Supplemental Table 1 Properties of measured 39 peptic fragments of α_1AT in H/D-EX

Region[a]	Position	Peptide	Xcorr[b]	RT[c]	z	N[d]	Theoretical m/z & mass				Observed m/z (average)										Exchanged deuterium content (ea)						Exchanged deuterium content (%)						D2-spepcific H/D-EX			Group[h]
											$D_{0\%}$		D_t						$D_{100\%}$																	
							$D_{0\%}$ m/z	D_{max} m/z	$D_{0\%}$ mass	D_{max} mass	H1 (2runs)	*stdev*	D1 (2runs)	*stdev*	D2 (2runs)	*stdev*	D3 (2runs)	*stdev*	D0 (2runs)	*stdev*	*D1*[e]	*stdev*	*D2*	*stdev*	*D3*	*stdev*	*D1 (%)*[f]	*stdev (%)*	*D2 (%)*	*stdev (%)*	*D3 (%)*	*stdev (%)*	*D2(%)-D1(%)*	*D2(%)-D3(%)*	*Average (%)*[g]	
N-term	1-23	MDPQGDAAQKTDTSHHDQDHPTF	2.50	4.74	3	20	860.9	867.6	2579.7	2599.7	860.9	0.0	863.7	0.5	864.5	0.0	864.3	0.2	864.9	0.2	13.8	2.7	17.8	0.1	16.9	1.1	68.9	13.6	89.0	0.3	84.3	5.7	20.1	4.7	12.4	A
N-term	1-30	MDPQGDAAQKTDTSHHDQDHPTFNKITPNL	3.28	5.53	3	26	1121.2	1129.7	3360.6	3386.6	1121.1	0.0	1124.7	0.4	1125.3	0.2	1123.8	0.6	1126.1	0.2	18.4	1.9	21.9	0.8	13.5	3.0	70.8	7.3	84.1	3.2	52.0	11.6	13.3	32.1	22.7	A
N-term-hA*	1-32	MDPQGDAAQKTDTSHHDQDHPTFNKITPNLAE	4.08	5.74	3	28	1187.9	1197.2	3560.7	3588.7	1187.9	0.1	1192.0	0.5	1192.8	0.2	1191.8	0.1	1193.5	0.4	20.6	2.5	24.8	1.1	19.5	0.3	73.5	9.0	88.5	4.1	69.7	1.1	15.0	18.8	16.9	A
hA	24-32	NKITPNLAE	3.02	4.81	2	7	500.5	503.6	999.0	1006.0	500.5	ND	502.6	0.1	502.8	0.1	502.3	0.4	503.1	0.2	5.7	0.3	6.3	0.3	5.0	1.0	81.4	3.6	89.3	4.4	71.7	14.0	7.9	17.7	12.8	A
hA-s6B*	38-51	YRQLAHQSNSTNIF	3.74	5.63	2	13	840.4	846.9	1678.8	1691.8	840.3	0.1	842.5	0.3	843.6	0.4	842.7	0.1	844.8	0.6	6.2	0.8	9.3	1.3	6.8	0.4	47.5	6.3	71.9	9.9	52.2	3.1	24.4	19.6	22.0	A
hB*	52-60	FSPVSIATA	1.87	7.38	1	7	893.0	900.0	892.0	899.0	892.9	0.0	893.4	0.1	893.1	0.1	893.1	0.1	898.0	0.0	0.5	0.2	0.2	0.1	0.1	0.1	7.6	2.8	2.4	2.0	2.0	2.0	-5.2	0.4	-	B
hB-hC	64-77	SLGTKADTHDEIL	3.06	5.11	2	12	700.8	706.8	1399.5	1411.5	700.8	0.1	702.3	0.0	702.4	0.1	702.6	0.1	704.2	0.5	5.5	0.1	5.8	0.3	6.3	0.4	45.7	1.1	48.1	2.2	52.3	3.7	2.5	-4.2	-	B
hB-hC*	65-77	LSLGTKADTHDEIL	3.24	6.56	2	13	757.3	763.8	1512.7	1525.7	757.3	0.1	758.6	0.1	758.8	0.1	758.7	0.0	760.6	0.4	4.9	0.4	5.7	0.4	5.4	0.2	37.3	3.0	44.0	3.0	41.9	1.3	6.7	2.1	4.4	B
hC1-hD	82-96	FNLTEIPEAQIHEGF	4.69	9.26	2	13	873.5	879.9	1744.9	1757.9	873.4	0.0	876.2	0.0	876.5	0.0	876.4	0.0	877.9	0.2	8.1	0.1	8.8	0.0	8.6	ND	62.1	0.8	67.9	0.3	66.5	ND	5.8	1.4	3.6	B
hC1-hD*	83-99	NLTEIPEAQIHEGFQEL	4.72	9.02	2	15	985.1	992.5	1968.1	1983.1	985.0	0.0	988.5	0.0	988.4	0.2	988.3	0.4	991.2	0.2	8.5	0.1	8.2	0.5	8.1	0.9	56.4	0.7	54.4	3.1	53.7	6.1	-2.1	0.7	-	B
s2A-hE-s1A*	120-142	LSEGLKLVDKFLEDVKKLYHSEA	4.93	9.45	4	22	666.5	672.4	2662.1	2684.1	666.5	0.0	667.4	ND	668.9	0.1	668.9	0.2	670.8	0.1	4.5	ND	12.2	0.3	12.1	1.2	20.6	ND	55.5	1.5	55.1	5.3	34.9	0.4	-	D
s1A-hF*	143-159	FTVNFGDTEEAKKQIND	4.23	7.83	2	16	979.0	986.9	1956.0	1972.0	978.8	0.0	982.2	0.1	982.3	0.1	981.9	0.2	984.6	0.5	9.2	0.4	9.5	0.3	8.2	0.7	57.5	2.5	59.6	1.9	51.4	4.3	2.1	8.1	4.9	B
hF-thFs3A	160-171	YVEKGTQGKIVD	3.14	4.63	2	11	669.3	674.8	1336.5	1347.5	669.2	0.0	672.2	0.3	672.6	0.0	672.3	0.0	673.1	0.1	8.4	1.0	9.7	0.1	8.9	ND	76.6	9.1	88.2	1.3	80.8	ND	11.6	7.4	9.5	A
hF-thFs3A*	160-172	YVEKGTQGKIVDL	2.68	5.22	2	12	725.8	731.8	1449.7	1461.7	725.8	0.0	728.9	0.2	729.3	0.1	729.1	0.1	730.0	0.3	9.0	0.7	10.2	0.2	9.5	0.3	75.1	5.5	85.0	1.9	79.0	2.6	9.9	6.0	7.9	A
thFs3A*	172-182	LVKELDRDTVF	2.41	6.53	2	10	668.3	673.3	1334.5	1344.5	668.3	0.1	670.9	0.1	671.1	0.1	670.7	0.1	671.4	0.1	8.3	0.3	9.0	0.2	7.8	0.3	82.9	3.2	89.6	2.3	77.7	3.0	6.7	11.9	9.3	A
thFs3A	173-182	VKELDRDTVF	2.54	5.87	2	9	611.7	616.1	1221.4	1230.4	611.7	ND	614.1	0.1	614.3	0.0	613.8	0.1	614.7	0.3	7.1	0.3	7.7	0.1	6.3	0.3	79.3	2.8	85.7	1.6	70.3	2.8	6.4	15.4	10.9	A
s3A*	183-189	ALVNYIF	1.83	9.11	1	6	840.0	845.3	839.0	845.0	839.8	0.0	840.3	0.4	840.0	0.0	840.0	ND	843.8	0.4	0.4	0.6	0.0	0.0	0.0	ND	7.3	9.5	0.0	0.6	0.0	ND	7.3	0.0	-	B
s3A-s4C	183-205	ALVNYIFFKGKWERPFEVKDTEE	2.30	8.80	4	21	712.6	718.8	2846.2	2867.2	712.5	ND	714.4	0.1	715.0	0.0	714.4	0.0	716.6	0.1	9.7	0.4	12.5	0.0	9.8	0.3	46.4	1.9	59.7	0.0	46.8	1.2	13.3	12.9	13.1	A
s3A-s4C*	190-205	FKGKWERPFEVKDTEE	3.96	5.39	3	14	676.1	680.8	2025.2	2039.2	676.1	0.0	678.3	0.1	678.7	0.0	678.1	0.1	678.8	0.4	11.1	0.3	13.5	0.1	10.1	0.5	79.1	2.2	96.2	1.0	72.0	3.7	17.1	24.2	20.7	A
s4C-s3C*	208-227	FHVDQVTTVKVPMMKRLGMF	4.42	8.91	4	18	592.2	596.5	2364.9	2382.9	592.2	ND	593.8	0.2	593.8	0.1	593.7	0.3	595.6	0.5	8.1	0.9	8.2	0.5	8.0	1.6	44.8	5.0	45.5	2.7	44.2	8.7	0.7	1.3	1.0	B
s4C-s3C	209-226	HVDQVTTVKVPMMKRLGM	4.99	8.40	4	16	518.7	522.4	2070.6	2086.6	518.5	ND	520.1	0.2	520.2	0.1	520.1	0.0	521.8	0.3	7.4	0.8	7.7	0.7	7.4	0.2	46.2	5.0	48.1	4.5	46.3	1.1	1.9	1.8	1.8	B
s4C-s3C	209-227	HVDQVTTVKVPMMKRLGMF	4.72	8.73	3	17	740.3	745.9	2217.8	2234.8	740.3	0.0	742.0	0.2	742.1	0.1	741.8	0.0	744.0	0.4	7.8	0.9	8.3	0.3	7.1	0.2	46.0	5.1	48.8	1.9	41.8	0.9	2.8	7.0	4.9	B
s3C	216-226	VKVPMMKRLGM	2.09	7.53	3	9	430.9	433.8	1289.8	1298.8	430.8	ND	431.7	0.3	431.6	0.0	431.5	0.2	432.8	0.2	3.8	1.5	3.1	0.2	2.7	0.8	42.3	16.9	34.0	2.3	29.9	8.8	-8.2	4.1	-	C
s1B-s2B*	227-238	FNIQHCKKLSSW	3.80	8.05	3	11	497.9	501.6	1490.8	1501.8	497.9	ND	498.6	0.3	498.6	0.2	498.4	0.0	500.1	0.7	3.5	1.4	3.4	0.9	2.6	0.2	31.7	12.6	30.8	8.1	23.8	1.5	-0.9	6.9	3.0	B
s2B-s3B	241-251	LMKYLGNATAI	2.32	7.96	2	10	598.2	603.2	1194.5	1204.5	598.2	ND	599.6	0.0	599.7	0.7	599.4	0.2	601.3	0.3	4.4	0.0	4.6	2.4	3.7	0.8	44.3	0.0	46.4	24.2	36.6	7.6	2.1	9.8	5.9	A
s2B-s3B*	242-251	MKYLGNATAI	1.75	6.20	2	9	541.7	546.2	1081.3	1090.3	541.9	ND	543.0	0.0	543.4	0.0	543.0	0.1	544.8	ND	3.9	0.1	5.0	0.1	3.8	0.3	43.2	0.9	55.0	0.7	42.1	3.0	11.8	12.9	12.3	A
s3B-hG*	253-266	FLPDEGKLQHLENE	4.05	6.75	2	12	835.4	841.3	1668.8	1680.8	835.4	0.1	837.5	0.2	837.9	ND	837.8	ND	839.1	0.0	6.7	0.6	8.1	ND	7.9	ND	56.0	5.4	67.2	ND	65.8	ND	11.2	1.4	6.3	A
hH*	267-275	LTHDIITKF	3.22	6.20	2	8	544.6	548.5	1087.3	1095.3	544.6	ND	545.7	0.0	545.5	0.0	545.4	ND	546.5	ND	4.4	0.1	3.8	0.0	3.0	ND	55.0	1.9	47.6	0.4	37.9	ND	-7.4	9.7	-	C
hH-s2C*	276-291	LENEDRRSASLHLPKL	2.46	7.66	3	14	627.0	631.7	1878.1	1892.1	627.0	0.0	628.0	0.4	627.9	0.0	627.7	ND	629.5	0.4	5.4	2.1	4.7	0.3	3.5	ND	38.5	14.9	33.4	2.0	24.7	ND	-5.1	8.7	-	C
hH-s6A	276-296	LENEDRRSASLHLPKLSITGT	3.14	8.34	4	19	585.4	590.2	2337.6	2356.6	585.5	0.0	586.8	0.3	586.9	0.1	586.6	0.3	588.5	ND	8.7	1.8	9.2	0.6	7.3	1.7	46.0	9.7	48.5	3.0	38.7	9.0	2.4	9.8	6.1	A
s6A*	291-300	LSITGTYDLK	2.98	6.68	2	9	556.1	560.3	1110.3	1119.3	556.0	ND	558.7	0.1	559.2	ND	559.1	0.0	560.0	0.2	5.9	0.3	7.2	ND	7.0	0.1	65.8	3.3	79.9	ND	78.0	1.2	14.1	1.9	8.0	A
hI-hI1*	304-317	GQLGITKVFSNGAD	2.74	8.01	2	13	704.3	711.3	1406.6	1419.6	704.2	0.1	706.6	0.1	706.7	0.1	706.5	0.0	708.6	0.3	7.0	0.3	7.4	0.4	6.6	ND	53.9	2.1	56.7	3.3	51.1	ND	2.9	5.7	4.3	B
thI1s5A-s5A*	318-338	LSGVTEEAPLKLSKAVHKAVL	4.32	8.07	4	19	548.7	553.5	2190.6	2209.6	548.7	ND	550.5	0.3	550.5	0.0	550.3	0.1	552.2	0.2	9.9	1.5	10.1	0.1	8.8	0.3	52.3	7.6	53.2	0.4	46.1	1.8	0.9	7.1	4.0	B
s5A*	325-338	APLKLSKAVHKAVL	2.97	4.85	3	12	492.6	496.6	1474.9	1486.9	492.6	ND	493.8	0.1	493.6	0.1	493.3	0.2	495.4	0.2	5.4	0.6	4.2	0.7	3.1	0.8	45.2	4.9	34.9	5.4	25.9	6.7	-10.3	8.9	-	C
s5A-RSL	339-351	TIDEKGTEAAGAM	2.02	4.70	2	12	647.7	653.6	1293.4	1305.4	647.7	0.1	651.2	0.1	651.5	0.1	651.4	0.1	652.1	0.5	9.5	0.3	10.4	0.2	10.0	0.4	78.8	2.9	86.5	1.9	83.2	3.0	7.7	3.3	5.5	A
s5A-RSL*	339-352	TIDEKGTEAAGAMF	2.47	6.49	2	13	721.3	727.5	1440.6	1453.6	721.1	ND	724.6	0.3	725.3	0.2	725.0	0.1	726.1	0.5	9.0	0.7	11.0	0.5	10.1	0.3	68.9	5.5	84.3	3.8	78.0	2.4	15.4	6.3	10.8	A
s4B-C-term*	373-394	LMIDQNTKSPLFMGKVVNPTQK	6.33	8.29	3	19	831.0	837.1	2490.0	2509.0	830.9	0.1	832.8	0.1	832.4	0.2	832.1	0.2	836.0	0.4	7.0	0.5	5.2	0.8	4.4	0.7	36.8	2.8	27.1	4.3	23.0	3.8	-9.6	4.1	-	C
s4B-C-term	374-394	MIDQNTKSPLFMGKVVNPTQK	6.24	7.75	3	18	793.3	799.3	2376.8	2394.8	793.3	ND	795.1	0.2	795.0	0.1	794.2	0.1	797.7	0.5	7.5	0.9	6.9	0.6	3.6	0.3	41.7	5.0	38.4	3.2	19.8	1.9	-3.3	18.6	-	C
s5B-C-term	385-394	MGKVVNPTQK	2.56	4.65	2	8	551.7	555.6	1101.3	1109.3	551.6	0.0	553.1	0.0	553.1	ND	552.5	0.4	554.7	0.3	3.8	0.1	3.8	ND	2.2	1.2	47.9	1.4	47.3	ND	28.1	14.8	-0.7	19.1	-	C
Average												**0.05**		**0.18**		**0.12**		**0.15**		**0.31**		**0.75**		**0.44**		**0.65**		**5.21**		**3.24**		**4.62**				

[a] The nomenclature of Huber and Carrell was followed (1).

[b] Searched scores by SEQUEST searching algorithm.

[c] Retention time (min)

[d] The number of theoretically exchangeable amide hydrogen. Proline residue has no exchangeable amide hydrogen on peptide bond.

[e] The deuterium content, *D* in each fragment was calculated from $D = N \cdot (m_t - m_{0\%}) / (m_{100\%} - m_{0\%})$, where m_t is the experimentally determined mass, $m_{0\%}$ is the average mass of 0% deuterium control, and $m_{100\%}$ represents the average mass of the 100% deuterium control (2). *D1* shows exchanged-deuterium content in native α_1AT, *D2* and *D3* show exchanged-deuterium content during complex formation and after complex formation, respectively.

[f] *D1(%), D2(%), and D3(%)* are portion of H/D-EX relation to the number of theoretically exchangeable amide hydrogen in each peptic fragment, for instance, *D2*(%) = *D2* / N x 100. *D2(%)-D1(%)* or *D2(%)-D3(%)* indicates the difference in percent exchange for D2-specific relation to D1 to D3

[g] Average of percentage differences for D2-specific H/D-EX, that is average of *D2(%)-D1(%)* and *D2(%)-D3(%)*.

[h] Each group (A~D) was categorized according to the pattern of H/D-EX for D1-D2-D3. The groups are the same as in Fig 5.

[*] Representative 23 peptic fragments that provide details of structural changes for most secondary structures were selected**.**

ND: error not determined for single measurement

Note that average of percent change error (n=2) in 39 common peptic fragments was ± 4.36% (D1, ± 5.21%; D2, ± 3.24%; D3, ± 4.62%).

References

1. Huber, R. & Carrell, R. W. (1989) Biochemistry 28, 8951-8966.

2. Smith, D. L., Deng, Y., & Zhang, Z. (1997) J Mass Spectrom 32, 135-146.