Elemental Composition

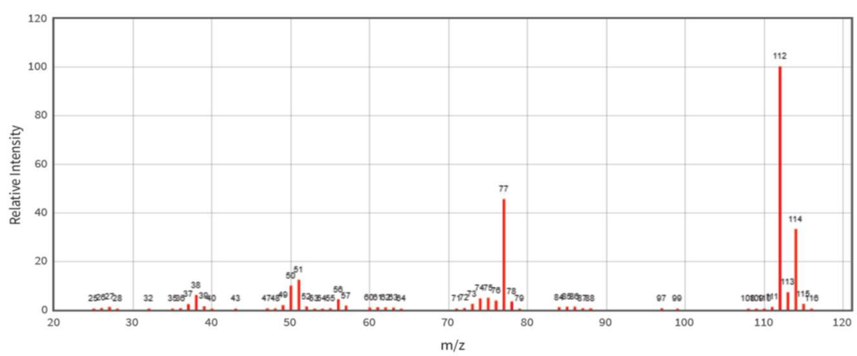
Standard interpretation procedure for EI spectra

1. ***Known information*** *(other spectra, history of the sample), clear requirements for the MS measurement, control the m/z assignment (calibration)*
2. **Elemental composition** – isotopic pattern (for all peaks in the spectrum)
3. **Molecular ion** (largest mass in the spectrum, odd number of electrons, logic neutral losses). Comparison with spectra obtained with CI or other soft-ionization method
4. **Important ions**: odd number of electrons, largest abundance, high mass, largest abundance in a group of the peaks
5. **Appearance of the spectrum**: stability of molecular ion, labile bonds
6. **Possible sub-structures**
   1. Important series of ions with low masses
   2. Important neutral losses from $M^{+\bullet}$ (fragment with high masses)
   3. Characteristic ions
7. **Suggest molecular structure**

   Comparison with a reference spectrum, with spectra of similar compounds, check with fragmentation mechanisms expected for the suggested molecular ion

Literature - Fred W. McLafferty, František Tureček: Interpretation of mass spectra

What is the elemental composition of the analyte?



1) The biggest peaks first
2) Select peak A - the peak with the largest mass containing the basic isotopes

Isotopic patterns

TYPE A

Element	Mass
H	1
F	19
P	31
I	127

TYPE A+1

Element	A Mass	A+1 Mass
C	12 (100%)	13 (1.1%)
N	14 (100%)	15 (0.37%)

TYPE A+2

Element	A Mass	A+1 Mass	A+2 Mass
O	16 (100%)	17 (0.04%)	18 (0.2%)
S	32 (100%)	33 (0.79%)	34 (3.4%)
Cl	35 (100%)		37 (32%)
Br	79 (100%)		81 (97.3%)

A+1 Elements: C, (N)

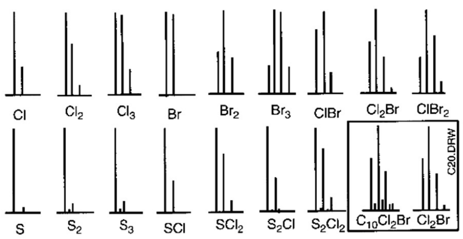
- $^{2}H/^{1}H$ very small, H considered as type A
- N – neglect
- C – the most important
  - Abundance of ^{13}C is ~ 1.1% (slightly differs based on the origin)
  - → we can deduce the number of carbon atoms in the given ion from the A+1 mass

Table 2.2. *Isotopic contributions for carbon and hydrogen. If the abundance of the peak A is 100 (after correction for isotopic contributions to it), then its isotopic contributions will be:*

	(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

A+2 Elements: O, S, Cl, Br

- Very characteristic – always start with
- More of A+2 elements in a molecule gives also characteristic patterns recognizable at the first sight



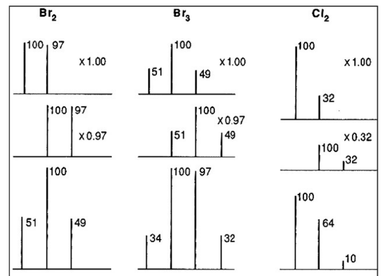


Figure 2.1. Linear superposition of bromine and chlorine peak patterns.

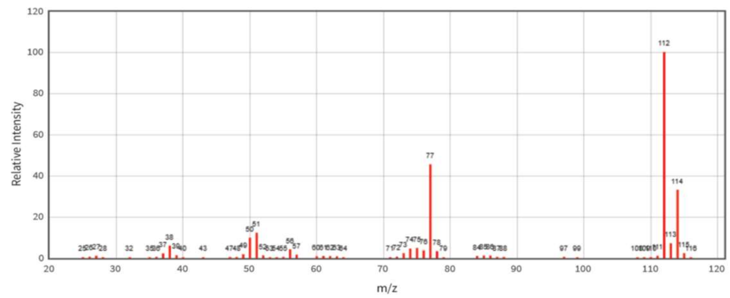
A Elements: H, F, P, I

- When we determine the number of A+1 and A+2 elements, we add A elements so that we obtain the correct final mass
  - Observe valences (carbon has only four-valences…)
  - If the missing mass is less than 19 (F), add just hydrogen atoms

m/z	Int.
127	100.
128	0.0
129	0.0

m/z	Int.	Int.
69	100.	100.
70	1.1	0.0
71	0.0	0.0

What is the elemental composition of the analyte?



1) The biggest peaks first
2) Select peak A
   a) The peak with the largest mass containing the basic isotopes (usually, the largest peak in the group)
   b) If [A-2]/[A] > 30% → then Cl, Br
   c) Determine elemental composition of A
   d) If elemental composition of A does not correspond to the isotopic pattern, then A was selected incorrectly

Tips for elemental composition determination

1) The biggest peaks first

   the smallest isotopic contamination
2) Select peak A
   a) The peak with the largest mass containing the basic isotopes (usually, the largest peak in the group)
   b) If [A-2]/[A] > 30% → then Cl, Br
   c) Determine elemental composition of A
   d) If elemental composition of A does not correspond to the isotopic pattern, then A was selected incorrectly
3) Use every group of the peaks
4) Control internal consistency of your assignment of peak compositions and fragmentations

   $M^{+\cdot}$ must have the largest number of given atoms of all elements