Real-time Broad Spectrum Characterization of Hazardous Wastes by Membrane Introduction Mass Spectrometry

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Overview

- This project addresses the need for characterization of waste streams associated with Mixed Low Level Waste (MLLW).
- The goal of this project is to extend the applicability of Membrane Introduction Mass Spectrometry (MIMS) to the *simultaneous* detection of a broad spectrum of environmental contaminants (Volatile and Semivolatile Organic Compounds (VOCs and SVOCs), and metal-containing compounds).
- Successful implementation of the basic analytical science being developed in this program could result in significant time and resource savings in the sampling and characterization of MLLW streams.

Motivation for Work

- DOE currently has >100 Waste Sites and >1400 Mixed Waste streams.
- Real-time, *in situ* characterization tools are needed to develop and optimize sampling strategies and minimize lab-based characterization costs.
- MIMS is well-established for on-line analysis of VOCs and SVOCs in air and water. In order to address the needs of EMSP/DOE, we are developing a single instrument/method MIMS platform for the characterization of a broad range of organic and metallic contaminants found in a variety of matrices and effluents.

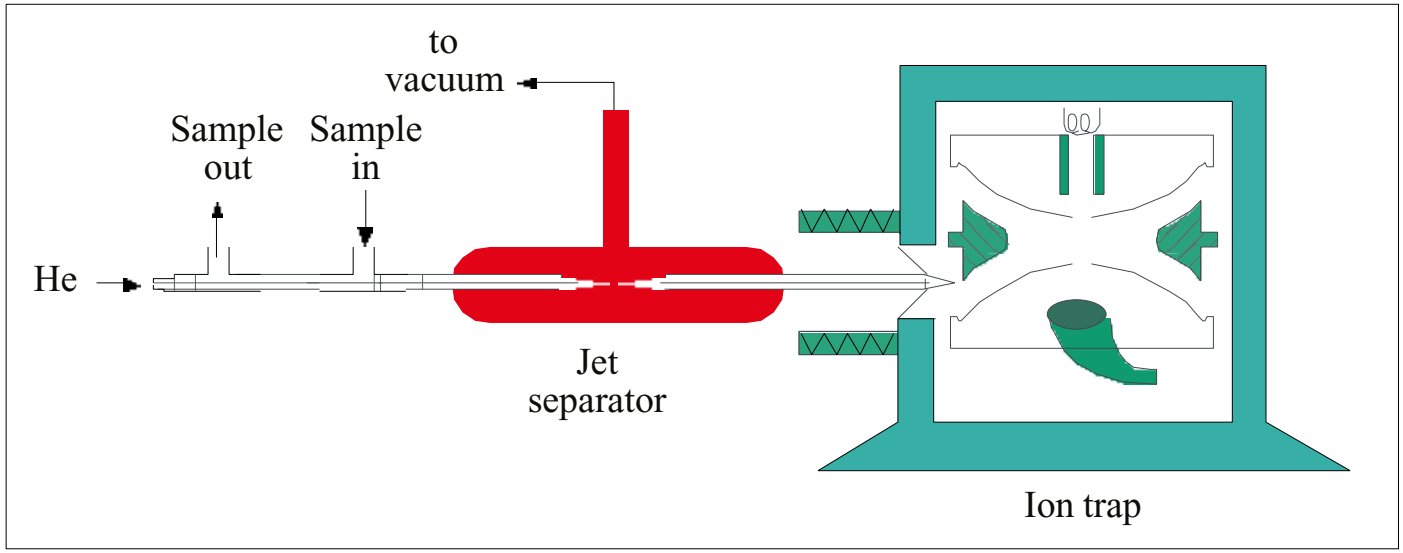
Potential DOE Site Applications

- INEEL, Advanced Mixed Waste Treatment Project Production Operations
  - Initial characterization and post-treatment analysis and monitoring of waste.
- Oak Ridge Reservation, Y-12 East Fork Poplar Creek Remedial Action
  - On-line monitoring of groundwater, surface water, and springs at Chestnut Ridge Security Pits to establish the effectiveness of treatment systems.
- Nevada Test Site, Industrial Sites
  - In-situ surveys; monitoring wells; effluent streams; long-term monitoring and surveillance

Membrane Introduction Mass Spectrometry

- "Flow injection" technique
  - Little or no sample preparation needed
  - Fast, sequential analysis of blanks, standards, and samples
  - Sample returned to waste stream - no new generation of hazardous waste
- Analytes "pervaporate" through membrane that separates mass spectrometer from sample
  - Limited selectivity provided by membrane
  - Instrument Typically not Contaminated by Bulk Matrix Constituents – Important for Sites with Radiological Issues
- Analyte identification and quantitation provided by mass spectrometer
- Large linear dynamic range ($\geq 10^3$)
- Low detection limits ($\leq$ ppt)
- Fast time response (0.5 – 5 minutes)

Typical MIMS Apparatus



- Membrane consists of a poly(propylene) microporous support fiber (240 μm i.d. x 300 μm o.d.) coated with
  1. an ultra-thin (approximately 0.5 μm) layer of highly crosslinked plasma polymerized poly(dimethylsiloxane) (commercial).
  2. Pulsed plasma polymerized allyl alcohol layer (custom).

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Ionization Mechanisms Investigated

Source	Frag.	
Electron Impact (EI)	High	$M + e^- \longrightarrow M^+ + 2e^-$
Chemical Ionization (CI)	Low	
– Charge Exchange (CE)		$X^+ + M \longrightarrow X + M^+$
– Protonation		$M + AH^+ \longrightarrow MH^+ + A$
Microwave Plasma (MIP)	Variable	
– Thermal Ionization		$M + e^- \longrightarrow M^+ + 2e^-$
– Penning Ionization		$Ar^* + M \longrightarrow Ar + M^+ + e^-$
– Charge Exchange		$Ar^+ + M \longrightarrow Ar + M^+$

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H_2O Charge Exchange CI

$$H_2O + e^- \rightarrow H_2O^{+\cdot} + 2e^- \quad (A)$$

$$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + OH^\cdot \quad (B)$$

$$H_3O^+ + M \rightarrow MH^+ + H_2O \quad (C)$$

$$H_2O^{+\cdot} + M \rightarrow MH^+ + OH^\cdot \quad (C')$$

In the first step (A), traditional electron impact ionization is used to generate an intermediate reagent ion, $H_2O^{+\cdot}$. Further reaction with H_2O (B) results in the formation of the active species (H_3O^+). Reaction C′ does not occur to any appreciable extent, because $H_2O^{+\cdot}$ is ejected from the trap at the end of the ionization period.

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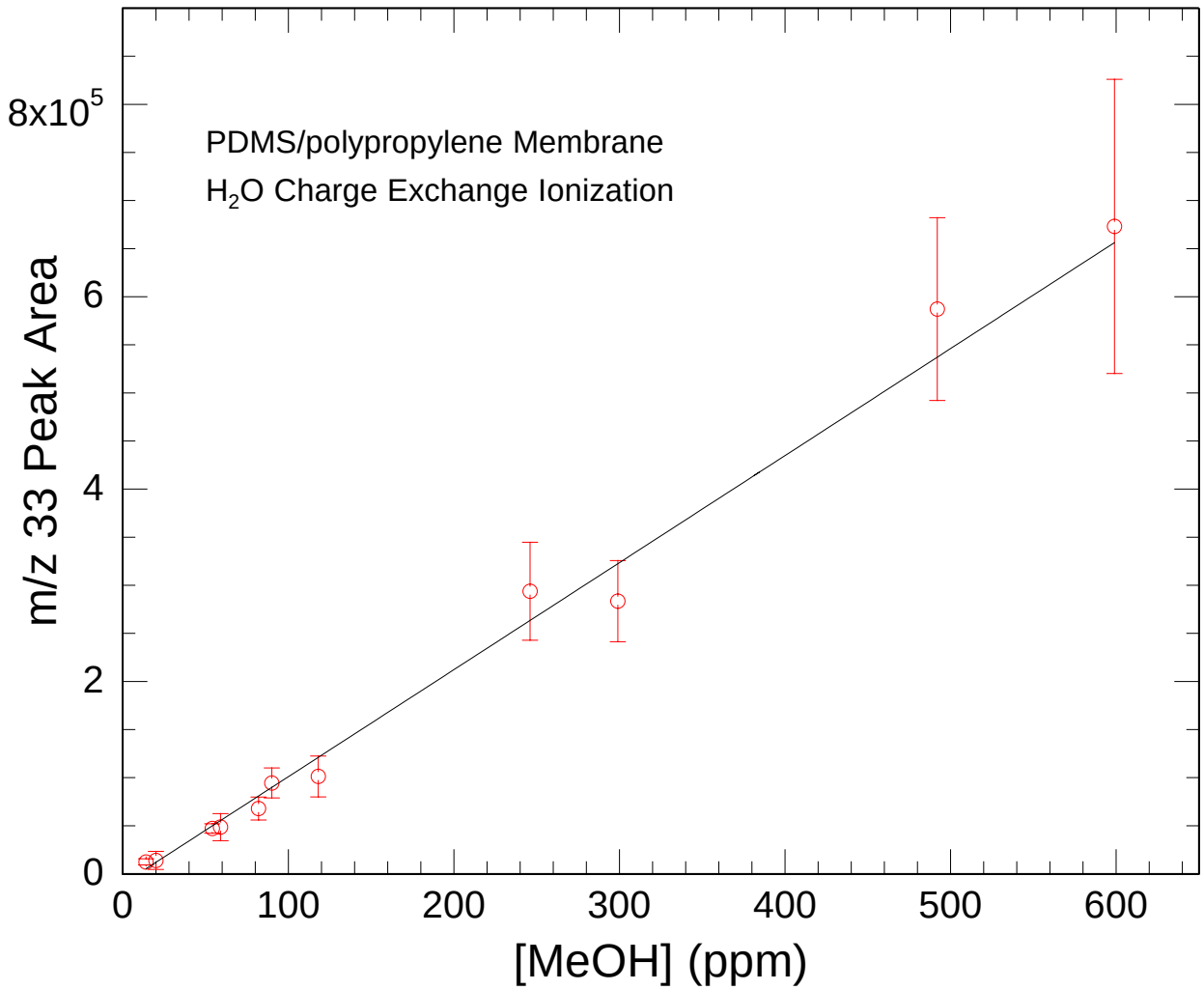
MIMS of Methanol in Air



T. M. Allen, T. M. Falconer, M. E. Cisper, A. J. Borgerding, C. W. Wilkerson, Anal. Chem., submitted.

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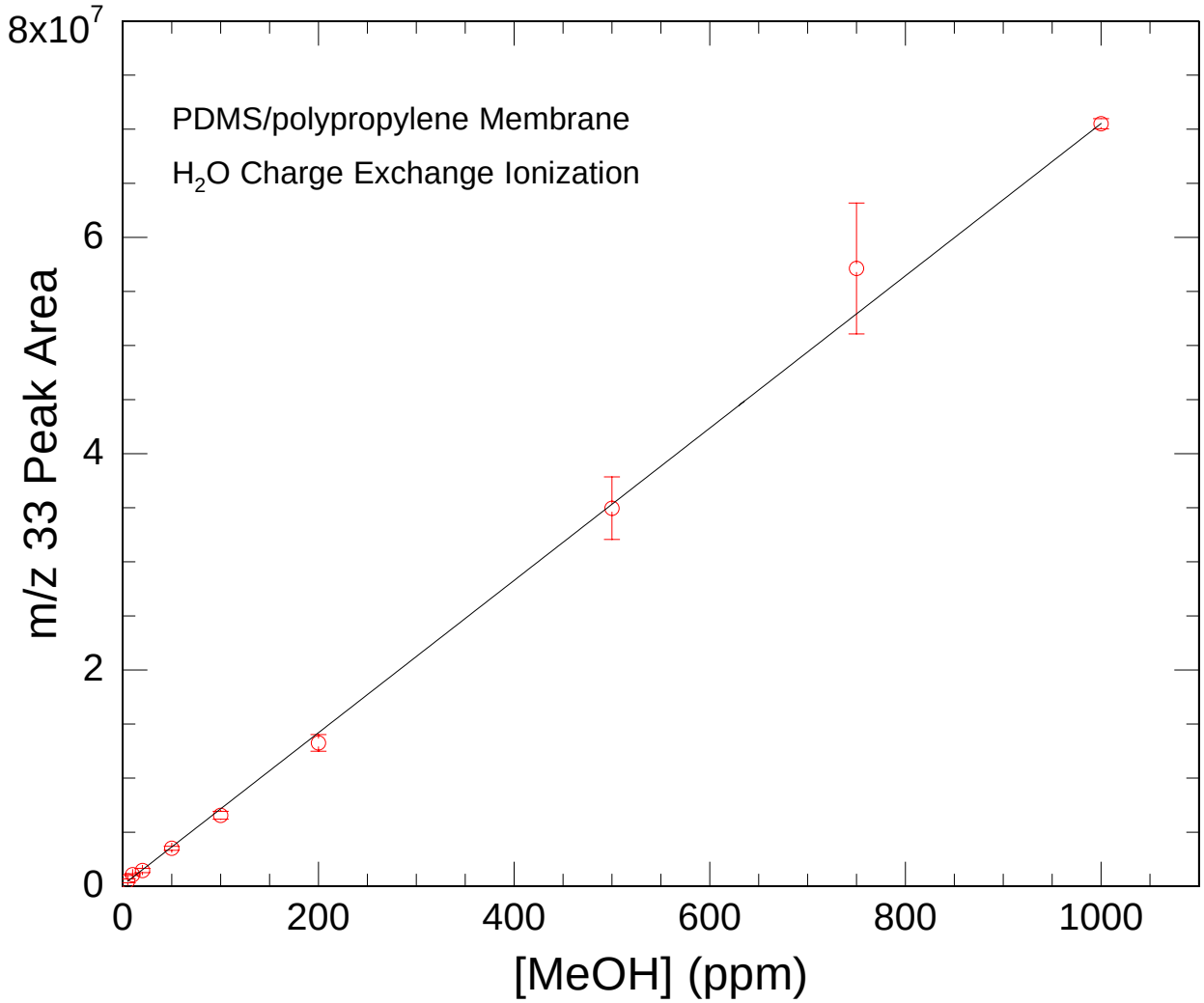
MIMS of Methanol in Water



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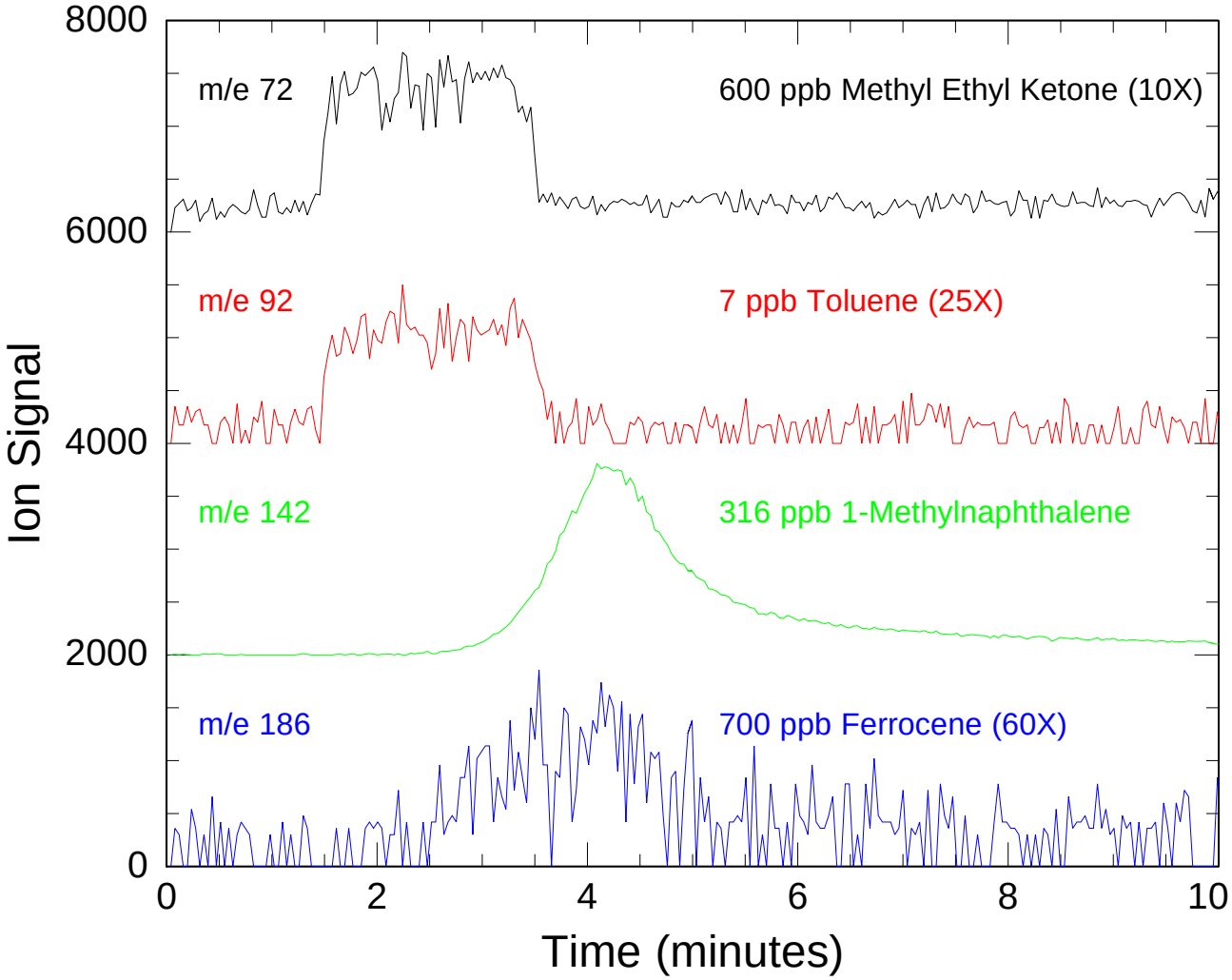
MIMS of VOC/SVOC/Organometal Sample in Air



M. E. Cisper, T. M. Allen, P. H. Hemberger, C. W. Wilkerson, manuscript in preparation

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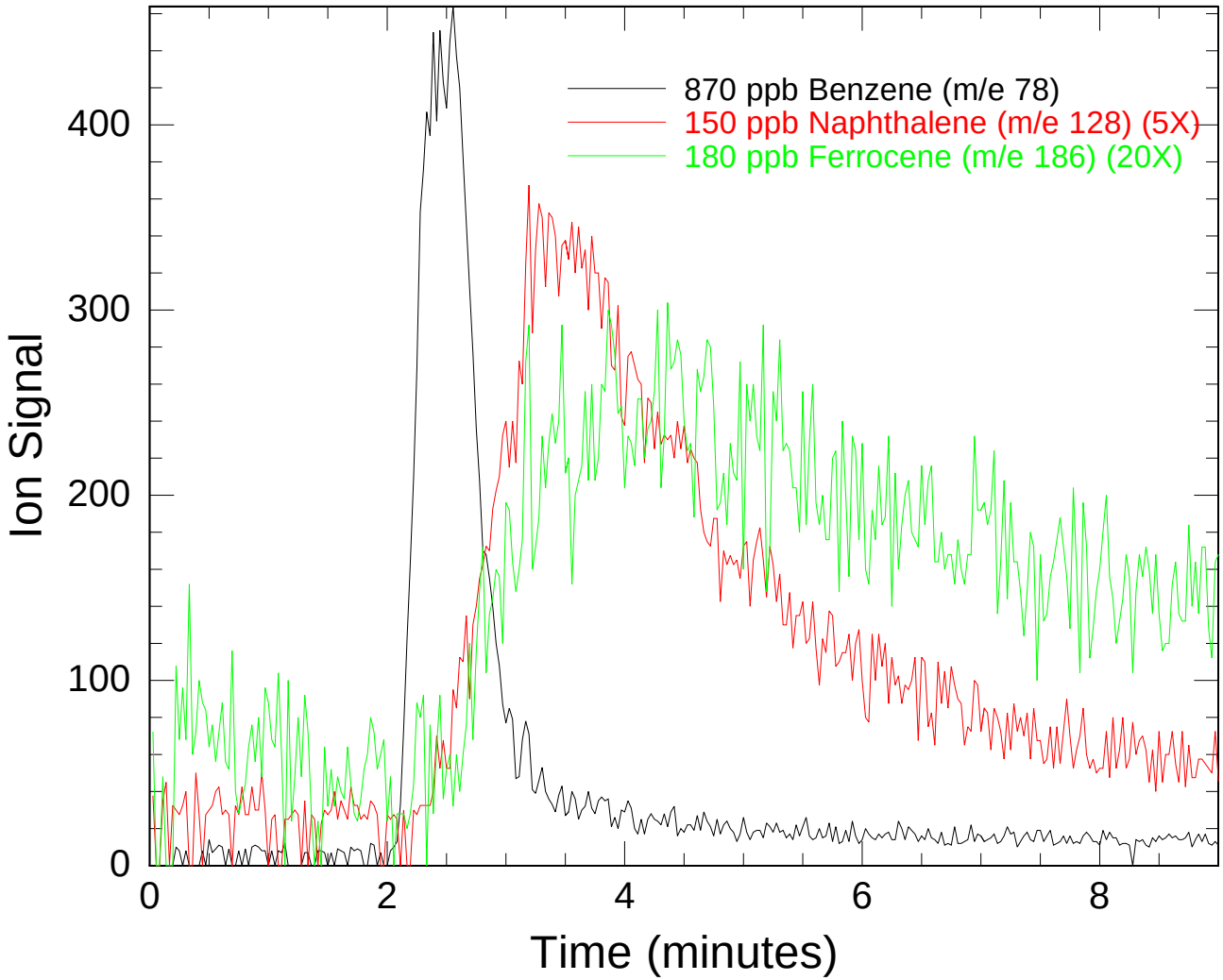
MIMS of VOC/SVOC/Organometal Sample in Water

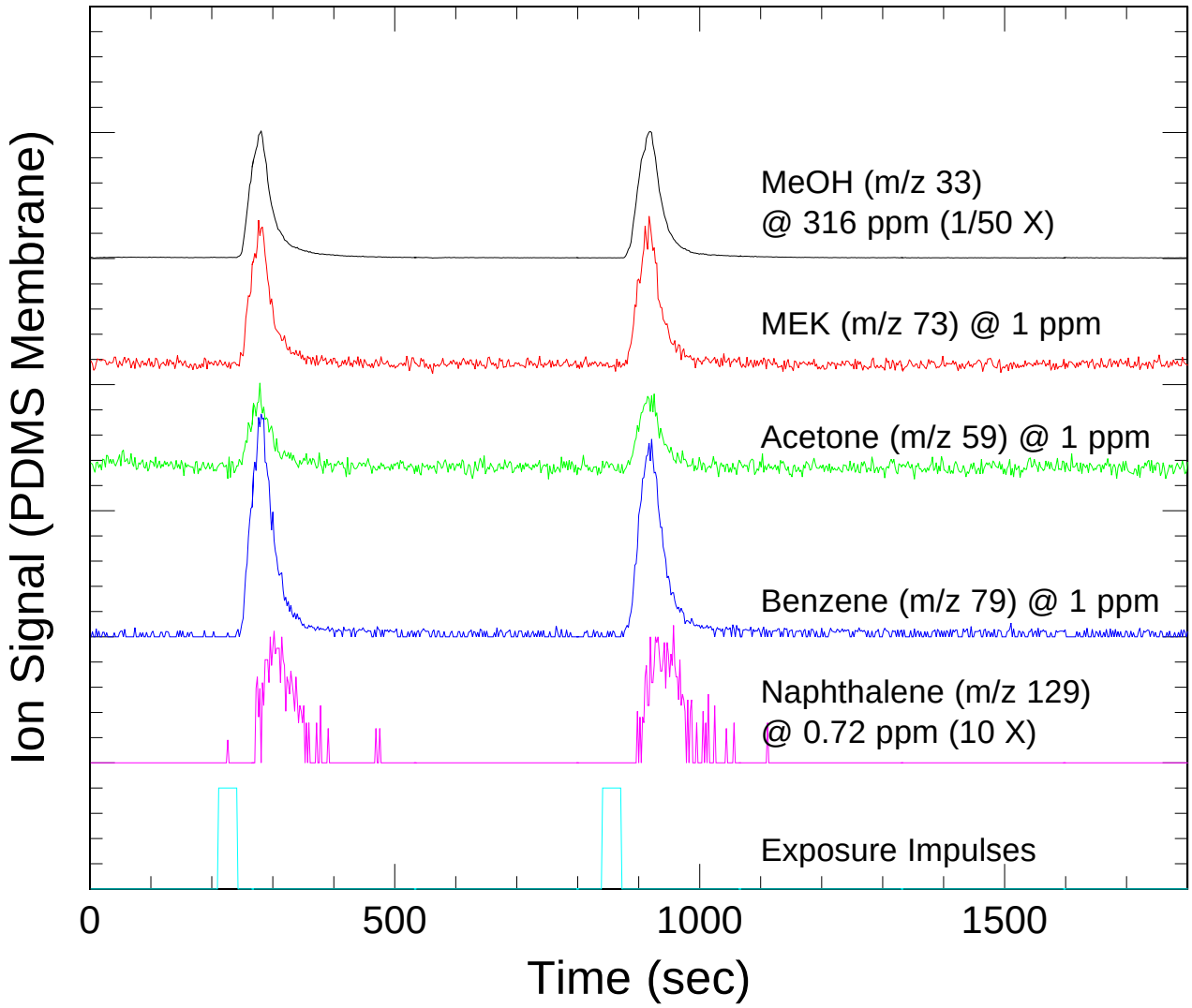


M. E. Cisper, T. M. Allen, P. H. Hemberger, C. W. Wilkerson, manuscript in preparation

Custom Membranes

- Performed by R. B. Timmons, U. Texas – Arlington
- Same poly(propylene) substrate as used in commercial PDMS membrane
- Allyl Alcohol (1-propene-3-ol) is deposited using a pulsed RF discharge (200 W peak 13.56 MHz).
- Two variants:
  - "1:2" (plasma on/off time in msec)
  - "1:15"

MIMS of Aqueous VOC/SVOC Mix - PDMS



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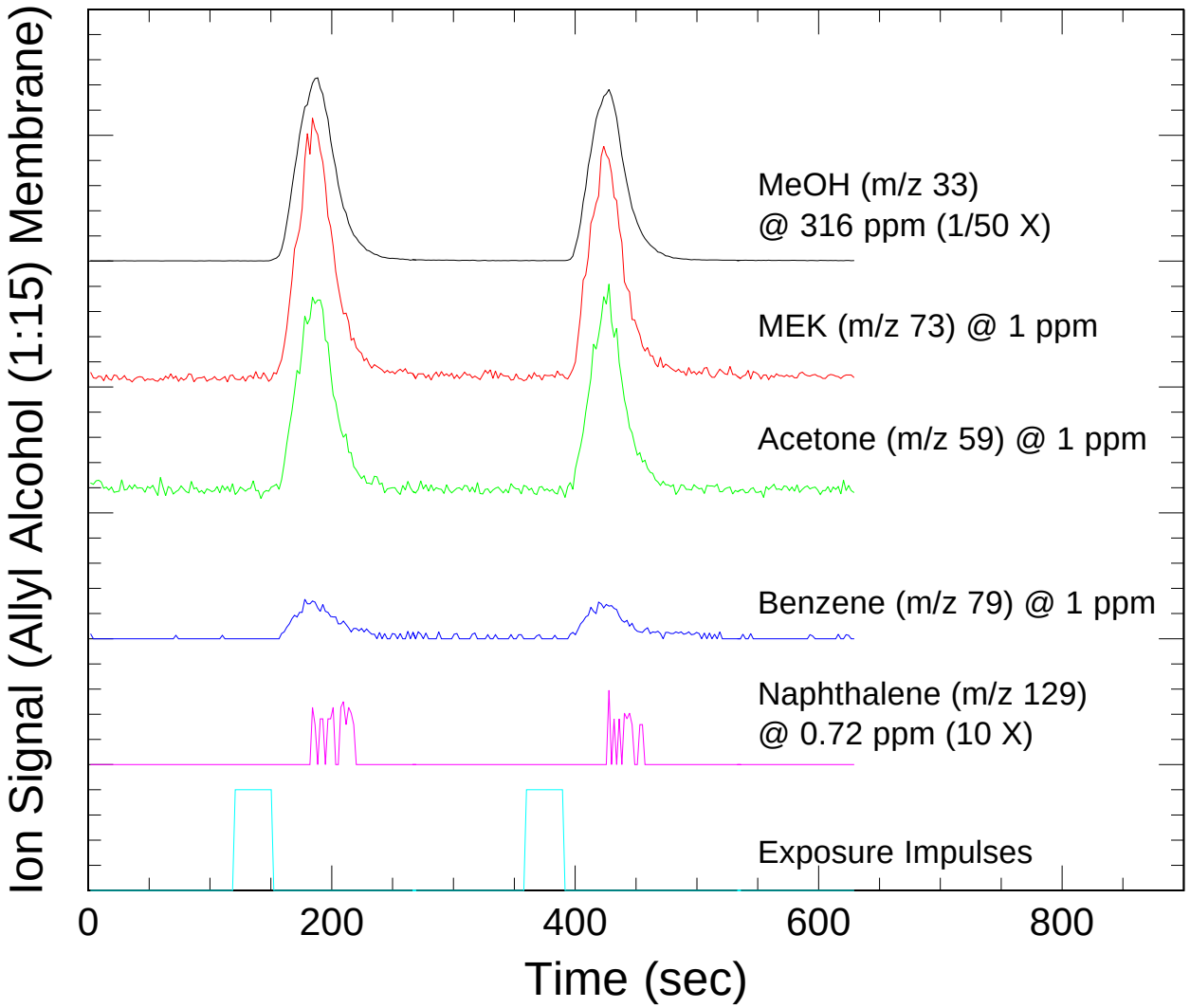
MIMS of Aqueous VOC/SVOC Mix - Allyl Alcohol (1:15)



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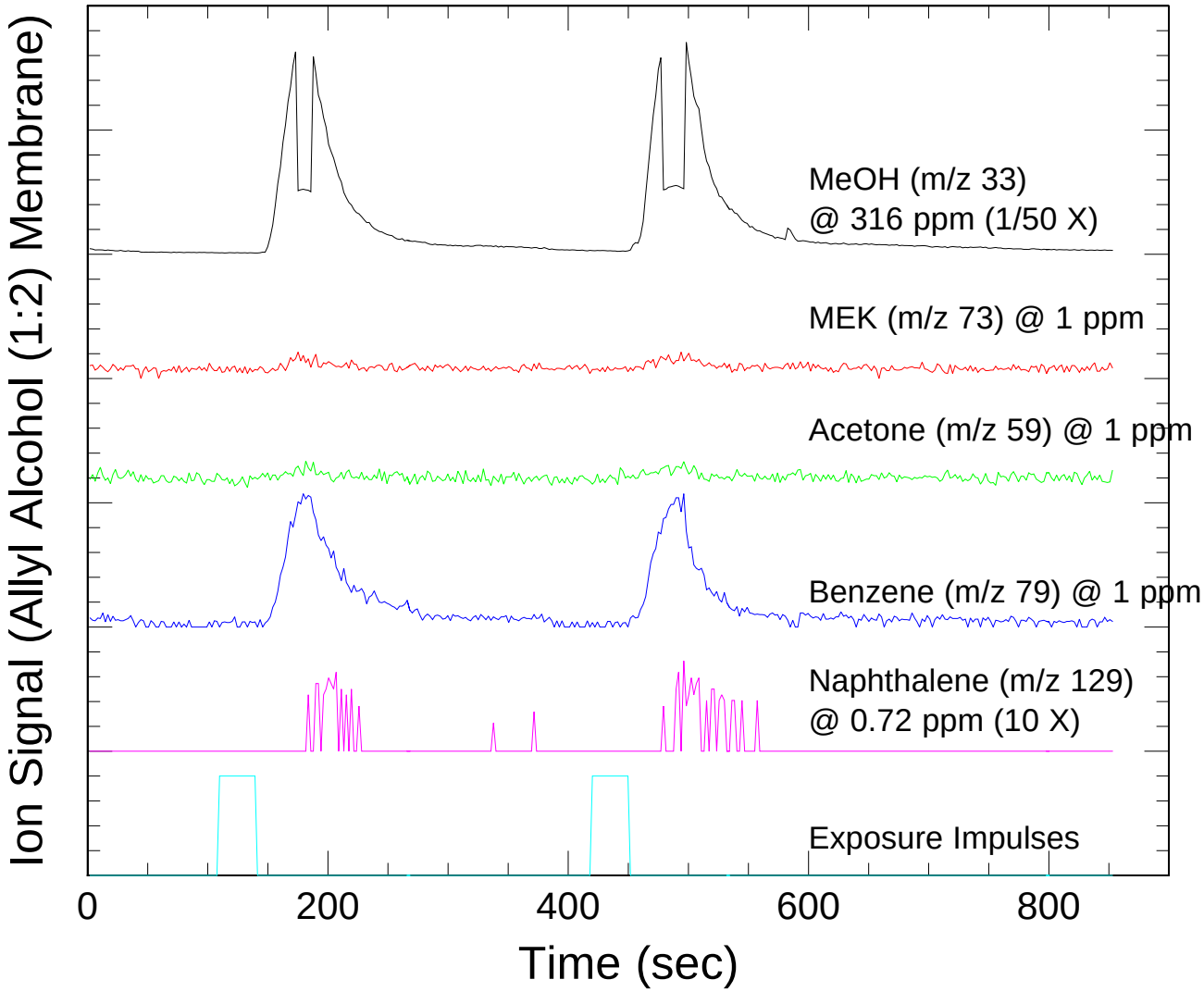
MIMS of Aqueous VOC/SVOC Mix - Allyl Alcohol (1:2)



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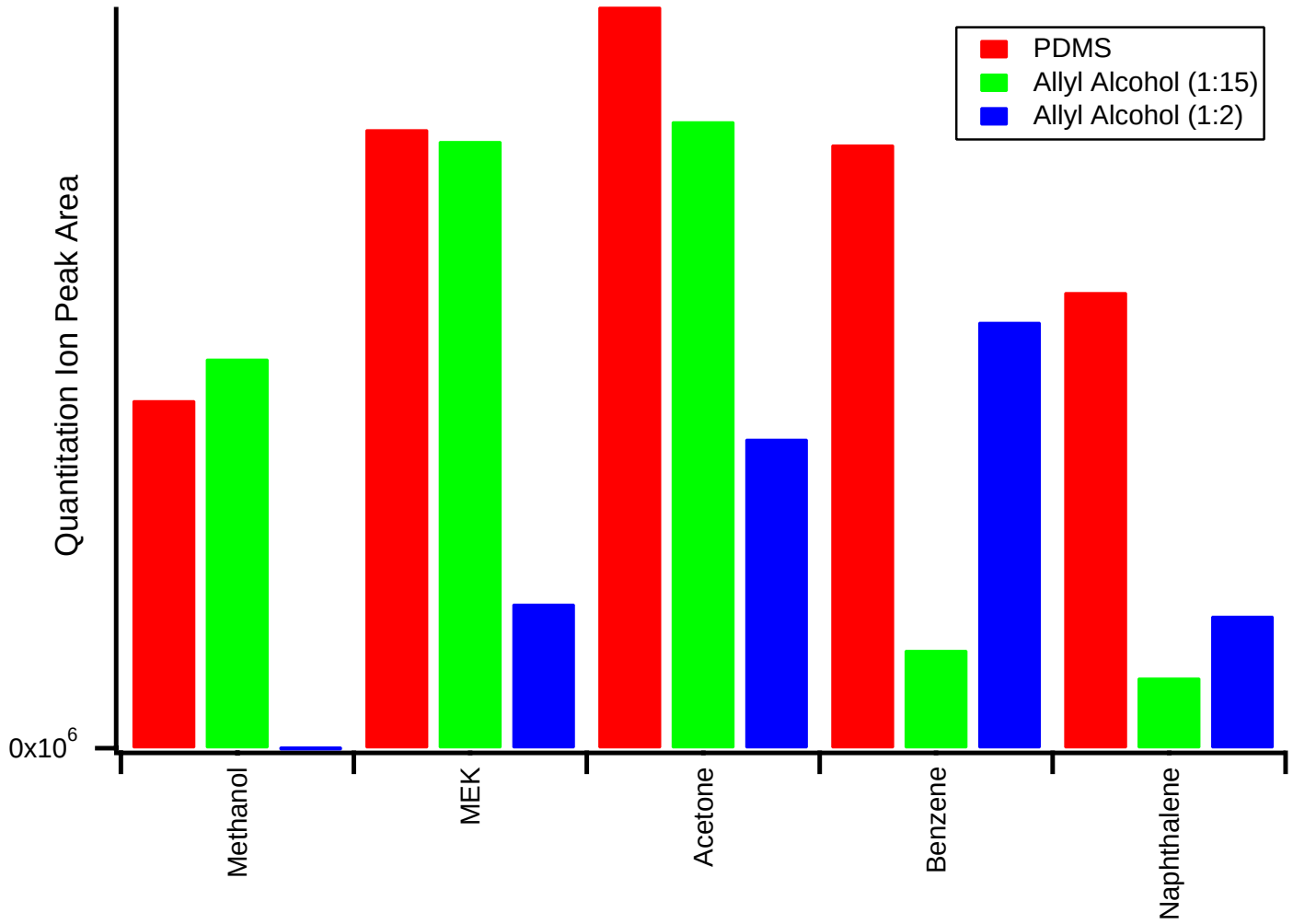
Comparison of Modified Membranes



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Polymerization Conditions Impact Performance

- "1:15" membrane is more hydrophilic
  - Prominent O-H stretch observed in IR spectrum[a]
  - More polar analytes (methanol, MEK, acetone) show larger signal
  - PAHs attenuated
- "1:2" membrane attenuates MIMS response of polar species
  - Very weak O-H band in IR

[a] C. L. Rinsch, X. Chen, V. Panchalingam, R. C. Eberhart, J. Wang, R. B. Timmons, Langmuir **12**, 2995 (1996)

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FY00 Accomplishments

- Published review of recent MIMS Applications and Trends.[a]
- One manuscript in review, one about to be submitted, reporting results on simultaneous detection and tailored membranes.
- Extension of MIMS to an environmentally significant polar volatile organic compound, such as methanol in air and water.
- Application of tailored membranes for selective measurement of specific classes of hazardous chemicals.

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[a] R. C. Johnson, R. G. Cooks, T. M. Allen, M. E. Cisper, P. H. Hemberger, Mass Spectrometry Reviews **19**, 1 (2000)

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Project Accomplishments

Over the course of this project, we have:

- Demonstrated detection of ≈ 50 VOCs, SVOCs, and organometallic species via MIMS.
- Demonstrated simultaneous detection of model VOC, SVOC, and organometallic compounds.
- Demonstrated the advantages of using chemically tailored membranes for selective measurement of classes of chemicals.
- Applied charge exchange (CE) ionization to achieve drastically improved sensitivity compared to electron impact ionization.

FY01 Plans

Pending renewal of the project, we plan to:

- Focus on design, fabrication, and evaluation of chemically tailored membranes for the simultaneous detection of compounds with particular functional groups (multiple membrane configuration).
- Further develop chemical ionization strategies, that take advantage of the unique features of ion trap mass spectrometry, in order to maximize both method selectivity and sensitivity.
- Expand range of matrices to include soils; apply method in air, water, and soil to the detection and quantitation of DOE/EPA priority pollutants.

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- Travis Falconer, U. North Dakota

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