Evolved Gas Analysis: Introduction to TGA/MS

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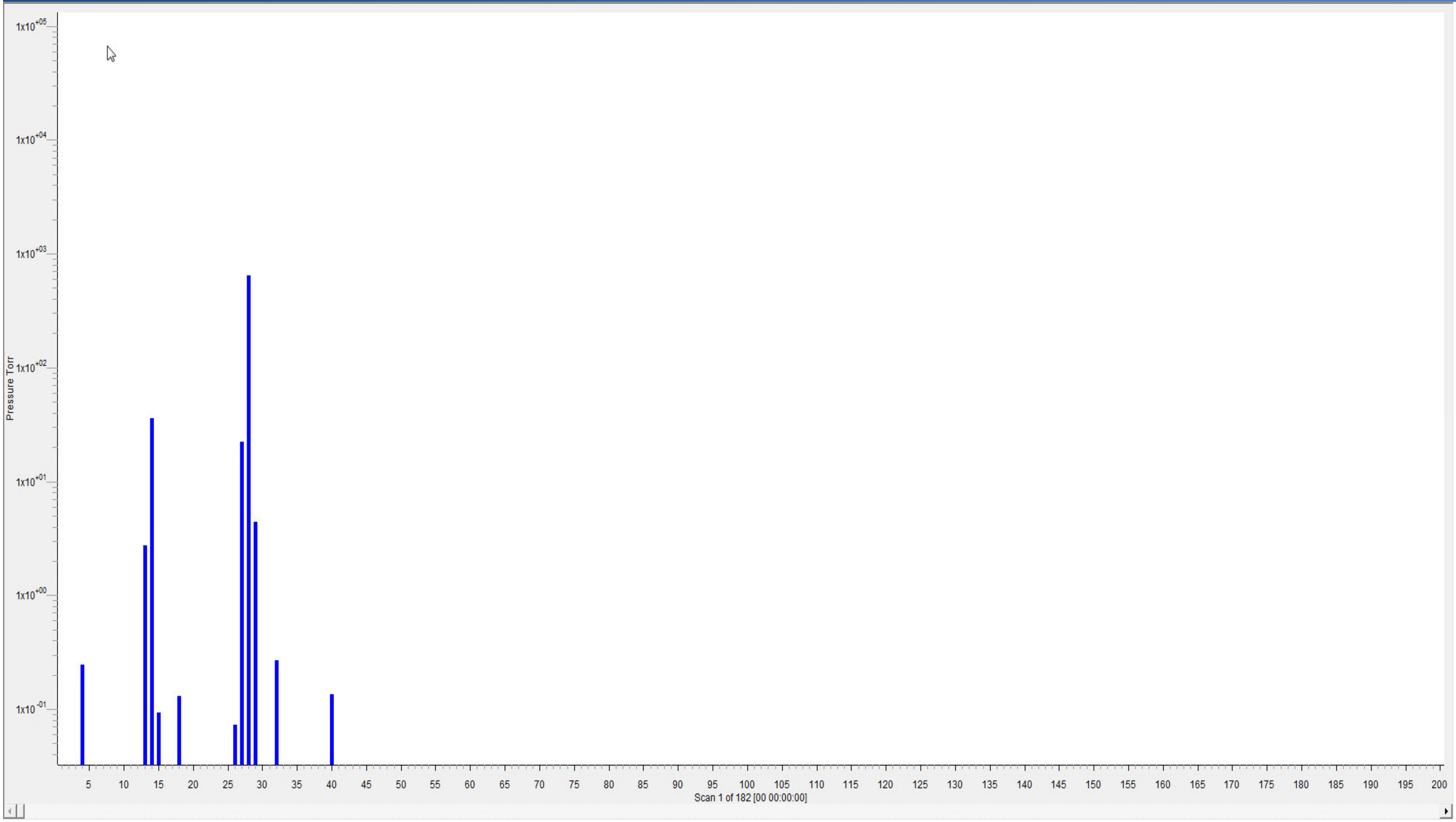
Evolved Gas Analysis

- Evolved Gas Analyses (EGA) are exciting techniques for today's analytical chemist.
- Sometimes referred to as 'hyphenated' techniques, they commonly combine TGA with FTIR (TGA/FTIR), mass spectrometry (TGA/MS) and gas chromatography and mass spectrometry (TGA/GC-MS).
- For TGA/MS, the sample is introduced by vaporizing in the TGA and introducing the sample gas into the mass spectrometer via a heated stainless steel capillary to the MS inlet orifice or molecular leak.

Examples of TGA/MS Data Presentation

- MS Data Formats:
  - Barchart – Scan from initial amu to final amu, inclusive
  - PeakJump – Scan of specific subset of amu
- TGA/MS Data Presentation
  - Weight Lose Data vs Temperature
  - Mass Spectral Data vs Temperature

Simplified Bar Chart Display: Background for Polyphenylene Oxide at Start of Experiment



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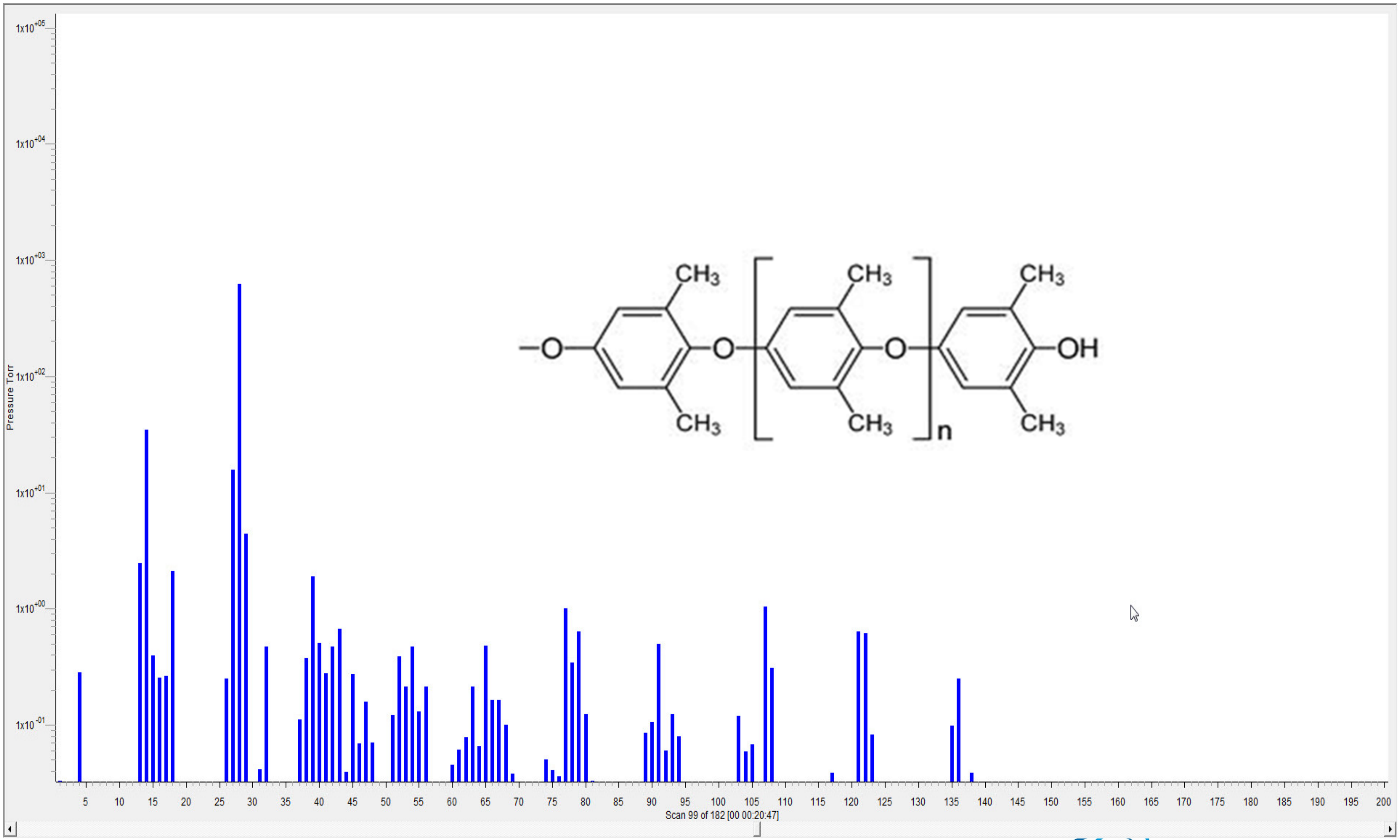
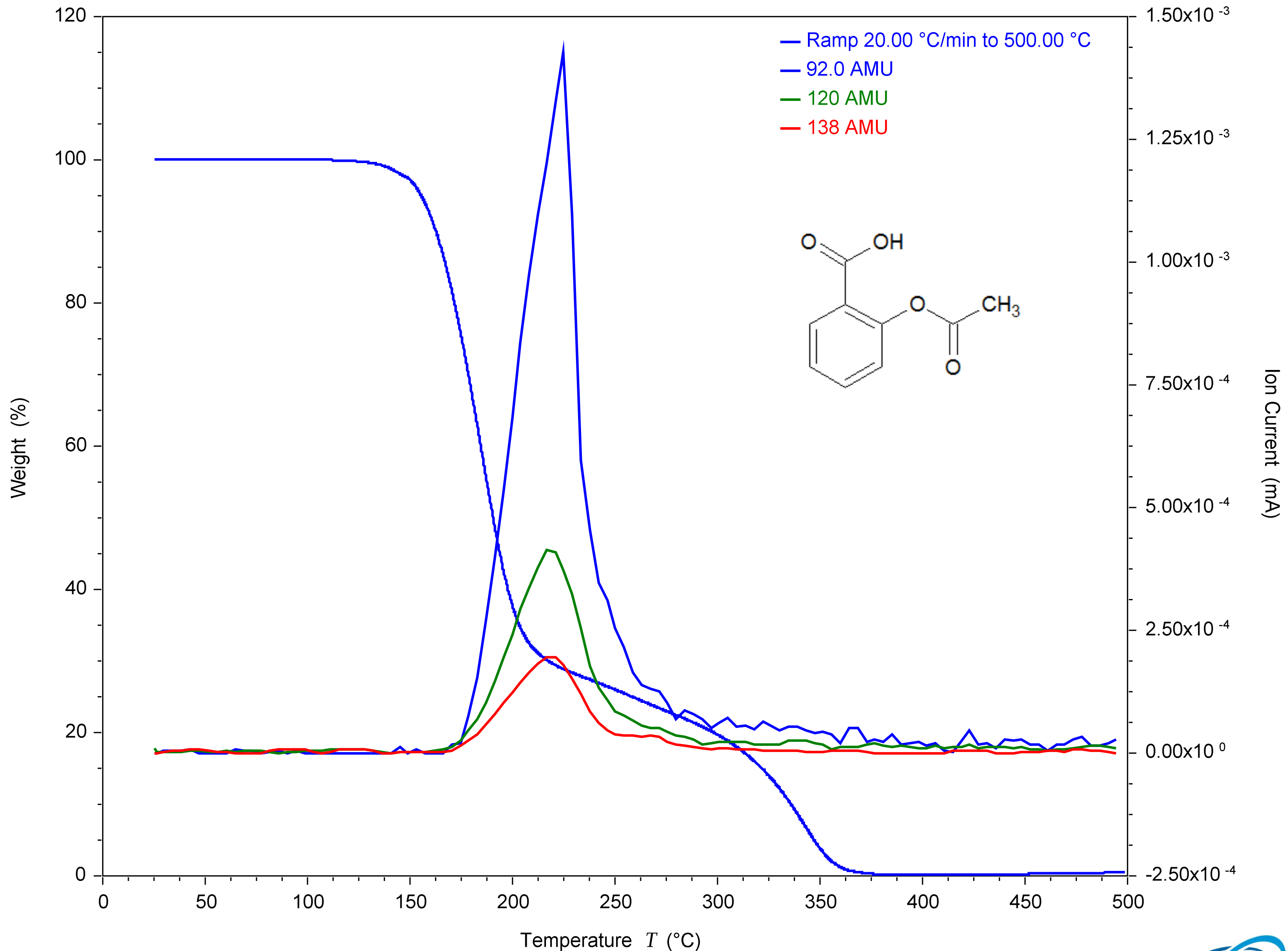
Typical Raw Data:
m/z vs Partial Pressure for Polyphenylene Oxide



Example: Typical TGA/MS Data Presentation



The Discovery Series II Mass Spectrometer (DMS)

- Benchtop, unit resolution quadrupole mass spec designed and optimized for evolved gas analysis (EGA)

- Quadrupole detection system includes…
  - a closed ion source
  - a quadrupole mass filter assembly
  - dual detector system (Faraday and Secondary Electron Multiplier)

  …ensuring excellent sensitivity from ppb to percent concentrations

DMS Series II System Overview

Heated SS Capillary Inlet Custom Interfaced to TGA Exhaust

- Inlet consists of a SS capillary tube with a 300 ℃ heater assembly

Dry Vacuum Pumps

- Hydrocarbon-free vacuum system
- 70 l/s wide range turbo molecular pump
- 4 headed, higher compression, diaphragm backing pump

Integrated Pressure Gauge

- Independent pressure measurement
- Trip signal to protect analyzer

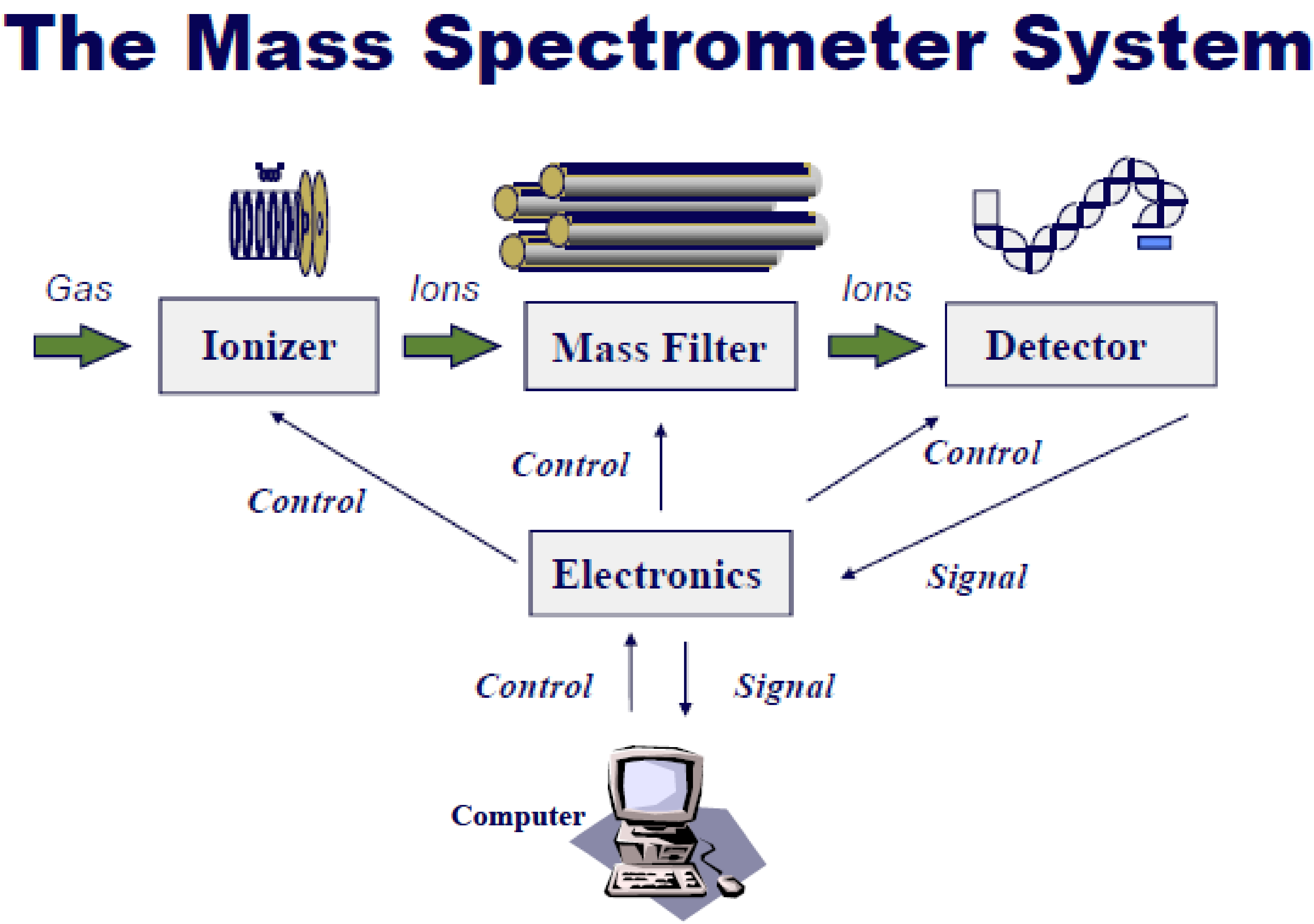
EM Thermal trip

- Protects the electron multiplier from damage if operated above 80 ˚C

24 Volt operation

- Mains supply independent
- Longer diaphragm lifetime on the pump, due to cooler operation

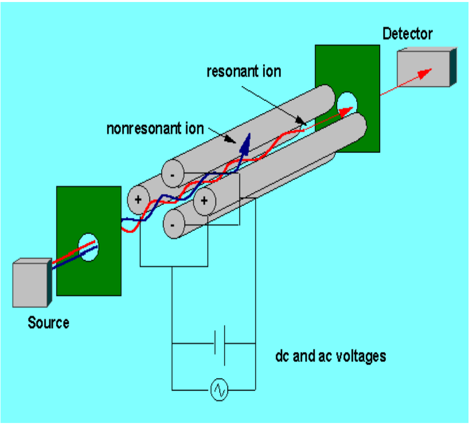
A Quadrupole Mass Spectrometer

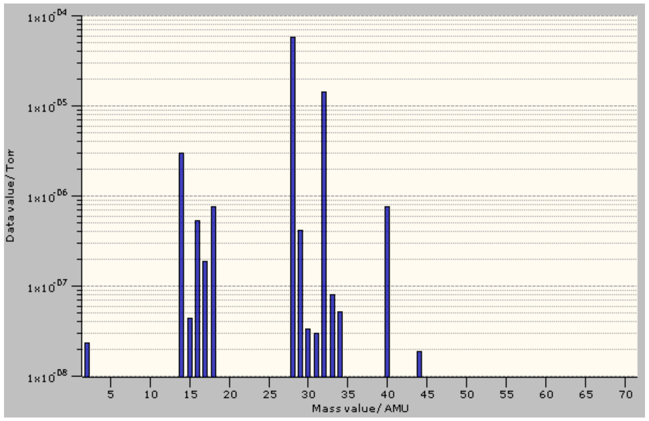


What is a Quadrupole Mass Spectrometer?

A Quadrupole Mass Analyzer

- Ionizes gas molecules and atoms
  - Electron impact knocks off an electron and fragments molecules forming positive ions
- Sorts by the mass/charge (m/z) ratio
- Measures the ion current
- Displays ion current vs. m/z ratio
- When calibrated against inlet pressure - can display partial pressure vs. m/z ratio



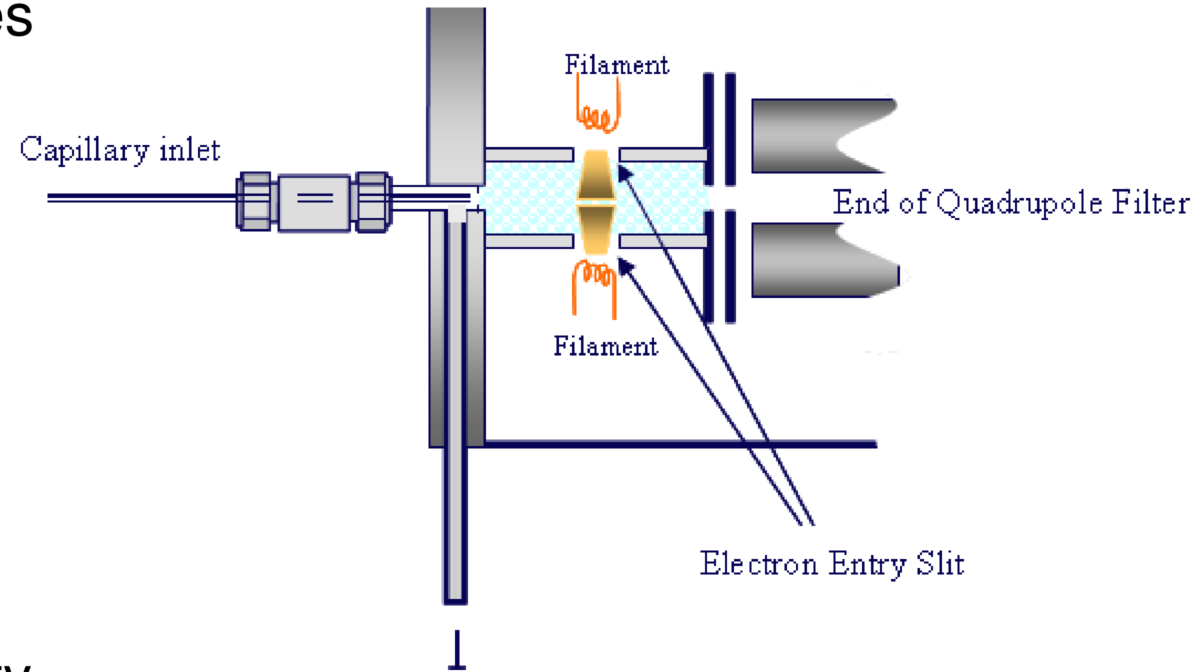


Ion source design

Closed Ion Source

- Significantly improves detection capability compared with open ion source designs

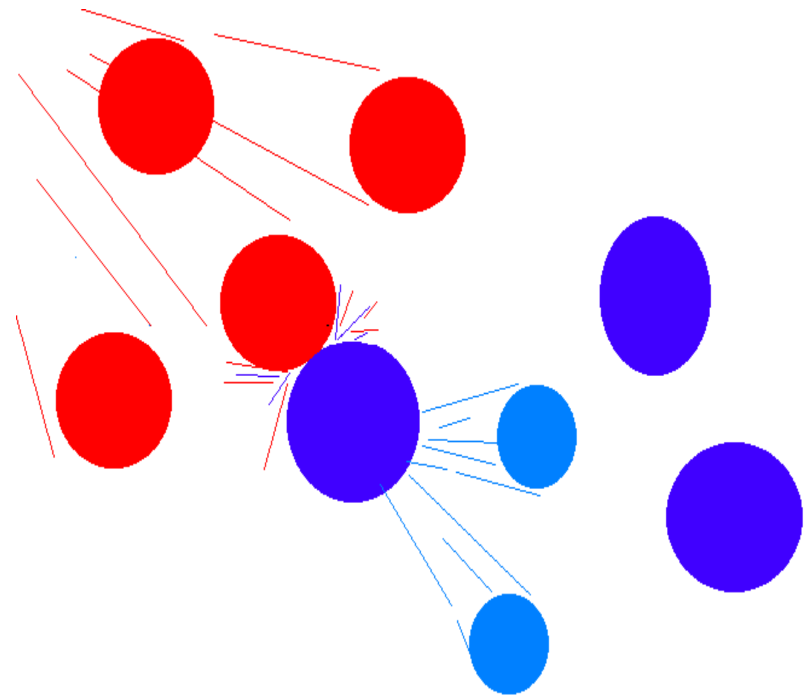
- Eliminates system background interference & maximizes sample peak intensity



What is a Mass Spectrometer?

Ionization Process

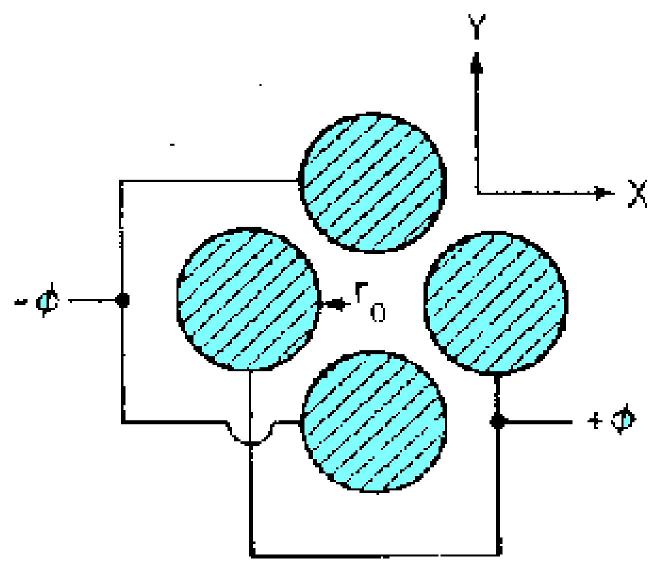
- Electrons are emitted from hot filaments and accelerated toward the source cage via an electrical bias voltage
- The fast moving electrons collide with gas molecules, dislodging electrons, thus ionizing them
- An ion is an atom or group of atoms which have become charged, positively or negatively, through losing or gaining electrons



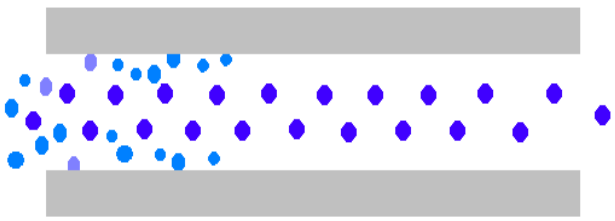
What is a Mass Spectrometer?

The Quadrupole Mass Filter Assembly

- The quadruple array is composed of four precision stainless steel rods
- RF power is applied to all rods with - DC to one pair and +DC to the opposing pair
- This creates a complex electrical field
- By varying the voltage, electrical field can be controlled



How a Quadrupole Mass Spec Filter Works



- The electrical field is varied by ramping the RF/DC voltages in a 6:1 ratio
- As ramp increases, ions with an appropriate m/z will oscillate in a stable three dimensional trajectory through the poles
- Ions of incorrect m/z will oscillate out of control and collide with the poles

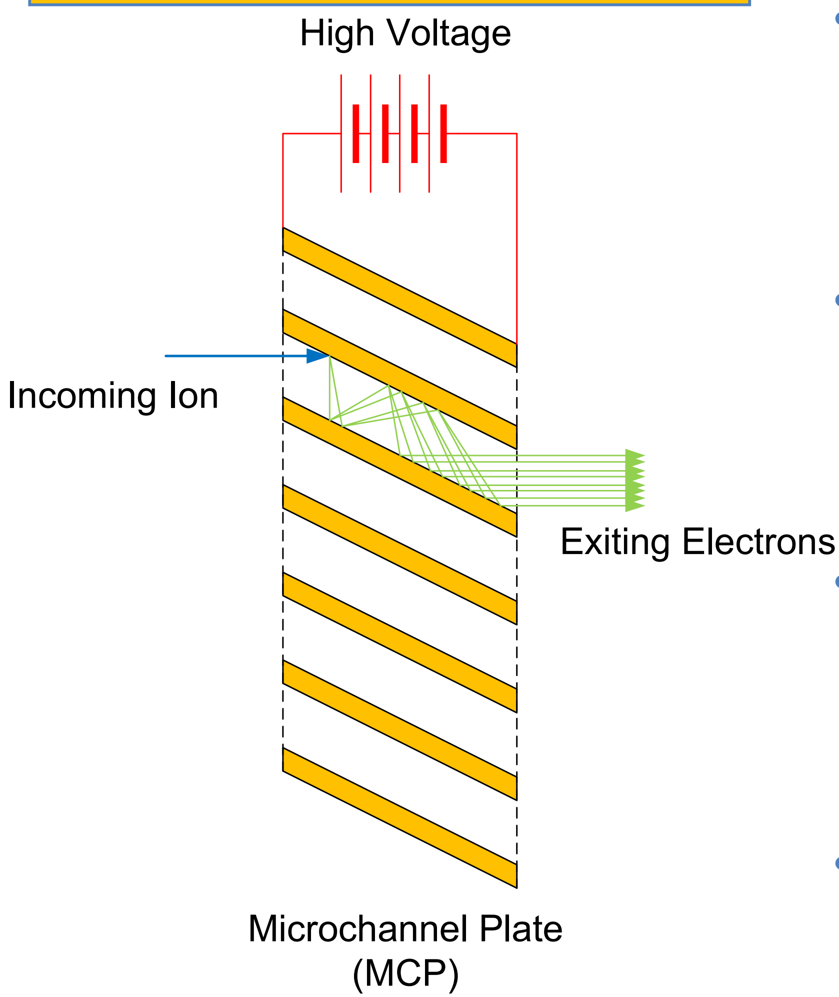
Ion Detector

- Faraday Cup
  - Ion current collected directly and fed to amplifier
  - Basic sensitivity is measured at the Faraday cup

- Electron Multiplier
  - Continuous Dynode
    - Microchannel Plate
  - Gain– ratio of output with multiplier to Faraday cup current (no multiplier)

Micro-Channel Plate Electron Multiplier

Active surface: $PbO\text{-}B_2O_3$ glass

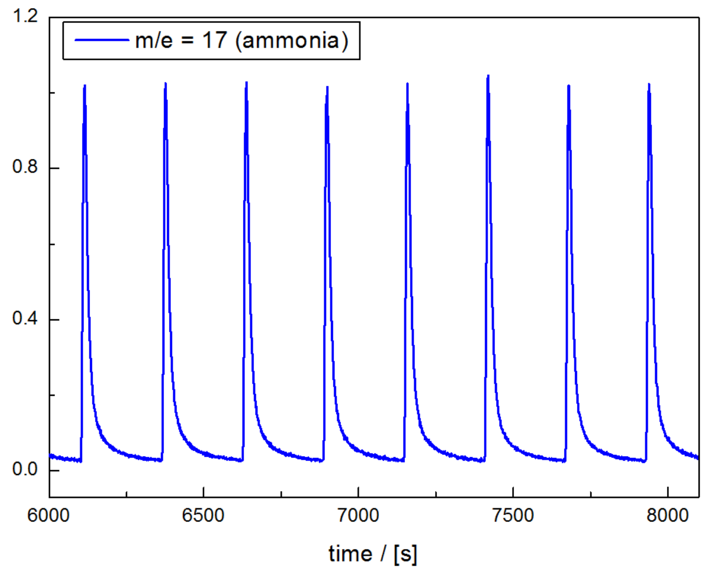


High-resistivity surface with a high secondary emission coefficient for electrons

- MCP is a plate made of small glass tubes of approximately 10 micron diameter
- Incoming ions cause emission of electrons from the surface of the tubes
- The ratio between incoming ions and exiting electrons is the multiplier gain
- MCP can give a gain of up to 3000

Heater and Inlet design

- Capillary and inlet materials minimize ad-/desorption effects even for reactive and corrosive species
- Consistent heating across the whole inlet and the spectrometer



Reproducibility of short NH3 pulses

Summary of DMS Series II System

- 1-300 AMU Quadruple Mass Filter
- Easy Maintenance
  - Capillary Inlet and Pressure Reduce Orifice
- High Sensitivity Detector
- High Speed Data Collection
- Integrated Control Via TGA Digital Trigger
- Easy to use software designed around the needs of the TGA user

Specific Benefits of Discovery Mass Spectrometer

TA Discovery Series II Mass Spectrometer offers a number of specific advantages:

- Rugged design
- Easy maintenance
- Excellent sensitivity
- Neat sample analysis – no need for solvents
- Ease of use – operation software features simple experimental design
- Automatic synchronization of TGA collection data including support of the TGA autosampler
- Powerful TRIOS software for TGA/MS data analysis
- Worldwide support
- Expert local knowledge

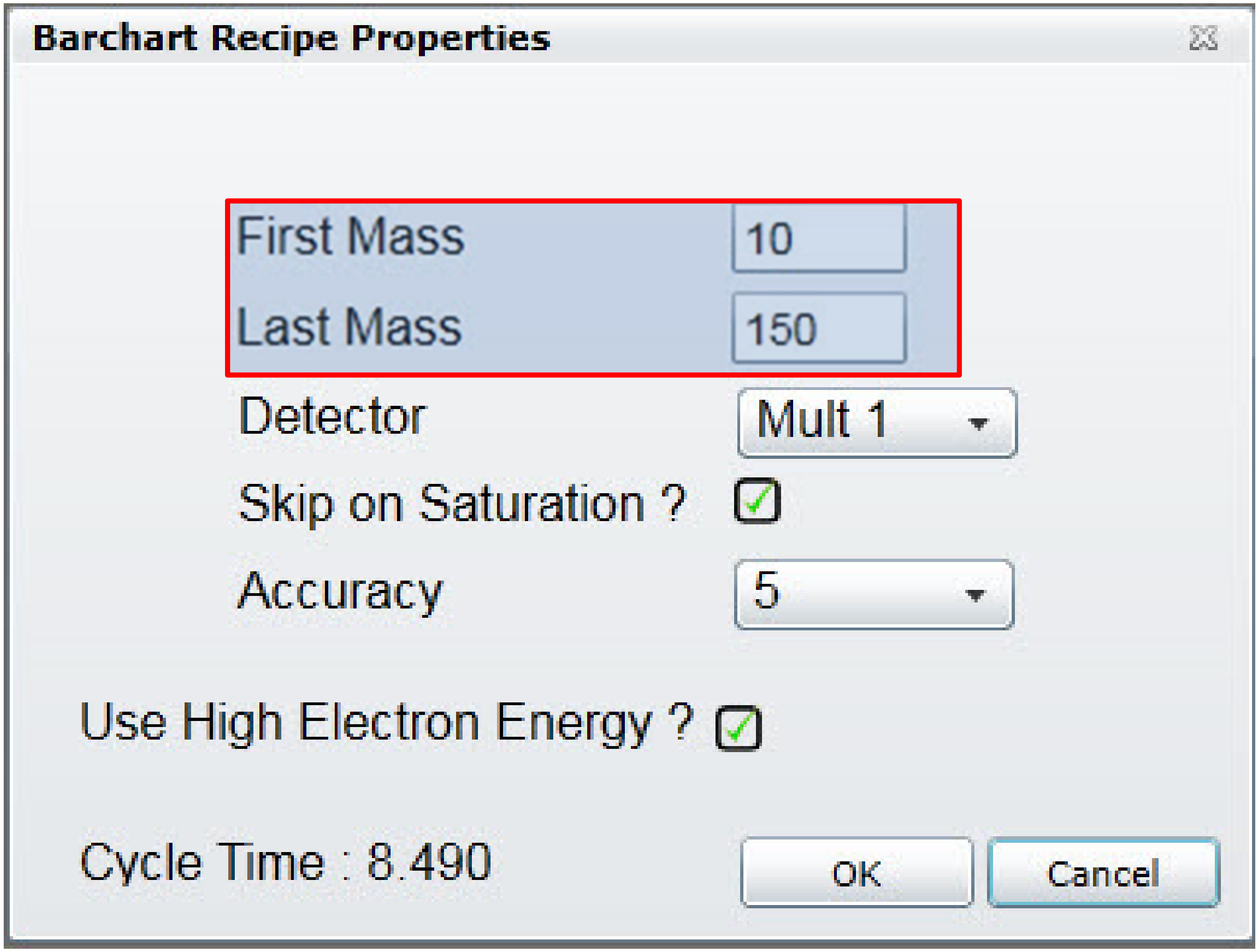
Applications

- Polymers
- Residual Solvent
- Pharmaceuticals
- Biomass
- Soil
- Excellent scouting instrument for GC/MS or HPLC/MS as a first pass for unknown or samples that may be fairly ‘dirty’.
- Many others!

TGA/MS: Experiments

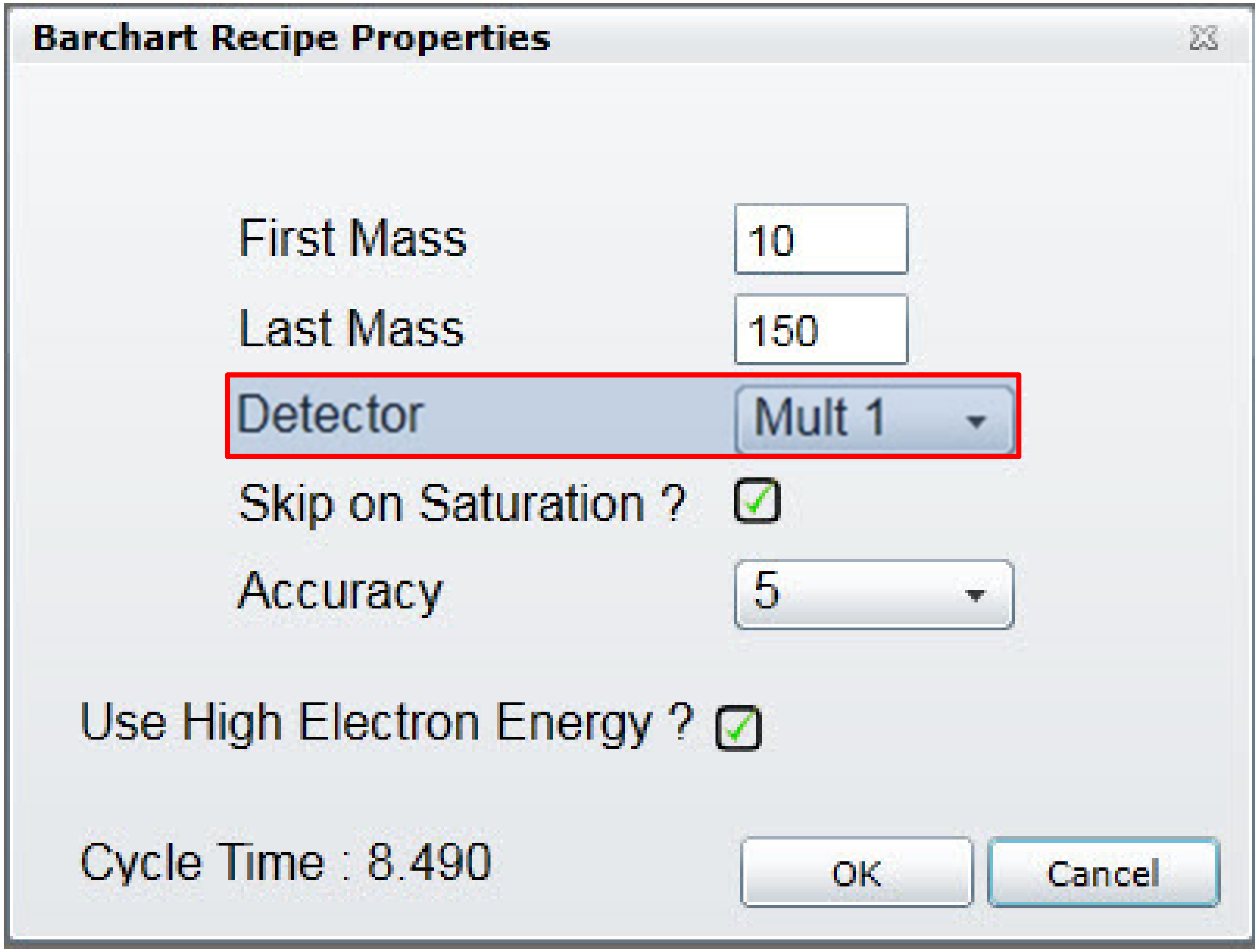
- Experiments are called ‘recipes’
- Barchart
  - Scan across specified ion range - m/z 1 to m/z 300
  - Typically used as first approach for an unknown compound
- Peak Jump
  - Scan specific ions
  - Example, scan m/z 91, 65, 51, 39 if you are looking for residual toluene

Basic System Operation: Selection of Parameters for Barchart Recipe



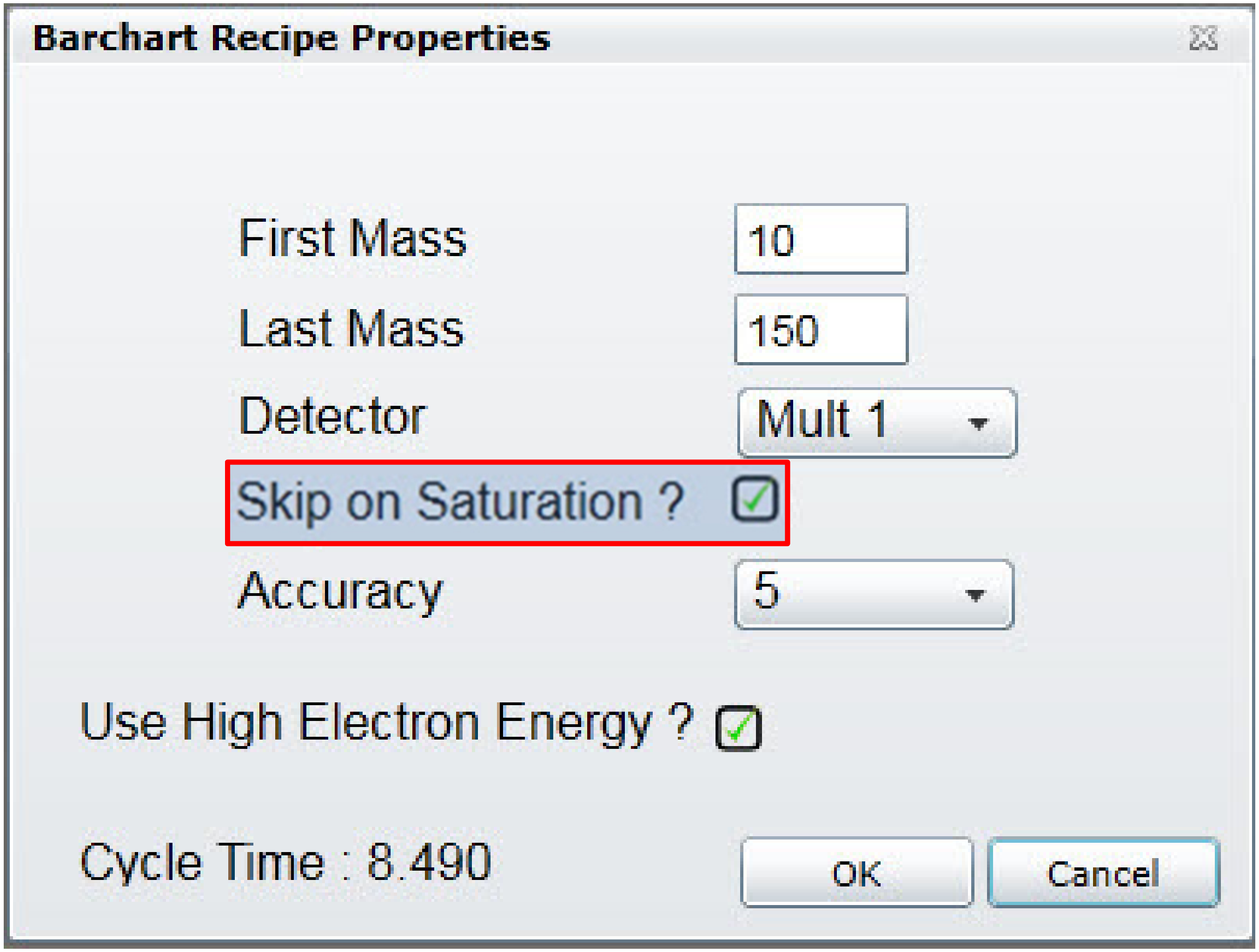
Choose your mass range by entering the desired values into the **First Mass** and **Last Mass** fields.

Basic System Operation: Selection of Parameters for Barchart Recipe



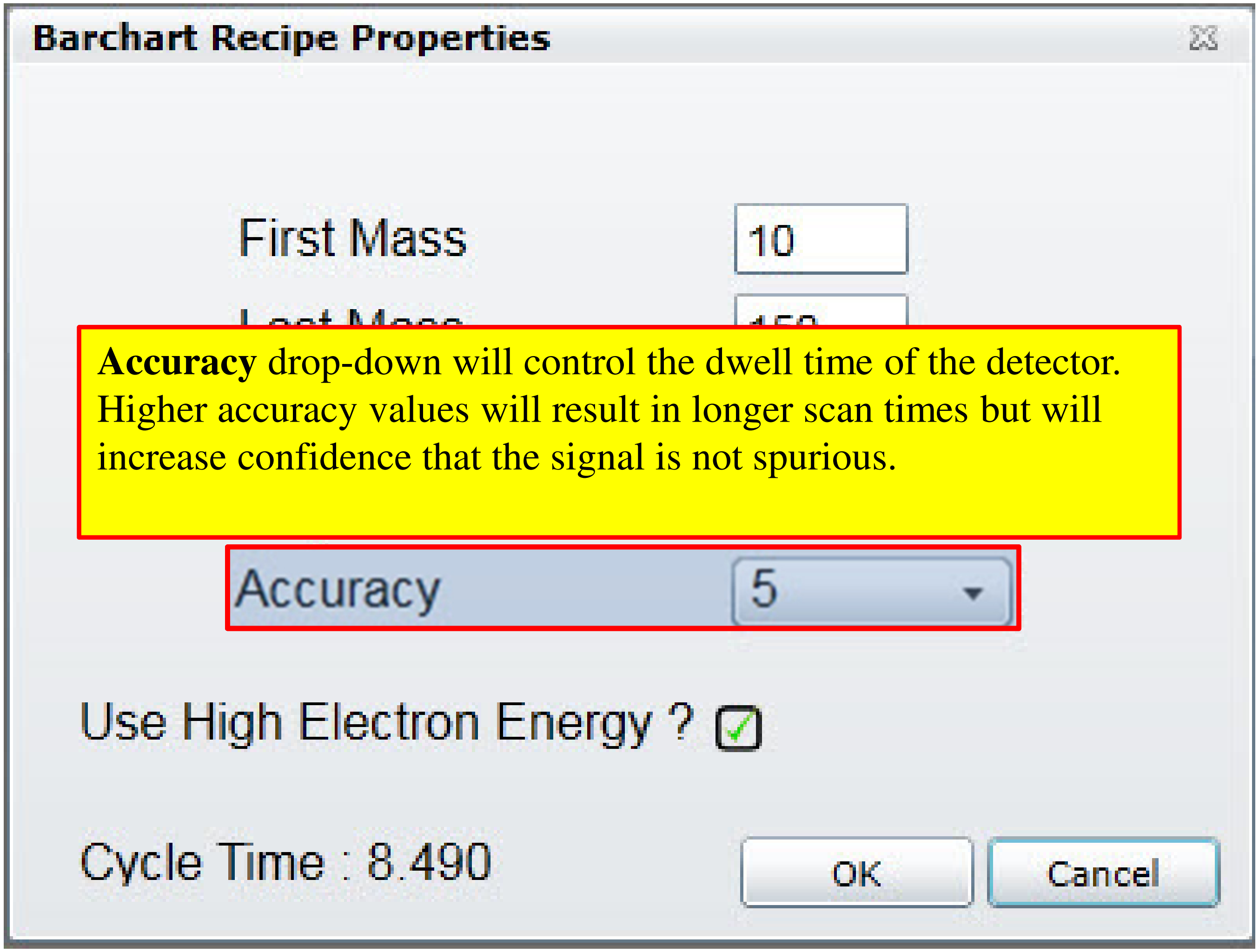
Choose the detector setting (gain) that you need. Typically either the **Faraday** or **Mult 1** will be sufficient.

Basic System Operation: Selection of Parameters for Barchart Recipe



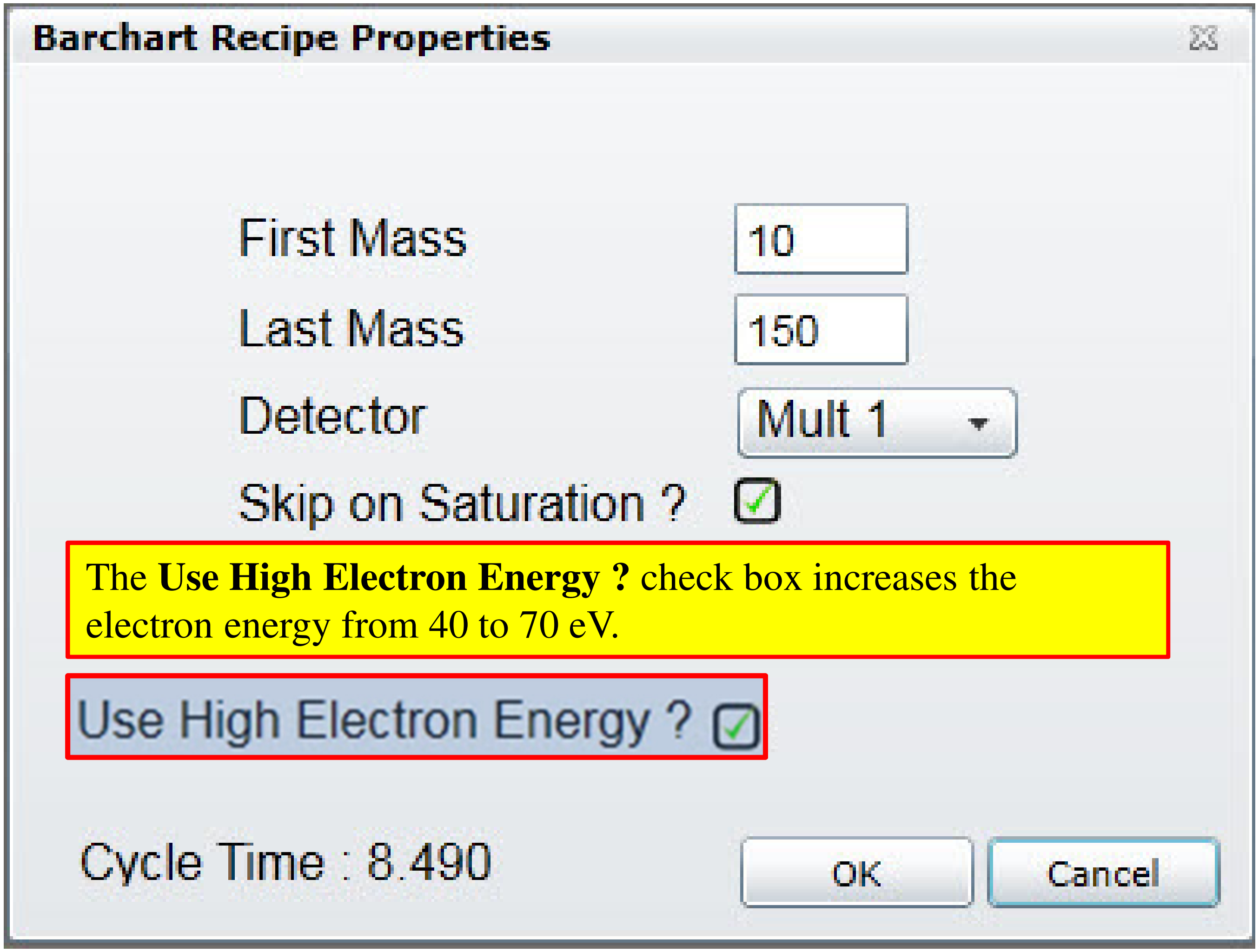
The **Skip on Saturation** check box will omit a mass if the signal saturates the detector.

Basic System Operation: Selection of Parameters for Barchart Recipe

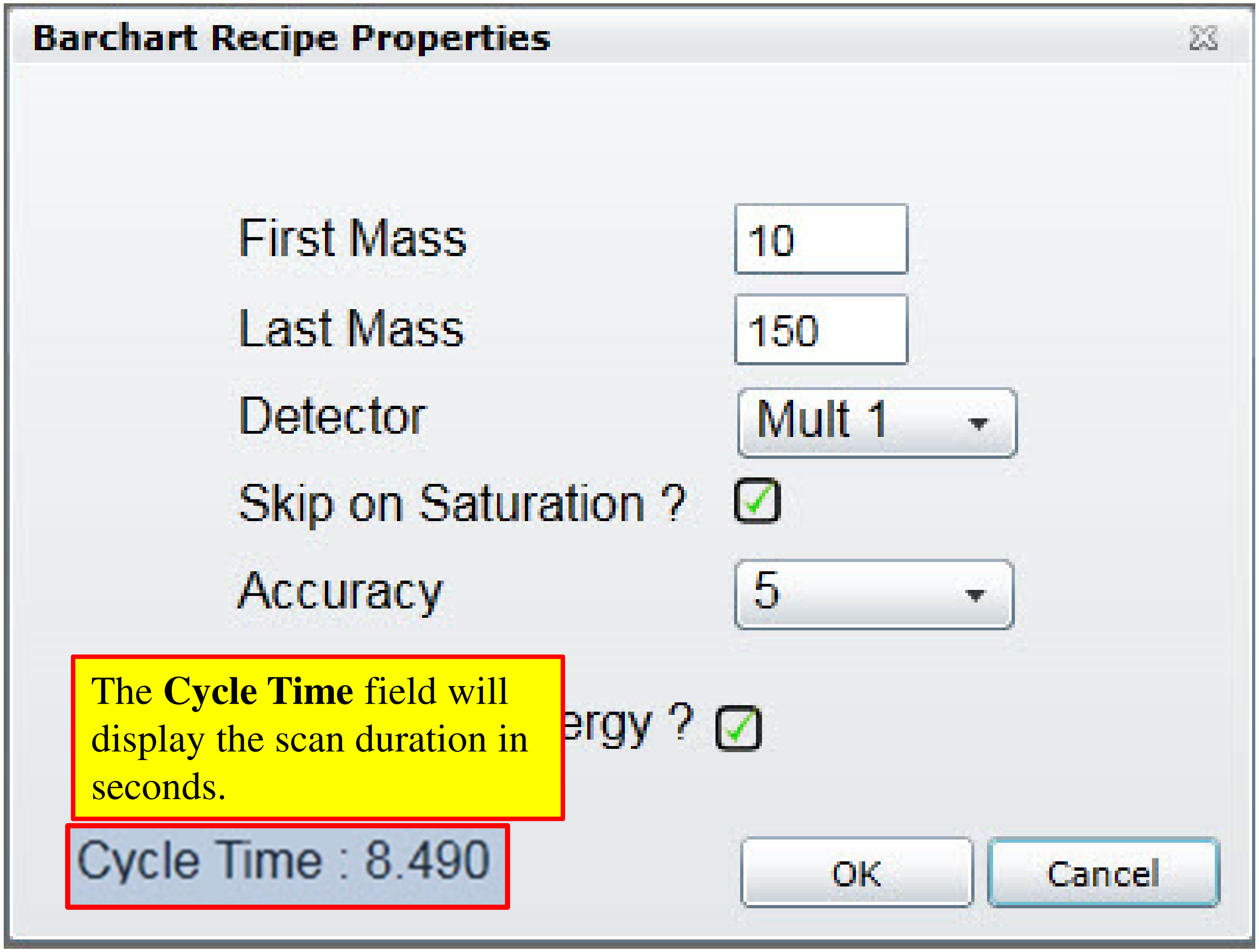


Accuracy drop-down will control the dwell time of the detector. Higher accuracy values will result in longer scan times but will increase confidence that the signal is not spurious.

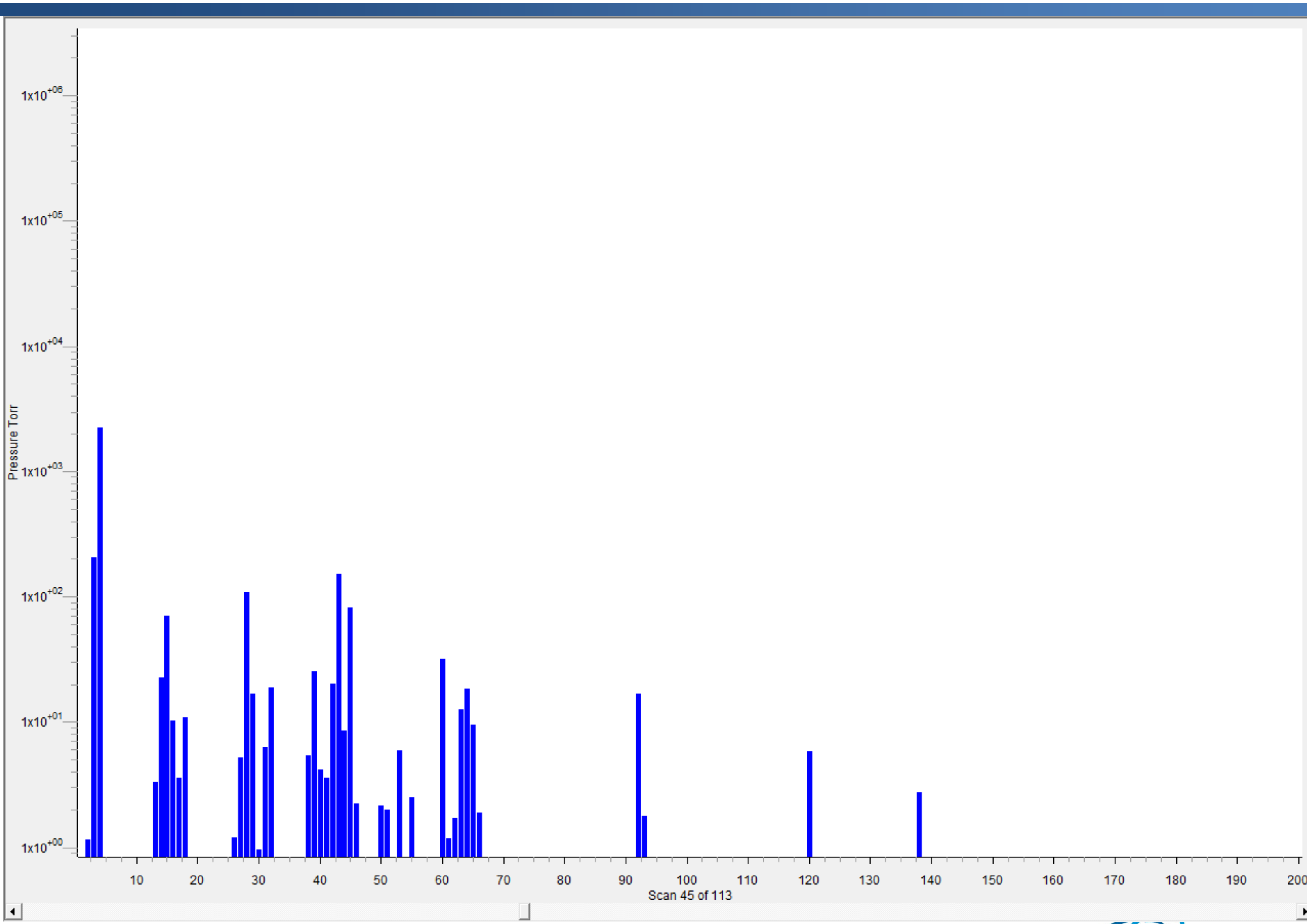
Basic System Operation: Selection of Parameters for Barchart Recipe



Basic System Operation: Selection of Parameters for Barchart Recipe



Example: Aspirin



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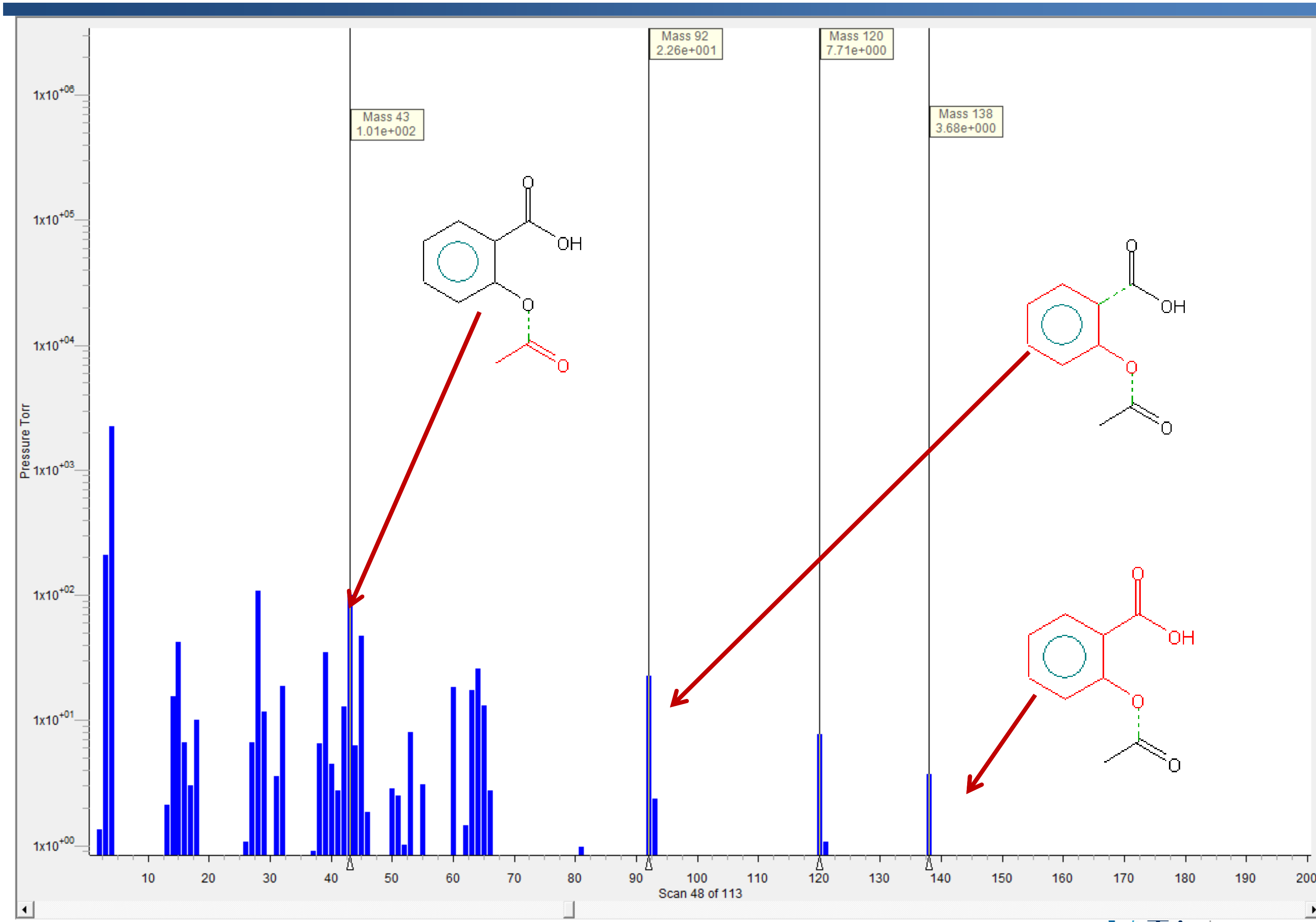

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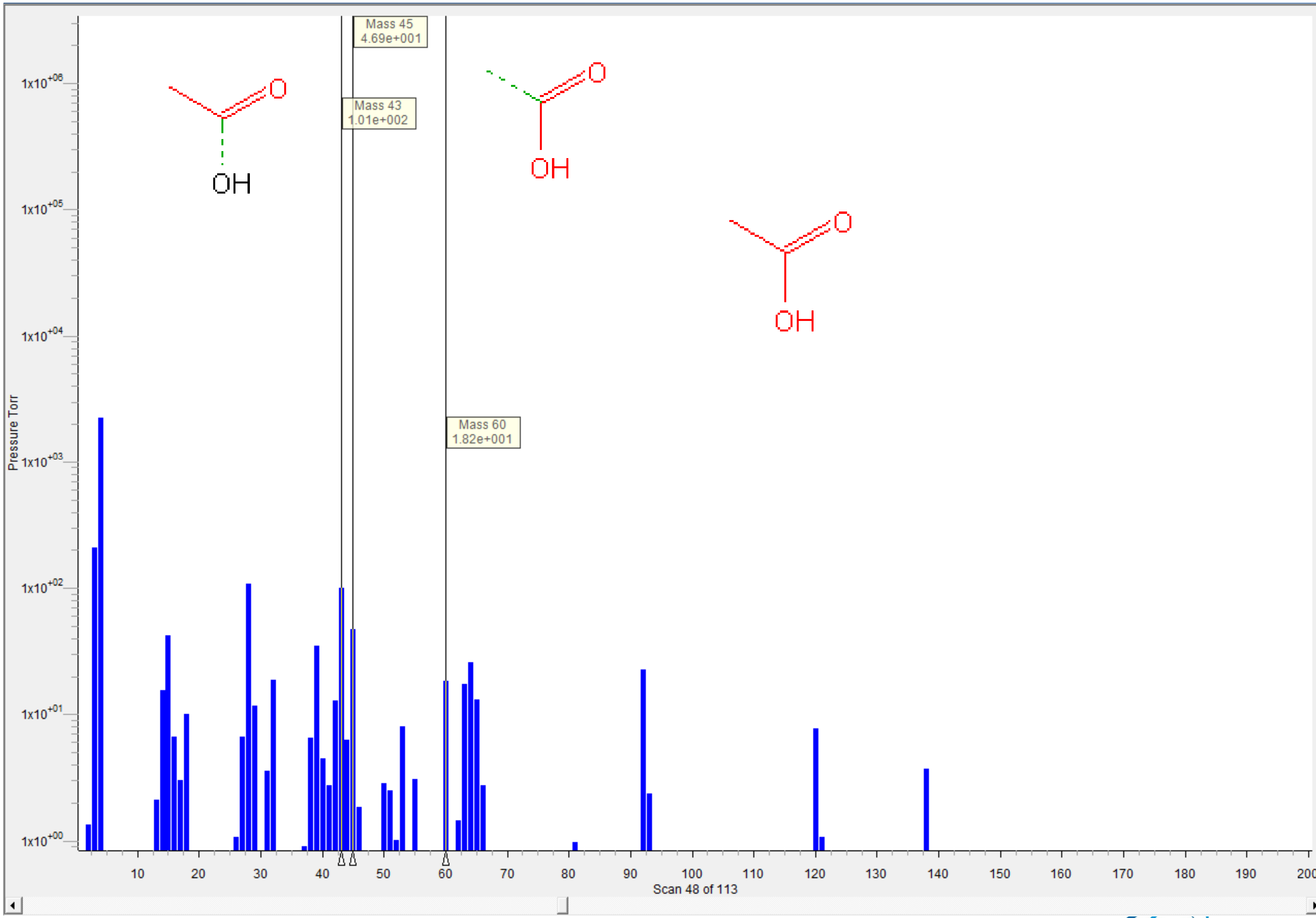

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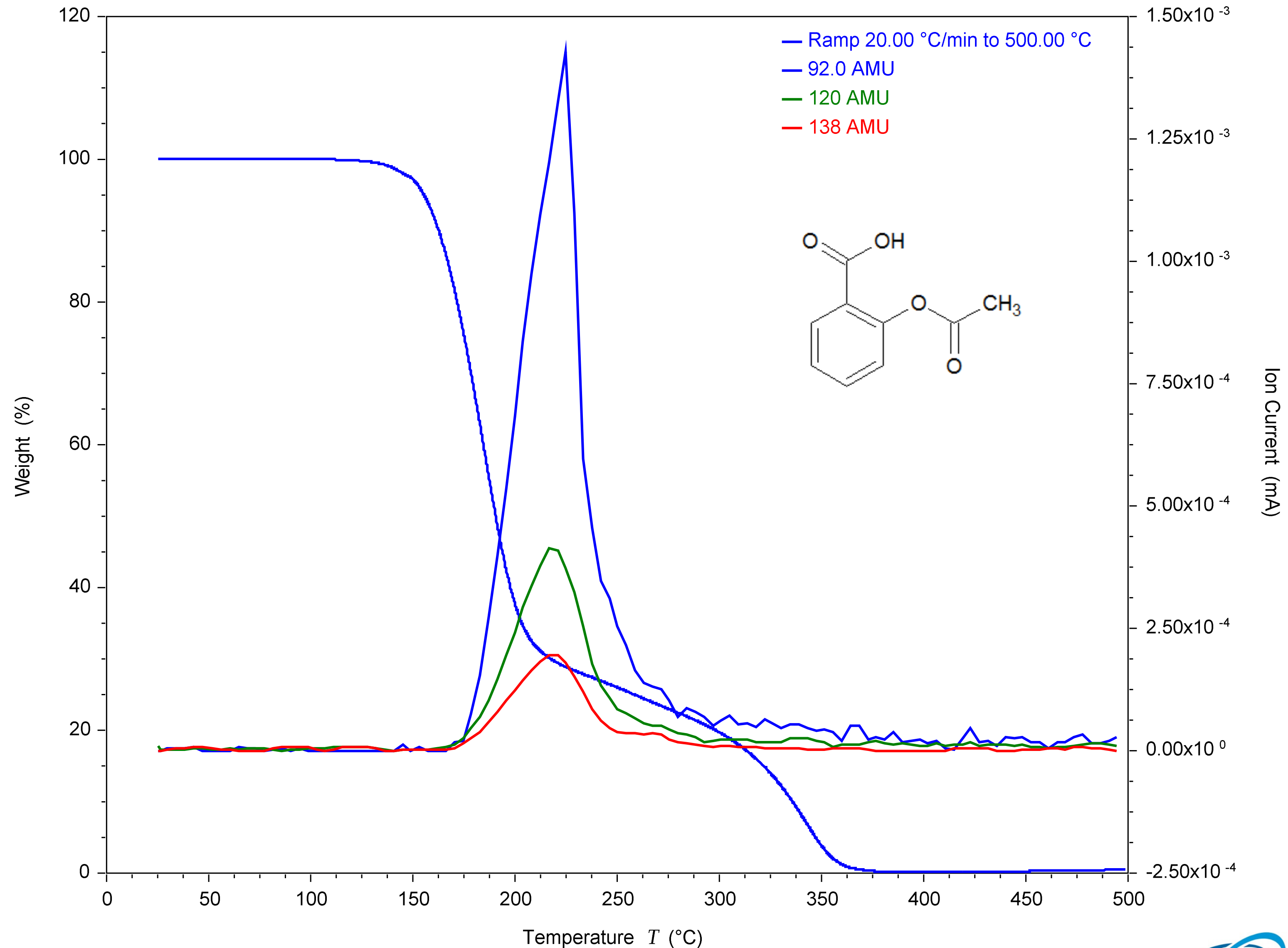

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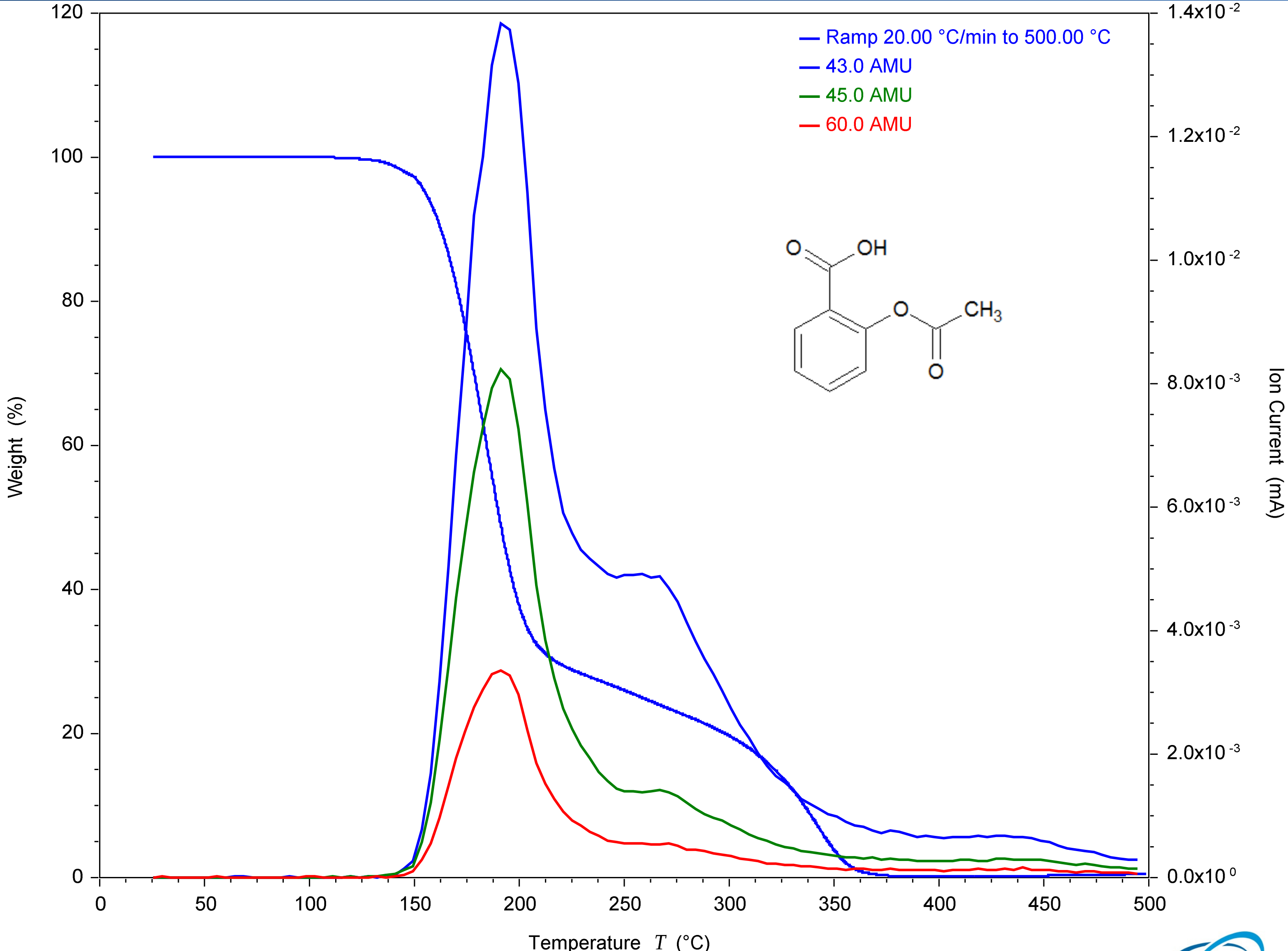
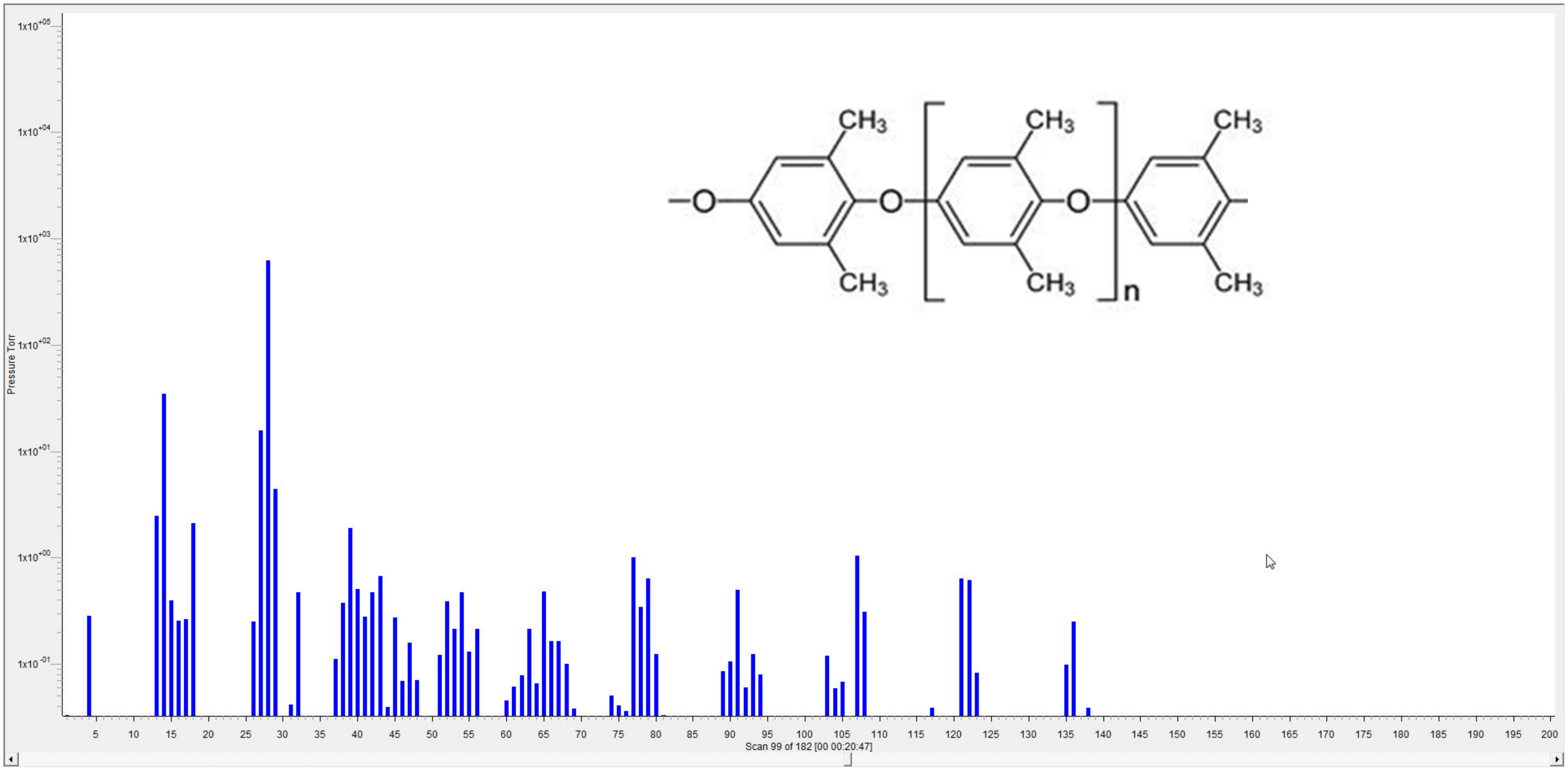


Example: Polyphenylene Oxide (PPO)



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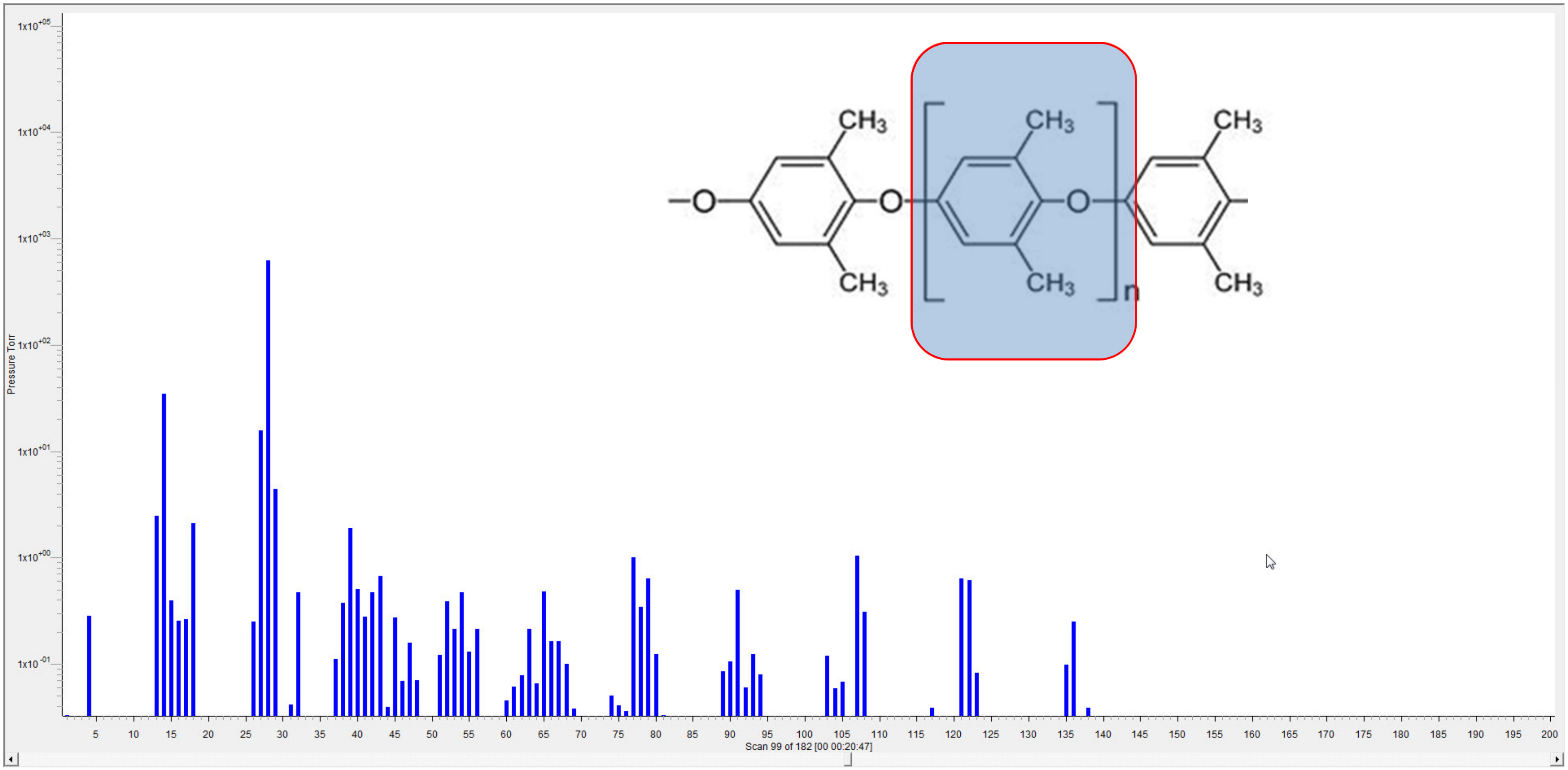

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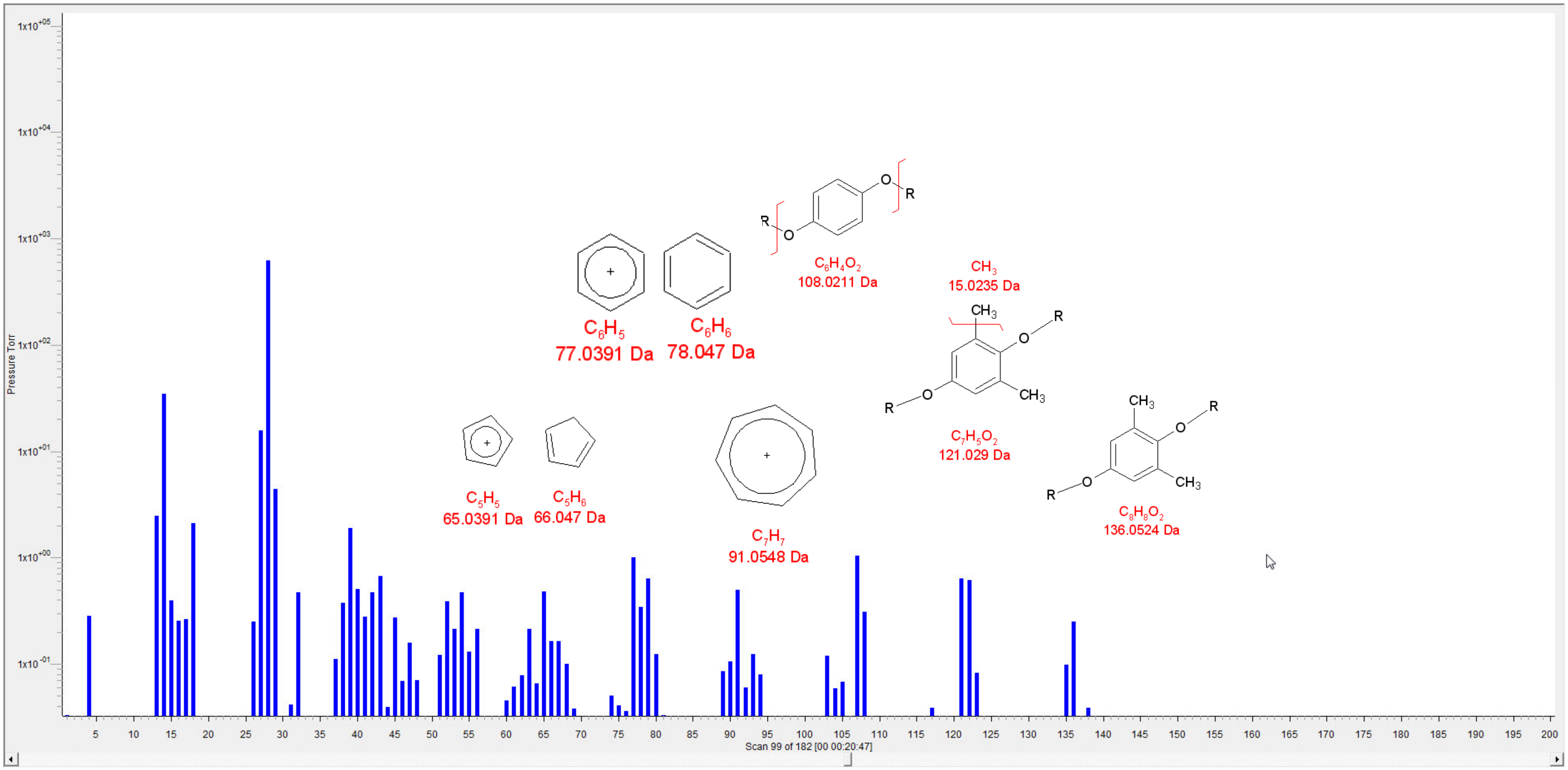

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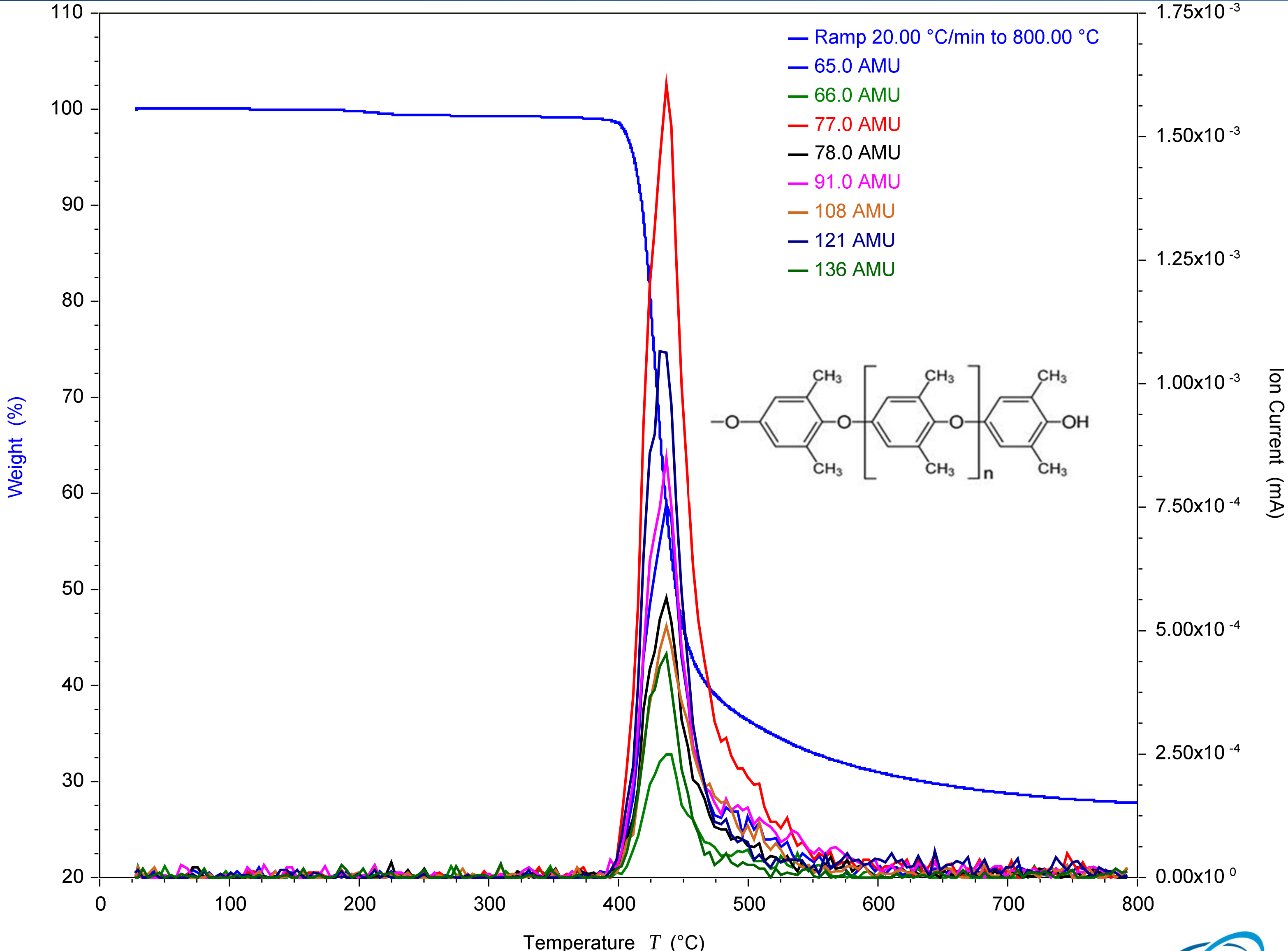
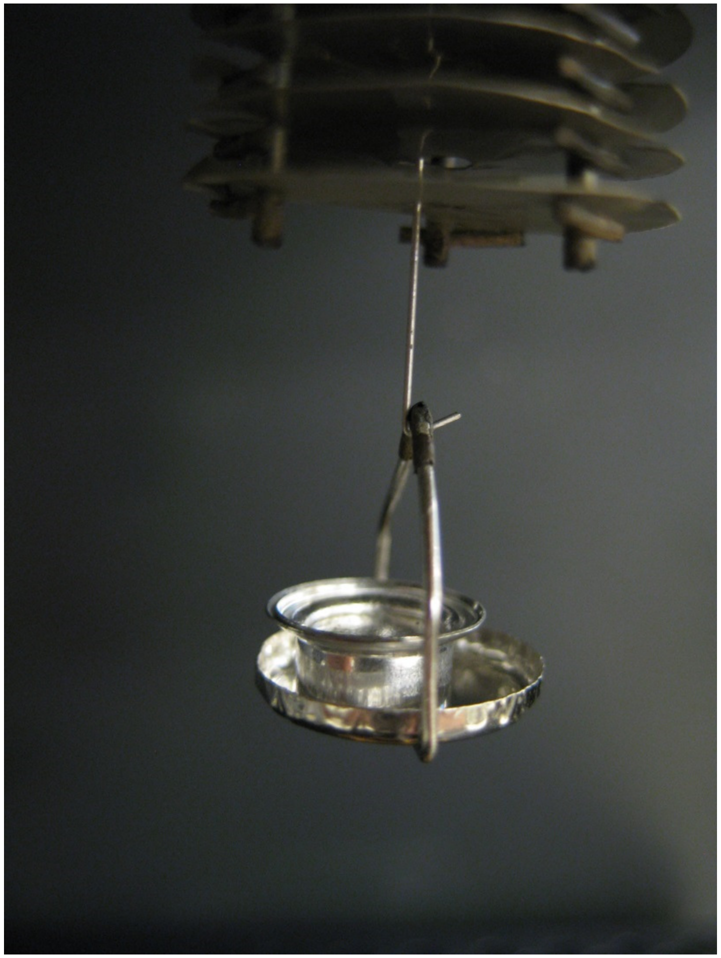


Experimental Design: Some Considerations

- Barchart experiment is a good place to start especially for unknowns.
- Peak Jump is very useful for ‘known’ samples; for example, monitoring residual solvent, reaction products, contaminants, etc.
- Start with small sample masses: 2-3 mg and increase if needed.
- Purge gas
  - Use High Purity (may still contain air)
  - He, N2, Ar, Air
- Monitor background before and after run.

Experimental Design: Some Considerations

- An isothermal before starting the heating ramp is effective for obtaining clean data showing minimal atmospheric changes as the furnace closes.
- For volatile samples, a DSC pinhole pan will often minimize the loss of sample during the isothermal.



Summary

- TGA/MS is powerful tandem and excellent addition to the analytical chemist's tools.
- High quality data is easy to obtain. Powerful software makes data reduction and reporting easy.
- Instrument is easy to operate and easy to maintain.
- Excellent analytical tool for 'difficult' samples

Thank You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