Supplementary Material

Enhancing characterization of organic nitrogen components in aerosols and droplets using high-resolution aerosol mass spectrometry

Xinlei Ge[1,2], Yele Sun[1,3], Justin Trousdell[1], Mindong Chen[2], Qi Zhang[1]

[1]Department of Environmental Toxicology, University of California at Davis, One Shields Avenue, California 95616, United States

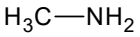
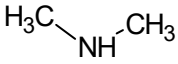
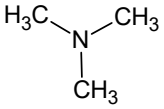
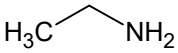
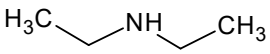
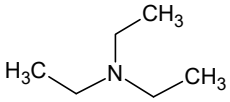
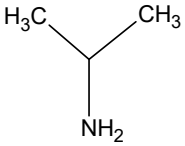
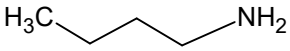
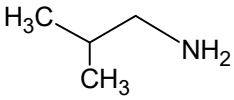
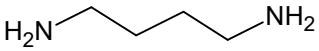
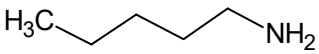
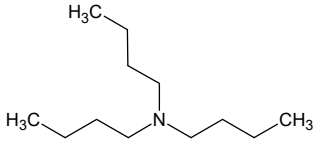
[2]Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (AEET), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

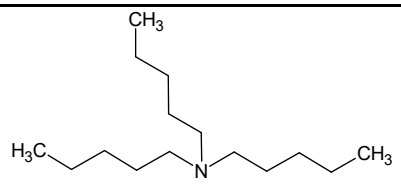
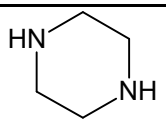
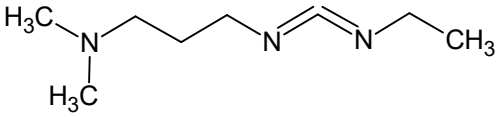
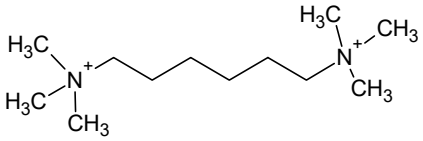
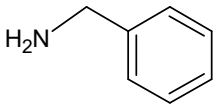
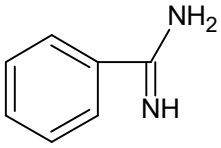
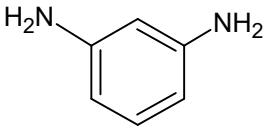
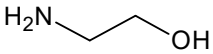
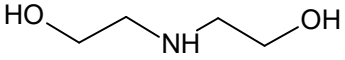
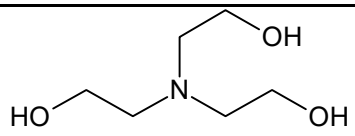
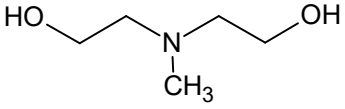
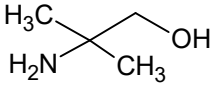
[3]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

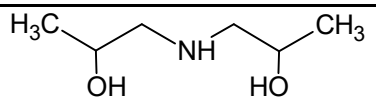
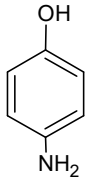
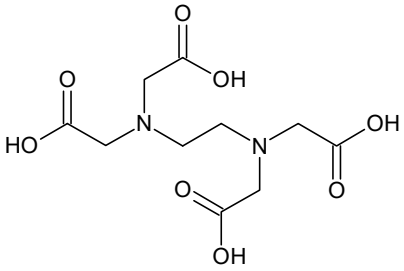
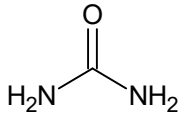
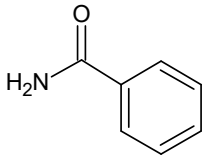
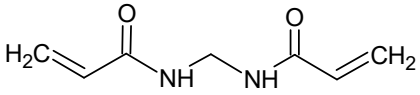
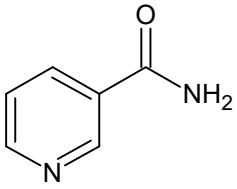
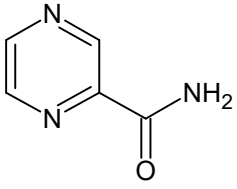
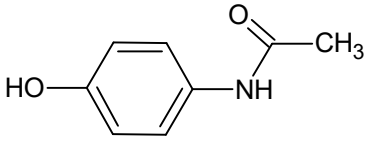
Correspondence to: Q. Zhang (dkwzhang@ucdavis.edu)

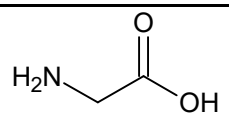
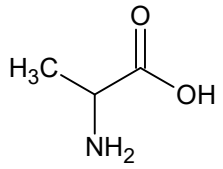
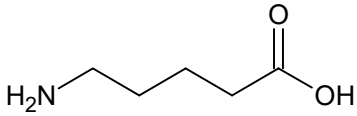
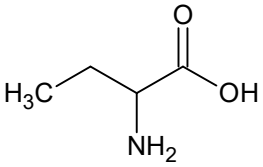
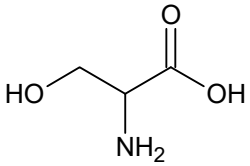
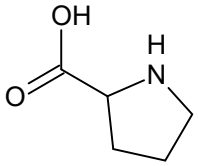
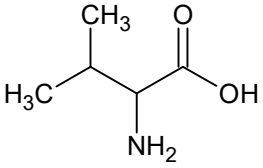
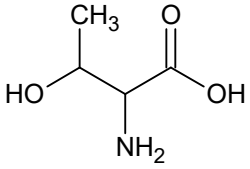
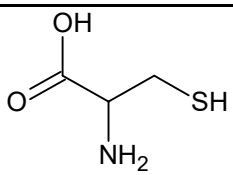
24 pages, 2 tables and 7 figures

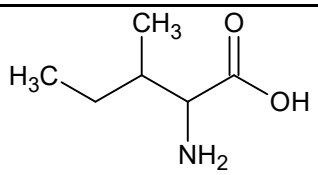
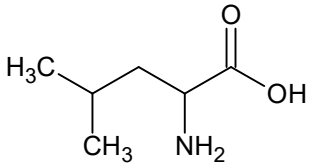
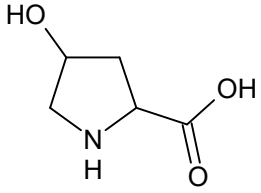
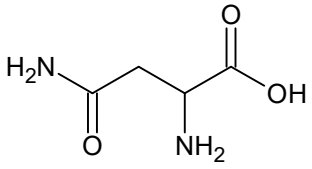
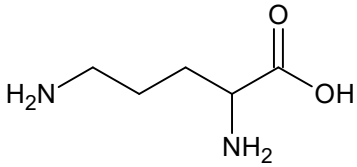
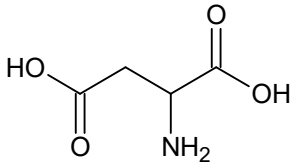
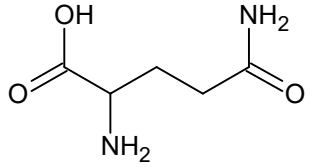
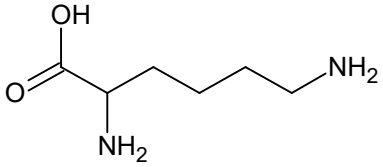
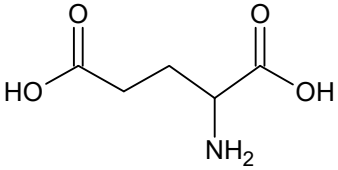
Table S1. List of N-containing organic (ON) standards analyzed in this study.

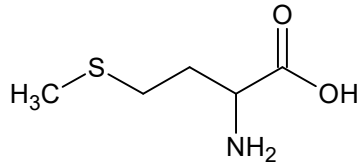
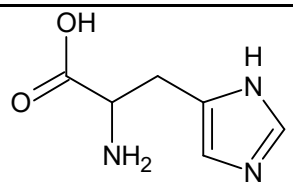
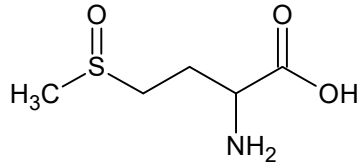
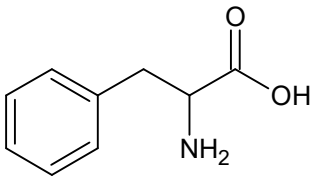
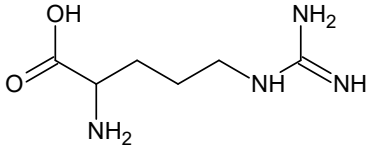
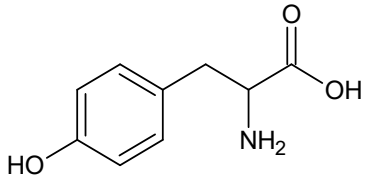
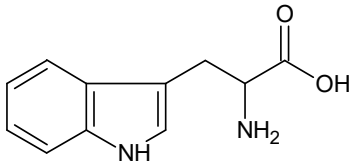
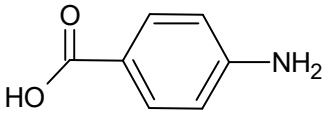
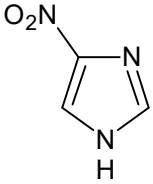
No.	Name	Abbr.	Functional Groups	Chemical Formula	Molecular weight	Structure
1	Methylamine (Hydrochloride)	MA	Amine	CH_5N (HCl)	31.0571 (36.4610)	
2	Dimethylamine (Hydrochloride)	DMA	Amine	C_2H_7N (HCl)	45.0837 (36.4610)	
3	Trimethylamine (Hydrochloride)	TMA	Amine	C_3H_9N (HCl)	59.1103 (36.4610)	
4	Ethylamine (Hydrochloride)	EA	Amine	C_2H_7N (HCl)	45.0837 (36.4610)	
5	Diethylamine (Hydrochloride)	DEA	Amine	$C_4H_{11}N$ (HCl)	73.1368 (36.4610)	
6	Triethylamine (Hydrochloride)	TEA	Amine	$C_6H_{15}N$ (HCl)	101.1900 (36.4610)	
7	Isopropylamine (Hydrochloride)	iPPA	Amine	C_3H_9N (HCl)	59.11 (36.4610)	
8	Butylamine (Hydrochloride)	BTA	Amine	$C_4H_{11}N$ (HCl)	73.14 (36.4610)	
9	Isobutylamine (Hydrochloride)	iBTA	Amine	$C_4H_{11}N$ (HCl)	73.14 (36.4610)	
10	1,4-Diaminobutane (Hydrochloride)	BDA	Amine	$C_4H_{12}N_2$ (2HCl)	88.15 (72.9220)	
11	Pentylamine (Hydrochloride)	PTA	Amine	$C_5H_{13}N$ (HCl)	87.16 (36.4610)	
12	Tributylamine (Hydrochloride)	TBA	Amine	$C_{12}H_{27}N$ (HCl)	185.3495 (36.4610)	

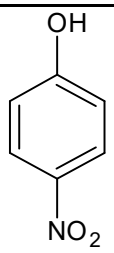
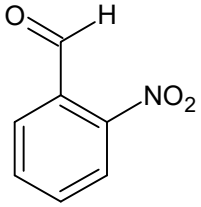
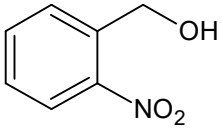
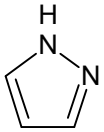
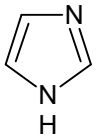
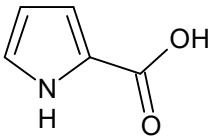
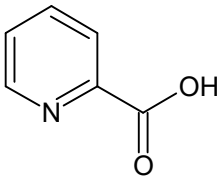
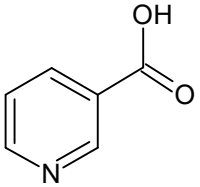
13	Tri-n-amylamie (Hydrochloride)	TAA	Amine	$C_{15}H_{33}N$ (HCl)	227.4292 (36.4610)	
14	Piperazine (Dihydrochloride)	PIP	Amine	$C_4H_{10}N_2$ (2HCl)	86.1356 (72.9220)	
15	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (Hydrochloride)	DMPED	Amine	$C_8H_{17}N_3$ (HCl)	155.2407 (36.4610)	
16	Hexamethonium chloride	HM	Amine	$C_{12}H_{30}N_2(Cl_2)$	202.3800 (70.9060)	
17	Benzylamine (Hydrochloride)	BZA	Amine	C7H9N (HCl)	107.1531 (36.4610)	
18	Benzamidine (Hydrochloride)	BZD	Amine	$C_7H_8N_2$ (HCl)	120.1518 (36.4610)	
19	1,3-phenylenediamine (Dihydrochloride)	PHLDA	Amine	$C_6H_8N_2$ (2HCl)	108.1411 (72.9220)	
20	Ethanolamine Also tried MEA.HCl	EAOH	Amine	C_2H_7NO	61.0831	
21	Diethanolamine (Hydrochloride)	DEAOH	Amine	$C_4H_{11}NO_2$ (HCl)	105.1356 (36.4610)	
22	Triethanolamine	TEAOH	Amine	$C_6H_{15}NO_3$	149.1882	
23	Methyldiethanolamine (Hydrochloride)	MDEA	Amine	$C_5H_{13}NO_2$ (HCl)	119.1622 (36.4610)	
24	2-Amino-2-methyl-1-propanol (Hydrochloride)	AMP	Amine	$C_4H_{11}NO$ (HCl)	89.1362 (36.4610)	

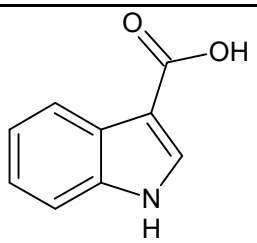
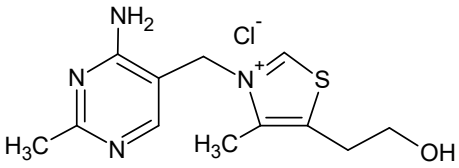
25	Bis(2-hydroxypropyl)amine	BOHA	Amine	$C_6H_{15}NO_2$	133.1888	
26	4-Aminophenol (Hydrochloride)	APA	Amine	C_6H_7NO (HCl)	109.1259 (36.4610)	
27	Ethylene diamine tetraacetic acid	EDTA	Amine	$C_{10}H_{16}N_2O_8$	292.2426	
28	Urea	UREA	Amide	CH_4N_2O	60.0553	
29	Benzamide	BZAM	Amide	C7H7NO	121.1366	
30	N,N'-Methylenebisacrylamide	NMAM	Amide	$C_7H_{10}N_2O_2$	154.1665	
31	Nicotinamide	NCAM	Amide	$C_6H_6N_2O$	122.1246	
32	Pyrazinecarboxamide	PRCAM	Amide	$C_5H_5N_3O$	123.1127	
33	Acetaminophenol	AAP	Amide	$C_8H_9NO_2$	151.1626	

34	Glycine	GLY	Amino Acid	$C_2H_5NO_2$	75.0666	
35	L-Alanine	ALA	Amino Acid	$C_3H_7NO_2$	89.0932	
36	γ-Aminobutyric acid	GABA	Amino Acid	$C_4H_9NO_2$	103.1198	
37	R-2-aminobutyric acid	RGABA	Amino Acid	$C_4H_9NO_2$	103.1198	
38	L-Serine	SER	Amino Acid	$C_3H_7NO_3$	105.0926	
39	L-Proline	PRO	Amino Acid	$C_5H_9NO_2$	115.1305	
40	L-Valine	VAL	Amino Acid	$C_5H_{11}NO_2$	117.1463	
41	L-Threonine	THR	Amino Acid	$C_4H_9NO_3$	119.1192	
42	L-Cysteine	CYS	Amino Acid	$C_3H_7NO_2S$	121.1580	

43	L-Isoleucine	ILE	Amino Acid	$C_6H_{13}NO_2$	131.1729	
44	L-Leucine	LEU	Amino Acid	$C_6H_{13}NO_2$	131.1729	
45	trans-4-hydroxyl-proline	PROOH	Amino Acid	$C_5H_9NO_3$	131.1299	
46	L-Asparagine	ASN	Amino Acid	$C_4H_8N_2O_3$	132.1179	
47	L-Ornithine (Hydrochloride)	ORN	Amino Acid	$C_5H_{12}N_2O_2$ (HCl)	132.1610 (34.4610)	
48	L-Aspartic Acid	ASP	Amino Acid	$C_4H_7NO_4$	133.1027	
49	L-Glutamine	GLN	Amino Acid	$C_5H_{10}N_2O_3$	146.1445	
50	L-Lysine	LYS	Amino Acid	$C_6H_{14}N_2O_2$	146.1876	
51	L-Glutamic Acid	GLU	Amino Acid	$C_5H_9NO_4$	147.1293	

52	L-Methionine	MET	Amino Acid	$C_5H_{11}NO_2S$	149.2110	
53	L-Histidine (Monochloride. Monohydrate)	HIS	Amino Acid	$C_6H_9N_3O_2$ ($HCl \cdot H_2O$)	155.1546 (36.4610+18.013)	
54	L-Methionine Sulfoxide	METSO	Amino Acid	$C_5H_{11}NO_3S$	165.2110	
55	L-Phenylalamine	PHE	Amino Acid	$C_9H_{11}NO_2$	165.1891	
56	L-Arginine (Hydrochloride)	ARG	Amino Acid	$C_6H_{14}N_4O_2$ (HCl)	174.2010 (36.4610)	
57	L-Tyrosine	TYR	Amino Acid	$C_9H_{11}NO_3$	181.1885	
58	L-Tryptophan	TRP	Amino Acid	$C_{11}H_{12}N_2O_2$	204.2252	
59	4-Aminobenzonic acid	ABA	Amino acid	$C_7H_7NO_2$	137.1360	
60	4-Nitroimidazole	NID	Nitro-compounds	$C_3H_3N_3O_2$	113.0748	

61	4-Nitrophenol	NPH	Nitro-compounds	$C_6H_5NO_3$	139.1088	
62	2-Nitrobenzaldehyde	NBAD	Nitro-compounds	$C_7H_5NO_3$	151.1195	
63	2-nitrobenzyl alcohol	NBAC	Nitro-compounds	$C_7H_7NO_3$	153.1354	
64	Pyrazole	PRZ	N-heterocycle	$C_3H_4N_2$	68.0773	
65	Imidazole	ID	N-heterocycle	$C_3H_4N_2$	68.0773	
66	Pyrrole-2-carboxylic acid	PRCA	N-heterocycle	$C_5H_5NO_2$	111.0987	
67	2-Picolinic acid	PCA	N-heterocycle	$C_6H_5NO_2$	123.1094	
68	Nicotinic acid	NCA	N-heterocycle	$C_6H_5NO_2$	123.1094	

69	Indole-3-carboxylic acid	IDCA	N-heterocycle	$C_9H_7NO_2$	161.1574	
70	Thiamine (hydrochloride)	THA	N-heterocycle	$C_{12}H_{17}ClN_4OS$ (HCl)	300.8076 (36.4610)	
71	Amino acid standard	AS	Amino Acid	-	-	Physiological acidics and neutrals
72	Protein	PROTEIN	Protein	-	-	Cytochrome C from horse heart
73	Elliott Soil	HA	Humic substance	-	-	Standard HA from IHSS*, No. 1S102H
74	Waskish Peat	FA	Humic substance	-	-	Reference HA from IHSS, No. 1R107F
75	Suwannee River	NOM	Humic substance	-	-	Aquatic NOM (Natural Organic Matter) from IHSS, No. 1R101N

*International Humic Substances Society (http://www.ihss.gatech.edu/).

Table S2. List of the N-containing organic (ON) standards used to make the 1:1 (mass ratio) mixtures with sulfate (in ammonium sulfate).

No.	ID. in Table S1	Name	No.	ID. in Table S1	Name
1	1	Methylamine (Hydrochloride)	**10**	34	Glycine
2	2	Dimethylamine (Hydrochloride)	**11**	35	L-Alanine
3	3	Trimethylamine (Hydrochloride)	**12**	39	L-Proline
4	4	Ethylamine (Hydrochloride)	**13**	41	L-Threonine
5	5	Diethylamine (Hydrochloride)	**14**	42	L-Cysteine (Hydrochloride)
6	6	Triethylamine (Hydrochloride)	**15**	59	4-Aminobenzonic acid
7	20	Ethanolamine (Hydrochloride)	**16**	68	Nicotinic acid
8	19	1,3-phenylenediamine (Dihydrochloride)	**17**	23	Methyldiethanolamine (Hydrochloride)
9	33	Acetaminophenol	**18**	14	Piperazine (Dihydrochloride)

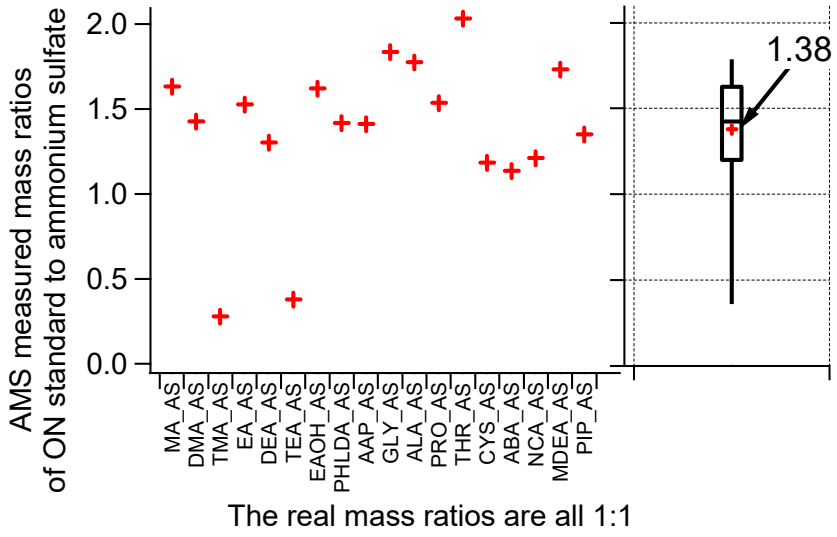


Figure S1. AMS measured mass ratios of the mixtures of different ON standards with ammonium sulfate. All mass ratios of the mixtures are prepared in 1:1 (the whiskers above and below the boxes indicate the 90th and 10th percentiles, the upper and lower boundaries of the boxes indicate the 75th and 25th percentiles, and the lines in the boxes indicate the median values and the cross symbols indicate the mean values).

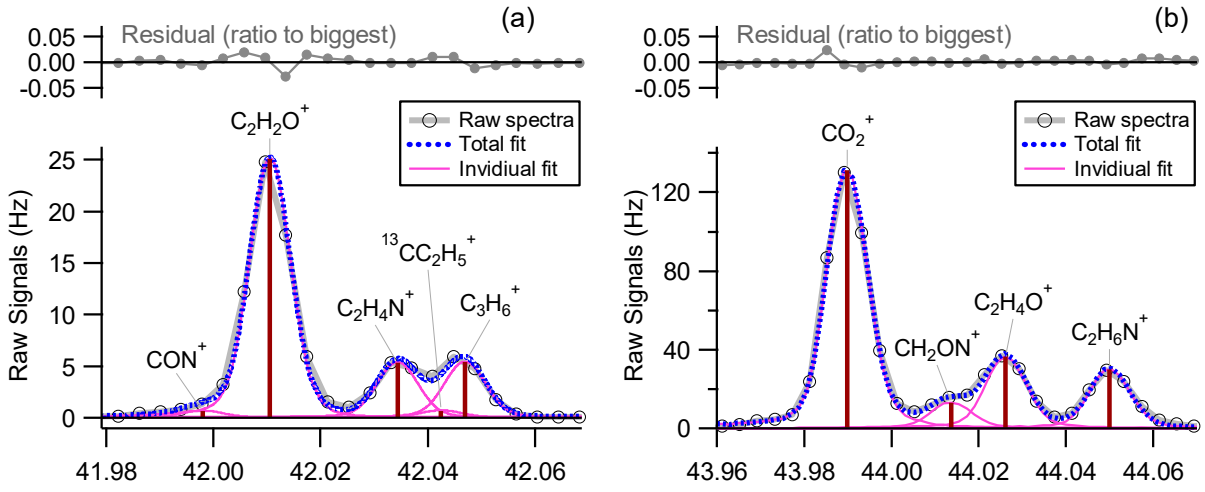
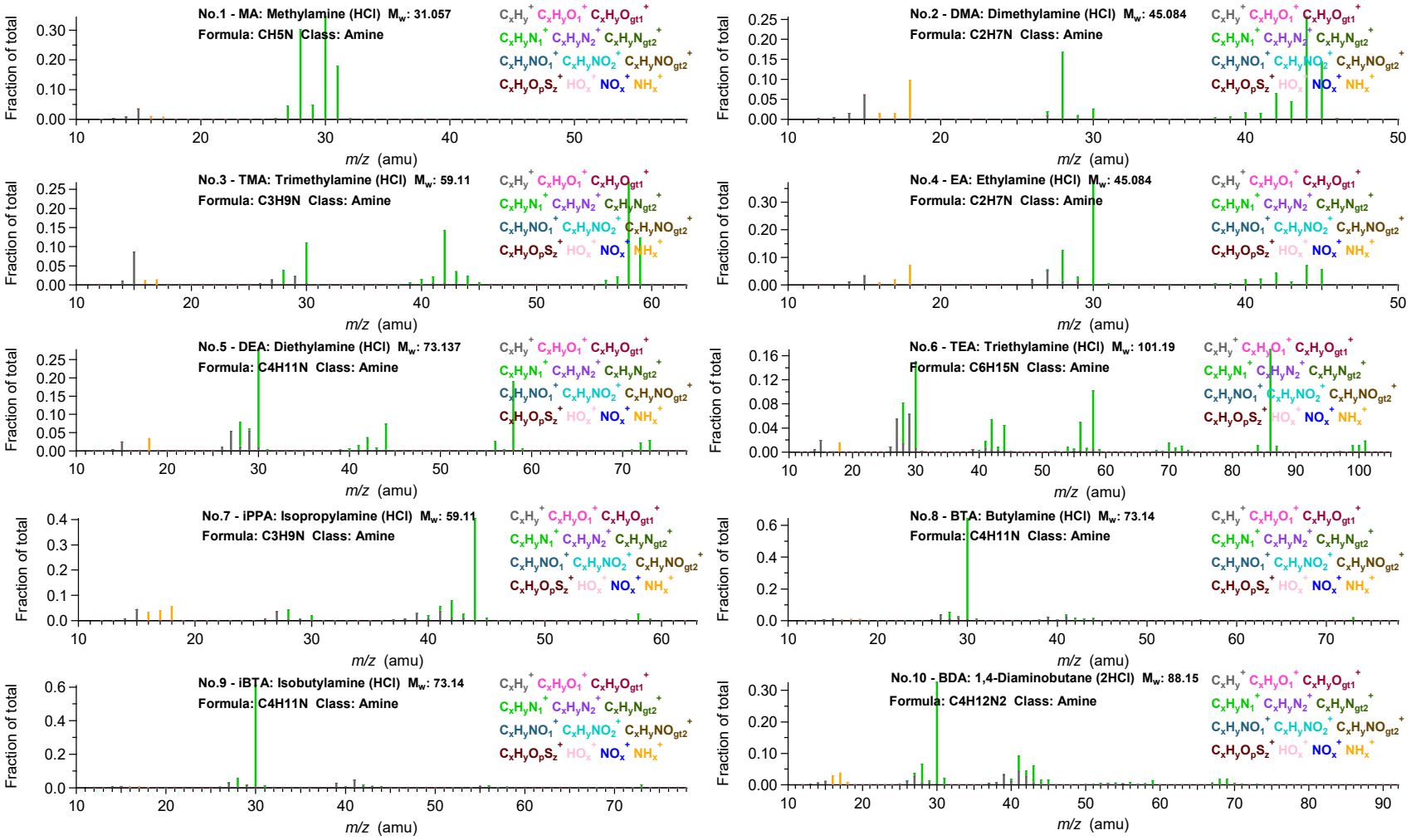
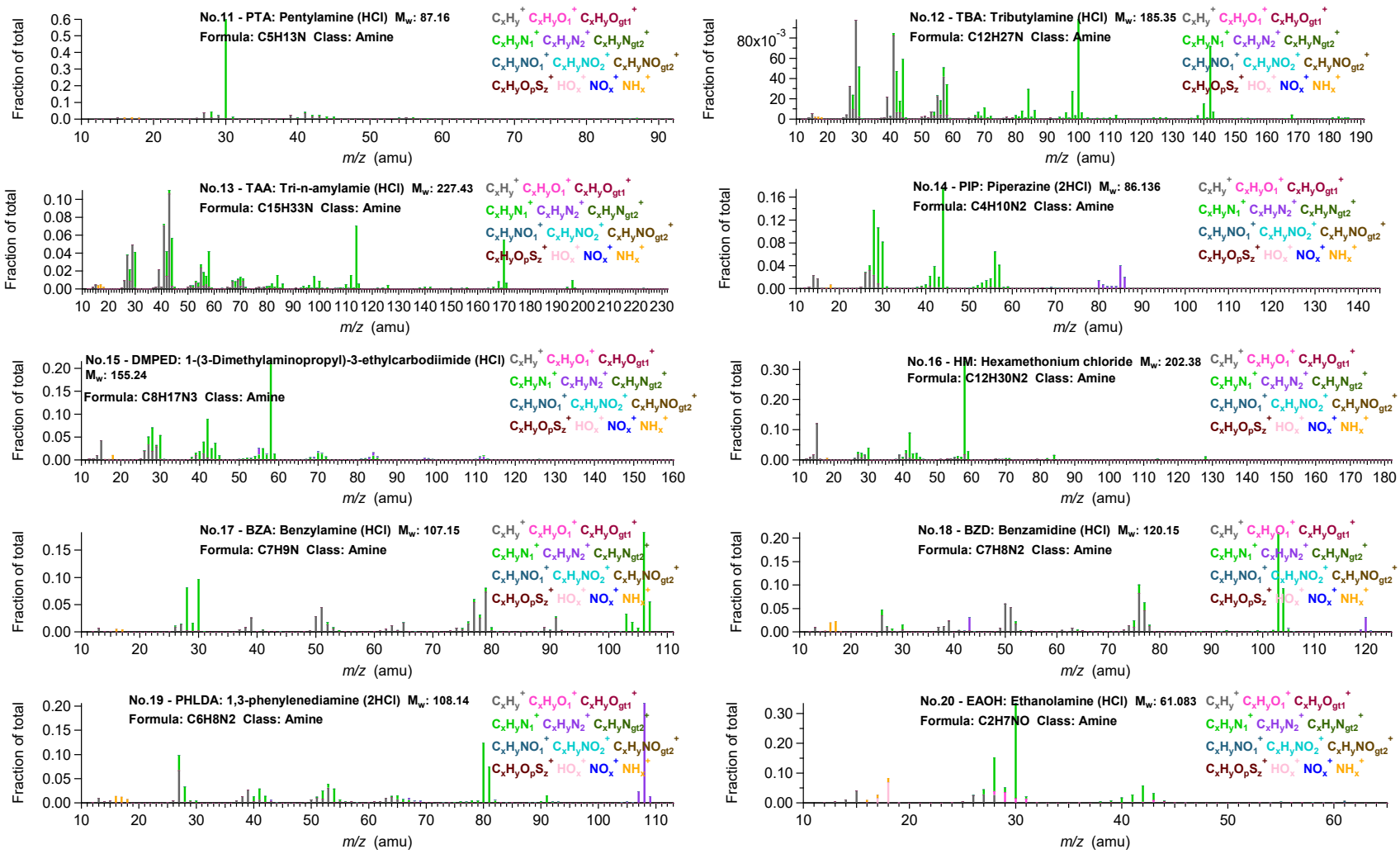
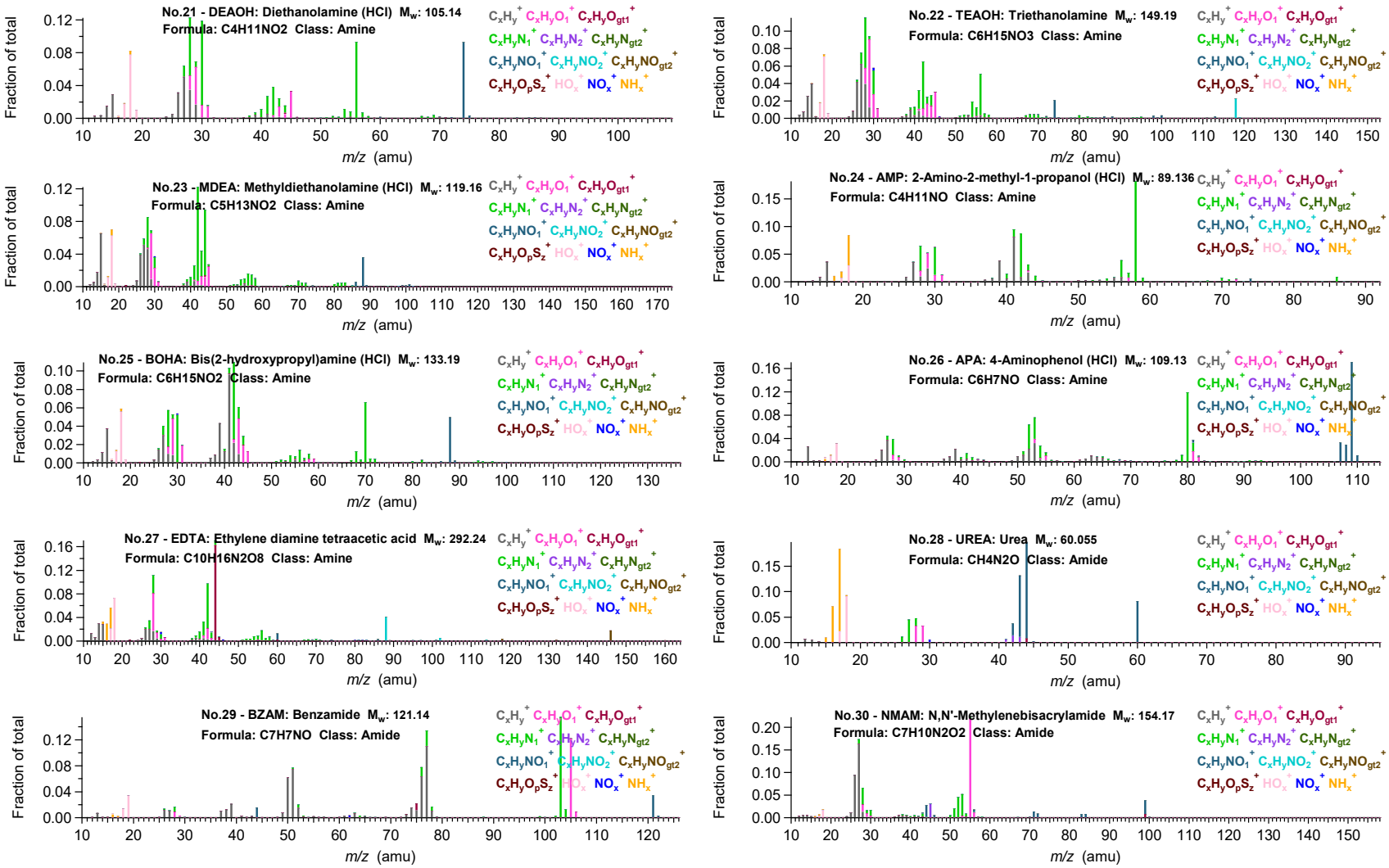
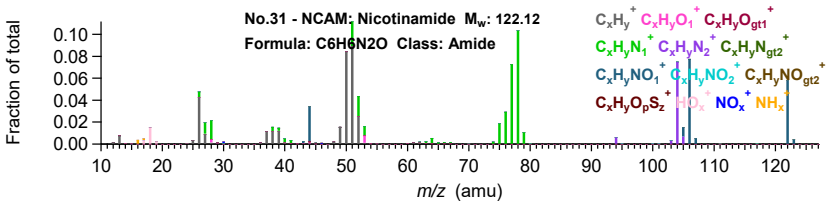


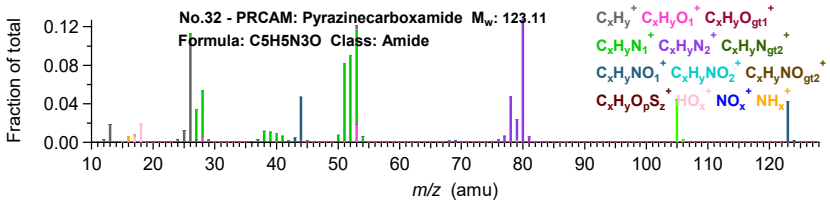
Figure S2. Examples of high resolution mass spectral analysis of (a) *m/z* 42 and (b) *m/z* 44.

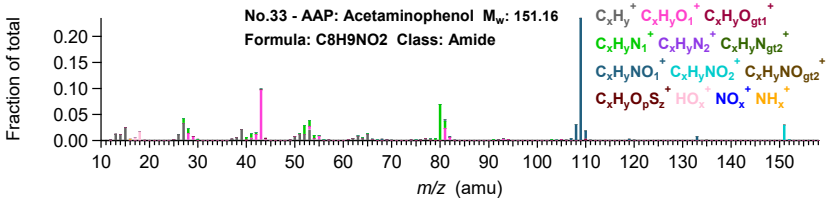

No.1 - MA: Methylamine (HCl) Mw: 31.057
Formula: CH5N Class: Amine
No.2 - DMA: Dimethylamine (HCl) Mw: 45.084
Formula: C2H7N Class: Amine
No.3 - TMA: Trimethylamine (HCl) Mw: 59.11
Formula: C3H9N Class: Amine
No.4 - EA: Ethylamine (HCl) Mw: 45.084
Formula: C2H7N Class: Amine
No.5 - DEA: Diethylamine (HCl) Mw: 73.137
Formula: C4H11N Class: Amine
No.6 - TEA: Triethylamine (HCl) Mw: 101.19
Formula: C6H15N Class: Amine
No.7 - iPPA: Isopropylamine (HCl) Mw: 59.11
Formula: C3H9N Class: Amine
No.8 - BTA: Butylamine (HCl) Mw: 73.14
Formula: C4H11N Class: Amine
No.9 - iBTA: Isobutylamine (HCl) Mw: 73.14
Formula: C4H11N Class: Amine
No.10 - BDA: 1,4-Diaminobutane (2HCl) Mw: 88.15
Formula: C4H12N2 Class: Amine
Fraction of total
m/z (amu)

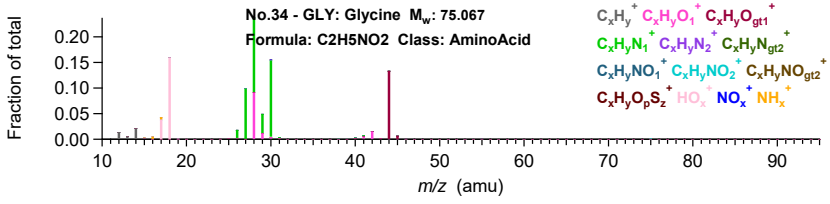

No.11 - PTA: Pentylamine (HCl) Mw: 87.16
Formula: C5H13N Class: Amine
No.12 - TBA: Tributylamine (HCl) Mw: 185.35
Formula: C12H27N Class: Amine
No.13 - TAA: Tri-n-amylamie (HCl) Mw: 227.43
Formula: C15H33N Class: Amine
No.14 - PIP: Piperazine (2HCl) Mw: 86.136
Formula: C4H10N2 Class: Amine
No.15 - DMPED: 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (HCl)
Mw: 155.24
Formula: C8H17N3 Class: Amine
No.16 - HM: Hexamethonium chloride Mw: 202.38
Formula: C12H30N2 Class: Amine
No.17 - BZA: Benzylamine (HCl) Mw: 107.15
Formula: C7H9N Class: Amine
No.18 - BZD: Benzamidine (HCl) Mw: 120.15
Formula: C7H8N2 Class: Amine
No.19 - PHLDA: 1,3-phenylenediamine (2HCl) Mw: 108.14
Formula: C6H8N2 Class: Amine
No.20 - EAOH: Ethanolamine (HCl) Mw: 61.083
Formula: C2H7NO Class: Amine
Fraction of total
m/z (amu)

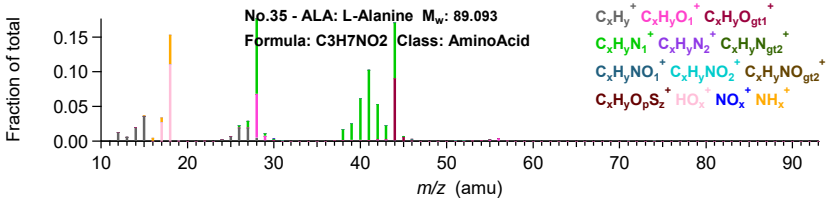

No.21 - DEAOH: Diethanolamine (HCl) Mw: 105.14
Formula: C4H11NO2 Class: Amine
No.22 - TEAOH: Triethanolamine Mw: 149.19
Formula: C6H15NO3 Class: Amine
No.23 - MDEA: Methyldiethanolamine (HCl) Mw: 119.16
Formula: C5H13NO2 Class: Amine
No.24 - AMP: 2-Amino-2-methyl-1-propanol (HCl) Mw: 89.136
Formula: C4H11NO Class: Amine
No.25 - BOHA: Bis(2-hydroxypropyl)amine (HCl) Mw: 133.19
Formula: C6H15NO2 Class: Amine
No.26 - APA: 4-Aminophenol (HCl) Mw: 109.13
Formula: C6H7NO Class: Amine
No.27 - EDTA: Ethylene diamine tetraacetic acid Mw: 292.24
Formula: C10H16N2O8 Class: Amine
No.28 - UREA: Urea Mw: 60.055
Formula: CH4N2O Class: Amide
No.29 - BZAM: Benzamide Mw: 121.14
Formula: C7H7NO Class: Amide
No.30 - NMAM: N,N'-Methylenebisacrylamide Mw: 154.17
Formula: C7H10N2O2 Class: Amide
Fraction of total
m/z (amu)

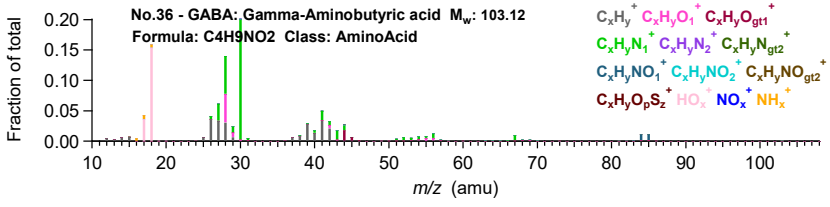

No.31 - NCAM: Nicotinamide Mw: 122.12
Formula: C6H6N2O Class: Amide
Fraction of total
m/z (amu)

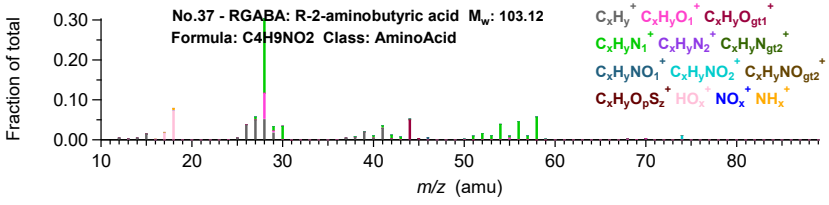

No.32 - PRCAM: Pyrazinecarboxamide Mw: 123.11
Formula: C5H5N3O Class: Amide
Fraction of total
m/z (amu)

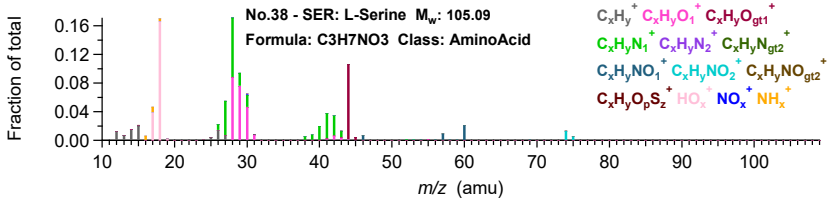

No.33 - AAP: Acetaminophenol Mw: 151.16
Formula: C8H9NO2 Class: Amide
Fraction of total
m/z (amu)

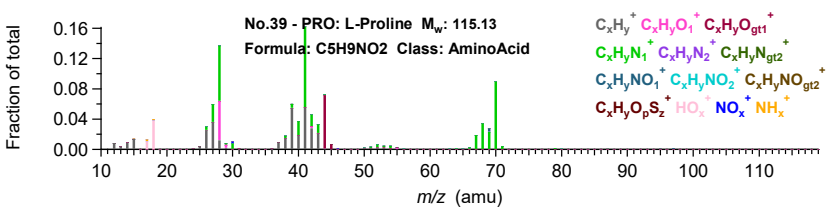

No.34 - GLY: Glycine Mw: 75.067
Formula: C2H5NO2 Class: AminoAcid
Fraction of total
m/z (amu)

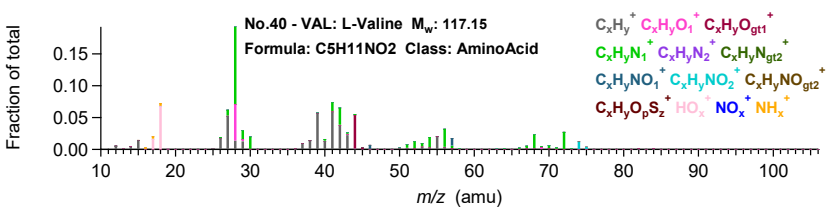

No.35 - ALA: L-Alanine Mw: 89.093
Formula: C3H7NO2 Class: AminoAcid
Fraction of total
m/z (amu)

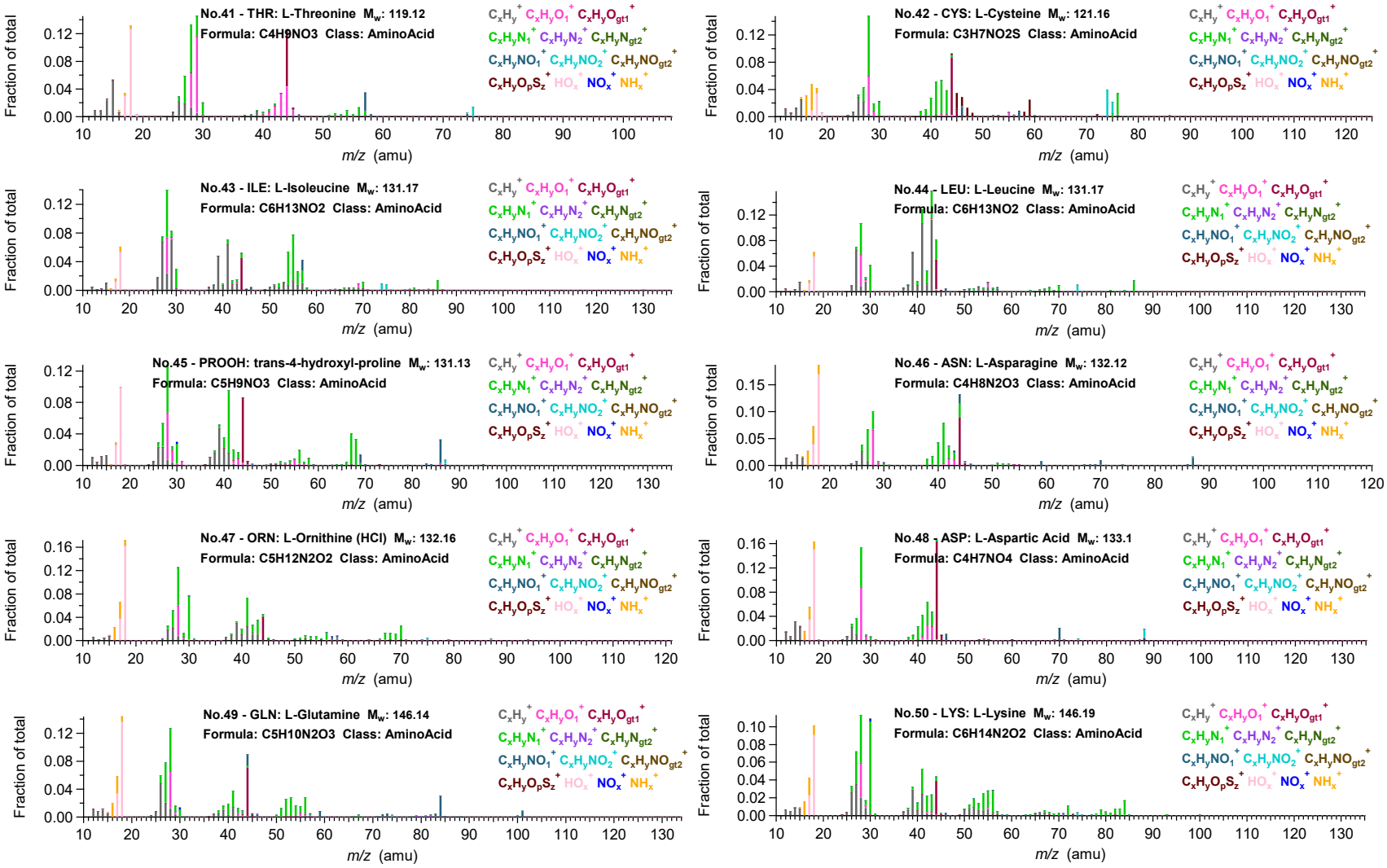

No.36 - GABA: Gamma-Aminobutyric acid Mw: 103.12
Formula: C4H9NO2 Class: AminoAcid
Fraction of total
m/z (amu)

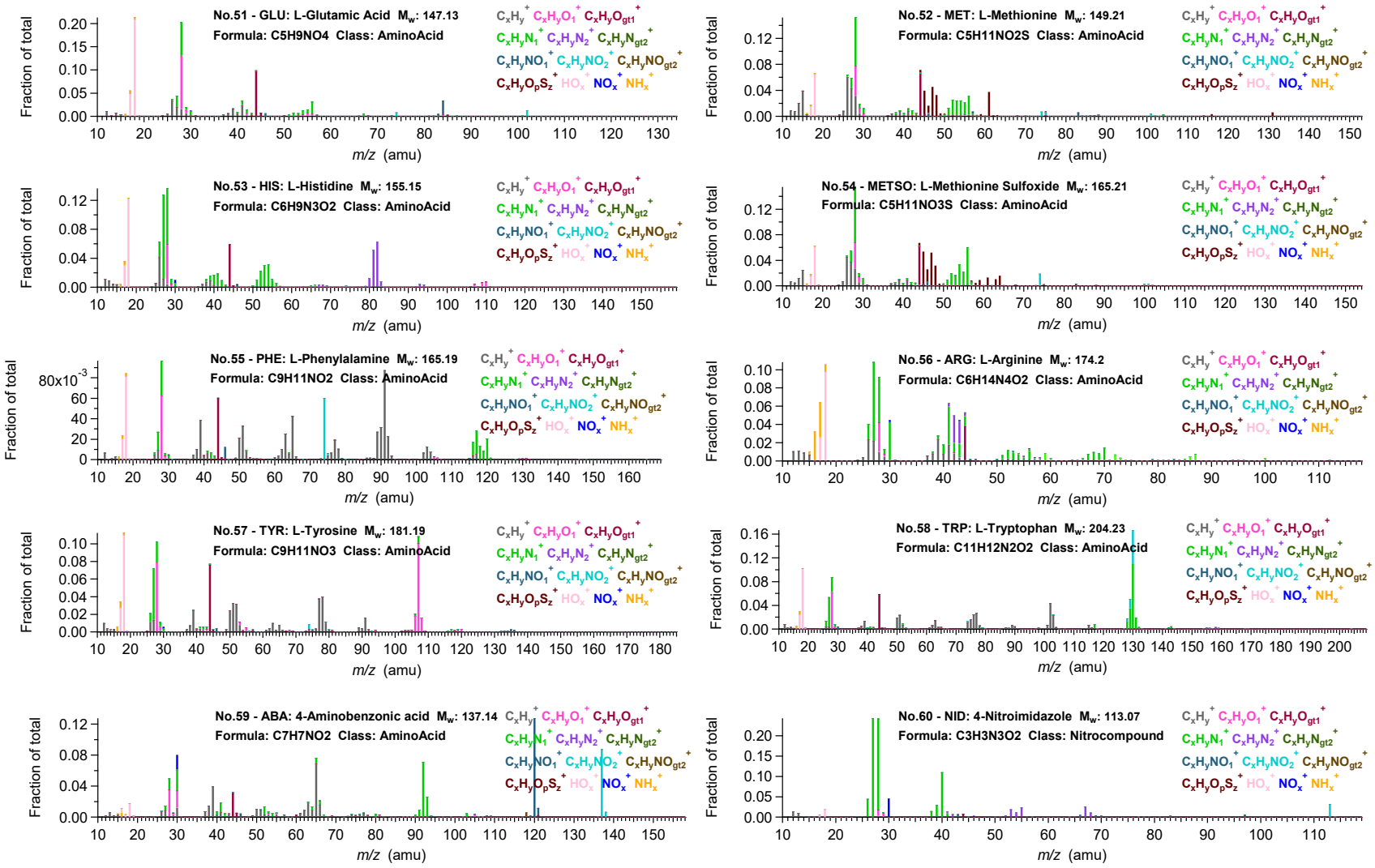

No.37 - RGABA: R-2-aminobutyric acid Mw: 103.12
Formula: C4H9NO2 Class: AminoAcid
Fraction of total
m/z (amu)

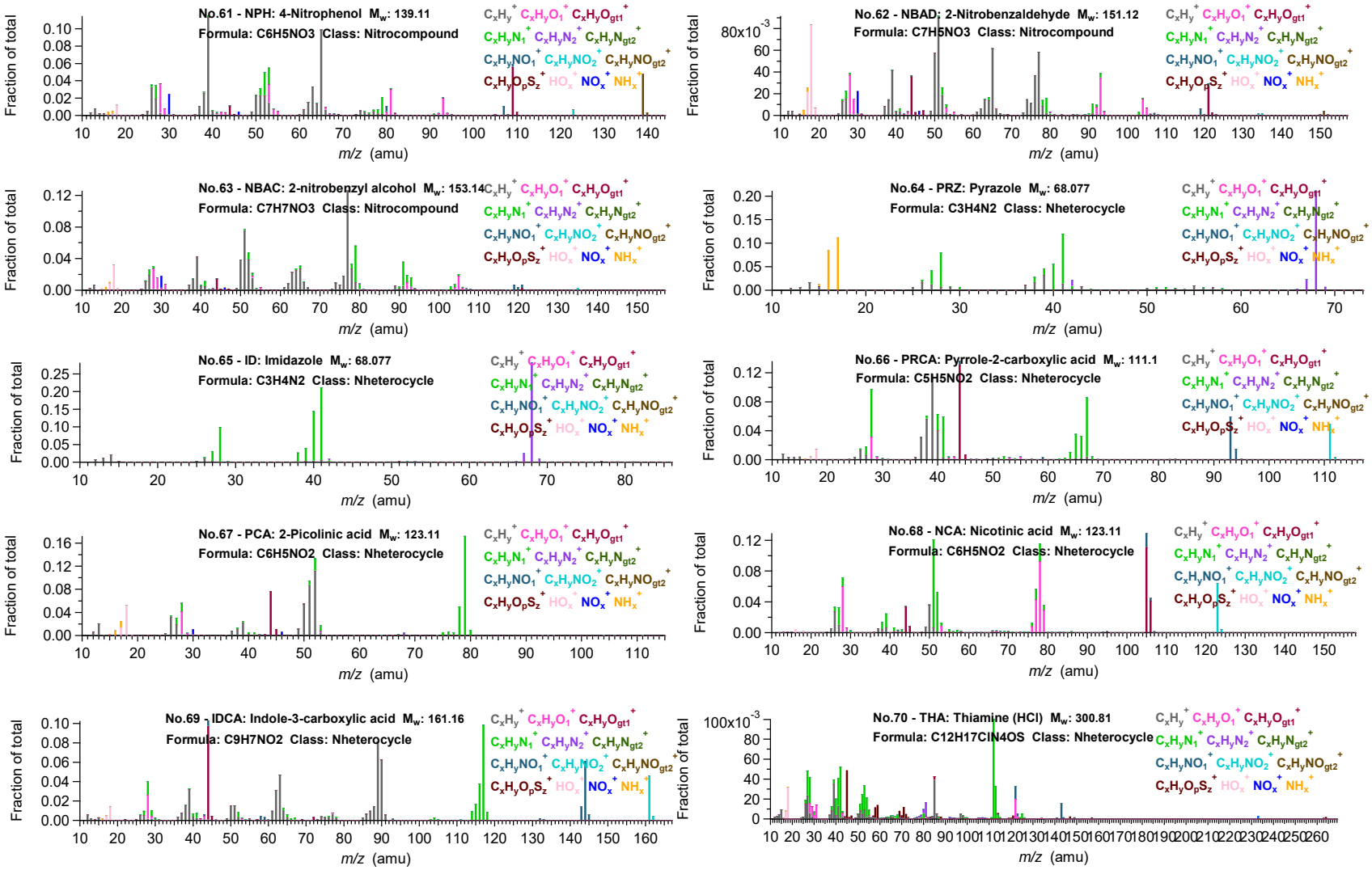

No.38 - SER: L-Serine Mw: 105.09
Formula: C3H7NO3 Class: AminoAcid
Fraction of total
m/z (amu)


No.39 - PRO: L-Proline Mw: 115.13
Formula: C5H9NO2 Class: AminoAcid
Fraction of total
m/z (amu)


No.40 - VAL: L-Valine Mw: 117.15
Formula: C5H11NO2 Class: AminoAcid
Fraction of total
m/z (amu)


No.41 - THR: L-Threonine Mw: 119.12
Formula: C4H9NO3 Class: AminoAcid
No.42 - CYS: L-Cysteine Mw: 121.16
Formula: C3H7NO2S Class: AminoAcid
No.43 - ILE: L-Isoleucine Mw: 131.17
Formula: C6H13NO2 Class: AminoAcid
No.44 - LEU: L-Leucine Mw: 131.17
Formula: C6H13NO2 Class: AminoAcid
No.45 - PROOH: trans-4-hydroxyl-proline Mw: 131.13
Formula: C5H9NO3 Class: AminoAcid
No.46 - ASN: L-Asparagine Mw: 132.12
Formula: C4H8N2O3 Class: AminoAcid
No.47 - ORN: L-Ornithine (HCl) Mw: 132.16
Formula: C5H12N2O2 Class: AminoAcid
No.48 - ASP: L-Aspartic Acid Mw: 133.1
Formula: C4H7NO4 Class: AminoAcid
No.49 - GLN: L-Glutamine Mw: 146.14
Formula: C5H10N2O3 Class: AminoAcid
No.50 - LYS: L-Lysine Mw: 146.19
Formula: C6H14N2O2 Class: AminoAcid
Fraction of total
m/z (amu)


No.51 - GLU: L-Glutamic Acid Mw: 147.13
Formula: C5H9NO4 Class: AminoAcid
No.52 - MET: L-Methionine Mw: 149.21
Formula: C5H11NO2S Class: AminoAcid
No.53 - HIS: L-Histidine Mw: 155.15
Formula: C6H9N3O2 Class: AminoAcid
No.54 - METSO: L-Methionine Sulfoxide Mw: 165.21
Formula: C5H11NO3S Class: AminoAcid
No.55 - PHE: L-Phenylalamine Mw: 165.19
Formula: C9H11NO2 Class: AminoAcid
No.56 - ARG: L-Arginine Mw: 174.2
Formula: C6H14N4O2 Class: AminoAcid
No.57 - TYR: L-Tyrosine Mw: 181.19
Formula: C9H11NO3 Class: AminoAcid
No.58 - TRP: L-Tryptophan Mw: 204.23
Formula: C11H12N2O2 Class: AminoAcid
No.59 - ABA: 4-Aminobenzonic acid Mw: 137.14
Formula: C7H7NO2 Class: AminoAcid
No.60 - NID: 4-Nitroimidazole Mw: 113.07
Formula: C3H3N3O2 Class: Nitrocompound
Fraction of total
m/z (amu)


No.61 - NPH: 4-Nitrophenol Mw: 139.11
Formula: C6H5NO3 Class: Nitrocompound
No.62 - NBAD: 2-Nitrobenzaldehyde Mw: 151.12
Formula: C7H5NO3 Class: Nitrocompound
No.63 - NBAC: 2-nitrobenzyl alcohol Mw: 153.14
Formula: C7H7NO3 Class: Nitrocompound
No.64 - PRZ: Pyrazole Mw: 68.077
Formula: C3H4N2 Class: Nheterocycle
No.65 - ID: Imidazole Mw: 68.077
Formula: C3H4N2 Class: Nheterocycle
No.66 - PRCA: Pyrrole-2-carboxylic acid Mw: 111.1
Formula: C5H5NO2 Class: Nheterocycle
No.67 - PCA: 2-Picolinic acid Mw: 123.11
Formula: C6H5NO2 Class: Nheterocycle
No.68 - NCA: Nicotinic acid Mw: 123.11
Formula: C6H5NO2 Class: Nheterocycle
No.69 - IDCA: Indole-3-carboxylic acid Mw: 161.16
Formula: C9H7NO2 Class: Nheterocycle
No.70 - THA: Thiamine (HCl) Mw: 300.81
Formula: C12H17ClN4OS Class: Nheterocycle
Fraction of total
m/z (amu)

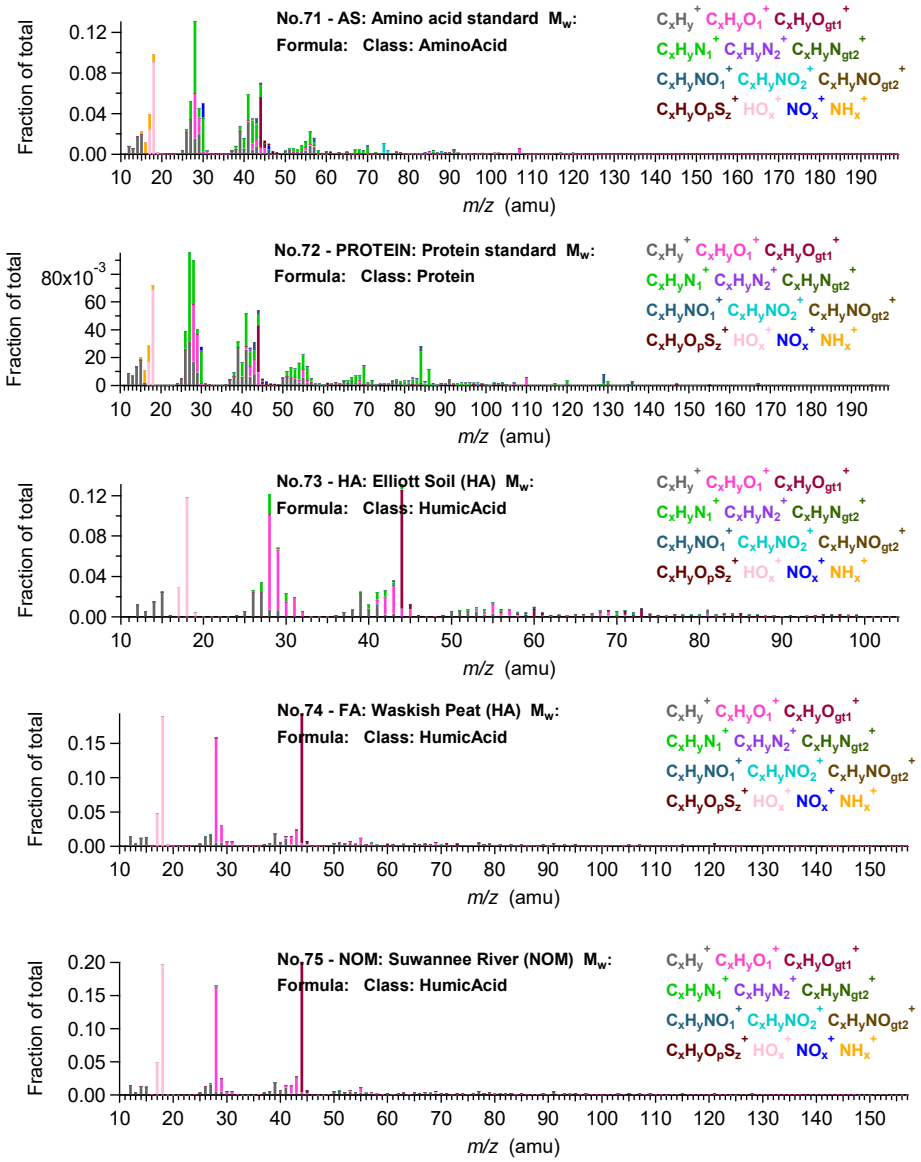


Figure S3. High resolution mass spectra of the 75 ON standards determined in this study.

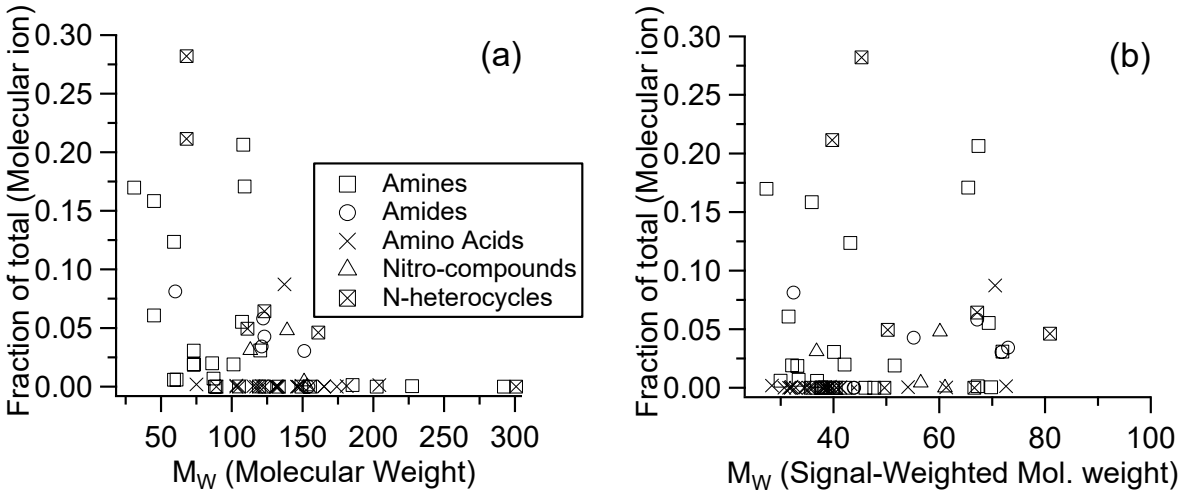


Figure S4. Mass fractions of the molecular ions in the HR-AMS spectra of the ON standards as a function of the molecular weights (M_w) (a), and the signal-weighted molecular weights (b) (calculated as $\sum f_i * i_{m/z}$, where $i_{m/z}$ is the exact mass of ion i and f_i is the mass fraction of that ion in the compound's spectrum).

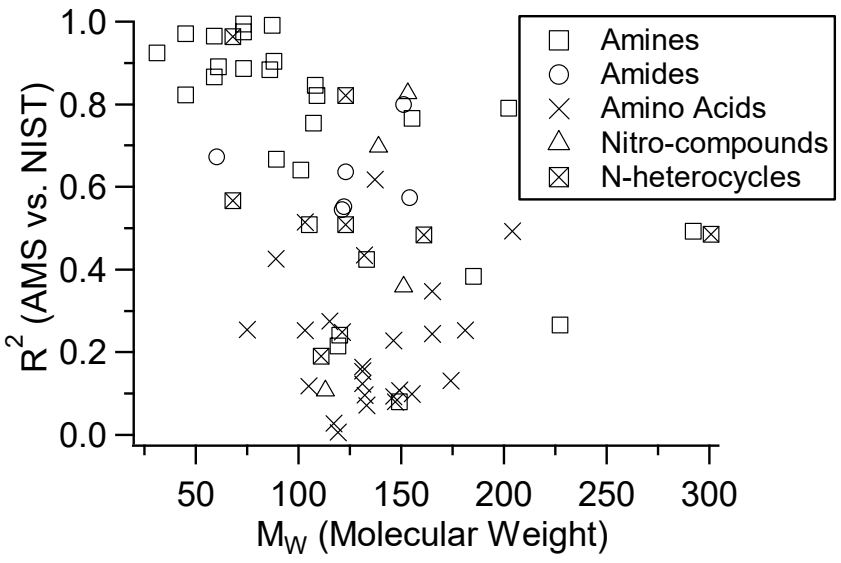


Figure S5. Correlation coefficients (Pearson's r^2) between the HR-AMS spectra and the NIST spectra as a function of the molecular weights of the ON standards.

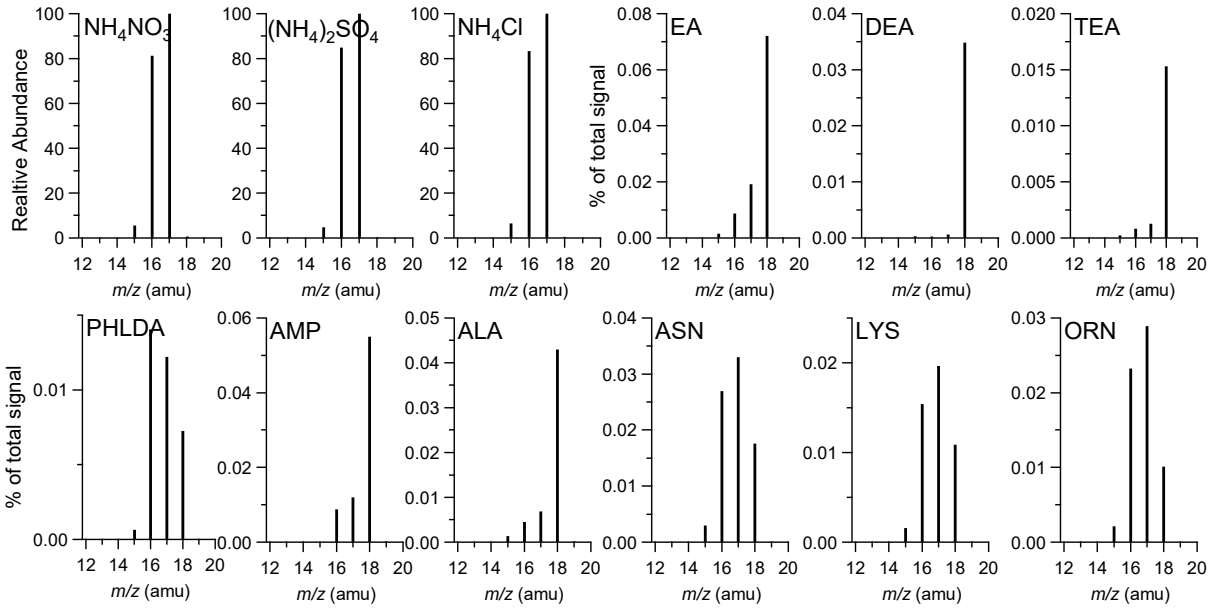


Figure S6. Mass fractional contributions of NH_x^+ ion fragments in the HR-AMS spectra of ammonium nitrate, ammonium sulfate and ammonium chloride, and a few selected amines and amino acids.

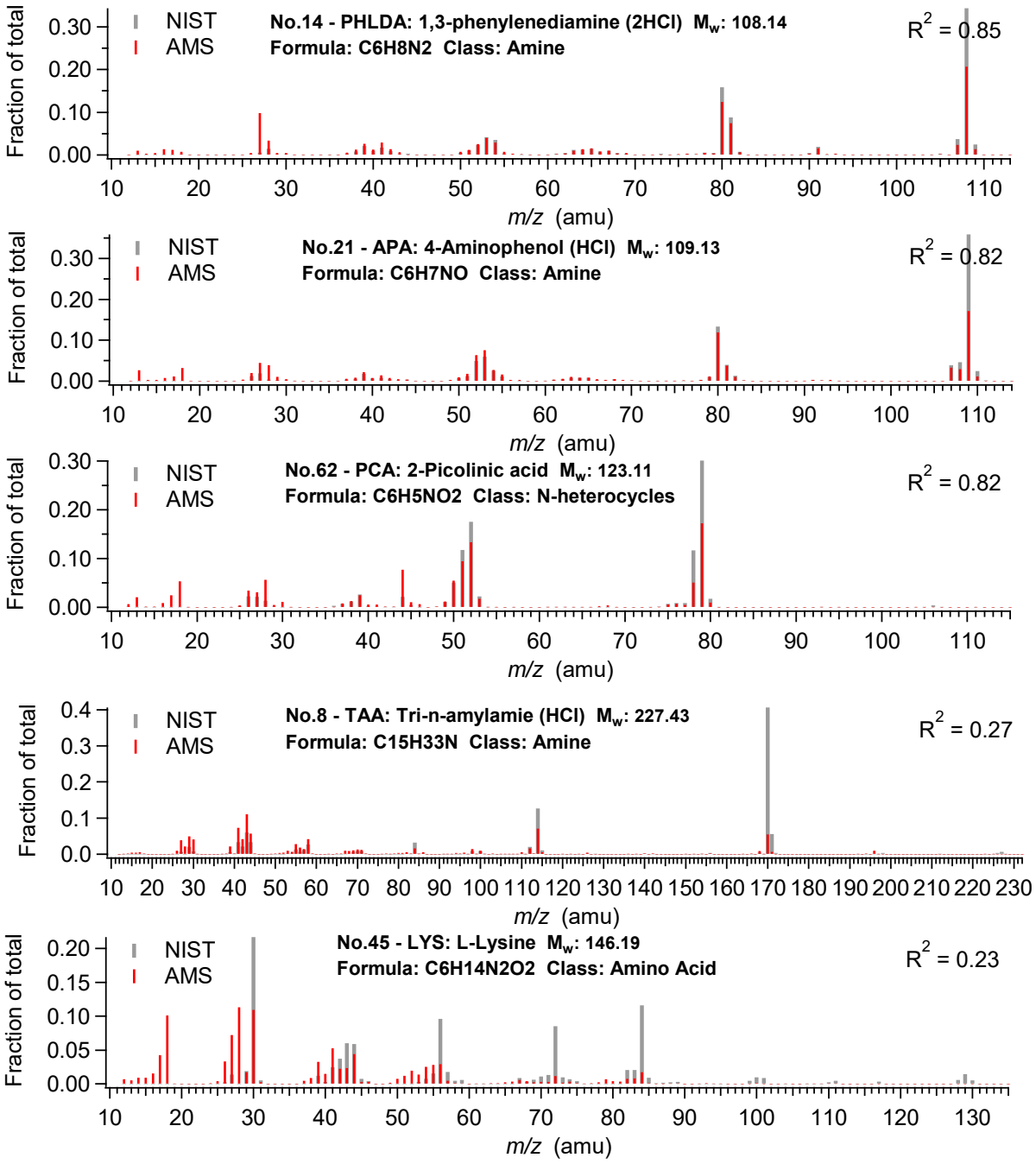


Figure S7. AMS spectra (summed in unit mass resolution from HR spectra) versus NIST spectra for a few selected ON standards.