

Three and Four Mass Spectrometers in Parallel for Lipid Analysis – How Many Instruments are Enough?



Agricultural
Research
Service

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Development Laboratory**

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Nutrition Research Center**

Beltsville, MD

Why Parallel Mass Spectrometry?

So many experiments to perform...

**So Little Time!
(and Sample!)**

Why Parallel Mass Spectrometry?

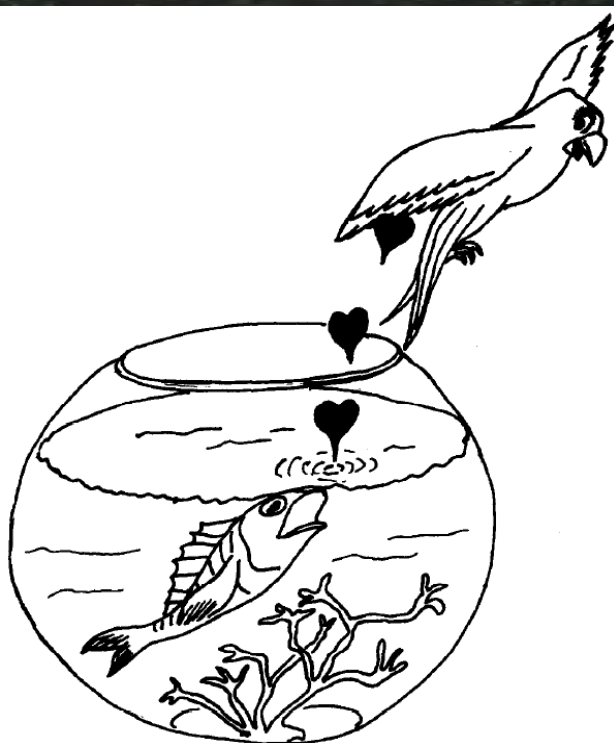


Fig. 1. A difficult courtship.

Like the Fish who
loves the Bird,
LC-MS must bridge
the gap between
liquid and air.

Why Parallel Mass Spectrometry?

- **Three primary types of Atmospheric Pressure Ionization (API) techniques for LC-MS:**
 - Atmospheric Pressure Chemical Ionization (**APCI**)
 - Electrospray Ionization (**ESI**)
 - Atmospheric Pressure Photoionization (**APPI**)
- Each provides **Valuable**, but **Complementary** information

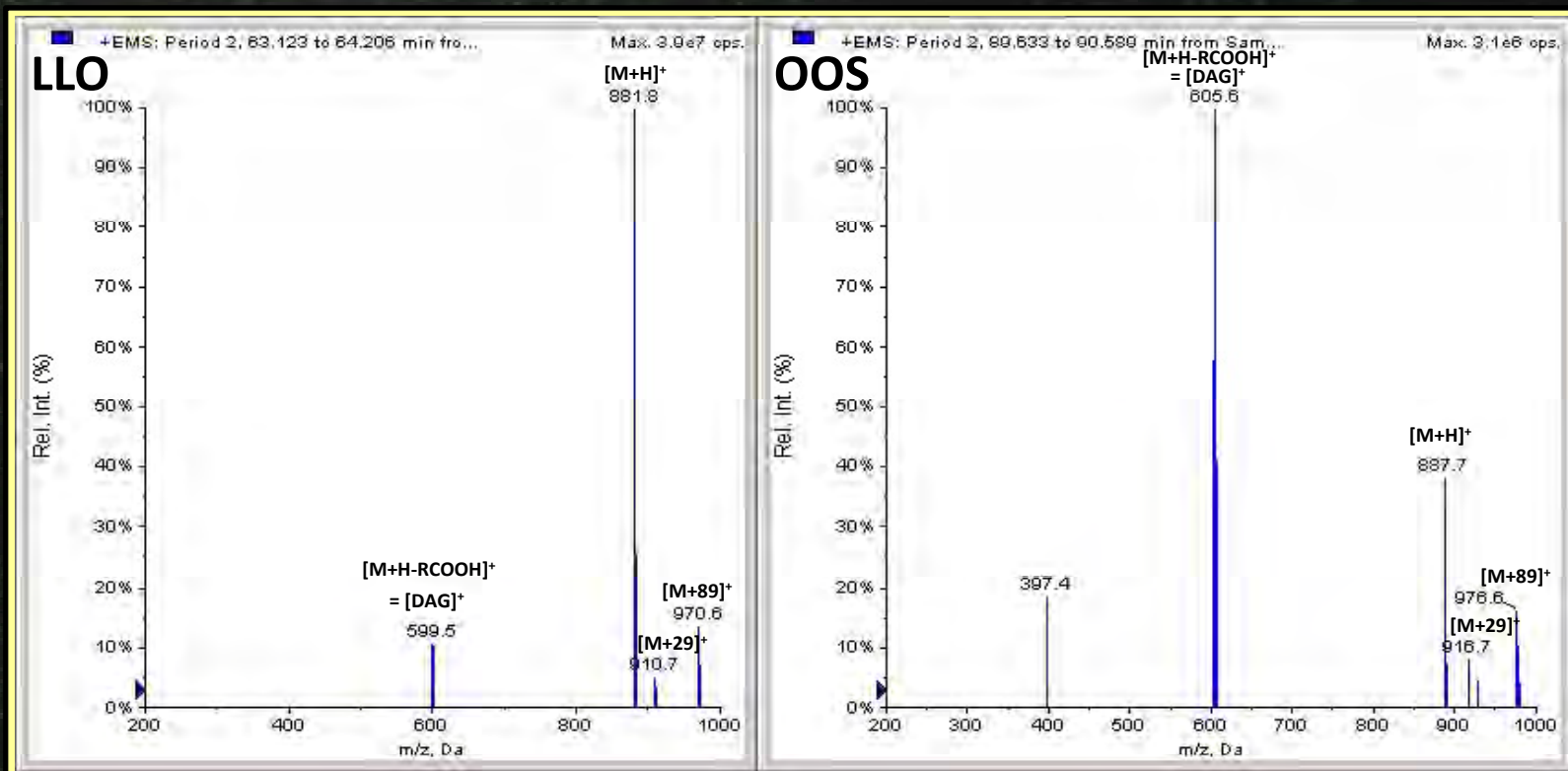
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Chemical Ionization (APCI)

- Relatively simple spectra
- Produces some, but maybe not a lot, of $[M+H]^+$
- Often produces major fragments as base peaks
- Produces some ACN adducts ('chemical ionization')
- Some, but minimal, discrimination between classes
- Substantial dependence of $[M+H]^+$ on the degree of unsaturation in triacylglycerols (TAGs)

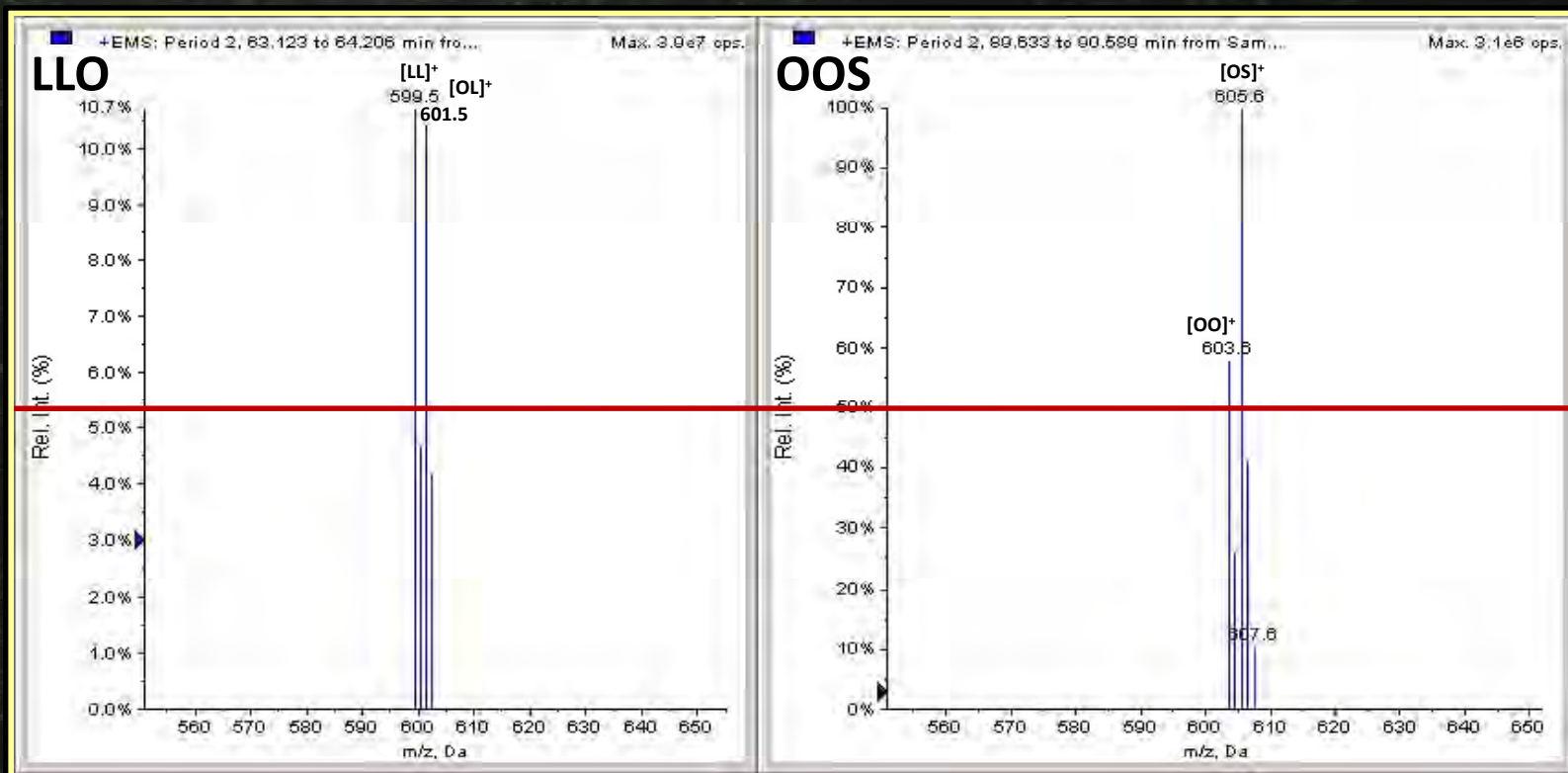
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Chemical Ionization (APCI)



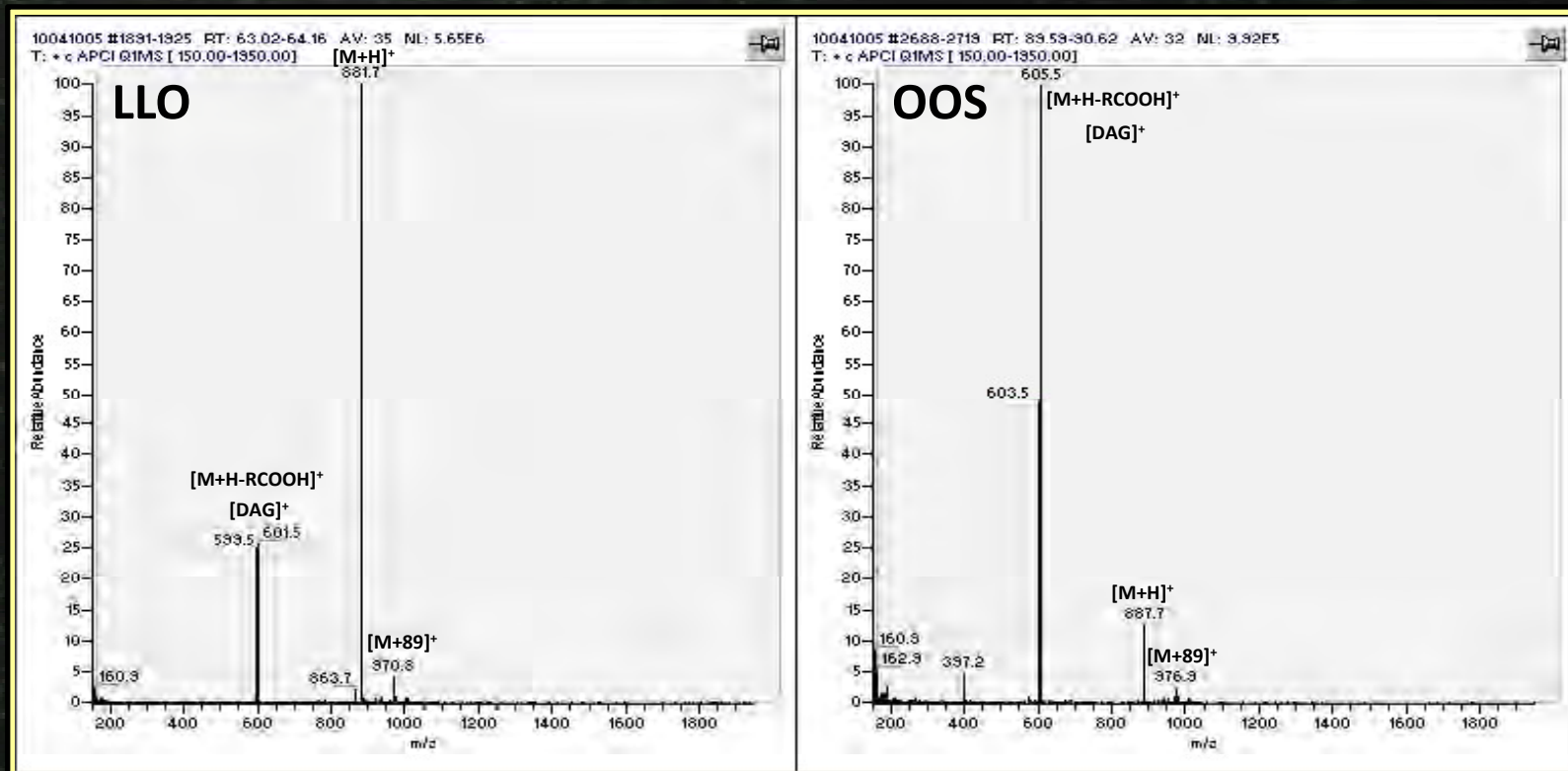
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Chemical Ionization (APCI)



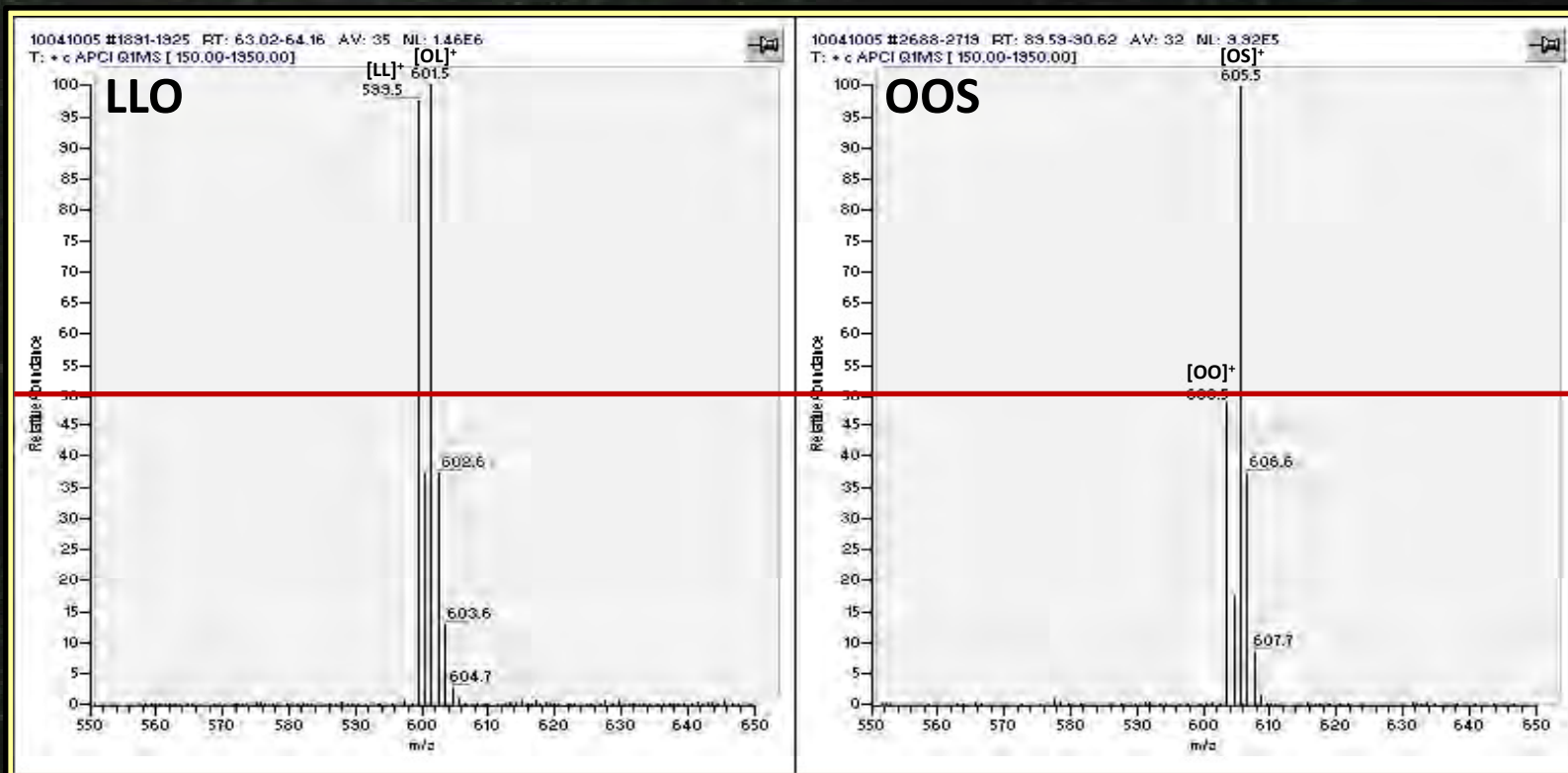
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Chemical Ionization (APCI)



Atmospheric Pressure Ionization (API)

Atmospheric Pressure Chemical Ionization (APCI)



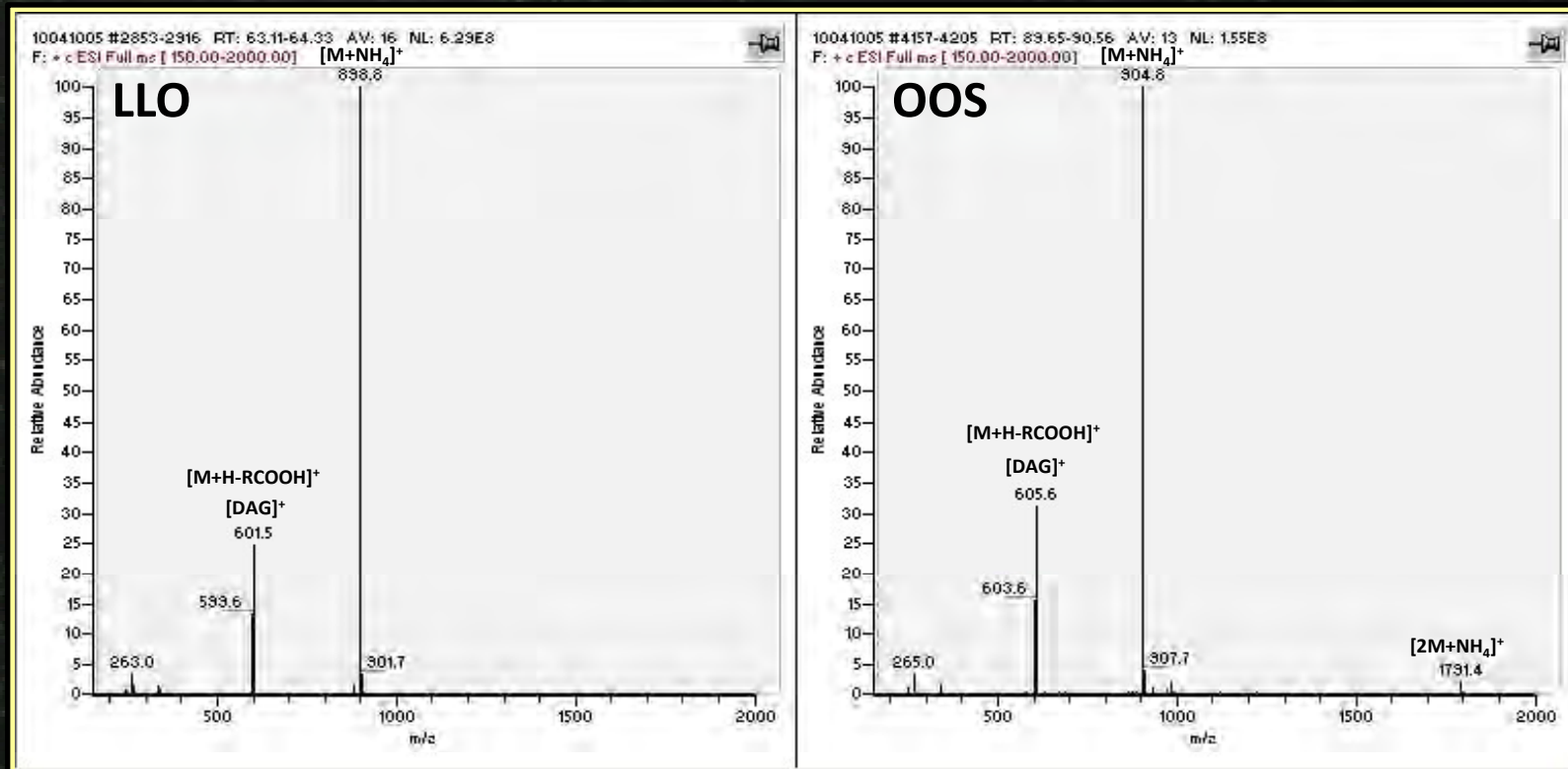
Atmospheric Pressure Ionization (API)

Electrospray Ionization (ESI)

- Produces mostly $[M+X]^+$, where X is adduct (e.g., NH_4^+ from NH_4OCOH)
- Except: Produces $[M+H]^+$ from phospholipids
- Produces minimal fragmentation
- Best suited to producing precursors for MS/MS
- Substantial discrimination between classes
- Requires electrolyte (LC or via tee)

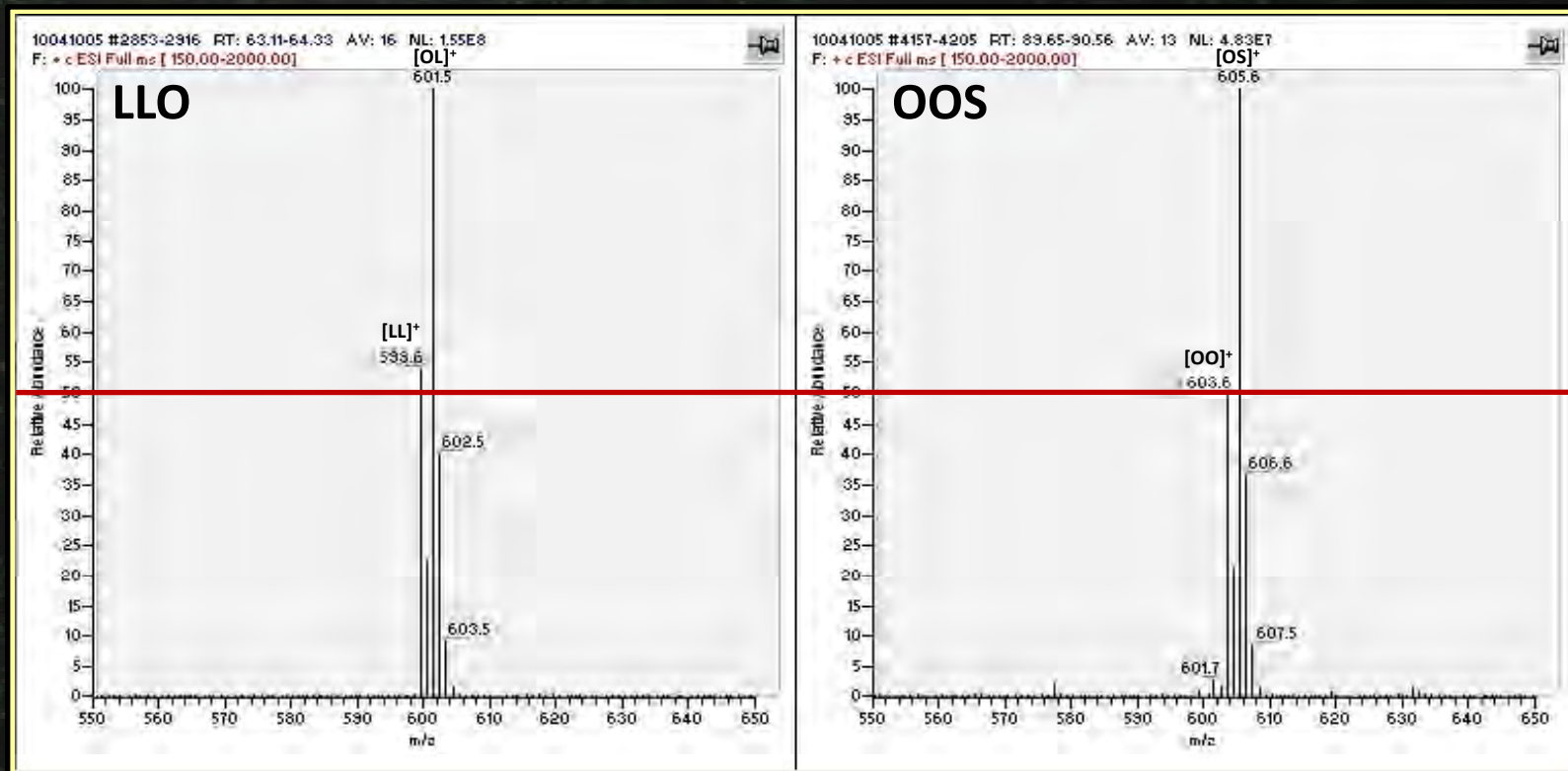
Atmospheric Pressure Ionization (API)

Electrospray Ionization (ESI)

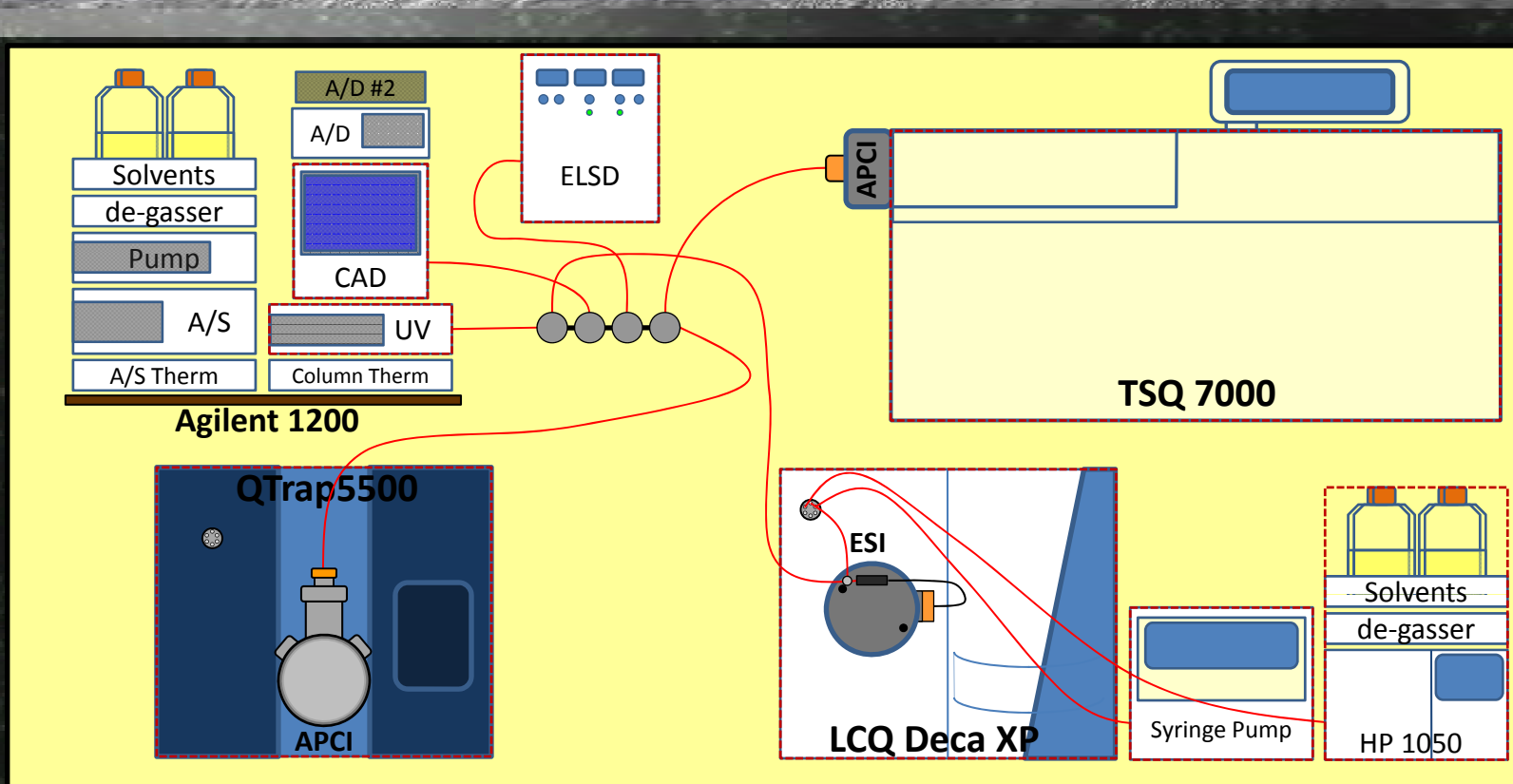


Atmospheric Pressure Ionization (API)

Electrospray Ionization (ESI)



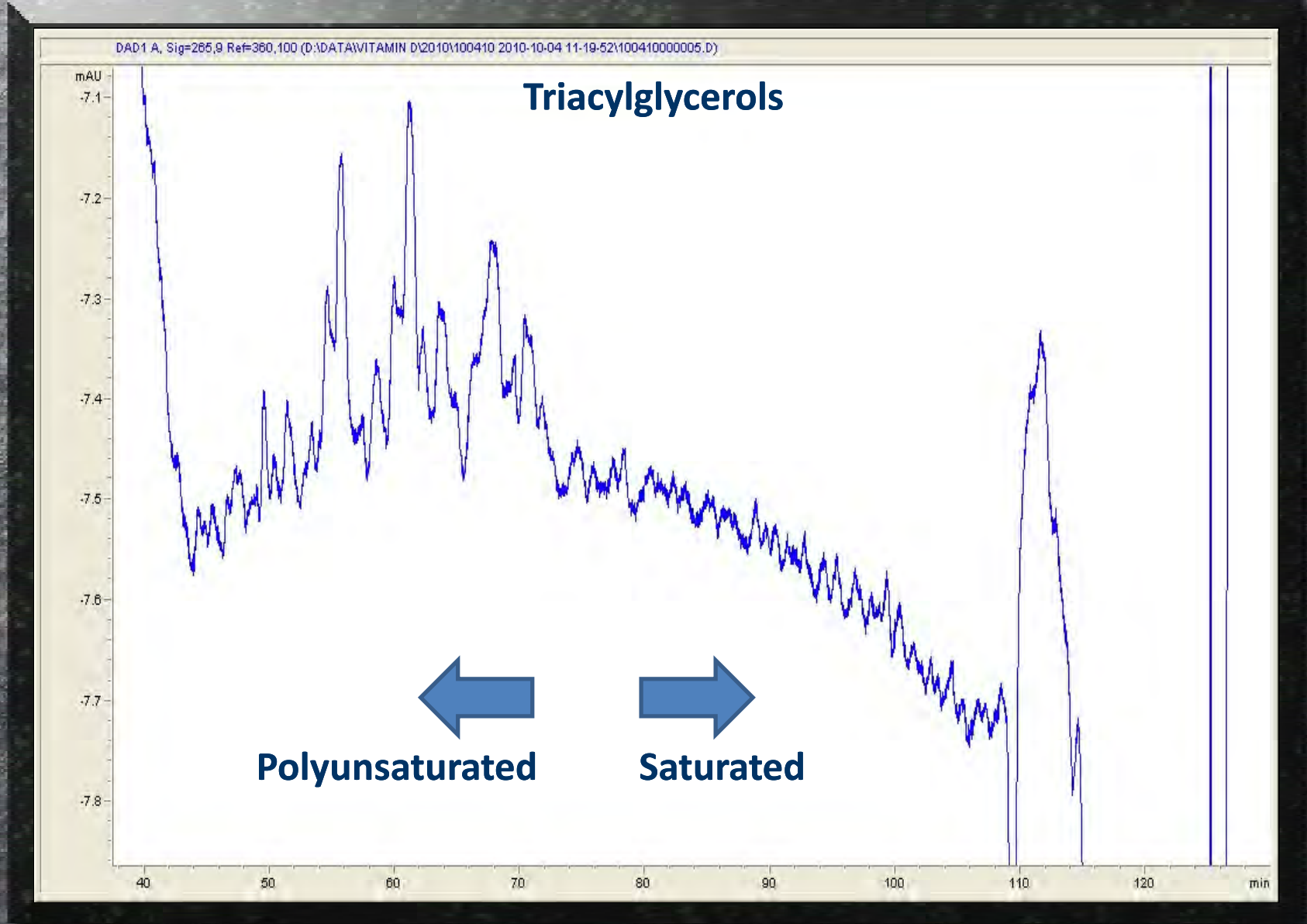
Triple Parallel MS Instrumentation



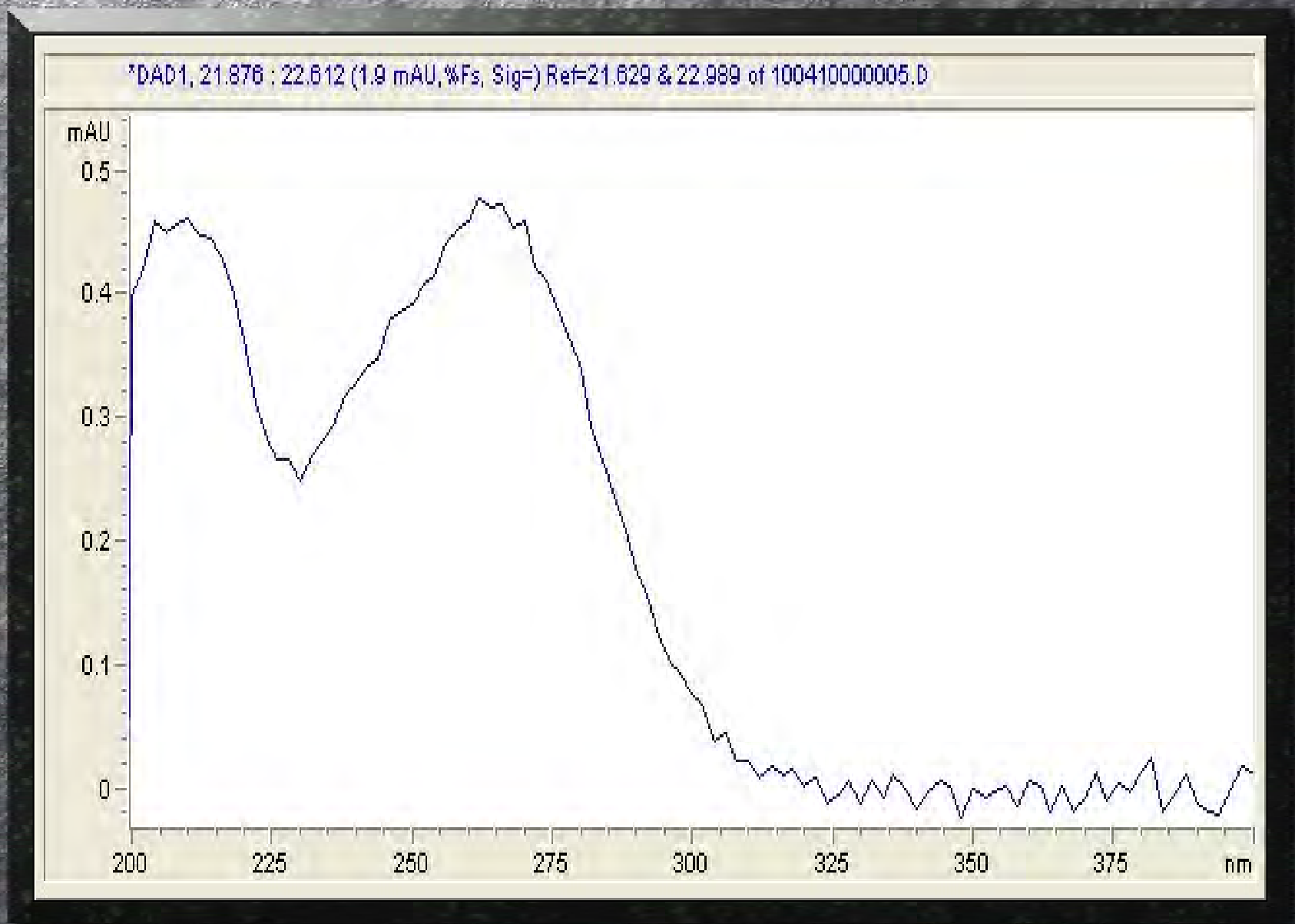
Oil-filled Vitamin D₃ Supplement Gelcaps



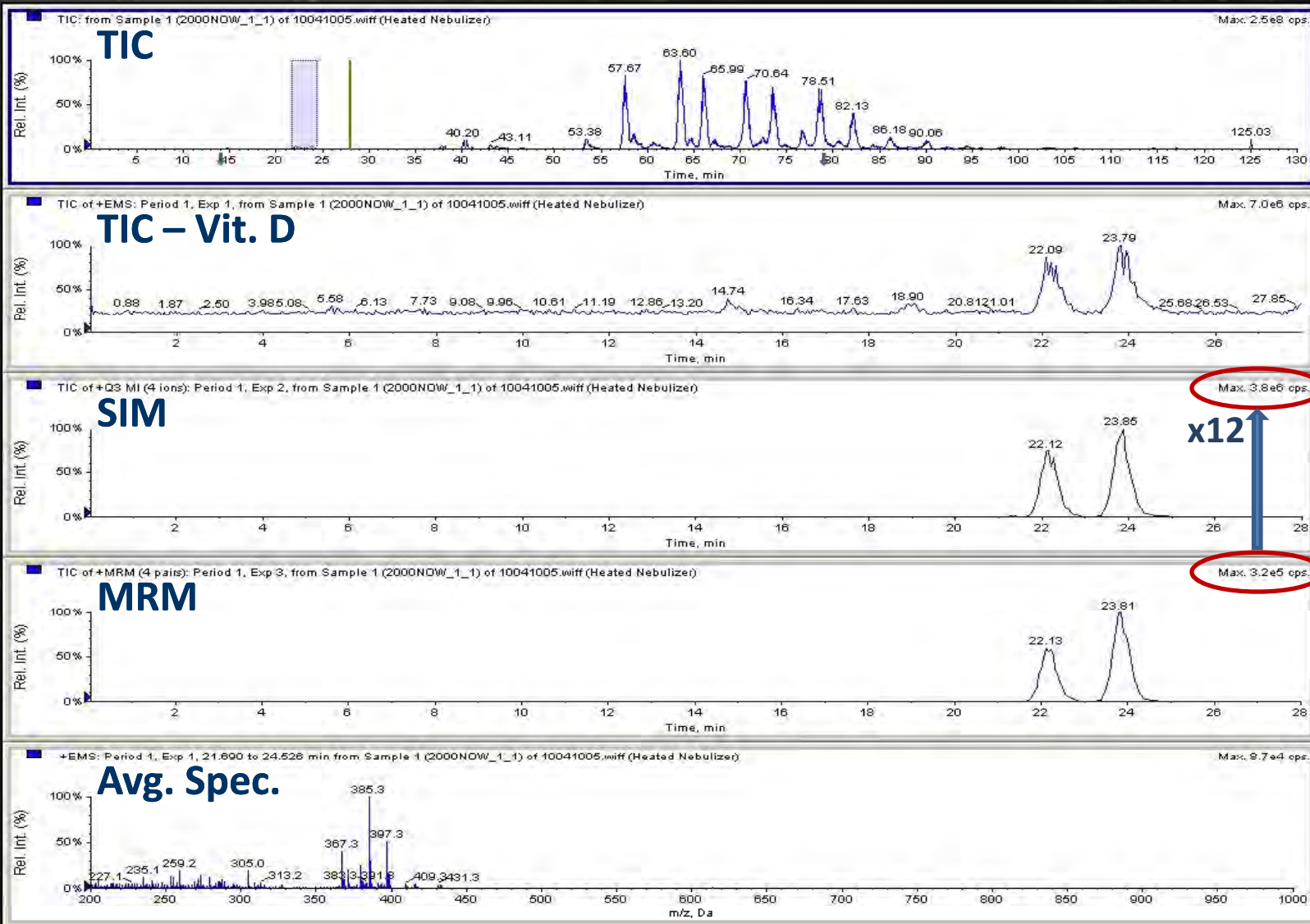
UV Chromatogram @ 265 nm



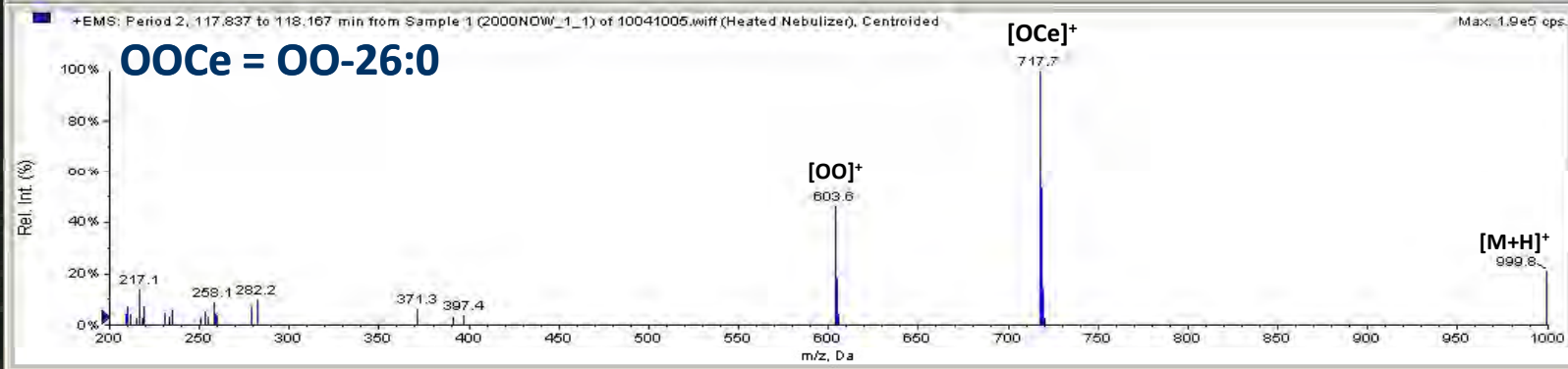
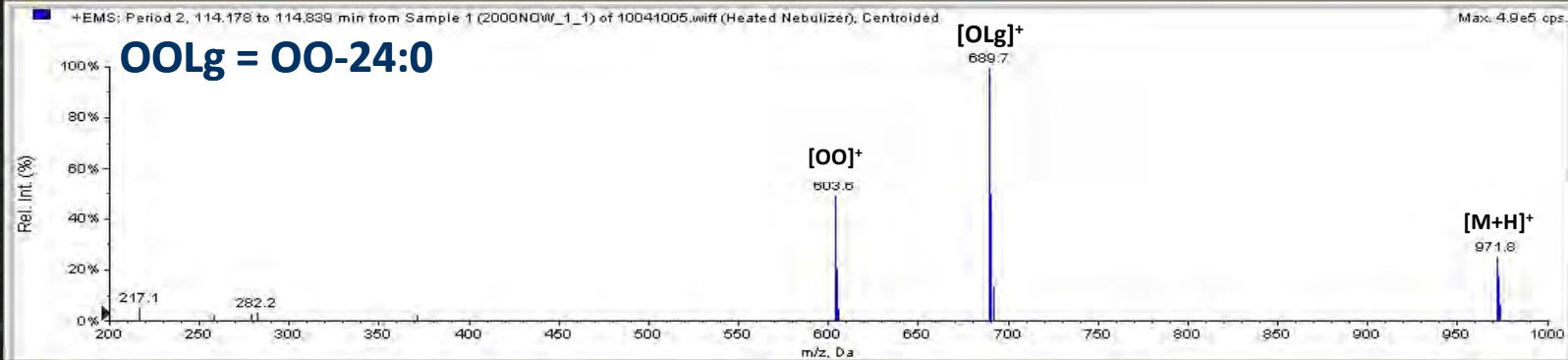
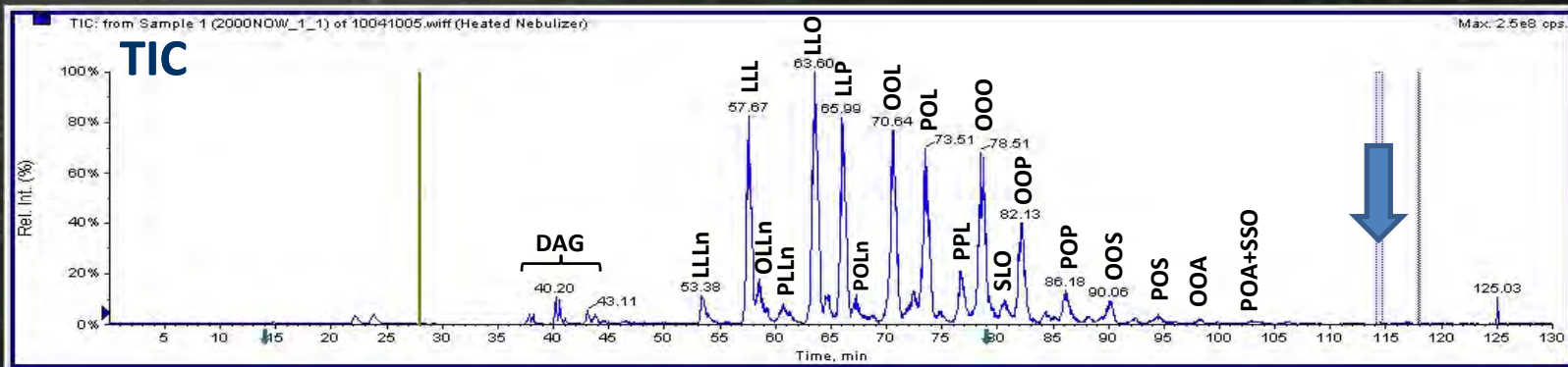
UV Full Scan Chromatogram



APCI-MS on QTrap 5500

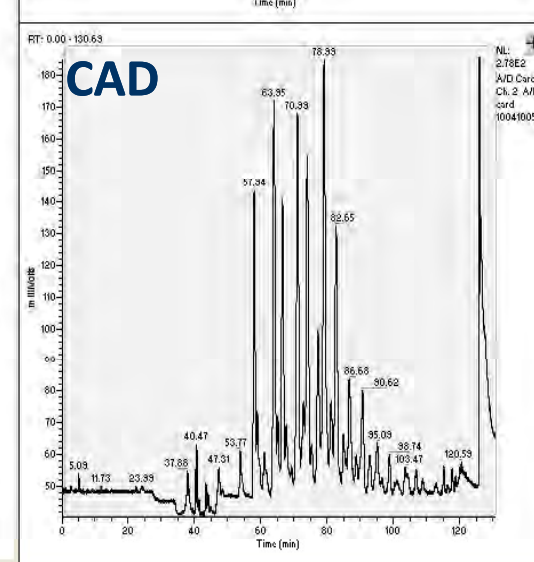
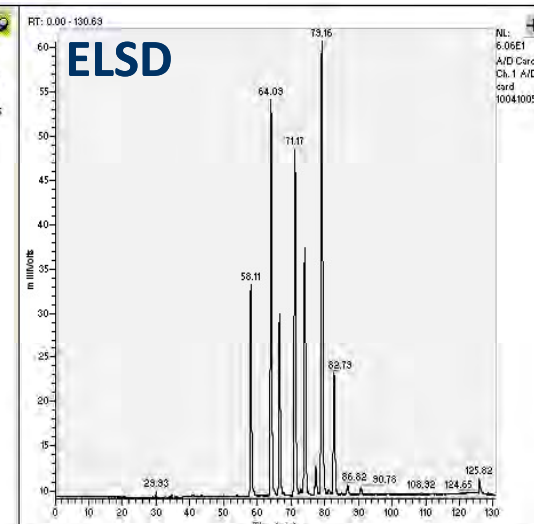
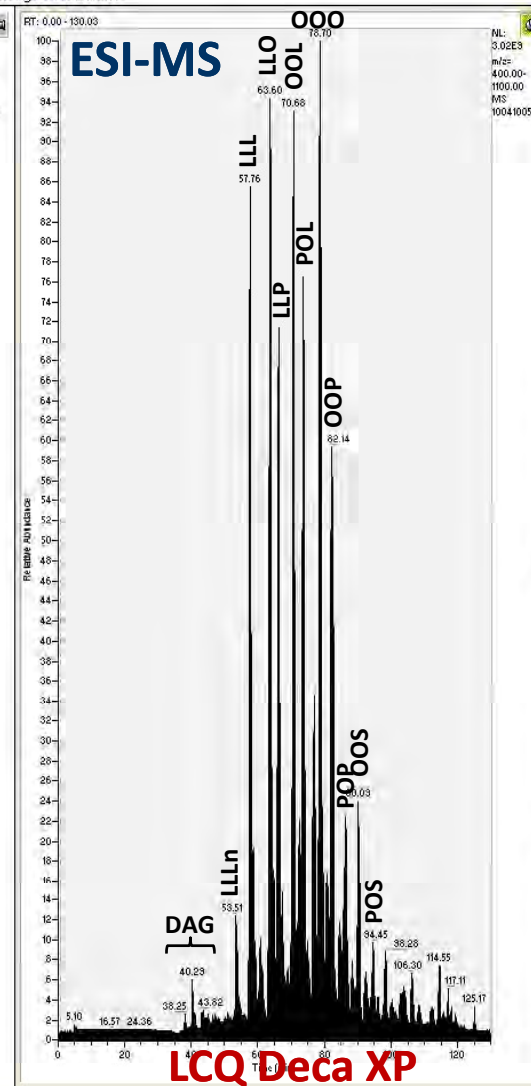
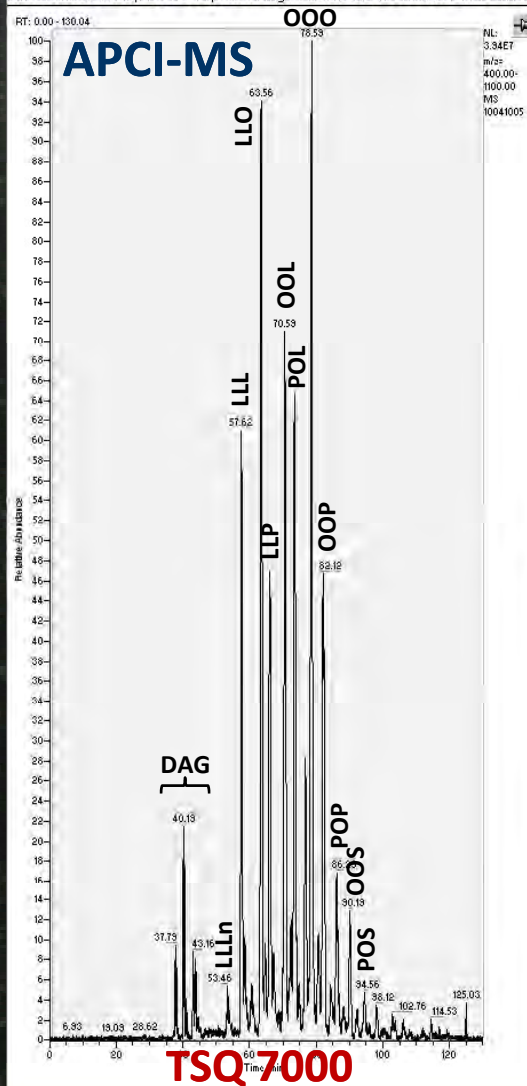


APCI-MS on QTrap 5500



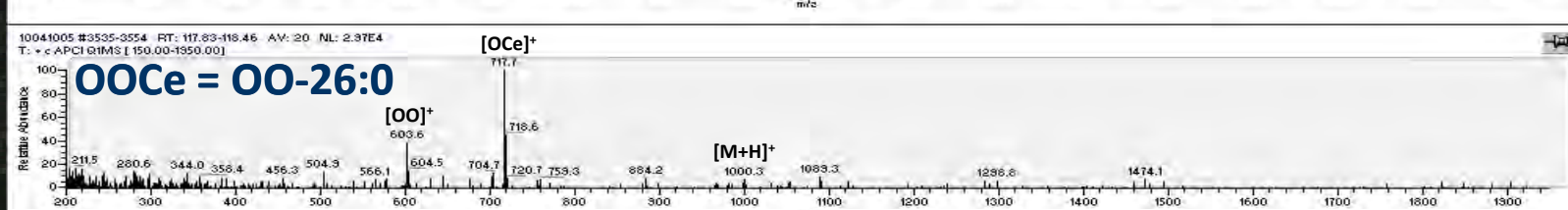
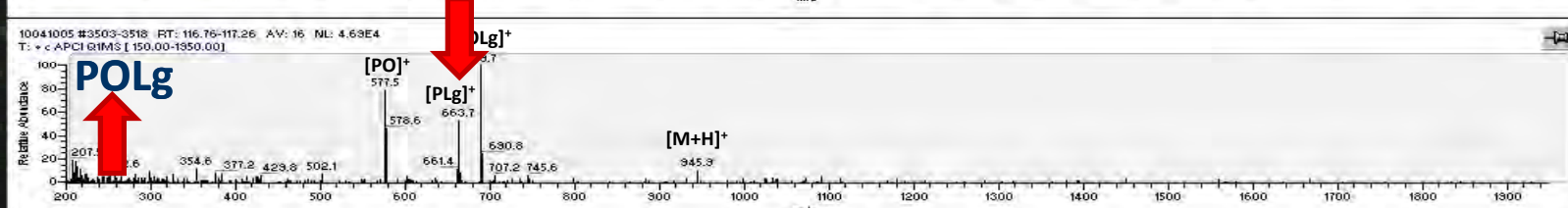
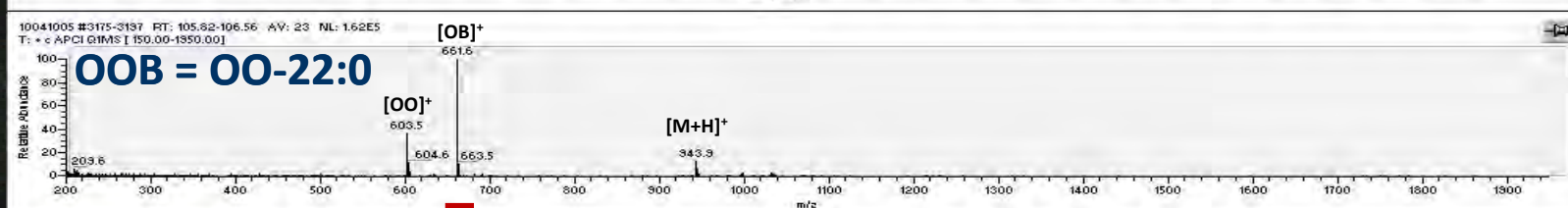
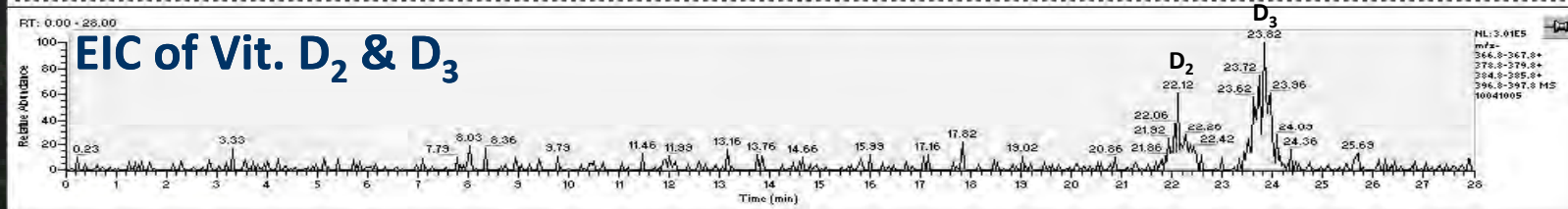
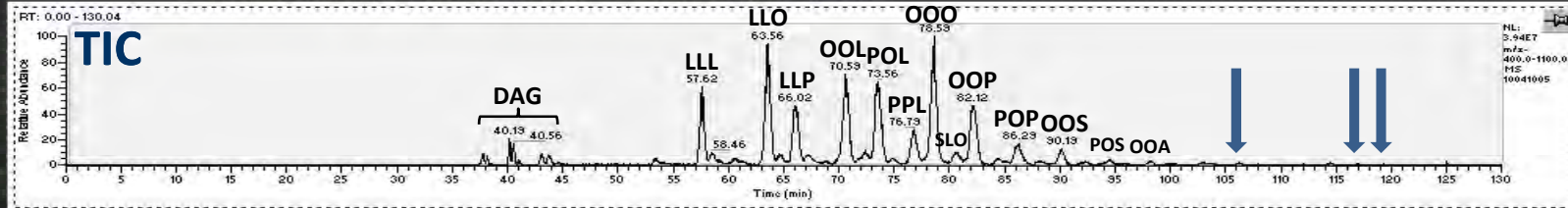
MS and Aux. Det. Chromatograms

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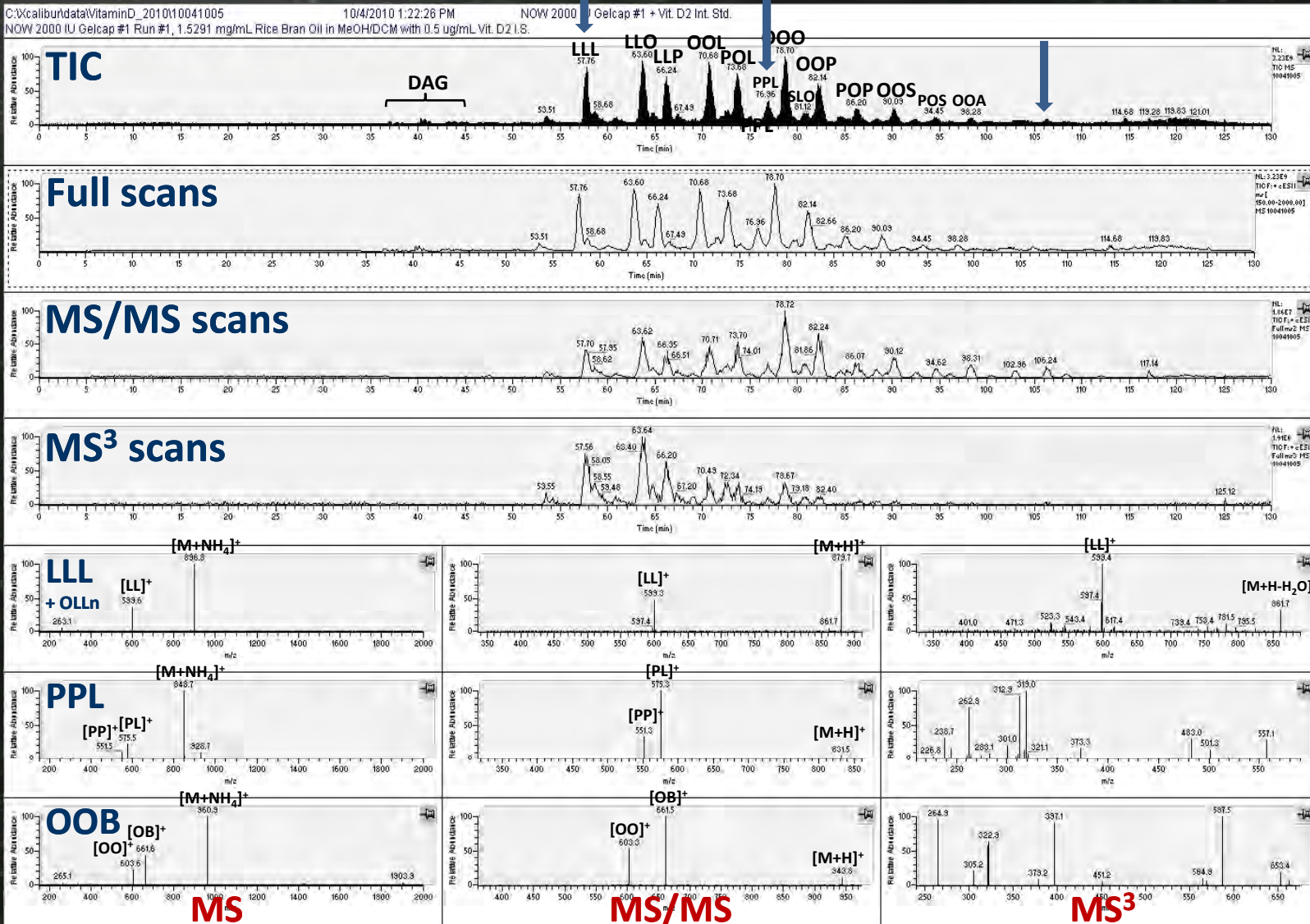


APCI-MS on TSQ 7000

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ESI-MS on LCQ Deca XP



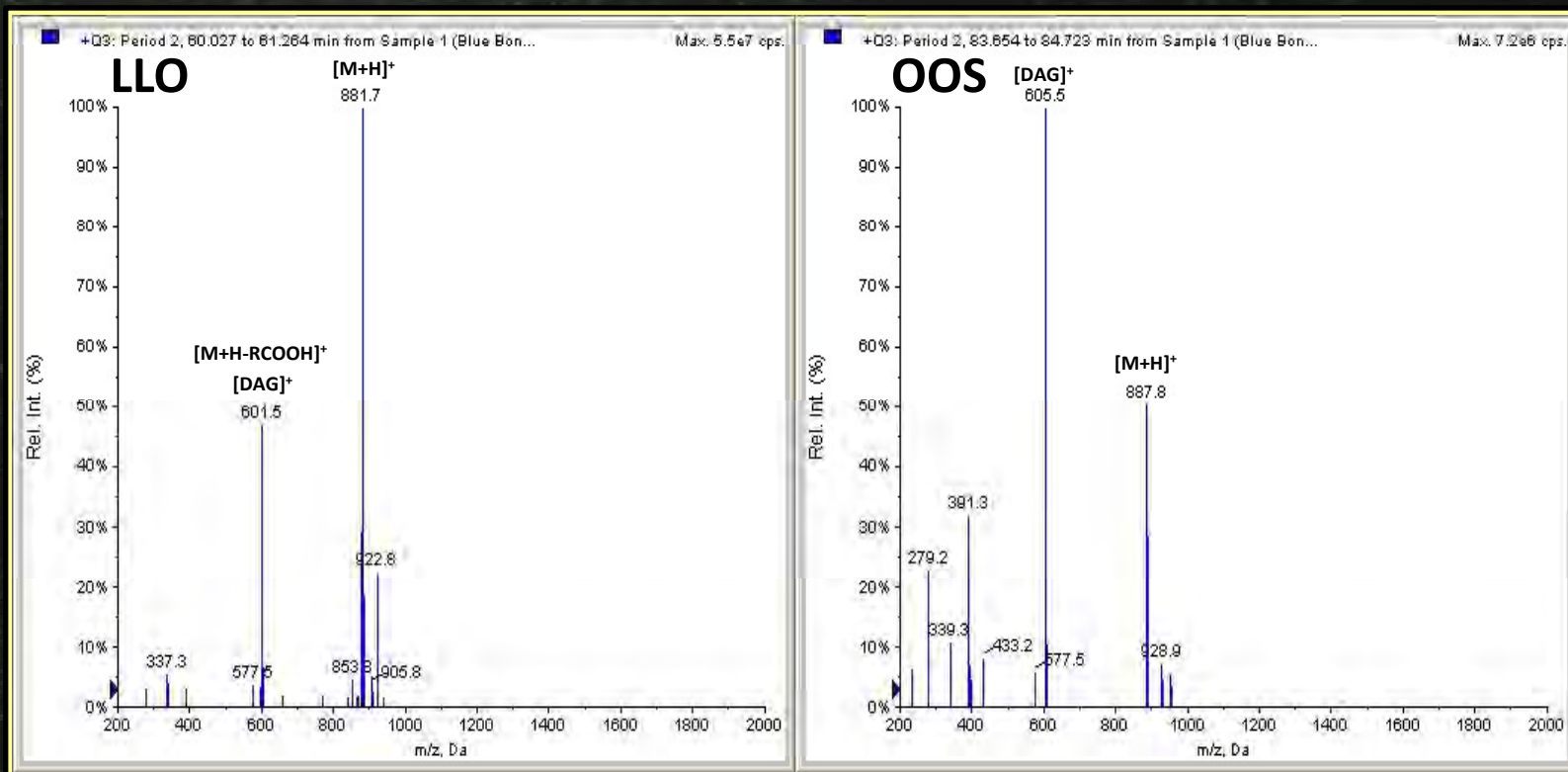
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Photoionization (APPI)

- Very similar spectra to APCI-MS
- Produces some, but maybe not a lot, of $[M+H]^+$
- Often produces major fragments as base peaks
- More discrimination between classes than APCI
- Requires dopant for most lipids (Acetone or Toluene @ 10-50 $\mu\text{L}/\text{min}$)

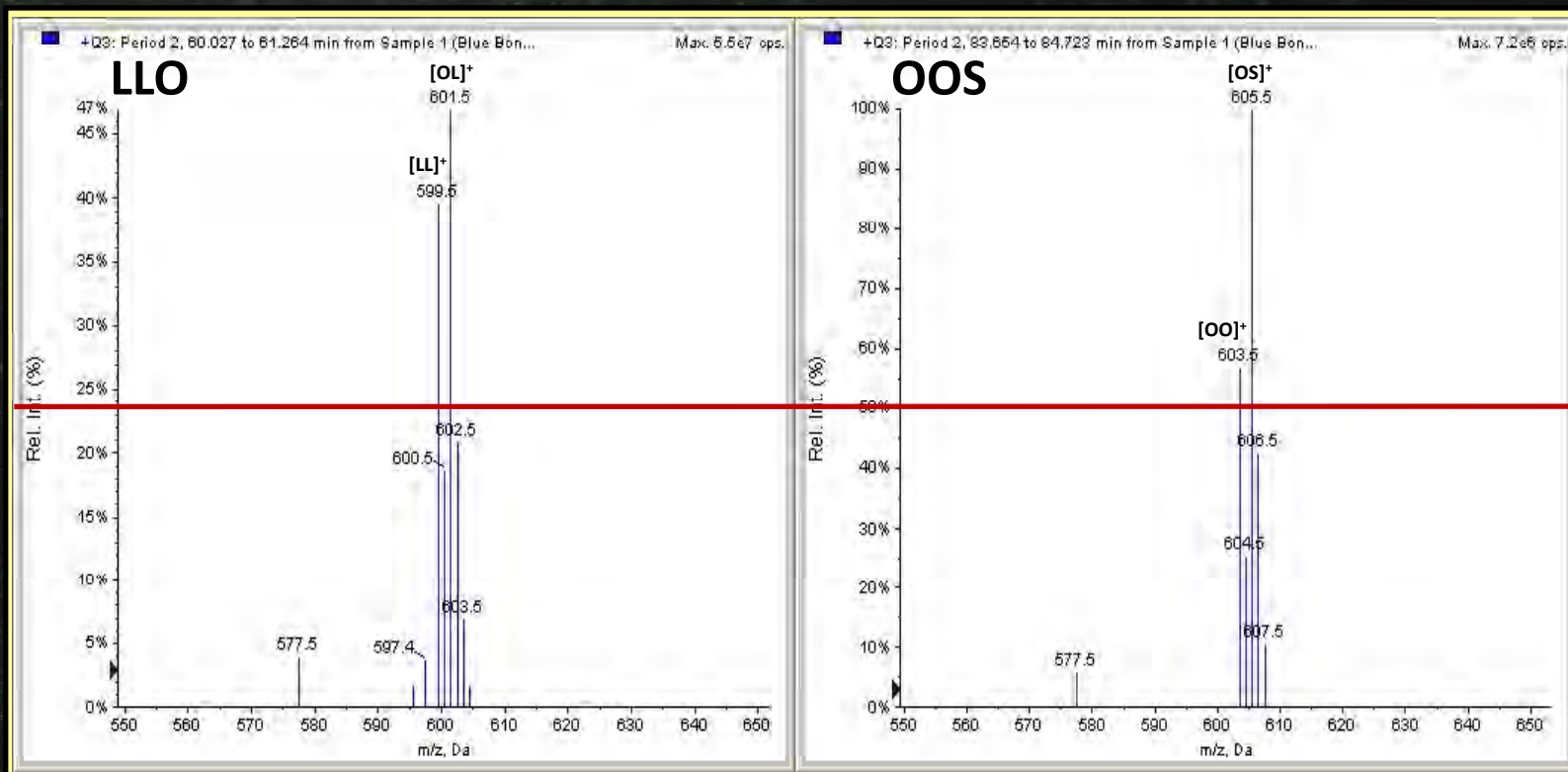
Atmospheric Pressure Ionization (API)

Atmospheric Pressure Photoionization (APPI)

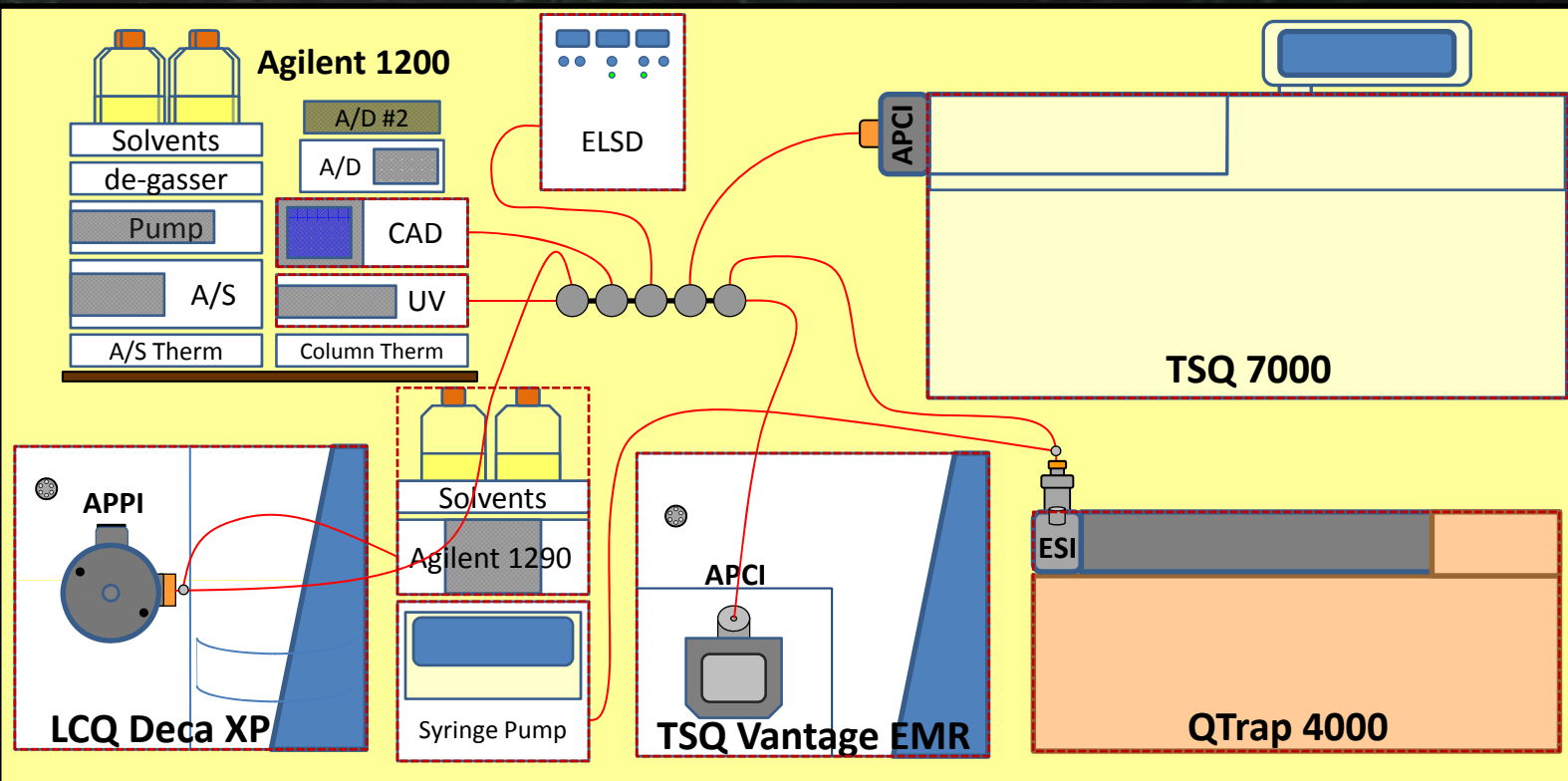


Atmospheric Pressure Ionization (API)

Atmospheric Pressure Photoionization (APPI)

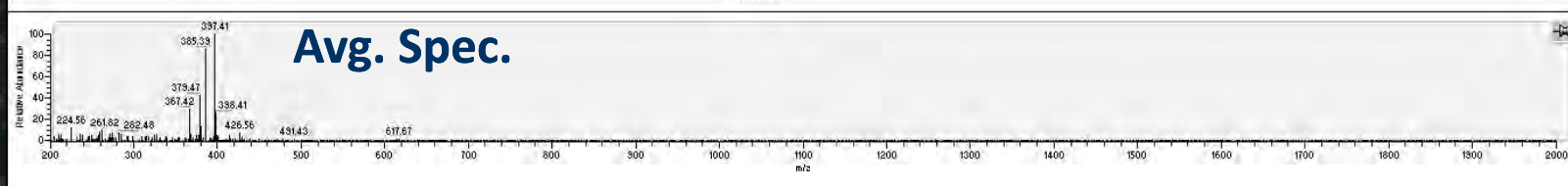
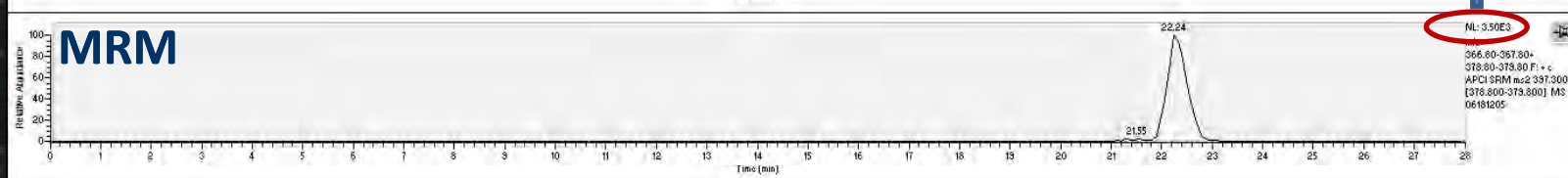
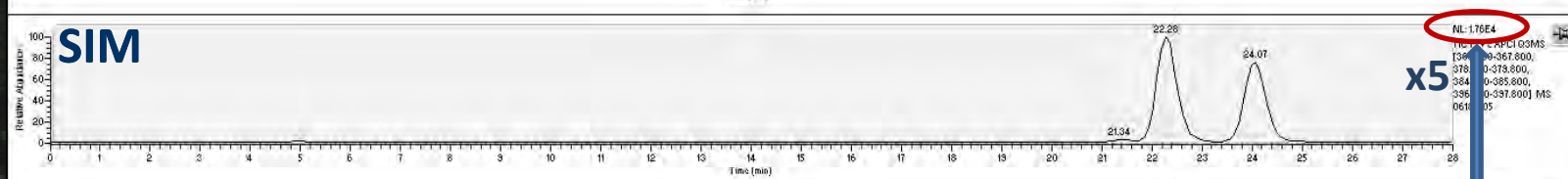
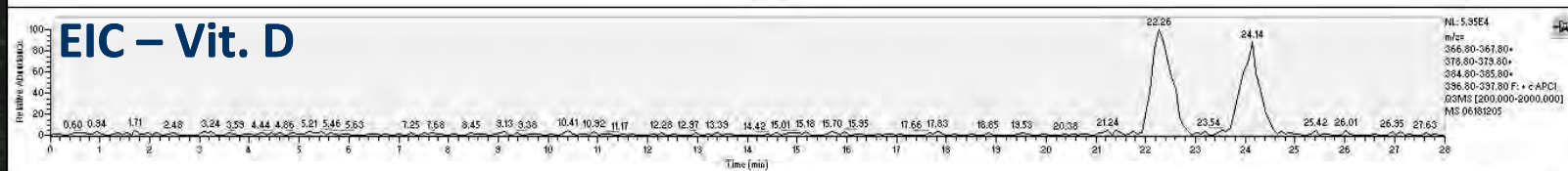
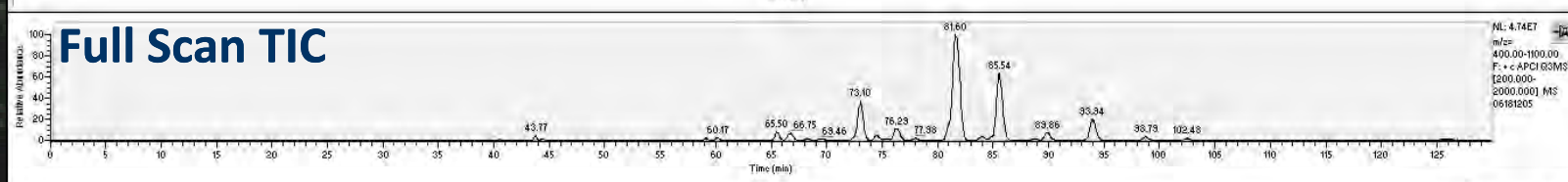
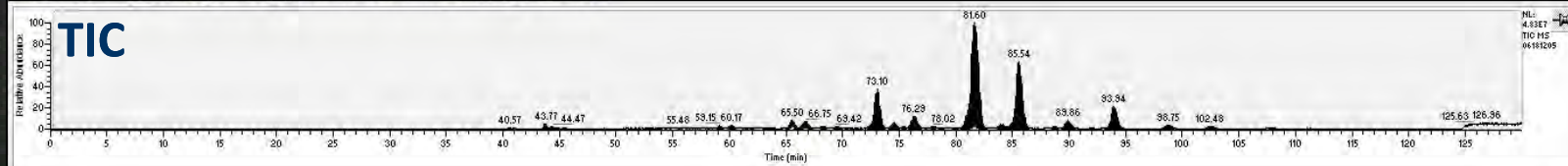


Quadruple Parallel MS Instrumentation



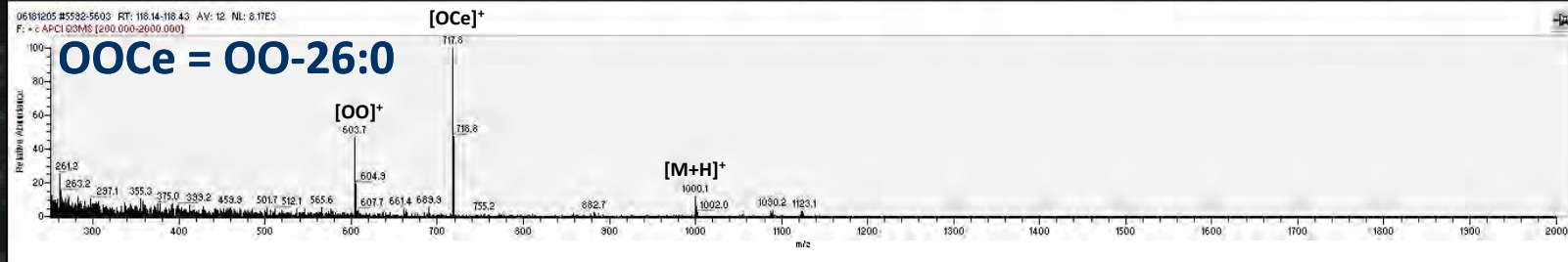
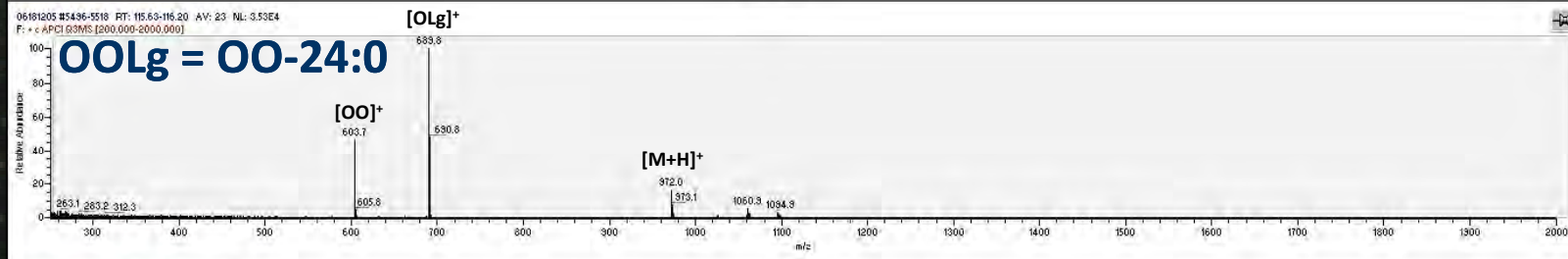
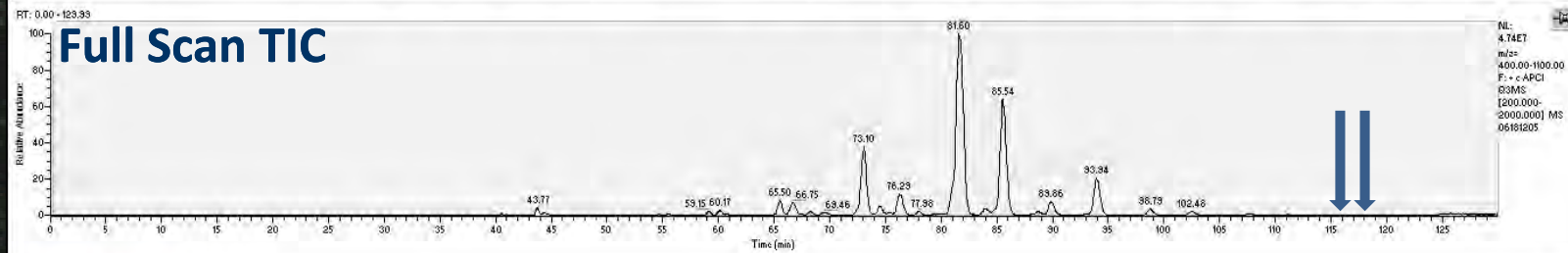
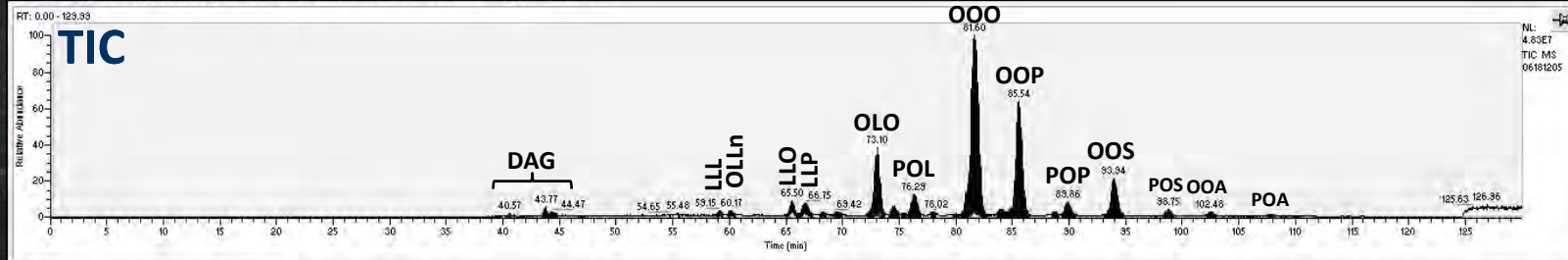
APCI-MS on TSQ Vantage

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 Now 1000 IU Gelcap #1 Run #1, 1.0524 mg/mL Olive Oil in MeOH/DCM with 0.5 ug/mL Vit. D2 I.S.



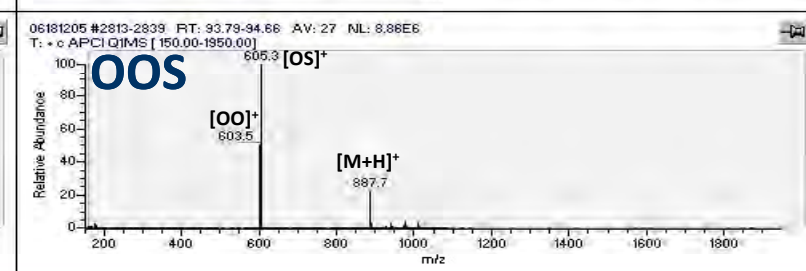
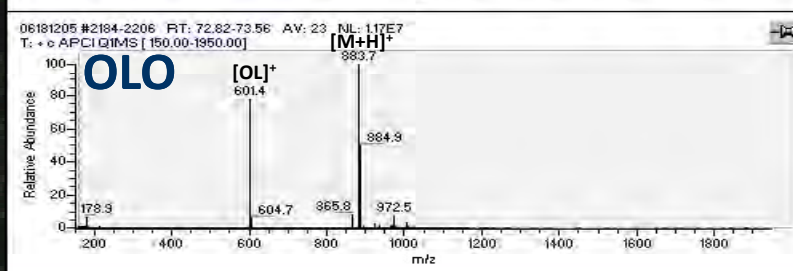
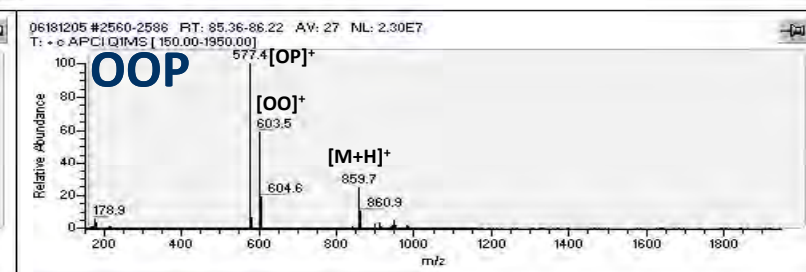
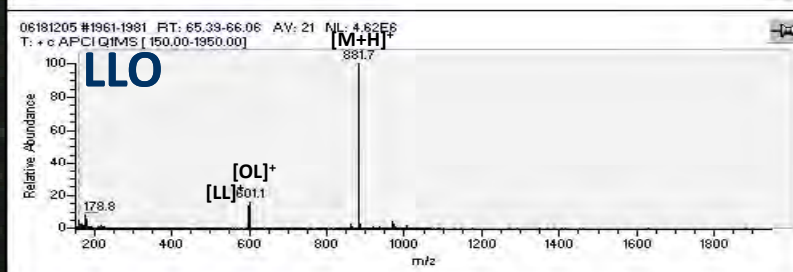
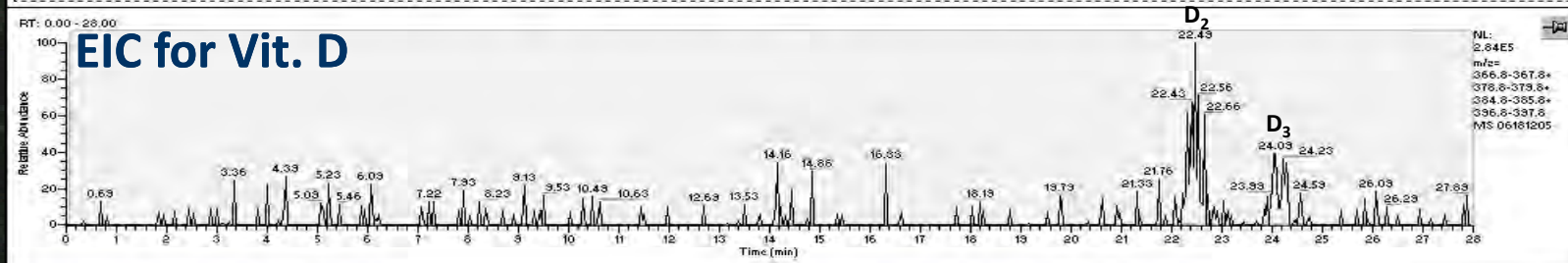
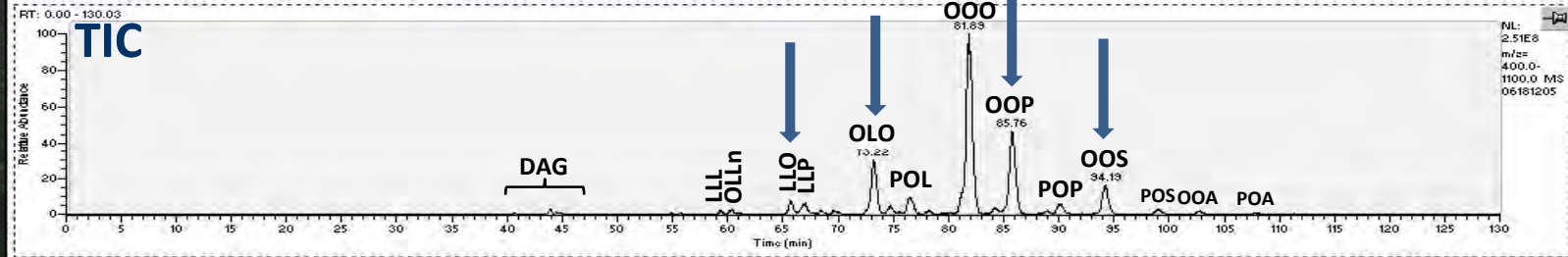
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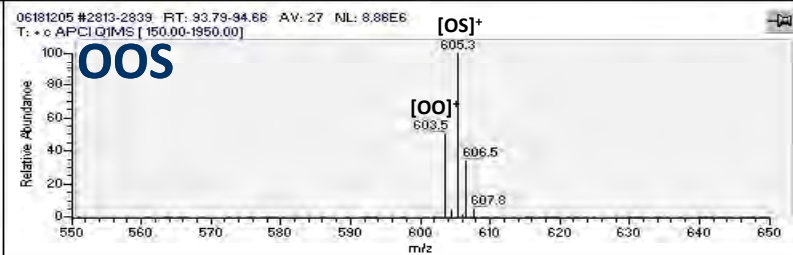
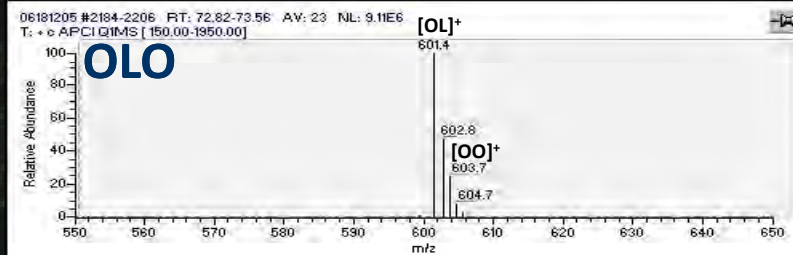
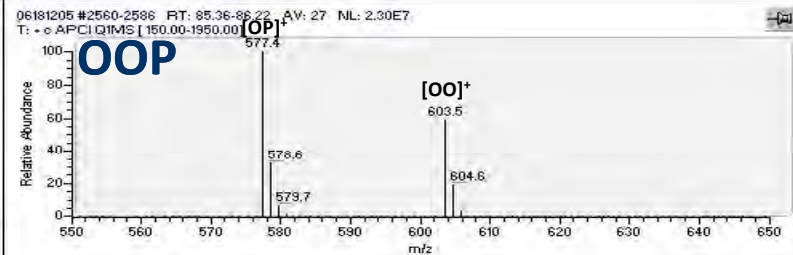
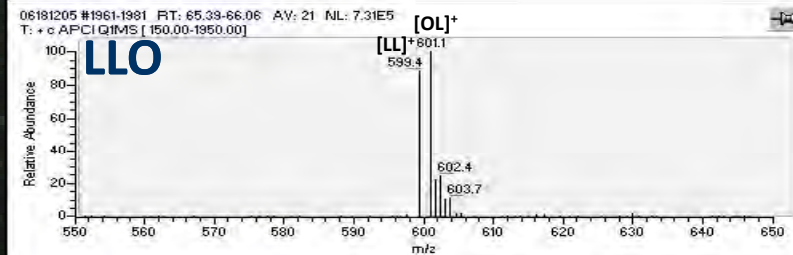
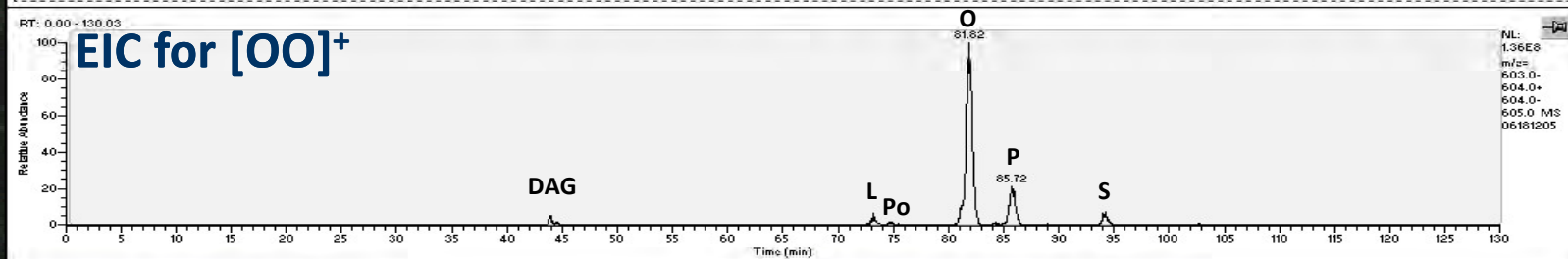
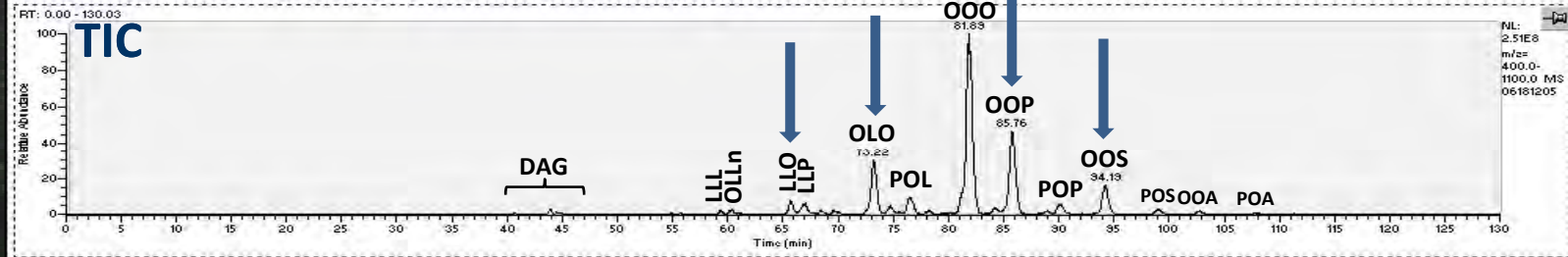
APCI-MS on TSQ7000

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APCI-MS on TSQ7000

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 Now 1000 IU Gelcap #1 Run #1, 1.0524 mg/mL Olive Oil in MeOH/DCM with 0.5 ug/mL Vit. D2 I.S.



ESI-MS on QTrap 4000

