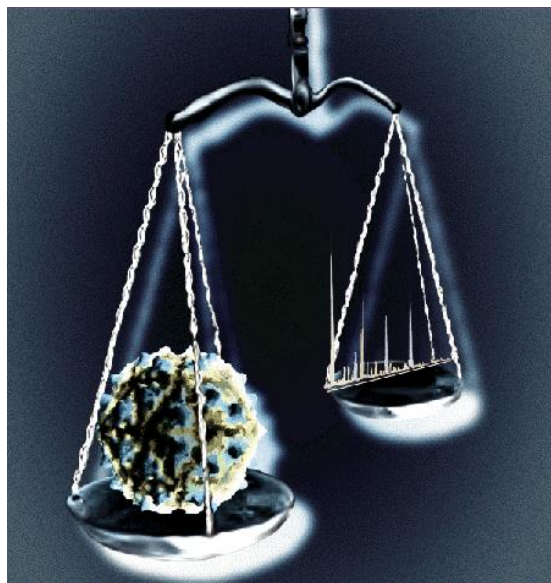# Mass Spectrometry

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Introduction to Mass Spectrometry

➢ At the most fundamental level, matter is characterized by two quantities:

FREQUENCY AND MASS.

➢ Measuring:
(1) the frequencies of emitted, absorbed, and diffracted electromagnetic radiation and

Introduction to
Mass Spectrometry

➢At the most fundamental level, matter is characterized by two quantities:

FREQUENCY AND MASS.

➢Measuring:
(1) the frequencies of emitted, absorbed, and diffracted electromagnetic radiation and

(2) the masses of intact particles & pieces of fragmented particles are the principal means by which we can investigate the structural features of atoms and molecules.

Mass Spectrometry

Mass spectrometry refers to that branch of analytical science devoted to:

1) **developing and using instruments to determine the masses of atoms and molecules**

2) **Deducing the identities or abundances of atoms in physical and biological samples, and**

2: Mass Analysis

•**Sorting and counting**
- •*Pocket change (mixture of coins)*
- •*Penny, dime, nickel, quarter, half $*
- •*Sorting change by value or size*
- •*Concept of visual interpretation*

Quantity (Abundance)

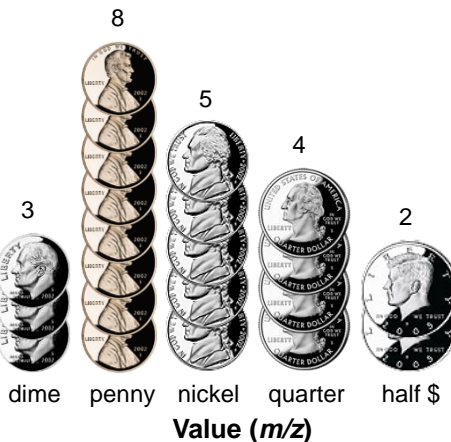dime   penny   nickel   quarter   half $

Value (*m/z*)

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- •*Mixture of molecules*
- •*Molecules of different weight, size*
- •*Separation by mass spectrum*

Quantity (Abundance)

3   8   5   4   2

dime   penny   nickel   quarter   half $

Value (*m/z*)

"What is Mass Spectrometry?" D.H. Chace, O.D. Sparkman, American Society for Mass Spectrometry, 2005: D.C. Muddiman; D. Ayerhart

3

Mass Spectrometry

Mass spectrometry refers to that branch of analytical science devoted to:

1) **developing and using instruments to determine the masses of atoms and molecules**

2) **Deducing the identities or abundances of atoms in physical and biological samples, and**

3) **elucidating the structural properties or deducing the identities, or determining the concentrations of molecules in physical/biological samples.**

Mass Spectrometry

Is powerful and versatile because it can be used to qualitatively and/or quantitatively analyze

1) **All elements and essentially all compounds**

2) **Samples in all states of matter**

3) **Particles whose masses range from < 1 u to > 1,000,000 u, and**

4) **Sample amounts down to < 1 attomole (10^{-18} of a mole)**

Mass Spectrometry Uses and Benefits:

1) Elemental composition of samples of matter

2) Structures of inorganic, organic, and biological molecules

3) Qualitative and quantitative composition of complex mixtures

4) Structure and composition of solid surfaces

5) Isotopic ratios of atoms in samples

- ➤ Analysis is fast (normally a few seconds or less);
- ➤ Mass resolution can be very good (100,000 or better);
- ➤ detection limits are often much better than for optical methods;
- ➤ spectra are relatively simple;
- ➤ unambiguous identification can often be obtained.

The Mass Spectrometer

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2. **separates the ions according to their respective ratios of *mass-to-charge* (*m/z*), and**

3. **produces a record of the ions' abundances versus their respective values of *m/z*.**

Anatomy of a Mass Spectrometer II
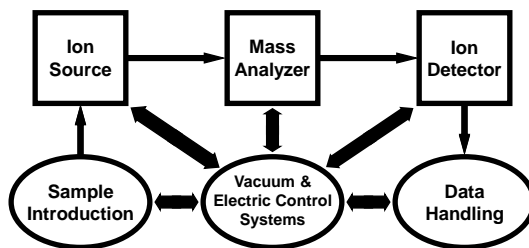
> The ion source forms an ion beam from a sample.
> The mass analyzer disperses the ion beam into component beams of different mass-to-charge ratios.
> The ion detector converts the ion beam currents into a current or voltage signal.

What does *m/z* practically mean?

The mass-to-charge ratio, m/z, (read "m over z") is **dimensionless** by definition.

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So, practically this means it is always denoted *before* the number:

m/z **180**

What does *m/z* practically mean?

Consequently, the *m/z*, of $C_{20}N_8O_6H_{24}^{2+}$ would (approximately) be:

m/*z* **236** (m=(472))/z=2)

Try $C_{20}N_8O_6H_{25}^{3+}$ for yourselves…

$^{12}C = 12.00000$ g/mol; $^{14}N = 14.0030$ g/mol; $^{16}O = 15.9949$ g/mol; $^1H = 1.0078$ g/mol

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What do you notice about this number?

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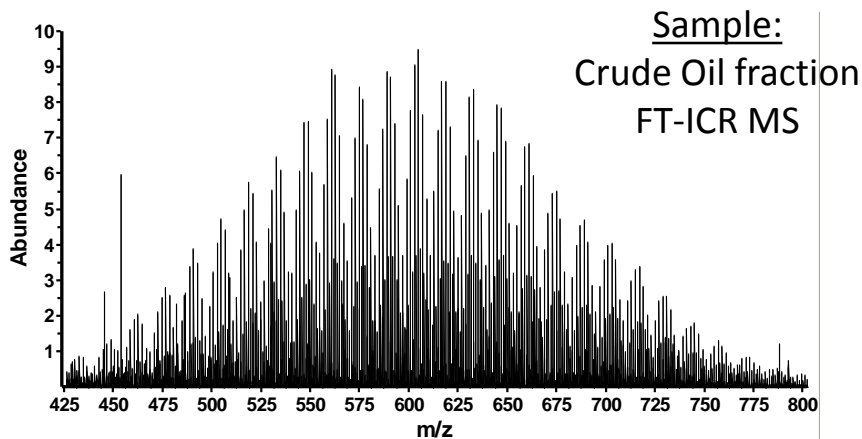
The Mass Spectrum

➢**Mass spectrometers measure the relative mass-to-charges (m/z) and relative abundances, producing a mass spectrum.**

➢ 1 mass spectrum, many mass spectra!

➢**From the mass-to-charges (m/z) we can calculate the molecular mass(es) present**

The Mass Spectrum

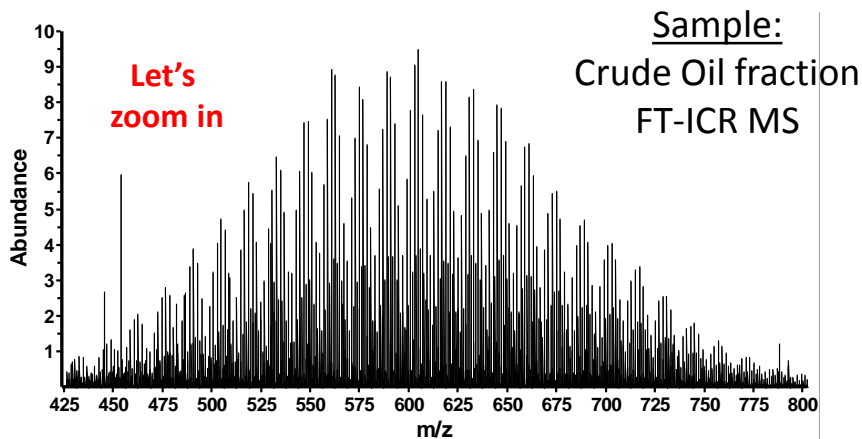➢**Mass spectrometers measure the relative mass-to-charges (m/z) and relative abundances of**

1.Intact molecular ions

<u>Sample:</u>
Crude Oil fraction
FT-ICR MS

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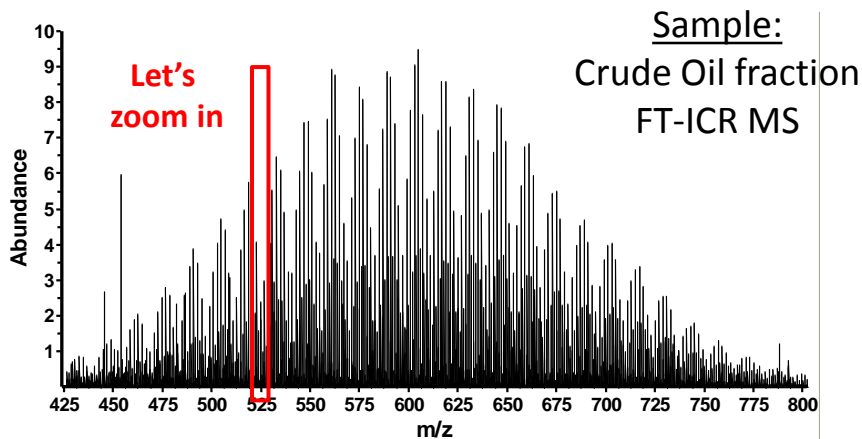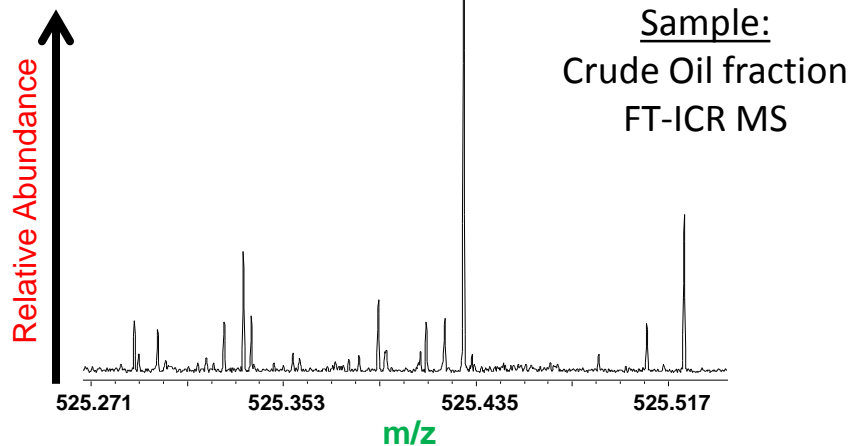FT-ICR MS

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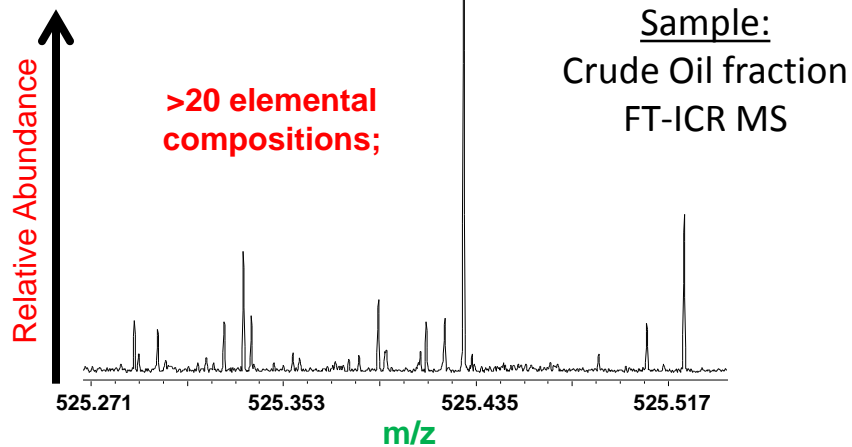FT-ICR MS

The Mass Spectrum

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>20 elemental compositions;

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An atom or molecule in which the total number of electrons is **<u>not equal</u>** to the total number of protons, thereby giving the atom or molecule a net positive or negative electrical charge.

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If we have **more electrons** than protons, the ion will be **negatively** charged.

What types of ion are possible?

Or, how can we make ions?

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   E.g., metal cations (Na, Li, Ag, etc.) or anions (NO_3^-, Cl^-, etc.)

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FOR THIS CLASS: we will concentrate (mostly) on ionization involving removal of an electron from the analyte molecule.

Mass-to-Charge (m/z) Ratio

Atomic & Molecular Weights - atomic mass units (amu) or daltons (Da)

1 amu = 1 Da = 1/12 mass of carbon-12 atom = 1.66054×10^{-24} g

Examples: **Chlorine atom:** $^{35}_{17}Cl$ **= 34.9688 Da**

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$^{13}C^1H_4$ **= 17.0347 Da ; (13.00335 + 4x1.007825)**
$^{12}C^1H_3{}^2H_1$ **= 17.0376 Da ; (12 + 3x1.007825 + 2.0141)**

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NOTE:

Periodic tables report ***average*** atomic weights for ***all stable isotopes***, not any specific individual isotope. A good mass spectrometer can often separate isotopic compositions.

Nomenclature

mass number

atomic number C

Isotope specific!

$^{12}_{6}C = 12.000000$ **Da**

mass number => **What we measure in mass spectrometry**

Atomic number = Number of protons

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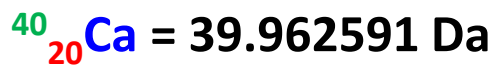$^{40}_{20}Ca = 39.962591$ Da

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Nomenclature

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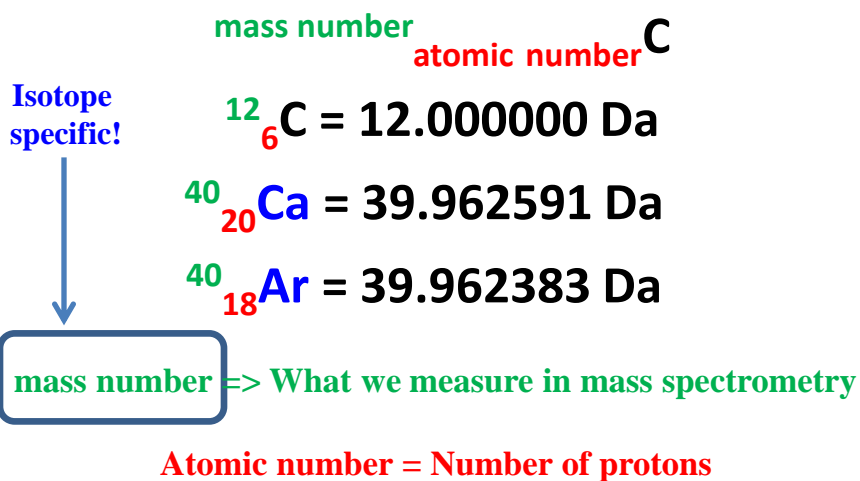**Isotope specific!**

$^{12}_{6}C$ = **12.000000 Da**

$^{40}_{20}Ca$ = **39.962591 Da**

$^{40}_{18}Ar$ = **39.962383 Da**

mass number => **What we measure in mass spectrometry**

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Monoisotopic Elements

1. Have only 1 naturally occurring isotope.
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3. Examples include:
   ^{19}F, ^{23}Na, ^{31}P, ^{127}I, ^{9}Be, ^{27}Al, amongst others.

Multi-isotopic Elements

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4. Similarly, there **is often variation in isotopic abundances** particularly for **transition elements** (metals) & relevantly for biology *oxygen* **^{18}O** is more abundant than **^{17}O**, but much less abundant than **^{16}O**.

Multi-isotopic Elements E.g.,
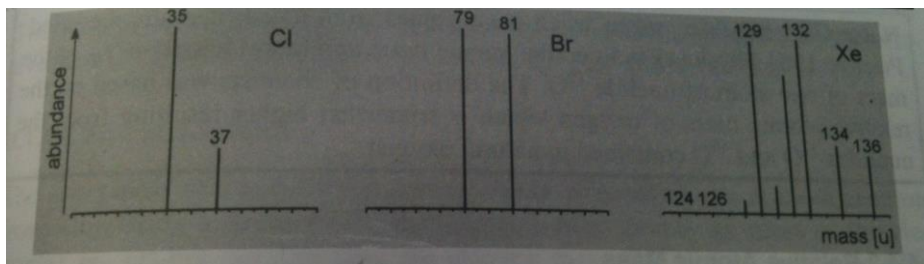
^{37}Cl ^{37}Cl ^{79}Br ^{81}Br $^{Various}Xe$ (9 isotopes)

See Table 3.1 and the Appendix of the book: note these are
normalized to the most abundant isotope = 100.

Isotopic Abundance

Element	Major Isotope	Minor Isotope(s)	Abundance*
Hydrogen	^1H	^2H	0.015
Carbon	^{12}C	^{13}C	1.08
Nitrogen	^{14}N	^{15}N	0.37
Oxygen	^{16}O	$^{17}O, ^{18}O$	0.04, 0.20
Sulfur	^{32}S	$^{33}S, ^{34}S$	0.80, 4.40
Chlorine	^{35}Cl	^{37}Cl	32.5
Bromine	^{79}Br	^{81}Br	98.0

*Abundance is relative to 100 parts of the most abundant isotope

Nominal Mass

The integer mass of the most abundant naturally occurring stable isotope of an element.

So for:

C, the nominal mass is 12 u; for oxygen, the nominal mass is 16 u; for H the nominal mass is 1 u.

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Thus for $C_3H_6O^{+\bullet}$ the nominal mass is $12(3)+1(6)+16(1) = 58$ u.

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For small ions, this is often the equal to the mass number, for large ions it is not necessarily the case.

This is useful for initial estimation when looking for you analyte ions.

Monoisotopic Mass

The exact mass of the most abundant naturally occurring stable isotope of an element.

So for a molecule, C_3H_6O, the exact mass is:

12.00000(3)+ 1.007825(6)+ 15.994915(1) = 58.041865 u.

Exact Ionic Mass:

The exact ionic mass = Monoisotopic mass– mass of 1 mole electrons

The exact ionic mass = Monoisotopic Mass – 0.000548 u

The exact ionic mass = 58.041865 u – 0.000548 u = 58.041347 u

Isotopic Distribution Calculation

A mass spectrum is ordinarily composed of a superimpositions of all of the mass spectra of all of the isotopic species involved.

Consequently, when we have multiple isotopic types and abundances together we get a unique pattern that if resolvable, we can use to help identify our analyte ions immediately.

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A simple example of this is with the important element carbon (see HW too).

If we have 1000 CH_4 molecules, the

$^{12}C/^{13}C$ ratio will be roughly 989/11 using nominal masses. Thus we can approximate using this ratio = 100/1.1

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What does this buy us?

Peak Relative Abundance/Intensity:

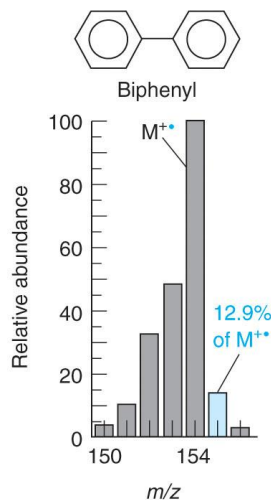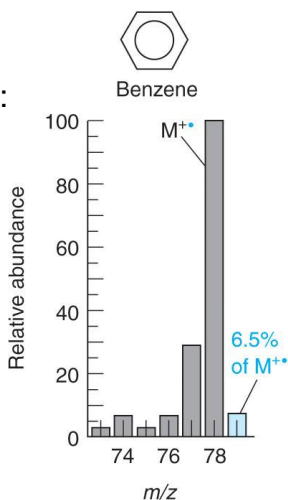➤ Related directly to how much of the ion reaches the detector.

➤ **M+1: ^{13}C**

m/z 78 vs 79:

100/6.5%

6x1.1 =6.6%

What about for Biphenyl?

Benzene — $M^{+\bullet}$, 6.5% of $M^{+\bullet}$

Biphenyl — $M^{+\bullet}$, 12.9% of $M^{+\bullet}$

Peak Abundance/Intensity: Carbon and Hydrogen

➢ For **Benzene radical cation, $[C_6H_6]^{\bullet+}$**

➢ n = 6 C

➢ **M+1 intensity =**   6 x **1.1%**
➢ **M+1 intensity =**   6.6%   Expt: 6.5% (previous slide)

➢ **For you to try Biphenyl radical cation, $[C_{12}H_{10}]^{\bullet+}$**

➢ **Answer: 13.1% $[C_{12}H_{10}]^{\bullet+}$**   Expt: 12.9%

Peak Abundance/Intensity: Carbon

➢ Number of Carbon atoms can be determined ***roughly*** using:

Number of C atoms = peak intensity of $[X+1]^{\bullet+}$
                    contribution per C atom

For Benzene:
Number of C atoms = 6.5%/1.1% = 5.909… = 6

For Biphenyl:
Number of C atoms = 12.9%/1.1% = 11.72…= 12

In general, to be really accurate you need to add in the
contributions from all elements ^2D, ^{17}O, ^{15}N, etc.

Isotopic Distribution Calculation

We can calculate this for a general pair of isotopes using:

The Binomial Series

$(a + b)n = a^n + na^{n-1}b + n(n-1)a^{n-2}b^2/(2!) + n(n-1)(n-2)a^{n-3}b^3/(3!) + \ldots$

and you should be able to work out that $(a + b)^3 = a^3 + 3a^2b + 3b^2a + b^3$.

It should also be obvious to you that $(a + b)^1 = a + b$.

so $(a + b)^1 = \quad a + b$

$(a + b)^2 = \quad a^2 + 2ab + b^2$

$(a + b)^3 = \; a^3 + 3a^2b + 3b^2a + b^3$

a = abundance of isotope 1
b = abundance of isotope 2
For carbon: a = 100 & b = 1.1

So for n = 1,2,3,4 this is simple to solve by multiplication. Beyond this however things rapidly get tedious and mistakes more likely.

Isotopic Distribution Calculation

For larger things we can either be very careful or use something provided by someone else:

http://www.sisweb.com/mstools/isotope.htm

This provides peak abundances and m/z values for neutral compositions (i.e., you will have to adjust for the loss/gain of electrons).

Can be run at high or low resolution. Try this out for something with multiple CHNOPS values and look at how things differ.

Also try this with Pd or several Pd atoms (6 isotopes) look at how the pattern changes.

Peak Abundance/Intensity: Halogens

➤ Abundances are much higher for Cl and Br isotopes.

➤ Things get complicated when there's more than one.

➤ Notice that M+2, M+4 or even M+6 matter here.

➤ Fragments of the precursor also may be mixtures

➤ This can be highly diagnostic and thus helpful.
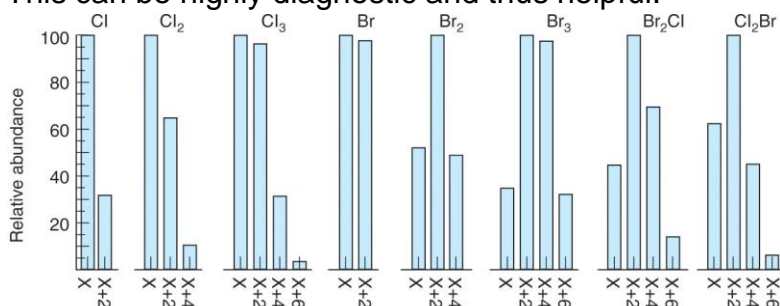
For you to do at home:

➤ Why does this obviously contain Bromine?

➤ Can you explain the fragment M-29?

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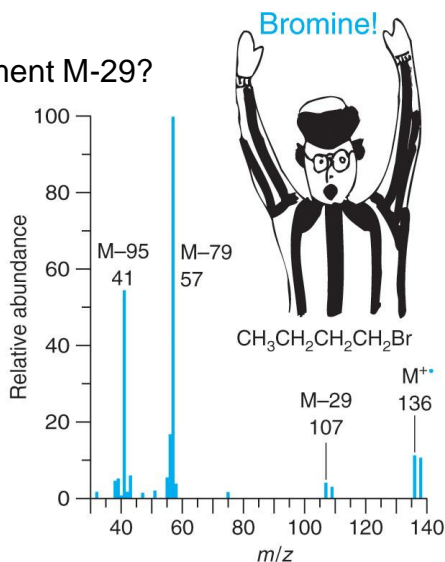
Some very basic questions

1. What is the approximate mass (nearest integer) of toluene?

2. If we remove an electron from toluene what is the approximate m/z?

3. If we remove a second electron from toluene what is the approximate m/z?

4. If instead we add an electron to toluene what is the approximate m/z?

Some very basic questions

1. What is the approximate mass (nearest integer) of toluene?
   A. MW(C7H8) = 12*7 + 6*8 = 92 g/mol

2. If we remove an electron from toluene what is the approximate m/z?
   A. m/z = 92/1 = 92

3. If we remove a second electron from toluene what is the approximate m/z?
   A. m/z = 92/2 = 46

4. If instead we add an electron to toluene what is the approximate m/z?
   A. m/z = 92/1 = 92