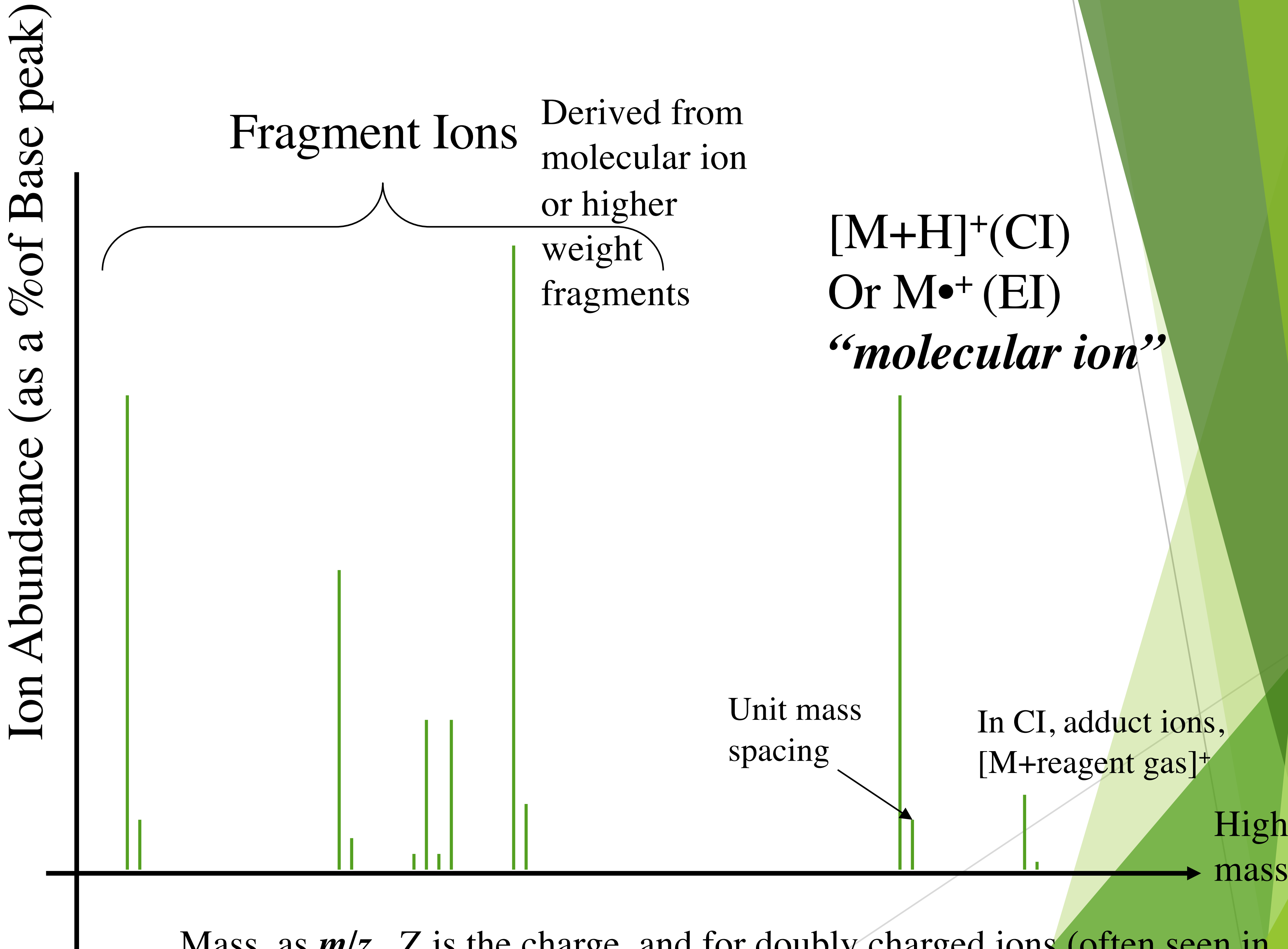
Front Ends:
- GC
- LC
- SPME
- Electrophoresis
- Ion Mobility

Ionization Sources:
- Electron Impact (EI)
- Atmospheric Pressure Chemical Ionization (APCI)
- MALDI
- Electrospray/ Nanospray Ionization (ESI)
- Corona Discharge
- Inductively Coupled Plasma (ICP)
- FAB, SIMS

Mass (Ion) Analyzers:
- Linear Quadrupole
- Quadrupole Ion Trap (QIT)
- Time-of-Flight (TOF)
- Ion Cyclotron Resonance (FT-MS)
- Sectors
- OrbiTrap
- Ion Mobility
- Any Combination Hybrids (Triple Quads, Q-TOF, TOF-TOF, IM-TOF, IM-Q)

Detection:
- Faraday Cup
- Electron Multiplier
- Microchannel Plate

What's in a Mass Spectrum?



Mass, as ***m/z***. Z is the charge, and for doubly charged ions (often seen in macromolecules), masses show up at half their proper value

Molecular Ions
give us the molecular mass

Electron Impact

$^{-}e\bullet$ $^{-}e\bullet$

M

$^{-}e\bullet$ $^{-}e\bullet$ $^{-}e\bullet$ $^{-}e\bullet$

$2e^{-}\bullet$

Dislodges an electron

$M^{+}\bullet$

Chemical Ionization

H^{+} H^{+} H^{+}

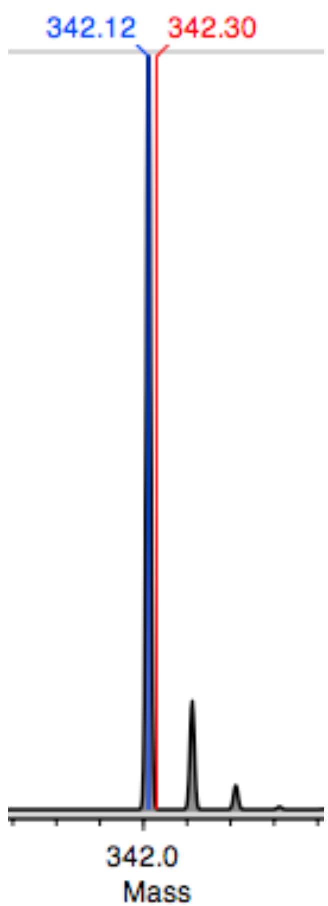
M

H^{+} H^{+}

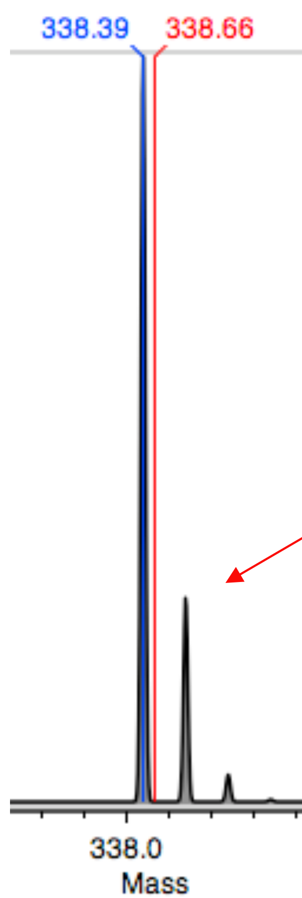
$[M+H]^{+}$

Weighs ***one more*** than MW

Isotope Patterns in Ion Clusters



$C_{24}H_{50}$



$C_{12}H_{22}O_{11}$

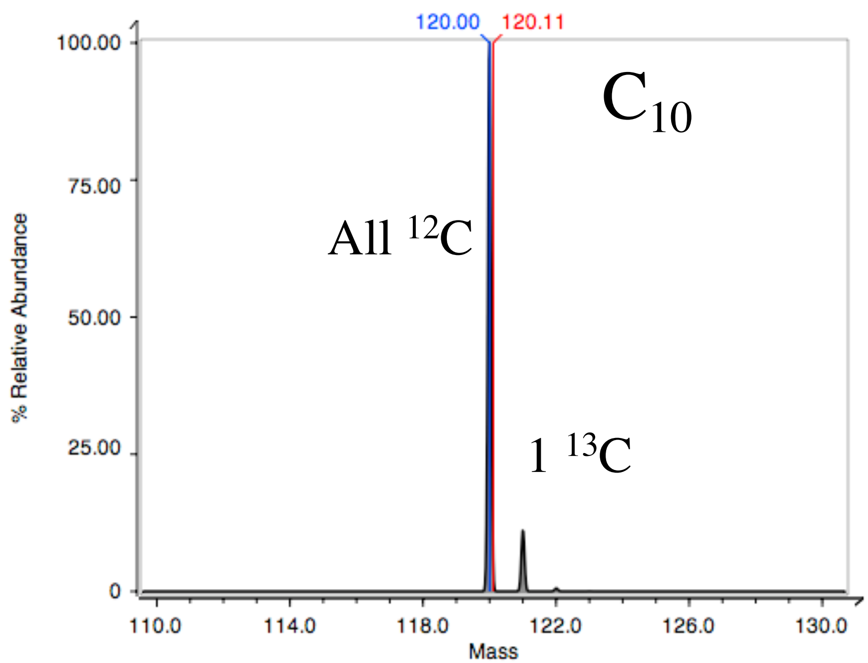
Here are two molecular ions of nearly the same m/z. One of them is "carbon-rich", and has a larger number of ^{13}C's

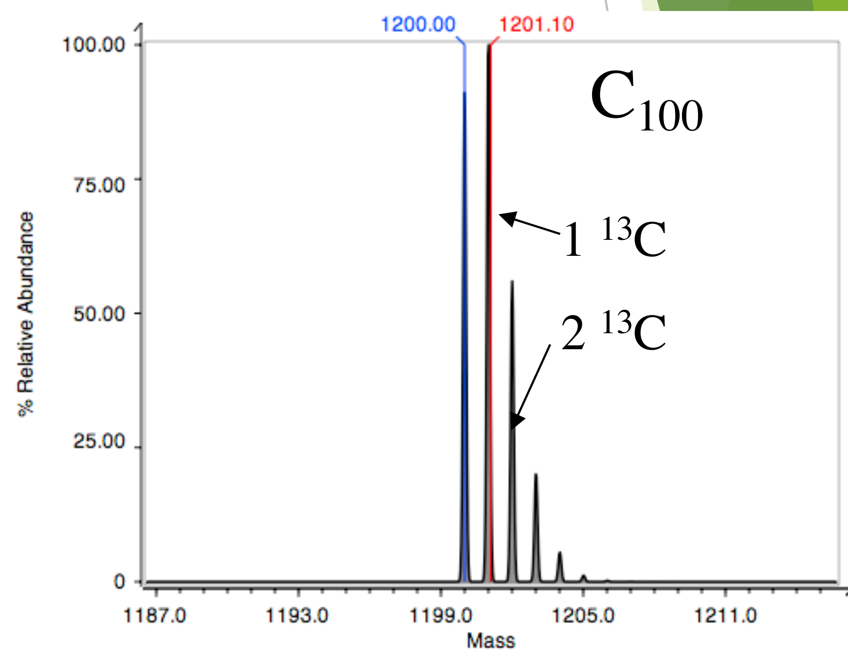
The other, presumably has proportionately, more heteroatoms

Why is this Important?

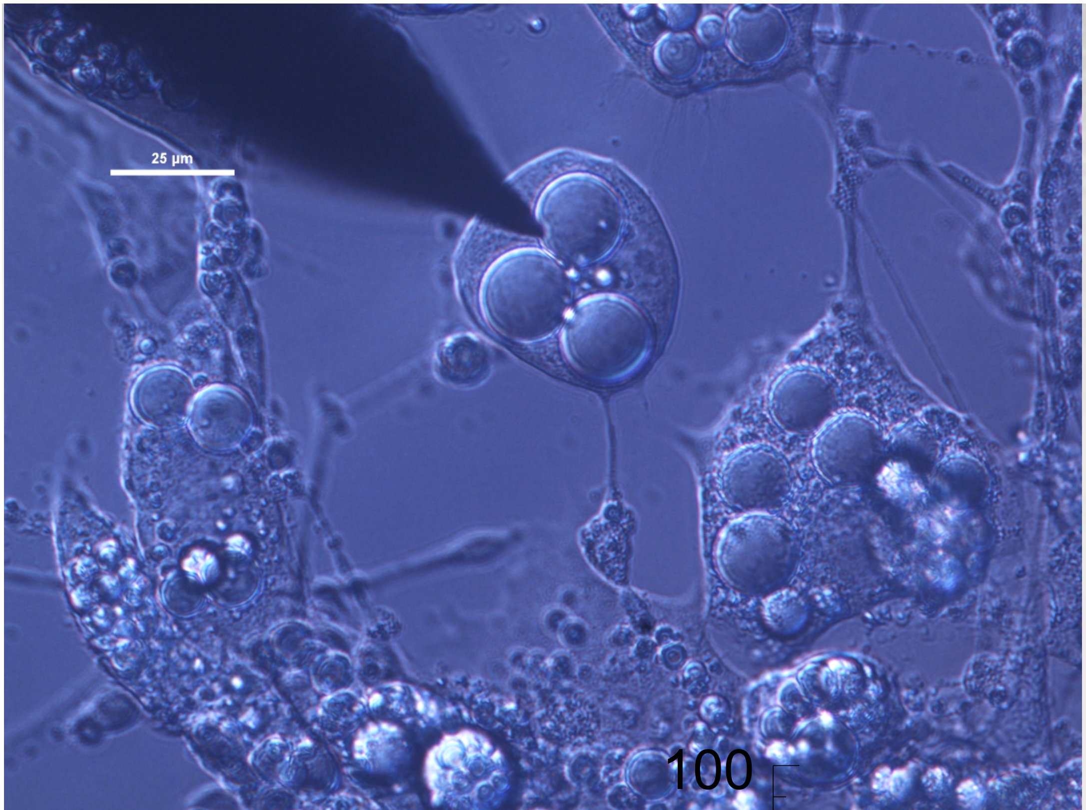
A rule of thumb, made possible by knowing the isotopic abundance is that the number of C in a formula is given by:

$$N = Intensity\frac{[M+1]}{[M]}x90.1$$

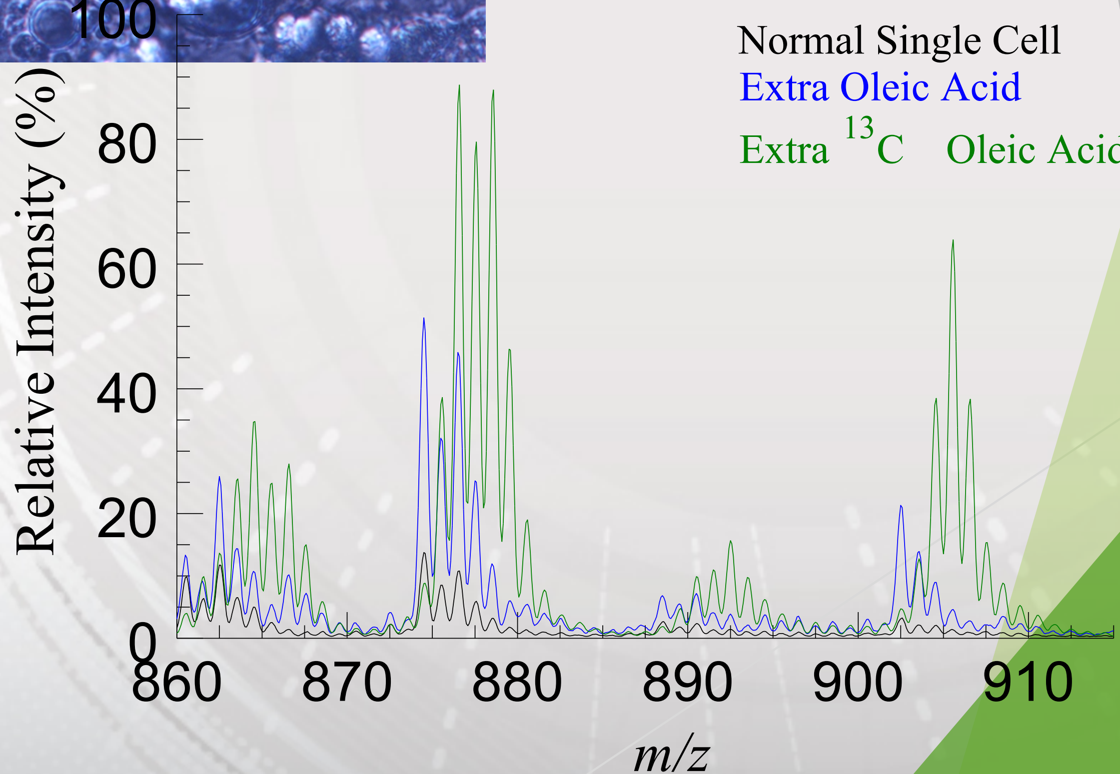




From this, it is clear that for large or macromolecules, there will be practically no population having all ^{12}C or even only 1 ^{13}C



Phelps, M.; Hamilton, J.; Verbeck, G.F., "Nanomanipulation-coupled nanospray mass spectrometry as an approach for single cell analysis", Rev. Sci. Inst., 85 (2014) 124101.



Reading a Mass Spec from the $M^{+}\bullet$ Down (EI)

Fragment	Due to loss of…	Interpretation
$M^{+}\bullet$ -1	-H•	Aldehydes, tert. Alcohols, cyclic amines
$M^{+}\bullet$ -2	Multiple -H•	Secondary alcohols
$M^{+}\bullet$ -3	Multiple -H•	Primary alcohols
$M^{+}\bullet$ -4 to -13	(doubtful)	Consider contaminants
$M^{+}\bullet$ -14	(doubtful)	$CH_2\bullet$, N• not good losses
$M^{+}\bullet$ -15	$CH_3\bullet$	Available methyl groups, methylesters
$M^{+}\bullet$ -16	O•	Peroxides
$M^{+}\bullet$ -17	OH•	Alcohols, phenols, RCO_2H
$M^{+}\bullet$ -18	H_2O	alcohols
$M^{+}\bullet$ -19	-F•	
$M^{+}\bullet$ -20	-HF	
$M^{+}\bullet$ -21 to -25	No peaks expected	
$M^{+}\bullet$ -26	HC≡CH	
$M^{+}\bullet$ -27	•HC=CH2 or HCN	HCN from pyridine, anilines
$M^{+}\bullet$ -28	C≡O or CH_2=CH_2	Check for McLafferty R&R

Nominal Mass

199.

Molecular Weight	Empirical Formula	Compound Name, Monograph Number
199.852089	C_2HCl_5	Pentachloroethane, 6900
199.883622	$C_3H_6Br_2$	Propylene Dibromide, 7642 Trimethylene Bromide, 9383
199.947291	$C_7H_5BrO_2$	p-Bromobenzoic Acid, 1407
199.983614	$C_3H_5ClN_2O_6$	Clonitrate, 2355
199.983676	C_8H_9BrO	p-Bromophenol, Ethyl ether, 1432
199.987226	C_4F_8	Octafluorocyclobutane, 6555
199.995703	$C_7H_4O_7$	Meconic Acid, 5608, 6253
199.998870	$C_7H_5ClN_2O_3$	Aklomide, 188
200.006936	$C_6H_4N_2O_6$	2,4-Dinitroresorcinol, 3281
200.008591	$C_4H_9O_7P$	D-Erythrose 4-Phosphate, 3614
200.017498	$C_8H_9ClN_2S$	p-Chlorobenzylpseudothiourea, 2102
200.024022	$C_9H_9ClO_3$	(4-Chloro-o-toloxy)acetic Acid, 2158
200.050716	$C_9H_{12}O_3S$	Ethyl p-Toluenesulfonate, 3808
200.054555	$C_6H_8N_4O_4$	Ronidazole, 8021
200.059721	$C_8H_9FN_2O_3$	Ftorafur, 4126
200.061950	$C_8H_{12}N_2O_2S$	Thiobarbital, 9051
200.083730	$C_{13}H_{12}O_2$	Monobenzone, 6085
200.094963	$C_{12}H_{12}N_2O$	Harmalol, 4469
200.104859	$C_{10}H_{16}O_4$	Camphoric Acid, 1735, 1450
200.131349	$C_{13}H_{16}N_2$	Tetrahydrozoline, 8934
200.177630	$C_{12}H_{24}O_2$	Ethyl Caprate, 3707 Lauric Acid, 5230
200.641549	$[C_{27}H_{35}N_3]^{2+}$	Methyl Green, Cation (half mass) 5949
200.906979	$C_3AlN_3S_3$	Aluminum Thiocyanate, 371

Here for example is a list of the compounds in the Merck Index (9th ed) that weigh nominally, 200

Exact mass measurements can easily distinguish

These instruments (and other) can generate exhaustive lists of possible structure formulas near the exact mass value.

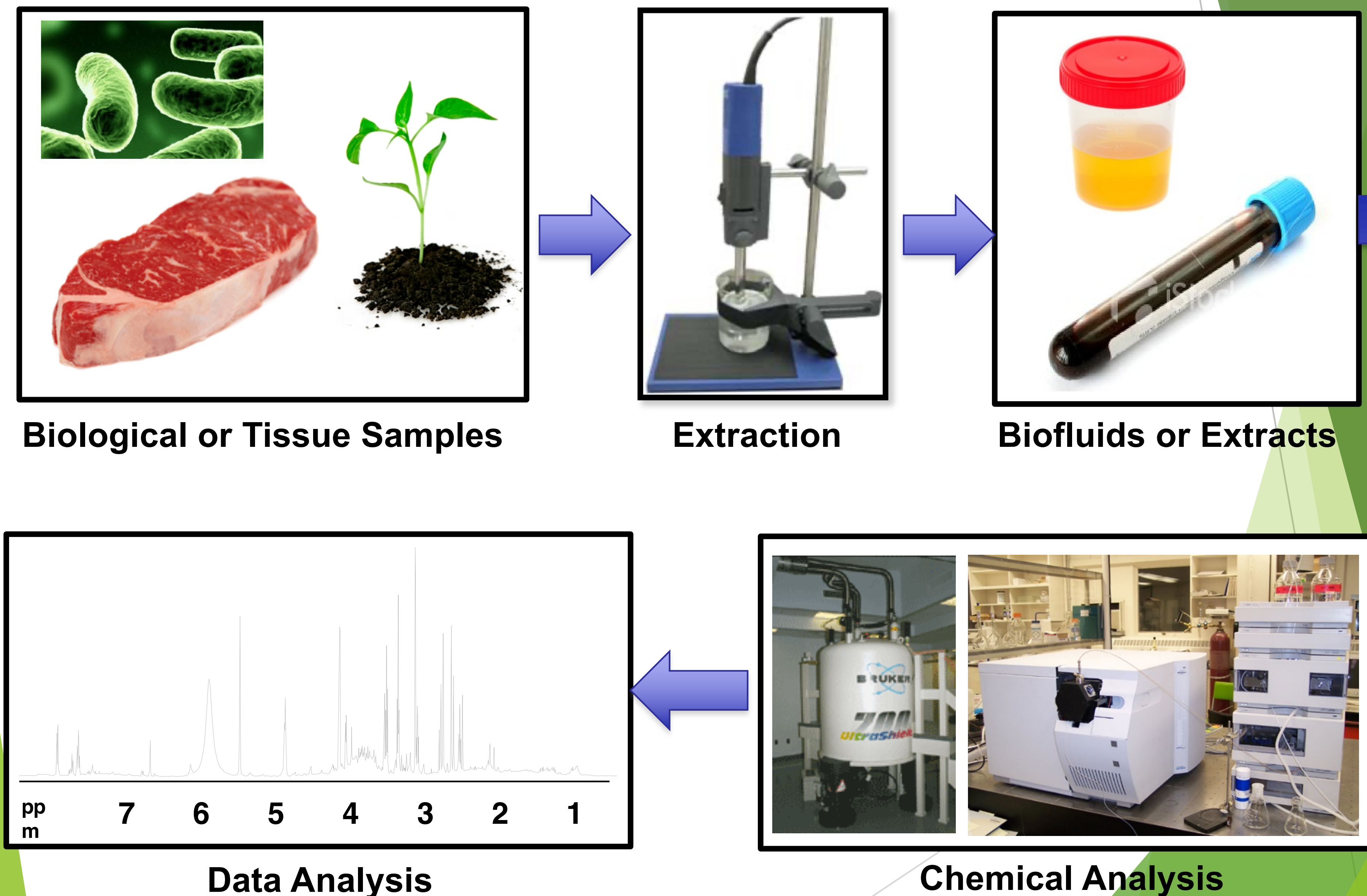
Example, m/z's for 157

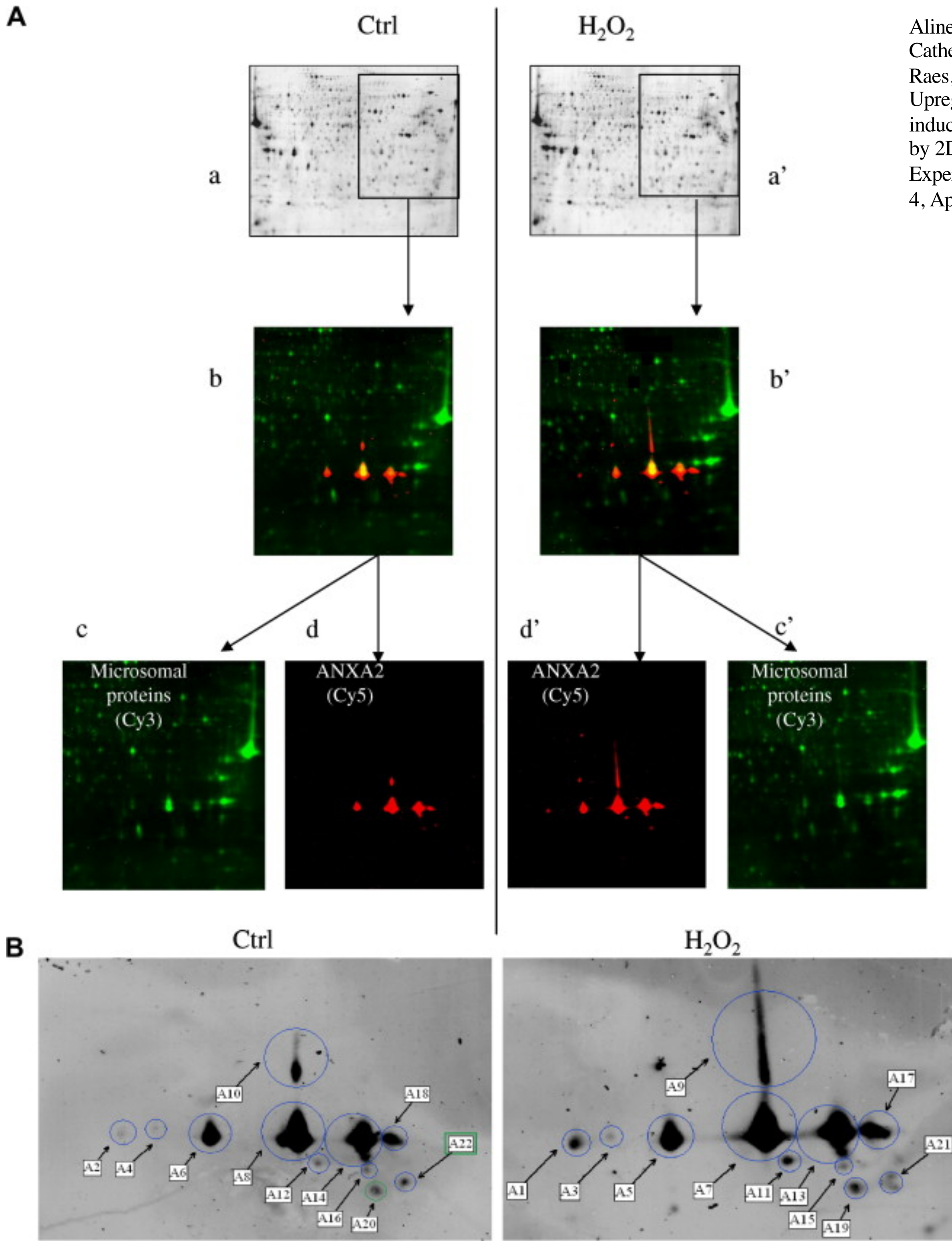
molar mass: 157

Formula	M+1	M+2	MM	e/o	dbr
HN2O8	1.05	1.60	156.9732	e	1.5
HN10O	3.75	0.20	157.0337	e	5.5
H3N3O7	1.41	1.40	156.9971	o	1
H3N11	4.12	0.00	157.0576	o	5
H5N4O6	1.78	1.20	157.021	e	0.5
H7N5O5	2.14	1.00	157.0448	o	0
CHO9	1.45	1.80	156.9619	e	1.5
CHN8O2	4.15	0.43	157.0224	e	5.5
CH3NO8	1.81	1.60	156.9858	o	1
CH3N9O	4.51	0.24	157.0463	o	5
CH5N2O7	2.17	1.41	157.0096	e	0.5
CH5N10	4.88	0.04	157.0702	e	4.5
CH7N3O6	2.54	1.21	157.0335	o	0
C2HN6O3	4.55	0.66	157.0111	e	5.5
C2H3N7O2	4.91	0.47	157.0350	o	5
C2H5O8	2.57	1.61	156.9983	e	0.5
C2H5N8O	5.27	0.28	157.0589	e	4.5
C2H7NO7	2.93	1.42	157.0222	o	0
C2H7N9	5.64	0.09	157.0827	o	4
C3HN4O4	4.94	0.89	156.9998	e	5.5
C3H3N5O3	5.31	0.70	157.0237	o	5
C3H5N6O2	5.67	0.51	157.0476	e	4.5
C3H7N7O	6.03	0.33	157.0714	o	4
C3H9N8	6.4	0.14	157.0953	e	3.5
C4HN2O5	5.34	1.11	156.9885	e	5.5
C4H3N3O4	5.70	0.93	157.0124	o	5
C4H5N4O3	6.07	0.74	157.0362	e	4.5
C4H7N5O2	6.43	0.56	157.0601	o	4
C4H9N6O	6.79	0.38	157.0840	e	3.5
C4H11N7	7.16	0.20	157.1078	o	3
C5HO6	5.74	1.32	156.9772	e	5.5
C5H3NO5	6.10	1.15	157.0011	o	5
C5H5N2O4	6.46	0.97	157.025	e	4.5
C5H7N3O3	6.83	0.79	157.0488	o	4
C5H9N4O2	7.19	0.61	157.0727	e	3.5
C5H11N5O	7.55	0.44	157.0965	o	3
C5H13N6	7.92	0.26	157.1204	e	2.5
C6HN6	8.84	0.33	157.0264	e	9.5
C6H5O5	6.86	1.19	157.0136	e	4.5
C6H7NO4	7.22	1.02	157.0375	o	4
C6H9N2O3	7.59	0.84	157.0614	e	3.5
C6H11N3O2	7.95	0.67	157.0852	o	3
C6H13N4O	8.31	0.50	157.1091	e	2.5
C6H15N5	8.68	0.32	157.1329	o	2
C7HN4O	9.23	0.58	157.0151	e	9.5
C7H3N5	9.60	0.41	157.0390	o	9
C7H9O4	7.98	1.07	157.0501	e	3.5
C7H11NO3	8.35	0.90	157.0739	o	3
C7H13N2O2	8.71	0.73	157.0978	e	2.5
C7H15N3O	9.07	0.56	157.1217	o	2
C7H17N4	9.44	0.40	157.1455	e	1.5
C8HN2O2	9.63	0.81	157.0038	e	9.5
C8H3N3O	9.99	0.65	157.0277	o	9
C8H5N4	10.36	0.49	157.0516	e	8.5
C8H13O3	9.11	0.96	157.0865	e	2.5
C8H15NO2	9.47	0.80	157.1104	o	2
C8H17N2O	9.83	0.64	157.1342	e	1.5
C8H19N3	10.20	0.47	157.1581	o	1
C9HO3	10.03	1.05	156.9925	e	9.5
C9H3NO2	10.39	0.89	157.0164	o	9
C9H5N2O	10.75	0.73	157.0403	e	8.5
C9H7N3	11.12	0.57	157.0641	o	8
C9H17O2	10.23	0.87	157.1229	e	1.5
C9H19NO	10.59	0.71	157.1468	o	1
C9H21N2	10.96	0.55	157.1706	e	0.5
C10H5O2	11.15	0.97	157.029	e	8.5
C10H7NO	11.51	0.81	157.0528	o	8
C10H9N2	11.88	0.66	157.0767	e	7.5
C10H21O	11.35	0.79	157.1593	e	0.5
C10H23N	11.72	0.64	157.1832	o	0
C11H9O	12.27	0.90	157.0654	e	7.5
C11H11N	12.64	0.75	157.0892	o	7
C12H13	13.40	0.84	157.1018	e	6.5
C13H	14.32	0.97	157.0078	e	13.5

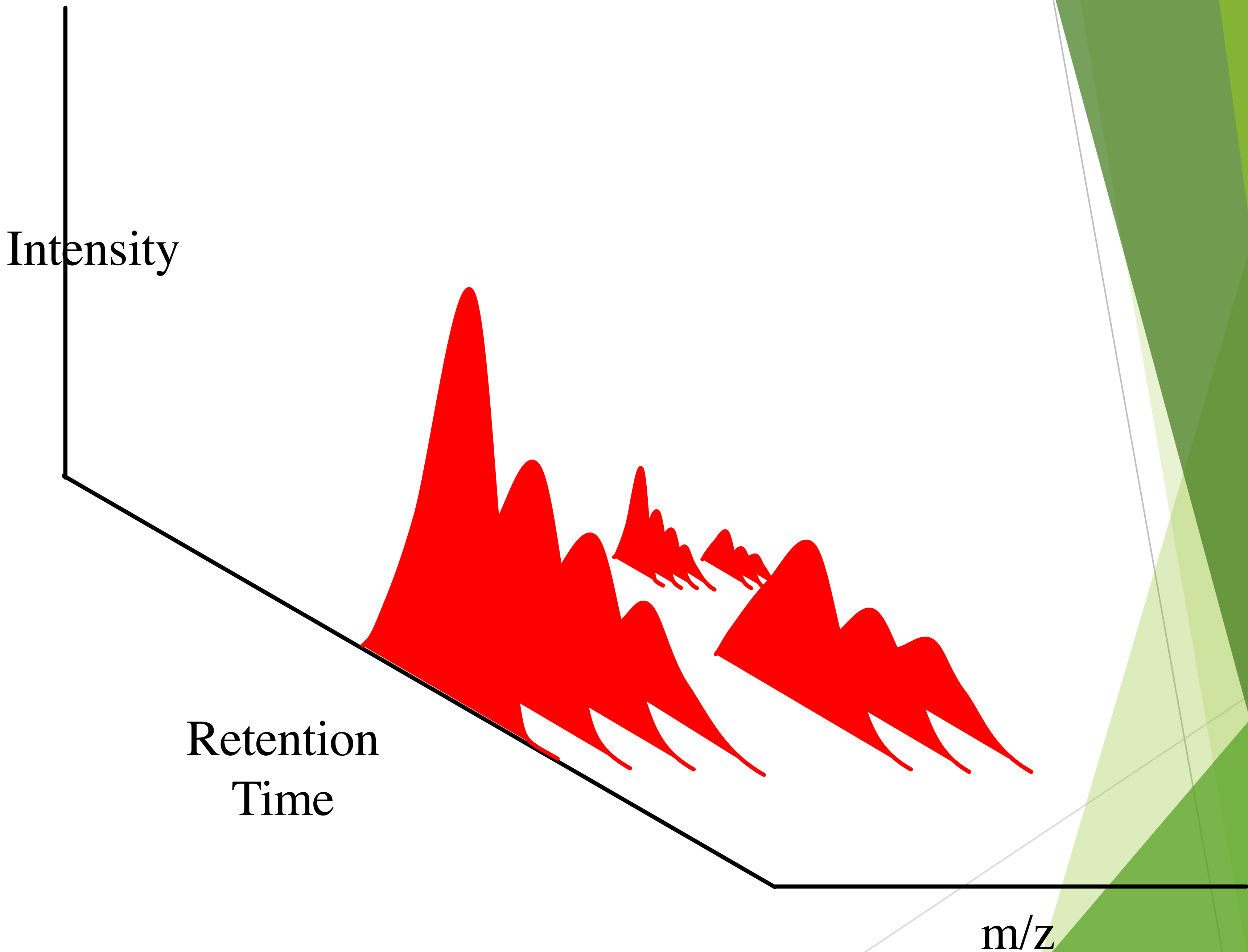
Clearly, some are not realistic!

Metabolomics Workflow





Aline Chrétien, Edouard Delaive, Marc Dieu, Catherine Demazy, Noëlle Ninane, Martine Raes, Olivier Toussaint
Upregulation of annexin A2 in H2O2-induced premature senescence as evidenced by 2D-DIGE proteome analysis
Experimental Gerontology, Volume 43, Issue 4, April 2008, Pages 353–359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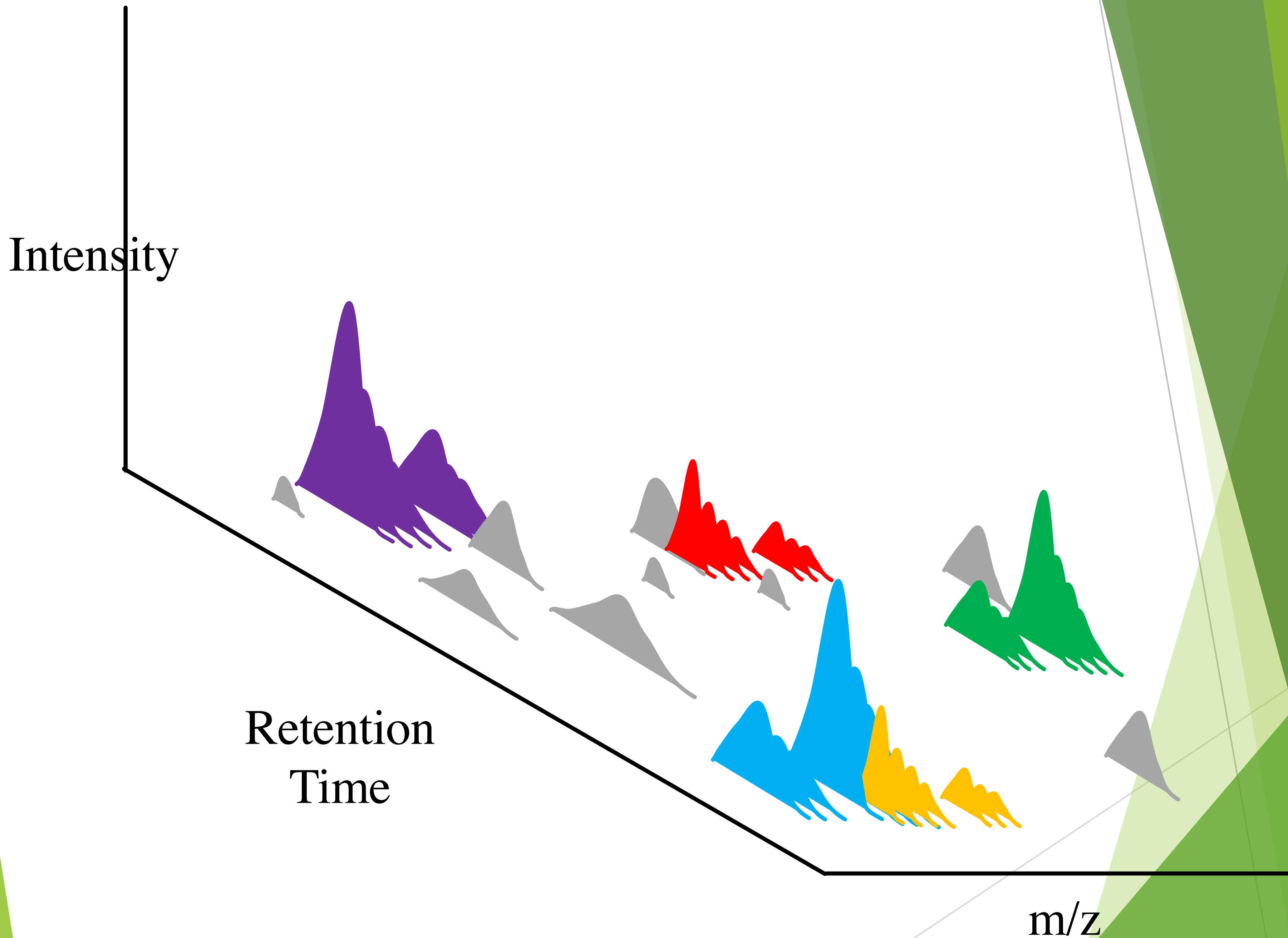
Retention
Time
m/z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m/z