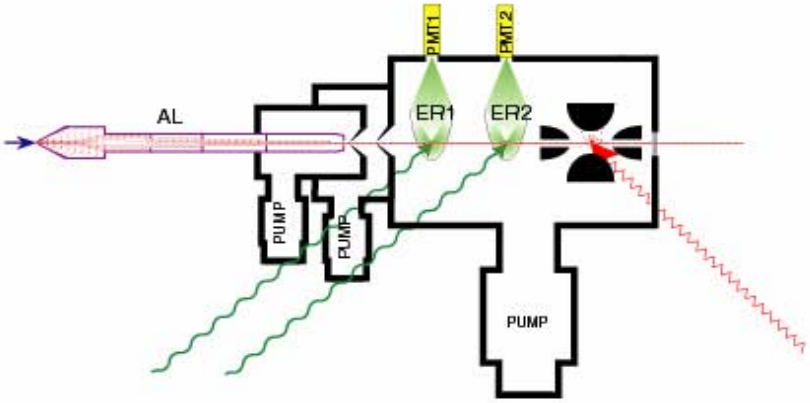
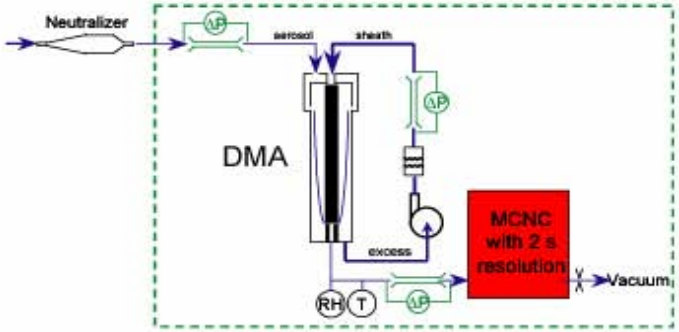
Real Time Tailpipe Emission Measurements

Single particle size and composition by chemical ionization mass spectroscopy



Rapid size distribution from 2.9nm to 1000nm measurements with 2 second time resolution



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ROAD MAP

Objective

Where we are

Steps to get there

Objective

Develop and deploy a system capable of providing *size resolved composition* of tailpipe-emitted particulates and their time evolution for assessing health effects and engine performance

Requirements

- *Real-time*
- *Easy to interpret* format
- Size range from a few nanometers to microns
- Temporal resolution on order seconds

Approach

Hardware (RT-SPMS): Develop a *Real-Time Single Particle Mass Spectrometer* capable of measuring the size and composition of individual particles 20nm to 3μm in diameter, while measuring complete *size distributions* with 2 seconds time resolution.

Software (SpectraMiner): Develop the software package for real-time data analysis and an interactive visual interface.

The Challenge

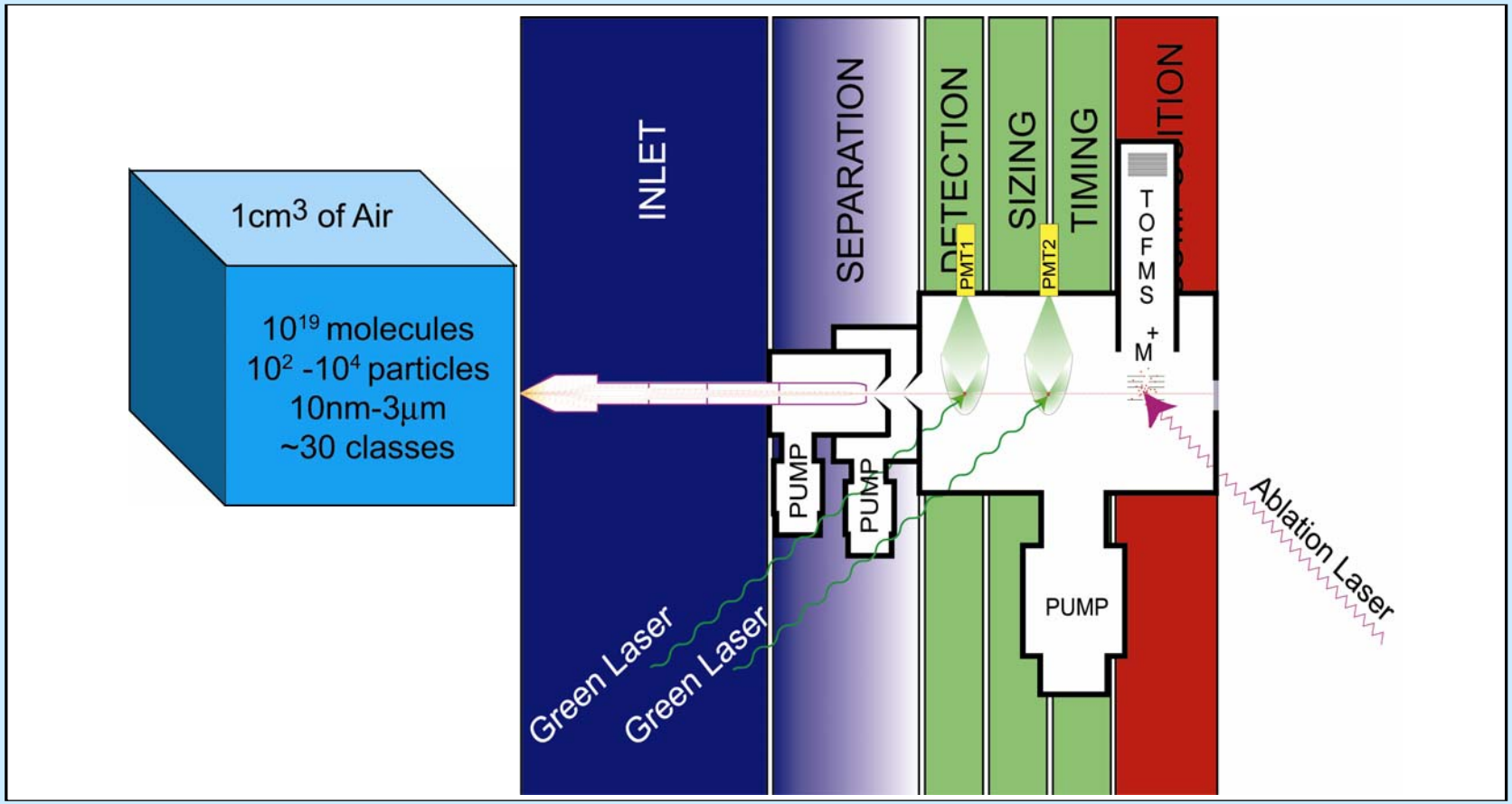
The Instrument (RT-SPMS)

- Particle number ***concentrations*** are very ***low***
- Particles are ***small***
- Transient events occur over ***short times***
- Chemical composition is ***complex***
- The road to ***quantitative*** analysis is long and arduous

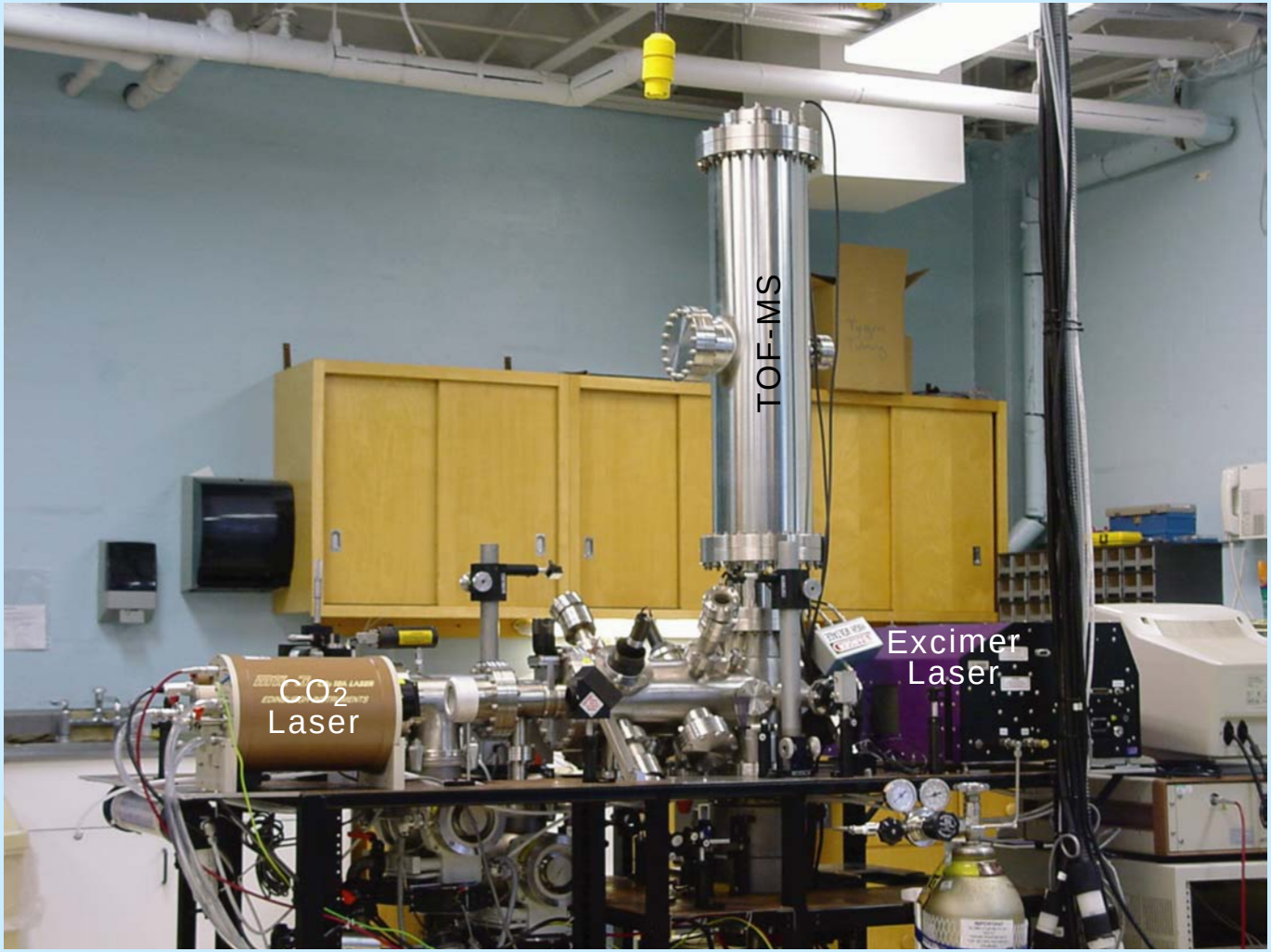
Data Analysis and Visualization (SpectraMiner)

- The data are ***complex***
- Data sets are ***large***
- ***Real-time*** data analysis and visualization is the key
- ***User-friendly*** visual interface is a must

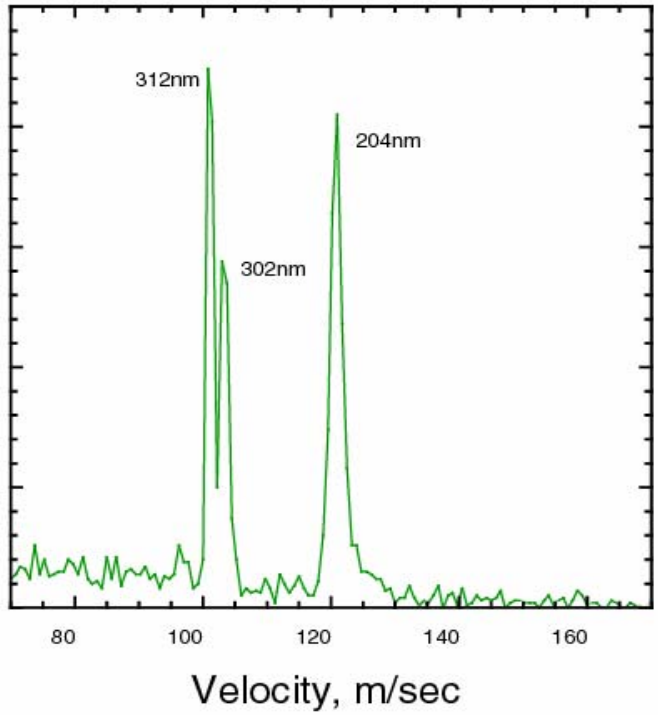
Single Particle Mass Spectrometry: Basics

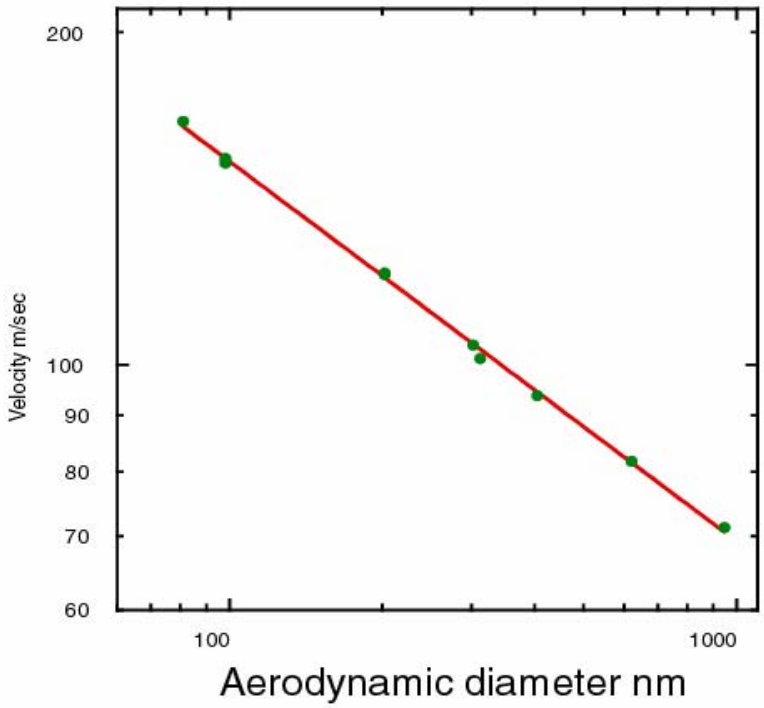


BNL's Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT-MS)

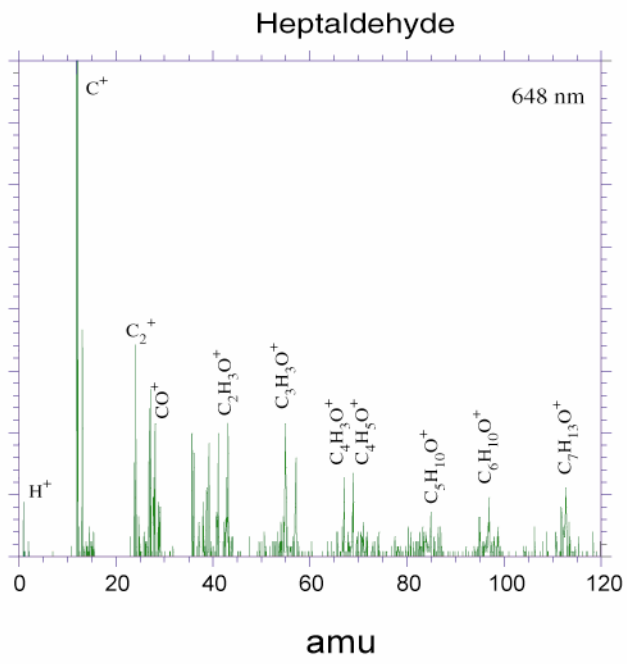


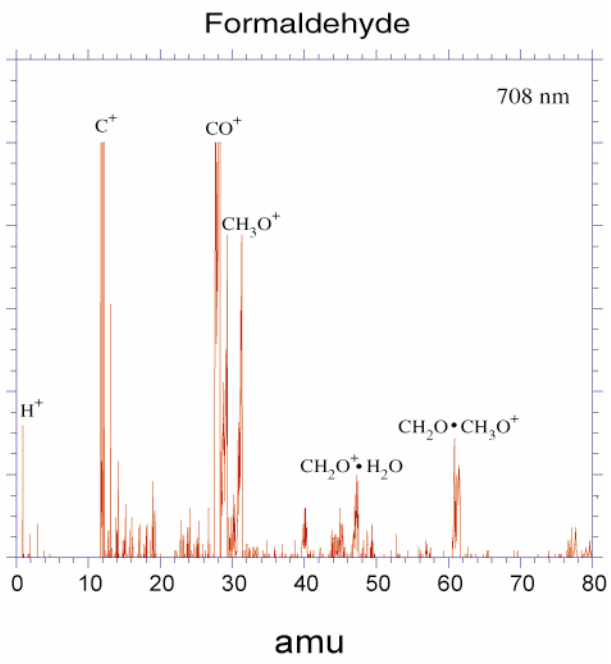
AERODYNAMIC PARTICLE SIZING



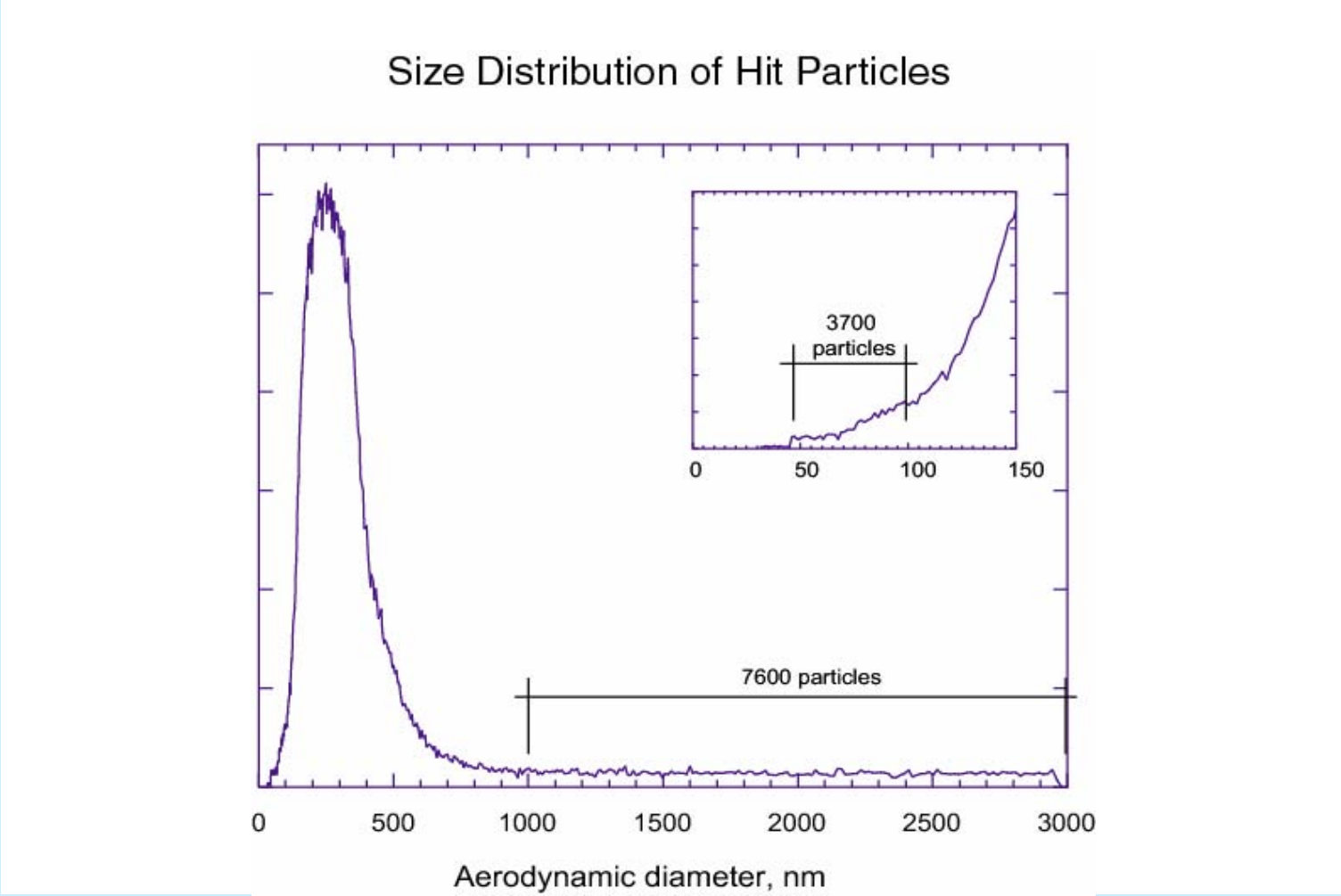


Aldehyde Particles MS

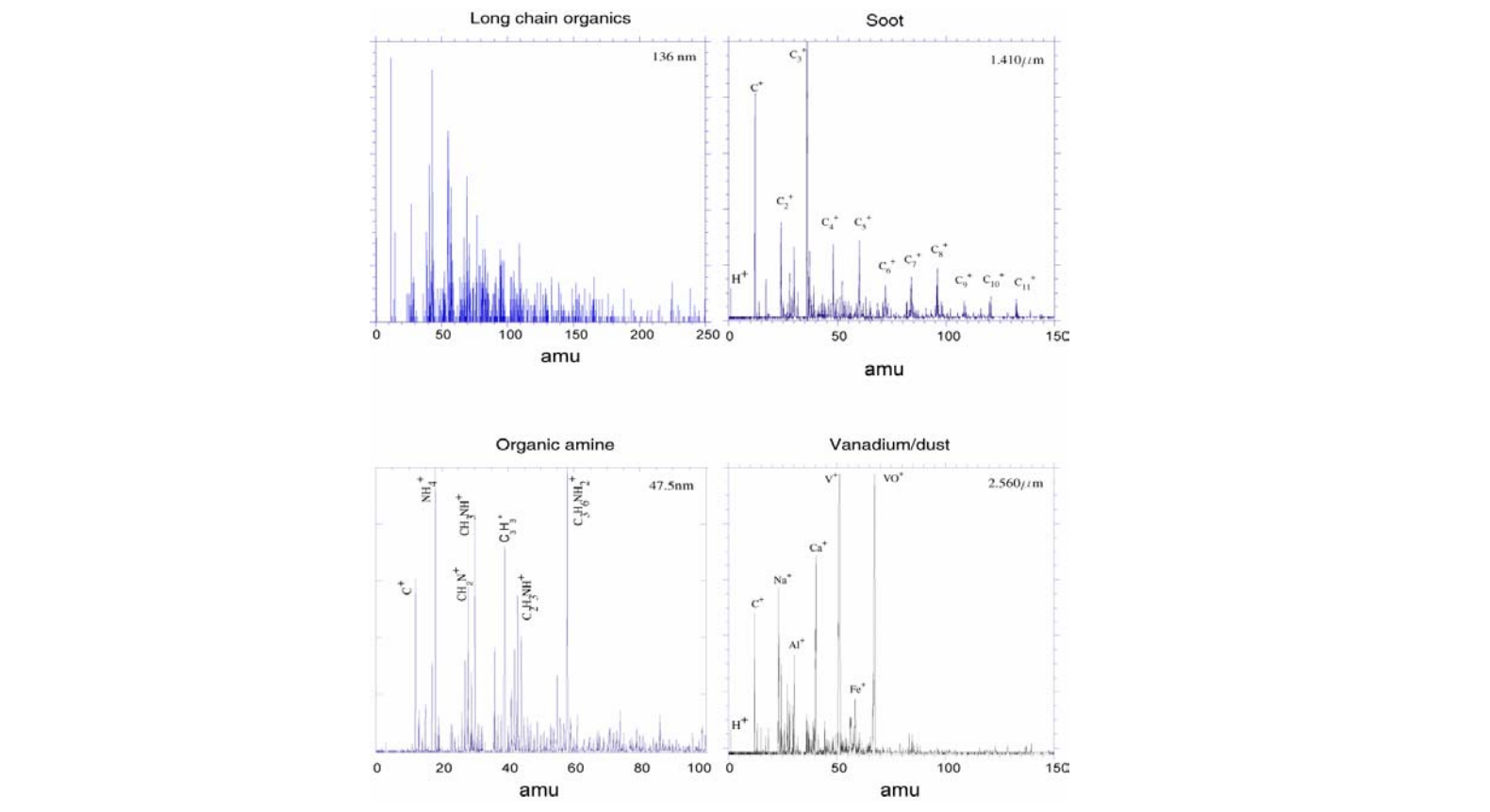




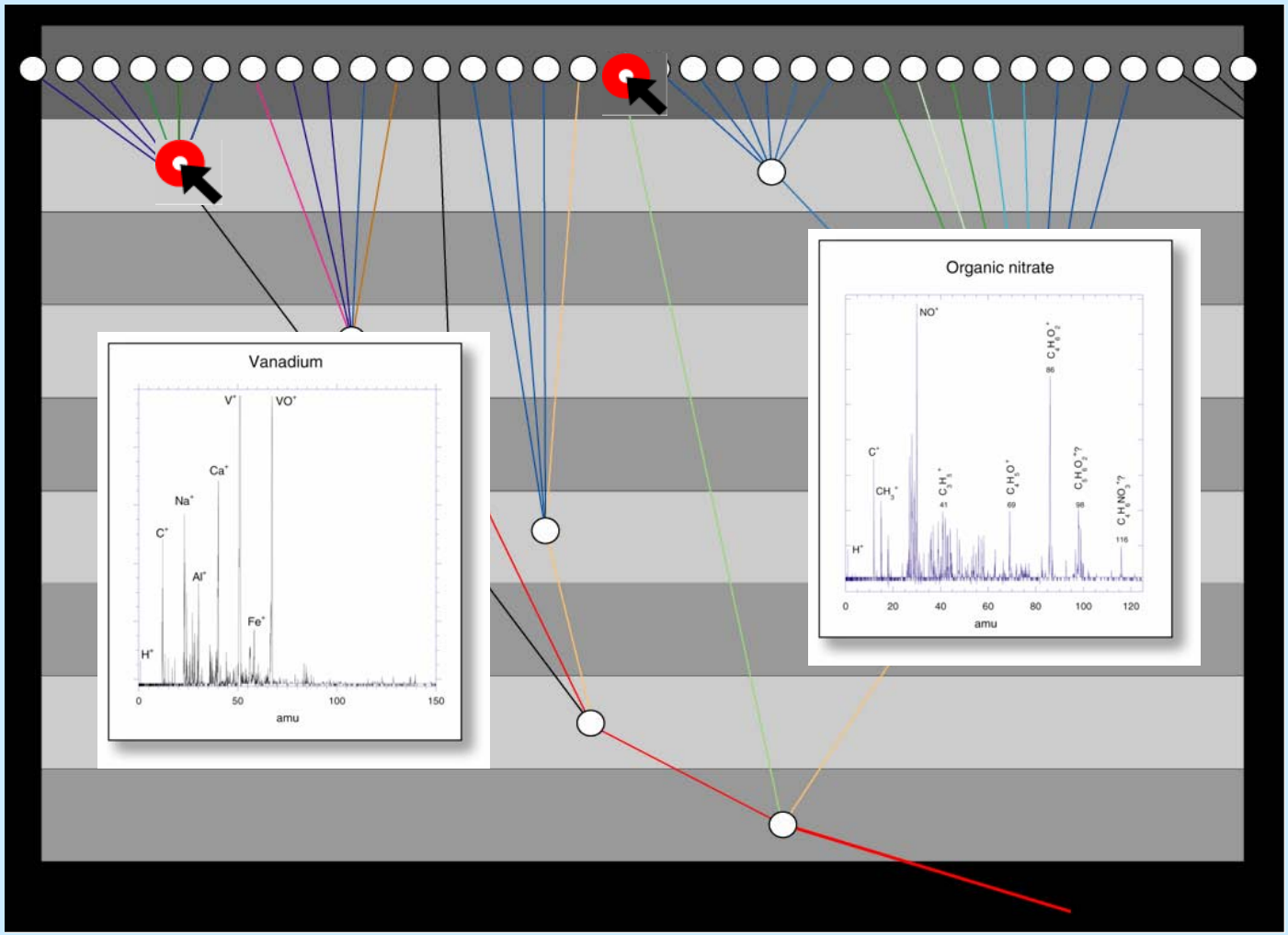
Field Measurements Houston TX



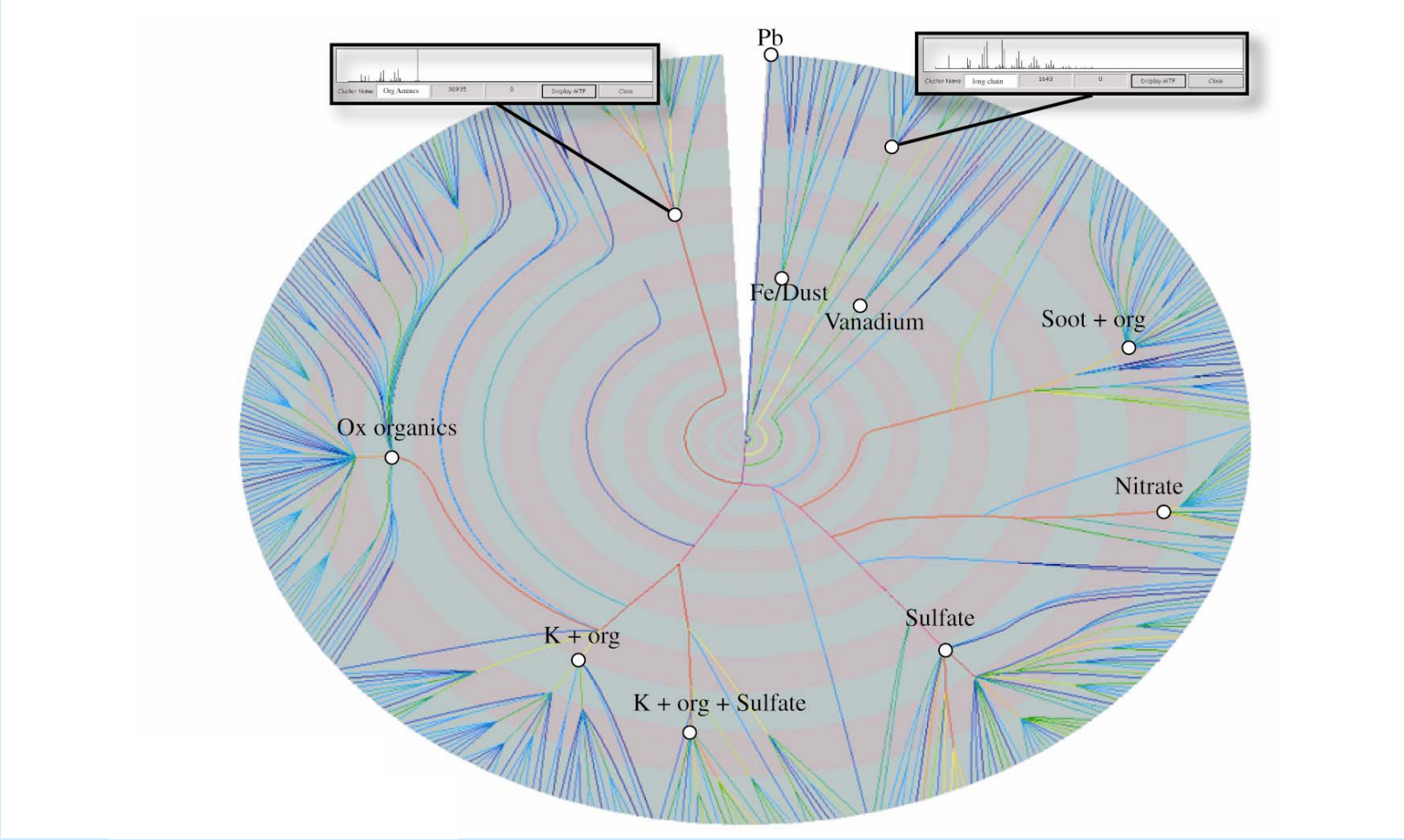
4 Little Particles From Houston TX



The Dendogram or Classification Tree



The Interactive Circular Dendogram
Representing 233699 Particles From Houston TX



Application to Exhaust Emissions

An exploratory study on 5 automobiles

2002 Audi A4

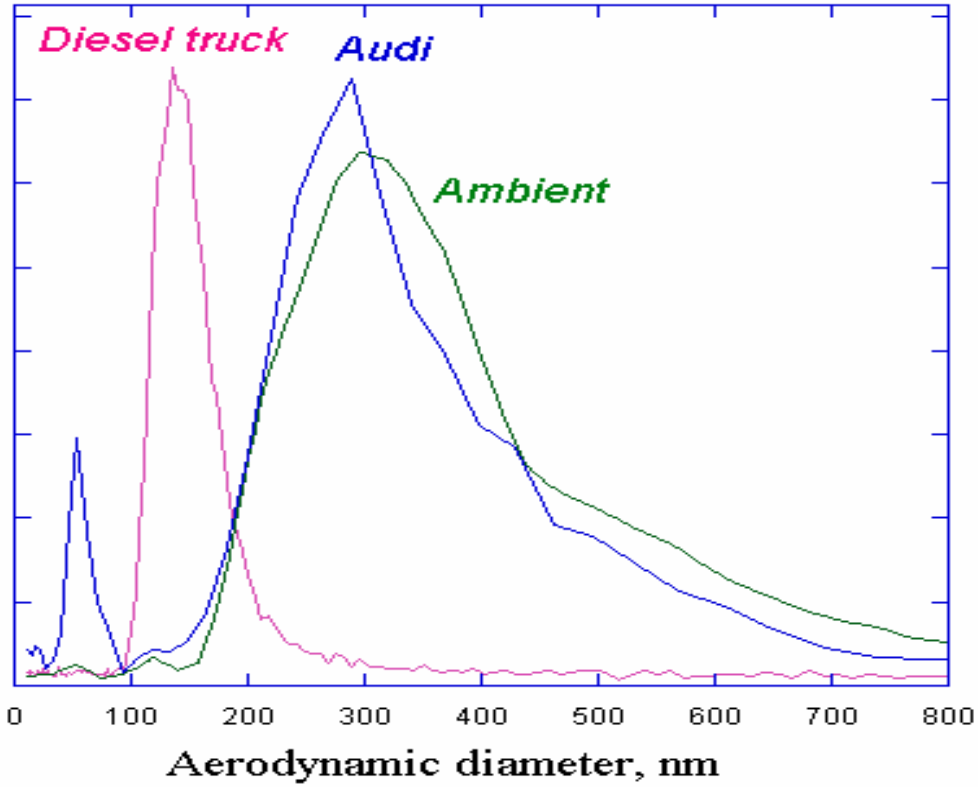
1998 Corvette

An old diesel garbage truck (no emission controls)

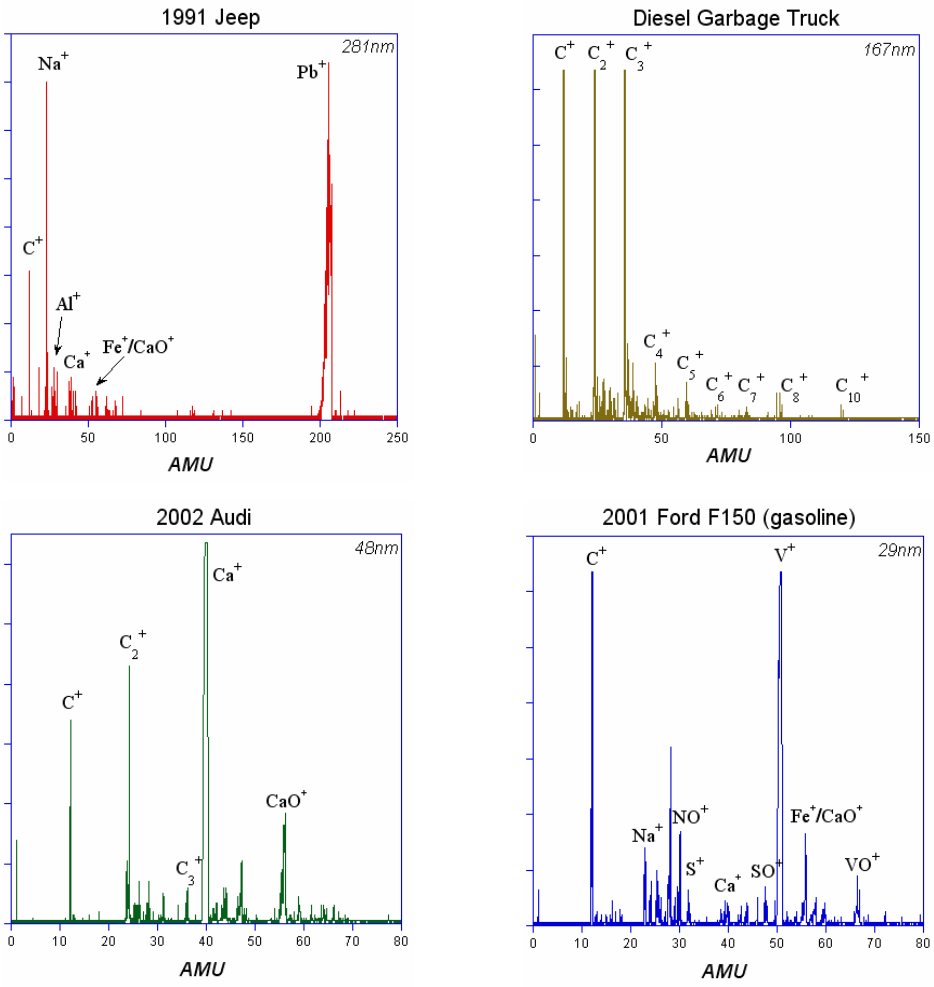
1991 Jeep Cherokee

2001 Ford F150 truck running on CNG or on gasoline

Size Distribution of Hit Particles



4 Little Exhaust Particles



Lessons

- **The RT-SPMS** has the required sensitivity and temporal resolution

- **SpecraMiner** analyzes and provides a visual display of the data in near real-time with a user friendly interactive interface

Where Do We Go From Here (easy)

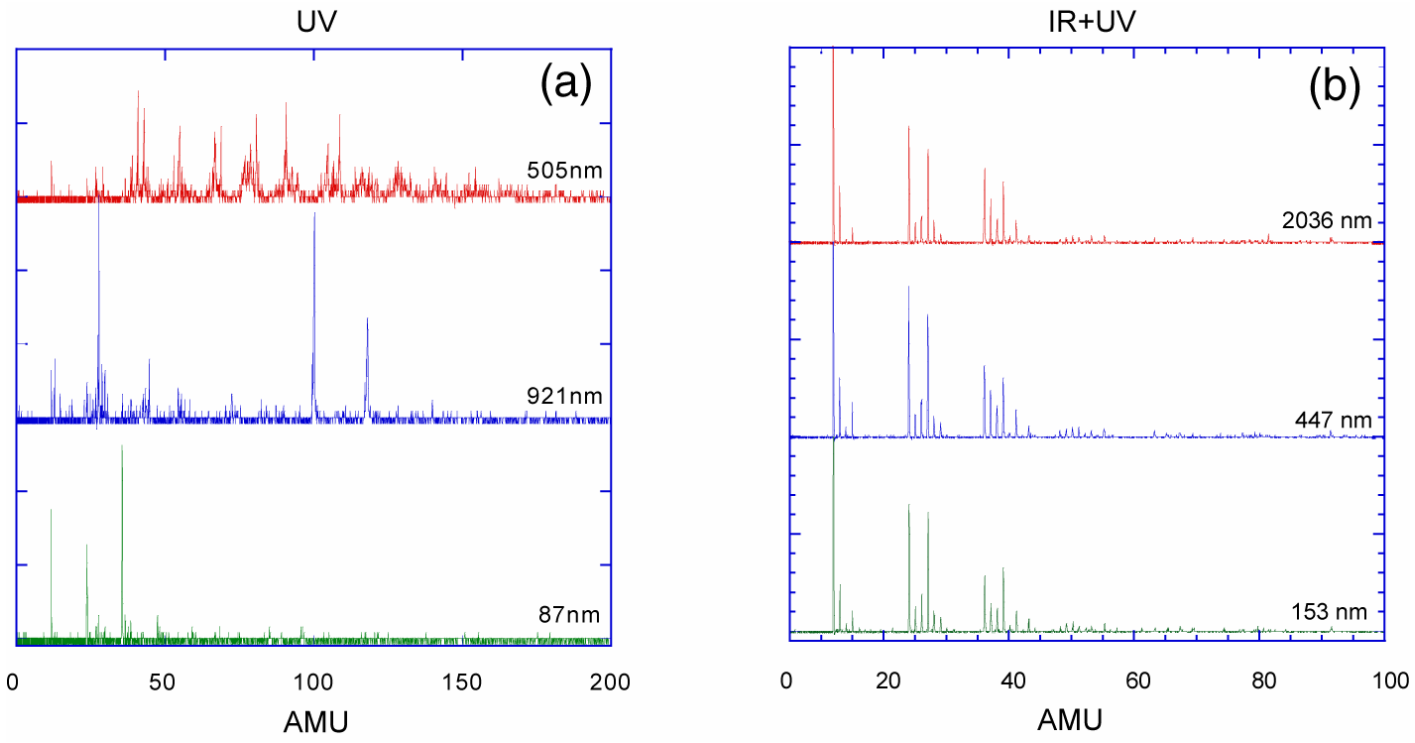
- Improve RT-SPMS ability to characterize small particles by using a UV laser for light scattering and modifying the aerodynamic lens inlet
- Build a smaller ruggedized version of RT-SPMS
- Generate a spectral library
- Upgrade SpecraMiner to perform analysis, which includes particle and gas phase emission information and engine performance parameters, in *true* real-time

Where Do We Go From Here (hard)

- Turn RT-SPMS into a quantitative tool by producing ions in a two step process of evaporation followed by gas phase ionization

- Make the spectra produced by RT-SPMS easier to interpret by elimination fragmentation through chemical ionization

TWO STEP ION FORMATION:
IR EVAPORATION FOLLOWED BY UV IONIZATION



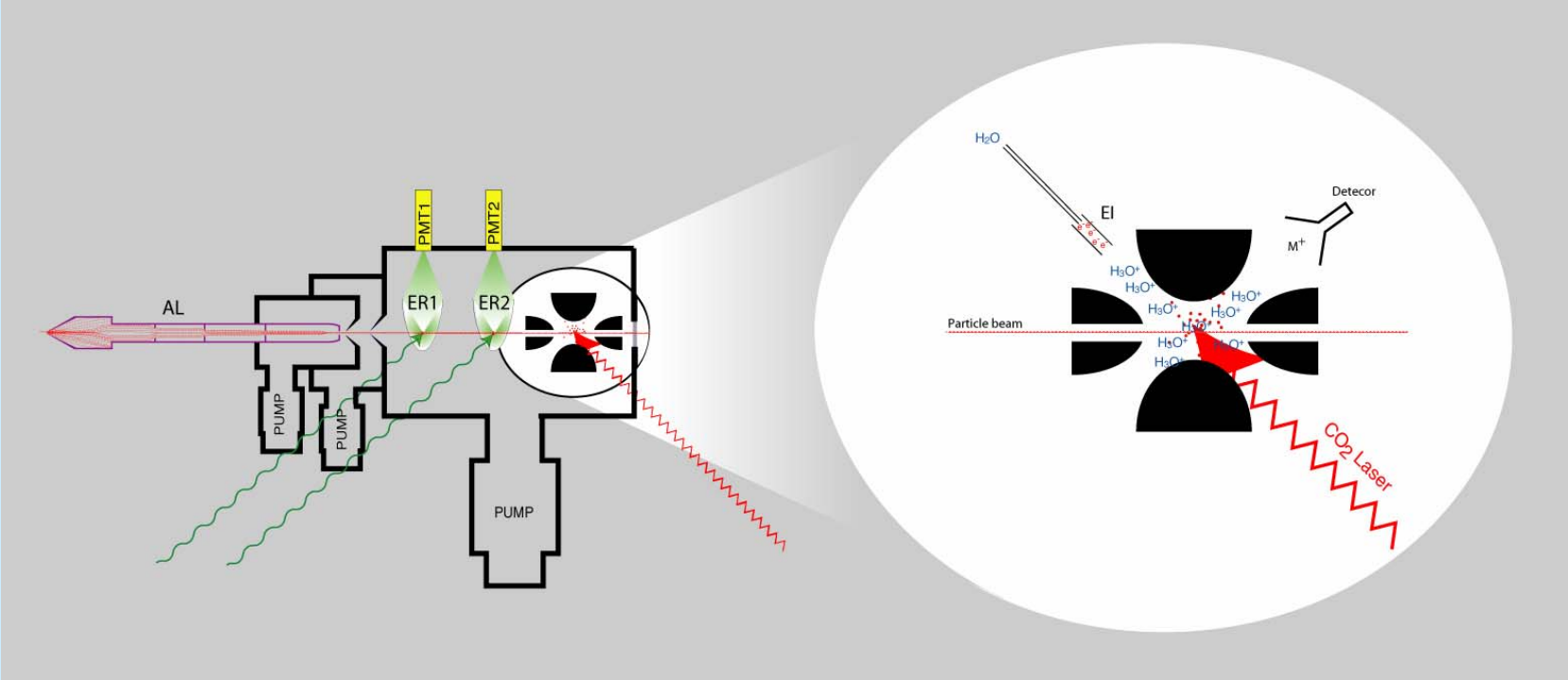
Beyond IR-UV to Chemical Ionization

- **Proton Transfer Reaction Mass Spectrometry** (PTR-MS) **:** is based on the non-dissociative and very efficient proton transfer reactions of H_3O^+ ions with most common organic molecules

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

- **PTR-MS in Ion Trap:** The RF ion trap mass spectrometer possesses the unique ability to store H_3O^+ ions prior to particle arrival to be reacted with the gas plume that is formed by CO_2 laser particle evaporation

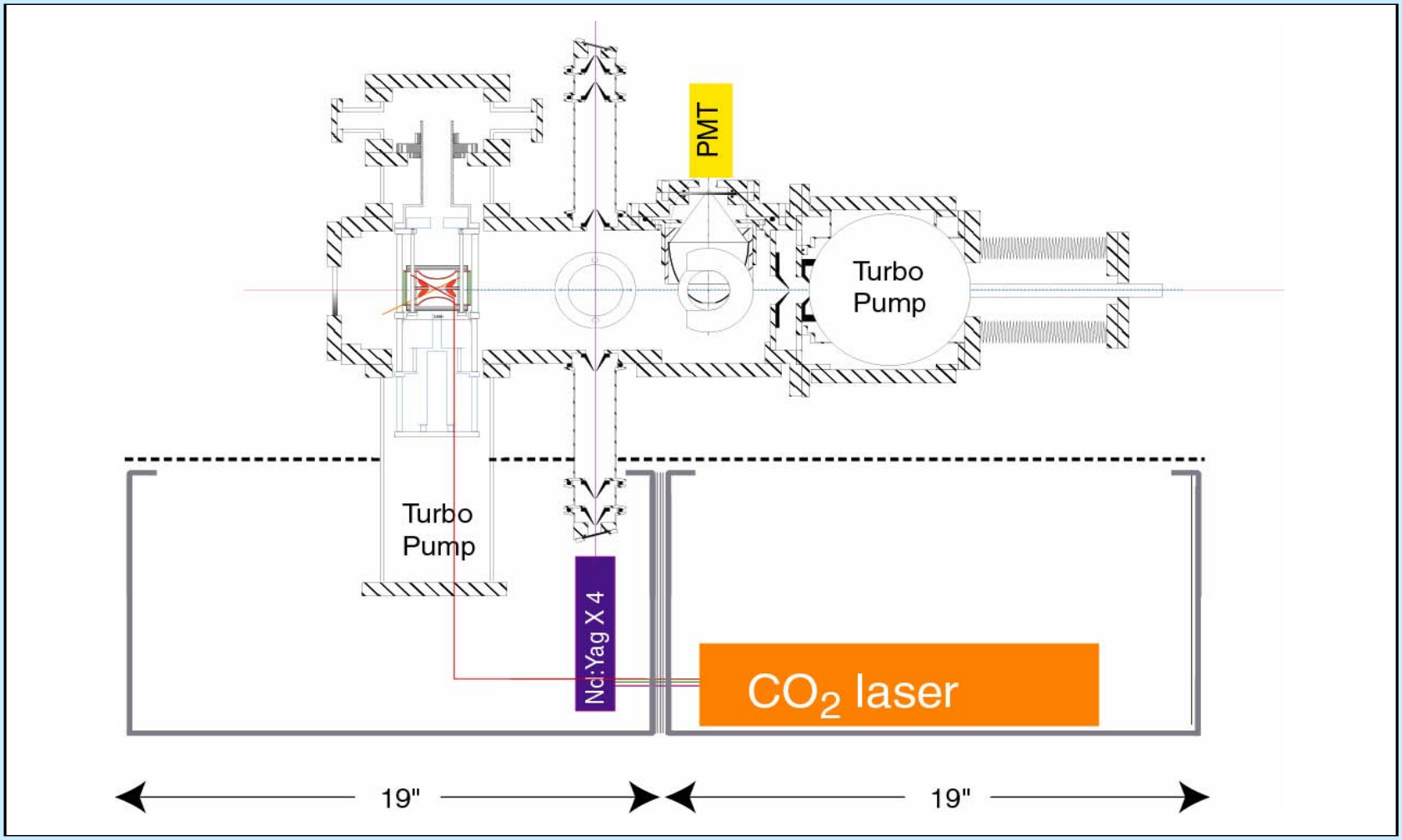
PROTON TRANSFER ION TRAP MASS SPECTROSCOPY



SINGLE PARTICLE CO_2 EVAPORATION PROTON TRANSFER REACTION ION TRAP MASS SPECTROSCOPY

Conclusion

RT-SPMS, rapid size distribution and SpectraMiner provide:

- *In-situ* measurement of individual particle size and composition
- Wide size range (from 20nm to 3 microns)
- High temporal resolution of ~50 particle/sec
- Capability to capture and characterize transients
- Analysis of organics by chemical ionization MS
- Characterization of semivolatile
- Simple and analytical quality fringerprinting
- Real-time data visualization and analysis

Compact Field Deployable RT-SPMS