MS Interpretation I

Identification of the Molecular Ion

Molecular Ion: EI

- Requirements for the Molecular Ion
  - Must be the highest m/z peak in the spectrum
    - Highest Isotope Cluster
- Must be an odd-electron ion
- High mass fragments must be explained
  - must come from logical neutral losses

- These are necessary but insufficient conditions for molecular ion identification

Odd-Electron Ions

- Molecular Ion in EI must be odd-electron
  - Referred to as “OE” (with symbol “+•”)
  - Even electron ions “EE” (with symbol “+”)
- Most fragment peaks are EE ions
- OE ions have integer RDB numbers
- Must follow the nitrogen rule
  - A compound with an even number of nitrogens will have an even mass number

EI: Logical Neutral Losses

- Neutral certain masses are highly unlikely
  - Mass 4 to 14
  - Mass 21 to 25

- If high-resolution data is available, then the test is more clear
  - M-15 is common (M-CH_3) but if HRMS can determine that M-15 is M-NH, then M is probably not the molecular ion

Molecular Ion

- Sometimes EI will not give a molecular ion peak
  - Molecular ion peak may be very small
- Small background peaks may be incorrectly identified
  - Software background subtraction can eliminate some spurious peaks
- Confirmation by a “soft” ionization technique
  - CI, ESI, APCI, MALDI

Molecular Ion: ESI

- Not necessarily the highest mass peak in the spectrum
- Pseudomolecular ions are formed
  - Multiple ions (M+H, M+Na etc.) could come from the same molecule
  - Cluster ions (2M+H, 2M+Na etc.) can be observed at higher concentration
  - Usually dilution of the sample will indicate whether an ESI dimer is covalent.
- Cluster ions can identify ionizing group

Molecular Ions: ESI

- Other species can form depending on the functional groups present in the molecule
  - Acidic/exchangeable protons can exchange with sodium/other metal ions to form:
    - M-H+2Na, M-2H+3Na, etc. depending on the amount of sodium present and the number of sites.
- Multiply charged peaks can give even more complex patterns
- Addition of a homogeneous ionizing agent can simplify spectra and confirm molecular ion

Molecular Ions: ESI

- Sometimes chemistry can occur between the analyte and the solvent.
  - May be an equilibrium process
- Aldehydes and α,β-unsaturated carbonyls can add solvents like water or methanol
  - These peaks can be confirmed by re-running the sample in a different solvent

Molecular Ions: ESI

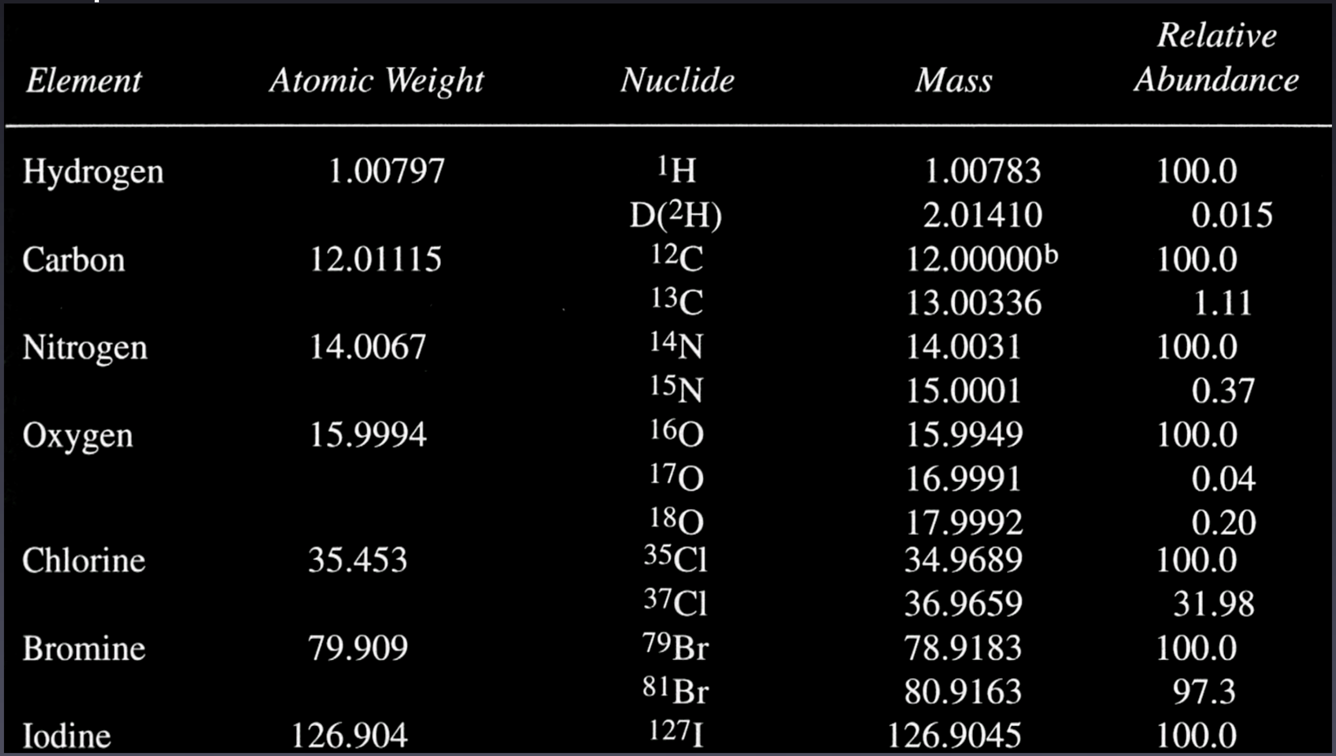
- Ambiguous cases can sometimes be resolved by running both positive and negative ion spectra
  - Ions may be separated by 2 or 24 amu
- Addition of deuterated solvent can expose the number of exchangeable protons
  - In some cases, kinetics of H/D exchange can be measured this way

Molecular Ion

- Once molecular ion is established, the peak (and it’s surrounding isotopic peaks) should be examined
  - Compound Molecular Weight
    - Begins to limit possible molecular formula (MF)
  - Isotopic distribution
    - Certain elements are quite characteristic
  - High resolution measurement
    - Further limit MF
  - Software evaluates exact mass and isotopic pattern together to limit MF

Isotopic Abundance and Peaks

- For nearly all elements, there are multiple isotopes with some natural abundance.
- Every atom in a molecule has a chance of being one of these isotopes. So, there will be some fraction of molecules that will be heavier than expected parent mass.



Element	*Atomic Weight*	*Nuclide*	*Mass*	*Relative Abundance*
Hydrogen	1.00797	^{1}H	1.00783	100.0
		D(^{2}H)	2.01410	0.015
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Iodine	126.904	^{127}I	126.9045	100.0

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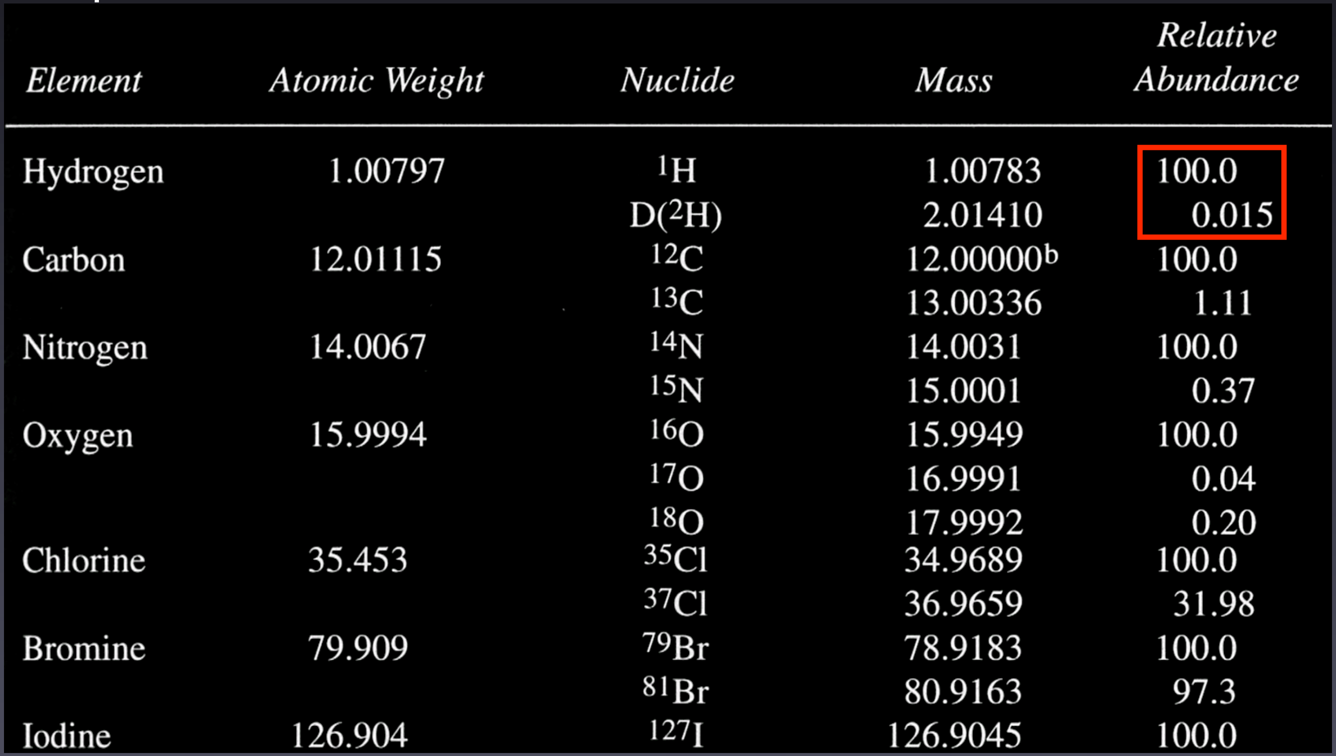

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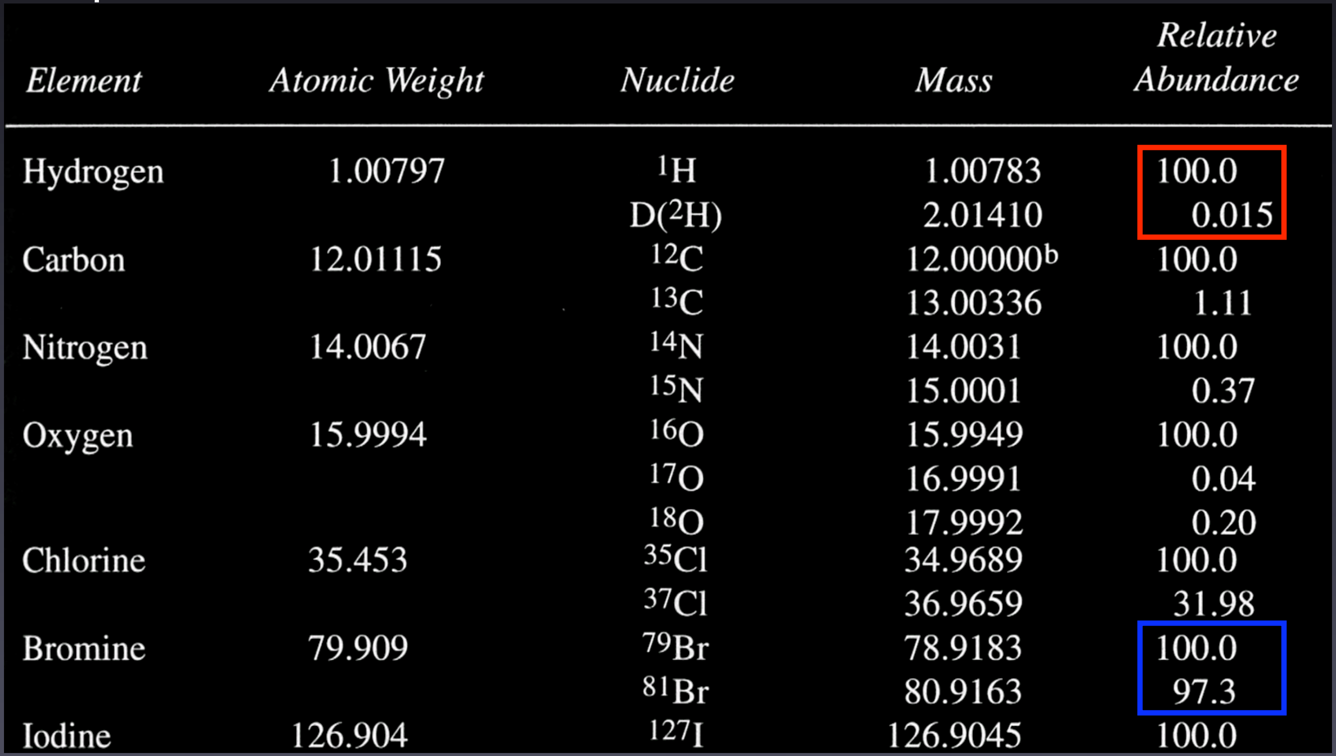

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For others, isotope abundance is high.

These differences are exhibited in peak intensities in mass spec.

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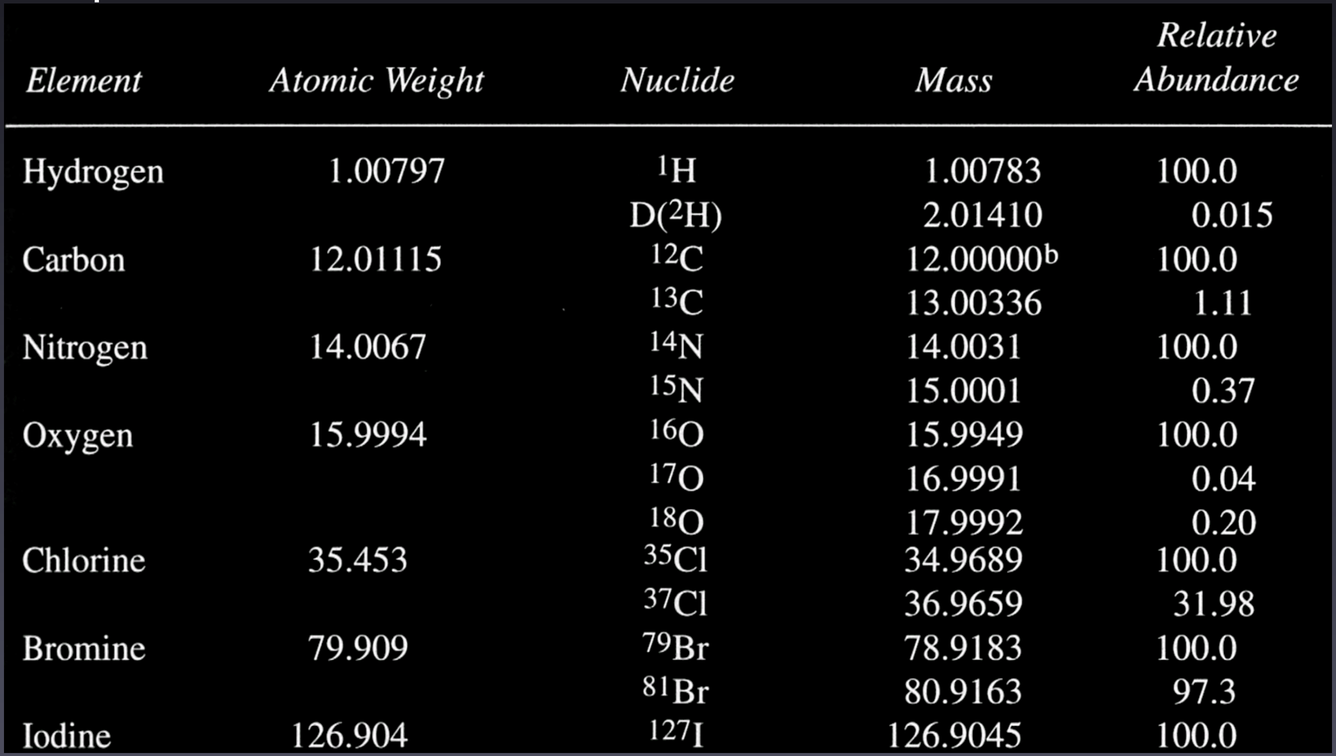

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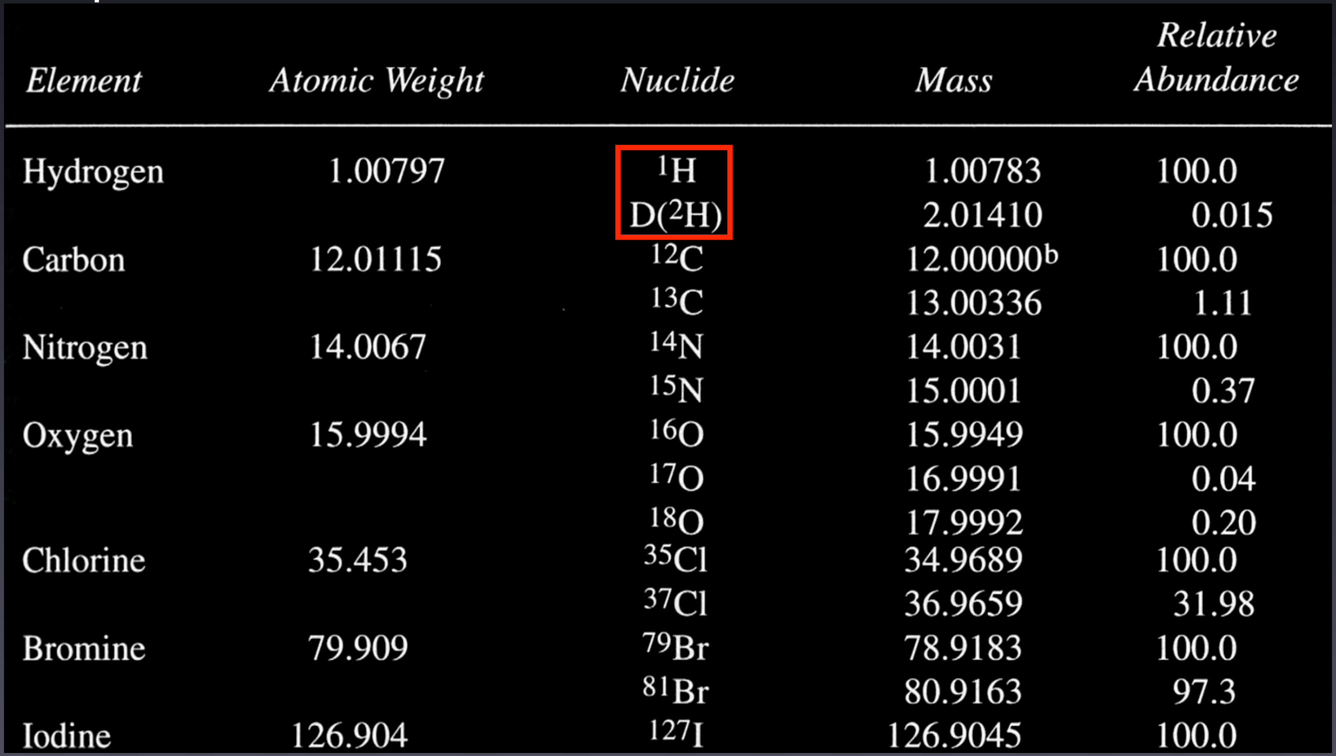

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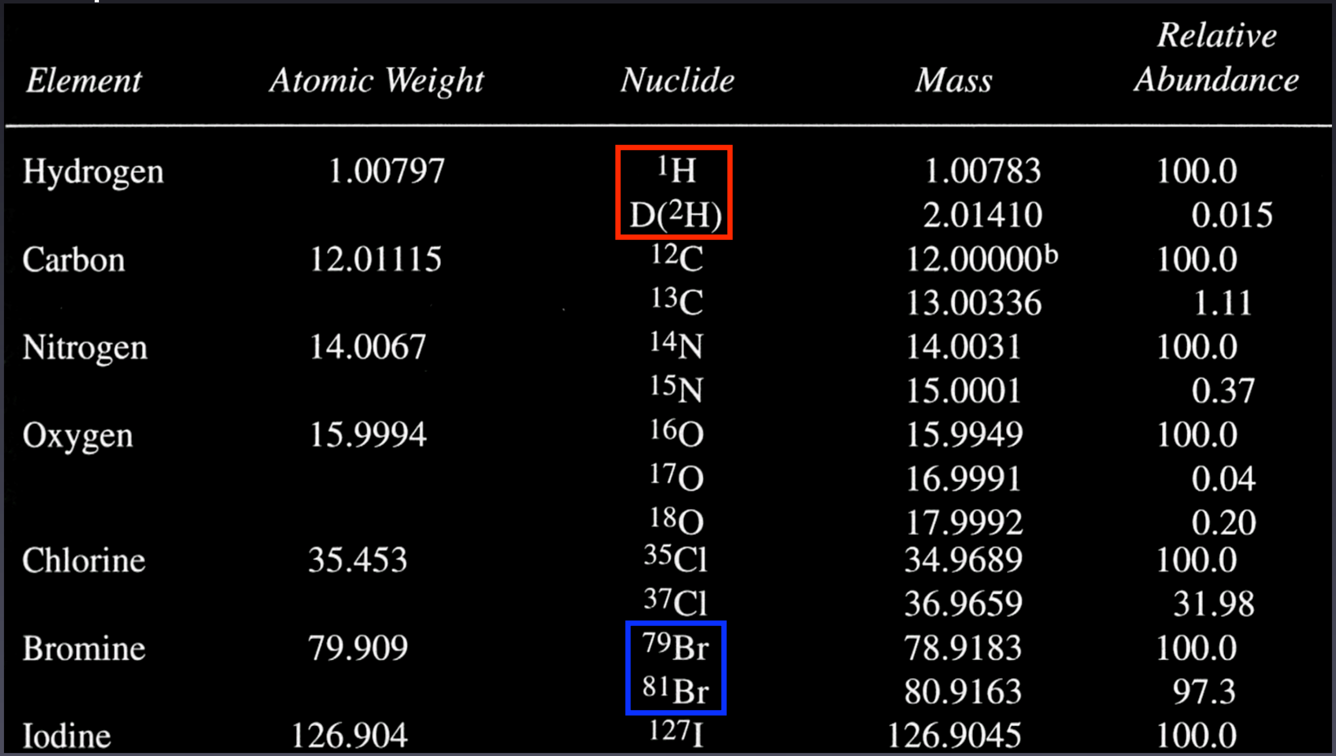

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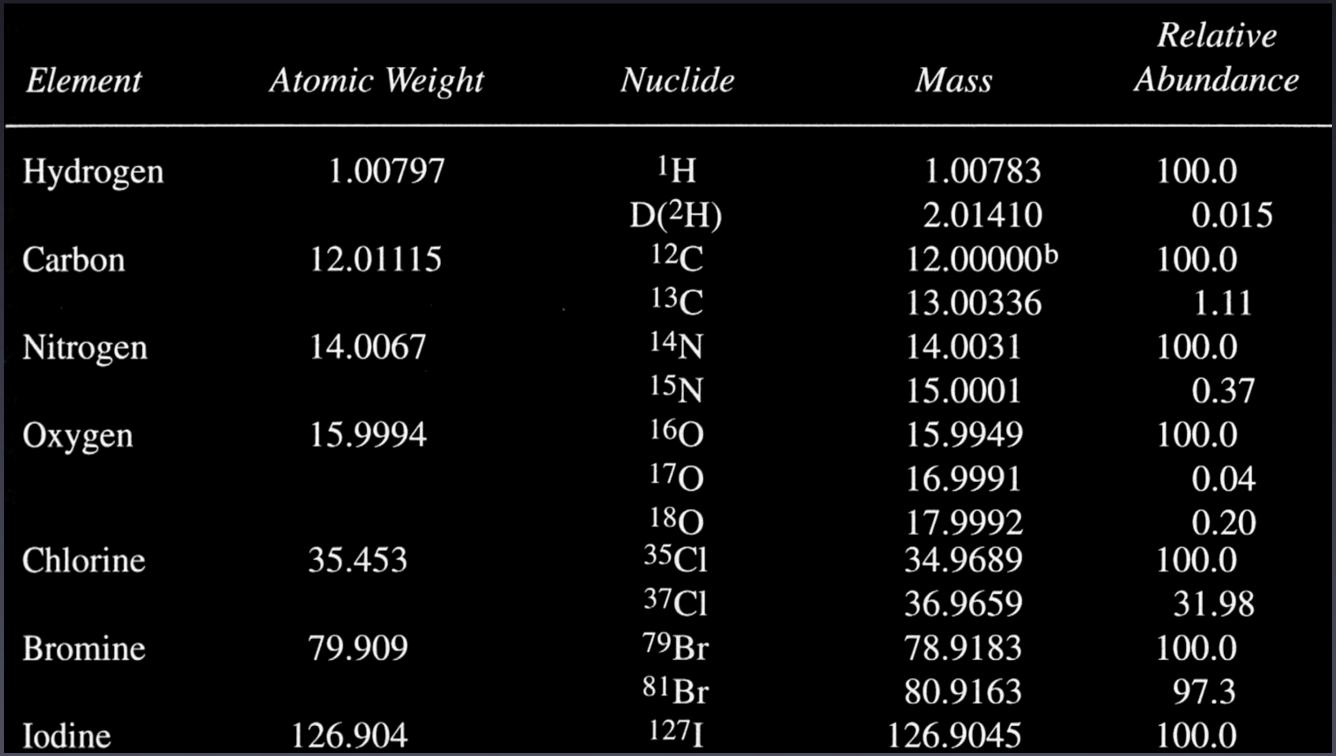
For some, isotope mass difference is 1.

For others, mass difference is >1.

These differences are exhibited as multiple peaks in mass spec.

Isotopic Abundance and Peaks

Atoms are nicknamed “A + *n*” in mass spec, based on most prevalent higher isotope mass.



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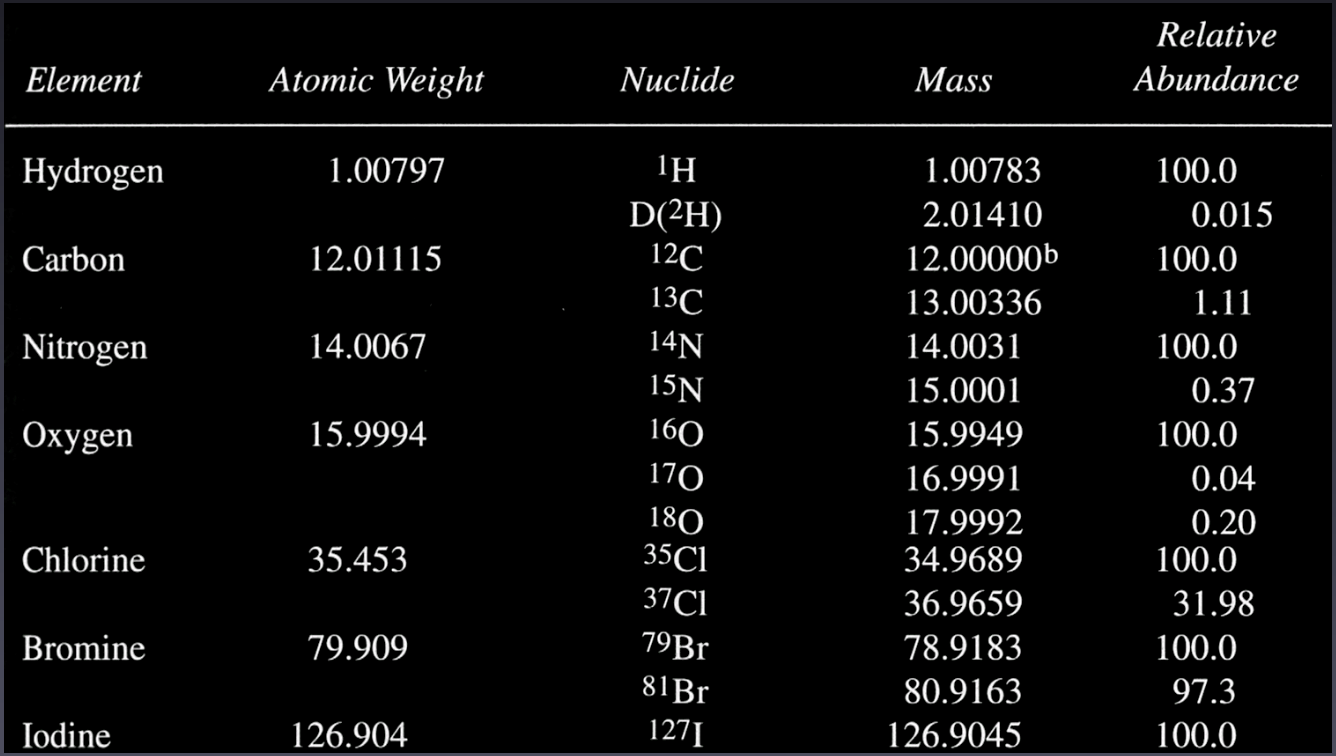

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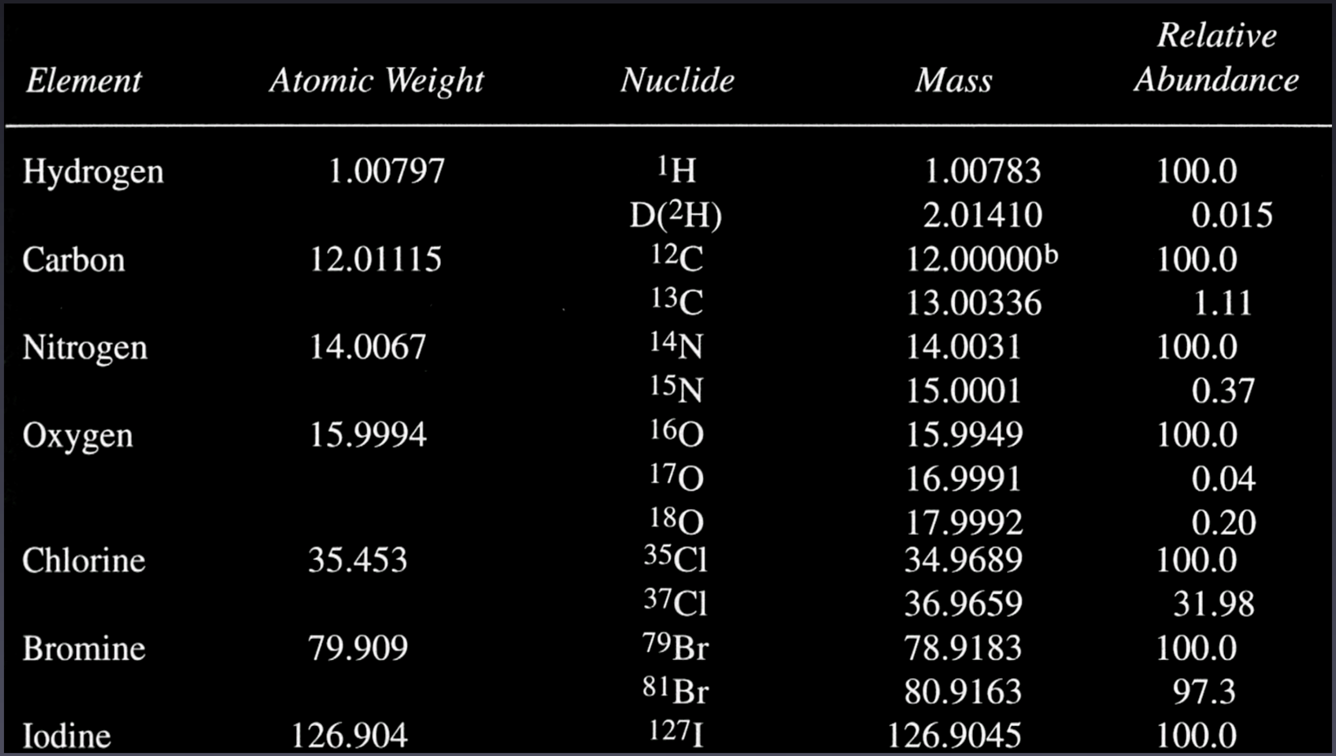

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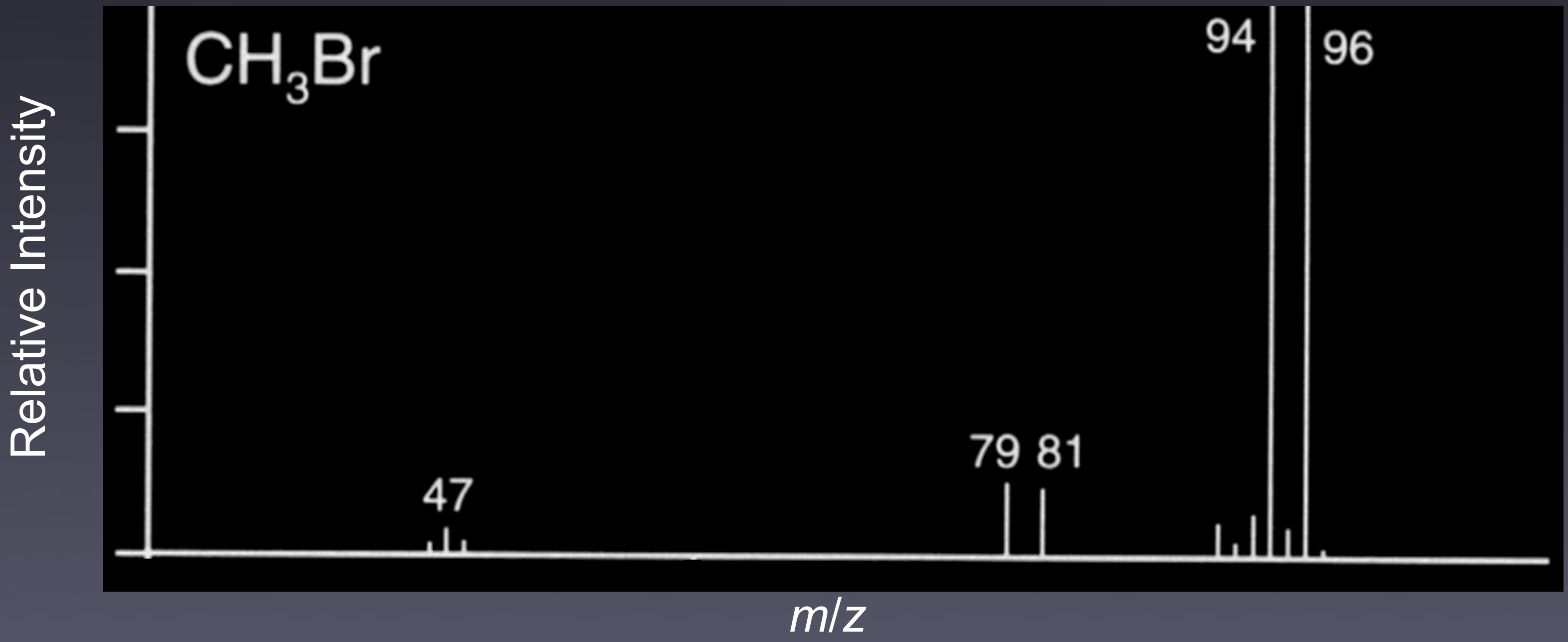
Br: “A + 2”. Contributes to peak at M + 2 in MS.

Isotopic Abundance and Peaks

A + *n* isotopes generate characteristic patterns in mass spectra.



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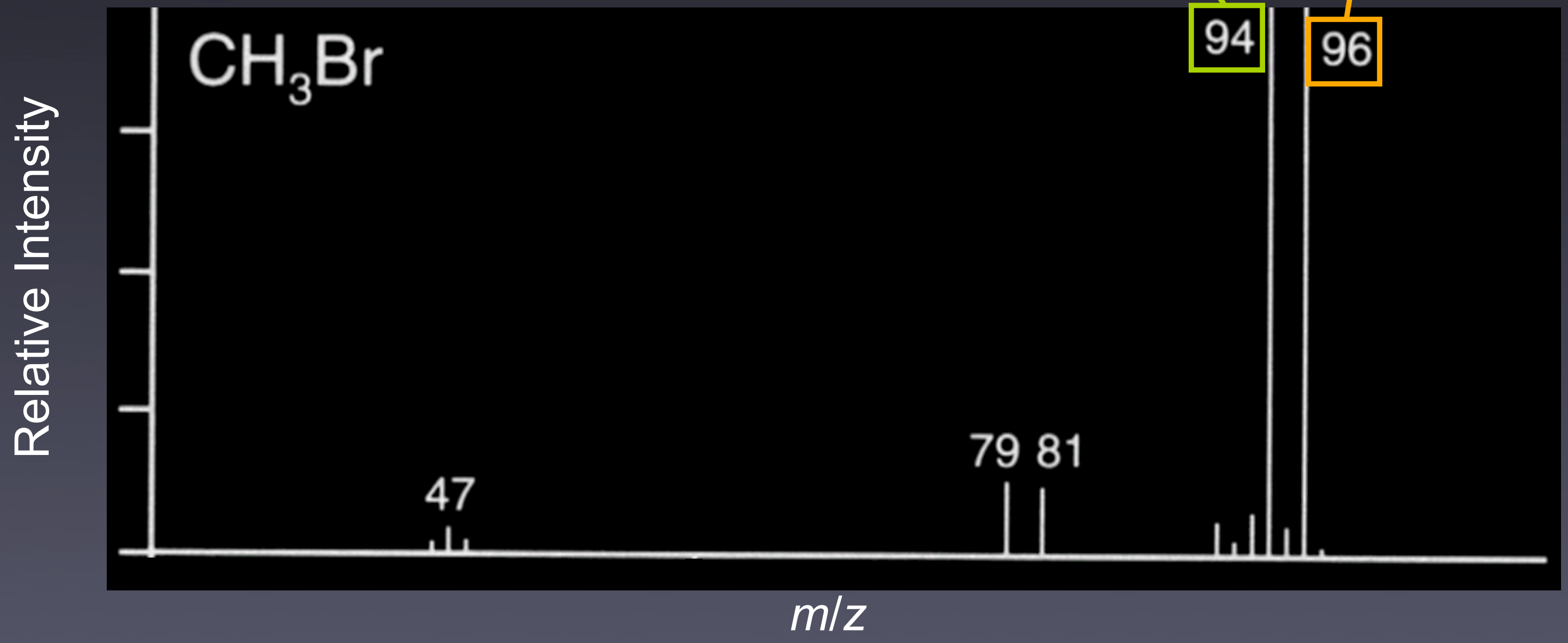
$CH_3(^{79}Br)$

isotopic abundance (^{79}Br): 50.5%

$CH_3(^{81}Br)$

isotopic abundance (^{81}Br): 49.5%



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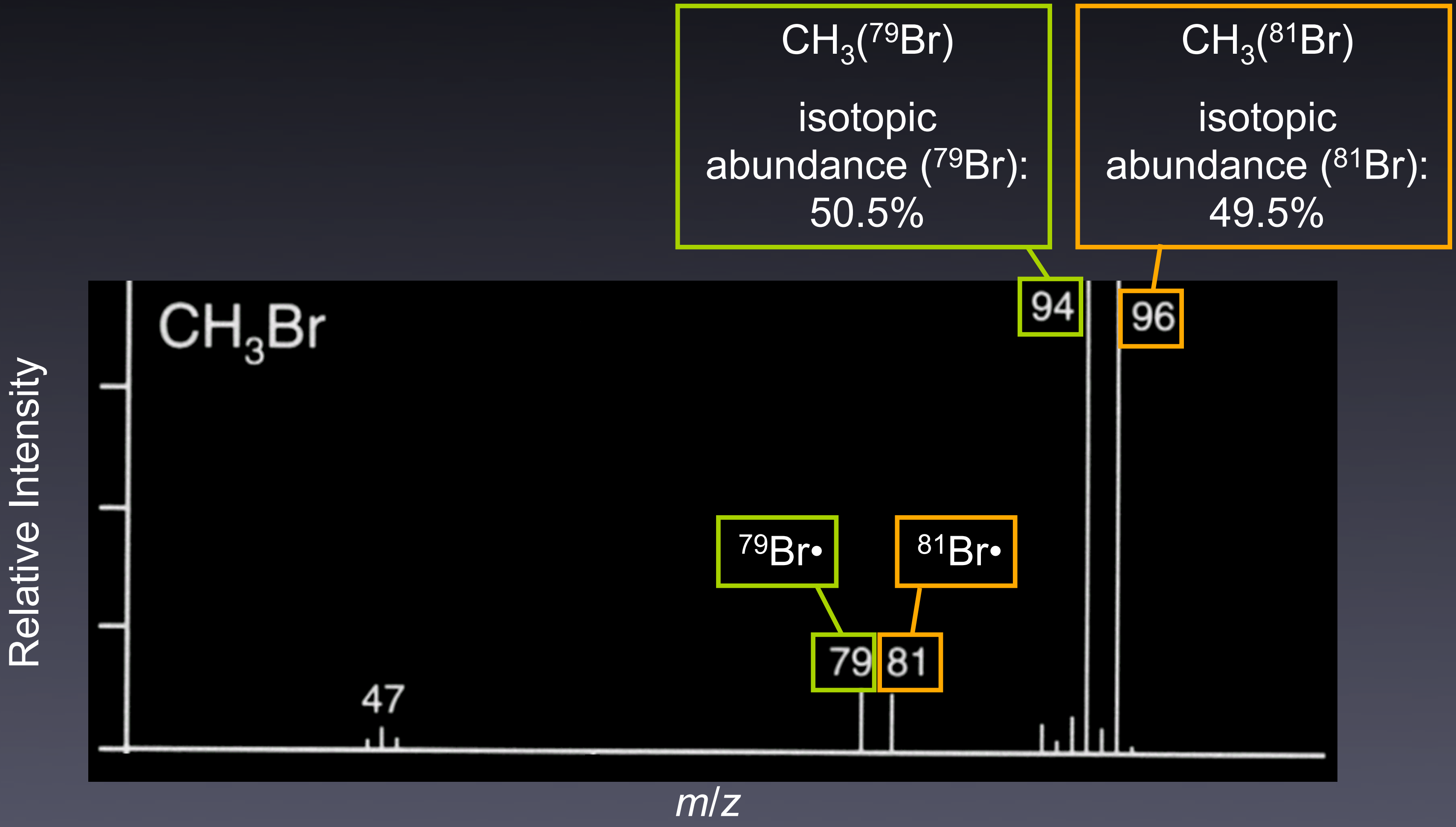

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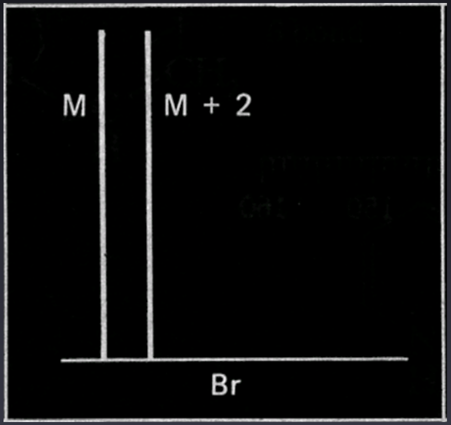
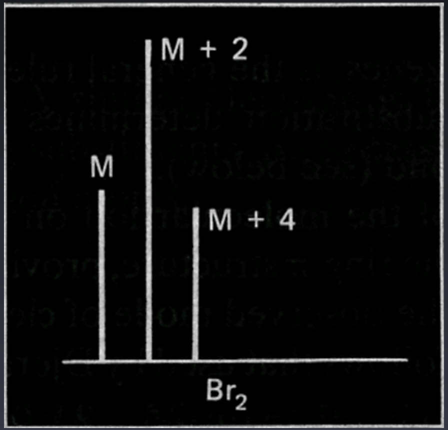
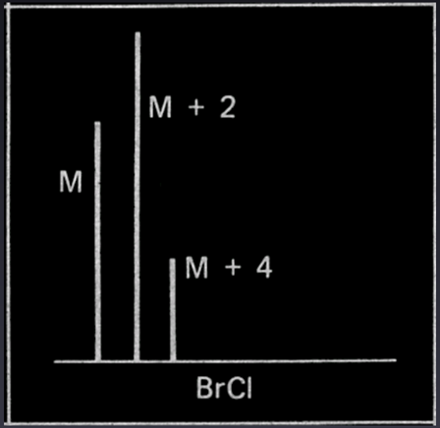
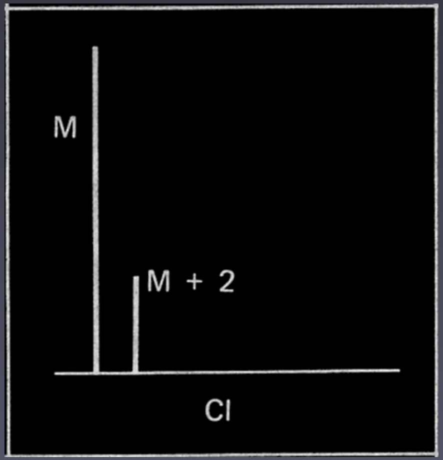
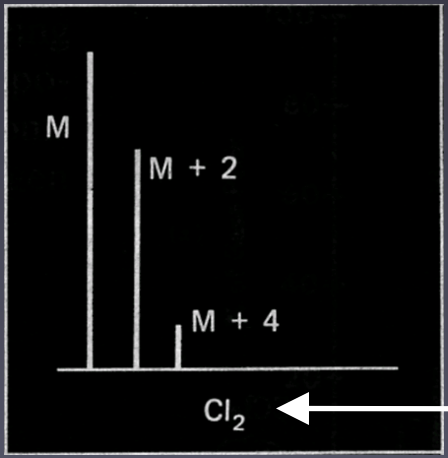
Halogen isotopes generate characteristic patterns in mass spectra.











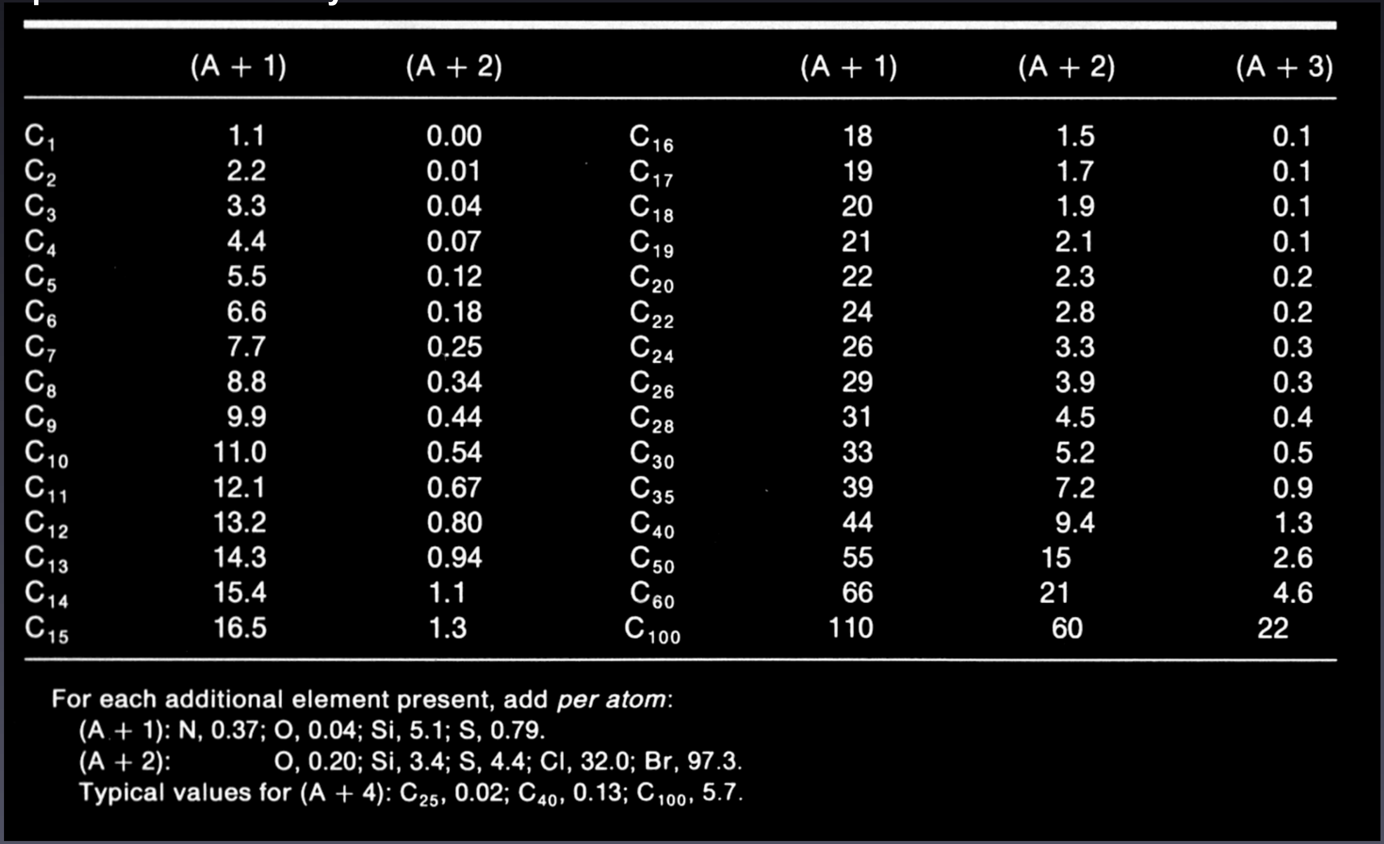
Pictures of these patterns available in textbook, Pretsch.

(Refers to two chlorines in any molecule, not just Cl_2.)

Isotopic Abundance and Peaks

Though isotopic contributions of ^{13}C, ^{2}H to MS are small, they add up.

If, for a carbon-containing compound, peak A has intensity 100, then higher-mass peaks have intensity:



	(A + 1)	(A + 2)		(A + 1)	(A + 2)	(A + 3)
C_1	1.1	0.00	C_{16}	18	1.5	0.1
C_2	2.2	0.01	C_{17}	19	1.7	0.1
C_3	3.3	0.04	C_{18}	20	1.9	0.1
C_4	4.4	0.07	C_{19}	21	2.1	0.1
C_5	5.5	0.12	C_{20}	22	2.3	0.2
C_6	6.6	0.18	C_{22}	24	2.8	0.2
C_7	7.7	0.25	C_{24}	26	3.3	0.3
C_8	8.8	0.34	C_{26}	29	3.9	0.3
C_9	9.9	0.44	C_{28}	31	4.5	0.4
C_{10}	11.0	0.54	C_{30}	33	5.2	0.5
C_{11}	12.1	0.67	C_{35}	39	7.2	0.9
C_{12}	13.2	0.80	C_{40}	44	9.4	1.3
C_{13}	14.3	0.94	C_{50}	55	15	2.6
C_{14}	15.4	1.1	C_{60}	66	21	4.6
C_{15}	16.5	1.3	C_{100}	110	60	22

For each additional element present, add *per atom*:
(A + 1): N, 0.37; O, 0.04; Si, 5.1; S, 0.79.
(A + 2): O, 0.20; Si, 3.4; S, 4.4; Cl, 32.0; Br, 97.3.
Typical values for (A + 4): C_{25}, 0.02; C_{40}, 0.13; C_{100}, 5.7.

McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra.*

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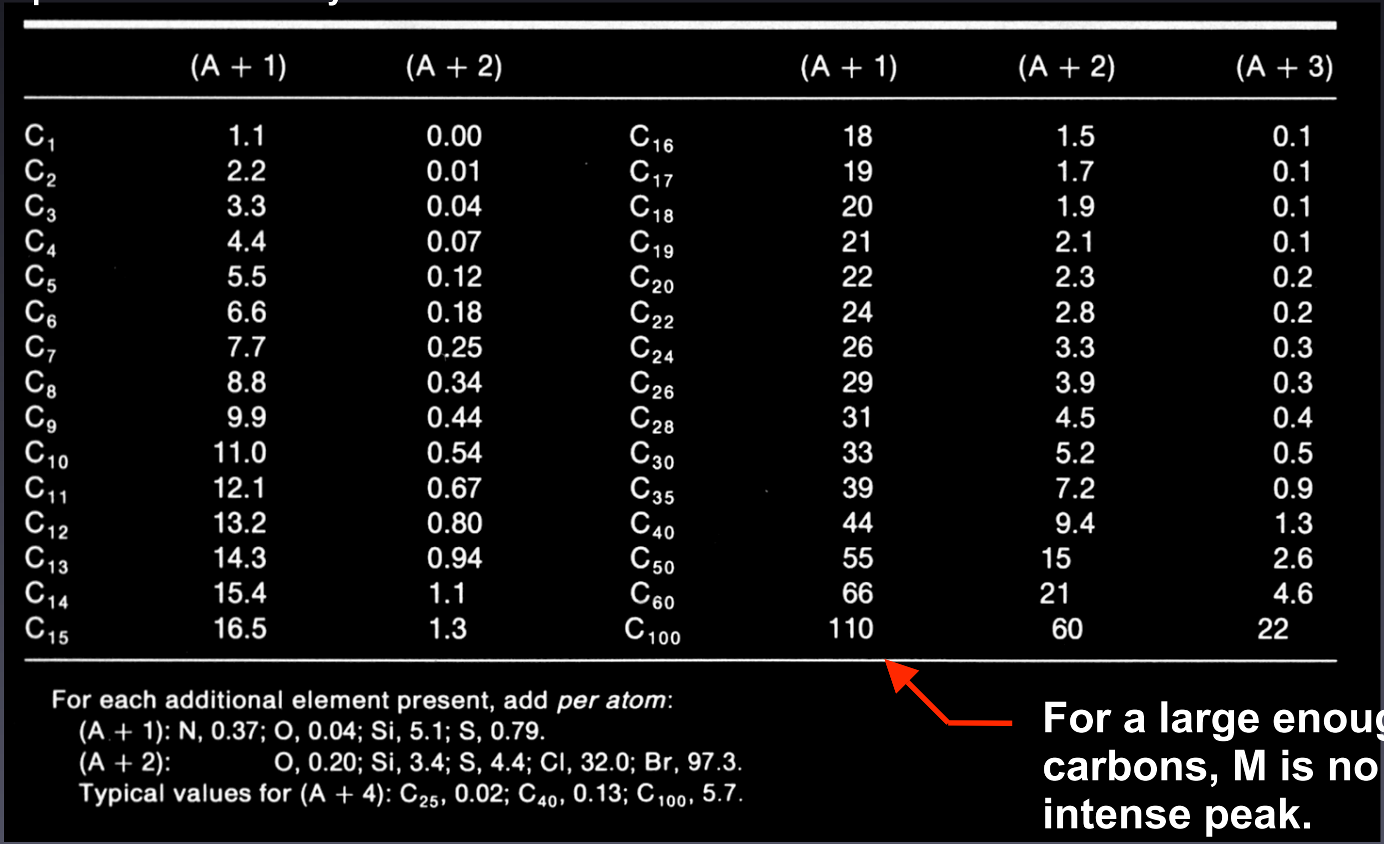

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C_9	9.9	0.44	C_{28}	31	4.5	0.4
C_{10}	11.0	0.54	C_{30}	33	5.2	0.5
C_{11}	12.1	0.67	C_{35}	39	7.2	0.9
C_{12}	13.2	0.80	C_{40}	44	9.4	1.3
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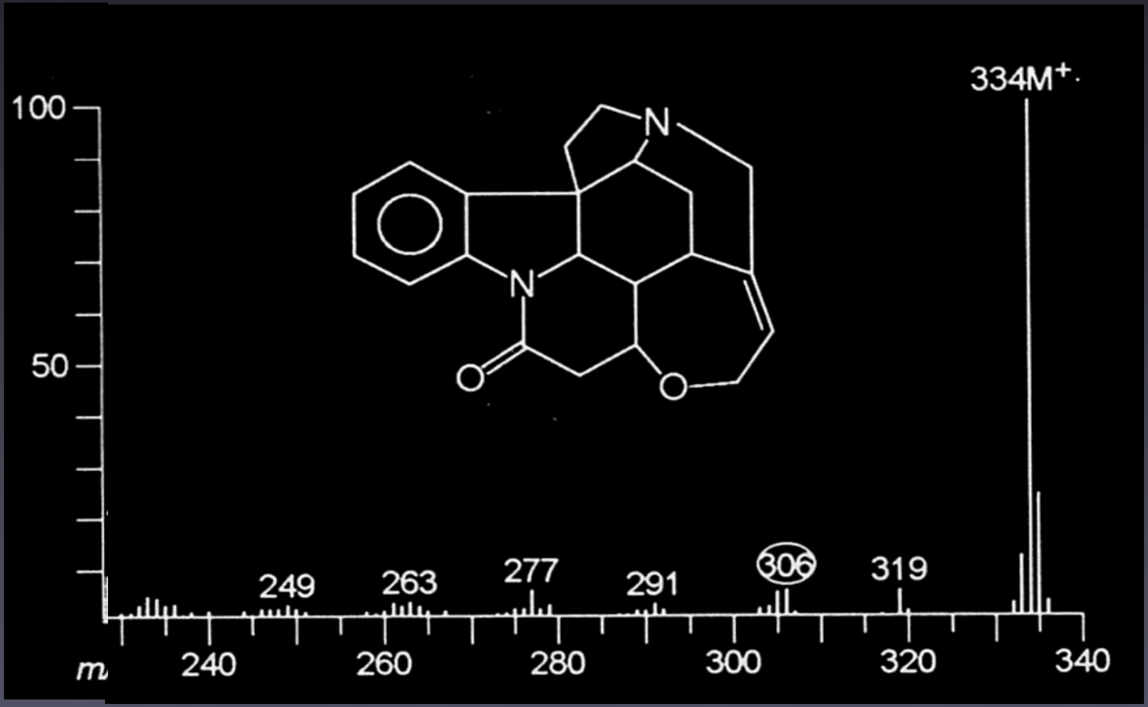
For a large enough number of carbons, M is no longer most intense peak.

McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra.*

Isotopic Series in Large Molecules

For the EI-MS of strychnine ($C_{21}H_{22}N_2O_2$), what should the intensity of (M + 1), *m*/*z* = 335, be?



$P_{^{13}C} = 21(1.1\%)$

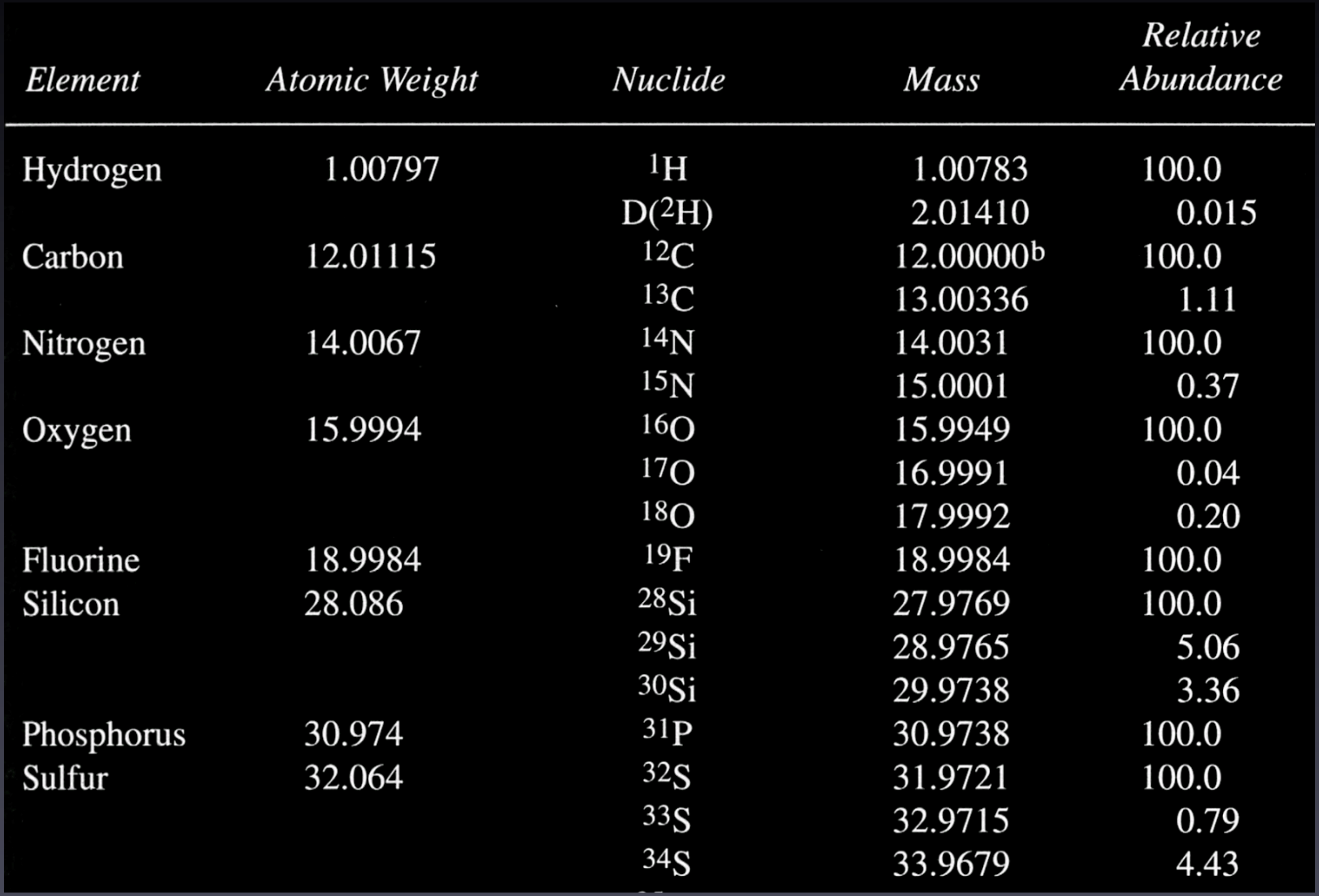
$P_{^{2}H} = 22(0.015\%)$

$P_{^{15}N} = 2(0.37\%)$

$P_{^{17}O} = 2(0.04\%)$

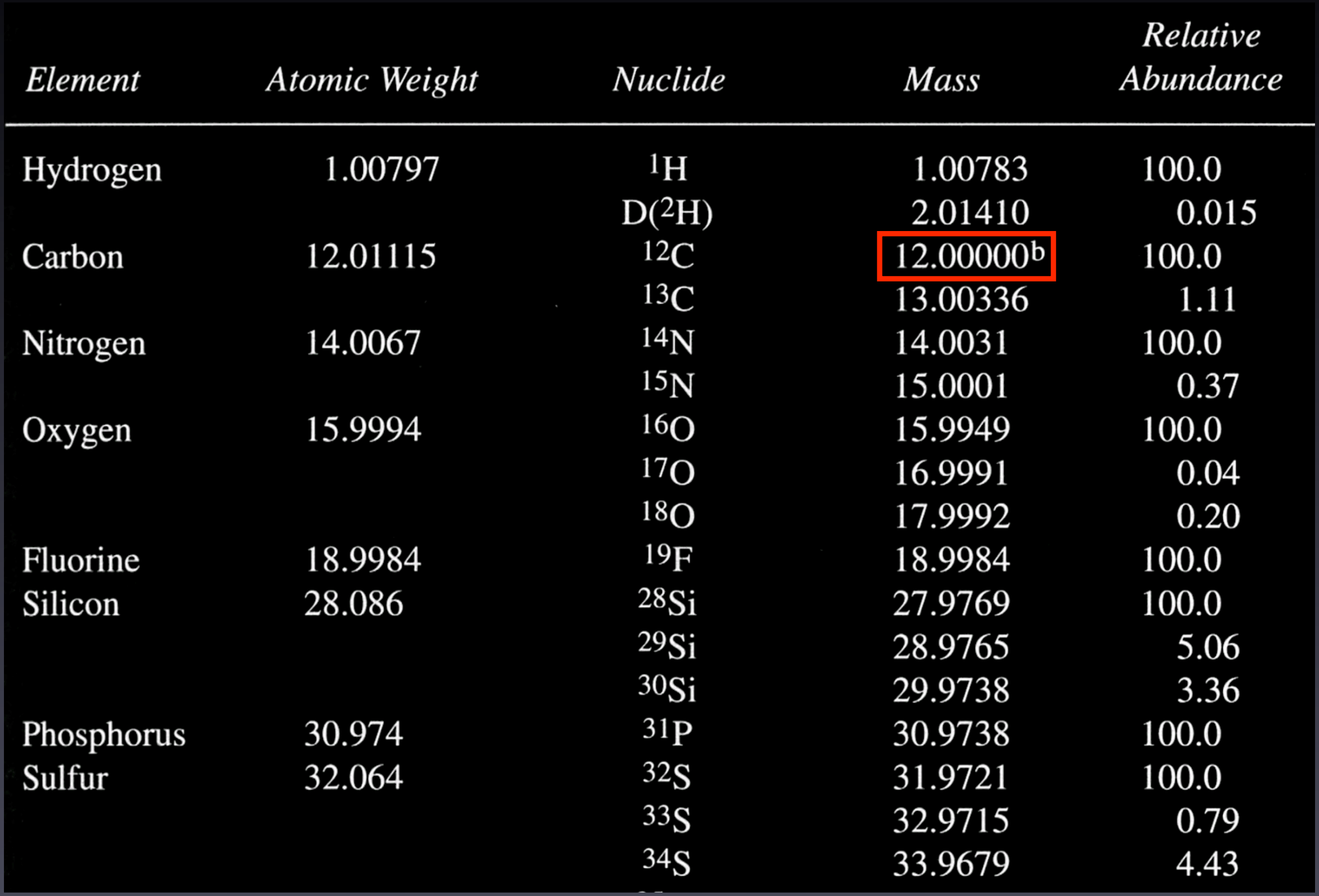
= **24%**

Exact Masses and Molecular Formulae



Element	*Atomic Weight*	*Nuclide*	*Mass*	*Relative Abundance*
Hydrogen	1.00797	^{1}H	1.00783	100.0
		$D(^{2}H)$	2.01410	0.015
Carbon	12.01115	^{12}C	12.00000[b]	100.0
		^{13}C	13.00336	1.11
Nitrogen	14.0067	^{14}N	14.0031	100.0
		^{15}N	15.0001	0.37
Oxygen	15.9994	^{16}O	15.9949	100.0
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
Fluorine	18.9984	^{19}F	18.9984	100.0
Silicon	28.086	^{28}Si	27.9769	100.0
		^{29}Si	28.9765	5.06
		^{30}Si	29.9738	3.36
Phosphorus	30.974	^{31}P	30.9738	100.0
Sulfur	32.064	^{32}S	31.9721	100.0
		^{33}S	32.9715	0.79
		^{34}S	33.9679	4.43

Exact Masses and Molecular Formulae



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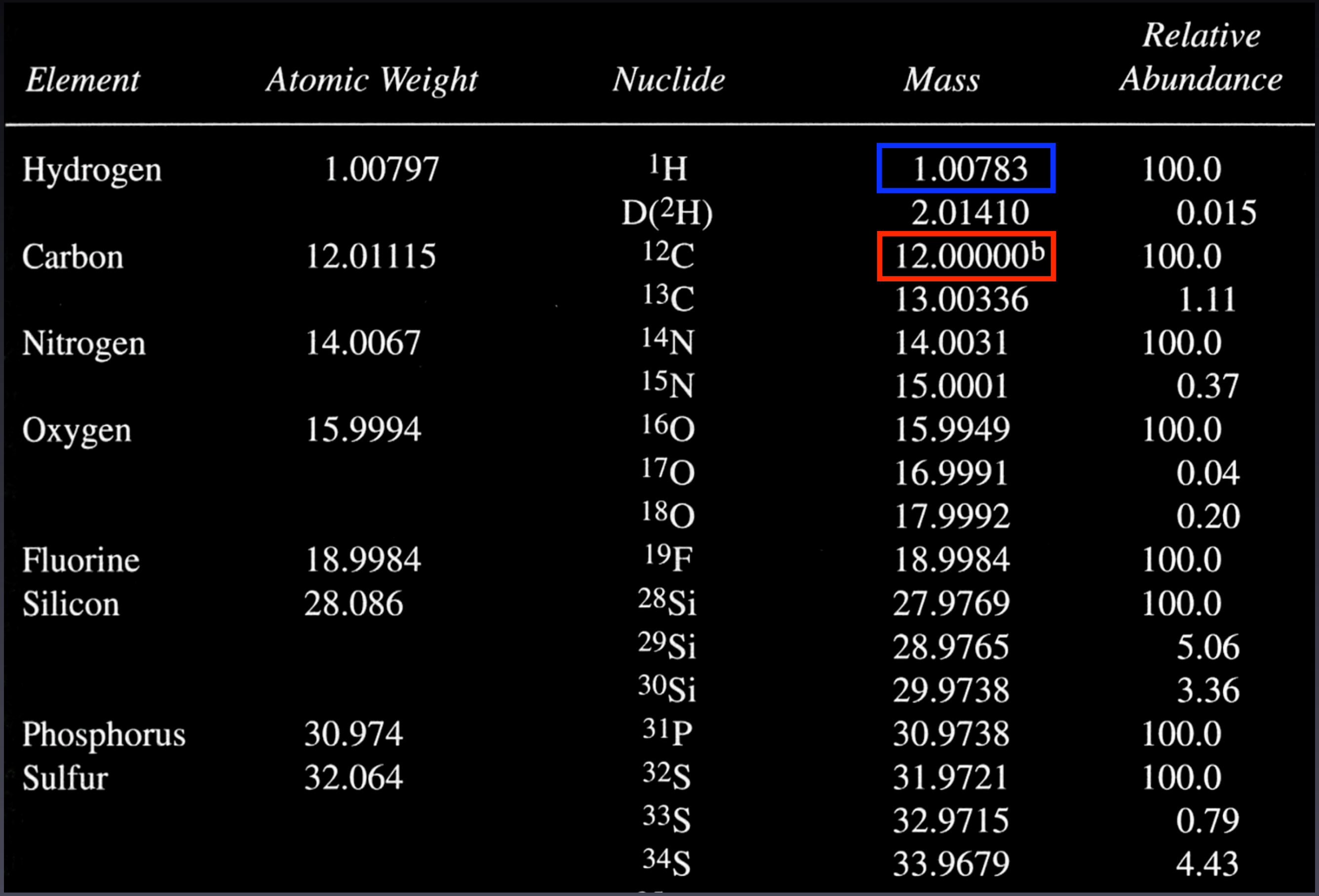
		^{34}S	33.9679	4.43

^{12}C mass set to 12 amu, exactly.

Exact Masses and Molecular Formulae



Element	*Atomic Weight*	*Nuclide*	*Mass*	*Relative Abundance*
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		$D(^{2}H)$	2.01410	0.015
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As a result, ^{1}H mass is actually higher than 1 amu.

Exact Masses and Molecular Formulae

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As a result, ^{1}H mass is actually higher than 1 amu.

And ^{16}O mass is lower than 16 amu.

Exact Masses and Molecular Formulae

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		D(^{2}H)	2.01410	0.015
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Phosphorus	30.974	^{31}P	30.9738	100.0
Sulfur	32.064	^{32}S	31.9721	100.0
		^{33}S	32.9715	0.79
		^{34}S	33.9679	4.43

^{12}C mass set to 12 amu, exactly.

As a result, ^{1}H mass is actually higher than 1 amu.

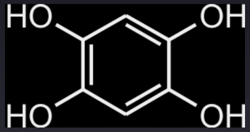
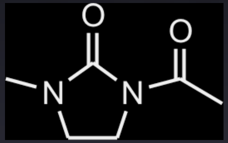
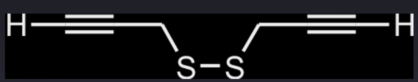
And ^{16}O mass is lower than 16 amu.

Isotopes vary from unit masses by “mass defect”.

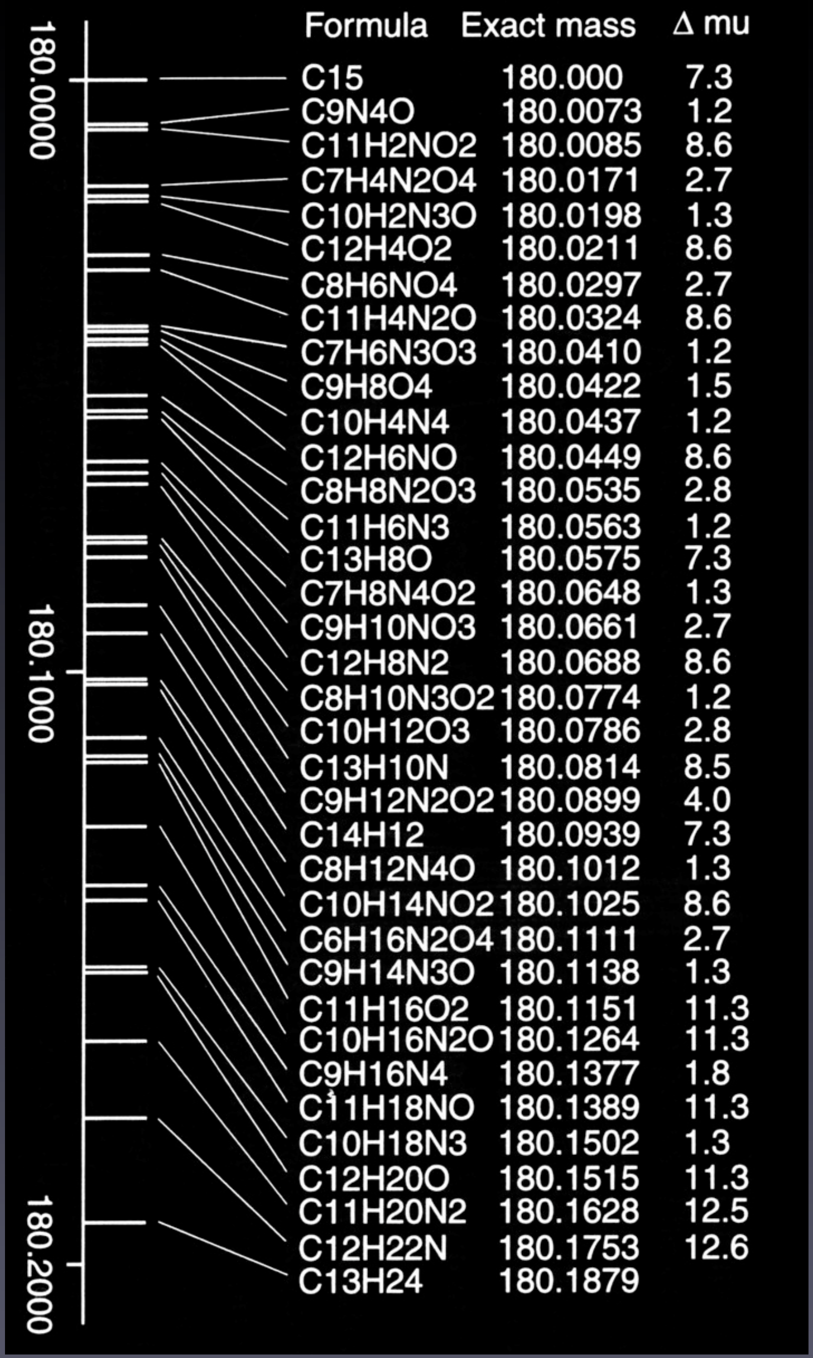
^{1}H has positive mass defect; ^{16}O has negative mass defect.

Exact Masses and Molecular Formulae

So, molecules with different molecular formulae have different exact masses.

				
molecular formula	$C_{10}H_{22}$	$C_6H_6O_4$	$C_6H_{10}N_2O_2$	$C_6H_6S_2$
m/*z* (unit)	142	142	142	142
m/*z* (exact mass)	142.1723	142.0264	142.0743	141.9911

For small molecules,
it’s possible to distinguish
all possibilities with ~5ppm
mass accuracy

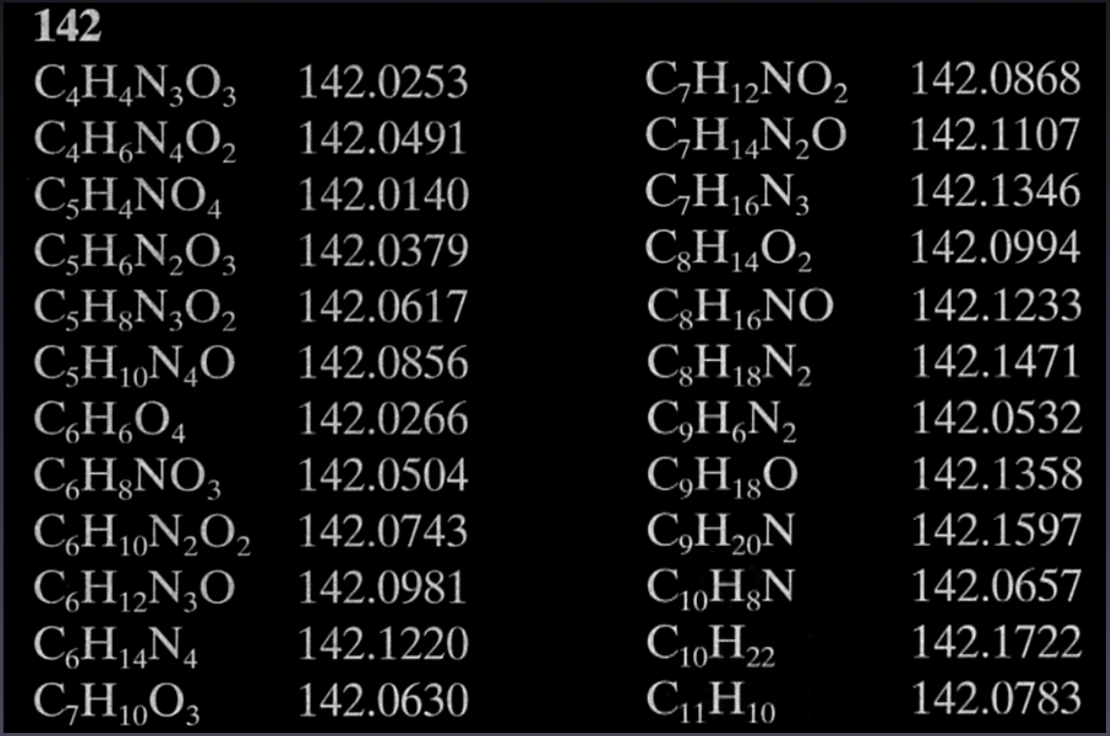


Formula	Exact mass	Δ mu
C15	180.000	7.3
C9N4O	180.0073	1.2
C11H2NO2	180.0085	8.6
C7H4N2O4	180.0171	2.7
C10H2N3O	180.0198	1.3
C12H4O2	180.0211	8.6
C8H6NO4	180.0297	2.7
C11H4N2O	180.0324	8.6
C7H6N3O3	180.0410	1.2
C9H8O4	180.0422	1.5
C10H4N4	180.0437	1.2
C12H6NO	180.0449	8.6
C8H8N2O3	180.0535	2.8
C11H6N3	180.0563	1.2
C13H8O	180.0575	7.3
C7H8N4O2	180.0648	1.3
C9H10NO3	180.0661	2.7
C12H8N2	180.0688	8.6
C8H10N3O2	180.0774	1.2
C10H12O3	180.0786	2.8
C13H10N	180.0814	8.5
C9H12N2O2	180.0899	4.0
C14H12	180.0939	7.3
C8H12N4O	180.1012	1.3
C10H14NO2	180.1025	8.6
C6H16N2O4	180.1111	2.7
C9H14N3O	180.1138	1.3
C11H16O2	180.1151	11.3
C10H16N2O	180.1264	11.3
C9H16N4	180.1377	1.8
C11H18NO	180.1389	11.3
C10H18N3	180.1502	1.3
C12H20O	180.1515	11.3
C11H20N2	180.1628	12.5
C12H22N	180.1753	12.6
C13H24	180.1879	

Exact Masses and Molecular Formulae

How to determine a molecular formula from an exact mass:

- Look up in a table, *or*



142

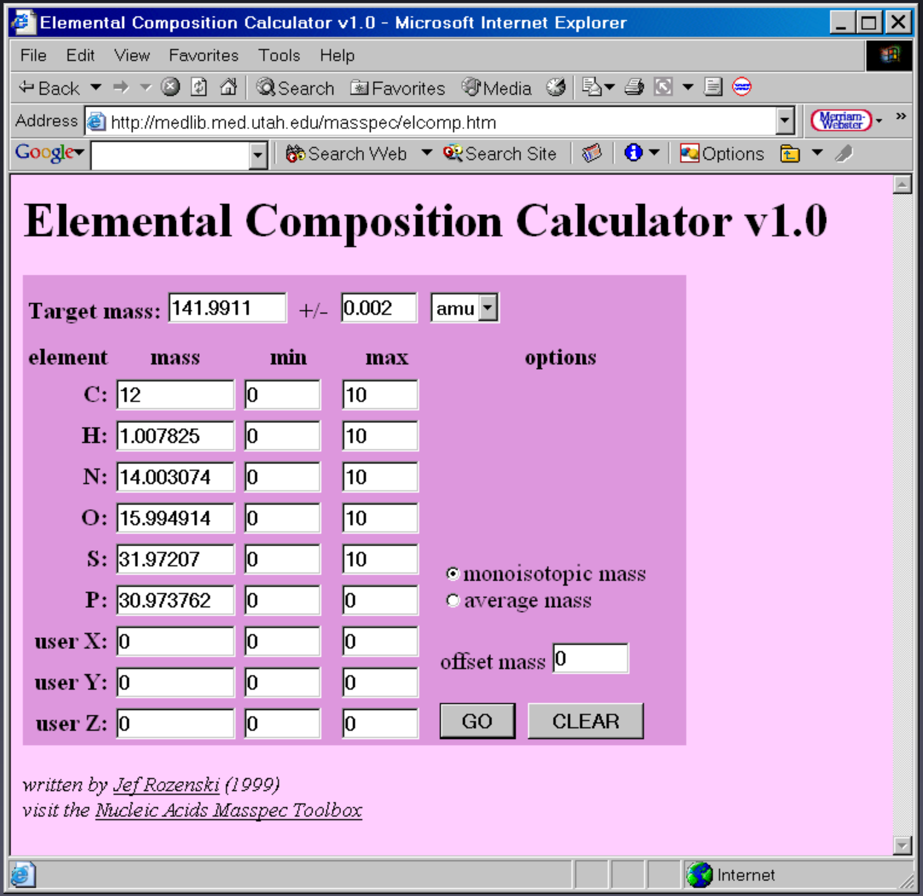
$C_4H_4N_3O_3$	142.0253	$C_7H_{12}NO_2$	142.0868
$C_4H_6N_4O_2$	142.0491	$C_7H_{14}N_2O$	142.1107
$C_5H_4NO_4$	142.0140	$C_7H_{16}N_3$	142.1346
$C_5H_6N_2O_3$	142.0379	$C_8H_{14}O_2$	142.0994
$C_5H_8N_3O_2$	142.0617	$C_8H_{16}NO$	142.1233
$C_5H_{10}N_4O$	142.0856	$C_8H_{18}N_2$	142.1471
$C_6H_6O_4$	142.0266	$C_9H_6N_2$	142.0532
$C_6H_8NO_3$	142.0504	$C_9H_{18}O$	142.1358
$C_6H_{10}N_2O_2$	142.0743	$C_9H_{20}N$	142.1597
$C_6H_{12}N_3O$	142.0981	$C_{10}H_8N$	142.0657
$C_6H_{14}N_4$	142.1220	$C_{10}H_{22}$	142.1722
$C_7H_{10}O_3$	142.0630	$C_{11}H_{10}$	142.0783

From R. M. Silverstein, F. X. Webster, *Spectrometric Identification of Organic Compounds* (Wiley, 1998), 6th ed.

Exact Masses and Molecular Formulae

How to determine a molecular formula from an exact mass:

- Look up in a table, *or*
- Use a web-based calculator.



Address: http://medlib.med.utah.edu/masspec/elcomp.htm

Elemental Composition Calculator v1.0

Target mass: 141.9911 +/- 0.002 amu

element	mass	min	max
C:	12	0	10
H:	1.007825	0	10
N:	14.003074	0	10
O:	15.994914	0	10
S:	31.97207	0	10
P:	30.973762	0	0
user X:	0	0	0
user Y:	0	0	0
user Z:	0	0	0

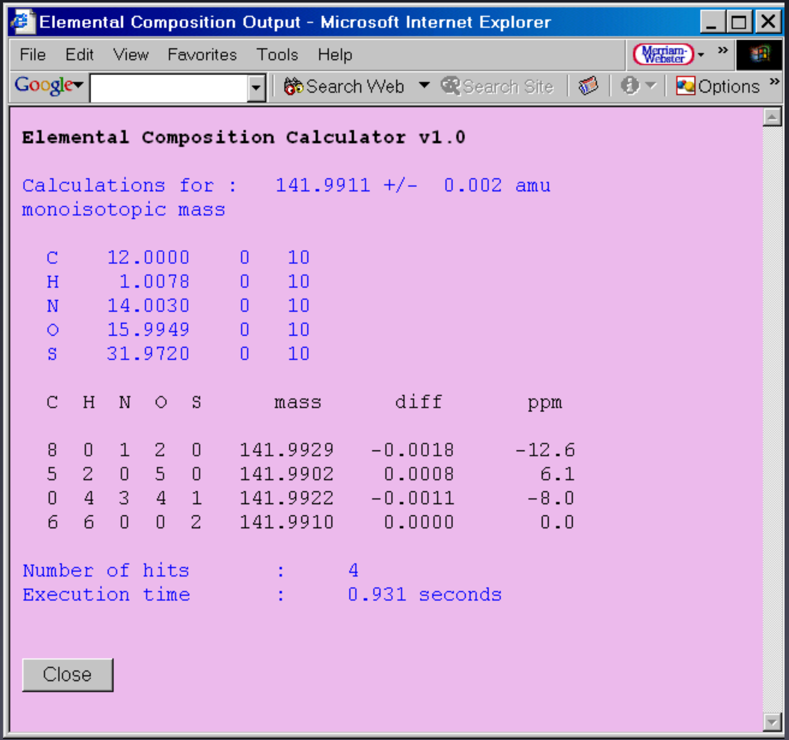
options

● monoisotopic mass
○ average mass

offset mass 0

GO CLEAR

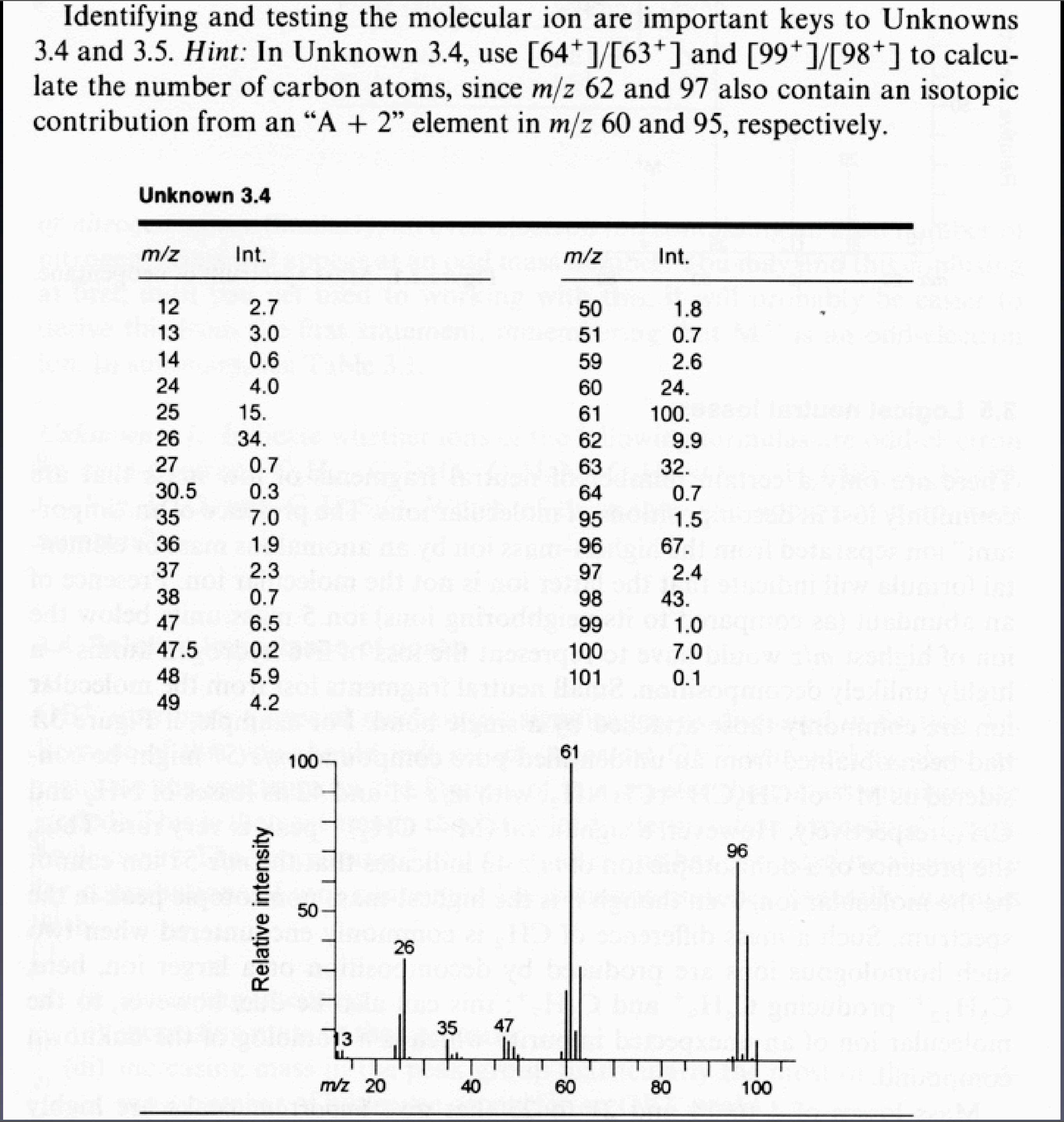
written by Jef Rozenski (1999)
visit the Nucleic Acids Masspec Toolbox



```
Elemental Composition Calculator v1.0

Calculations for :   141.9911 +/-   0.002 amu
monoisotopic mass

  C    12.0000    0    10
  H     1.0078    0    10
  N    14.0030    0    10
  O    15.9949    0    10
  S    31.9720    0    10

  C   H   N   O   S       mass       diff        ppm

  8   0   1   2   0    141.9929   -0.0018      -12.6
  5   2   0   5   0    141.9902    0.0008        6.1
  0   4   3   4   1    141.9922   -0.0011       -8.0
  6   6   0   0   2    141.9910    0.0000        0.0

Number of hits        :     4
Execution time        :     0.931 seconds
```

$C_6H_6S_2$ is closest match.

Quiz



Identifying and testing the molecular ion are important keys to Unknowns 3.4 and 3.5. *Hint:* In Unknown 3.4, use $[64^+]/[63^+]$ and $[99^+]/[98^+]$ to calculate the number of carbon atoms, since *m/z* 62 and 97 also contain an isotopic contribution from an "A + 2" element in *m/z* 60 and 95, respectively.

Unknown 3.4

m/z	Int.	*m/z*	Int.
12	2.7	50	1.8
13	3.0	51	0.7
14	0.6	59	2.6
24	4.0	60	24.
25	15.	61	100.
26	34.	62	9.9
27	0.7	63	32.
30.5	0.3	64	0.7
35	7.0	95	1.5
36	1.9	96	67.
37	2.3	97	2.4
38	0.7	98	43.
47	6.5	99	1.0
47.5	0.2	100	7.0
48	5.9	101	0.1
49	4.2		