

A photograph of a sunset over the ocean. The sun is low on the horizon, creating a bright orange and yellow glow that spreads across the sky and reflects on the water. The sky is filled with soft, wispy clouds. In the foreground, two people are sitting on a sandy beach, looking out at the sea. The overall mood is peaceful and serene.

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

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**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

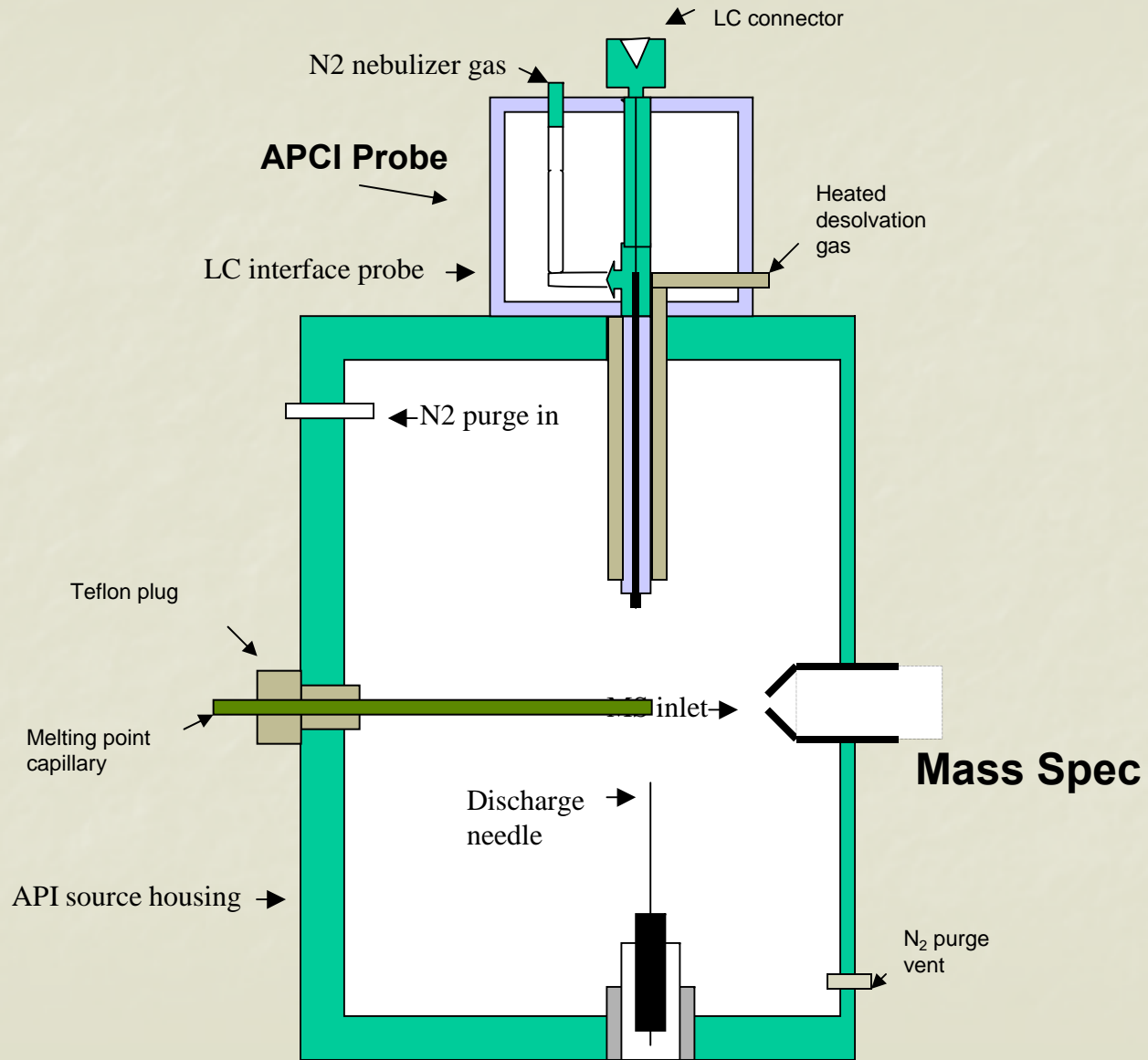
Exception is photoionization (not acid/base ionization) but still mediated by solvent

**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**

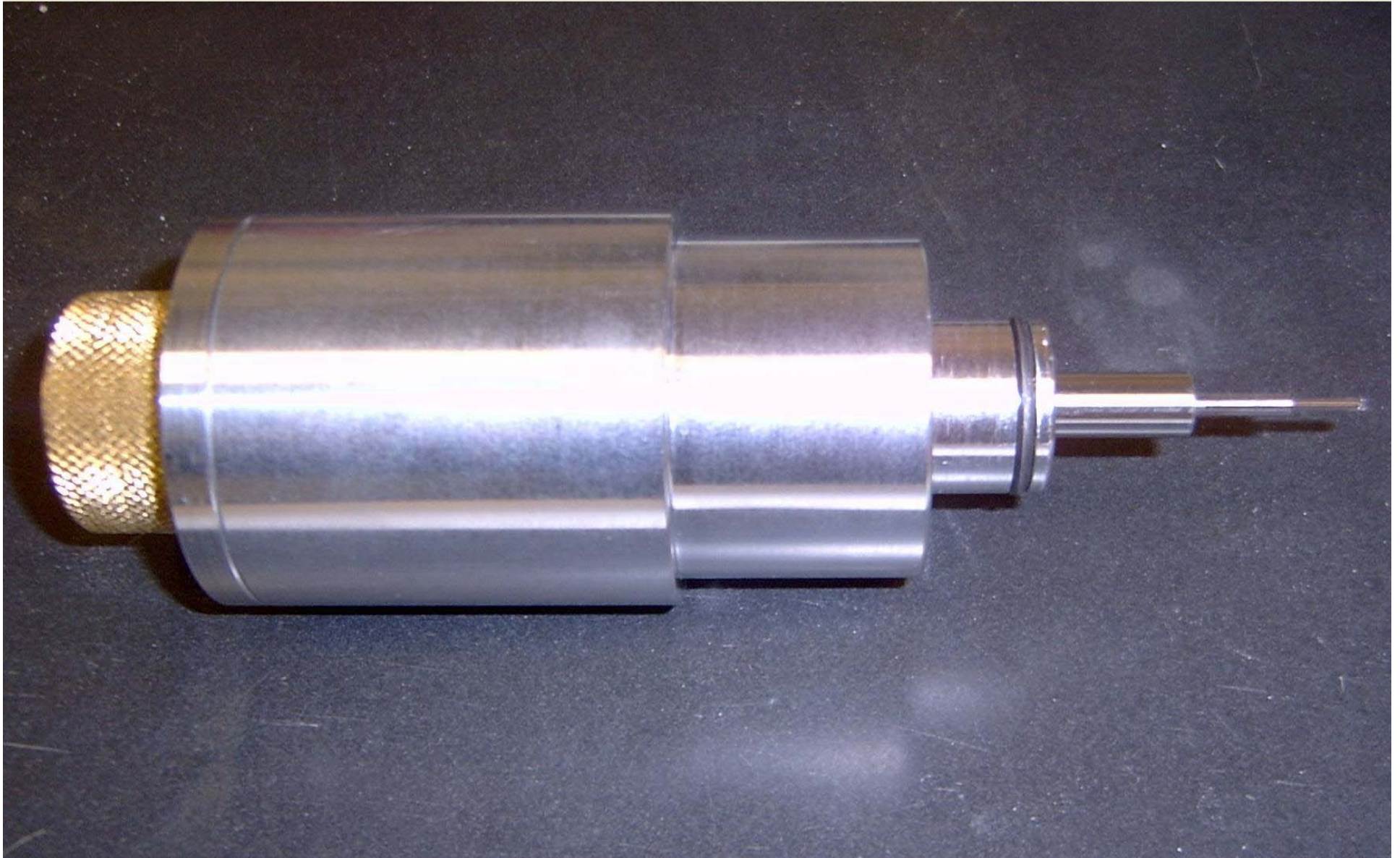
# ASAP Ion Source

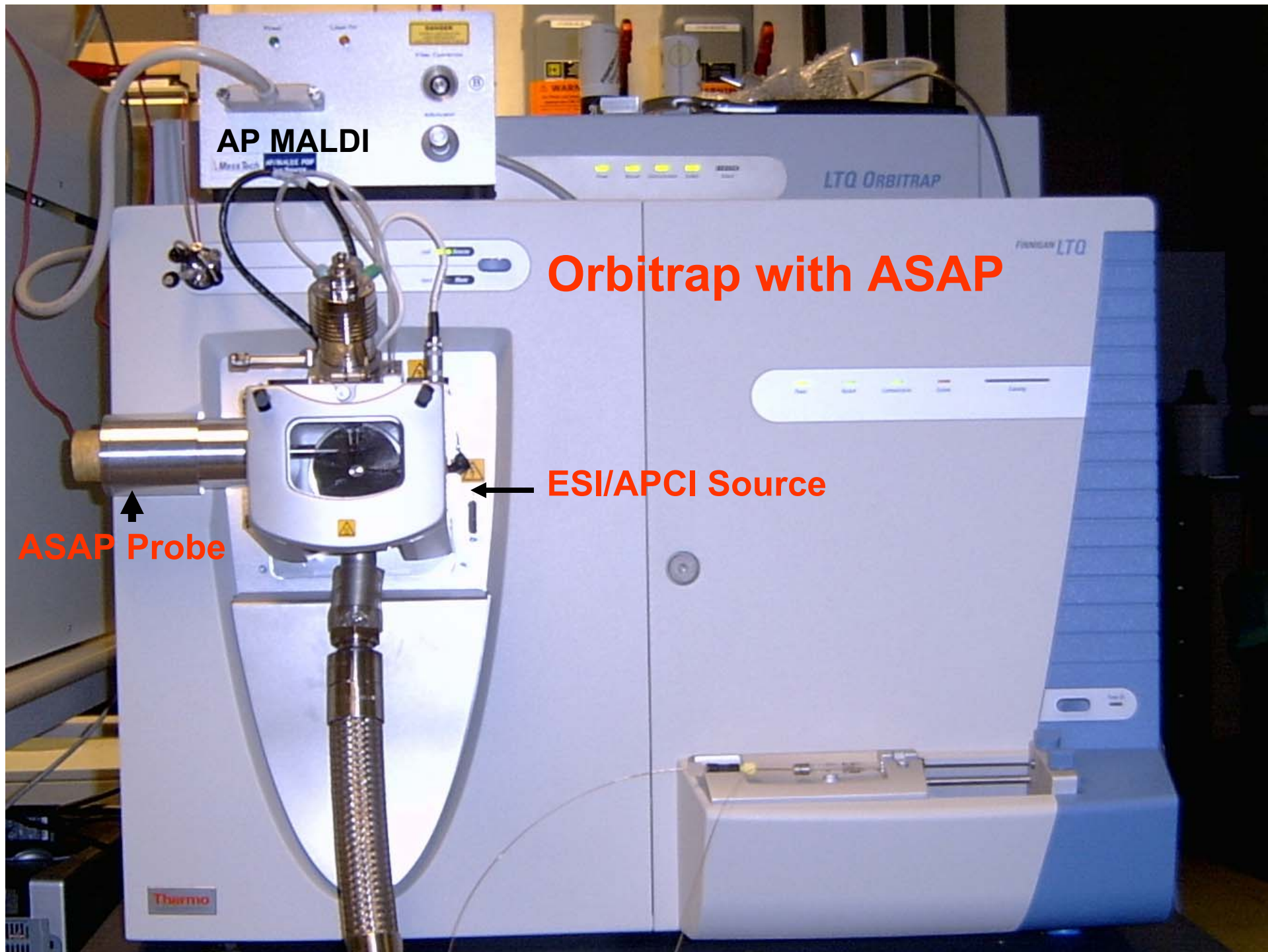


# Safety First

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

# ASAP Probe





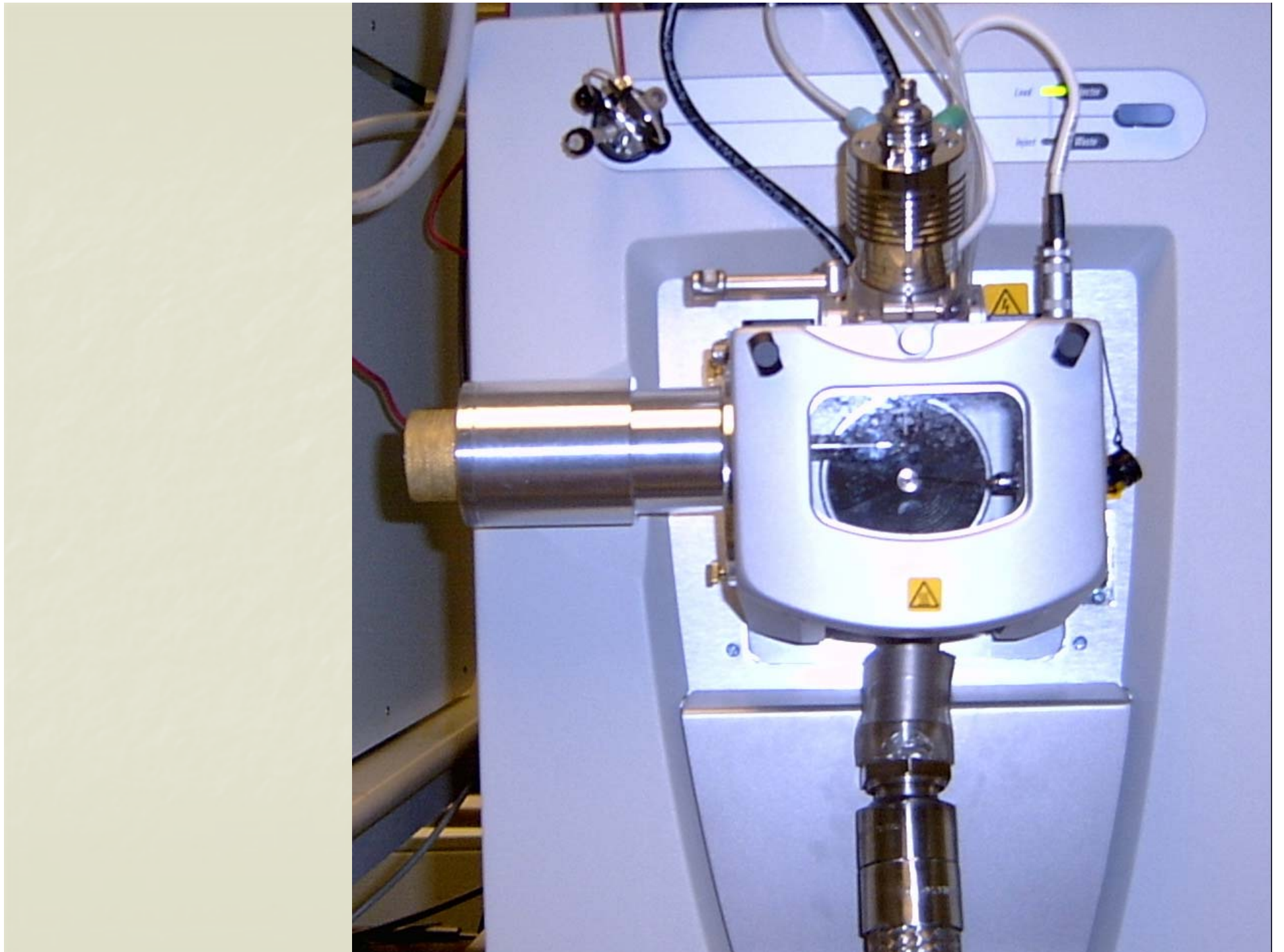
AP MALDI

Orbitrap with ASAP

ESI/APCI Source

ASAP Probe

Thermo



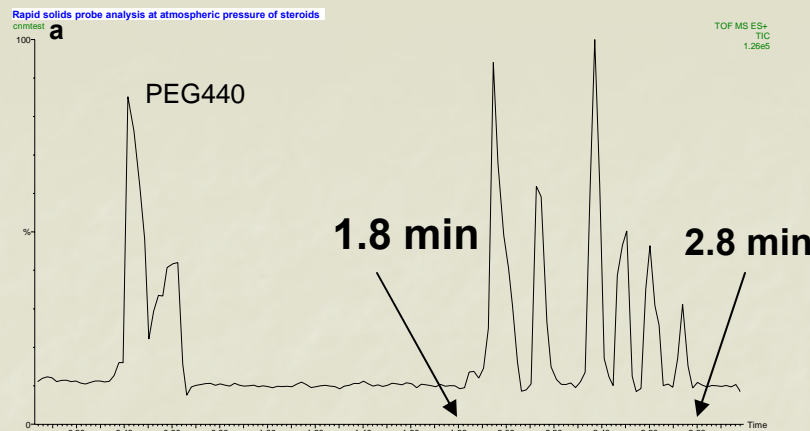
# ASAP Examples

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

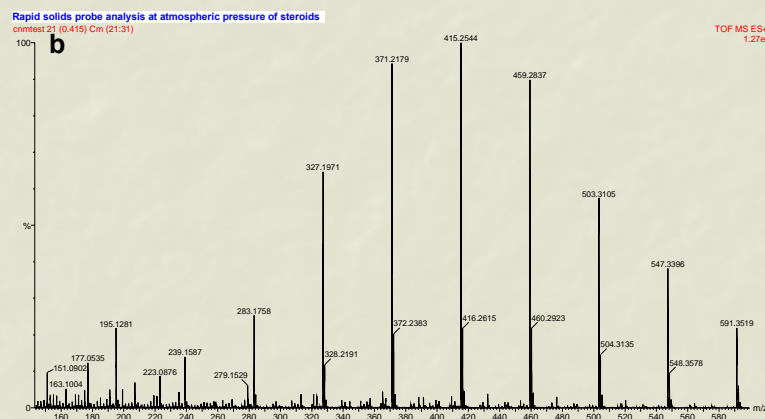
# Replacement for Solids Probe

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

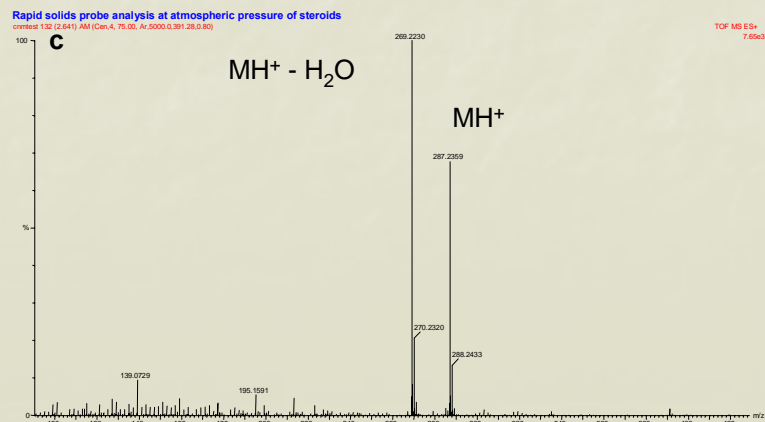
# ASAP on QToF Showing Instrument Calibration and 6 Steroid Samples in 3 min.



Total Ion Current Chromatogram of ASAP analysis of 6 steroids



PEG for Instrument Calibration

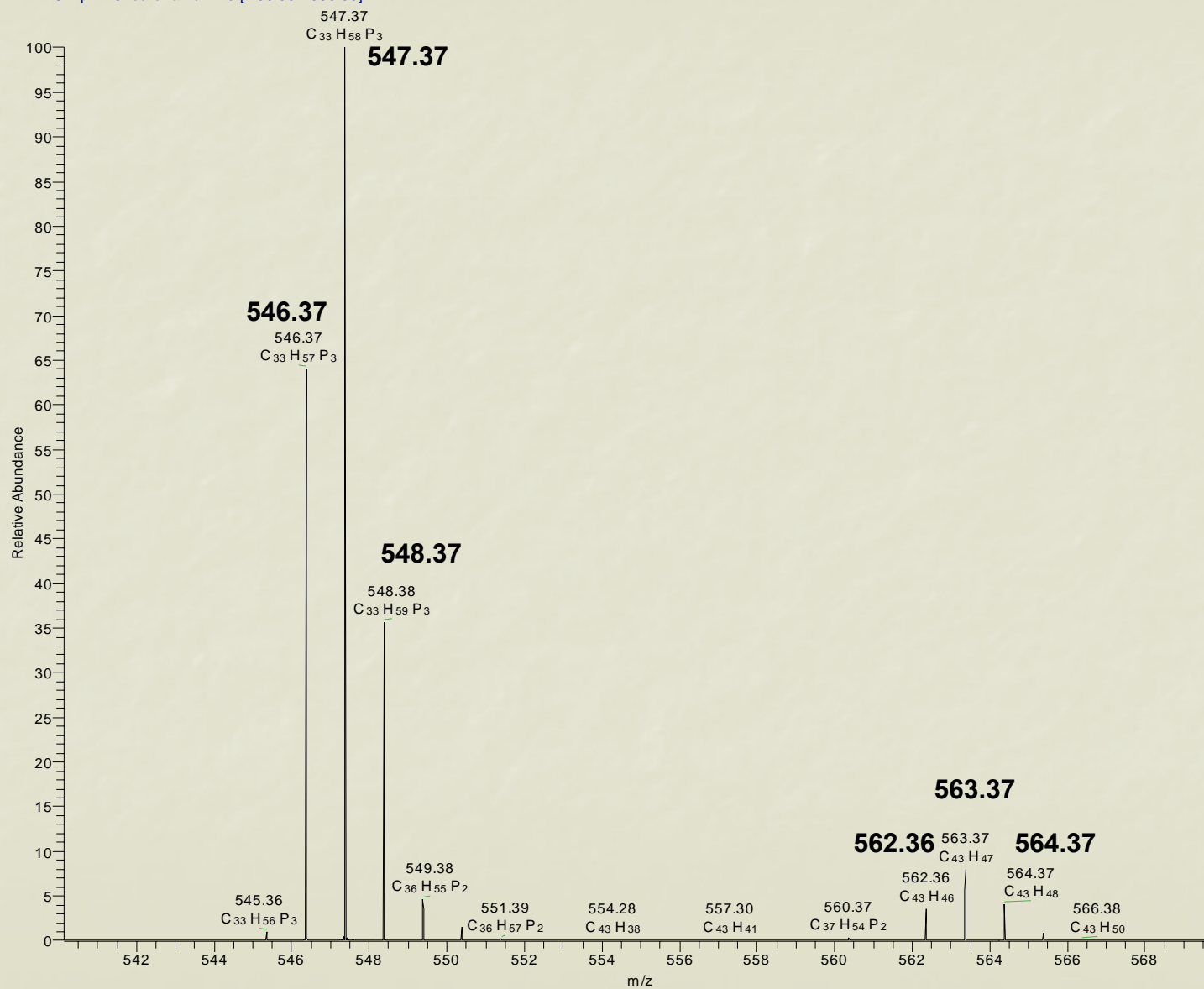


Atmospheric Pressure Mass Spectrum of Steroid

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

# Solids Probe Sample for Accurate Mass

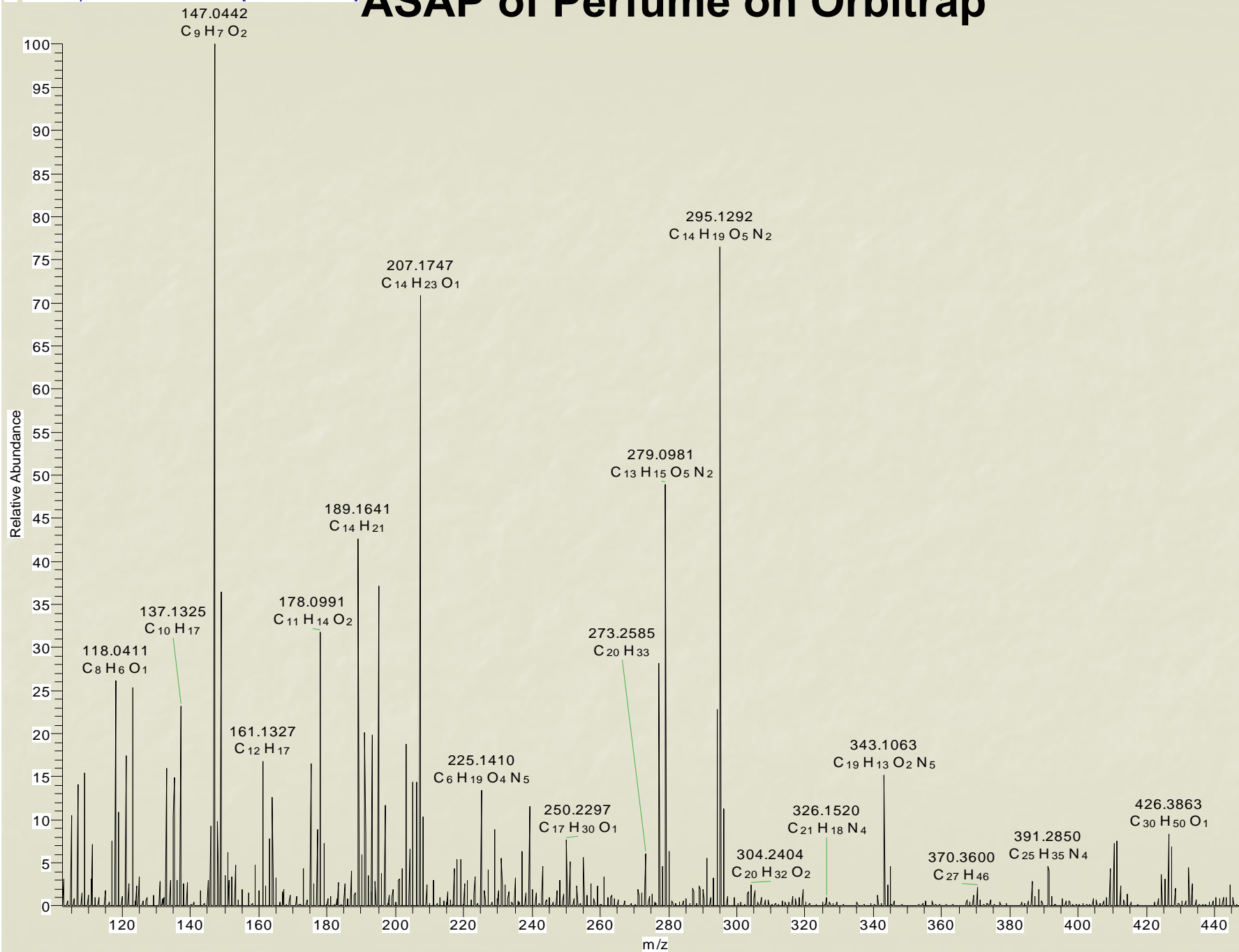
fish-111034-71-tube2-asap1\_060718095705 #15 RT: 0.89 AV: 1 SB: 1 0.32 NL: 3.39E7  
T: FTMS + p APCI corona Full ms [ 100.00-1000.00]



# 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

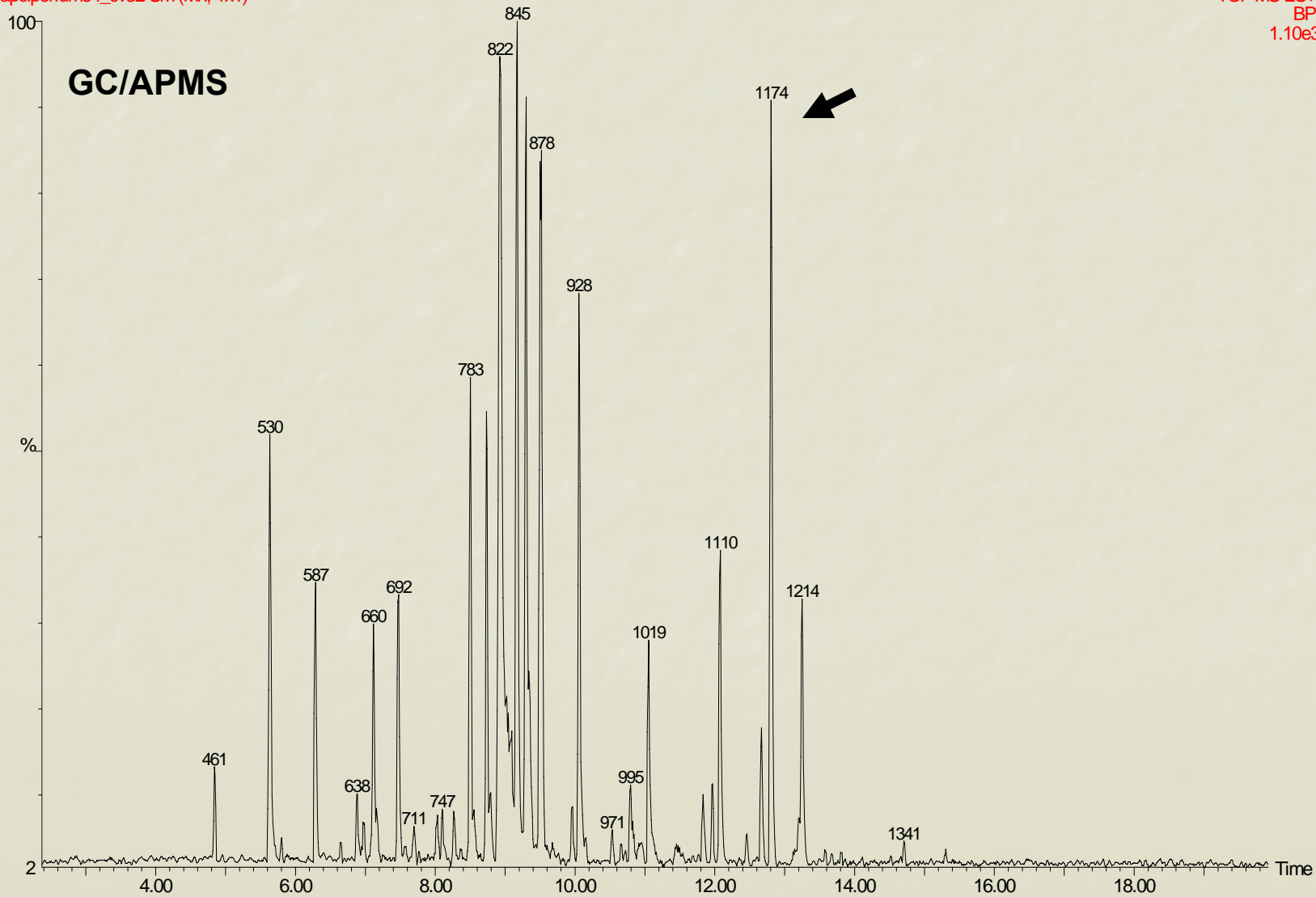
# ASAP of Perfume on Orbitrap



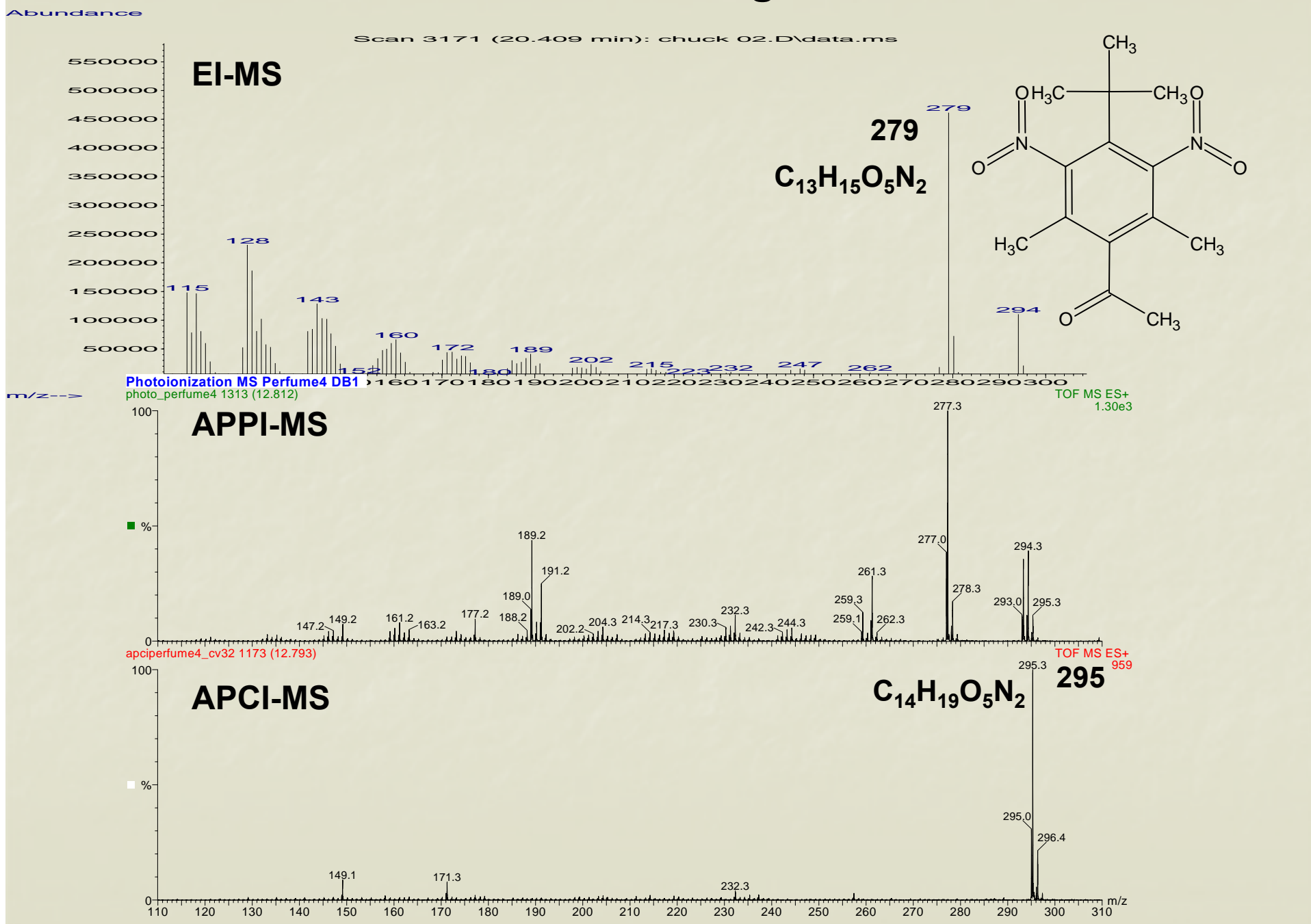
# Perfume Analysis

APGCMS Perfume4 30m DB1  
apciperfume4\_cv32 Sm (Mn, 1x1)

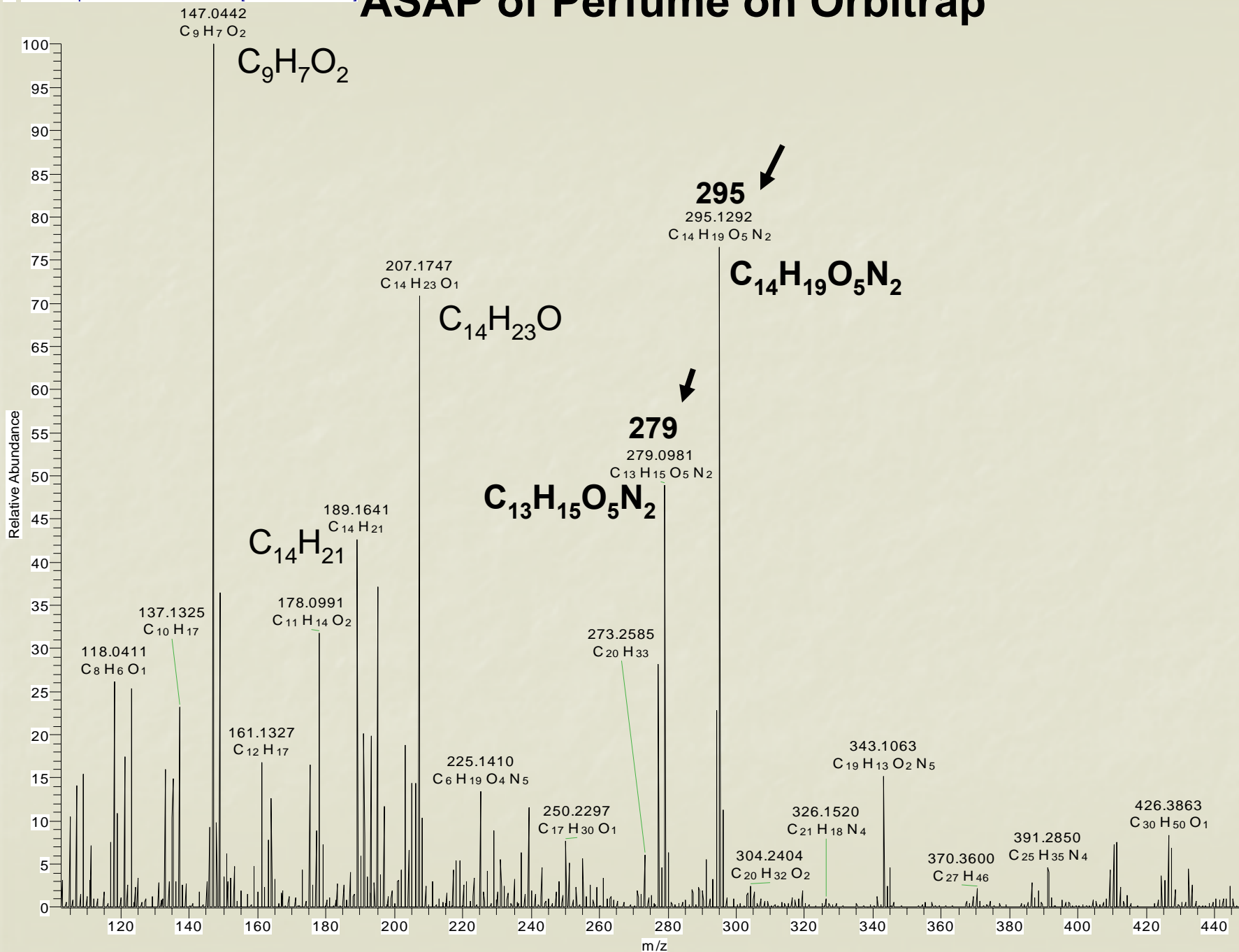
TOF MS ES+  
BPI  
1.10e3



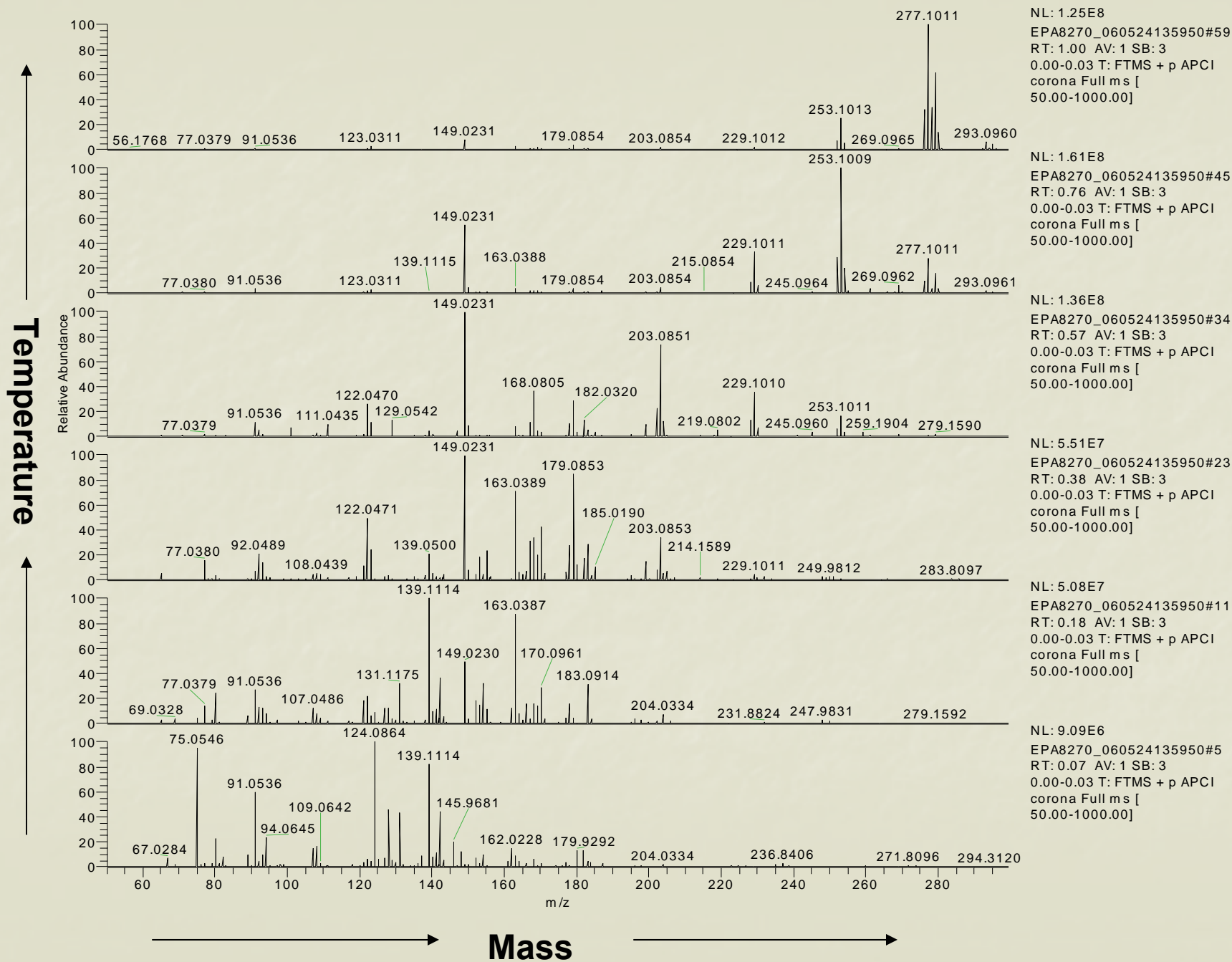
# GC/MS of Musk Ketone Using EI, APPI, and APCI



# ASAP of Perfume on Orbitrap

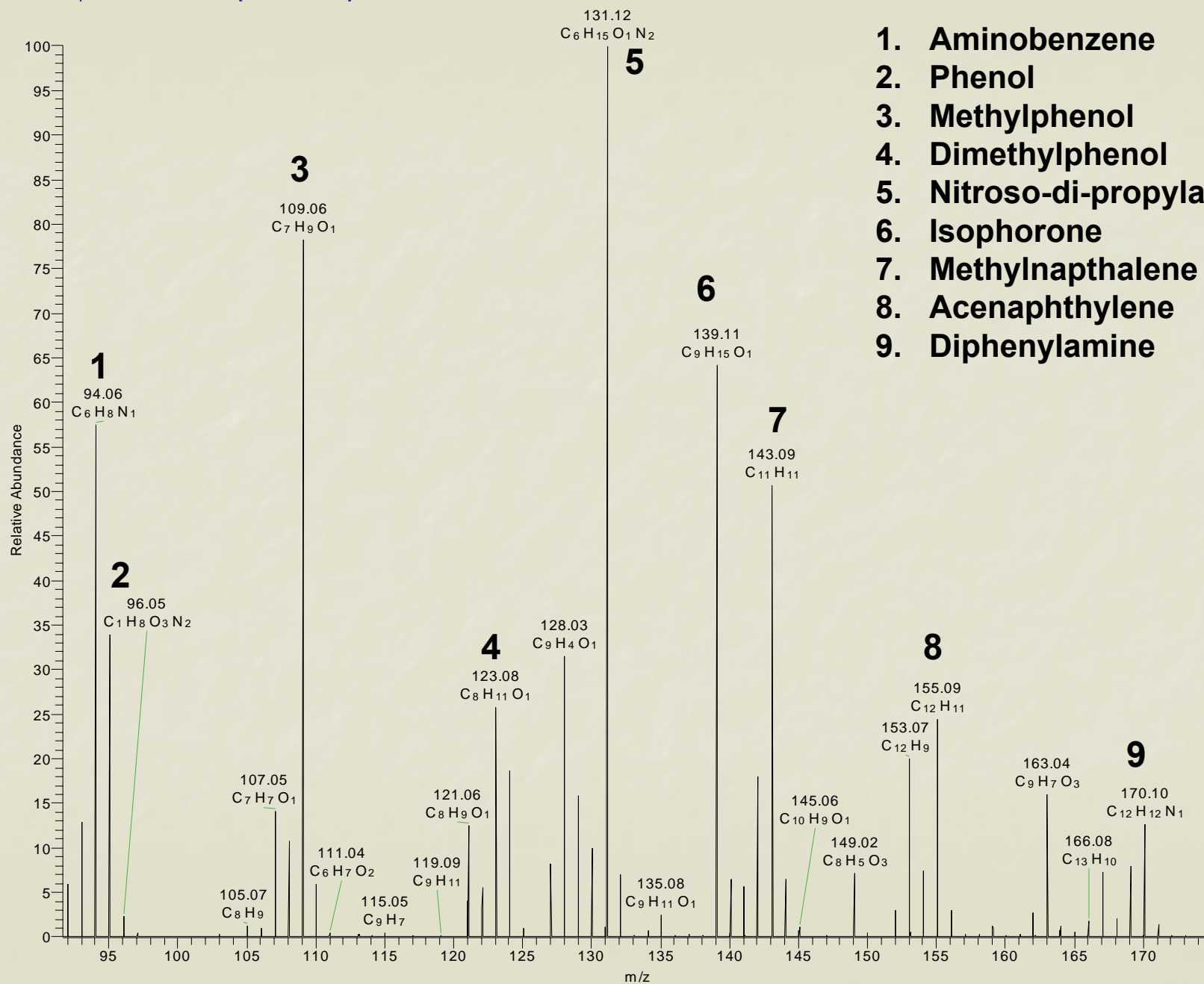


# EPA 8270 Megamix by ASAP as a Function of Time/Temperature



# ASAP of Restek EPA 8270 Megamix

EPA8270\_060524143111 #4 RT: 0.06 AV: 1 NL: 6.03E7  
T: FTMS + p APCI corona Full ms [50.00-1000.00]

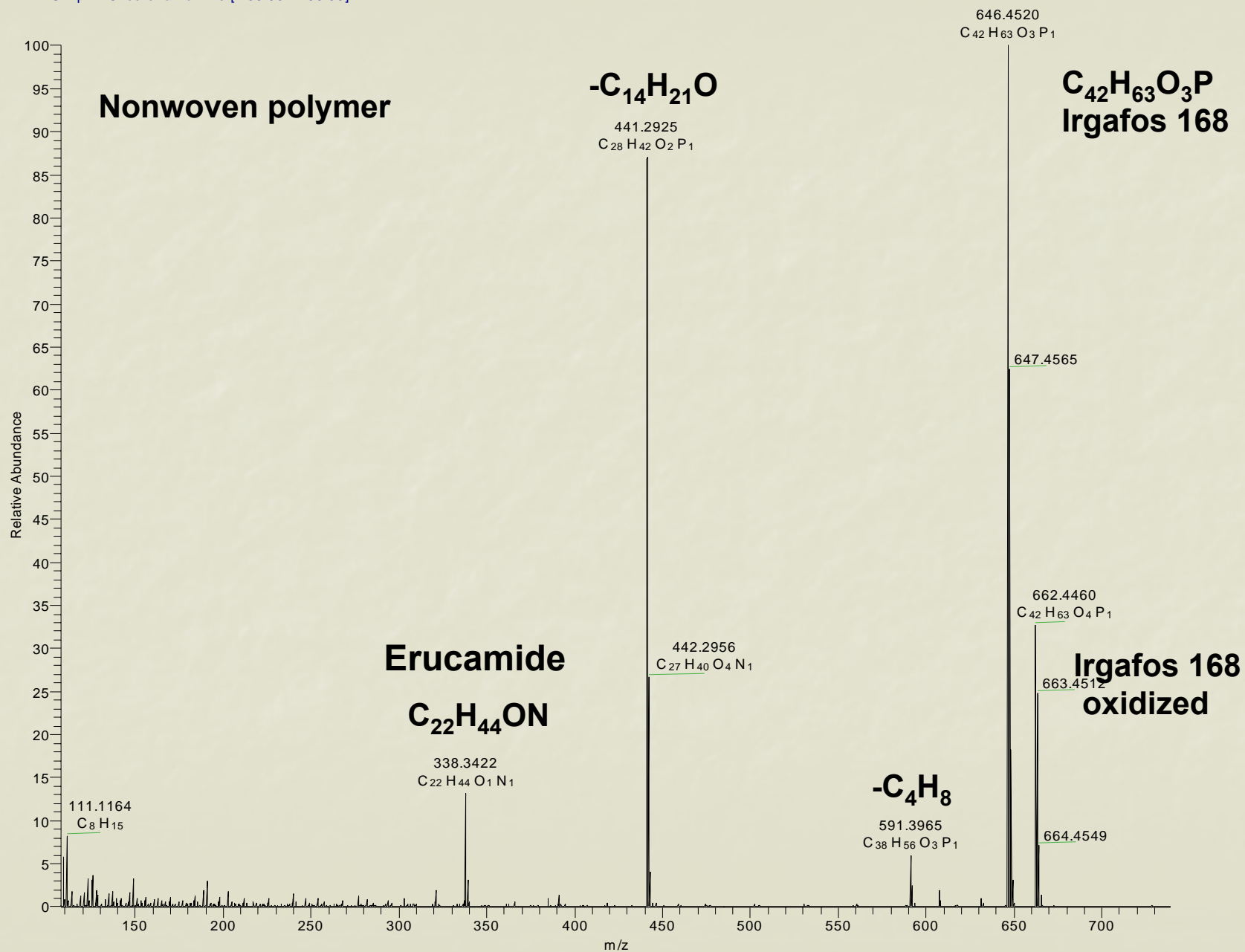


# Polymer Additive Analysis

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

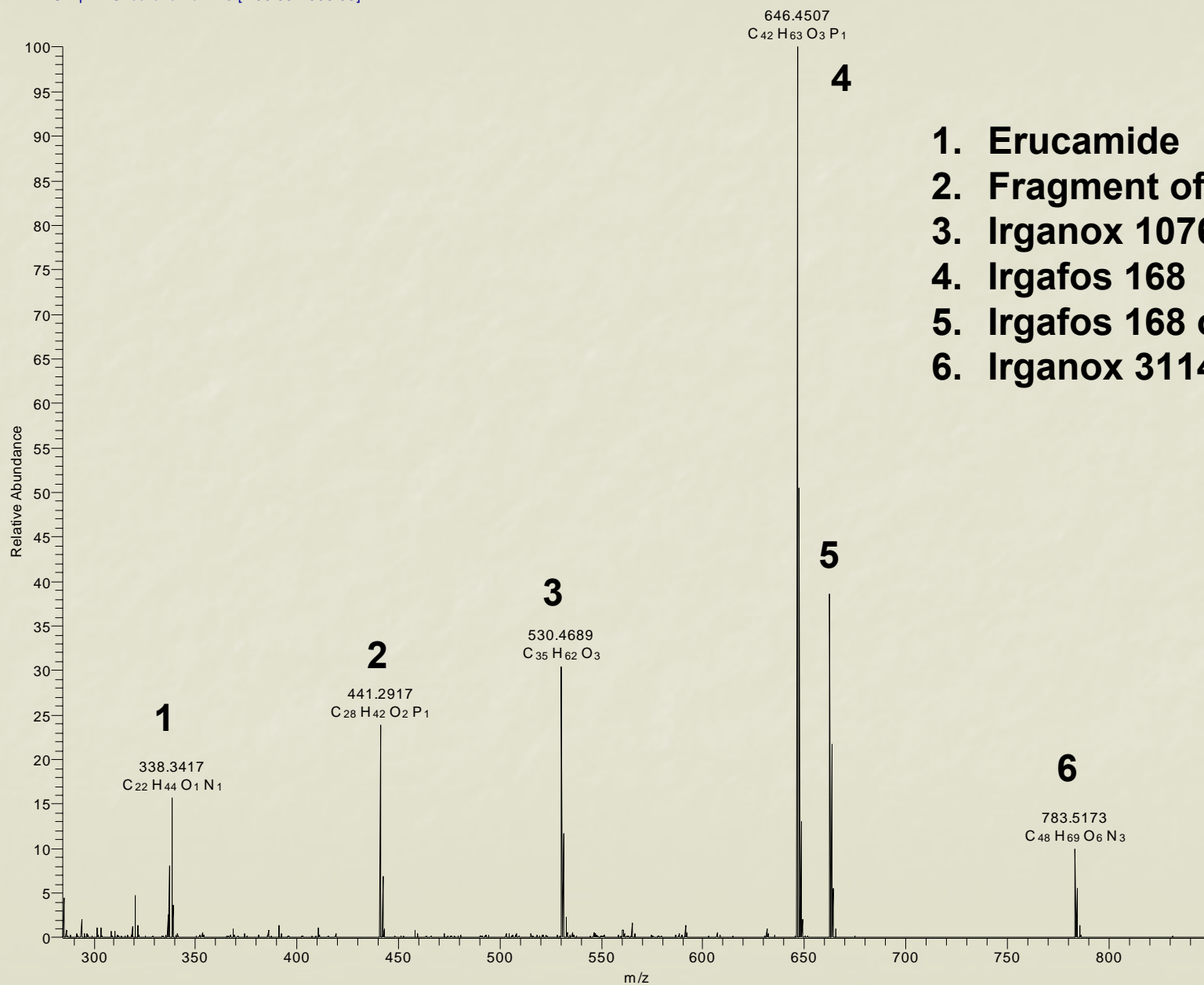
# ASAP of Additives in Polymer

MASSOUDA\_1\_PELLET\_060504125118 #42 RT: 1.26 AV: 1 NL: 1.76E7  
T: FTMS + p APCI corona Full ms [ 100.00-1200.00]



# ASAP of Nonwoven Fiber

nonwovan\_fabric\_060118155342 #63 RT: 1.89 AV: 1 NL: 1.00E7  
T: FTMS + p APCI corona Full ms [ 100.00-2000.00]



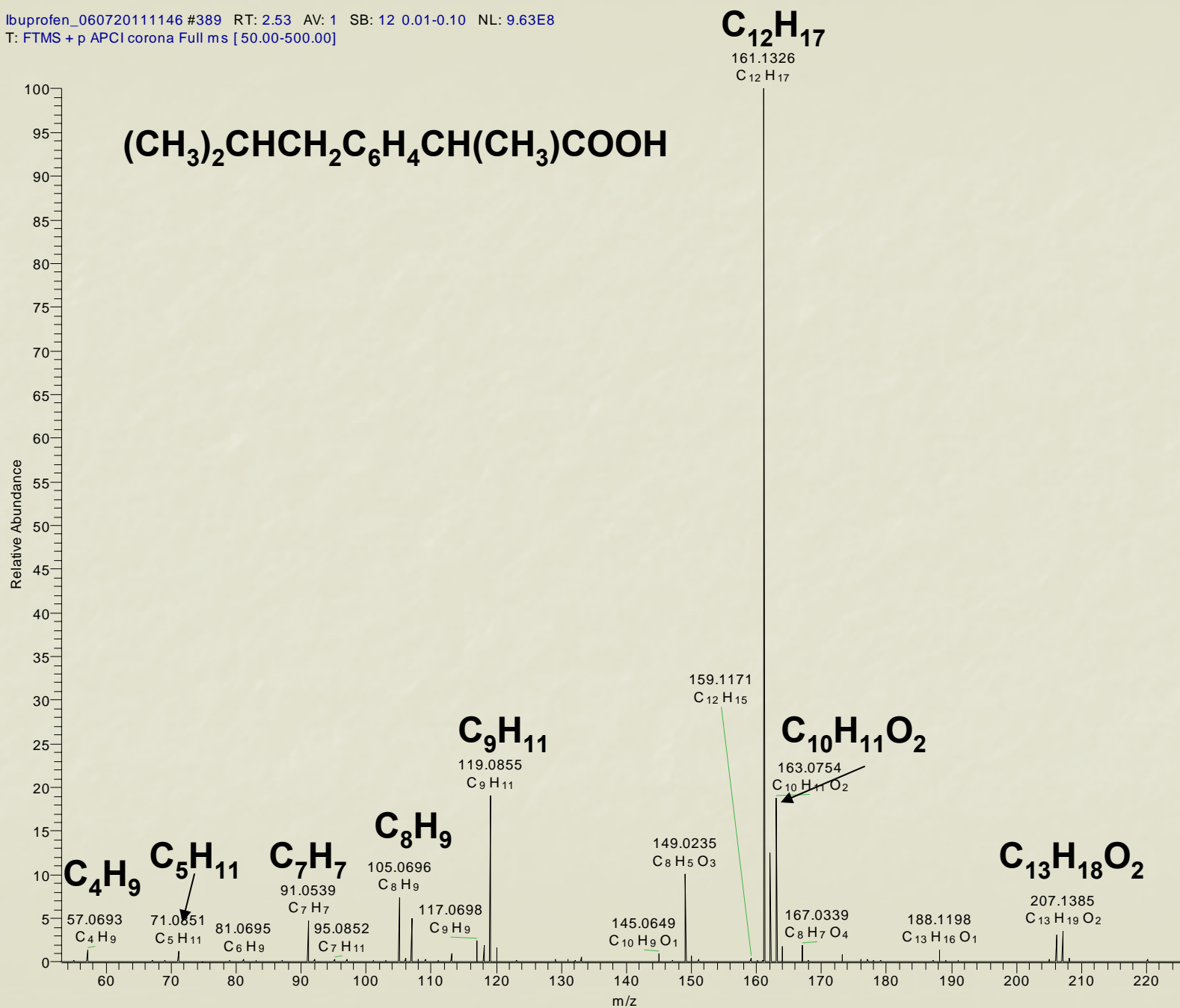
1. Erucamide
2. Fragment of 4
3. Irganox 1076
4. Irgafos 168
5. Irgafos 168 oxidized
6. Irganox 3114

# **ASAP of Drugs**

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

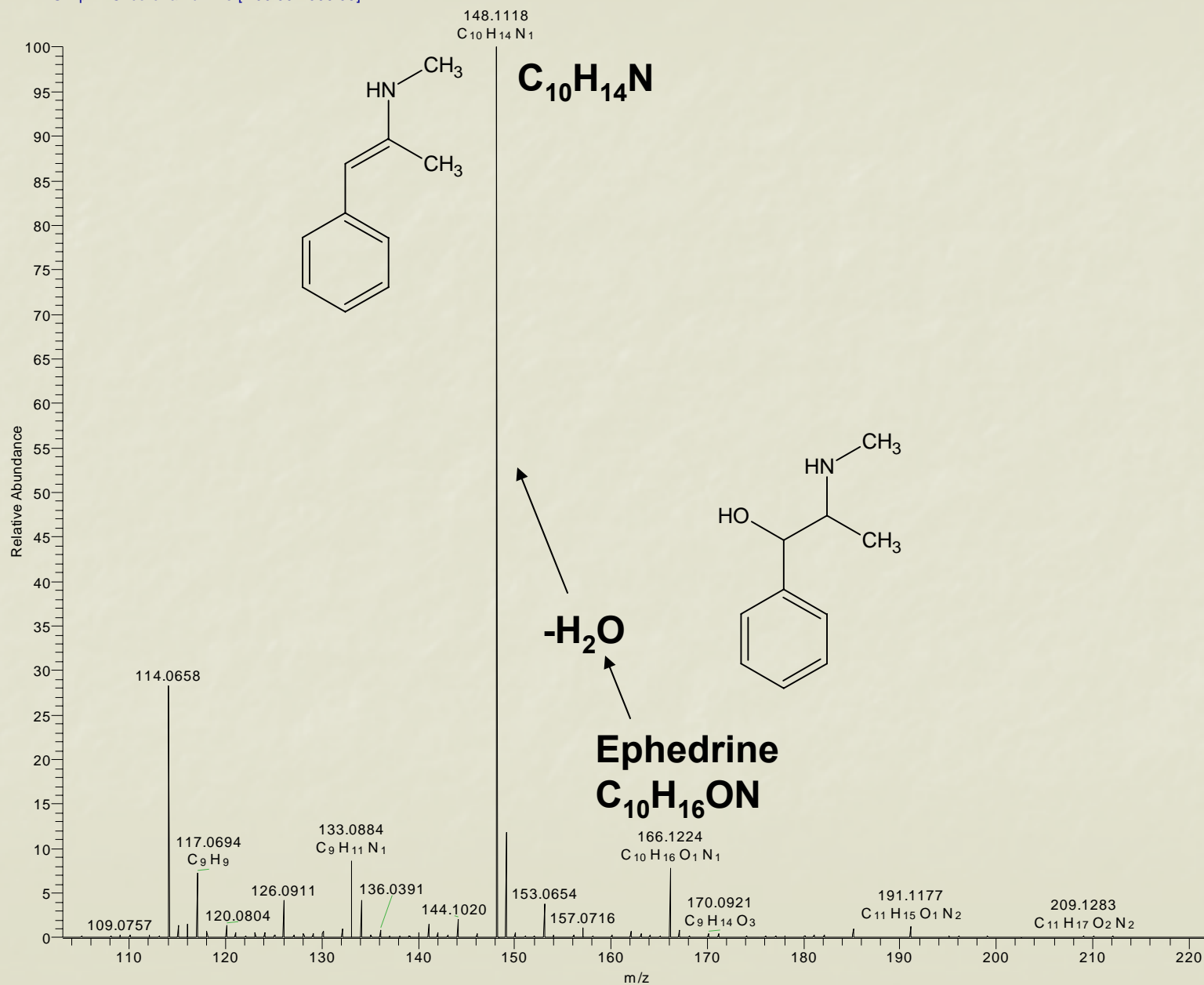
# ASAP of Ibuprofen Tablet

Ibuprofen\_060720111146 #389 RT: 2.53 AV: 1 SB: 12 0.01-0.10 NL: 9.63E8  
T: FTMS + p APCI corona Full ms [ 50.00-500.00]



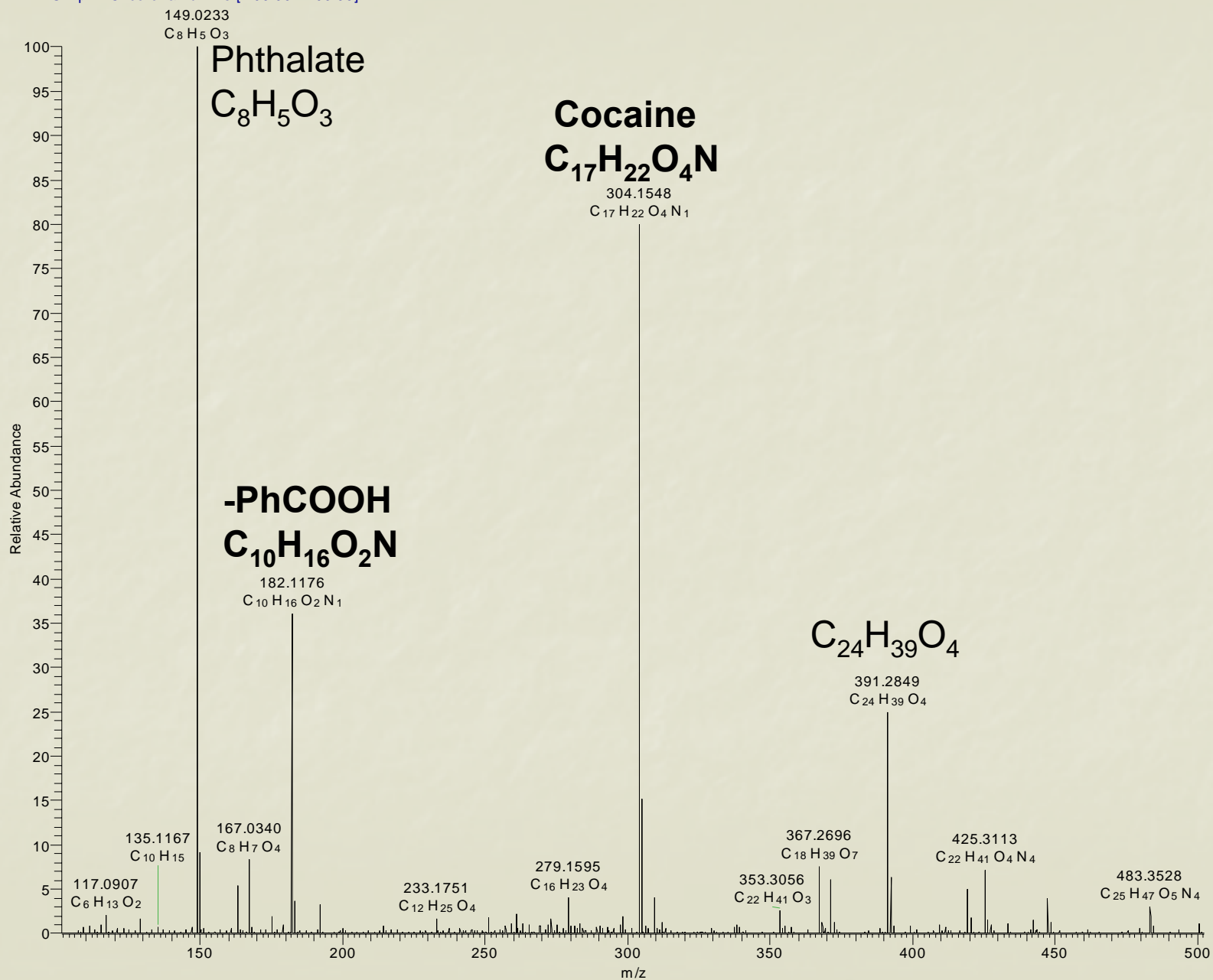
# Direct ASAP Analysis of Urine Sample 9 hrs After 12 hr Sedarfed<sup>®</sup>

cnmurin\_psuedo\_caf\_060324101339 #33 RT: 1.05 AV: 1 SB: 7 0.04-0.24 NL: 5.77E7  
T: FTMS + p APCI corona Full ms [ 100.00-1000.00]



# The Famous Cocaine on a Dollar Bill

dollar\_bills\_051118165312 #198 RT: 1.72 AV: 1 NL: 8.56E8  
T: FTMS + p APCI corona Full ms [ 100.00-1200.00]

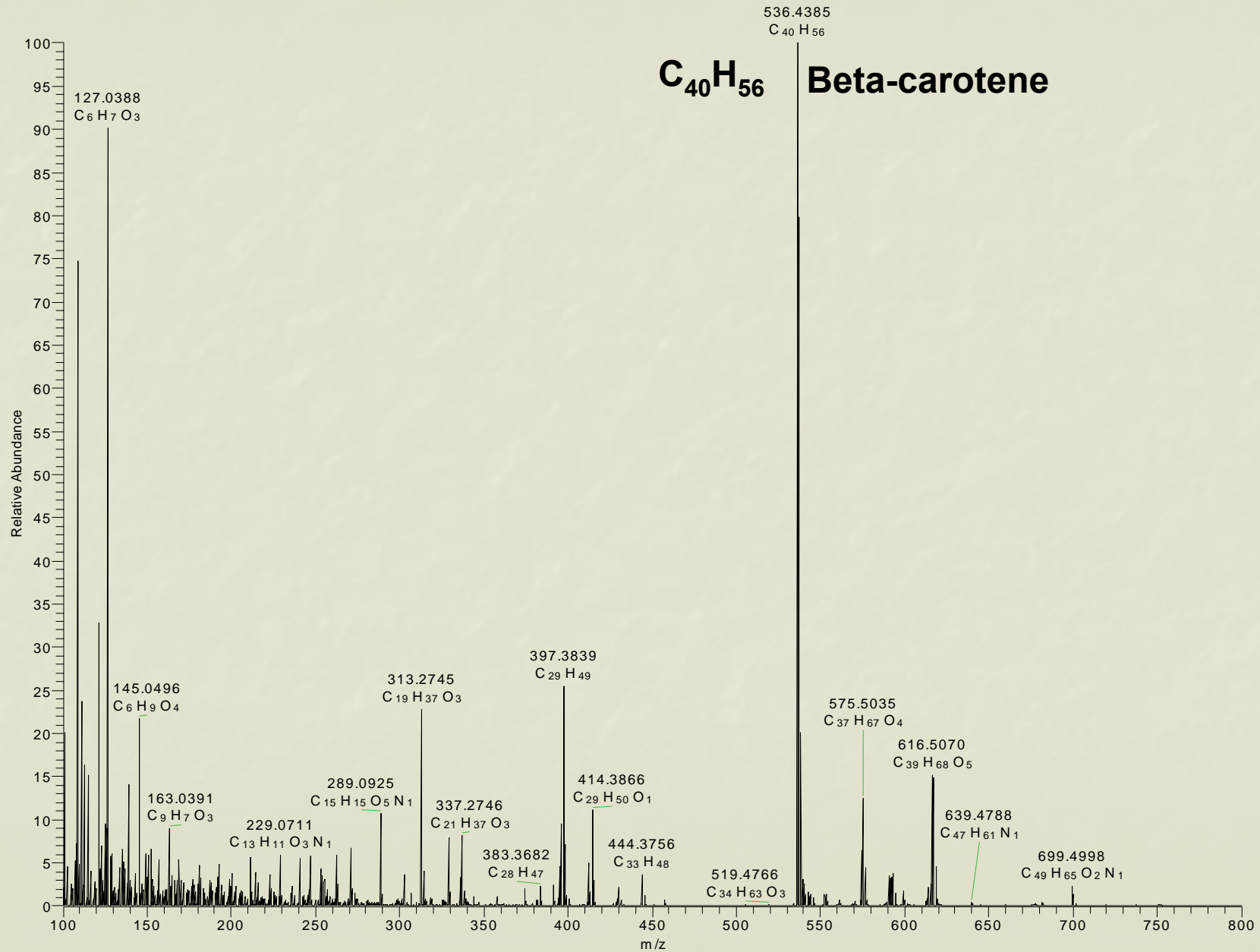


# **ASAP of Biological Samples**

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

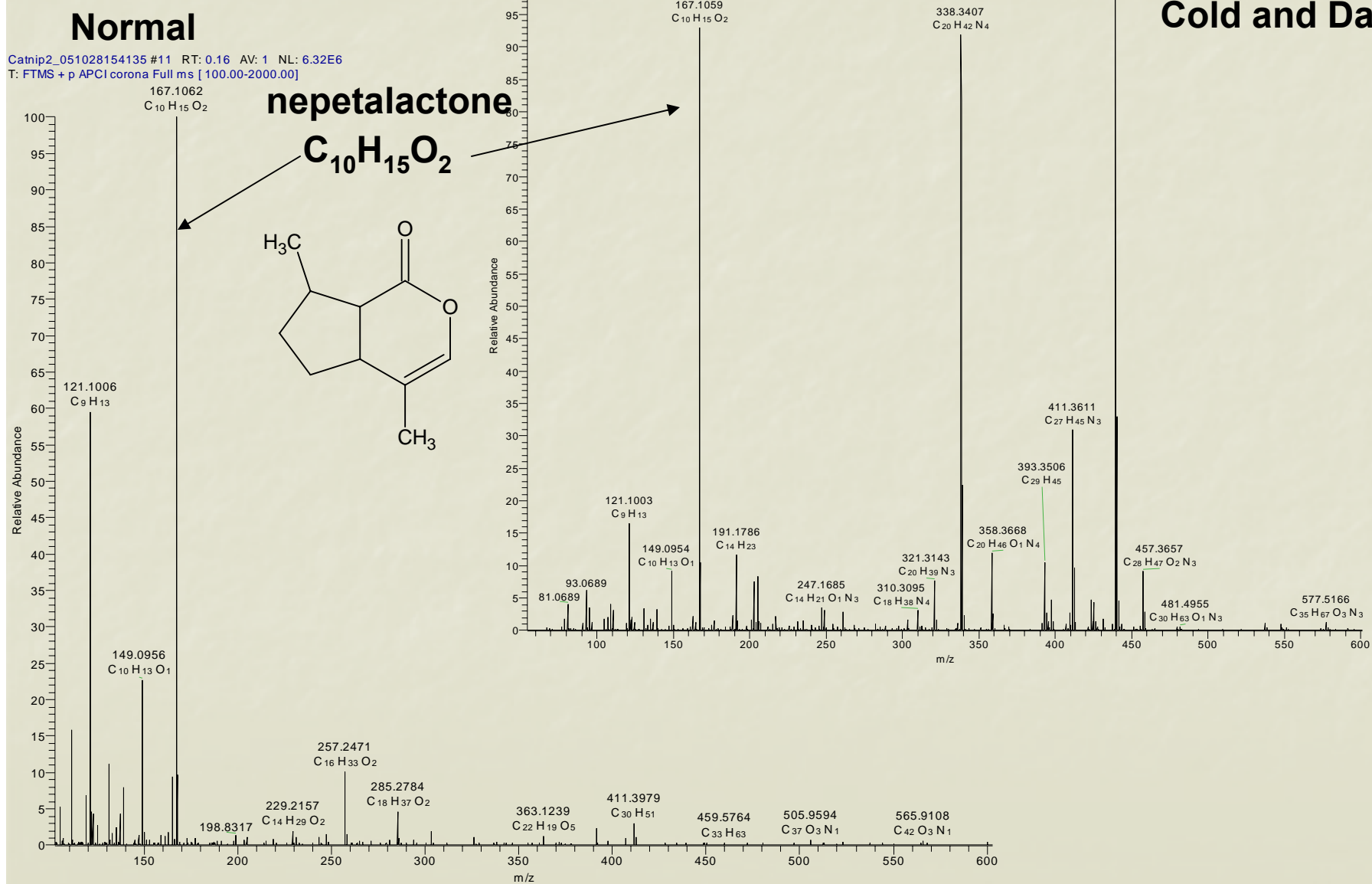
# ASAP of Carrot

carot\_060329155429 #20 RT: 0.57 AV: 1 NL: 4.25E6  
T: FTMS + p APCI corona Full ms [100.00-800.00]

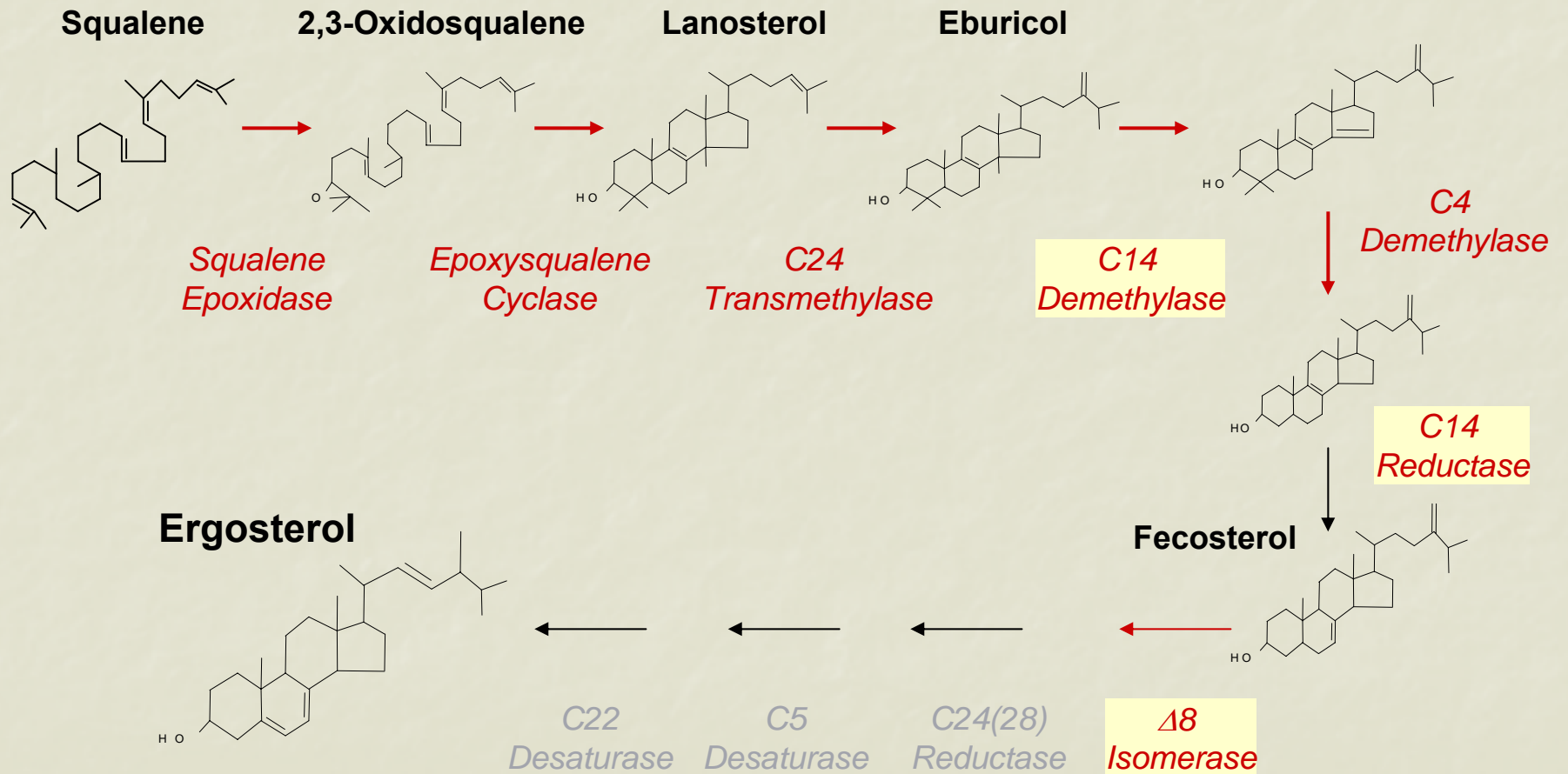


# ASAP of Catnip Leaf Normal Growth and After Growth in Cold and Dark

catnip\_cold\_060111151518 #54 RT: 1.47 AV: 1 NL: 1.10E8  
T: FTMS + p APCI corona Full ms [50.00-1000.00]

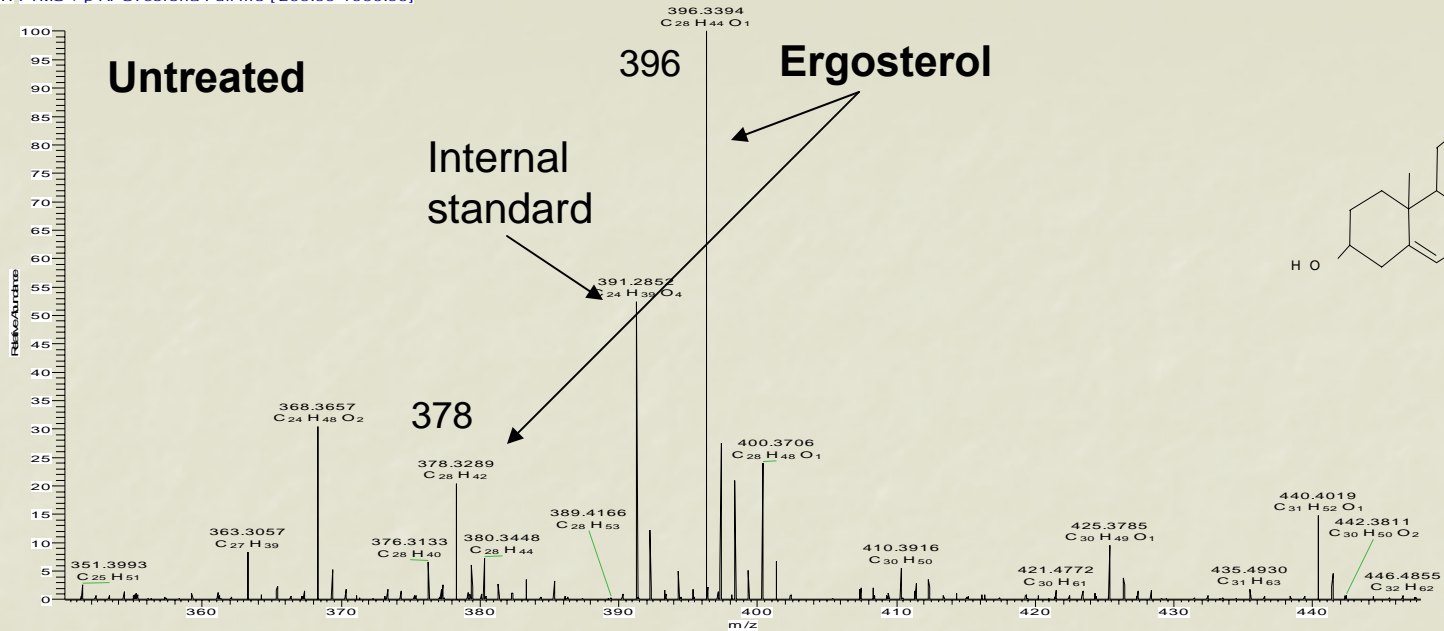


# Ergosterol Biosynthesis

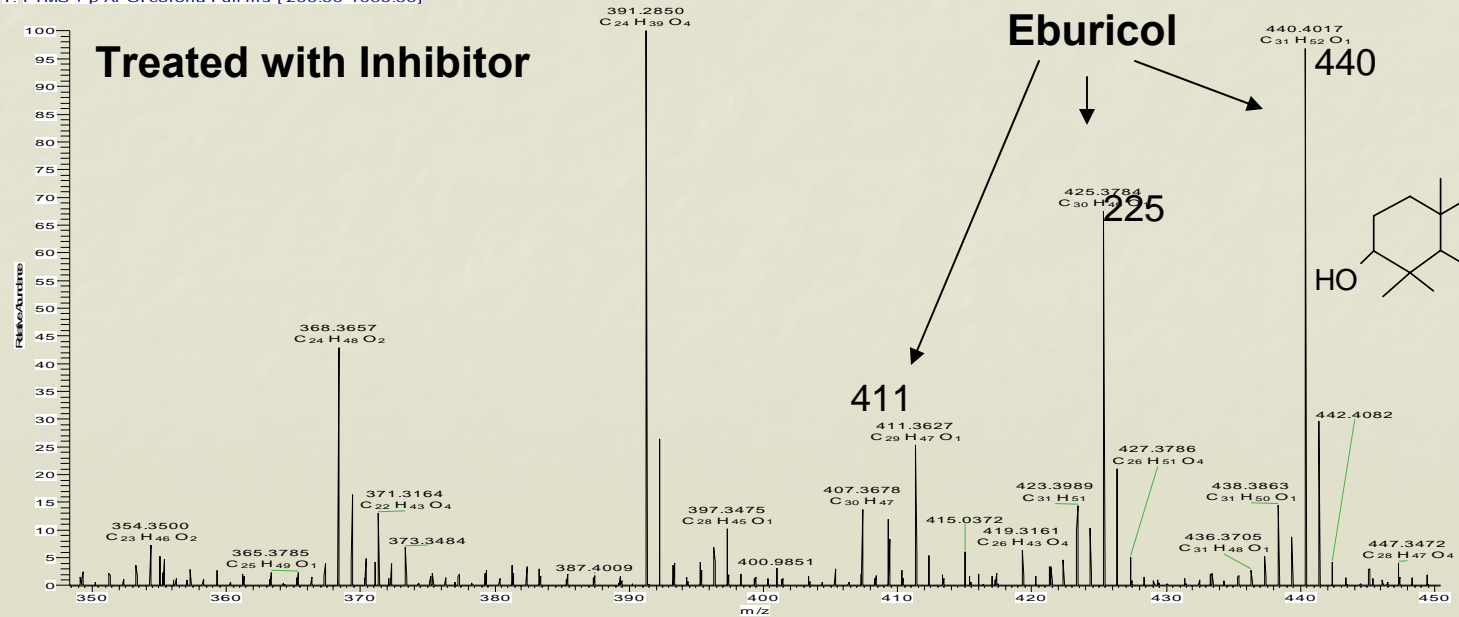


# ASAP of Fungus Cells

AG\_FUNGUS\_CONTROL\_S\_060228154133 #22 RT: 0.65 AV: 1 SB: 3 0.00-0.07 NL: 1.05E5  
T: FTMS + p APCI corona Full ms [ 200.00-1000.00]

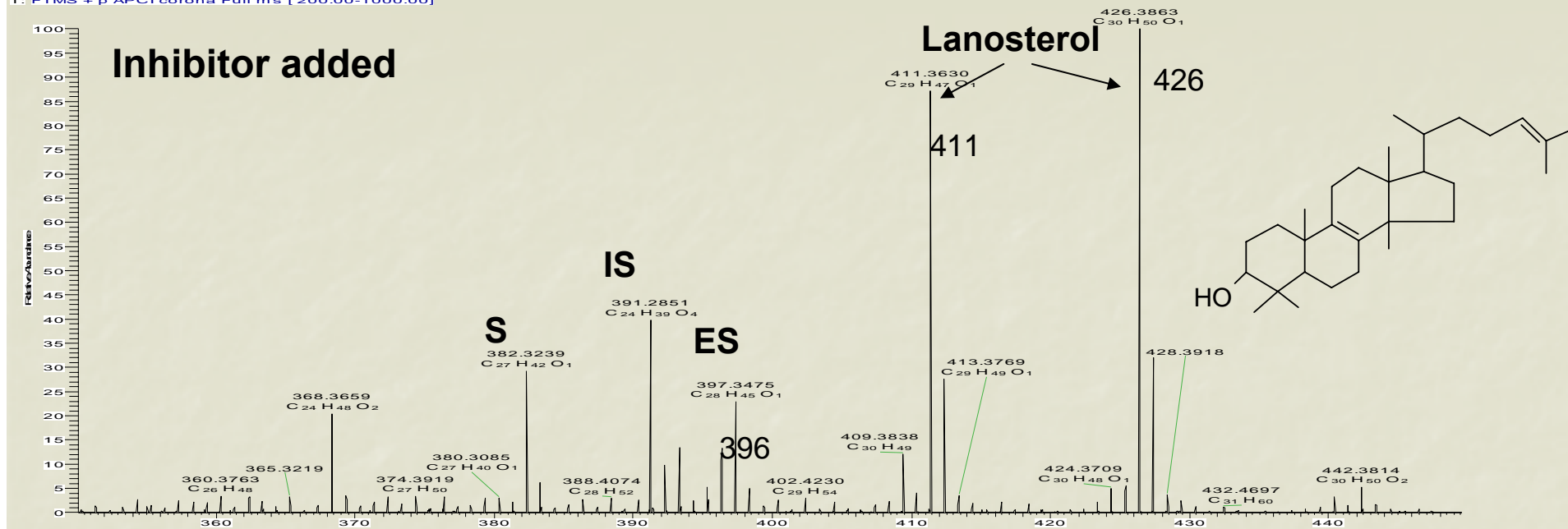


AG\_FUNGUS\_H6573\_S\_060228172336 #25 RT: 0.73 AV: 1 SB: 3 0.01-0.07 NL: 3.85E4  
T: FTMS + p APCI corona Full ms [ 200.00-1000.00]

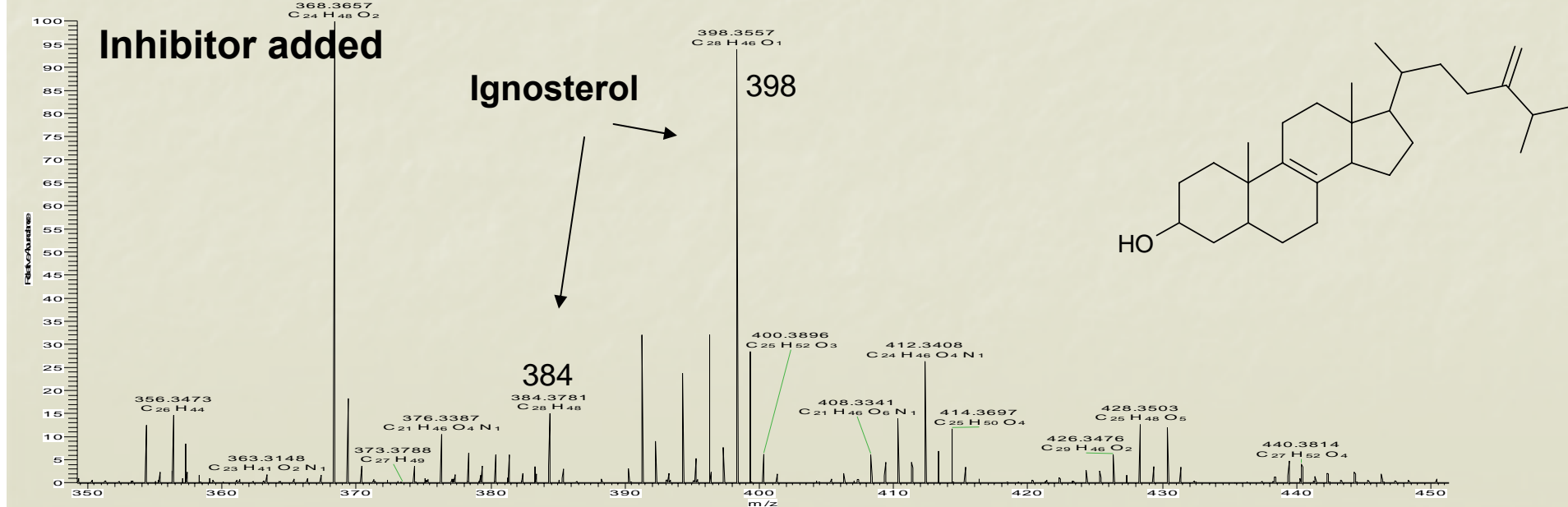


# ASAP of Treated Fungus

AG\_FUNGUS\_JP355\_S\_060228172336 #23 RT: 0.60 AV: 1 SB: 3 0.01-0.07 NL: 2.53E5  
T: FTMS + p APCI corona Full ms [ 200.00-1000.00]



AG\_FUNGUS\_YB837\_S\_060228172336 #23-27 RT: 0.54-0.63 AV: 5 SB: 3 0.01-0.07 NL: 4.52E5  
T: FTMS + p APCI corona Full ms [ 200.00-1000.00]

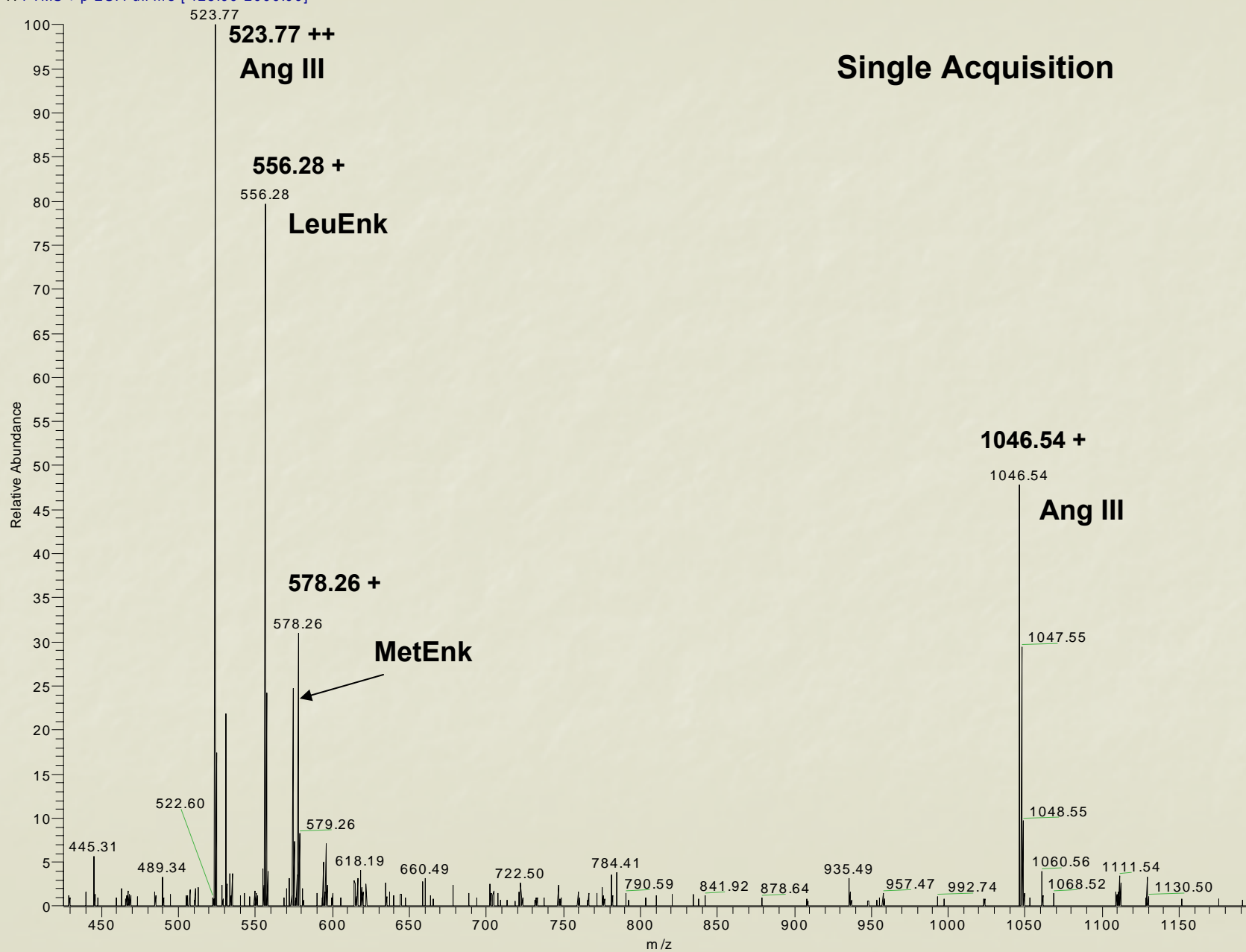


# ASAP Probe for DESI

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

# Sigma Peptide Mixture by ASAP Probe DESI

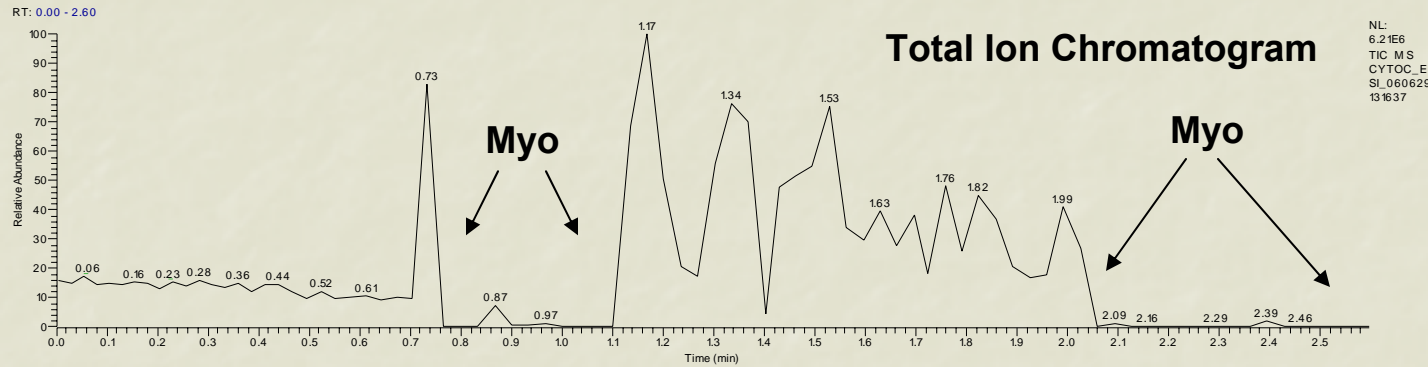
SIGMAPEP\_ESI\_060629131637 #109 RT: 3.42 AV: 1 NL: 5.56E4  
T: FTMS + p ESI Full ms [425.00-2000.00]



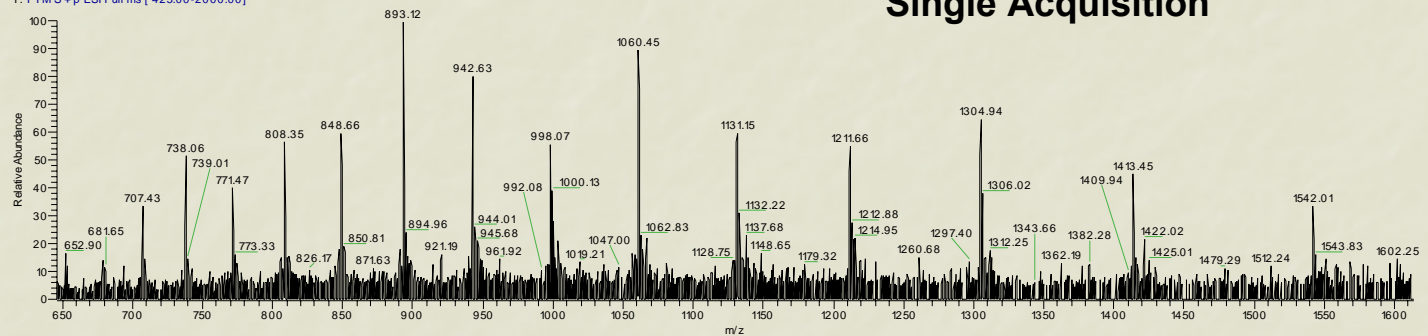
# Myoglobin by ASAP Probe DESI

XtractTemp\_20060710162342

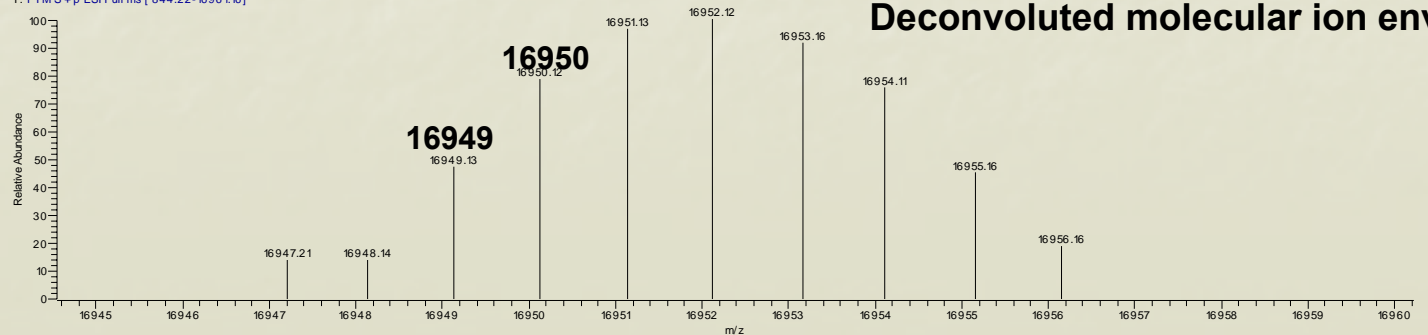
7/10/2006 4:23:46 PM



CYTOC\_ESI\_060629131637#28 RT: 0.73 AV: 1 NL: 149E4  
T: FTM S+p ESI Full ms [ 425.00-2000.00]



XtractTemp\_20060710162342#1 RT: 100 AV: 1 NL: 136E3  
T: FTM S+p ESI Full ms [ 844.22-1696.16]



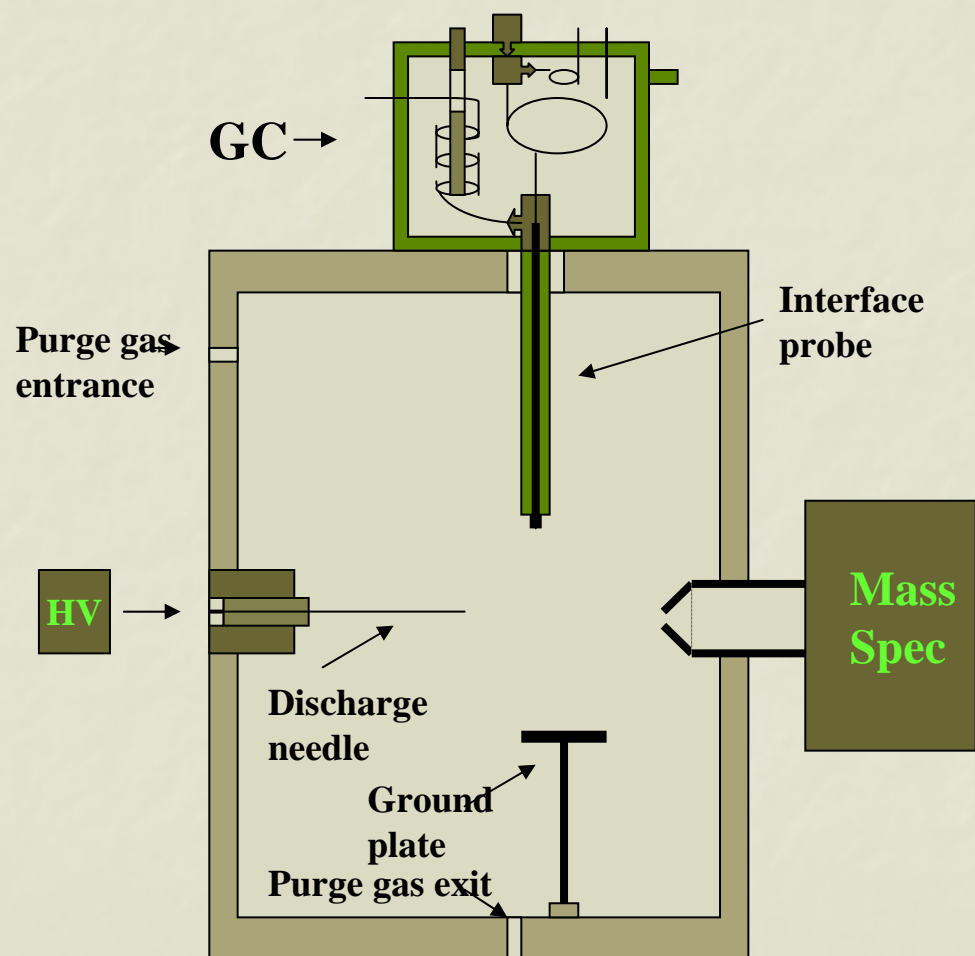
# Conclusions

- 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

- o **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.**
- o **Any LC/MS instrument can also be used as a GC/MS instrument.**
- o **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.

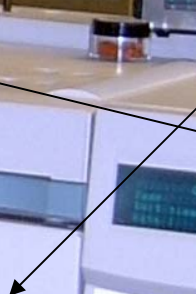
### Advantages over vacuum GC/MS

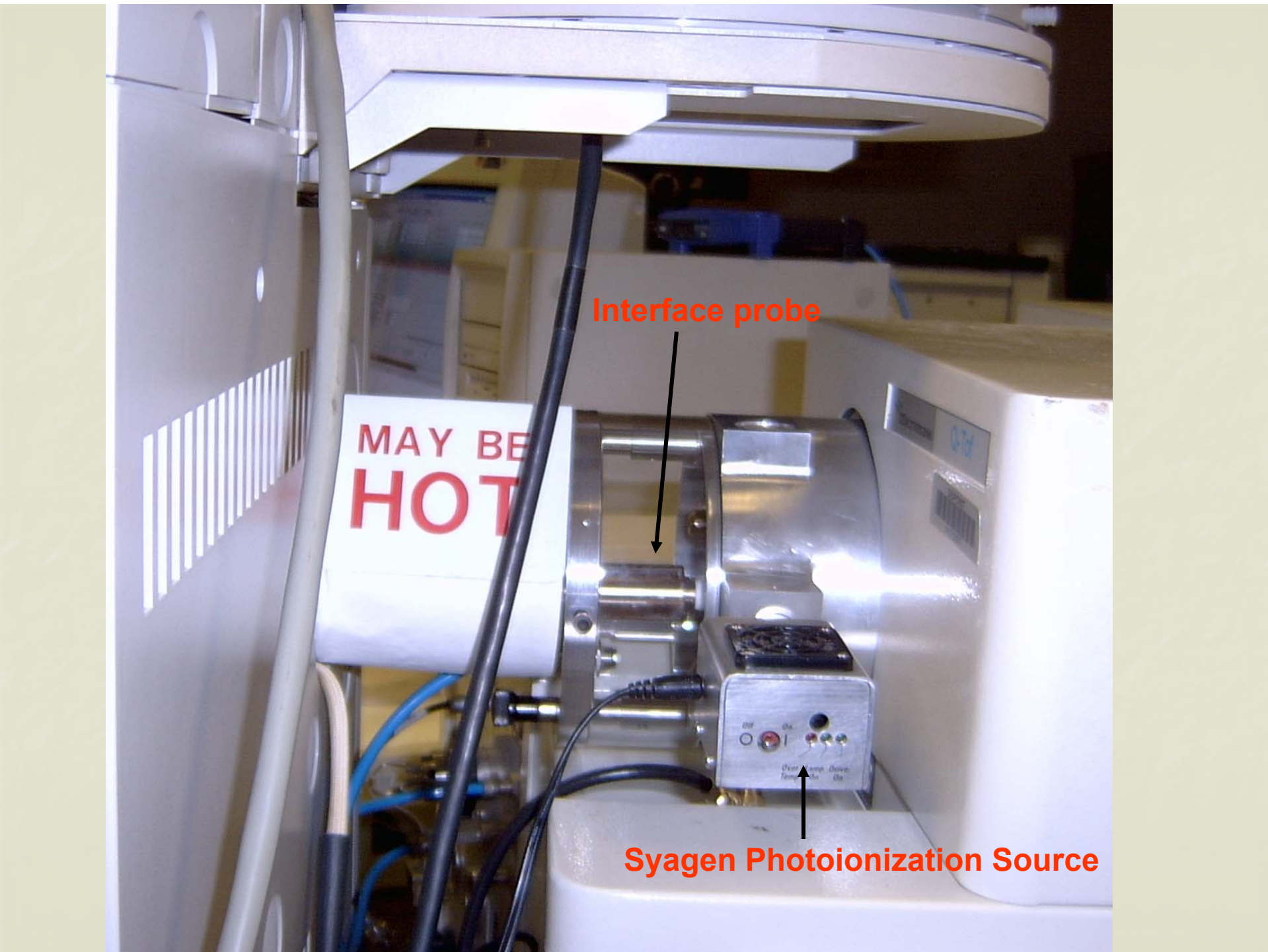
- Uses high performance LC/MS instrumentation
- Mass selected fragmentation for GC/MS Quantitation

**Waters QTof**



**Agilent GC  
With autosampler**



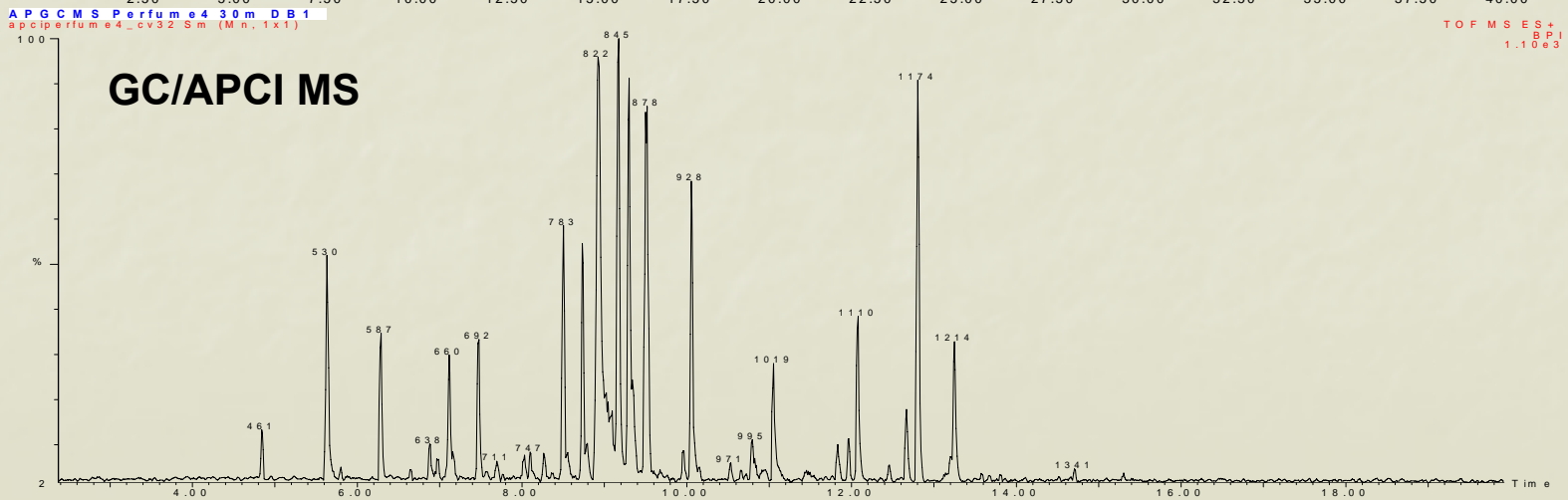
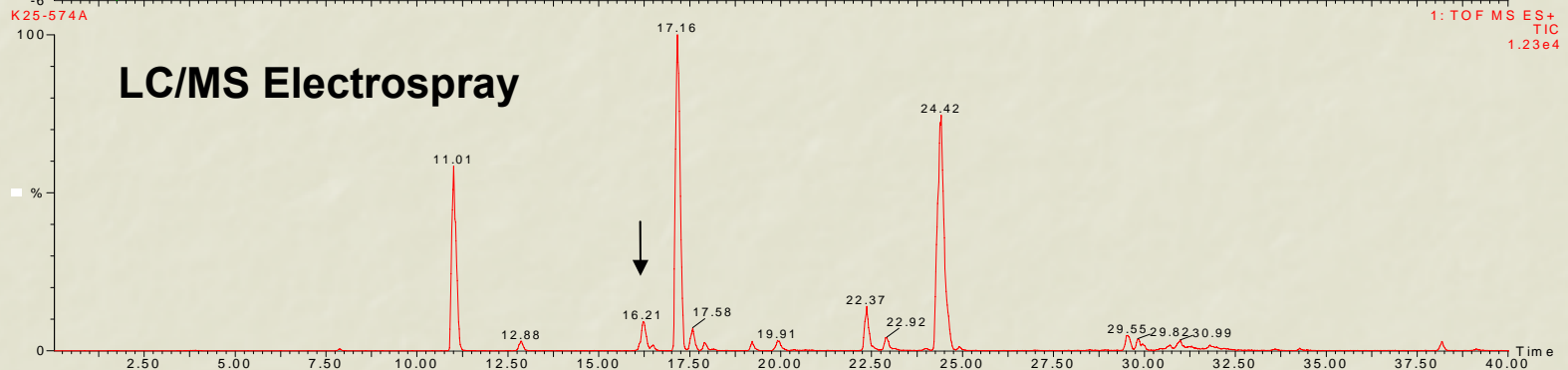
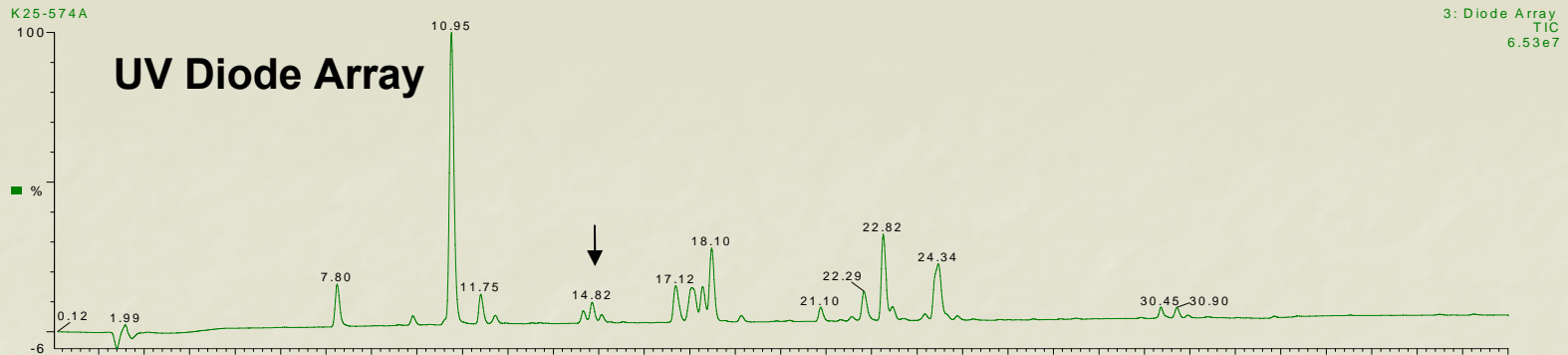


MAY BE  
**HOT**

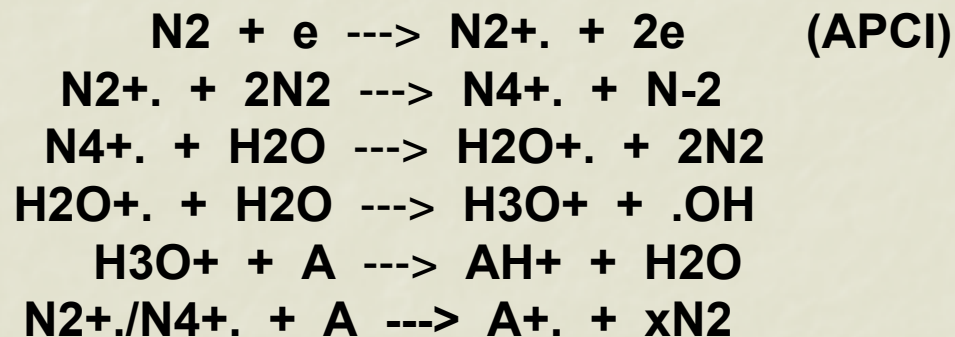
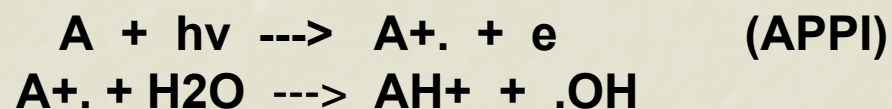
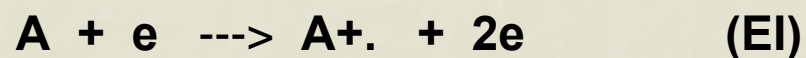
Interface probe

Syagen Photoionization Source

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



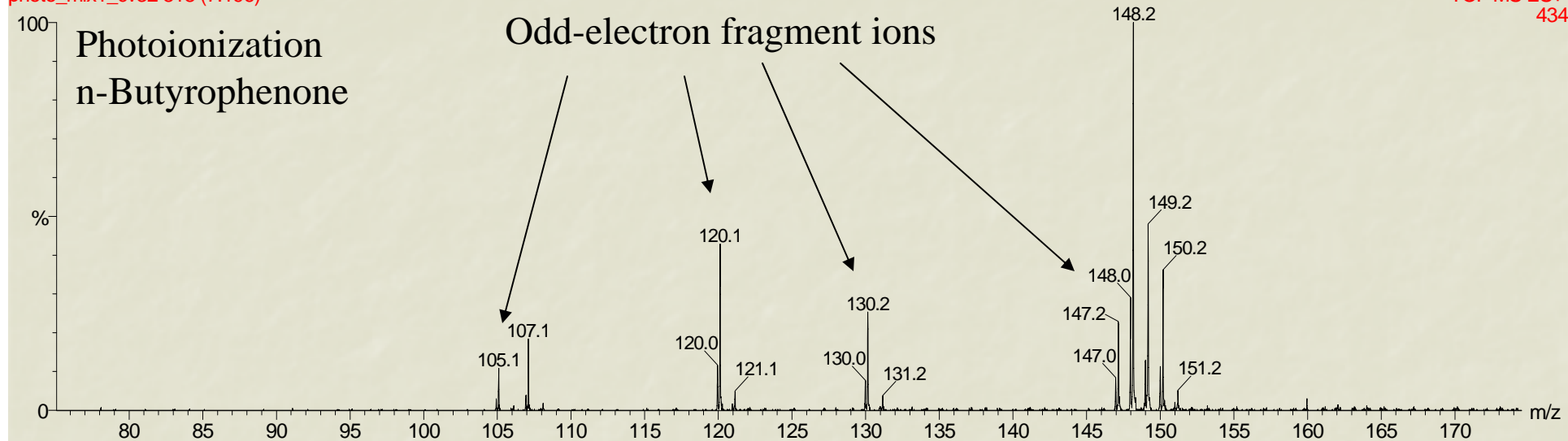
## Molecular and MH<sup>+</sup> Ion Generation



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

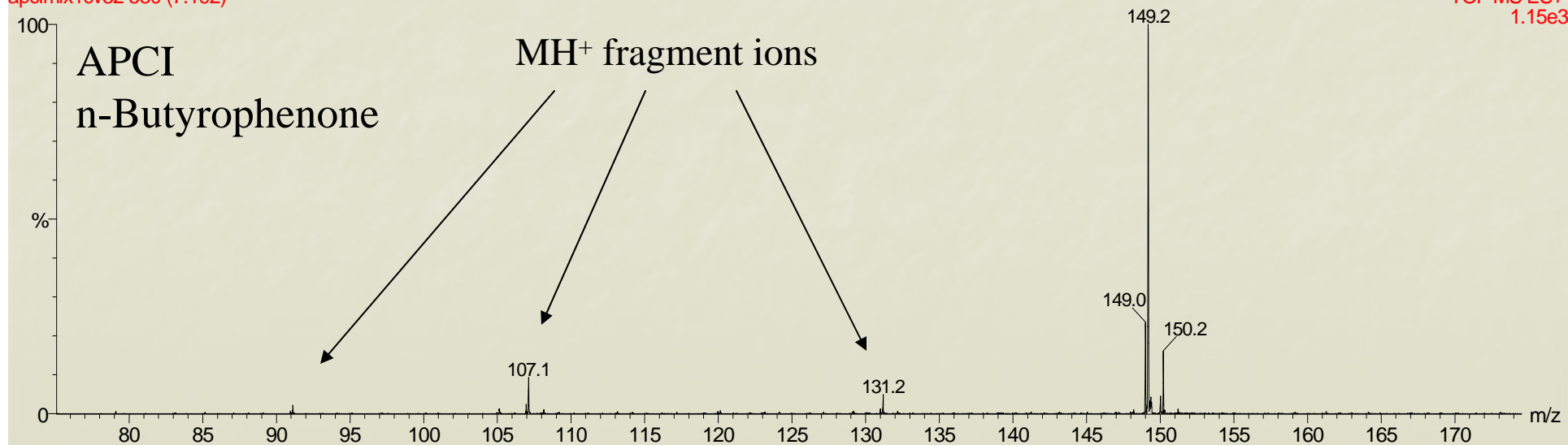
Photoionization MS photoMix1 30m DB1

photo\_mix1\_cv32 818 (7.196)



APGCMS photomix1 30m DB1

apcimix1cv32 530 (7.192)

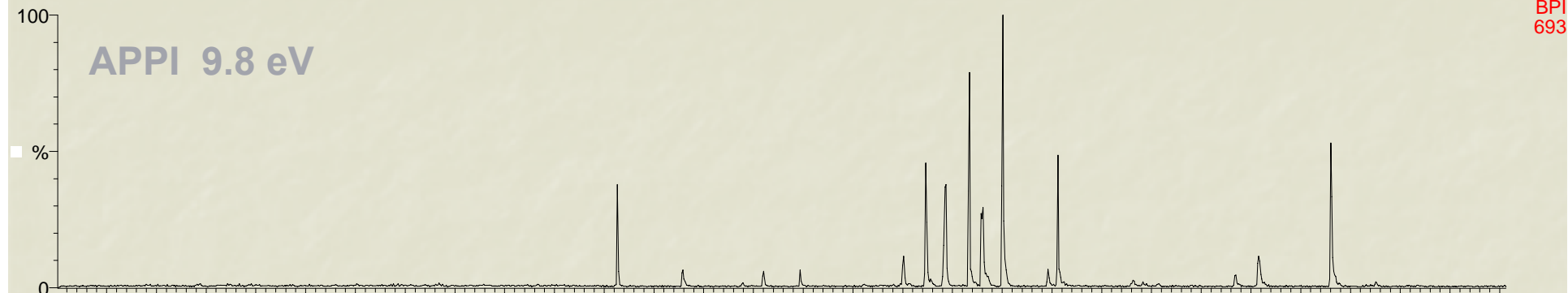


# Perfume Analysis by API-GC/MS

- 1) Rose oil 2) Linalool 3) C<sub>14</sub>H<sub>12</sub> 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

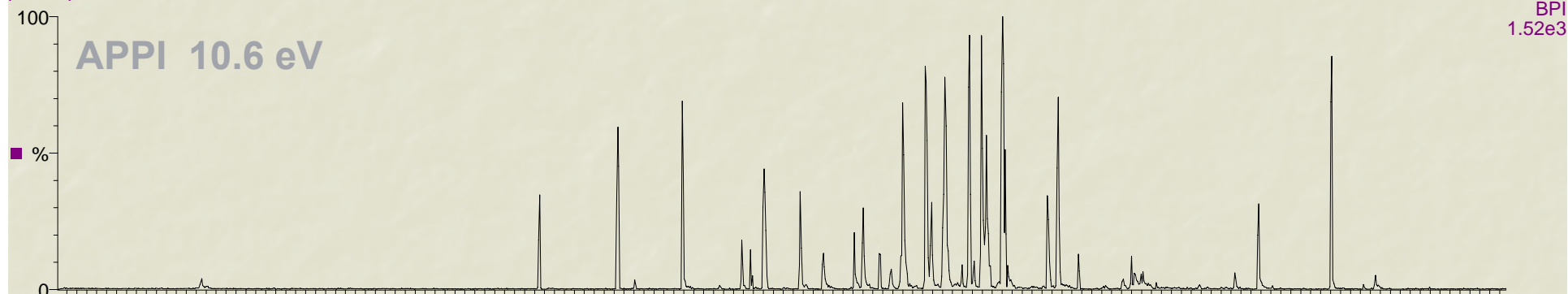
photoperfume4\_cv33

TOF MS ES+  
BPI  
693



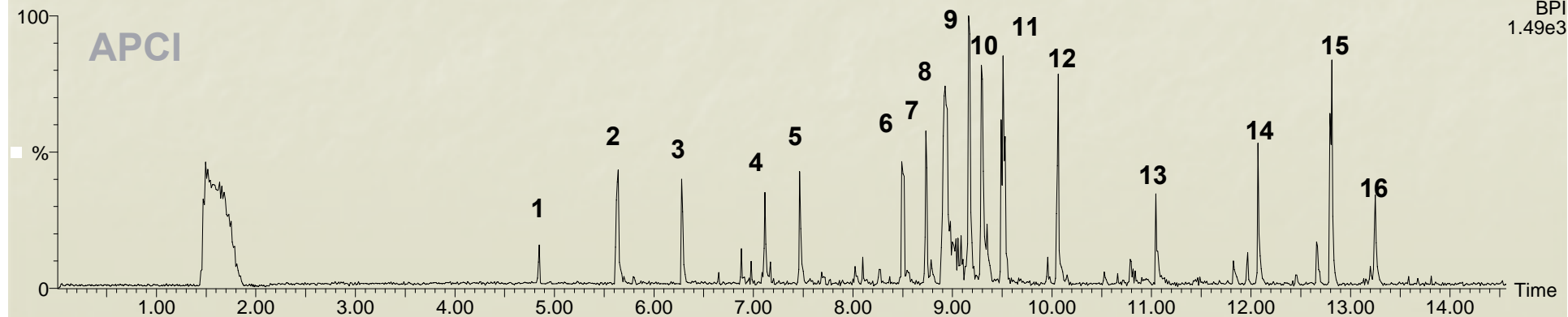
photo\_perfume4

TOF MS ES+  
BPI  
1.52e3



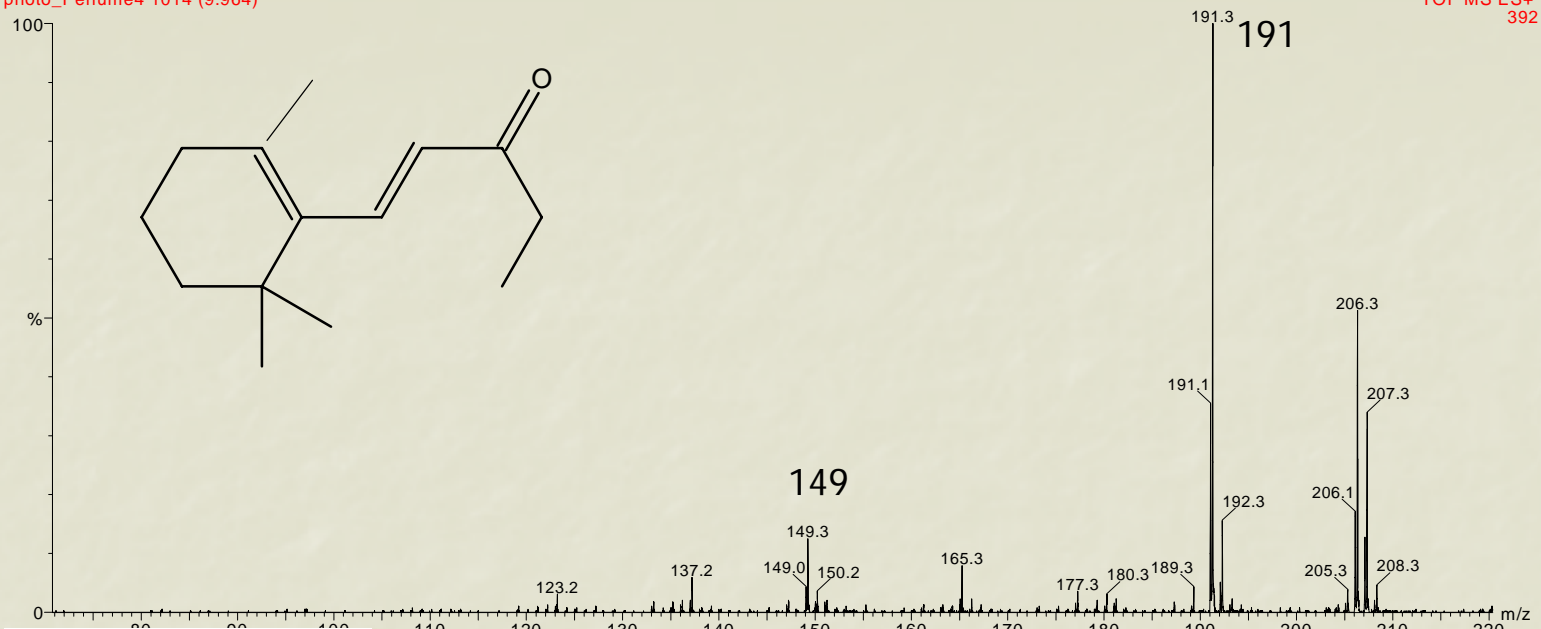
apciperfume4\_cv32

TOF MS ES+  
BPI  
1.49e3

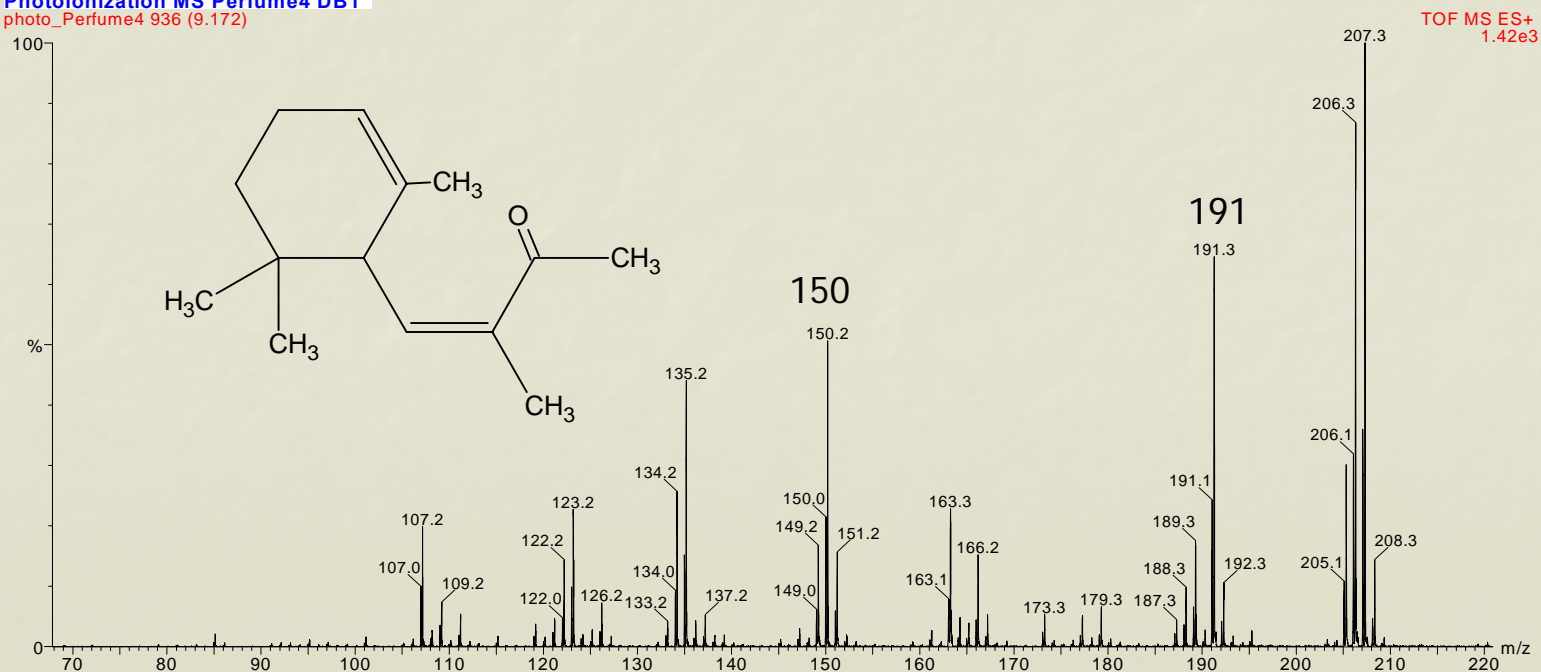


# APPI Spectra of Isomers of methyl-ionone

Photoionization MS Perfume4 DB1  
photo\_Perfume4 1014 (9.964)



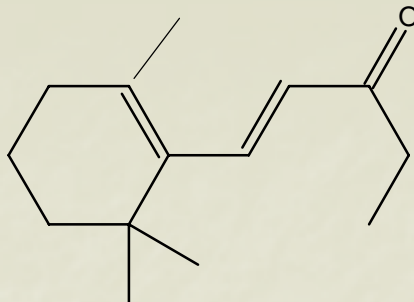
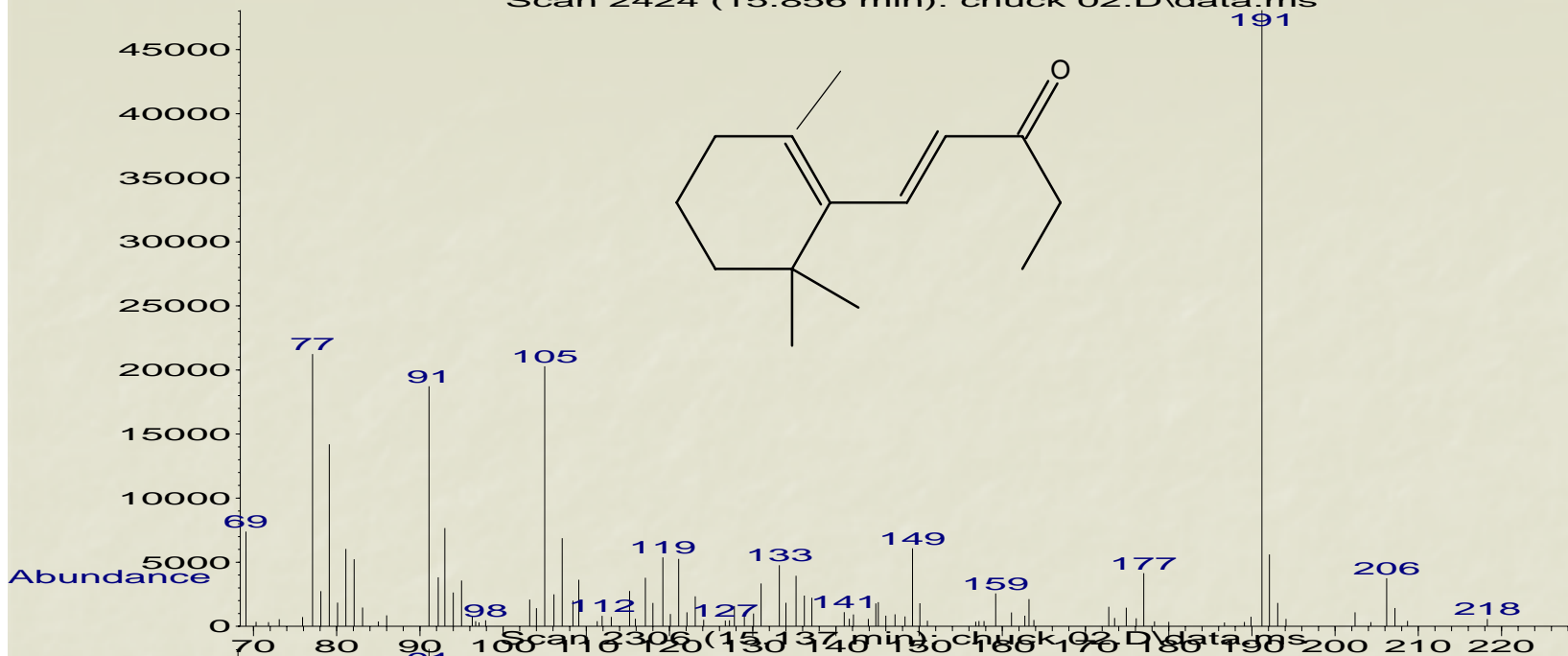
Photoionization MS Perfume4 DB1  
photo\_Perfume4 936 (9.172)



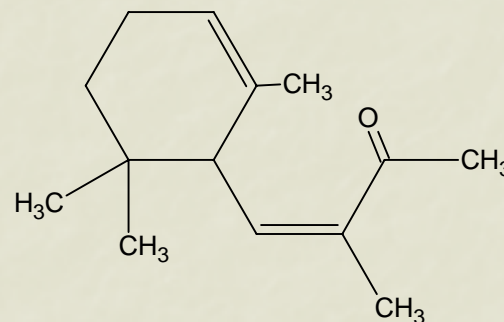
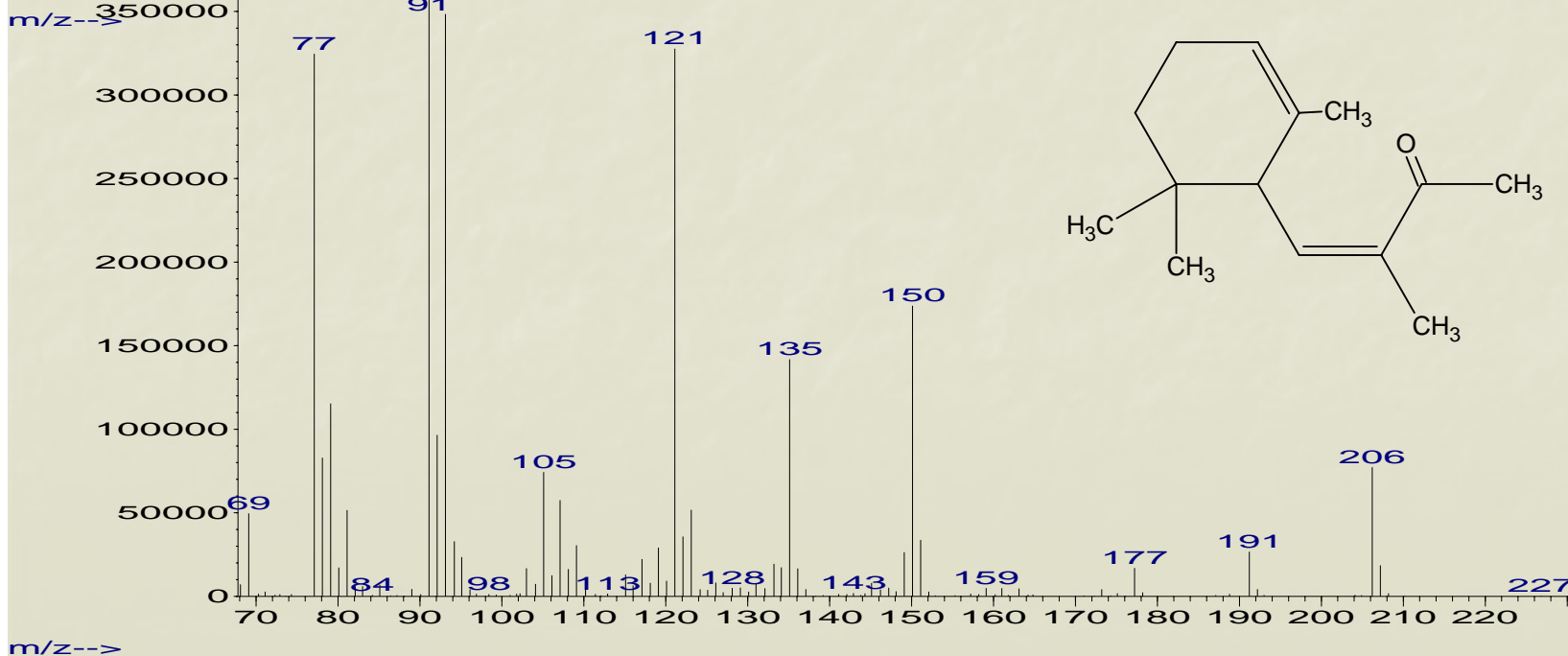
Abundance

# Electron Impact Spectra of Methyl-ionone Isomers

Scan 2424 (15.856 min): chuck 02.D\data.ms

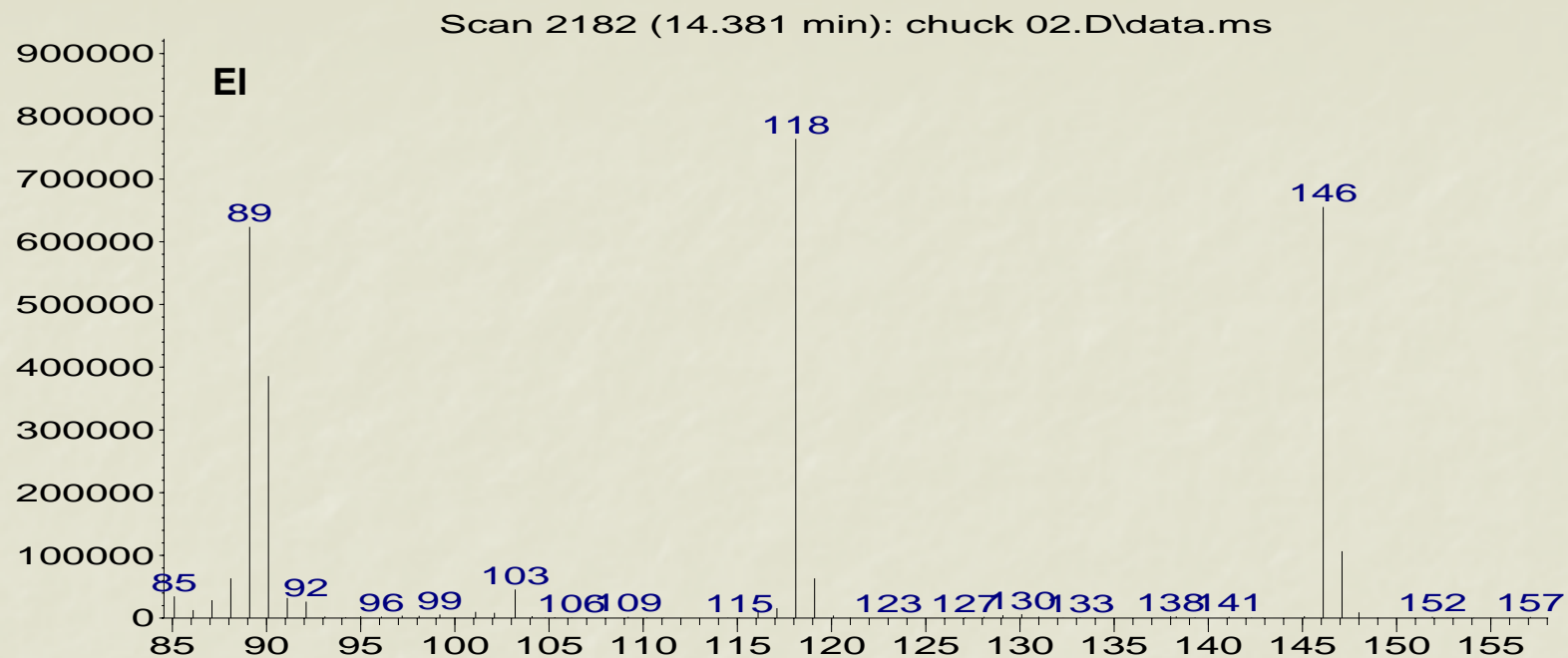


Abundance

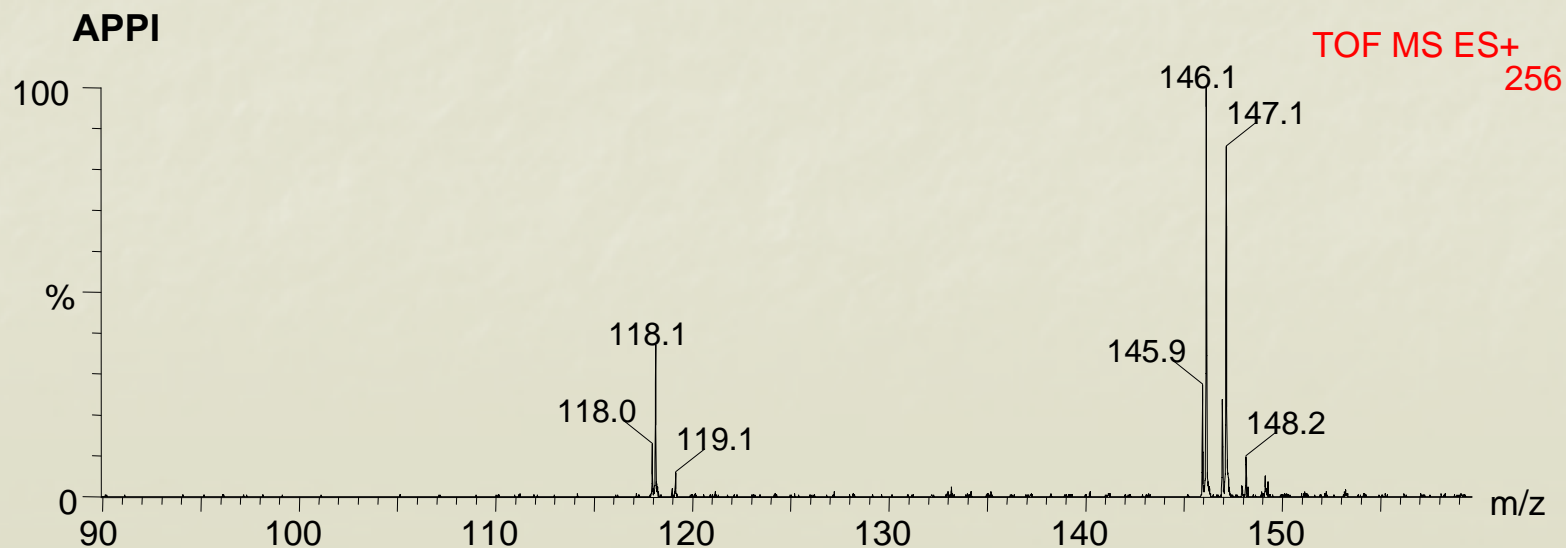


# Comparison of Electron Impact to APPI Spectra of Benzopyran-2-one

Abundance



m/z-->

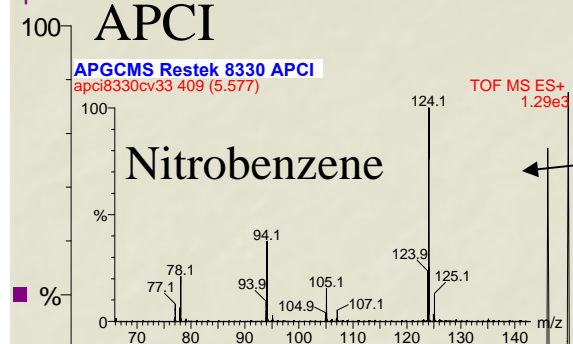


# GC/APMS Restek 8270 EPA Mixture

APGCMS Restek 8330 APCI

apci8330\_cv33

## APCI



APGCMS Restek 8330 APCI  
apci8330\_cv33 409 (5.577)

## Nitrobenzene

APGCMS Restek 8330 APCI

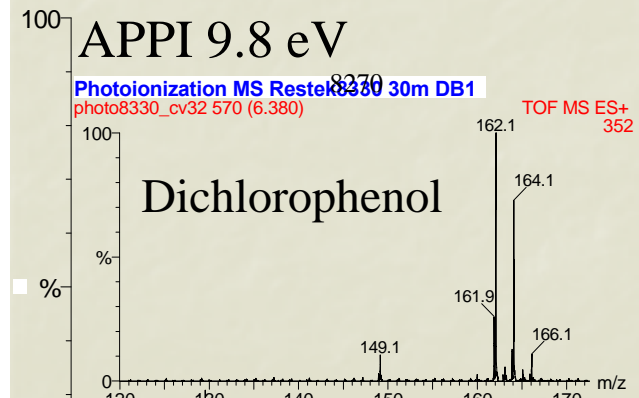
apci8330\_cv33



TOF MS ES+  
BPI  
1.47e3

photo8330\_cv32

## APPI 9.8 eV

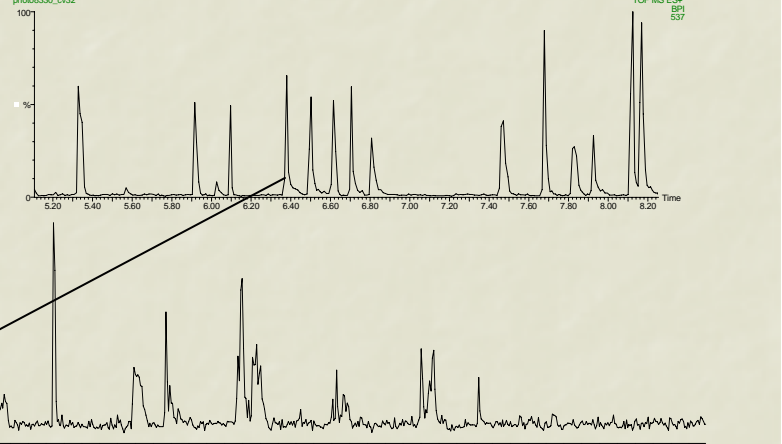


Photoionization MS Restek 8330 30m DB1  
photo8330\_cv32 570 (6.380)

## Dichlorophenol

APGCMS Restek 8330 APCI

photo8330\_cv32



TOF MS ES+  
BPI  
1.10e3

Time

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

photo8271megamix3

TOF MS ES+  
BPI  
1.76e3

Peak width 1.5 sec  
0.5 sec acquisition

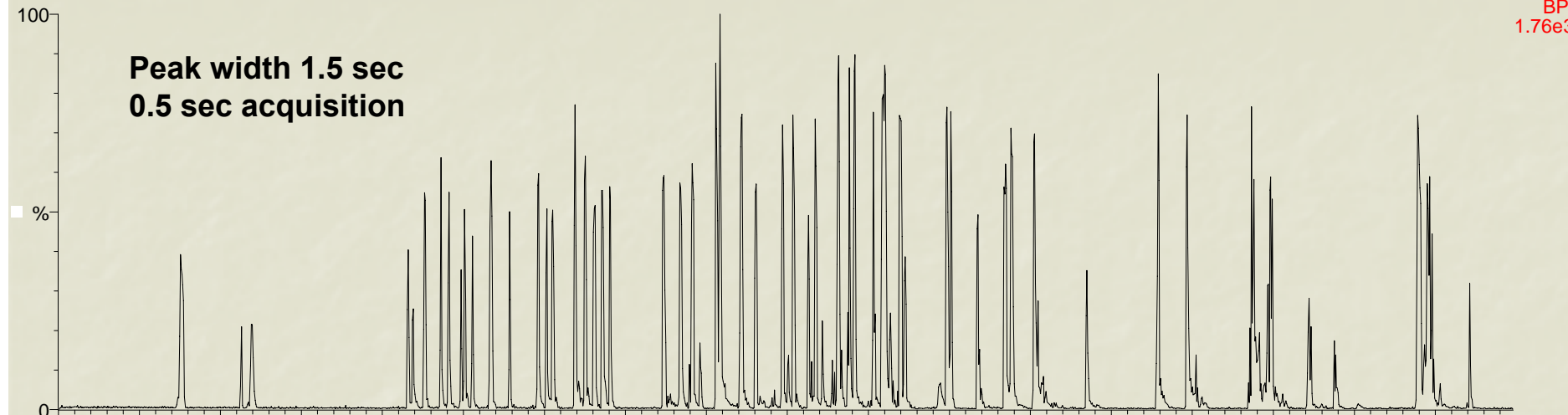
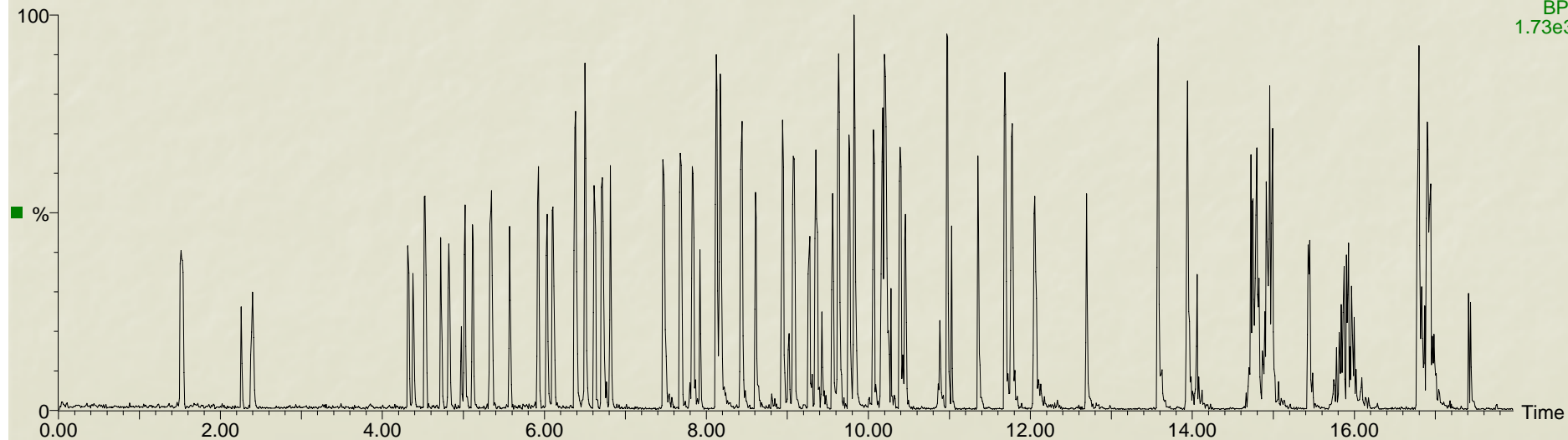


photo8271megamix2

TOF MS ES+  
BPI  
1.73e3



# Conclusion

- o AP-GC/MS extends the capabilities of LC/MS instrumentation.
- o APPI GC/MS is almost a universal ionization method for volatile compounds.
- o High sensitivity.
- o Library search possible with APPI?
- o Positive/negative ionization, accurate mass, MS/MS, quantitation.
- o 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**



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