseous organics emitted from an industrial source. … designed for ppm level sources, <u>some detectors are quite capable of detecting compounds at ambient levels</u>, e.g., ECD, ELCD, and "HID".
- <u>Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years."</u>
- We are there now

Direct or Thermal Desorption PTR-TOF-MS Compliance Methods Analogous to Validated EPA Test Method 8265:

- EPA M8265 Volatile Organic Compounds (VOCs) in Water, Soil, Soil Gas, and Air by Direct Sampling Ion Trap Mass Spectrometry (DSITMS)
- "method uses direct sampling ion trap mass spectrometry (DSITMS) for the rapid quantitative measurement, continuous real-time monitoring, and qualitative and quantitative preliminary screening of volatile organic compounds (VOCs) in water, soil, soil gas, and air."
- Complementary molecular ion information is obtained in the Chemical Ionization (CI) mode also provides enhanced sensitivity and improved selectivity for certain compounds, including alkyl-aromatics, ketones, and aldehydes.
- NOTE: Other mass spectrometers may be used if they have capabilities and performance specifications appropriate for the intended application.

PTR TOF MS Case Study BTEX Ambient



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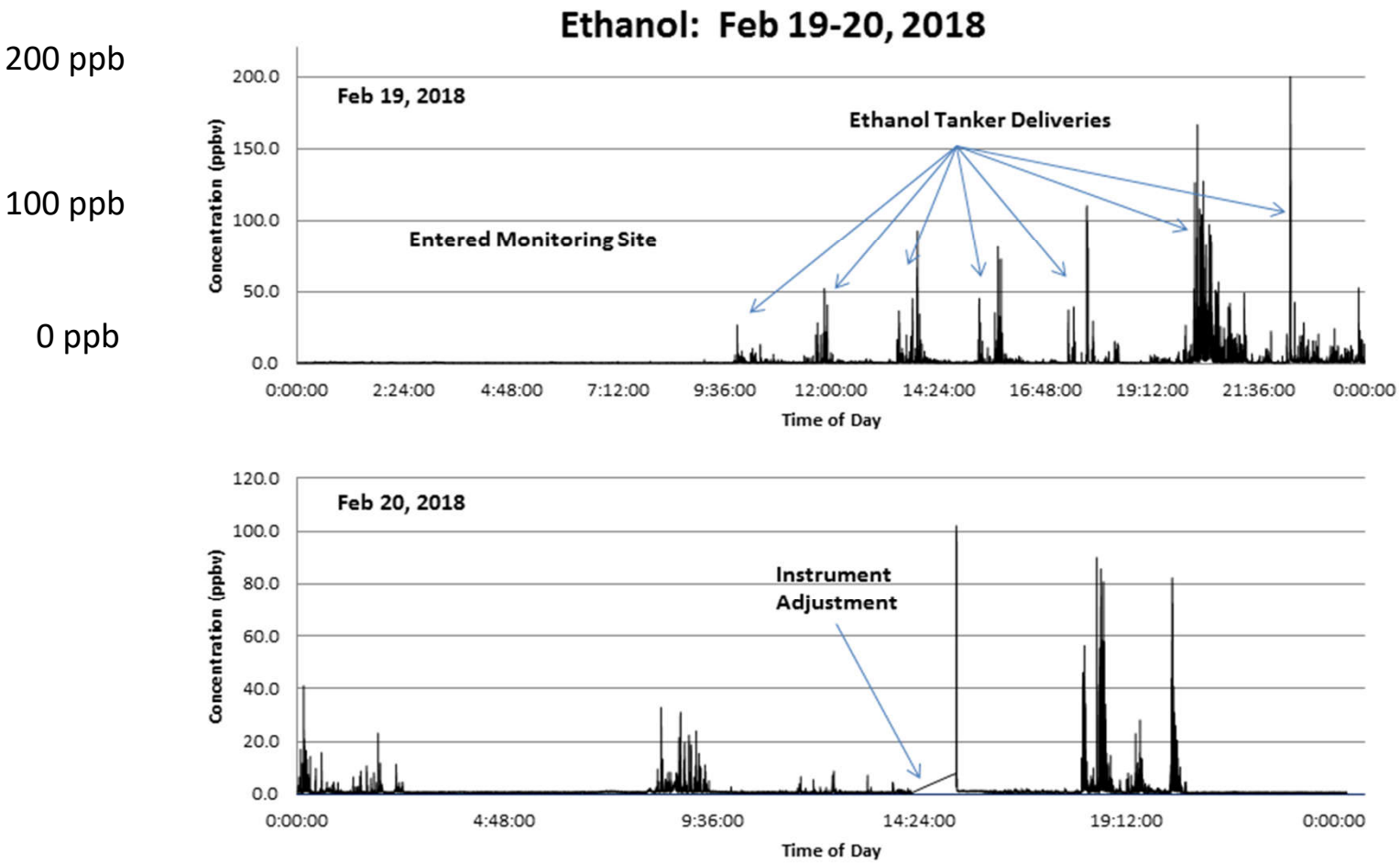
PTR-TOF-MS – Real VOC and BTEX



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Case Study: Process (Fermentation/Ethanol Plants)

Table I. Time averaged concentrations of six sampling locations in parts-per-billion (ppbv).

Concentrations (ppbv)	CO2 Scrubber	DDGS Bag House	RTO Inlet	RTO Out	Syrup Tank	Fluid Out	Detection limit**
Formaldehyde	295	322	9300	679	377	540	6.5
Methanol	828	371	7060	893	5300	906	7.7
Hydrogen sulfide	852	16.0	75.8	50.0	39.5	34.8	0.5
Acetaldehyde	12800	718	20400	4228	6070	2640	49
Formic acid	3960	1110	5000	3930	1160	1230	21
Ethanol	10400	66.7	11700	146	5910	305	0.4
CH_4S	953	10.6	245	29.7	142	13.8	0.3
Acrolein	834	43.5	3996	182	341	52.3	1.4
Acetic acid*	13000	594	16400	1360	4210	4250	4.9
C_2H_6S	3.6	1.8	308	8.0	8.9	6.3	0.1
Isoamyl alcohol	1160	117	12300	423	399	277	1.6
2,3-butanedione	93.9	141	10100	276	879	1020	1.6
$C_4H_{10}S$	114	26.5	293	158	54.3	68.2	2.4
2-furaldehyde	24.0	31.8	3010	56	3940	250	0.2
Ethyl acetate	14800	85.6	22200	406	250	473	2.2
Carbonyl sulfide	46.3	6.8	55.1	9.1	10.1	10.8	0.4
Carbon disulfide	7.0	5.2	19.0	8.6	13.7	2.8	0.2

Notes: Data are 5-minute averages of the most appropriate irradiation setting.

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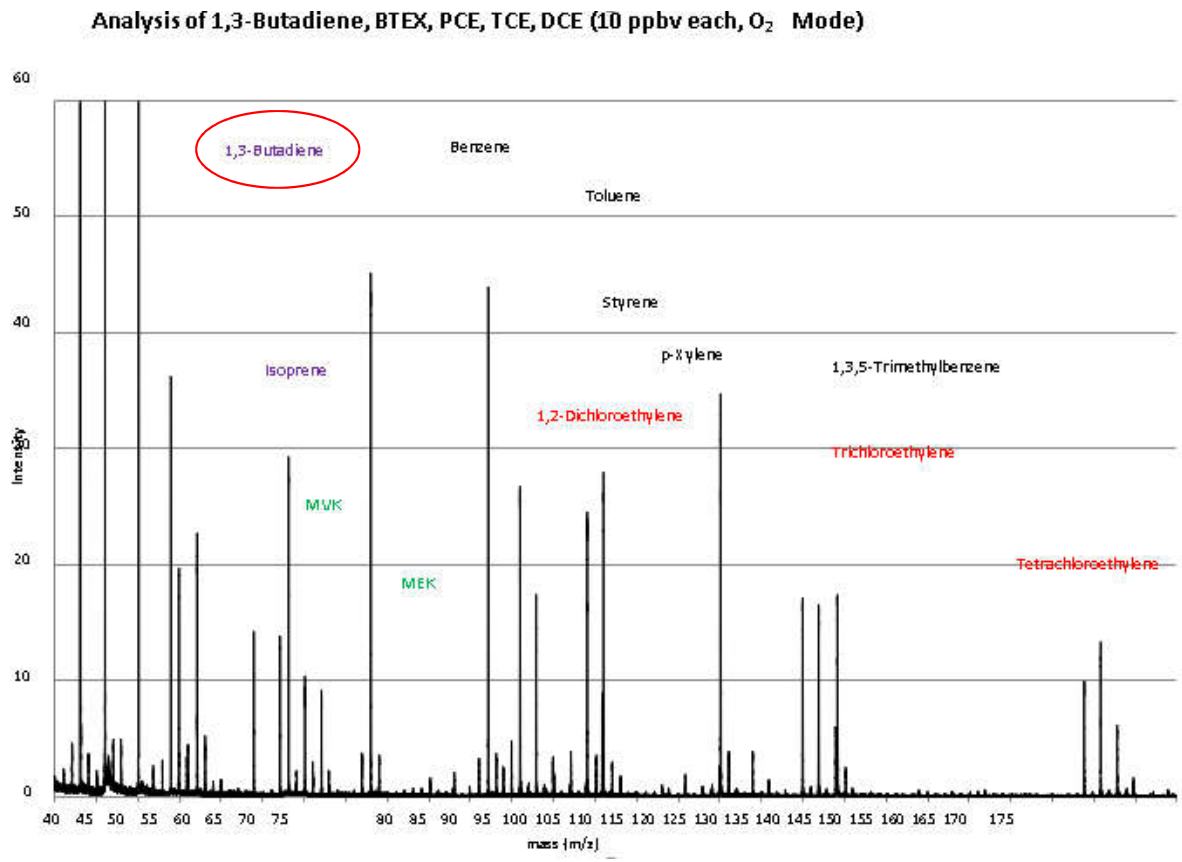
Method Development; 1,3 Butadiene, PCCs



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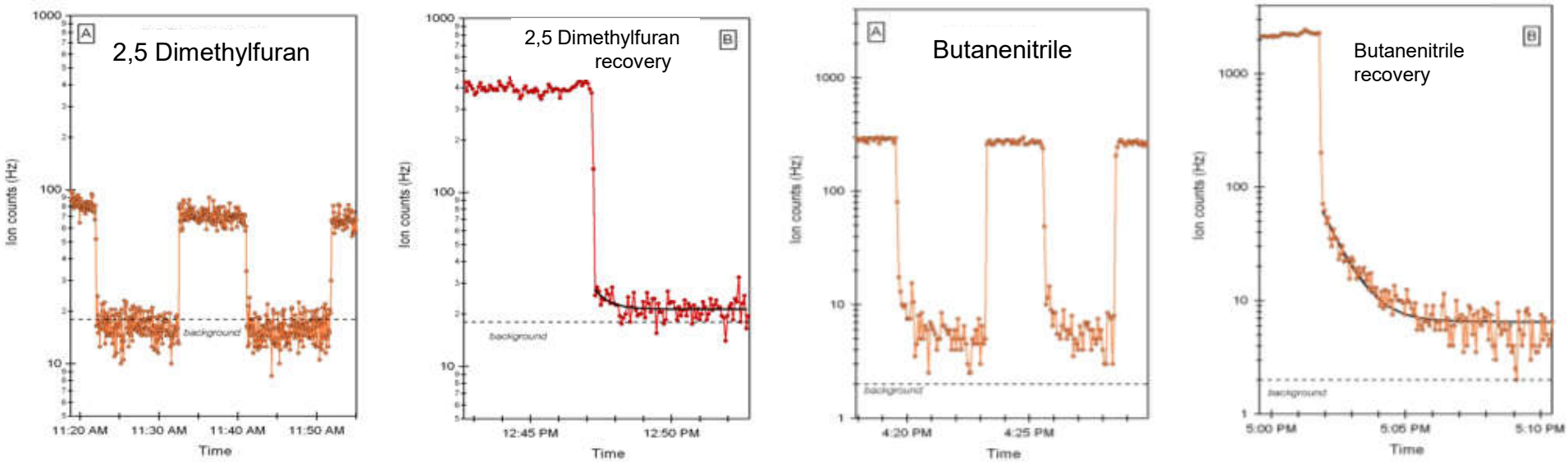
Method Dev:
Hard to Measure Compounds- Furans, Nitrosamines

Fast response time – Small to no memory effects



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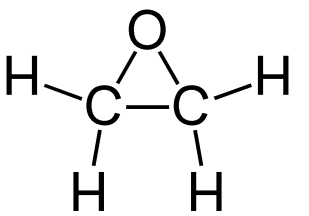
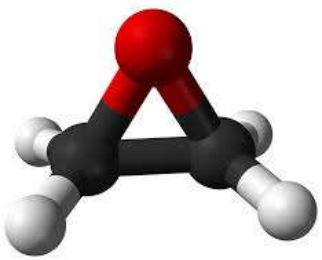
Case Study
Ethylene Oxide/Acetaldehyde Ambient Air

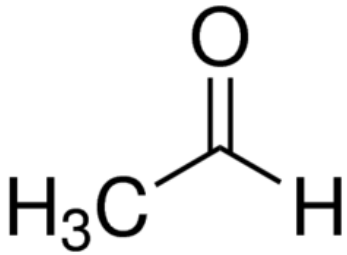
Ethylene Oxide

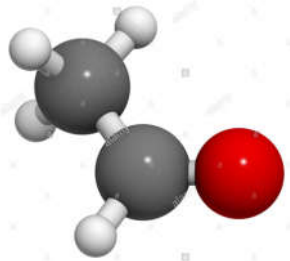




- Mass Spec gives same m/z peak
- Acetaldehyde may be high in Ambient but higher in Combustion
- Similar characteristics make it co-elute – only now new columns coming out
- Typical MS or GC cant get low enough and concentration needed (50-100 ppt)
- PTR reagent chemistry can do real time to <100 ppt ambient

Acetaldehyde





Molar mass: 44.05 g/mol
Formula: **C2H4O**
Boiling point: 51.26°F (10.7°C)
Density: 882 kg/m³

Same Molecular Weight
Similar boiling points

Molar mass: 44.05 g/mol
Formula: **C2H4O**
Boiling point: 68.36°F (20.2°C)
Density: 788 kg/m³

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Method 18 Compliance – GC-FID or PTR (New Column Found) EtO/Acetaldehyde

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Analysis Method : C:\HPCHEM\1\METHODS\ETO-AA.M
Last changed    : 2/21/2019 7:18:42 PM by AH
                  (modified after loading)
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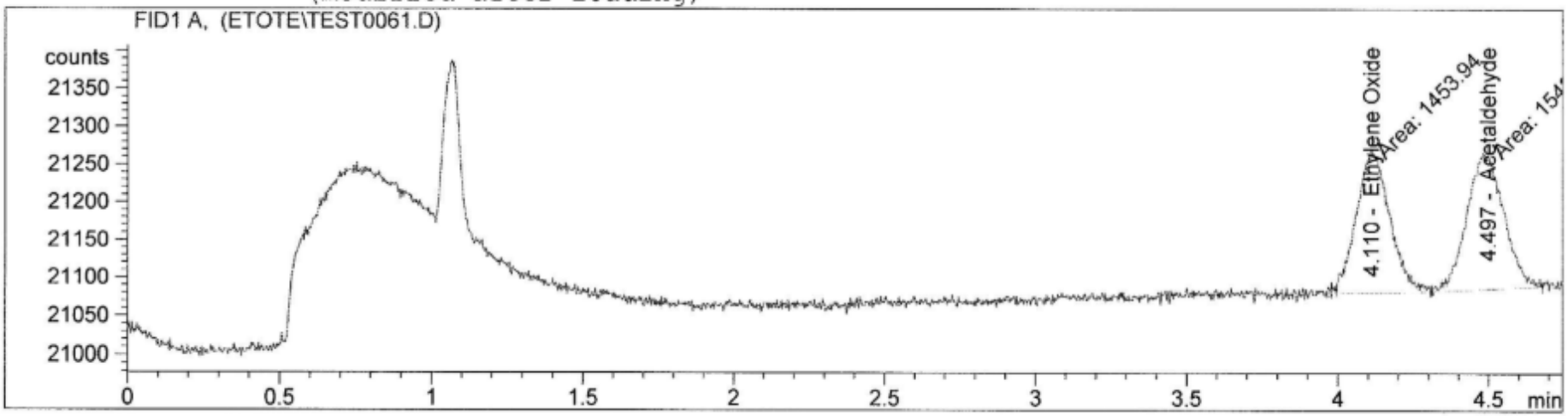


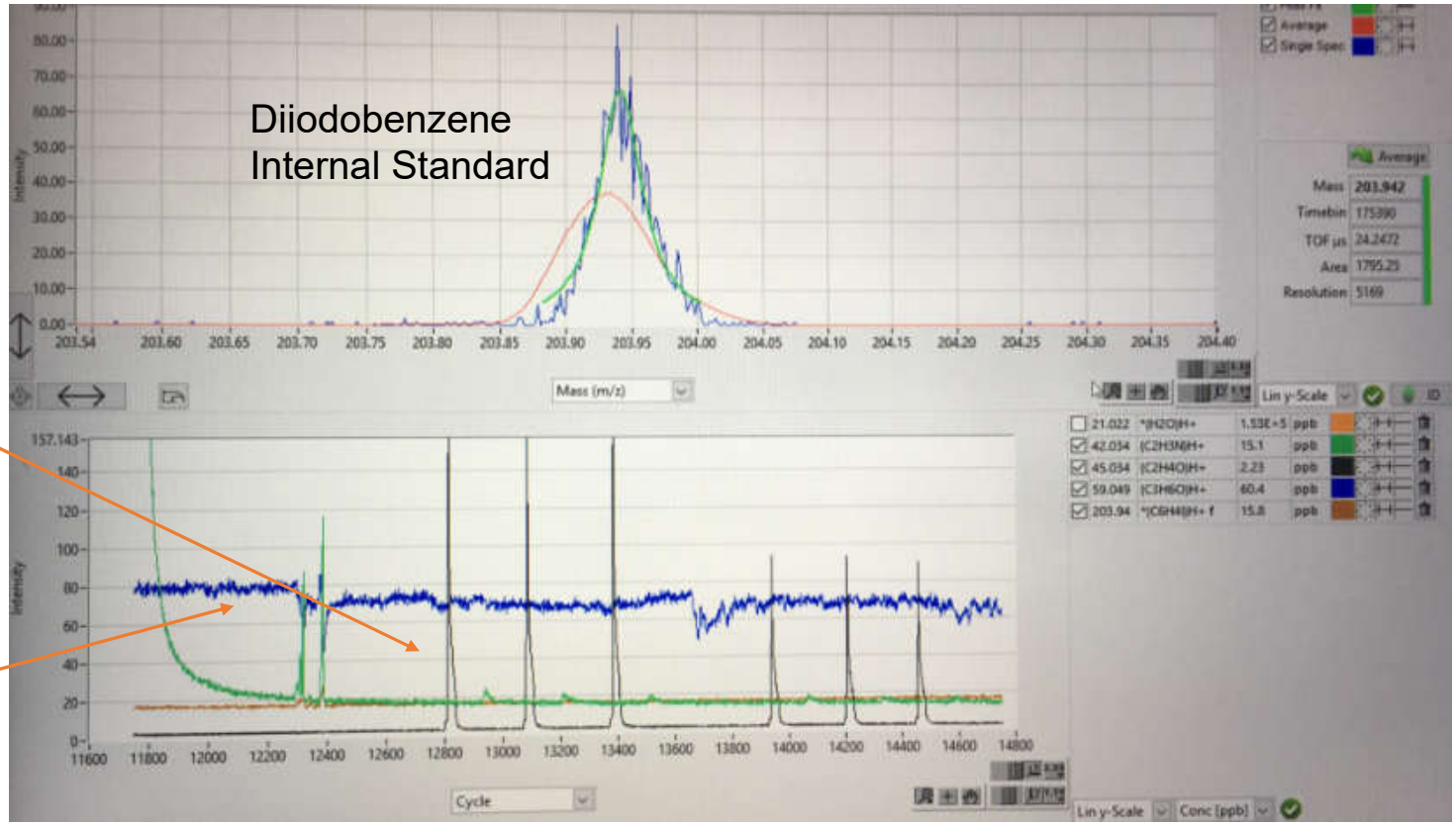
- GC-FID Still not sensitive enough (~10 ppb) for Ambient Air
- Switch to PTR as Detector

Case Study – Try GC-PTR-TOF EtO/Acetaldehyde

- Tried NH+ (Ammonium from Literature) = NG

- Coupled to GC
- Reagent H3O+
- Co-Elution EtO/Acetaldehyde

- Acetone monitored as leak detection (a lot in indoor air)



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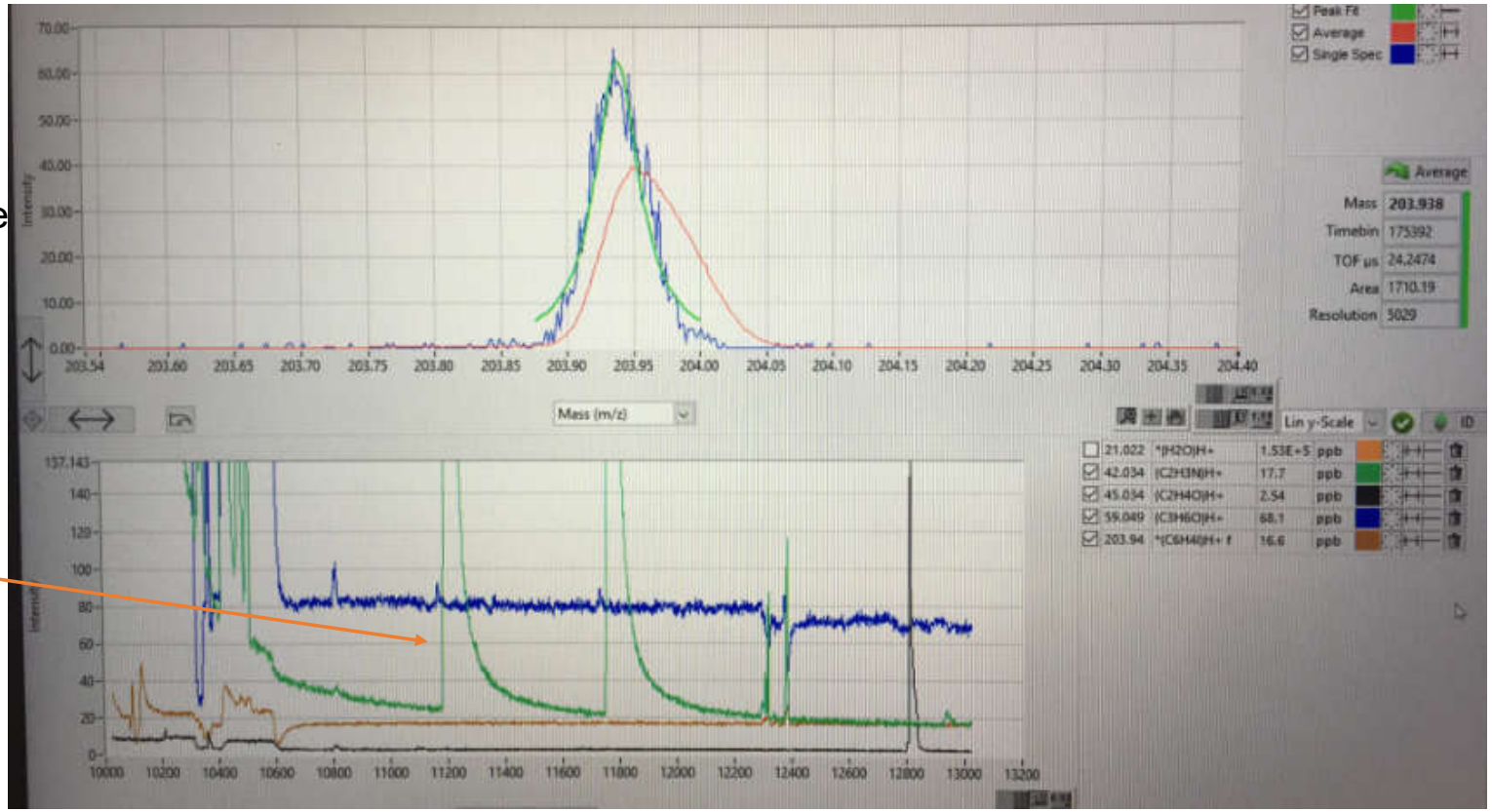
Case Study – Try GC-PTR-TOF with DNPH Tube (Inlet to GC) EtO/Acetaldehyde

- Switch Back to H3O+
- Add Dinitrophenylhydrazine (DNPH Tube)
- Removes 99% Acetaldehyde But Sil Gel removes EtO
- DNPH dissolved in acetonitrile
- TO5 DNPH glass fiber cartridge underway

Acetonitrile (Green Line)



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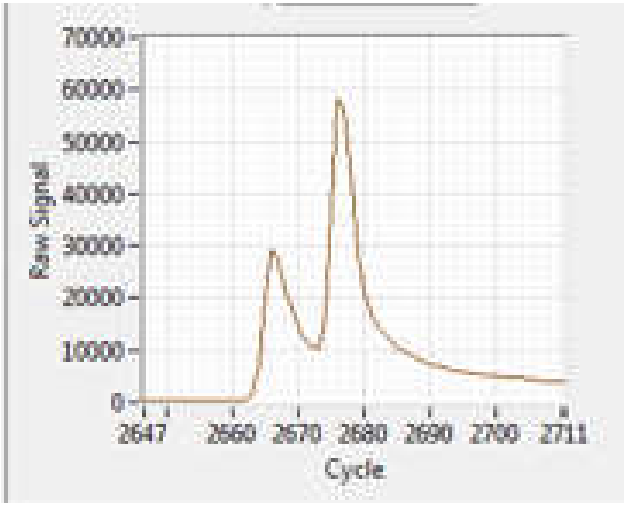
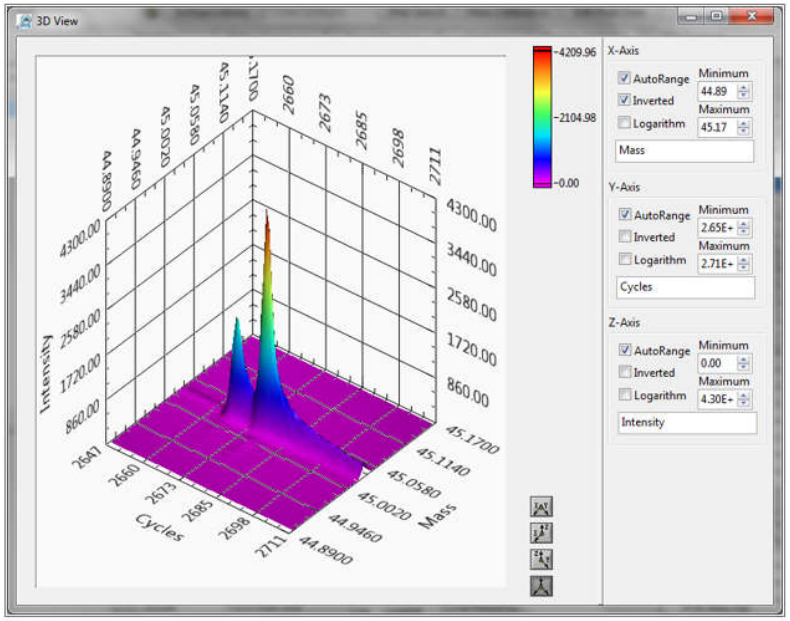
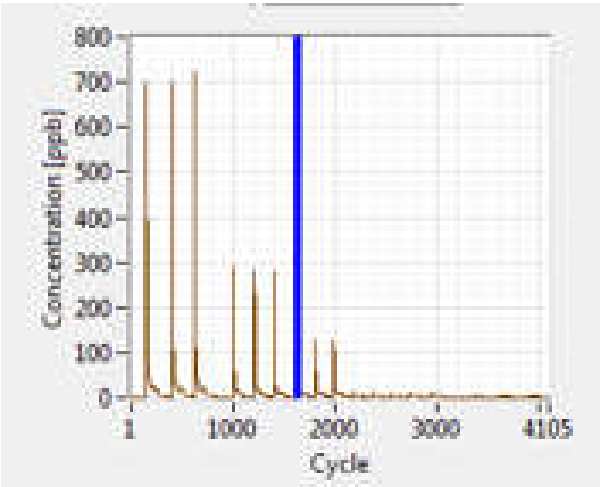
Case Study – GC-PTR-TOF-MS
New Column
EtO/Acetaldehyde

- GC-PTR-TOF-MS
- Separation on GC
- PTR-TOF-MS Integrations
- Extremely Reproducible







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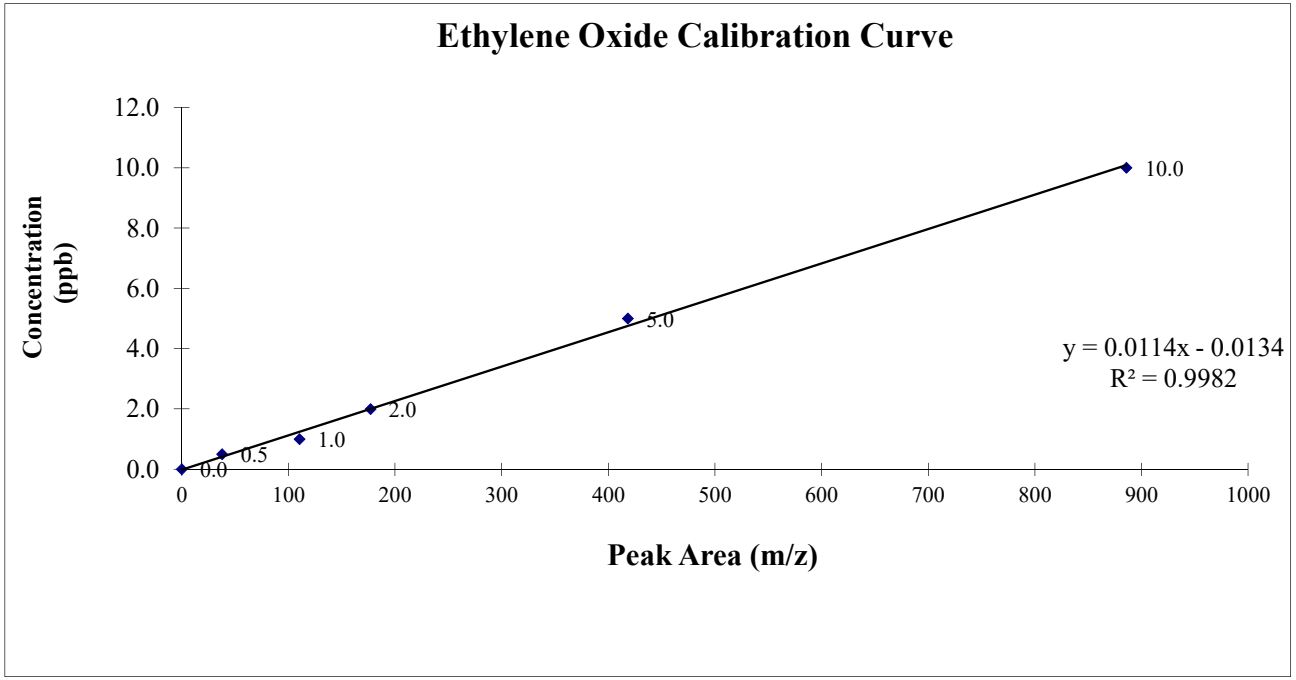
GC-PTR-TOF-MS EtO Linearity



NIST Traceable
1% Accuracy MFCs
1000:1 Dilution Capability
GC Injections each point
+-5% diff precision criteria met

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GC-PTR-TOF-MS EtO Detection Limit

Company: PTR Validation
Location: Wauconda, IL
Monitor: PTR-TOF
Manufacturer: Ionicon
Model: 6000
Date: 2/21/2019
Operator: D. Chapman
Compound: Ethylene Oxide

Repetition	Average PTR Reading (ppb v)
1	0.95
2	1.19
3	1.00
4	1.03
5	1.31
6	1.30
7	1.02
8	1.24
9	1.13
10	1.04
11	1.12
12	1.28

Total Population	12
t-Test Population (n-1)	11
Average RM reading	1.13
Standard Deviation	0.128
Student t- Test Value	2.718

	ppb v	ppt v
MDL (LOD)	0.347	347
PQL (LOQ) (3 x MDL)	1.041	1041

The USEPA defines MDL as "the minimum concentration that can be determined with 99% confidence that the true concentration is greater than zero." This procedure is outlined in 40CFR 136 and TTN EMC.
The NELAC Standard (TNI) now define detection limits as Limit of Detection - LOD and Limit of Quantification - LOQ. These terms were historically known as Method Detection Limit - MDL and Practical Quantification Limit -PQL.

Student t-Test Values	
t-Test Population	t-Test Value
7	2.998
8	2.896
9	2.821
10	2.764
11	2.718
12	2.681

- **Limit of Detection GC-Integration-PTR-TOF-MS = 350 parts per trillion (ppt) Real Time 100 ppt**
- **Lower LOD with larger sample loop**
- **Current ONGOING Real Time Direct PTR-TOF-MS (New Reagent Chemistry) = <100 ppt**
- **PTR also being retrofitted with new Lens to gain 3x better sensitivity**

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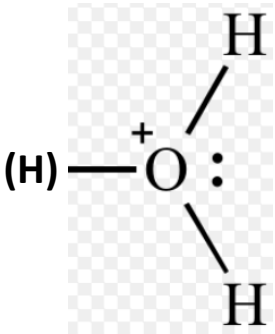
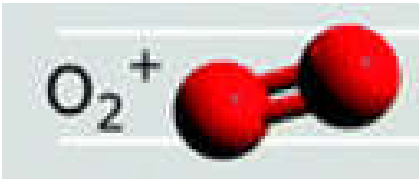
REAL TIME Mthd Dev - Dioxygenyl Association



Oxonium
or Hydronium
18 or 19 amu



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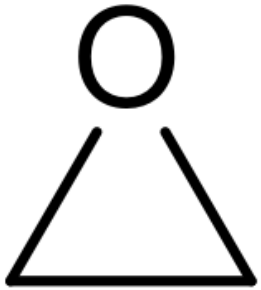

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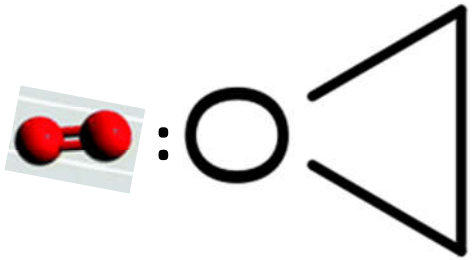

Dioxygenyl
O2+
32 & 33 amu

EtO
44 amu

EtO - O2
Association
76 & 77 amu

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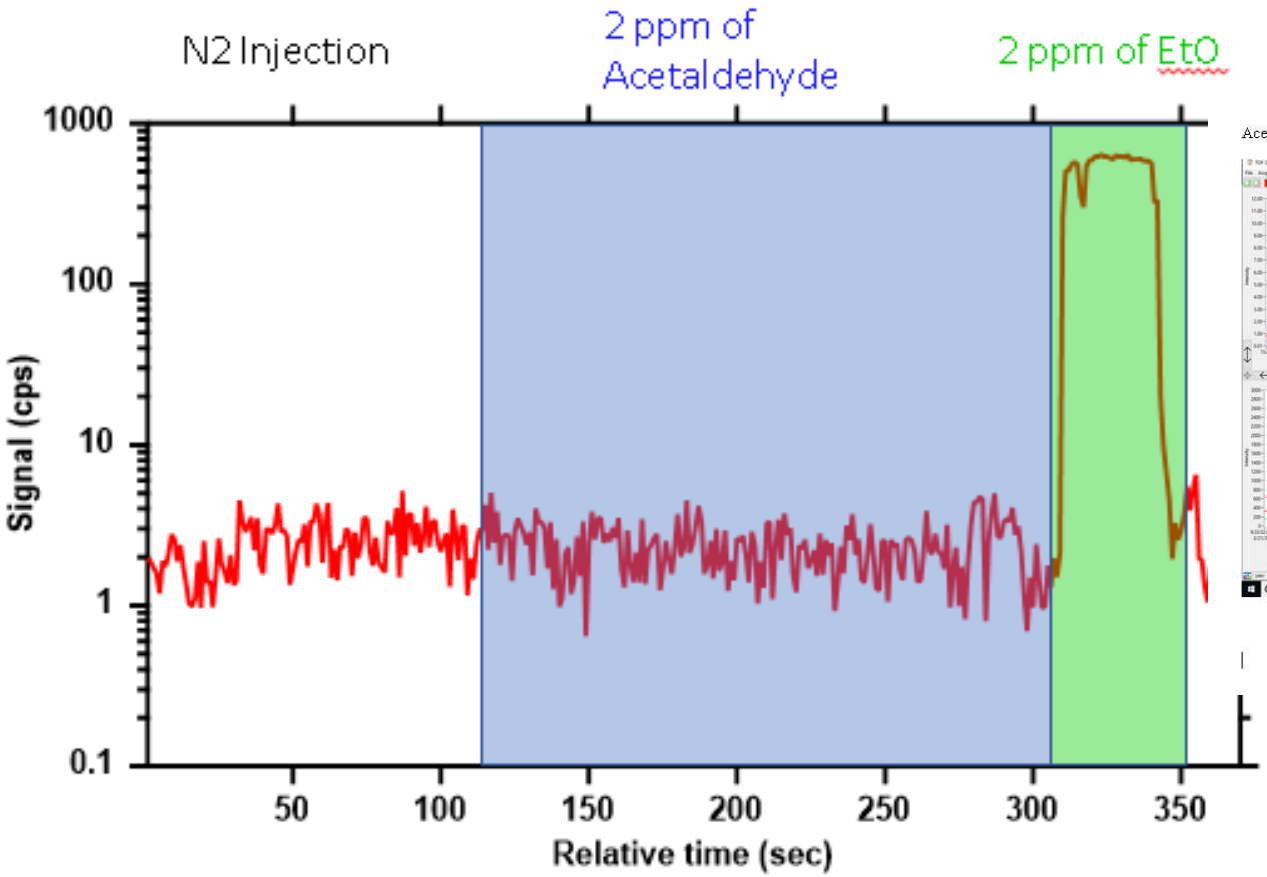
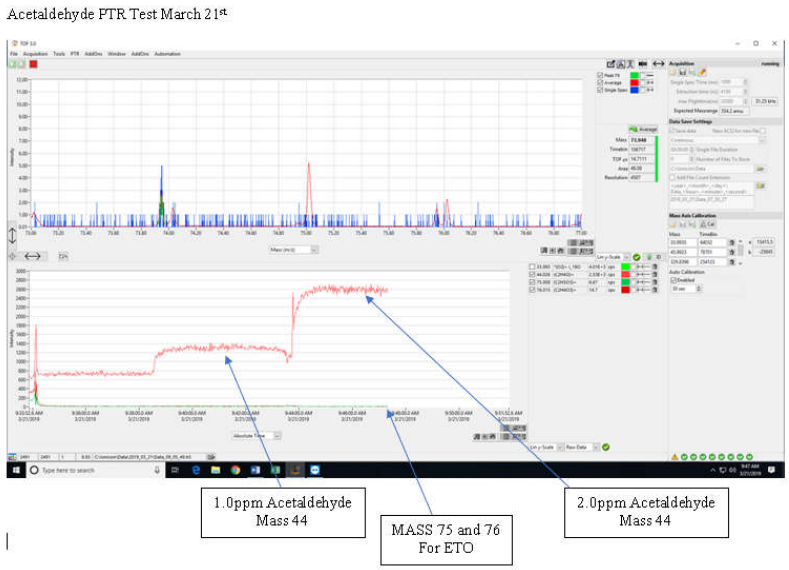
Optimized method for the detection of EtO

No interferences from isobaric compounds





Mass 76 and 77 EtO

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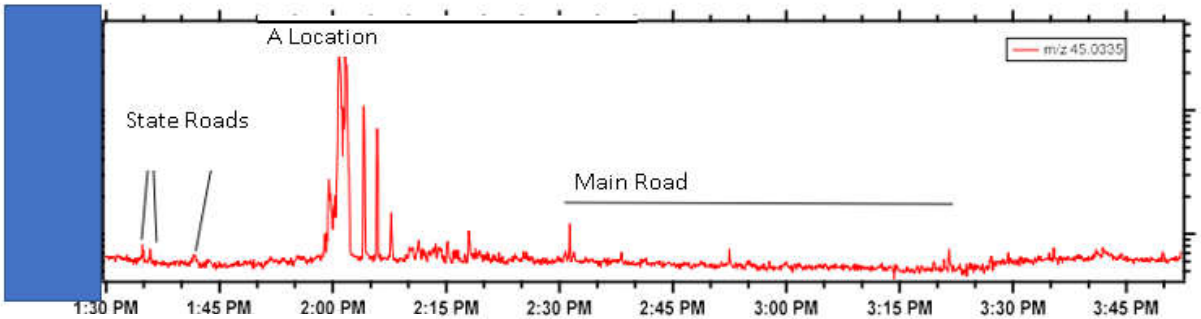
Real Time Mapping



- **GPS Coordinates**
- **Video Corellation**
- **Wind Velocity -Sonic Anemometer**
- **Wind Direction**
- **Montrose Triangulation Platform**

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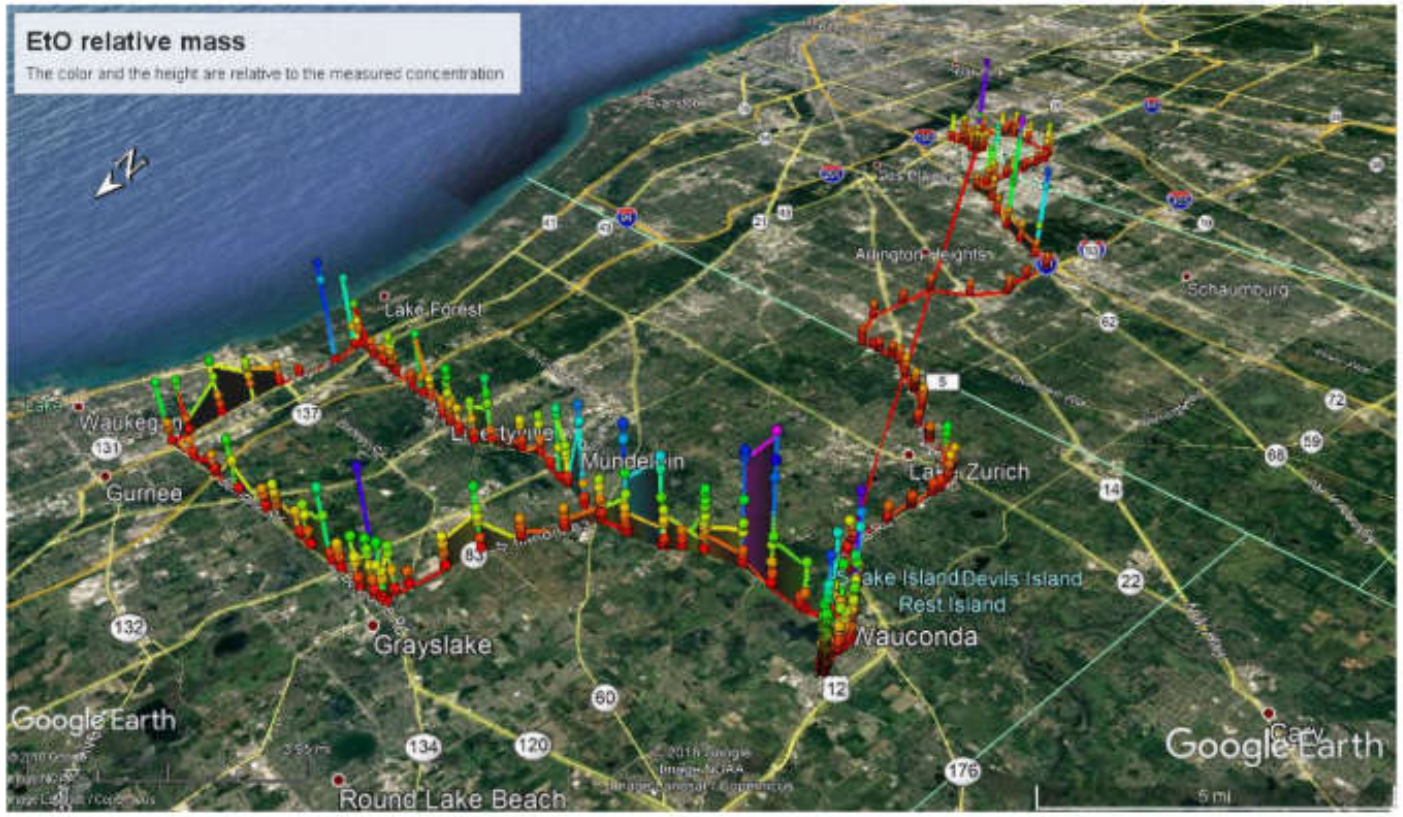
Visualization of EtO Dispersion



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EtO and Other Targets Everyday Sources

EtO & Acetaldehyde

Source	EtO and Acetaldehyde	Benzene	Toluene	Xylene
	Concentration (ppb)			
N2 injection	0	0	0	0
Laboratory background	0	2.2	9.5	40
Breath test	0	6.1	25	96
Breath test 2	2.5	5.8	23	79
Korean cabbage kimchi	4153	0	37	116
Cigarette smoke	2	150	226	186
Unlit cigar	0	2.3	6.1	15
Candle	6	1	5.7	17
Heated vegetable oil (80% soy)	3	32	7.9	19
Diesel exhaust (ignition stage)	0	1016	454	475
De-icer	2	0	0.2	0.2
Burning leaves	0	250	108	66
Breath test 3	0	2.2	6.9	14

EtO Alone

Sources	Concentration (ppb)	
	EtO	Ethylene
Kimchi cabbage	10	-
Cigarette combustion	176	135
Biomass burning	199	56500
Gas exhaust	0	-
Diesel exhaust	1.3	-
Diesel exhaust no catalytic converter	2.5	-
Diesel exhaust from an older truck	26	-
Cigarette breath	12	-

"-" identifies materials that were not measured for Ethylene.

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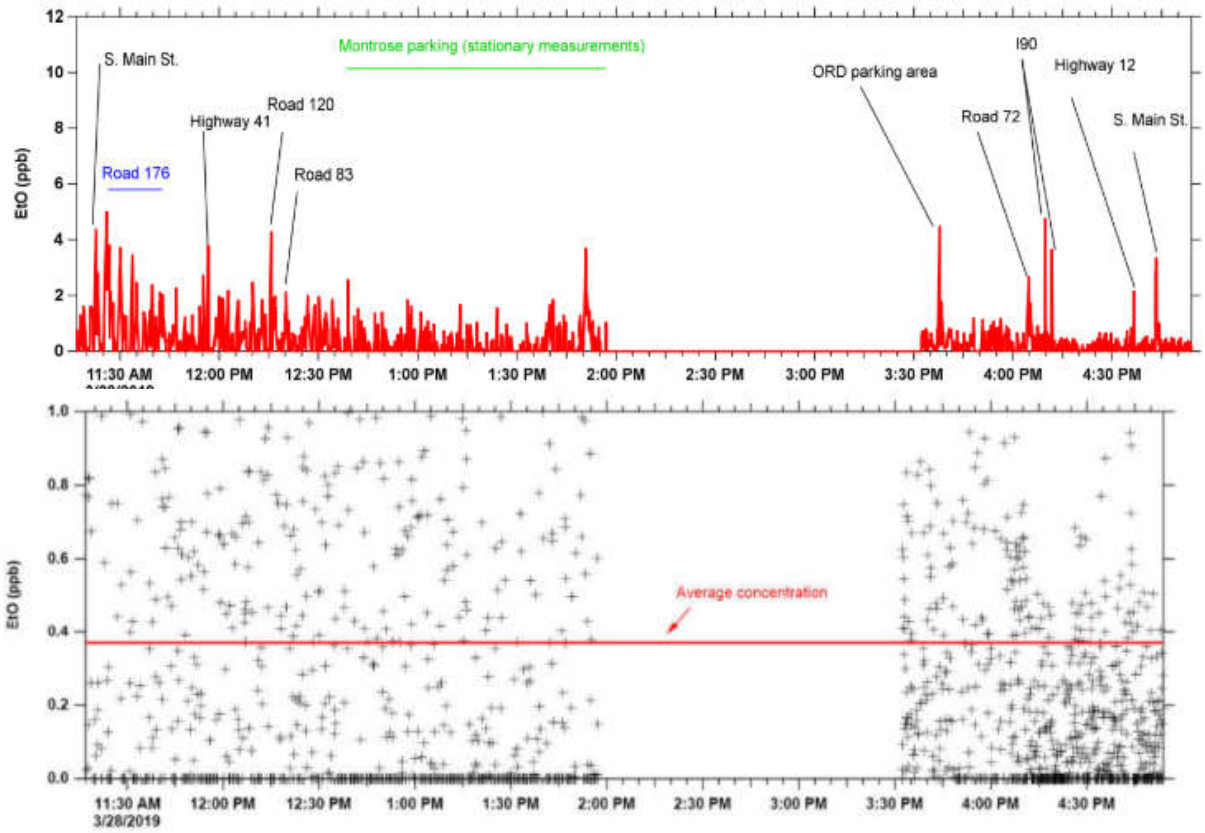
Industry Defense Studies 2 – Real Time



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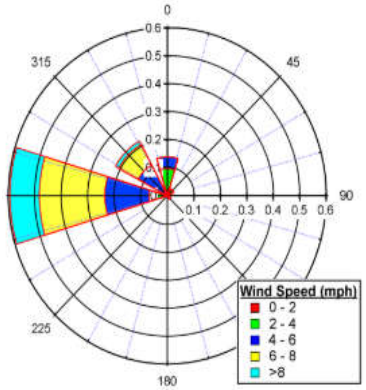
EtO Statistics and Wind Roses

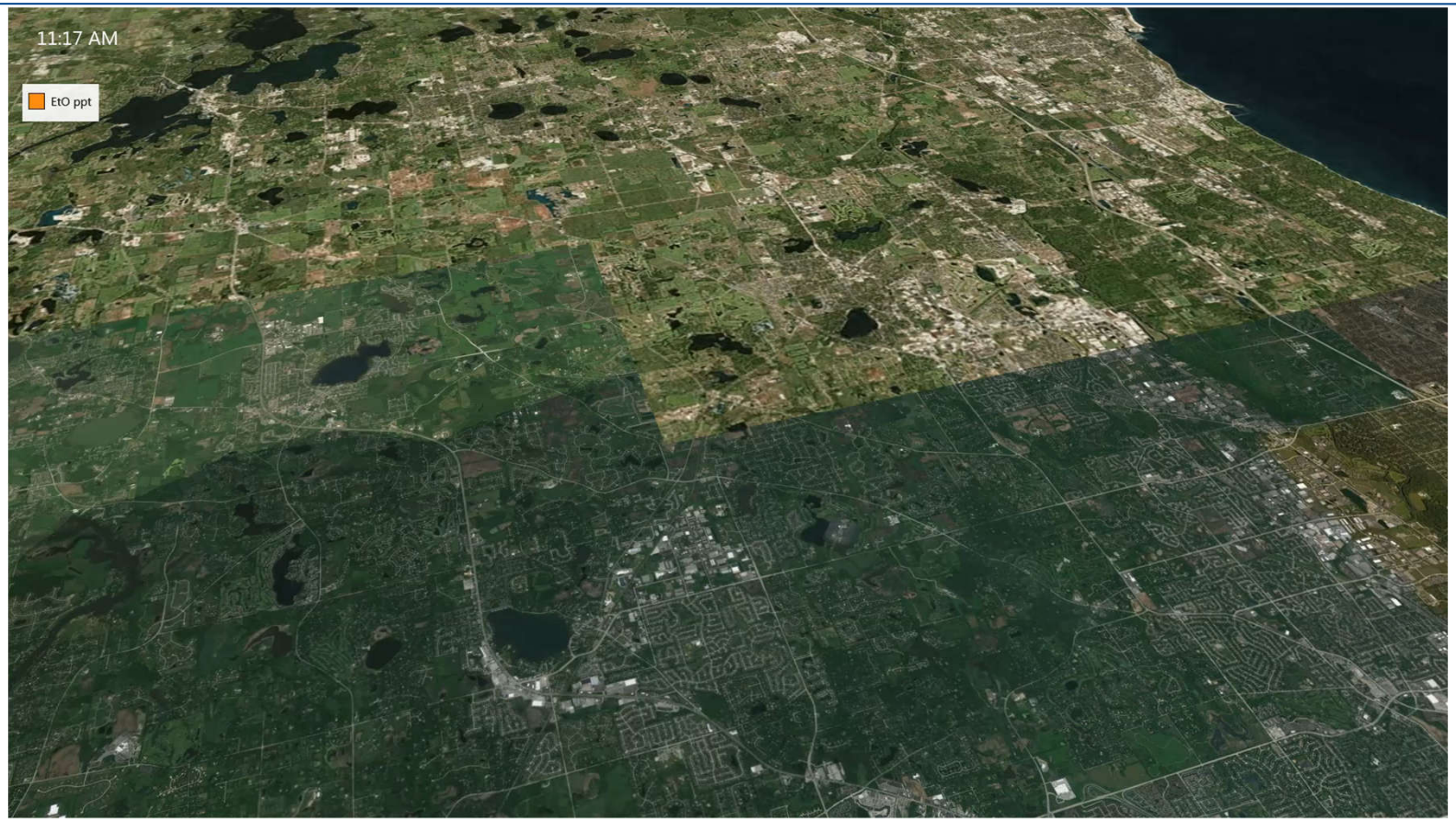
ppbv

location	start time	stop time	average	stdev	min	max
Road 176	11:22	11:54	0.78	1.04	<0.42	5.02
Highway 41	11:54	12:02	0.64	0.90	<0.42	3.80
Road 120	12:02	12:16	0.61	0.75	<0.42	4.30
Road 83	12:17	12:23	0.48	0.53	<0.42	2.14
Road 176	12:23	12:31	0.54	0.59	<0.42	2.02
Montrose stationary measurements	12:32	13:51	<0.42	--	<0.42	3.70
S. Main St.	13:52	13:57	<0.42	--	<0.42	1.16
ORD	15:32	15:57	<0.42	--	<0.42	4.50
Road 72	15:57	16:06	<0.42	--	<0.42	2.69
I-90	16:06	16:12	0.47	0.79	<0.42	4.78
Road 53	16:12	16:20	<0.42	--	<0.42	0.50
Highway 12	16:25	16:42	<0.42	--	<0.42	2.17
S. main St	16:42	16:53	<0.42	--	<0.42	3.36



MONTROSE ENVIRONMENTAL

Visualization of EtO Ambient Dispersion



MONTROSE ENVIRONMENTAL

Summary

- PTR-TOF-MS may be used to measure ultra-low real time detection limits for hard to measure compounds (Methodologies developing quickly) in real time
- Other Test Method (OTM) may be developed for sources with EPA approval
- Integrated GC-PTR-TOF-MS represents legally defensible EPA Reference Method 18 Direct Interface if all QA/QC in Method followed
- GC Integrated or Direct Real Time PTR-TOF-MS is a cost effective solution – Same as a typical FTIR test (Pay by day) - Reasonable Rates