ELECTRONIC SUPPLEMENTARY MATERIAL

Effect of Cu(II) on *in vitro* glycation of human serum albumin by methylglyoxal: LC-MS - based proteomic approach

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Figure 1S. Typical capHPLC-ESI-QTOFMS chromatograms obtained for: (a) non-modified HSA; (b) HSA incubated with methylglyoxal, HSA_MGo; (c) incubated with methylglyoxal in the presence of Cu(II) 5mgCu L^{-1}, HSA_MGo_Cu5.

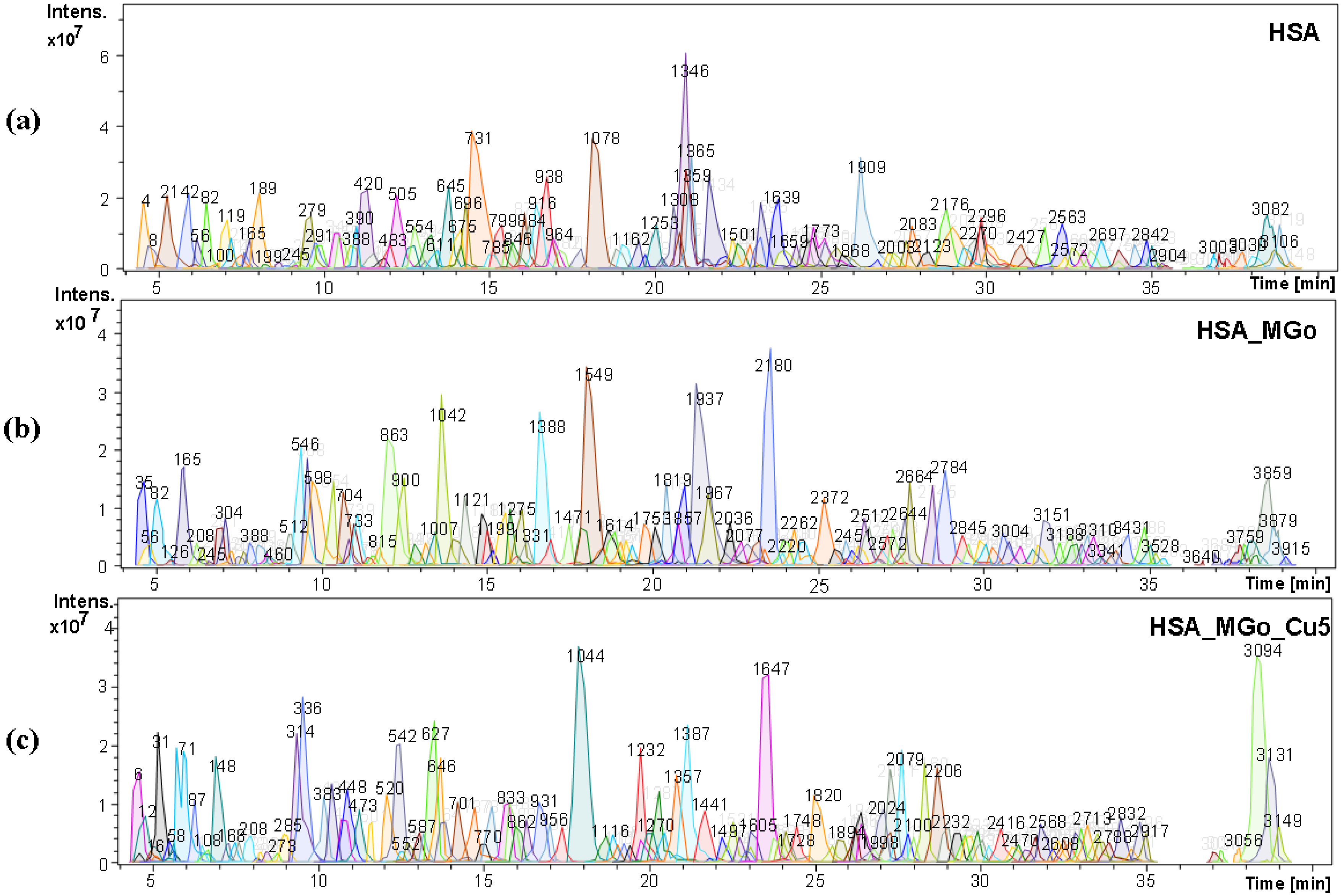


Figure 2S. Total number of peptides detected in HSA after incubation with methylglyoxal in the absence (HSA_MGo) or in the presence of three different Cu(II) concentrations (HSA_MGo_Cu01, HSA_MGo_Cu1, HSA_MGo_Cu5), assessed using ProteinScape platform.

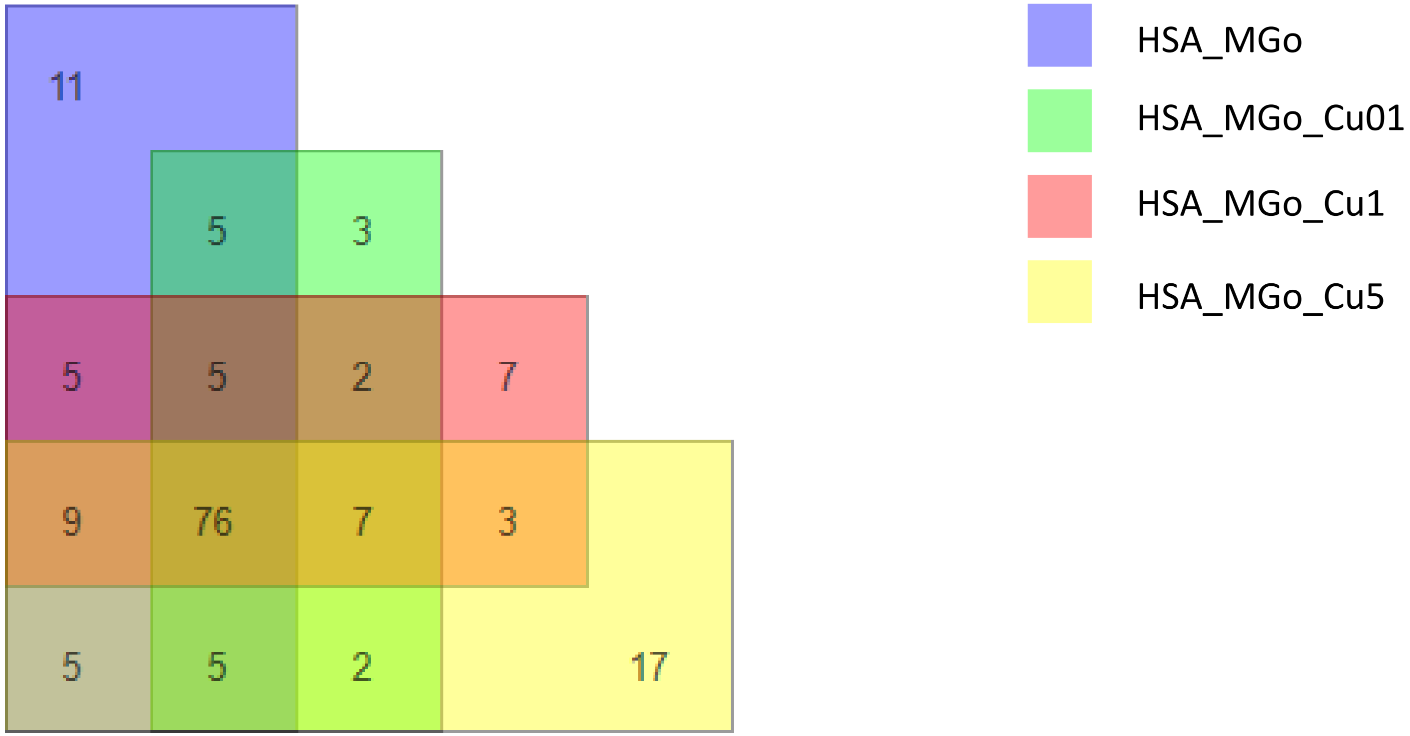
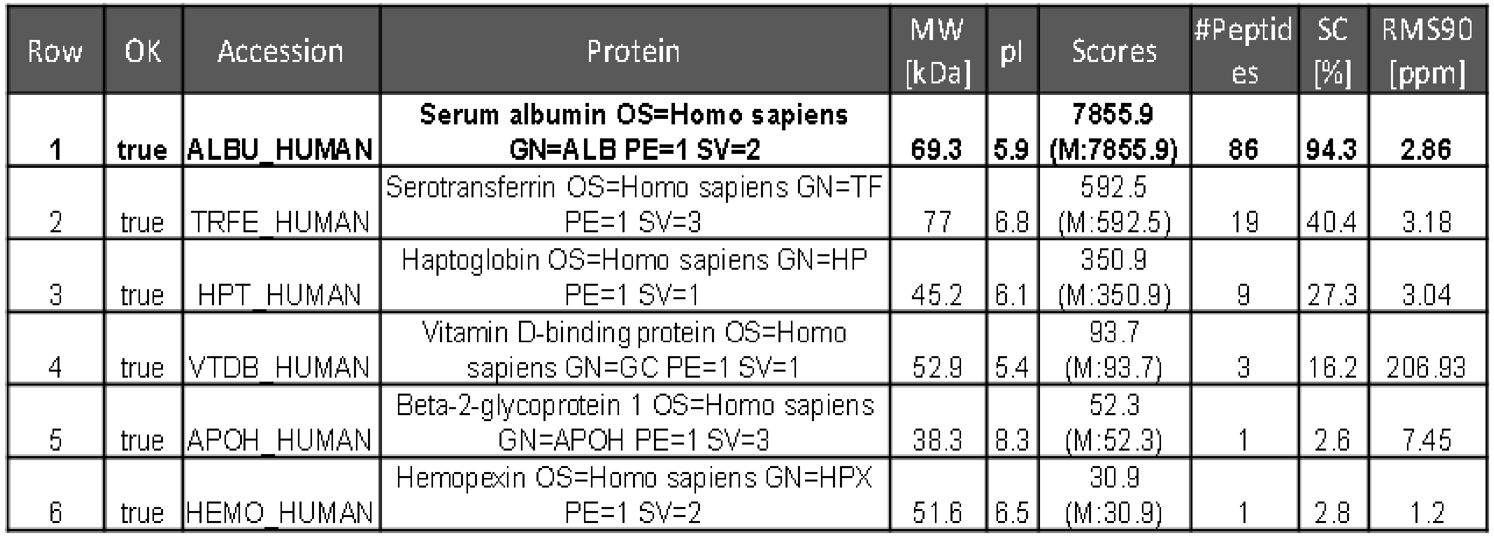


Figure 3S. Protein identification/confirmation. (a) Mascot search outcome obtained for human serum albumin incubated without methylglyoxal and in the absence of Cu(II); the highest score (based on 609 AA sequence encoded by ALB gene) correspond to HSA (P02768, Uniprot KB/ Swiss-prot). (b) Sequence coverage of P02768 obtained for albumin incubated under different conditions.

(a)

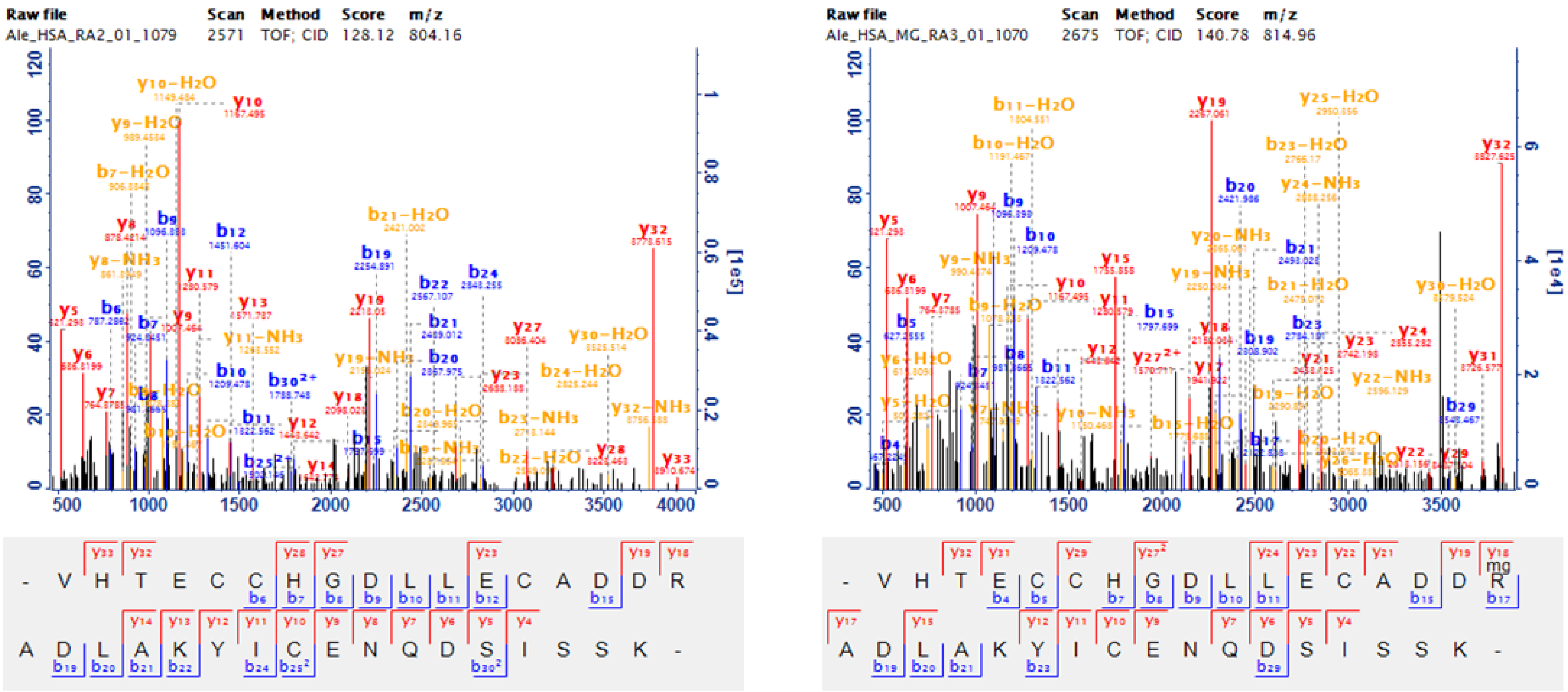


Row	OK	Accession	Protein	MW [kDa]	pI	Scores	#Peptides	SC [%]	RMS90 [ppm]
1	**true**	**ALBU_HUMAN**	**Serum albumin OS=Homo sapiens GN=ALB PE=1 SV=2**	**69.3**	**5.9**	**7855.9 (M:7855.9)**	**86**	**94.3**	**2.86**
2	true	TRFE_HUMAN	Serotransferrin OS=Homo sapiens GN=TF PE=1 SV=3	77	6.8	592.5 (M:592.5)	19	40.4	3.18
3	true	HPT_HUMAN	Haptoglobin OS=Homo sapiens GN=HP PE=1 SV=1	45.2	6.1	350.9 (M:350.9)	9	27.3	3.04
4	true	VTDB_HUMAN	Vitamin D-binding protein OS=Homo sapiens GN=GC PE=1 SV=1	52.9	5.4	93.7 (M:93.7)	3	16.2	206.93
5	true	APOH_HUMAN	Beta-2-glycoprotein 1 OS=Homo sapiens GN=APOH PE=1 SV=3	38.3	8.3	52.3 (M:52.3)	1	2.6	7.45
6	true	HEMO_HUMAN	Hemopexin OS=Homo sapiens GN=HPX PE=1 SV=2	51.6	6.5	30.9 (M:30.9)	1	2.8	1.2

(b)

Sample	Sequence coverage, % (609 AA)	Sequence coverage, % (585 AA)
HSA	94	98
HSA_MGo	92	96
HSA_MGo_Cu01	89	93
HSA_MGo_Cu1	93	97
HSA_MGo_Cu5	89	93

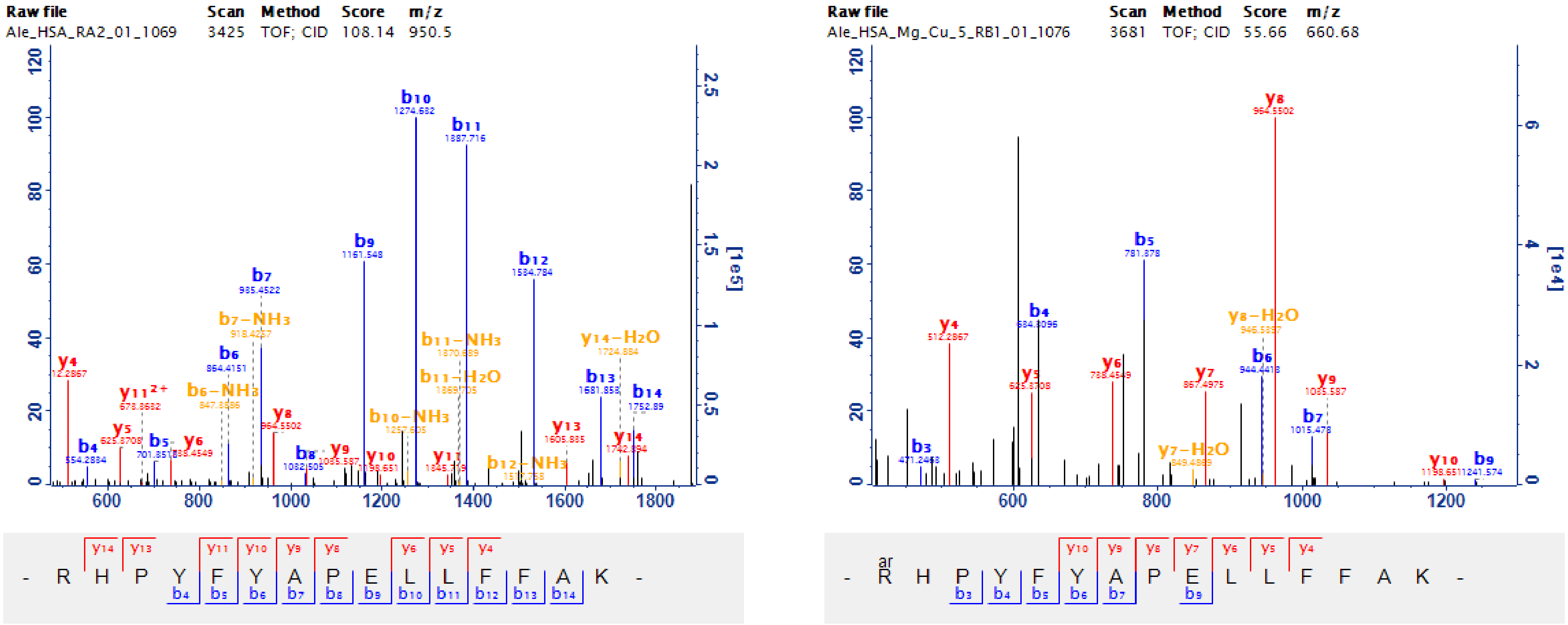
Figure 4S. De novo sequencing of K.VHTECCHGDLLECADDRADLAKYICENQDSISSK.L peptide (265-298, based on 609 AA sequence) found to be modified by MG-H on ^{280}R. (MaxQuant platform)



non-modified
charge state +5

^{280}R(MG-H)
charge state +5

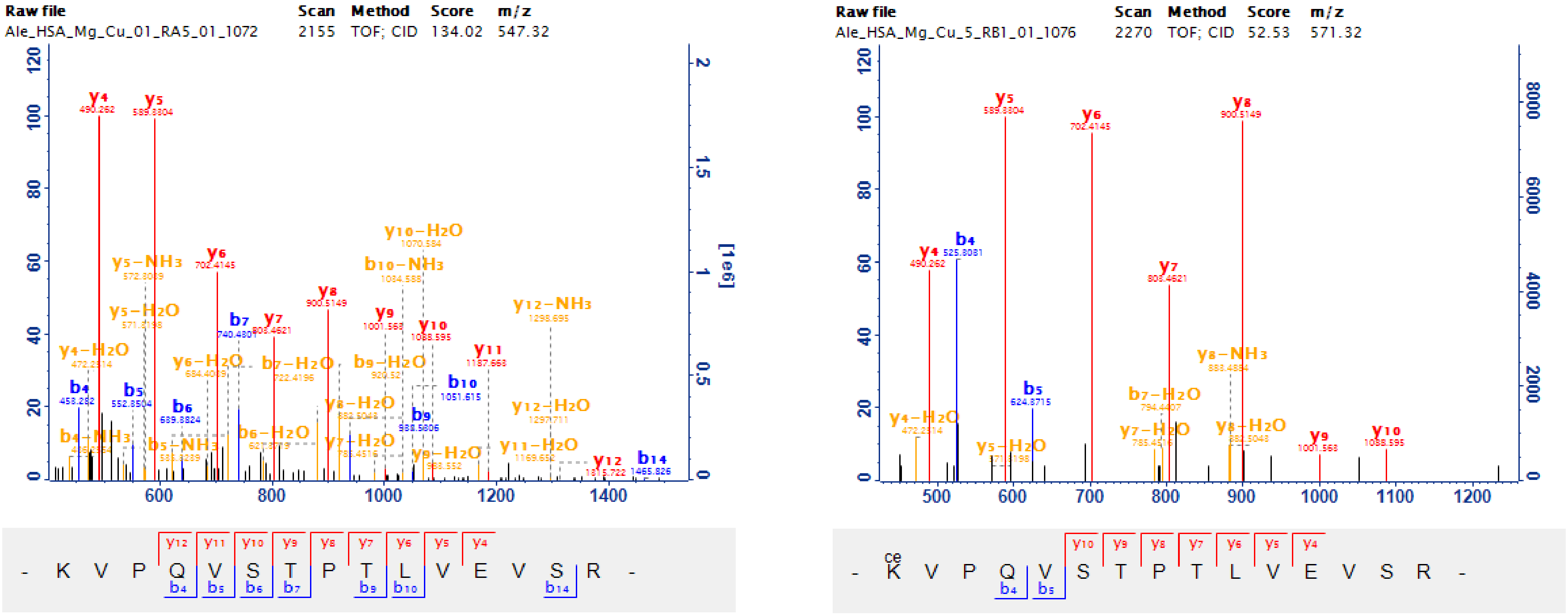
Figure 5S. De novo sequencing of R.RHPYFYAPELLFFAK.R peptide (169-183, based on 609 AA sequence) found to be modified by ArgPyr on ^{169}R. (MaxQuant platform)



non-modified
charge state +2

^{169}R(ArgPyr)
charge state +3

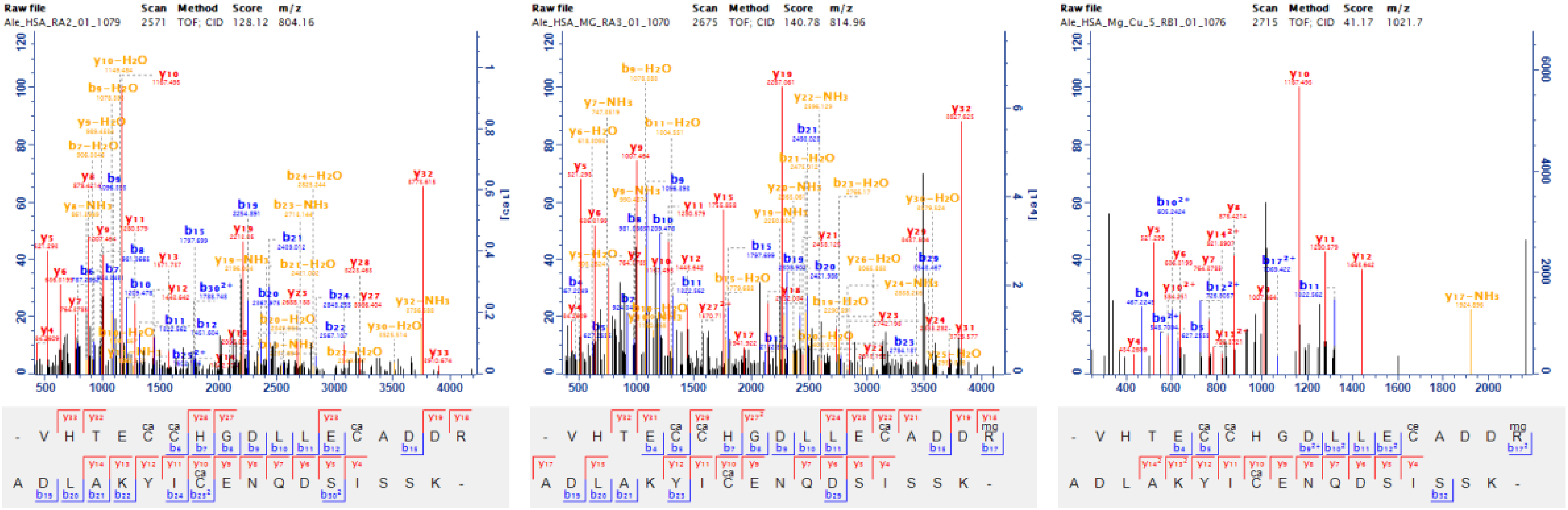
Figure 6S. De novo sequencing of K.KVPQVSTPTLVEVSR.N peptide (438-452, based on 609 AA sequence) found to be modified by CEL ^{438}K. (MaxQuant platform)



non-modified
charge state +3

^{438}K(CEL)
charge state +3

Figure 7S. De novo sequencing of K.VHTECCHGDLLECADDRADLAKYICENQDSISSK.L peptide (265-298, based on 609 AA sequence) found to be modified by CECys on ^{277}C and by MG-H1 on ^{280}R. (MaxQuant platform)



non-modified
charge state +5

^{280}R(MG-H1)
charge state +5

^{277}C(CECys)
charge state +4