

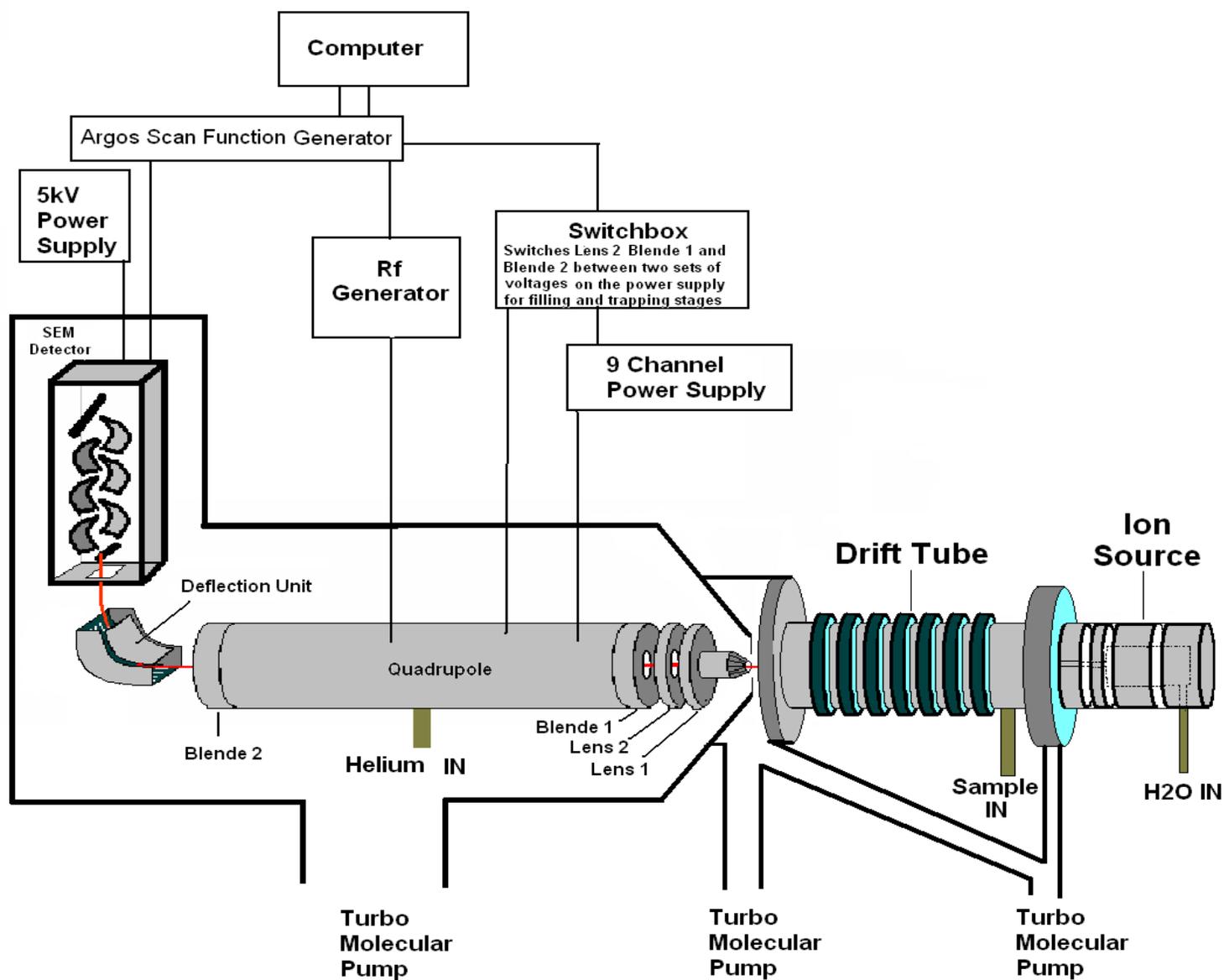
**“Production of Secondary Organic
Aerosol from Multiphase Terpene
Photooxidation”**

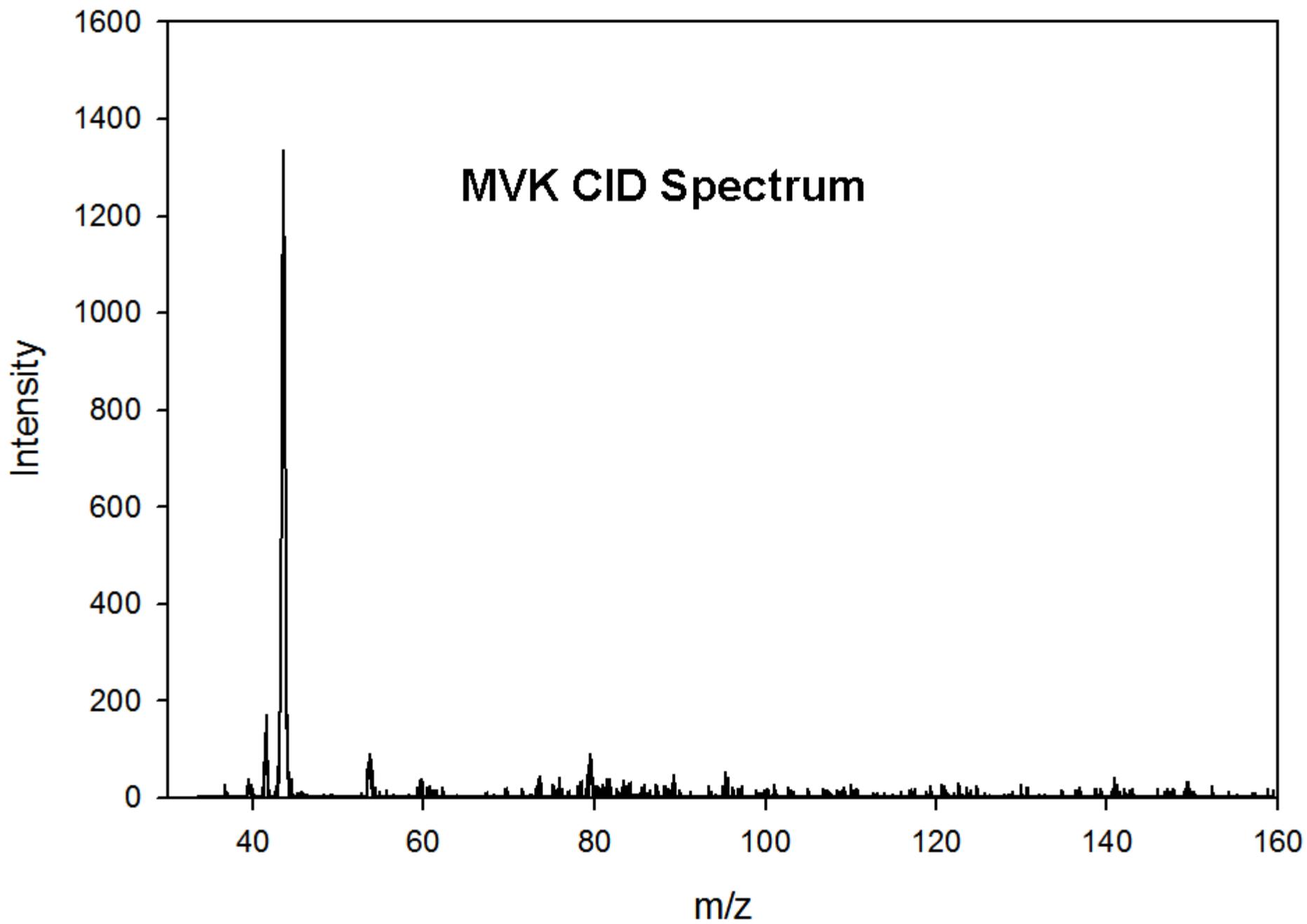
**Shepson Group
Purdue Climate Change Research Center**

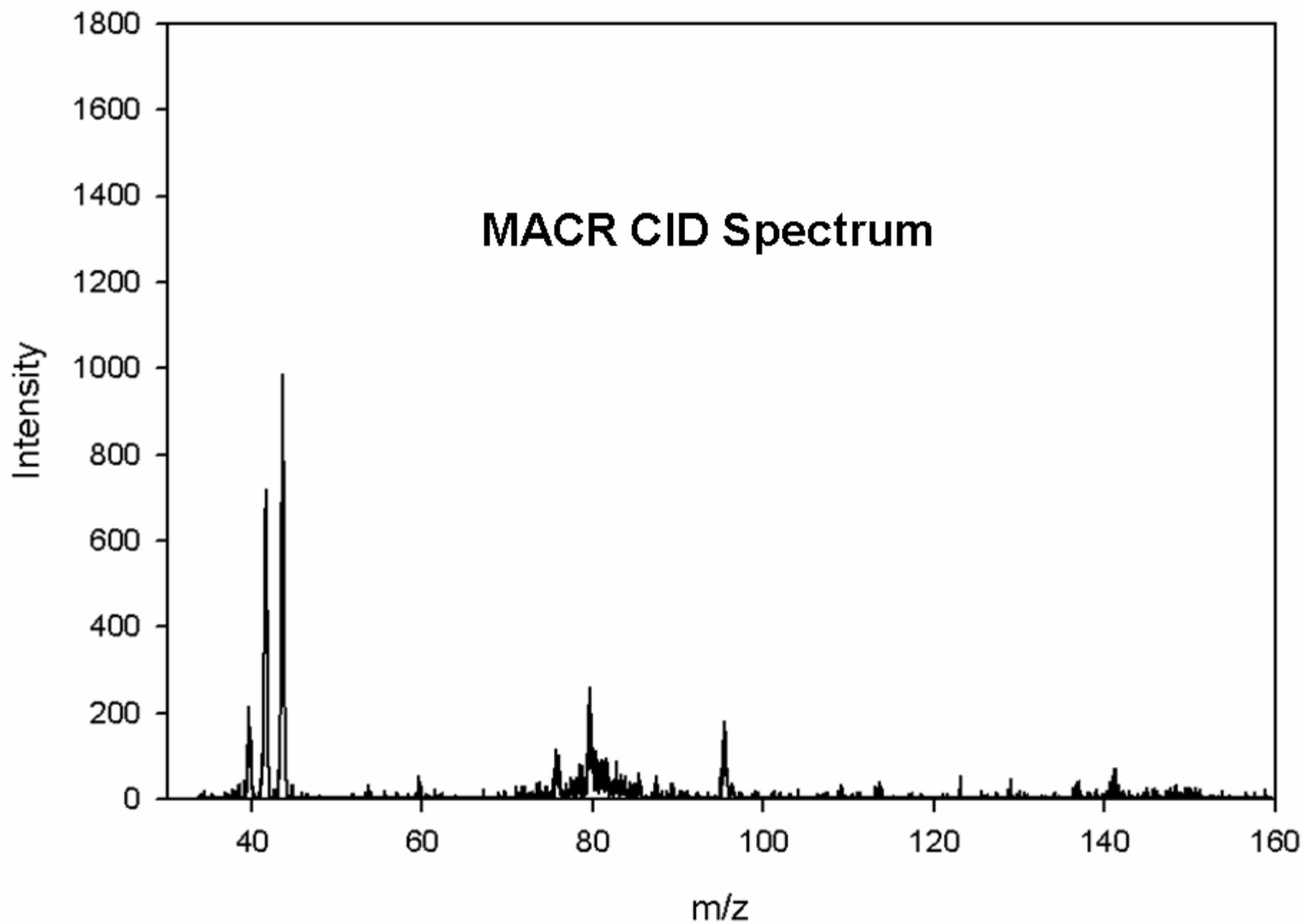
Project Hypotheses

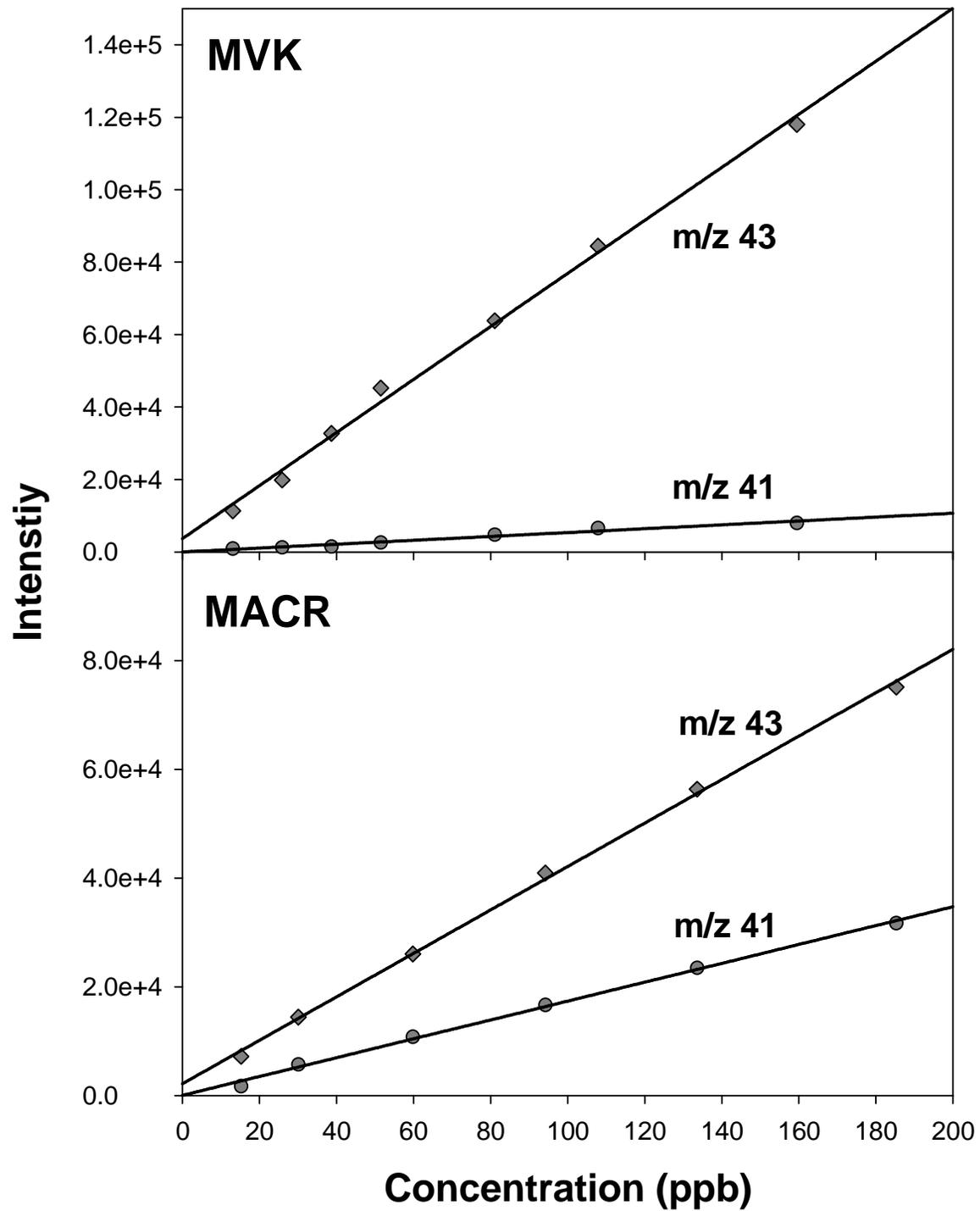
- **PTRLIT can be used to vastly improve our ability to identify and quantify the photooxidation products of BVOCs that are important aerosol precursors.**
- **DESI can be used in conjunction with smog chamber-based studies of BVOC/NO_x irradiations to investigate the nature of oxidation products that are important SOA precursors.**
- **Aerosol can age both as a result of polymerization chemistry, but also because of aerosol-phase photochemistry, and this processing influences the distribution of species between the gas and aerosol phase.**
- **We can quantitatively assess the contribution of α - and β -pinene to ambient SOA production in forest environments through simultaneous measurement of their oxidation products and aerosol growth.**

Proton Transfer Reaction Linear Ion Trap (PTR-LIT)

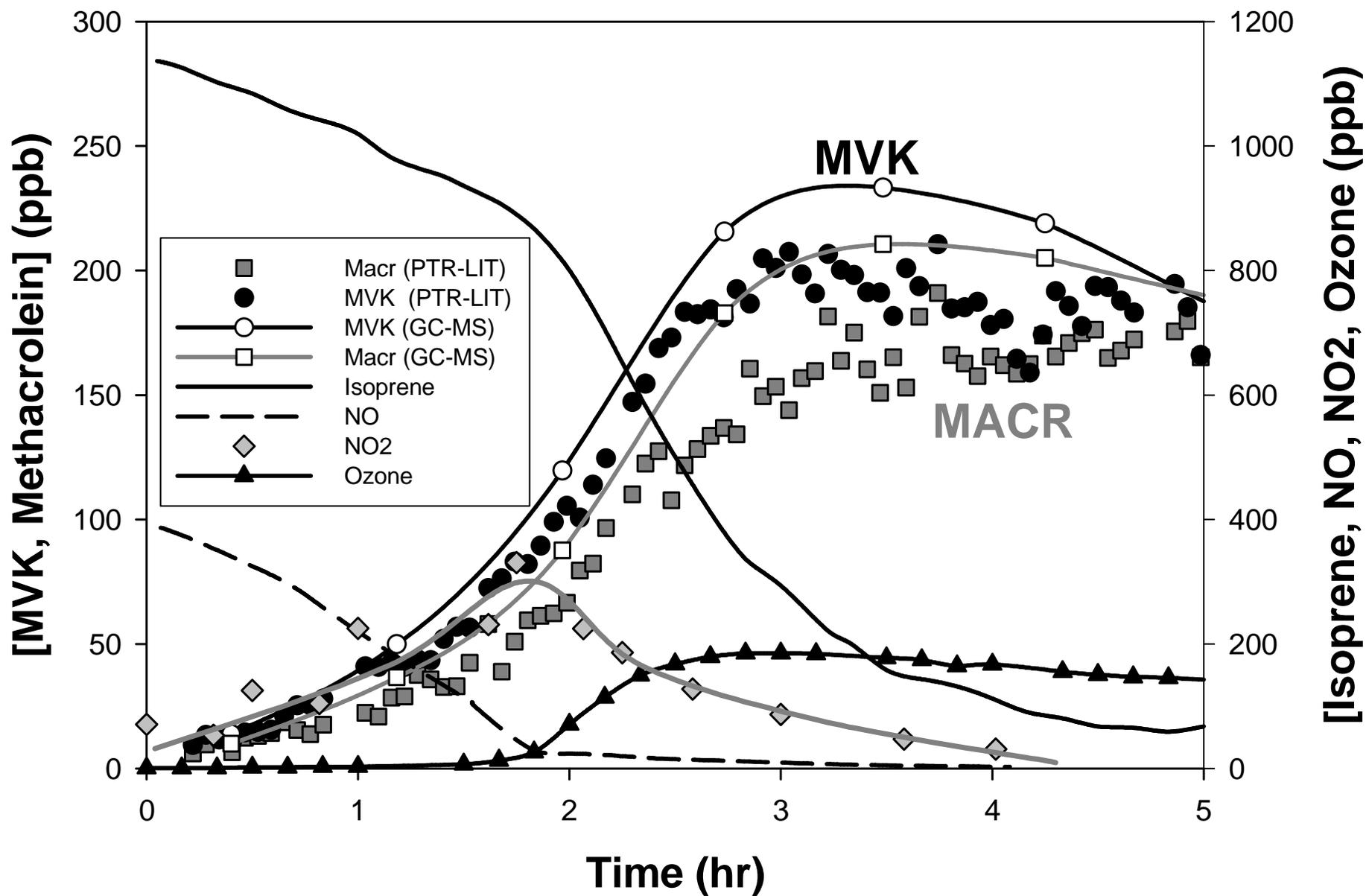






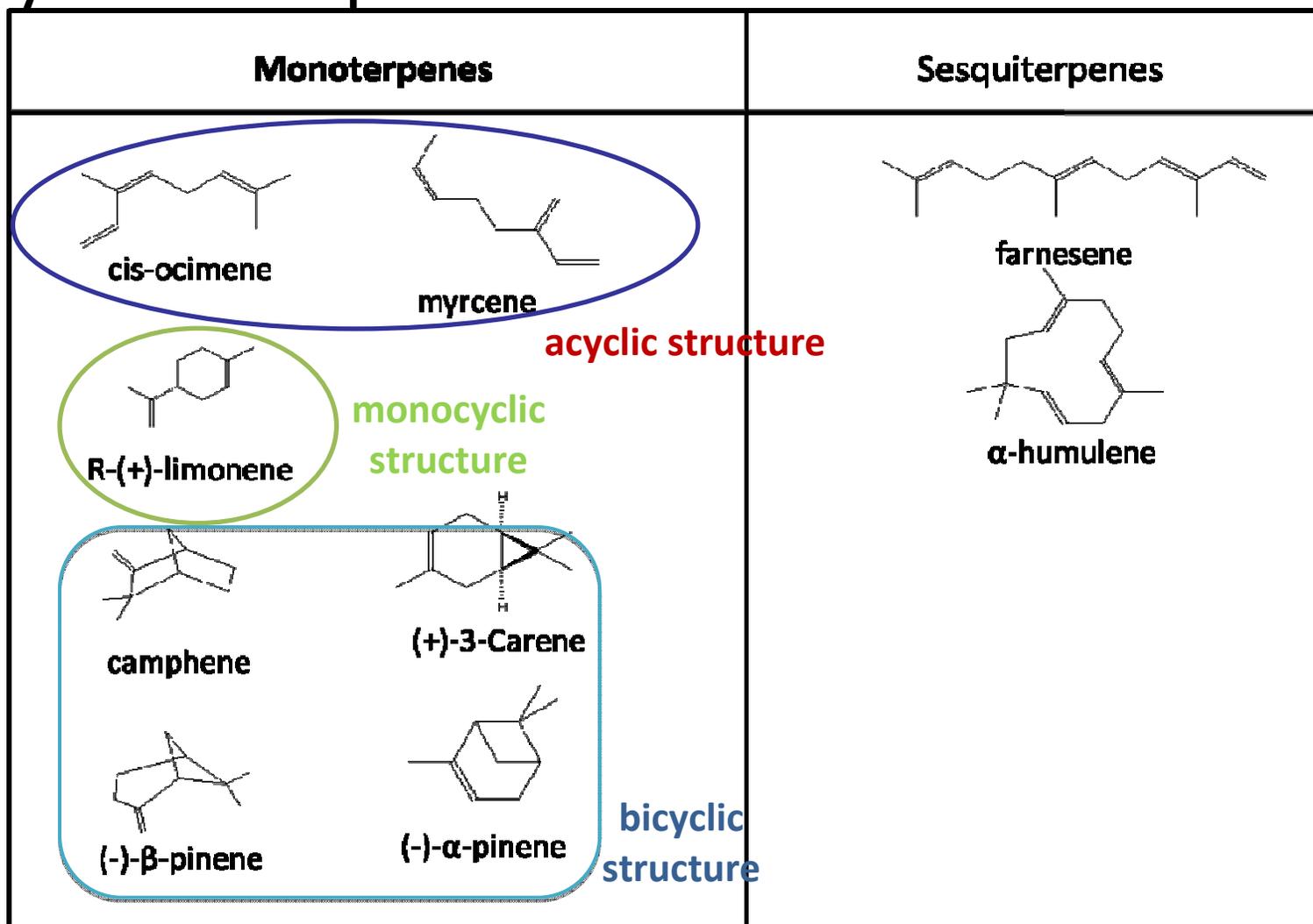


Isoprene/NO_x Smog Chamber Irradiation





Analysed Compounds:



Griffin System Software - [C:\Griffin\Scan Functions\11-6-2007 Limonene]

File Edit View Setup Instrument Window Help

Scan Device MS Quant. Method Open Save Print Undo Cut Copy Paste Comm System Monitor Tune Config Library Users

Control Panel

Result Setup

WF1

WF2

Show

- Spectrum
- Chronogram

Scans/Avg 200

View

- Peak Labels
- Detailed Data

X-Axis: M/z Time

Peaks

Spread (ms) 1.5

Peak Floor 150

Valley (%) 100

Filter

- Noise

Spectrum Baseline

- Manual 0
- Auto

Background Capture

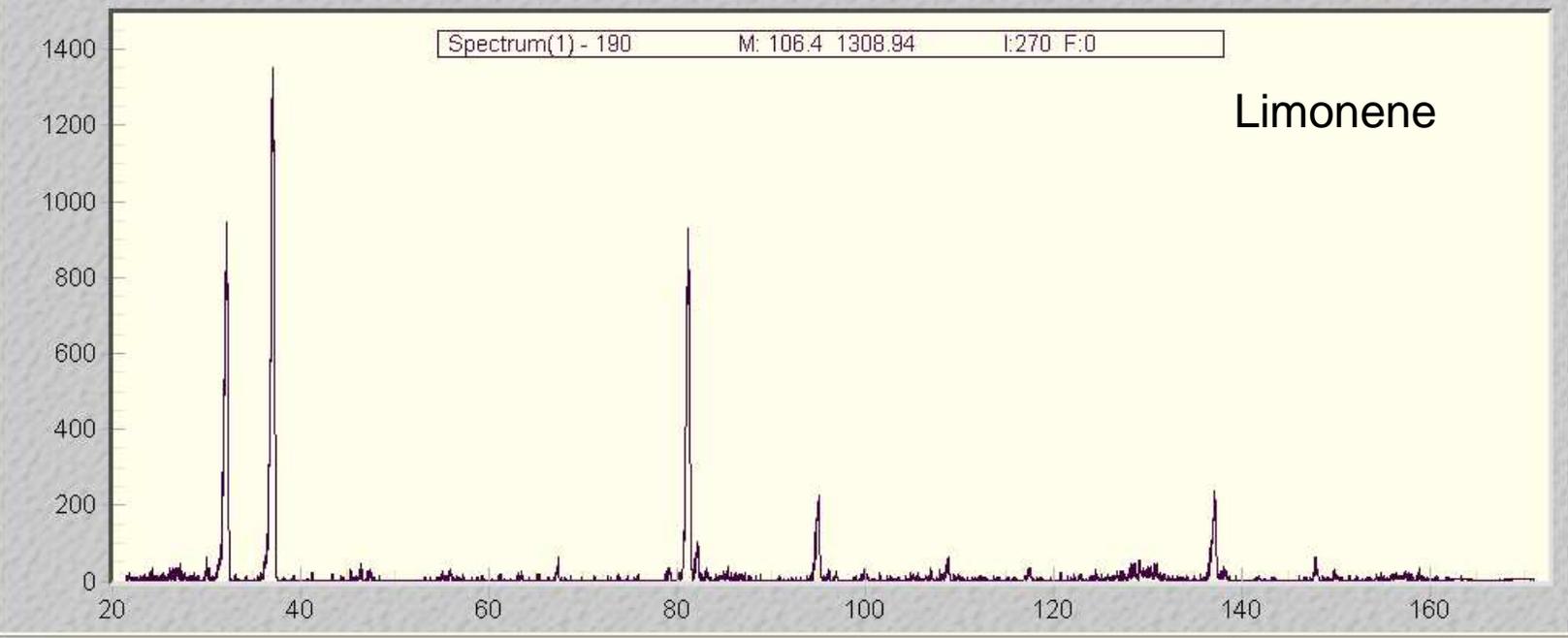
TIC Threshold 0

Result Data

C:\Griffin\11-6-07 limonene CID 2

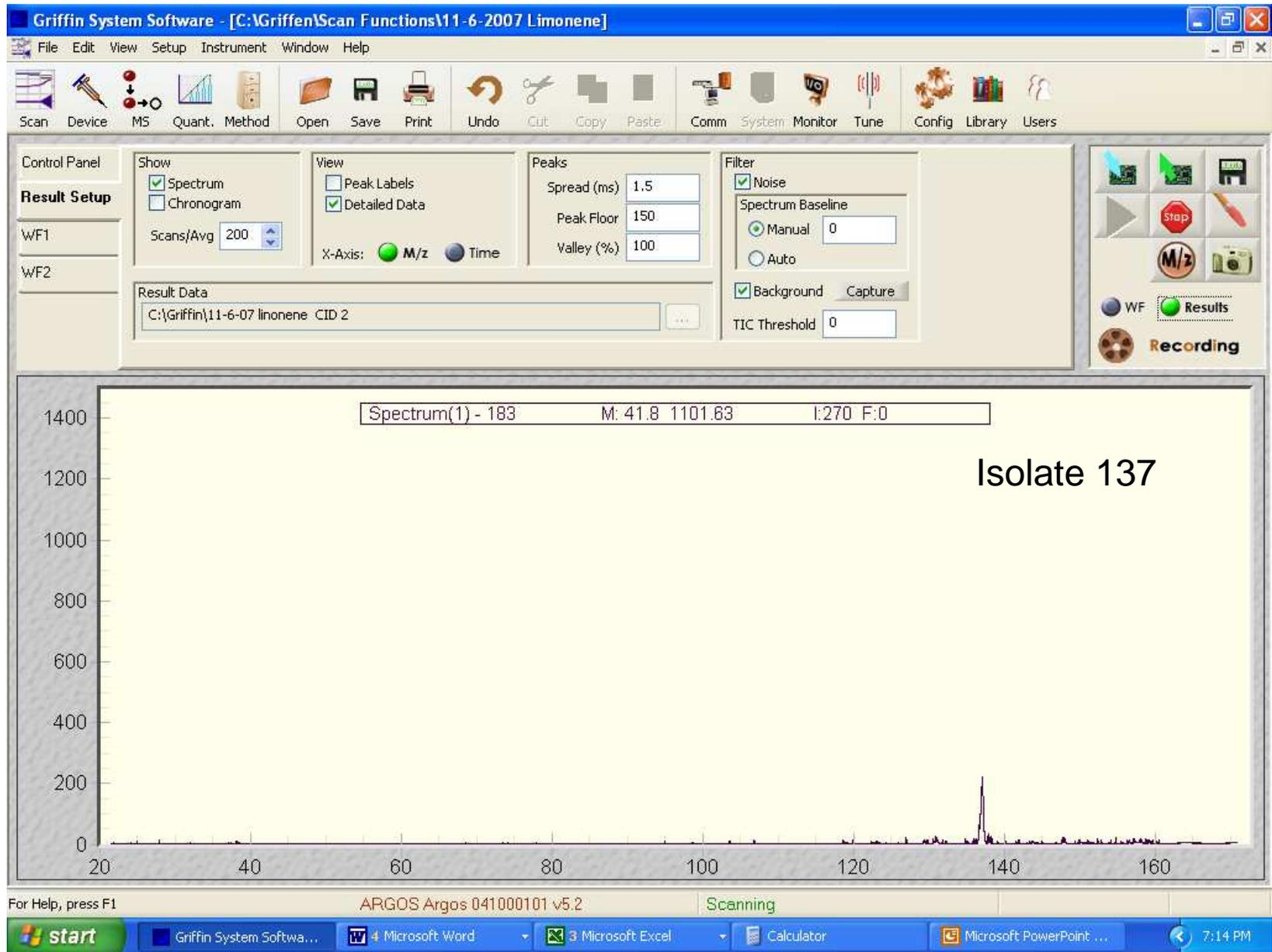
WF Results

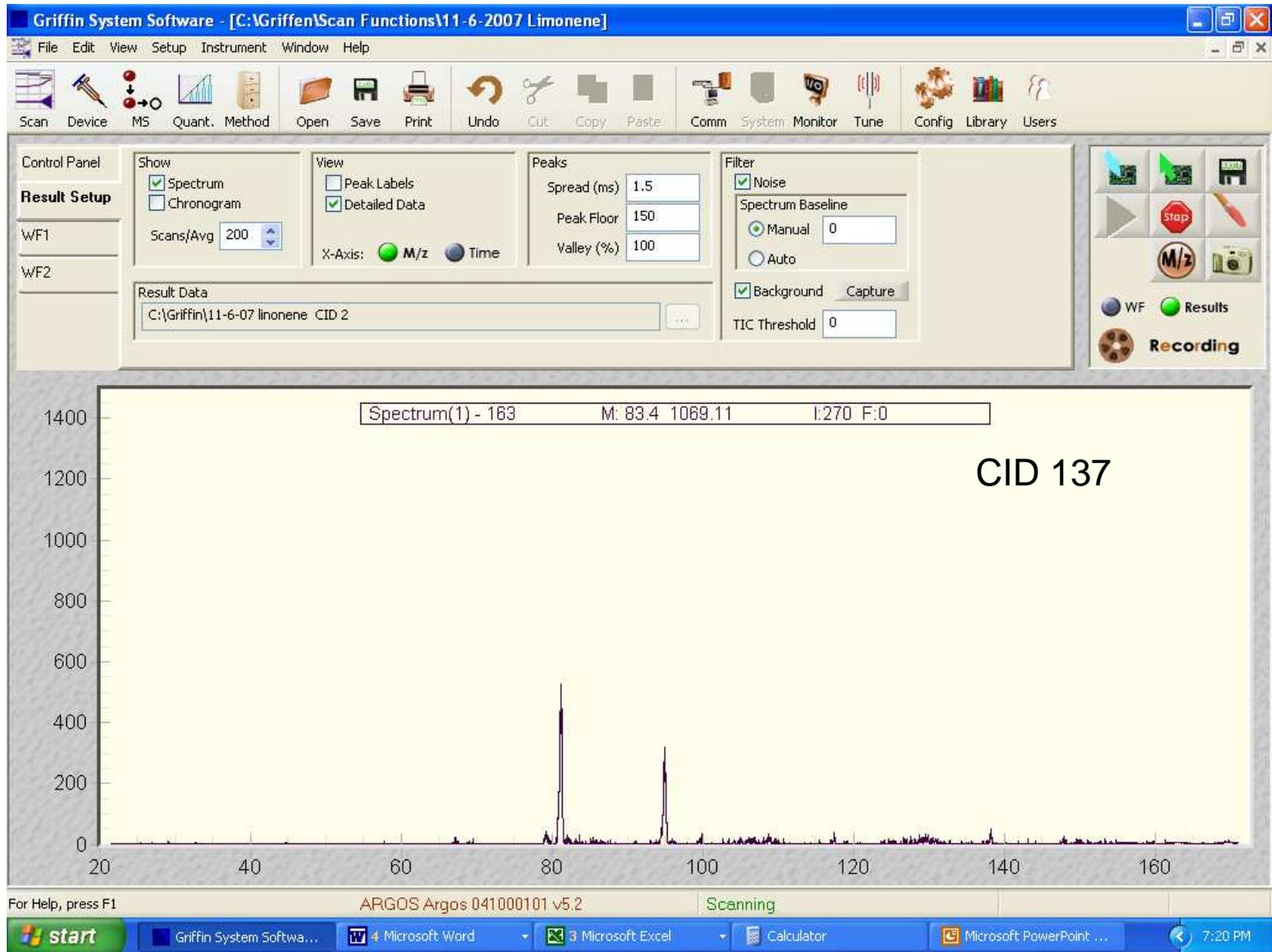
Recording

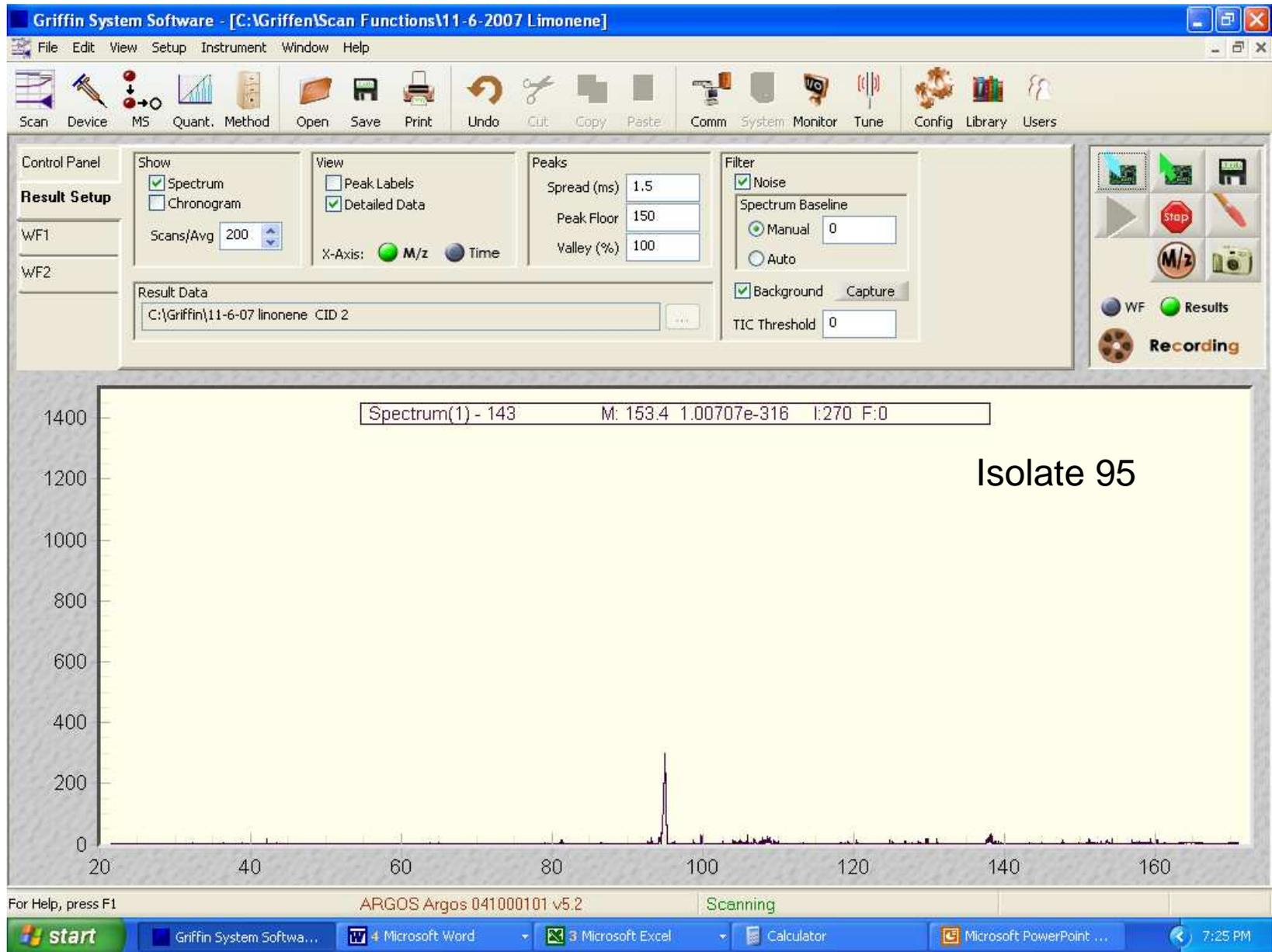


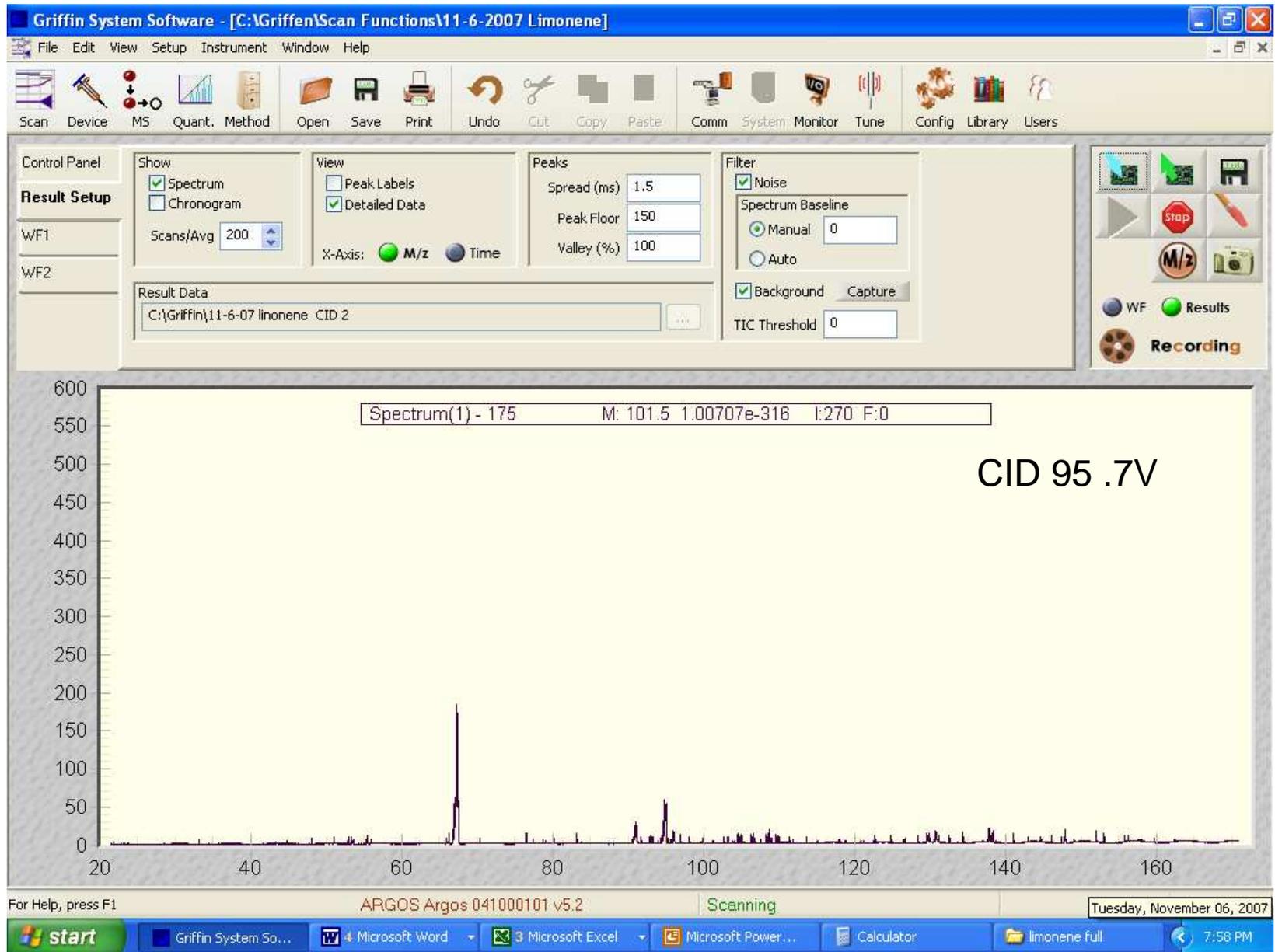
For Help, press F1 ARGOS Argos 041000101 v5.2 Scanning

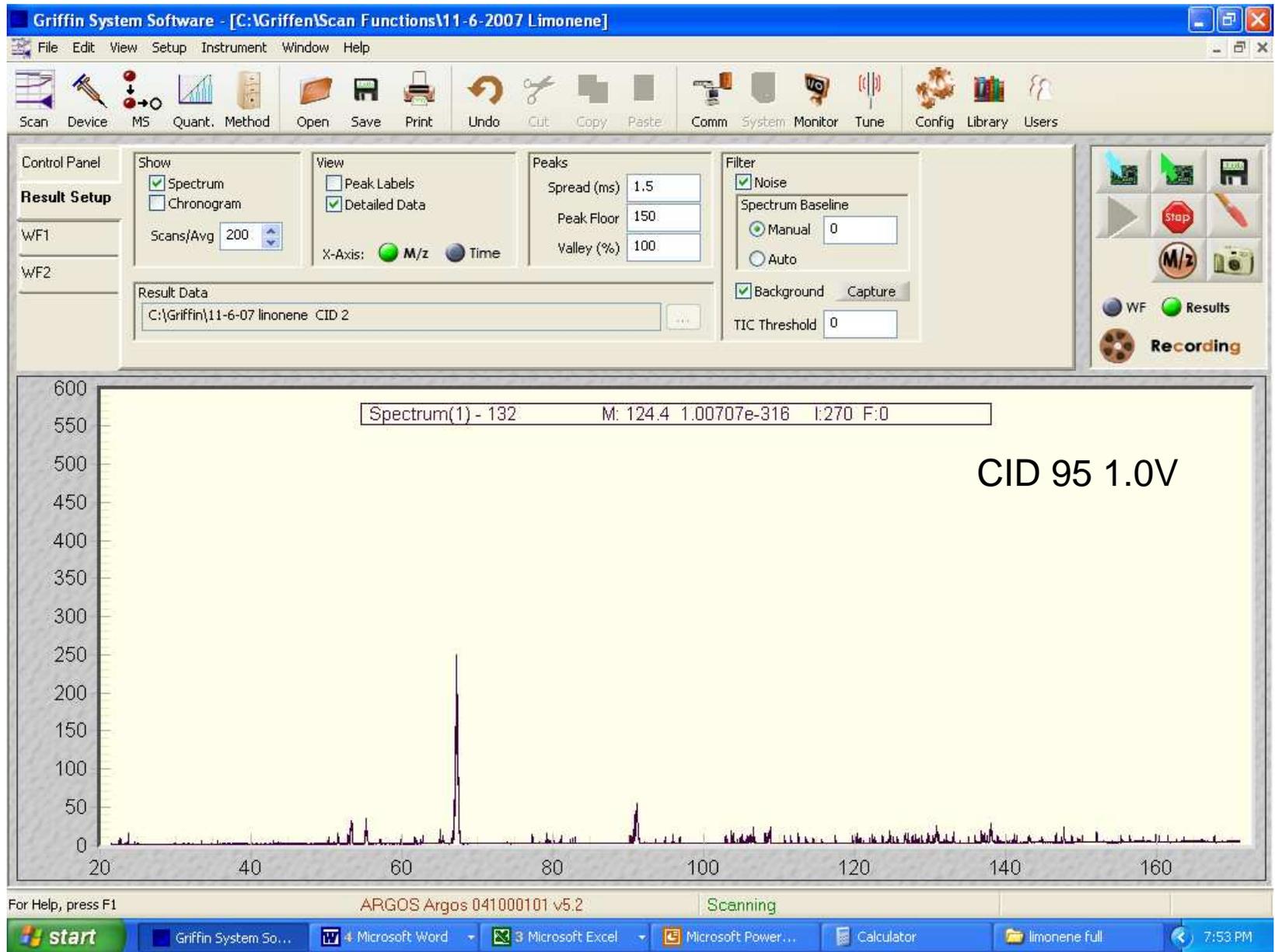
start Griffin System Softwa... 4 Microsoft Word 3 Microsoft Excel Calculator 7:09 PM

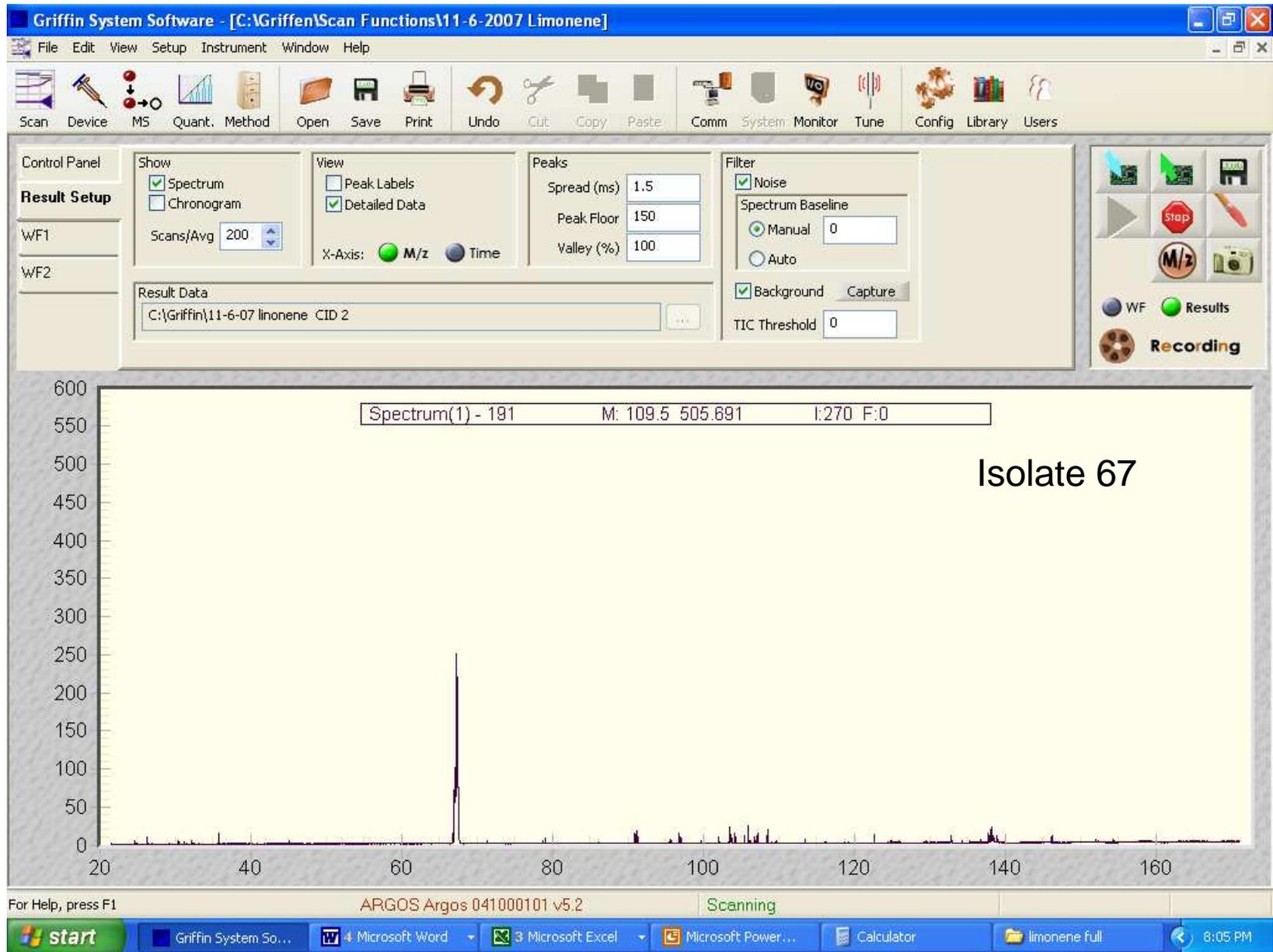


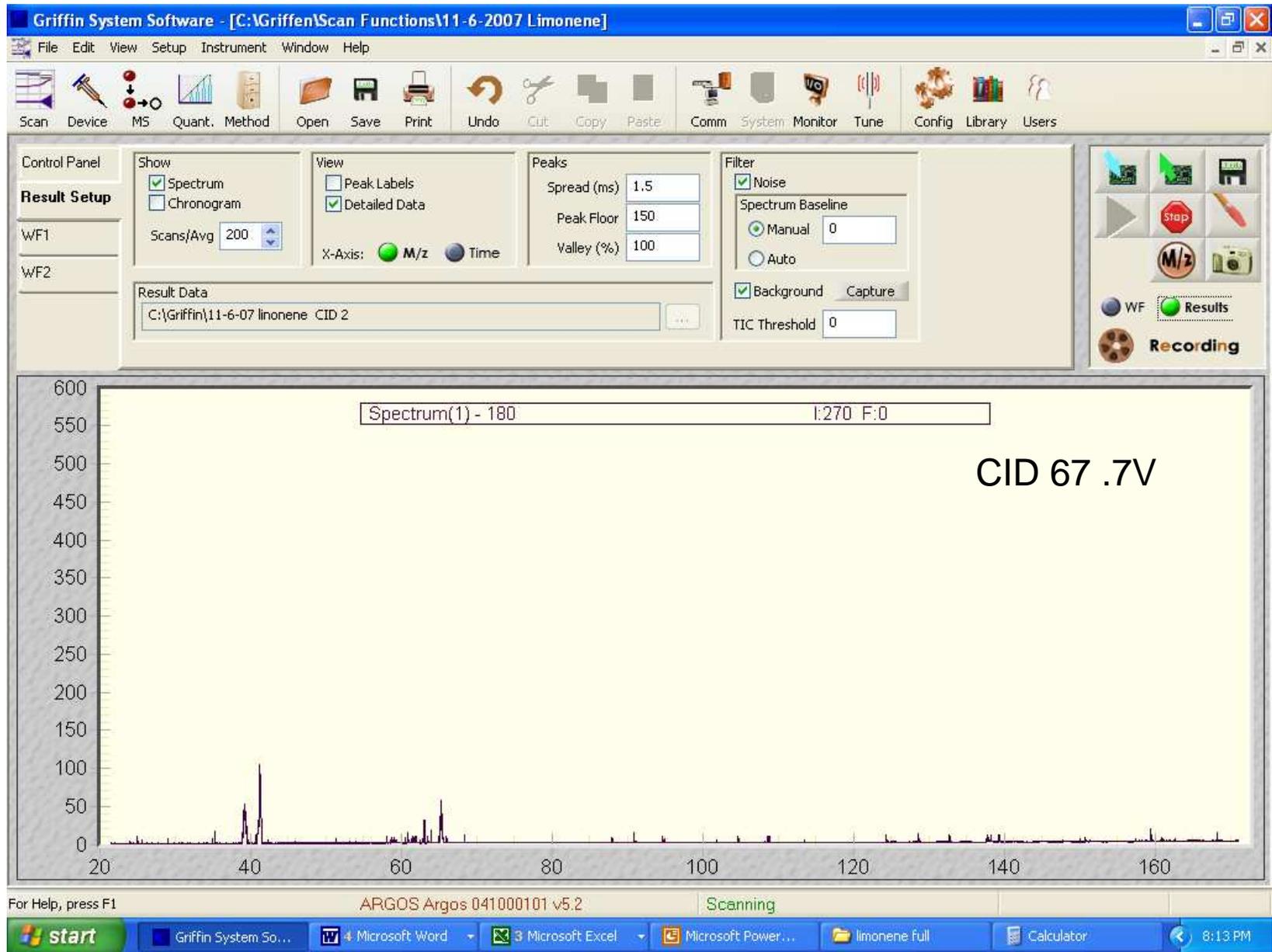








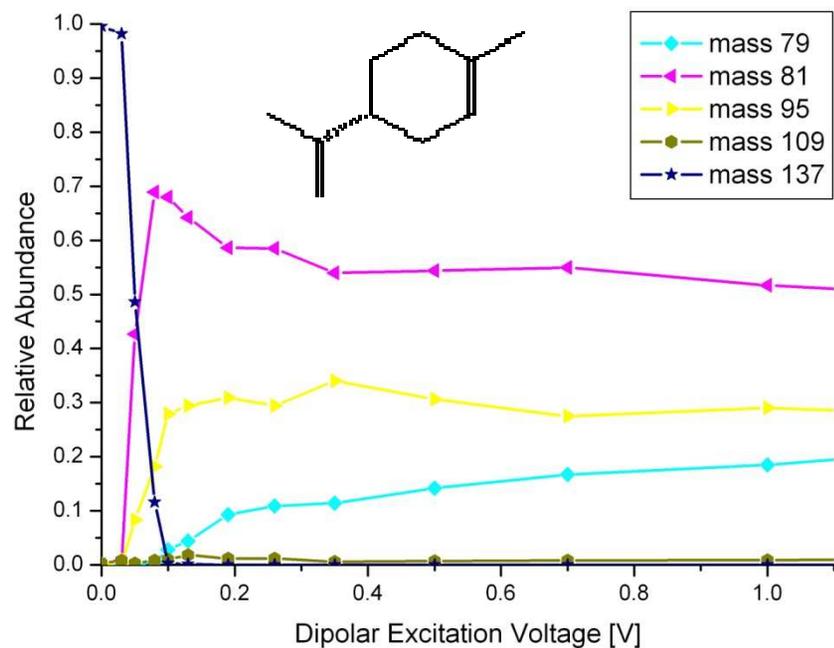




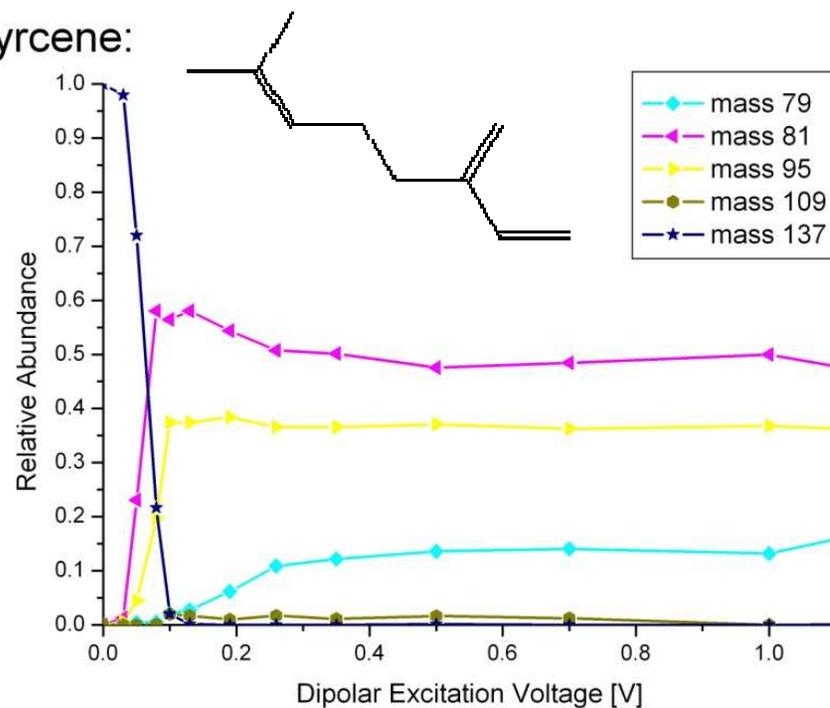


PTR-LIT MS/MS Fragmentation Patterns:

limonene:



myrcene:





Oligomer Production and Analysis

● Source Conditions

Spray Voltage: 4.5 kV

Spray Flow: 3 $\mu\text{L}/\text{min}$

Spray Solvent: 1:1 Methanol:Water
with 10^{-5} M NaOH

Nebulization Gas: 120 psi N_2

Capillary Temp: 200 $^{\circ}\text{C}$

Tube Lens Voltage: 65 V

Capillary Voltage: 20 V

α : 35 $^{\circ}$

h : 1 mm

d : 2 mm

Spot Diameter: 0.8 mm

Sample Loading: 90 ng/spot

● Sample Preparation

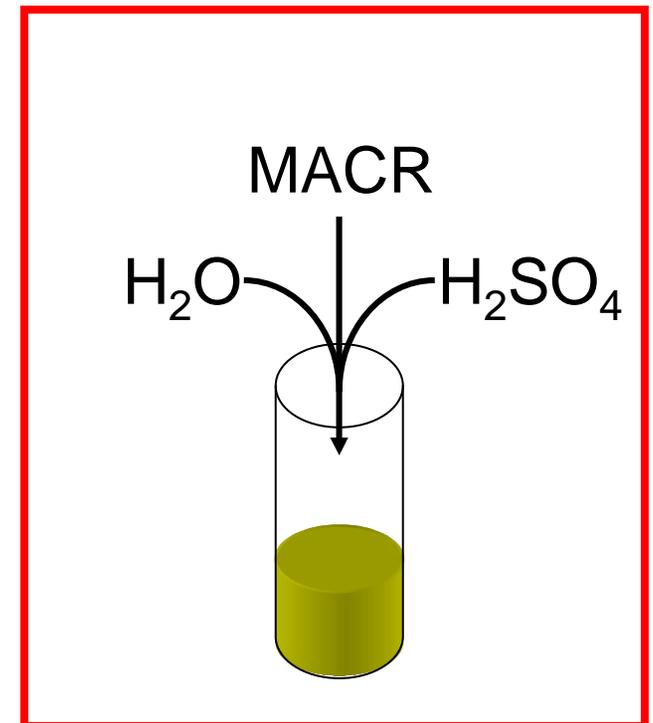
Concentrated Oligomer

100 μL methacrolein

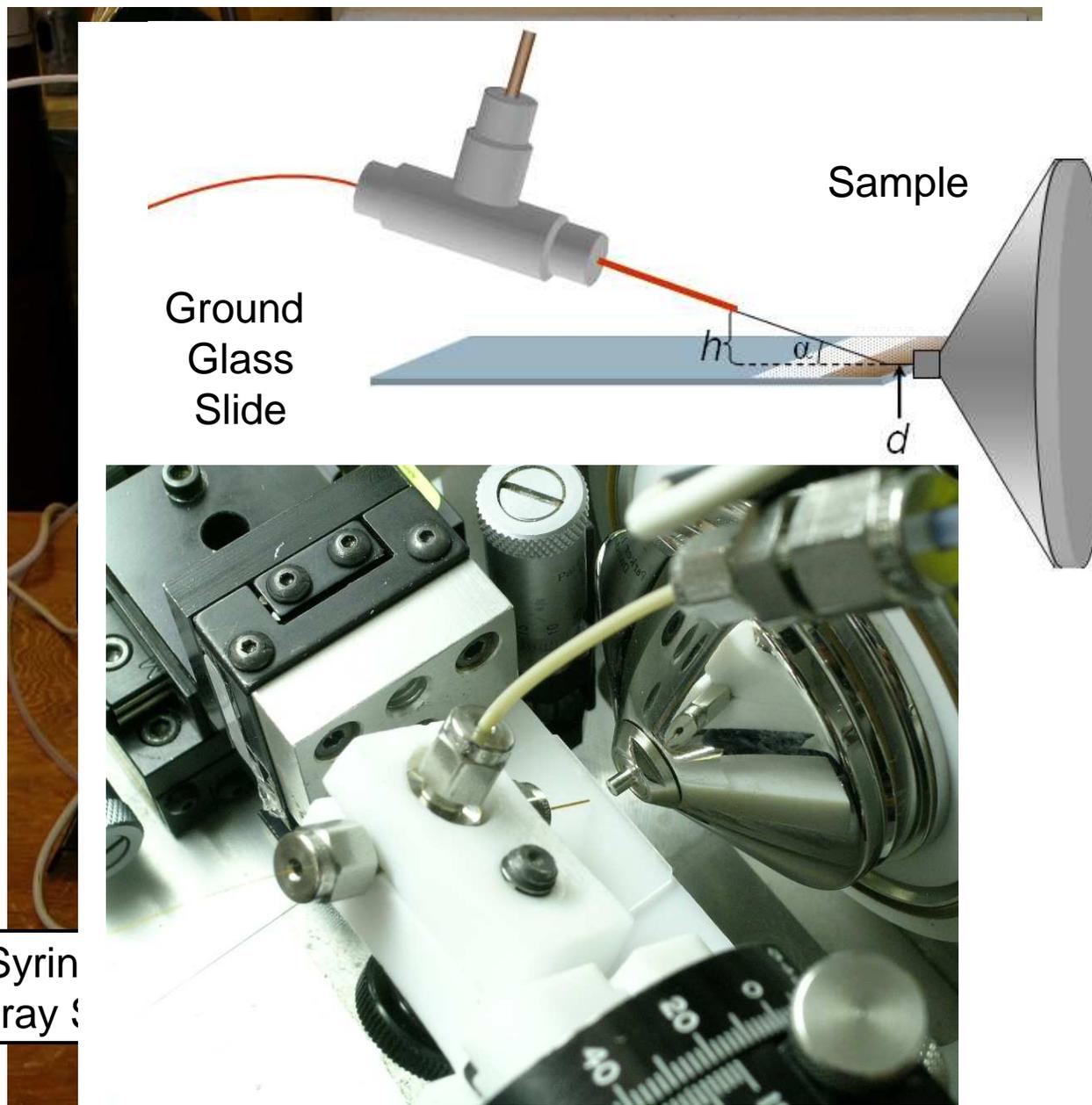
100 μL H_2SO_4

80 μL water

Diluted with acetonitrile

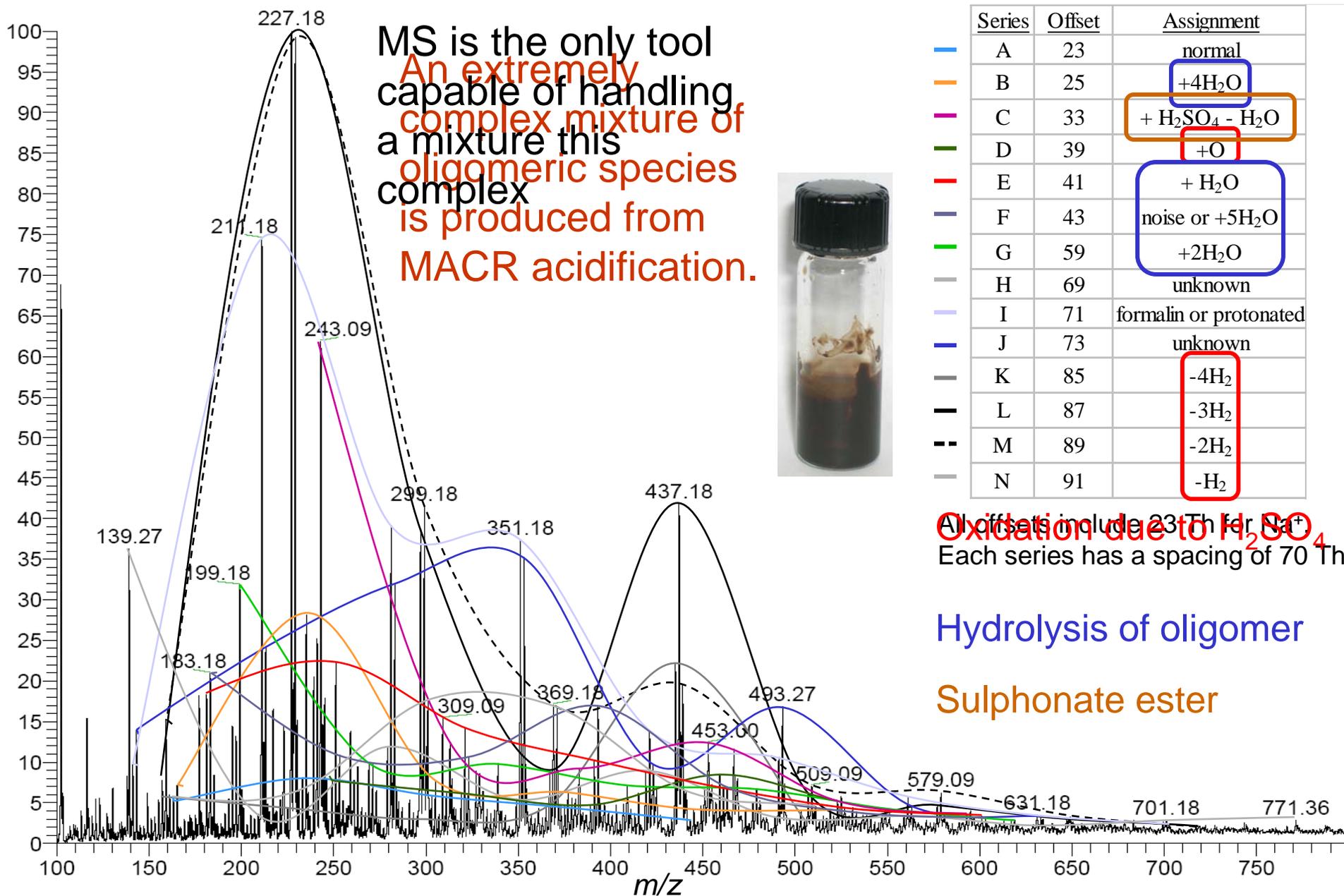


DESI Mass Spectrometry



Syrin
Spray S

MACR Oligomer from H₂SO₄ Catalysis



MS is the only tool capable of handling a complex mixture of oligomeric species is produced from MACR acidification.

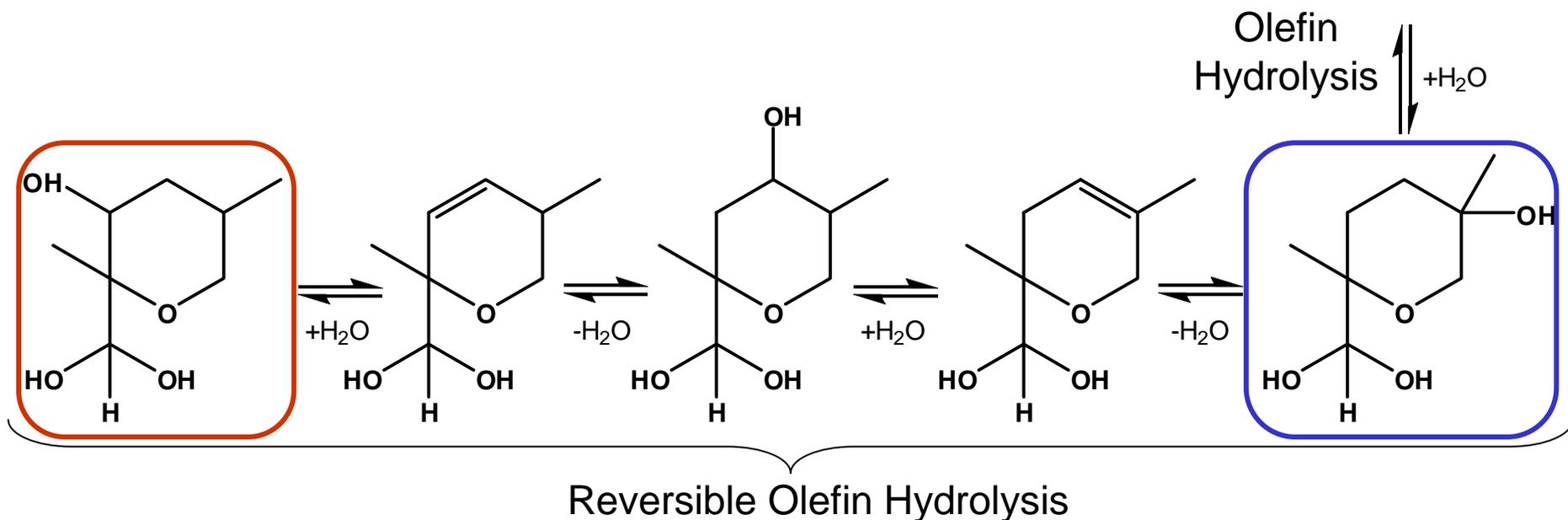
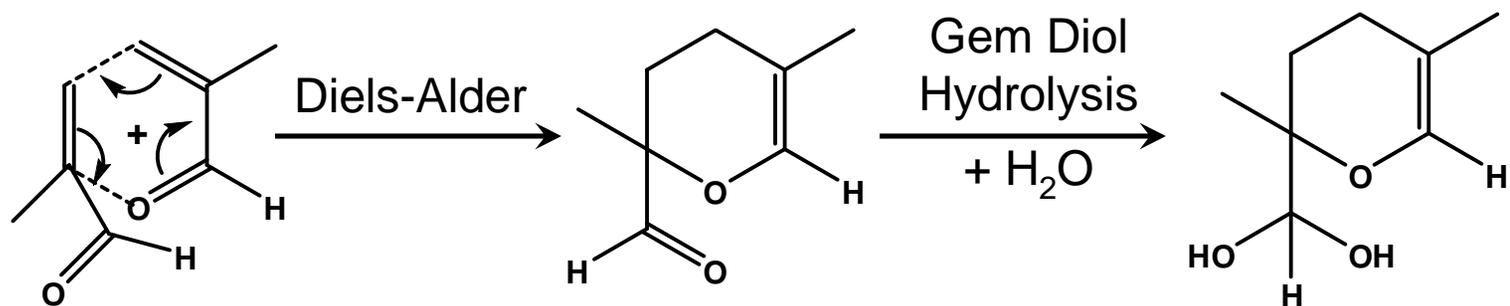


Oxidation due to H₂SO₄.
Each series has a spacing of 70 Th.

Hydrolysis of oligomer

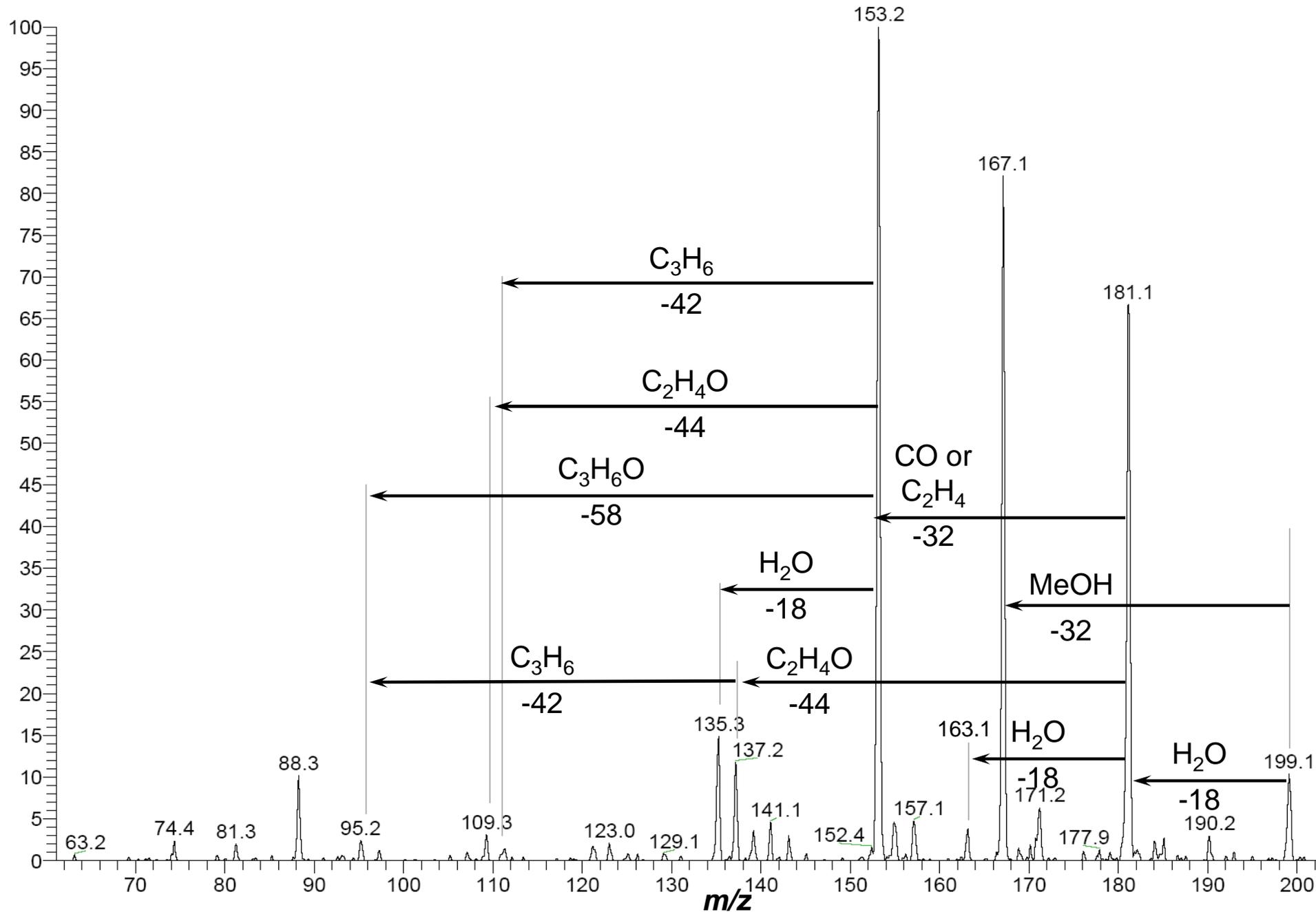
Sulphonate ester

Formation of [MACR₂ + 2H₂O]

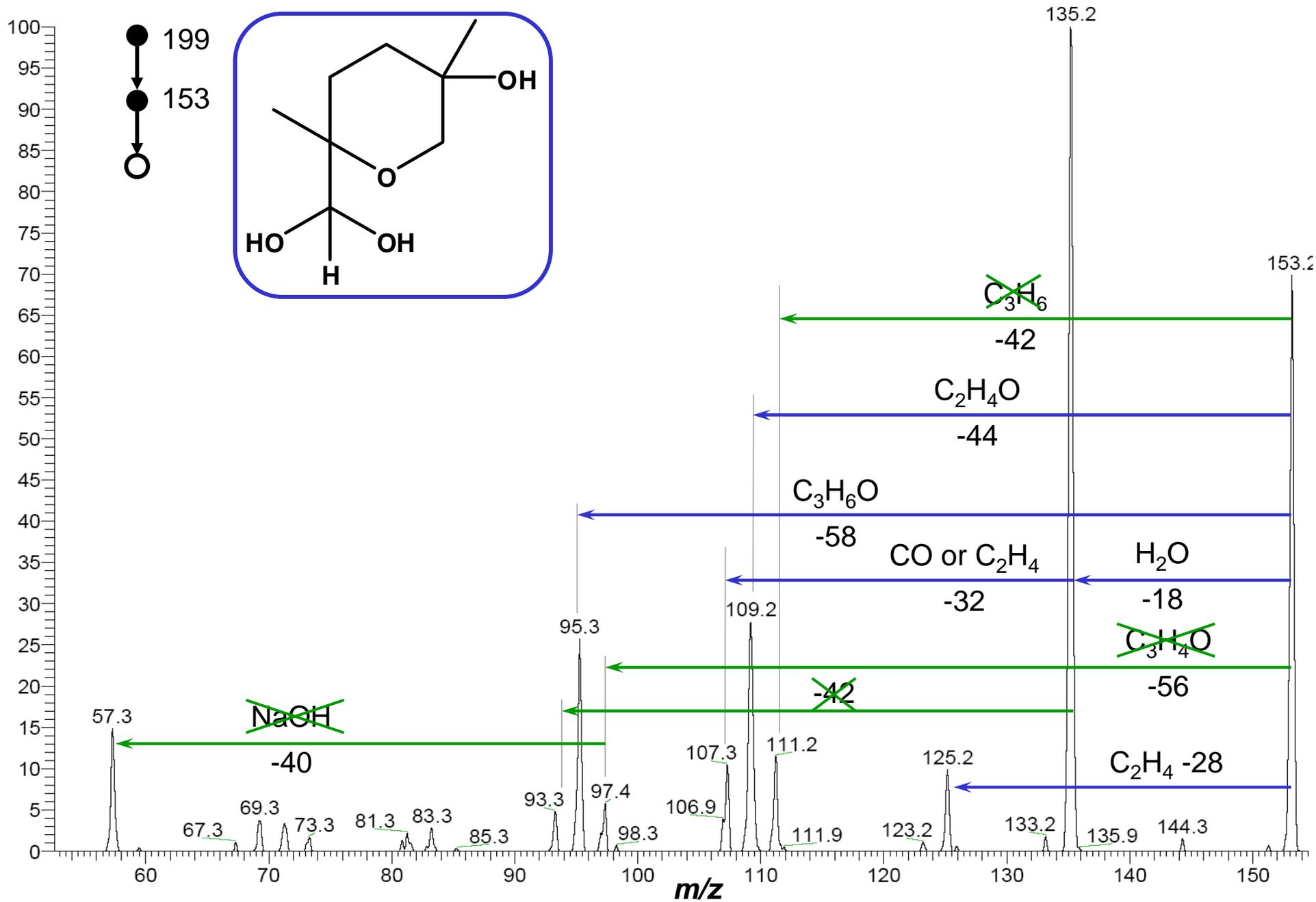


- Diels-Alder has been observed in MACR oligomer, but not in SOA oligomer
- At least two structures cover the range of fragments for *m/z* 199

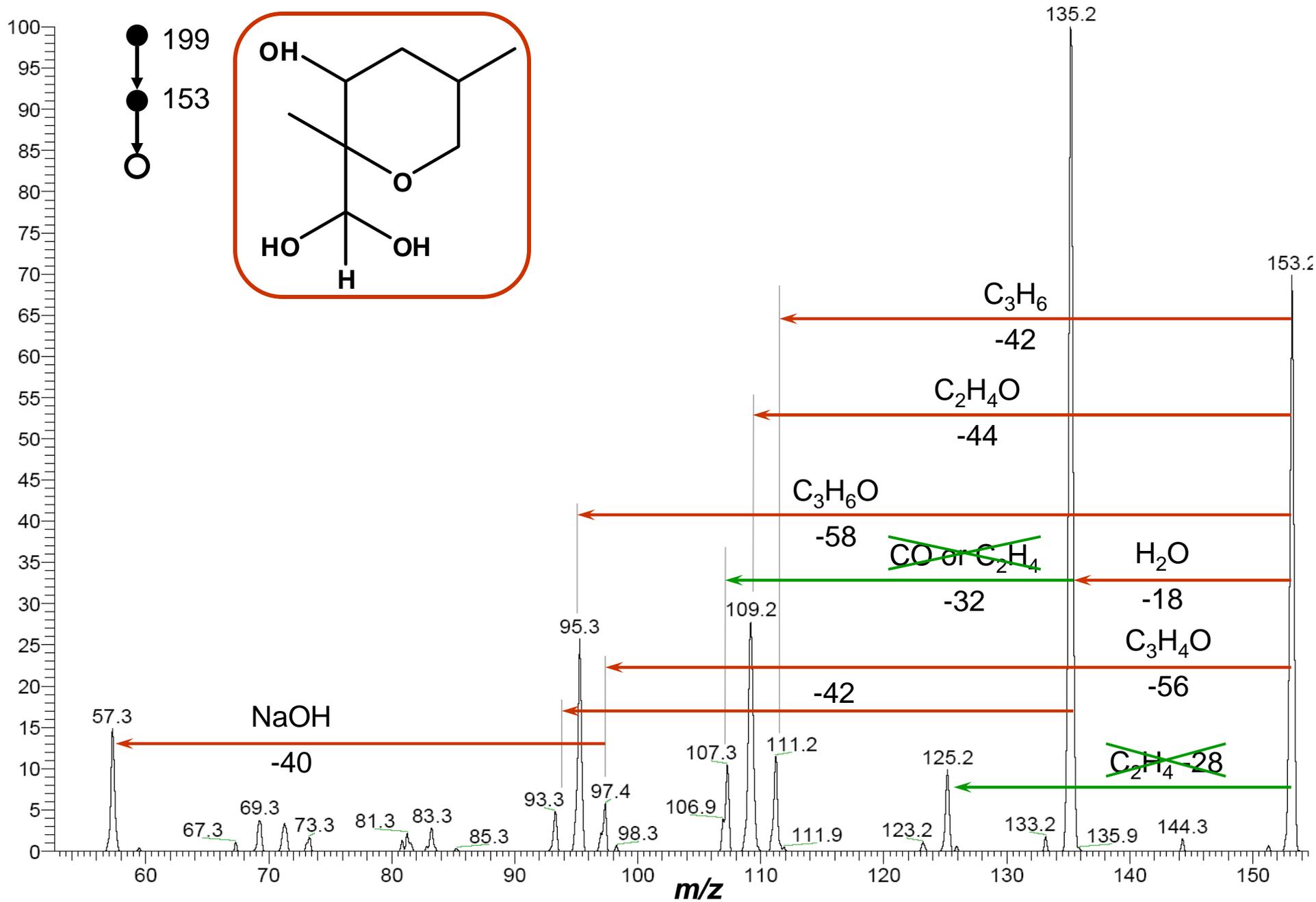
DESI-MS² of m/z 199: $[\text{MACR}_2 + 2\text{H}_2\text{O}]\text{Na}^+$



DESI-MS³ of m/z 199: $[\text{MACR}_2 + 2\text{H}_2\text{O}]\text{Na}^+$



DESI-MS³ of m/z 199: $[\text{MACR}_2 + 2\text{H}_2\text{O}]\text{Na}^+$

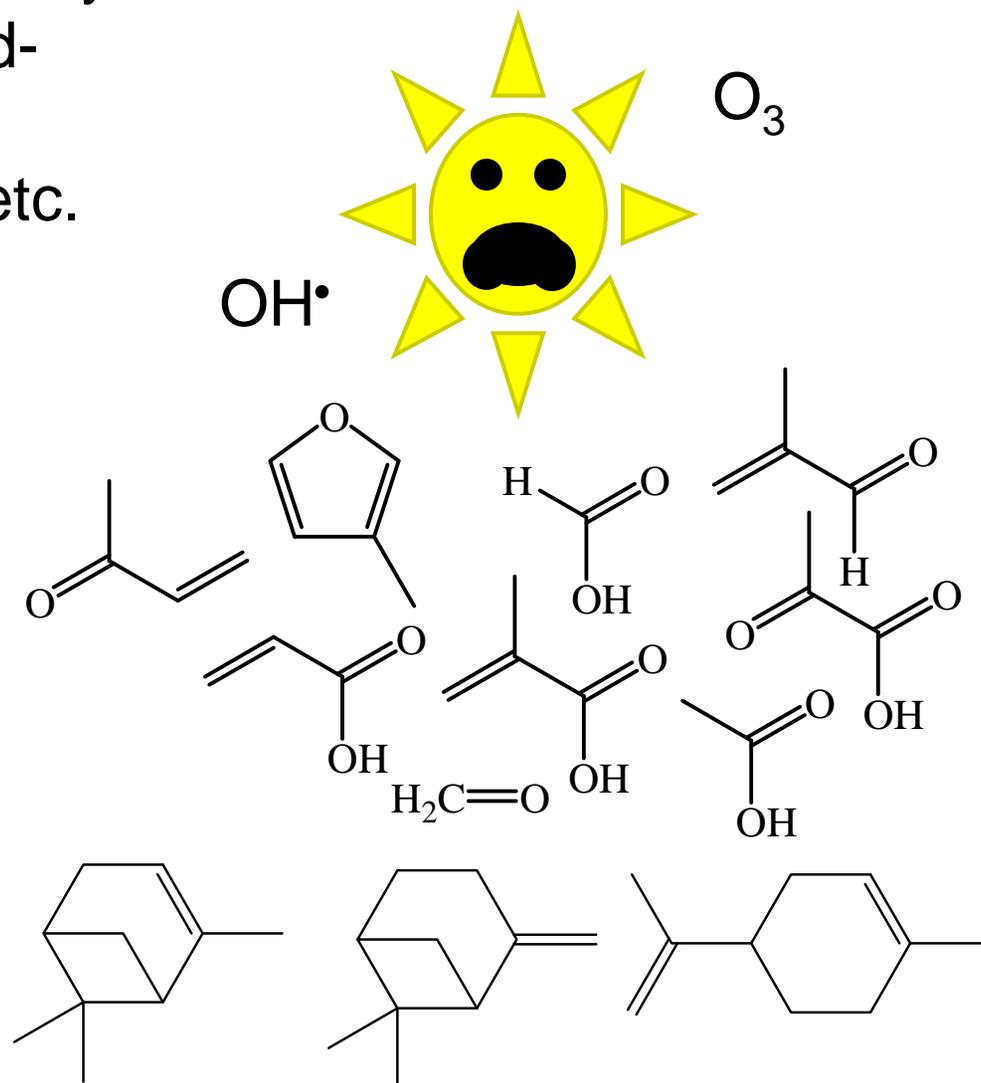


A simplified case, addressing only one monomer undergoing acid-catalyzed reactions without light, heat, radical chemistry, etc.



Can we really do this on a real system???

...but in the real world...





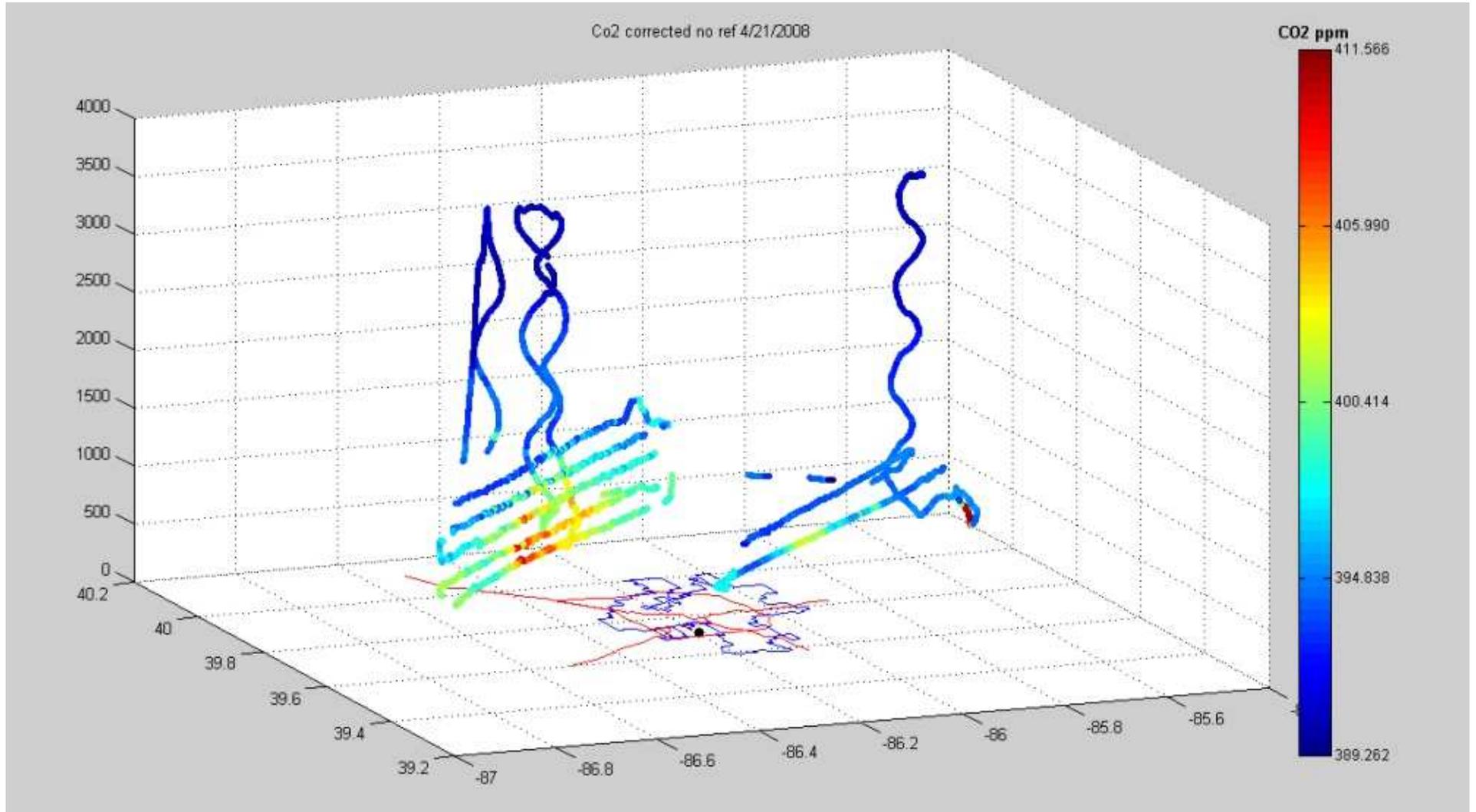
**Airborne Laboratory for
Atmospheric Research
(ALAR)**



<http://www.purdue.edu/climate>

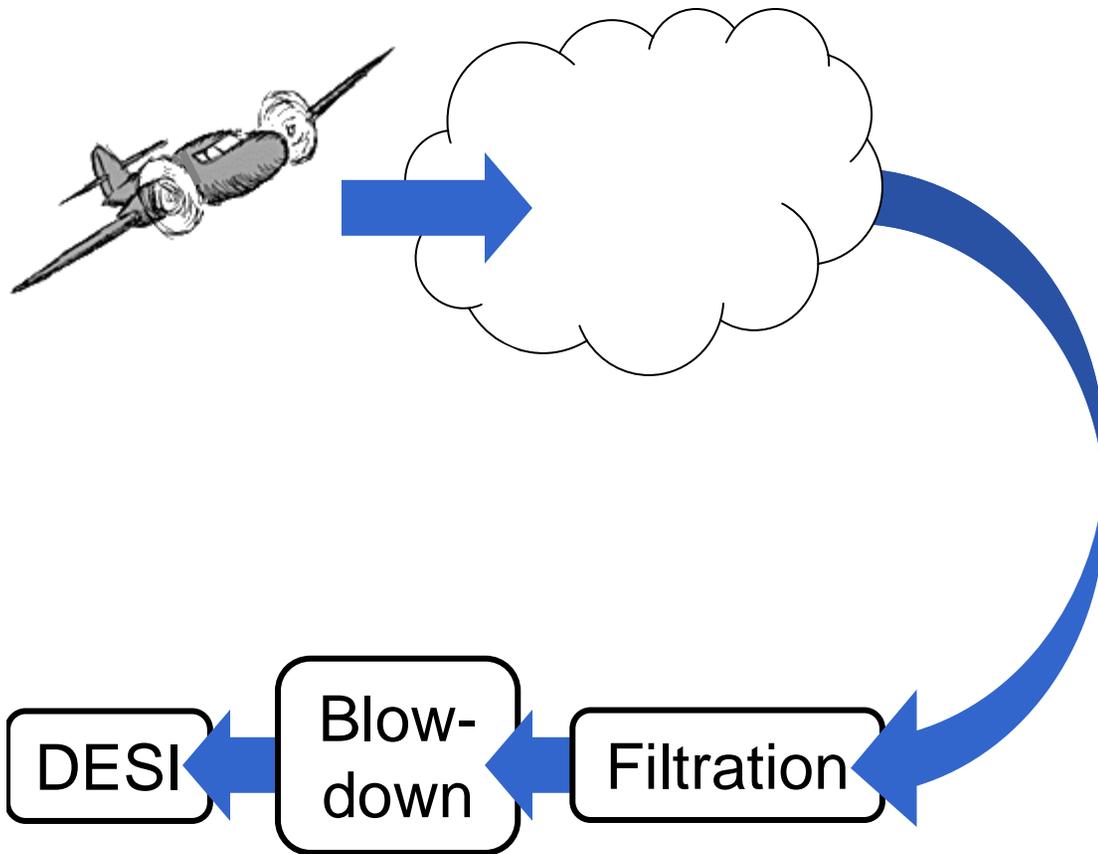


ALAR emission flux experiments

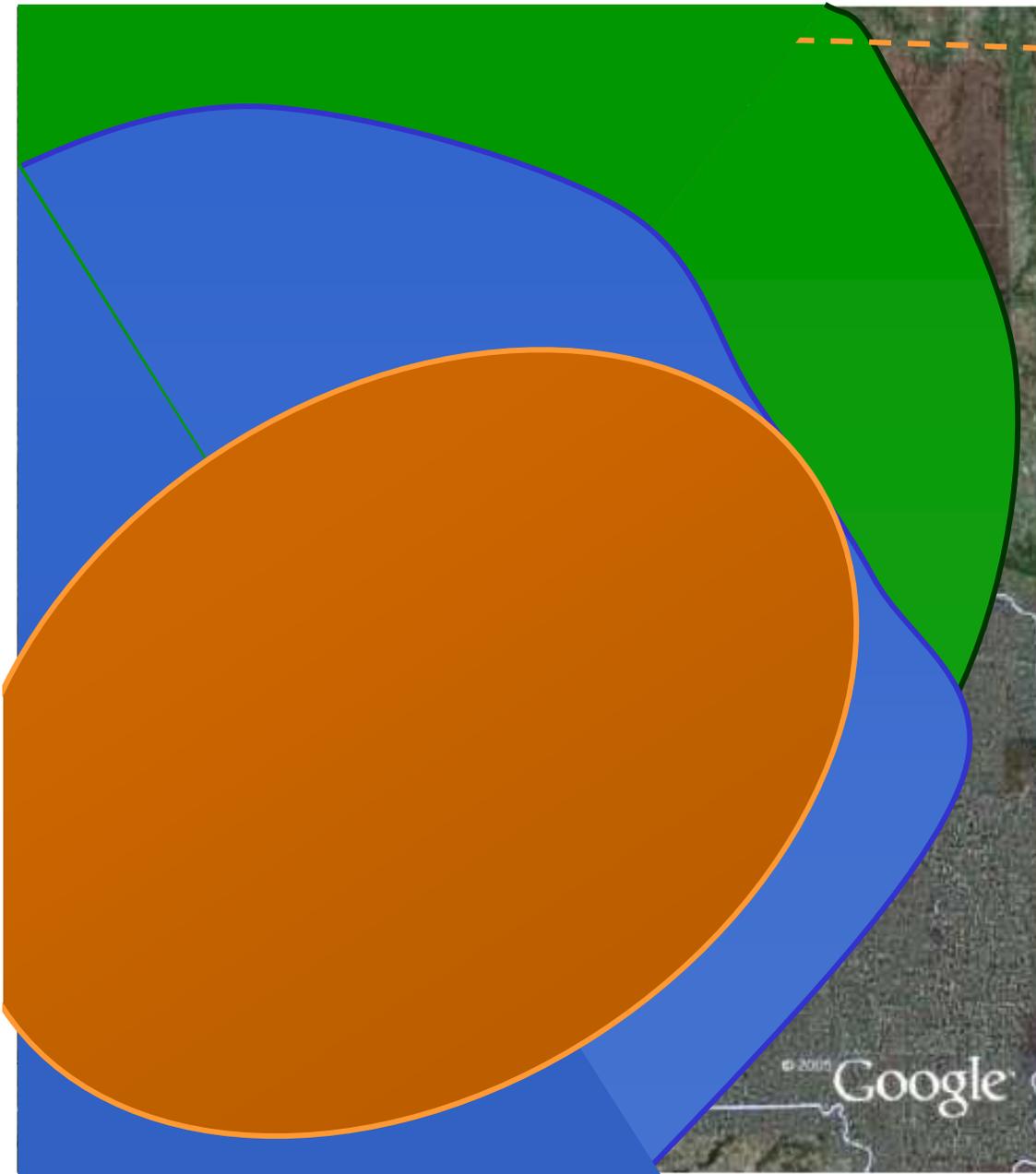


Cloud Water Analysis

Sampling cloud water using our Airborne Laboratory for Atmospheric Research (ALAR)



Cloud Water Collection Site: Central Missouri



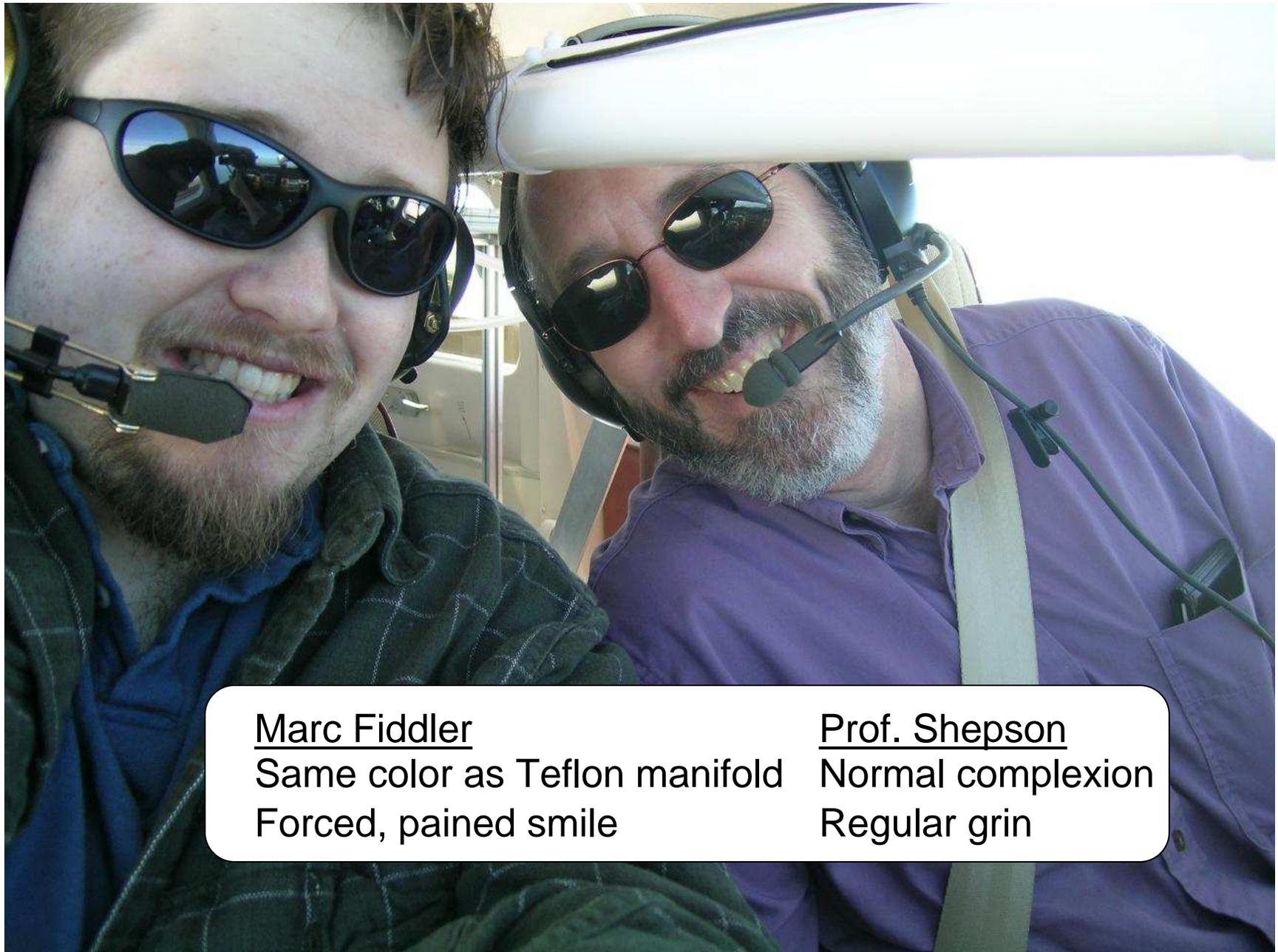
BEIS-estimated isoprene emissions

MEGAN, elevated isoprene

GOME CH₂O

Winds came from the NW this day.

The Thrill of Flight



Marc Fiddler

Same color as Teflon manifold
Forced, pained smile

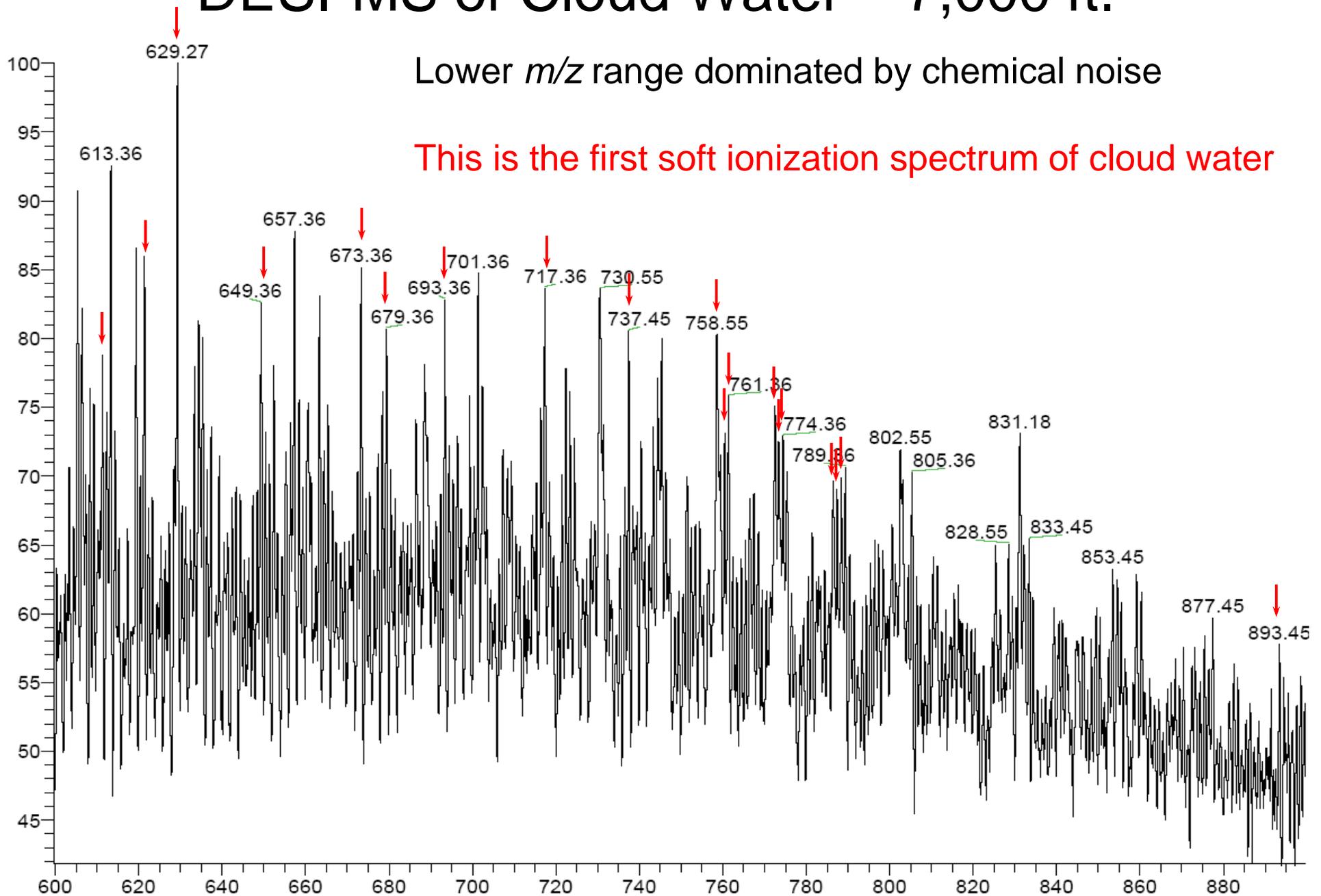
Prof. Shepson

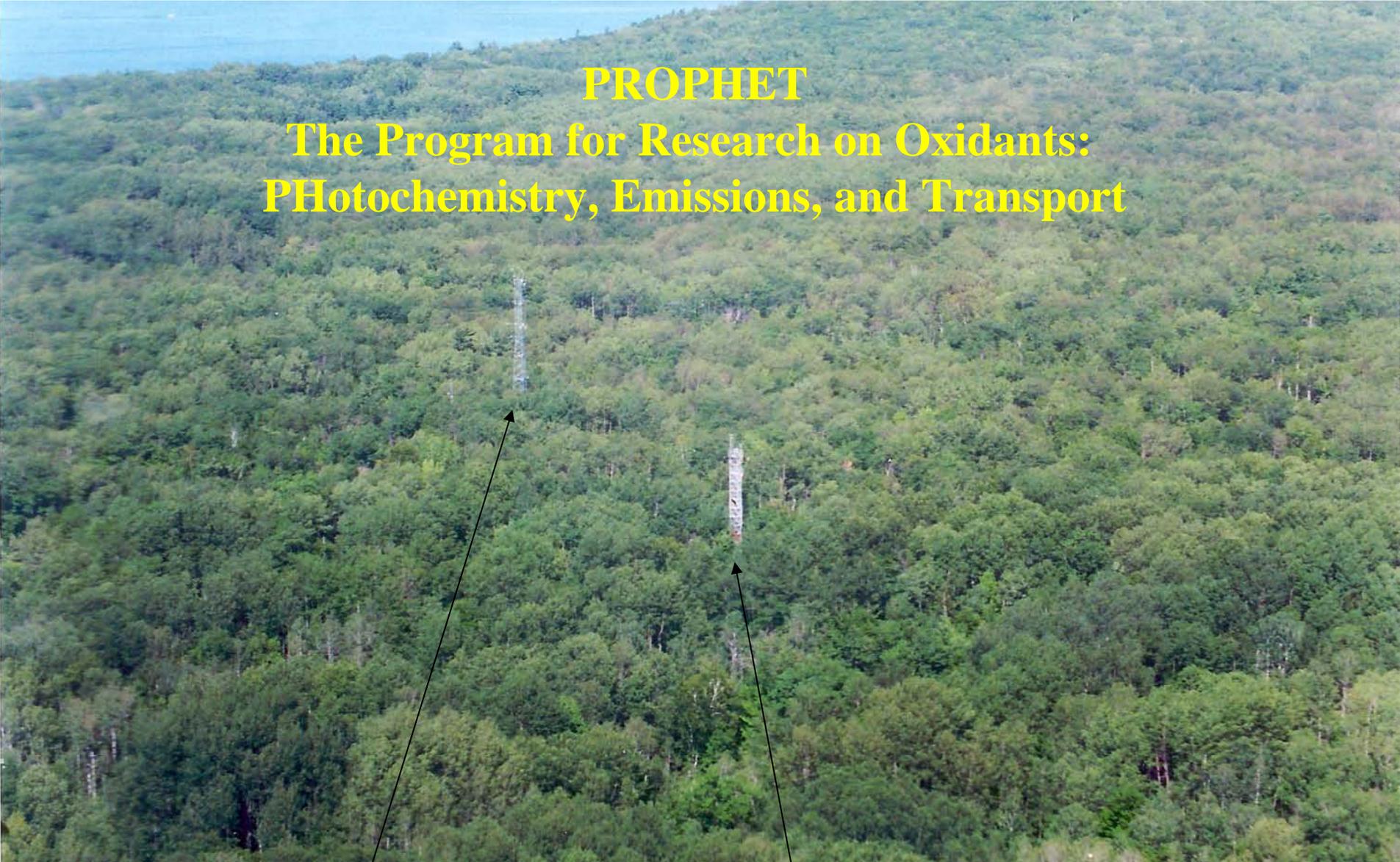
Normal complexion
Regular grin

DESI-MS of Cloud Water – 7,000 ft.

Lower m/z range dominated by chemical noise

This is the first soft ionization spectrum of cloud water

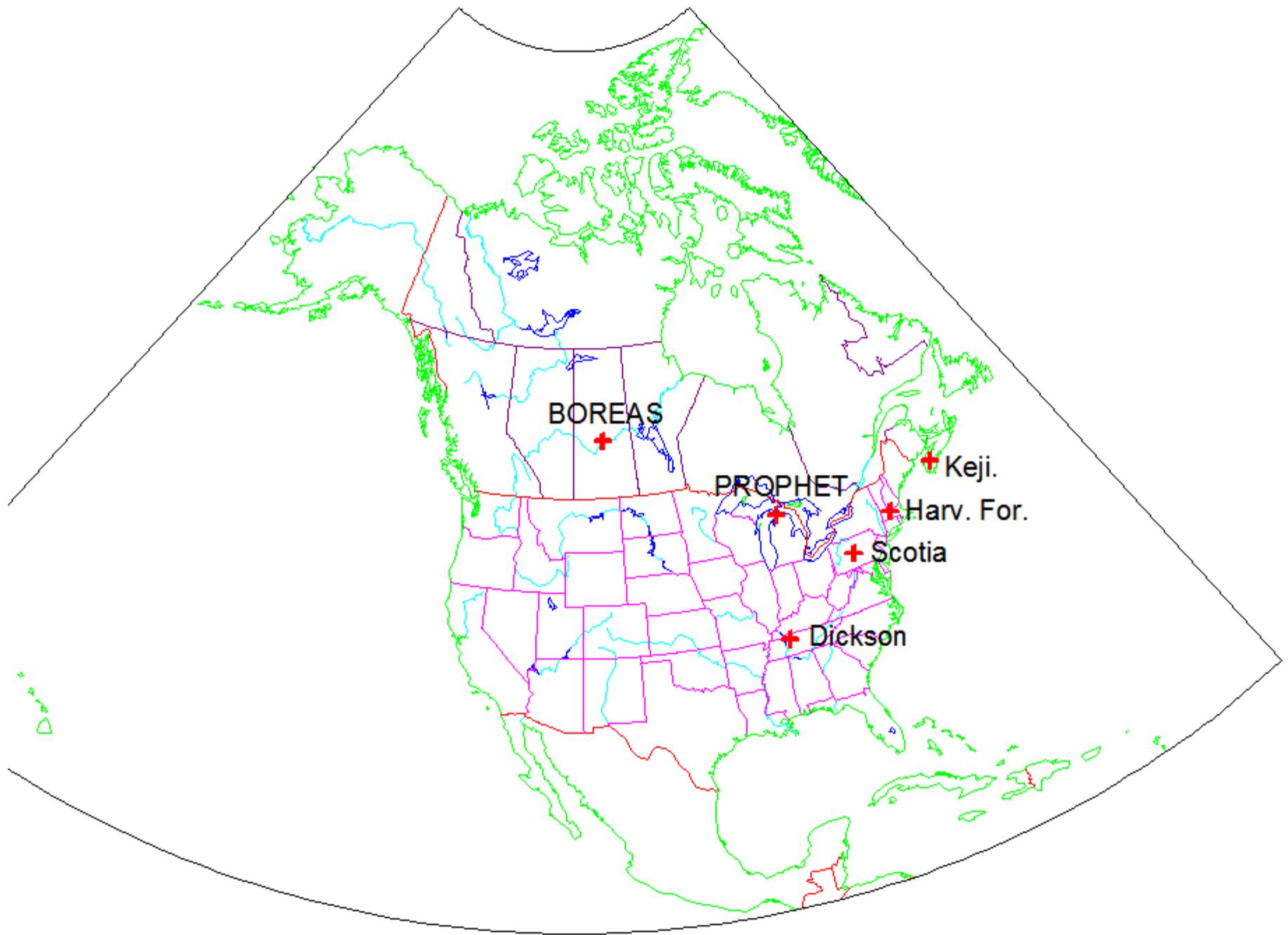




PROPHET
The Program for Research on Oxidants:
PHotochemistry, Emissions, and Transport

Ameriflux Tower

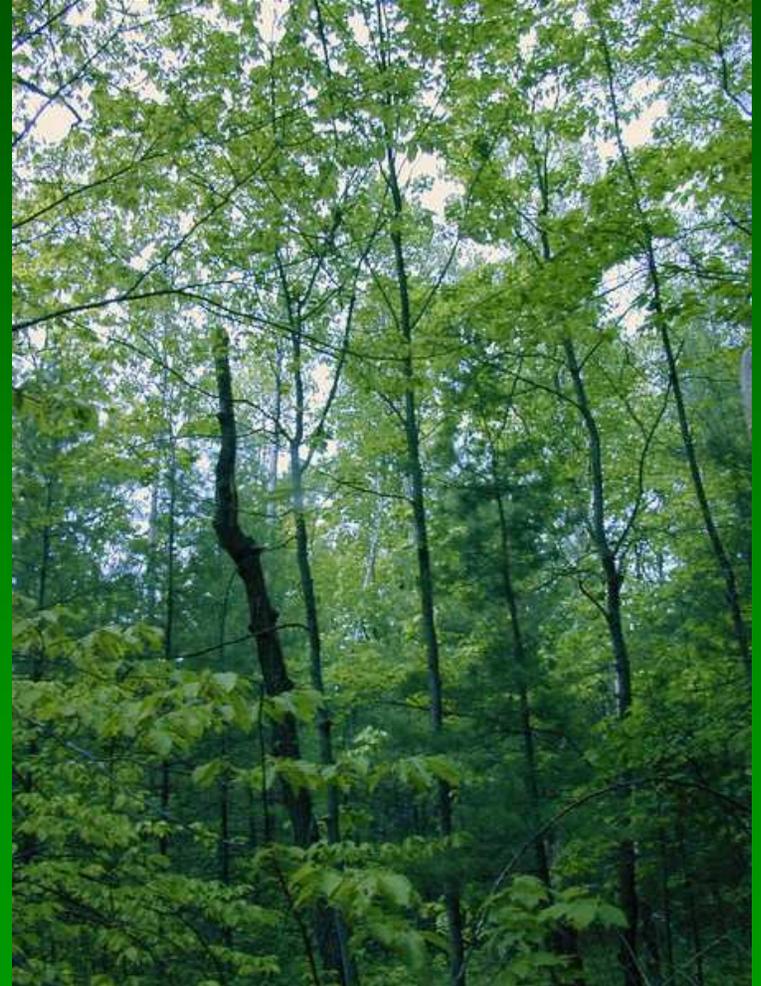
PROPHET Tower



Background

Carbon cycling in forests of the future

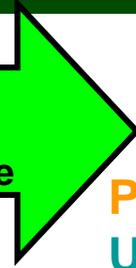
- Across the upper Midwest, aspen and birch in the canopy are dying and being replaced by pine, oak, and maple.
- This is prompting a major successional transition, altering microclimate and increasing species and structural complexity of the forest canopy.
- These changes will have a profound effect on the region's carbon cycle.



Experimental treatment

Accelerated succession
via experimental disturbance

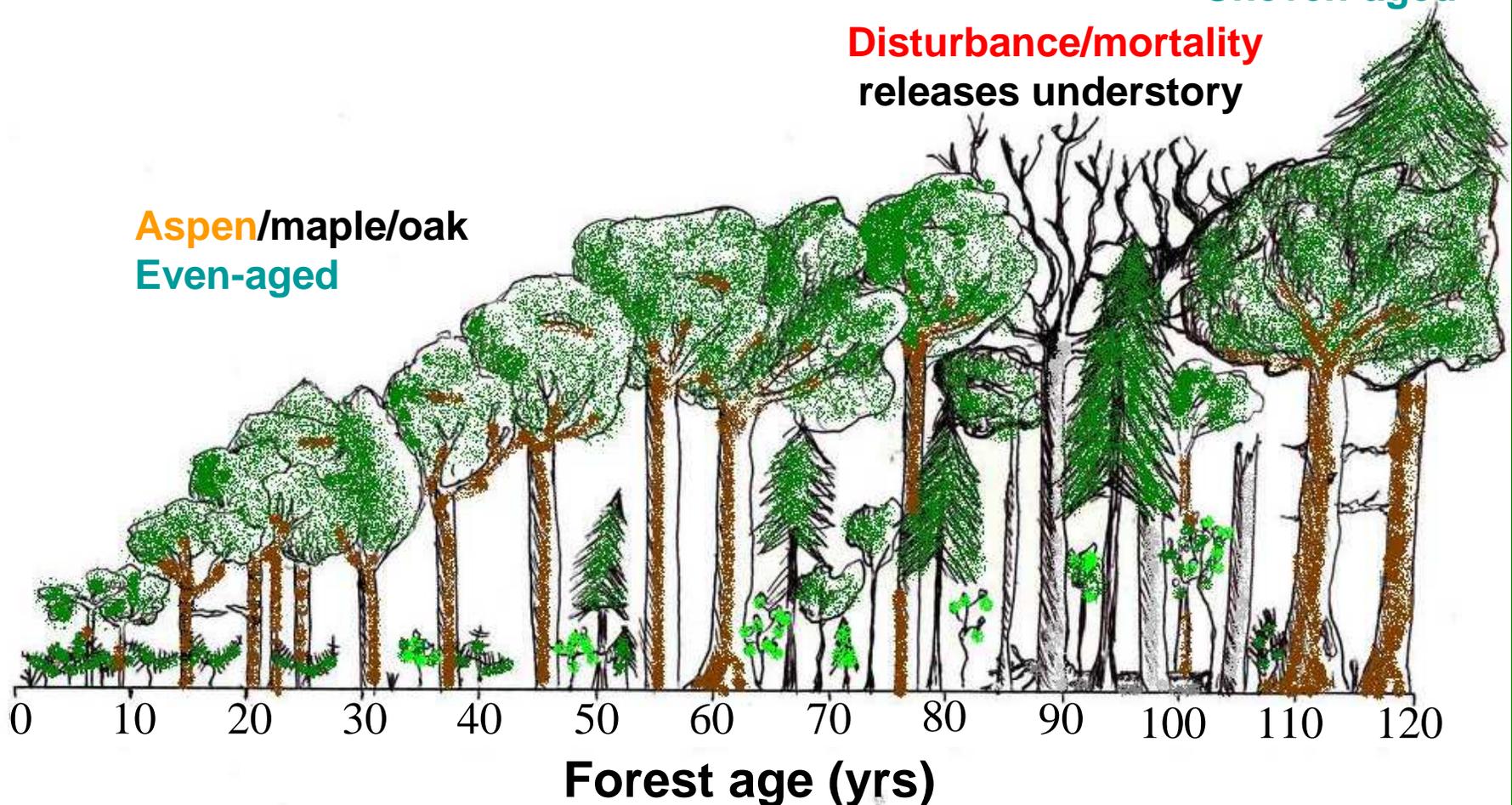
Insects
Pathogens
Natural senescence



Pine/maple/oak
Uneven-aged

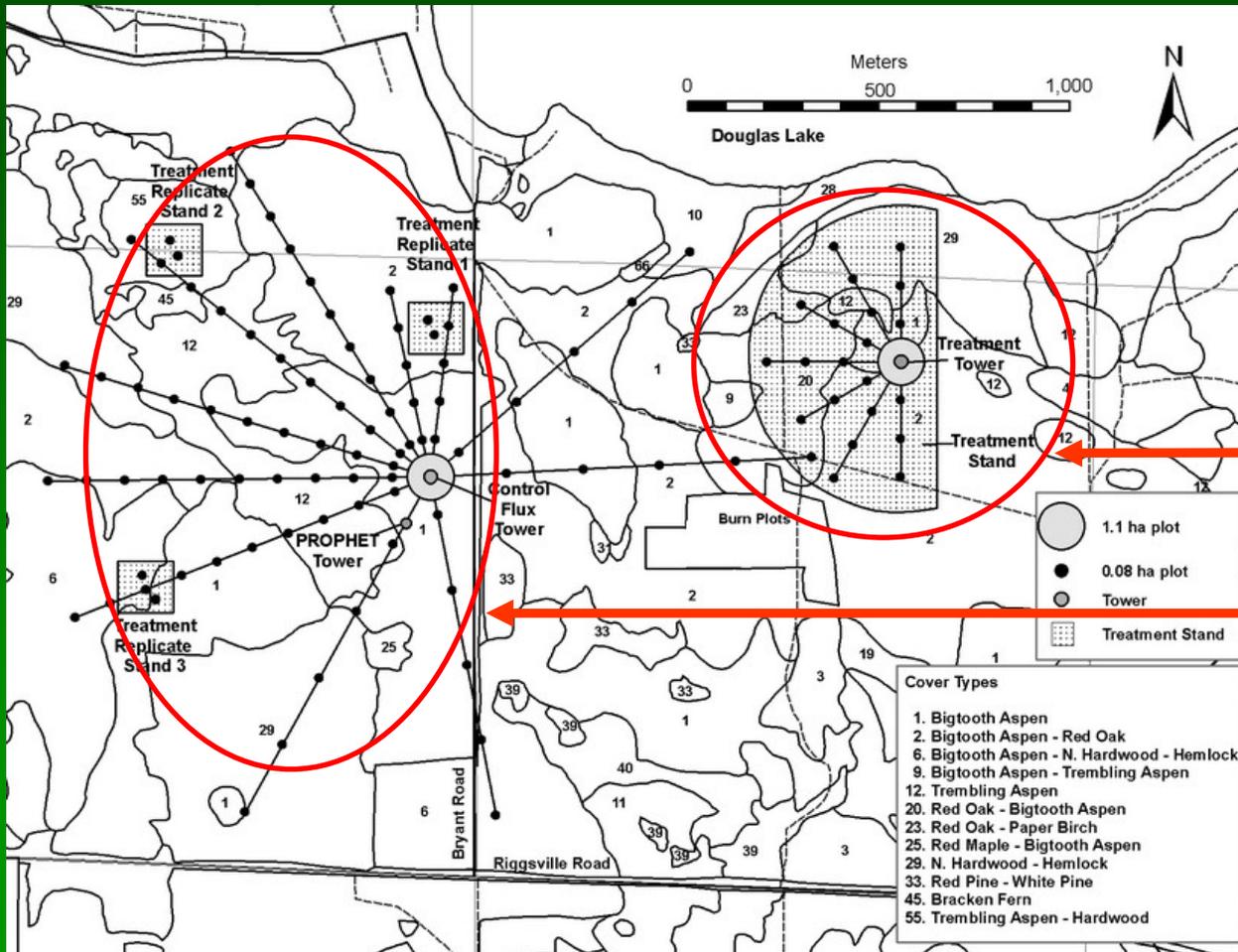
Disturbance/mortality
releases understory

Aspen/maple/oak
Even-aged



Experimental design

A large-scale forest succession experiment



➤ In 2008, accelerated succession will be initiated by killing canopy aspen and birch, or ~40 % of the leaf area.

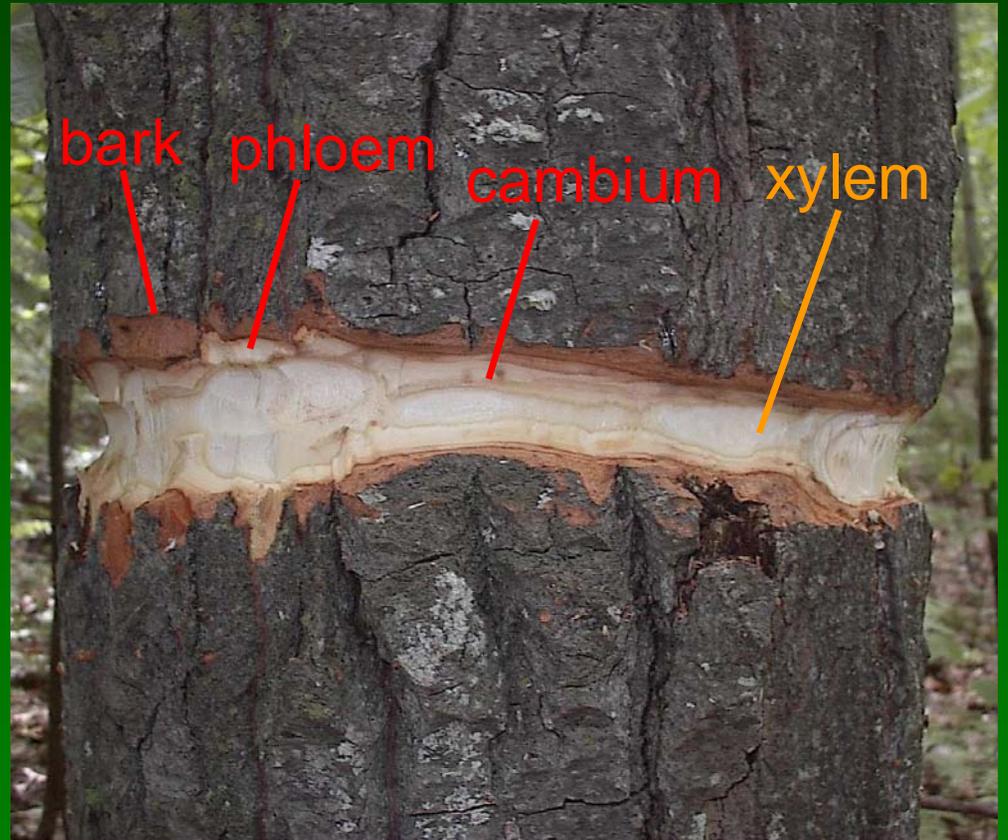
➤ One 33 ha stand

➤ Three 2 ha replicate stands

Girdling procedure



Waist girdler



Phloem girdling



Methods

VOC Measurement

- PTR-LIT
- Fast Isoprene Sensor
- PTR-MS at FASET Tower

Aerosol Measurement

- Aerosol Counter
- SPMS (Aerosol Sizer)

Meteorological Data

- Temp, RH
- PAR, Diffuse Radiation
- Sonic Anemometer

Proxy for Net Primary Productivity

- CO₂ flux from Ameriflux tower



Thank you!

Input?