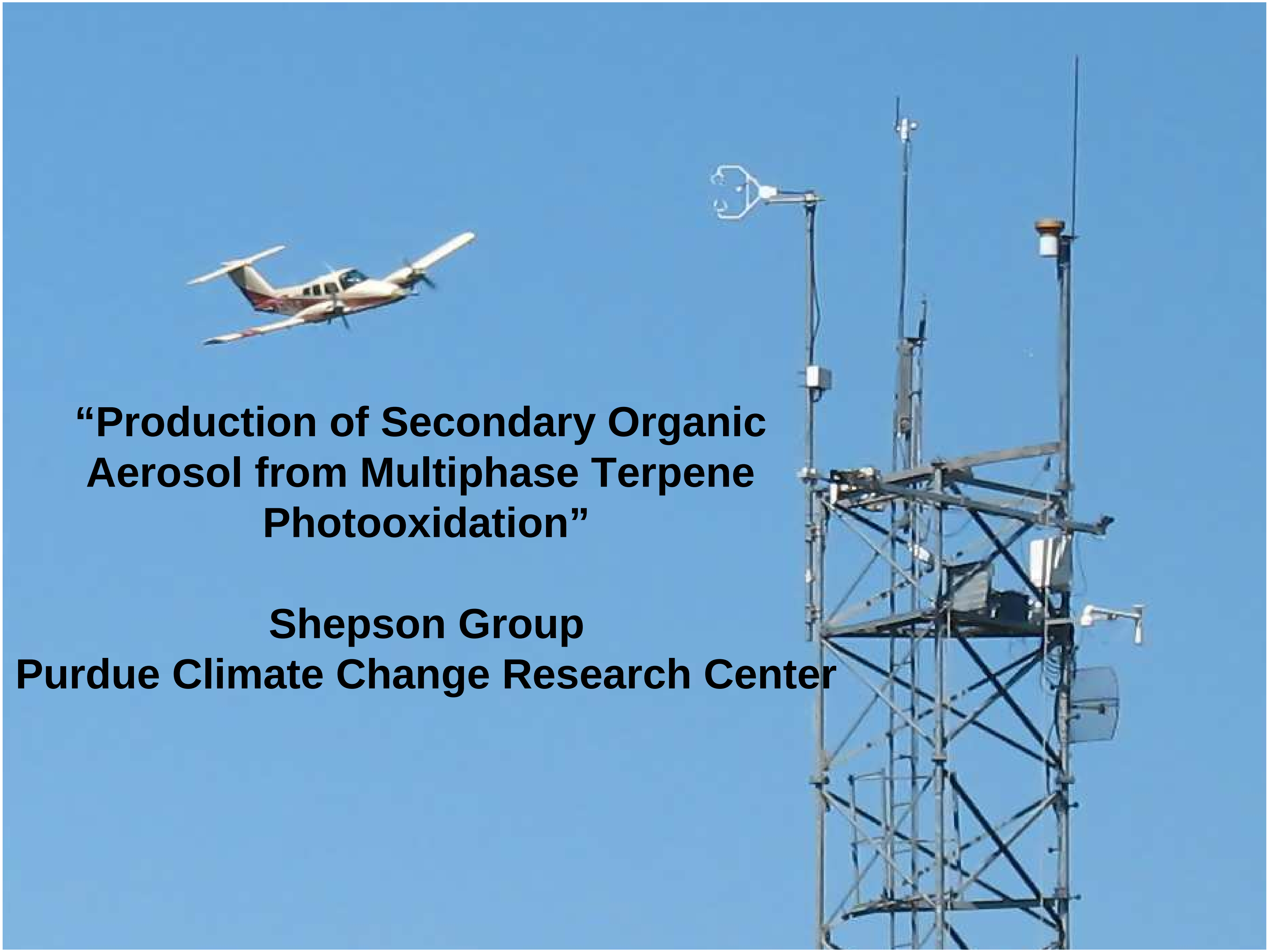


“Production of Secondary Organic Aerosol from Multiphase Terpene Photooxidation”

Shepson Group
Purdue Climate Change Research Center

Project Hypotheses

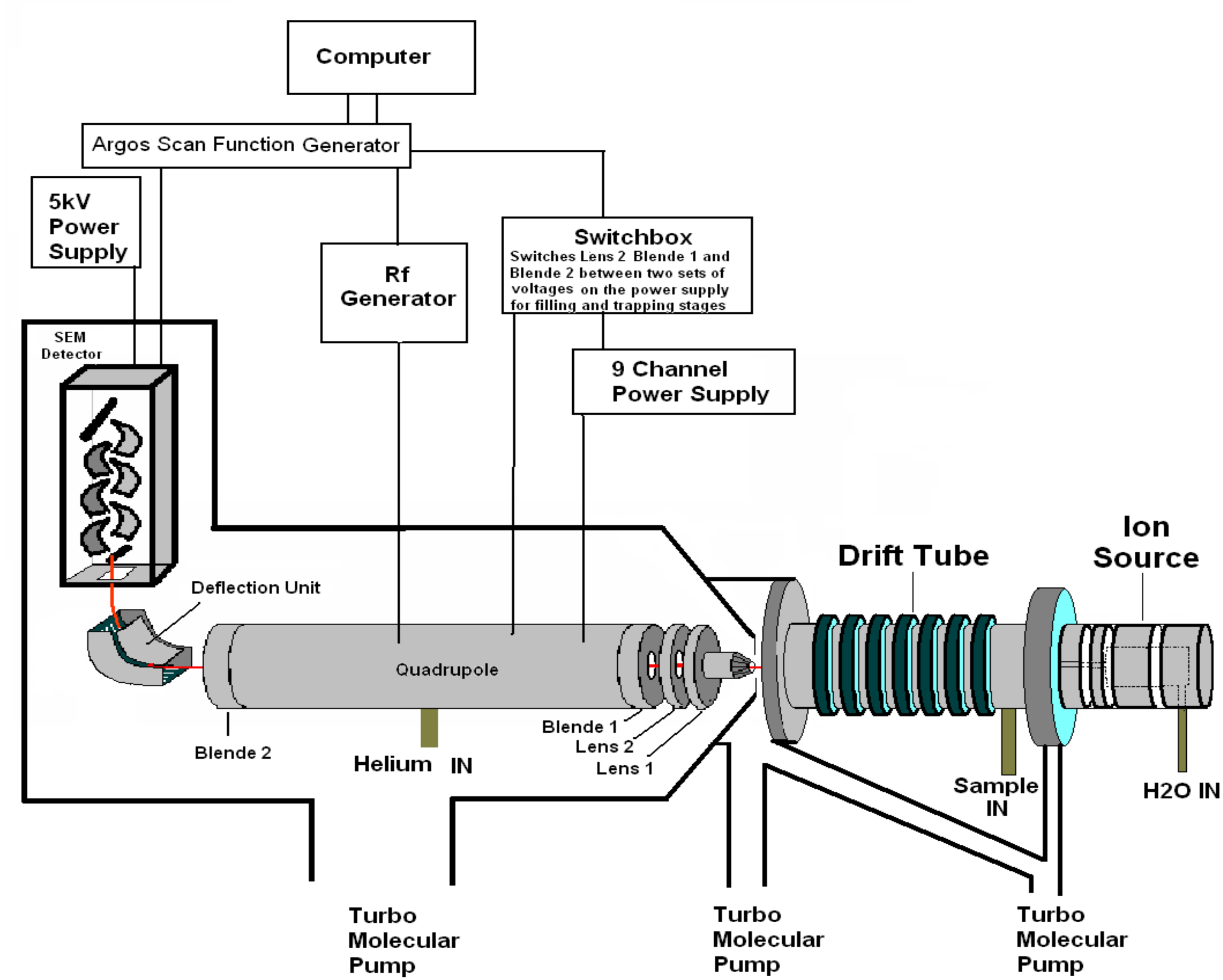
•PTRLIT can be used to vastly improve our ability to identify and quantify the photooxidation products of BVOCs that are important aerosol precursors.

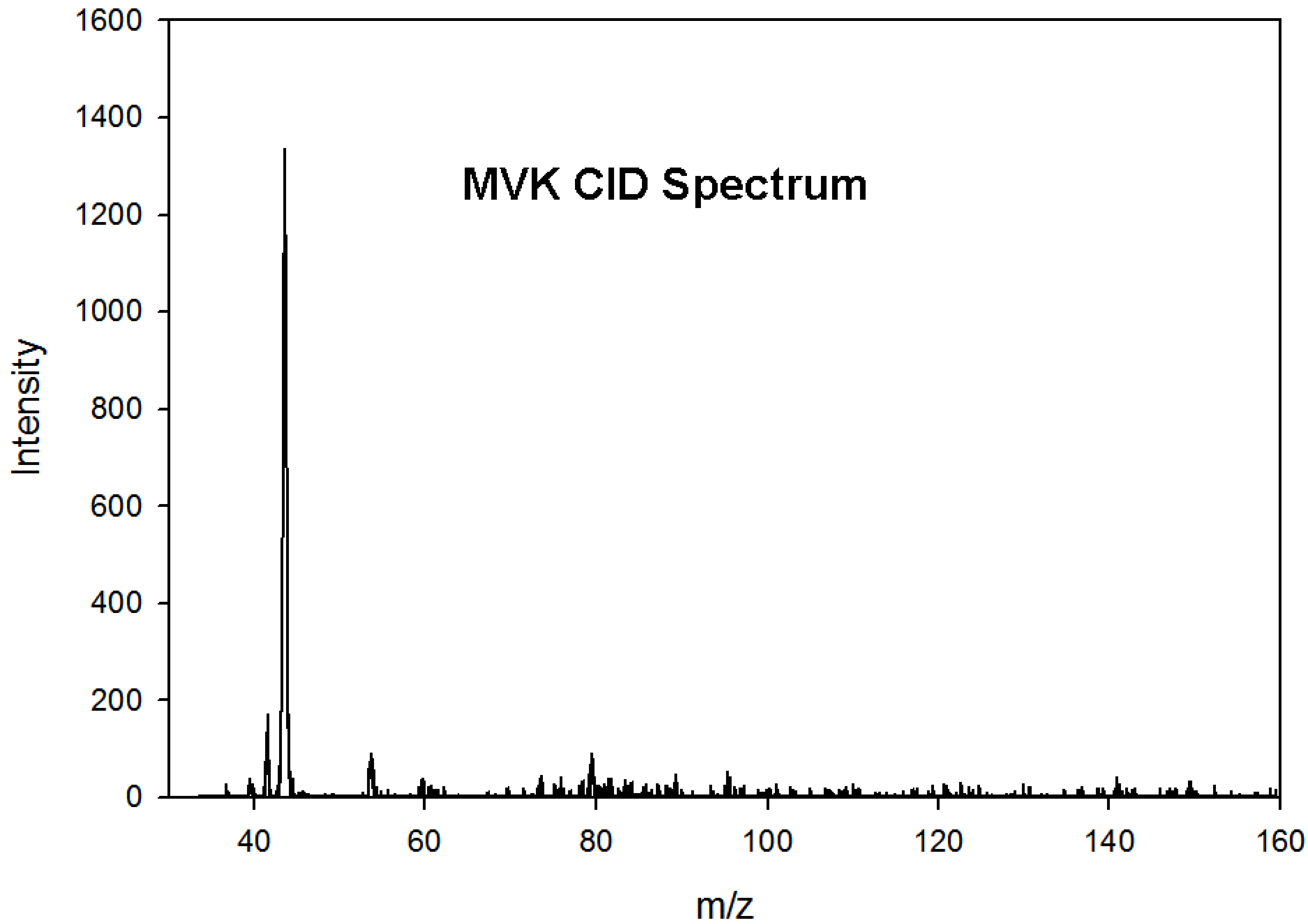
•DESI can be used in conjunction with smog chamber-based studies of BVOC/NOx irradiations to investigate the nature of oxidation products that are important SOA precursors.

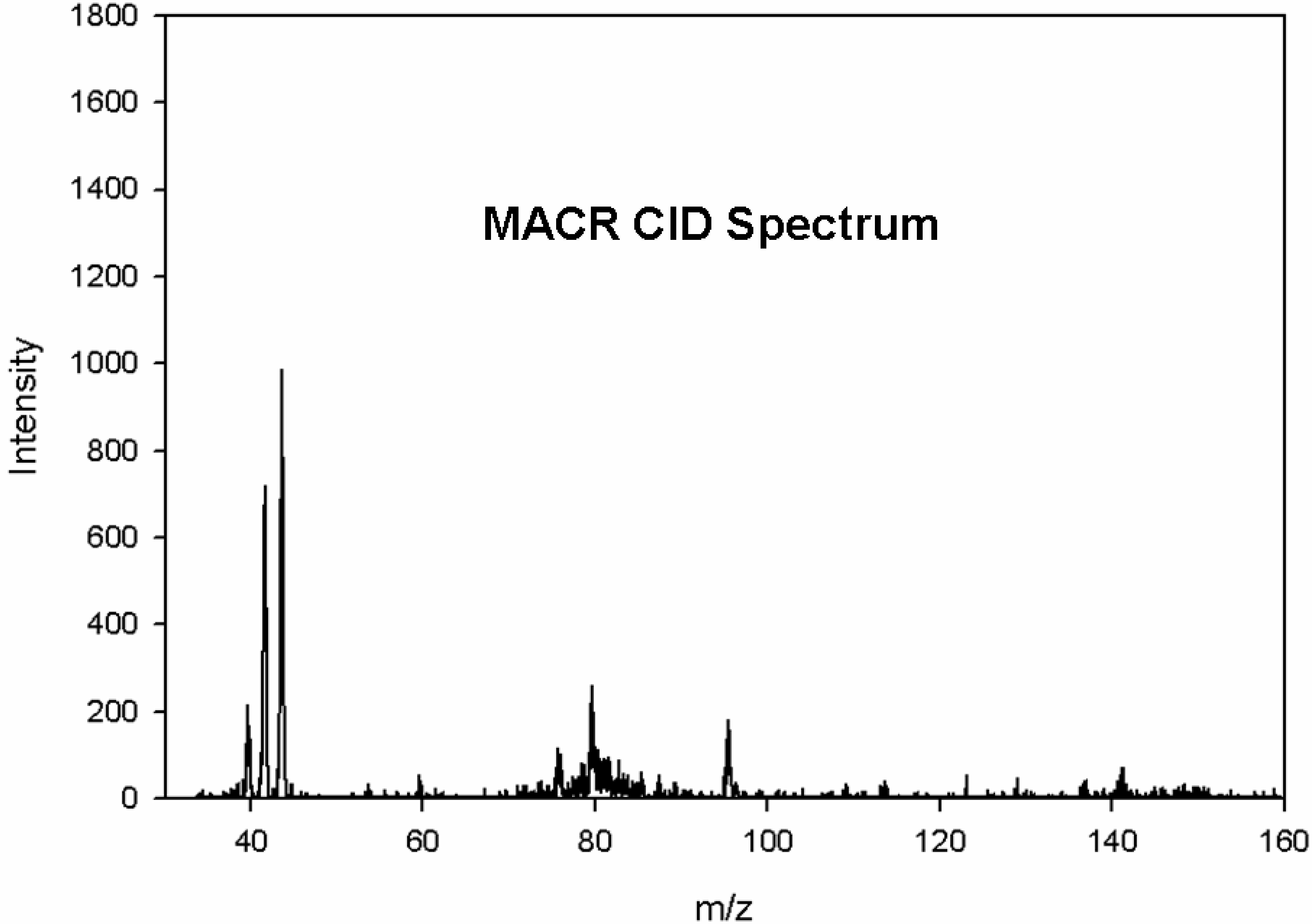
•Aerosol can age both as a result of polymerization chemistry, but also because of aerosol-phase photochemistry, and this processing influences the distribution of species between the gas and aerosol phase.

•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)




MVK CID Spectrum
Intensity
m/z
0
200
400
600
800
1000
1200
1400
1600
40
60
80
100
120
140
160


MACR CID Spectrum
Intensity
m/z
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400
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800
1000
1200
1400
1600
1800
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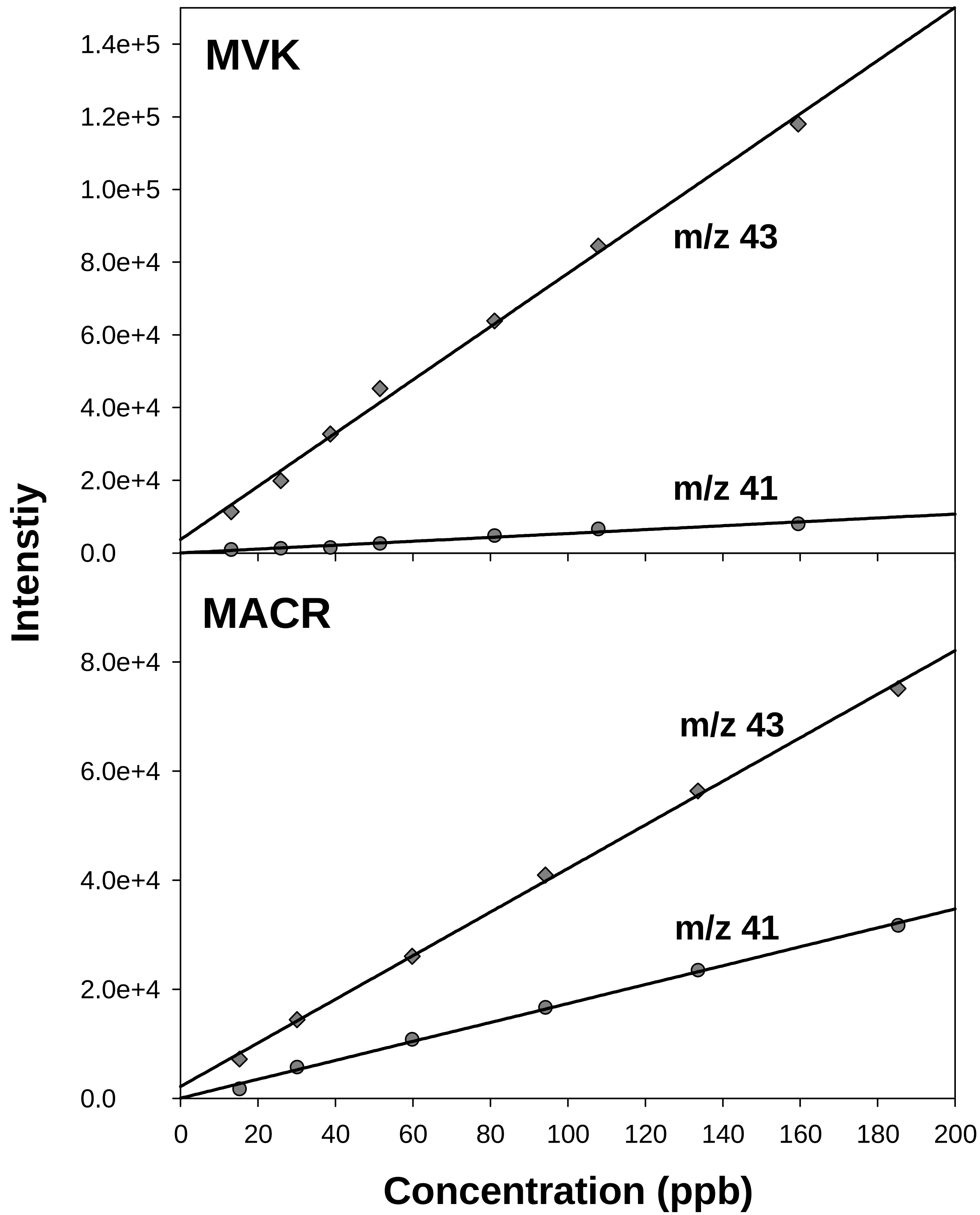
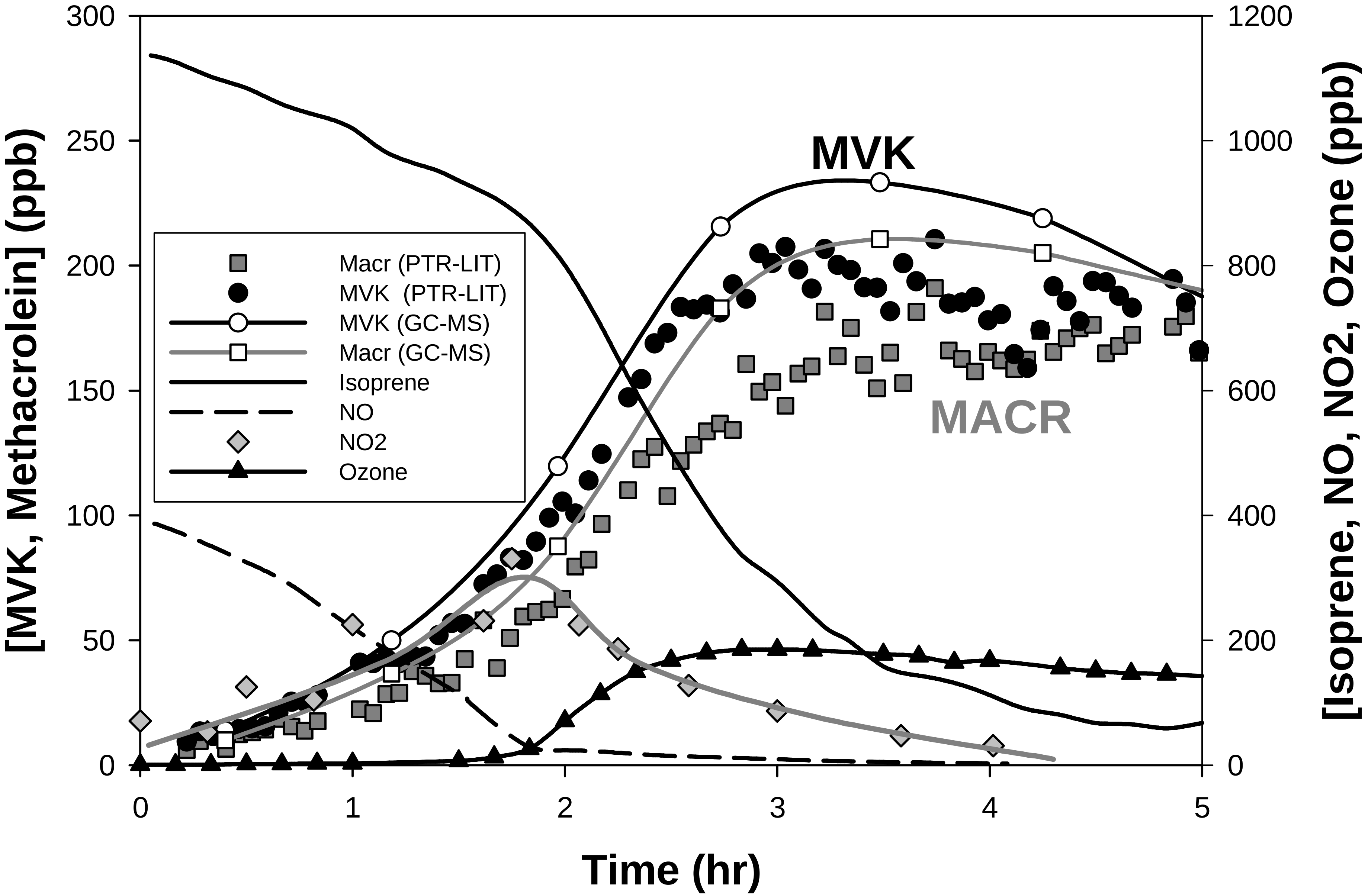
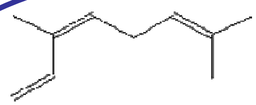
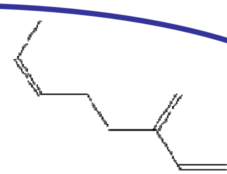
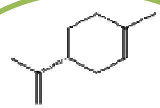
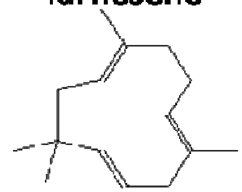
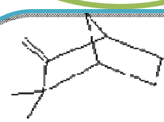
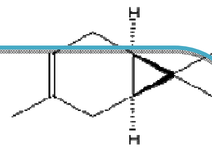
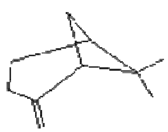
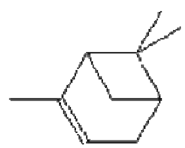
120
140
160


MVK
m/z 43
m/z 41
MACR
m/z 43
m/z 41
Intenstiy
Concentration (ppb)
1.4e+5
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
0
20
40
60
80
100
120
140
160
180
200

Isoprene/NO_x Smog Chamber Irradiation



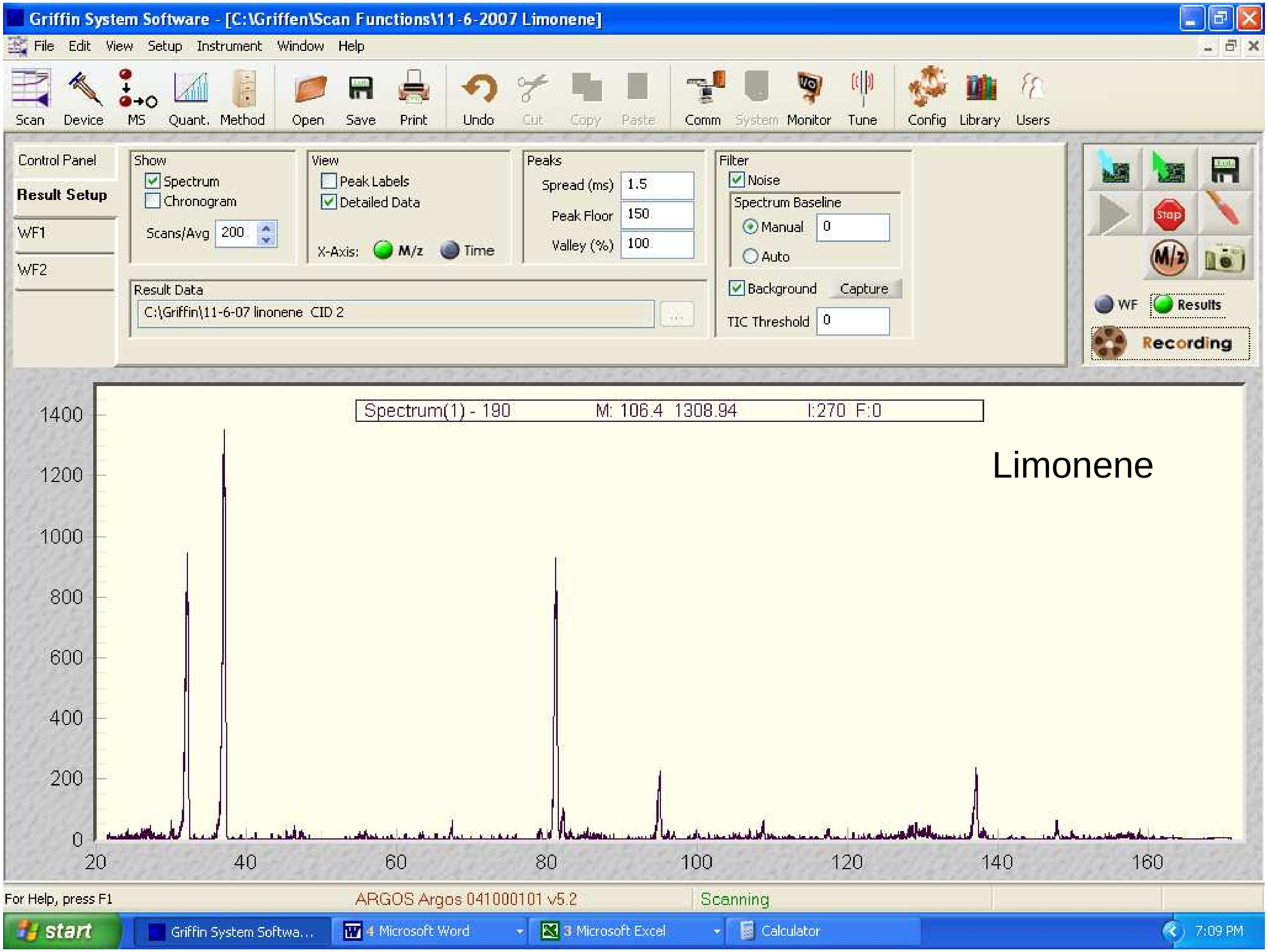
Analysed Compounds:

Monoterpenes		Sesquiterpenes
 cis-ocimene	 myrcene	 farnesene
 R-(+)-limonene		 α-humulene
 camphene	 (+)-3-Carene	
 (-)-β-pinene	 (-)-α-pinene	

acyclic structure

monocyclic structure

bicyclic structure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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 linonene CID 2
Stop
M/z
WF
Results
Recording
Spectrum(1) - 190 M: 106.4 1308.94 I:270 F:0
Limonene
1400
1200
1000
800
600
400
200
0
20 40 60 80 100 120 140 160
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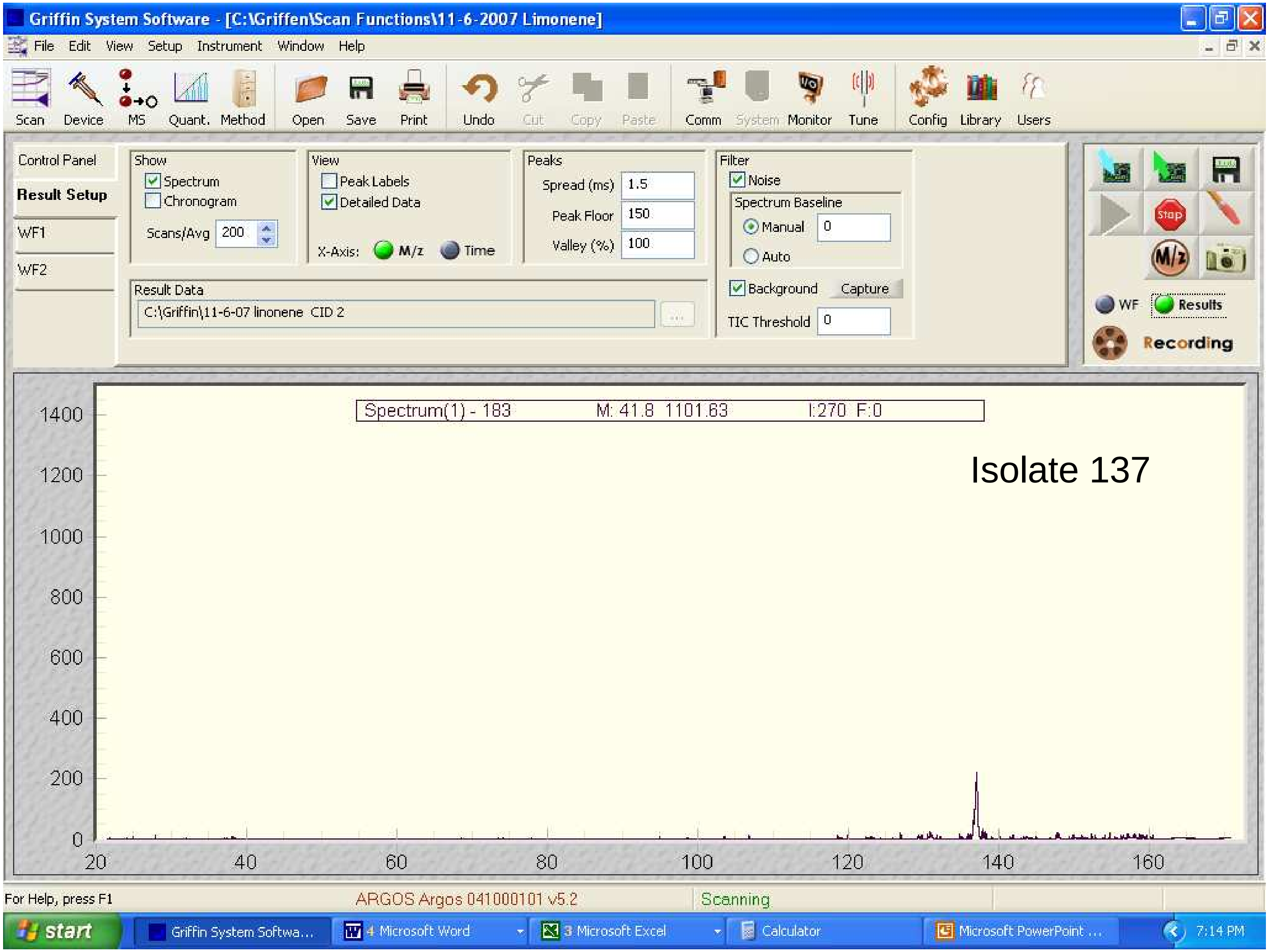
3 Microsoft Excel
Calculator
7:09 PM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View
Peak Labels
Detailed Data
X-Axis: M/z Time
Peaks
Spread (ms) 1.5
Peak Floor 150
Valley (%) 100
Filter
Noise
Spectrum Baseline
Manual 0
Auto
Background Capture
TIC Threshold 0
Result Data
C:\Griffin\11-6-07 linonene CID 2
WF Results
Recording
Spectrum(1) - 183 M: 41.8 1101.63 I:270 F:0
Isolate 137
1400
1200
1000
800
600
400
200
0
20 40 60 80 100 120 140 160
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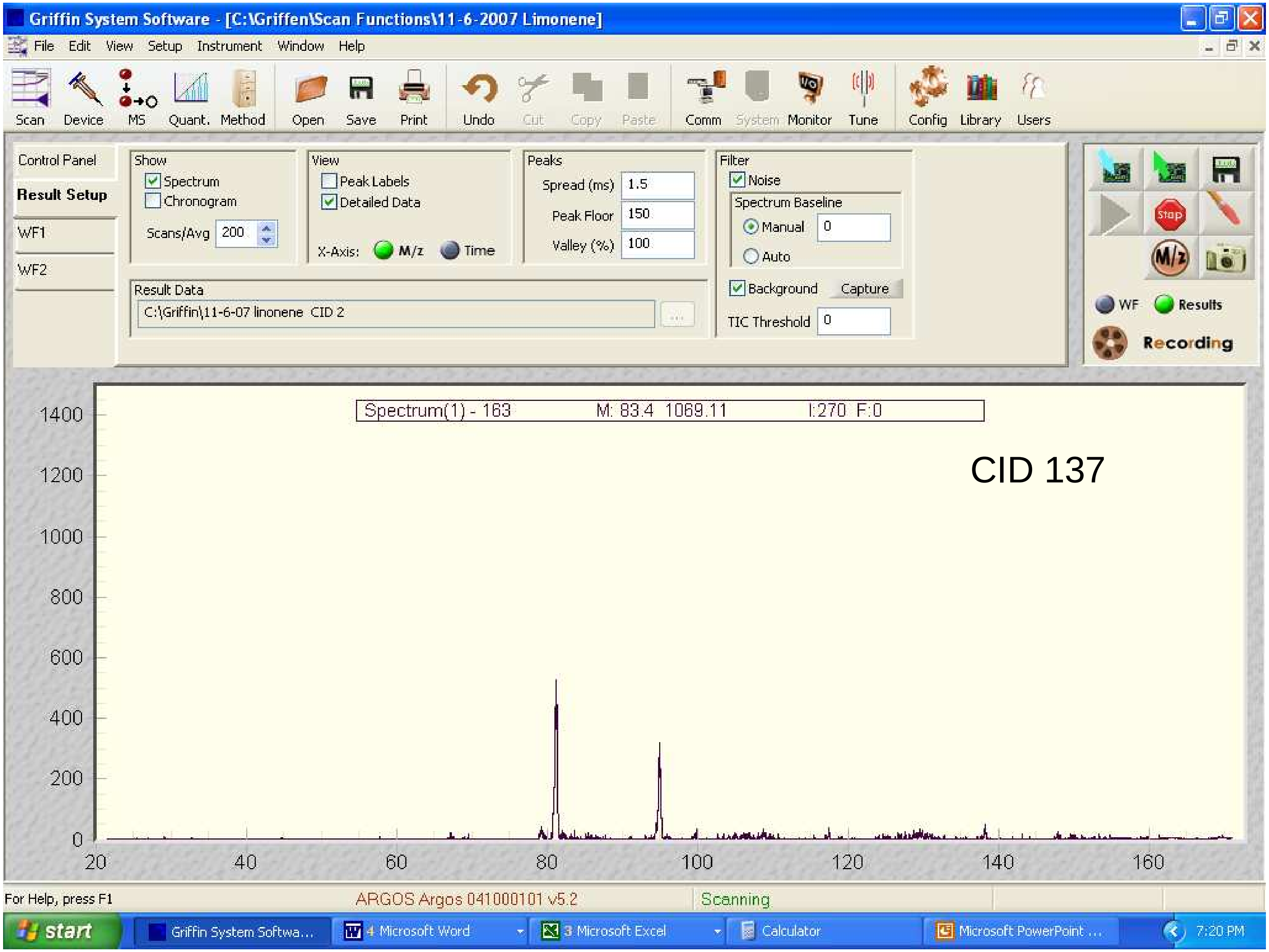

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Control Panel
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WF2
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Spectrum
Chronogram
Scans/Avg 200
View
Peak Labels
Detailed Data
X-Axis: M/z Time
Peaks
Spread (ms) 1.5
Peak Floor 150
Valley (%) 100
Filter
Noise
Spectrum Baseline
Manual 0
Auto
Background Capture
TIC Threshold 0
Result Data
C:\Griffin\11-6-07 linonene CID 2
WF Results
Recording
Spectrum(1) - 183 M: 83.4 1069.11 I:270 F:0
CID 137
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Calculator
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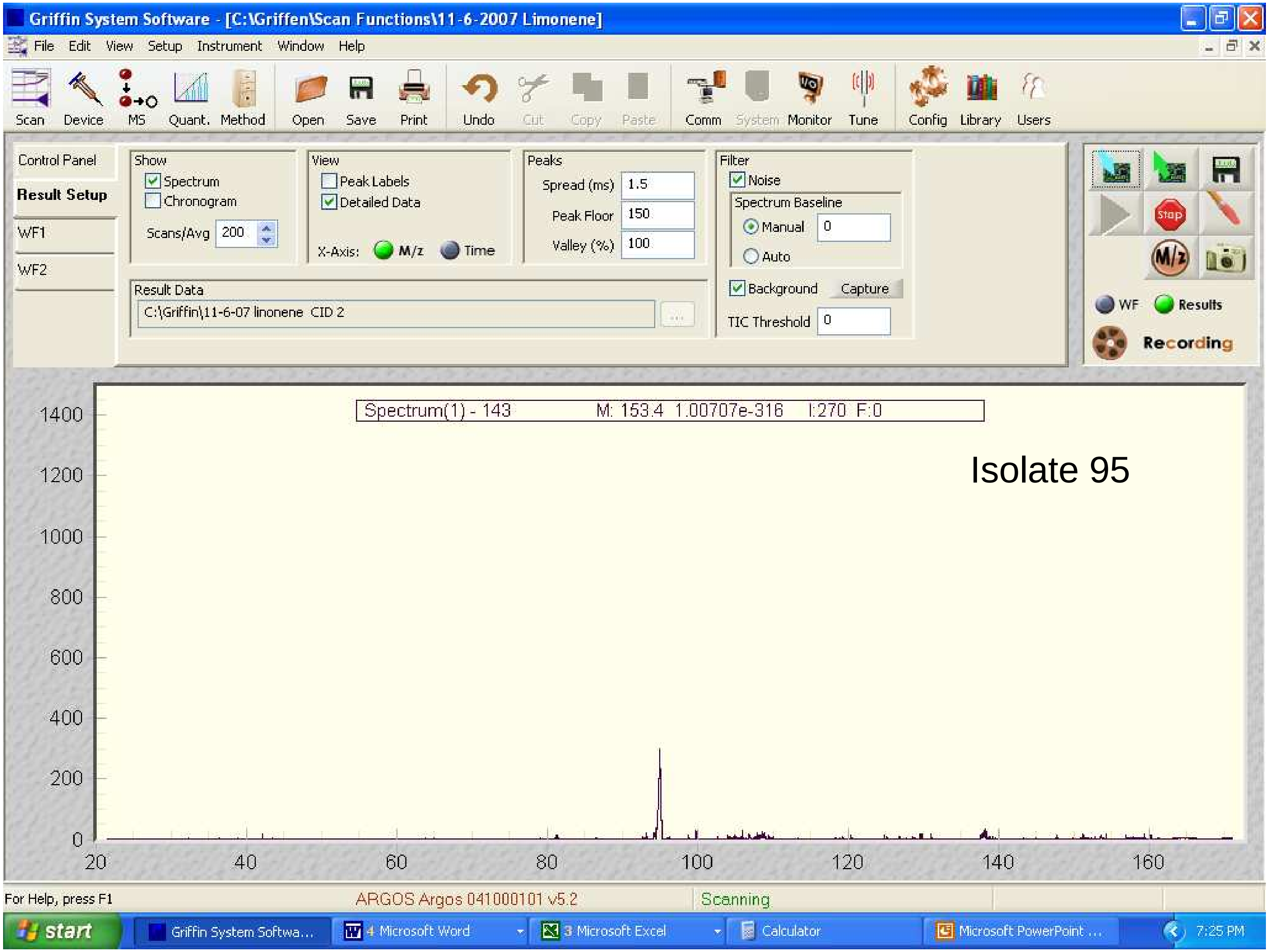
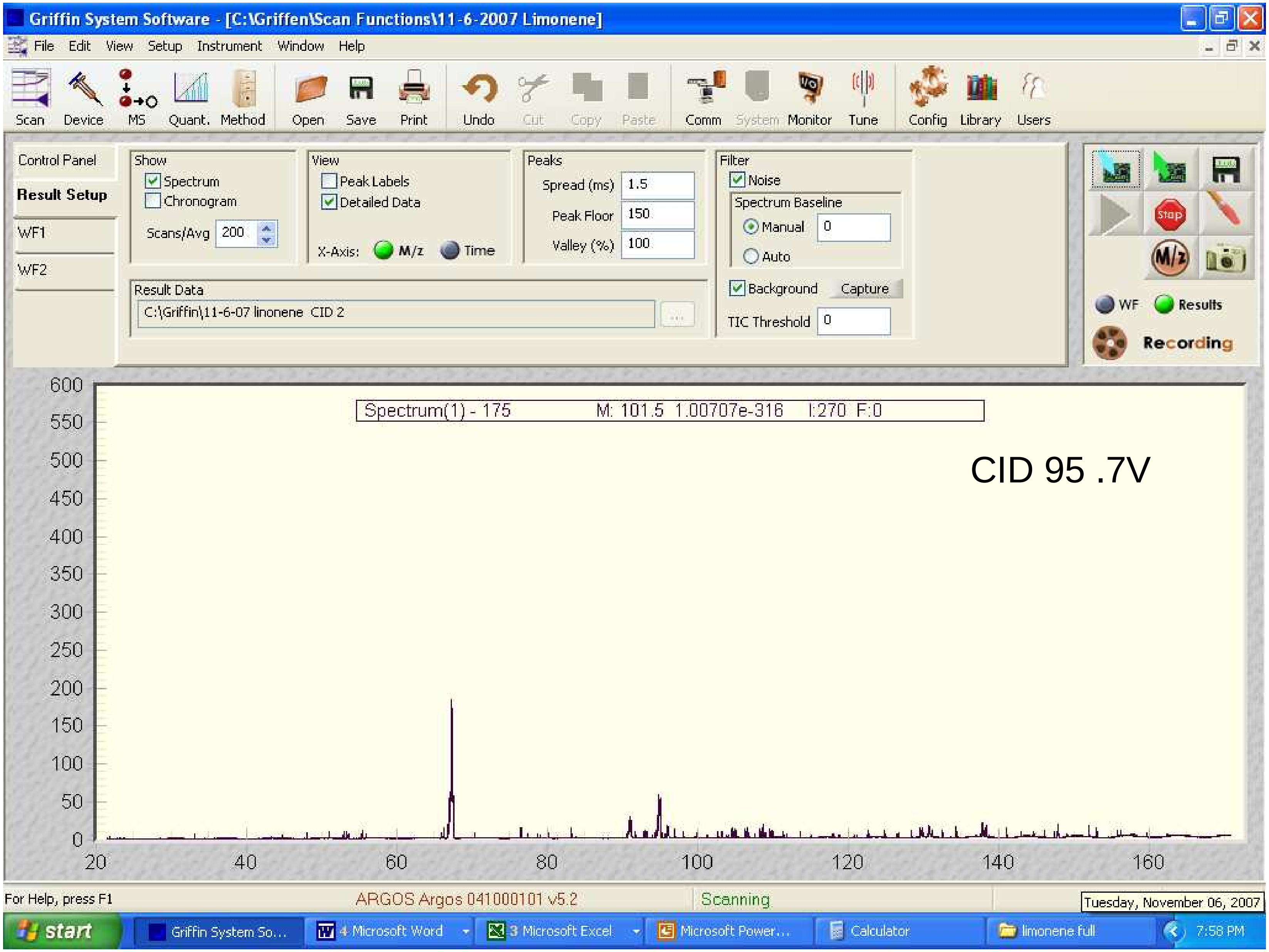
US EPA ARCHIVE DOCUMENT



Isolate 95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Control Panel
Result Setup
WF1
WF2
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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 linonene CID 2
WF Results
Recording
Spectrum(1) - 175 M: 101.5 1.00707e-316 I:270 F:0
CID 95 .7V
600 550 500 450 400 350 300 250 200 150 100 50 0
20 40 60 80 100 120 140 160
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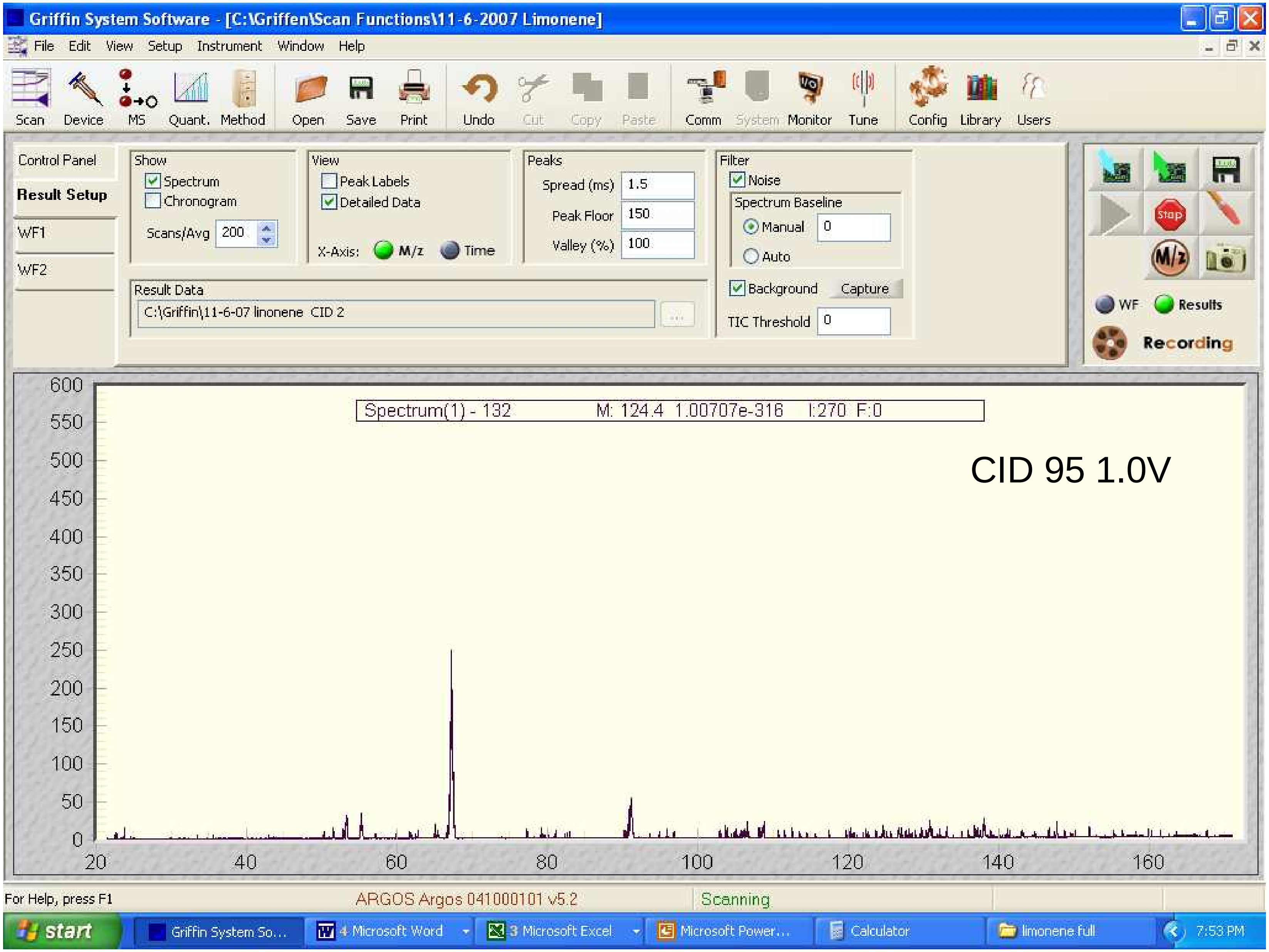
Microsoft Power...
Calculator
limonene full
7:58 PM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Control Panel
Result Setup
WF1
WF2
Show
Spectrum
Chronogram
Scans/Avg 200
View
Peak Labels
Detailed Data
X-Axis: M/z Time
Peaks
Spread (ms) 1.5
Peak Floor 150
Valley (%) 100
Filter
Noise
Spectrum Baseline
Manual 0
Auto
Background Capture
TIC Threshold 0
Result Data
C:\Griffin\11-6-07 linonene CID 2
Stop
M/z
WF Results
Recording
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CID 95 1.0V
600
550
500
450
400
350
300
250
200
150
100
50
0
20
40
60
80
100
120
140
160
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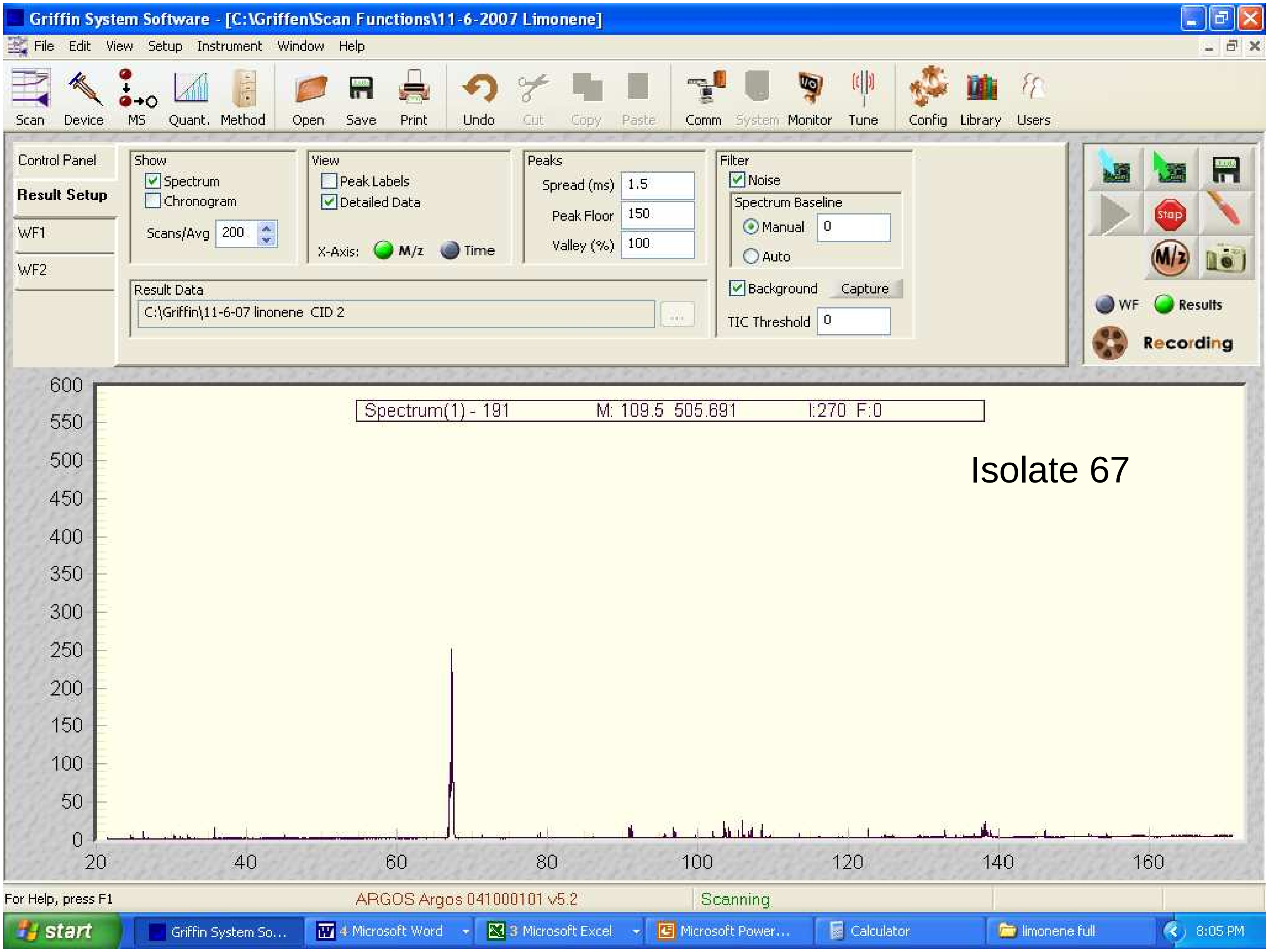
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Chronogram
Scans/Avg 200
View
Peak Labels
Detailed Data
X-Axis: M/z Time
Peaks
Spread (ms) 1.5
Peak Floor 150
Valley (%) 100
Filter
Noise
Spectrum Baseline
Manual 0
Auto
Background Capture
TIC Threshold 0
Result Data
C:\Griffin\11-6-07 linonene CID 2
Stop
WF Results
Recording
Spectrum(1) - 191 M: 109.5 505.691 I:270 F:0
Isolate 67
600
550
500
450
400
350
300
250
200
150
100
50
0
20 40 60 80 100 120 140 160
For Help, press F1
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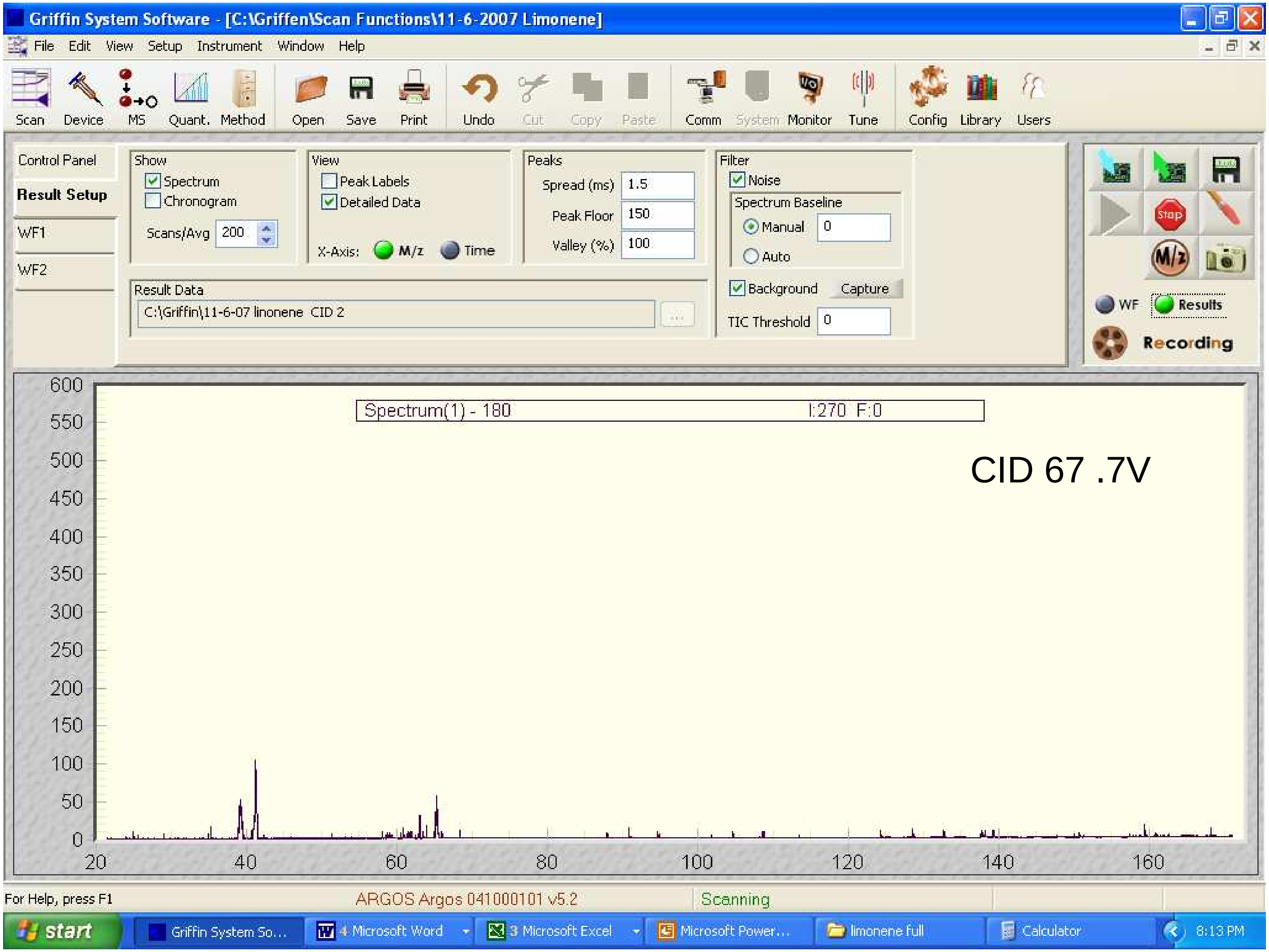
Calculator
limonene full
8:05 PM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Result Setup
WF1
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Show
Spectrum
Chronogram
Scans/Avg 200
View
Peak Labels
Detailed Data
X-Axis: M/z Time
Peaks
Spread (ms) 1.5
Peak Floor 150
Valley (%) 100
Filter
Noise
Spectrum Baseline
Manual 0
Auto
Background Capture
TIC Threshold 0
Result Data
C:\Griffin\11-6-07 linonene CID 2
WF Results
Recording
Spectrum(1) - 180 I:270 F:0
CID 67 .7V
600
550
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450
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350
300
250
200
150
100
50
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40
60
80
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120
140
160
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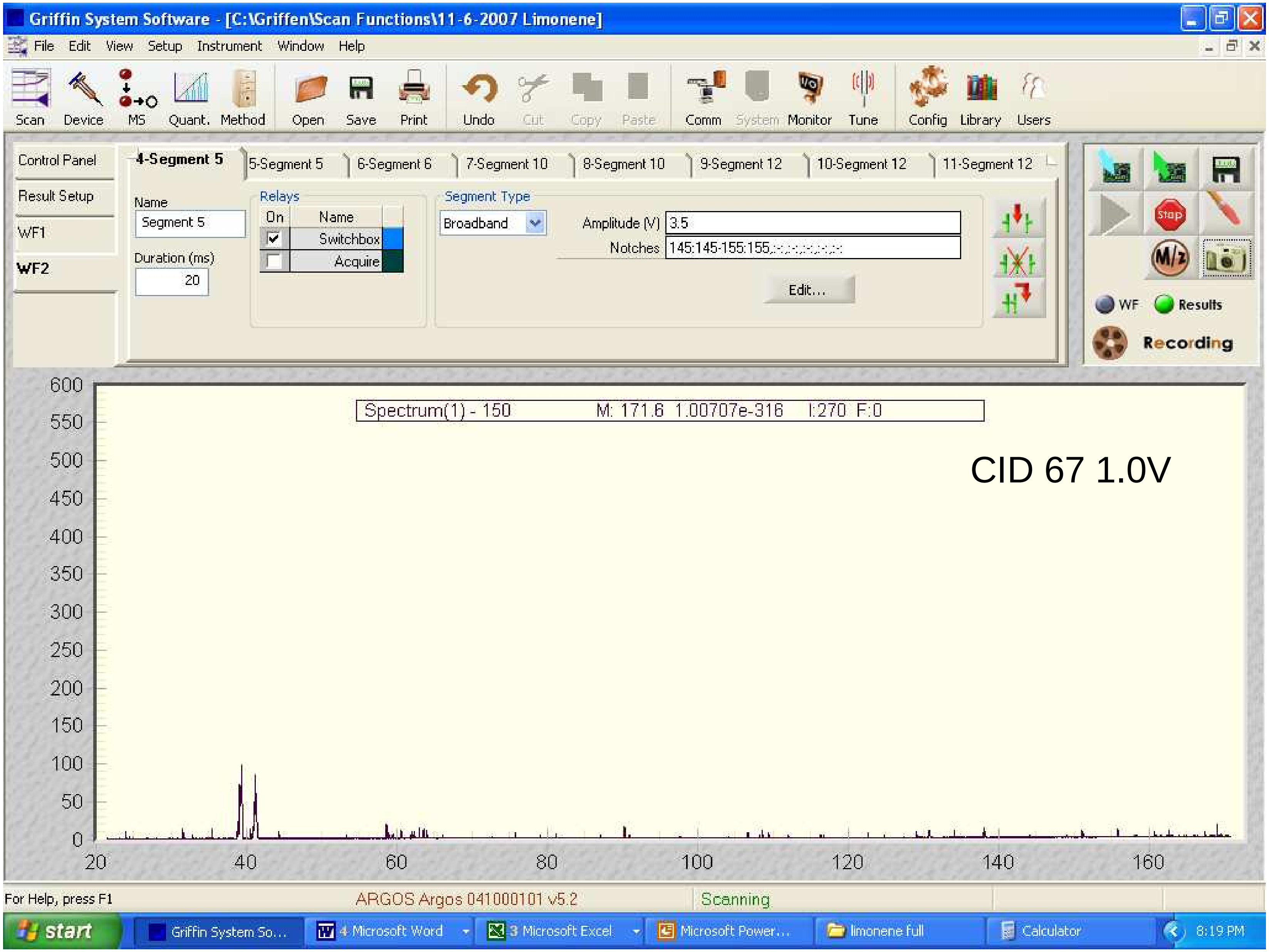
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Control Panel
Result Setup
WF1
WF2
4-Segment 5 5-Segment 5 6-Segment 6 7-Segment 10 8-Segment 10 9-Segment 12 10-Segment 12 11-Segment 12
Name
Segment 5
Duration (ms)
20
Relays
On Name
Switchbox
Acquire
Segment Type
Broadband
Amplitude (V) 3.5
Notches 145:145-155:155,:-:,:-:,:-:,:-:,:-:
Edit...
WF Results
Recording
Spectrum(1) - 150 M: 171.6 1.00707e-316 I:270 F:0
CID 67 1.0V
600 550 500 450 400 350 300 250 200 150 100 50 0
20 40 60 80 100 120 140 160
For Help, press F1
ARGOS Argos 041000101 v5.2
Scanning
start
Griffin System So...
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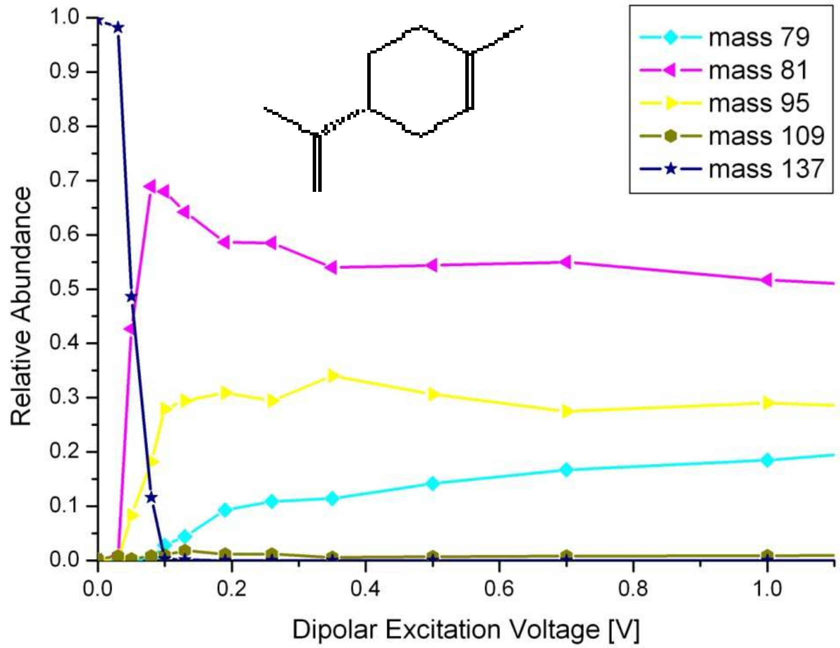
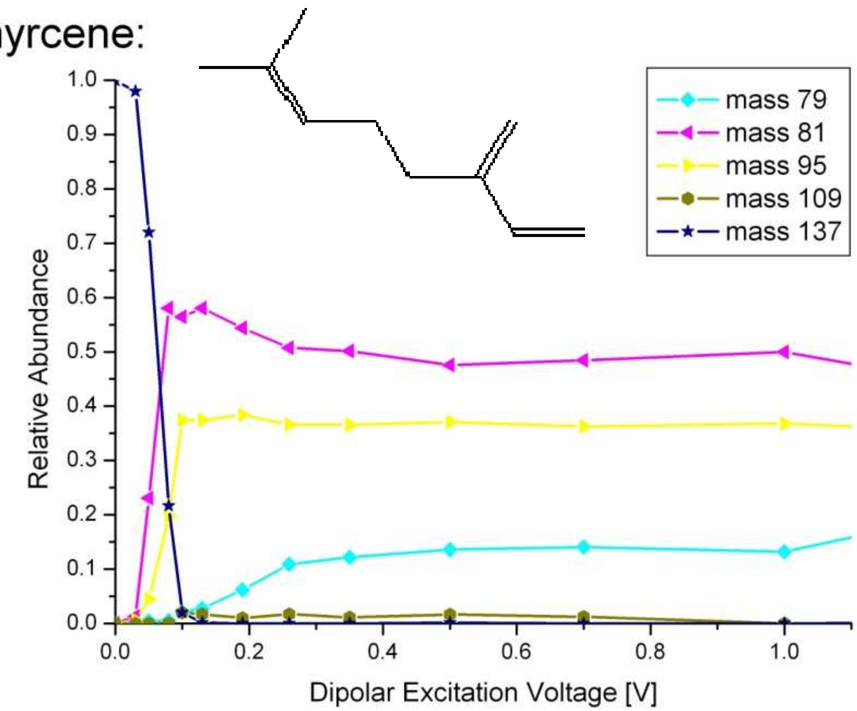
3 Microsoft Excel
Microsoft Power...
limonene full
Calculator
8:19 PM

PTR-LIT MS/MS Fragmentation Patterns:

limonene:



myrcene:




"BOB"
+ OH, NO
ONO2
OH

Oligomer Production and Analysis

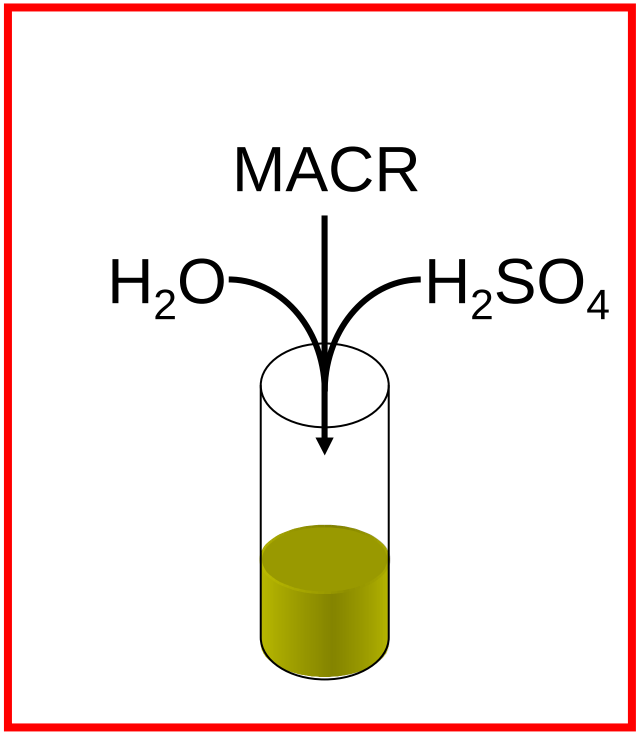
- Source Conditions

Spray Voltage: 4.5 kV
Spray Flow: 3 µL/min
Spray Solvent: 1:1 Methanol:Water with 10^{-5} M NaOH
Nebulization Gas: 120 psi N_2
Capillary Temp: 200 ℃
Tube Lens Voltage: 65 V
Capillary Voltage: 20 V

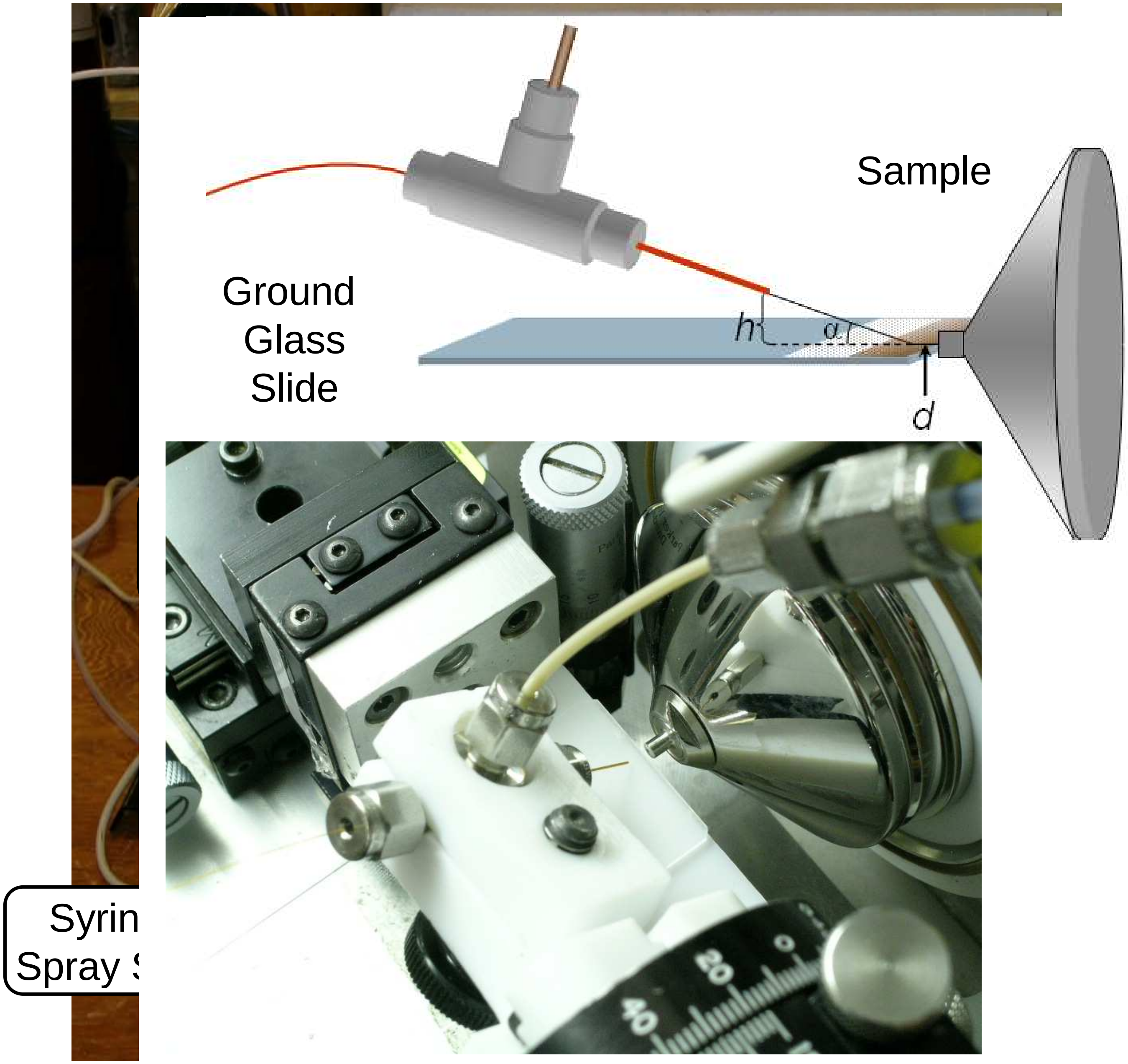
α: 35°
h: 1 mm
d: 2 mm
Spot Diameter: 0.8 mm
Sample Loading: 90 ng/spot

- Sample Preparation

<u>Concentrated Oligomer</u>
100 µL methacrolein
100 µL H_2SO_4
80 µL water
Diluted with acetonitrile

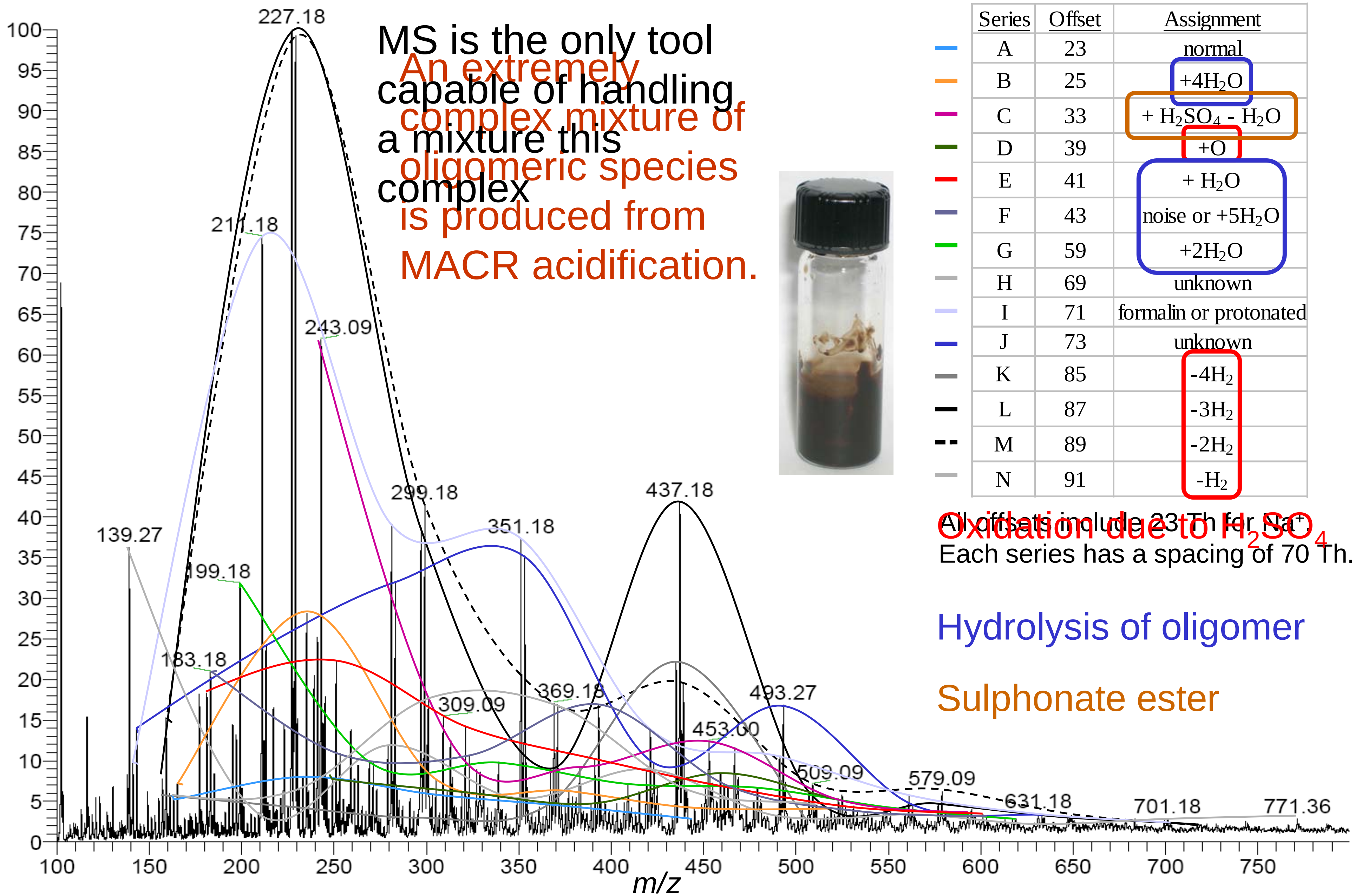


DESI Mass Spectrometry



Takáts, Z., *et al.*, *Science*, **2004**, *306*, 471-473. Cooks, R.G., et al., *Science*, **2006**, *311*, 1566-1570.

MACR Oligomer from H_2SO_4 Catalysis



MS is the only tool capable of handling a mixture this complex

An extremely complex mixture of oligomeric species is produced from MACR acidification.

Series	Offset	Assignment
A	23	normal
B	25	$+4H_2O$
C	33	$+ H_2SO_4 - H_2O$
D	39	+O
E	41	$+ H_2O$
F	43	noise or $+5H_2O$
G	59	$+2H_2O$
H	69	unknown
I	71	formalin or protonated
J	73	unknown
K	85	$-4H_2$
L	87	$-3H_2$
M	89	$-2H_2$
N	91	$-H_2$

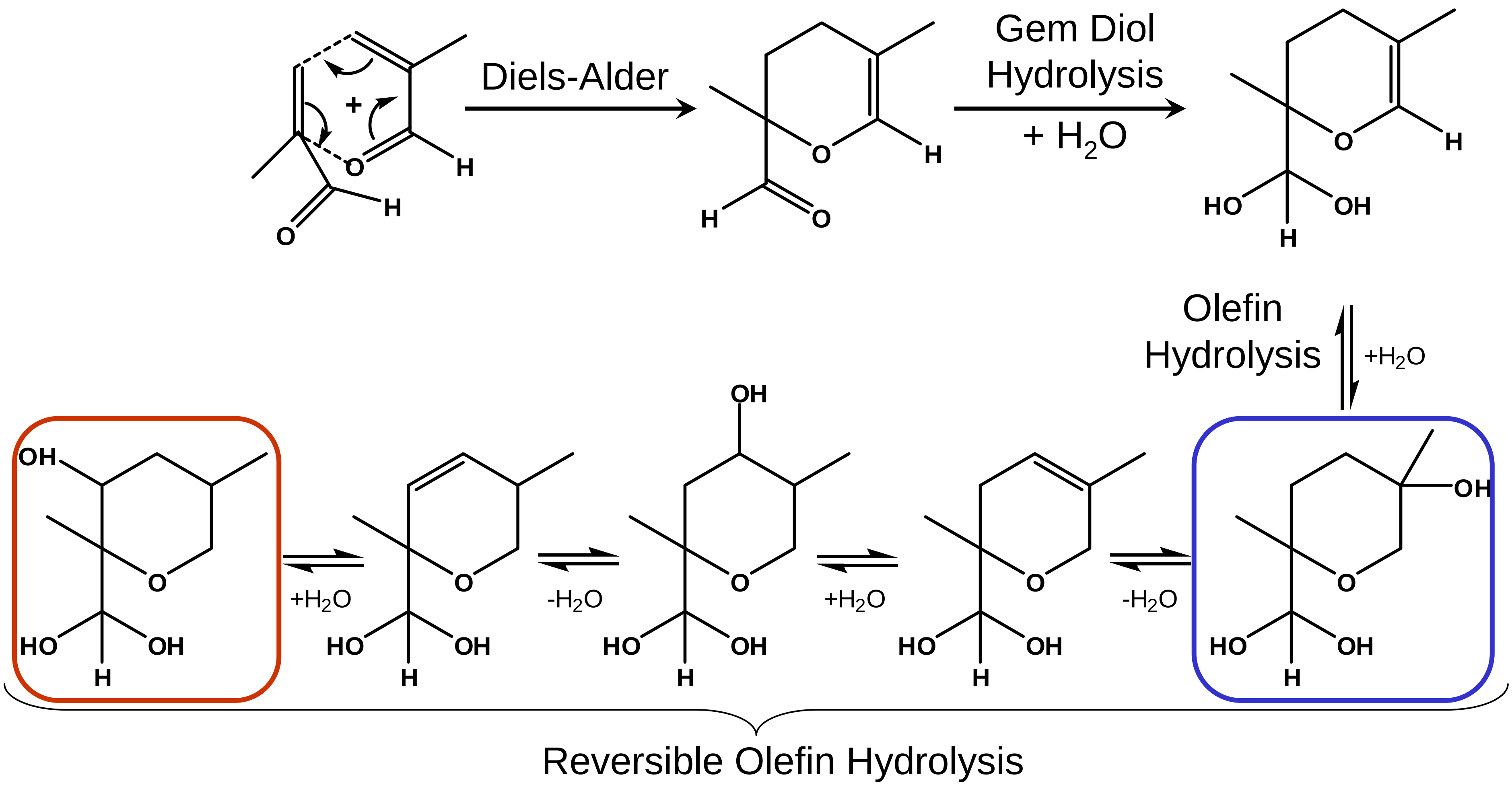
All offsets include 23 Th for Na^+.
Each series has a spacing of 70 Th.

Oxidation due to H_2SO_4

Hydrolysis of oligomer

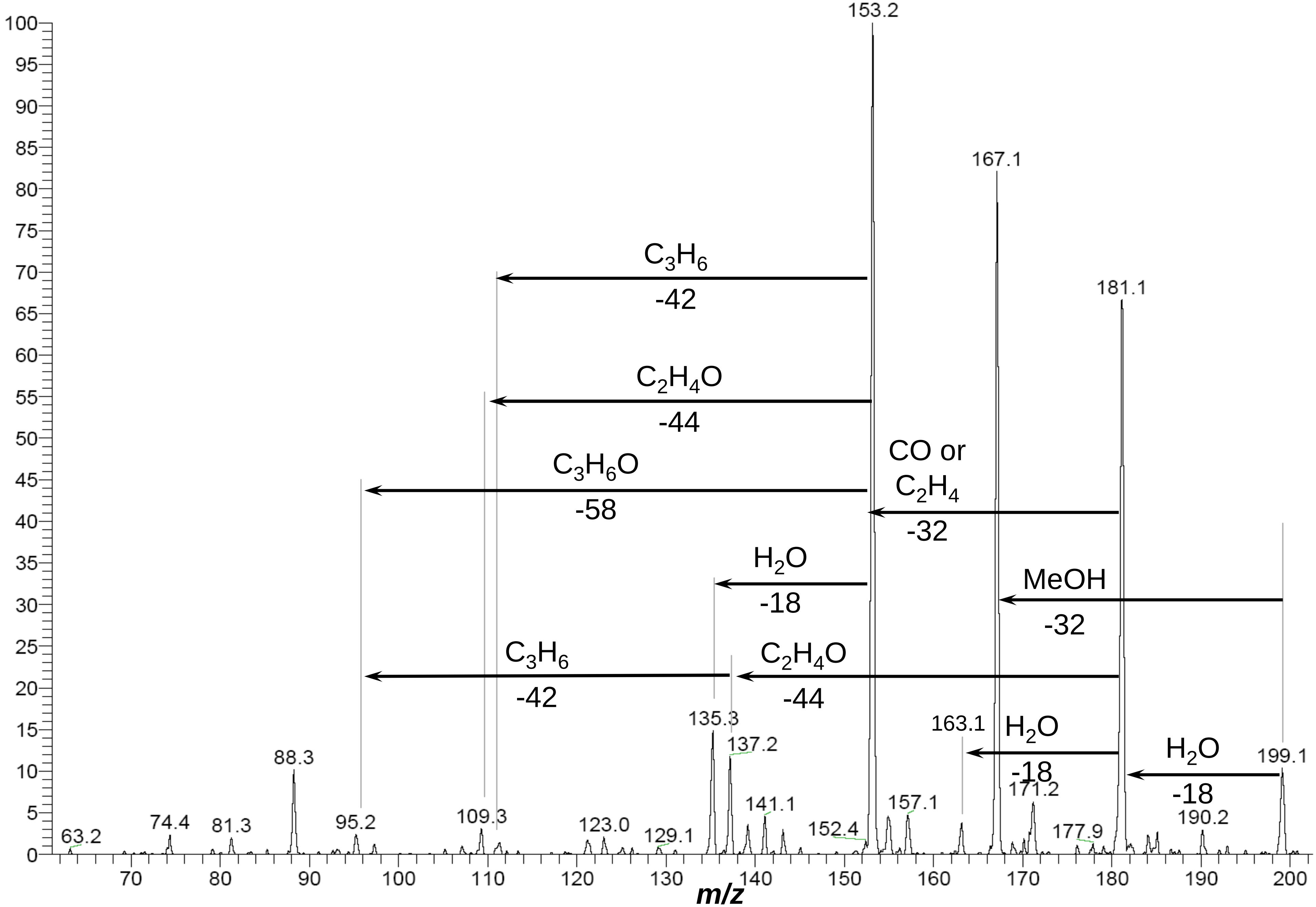
Sulphonate ester

Formation of [$MACR_2 + 2H_2O$]

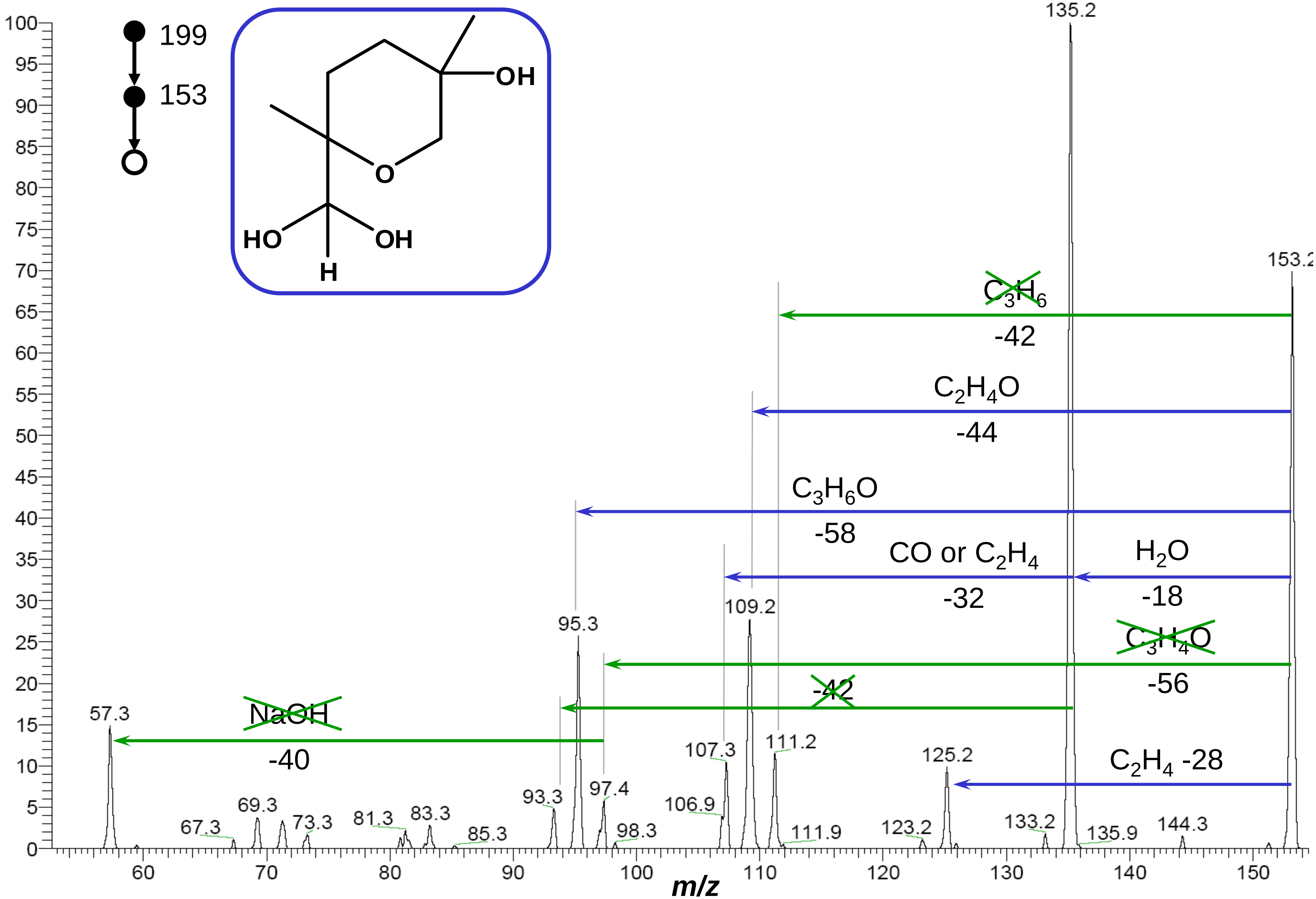


- Diels-Alder has been observed in MACR oligomer, but not in SOA oligomer
- At least two structures cover the range of fragments for *m/z* 199

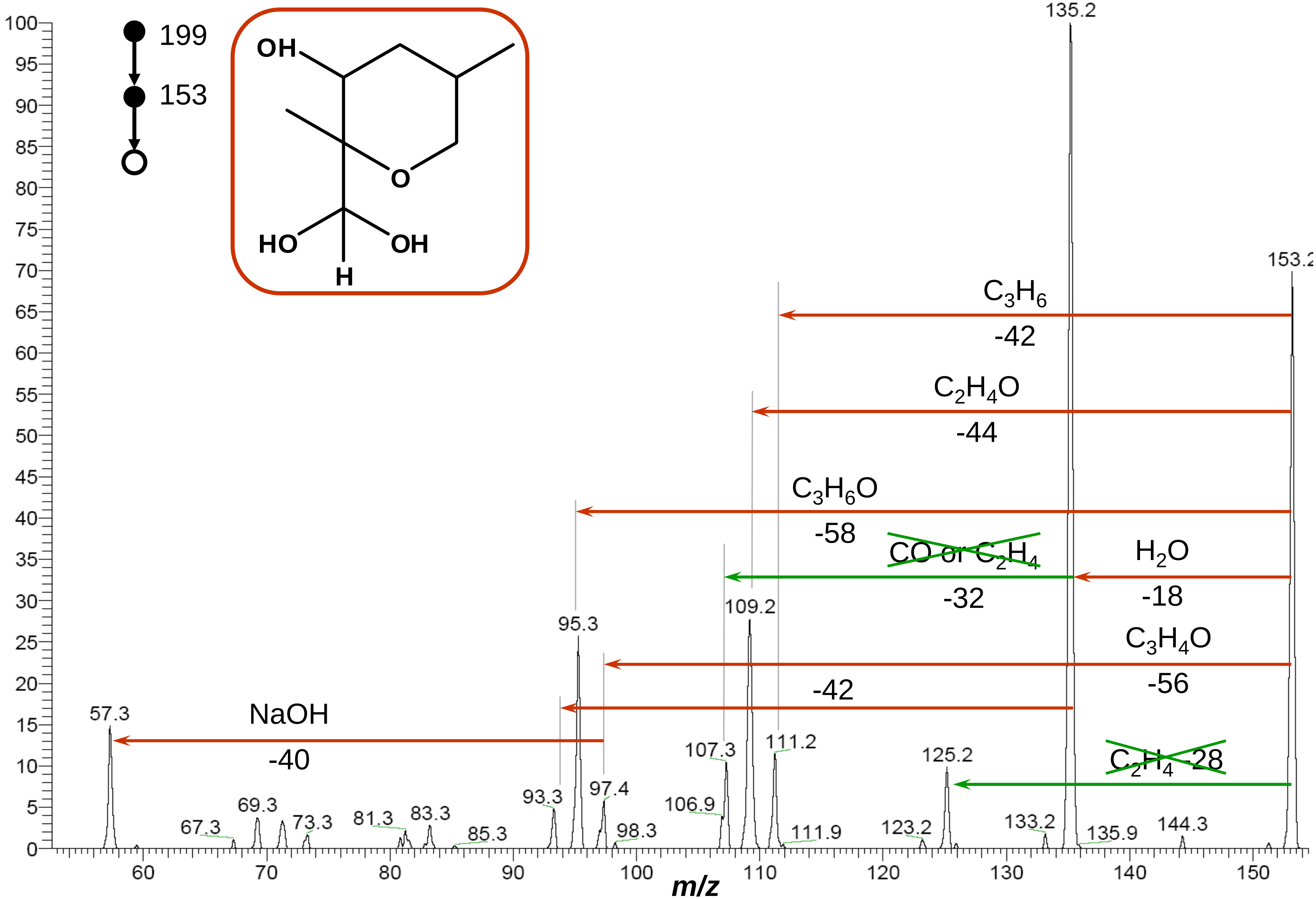
DESI-MS^2 of *m/z* 199: $[MACR_2 + 2H_2O]Na^+$



DESI-MS^3 of *m/z* 199: $[MACR_2 + 2H_2O]Na^+$

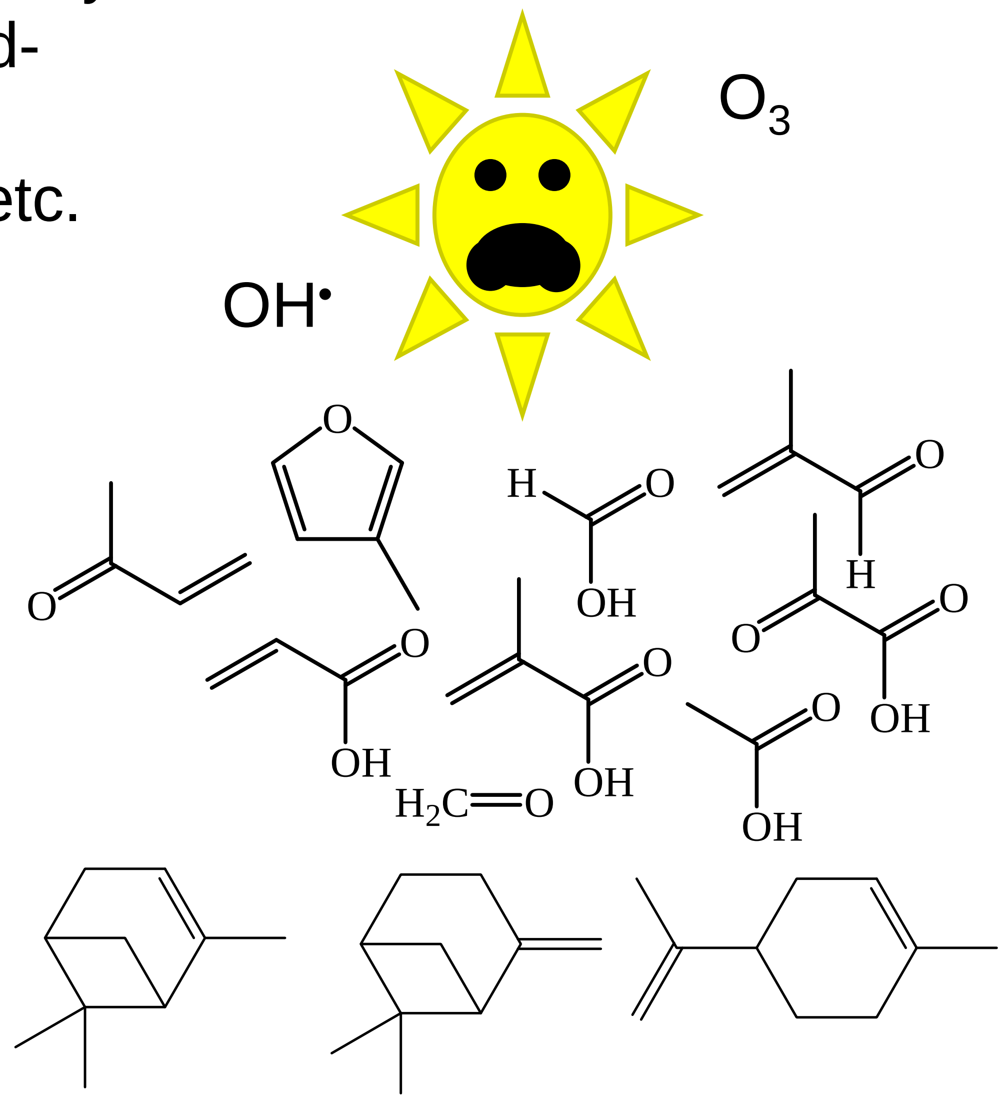


DESI-MS^3 of *m/z* 199: $[MACR_2 + 2H_2O]Na^+$

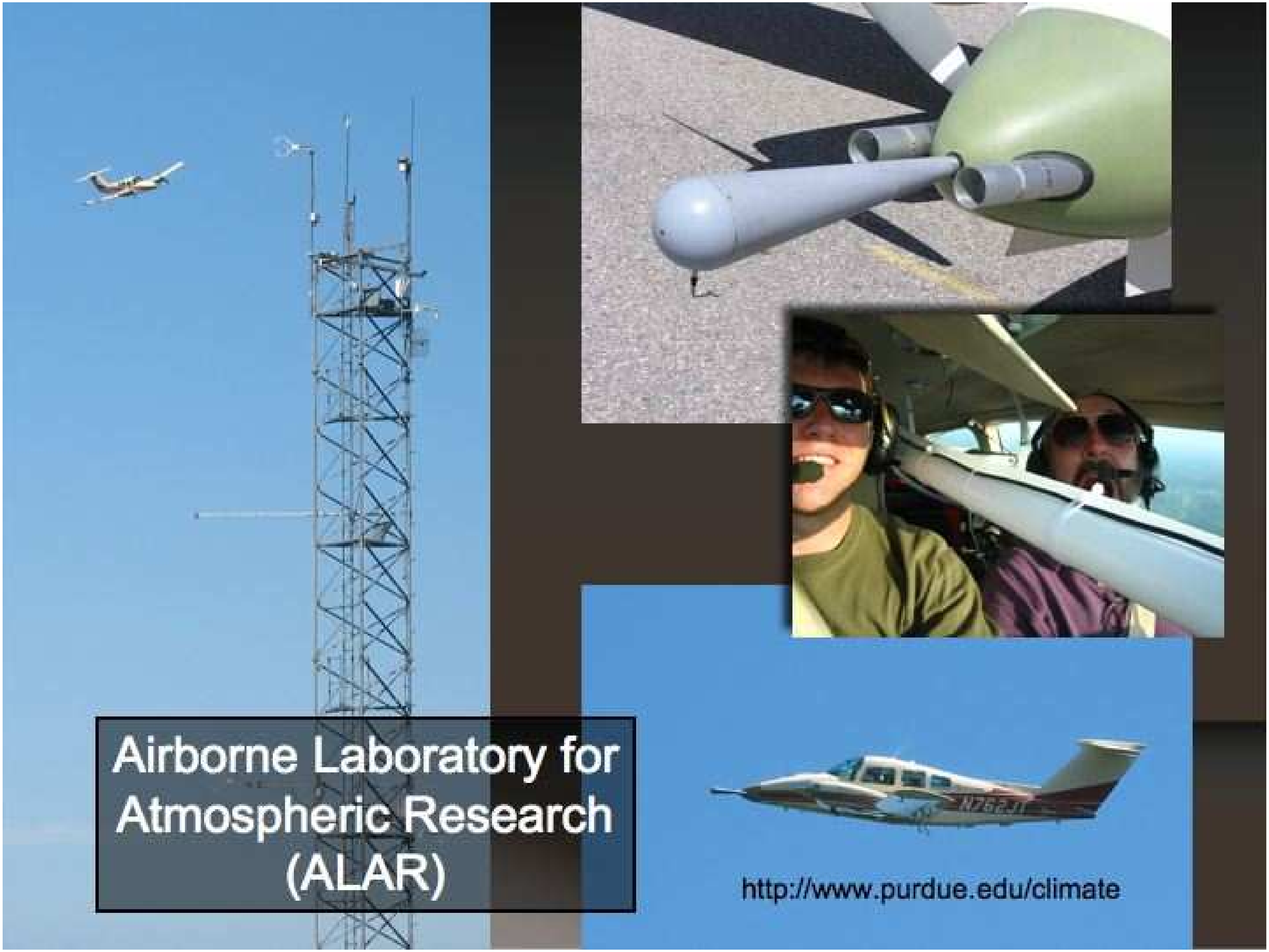


A simplified case, addressing only one monomer undergoing acid-catalyzed reactions without light, heat, radical chemistry, etc.

…but in the real world…

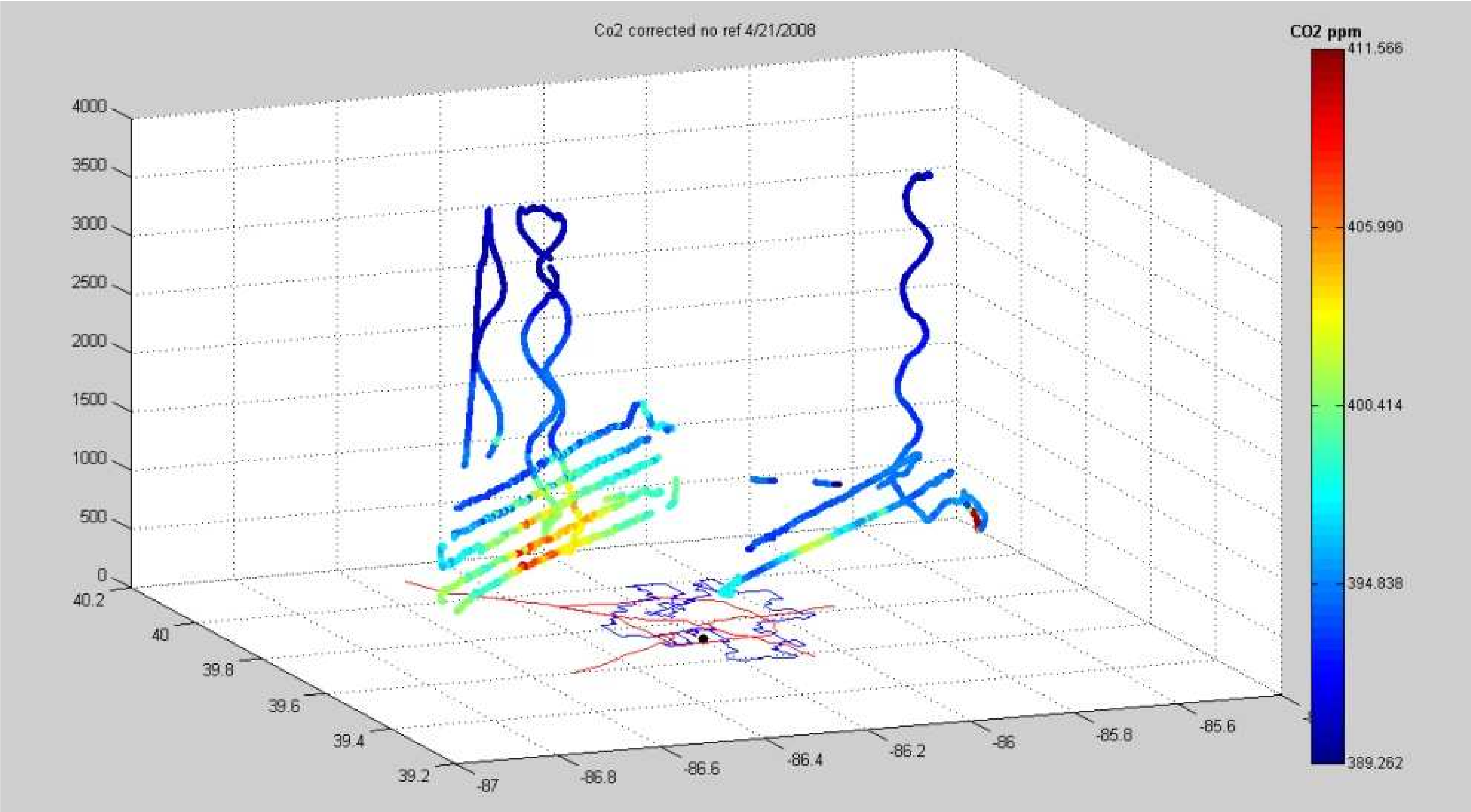


Can we really do this on a real system???


Airborne Laboratory for
Atmospheric Research
(ALAR)
http://www.purdue.edu/climate

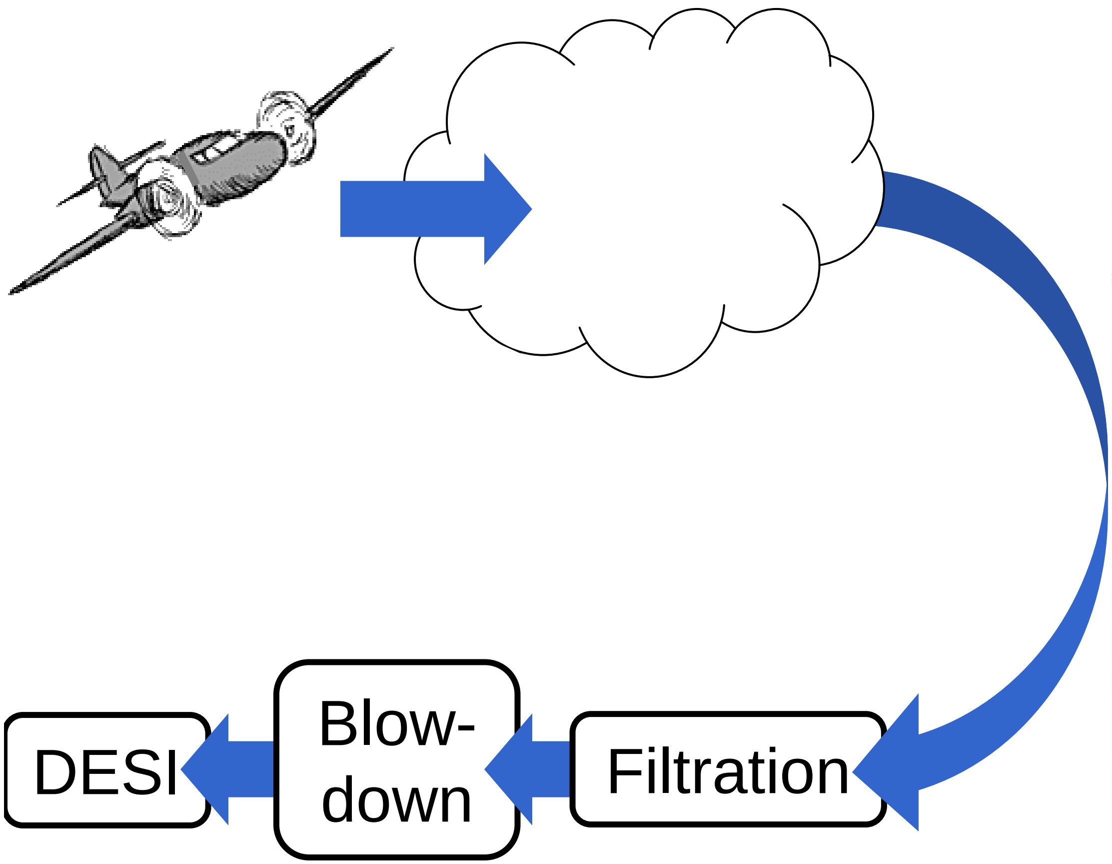

N762JT

ALAR emission flux experiments

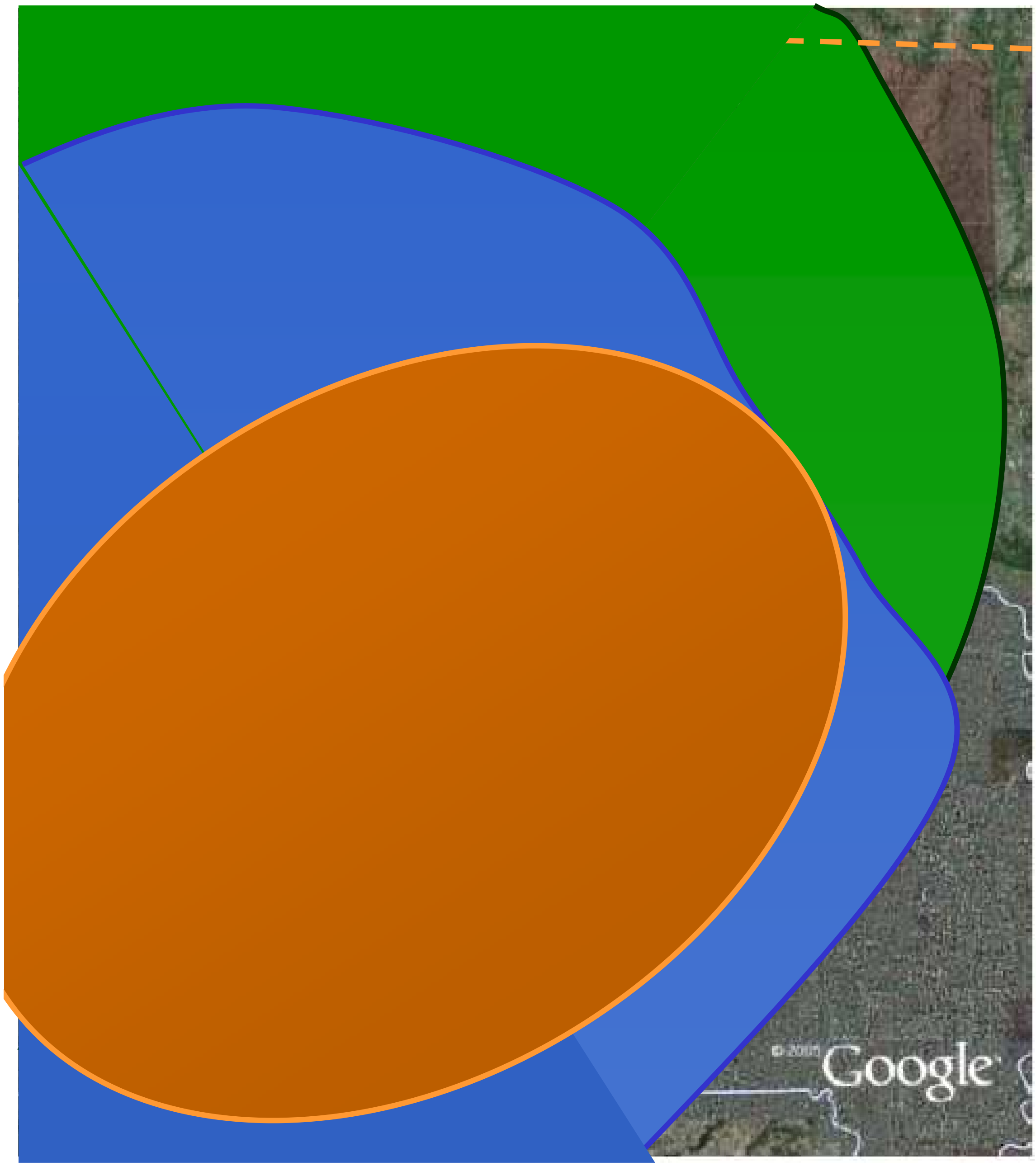


Cloud Water Analysis

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



Cloud Water Collection Site: Central Missouri



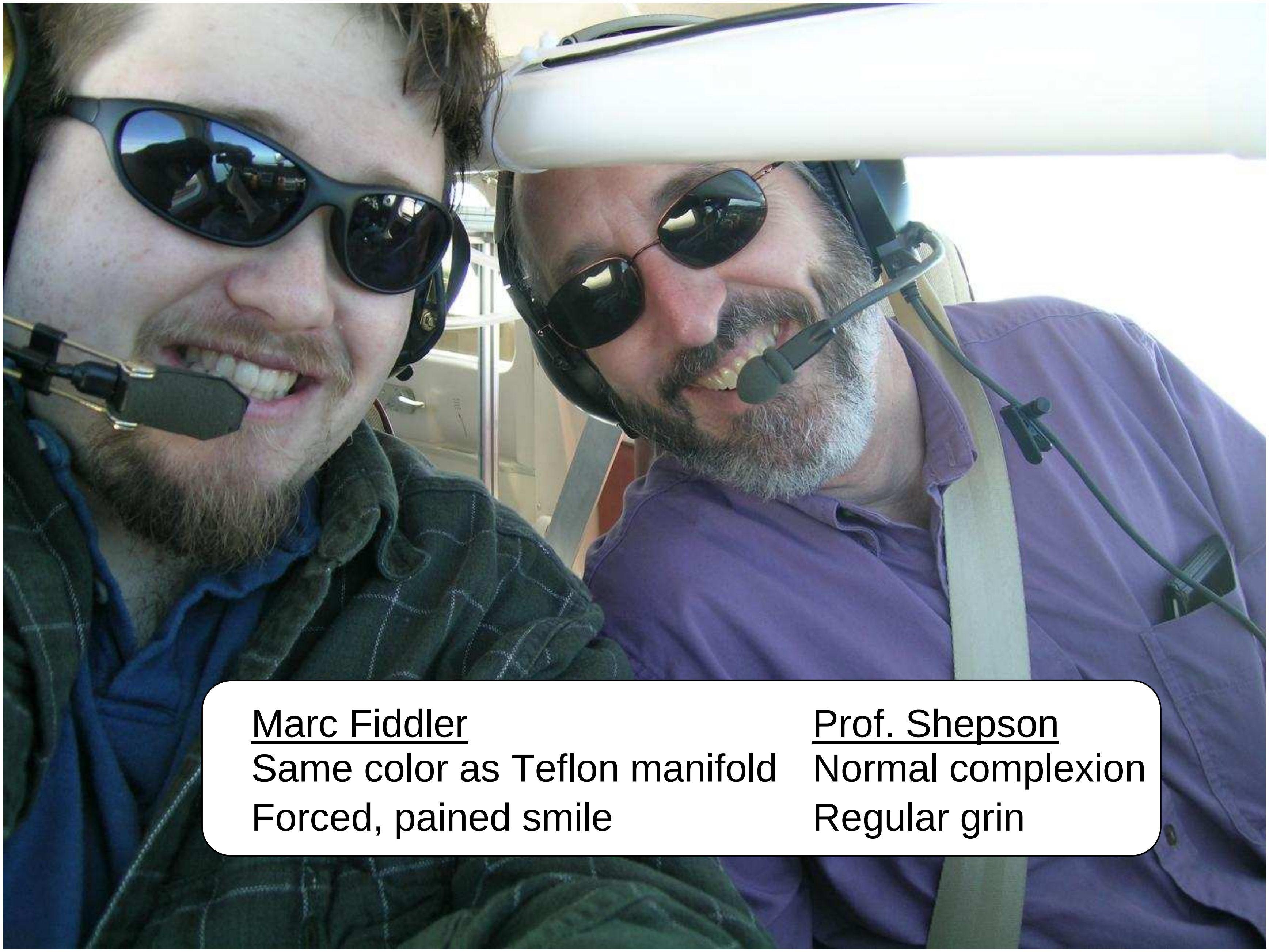
BEIS-estimated isoprene emissions

MEGAN, elevated isoprene

GOME CH_2O

Winds came from the NW this day.

The Thrill of Flight



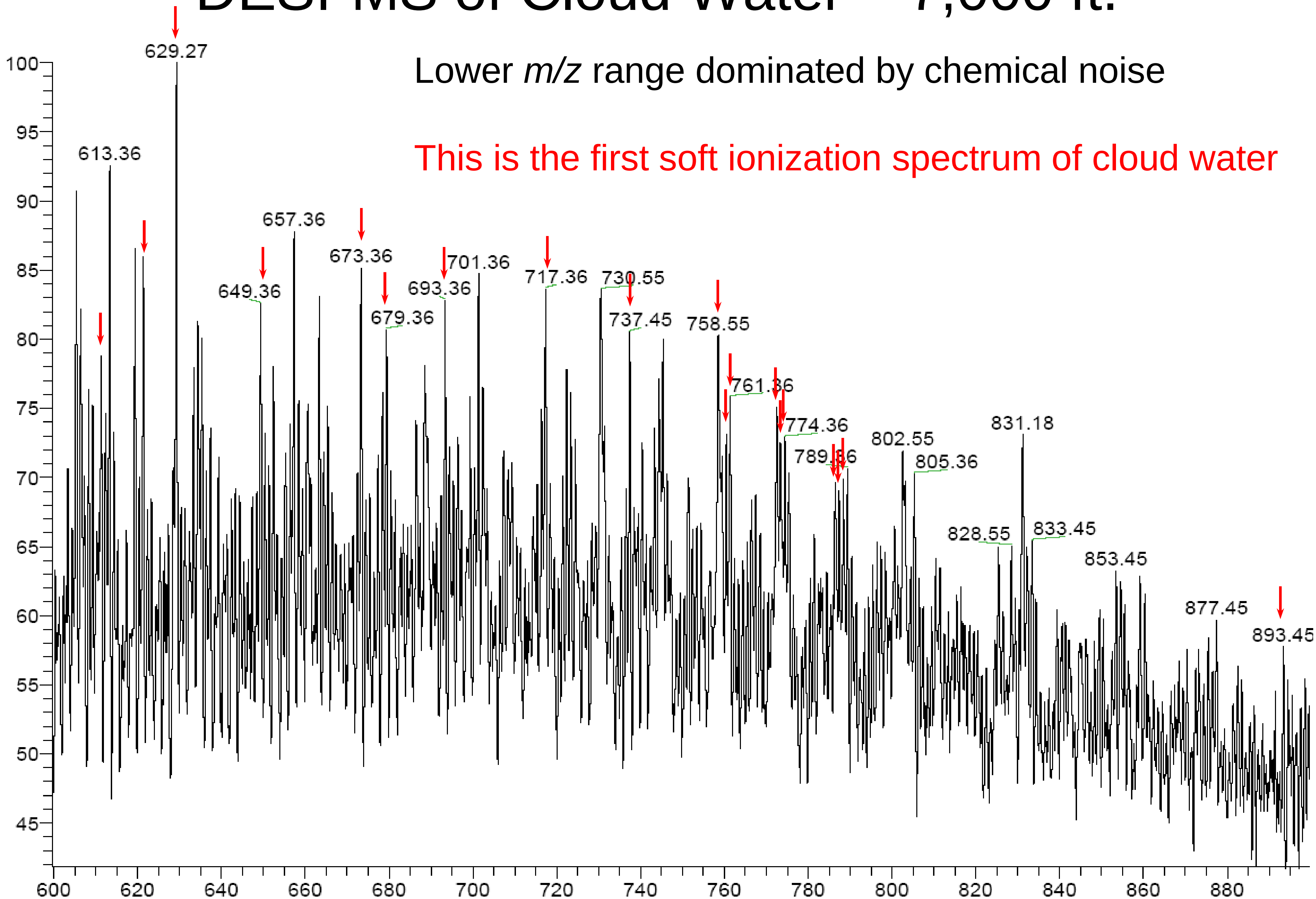
Marc Fiddler
Same color as Teflon manifold
Forced, pained smile

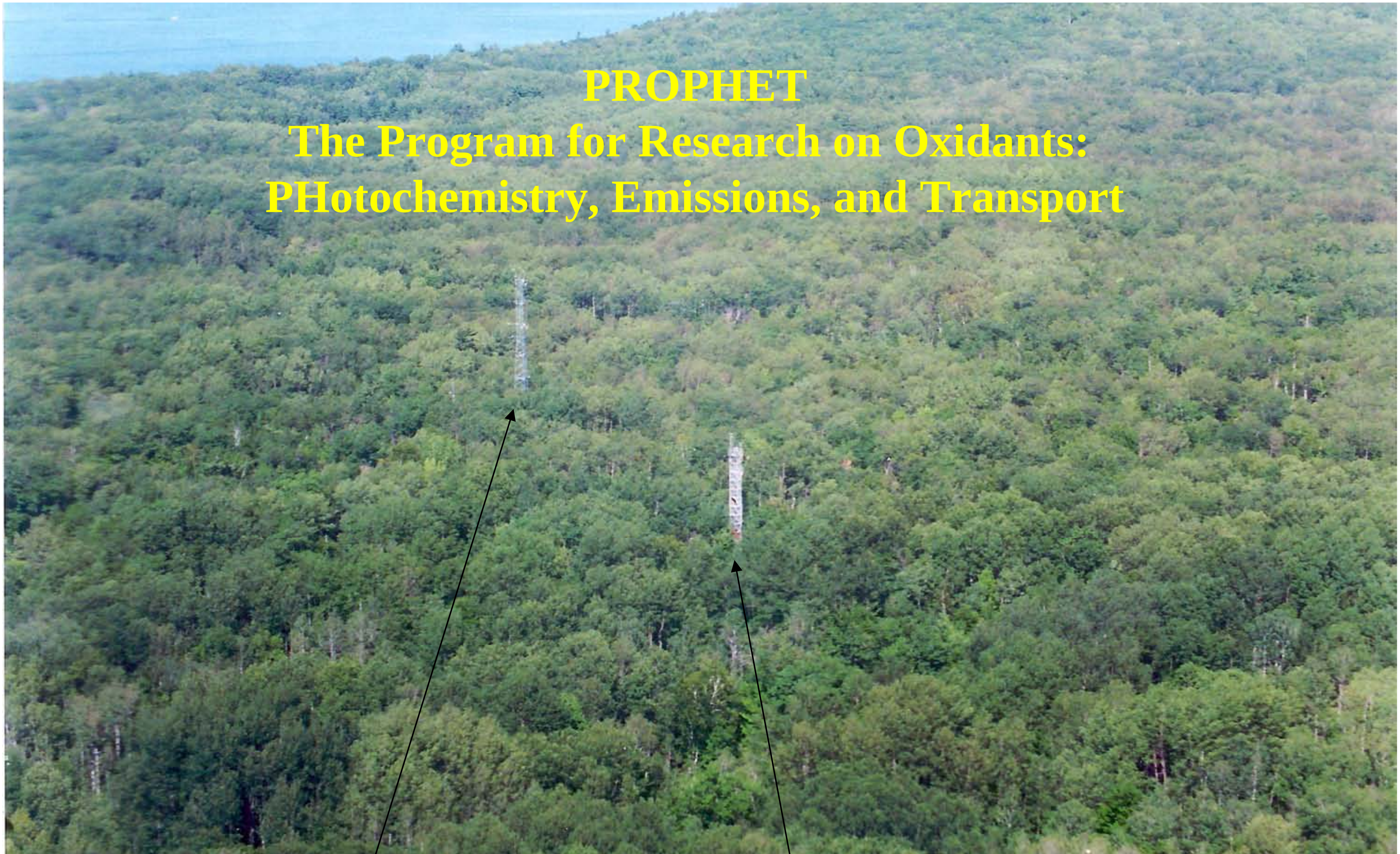
Prof. Shepson
Normal complexion
Regular grin

DESI-MS of Cloud Water – 7,000 ft.

Lower *m/z* range dominated by chemical noise

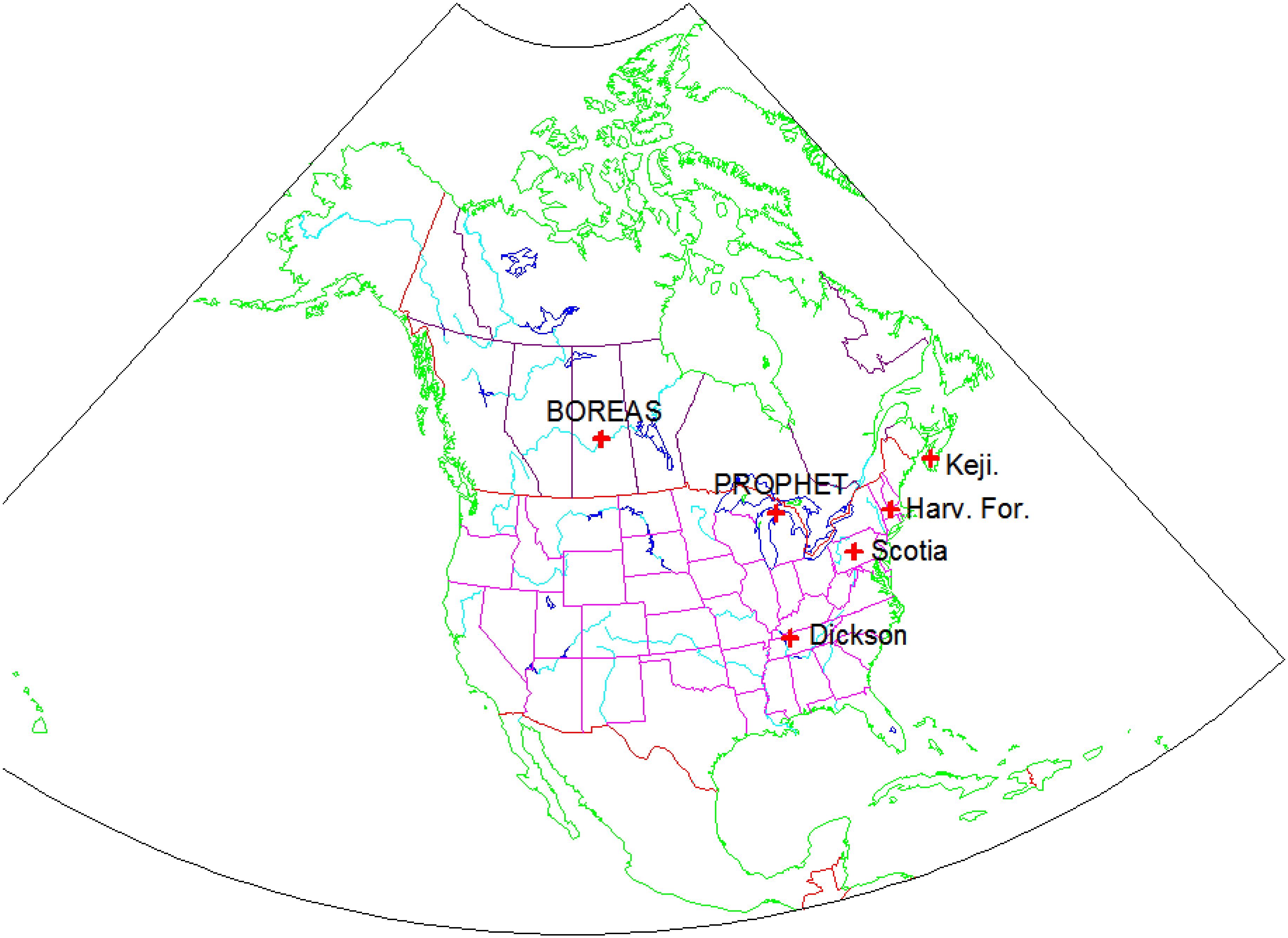
This is the first soft ionization spectrum of cloud water





Ameriflux Tower

PROPHET Tower


BOREAS
PROPHET
Keji.
Harv. For.
Scotia
Dickson

Background

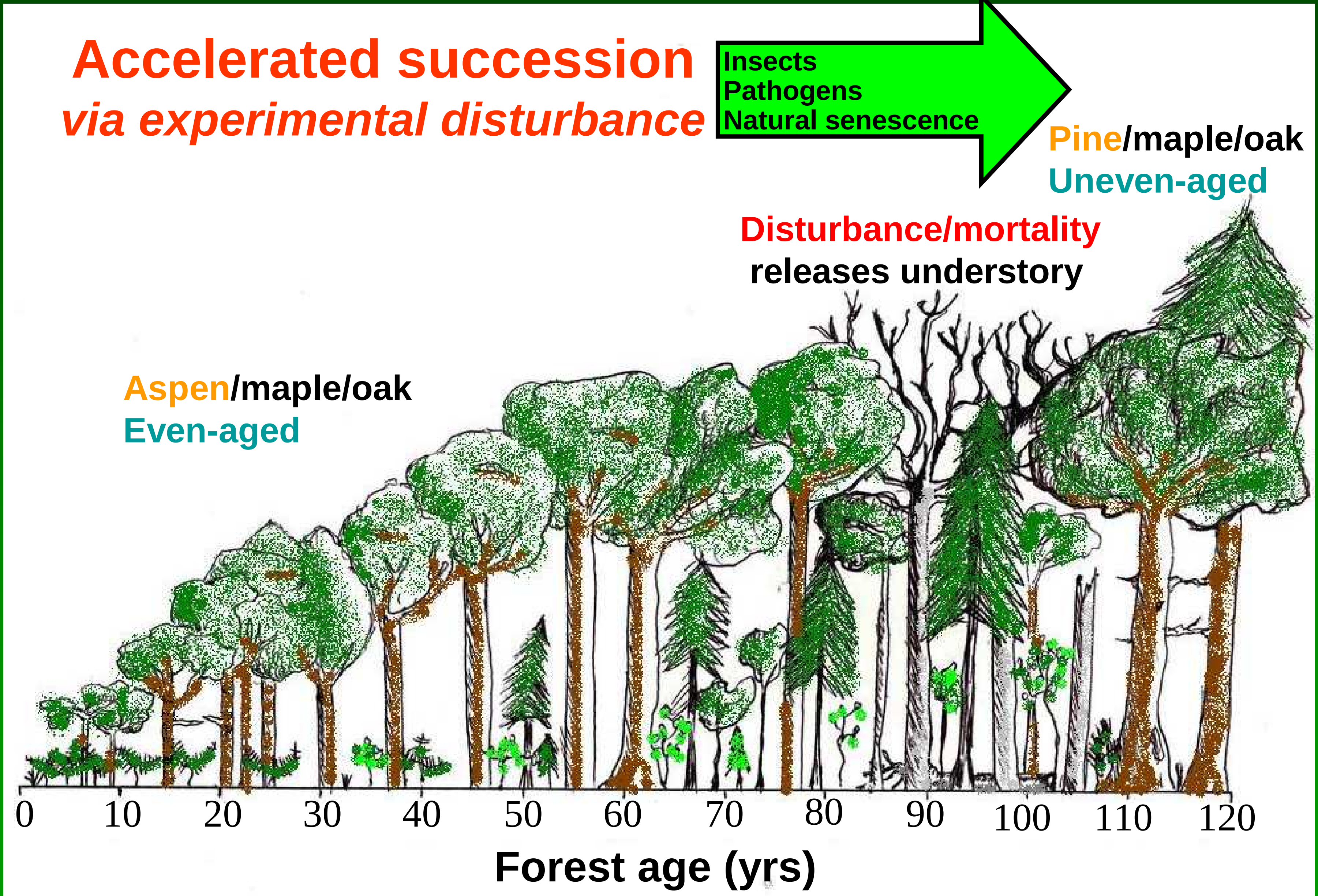
Carbon cycling in forests of the future

- 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.

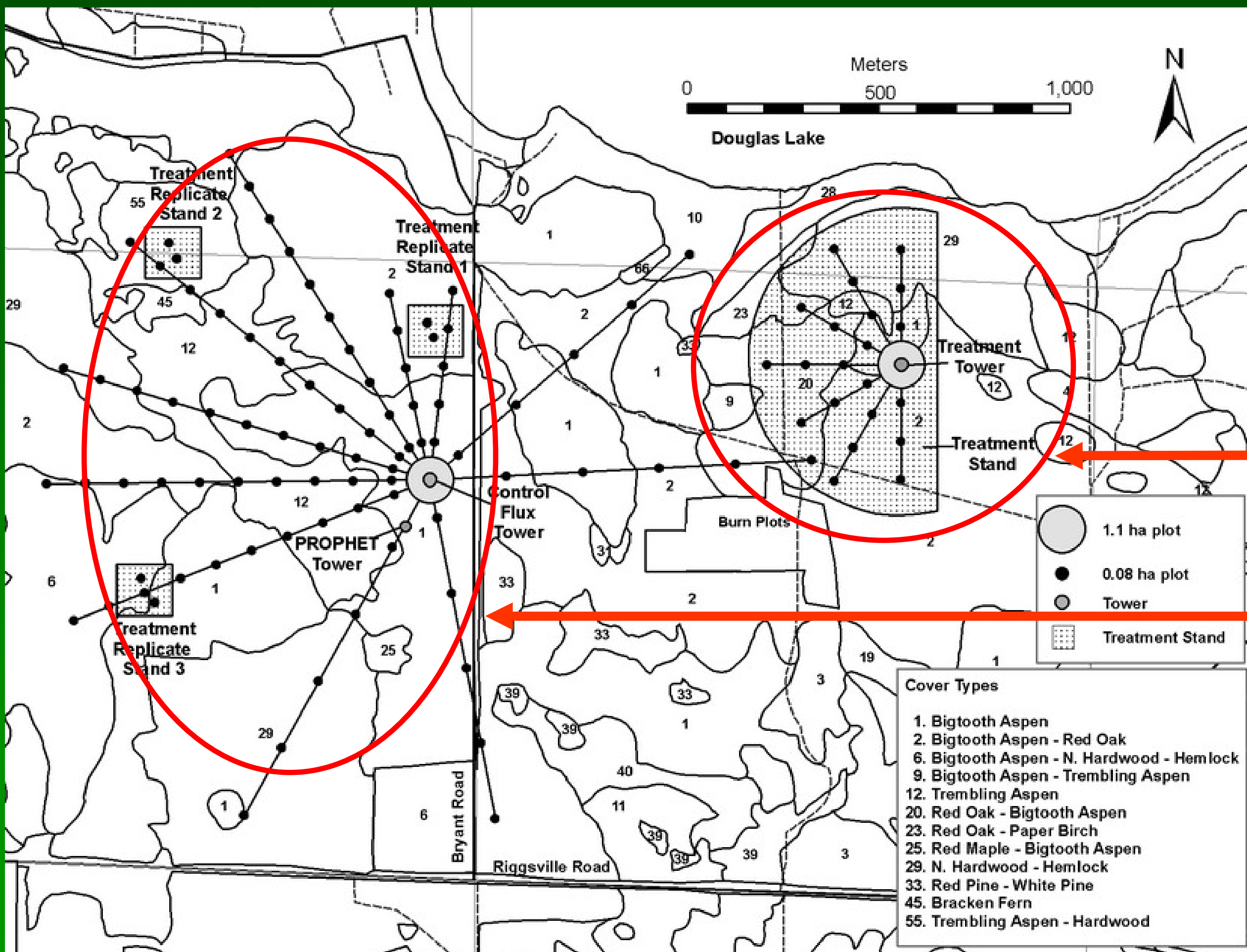
- These changes will have a profound effect on the region's carbon cycle.

Experimental treatment



Experimental design

A large-scale forest succession experiment



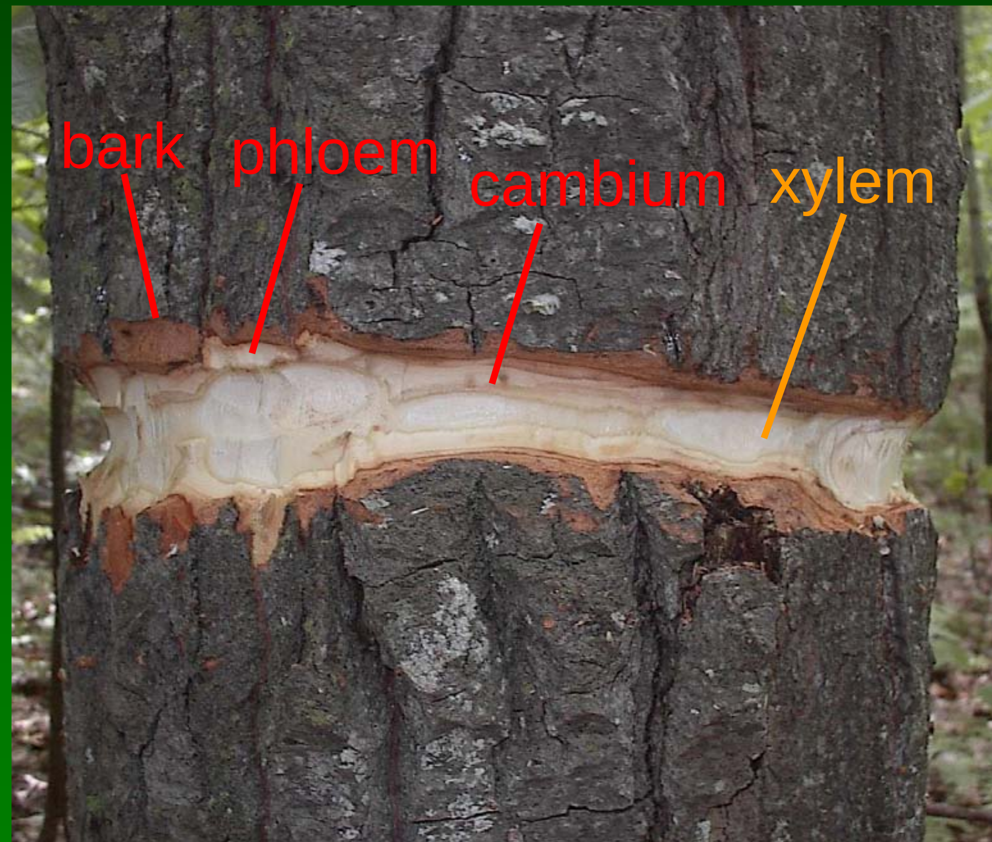
- In 2008, accelerated succession will be initiated by killing canopy aspen and birch, or ~40 % of the leaf area.

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

- CO_2 flux from Ameriflux tower

Thank you!

Input?