Real-Time Broad Spectrum Characterization of Hazardous Waste by Membrane Introduction Mass Spectrometry

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Background

- Many of the Mixed Hazardous Wastes at DOE sites are complex mixtures containing volatile and semi-volatile organic solvents, heavy metals, and radionuclides. Characterization of mixed wastes is necessary for developing suitable remediation strategies (i.e., storage, treatment, and disposal).
- MIMS is currently well-established for the on-line analysis of VOCs in air and water. We are developing MIMS for a broad range of organics and heavy metal contaminants in a variety of matrices and effluents to address the problems at DOE sites.

Project Goal

- Many DOE sites would benefit from the implementation of MIMS as a near real-time, on-line analytical method. ***We seek to expand the real-time monitoring capabilities of Membrane Introduction Mass Spectrometry to the problem of Mixed Hazardous Waste***, with secondary emphasis on monitoring incinerator stack gases for both organics and toxic metals.
- The MIMS methodology could also be applied to other environmental and effluent monitoring problems that require rapid detection of contaminants including both VOCs, SVOCs, and heavy metals.

Potential Applications of MIMS

- 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 and Melton Valley Watershed to establish the effectiveness of treatment systems

- Nevada Test Site, Industrial Sites

  --in situ surveys; monitoring wells, effluent streams; maintenance of remedial systems; long term monitoring and surveillance

MIMS Analysis of Mixed Hazardous Wastes

- Sample can be returned to the waste stream--no new generation of hazardous waste.
- The mass spectrometer can remain free of contamination in the analysis of organics in a radioactive waste matrix.

1998 Objectives

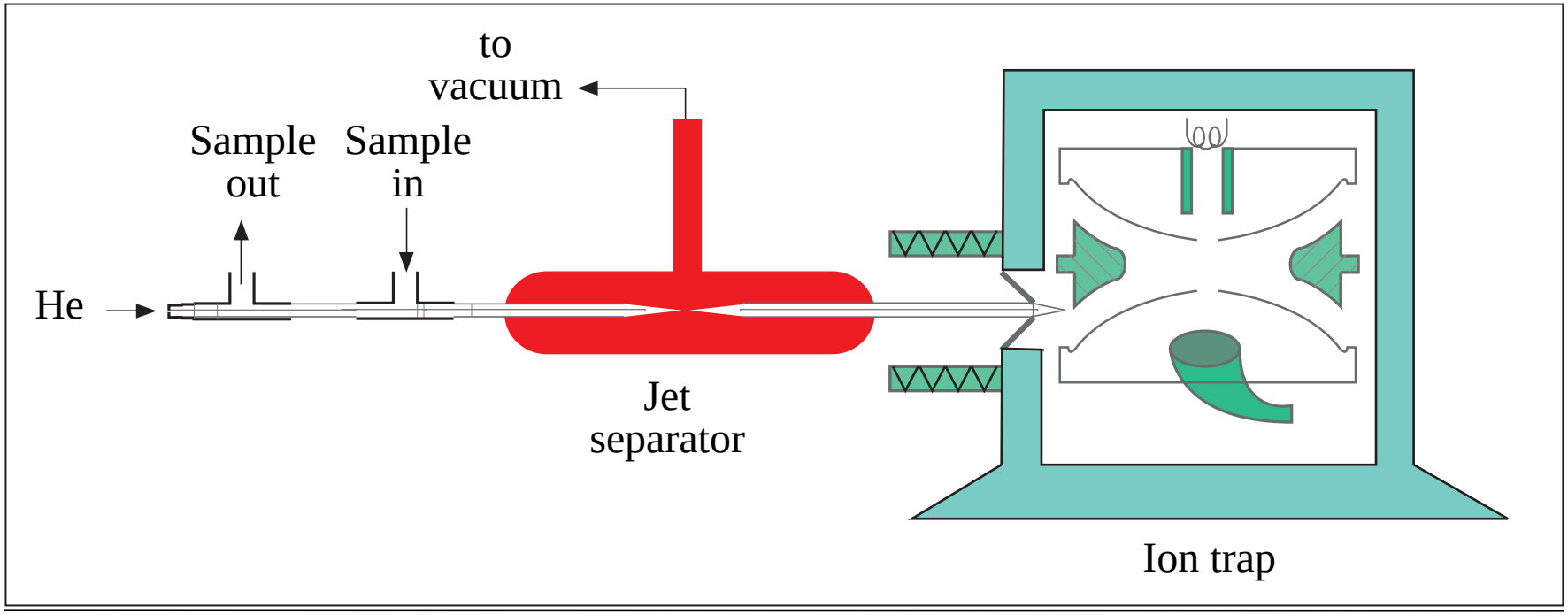
- Design, build, and test a rare-gas supported discharge ionization source, associated ion injection optics, and ion trap mass spectrometer. *To fully utilize the broad capabilities of MIMS, an alternative ionization source to electron impact may be more suitable for the analysis of both organics and metal-containing compounds found in complex Mixed Hazardous Wastes.*
- Extend MIMS to semi-volatile compounds.
- Explore ion chemistry of these compounds.

The first two objectives have been met; we are currently investigating ion chemistry.

Advantages of the MIMS Methodology

- Near real-time.
- No sample preparation for organics; minimal sample prep expected for heavy metals.
- Analysis time takes seconds to minutes.
- Broad dynamic range, minimal memory effects.
- Flow injection allows continuous sequential analysis of blanks, standards, and samples.
- Sample can be returned to the waste stream--no new generation of hazardous waste.
- The ion trap mass spectrometer can be kept free of radioactive contamination by the membrane interface.
- Applicable to *simultaneous* detection of VOCs, SVOCs, and organometals.

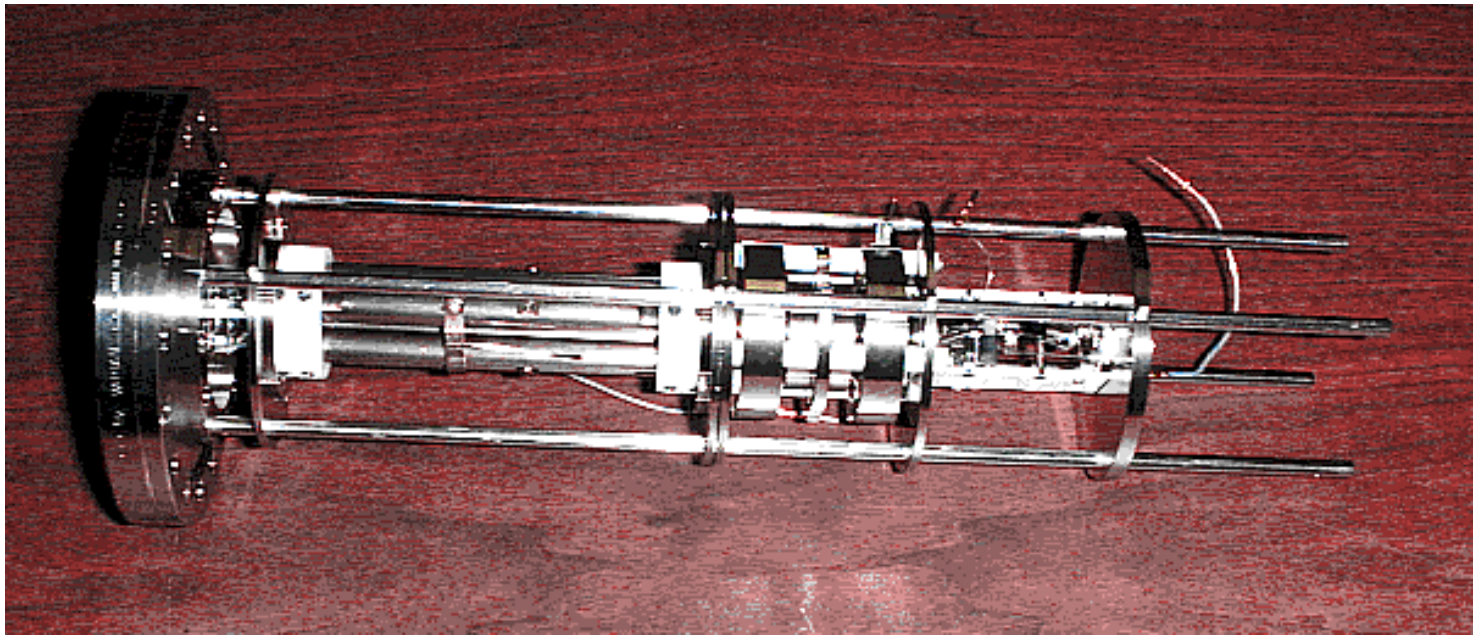
Analysis of Air or Water by Membrane Introduction Mass Spectrometry



Accomplishments in FY98

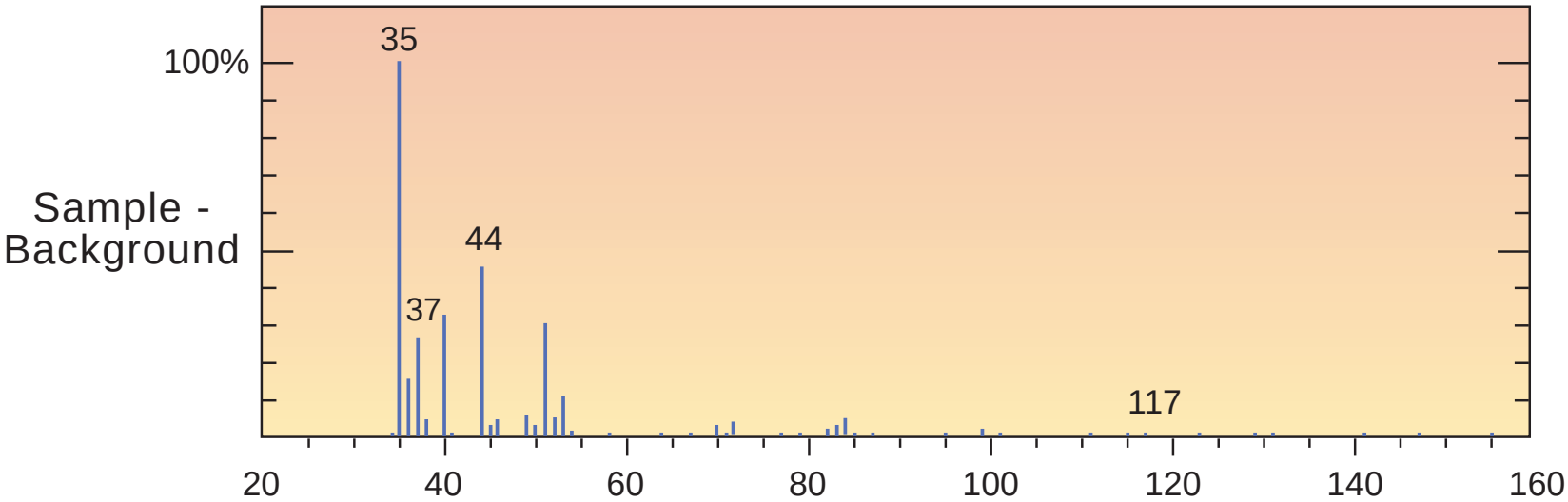
Plasma Source Ion Trap

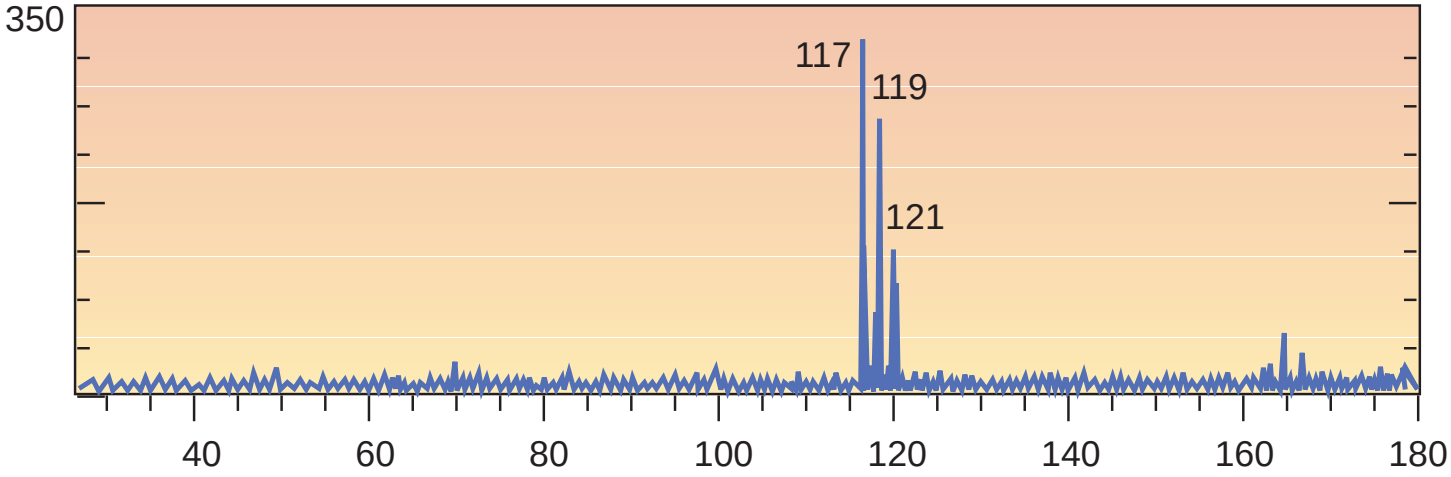
- Designed and tested the microwave plasma source ion trap mass spectrometer. We are investigating operating conditions for both elemental and molecular analysis.



A paper describing this instrument and the analysis of rare atmospheric gases has been accepted by *Int. J. Mass Spectrom. Ion Proc.*

Detection of identifying elemental and molecular ions for CCl_4 with the microwave plasma source





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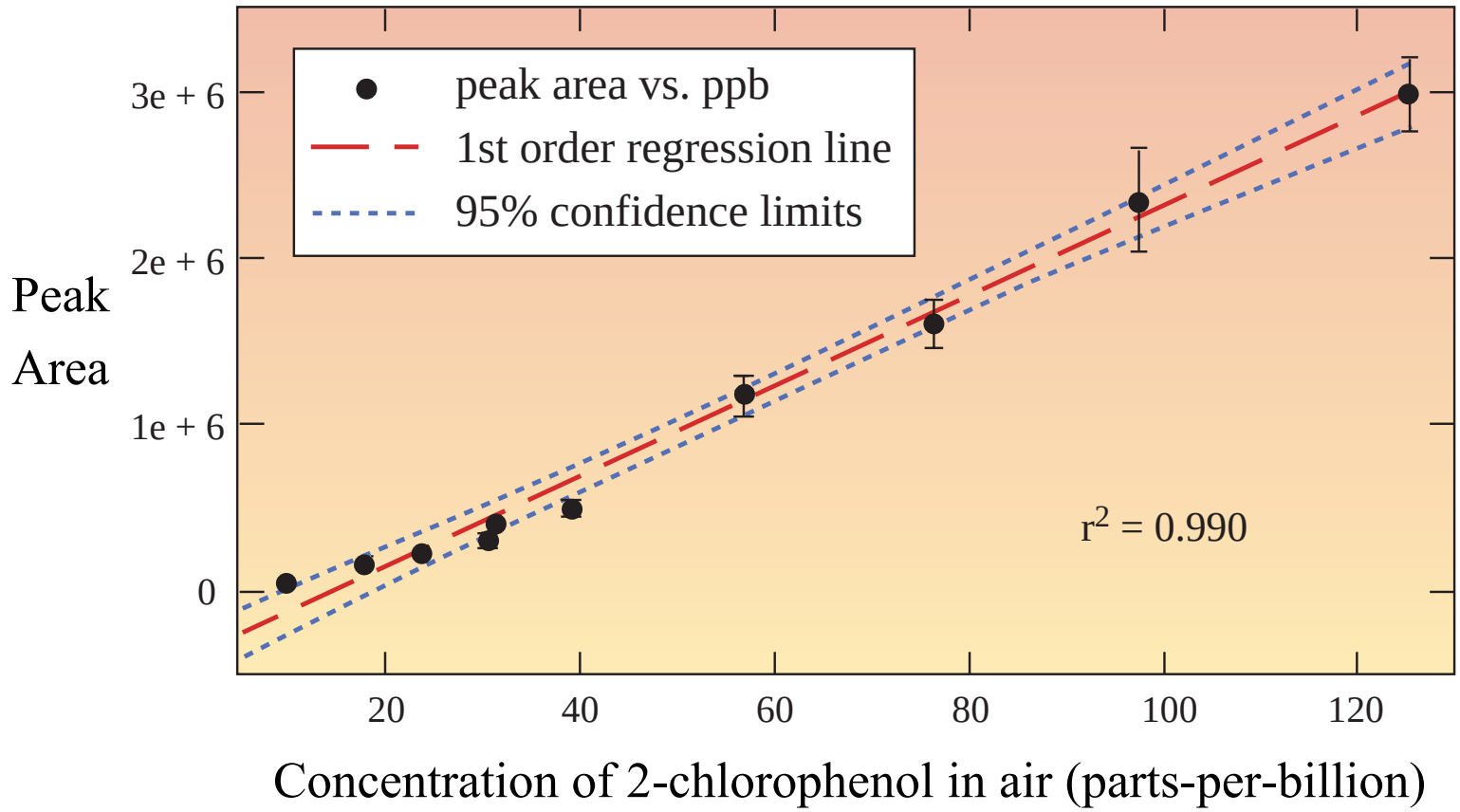
MIMS



Demonstrated the detection of 15 VOCs, 25 SVOCs, and 5 organometallics by MIMS including:

- chlorinated and oxygenated solvents
- phenols and chlorophenols
- lead, nickel, and tin compounds

Compounds Detected by MIMS

VOCs	SVOCs		Organometallics
Acetaldehyde	Acenaphthene	4-hydroxy-4-methyl-2-pentanone	Ferrocene
Acetone	Acetophenone	Malathion	Molybdenum hexacarbonyl
Benzene	Aniline	Methyl salicylate	Lead acetylacetonate
Carbon tetrachloride	2-chlorophenol	1-methyl-naphthalene	Nickel acetylacetonate
Chlorobenzene	3-chlorophenol	Naphthalene	Triphenyl tin chloride
Hydroxy acetone	Cyclohexanol	Nitrobenzene	
1-hydroxy-2-butanone	1,3-dichloro-benzene	Phenol	
Isopropyl alcohol	1,4-dichloro-benzene	Pyruvic acid	
Methyl ethyl ketone	2,4-dichloro-phenol	1,2,4-trichloro-benzene	
Methyl isobutyl ketone	2-(diethylamino) ethanol		
3-pentanone	Diethyl malonate		
Propanal	Diisopropyl aminoethanol		
Toluene	Dimethyl methyl-phosphonate		
Trichloroethane	2,4-dimethylphenol		
Trichloroethylene	Dimethyl sulfoxide		

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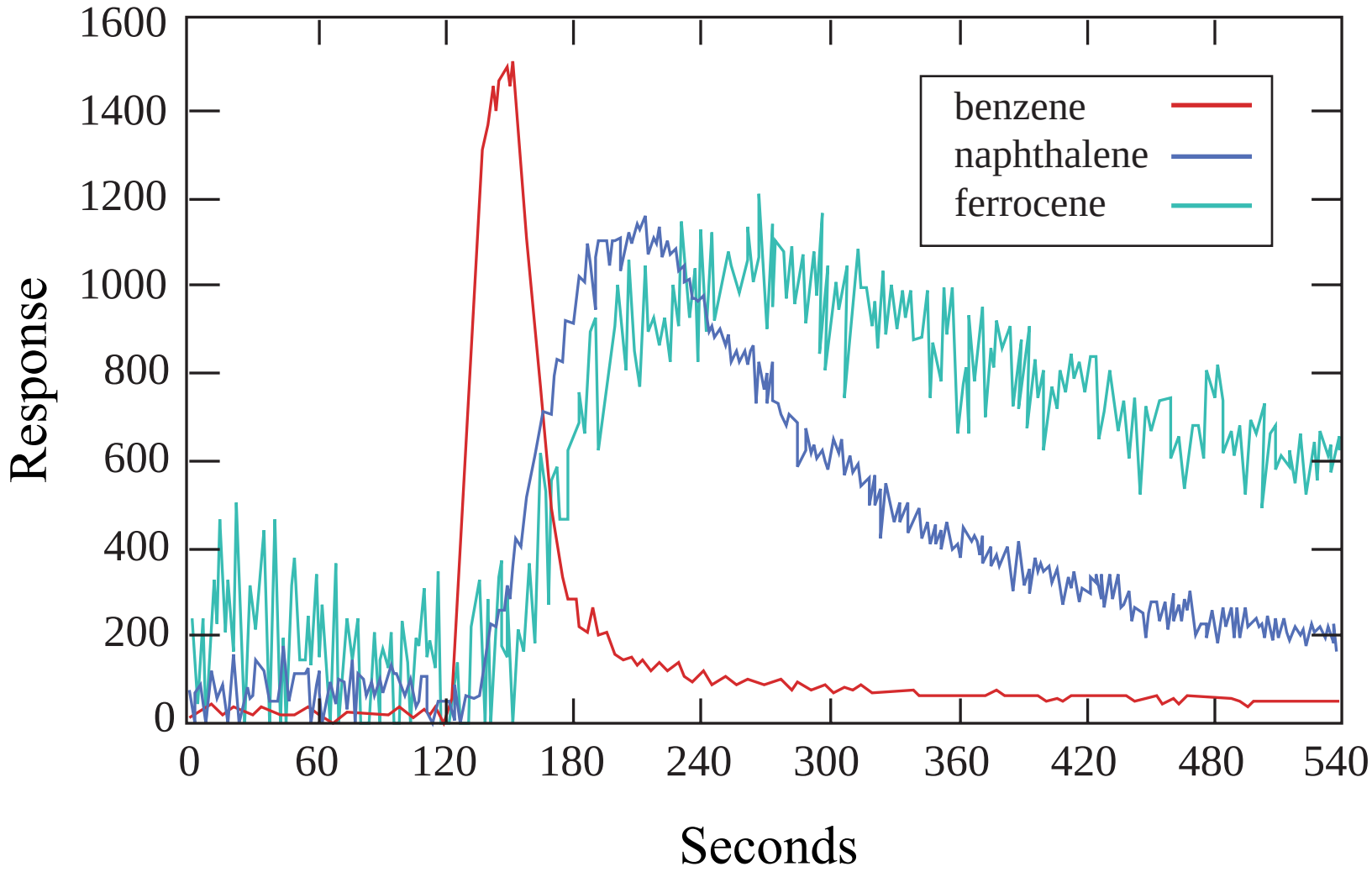
Simultaneous Detection of VOC, SVOC, and Organometallic Compound by MIMS

- Our preliminary studies have centered on model compounds, not necessarily environmentally significant contaminants.
- We have a listing of the VOCs, SVOCs, and metal compounds we have detected by MIMS available in a handout.
- For our next phase of investigation *we are seeking input on relevant compounds* pertinent to current mixed waste problems.

Simultaneous detection of 870 ppb benzene, 150 ppb naphthalene, and 180 ppb ferrocene in aqueous solution



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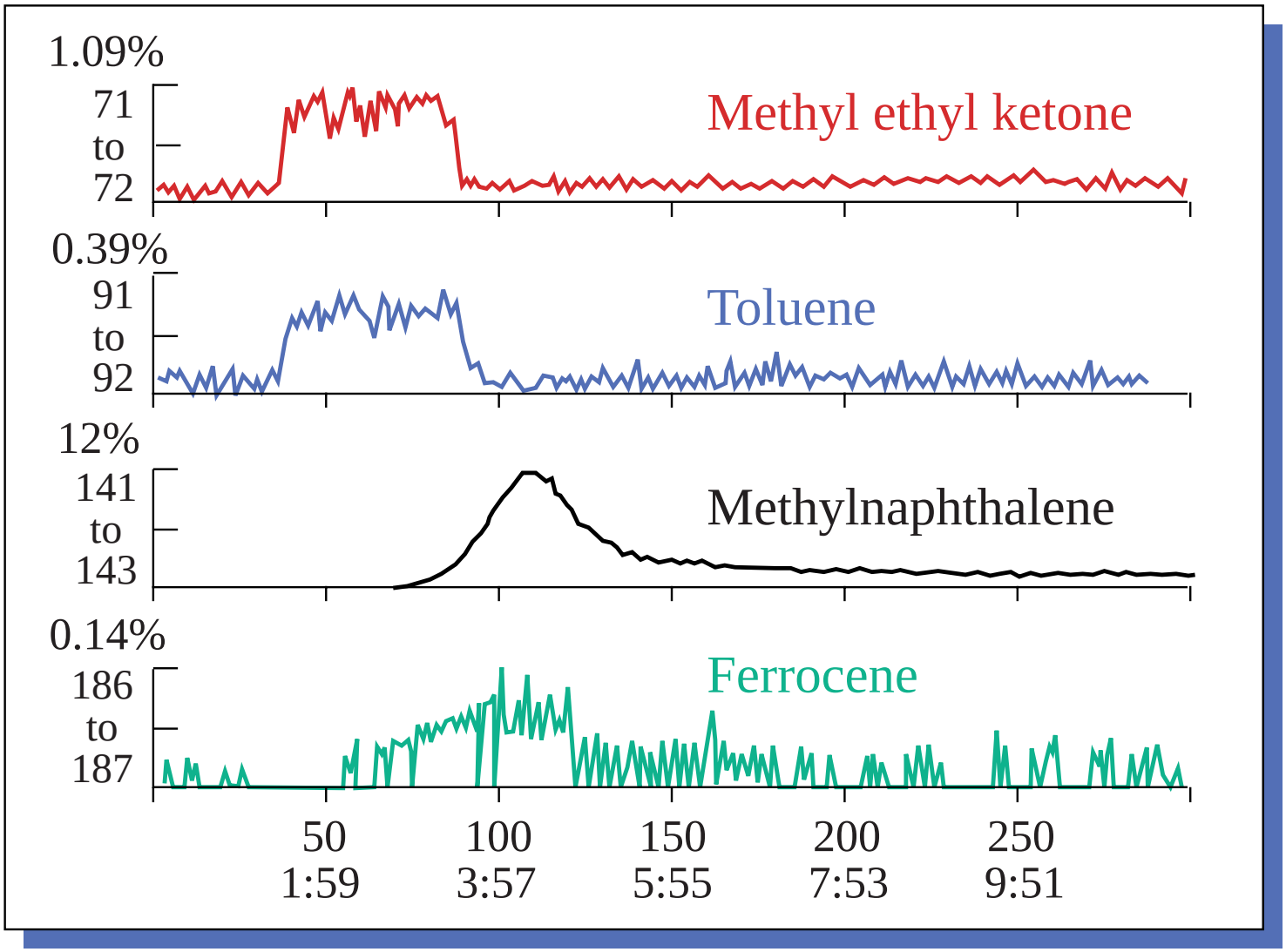
Simultaneous detection of 660 ppb methyl ethyl ketone, 7 ppb toluene, methylnaphthalene, and 700 ppb ferrocene in air



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Avenues for Further Technical Exploration

We have observed interesting ionization phenomena for some organometallics. The organic substituent is seen in the mass spectrum, but metal-containing fragment ions are missing. We speculate that this is due to the presence of oxygen, one of the predominating species in the ion trap environment.

FY99 Goals

- Focus on semi-volatile compounds

  -- ion chemistry in discharge source

  -- SVOC transport and membrane properties.

- Begin parallel work with organometallics.
- Evaluation of the discharge source.
- Obtain customer input on analytical needs and relevant compounds.

Conclusion

- Plasma source-ion trap combination looks like a productive marriage; operating conditions need further study.
- Detection of 25 SVOCs from various compound classes by MIMS was accomplished.
- Demonstration of simultaneous detection of VOC, SVOC, and organometallic by MIMS is very promising for eventual on-line analysis of Mixed Waste.