Proton Transfer Reaction Mass Spectrometry (PTR-MS) for Ambient and (Compliance) Source Testing Discussion

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ABSTRACT

Proton transfer reaction time of flight mass spectrometry (PTR-TOF-MS) is a continuous monitoring technique primarily used for ambient environmental measurements. It is an extremely sensitive and real-time instrument capable of measuring into the part per billion (ppb) and parts per trillion (ppt) levels for many organic and inorganic compounds. In recent years, its abilities were investigated to be used in identifying, quantifying, and monitoring stationary sources, typically after dilution. Although regulatory acceptance for PTR-TOF-MS is sparse, there is an accepted instrument for use with modified EPA Method 8265 for vapor intrusion and sewer gas studies. Anecdotal discussions with regulatory personnel indicate a reluctance to embrace PTR technology due to its cost and general availability to industry. A recent example of this phenomenon is Fourier Transform Infrared (FTIR) spectrometry. There was an initial reluctance to embrace the technology; however, after roughly a decade, it became fully integrated as a compliance source testing tool. Cost and availability of the PTR technology to industry for testing are quickly being addressed and acceptable methodologies are being developed for United States Environmental Protection Agency (EPA) consideration. The need for real-time, ultra-low-level measurements is real as can be demonstrated with the recent ethylene oxide risk assessment reviews. Real-time or near real-time (<15 min per data point) detection limits of ethylene oxide in ambient air have already been demonstrated down to 100 ppt.

A draft ASTM method is also being developed, "Standard Guide for Selection of Real-Time and Near Real-Time Mass Spectrometer-Based Technologies for Online Measurements of Volatile Organic Compounds in Ambient Air." Additionally, placement of a gas chromatograph (GC) or "fast GC" in front of the PTR, with the PTR-TOF-MS acting as the detector, fits the definition of EPA Method 18 direct interface, "Measurement of gaseous organic compound emissions by gas chromatography."

INTRODUCTION

Several test studies have been performed on ambient and indoor air projects with good success, which begs the question can PTR-MS measure stationary or mobile sources. Due to its ability to monitor in one- (1-) second increments, a high temporal resolution of emissions can be achieved which, in return, can provide unseen spatial resolution in ambient measurements but also in process or control device optimization. With detection limits in the ppb to ppt level for volatile organics, a PTR instrument performs at the same level or better than any of the existing technologies presently employed in the field. However, a PTR has the time resolution of seconds to minutes when coupled with a front-end separatory technique. For projects employing PTR techniques at large area sites and remediation operations that require immediate response, this method can be a solid cost-saving option. As more PTR instruments are employed in the field and acceptance of the technology advances, costs for testing are anticipated to drop. Present costs for testing one source are not much higher than a typical FTIR or GC test.

Several applications show a need for more sensitive and accurate measurements in real time. This paper will report on recent advances in measuring the following compounds with either simulated or field data results. The compounds investigated are ethylene oxide, 1,3 Butadiene, several other HAPs including the oxygenated HAPs (OHAPs) critical to the wood products and cement industries, and Highly Reactive HAPs (HRVOC) and VOCs from an ethanol plant.

DISCUSSION

PTR-MS instruments may use different reagent ions to protonate many different species to be detected simultaneously. Different reagent ions allow the user to employ different ionization schemes to increase selectivity. Sample matrix compounds are not fully ionized and react differently when exposed to differing reagent compounds. To provide a wider range of detected compounds, different reagents provide a differing spectrum fingerprint that is used to prove or disprove the target compound of interest in the sample matrix [1,2]. The most recent instruments allow switching between reagents in seconds and on the fly. However, if the target compound is known and no isomers are found or expected, a single reagent is used.

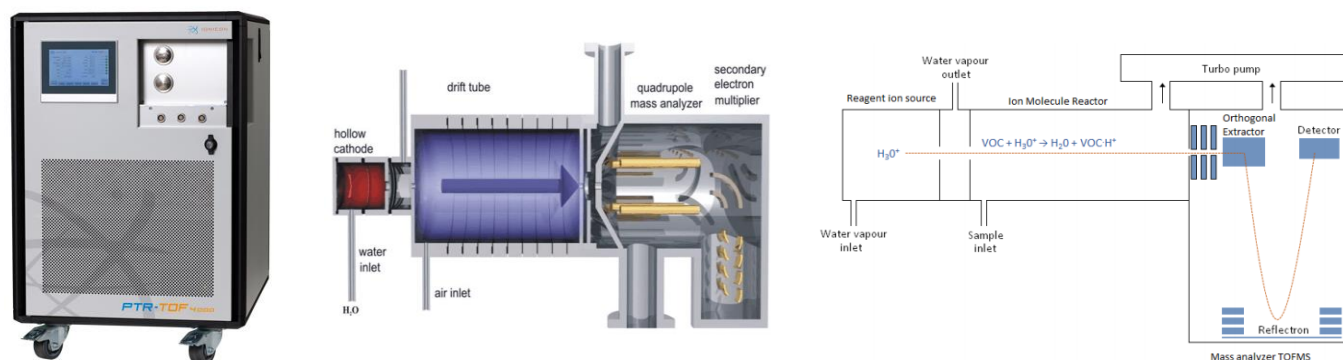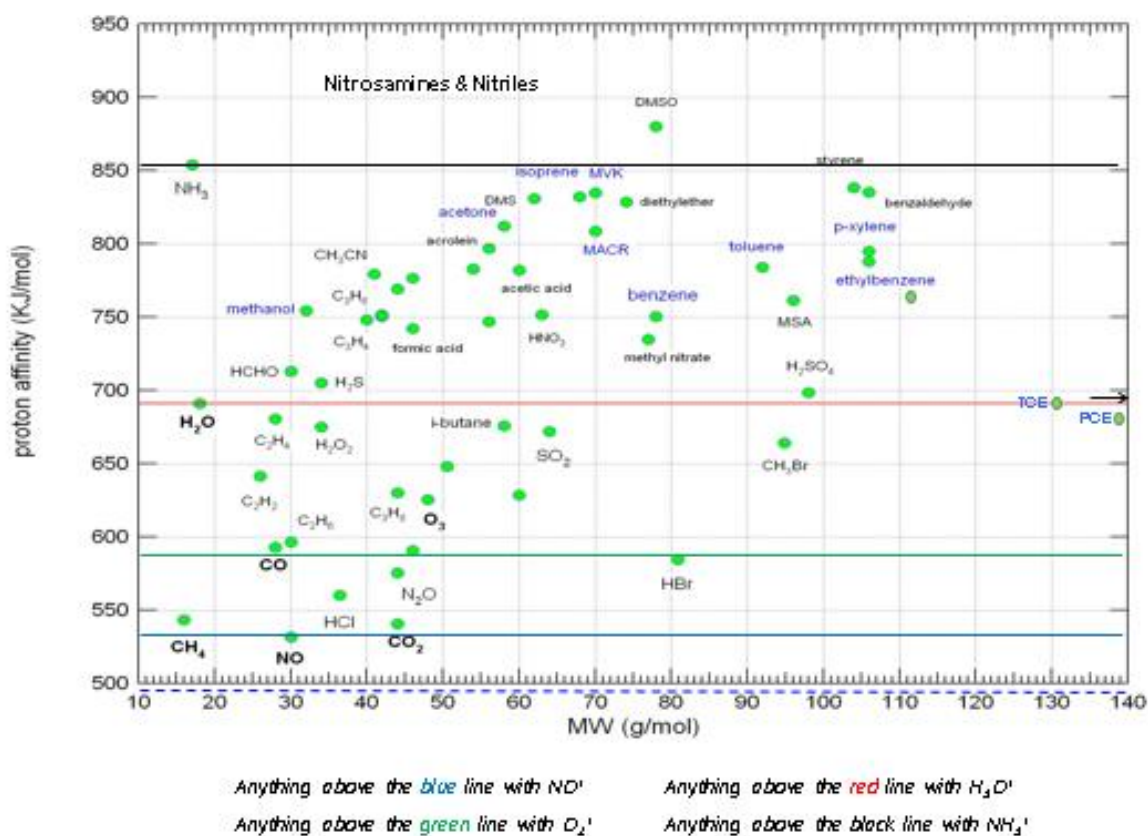**Figure 1. Typical PTR-TOF-MS Schematic Showing Drift Tube and TOF**

Table 1. Typical Common Reagents employed for different target compound species [2]

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Anything above the blue line with NO⁺   Anything above the red line with H₃O⁺
Anything above the green line with O₂⁺   Anything above the black line with NH₄⁺

PTR instruments are sometimes coupled to various types of GC, thermal desorption instruments, or ion mobility spectrometers (IMS) that allow a user to concentrate or pre-separate target compounds or their isomers prior to detection and quantification by the PTR-MS-type.   The use of these additional capability technologies add time to the typical 1-reading-per-second real-time data to near real-time data. Improved sensitivity or improved selectivity is typical.

Time of Flight (TOF) MS instruments have improved resolution and speed. Improvements in mass accuracy, which assists in identifying individual ion signals, mass, range, and multi-ion sensitivity, are common. In place of mass overlaps, which cannot be separated without the use of a front-end GC, this improved resolution becomes very important.

A fast GC is an easy way to reduce analysis times but keep the resolving power of the GC.   A typical fast GC may produce separation of sample matrix components in less than 10 minutes and many times with back-flush capability on the column to below 5 minutes per sample data point.

A PTR-MS coupled to a standard or fast GC [3,4] enhances selectivity and sensitivity and increases the types of compounds and isomers in a sample matrix [5]. A PTR MS without a front-end separatory technique provides high temporal resolution to be an advantage in several applications, including intermediaries, transients, and process optimization. Ten to fifteen minutes is typical for a coupled GC PTR MS [5,7] or even lower with back-flush capability or a limited number of constituents in the sample matrix allowing the use of a reduced-length column or temperature and/or pressure programming.

Case Study 1: Ethanol Processing

On Table 1, an ethanol (fermentation) facility was sampled at six exhaust points along the process line using different reagents on the fly (switching between reagents in approximately 10 to 20 seconds), which allows the compounds to be identified and confirmed, but also identified by their different chemistry and/or proton affinity where some will react only to a specific reagent used with a lower proton affinity than the target compound. Additionally, the parameters of the chemical ionization (CI) source and funnel lens of the "drift tube," such as voltages, may be adjusted to increase electron ionization (EI) and further fragment the target species or completely destroy it if it interferes with another species.

The Table demonstrates a wide array of compounds that may be identified and the wide range of concentrations demonstrates the ability of the instrument to measure over several orders of magnitude.   Depending on the instrument series, some PTR-TOF-MS systems will "saturate," meaning complete transfer of available protons from the reagent to the target leaving no other protons available for transfer. Several other factors may cause saturation of the TOF detection system, such as saturation of an analog to digital semi-conductor chip (ADC) in the electronics path.

In these high source concentration events where you have mixtures of different compounds at high concentrations and low or even ultra-low concentrations, a series of dilutions may need to be performed if all compound concentrations are needed to be known. This is typically performed using ultrapure or research-grade nitrogen or synthetic air. Synthetic air may be useful if reactions with oxygen are needed to be seen.   In any case, the inlet of the PTR has a limit of 120°C, so the sample must be received at a non-condensing moisture content below the

sampling system or PTR inlet temperature of moisture and/or target compound saturation/condensation.

Table 2. Ethanol Plant Emissions from Six (6) Sources. Up to 40% Moisture by Volume.

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.
* This results may contain contributions by fragments of other volatile organics that dissociate into acetic acid, in particular ethyl acetate.
** Detection limits are reported as average 3-sigma values based on daily zero air measurements over the course of the sampling campaign.

Table 3. Ethanol Plant Target Compounds Concentrations, Standard Deviation Under Different PTR Conditions

High Voltage Mode											
Periods		Average (ppb)					Standard deviation (ppb)				
Period start	Period end	Methanol	Acetaldehyde	Ethanol	Acrolein	Acetic Acid	Methanol	Acetaldehyde	Ethanol	Acrolein	Acetic Acid
9:03:24	9:10:39	5920	4636	682	2313	2478	236	129	27	123	155
9:16:19	9:21:49	3656	2969	378	1458	1659	33	37	12	17	34
9:25:49	9:28:09	1993	1796	194	750	903	32	21	6.5	13	11
9:40:04	9:46:14	1138	1168	99	383	508	21	16	6.0	8.7	12
9:48:24	9:51:29	752	895	58	219	331	27	14	4.5	6.7	5.5
10:06:04	10:07:19	512	731	38	117	223	14	11	4.5	3.8	6.0
10:16:04	10:17:04	302	577	10	27	144	9.3	12	2.2	1.8	4.7

Low Voltage Mode			
Periods		Ethyl Acetate	
Period start	Period end	Average (ppb)	Standard deviation (ppb)
9:29:34	9:36:39	725	32
9:36:49	9:38:09	372	7.6
9:53:44	9:58:39	204	20
9:58:49	10:01:19	123	3.1
10:12:09	10:15:04	50	2.8

Figure 2. HAP Compound Batch Process Concentration Over Time
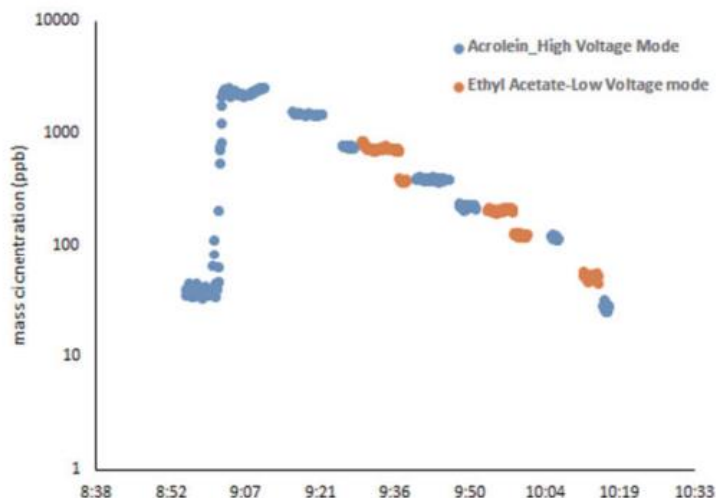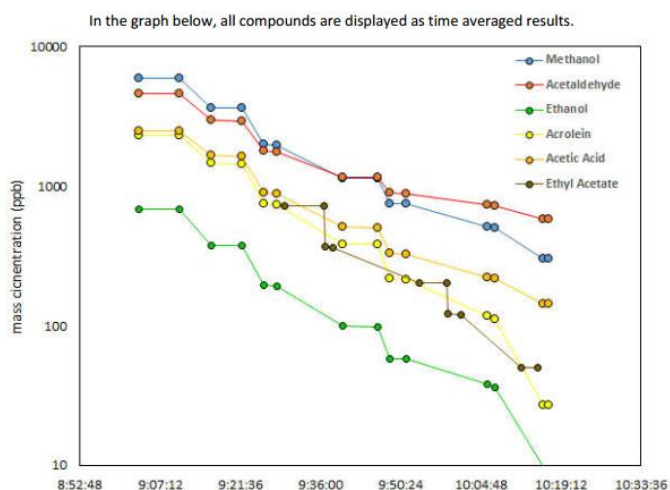

Figure 3. Additional HAP Target Compound Batch Process Concentration Over Time

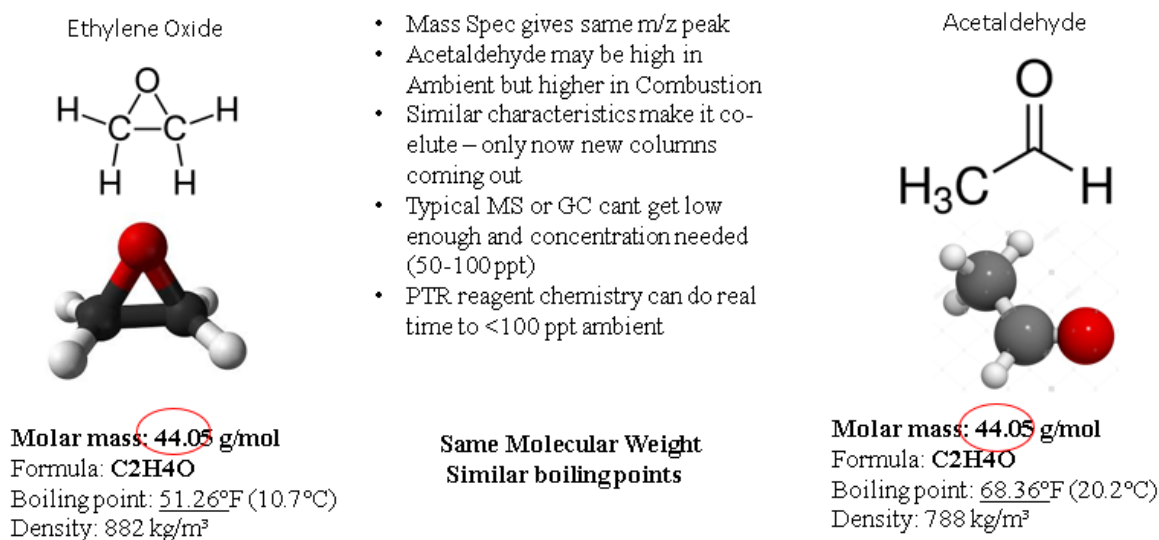**Case Study 2.0 – Ethylene Oxide (EtO)**

The current news outlets report [8,9,10] on ethylene oxide manufactures and sterilization facilities have resulted in a focus on ethylene oxide concentrations from stacks and ducts, as well as ambient air levels near these facilities. There has been a push to also determine geographical concentrations of ambient levels of ethylene oxide and contributions from other contributory sources, such as lawnmowers, barbecue grills, airports, and diesel engines. Montrose has performed many of these tests, including building temporary total enclosures for these measurements. However, the need is still present for low-level ambient measurements at or

below typical normal ambient concentrations in urban and/or metropolitan areas with one community measuring 26.4 ug/CuM or 1,000 times above EPA limits [10]. Ambient measurement references cover a wide range of published data from the lowest concentration found at 16 parts per trillion (ppt) at remote coastal locations. This is believed to represent the hemispheric background for this persistent chemical. In the Los Angeles area in 1988, concentrations ranged from about 30 ppt in the suburbs to 800 ppt downtown [11].

ETHYLENE OXIDE INTERFERENCES

As presented in the diagram below, it is not easy to measure ethylene oxide due to its relationship to a common aldehyde with a similar chemical nature and same molecular weight. It has been difficult to measure one without interference from the other by either gas chromatography or various types of mass spectrometry such as those operated in CI mode, which includes the PTR.

Figure 4. Chemical Parameter Comparisons of Ethylene Oxide and Acetaldehyde

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

An attempt is ongoing to use a dinitrophenyl hydrazine (DNPH) impregnated glass fiber filter to derivatize the acetaldehyde and allow the EtO to pass through with a recovery experiment.   This would allow real time PTR-TOF-MS measurements. Experiments are ongoing.

SEPARATION TECHNIQUES USING GC-PTR-TOF-MS

The integration of a front-end GC to the PTR allows for the separation of a complex matrix or isomers of a compounds such as ortho-, meta-, para-xylene, or acetaldehyde and ethylene oxide. The limitation is that the integration process has been tested with various carrier gases such as hydrogen (H_2) and nitrogen (N_2). Currently, the most recent experiments with the PTR-TOF-MS instrument used in this study, hydrogen was first attempted to be used as a carrier gas for the GC column, but because the instrument has several integrated mass flow controllers, the H_2 was causing issues with the controllers due to density differences. At this time, no further

experiments were performed with hydrogen, although it does remain a better chromatographic carrier gas to produce enhanced separation and peak shapes.

Nitrogen was used as the carrier gas and several different columns were tried in these experiments to separate EtO from acetaldehyde. A newer type porous layer open tubular (PLOT) column was also tried in these experiments and although separation was achieved, there was a good deal of retention time (RT) shifting from calibration RT attributed to differences in moisture content. This added another layer of complexity and it was decided that would not be chosen for these experiments. Additionally, PLOT columns will bleed off stationary phase that would be problematic to keeping the DRIFT tube on the PTR clean of debris and contaminants.

A mega-bore 0.53 um capillary column was utilized for these experiments and separation was achieved with nitrogen carrier gas and a large 5 mL sample loop was used to achieve the largest mass entering the PTR for improved sensitivity. The mass leaving the capillary column will determine the detection limit on the integrated instrument as in any chromatographic system. The challenge is to match the flow rate of the carrier gas to the PTR inlet flow rate so as to not cause a vacuum on the capillary column or require make-up gas to achieve the required flowrate of the PTR. The PTR is optimally factory set-up to require ~30 mL of flow, but we were able to turn down the flow rate using a Peek™ needle valve on the inlet to 11 sccm without any issues with the PTR, which was surprising to the manufacturer.

The results of the chromatographic injections of EtO and acetaldehyde are depicted in Figure 5.

Figure 5. GC Chromatographic Separation of EtO and Acetaldehyde Prior to Integration to PTR
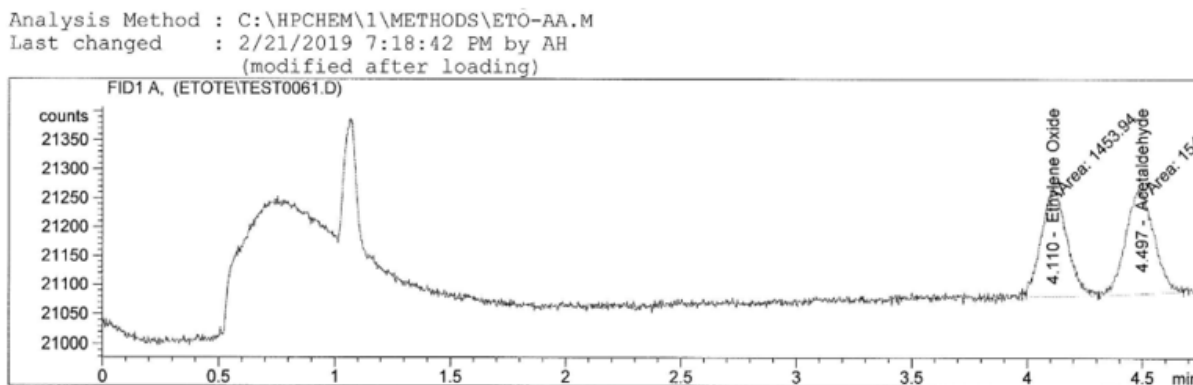
Figure 6. Chromatographic Peak Shape and Concentration Levels for EtO Integrated To A PTR-TOF-MS as the Detector

- Internal Standard diiodobenzene
- Coupled to GC
- Reagent H3O+
- Co-Elution EtO/Acetaldehyde
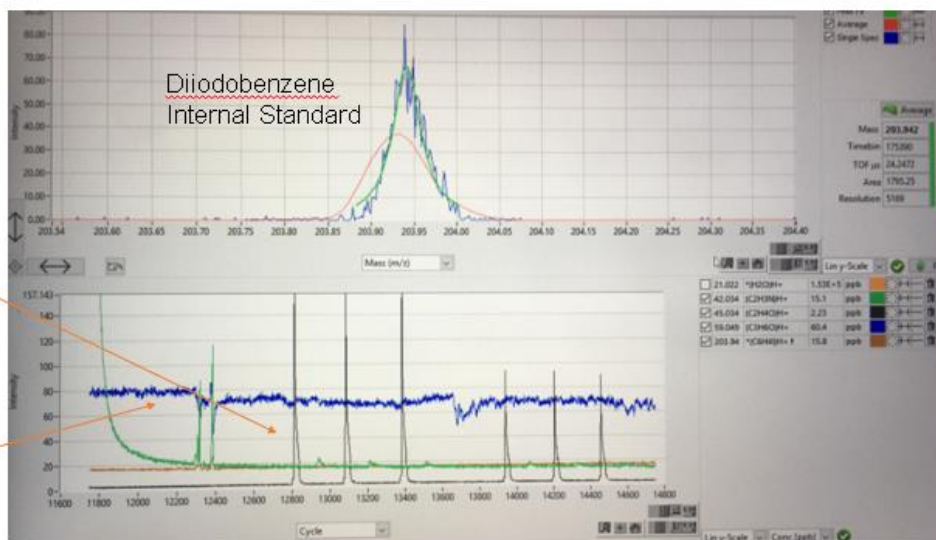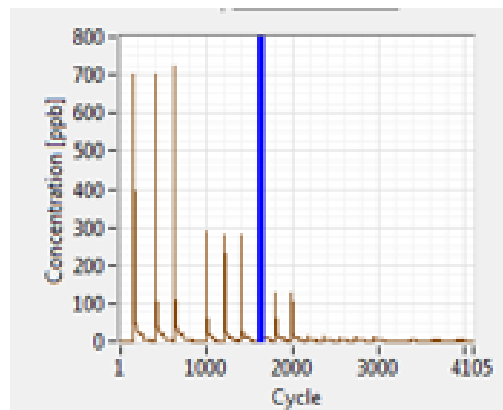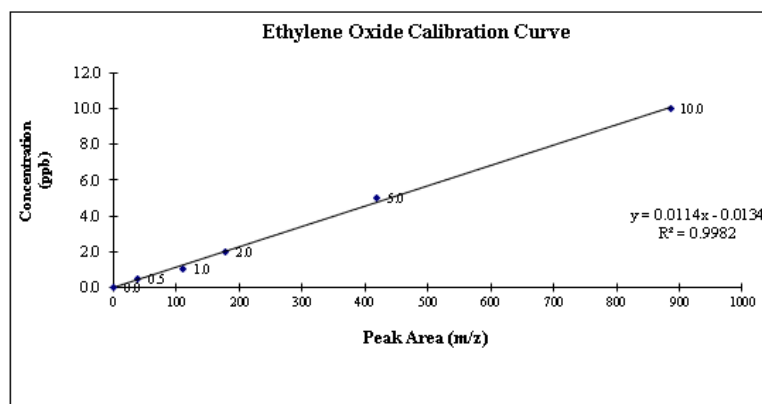- Acetone monitored as leak detection (a lot in indoor air)

Figure 7. Ethylene Oxide Linearity and Limits of Detection and Recoveries by GC-PTR-TOF-MS

Ethylene Oxide Calibration Curve

$y = 0.0114x - 0.0134$
$R^2 = 0.9982$

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.

REAL-TIME MEASUREMENTS (1HZ)

Tests are ongoing to differentiate EtO and acetaldehyde in real time by either filtering out the aldehyde by DNPH derivatization, or adjusting the PTR and DRIFT tube settings to completely fragment the acetaldehyde leaving only the EtO representative of the 44 + 1 amu peak on the TOF-MS. However, several customers were interested in a combined worst-case EtO and acetaldehyde combined real-time measurement while driving around different areas of Chicago, IL. When a high-concentration plume was detected, the vehicle was pulled over and a SUMMA canister was collected to confirm the ratio of acetaldehyde to EtO by GC-MS electron impact (EI) mode. Analysis of the high-concentration peaks collected in Summa Canisters are ongoing at the time of writing.

On-road measurements of ambient air were performed on February 28 to March 01, 2019, in the Chicago, IL, area. The target analyte was EtO and areas of interest were chosen after consultation with our customers.

The instrument used was a Proton Transfer Reaction Mass Spectrometer (Ionicon PTR-TOF-MS T-6000x2) attached to the main Peek™ sampling line within the mobile laboratory van platform. The main intake was set to 20L/minute and was not diluted. A subset of 100 sccm was slipstream transferred into the PTR-MS inlet.

In pre-analyses testing, two different analytical conditions were validated, one using hydronium ions (H_3O^+) as primary ionization source, one using O_2^+. In-field studies have shown a detection limit of 330 ppt. The results reported in the accompanying figures (below) are 5-second data for the combined emission signal of ethylene oxide and acetaldehyde. Daily zero-air measurements were performed to identify sampling equipment background and instrument background during the analyses. Mass calibration of the PTR-MS was performed using the integrated "PerMaScale" function. A description of this technique is not part of this discussion.

Sampling was performed using the above-roof snorkel, subsamples were delivered to the CO2, H2O monitors and the PTR-MS. GPS and weather data were gathered with the onboard weather station and reported in 1-second increments. During the first day, 02/28/19, the PTR-MS was operated in O2 + mode and at E/N=19 Td. The GPS and weather station operated until 12:34 accounting for 45% of the measurements due to loss of the signal from the satellite after performing underground measurements in the Chicago downtown tunnel area.

On 03/01/19 the PTR-MS was operated in H3O + mode and at E/N=120 Td. The concentrations provided in this report are based on the EtO calibration curves (sensitivities).

Figure 8. Ethylene Oxide and Acetaldehyde Linearity by Real Time PTR-TOF-MS (O2$^+$ mode)
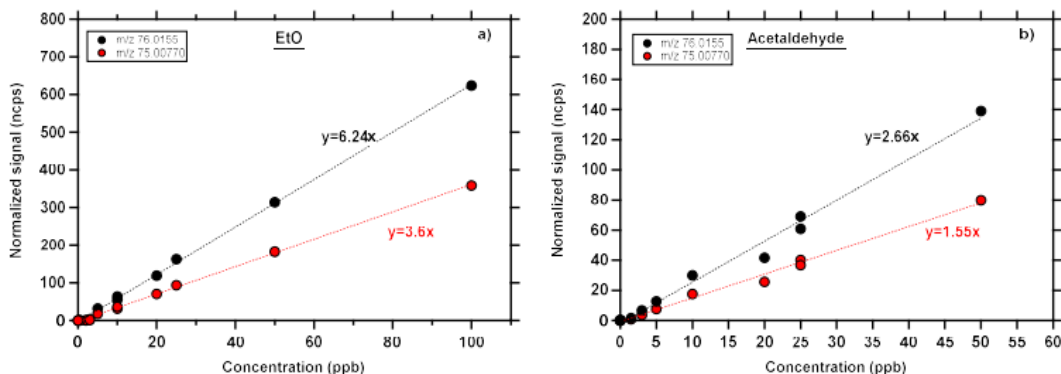
On both days, the average ambient temperature was below freezing. On 02/28/19, the temperature range was -8.2±2.4°C, while on 03/01/1912, the temperature was -1.8±0.9°C. As ambient acetaldehyde is an oxidation product in the atmosphere, we expect a different background concentration between the two days. On 2/28/19, the combined average concentrations of EtO and/or acetaldehyde was 1.13±1 ppb with a maximum at 21.2 ppb, while on 03/01/19, the average was 7.9±18 ppb with a maximum at 308 ppb. Ambient air near several facilities was tested, but for confidentiality matters, some of the data near these facilities have been scrubbed in this report.

Figure 9. a) Measurements of the EtO and/or acetaldehyde concentration at mass 76 at the first facility and regional background with red. b) Timeseries of the EtO and/or acetaldehyde mass based on their fragment at mass 75. Wind rose near a facility.
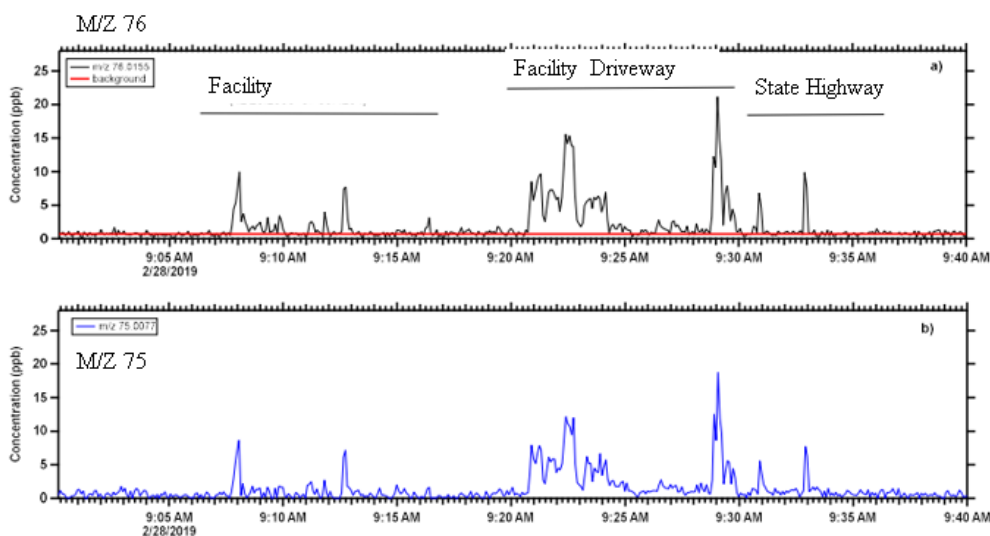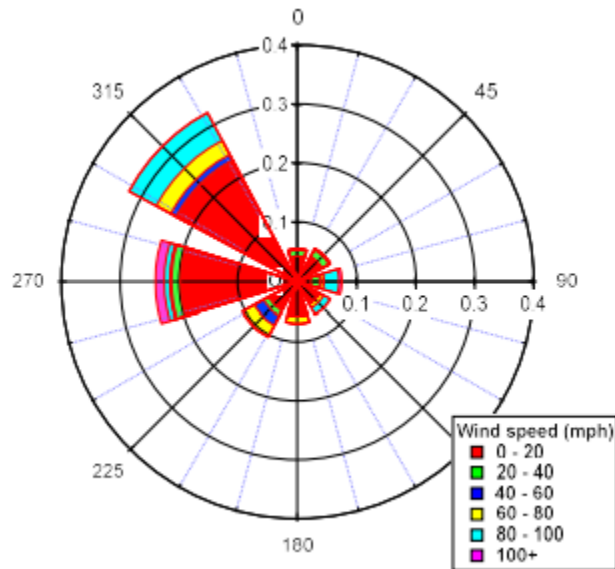
Sampling continued in downtown Chicago with concentrations up to 4 ppb. At 13:35, the van entered the underground tunnels downtown. The concentration was almost similar to the surface. At 14:00, sampling stopped underground and continued on the surface in downtown Chicago. At 14:29, the sampling continued away from the downtown Chicago area. At 15:18, sampling continued on route 41 North and, at 15:24, on I- 94 West. Figure 8 show the mass 76 time series of the whole day for comparison with relative concentrations.

Figure 10. a) Measurements of the EtO and/or Acetaldehyde Concentration at Mass 76 at a Facility and Airport and Downtown Chicago with Regional Background in Red.
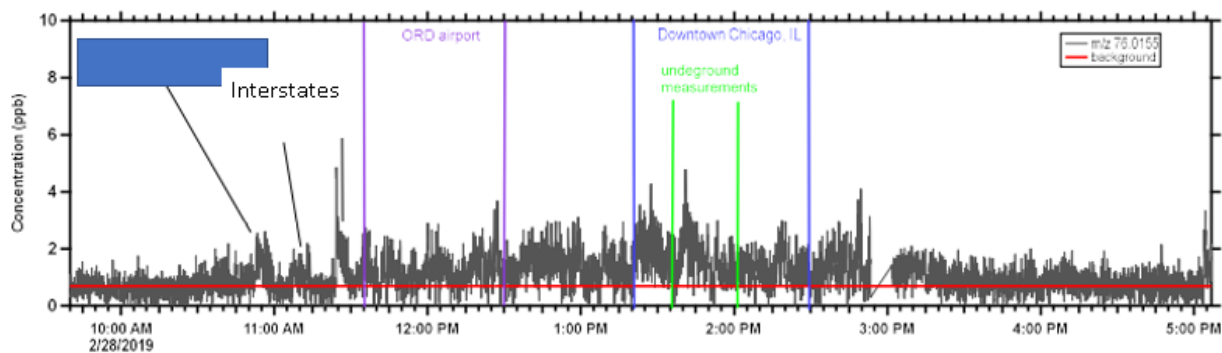
Figure 11. Measurements of the EtO and/or Acetaldehyde Concentration at Mass 45 Near a Facility (Confidential Data Blocked)
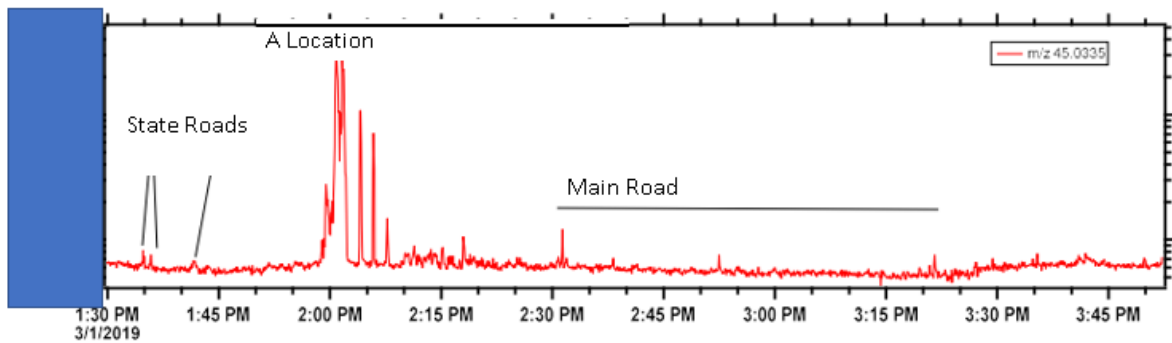

Figure 12. Measurements of the EtO and/or Acetaldehyde Concentration Along Some Routes Traveled (Confidential Data Blocked)
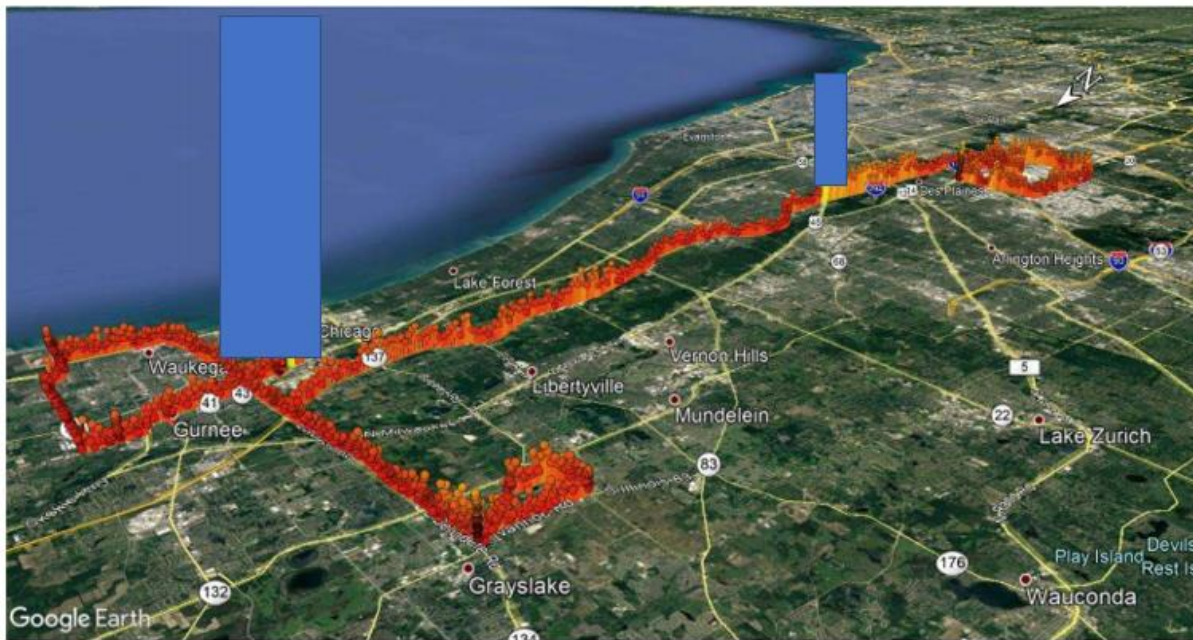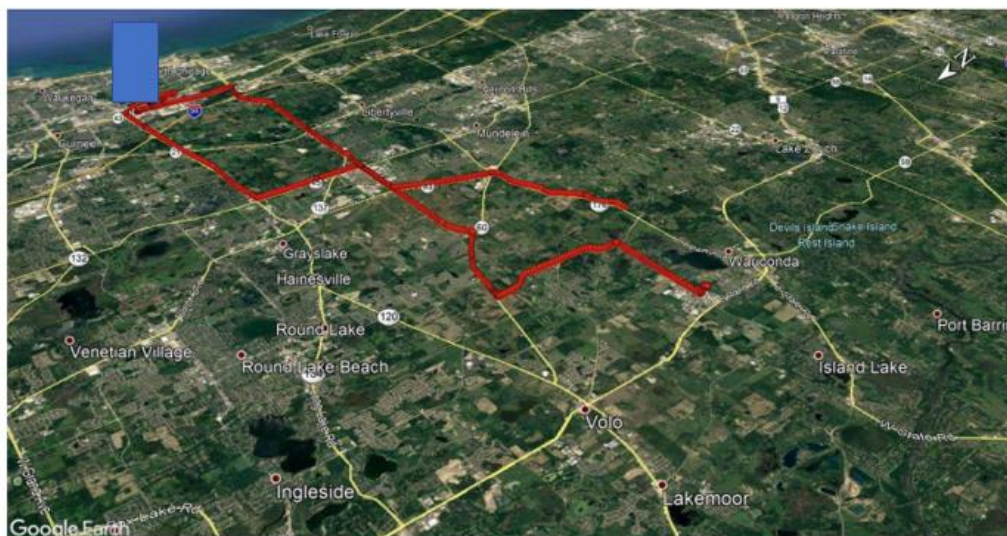
Figure 13. Measurements of the EtO and/or Acetaldehyde Concentration Along All Routes Traveled (Confidential Data Blocked)

Area	start time	end time	EtO (ppb) average	stdev	min	max
Waukegan regional background			0.7	0.3	0.1	1.7
▄▄▄▄ parking			1.5	1.6	0.1	10
Driveway to south parking			4.0	4.1	0.2	21
Route ▪ east of the facility			1.7	2.2	0.5	9.9
▄▄▄▄ Generating Station			0.7	0.3	0	1.4
▄▄▄ chemicals			0.6	0.4	0	1.8
North of the second ▄▄▄			0.9	0.5	0	2.6
I-94			0.9	0.5	0	2.2
I-294			1.2	0.9	0	4.9
ORD airport			1.2	0.7	0	4.9
Downtown Chicago part 1			1.8	0.6	0.6	4.3
Underground Chicago			1.6	0.7	0	4.8
Downtown Chicago part 2			1.3	0.5	0	3.0

EtO (ppb) average	stdev	min	max
37	69	5.5	308
16	26	5.9	108
6.7	0.9	5.7	15
5.6	0.5	1.8	12

OTHER SOURCES ETO

Figure 14. Measurements of EtO and/or Acetaldehyde and BTX Concentration from Common Items During This Mobile Deployment

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

SUMMARY

PTR-TOF-MS has demonstrated its ability to measure a wide array of organic and inorganic compounds to ultra-low levels previously only available in a brick and mortar laboratory or with concentration techniques. System sensitivity will depend predominantly on the volume of the sample matrix sampled, the analytical system parameter settings, and the type of mass spectrometer employed. Typical detection limits range from 0.1 ppbv using a quadrupole mass spectrometer (full scan mode) to ppt when using triple-quad or quad-SIM or MS (single target compound) or modern TOF MS instruments (target compounds and unknown compound scanning).

Ethylene oxide, although an isomer of acetaldehyde, may be measured in real time in ambient air and in stacks and ducts by using established EPA reference methodology with the use of a GC on the front end. PTR technology is also being investigated with dilution as a viable tool for source testing measurements in real-time or near real-time compliance measurements. These data agree with the literature performed by others on other compounds and PTR-TOF-MS capabilities.

ACKNOWLEDGEMENTS

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