Supplemental Figures 1-5 (General Description): Raw, baseline subtracted, and charge deconvoluted mass spectra for the spectra shown in Fig. 1. Tables of observed and calculated *m/z* values are provided as Supplemental Tables 1-5. For albumin, the Bruker Daltonics charge deconvolution algorithm took into account a minimum of the 20 most abundant charge states, summing the raw signal surrounding each individual peak. This procedure results in the simultaneous enhancement of signal/noise for true peaks and the canceling of noise or inconsistent baseline anomalies. For apoA-I, a minimum of at least the 5 most abundant charge states were used in the deconvolution algorithm. PH indicates peak height.

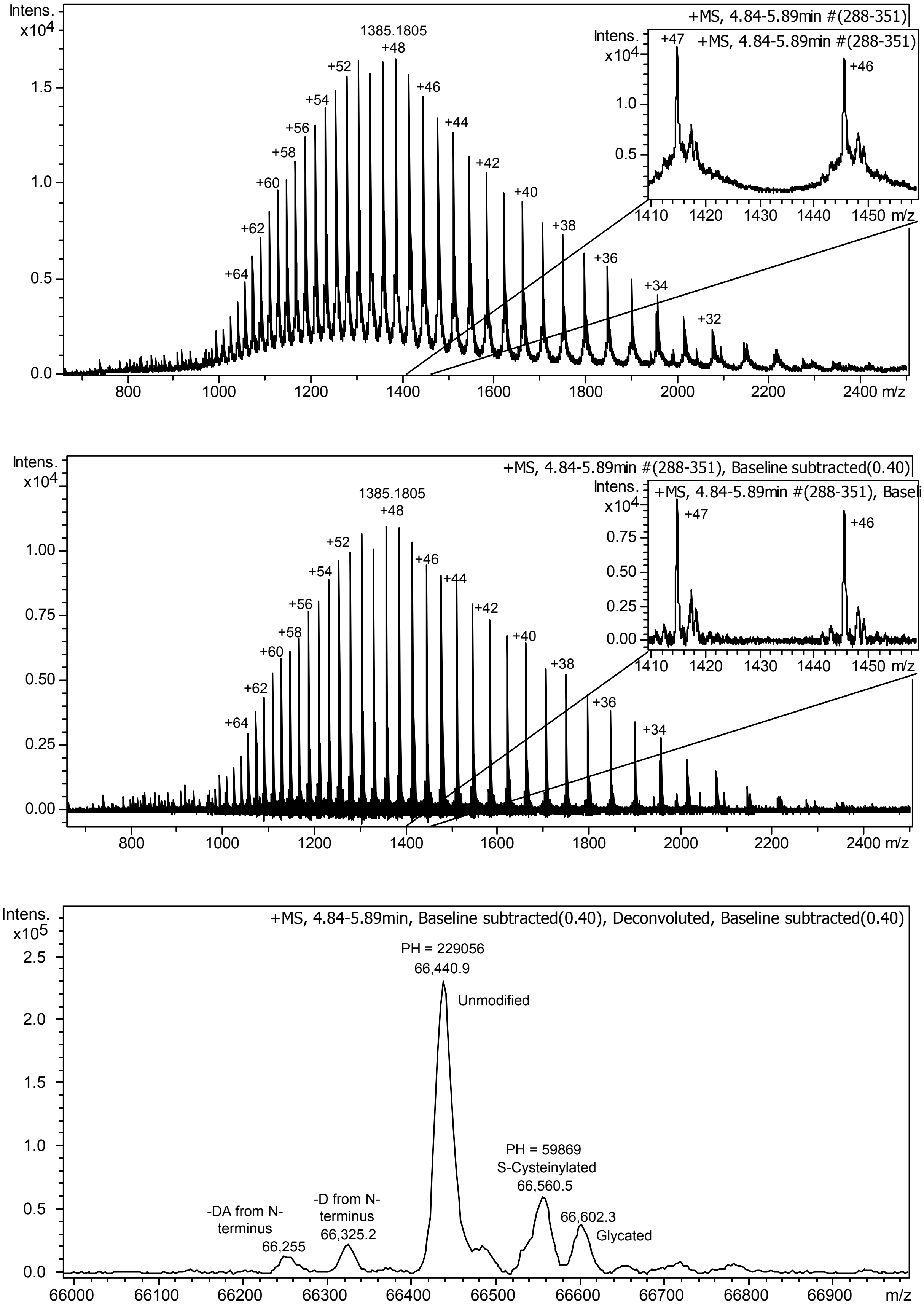
Supplemental Figure 1: Albumin from a fresh, never frozen EDTA plasma sample provided by a healthy donor.

Supplemental Figure 2: ApoA-I from the same fresh, never frozen EDTA plasma sample provided by a healthy donor.

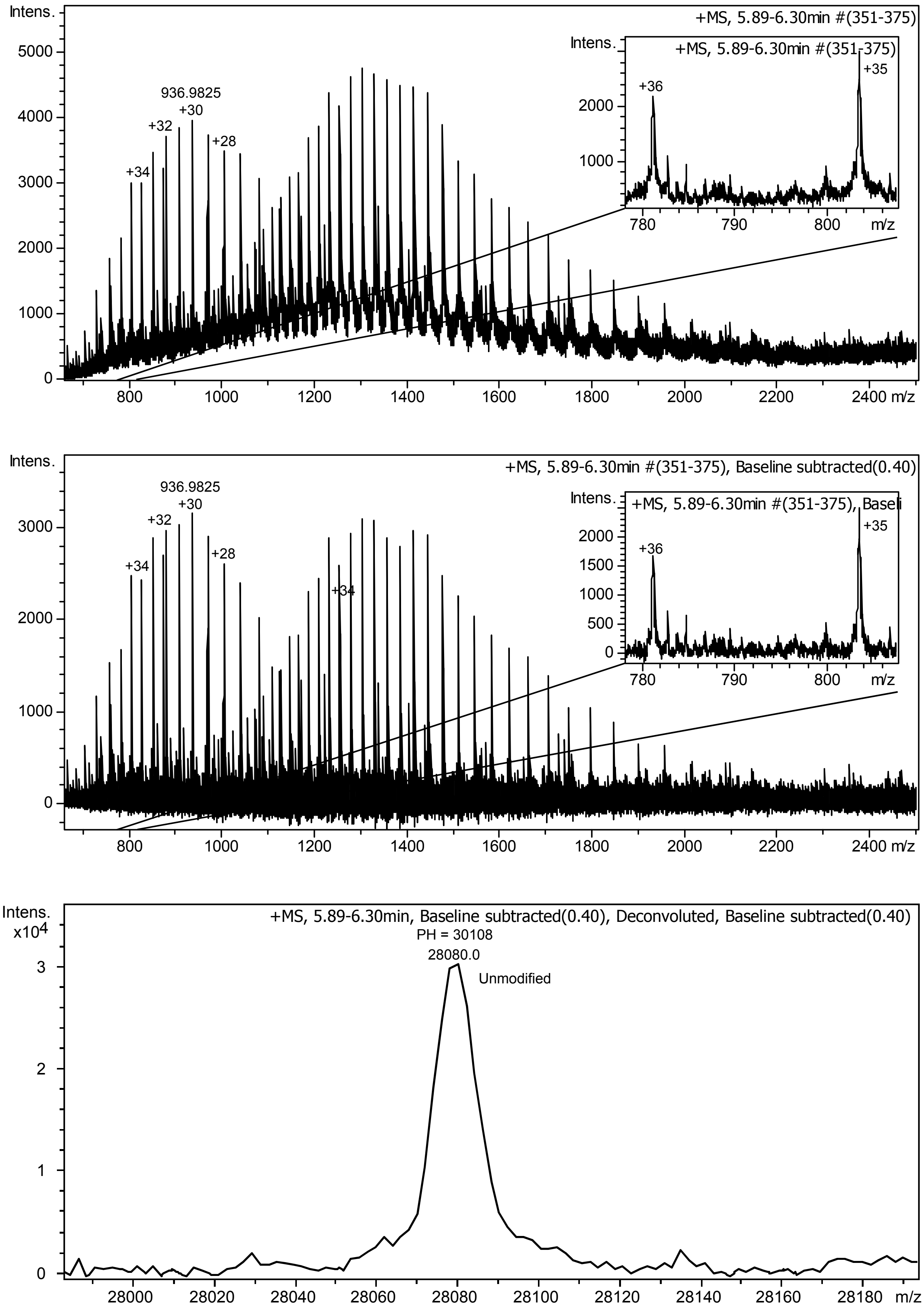
Supplemental Figure 3: Albumin from the same sample shown in Supp. Figs. 1-2, aged for 60 days at -20 °C.

Supplemental Figure 4: ApoA-I from the same sample shown in Supp. Figs. 1-2, aged for 11 days at 25 °C.

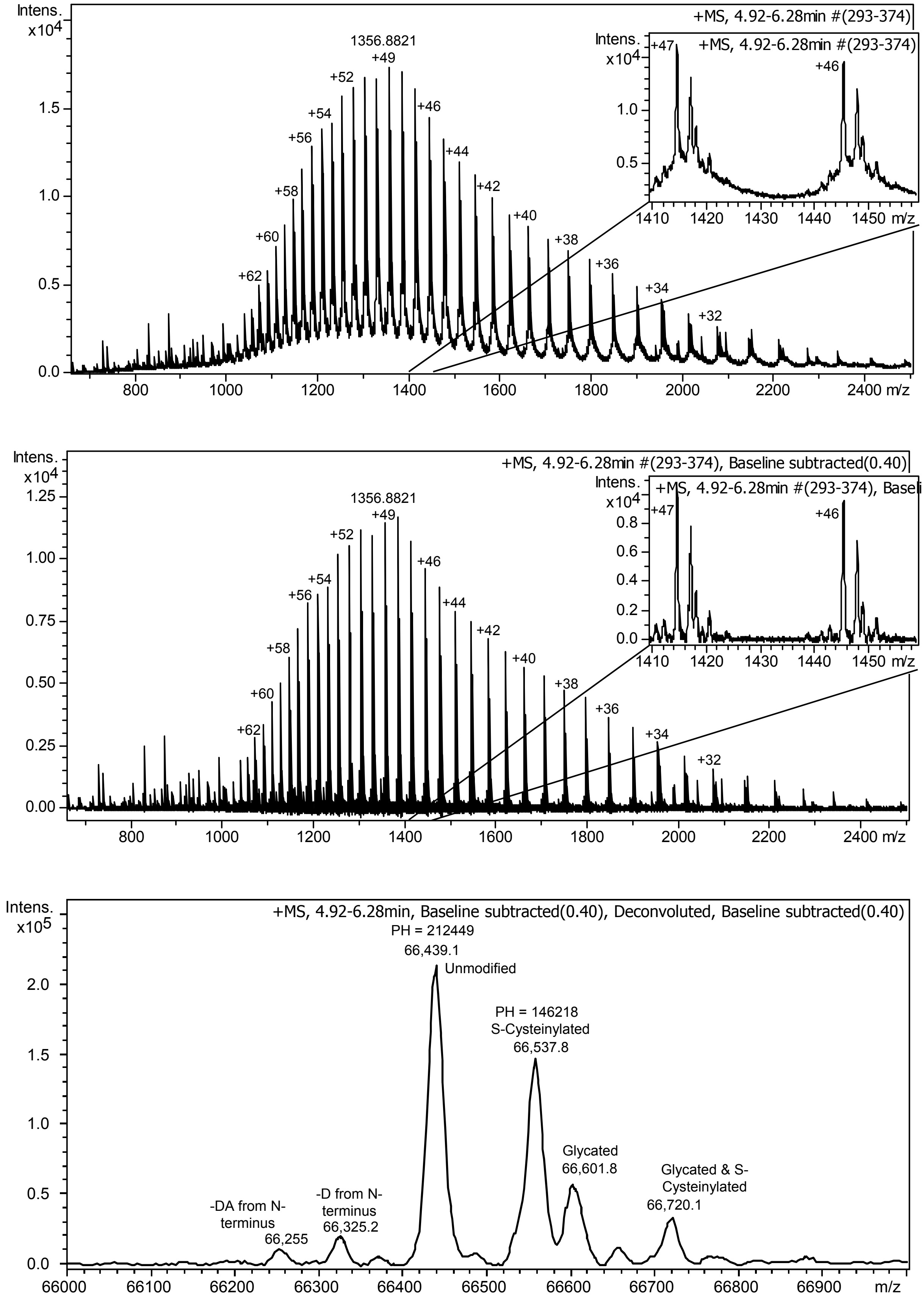
Supplemental Figure 5: ApoA-I from a healthy donor sample purchased from a for-profit biobank, aged for 4 years under unspecified “frozen” conditions. No peaks corresponding to albumin are observed in the raw spectrum because data from this particular sample were acquired by pre-isolation of apoA-I by mass spectrometric immunoassay (MSIA) [Niederkofler, E. E. et al. (2003) Novel mass spectrometric immunoassays for the rapid structural characterization of plasma apolipoproteins. J Lipid Res 44, 630-639]. When samples are injected onto the LC-MS immediately after immunocapture, MSIA does not result in any artifactual oxidation. No other data collected for this study were acquired by MSIA. This spectrum was included because the data from this spectrum served as one of the initial impetuses for this study.



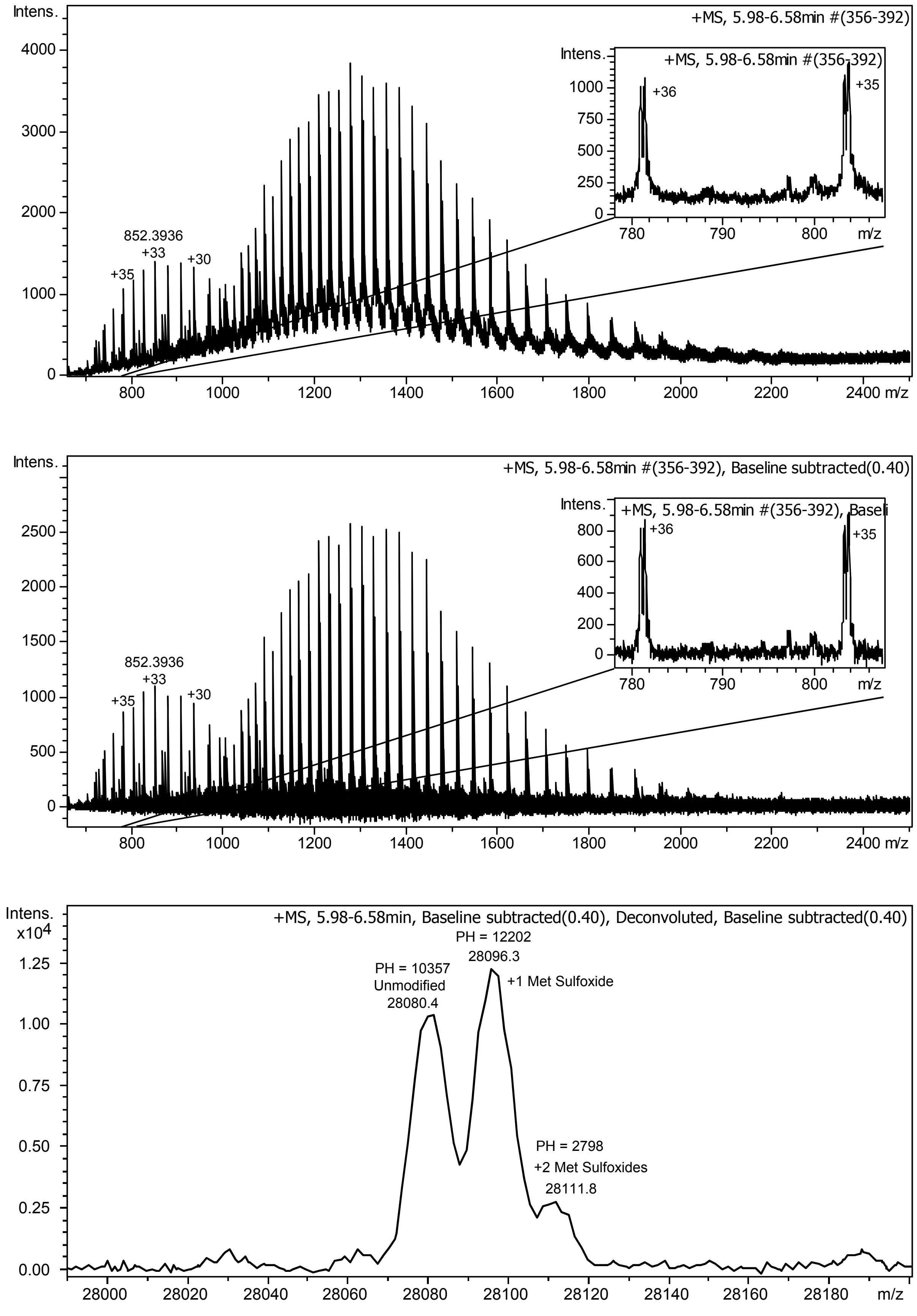
Supplemental Figure 1



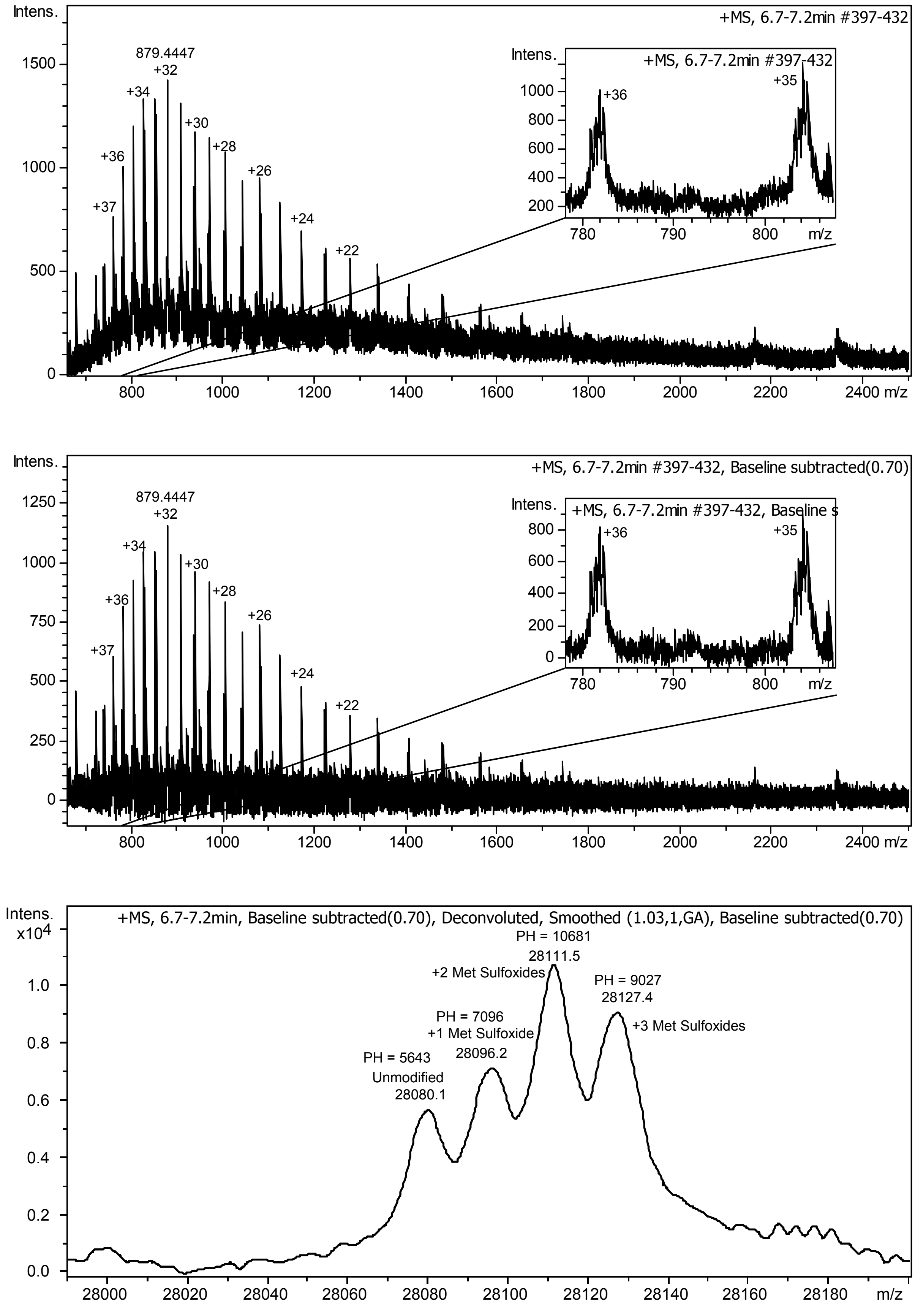
Supplemental Figure 2



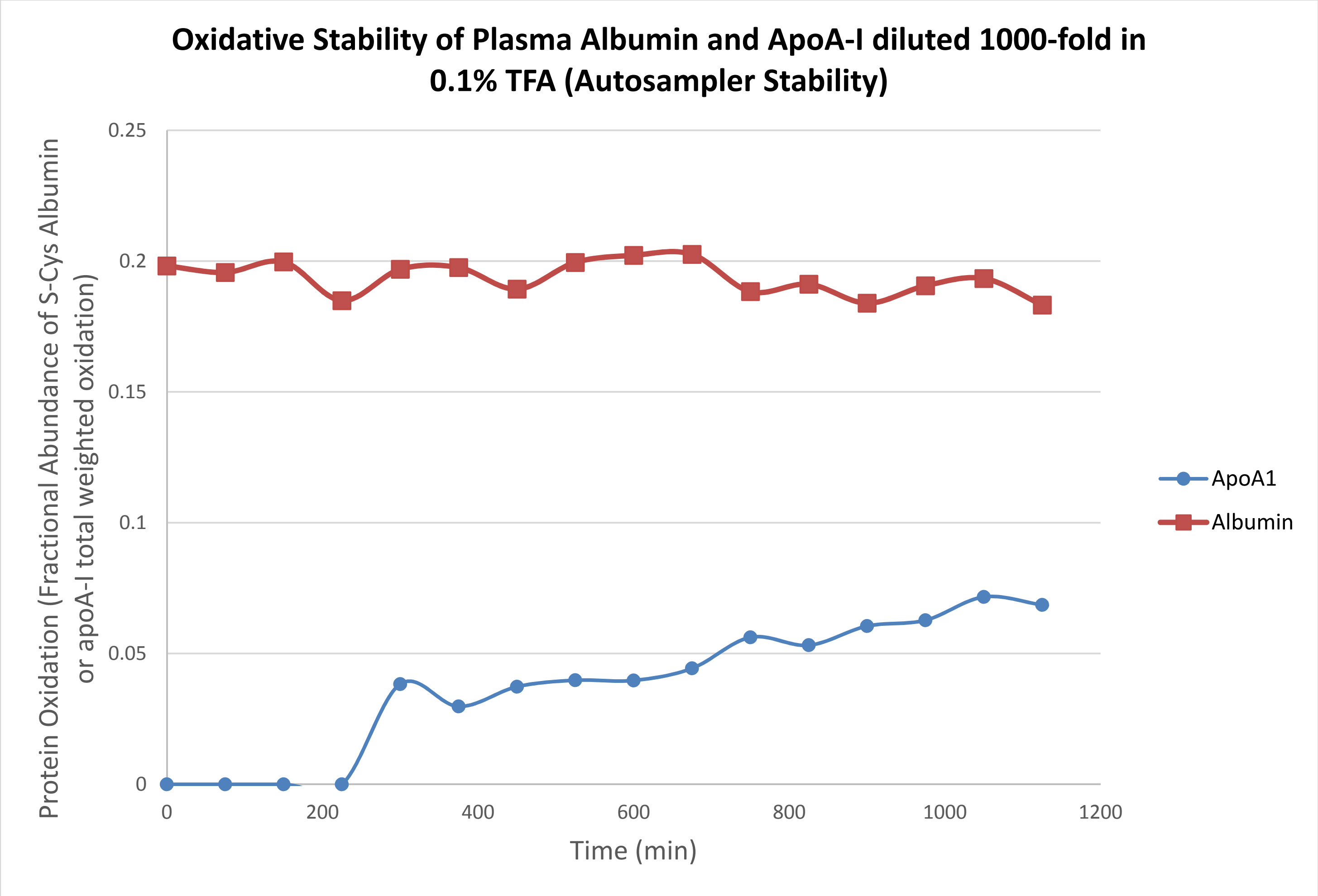
Supplemental Figure 3



Supplemental Figure 4



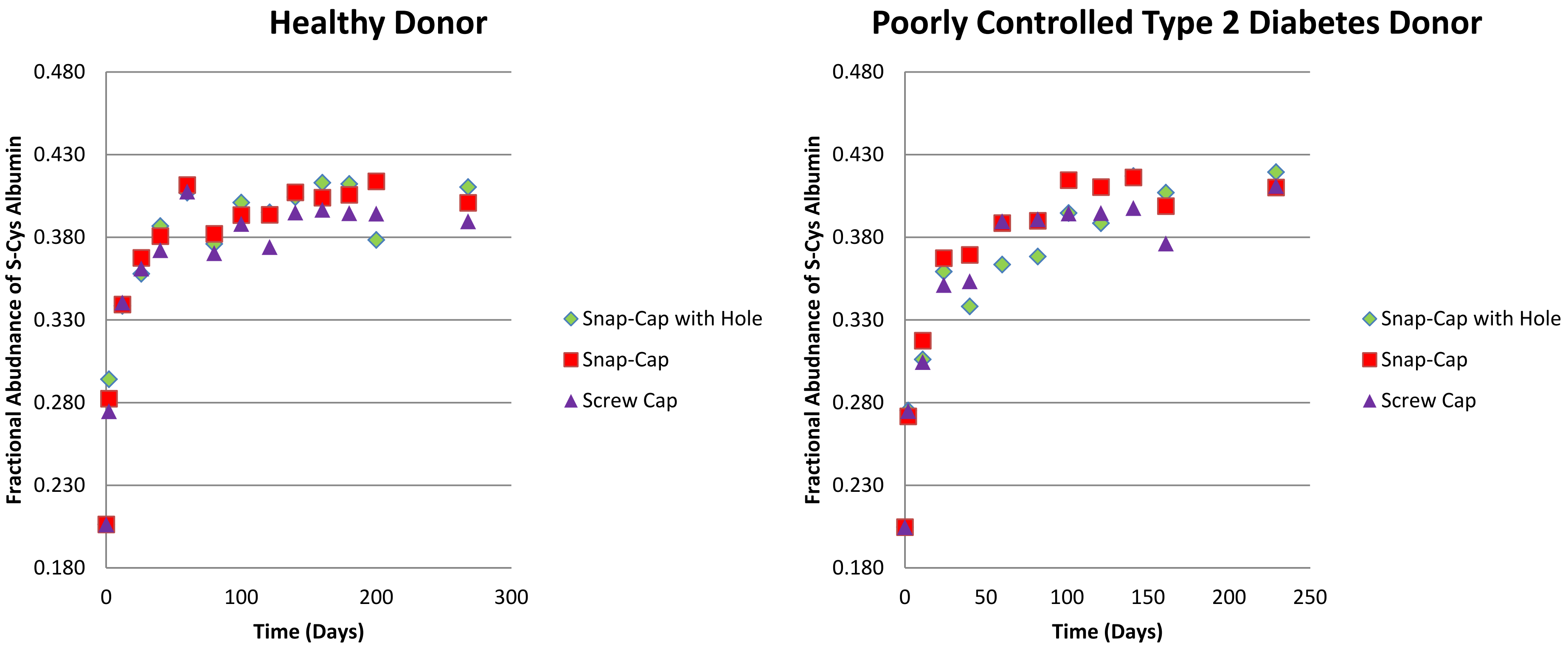
Supplemental Figure 5



Supplemental Figure 6: Autosampler stability of albumin and apoA-I diluted 1000-fold in 0.1% trifluoroacetic acid and placed on an autosampler at 10 °C. The time frame shown is that required to analyze 96 samples using the methodology described here. Albumin S-cysteinylation was stable, but apoA-I methionine oxidation was not.

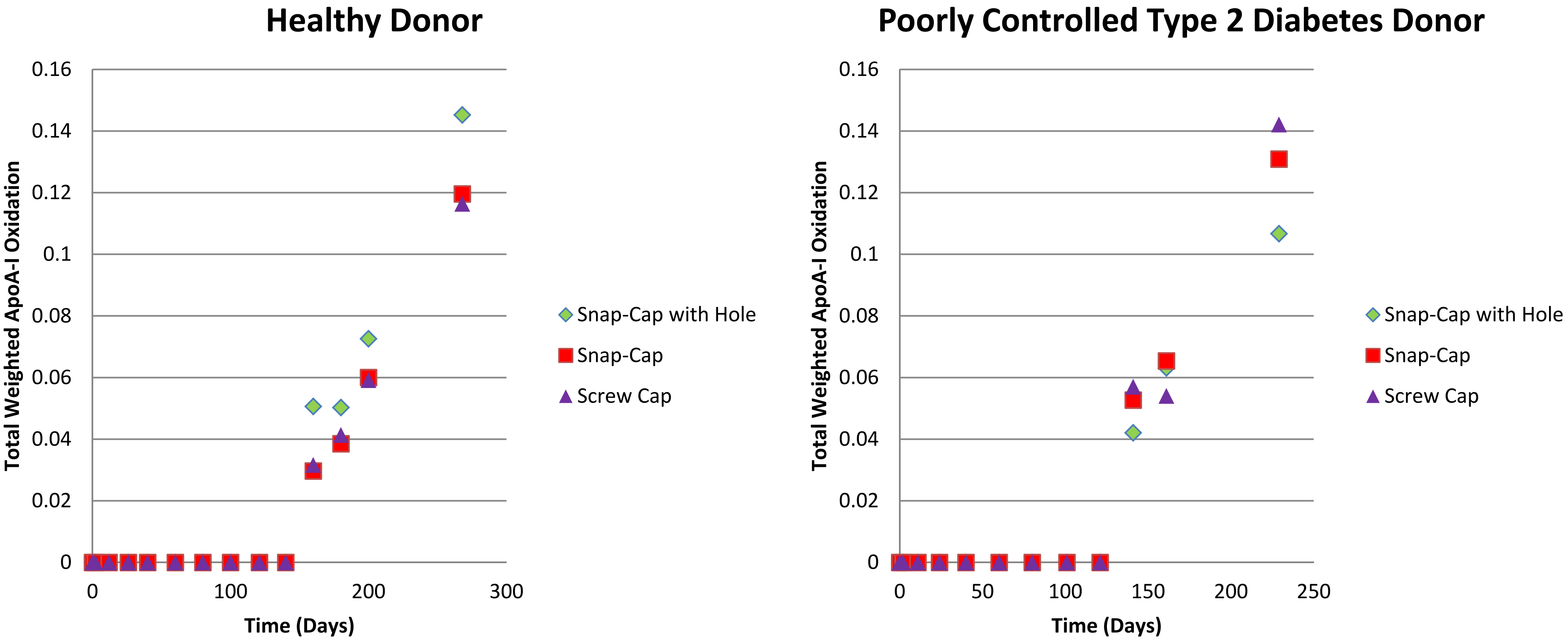
Supplemental Figure 7: Photograph illustrating plasma sample dehydration from storage in an auto defrost freezer.

Albumin Oxidation at -20 °C is Independent of Vial Headspace / Degree of Sealing



Supplemental Figure 8: Albumin oxidation (S-cysteinylation) in the samples from the healthy donor and poorly controlled type 2 diabetic stored in a manual defrost freezer at -20 °C. Data are the same as in Fig. 2, but replicates are separated out with regard to storage vessel type.

ApoA-I Oxidation at -20 °C is not Determined by Vial Headspace / Degree of Sealing



Healthy Donor

Poorly Controlled Type 2 Diabetes Donor

Supplemental Figure 9: ApoA-I methionine oxidation in the samples from the healthy donor and poorly controlled type 2 diabetic stored in a manual defrost freezer at -20 °C. Data are the same as in Fig. 3, but replicates are separated out with regard to storage vessel type.

Supplemental Table 1: Mass Table for Supplemental Figure 1 – Albumin at time zero from a healthy donor. Only the *m/z* values corresponding to the base peak in the charge deconvoluted spectrum are shown.

		Observed	Calculated	Observed	Calculated
	Charge State	*Raw m/z*	*Raw m/z*	*Deconvoluted* MH^+ *Mass*	*Deconvoluted* MH^+ *Mass*
Albumin	+65	1,023.1604	1,023.1215	**66,440.9**	**66,438.9**
	+64	1,039.1096	1,039.0922		
	+63	1,055.5693	1,055.5698		
	+62	1,072.6320	1,072.5790		
	+61	1,090.1919	1,090.1459		
	+60	1,108.3717	1,108.2983		
	+59	1,127.1101	1,127.0661		
	+58	1,146.5066	1,146.4810		
	+57	1,166.6453	1,166.5772		
	+56	1,187.4467	1,187.3911		
	+55	1,208.9789	1,208.9618		
	+54	1,231.3553	1,231.3315		
	+53	1,254.6126	1,254.5453		
	+52	1,278.7039	1,278.6519		
	+51	1,303.7446	1,303.7039		
	+50	1,329.8544	1,329.7580		
	+49	1,356.9385	1,356.8755		
	+48	1,385.1805	1,385.1229		
	+47	1,414.6435	1,414.5723		
	+46	1,445.3864	1,445.3022		
	+45	1,477.4614	1,477.3978		
	+44	1,511.0278	1,510.9523		
	+43	1,546.0870	1,546.0674		
	+42	1,582.8779	1,582.8548		
	+41	1,621.4989	1,621.4366		
	+40	1,661.9439	1,661.9475		
	+39	1,704.6050	1,704.5359		
	+38	1,749.4310	1,749.3658		
	+37	1,796.5972	1,796.6189		
	+36	1,846.4743	1,846.4972		
	+35	1,899.2539	1,899.2257		
	+34	1,955.0667	1,955.0559		
	+33	2,014.3384	2,014.2697		
	+32	2,077.1730	2,077.1844		
	+31	2,144.1840	2,144.1581		

Supplemental Table 2: Mass Table for Supplemental Figure 2 – ApoA-I at time zero from a healthy donor. Only the *m/z* values corresponding to the base peak in the charge deconvoluted spectrum are shown.

		Observed	Calculated	Observed	Calculated
	Charge State	*Raw m/z*	*Raw m/z*	*Deconvoluted MH⁺ Mass*	*Deconvoluted MH⁺ Mass*
ApoA-I	+36	780.9446	780.9611	**28,080.0**	**28,079.6**
	+35	803.2088	803.2457		
	+34	826.8395	826.8412		
	+33	851.8577	851.8667		
	+32	878.4926	878.4563		
	+31	906.7825	906.7613		
	+30	936.9825	936.9533		
	+29	969.2562	969.2276		
	+28	1,003.8416	1,003.8071		
	+27	1,040.9965	1,040.9481		

Supplemental Table 3: Mass Table for Supplemental Figure 3 – Albumin from a healthy donor after 60 days at -20 °C. Only the *m/z* values corresponding to the base peak in the charge deconvoluted spectrum are shown.

		Observed	Calculated	Observed	Calculated
	Charge State	*Raw m/z*	*Raw m/z*	*Deconvoluted MH^+ Mass*	*Deconvoluted MH^+ Mass*
Albumin	+64	1,039.0976	1,039.0922	**66,439.1**	**66,438.9**
	+63	1,055.5643	1,055.5698		
	+62	1,072.5625	1,072.5790		
	+61	1,090.1465	1,090.1459		
	+60	1,108.3033	1,108.2983		
	+59	1,127.0590	1,127.0661		
	+58	1,146.4920	1,146.4810		
	+57	1,166.5926	1,166.5772		
	+56	1,187.3840	1,187.3911		
	+55	1,208.9827	1,208.9618		
	+54	1,231.3319	1,231.3315		
	+53	1,254.5481	1,254.5453		
	+52	1,278.6460	1,278.6519		
	+51	1,303.6930	1,303.7039		
	+50	1,329.7656	1,329.7580		
	+49	1,356.8821	1,356.8755		
	+48	1,385.1356	1,385.1229		
	+47	1,414.5951	1,414.5723		
	+46	1,445.3325	1,445.3022		
	+45	1,477.4243	1,477.3978		
	+44	1,510.9507	1,510.9523		
	+43	1,546.0798	1,546.0674		
	+42	1,582.8689	1,582.8548		
	+41	1,621.4249	1,621.4366		
	+40	1,661.9561	1,661.9475		
	+39	1,704.5380	1,704.5359		
	+38	1,749.3688	1,749.3658		
	+37	1,796.6358	1,796.6189		
	+36	1,846.5239	1,846.4972		
	+35	1,899.2072	1,899.2257		
	+34	1,955.0347	1,955.0559		
	+33	2,014.3156	2,014.2697		
	+32	2,077.1643	2,077.1844		
	+31	2,144.1838	2,144.1581		

Supplemental Table 4: Mass Table for Supplemental Figure 4 – ApoA-I at from a healthy donor after 11 days at 25 °C. Only the *m/z* values corresponding to the base peak in the charge deconvoluted spectrum are shown.

		Observed	Calculated	Observed	Calculated
	Charge State	*Raw m/z*	*Raw m/z*	*Deconvoluted MH$^+$ Mass*	*Deconvoluted MH$^+$ Mass*
ApoA-I	+37	760.3156	760.3135	**28,096.3**	**28,095.6**
	+36	781.4401	781.4056		
	+35	803.6990	803.7029		
	+34	827.3394	827.3118		
	+33	852.3936	852.3515		
	+32	878.9726	878.9563		
	+31	907.3103	907.2774		
	+30	937.4766	937.4867		
	+29	969.8069	969.7793		
	+28	1,004.4410	1,004.3786		

Supplemental Table 5: Mass Table for Supplemental Figure 5 – ApoA-I at from a healthy donor after 4 years of unknown “frozen” storage conditions. Only the *m/z* values corresponding to the base peak in the charge deconvoluted spectrum are shown.

		Observed	Calculated	Observed	Calculated
	Charge State	*Raw m/z*	*Raw m/z*	*Deconvoluted MH^+ Mass*	*Deconvoluted MH^+ Mass*
ApoA-I	+37	760.7210	760.7459	**28,111.5**	**28,111.6**
	+36	781.8752	781.8500		
	+35	804.1406	804.1600		
	+34	827.7999	827.7824		
	+33	852.8060	852.8364		
	+32	879.4447	879.4563		
	+31	907.7673	907.7935		
	+30	938.0634	938.0200		
	+29	970.3279	970.3310		
	+28	1,004.9485	1,004.9500		
	+27	1,042.1198	1,042.1333		
	+26	1,082.1860	1,082.1769		
	+25	1,125.4339	1,125.4240		
	+24	1,172.3009	1,172.2750		
	+23	1,223.2221	1,223.2000		
	+22	1,278.6884	1,278.7545		

Supplemental Table 6: Basic clinical information of patients with myocardial infarction (n = 24). Twelve patients were male and twelve were female.

Demographics	Mean	SE (+/-)
Age (years)	60.1	11.2
Height (cm)	167	10.9
Weight (kg)	94.7	24.0
BMI %	33.5	7.23

Supplemental Table 7: Clinical laboratory measurements of patients with myocardial infarction (n = 24)

Laboratory parameters	Mean	SE (+/-)
HDL (mg/dl)	42	8.7
LDL (mg/dl)	101	42.7
Total Cholesterol (mg/dl)	175	45.6
Triglycerides (mg/dl)	163	72.6
CPK-MB (mg/dl)	45	127
Troponin I (ng/ml)	2.9	9.4
Creatinine (mg/dl)	1.1	0.42
HbA1c (only diabetics)	8.5	1.3
Systolic BP (mmHg)	136	33
Diastolic BP (mmHg)	80	21
HR	74	12
TIMI [a]	3.6	1.3

[a] Thrombolysis in Myocardial Infarction risk score. Based on parameters described in: Antman, E. M., et al (2000) The TIMI risk score for unstable angina/non-ST elevation MI: A method for prognostication and therapeutic decision making. *JAMA* 284, 835-842

Supplemental Table 8: Clinical characteristics of prostate cancer patients (n = 24). All cases were diagnosed as adenocarcinoma. Twenty three subjects were white, one was African-American.

Subject Parameter	Mean	SE (+/-)
Age (yrs)	62.7	5.7
Stage	2.1	0.34
Gleason Score	(3.08 + 3.75)	(0.28 + 0.68, resp.)
PSA (ng/mL)	5.9	2.1