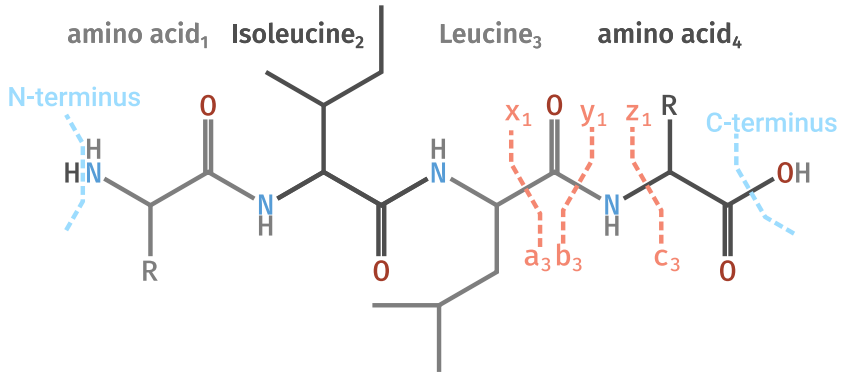
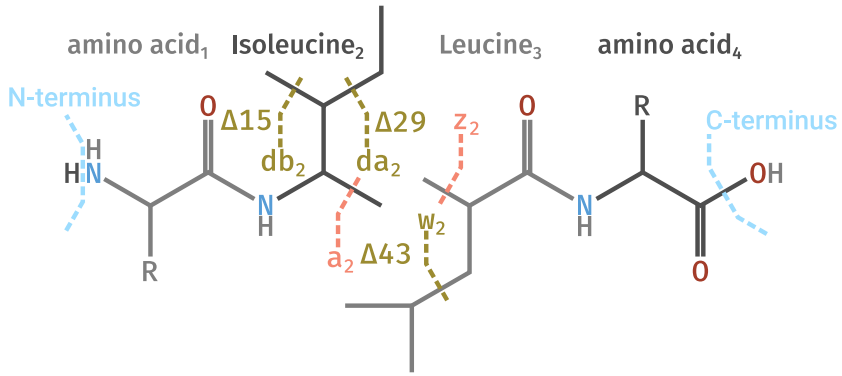
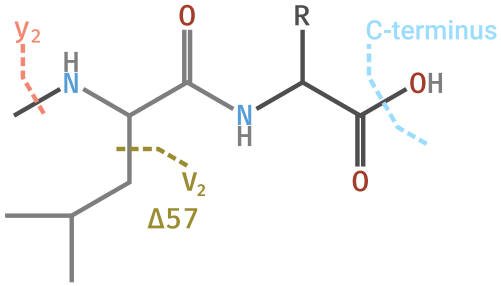
Backbone fragmentation



	Formula (h = H^+ × z)	Mass (h = 1.008 × z)
a	$\sum^{n}$(AA) − CO + h	$\sum^{n}$(AA) − 27.995 + h
b	$\sum^{n}$(AA) + h	$\sum^{n}$(AA) + h
c	$\sum^{n}$(AA) + NH_3 + h	$\sum^{n}$(AA) + 17.027 + h
The "c-1" radical ion, which arises when the c ion loses a hydrogen to the z·+ ion, is also observed in ETD.		
d	$\sum^{n-1}$(AA) + C_2H_3N + h	$\sum^{n-1}$(AA) + 41.027 + h
v	$\sum^{c-1}$(AA) + C_2H_2NO + h	$\sum^{c-1}$(AA) + 56.014 + h
w	$\sum^{c-1}$(AA) + C_3H_3O + h	$\sum^{c-1}$(AA) + 55.018 + h
x	$\sum^{c}$(AA) + CO − H_2 + h	$\sum^{c}$(AA) + 25.979 + h
y	$\sum^{c}$(AA) + H_2O + h	$\sum^{c}$(AA) + 18.011 + h
z	$\sum^{c}$(AA) + O − NH + h	$\sum^{c}$(AA) + 0.984 + h
The z·+ radical ion, which is heavier by one hydrogen than the "z ion" originally defined by Biemann, is also observed in ETD spectra. Likewise for the "z·+1" ion, which is one hydrogen heavier still.		

Side chain fragmentation / satellite ions

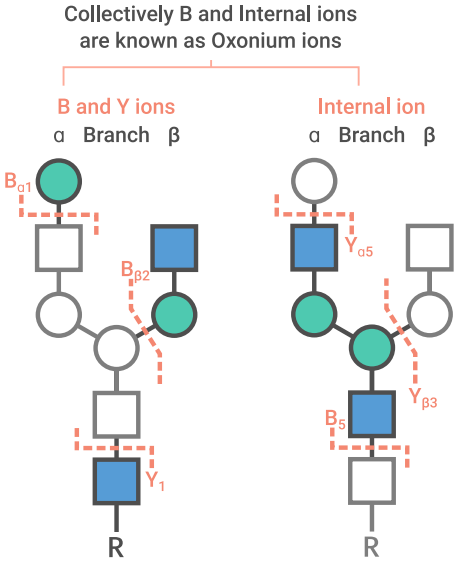




The satellite ions are formed as secondary fragmentation, d from an a ion, w from a z ion. For Threonine and Isoleucine there are two possible d and w ions. These can be listed as 'd/wa_N' and 'd/wb_N' where a is the heaviest of the two options. For Threonine wa has an additional group of OH and wb a group of CH_3. Isoleucine wa has an additional group of C_2H_5, and wb a group of CH_3. Valine is a special case; it has CH_3 as additional mass. Glycine, alanine, and proline have no satellite ions. The v ion is full loss of the sidechain from a y ion. For ETD, side chain loss as seen in v ions can be observed on any fragment with any sidechain loss. This is most often visible from the precursor.

Glycan

Collectively B and Internal ions are known as Oxonium ions



Ion	Formula	Mass	Ion	Formula	Mass
H-$C_2H_6O_3$	$C_4H_5O_2$	85.0284	S-H_2O	$C_{11}H_{16}NO_7$	274.0921
H-CH_6O_3	$C_5H_5O_2$	97.0284	S	$C_{11}H_{18}NO_8$	292.1027
H-2H_2O	$C_6H_7O_3$	127.0390	G-H_2O	$C_{11}H_{16}NO_8$	290.0870
H-H_2O	$C_6H_9O_4$	145.0495	G	$C_{11}H_{18}NO_9$	308.0976
H	$C_6H_{11}O_5$	163.0601	H+N	$C_{14}H_{24}NO_{10}$	366.1395
N-$C_4H_8O_4$	C_4H_6NO	84.0444	2N	$C_{16}H_{27}N_2O_{10}$	407.1660
N-$C_2H_6O_3$	$C_6H_8NO_2$	126.0550	H+2N	$C_{22}H_{37}N_2O_{15}$	569.2188
N-CH_6O_3	$C_7H_8NO_2$	138.0550	H+N+S	$C_{25}H_{41}N_2O_{18}$	657.2349
N-$C_2H_4O_2$	$C_6H_{10}NO_3$	144.0655			
N-2H_2O	$C_8H_{10}NO_3$	168.0655			
N-H_2O	$C_8H_{12}NO_4$	186.0761			
N	$C_8H_{14}NO_5$	204.0867			

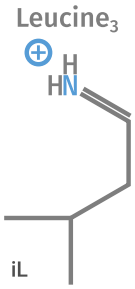
H=Hex
N=HexNAc
S/A=Neu5Ac
G=Neu5Gc

Formula & Mass are MH+

doi: 10.1016/j.trac.2018.09.007

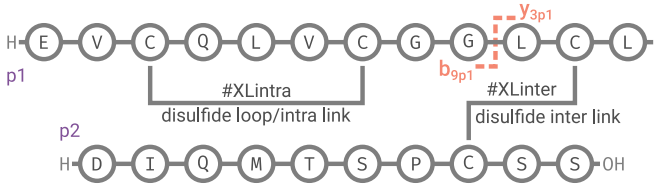
Immonium

Formed by double backbone cleavage. Commonly fragments further by neutral loss. These fragments indicate existence of certain amino acids, but not all amino acids form immonium ions. The immonium ions have a mass between 0 and 160 Da. Formula: amino acid - CO + H



Amino Acid	Formula	Mass	Amino Acid	Formula	Mass
A	C_2H_6N	44.050	K	$C_5H_{13}N_2$	101.108
R	$C_5H_{13}N_4$	129.114	M	$C_4H_{10}NS$	104.053
N	$C_3H_7N_2O$	87.056	F	$C_8H_{10}N$	120.081
D	$C_3H_6NO_2$	88.040	P	C_4H_8N	70.066
C	C_2H_6NS	76.022	S	C_2H_6NO	60.045
E	$C_4H_8NO_2$	102.056	T	C_3H_8NO	74.061
Q	$C_4H_9N_2O$	101.071	W	$C_{10}H_{11}N_2$	159.092
G	CH_4N	30.034	Y	$C_8H_{10}NO$	136.076
H	$C_5H_8N_3$	110.072	V	$C_4H_{10}N$	72.081
I/L/J	$C_5H_{12}N$	86.097	Formula & Mass are MH+		

Cross-links



Two possible masses for y_{3p1}

y_{3p1}└┐#XLinter LCL + OH - $H_{(broken\ disulfide)}$

y_{3p1}└┐#XLinter LCL + OH - $2H_{(intact\ disulfide)}$ + p2

One possible mass for b_{9p1}

b_{9p1}└┐#XLintra EVCQLVCGG + H - $2H_{(disulfide)}$

This disulfide is a loop link, so it could break either in the linker or in any of the contained amino acids without changing the final mass of the fragment.

Note that if you want to see breaking cross-linkers you will need to define your own custom linkers in the Annotator as the breaking is not defined in any of the used modification databases.

To annotate these and more on your own data see: github.com/snijderlab/annotator

"An easy tool empowering everyone to annotate complex spectra"

Author : Douwe Schulte
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V1.0