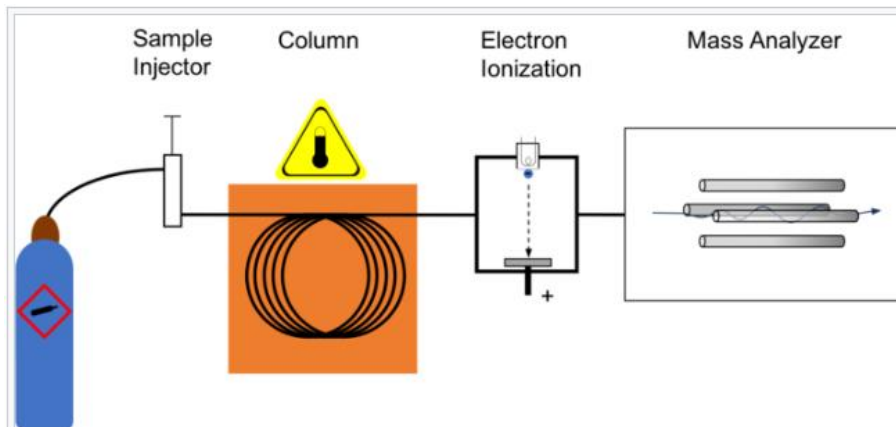


Free NIST GC-MS Software Lab
for Universities:
Part 1: Very Basic Theory of
GC-MS Analyses



James Little
August 29, 2023

38 years Eastman Chemical Company
7 years Mass Spec Interpretation Services

<https://littlemsandsailing.wpcomstaging.com/>

[Link to GCMS Schematic Above](#)

[Link to University Logos](#)

Free NIST GC-MS Software Lab for Universities

Part 1: Very Basic Theory of GCMS Analyses

Part 2: Installation of Software

Part 3: Library Searches

Part 4: Processing GCMS Data with AMDIS

Part 5: Understanding EI Fragmentation with MS Interpreter

Part 6: Structure Searches with Input from ChemSketch

Part 7: Creating a User Library

Part 8: Advanced Processing with NIST Software

A "Little" Mass Spec and Sailing
Organic Mass Spectrometry, NMR, Sailing, Tesla, Duplicate Bridge

Mass Spec Interpretation Services

100
50
0

10 20 30 40 50 60

15 16 27 31 39 40 44 51 53

43

MASSMAN
WILLIAMS

SPRAY

569.2876

CAS NO.
20583873

C₆H₁₂O
CAN COATING

About Me My Topics Others Links

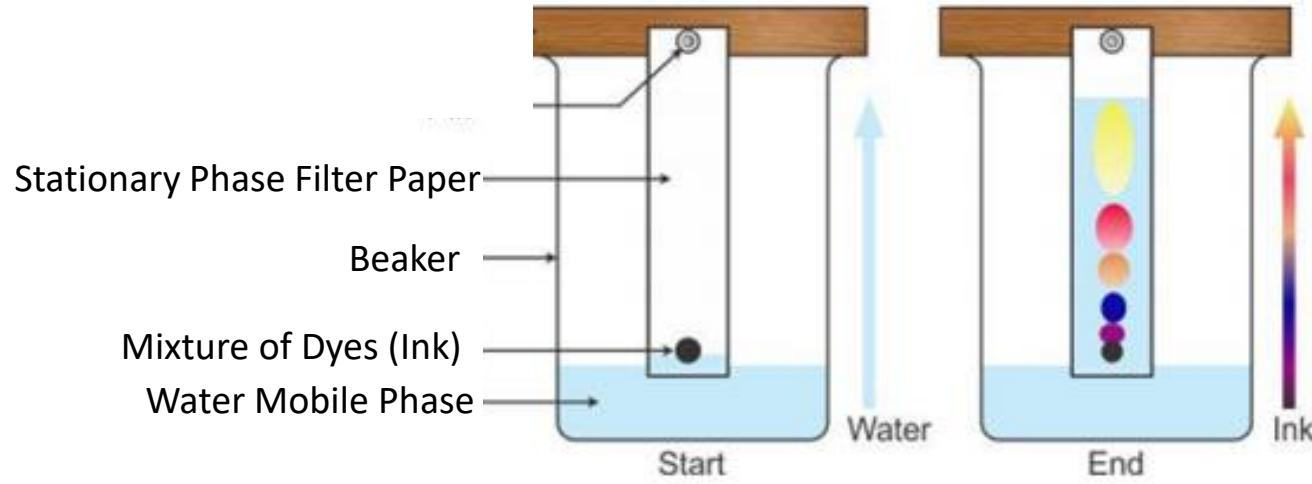
[Link to Training Website](#)

Hyphenated Technique: Gas Chromatography-Mass Spectrometry (GC-MS)

“GC-MS remains one of the most powerful, flexible, and widely used tools for analyzing chemical mixtures in drug screening, forensic, environmental, and trace analysis, as well as other applications.”

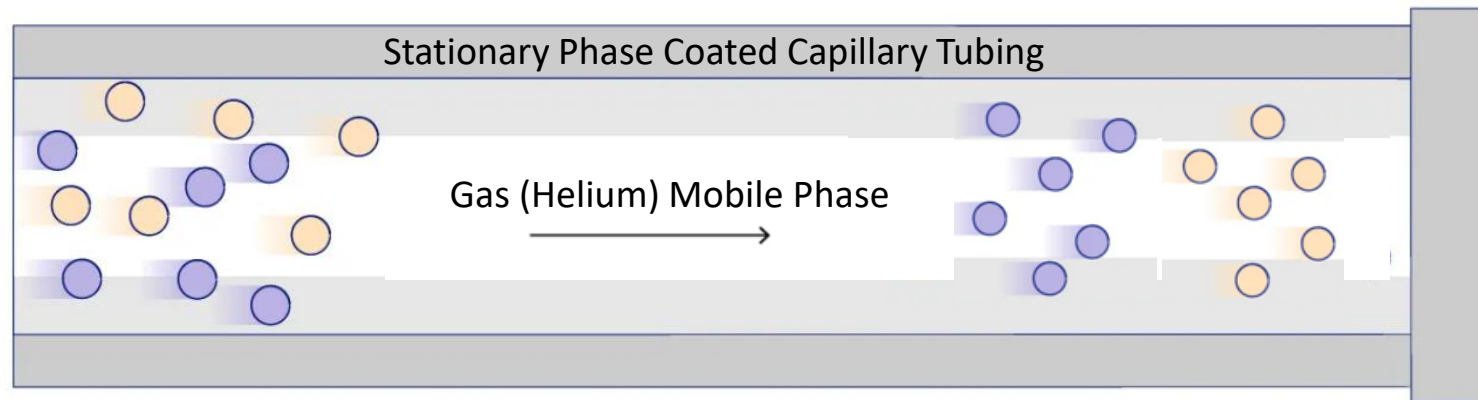
[Link to American Chemical Society: What Is Chemistry](#)

Complex Mixtures Separated by Chromatography for Mass Spec Analyses



Separated by Polarity

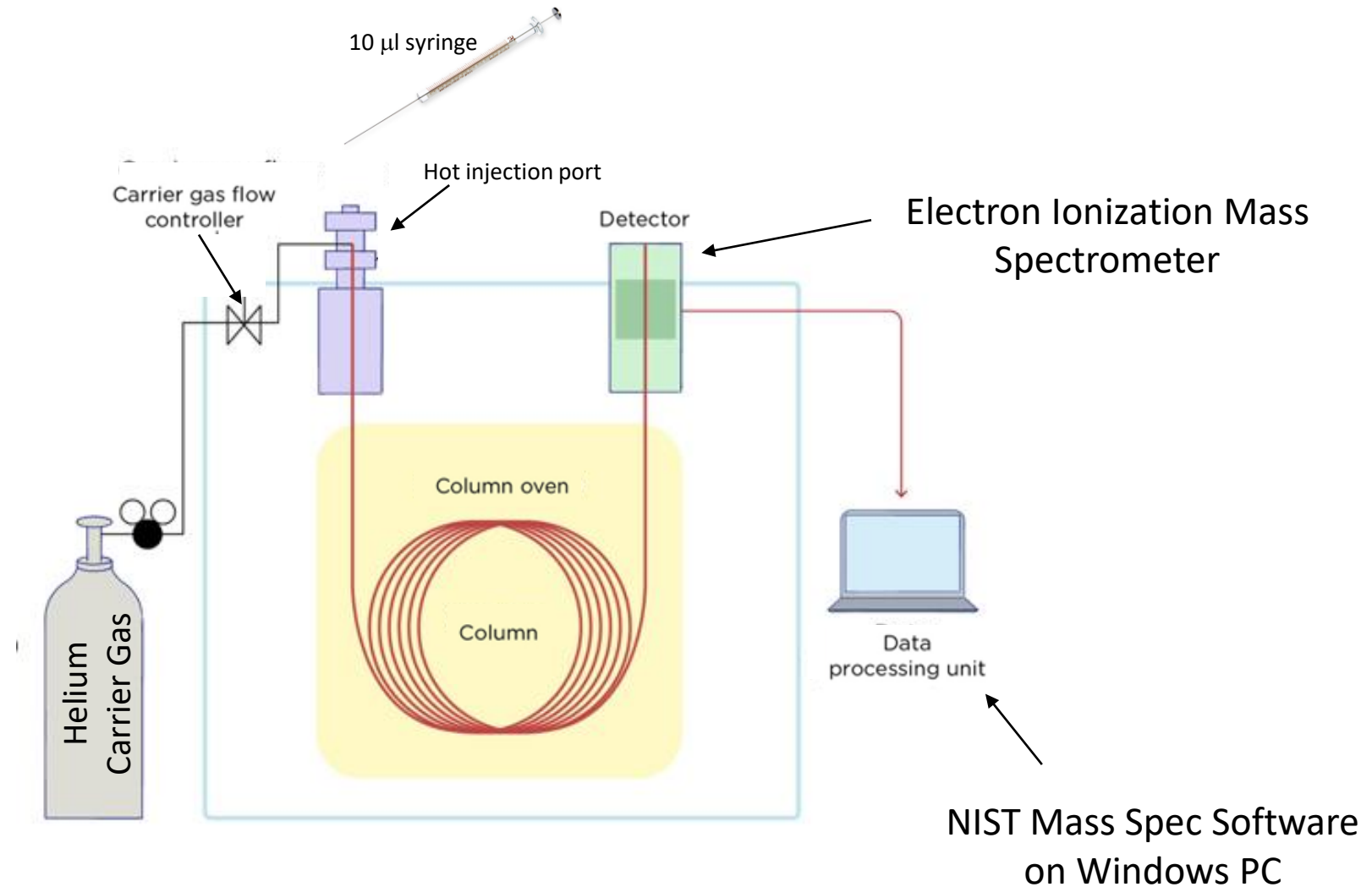
[Paper Chromatography \(link\)](#)



Separated by Polarity and/or Boiling Point

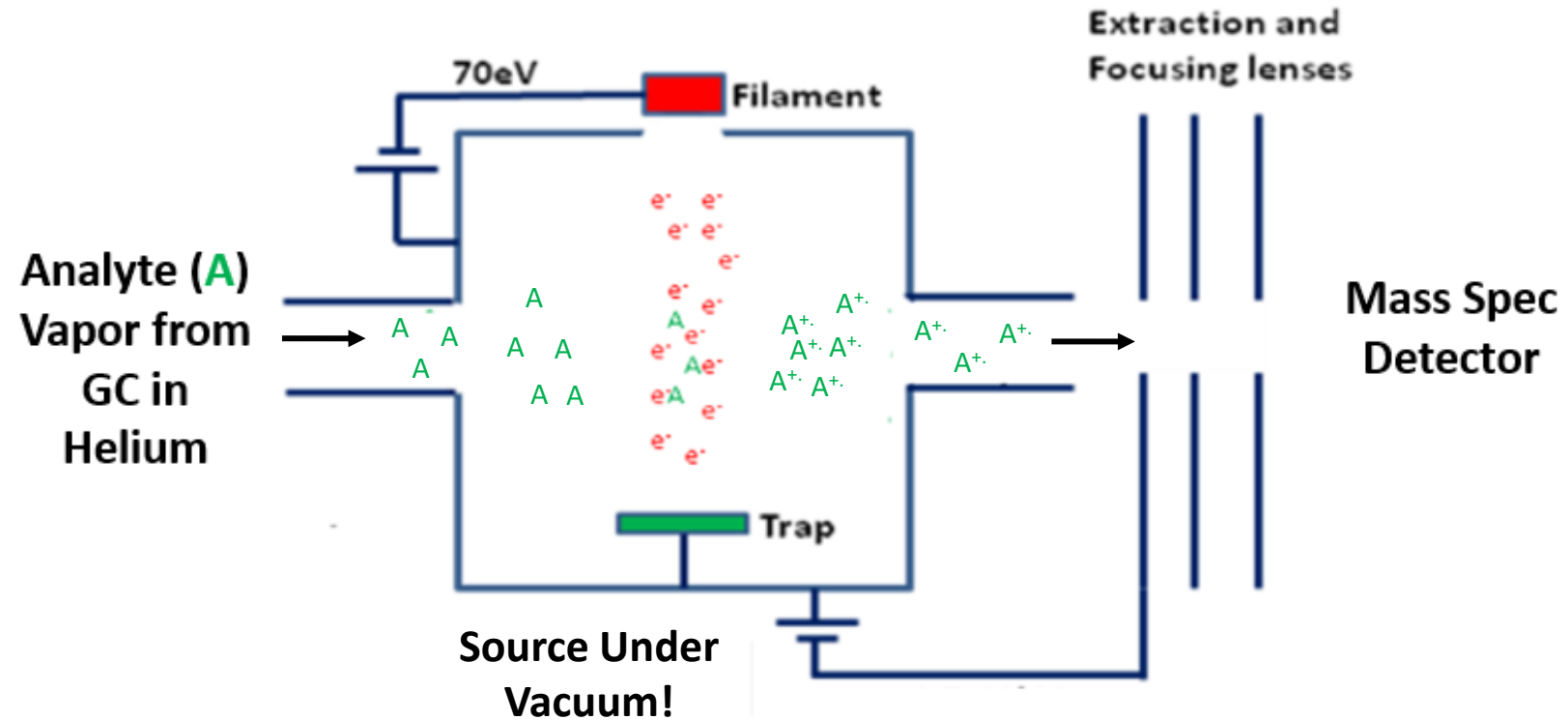
[Gas Chromatography Link](#)

Typical Gas Chromatography System Equipped with EI Mass Spectrometer as Detector



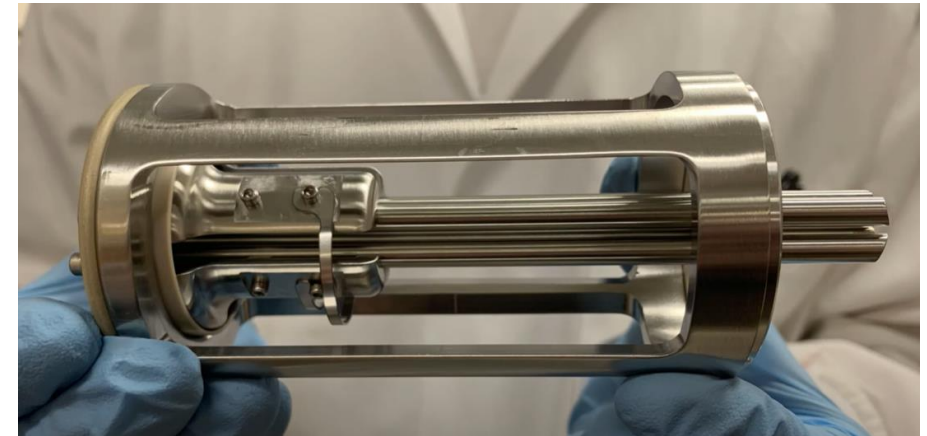
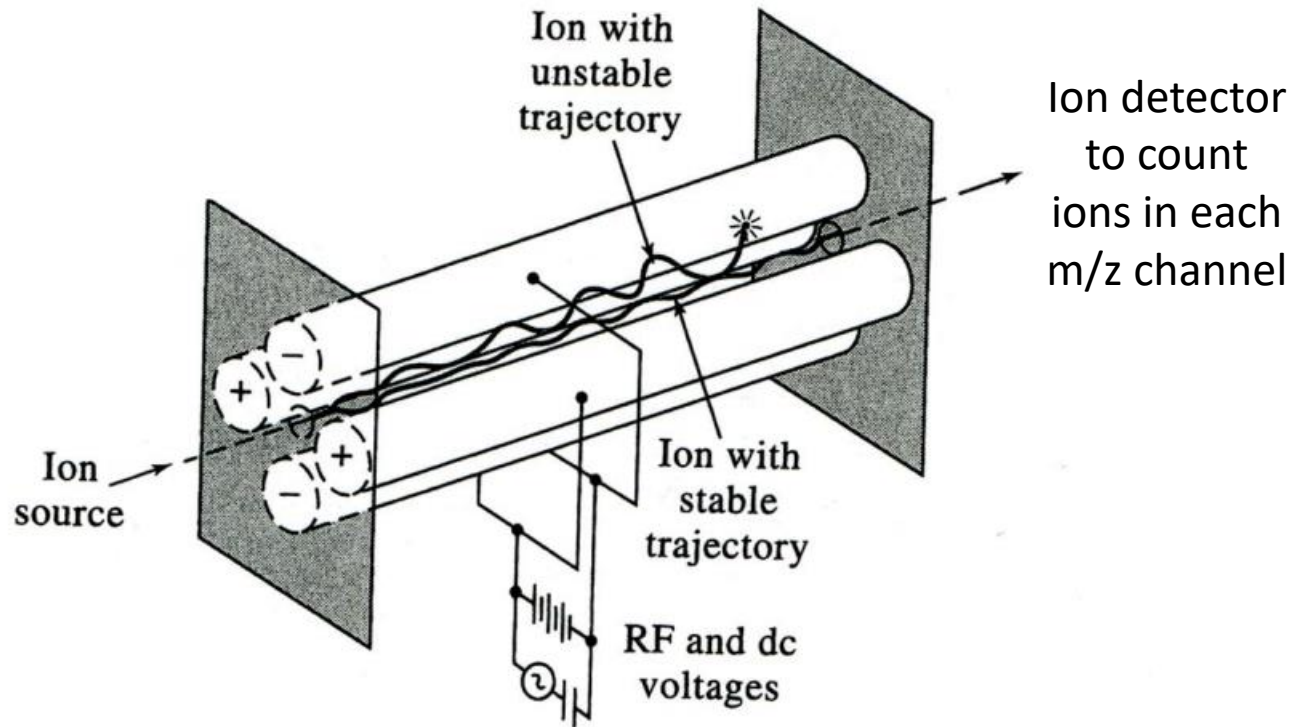
[Link to Diagram Above](#)

Electron Ionization (EI) Source



[Link to EI Source Diagram](#)

Quadrupole Mass Spec (MS) Detector *Under Vacuum*



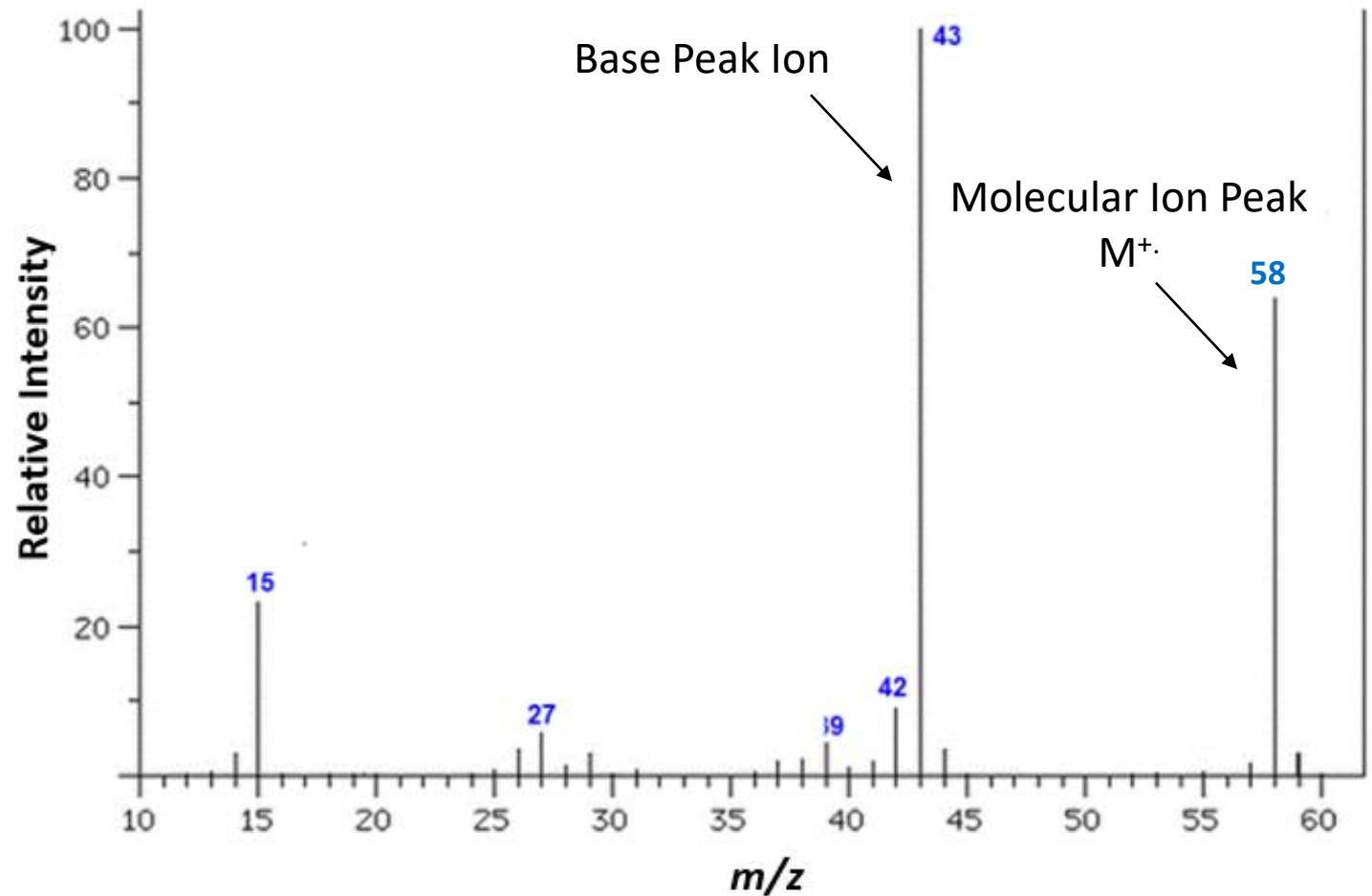
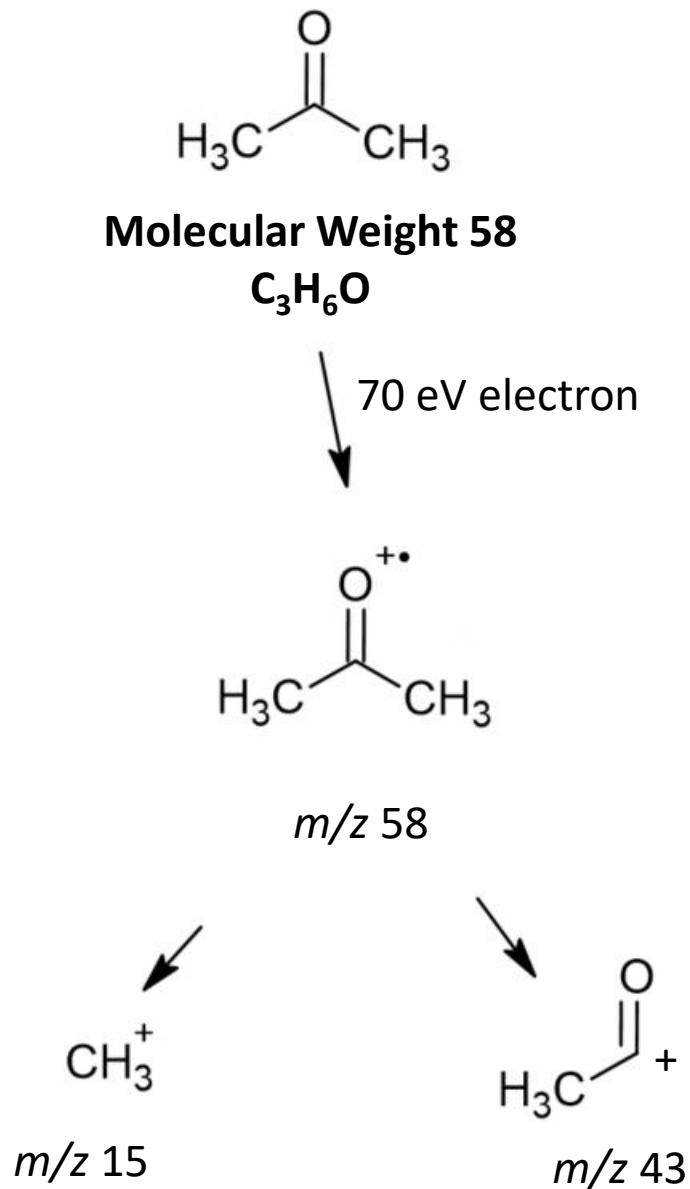
[Agilent MSD Quadrupole Assembly Link](#)

- Change RF and DC Voltages to send **one** m/z value to detector at a time
- e.g. the quad scan starts at m/z 10, 11,..., 800 in <1 second to generate a mass spectrum
- Fast enough to get several spectra across a GC peak for one component
- Mass/charge vs. intensity pairs stored on PC for processing with NIST software

[Link to Quadrupole Diagram](#)

Electron Ionization (EI) Mass Spectrum of Acetone

Very Reproducible, *Easily* Found in Spectral Library Search via Computer



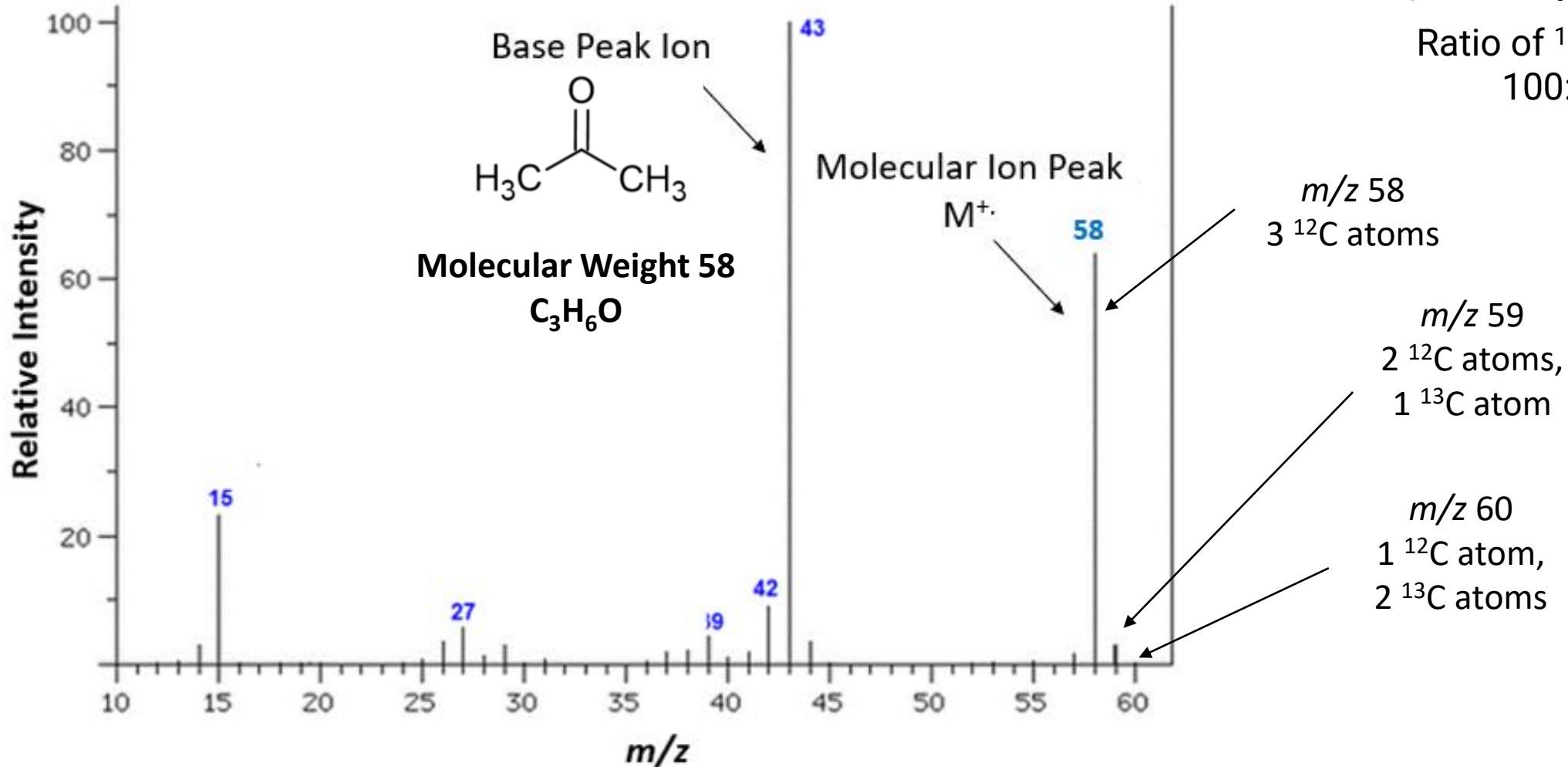
[Link to EI Spectrum](#)

Electron Ionization (EI) Mass Spectrum of Acetone

Isotopic Ions from Presence of ^{13}C

Carbon A+1 Element
(A=abundance)
(Shifted by 1 Dalton)

Ratio of ^{12}C to ^{13}C
100:1.1



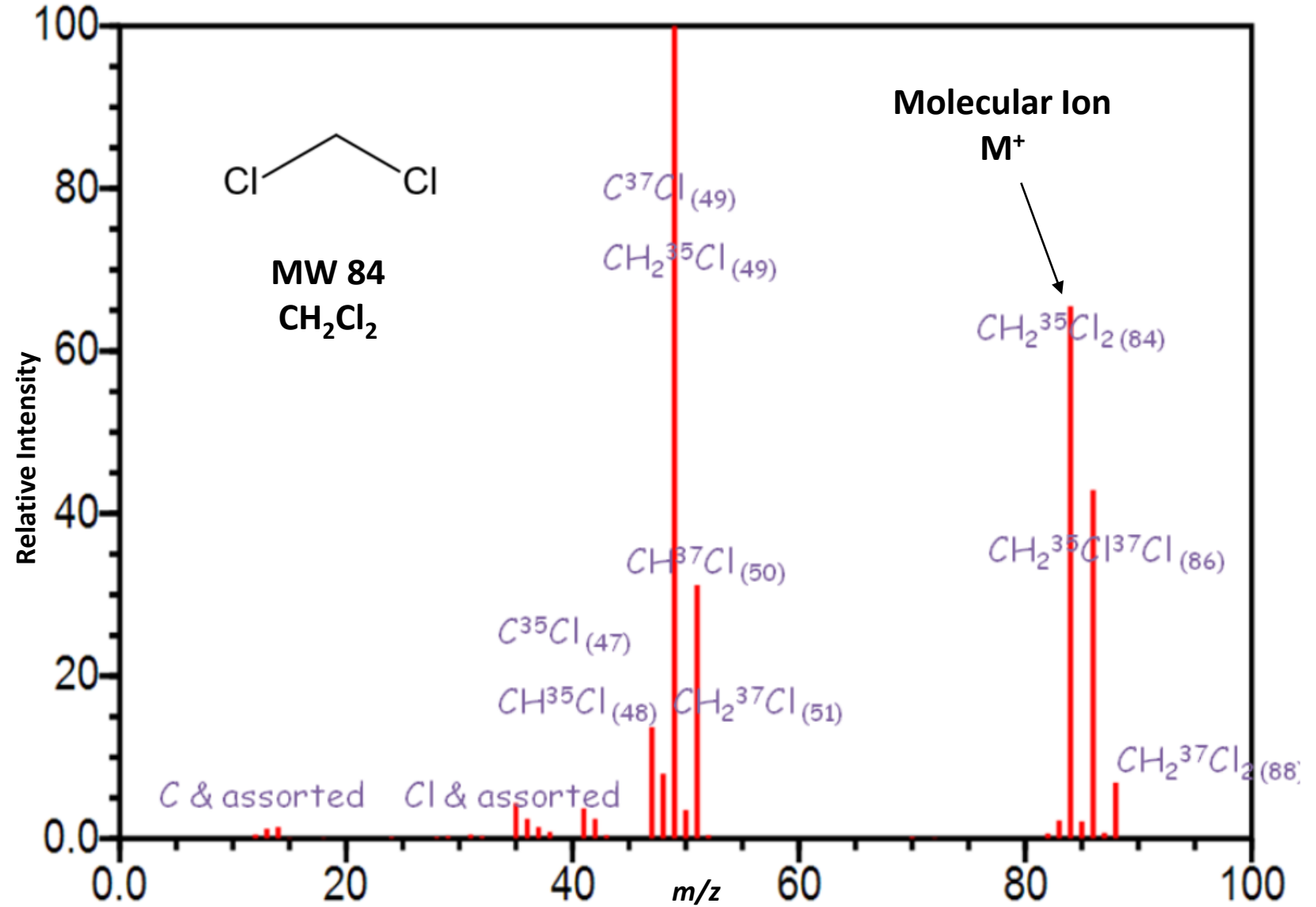
[Link to EI Spectrum](#)

Electron Ionization (EI) Mass Spectrum of Methylene Chloride

More Abundant Isotopes *Easily* Noted and Found in Computer Search

Chlorine A+2 Element
(Shifted 2 Daltons)

Ratio of ^{35}Cl to ^{37}Cl
100:32.0



[Link to EI Spectrum](#)

Natural Abundances of Stable Isotopes

Table 2.1. Natural isotopic abundances of common elements.^a

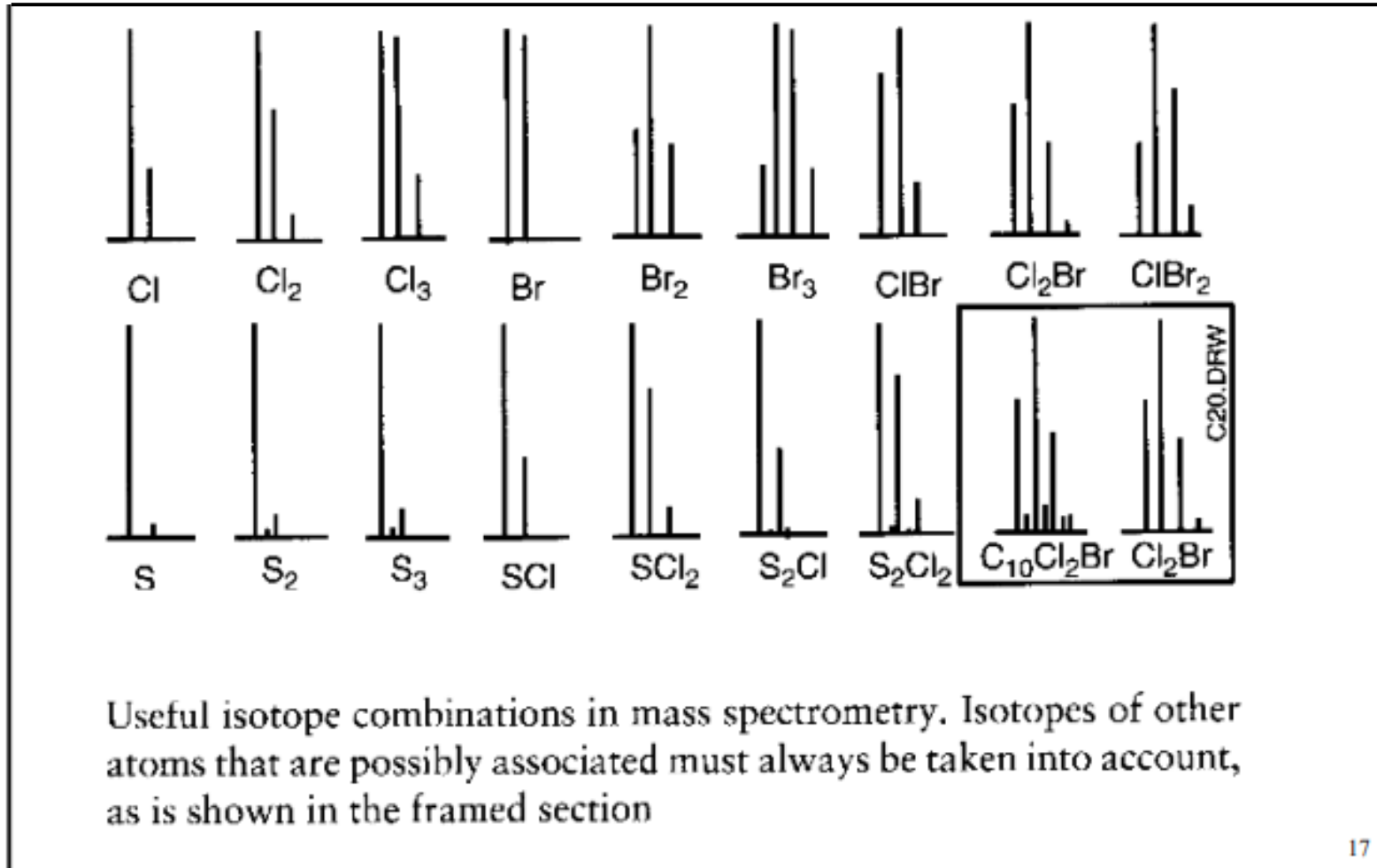
Element	A		A + 1		A + 2		Element type
	Mass	%	Mass	%	Mass	%	
H	1	100	2	0.015			H "A"
C	12	100	13	1.1 ^b			C "A + 1"
N	14	100	15	0.37			N "A + 1"
O	16	100	17	0.04	18	0.20	O "A + 2"
F	19	100					F "A"
Si	28	100	29	5.1	30	3.4	Si "A + 2"
P	31	100					P "A"
S	32	100	33	0.79	34	4.4	S "A + 2"
Cl	35	100			37	32.0	Cl "A + 2"
Br	79	100			81	97.3	Br "A + 2"
I	127	100					I "A"

^aWapstra and Audi (1986).

^b1.1 ± 0.02, depending on source.

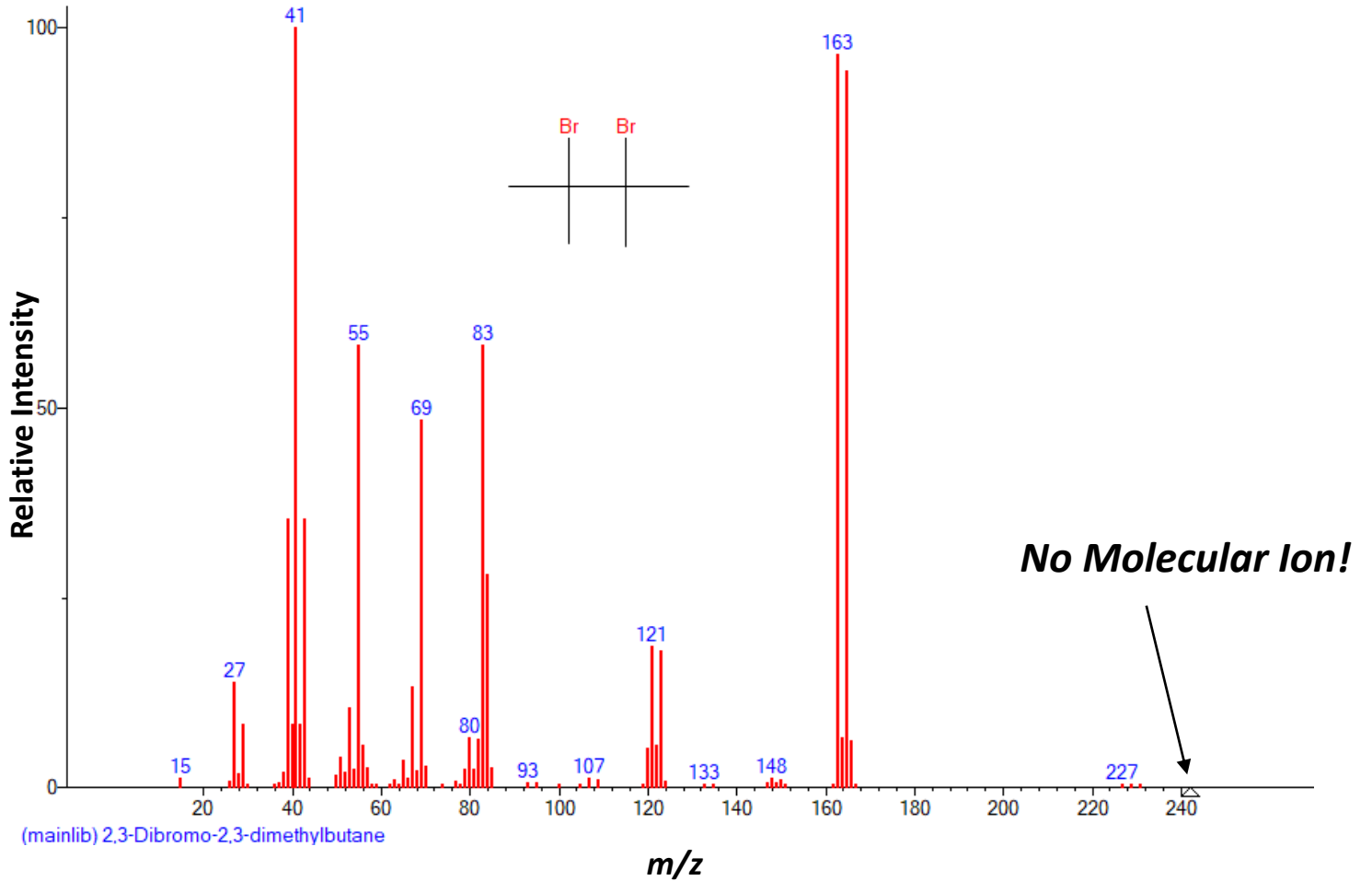
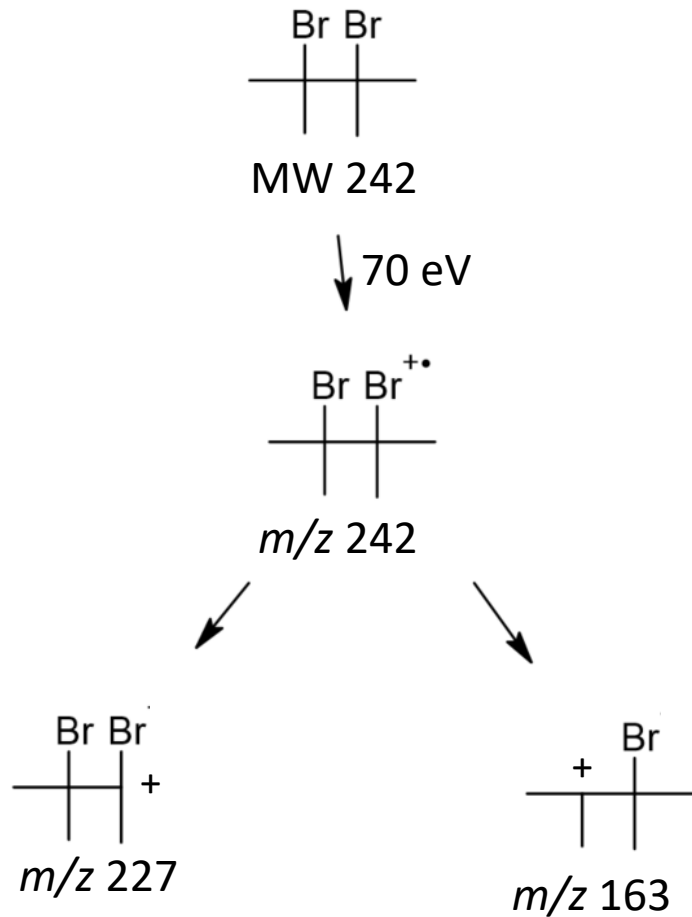
- Note that the isotope of lowest mass is the most abundant for all of **these** elements
 - “A”, “A+1”, and “A+2” elements

Examples of Very Distinct Presence of A+2 Elements in a Molecular Ion Very Obvious and Easily Found in Computer Search

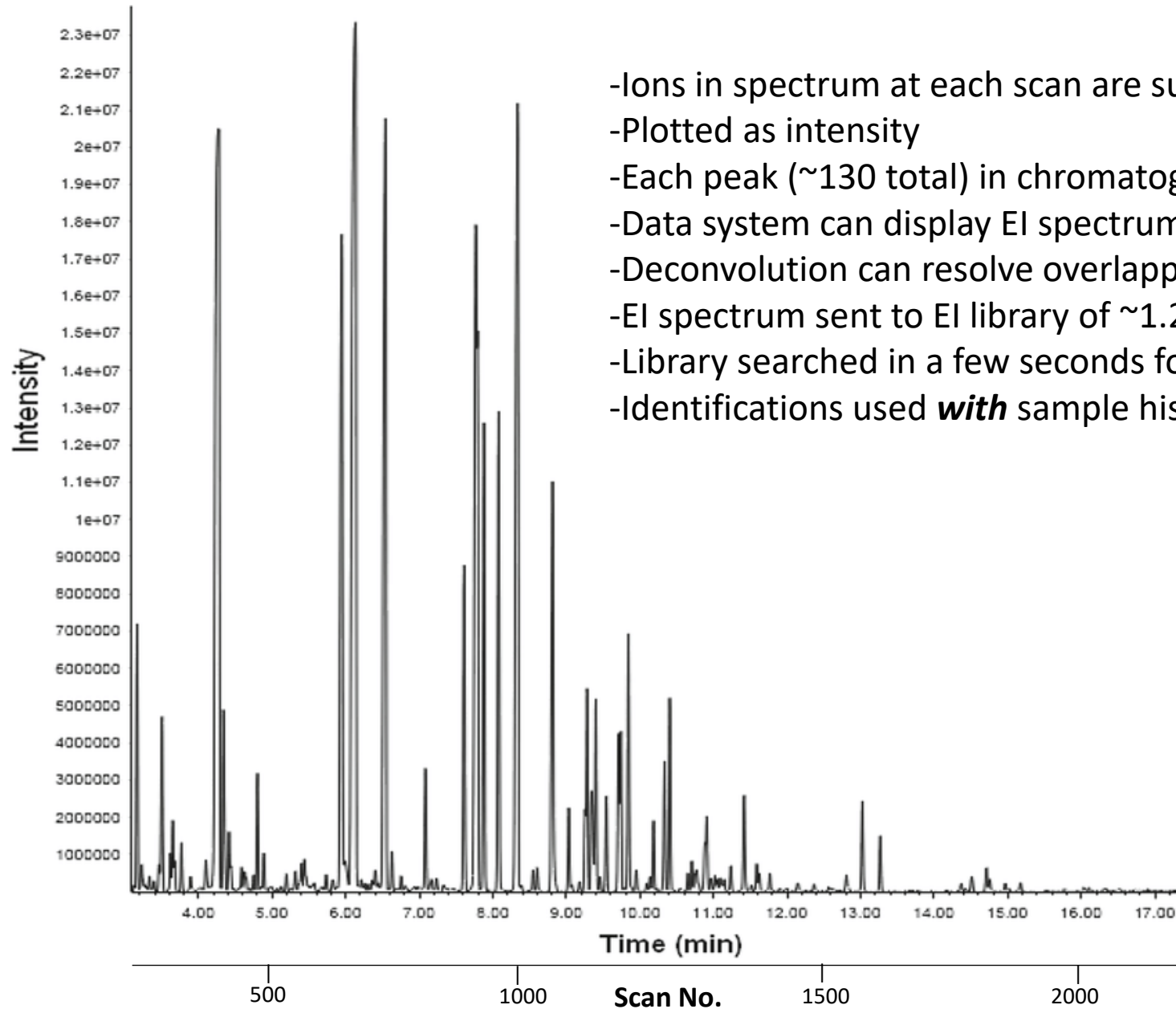


Not All Compounds Have a Molecular Ion!

- Molecular ion not stable
- Immediately fragments
- However**, still easily identified by computer search



Example of Total Ion Chromatogram for a GC-MS Analysis



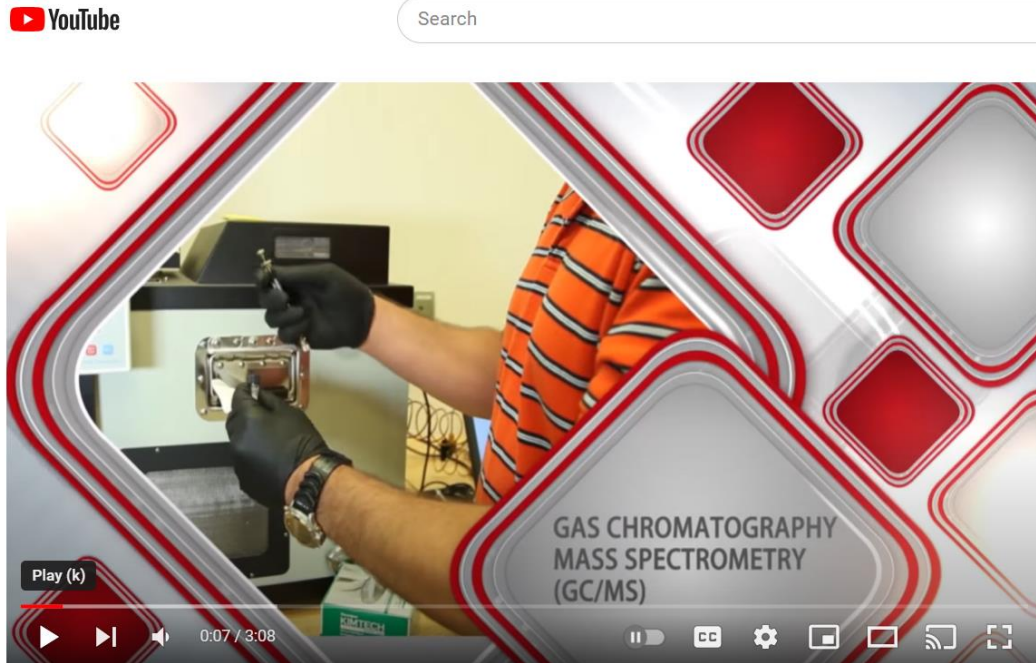
- Ions in spectrum at each scan are summed giving a total ion current
- Plotted as intensity
- Each peak (~130 total) in chromatogram is one or more components
- Data system can display EI spectrum for every scan or point in time
- Deconvolution can resolve overlapping components in a peak
- EI spectrum sent to EI library of ~1.2 million spectra
- Library searched in a few seconds for **proposed** identification
- Identifications used **with** sample history/knowledge organic chemistry **to confirm**

[Link to Literature Chromatogram](#)

Brief Videos of GC-MS

1st Manual Injection (3:08 min)

2nd Automated Injection (3:10 min)



[Link to Manual Injection 1st YouTube Video](#)



[Link to Automated Injection 2nd YouTube Video](#)