Motor Vehicle Exhaust Analysis with a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) – Comparison Study with Conventional Methods for BTEX and Other Toxic Air Contaminants

California Environmental Protection Agency
Air Resources Board

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Introduction

Importance of VOC Quantification

- Health issue: Toxicity of volatile organic compounds (VOCs) and their atmospheric photochemical reaction products
- Air quality issues: Ozone formation and secondary organic aerosol (SOA) formation

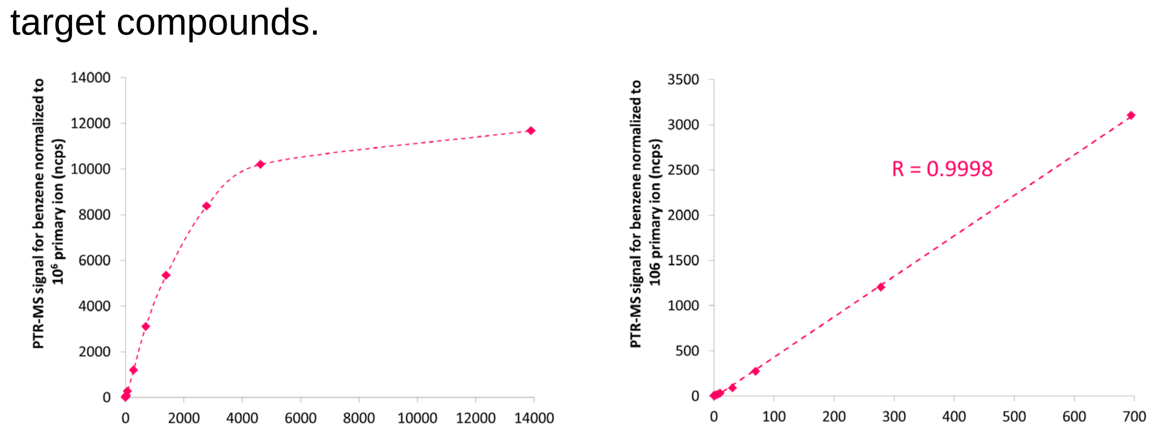
Labile VOC and SVOC Quantification – Difficulties

- Most of the conventional quantification methods for VOCs are offline, so a sample storage medium is required.
- Loss of labile VOCs and SVOCs which occur during sample collection leads to underestimation of the target compounds concentration.
  - Derivatization product of acrolein in a 2,4-dinitrophenylhydrazine (DNPH) cartridge (acidified) is known to be unstable.
  - Naphthalene is known to have significant loss in a Tedlar bag.

PTR-MS – Advantages and Disadvantages

Advantages
- Online analysis eliminates need for sample collection or derivatization.
- Provides second-by-second concentration profiles, which are useful for evaluating impacts of control technologies that reduce toxic VOC emissions.
- Does not require an authentic standard of the compounds of interest. This is a great advantage in the analysis for compounds without any reliable standard due to their toxicity or stability.

Disadvantages
- Linearity range of the PTR-MS was found to be up to ~700 ppbv of total reactive VOC, but peak VOC concentrations for vehicle tests typically reach the ppmv level.
- PTR-MS may be saturated for some cold start or hard acceleration episodes during transient chassis dynamometer testing, and saturation will cause underestimation of the target compounds.



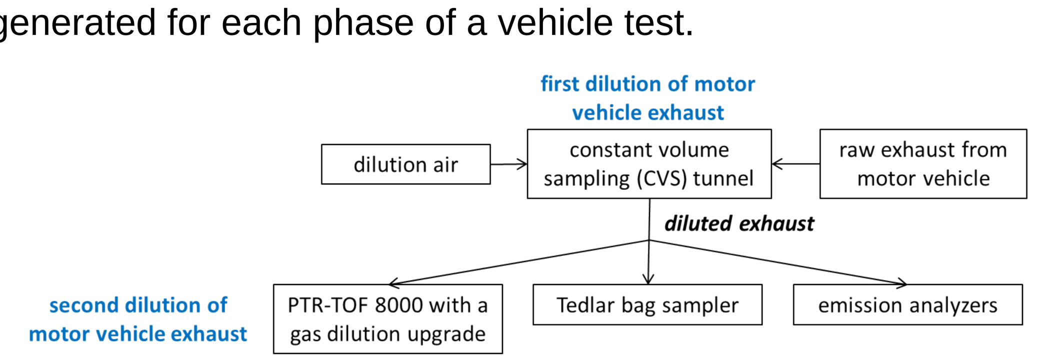
Normalized PTR-MS signal for benzene (ncps) up to 14000 ppbv (left) and 700 ppbv (right) of total reactive VOC

Objectives

- Develop a gas dilution unit to upgrade the PTR-TOF 8000 for exhaust analysis.
- Compare measurements of benzene, toluene, ethylbenzene, and xylene (BTEX) in automotive exhaust using the PTR-MS with measurements utilizing ARB's conventional GC-FID method (SOP MLD 102/103) to verify potential automotive applications.
- Conduct preliminary correlation analyses of real-time emission profiles from the PTR-MS and real-time profiles of engine parameters to assess sensitivity and responsiveness of the PTR-MS to engine and emission control events.

Experimental Methods – Vehicle Test Setup

- 17 automotive vehicle exhaust samples from chassis dynamometer tests were analyzed.
- Test cycles include Unified Cycle (UC), Federal Test Procedure (FTP), and Supplemental FTP which consists of 3 phases, 3 phases, and 1 phase, respectively.
- PTR-MS was configured for online analysis. (1 second resolution; H_3O^+ primary ion)
- GC-FID was carried out with offline analysis on samples collected in Tedlar bags; one bag sample was generated for each phase of a vehicle test.

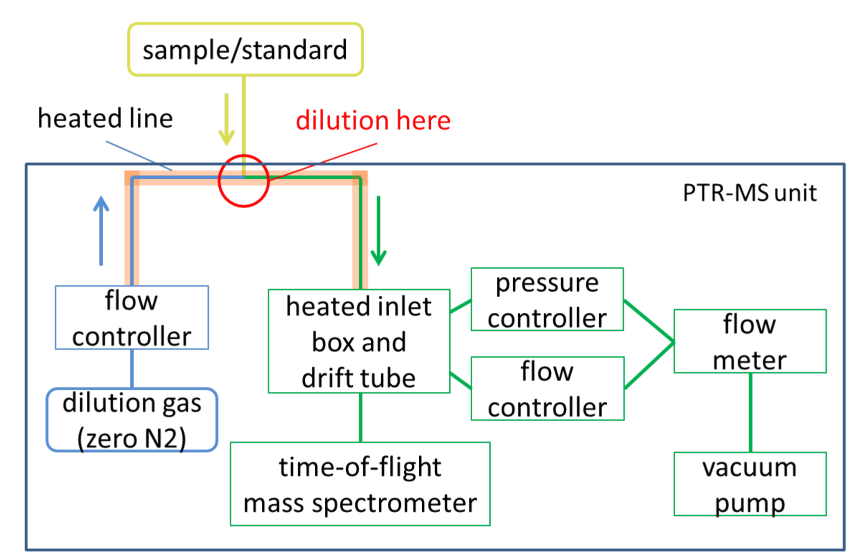


chassis dynamometer vehicle test setup

Gas Dilution Upgrade for the PTR-TOF 8000

Gas Dilution Upgrade Setup

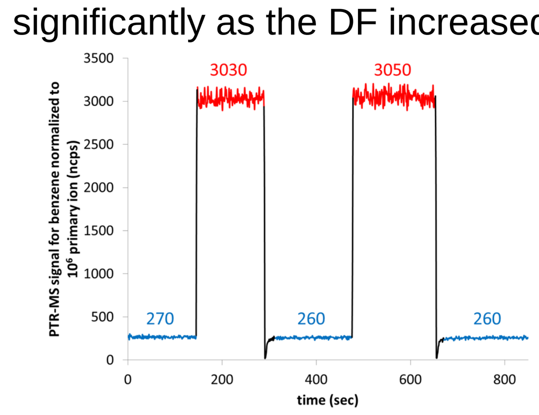
- Gas dilution upgrade is developed in collaboration with the PTR-TOF 8000 manufacturer, Ionicon Analytik Ges.m.b.H.
- Ionicon PTR-Manager software is upgraded to monitor flows from all additional flow controllers and a meter.



PTR-TOF 8000 with a gas dilution upgrade

Dilution Factor Calculation

- The dilution factor (DF) was calculated from the ratios of benzene standard gas signals which were measured prior to every vehicle test. (below left)
- Differences between measured flow rates and those determined from benzene dilution increased significantly as the DF increased. (below right)



PTR-MS signal for benzene with (blue) and without (red) dilution (DF = 11)

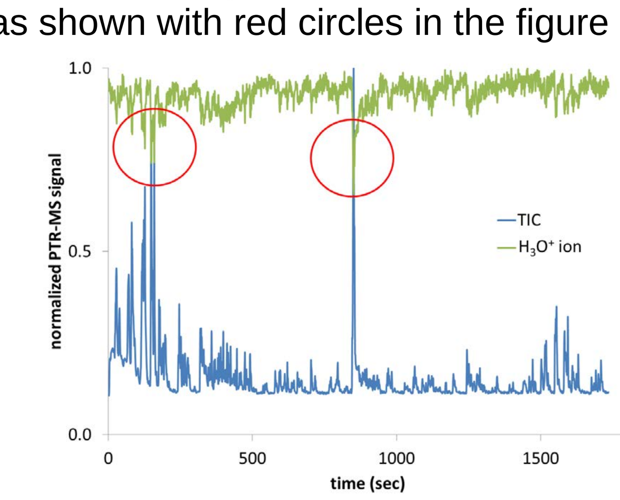
flow rate (sccm)		PTR-MS benzene	DF		% difference
dilution gas	standard gas	signal (ncps)	flow-base	signal-base	
0.00	0.00	747.45	n/a	n/a	n/a
499.94	125.02	152.72	5.00	4.89	2.20
499.99	55.06	77.19	10.1	9.68	4.16
500.00	26.40	39.06	19.9	19.1	4.02
499.99	17.29	26.32	29.9	28.4	5.02
500.01	10.28	16.24	49.6	46.0	7.26
500.01	6.88	11.19	73.7	66.8	9.36
500.01	5.19	8.38	97.3	89.2	8.32

DF calculated from the flow rates and the PTR-MS signal for benzene

Comparison of the Measurements between PTR-MS and GC-FID

PTR-MS Saturation

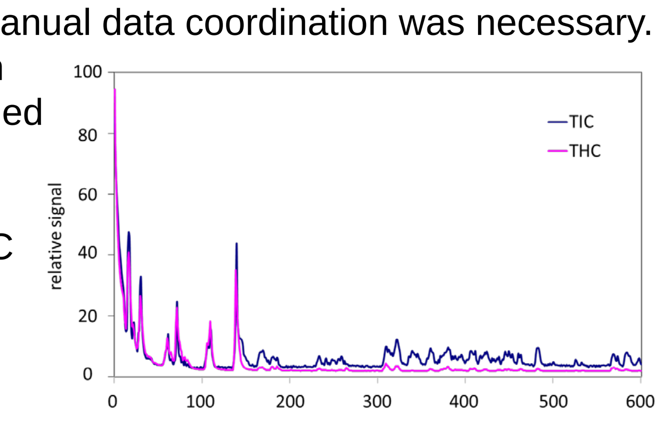
- When the PTR-MS was saturated, the primary ion (H_3O^+) was depleted significantly as shown with red circles in the figure below.



PTR-MS signal for the total ion count (TIC, m/z 25-497) and the primary ion ($H_3{}^{18}O^+$, m/z 21)

Data Synchronization

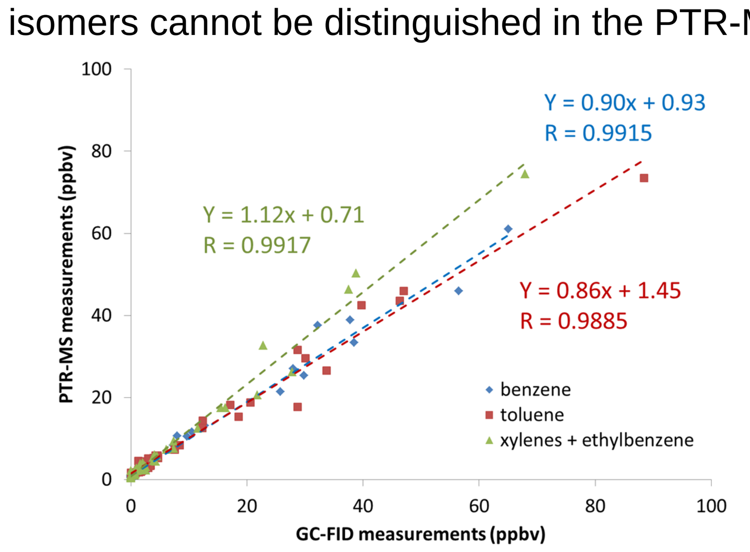
- The PTR-MS was not set to automatically synchronize with the bag sampling device and the emission analyzers, so manual data coordination was necessary.
- Synchronization was accomplished by aligning the peak pattern of the PTR-MS TIC and the total hydrocarbon (THC) measurements from the THC analyzer.



TIC (m/z 21-497) signal from the PTR-MS and THC measurements from the THC analyzer

PTR-MS and GC-FID Comparison

- Xylene and ethylbenzene concentrations from the GC-FID measurements were combined for comparison with the PTR-MS measurements, because those isomers cannot be distinguished in the PTR-MS analysis.
- The agreement between the measurements from two methods for BTEX were within 15 % for concentrations above 4 ppbv

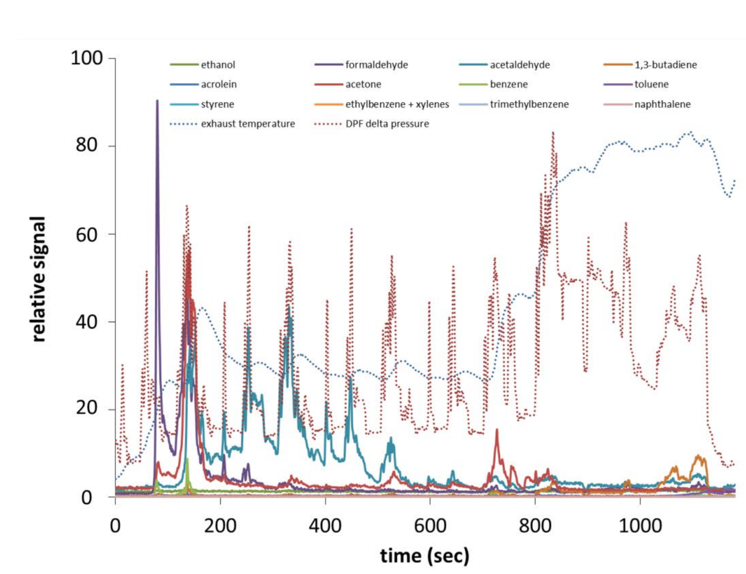


	PTR-MS / GC-FID
benzene	0.96
toluene	0.96
ethylbenzene and xylene	1.15

Correlation of the measurements from the PTR-MS and the GC-FID

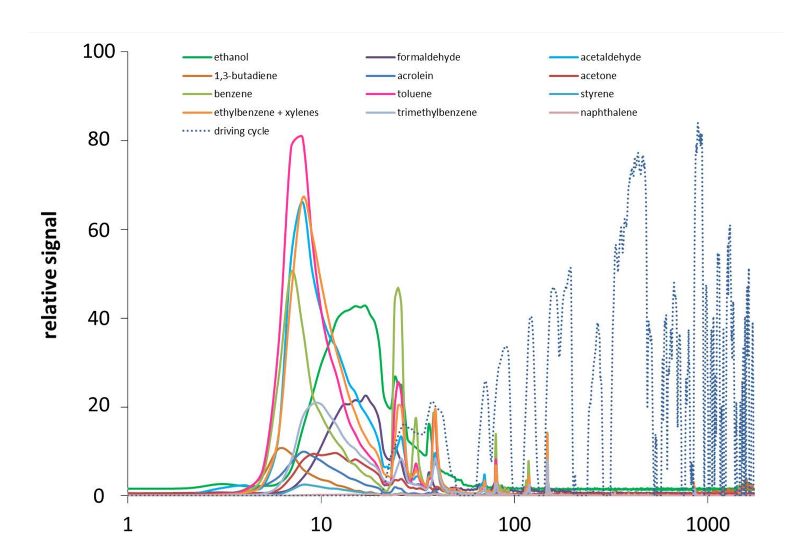
Examples of Automotive Applications of Real-Time VOC Emission Analysis

DPF Regeneration



PTR-MS signals for selected VOCs and on-board diagnostics signals for exhaust gas temperature and pressure drop in a diesel particle filter for a light-duty diesel vehicle

Driving Cycle and Emission



PTR-MS signals for selected VOCs and driving cycle (UC) for a light-duty gasoline vehicle

Future Study

- Investigate potential errors introduced by real-time flow changes during vehicle test.
- Develop methods for quantifying labile VOCs and SVOCs including acrolein, 1,3-butadiene, and naphthalene.
- Study different primary ions (O_2^+ and NO^+) for their applications in mobile source toxic compounds analysis.

Summary

- The PTR-MS was upgraded with a gas dilution unit for exhaust testing.
- The agreement between the GC-FID and the PTR-MS measurements for BTEX was within 15 % for concentrations above 4 ppbv.
- PTR-MS enables real-time measurements of selected exhaust VOC emissions which permits evaluation of engine and control technology events.

Acknowledgement

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- Dr. Christopher Brandow (formerly with ECARS, CARB) for NMHC analysis with the GC-FID.