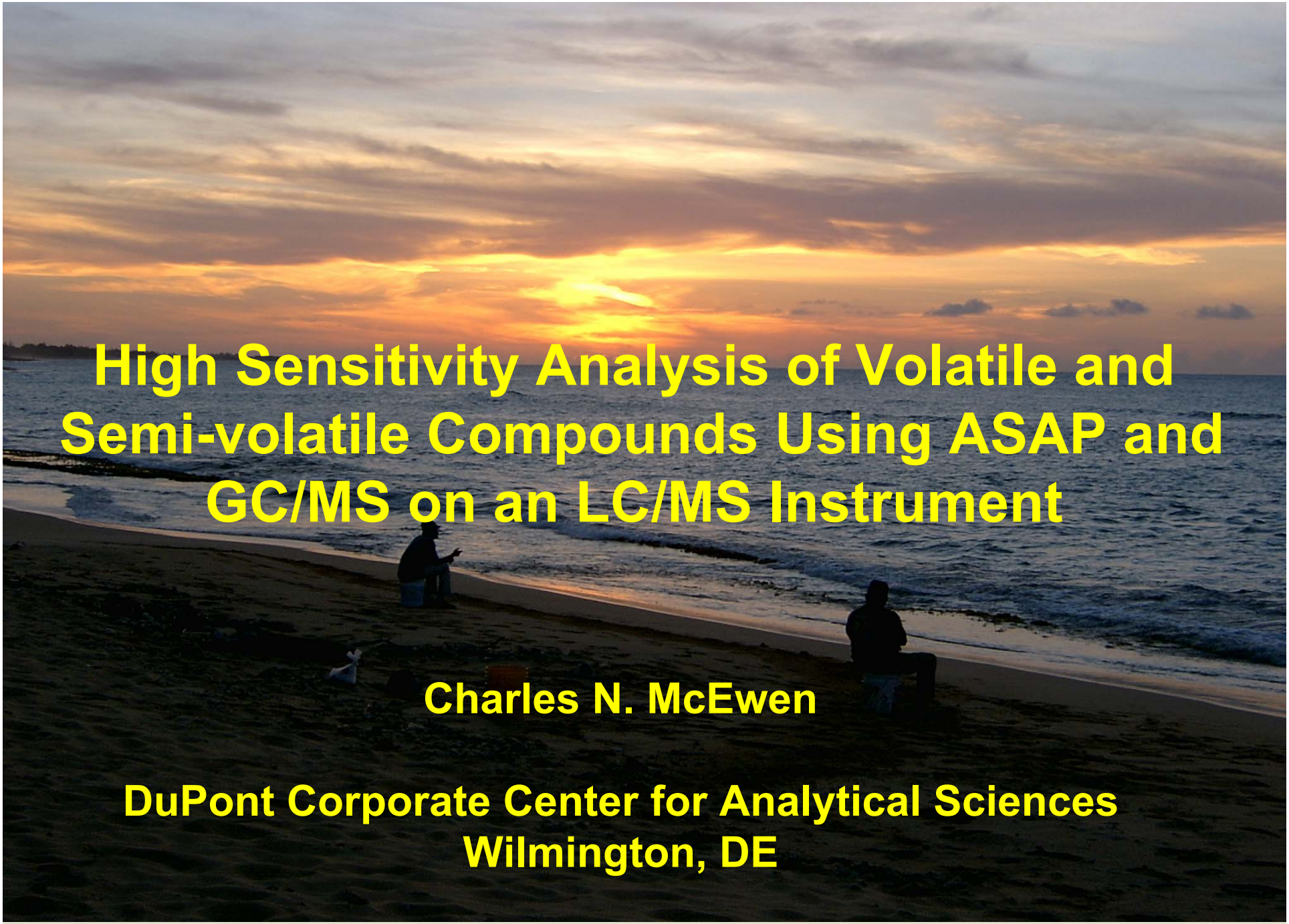


High Sensitivity Analysis of Volatile and Semi-volatile Compounds Using ASAP and GC/MS on an LC/MS Instrument

Charles N. McEwen

DuPont Corporate Center for Analytical Sciences
Wilmington, DE

Why is Solvent Bad for Ionization?

Solvent in the gas phase limits ionization to molecules more basic than the solvent

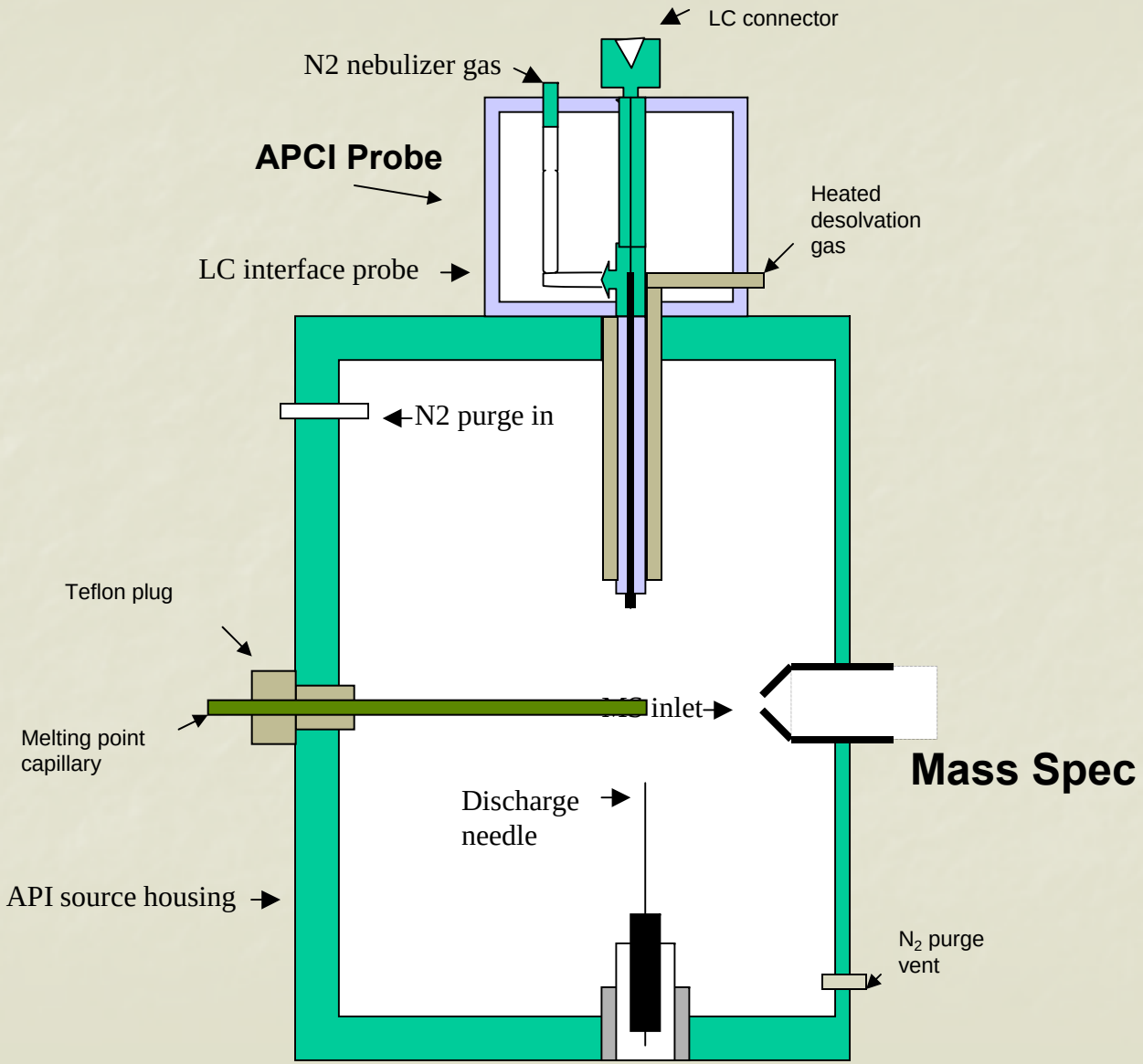
Exception is photoionization (not acid/base ionization) but still mediated by solvent

Removing solvent and water vapor from ionization region increases types of compounds that can be ionized at atmospheric pressure

ASAP

- Atmospheric-pressure Solids Analysis Probe
- A rapid method for analysis of volatile and semivolatile compounds in solids, liquids, polymers, and biological tissue

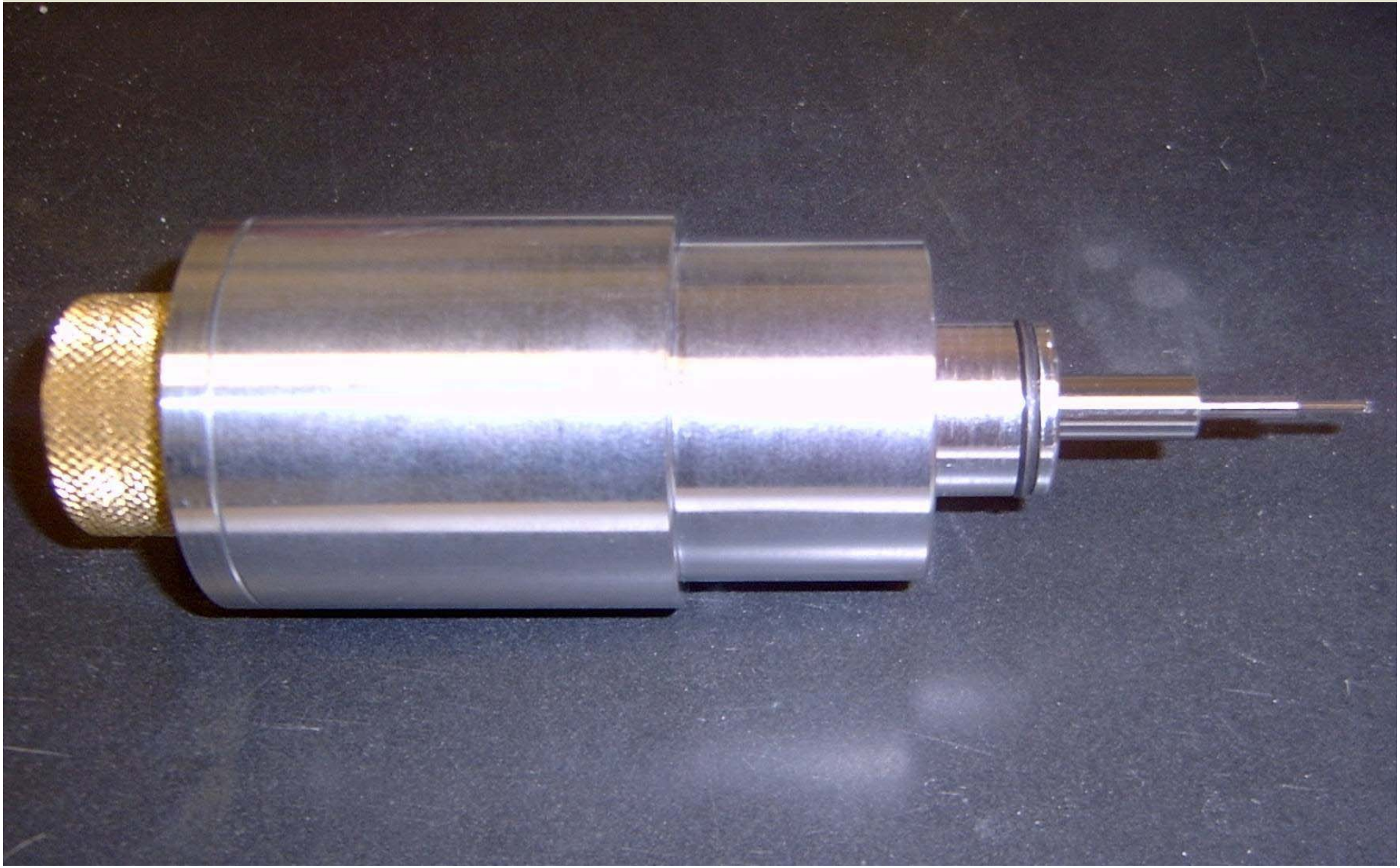
ASAP Ion Source

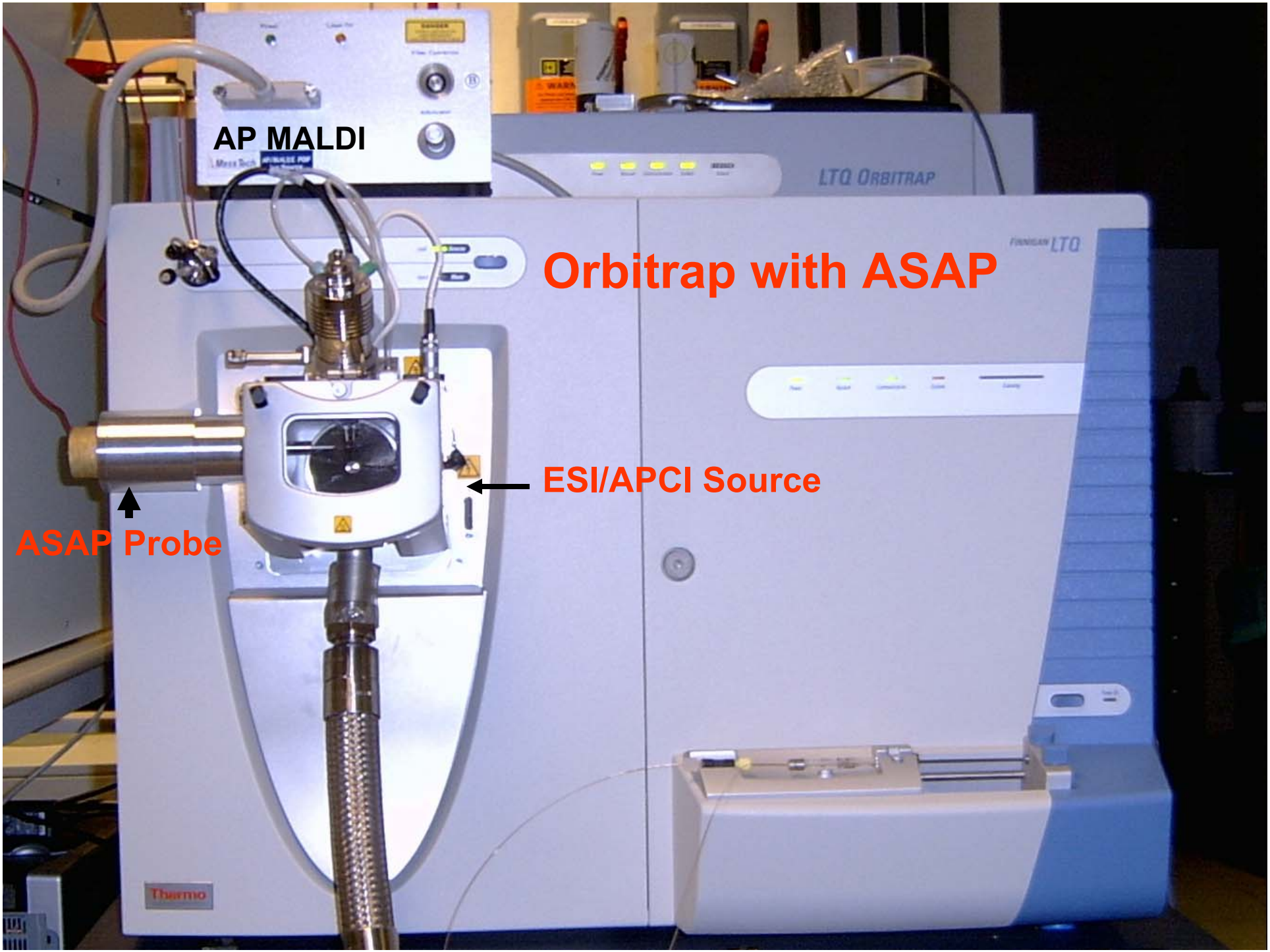


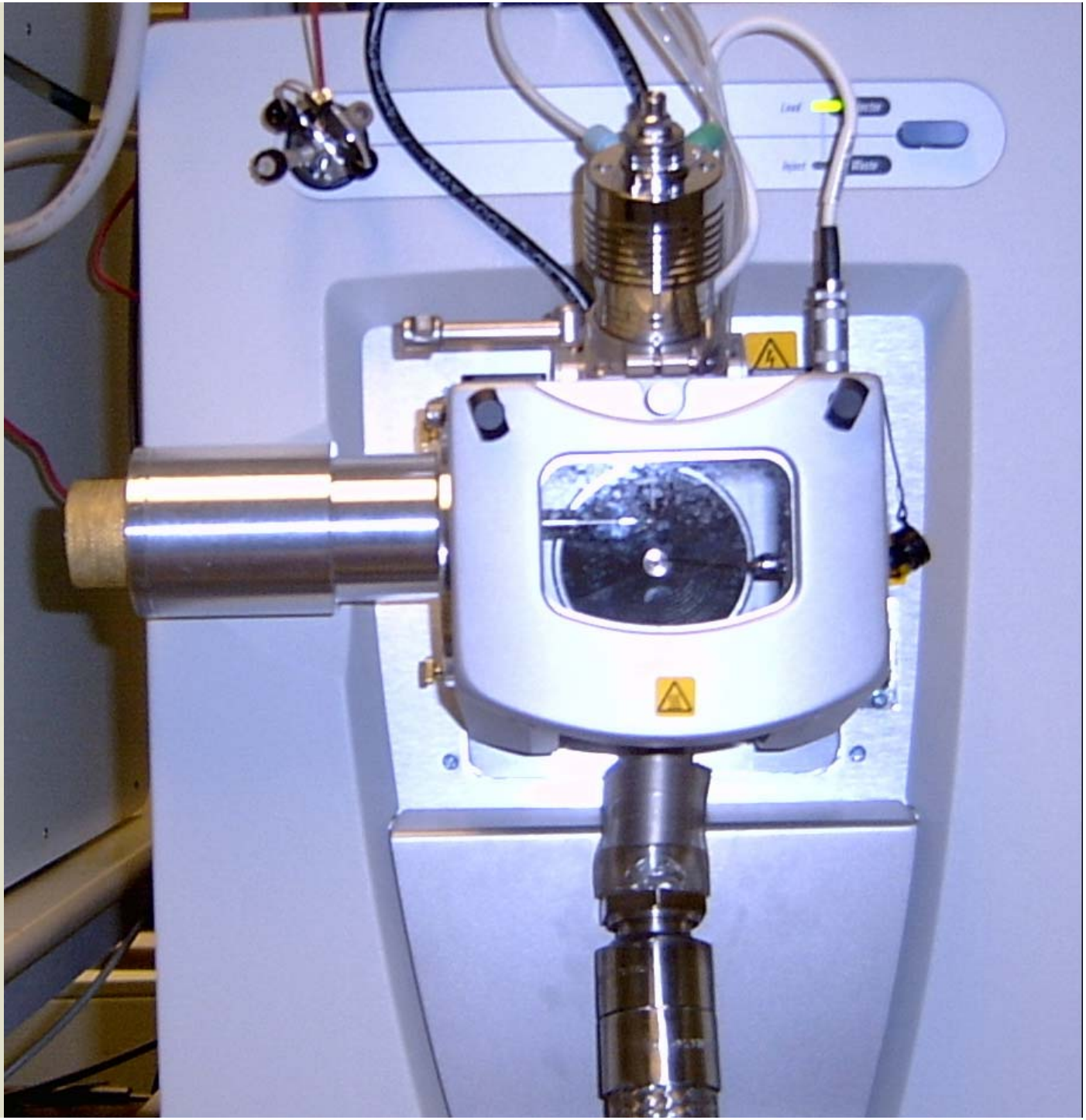
Safety First

- ASAP vaporizes materials
- The ion source should be sealed during analysis (Just as ESI and APCI) and
- Vented to a hood

ASAP Probe




AP MALDI
LTQ ORBITRAP
FINNIGAN LTQ
Orbitrap with ASAP
ESI/APCI Source
ASAP Probe
Thermo



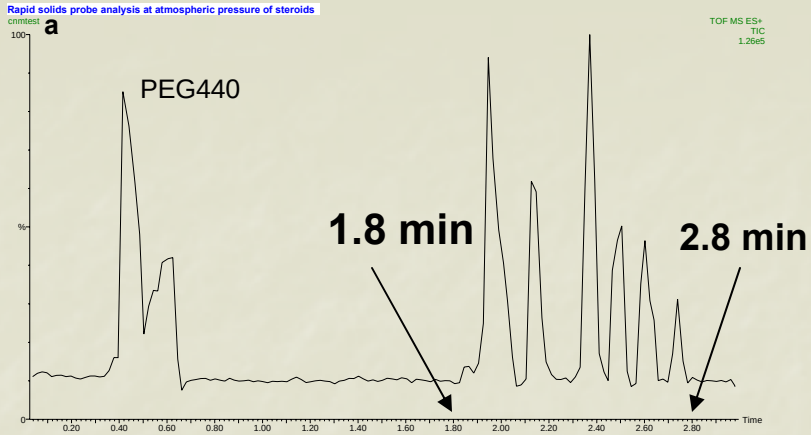
ASAP Examples

- Solids probe replacement
- Accurate mass of mixtures
- Analysis of polymer additives
- Analysis of drugs (or explosives)
- Analysis of biological tissue

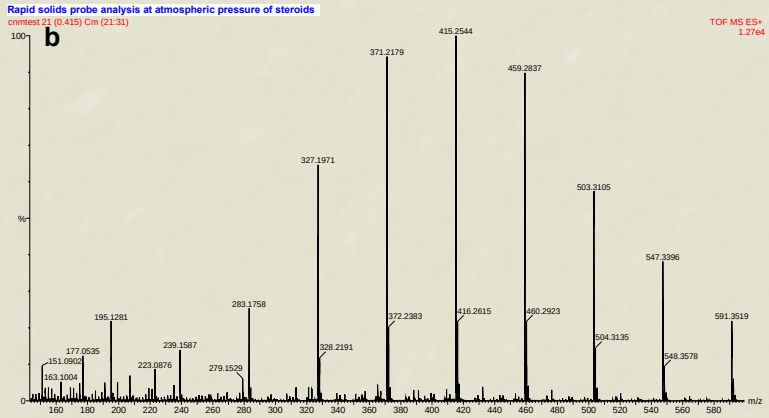
Replacement for Solids Probe

- No vacuum lock
- Fast analysis
- MH^+ ions with minimal fragmentation
- Accurate mass
- MS/MS for structural information

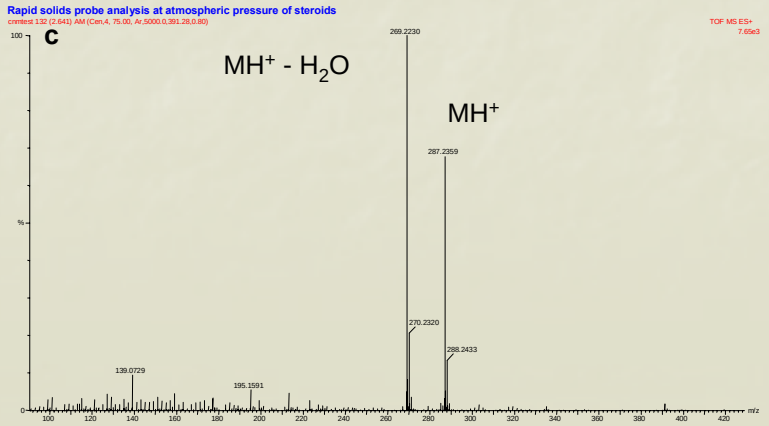
ASAP on QTof Showing Instrument Calibration and 6 Steroid Samples in 3 min.



Total Ion Current Chromatogram of ASAP analysis of 6 steroids



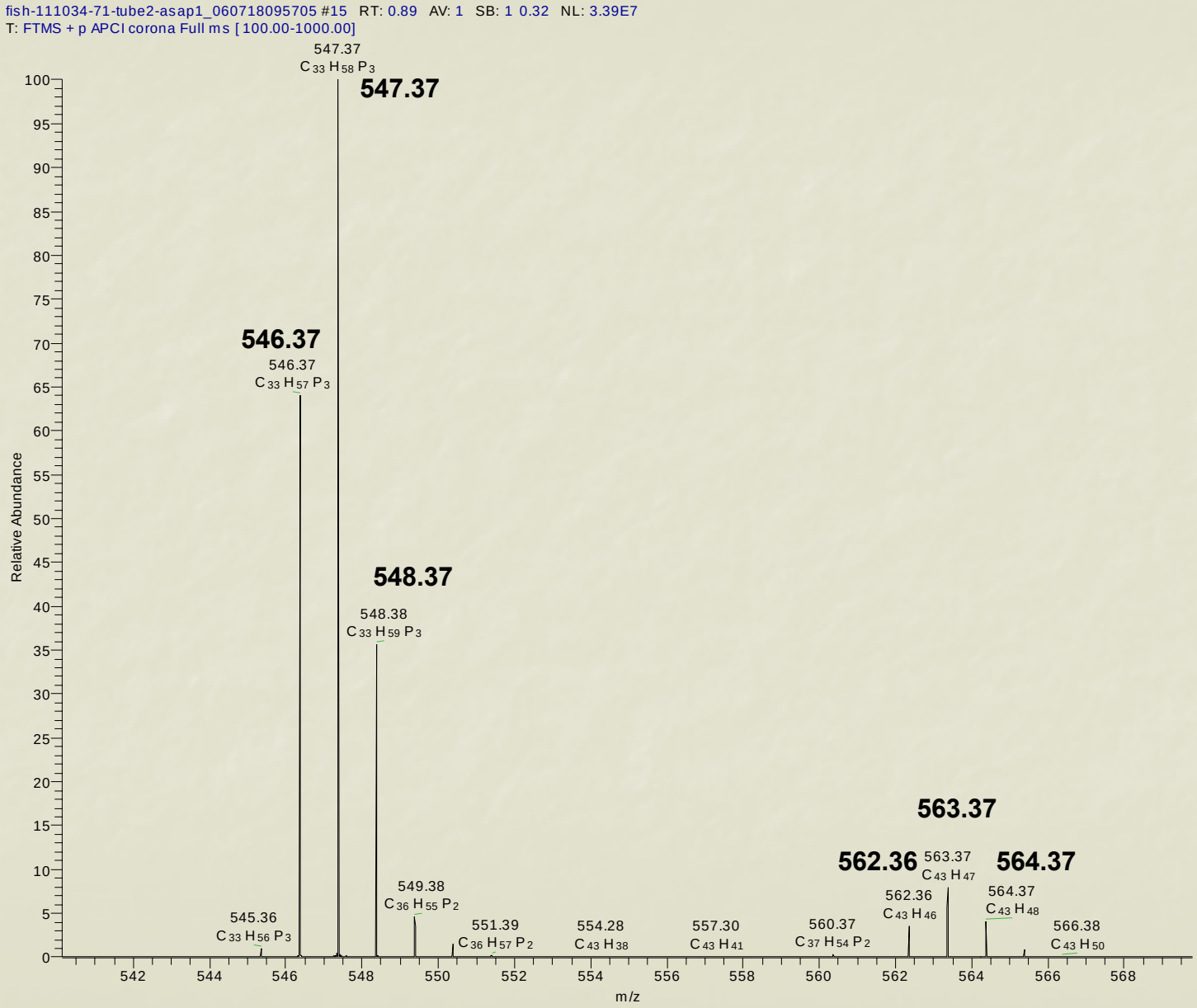
PEG for Instrument Calibration



Atmospheric Pressure Mass Spectrum of Steroid

Anal. Chem., 2005, 77,7826-7831

Solids Probe Sample for Accurate Mass

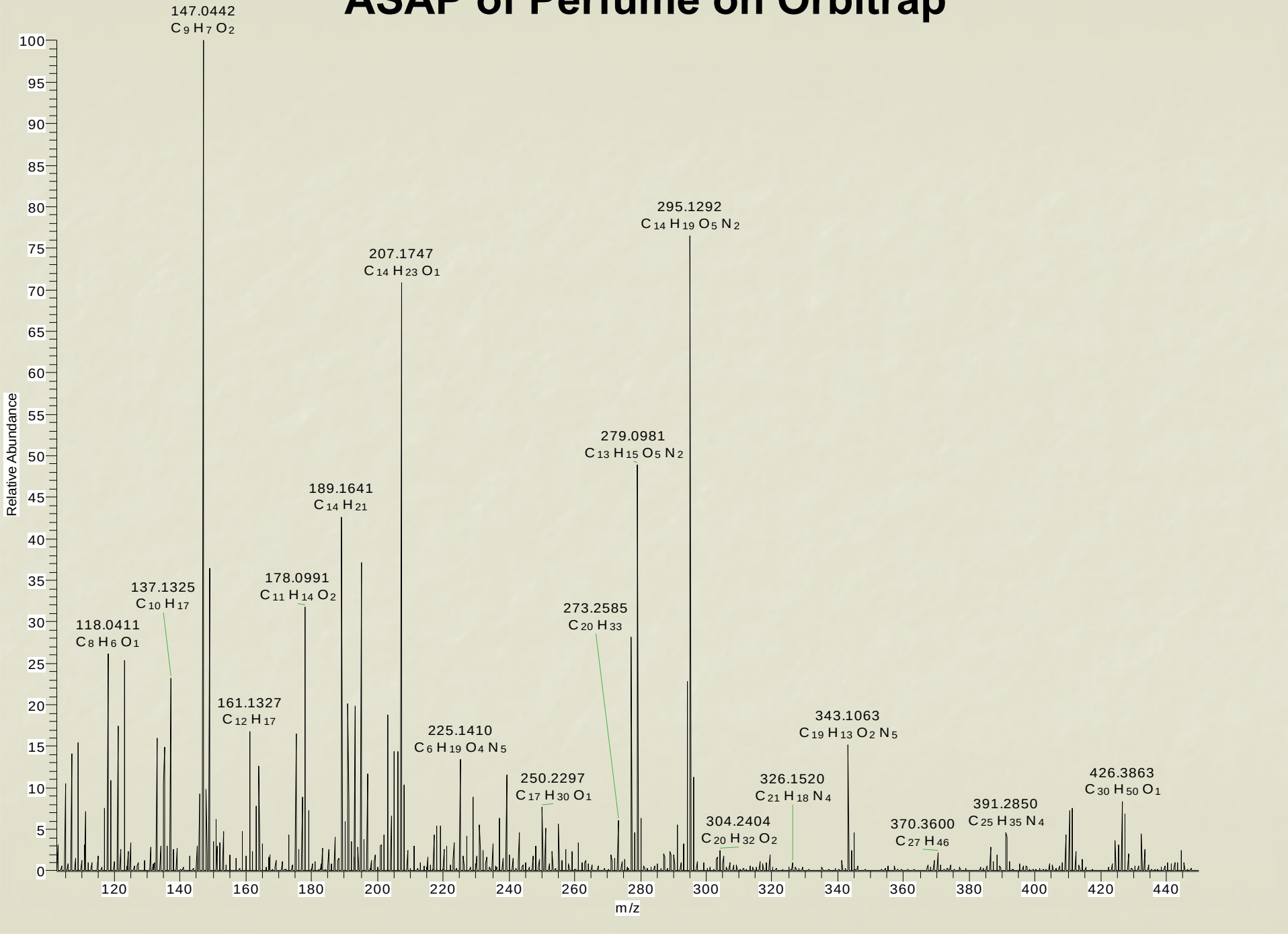


Accurate Mass Measurement for GC/MS

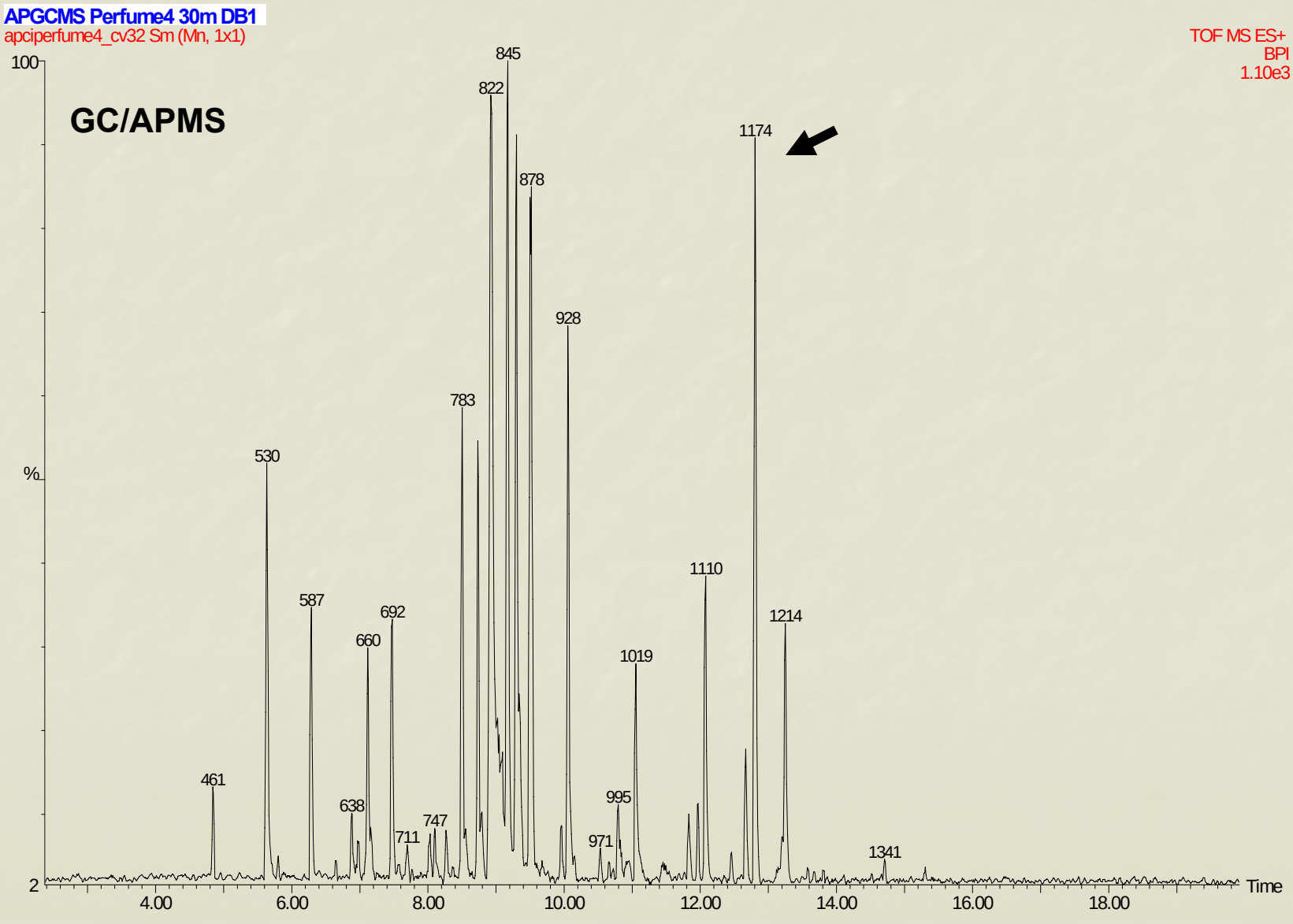
- GC/MS using low performance MS
- ASAP on high performance MS for elemental compositions
- High resolution required
- MS/MS with accurate mass

PrefumeX_051219134717 #8-18 RT: 0.18-0.29 AV: 11 NL: 2.03E7
T: FTMS + p APCI corona Full ms [100.00-800.00]

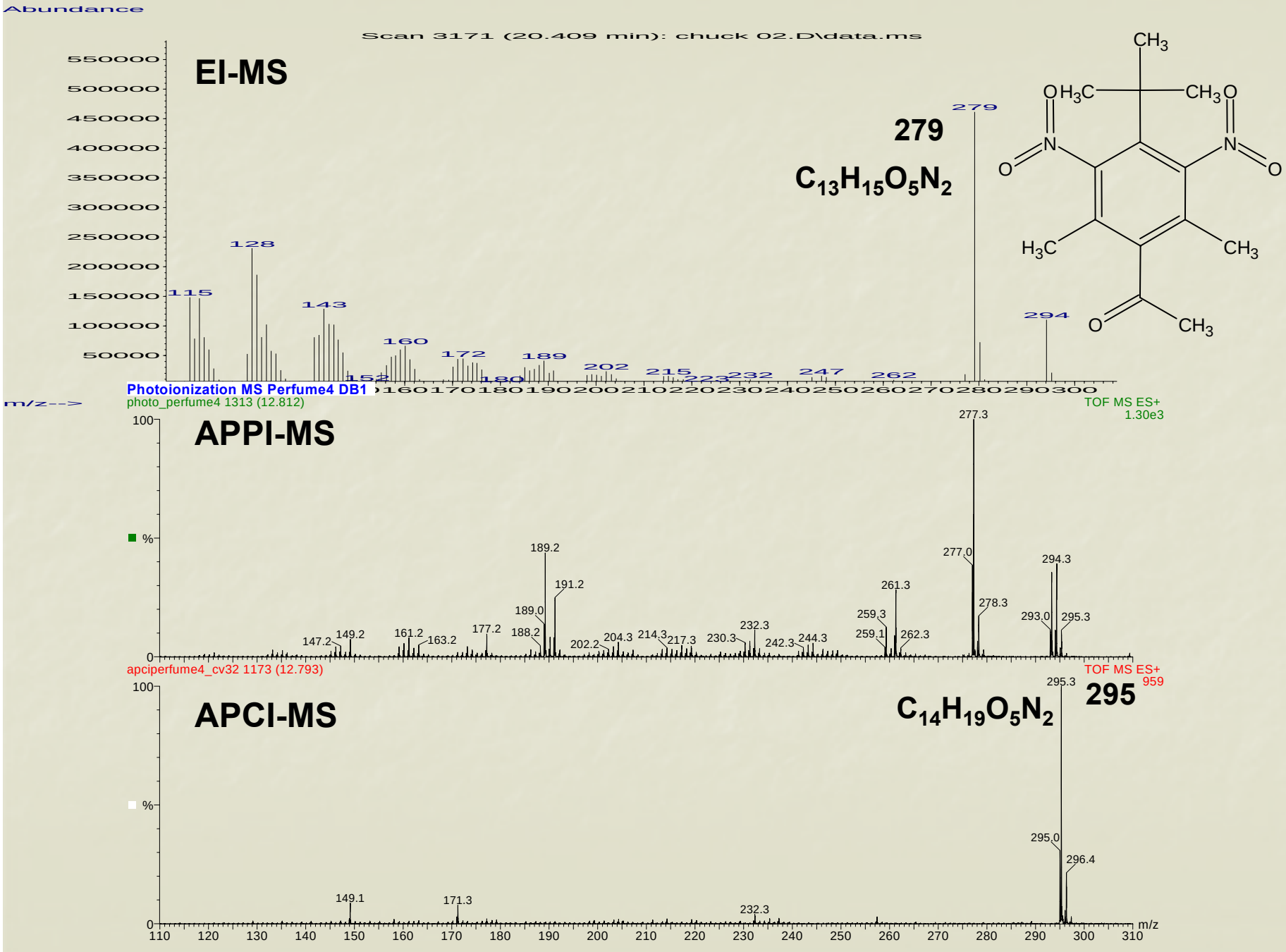
ASAP of Perfume on Orbitrap

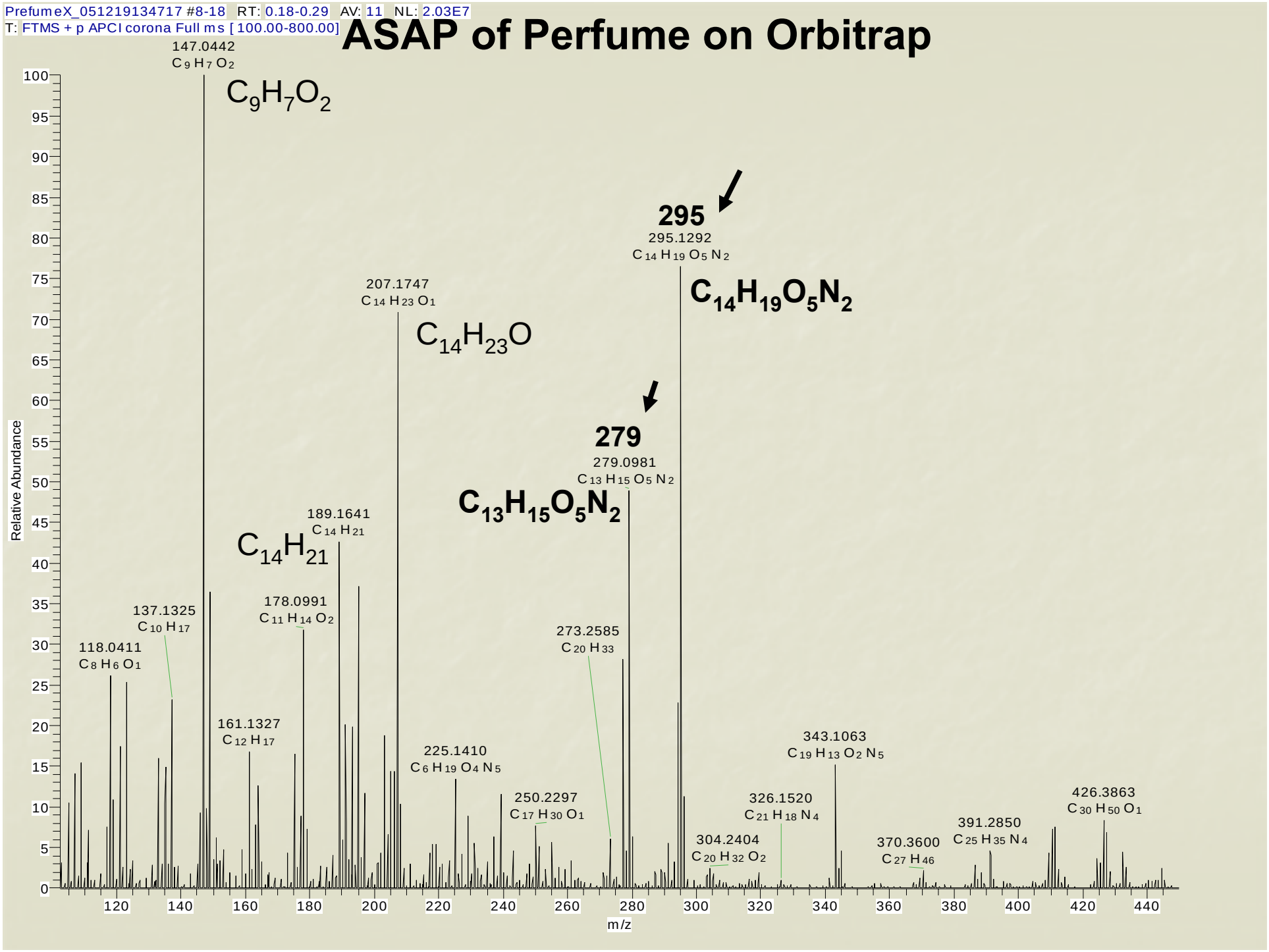


Perfume Analysis

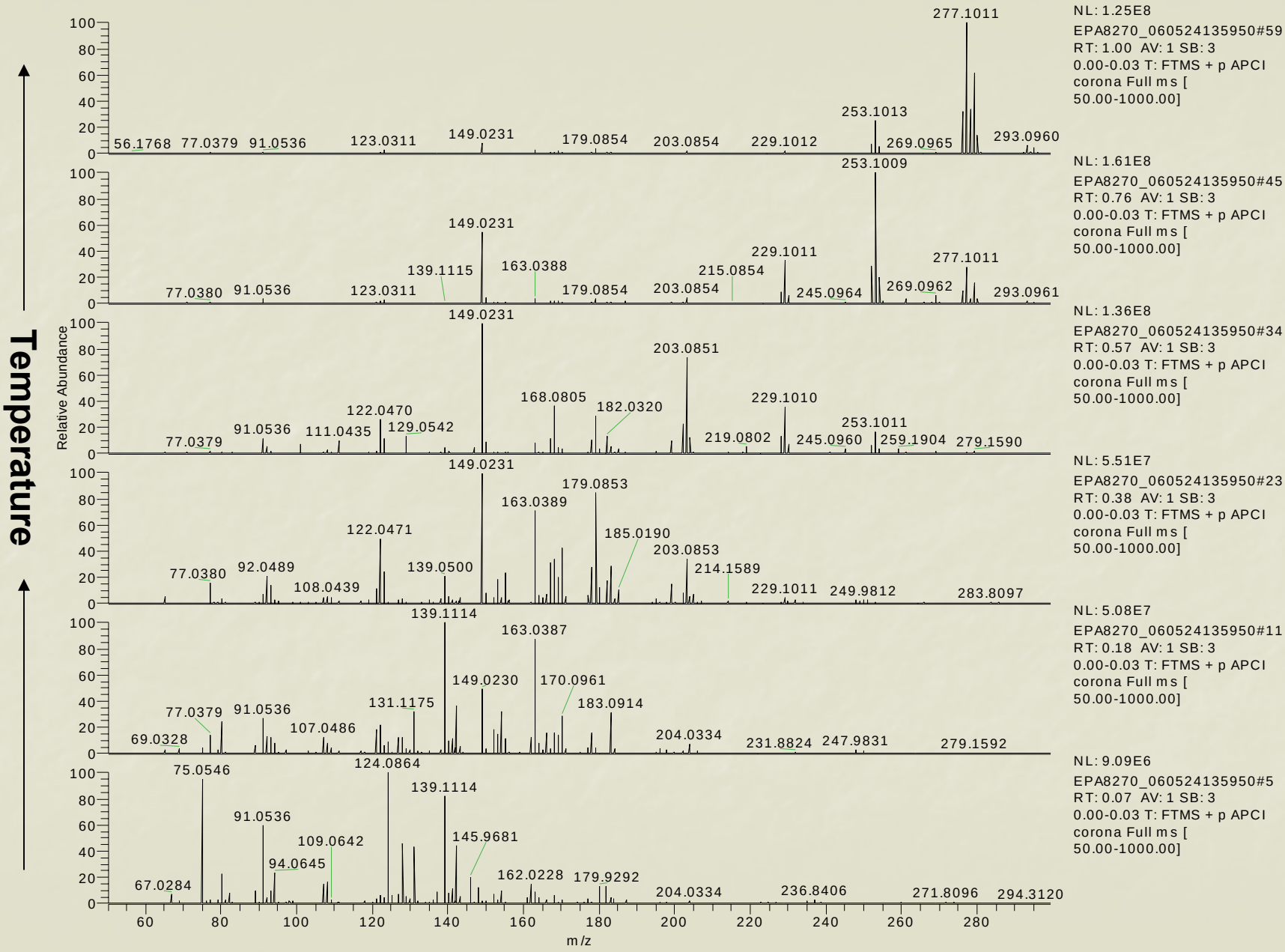


GC/MS of Musk Ketone Using EI, APPI, and APCI

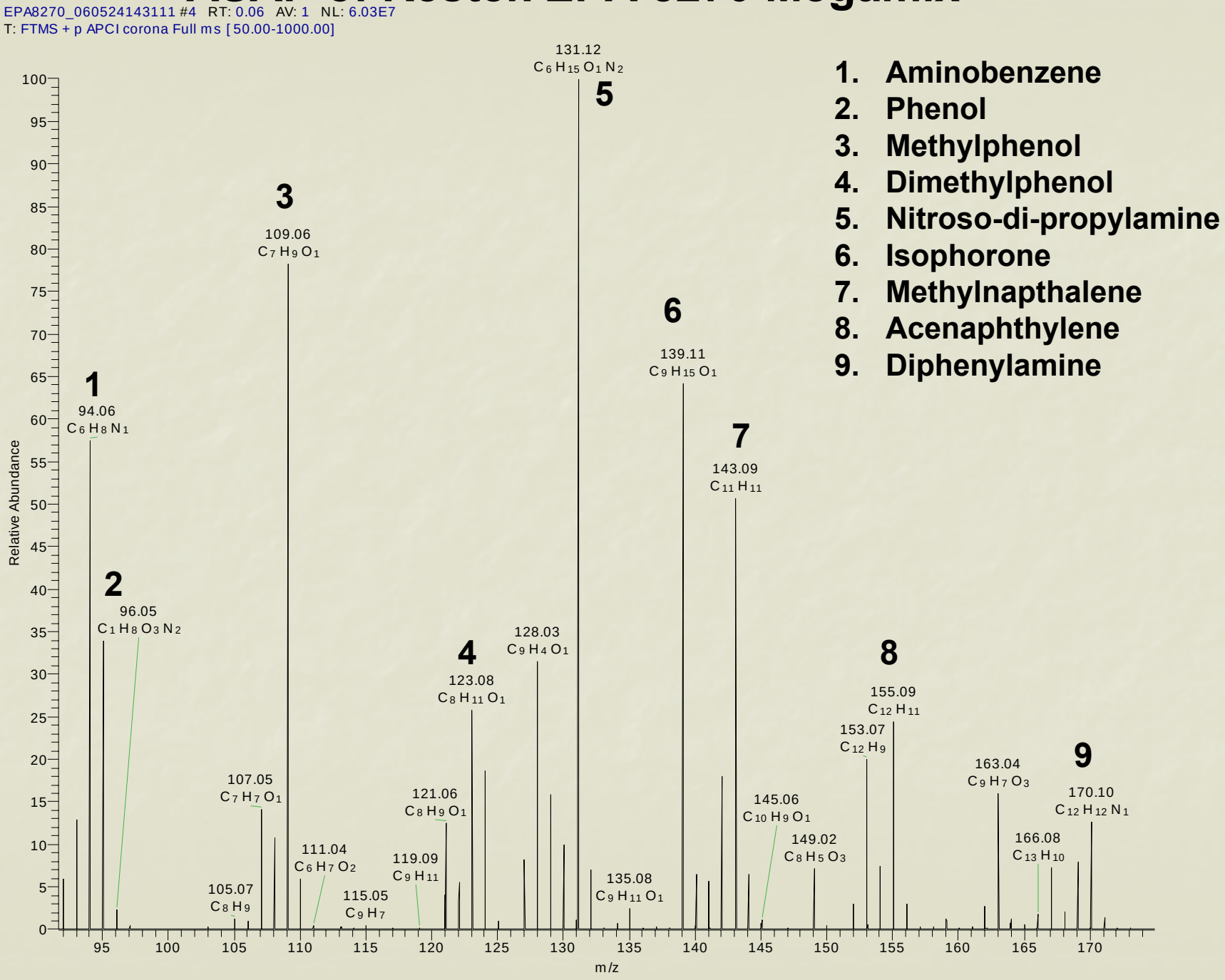



PrefumeX_051219134717 #8-18 RT: 0.18-0.29 AV: 11 NL: 2.03E7
T: FTMS + p APCI corona Full ms [100.00-800.00]
ASAP of Perfume on Orbitrap
147.0442
C9 H7 O2
C9H7O2
295
295.1292
C14 H19 O5 N2
C14H19O5N2
207.1747
C14 H23 O1
C14H23O
279
279.0981
C13 H15 O5 N2
C13H15O5N2
189.1641
C14 H21
C14H21
178.0991
C11 H14 O2
137.1325
C10 H17
118.0411
C8 H6 O1
161.1327
C12 H17
225.1410
C6 H19 O4 N5
250.2297
C17 H30 O1
273.2585
C20 H33
304.2404
C20 H32 O2
326.1520
C21 H18 N4
343.1063
C19 H13 O2 N5
370.3600
C27 H46
391.2850
C25 H35 N4
426.3863
C30 H50 O1
Relative Abundance
m/z

EPA 8270 Megamix by ASAP as a Function of Time/Temperature



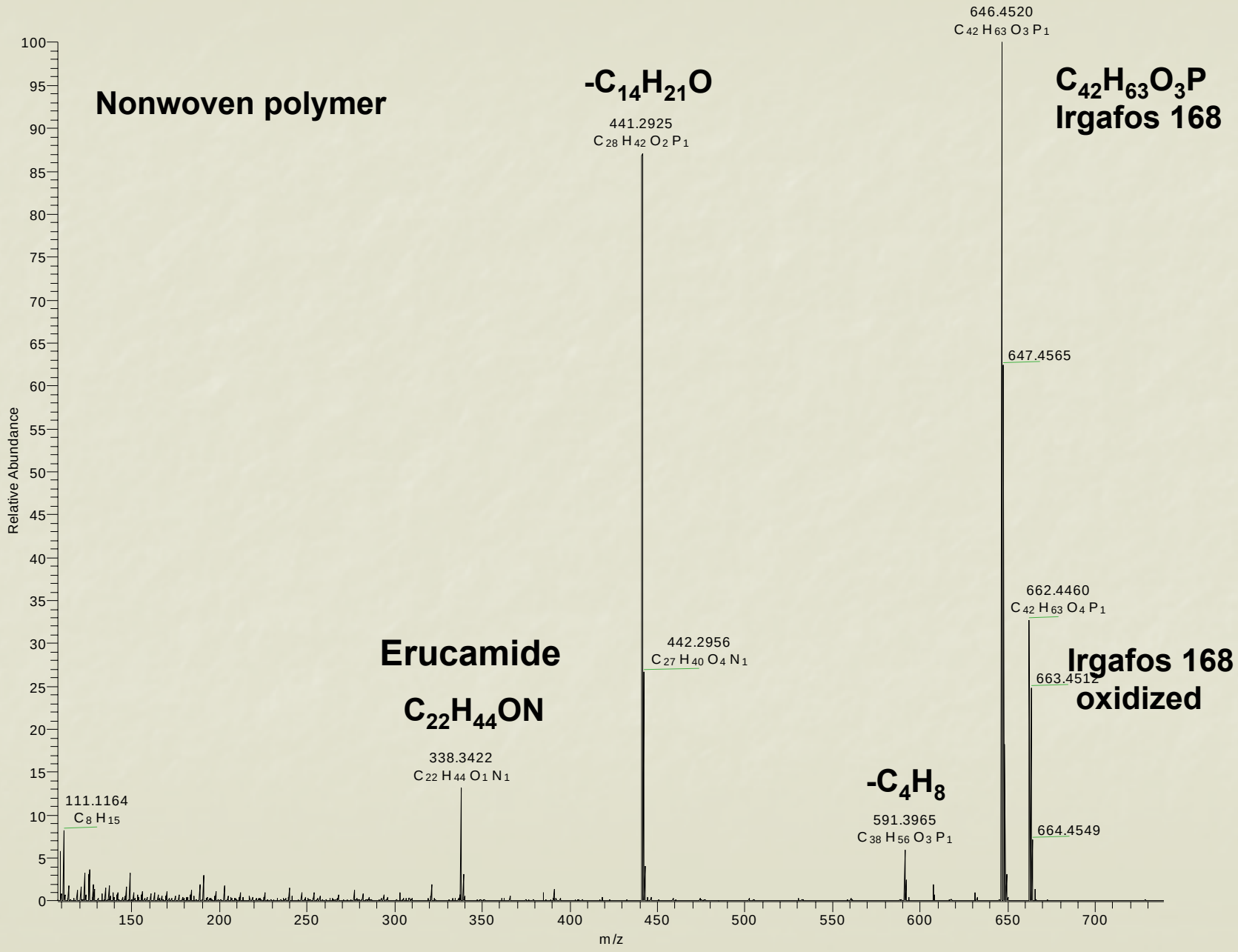
ASAP of Restek EPA 8270 Megamix



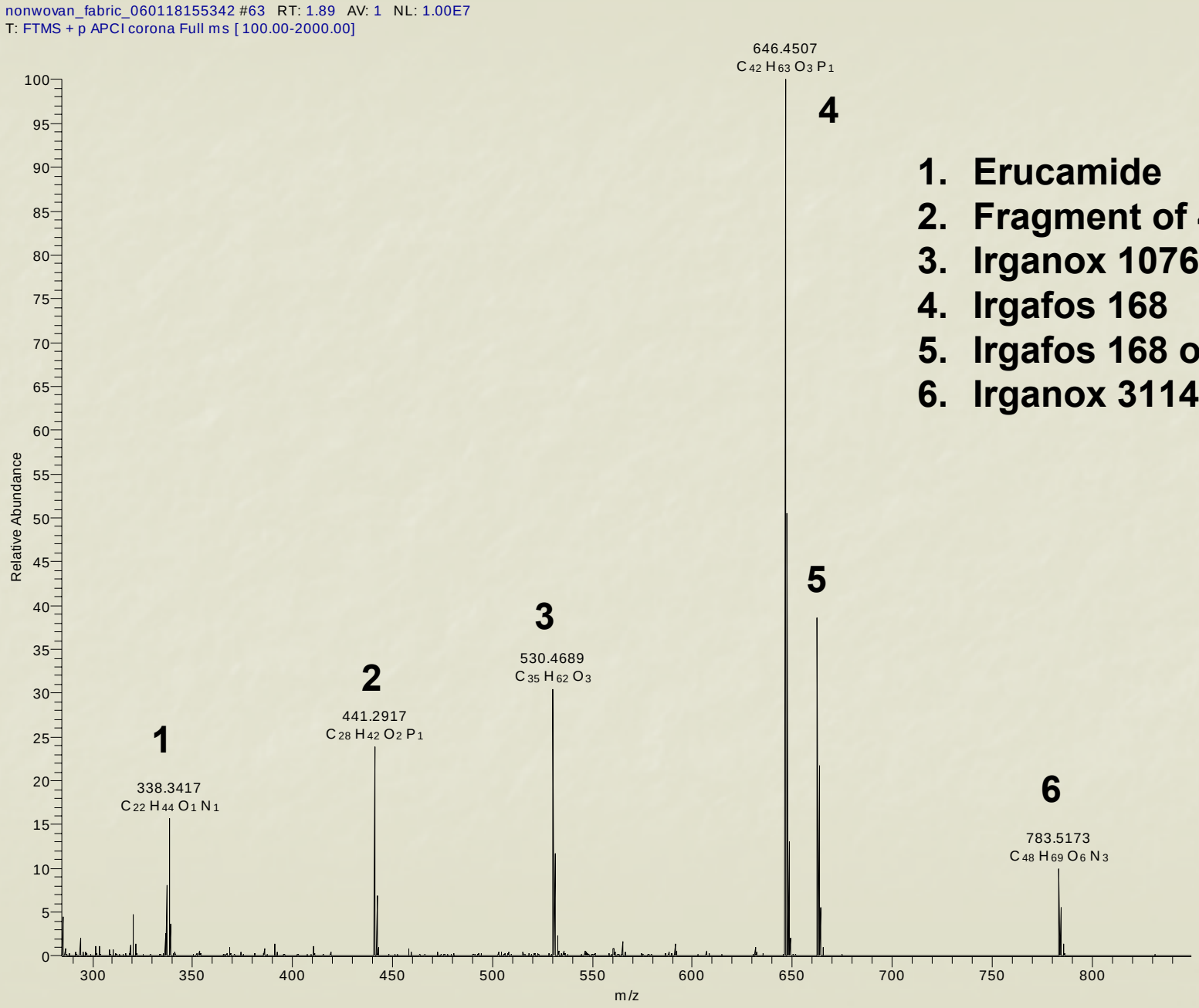
Polymer Additive Analysis

- Obtain additive elemental compositions in seconds
- No sample extraction required
- MS/MS for confirmation

ASAP of Additives in Polymer



ASAP of Nonwoven Fiber

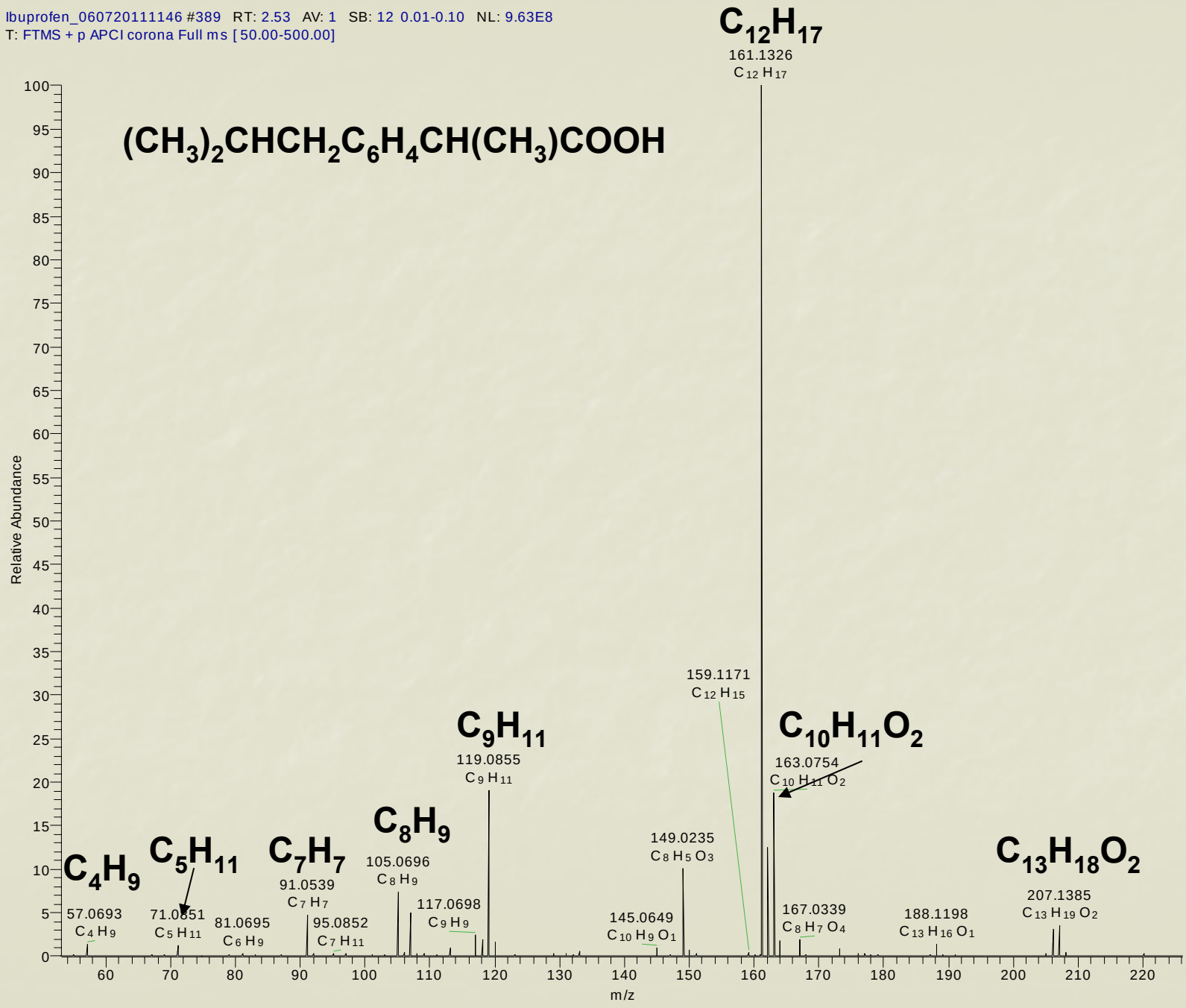


1. Erucamide
2. Fragment of 4
3. Irganox 1076
4. Irgafos 168
5. Irgafos 168 oxidized
6. Irganox 3114

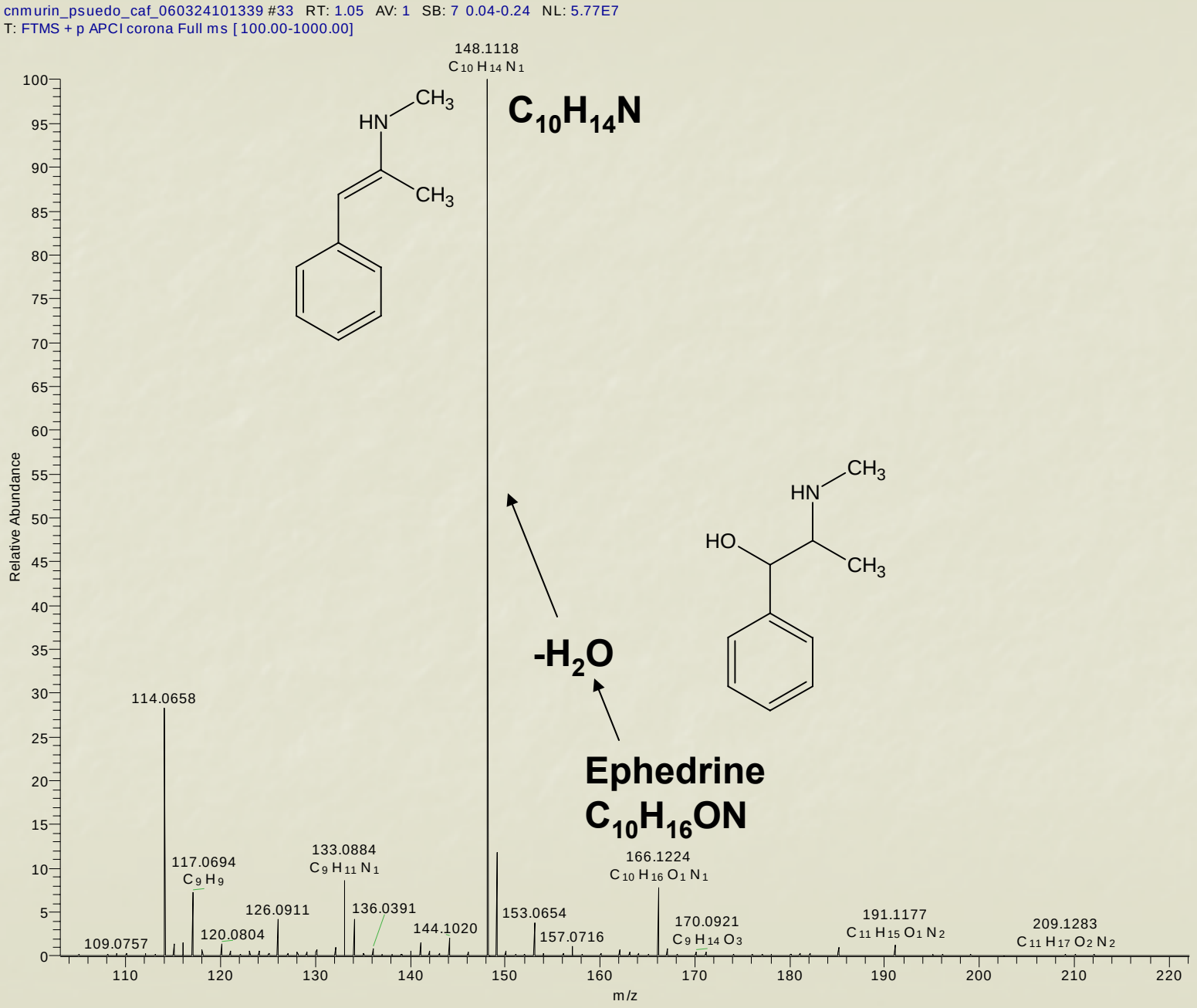
ASAP of Drugs

- On objects
- In urine or spit without sample preparation
- Accurate mass
- MS/MS

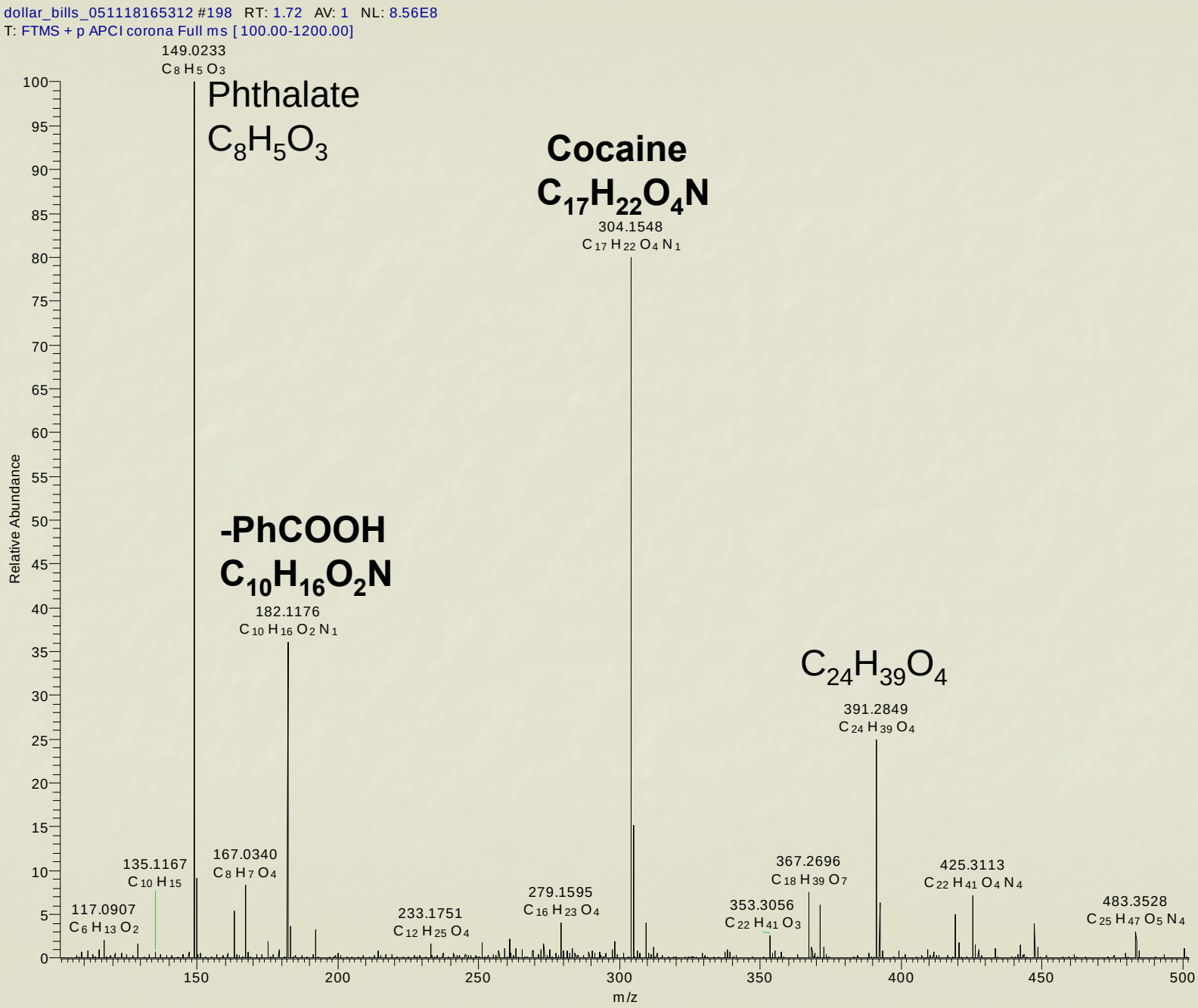
ASAP of Ibuprofen Tablet



Direct ASAP Analysis of Urine Sample 9 hrs After 12 hr Sedafed®



The Famous Cocaine on a Dollar Bill

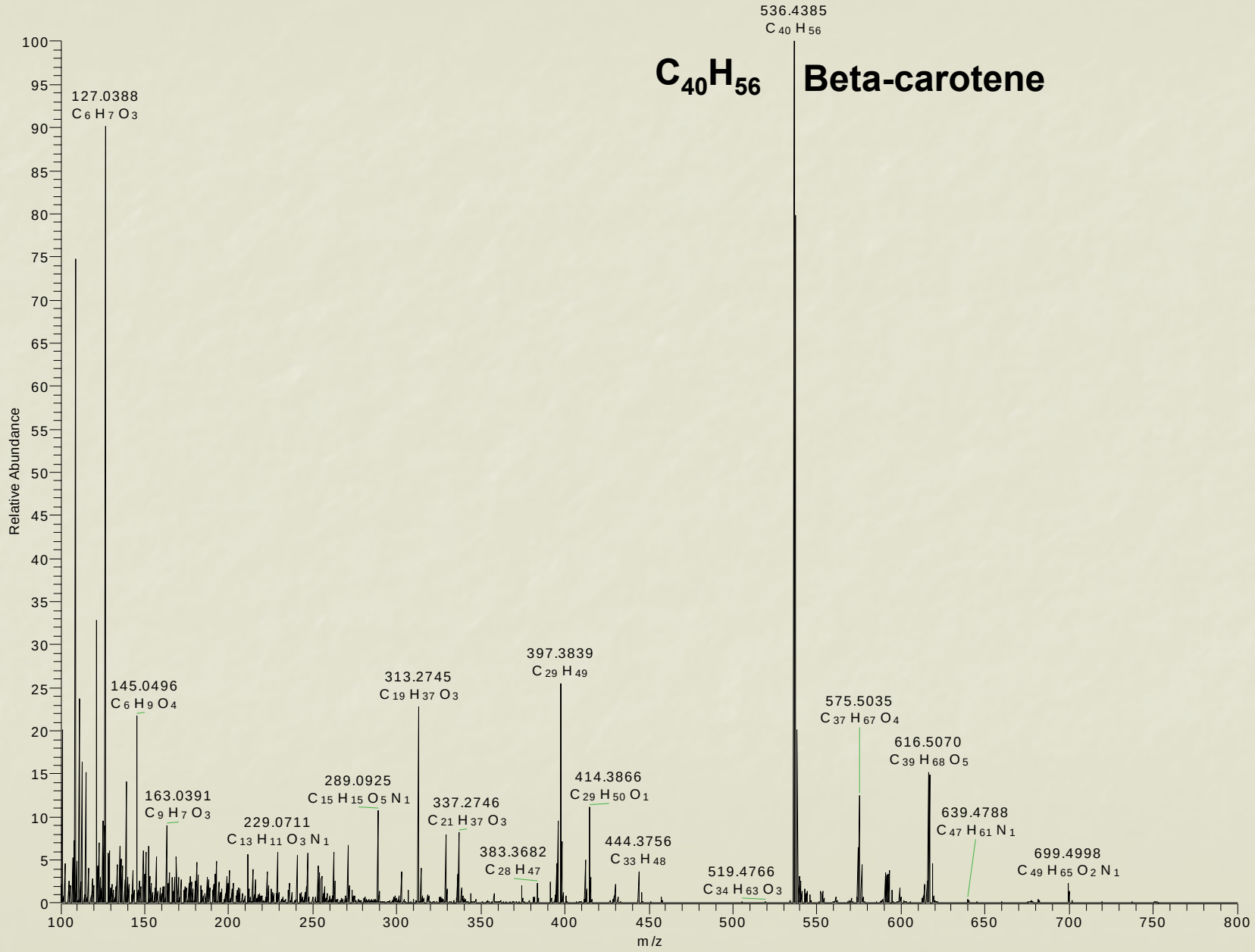


ASAP of Biological Samples

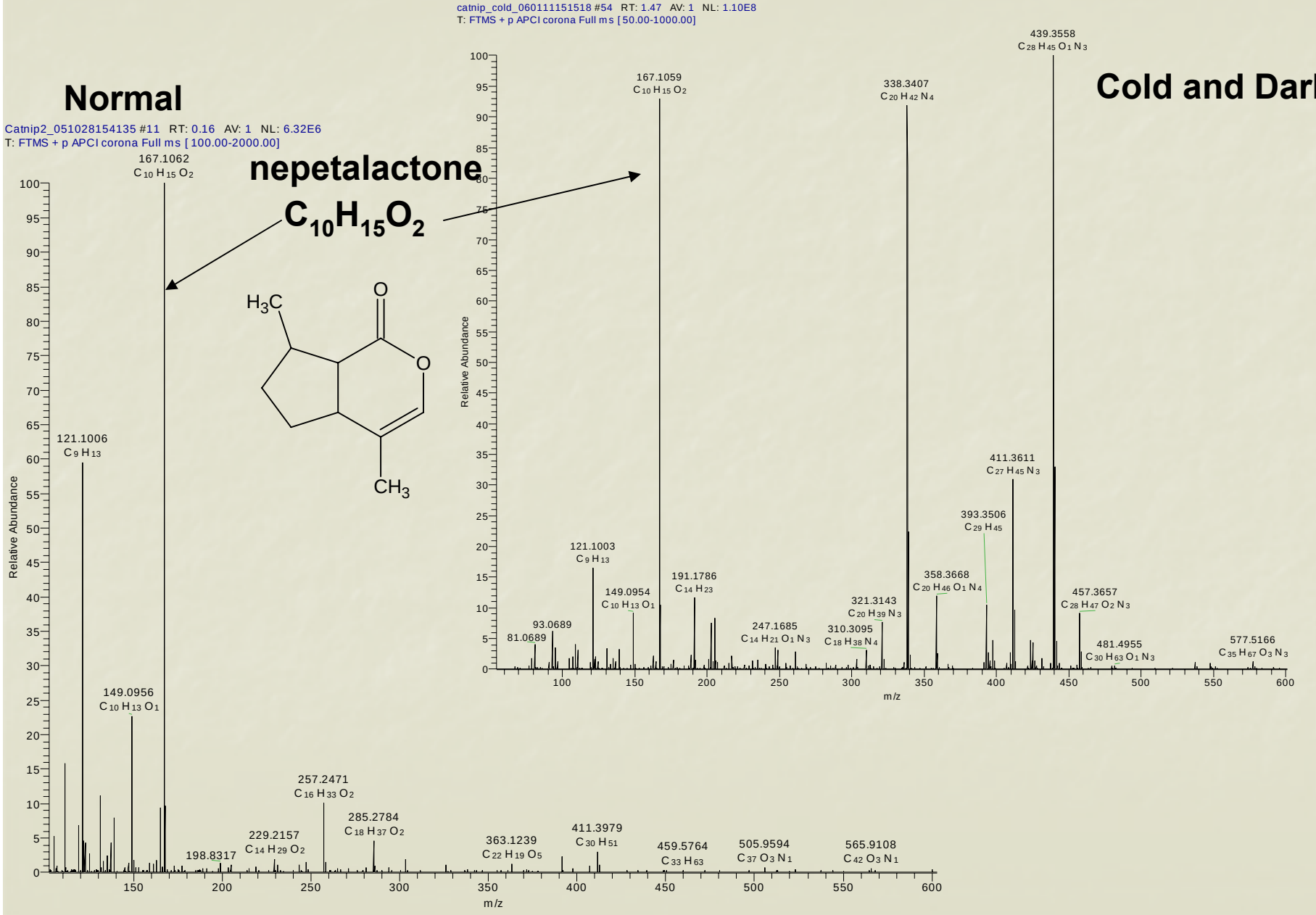
- Rapid analysis of volatiles in tissue
- No sample preparation
- Accurate mass and MS/MS
- High resolution desirable

ASAP of Carrot

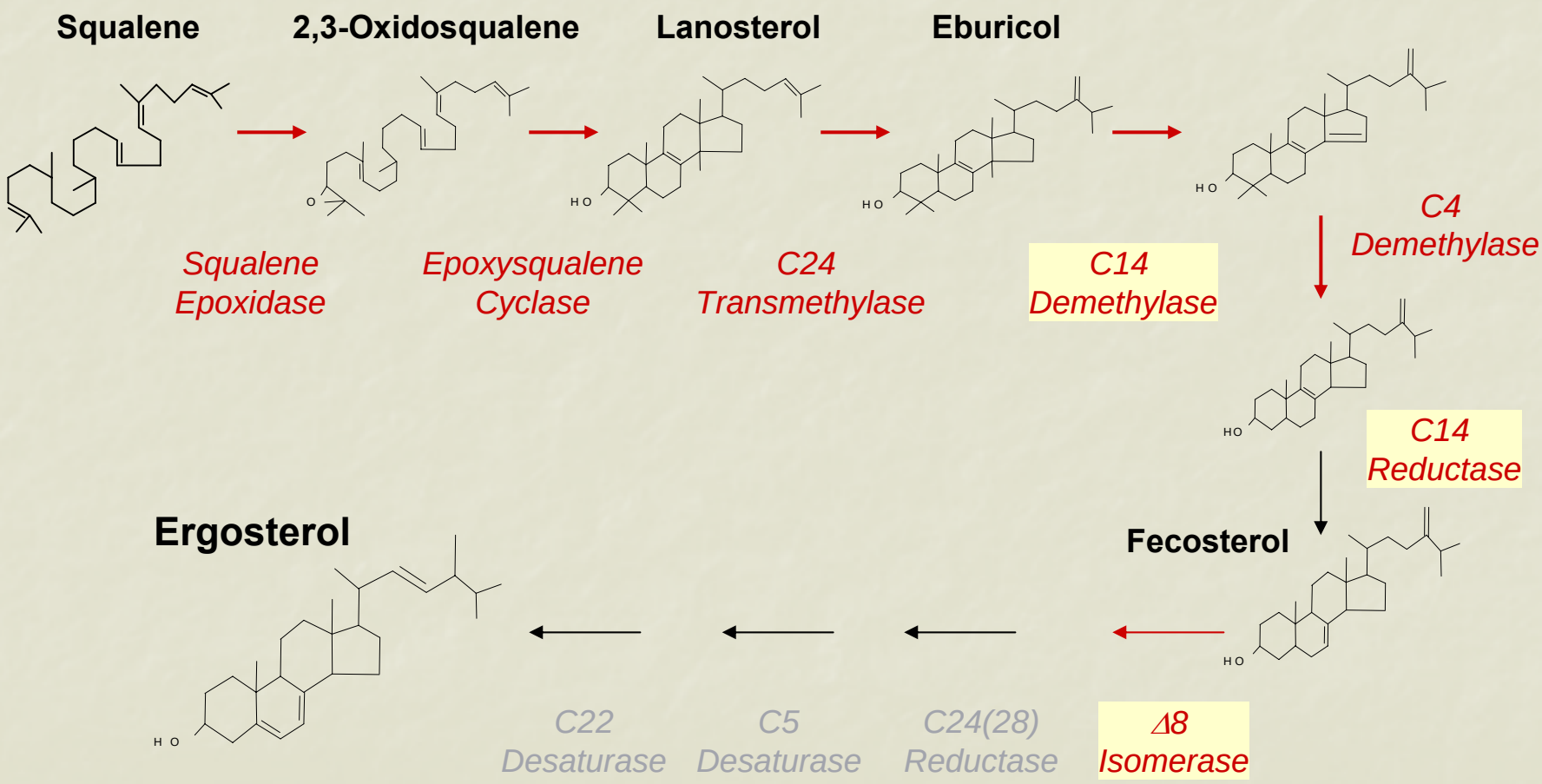
carot_060329155429 #20 RT: 0.57 AV: 1 NL: 4.25E6
T: FTMS + p APCI corona Full ms [100.00-800.00]



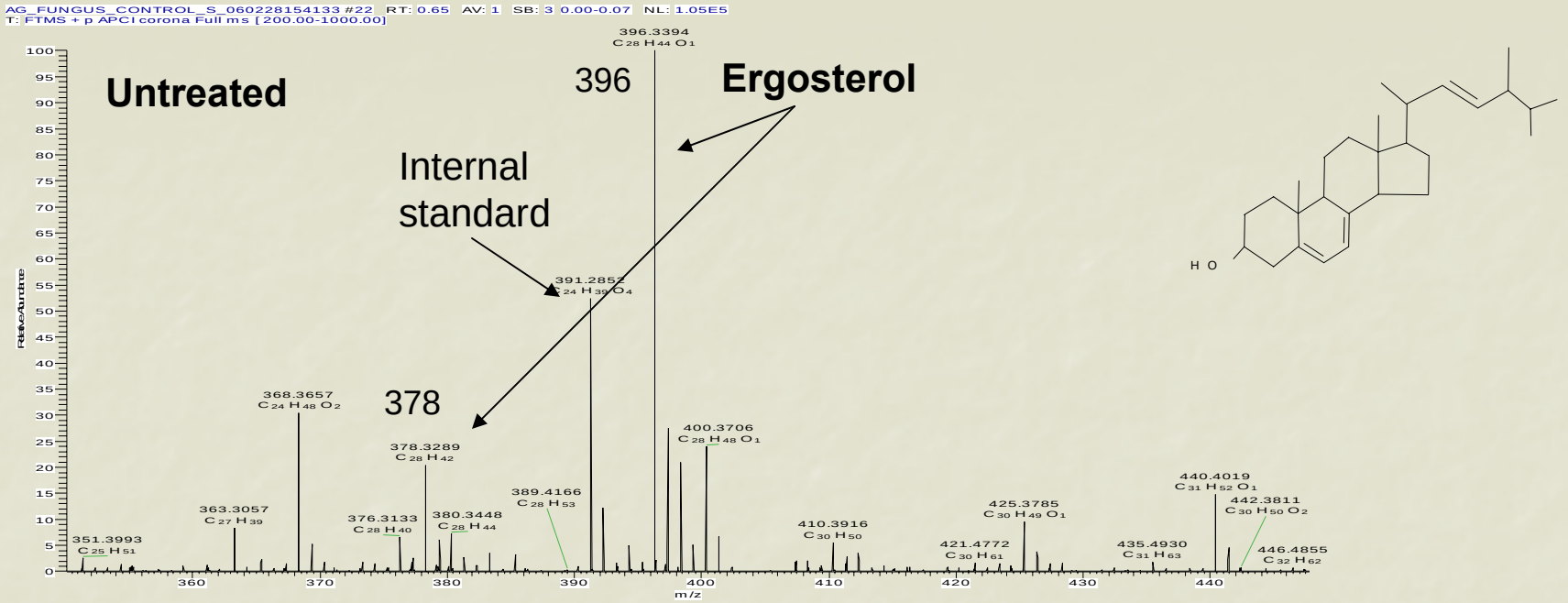
ASAP of Catnip Leaf Normal Growth and After Growth in Cold and Dark

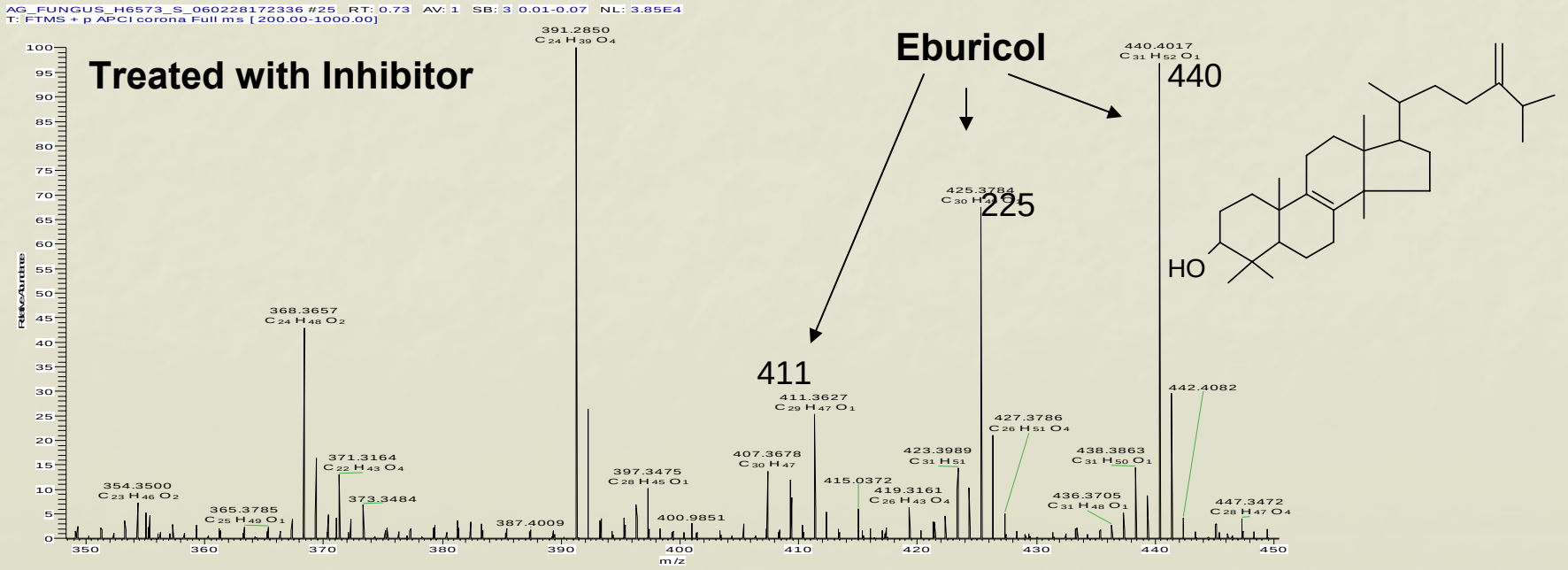


Ergosterol Biosynthesis

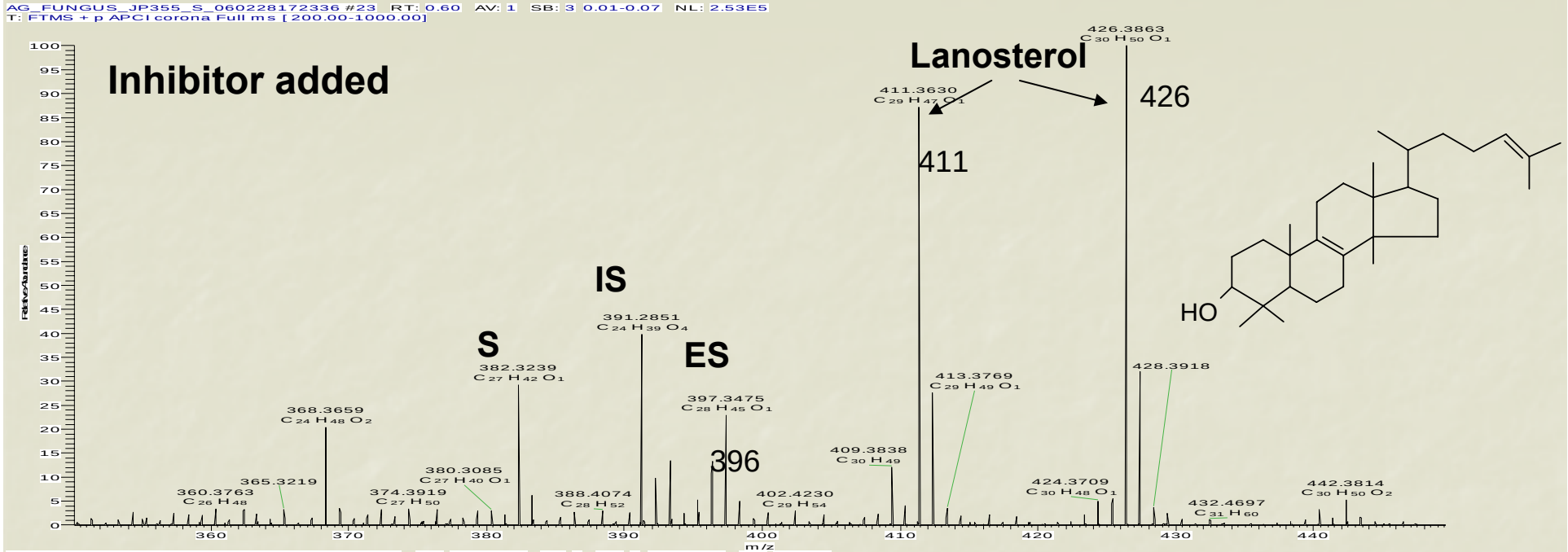


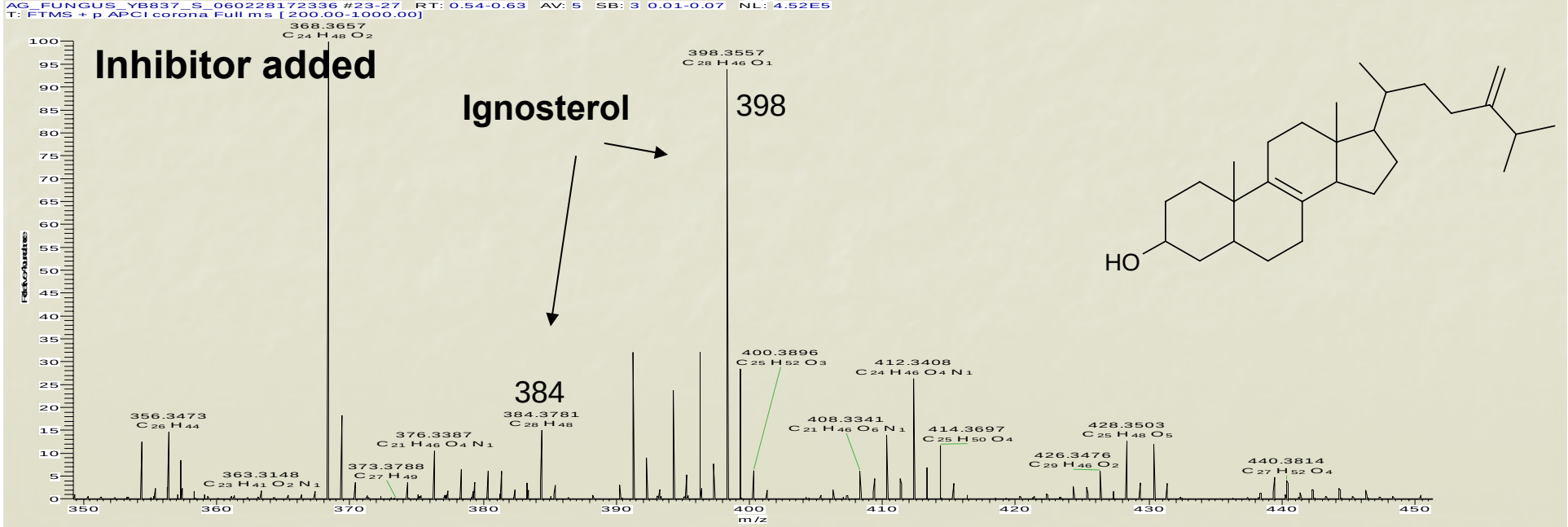
ASAP of Fungus Cells





ASAP of Treated Fungus

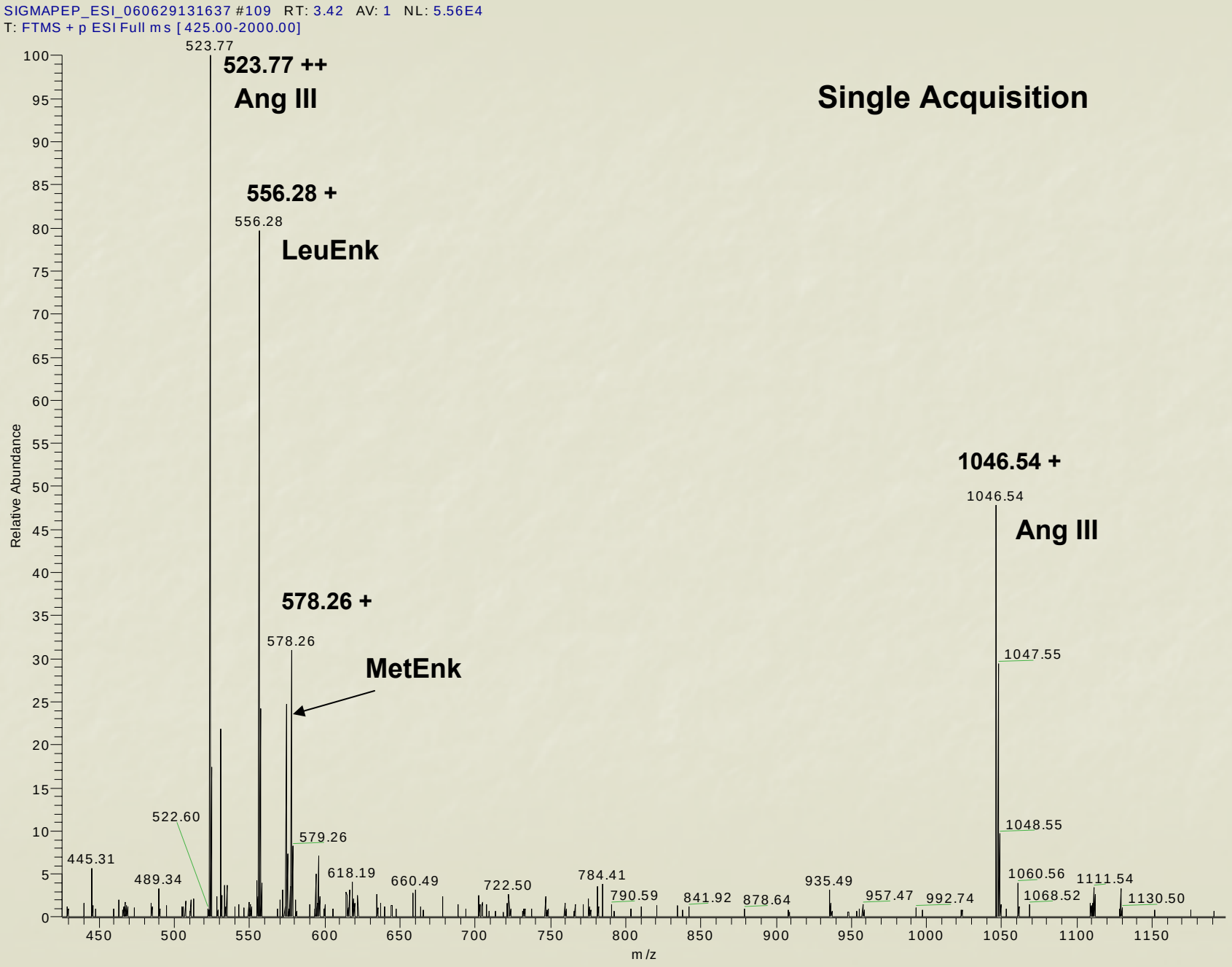




ASAP Probe for DESI

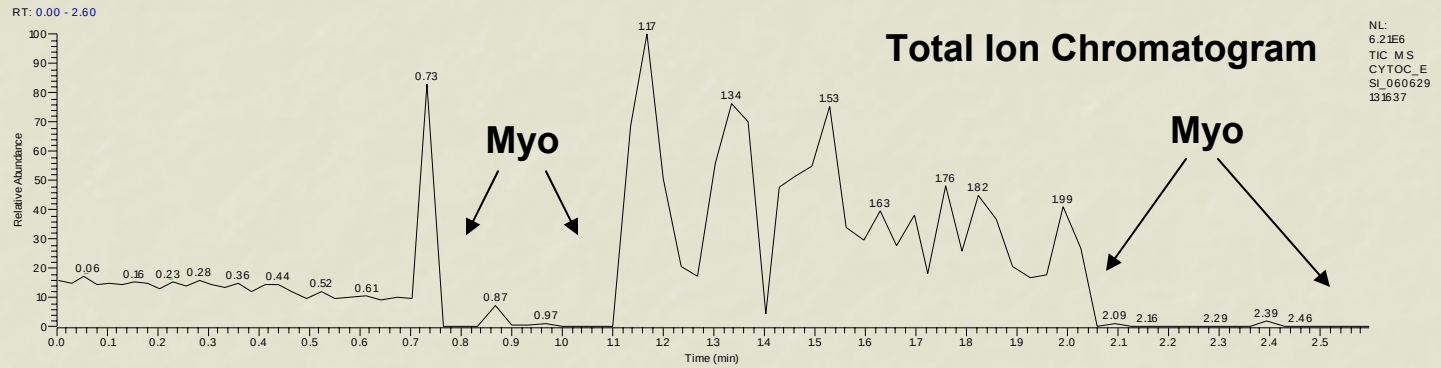
- **Analysis of nonvolatiles such as peptides and proteins**
- **Patented technology**

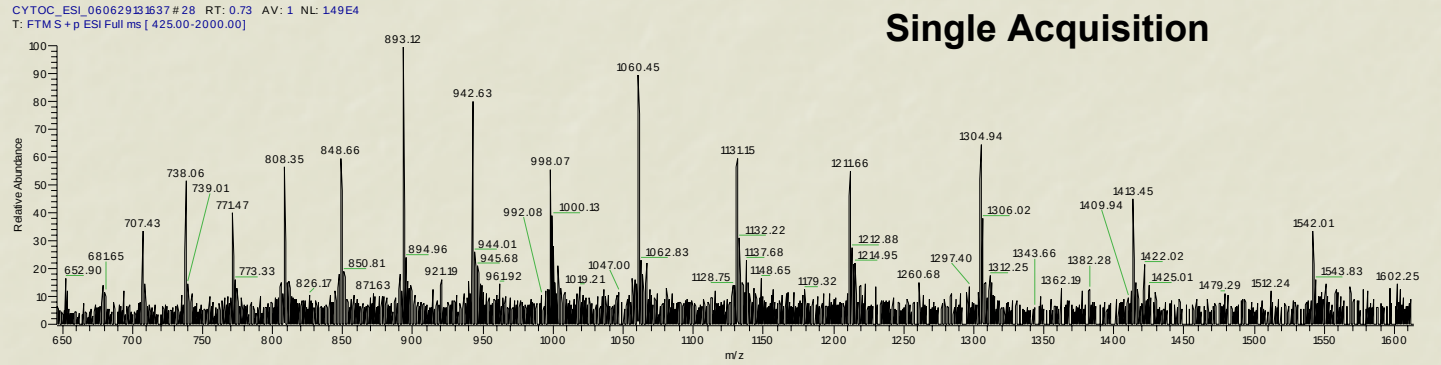
Sigma Peptide Mixture by ASAP Probe DESI

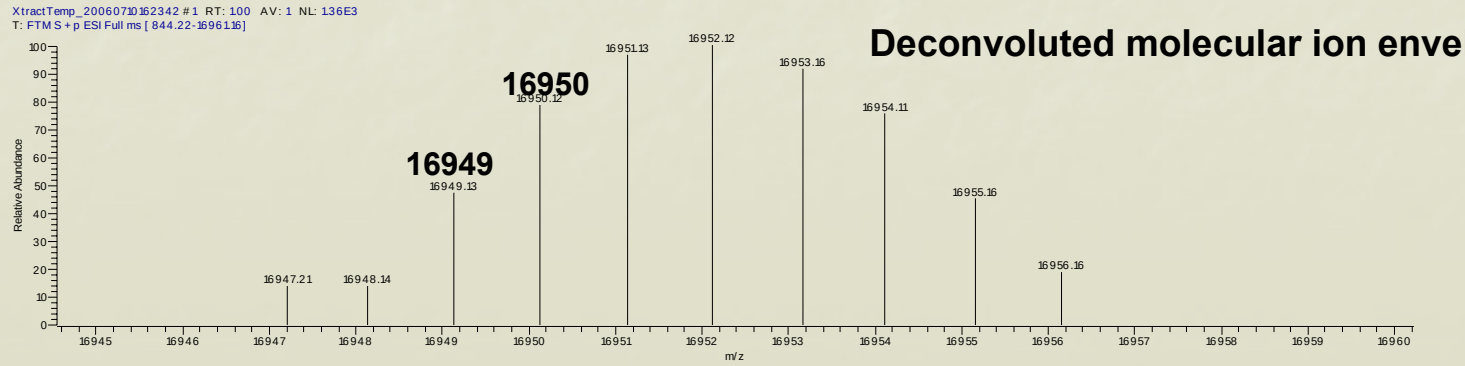


Myoglobin by ASAP Probe DESI

XtractTemp_20060710162342 7/10/2006 4:23:46 PM







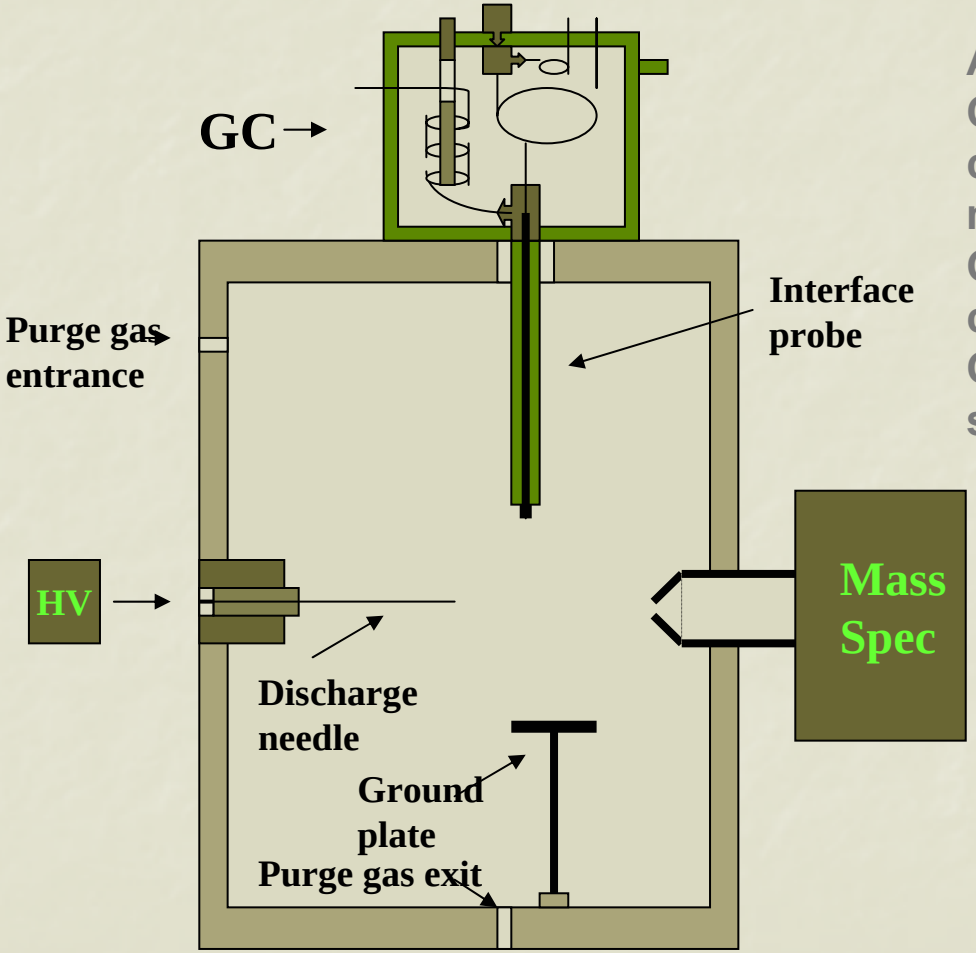
Conclusions

- ASAP is a rapid method for Analysis of Samples at Atmospheric Pressure
- ASAP is compatible with LC/MS and AP GC/MS and requires only a simple ion source modification
- Volatile and semivolatile compounds in solids, liquids, polymers, and biological tissue can be analyzed in seconds
- The method is especially powerful on high performance mass spectrometers

GC/MS on an LC/MS Instrument

- **Atmospheric Pressure Ionization (API) has primarily been interfaced with liquid chromatography, but it is also an ionization method that can be applied to gas chromatograph.**
- **Any LC/MS instrument can also be used as a GC/MS instrument.**
- **Either APCI or APPI can be used**

LC/MS Ion Source: GC Interface Probe Replaces LC Probe

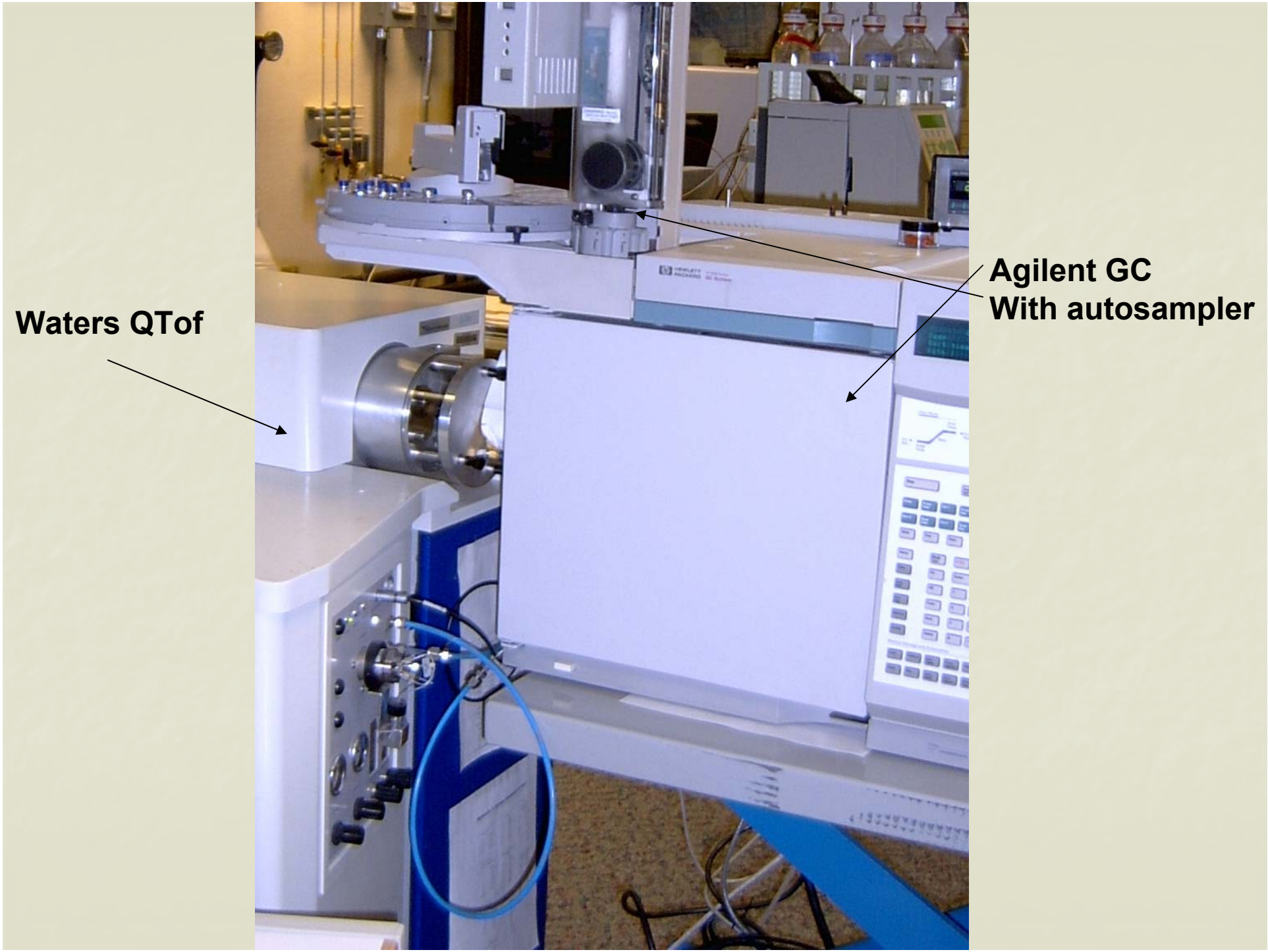


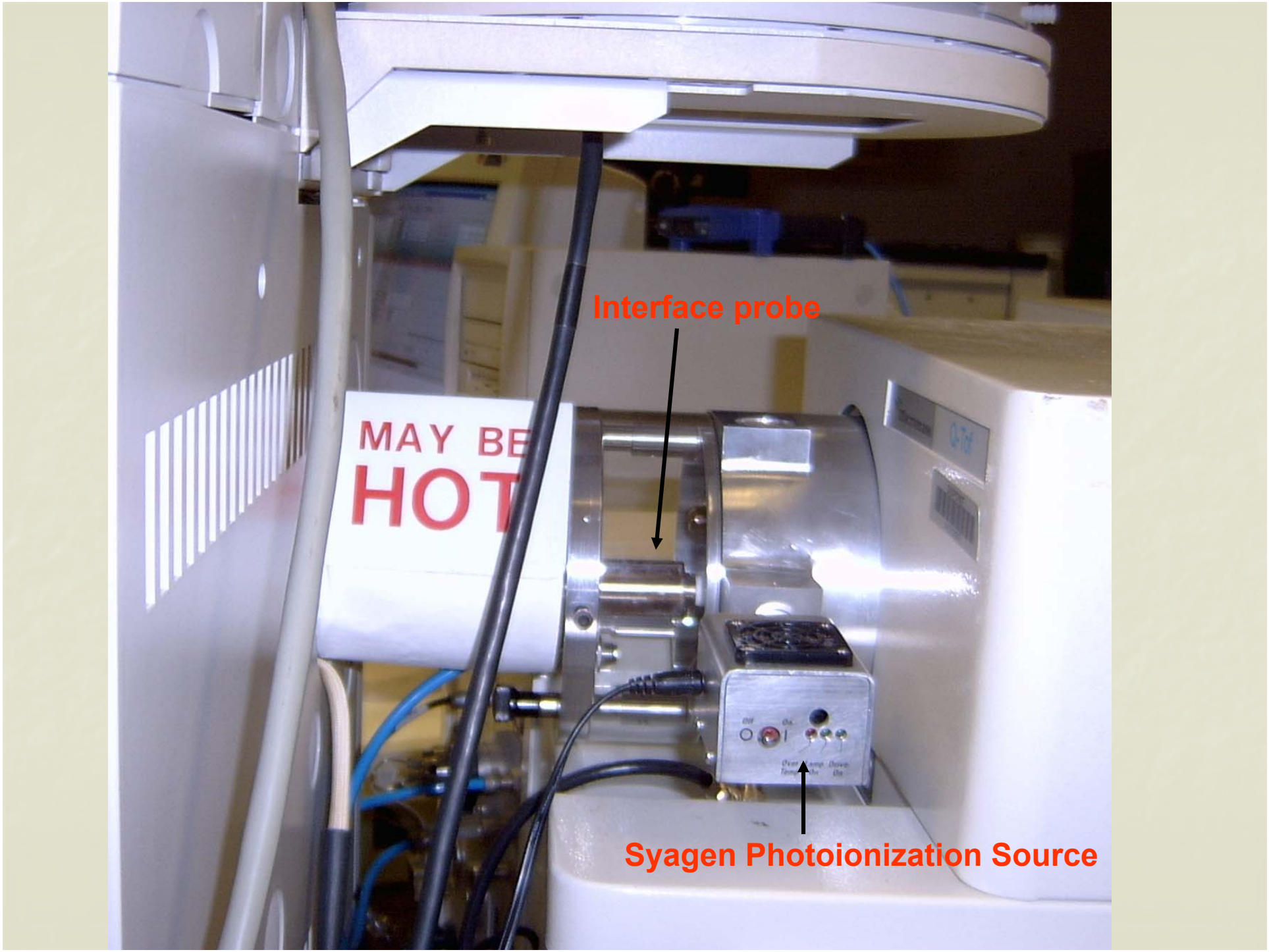
Advantages over LC/MS

- GC provides higher chromatographic resolution and more peak capacity than LC.
- Higher sensitivity for certain compounds.
- Less problems with analyte solubility.

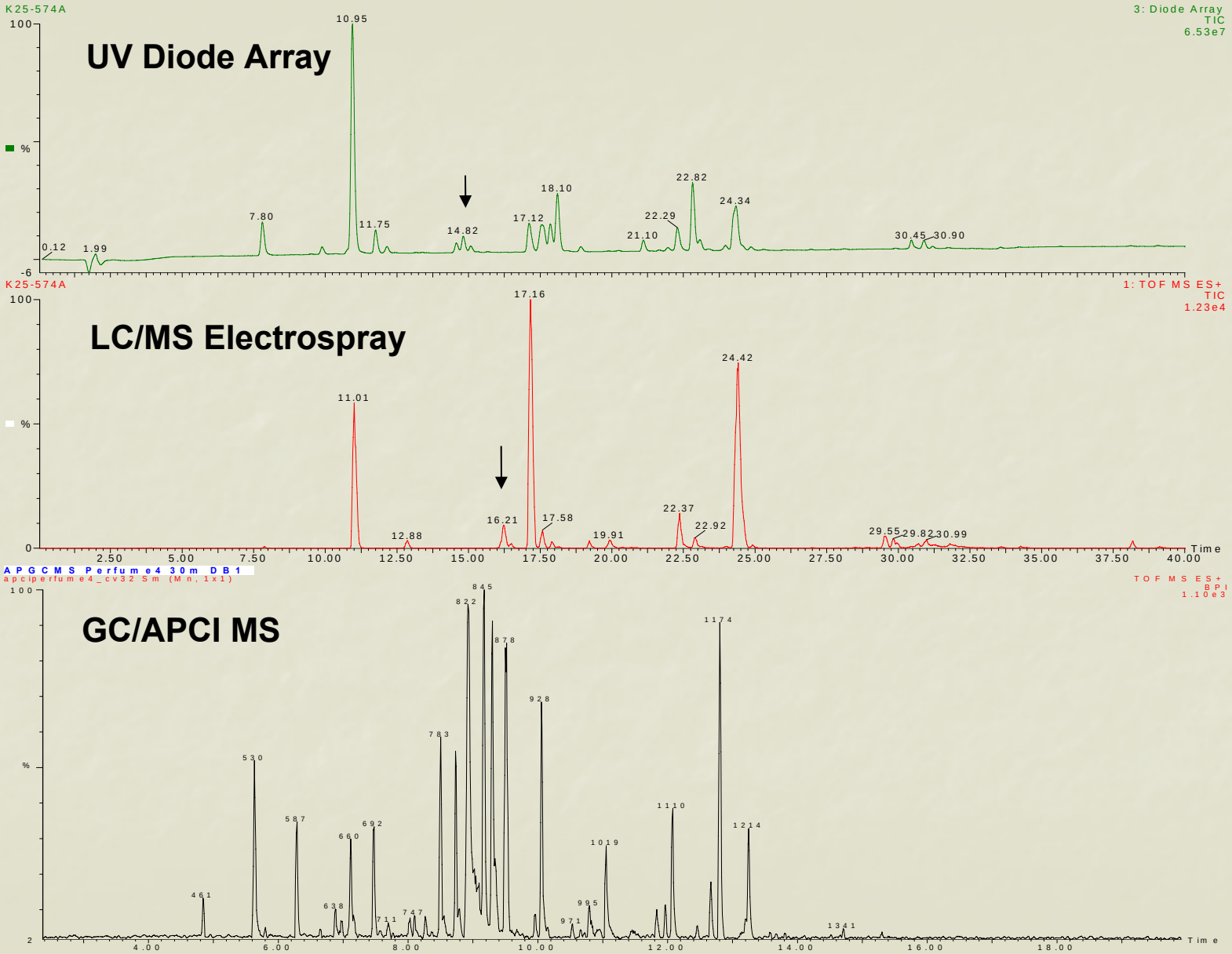
Advantages over vacuum GC/MS

- Uses high performance LC/MS instrumentation
- Mass selected fragmentation for GC/MS Quantitation


Waters QTof
Agilent GC
With autosampler


Interface probe
MAY BE
HOT
Syagen Photoionization Source

Perfume Analysis: Comparison of UV, LC/MS, GC/APMS



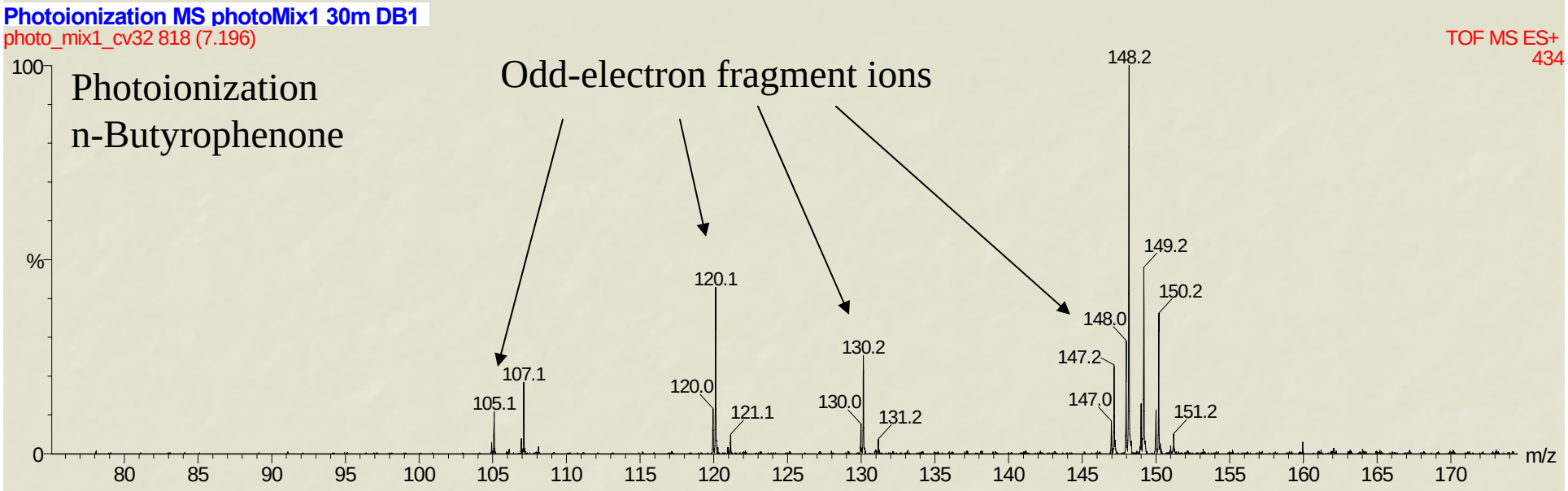
Molecular and MH^+ Ion Generation

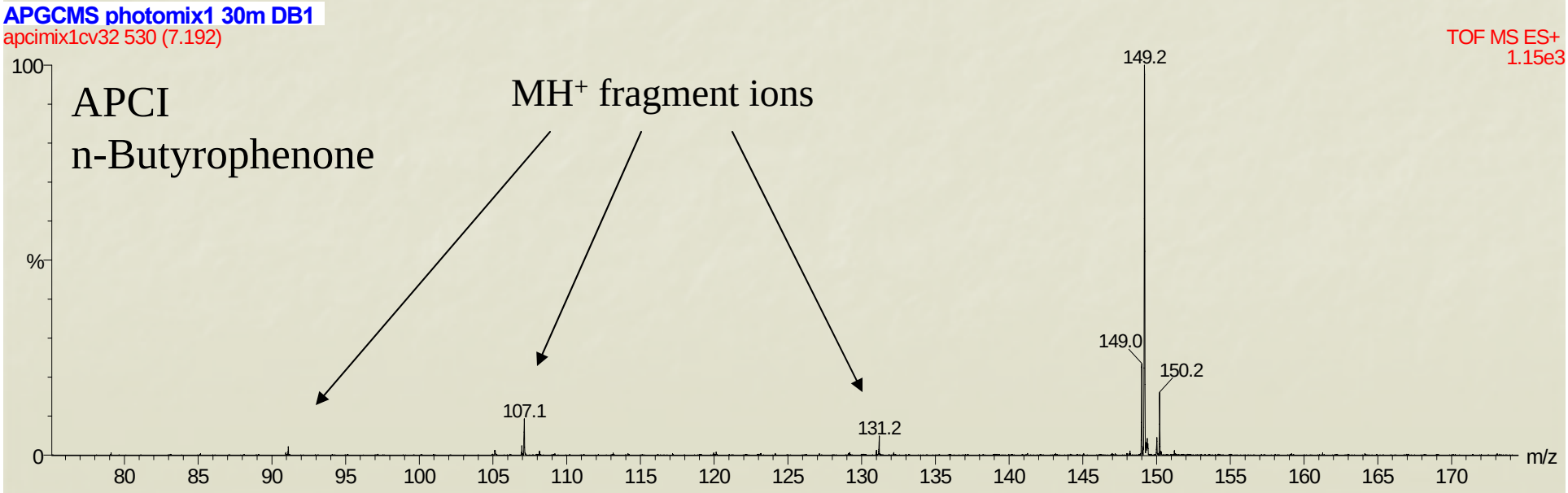
$$A + e \rightarrow A^{+\cdot} + 2e \quad \text{(EI)}$$

$$A + h\nu \rightarrow A^{+\cdot} + e \quad \text{(APPI)}$$
$$A^{+\cdot} + H_2O \rightarrow AH^+ + {\cdot}OH$$

$$N_2 + e \rightarrow N_2^{+\cdot} + 2e \quad \text{(APCI)}$$
$$N_2^{+\cdot} + 2N_2 \rightarrow N_4^{+\cdot} + N_{-2}$$
$$N_4^{+\cdot} + H_2O \rightarrow H_2O^{+\cdot} + 2N_2$$
$$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + {\cdot}OH$$
$$H_3O^+ + A \rightarrow AH^+ + H_2O$$
$$N_2^{+\cdot}/N_4^{+\cdot} + A \rightarrow A^{+\cdot} + xN_2$$

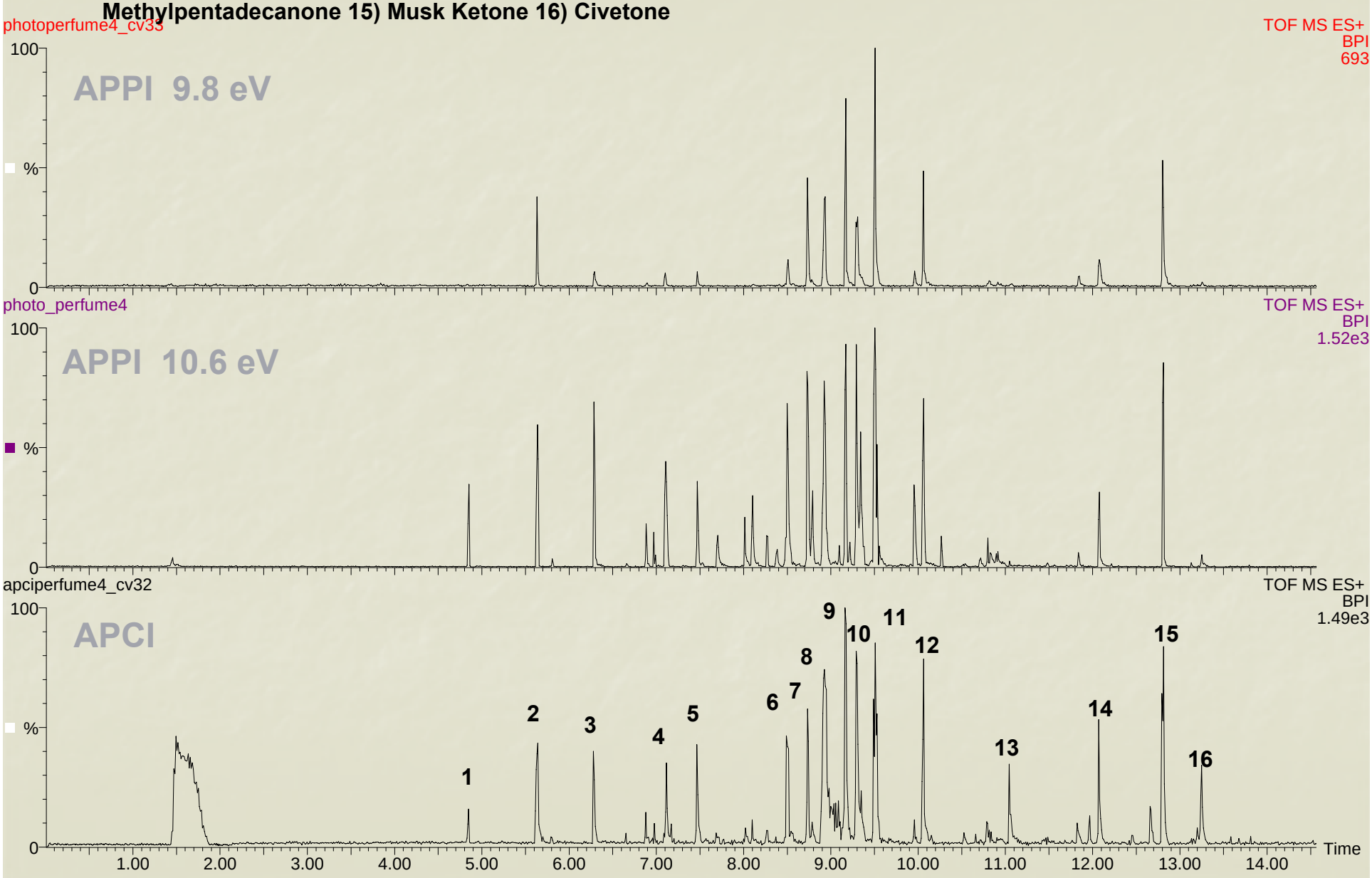
Comparison of AP GC/MS of n-Butyrophenone Using APPI and APCI



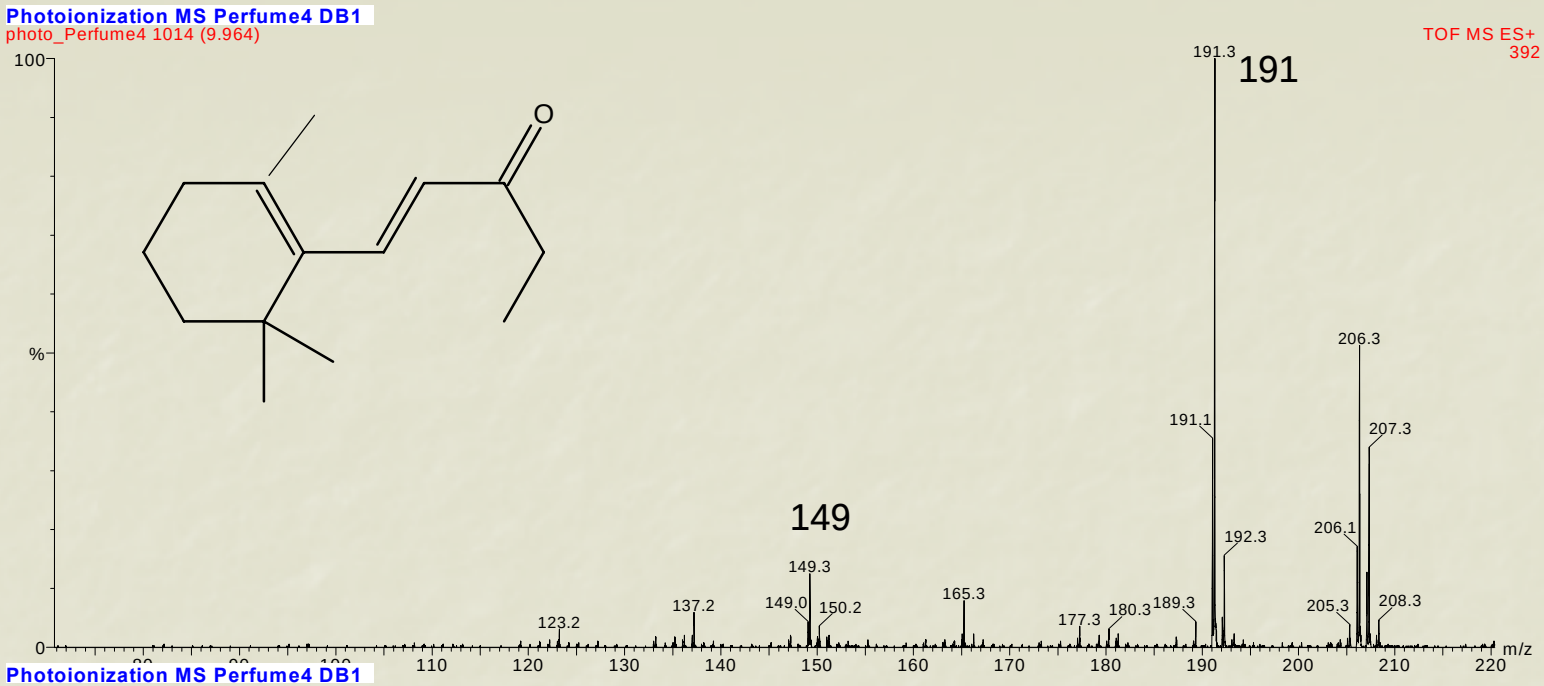


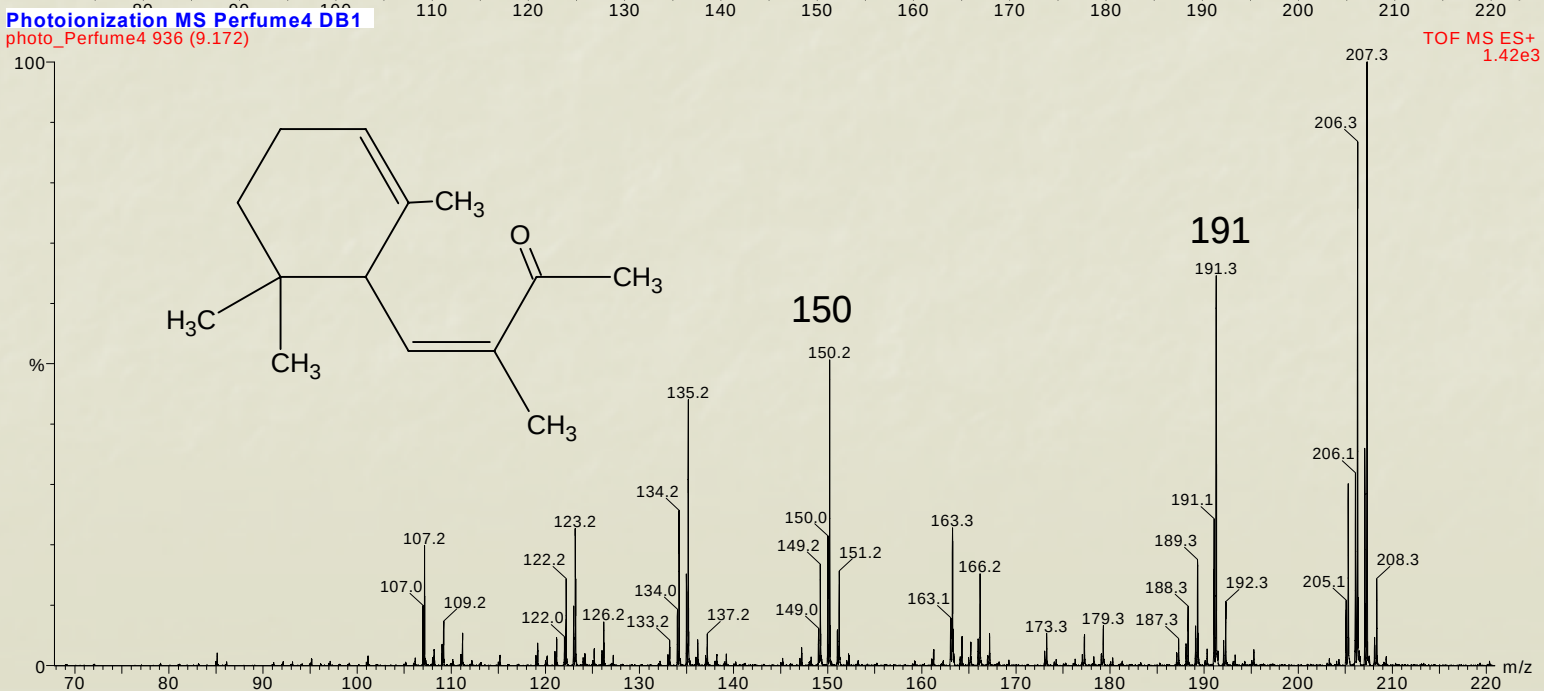
Perfume Analysis by API-GC/MS

1)Rose oil 2) Linalool 3) C14H12 4) Geraniol 5) Dimethyl-2,6-octadien-1-ol 6) Vanillin 7) Ionone 8) Coumarin 9)Cetone 10) Dimethoxypropenylbenenee 11) Isomethylionine 12) Diethylphthalate 13) Methyltetradecanoic acid 14) Methylpentadecanone 15) Musk Ketone 16) Civetone

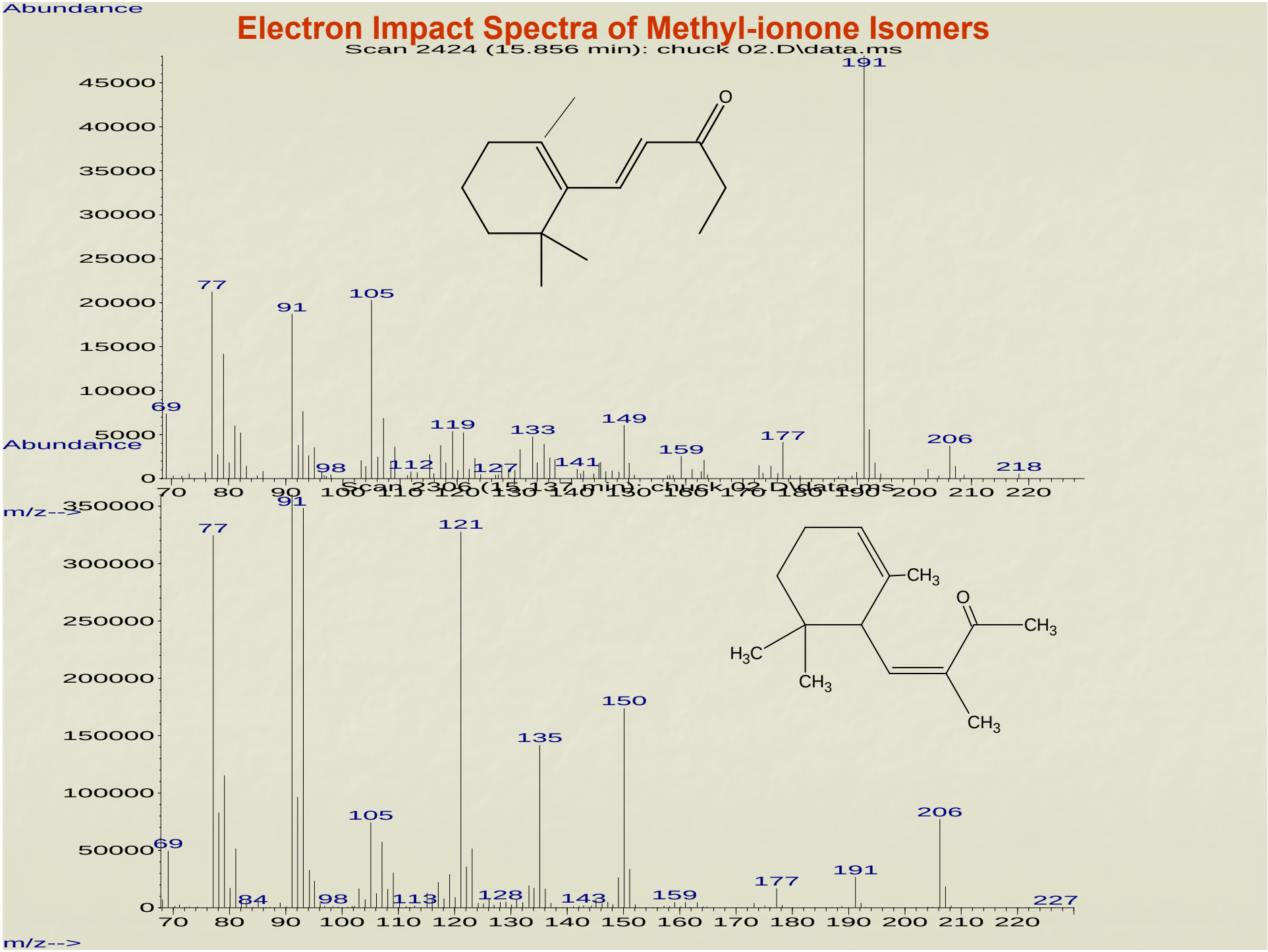


APPI Spectra of Isomers of methyl-ionone

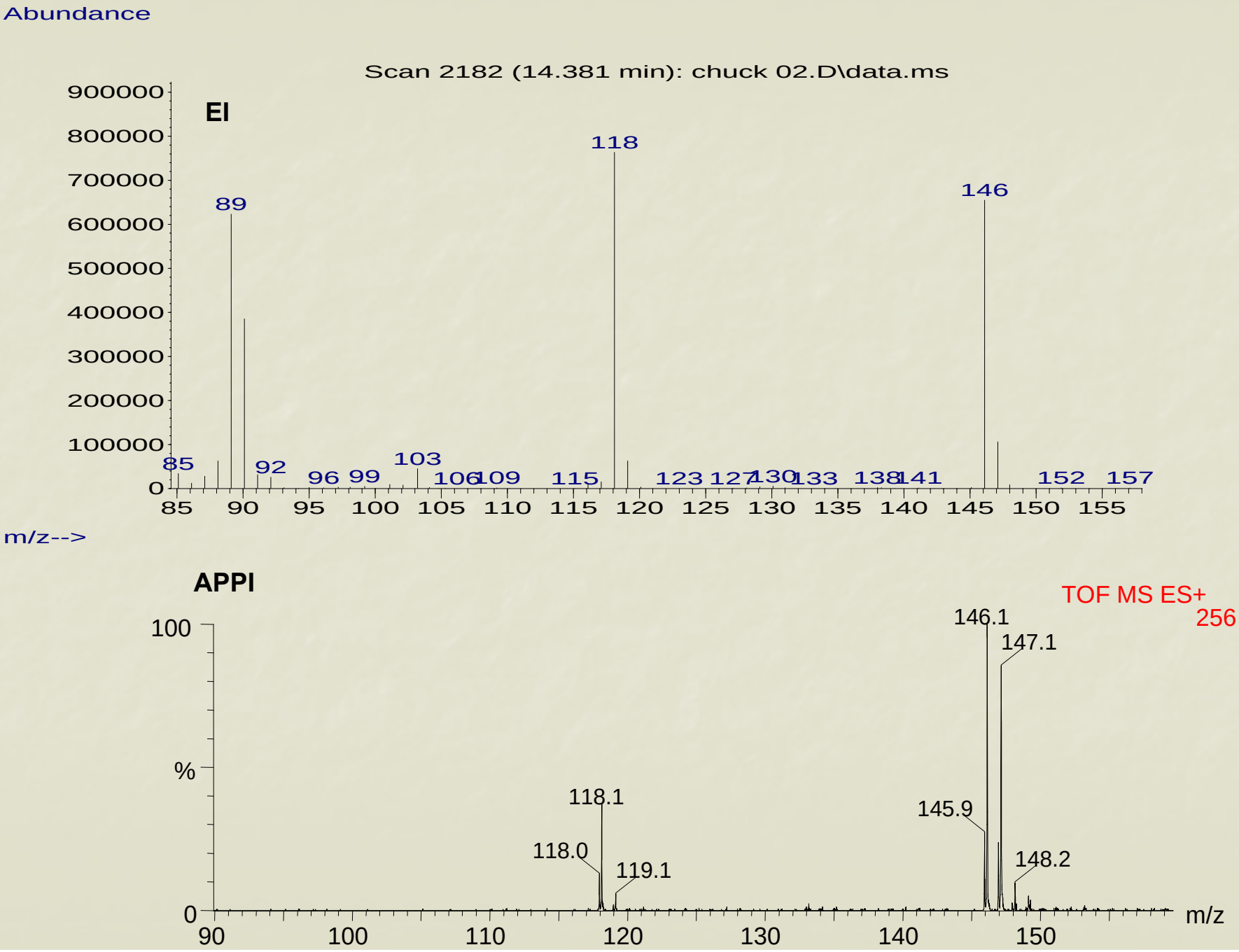




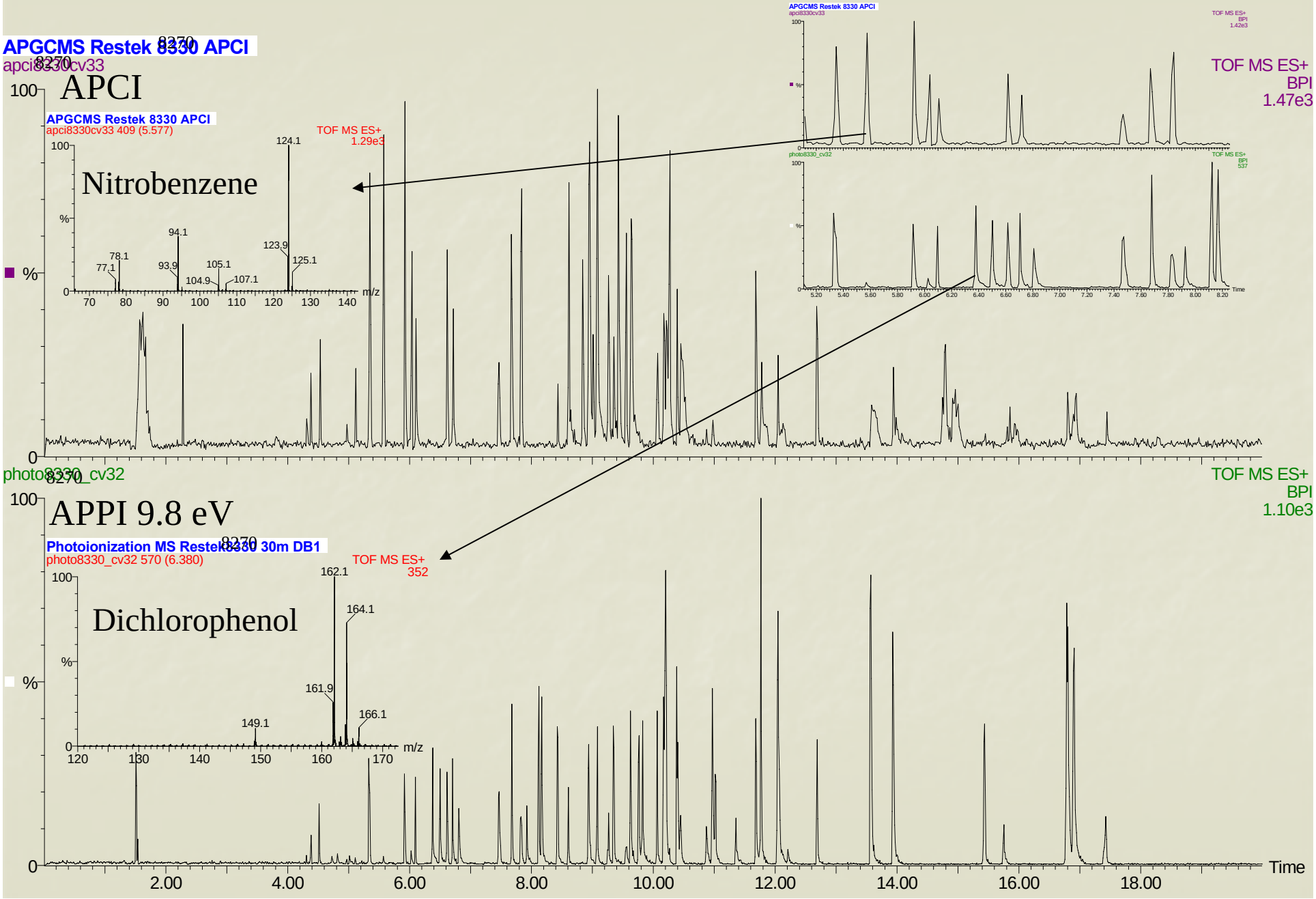
Electron Impact Spectra of Methyl-ionone Isomers



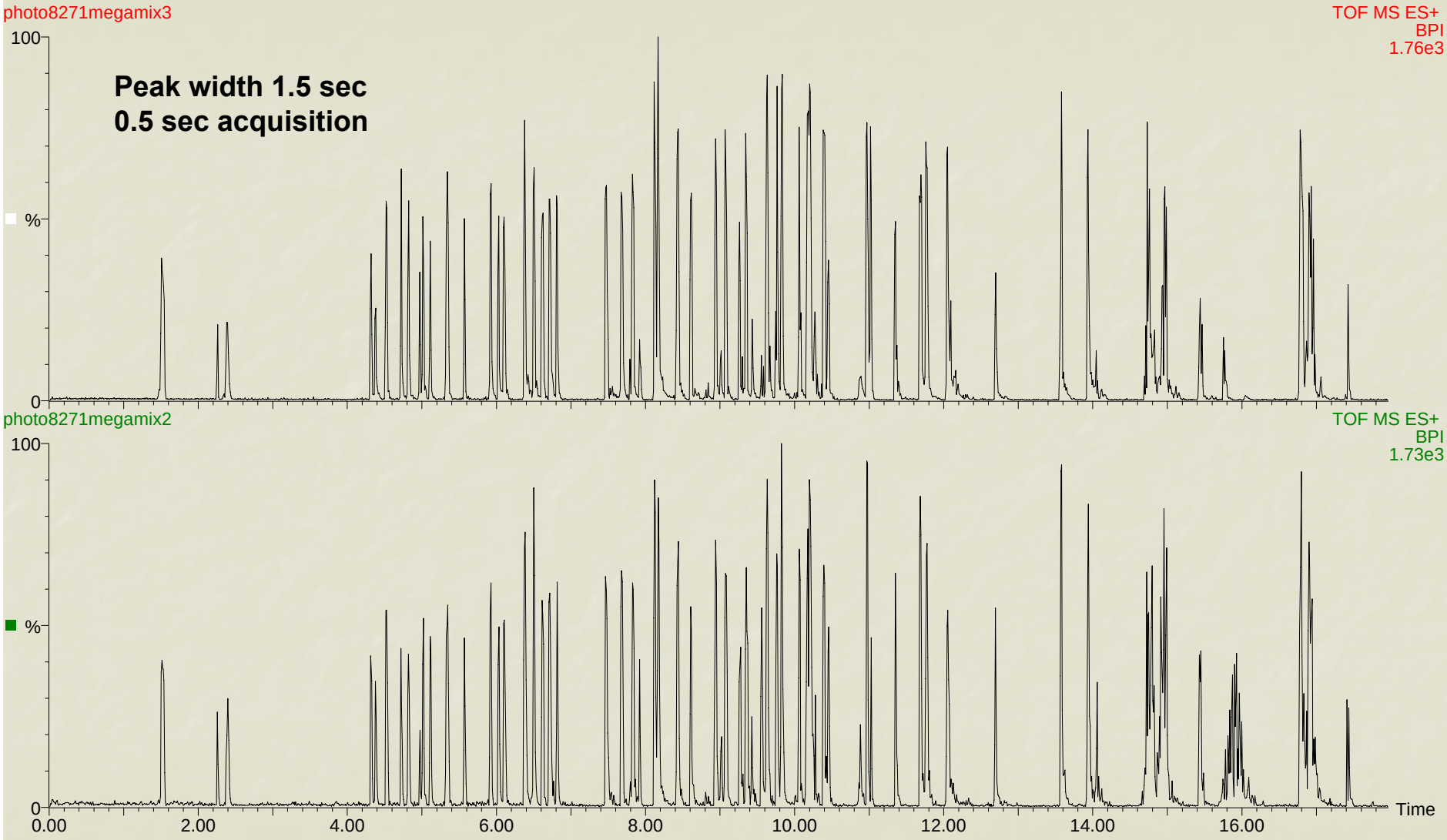
Comparison of Electron Impact to APPI Spectra of Benzopyran-2-one



GC/APMS Restek 8270 EPA Mixture



Reproducibility Study Restek 8270 Megamix by GC/10.6 eV APPI-MS

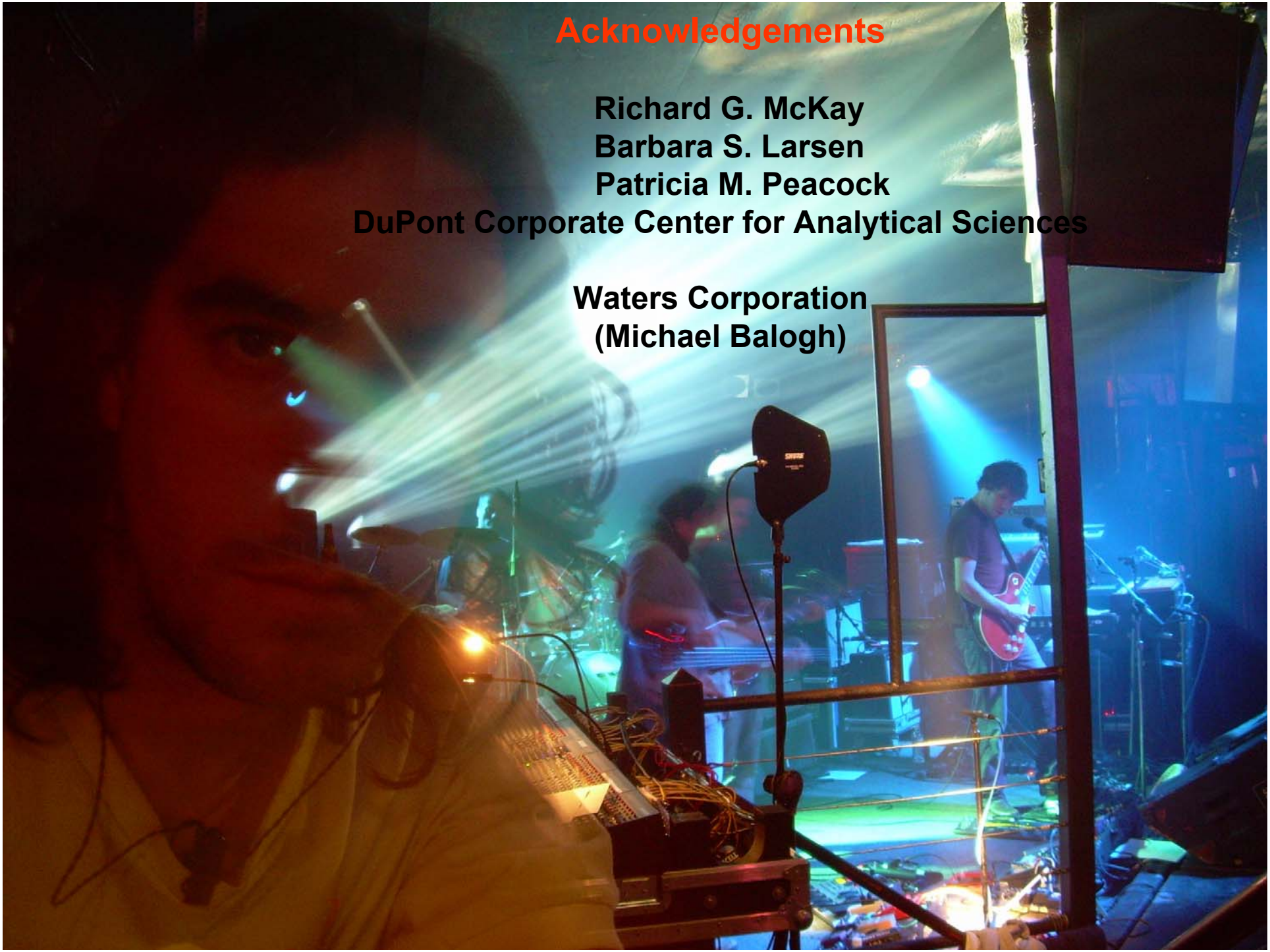


Conclusion

- AP-GC/MS extends the capabilities of LC/MS instrumentation.
- APPI GC/MS is almost a universal ionization method for volatile compounds.
- High sensitivity.
- Library search possible with APPI?
- Positive/negative ionization, accurate mass, MS/MS, quantitation.
- This work has shown that LC/MS instrumentation can be made more powerful and more universal by incorporating the ability to also perform AP GC/MS.

Additional Information

- **ASAP: McEwen, McKay, Larsen *Anal. Chem.,* 2005, 77, 7826-7831.**
- **AP GC/MS: McEwen, McKay *J. Am. Soc. Mass Spectrom.,* 2005, 16, 1730-1738.**
- **EMAIL: ASAPMS-info@comcast.net**



Acknowledgements

Richard G. McKay
Barbara S. Larsen
Patricia M. Peacock
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