MS Interpretation-1: Introduction + Elemental Composition I

CU- Boulder
CHEM 5181
Mass Spectrometry & Chromatography

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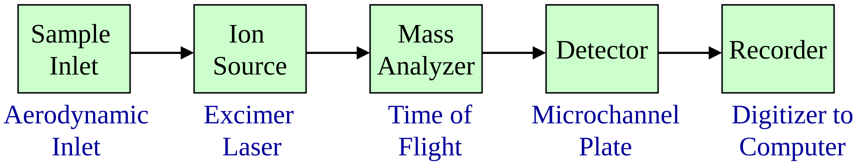
A few slides adapted from an earlier version of notes from Dr. Dan Czizco (then @ NOAA, now @ MIT

Last updated: Oct 2013

Business Items

- Note: doing the McLafferty reading includes solving ALL the unknowns
  - Like for Igor, here each lecture builds quickly on the previous one
  - If you don’t, you’ll quickly fall behind!
- HW7 due Thu before the start of class
  - Submitted via email, discussed in class as usual
  - No printouts this time
- HW8 due next Thu, to be posted on Thu
- Discussion of reading & comments

Introduction to Interpretation



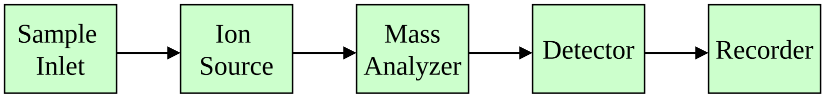
Sample Inlet → Ion Source → Mass Analyzer → Detector → Recorder

Aerodynamic Inlet | Excimer Laser | Time of Flight | Microchannel Plate | Digitizer to Computer

PALMS instrument in nose of WB-57 stratospheric aircraft. *Murphy, Czizco et al.*

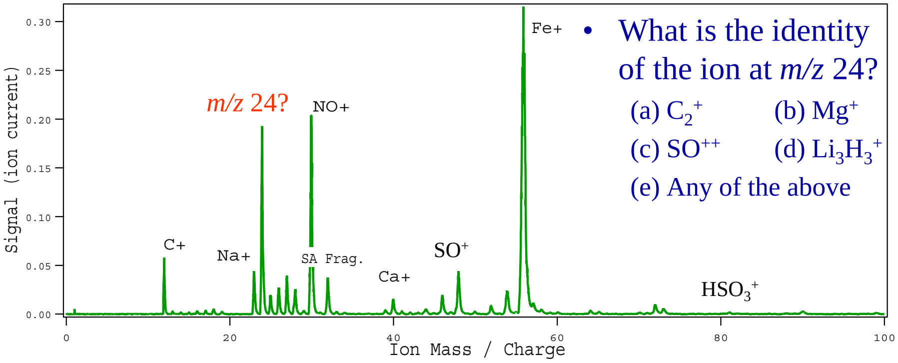
From Dr. Dan Czizco

...Now What? - I



Sample Inlet → Ion Source → Mass Analyzer → Detector → Recorder

PALMS single particle spectrum (stratosphere)



- What is the identity of the ion at *m/z* 24?

  (a) C_2^+ (b) Mg^+

  (c) SO^{++} (d) $Li_3H_3^+$

  (e) Any of the above

From Dr. Dan Czizco

...Now What? - II

- Most mass spectra are not trivial to decipher due to:
  - interferences (Mg^+ or C_2^+ on last page)
  - complexities of fragmentation

- Instead, MS Interpretation is problem solving, ‘playing chess’, or ‘cracking a code’
  - Use all available information in a logical and organized manner
- Focus: EI spectra of “small” organic molecules: $M^{+\bullet}$
  - Easiest for teaching / learning, most logical progression
  - Most interpretation techniques are applicable to spectra obtained with other ionization techniques
  - See chapter 7 of de Hoffmann for introduction and references for fragmentation with other techniques (e.g. MH^+)

Interpretation Lectures vs. McLafferty Chapters

- Ch. 1: Introduction
- Ch. 2: Elemental Composition
- Ch. 3: The Molecular Ion
- Ch. 4: Basic Fragmentation Mechanisms
- Ch. 5: Postulation of Molecular Structures
- Ch. 6: Auxiliary Techniques
- Ch. 7: Theory of Unimolecular Ion Decomp.
- Ch. 8: Detailed Fragmentation Mechanisms
- Ch. 9: Fragmentation of Compound Classes
- Ch. 10: Computer Methods

Covered in instrum. part

This part of course

Advanced version, not covered in course

Useful for understanding how databases work

Standard Intepretation Procedure

1. Elemental Composition ☐
    - 1.1. Choose peak group(s) ☐
    - 1.2. Build Table ☐
    - 1.3. A+2 elements ☐
    - 1.4. A+1 elements ☐
    - 1.5. Oxygen ☐
    - 1.6. Hydrogen losses ☐
    - 1.7. A elements ☐
    - 1.8. Exotic elements ☐
    - 1.9. RPDB ☐
    - 1.10. Noise level ☐

2. Molecular ion identity
    - 2.1. Identify Candidate $M^{+\cdot}$ ☐
    - 2.2. Check that $M^{+\cdot}$ is $OE^{+\cdot}$ ☐
    - 2.3. N-Rule: N in $M^{+\cdot}$, frags ☐
    - 2.4. Check most frag. are EE^{+} ☐
    - 2.5. Mark important $OE^{+\cdot}$ ☐
    - 2.6. Even vs odd at low m/z ☐
    - 2.7. Explain important frags ☐
    - 2.8. Logical neutral losses ☐
    - 2.9. $M^{+\cdot}$:most atoms each el. ☐
    - 2.10. $M^{+\cdot}$ abundance vs struct. ☐

3. Study General Appearance of the Spectrum
    - 3.1. Molecular stability ☐
    - 3.2. Low-mass ion series ☐
    - 3.3. Imp. characteristic ions ☐

4. Check your ID
    - 4.1. Compare to MS of similar ☐
    - 4.2. Check against database ☐

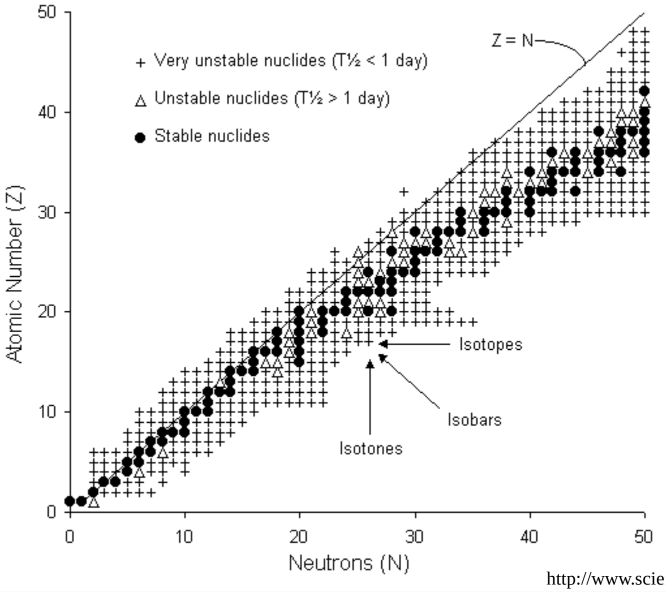
Adapted by Jose from McLafferty & Turececk
Suggestions for Improvement most welcome.

- ALWAYS Follow & annotate with step name

References on MS Interpretation

- McLafferty & Turecek, Interpretation of Mass Spectra, 4th Ed., 1993.
    - Best book on the subject, must have for class
    - We will follow it closely
- Smith & Busch,Understanding Mass Spectra, 1999.
    - Alternative to McLafferty, somewhat easier to read
- Lee, A beginner’s Guide to Mass Spectral Interpretation, 1998.
    - More basic, easy to read. Useful introduction before tackling McLafferty.
- Sorrell, Interpreting Spectra of Organic Molecules, 1988.
    - Older and more general.

Why are there isotopes?



- Q: what explains these observed trends?

http://www.science.uottawa.ca/eih/ch1/ch1.htm

Natural Abundances of Stable Isotopes

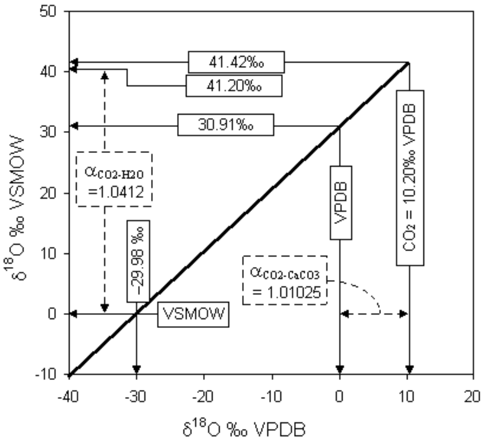
Table 2.1. *Natural isotopic abundances of common elements.*[a]

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

[a] Wapstra and Audi (1986).
[b] 1.1 ± 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

What about deviations from natural abundances?



- VSMOW: Vienna Standard Mean Ocean Water
- Vienna Pee Dee Belemnite

Clicker Q: the chart to the right shows the converstion between two standards for ^{18}O, as well as the fractionation due to some processes. Do we have to worry about such fractionations in class?

A. Always
B. Never
C. In some cases (frequent)
D. In some cases (rare)
E. I don’t know

http://www.science.uottawa.ca/eih/ch1/ch1.htm

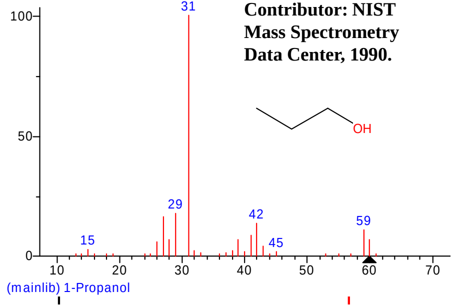
What about noise in the spectra?

- McLafferty states the level of noise to expect in all his spectra:
  - Convention of always assigning 100% to the strongest peak in the spectrum
    - Other fields of MS such as my group use other conventions, so beware that's not universal!
  - Noise: 10% of the intensity of the peak, or +/- 0.2% of the base peak, *whichever is greater.*
- Questions:
  - For the base peak its intensity is 100%, what is the level of noise to expect?
  - For a peak with an intensity of 1%-absolute (i.e. 1% of the intensity of the base peak), what is the level of noise to expect?
  - For which intensity do both sources of noise equal?
    - This separates small vs large peaks
  - This applies ONLY to the McLafferty unknowns!
- Unknowns from other sources (most class examples, exams, your own research, the literature, etc.):
  - You don't know a priory the magnitude of the noise
  - Large ions should always have better SNR than the small ones
  - You can estimate the level of noise from the spectra (step 1.10 of the SIP).

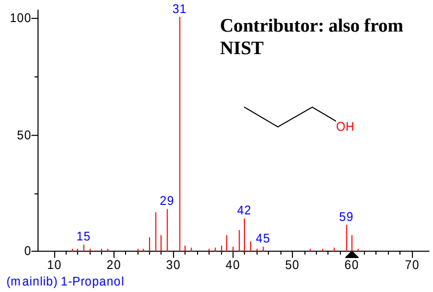
Reproducibility / Signal-to-Noise

- Be aware that database (and other) spectra have limited signal-to-noise and some instrument-to-instrument variability
- Database examples depend on instrument used
- Be aware that background / leak / contaminant peaks may be present that are not related to the molecule of interest
  - Take a “background” spectrum just before your analysis
- Make sure *m/z* values are correct!

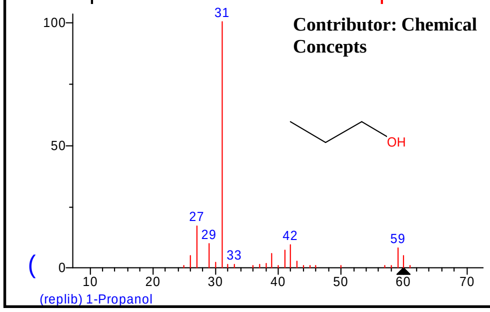
Reproducibility: 4 Spectra of 1-Propanol in NIST



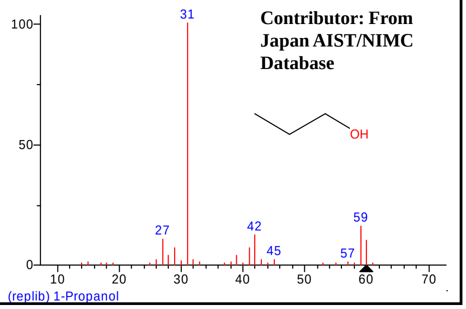
Contributor: NIST Mass Spectrometry Data Center, 1990.



Contributor: also from NIST



Contributor: Chemical Concepts



Contributor: From Japan AIST/NIMC Database

A+2 Elements IV

- Linear superposition of isotopic patterns
  - If there is more than one atom in the molecule of one of the A+2 elements, the result is even more striking

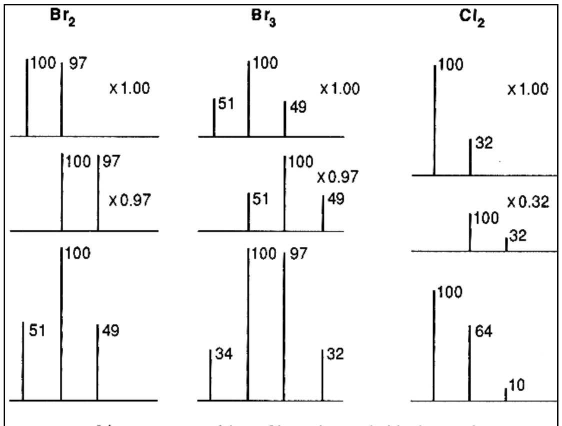


Figure 2.1. Linear superposition of bromine and chlorine peak patterns.

Isotopic peaks for 'n' atoms of same element

- Combinatorial problem
  - Same as coefficients of binomial formula $(a+b)^n$

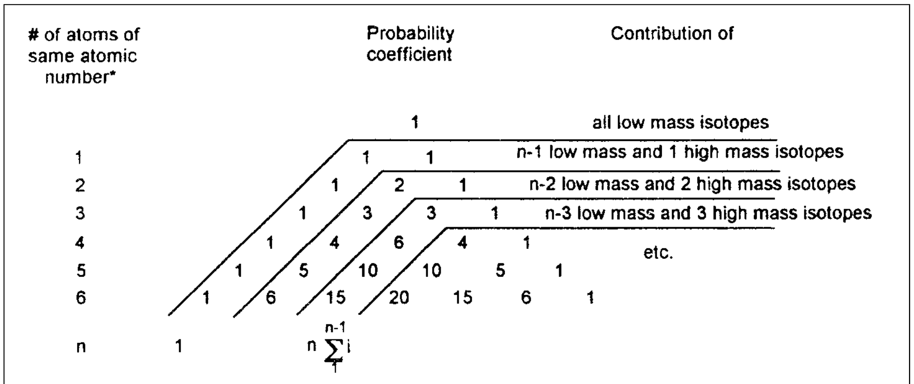


Figure 2.8. Binomial expansion (Pascal's) triangle. $\sum_{1}^{n-1} i = n(n-1)/2$. (*Assume the element in question has only two isotopes contributing to isotope peak ratios.)

From Smith and Busch, 1999

More Isotopic Peaks

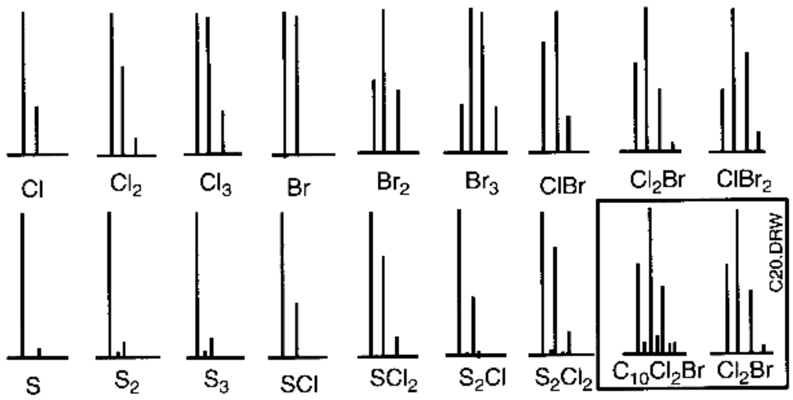


Figure 5.3
Useful isotope combinations in mass spectrometry. Isotopes of other atoms that are possibly associated must always be taken into account, as is shown in the framed section

Group Question

MT.2 How many isotopic forms of the molecular ion of $C_{11}Cl_{11}$ exist? How many nominal masses are represented?

A+2 Elements V

- Oxygen isotopes
  - The A+2 abundance of O is low (0.2%)
  - Need high abundance accuracy & precision
  - Other isotopic patterns can interfere (C), thus estimate number of oxygen after A+1 and other A+2 elements
- Absence of A+2 elements
  - Often they are not there. Value of negative info
  - If [(X+2)]/[X] < 3%, the peak X *cannot* contain the most abundant isotope of Si, S, Cl, or Br

A+1 Elements: C and N

- $^{2}H/^{1}H$ is so small that it is considered “A”
- Increasing number of C atoms linearly increases the probability that one of them is a ^{13}C (see table 2.2)
  - A way to deduce the number of carbon atoms
  - 1.1% of ^{13}C changes ~2% with source
- Don’t worry about N for now (next class)
  - “Nitrogen Rule” will come to our rescue

Number of Carbon Atoms

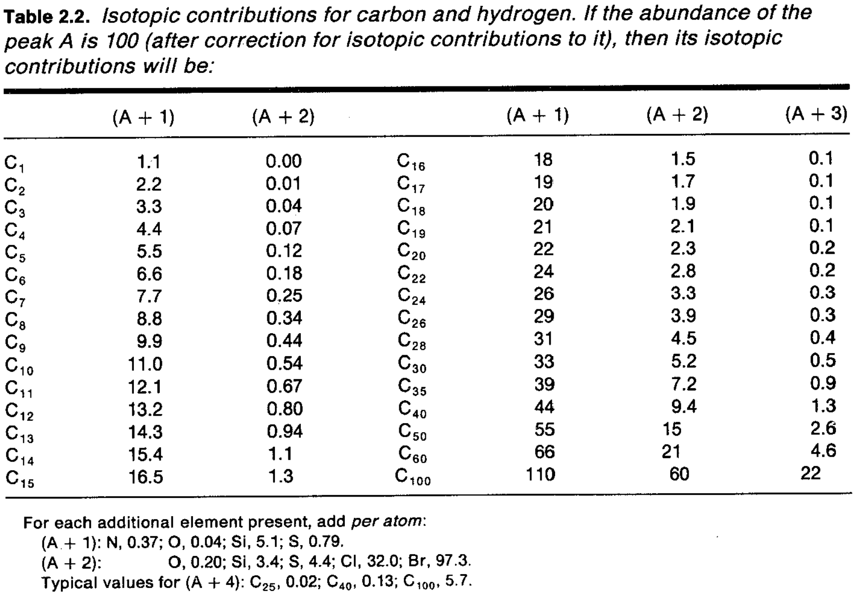


Table 2.2. *Isotopic contributions for carbon and hydrogen. If the abundance of the peak A is 100 (after correction for isotopic contributions to it), then its isotopic contributions will be:*

	(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

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.

Note from Unknown 2.4

- Note the many small peaks below the major ones, due to neutral losses of H and H_2
- *If you don't see those, the molecule likely has no H*
  - As simple as this seems, not using this rule has led to losing tons of points in past CHEM-5181!
- Also note that those peaks are less important in determining the structure
  - E.g. can't do C isotopes w/ 27 or 41
  - Start with the higher m/z (overall and in each group of peaks)

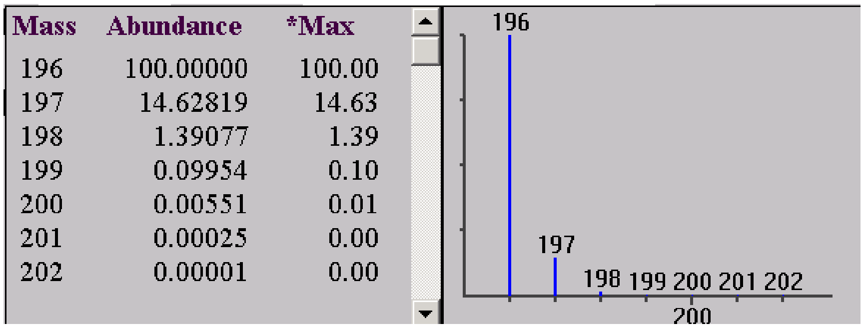
Possible Interferences

- We assumed that the only contributions to A+1 and A+2 peaks where from isotopes of the A peak
- Fragment ions can also add to the signal at A+1 and A+2
- A+2 elements of A-2 peak (or A+1 elements of A-1 peak) can add to A peak
  - Would produce erroneously low values for an element

A Elements: H, F, P, and I

- After the number of A+1 and A+2 elements have been assigned, A elements should provide the balance of the mass
  - Use number of atoms consistent with rules of bonding (no CH_6 please!)
  - Note that only H can be used until we need to add 19 (F)

Group Question

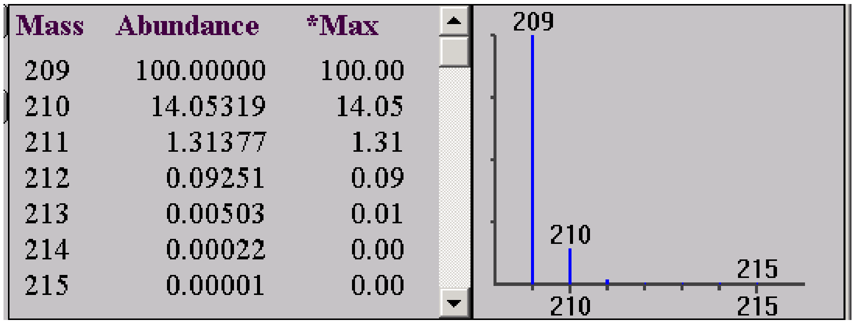


Mass	Abundance	*Max
196	100.00000	100.00
197	14.62819	14.63
198	1.39077	1.39
199	0.09954	0.10
200	0.00551	0.01
201	0.00025	0.00
202	0.00001	0.00

Determine the elemental composition of the following molecular ion. Note that there isotopic abundances are exact, there is no error.

- Work in groups, list evidence in board IN ORDER of use
- Note: this was in a cume in 2006

Group Question II

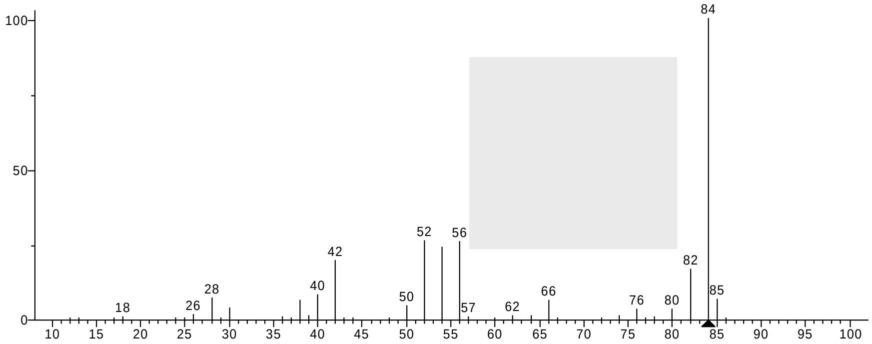


Mass	Abundance	*Max
209	100.00000	100.00
210	14.05319	14.05
211	1.31377	1.31
212	0.09251	0.09
213	0.00503	0.01
214	0.00022	0.00
215	0.00001	0.00

Determine the elemental composition of the following molecular ion. Note that there isotopic abundances are exact, there is no error.

- Work in groups, list evidence in board IN ORDER of use
- Note: this was in a cume in 2006

Group Question: identify this molecule



10 largest peaks:

84 999 |	52 261 |	56 259 |	54 239 |	42 197 |
82 167 |	40 81 |	28 72 |	85 68 |	66 65 |

- Work in groups, list evidence in board IN ORDER of use
- Note: this has been a past HW & exam

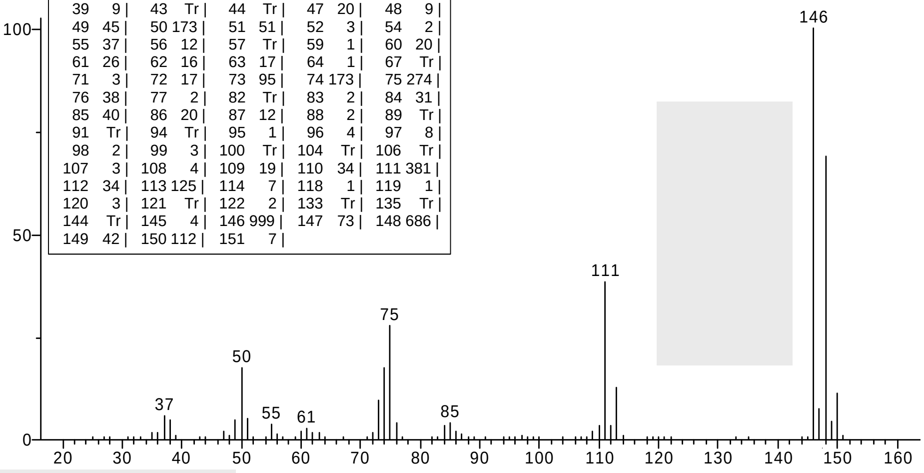
Group Question: identify this molecule

10 largest peaks:

146 999 |	148 686 |	111 381 |	75 274 |	50 173 |
74 173 |	113 125 |	150 112 |	73 95 |	147 73 |

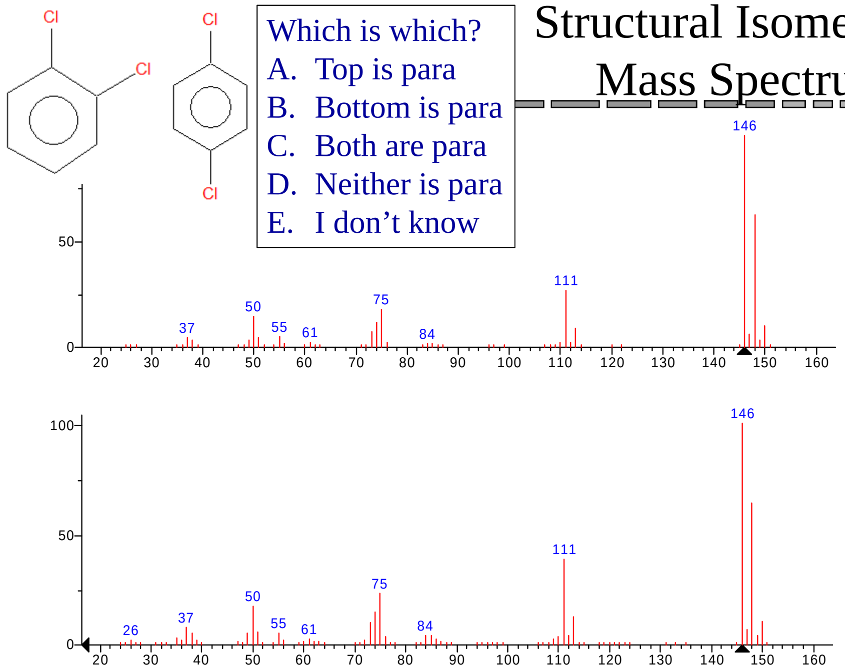
78 m/z Values and Intensities:

25	5 |	27	2 |	28	5 |	31	Tr |	32	3 |
33	Tr |	35	17 |	36	14 |	37	58 |	38	47 |
39	9 |	43	Tr |	44	Tr |	47	20 |	48	9 |
49	45 |	50	173 |	51	51 |	52	3 |	54	2 |
55	37 |	56	12 |	57	Tr |	59	1 |	60	20 |
61	26 |	62	16 |	63	17 |	64	1 |	67	Tr |
71	3 |	72	17 |	73	95 |	74	173 |	75	274 |
76	38 |	77	2 |	82	Tr |	83	2 |	84	31 |
85	40 |	86	20 |	87	12 |	88	2 |	89	Tr |
91	Tr |	94	Tr |	95	1 |	96	4 |	97	8 |
98	2 |	99	3 |	100	Tr |	104	Tr |	106	Tr |
107	3 |	108	4 |	109	19 |	110	34 |	111	381 |
112	34 |	113	125 |	114	7 |	118	1 |	119	1 |
120	3 |	121	Tr |	122	2 |	133	Tr |	135	Tr |
144	Tr |	145	4 |	146	999 |	147	73 |	148	686 |
149	42 |	150	112 |	151	7 |				



- Work in groups, list evidence in board IN ORDER of use
- Note: this has been a past HW & exam

Structural Isomers vs. Mass Spectrum

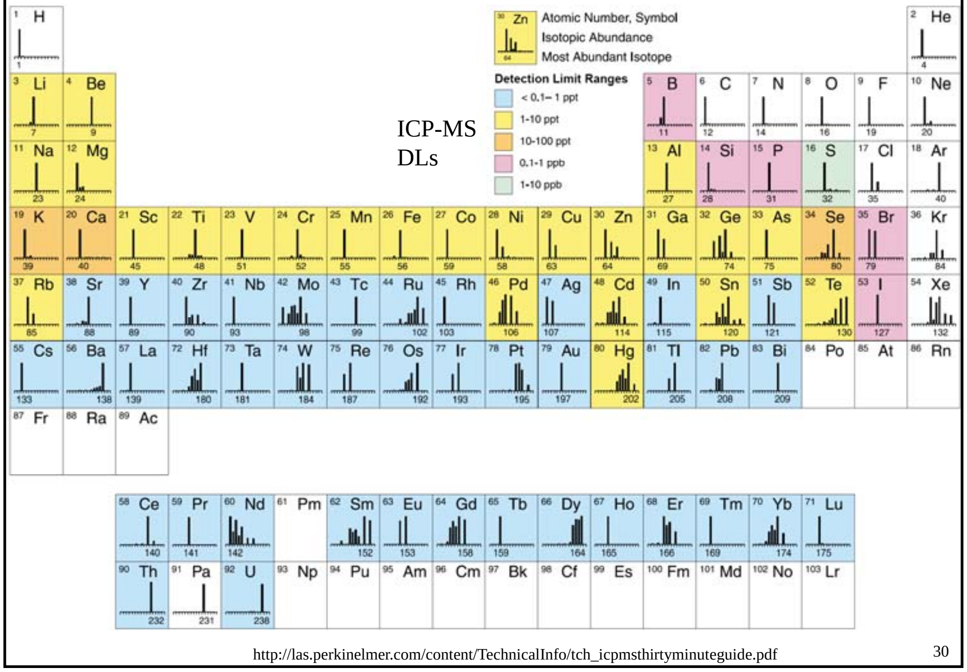


Which is which?

A. Top is para
B. Bottom is para
C. Both are para
D. Neither is para
E. I don’t know

B.S.

Isotopes of other Elements



ICP-MS
DLs

http://las.perkinelmer.com/content/TechnicalInfo/tch_icpmsthirtyminuteguide.pdf

Find Unusual Element in this Molecule