SUPPLEMENTAL DATA

Figure S1. Number of peptides as function of peptide length for all proteolytically derived peptides examined.



Figure S2. ECD of $[M + 6H]^{6+}$ precursor ions from the peptide KGDVAFVKHQTVPQNTGGKNPDPWAKNLNEKDYE, derived from Glu C digestion of apo-transferrin. A triply charged (z · H)-type product ion is indicated (see inset).



Figure S3. ECD sequence coverage as function of peptide mass for Glu C derived peptides detected in more than one charge state.



Figure S4. ECD sequence coverage as function of peptide mass for Lys N derived peptides detected in more than one charge state.



Charge	Peptide Sequence	Seq. Cov. %
+3	GACLLPKIETMREK	83%
+3	AEFVENTKLVTDUTK	86%
+3	CSTSSLLEACTFRRP	69%
+3	LFTFHADICTLPDTEK*	93%
+3	EFQLFSSPHGKDLLFK	100%
+3	LGEYGFQNALIVRYTRK*	80%
+3	FPKAEFVEVTKLVTDLITK	81%
+3	DFPIANGEROSPYDIDTK*	93%
+3	vpqvstptlvevskslgk*	100%
+3		89%
+3	SRSFQLFGSPPGQRDLLFK	100%
+3		89%
+3	GLVLIAFSQYLQQCPFDEHVK*	53%
+3	YLYEIARRHPVFYAPELLYYANK*	50%
+3	schitavgritagwnipmglillynk	90%
+3	LGGRPTTYEEYLGTEYVTAJANUK	86%
+3	EGYYGYTGAFROLVEKGDVAFyK*	64%
+3	COTESLVNRRPCFSALTPDETYVPK*	33%

 Table S1. ECD fragmentation summary of all triply protonated peptides from Lys C digestion.

* Peptides of the same composition but with a lysine residue at the N-terminus rather than the C-terminus were generated by Lys N digestion and also examined with ECD (see also Table S2).

The peptide CSTSSLLEACTFRRP corresponds to the C-terminus of the protein (apotransferrin).

Charge	Peptide Sequence	Seq. Cov. %
+3	KEDPQTFYYAVAVVjK	85%
+3	KPDPNJIJCDEFKADE	92%
+3	ĸцӻҭӻӊѧѹҁҭӏҎѻҭе*	100%
+3	KLKPDPNTLCDEFKADE	86%
+3	KLIGEYGEGNALIVRYTR*	94%
+3	KEDLIWELLINGAQEHFG	88%
+3	VPDKIJVRWCAYSEHEAT	93%
+3	KDFPIANGERQSPVDIDT*	73%
+3	KVPQVSTPTLVEVSRSLG*	100%
+3	KVASLRETYGDMADCCE	75%
+3	ĸhĺypĺepoĺnĺlíkoncpafe	65%
+3	кесснбріцесарряарца*	94%
+3	KSDNCEDTPEAGYFAVAVVK	94%
+3	KINHCRFDEFFSEGCAPGSK*	83%
+3	KGLYLJAFSQYLQQCPFDEHV*	84%
+3	ĸĹĸĸĸĸĸ	72%
+3	ĸŶŊŊĠŶſŦQĘĊĊQĂĘĎŔĠĂĊĻĿP	89%
+3	KYLYEJARRHPVFYAPELLYYAN*	35%
+3	KEGYYGYTGAFROLVEKGDYAFV*	77%
+3	ĸĸĸschttavgrtagwnipmglyn	43%
+3	KCCJJESLVNRRPCFSALTPDEJJYJVP*	29%

Table S2. ECD fragmentation summary for all triply protonated Lys N derived peptides.

* Peptides of the same composition but with a lysine residue at the C-terminus rather than the N-terminus were generated by Lys C digestion and also examined with ECD (see also Table S1). The peptide VPDTVRWCAVSEHEAT contains the N-terminus of the protein (apotransferrin).

Charge	Peptide Sequence	Seq. Cov. %
+3	KSHCIAEVEKDAIPE	92%
+3	AGRIDPYKLIRPYAAE	82%
+3	VPDKTYRWCAVSEHE	85%
+3	APRKNVRWCTISQPE	58%
+3	YVTAJANIJKKCSTSPLLE	94%
+3	YVKAVGNLRKCSTSSLLE	84%
+3	CLÁKLGGRPTYEEYLGTE	69%
+3	NLPPLTADFAEDKDYCKNYQE	72%
+3	YLGTEYVTAIANLKKCSTSPLLE	76%
+3	YGFQNALIVRYTRKVPQVSJTPTJLYE	36%
+3	SLVNRRPCFSALTPDETYVPKAFDE	43%
+3	GLSDGEWQQVLNVWGKVEADIAGHGQE	69%

 Table S3. ECD fragmentation summary for all triply protonated species from Glu C

 digestion.

Charge	Peptide Sequence	Seq. Cov. %
+4	LGEYGFONALÍVRYTRK	94%
+4	FPKAEFMEVTKLVTDLITK	69%
+4	skefolfssphckdllfk	100%
+4	SRSFQLFGSPPGQRDLLFK	100%
+4	INHCRFDEFFSEGCAPGSKK*	83%
+4	GLVLÍAFSQVLQQCPFDEHYK	63%
+4	YLYEIARRHPYFYAPELLYYANK*	100%
+4	ADROQYELLOLONTRKPVDEYK*	85%
+4	DLLFRODTVCLAKLHDRNTYEK	90%
+4	schtaygrtagwnipmgllynk	85%
+4	ĴGAPSIJJCVRRAFALECIRAJAEK	68%
+4	ĹĠĠŔ₽ſŢŶĔĔſŶĹĠſŦĔſŶIJŢĄĮĄŃĹĶĶ	91%
+4	EGYYGYTGAFROLVEKGDVAFVK	95%
+4	CCTESLYNRRPCFSALTPDETMVPK	95%
+4	SHCIAEVEKDAIRENLPPLTADFAEDK*	78%
+4	FRITLINFINAEGEPELLMLANWRPAQPLK	91%
+4	DAFLGSFLYEYSRRHPEYAVSVLLRLAK	62%
+4	SHQIAEVEKDAIPENLPPLTADFAEDKDVCK*	84%
+4	SCHTGLGRSAGWNIPIGLLYCDLPEPRKPLEK	52%

Table S4. ECD fragmentation summary for all quadruply protonated species from Lys C

 digestion.

* Peptides with the same composition but with a lysine residue at the N-terminus rather than the C-terminus were generated by Lys N digestion and also examined with ECD (see also Table S5). $^{\circ}$ = Product ions that cannot be distinguished based on their mass.

Charge	Peptide Sequence	Seq. Cov. %
+4	VPDKTYRWGAYSEHEAT	93%
+4	ĸŊĹŃŔĖĎFŖIJĻĊĹĎĠŤŔ	94%
+4	ĸĻĘſſĘŀŀĄŊĮĊſſĿPŎſŢĘŀŔQĨſĸ	100%
+4	ĸĦĹvþepqnljíkgngþþfe	88%
+4	KINHCRFDEFFSEGCAPGS	88%
+4	кңатуралтаакиррыма	86%
+4	KINHCRFDEFFSEGCAPGSK*	89%
+4	KLKHLVDEPONLIKONCOQFE	84%
+4	ĸŀŀſsſslpcylſĸpſtſĘſġſylaŴaŴyĸ	90%
+4	ĸŸĹŸĿĨĄŔŔĦ₽VFYAŖĘĻĻŸŸĄŊ*	80%
+4	KPVEEYANCHUARAPNHAVVITR	100%
+4	KADRDQYELLCLDNTRKPYDEY*	85%
+4	ĸĸſschtfavgſĸŢagſwnipmgĹĹyjn	95%
+4	KSHCIAEVEKDAIPENLPPLTADFAED*	61%
+4	KDFPIANGERQSPVDIDTKAVVQDPAL	91%
+4	ĸĘĊĦĹĄĠVPŚĦĄŴVĄŔŚVPGŔĘĎĻĮW	83%
+4		89%
+4	ĸſMYĹĠĔſŸVſŦĂIŖŃĻŖĘĠŦĊ₽ĔĂ₽ŦĎĘĊŔ₽Ÿ	85%
+4	KPLALVYGEATSRRMVNNGHSFNVEYDDSQD	69%
+4	ĸĸĸĸĸ	61%

Table S5. ECD fragmentation summary for all quadruply protonated species derived

 from Lys N digestion.

* Peptides with the same amino acid composition but with a lysine residue at the Cterminus rather than the N-terminus were generated by Lys C digestion and also examined with ECD (see also Table S4). The peptide VPDTVRWCAVSEHEAT contains the N-terminus of the protein (apotransferrin).

Charge	Peptide Sequence	Seq. Cov. %
+4	ѵҭӄӷѵҭҏц҉ҭҝѵӈҝ҉ѥ	85%
+4	DFRLLCLDGTRKPYTE	86%
+4	VPDKTVRWCAVSEHE	92%
+4	vskslgkvgtrggtkpe	80%
+4	LLKHKPKATEEQLKTVME	94%
+4	RALKAWSVARLSQKFPKAE	88%
+4	CCQAEDKGACLLPKIETMRE	83%
+4	YANCHLARAPNHAWTRKOKE	89%
+4	RALKAWSVARLSQKFPKAEFVE	90%
+4	TKOLLFRODTVCLAKLHORNTYE	86%
+4	ĸŶĹĠĔĔſŶVſĸſAVſĠſŊĹŖſĸĊŊŢŊŚĿĻĿĔ	87%
+4	YGFQNALIVRYTRKVPQVSjTPTJLME	76%
+4	CADDRADLAKYICDNODTISSKLKE	83%
+4	CFLSHKDDSPDLPKLKPDPNTLCDE	80%
+4	SLVNRRPCFSALTPDETYVPKAFDE	95%
+4	FAKIJQVADESHAGCEKSLHITLFGDE	83%
+4	YKDCHLAQVPSHTYYARSMGGKEDLIWE	81%
+4	FISDAIIHVLHSKHPGDFGADAQGAMTKALE	86%

 Table S6.
 ECD fragmentation summary for all quadruply protonated Glu C derived

 peptides.

Charge	Peptide Sequence	Seq. Cov. %
+5	skéfolfssphakóllfk	63%
+5	YLYEIARRHPYFYAPELLYYANK	90%
+5	INHCRFDEFFSEGCAPGSKKpSSLCK	88%
+5	HNGPEHWHKDFPIANGERQSPYDIDTK	78%
+5	DAFLGSFUYEYSRRHPEYAVSYLURUAK*	88%
+5	MYLGYEYVTAIRNLREGTJCPEAPTDECKPVK	81%
+5	SCHTGLERSAGWNIPIGLLYCDLPEPRKPLEK	74%
+5	LGEYGFQNALIVRYTRKVPQVSTPJJVEVSRSLGK	78%
+5	LCMG\$GLNLCEPNNKEGYYGYTGAFROLVEKGDVAFVK	78%
+5	aWQDPALKPLALWYGEATSRRMVNNGHSFNVEYDDSQDK	78%
+6	VotrgcftkpesermpgtebylskjilnrlqVlhek	87%
+6	DYELLCLOGTRKPVEEYANCHLARAPINHAVMTRK*	74%
+6	avvoldpallkplallyydejatskrynynghisfnyelyddigodk	84%

Table S7. ECD fragmentation summary for all $[M + 5H]^{5+}$ and all $[M + 6H]^{6+}$ precursor ions from Lys C digestion.

* Peptides with the same composition but with a lysine residue at the N-terminus rather than the C-terminus were generated by Lys N digestion and also examined with ECD (see also Table S8). ^ = Product ions that cannot be distinguished based on their mass.

Table S8. ECD fragmentation summary for all $[M + 5H]^{5+}$ and all $[M + 6H]^{6+}$ precursor ions from Lys N digestion.

Charge	Peptide Sequence	Seq. Cov. %
+5	KPVEEYANCHLARAPNHAYYTTR	79%
+5	ĸĘĊĦĹĬĂQVPSĦĂVVĂŔŚVŊĠĶĘĎĹIJŴ	79%
+5	ĸDAFLGSFLYEYSRRHPEYAVSVIJJRJA*	96%
+5	KNLRETAEEVKARYTRVVWCAYGPEEQK	92%
+5	KPLALVYGEATSRRMVNNGHSFNVEYDDSQD	100%
+5	ĸĎYĘĹĻĊĹŊĠŤŔĸ₽VĘĘŶĂŊĊŀĹĹĂŔĂ₽ŊŀŀÁŊŲŢŖ	81%
+6	ĸĸſschtiglgŖsaſgŴŊĺ₽jſġĹĹŊĊĎĹ₽Ę₽Ŗĸ₽ĻĘ	82%
+6	KDGPLITGTYRLVQFHFHWGSSDDQGSEHTVDR	67%
+6	ĸŊŶĘĹĹĊĹŊĠŢĸĸĸĸŧĘŶĄŊĊŀĹAŖaĸĸŀĬavvŢŢĸ*	77%
+6	ĸŇĹŊĘĸŊYĖĹĹĊĹŊĠŦŖĸ₽VĘĘŶĄŊĊŀĹĄŔĄ₽ŊŀĬĄvyŦŖ	75%

* Peptides with the same amino acid composition but with a lysine residue at the C-terminus rather than the N-terminus were generated by Lys C digestion and also examined with ECD (see also Table S7). $^{\circ}$ = Product ions that cannot be distinguished based on their mass.

Charge	Peptide Sequence	Seq. Cov. %
+5	YANCHLARAPNHAYYTRKOKE	95%
+5	RALKAWSVARLSQKFPKAEFVE	85%
+5	TKDĹĹĘŔŎĎŦVĊĹĄĶĹĦĎŔŊŢŊĔ	82%
+5	FAKTCVADESHAGCEKSLIHTLFGDE	75%
+5	ĸĹŀŦŗŦŀĄ₽ŀĊŢĹ₽ĎŢĔĸſŎĬĸĸŎŢĄĹŶĔ	96%
+5	YKDCHLAQVPSHTIVYARSMGGKEDLIWE	92%
+5	CFLSHKDDSPDLPKLKPDPNTLCDEFKADE	96%
+5	IAHRFKDLGEEHFKGUVLIAFSQYLQQCPFDE	80%
+5	MKASEDLKKHGTVVLTALGGILKKKGHHEAE	93%
+5	NRKSSKHSSLDCVLRPTEGYLAVAVVKKANE	86%
+5	GCAPGSKKDSSLCKLCMGSGLNLCEPNNKE	81%
+5	CHÍLÁQÍVPSHAVVARSÍVÞGKEÐLIWKLLÍSKAQE	73%
+5	cchgbluedabbrablakyjcbNgbtisskijke	78%
+5	FQLFSSPHGKDLLFKDSAHGFLKVPPRMDAKMYLGYE	70%
+6	YANCHLARAPNHAVVJTRKOKE	58%
+6	WFKCRRWQWRMKKLGAPSITCVRRAFALE	81%
+6	CCHGDLLECADDRADLAKYICDNODTIISSKLKE	75%
+6	KGÓVAFVKHQTVPQNTGGKNPÓPWAKNLNEKÓYE	90%
+6	FQLFSSPHGKDLLFKDSAHGFLKVPPRMDAKMYLGYE	91%
+6	ATKCOSFRDHMKSVIPSDGPSVACVKKASYLDCIRAJAANE	71%
+6	LLCLÓNTRKPVØEVKOCHLAGVPSHTVVARSMGGKEDUWE	66%

Table S9. ECD fragmentation summary for all $[M + 5H]^{5+}$ and all $[M + 6H]^{6+}$ precursor ions from Glu C digestion.