Electronic Supplementary Material (ESI) for Analyst.

Uncoiling Collagen: A Multidimensional Mass Spectrometry Study

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Supplementary Information

Table S1 Assignment table for the full MS spectrum (Figure 1) Peaks marked with a † were used to internally calibrate the spectrum. Peaks marked with a * have been further studied by MS/MS

Assignment	Peptide Elemental Composition	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
†HP MIX (8+)		2121.93315	2121.93460	-0.68
†HP MIX (7+)		1821.95231	1821.95285	0.29
†HP MIX (6+)		1521.97148	1521.96989	-1.04
$[\alpha1\ (802\text{-}861) + 3H + Na]^{4+}$	$C_{224}H_{339}N_{65}O_{77}$	1299.36800	1299.36756	-0.34
$[\alpha1\ (802\text{-}861) + 4H]^{4+}$	$C_{224}H_{339}N_{65}O_{77}$	1293.87251	1293.87286	0.27
$[\alpha2\ (518\text{-}571) + 3H + Na]^{4+}$	$C_{206}H_{320}N_{66}O_{76}$	1240.08287	1240.08551	2.13
$[\alpha2\ (518\text{-}571) + 4H]^{4+}$	$C_{206}H_{320}N_{66}O_{76}$	1234.58738	1234.58899	1.30
†HP MIX (5+)		1221.99063	1221.99097	0.28
$*[\alpha2\ (829\text{-}880) + 4H]^{4+}$	$C_{207}H_{322}N_{60}O_{75}$	1213.08796	1213.08920	1.03
$[\alpha2\ (829\text{-}880) + 4H]^{4+}$	$C_{207}H_{322}N_{60}O_{74}$	1209.08923	1209.08869	-0.44
$*[\alpha1\ (322\text{-}360) + 3H]^{3+}$	$C_{143}H_{219}N_{45}O_{52}$	1133.86981	1133.86999	0.16
$[\alpha2\ (947\text{-}972) + 2H]^{2+}$	$C_{99}H_{153}N_{29}O_{32}$	1131.06910	1131.07008	0.86
$[\alpha1\ (310\text{-}360) + 4H]^{4+}$	$C_{187}H_{291}N_{63}O_{66}$	1119.79106	1119.79151	0.40
$[\alpha2\ (505\text{-}541) + 3H]^{3+}$	$C_{137}H_{221}N_{49}O_{50}$	1118.54918	1118.54641	-2.47
$[\alpha2\ (449\text{-}484) + 3H]^{3+}$	$C_{145}H_{230}N_{44}O_{47}$	1114.23928	1114.23914	-0.13
$[\alpha2\ (572\text{-}607) + 3H]^{3+}$	$C_{141}H_{223}N_{45}O_{49}$	1111.21866	1111.21911	0.41
$[\alpha1\ (268\text{-}303) + 3H]^{3+}$	$C_{137}H_{213}N_{43}O_{52}S_1$	1109.17613	1109.17570	-0.39
$[\alpha1\ (\alpha1\ 538\text{-}573) + 3H]^{3+}$	$C_{136}H_{214}N_{44}O_{52}$	1099.52241	1099.52273	0.29
$[\alpha1\ (910\text{-}957) + 4H]^{4+}$	$C_{179}H_{281}N_{57}O_{67}$	1076.26561	1076.26544	-0.16
$[\alpha1\ (910\text{-}957) + 4H]^{4+}$	$C_{179}H_{281}N_{57}O_{66}$	1072.26689	1072.26761	0.68
$[\alpha1\ (947\text{-}994) + 4H]^{4+}$	$C_{182}H_{284}N_{60}O_{58}$	1060.53523	1060.53532	0.09
$[\alpha1\ (947\text{-}994) + 4H]^{4+}$	$C_{182}H_{284}N_{60}O_{57}$	1056.53650	1056.53588	-0.59
$[\alpha1\ (1062\text{-}1083) + 2H]^{2+}$	$C_{82}H_{134}N_{28}O_{29}$	988.50086	988.50120	0.35
$[\alpha1\ (763\text{-}795) + H + 2Na]^{3+}$	$C_{121}H_{193}N_{37}O_{43}$	966.46368	966.46382	0.15
$*[\alpha1\ (763\text{-}795) + 3H + CO]^{3+}$	$C_{122}H_{193}N_{37}O_{44}$	961.14068	961.14116	0.49
$*[\alpha1\ (763\text{-}795) + 2H + Na]^{3+}$	$C_{121}H_{193}N_{37}O_{43}$	959.13636	959.13651	0.16
$*[\alpha1\ (763\text{-}795) + 3H]^{3+}$	$C_{121}H_{193}N_{37}O_{44}$	957.14068	957.14091	0.24
†* $[\alpha1\ (763\text{-}795) + 3H]^{3+}$	$C_{121}H_{193}N_{37}O_{43}$	951.80905	951.80926	0.22
$[\alpha1\ (763\text{-}795) + 3H]^{3+}$	$C_{121}H_{193}N_{37}O_{42}$	946.47741	946.47750	0.10

[α2 (1022-1051) + 3H] $^{3+}$	$C_{115}H_{182}N_{40}O_{41}$	927.45349	927.45406	0.62
[α1 (310-360) + 5H]$^{5+}$	$C_{187}H_{291}N_{63}O_{66}$	896.03430	896.03552	1.36
[α2 (1016-1051) + 3H + Na]$^{4+}$	$C_{144}H_{229}N_{49}O_{46}$	851.67992	851.68054	0.72
*[α2 (422-448) + 3H]$^{3+}$	$C_{103}H_{169}N_{37}O_{37}S_1$	850.41397	850.41468	0.83
[α2 (1016-1051) + 4H]$^{4+}$	$C_{144}H_{229}N_{49}O_{46}$	846.18444	846.18557	1.34
[α1 (493-510) + 2H]$^{2+}$	$C_{71}H_{110}N_{22}O_{24}$	828.41045	828.41094	0.60
[α1 (538-573) + 4H]$^{4+}$	$C_{136}H_{214}N_{44}O_{52}$	824.89362	824.89397	0.42
[α2 (404-421) + 2H]$^{2+}$	$C_{66}H_{112}N_{24}O_{23}S_1$	821.40992	821.41035	0.52
[α1 (520-572) + 6H]$^{6+}$	$C_{203}H_{322}N_{66}O_{77}$	820.39578	820.39442	-1.65
[α1 (511-537) + 3H]$^{3+}$	$C_{100}H_{162}N_{32}O_{38}$	807.39821	807.39829	0.10
[α1 (511-537) + 3H]$^{3+}$	$C_{100}H_{162}N_{32}O_{37}$	802.06712	802.06739	0.34
[α1 (397-414) + 2H]$^{2+}$	$C_{67}H_{104}N_{22}O_{23}$	793.38951	793.39018	0.84
[α1 (574-597) + 3H]$^{3+}$	$C_{95}H_{152}N_{30}O_{32}S_1$	753.37093	753.37181	1.16
[α1 (865-880) + 2Na]$^{2+}$	$C_{61}H_{94}N_{20}O_{22}$	752.33180	752.33224	0.58
[α1 (574-597) + 3H]$^{3+}$	$C_{95}H_{152}N_{30}O_{31}S_1$	748.03930	748.03971	0.55
[α1 (865-880) + H +Na]$^{2+}$	$C_{61}H_{94}N_{20}O_{22}$	741.34083	741.34135	0.70
† *[α1 (865-880) + 2H]$^{2+}$	$C_{61}H_{94}N_{20}O_{22}$	730.34986	730.35057	0.98
[α2 (1016-1051) + 5H]$^{5+}$	$C_{144}H_{229}N_{49}O_{46}$	677.14901	677.14956	0.82
[α1 (1062-1083) + H + 2Na]$^{3+}$	$C_{82}H_{134}N_{28}O_{29}$	673.99096	673.99142	0.68
[α2 (973-994) + 2H + Na]$^{3+}$	$C_{83}H_{133}N_{31}O_{27}$	673.66750	673.66805	0.82
[α2 (973-994) + 2H + Na]$^{3+}$	$C_{83}H_{133}N_{31}O_{26}$	668.33586	668.33605	0.28
[α1 (1062-1083) + 2H + Na]$^{3+}$	$C_{82}H_{134}N_{28}O_{29}$	666.66364	666.66401	0.55
[α2 (973-994) + 3H]$^{3+}$	$C_{83}H_{133}N_{31}O_{27}$	666.34019	666.34046	0.41
[α2 (973-994) + 3H]$^{3+}$	$C_{83}H_{133}N_{31}O_{26}$	661.00855	661.00898	0.66
*[α1 (1062-1083) + 3H]$^{3+}$	$C_{82}H_{134}N_{28}O_{29}$	659.33633	659.33679	0.70
[α2 (326-340) + 2Na]$^{2+}$	$C_{53}H_{90}N_{18}O_{18}$	656.32325	656.32367	0.64
[α2 (326-340) + H + Na]$^{2+}$	$C_{53}H_{90}N_{18}O_{18}$	645.33228	645.33250	0.35
† *[α2 (326-340) + 2H]$^{2+}$	$C_{53}H_{90}N_{18}O_{18}$	634.34130	634.34193	0.99
[α1 (958-969) + 2H]$^{2+}$	$C_{51}H_{89}N_{19}O_{17}$	620.84147	620.84180	0.53
[α2 (1052-1065) + 2H]$^{2+}$	$C_{50}H_{82}N_{18}O_{18}$	612.31000	612.31058	0.94
[α2 (1066-1078) + 2H]$^{2+}$	$C_{52}H_{89}N_{17}O_{16}$	604.84094	604.84162	1.13
[α1 (685-696) + 2H]$^{2+}$	$C_{47}H_{76}N_{16}O_{15}$	553.29108	553.29166	1.05
† *[α1 (253-267) + 3H]$^{3+}$	$C_{62}H_{105}N_{21}O_{20}S_1$	499.59279	499.59327	0.95

RMS error = 0.79 ppm

Table S2 - Assignment table for the CAD spectrum of the tryptic digest peptide ion [α1 (763-795) + 3H] $^{3+}$ at *m/z* 951.80926 (Figure 3a). Peaks marked with a † were used to internally calibrate the spectrum. *P = hydroxyproline. Sequence: GLTGPIGP*PGPAGA*PGDKGEAGPSGPAGPTGAR

Assignment	Elemental Composition	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
$^{\dagger}y_{24}$	$C_{84}H_{134}N_{28}O_{32}$	2047.97918	2047.97953	0.17
b_{22}	$C_{81}H_{127}N_{23}O_{29}$	1886.92429	1886.9247	0.22
b_{21}	$C_{79}H_{124}N_{22}O_{28}$	1829.90283	1829.90392	0.60
y_{21}	$C_{74}H_{119}N_{25}O_{29}$	1822.86784	1822.87097	1.72
b_{20}	$C_{76}H_{119}N_{21}O_{27}$	1758.86571	1758.86643	0.41
$^{\dagger}y_{19}$	$C_{69}H_{111}N_{23}O_{27}$	1694.80926	1694.81009	0.49
?			1450.69557	
b_{17}	$C_{63}H_{97}N_{17}O_{22}$	1444.70669	1444.70745	0.53
?			1425.70793	
y_{16}	$C_{58}H_{96}N_{20}O_{21}$	1409.71317	1409.7138	0.45
GP*PGPAGA*PGDKGEAG	$C_{56}H_{85}N_{17}O_{22}$	1348.61279	1348.61332	0.39
y_{31}^{2+}	$C_{113}H_{179}N_{35}O_{41}$	1342.15717	1342.15797	0.60
y_{30}^{2+}	$C_{109}H_{172}N_{34}O_{39}$	1291.63333	1291.63371	0.30
y_{15}	$C_{52}H_{84}N_{18}O_{20}$	1281.61821	1281.61883	0.48
$^{\dagger}y_{29}^{2+}$	$C_{107}H_{169}N_{33}O_{38}$	1263.12260	1263.12308	0.38
y_{29}^{2+} - H_2O	$C_{107}H_{167}N_{33}O_{37}$	1254.11731	1254.1188	1.19
P*PGPAGA*PGDKGEA	$C_{52}H_{79}N_{15}O_{20}$	1234.56986	1234.57024	0.31
y_{14}	$C_{50}H_{81}N_{17}O_{19}$	1224.59675	1224.5972	0.37
GP*PGPAGA*PGDKGE	$C_{51}H_{77}N_{15}O_{20}$	1220.55421	1220.55492	0.58
y_{28}^{2+}	$C_{102}H_{162}N_{32}O_{37}$	1214.59621	1214.59686	0.53
y_{14} - H_2O	$C_{50}H_{79}N_{17}O_{18}$	1206.58618	1206.58692	0.61
GA*PGDKGEAGPSGP	$C_{49}H_{75}N_{15}O_{20}$	1194.53856	1194.53874	0.15
GPIGP*PGPAGA*PGD	$C_{51}H_{76}N_{14}O_{18}$	1173.55348	1173.55365	0.14
P*PGPAGA*PGDKGE	$C_{49}H_{74}N_{14}O_{19}$	1163.53275	1163.53309	0.29
y_{27}^{2+}	$C_{96}H_{151}N_{31}O_{36}$	1158.05418	1158.05454	0.31
$[y_{27}$ - $H_2O]^{2+}$	$C_{96}H_{149}N_{31}O_{35}$	1149.04890	1149.04942	0.45
b_{14} - H_2O	$C_{52}H_{80}N_{14}O_{15}$	1141.60004	1141.60048	0.39
PGPAGA*PGDKGEA	$C_{47}H_{72}N_{14}O_{19}$	1137.51710	1137.51728	0.16
y_{26}^{2+}	$C_{94}H_{148}N_{30}O_{35}$	1129.54345	1129.54383	0.34

$[y_{26} - H_2O]^{2+}$	$C_{94}H_{146}N_{30}O_{34}$	1120.53817	1120.53854	0.33
PIGP*PGPAGA*PGD	$C_{49}H_{73}N_{13}O_{17}$	1116.53202	1116.53232	0.27
$[y_{26} - 2H_2O]^{2+}$	$C_{94}H_{144}N_{30}O_{33}$	1111.53288	1111.53337	0.44
y_{13}	$C_{45}H_{74}N_{16}O_{16}$	1095.55415	1095.55474	0.54
y_{25}^{2+}	$C_{89}H_{141}N_{29}O_{34}$	1081.01707	1081.01757	0.46
$y_{25} - H_2O^{2+}$	$C_{89}H_{139}N_{29}O_{33}$	1072.01179	1072.01246	0.63
$b_{13} - H_2O$	$C_{49}H_{75}N_{13}O_{14}$	1070.56292	1070.56326	0.31
?			1054.49162	
P*PGPAGA*PGDKG	$C_{44}H_{67}N_{13}O_{16}$	1034.49015	1034.49067	0.50
b_{12}	$C_{47}H_{74}N_{12}O_{14}$	1031.55203	1031.5525	0.46
y_{12}	$C_{42}H_{69}N_{15}O_{15}$	1024.51704	1024.51749	0.44
$y_{24} - H_2O^{2+}$	$C_{84}H_{114}N_{28}O_{31}$	1015.48795	1015.48829	0.34
$b_{12} - H_2O$	$C_{47}H_{72}N_{12}O_{13}$	1013.54146	1013.54176	0.30
y_{23}^{2+}	$C_{82}H_{131}N_{27}O_{31}$	995.98250	995.98305	0.56
TGPIGP*PGPAGA	$C_{44}H_{68}N_{12}O_{14}$	989.50508	989.50572	0.65
P*PGPAGA*PGDK	$C_{42}H_{64}N_{12}O_{15}$	977.46869	977.46937	0.70
TGPIGP*PGPAGA - H_2O	$C_{44}H_{66}N_{12}O_{13}$	971.49451	971.49515	0.66
y_{11}	$C_{40}H_{66}N_{14}O_{14}$	967.49557	967.49607	0.51
?			953.80515	
$[M + 3H]^{3+}$	$C_{121}H_{193}N_{37}O_{43}$	951.80905	951.80945	0.42
$[M + 3H - H_2O]^{3+}$	$C_{121}H_{191}N_{37}O_{42}$	945.80552	945.80595	0.45
b_{21}^{2+}	$C_{79}H_{124}N_{22}O_{28}$	915.45505	915.45571	0.72
y_{21}^{2+}	$C_{74}H_{119}N_{25}O_{29}$	911.93756	911.93785	0.32
GP*PGPAGA*PGD	$C_{38}H_{55}N_{11}O_{15}$	906.39519	906.39568	0.54
y_{31}^{3+}	$C_{113}H_{179}N_{35}O_{41}$	895.10720	895.10759	0.43
$y_{31}^{3+} - H_2O$	$C_{113}H_{177}N_{35}O_{40}$	889.10368	889.10408	0.45
GPIGP*PGPAGA	$C_{40}H_{61}N_{11}O_{12}$	888.45740	888.45801	0.69
GP*PGPAGA*PGD - H_2O	$C_{38}H_{53}N_{11}O_{14}$	888.38463	888.38506	0.49
y_{20}^{2+}	$C_{72}H_{116}N_{24}O_{28}$	883.42683	883.42714	0.36
b_{20}^{2+}	$C_{76}H_{119}N_{21}O_{27}$	879.93649	879.93656	0.08
y_{10}	$C_{35}H_{59}N_{13}O_{13}$	870.44281	870.44292	0.13
$^{\dagger}y_{30}^{3+}$	$C_{109}H_{172}N_{34}O_{39}$	861.42464	861.4252	0.65
P*PGPAGA*PGD	$C_{36}H_{52}N_{10}O_{14}$	849.37373	849.37416	0.51

y_{19}^{2+}	$C_{69}H_{111}N_{23}O_{27}$	847.90827	847.9087	0.51
b_{10} - H_2O	$C_{39}H_{60}N_{10}O_{11}$	845.45158	845.45182	0.28
y_{29}^{3+}	$C_{107}H_{169}N_{33}O_{38}$	842.41749	842.41782	0.39
$[y_{19}$ - $H_2O]^{2+}$	$C_{69}H_{109}N_{23}O_{26}$	838.90299	838.9035	0.61
$[y_{29}$ - $H_2O]^{3+}$	$C_{107}H_{167}N_{33}O_{37}$	836.41397	836.41466	0.83
PIGP*PGPAGA	$C_{38}H_{58}N_{10}O_{11}$	831.43593	831.43644	0.61
y_9	$C_{32}H_{54}N_{12}O_{11}$	783.41078	783.41123	0.57
y_{27}^{3+}	$C_{96}H_{151}N_{31}O_{36}$	772.37188	772.37238	0.65
y_{17}^{2+}	$C_{62}H_{101}N_{21}O_{24}$	762.87370	762.87408	0.50
PIGP*PGPAG/GPIGP*PGPA	$C_{35}H_{53}N_9O_{10}$	760.39882	760.39949	0.88
y_{26}^{3+}	$C_{94}H_{148}N_{30}O_{35}$	753.36473	753.36505	0.43
*PGPAGA*PGD	$C_{31}H_{45}N_9O_{13}$	752.32096	752.32149	0.70
?			733.36329	
GA*PGDKGE	$C_{29}H_{45}N_9O_{13}$	728.32096	728.322145	1.62
y_8	$C_{30}H_{51}N_{11}O_{10}$	726.38932	726.38974	0.58
$^{\dagger}y_{16}^{2+}$	$C_{58}H_{96}N_{20}O_{21}$	705.36022	705.36078	0.79
b_8 - H_2O	$C_{32}H_{50}N_8O_8$	675.38244	675.38296	0.77
A*PGDKGE	$C_{27}H_{42}N_8O_{12}$	671.29950	671.30001	0.76
y_{15}^{2+}	$C_{52}H_{84}N_{18}O_{20}$	641.31274	641.31293	0.29
GPSGPAGP/GP*PGPAGA	$C_{27}H_{40}N_8O_9$	621.29910	621.29954	0.70
GPSGPAGP - H_2O	$C_{27}H_{38}N_8O_8$	603.28854	603.28913	0.98
*PGDKGE	$C_{24}H_{37}N_7O_{11}$	600.26239	600.26293	0.91
b_7	$C_{27}H_{45}N_7O_8$	596.34024	596.34062	0.64
b_7 - H_2O	$C_{27}H_{43}N_7O_7$	578.32968	578.33023	0.96
a_7	$C_{26}H_{45}N_7O_7$	568.34533	568.34589	0.99
PSGPAGP/P*PGPAGA	$C_{25}H_{37}N_7O_8$	564.27764	564.27811	0.83
y_6	$C_{22}H_{39}N_9O_8$	558.29944	558.29993	0.88
b_6	$C_{25}H_{42}N_6O_7$	539.31878	539.3192	0.79
?			534.30388	
b_6 - H_2O	$C_{25}H_{40}N_6O_6$	521.30821	521.30866	0.86
a_6	$C_{24}H_{42}N_6O_6$	511.32386	511.32378	-0.16
y_5	$C_{20}H_{36}N_8O_7$	501.27797	501.2784	0.85
P*PGPAG	$C_{22}H_{32}N_6O_7$	493.24053	493.24077	0.49

y_5 - NH_3	$C_{20}H_{33}N_7O_7$	484.25143	484.25201	1.21
$^{\dagger}b_5$ - H_2O	$C_{19}H_{29}N_5O_5$	408.22415	408.22469	1.33

RMS error = 0.64 ppm

Table S3 - Assignment table for the ECD spectrum of the tryptic digest peptide ion [α1 (763-795) + 3H] $^{3+}$ at *m/z* 951.80926 (Figure 3b). Peaks marked with a † were used to internally calibrate the spectrum. *P = hydroxyproline. Sequence: GLTGPIGP*PGPAGA*PGDKGEAGPSGPAGPTGAR

Assignment	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
† [M+3H]+ ••	2855.42823	2855.42940	0.41
[M+3H-OH]+ ••	2838.42549	2838.42416	-0.47
c_{31}	2625.29030	2625.29713	2.60
z_{30}	2568.26890	2568.27580	2.69
z_{30}•	2567.24850	2567.24986	0.53
†c_{27}	2313.14700	2313.14555	-0.63
c_{24}	2088.03560	2088.03228	-1.59
c_{21}	1846.92940	1846.92844	-0.52
c_{20}	1775.89230	1775.89148	-0.46
z_{20}•	1750.83550	1750.83301	-1.42
z_{20}	1749.82760	1749.82752	-0.05
c_{19}	1646.84970	1646.84893	-0.47
c_{18}	1589.82820	1589.82714	-0.67
z_{17}•	1509.72911	1509.72952	0.27
z_{17}	1508.72140	1508.72264	0.82
c_{17}	1461.73320	1461.73359	0.27
† $[M+3H]^{2+}$•	1427.71384	1427.71424	0.28
$[M+3H-NH_3]^{2+}$•	1419.20056	1419.20059	0.02
$[M+3H-CO]^{2+}$•	1413.71638	1413.71705	0.47
$[M+3H-2H_2O]^{2+}$•	1409.70327	1409.70251	-0.54
$[M+3H-CO_2H_2]^{2+}$•	1404.71110	1404.71150	0.29
$[M+3H-C_2H_4O_2]^{2+}$•	1397.70327	1397.70529	1.44
z_{16}	1393.69440	1393.69452	0.09
z_{32}^{2+}	1390.68980	1390.69222	1.74
c_{16}	1346.70630	1346.70816	1.38
z_{31}^{2+}	1334.14780	1334.14794	0.10
y_{30}^{2+}	1291.63330	1291.63246	-0.65
z_{30}•$^{2+}$	1284.12790	1284.12651	-1.08
z_{30}^{2+}	1283.62400	1283.62405	0.04

z_{15}	1266.60730	1266.60655	-0.59
z_{15}•	1265.59950	1265.59923	-0.21
z_{14}	1209.58580	1209.58762	1.50
z_{14}•	1208.57800	1208.57831	0.26
c_{13}	1105.60000	1105.60079	0.71
z_{13}	1079.53540	1079.53571	0.29
c_{12}	1048.57860	1048.57926	0.63
z_{12}	1008.49830	1008.49809	-0.21
c_{11}	977.54150	977.54190	0.41
† $[M+3H]^{3+}$	951.80900	951.80896	-0.04
$[M+3H_2O]^{3+}$	946.47736	946.47748	0.13
z_{10}	854.42410	854.42420	0.12
c_9	823.46720	823.46738	0.22
z_9•	768.39990	768.39994	0.05
z_9	767.39210	767.39201	-0.12
z_7	613.31780	613.31785	0.08
†z_6•	543.28854	543.28854	0.01
z_6	542.28070	542.28074	0.07
z_4•	389.21430	389.21450	0.51
z_3•	288.16660	288.16702	1.46
z_2•	231.14520	231.14567	2.03

RMS error = 0.91 ppm

Table S4 - Assignment table for the IRMPD spectrum of the tryptic digest peptide ion [α1 (763-795) + 3H] $^{3+}$ at *m/z* 951.80926 (Figure 3c). Peaks marked with a † were used to internally calibrate the spectrum. *P = hydroxyproline. Sequence: GLTGPIGP*PGPAGA*PGDKGEAGPSGPAGPTGAR

Assignment	Elemental Composition	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
b_{17}	$C_{63}H_{97}N_{17}O_{22}$	1444.70669	1444.70681	0.08
$^{\dagger}y_{16}$	$C_{58}H_{96}N_{20}O_{21}$	1409.71317	1409.71152	-1.17
y_{15}	$C_{52}H_{84}N_{18}O_{20}$	1281.61821	1281.61659	-1.26
y_{27}^{2+}	$C_{96}H_{151}N_{31}O_{36}$	1158.05418	1158.05447	0.25
b_{14} - H_2O	$C_{52}H_{80}N_{14}O_{15}$	1141.60004	1141.60083	0.69
y_{26}^{2+}	$C_{94}H_{148}N_{30}O_{35}$	1129.54345	1129.54412	0.59
b_{14} - $2H_2O$	$C_{52}H_{78}N_{14}O_{14}$	1123.58947	1123.59088	1.25
$[y_{26}$ - $H_2O]^{2+}$	$C_{94}H_{146}N_{30}O_{34}$	1120.53817	1120.53854	0.33
$^{\dagger}y_{13}$	$C_{45}H_{74}N_{16}O_{16}$	1095.55415	1095.55530	1.05
y_{25}^{2+}	$C_{89}H_{141}N_{29}O_{34}$	1081.01707	1081.01774	0.62
y_{12}	$C_{42}H_{69}N_{15}O_{15}$	1024.51704	1024.51878	1.70
y_{11}	$C_{40}H_{66}N_{14}O_{14}$	967.49557	967.49695	1.42
?			953.48490	
$[M + 3H]^{3+}$	$C_{121}H_{193}N_{37}O_{43}$	951.80905	951.81230	3.42
$[M + 3H - H_2O]^{3+}$	$C_{121}H_{191}N_{37}O_{42}$	945.80552	945.80757	2.16
y_{21}^{2+}	$C_{74}H_{119}N_{25}O_{29}$	911.93756	911.93993	2.60
GP*PGPAGA*PGD	$C_{38}H_{55}N_{11}O_{15}$	906.39519	906.39670	1.66
y_{31}^{3+}	$C_{113}H_{179}N_{35}O_{41}$	895.10720	895.10660	-0.67
y_{30}^{3+}	$C_{109}H_{172}N_{34}O_{39}$	861.42464	861.42303	-1.87
P*PGPAGA*PGD	$C_{36}H_{52}N_{10}O_{14}$	849.37373	849.37590	2.56
$^{\dagger}y_{19}^{2+}$	$C_{69}H_{111}N_{23}O_{27}$	847.90827	847.91000	2.04
y_{29}^{3+}	$C_{107}H_{169}N_{33}O_{38}$	842.41749	842.41791	0.50
y_9	$C_{32}H_{54}N_{12}O_{11}$	783.41078	783.41251	2.21
y_{26}^{3+}	$C_{94}H_{148}N_{30}O_{35}$	753.36473	753.36776	4.03
y_8	$C_{30}H_{51}N_{11}O_{10}$	726.38932	726.39071	1.92
y_{16}^{2+}	$C_{58}H_{96}N_{20}O_{21}$	705.36022	705.36179	2.22
*PGDKGEA	$C_{27}H_{42}N_8O_{12}$	671.29950	671.30037	1.30
y_{15}^{2+}	$C_{52}H_{84}N_{18}O_{20}$	641.31274	641.31397	1.91
GPSGPAGP - H_2O	$C_{27}H_{38}N_8O_8$	603.28854	603.28920	1.10

b_7 - H_2O	$C_{27}H_{43}N_7O_7$	578.32968	578.33039	1.24
P*PGPAGA	$C_{25}H_{37}N_7O_8$	564.27764	564.27824	1.06
y_6	$C_{22}H_{39}N_9O_8$	558.29944	558.29999	0.99
?			534.30364	
$^{\dagger}b_6$ - H_2O	$C_{25}H_{40}N_6O_6$	521.30821	521.30828	0.13
y_5	$C_{20}H_{36}N_8O_7$	501.27797	501.27782	-0.31
P*PGPAG	$C_{22}H_{32}N_6O_7$	493.24053	493.24033	-0.40
y_5 - NH_3	$C_{20}H_{33}N_7O_7$	484.25143	484.25099	-0.90
$^{\dagger}b_5$ - H_2O	$C_{19}H_{29}N_5O_5$	408.22415	408.22482	1.65

RMS error = 1.63 ppm

Table S5 - Assignment table for the CAD spectrum of the tryptic digest peptide ion [α2 (326-340)+ 2H] $^{2+}$ at *m/z* 634.34193 (Figure 5). Peaks marked with a † were used to internally calibrate the spectrum. *P = hydroxyproline. Sequence: GI*PGPVGAAGATGAR

Assignment	Elemental Composition	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
†y_{13}	$C_{45}H_{76}N_{16}O_{16}$	1097.56980	1097.56041	0.47
?			1088.54641	
y_{12}	$C_{40}H_{69}N_{15}O_{14}$	984.52212	984.51437	0.57
b_{12}	$C_{42}H_{68}N_{12}O_{14}$	965.50508	965.49770	0.71
?			959.50388	
b_{12} - H_2O	$C_{42}H_{66}N_{12}O_{13}$	947.49451	947.48704	0.37
y_{11}	$C_{38}H_{66}N_{14}O_{13}$	927.50066	927.49367	0.63
*PGPVGAAGATGA	$C_{39}H_{62}N_{12}O_{14}$	923.45813	923.45889	0.83
?			910.50379	
*PGPVGAAGATGA - H_2O	$C_{39}H_{60}N_{12}O_{13}$	905.44756	905.44809	0.59
b_{11}	$C_{38}H_{61}N_{11}O_{12}$	864.45740	864.45123	0.71
y_{10}	$C_{33}H_{59}N_{13}O_{12}$	830.44789	830.44220	0.83
?			809.42143	
*PGPVGAAGAT	$C_{34}H_{54}N_{10}O_{12}$	795.39955	795.40013	0.73
b_{10}	$C_{35}H_{56}N_{10}O_{11}$	793.42028	793.41509	0.97
*PGPVGAAGAT - H_2O	$C_{34}H_{52}N_{10}O_{11}$	777.38898	777.38963	0.83
?			768.37046	
?			760.89500	
?			750.03509	
?			749.36300	
?			746.38146	
b_9	$C_{33}H_{53}N_9O_{10}$	736.39882	736.39944	0.84
y_9	$C_{28}H_{50}N_{12}O_{11}$	731.37948	731.37481	0.83
?			717.35594	
a_9	$C_{32}H_{53}N_9O_9$	708.40390	708.40510	0.86
?			704.37111	
?			693.33253	
†y_8	$C_{26}H_{47}N_{11}O_{10}$	674.35802	674.35390	0.88

b_8	$C_{30}H_{48}N_8O_9$	665.36170	665.35768	0.90
?			663.83338	
$[M+2H]^{2+}$	$C_{53}H_{90}N_{18}O_{18}$	634.34130	634.33756	0.93
?			634.29253	
?			631.83302	
?			625.28302	
?			622.82770	
y_7	$C_{23}H_{42}N_{10}O_9$	603.32090	603.31742	0.94
?			597.28474	
b_7	$C_{27}H_{43}N_7O_8$	594.32459	594.32113	0.84
?			586.26060	
?			579.94049	
*PGPVGAA	$C_{25}H_{39}N_7O_8$	566.29329	566.29383	0.95
y_{13}^{2+}	$C_{45}H_{76}N_{16}O_{16}$	549.28854	549.28548	0.93
$[y_{13}\text{-}H_2O]^{2+}$	$C_{45}H_{74}N_{16}O_{15}$	540.28326	540.28010	0.78
b_6	$C_{25}H_{40}N_6O_7$	537.30313	537.30014	0.92
$^{\dagger}y_6$	$C_{20}H_{37}N_9O_8$	532.28379	532.28070	0.98
*PGPVGA	$C_{22}H_{34}N_6O_7$	495.25618	495.25607	1.06
y_{12}^{2+}	$C_{40}H_{69}N_{15}O_{14}$	492.76470	492.76213	1.12
y_5	$C_{18}H_{34}N_8O_7$	475.26232	475.25986	1.13
y_{11}^{2+}	$C_{38}H_{66}N_{14}O_{13}$	464.25397	464.25159	1.17
*PGPVG	$C_{19}H_{29}N_5O_6$	424.21906	424.21959	1.24
$^{\dagger}y_4$	$C_{15}H_{29}N_7O_6$	404.22521	404.22327	1.36

RMS error = 0.89 ppm

Table S6 - Assignment table for the CAD spectrum of the tryptic digest peptide ion [α1 (1062-1083) + 3H] $^{3+}$ at *m/z* 659.33679 (Figure 6). Peaks marked with a † were used to internally calibrate the spectrum. Sequence: SGDRGETGPAGPAGPIGPVGAR

Assignment	Elemental Composition	Theoretical Mass (*m/z*)	Observed Mass (*m/z*)	Error (ppm)
b_{17}	$C_{61}H_{96}N_{20}O_{23}$	1477.70300	1477.70334	-0.23
†b_{14}	$C_{48}H_{75}N_{17}O_{20}$	1210.54471	1210.54516	-0.37
b_{14} - H_2O	$C_{48}H_{73}N_{17}O_{19}$	1192.53415	1192.53470	-0.47
a_{14}	$C_{47}H_{75}N_{17}O_{19}$	1182.54980	1182.55029	-0.42
b_{13}	$C_{46}H_{72}N_{16}O_{19}$	1153.52325	1153.52376	-0.45
b_{13} - H_2O	$C_{46}H_{70}N_{16}O_{18}$	1135.51268	1135.51331	-0.55
y_{13}	$C_{49}H_{82}N_{16}O_{14}$	1119.62692	1119.62748	-0.50
?			1115.54623	
?			1113.49196	
?			1094.52299	
b_{12}	$C_{43}H_{67}N_{15}O_{18}$	1082.48613	1082.48655	-0.39
?			1068.47107	
?			1056.47091	
y_{12}	$C_{46}H_{77}N_{15}O_{13}$	1048.58981	1048.59038	-0.55
?			1042.45541	
?			1011.44959	
y_{11}	$C_{44}H_{74}N_{14}O_{12}$	991.56834	991.56891	-0.57
b_{11}	$C_{38}H_{60}N_{14}O_{17}$	985.43337	985.43395	-0.59
b_{11} - H_2O	$C_{38}H_{58}N_{14}O_{16}$	967.42280	967.42346	-0.68
a_{11}	$C_{37}H_{60}N_{14}O_{16}$	957.43845	957.43902	-0.59
†b_{10}	$C_{36}H_{57}N_{13}O_{16}$	928.41190	928.41251	-0.65
b_{10} - H_2O	$C_{36}H_{55}N_{13}O_{15}$	910.40134	910.40193	-0.65
a_{10}	$C_{35}H_{57}N_{13}O_{15}$	900.41699	900.41760	-0.68
y_{10}	$C_{39}H_{67}N_{13}O_{11}$	894.51558	894.51619	-0.68
?			884.38632	
b_9 - H_2O	$C_{33}H_{50}N_{12}O_{14}$	839.36423	839.36480	-0.69
?			827.36486	
y_9	$C_{36}H_{62}N_{12}O_{10}$	823.47847	823.47908	-0.75
y_9 - H_2O	$C_{36}H_{60}N_{12}O_9$	805.46790	805.46853	-0.78

?			786.33838	
y_8	$C_{34}H_{59}N_{11}O_9$	766.45700	766.45761	-0.79
b_8	$C_{28}H_{45}N_{11}O_{14}$	760.32203	760.32260	-0.75
y_8-H_2O	$C_{34}H_{57}N_{11}O_8$	748.44644	748.44705	-0.82
b_8 - H_2O	$C_{28}H_{43}N_{11}O_{13}$	742.31146	742.31204	-0.78
?			731.38009	
RGETGPAG	$C_{29}H_{47}N_{11}O_{11}$	726.35293	726.35348	-0.76
b_{16}^{2+}	$C_{59}H_{93}N_{19}O_{22}$	710.84441	710.84463	-0.31
b_7	$C_{26}H_{42}N_{10}O_{13}$	703.30056	703.30115	-0.84
?			698.32220	
b_7 - H_2O	$C_{26}H_{40}N_{10}O_{12}$	685.29000	685.29060	-0.88
?			679.38907	
$^{\dagger}y_7$	$C_{29}H_{52}N_{10}O_8$	669.40424	669.40482	-0.87
?			659.33028	
?			647.82013	
?			634.80598	
?			626.80931	
b_6	$C_{22}H_{35}N_9O_{11}$	602.25288	602.25344	-0.92
b_{14} - H_2O^{2+}	$C_{48}H_{73}N_{17}O_{19}$	596.77071	596.77122	-0.85
?			594.95513	
PIGPVGA	$C_{28}H_{45}N_7O_7$	592.34533	592.34590	-0.97
?			591.28905	
?			587.76588	
b_6 - H_2O	$C_{22}H_{33}N_9O_{10}$	584.24232	584.24280	-0.83
?			572.77487	
b_{13}^{2+}	$C_{46}H_{72}N_{16}O_{19}$	577.26526	577.26574	-0.83
a_6	$C_{21}H_{35}N_9O_{10}$	574.25797	574.25842	-0.79
b_{13} - H_2O	$C_{46}H_{70}N_{16}O_{18}$	568.25998	568.26049	-0.90
y_6	$C_{23}H_{41}N_9O_7$	556.32017	556.32071	-0.97
b_{12}^{2+}	$C_{43}H_{67}N_{15}O_{18}$	541.74670	541.74718	-0.88
y_6 - NH_3	$C_{23}H_{38}N_8O_7$	539.29362	539.29413	-0.94
y_{12}^{2+}	$C_{46}H_{77}N_{15}O_{13}$	524.79854	524.79905	-0.97
PIGPVG	$C_{25}H_{40}N_6O_6$	521.30821	521.30872	-0.98

$^{\dagger}y_5$	$C_{21}H_{38}N_8O_6$	499.29871	499.29923	-1.04
y_{11}^{2+}	$C_{44}H_{74}N_{14}O_{12}$	496.28781	496.28835	-1.09
b_{11}^{2+}	$C_{38}H_{60}N_{14}O_{17}$	493.22032	493.22084	-1.05
b_{11} - H_2O	$C_{38}H_{58}N_{14}O_{16}$	484.21504	484.21553	-1.01
y_5 - NH_2	$C_{21}H_{36}N_7O_6$	482.27216	482.27267	-1.06
b_5	$C_{17}H_{28}N_8O_8$	473.21029	473.21084	-1.16
b_{10} - H_2O^{2+}	$C_{36}H_{55}N_{13}O_{15}$	455.70431	455.70481	-1.10
b_4	$C_{15}H_{25}N_7O_7$	416.18883	416.18936	-1.29
y_9^{2+}	$C_{36}H_{62}N_{12}O_{10}$	412.24287	412.24334	-1.14
y_4	$C_{16}H_{31}N_7O_5$	402.24595	402.24651	-1.40
$^{\dagger}y_8^{2+}$	$C_{34}H_{59}N_{11}O_9$	383.73214	383.73269	-1.44
?			381.29808	
?			328.48422	
y_3	$C_{11}H_{22}N_6O_4$	303.17753	303.17808	-1.81
?			301.14148	

RMS error = 0.87 ppm

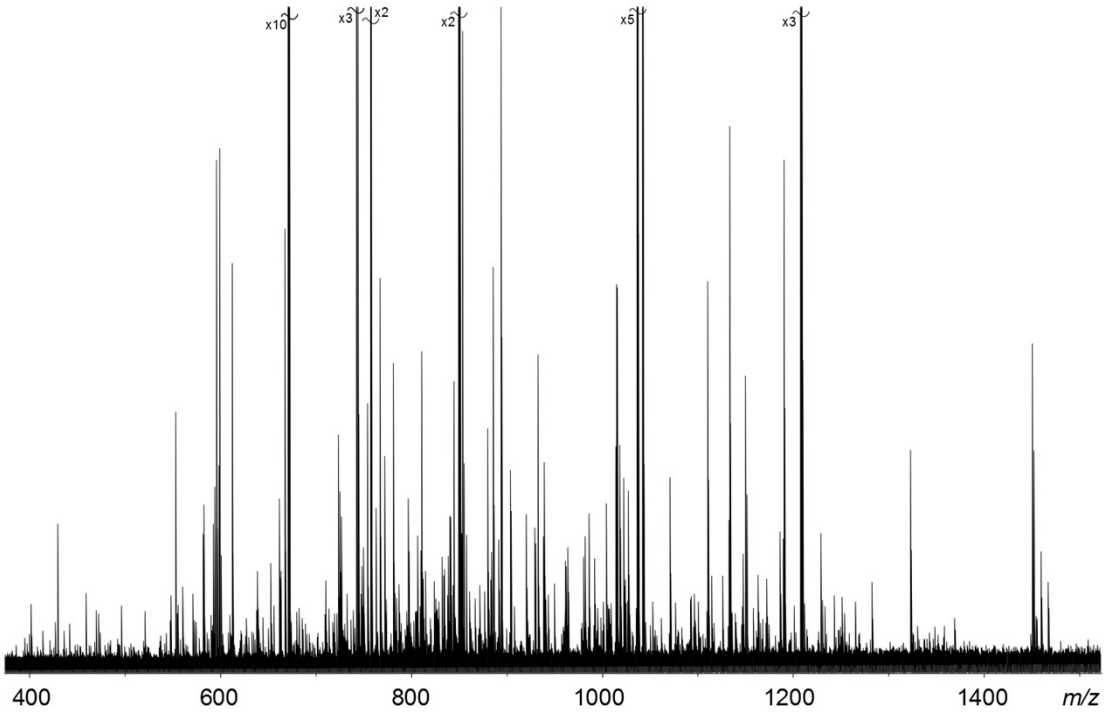

Figure S1 – Unlabelled CAD spectrum of multiple species at approximately *m/z* 850.41, highlighting the complexity and challenges during the assignment process. With the aid of 2D-FTICR-MS, however, the precursor at *m/z* 850.41468 has been assigned as $[\alpha 1\ (422\text{-}448) + 3H]^{3+}$