Supplementary Information for

Dual Cationic-Anionic Profiling of Metabolites in a Single Embryonic Cell in a Live Xenopus laevis Embryo by Microprobe CE-ESI-MS

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TABLES

Table S1. Molecular features detected by anionic analysis. Identified features are highlighted. Key: t_m, migration time.

m/z	t_m (min)
173.1027	**11.3**
145.0957	**13.9**
213.1135	14.4
211.0593	14.9
195.0857	15.0
145.0605	**15.1**
180.0331	15.8
194.0430	16.3
179.0555	**16.4**
185.9915	16.5
199.9901	16.5
242.0362	16.5
273.1059	16.5
172.0222	16.8
314.8748	17.3
204.0888	17.5
130.0613	**17.6**
170.0429	17.6
186.0166	17.7
192.0509	17.7
188.0169	17.9
183.0162	18.0
229.0413	18.0
223.0096	18.1
315.9317	18.2
116.0725	18.2
153.0272	18.3
190.0351	18.3
140.0112	18.5
169.0002	18.5
193.0701	18.5
131.0461	**18.6**
249.0243	18.6
138.0555	18.8
100.0410	19.0
214.0492	19.1
124.0068	19.1
400.1150	**19.9**

m/z	t_m (min)
343.8039	20.3
168.0413	**20.5**
126.0041	20.7
150.0570	20.8
164.0006	20.8
166.0519	**20.8**
114.9363	21.2
160.0599	21.7
173.1060	22.7
154.0614	23.2
112.9854	24.7
132.0286	**24.8**
331.5562	25.8
291.9683	25.8
152.0108	26.5
242.1145	26.6
78.9598	26.7
182.0581	26.7
96.9695	26.8
136.9618	26.8
156.9821	27.2
144.9751	27.3
238.9463	27.5
387.1692	27.9
140.0115	**28.2**
253.2161	28.4
180.0036	28.5
195.9774	28.5
299.9044	28.5
161.9930	28.6
201.9858	28.7
288.1824	28.8
272.1873	29.0
308.0998	29.2
256.1923	29.2
237.0919	29.3
254.1767	29.5
312.0709	29.6

m/z	t_m (min)
261.1350	29.6
257.1761	29.7
270.1717	29.7
364.1125	29.8
304.1518	29.8
348.1424	29.8
225.1499	29.8
264.1585	29.8
280.1324	29.8
293.1781	29.9
244.1559	30.3
211.1346	30.5
258.1714	30.9
294.1393	31.0
328.0466	31.2
214.1457	31.2
105.0191	**31.3**
209.1554	31.3
227.1269	31.4
245.0436	31.7
250.1466	31.7
363.0204	31.8
122.9933	31.8
199.1714	31.9
150.0415	**31.9**
233.1551	31.9
302.0854	31.9
218.1044	**32.0**
240.0860	32.0
262.0677	32.0
280.0777	32.0
324.0685	32.0
362.0244	32.0
274.0617	32.1
278.0417	32.1
340.0410	32.1
346.0513	32.1
146.0832	32.1

m/z	t_m (min)
200.1303	32.2
349.0044	32.2
243.0813	32.4
185.1554	32.6
144.0310	32.8
275.1325	32.8
216.0885	32.9
125.0981	33.2
186.1146	33.2
221.0824	33.3
321.0455	33.4
172.1431	33.5
217.9959	33.8
251.0712	34.0
236.0980	34.1
285.0446	34.1
149.1341	34.3
172.0999	34.5
175.0229	34.5
157.2450	34.8
159.1295	34.9
190.0551	35.2
177.0928	35.6
248.0784	35.6
127.0265	36.0
143.1086	36.5
181.0517	36.5
193.0913	37.1
171.0057	38.2
289.0316	38.3
322.0462	**38.4**
290.0891	38.5
129.0930	38.5
134.0482	**38.7**
165.0414	38.7

m/z	t_m (min)
179.0751	39.3
182.0472	**39.7**
138.9780	39.8
199.0001	39.9
176.9354	40.0
296.9767	40.1
131.0724	40.2
146.0472	**40.4**
149.0470	40.5
362.0071	40.9
380.0180	40.9
176.9372	40.9
323.0301	**40.9**
282.0396	40.9
272.9581	41.0
132.0420	41.0
213.0235	41.0
267.5315	42.4
282.0214	43.0
111.0211	43.1
241.0127	43.1
283.0236	43.1
117.0565	44.4
229.0107	44.5
231.0182	45.3
207.0131	45.4
135.0311	**45.4**
197.0312	45.4
298.9435	46.3
271.4403	47.3
110.0358	47.4
131.0727	47.7
150.0176	47.7
128.0364	47.8
119.0360	48.0

m/z	t_m (min)
290.9664	49.7
171.0125	50.5
213.9731	50.8
234.1102	50.9
173.0040	51.0
121.0305	51.1
210.0276	**53.4**
232.0090	53.4
112.0511	53.5
120.9804	53.5
88.0405	**53.6**
102.9703	53.6
166.9735	53.6
271.9400	53.6
285.9386	53.6
192.0174	53.7
247.9830	53.7
269.9646	53.7
130.0613	**53.9**
103.0760	55.2
192.9881	55.3
208.9613	55.3
248.9531	55.5
135.0131	57.3
105.0205	57.8
115.0761	60.8
100.9857	61.3
188.9389	61.3
200.9415	61.3
225.1867	61.3
239.2023	61.4
259.0234	**62.0**
130.0617	66.1

Table S2. Metabolites identified by cationic microprobe CE-ESI-MS. Key to symbols is in the footnote of **Table S3**.

ID	Metabolite	Formula	Time (min)	*m/z* measured	*m/z* theoretical	Δ*m/z* (mDa)	Δ*m/z* (ppm)
1	Spermidine (SPM)[**,R1]	$C_7H_{19}N_3$	15.5	146.1663	146.1652	-1.1	-7.5
2	Thiamine[**,R1]	$C_{12}H_{16}N_4OS$	17.8	265.1114	265.1118	0.4	1.4
3	Choline (Cho)[*,**,R1]	$C_5H_{13}NO$	18.6	104.1068	104.1070	0.2	1.9
4	Arg-Ala (RA)[**,R1]	$C_9H_{19}N_5O_3$	19.3	246.1570	246.1561	-0.9	-3.8
5	Lys-Ser (KS)[**,R1]	$C_9H_{19}N_3O_4$	19.3	234.1434	234.1448	1.4	6.1
6	Val-Lys (VK)[**,R2]	$C_{11}H_{23}N_3O_3$	19.6	246.1805	246.1812	0.7	2.9
7	S-adenosyl-methionine (SAM)[**,R1]	$C_{15}H_{22}N_6O_5S$	19.6	399.1430	399.1445	1.5	3.8
8	Ser-Arg (SR)[**,R1]	$C_9H_{19}N_5O_4$	19.6	262.1511	262.1510	-0.1	-0.4
9	Ornithine (Orn)[**,R1]	$C_5H_{12}N_2O_2$	19.8	133.0973	133.0972	-0.1	-0.8
10	Lysine (Lys)[*,**,R1]	$C_6H_{14}N_2O_2$	20.0	147.1132	147.1128	-0.4	-2.7
11	Arginine (Arg)[*,**,R1]	$C_6H_{14}N_4O_2$	20.4	175.1193	175.1190	-0.3	-2.0
12	Homolysine[**,R1]	$C_7H_{16}N_2O_2$	20.4	161.1287	161.1285	-0.2	-1.5
13	Tyr-Lys (YK)[**,R2]	$C_{15}H_{23}N_3O_4$	20.4	310.1749	310.1761	1.2	4.0
14	γ-aminobutyric acid (GABA)[*,**,R2]	$C_4H_9NO_2$	20.5	104.0707	104.0706	-0.1	-0.9
15	N6,N6,N6-trimethyl-lysine (TML)[**,R1]	$C_9H_{20}N_2O_2$	20.5	189.1599	189.1598	-0.1	-0.8
16	Histidine (His)[*,**,R1]	$C_6H_9N_3O_2$	20.5	156.0774	156.0768	-0.6	-4.1
17	Methylhistidine[**]	$C_7H_{11}N_3O_2$	20.7	170.0928	170.0924	-0.4	-2.3
18	Guanidinopropanoate[**]	$C_4H_9N_3O_2$	20.8	132.0761	132.0768	0.7	4.9
19	Acetylcholine (AcCho)[*,**,R1]	$C_7H_{15}NO_2$	20.8	146.1177	146.1176	-0.1	-1.0
20	Leu-Ala (LA)[**,R2]	$C_9H_{18}N_2O_3$	22.0	203.1388	203.1390	0.2	1.1
21	Cis-urocanate (cURA)[**,R1]	$C_6H_6N_2O_2$	22.2	139.0500	139.0502	0.2	1.4
22	Guanine[**,R1]	$C_5H_5N_5O$	22.3	152.0572	152.0567	-0.5	-3.4
23	Carnitine (Car)[*,**,R1]	$C_7H_{15}NO_3$	22.8	162.1131	162.1125	-0.6	-3.9
24	Trans-urocanate (tURA)[**,R1]	$C_6H_6N_2O_2$	23.0	139.0500	139.0502	0.2	1.4
25	Methylguanine[**,R2]	$C_6H_7N_5O$	23.3	166.0726	166.0723	-0.3	-1.8
26	Pyridoxal[**]	$C_8H_9NO_3$	23.4	168.0659	168.0655	-0.4	-2.3
27	Acetylcarnitine (AcCar)[**,R1]	$C_9H_{17}NO_4$	24.5	204.1231	204.1230	-0.1	-0.3
28	Methylaspartate[**,R2]	$C_5H_9NO_4$	25.4	148.0605	148.0604	-0.1	-0.4
29	Glycine[*,R2]	$C_2H_5NO_2$	25.3	76.0386	76.0393	0.7	9.3
30	Niacinamide[*,R2]	$C_6H_6N_2O$	25.4	123.0549	123.0553	0.4	3.2

ID	Metabolite	Formula	Time (min)	*m/z* measured	*m/z* theoretical	Δ*m/z* (mDa)	Δ*m/z* (ppm)
31	Creatine (CR)[*,**,R1]	$C_4H_9N_3O_2$	25.6	132.0779	132.0768	-1.1	-8.7
32	Pro-Val (PV)[**,R2]	$C_{10}H_{18}N_2O_3$	25.8	215.1378	215.1390	1.2	5.7
33	Alanine (Ala)[*,R1]	$C_3H_7NO_2$	27.4	90.0548	90.0550	0.2	1.7
34	Argininosuccinate (ASA)[**]	$C_{10}H_{18}N_4O_6$	28.5	291.1292	291.1299	0.7	2.4
35	Valine (Val)[*,**,R1]	$C_5H_{11}NO_2$	30.5	118.0864	118.0863	-0.1	-1.2
36	Serine (Ser) [*,**,R1]	$C_3H_7NO_3$	30.6	106.0498	106.0499	0.1	0.7
37	Isoleucine[*,‡,R1]	$C_6H_{13}NO_2$	30.7	132.1023	132.1019	-0.4	-3.0
38	Leucine[*,‡,R1]	$C_6H_{13}NO_2$	31.0	132.1023	132.1019	-0.4	-3.0
39	Asparagine (Asn)[**]	$C_4H_8N_2O_3$	32.1	133.0610	133.0608	-0.2	-1.7
40	Threonine (Thr)[*,**,R1]	$C_4H_9NO_3$	32.1	120.0654	120.0655	0.1	1.0
41	Tryptophan (Trp)[*,**,R1]	$C_{11}H_{12}N_2O_2$	32.6	205.0967	205.0972	0.5	2.2
42	Methionine (Met)[*,**,R1]	$C_5H_{11}NO_2S$	32.7	150.0588	150.0583	-0.5	-3.2
43	Glutamine (Gln)[**]	$C_5H_{10}N_2O_3$	32.8	147.0769	147.0764	-0.5	-3.3
44	2-Aminoadate[**,R2]	$C_6H_{11}NO_4$	32.9	162.0767	162.0761	-0.6	-3.8
45	Acetylhomoserine[†,R2]	$C_6H_{11}NO_4$	32.9	162.0767	162.0761	-0.6	-3.8
46	Citrulline (Cit)[**,R1]	$C_6H_{13}N_3O_3$	33.1	176.1027	176.1030	0.3	1.5
47	Homocitrulline[**,R1]	$C_7H_{15}N_3O_3$	33.2	190.1178	190.1186	0.8	4.3
48	Glutamic acid (Glu)[**]	$C_5H_9NO_4$	33.2	148.0610	148.0604	-0.6	-3.8
49	Phenylalanine (Phe)[**,R1]	$C_9H_{11}NO_2$	33.7	166.0867	166.0863	-0.4	-2.7
50	Acetyllysine[†,R2]	$C_8H_{16}N_2O_3$	34.0	189.1219	189.1234	1.5	7.8
51	Tyrosine (Tyr)[*,**,R1]	$C_9H_{11}NO_3$	34.1	182.0813	182.0812	-0.1	-0.7
52	Hypoxanthine (HPX)[**]	$C_5H_4N_4O$	34.3	137.0461	137.0458	-0.3	-2.3
53	Proline (Pro)[*,**,R1]	$C_5H_9NO_2$	34.6	116.0707	116.0706	-0.1	-0.8
54	Ser-Val (SV)[†,R2]	$C_8H_{16}N_2O_4$	34.9	205.1181	205.1183	0.2	0.9
55	Cysteine[*,**,R2]	$C_3H_7NO_2S$	35.8	122.0269	122.0270	0.1	1.0
56	Aspartic acid[*,**]	$C_4H_7NO_4$	36.0	134.0451	134.0448	-0.3	-2.4
57	Glycine betaine (GB) [*,‡,R1]	$C_5H_{11}NO_2$	36.6	118.0864	118.0863	-0.1	-1.2
58	Glutathione, oxidized (GSSG)[**,R1]	$C_{20}H_{32}N_6O_{12}S_2$	37.2	307.0826	307.0833	0.7	2.1
59	Hydroxyproline (Hyp)[**]	$C_5H_9NO_3$	38.3	132.0660	132.0655	-0.5	-3.6
60	Glutathione (GSH)[*,**,R1]	$C_{10}H_{17}N_3O_6S$	40.0	308.0908	308.0911	0.3	0.9

Table S3. Metabolites identified by anionic microprobe CE-ESI-MS.

ID	Metabolite (Abbrev)	Formula	Time (min)	*m/z* measured	*m/z* theoretical	Δ*m/z* (mDa)	Δ*m/z* (ppm)
1	Arginine (Arg)**	$C_6H_{14}N_4O_2$	11.3	173.1027	173.1033	0.6	3.5
2	Lysine (Lys)**	$C_6H_{14}N_2O_2$	13.9	145.0958	145.0971	1.3	9.2
3	Glutamine (Gln)**	$C_5H_{10}N_2O_3$	15.1	145.0605	145.0608	0.3	2.3
4	Glucose*,**	$C_6H_{12}O_6$	16.4	179.0555	179.0550	-0.5	-2.8
5	Asparagine (Asn)**	$C_4H_8N_2O_3$	17.3	131.0461	131.0451	-1.0	-7.6
6	Creatine (CR)**	$C_4H_9N_3O_2$	17.6	130.0613	130.0609	-0.4	-3.1
7	Phenethoxybenzamid - oxopentanoic acid**	$C_{19}H_{19}N_3O_7$	19.9	400.1150	400.1139	-1.1	-2.8
8	Phosphorylcholine**	$C_4H_{12}NO_4P$	20.5	168.0413	168.042	0.7	4.3
9	Pyridoxal**	$C_8H_9NO_3$	20.8	166.0519	166.0498	-2.1	-12.6
10	Aspartic acid (Asp)**	$C_4H_7NO_4$	24.8	132.0287	132.0291	0.4	3.3
11	Phosphoylethanolamine**	$C_2H_8NO_4P$	28.2	140.0115	140.0107	-0.8	-5.7
12	Glyceric acid**	$C_3H_6O_4$	31.3	105.0191	105.0182	-0.9	-8.6
13	Guanine**	$C_5H_5N_5O$	31.9	150.0415	150.041	-0.5	-3.3
14	Pantothenic acid**	$C_9H_{17}NO_5$	32.0	218.1044	218.1023	-2.1	-9.6
15	Cytidine phosphate (CMP)**	$C_9H_{14}N_3O_8P$	38.4	322.0462	322.0434	-2.8	-8.7
16	Adenine**	$C_5H_5N_5$	38.7	134.0482	134.0461	-2.1	-15.7
17	Pyridoxic acid (PHOS)**	$C_8H_9NO_4$	39.7	182.0472	182.0447	-2.5	-13.7
18	Glutamate (Glu)**	$C_5H_9NO_4$	40.4	146.0472	146.0456	-1.6	-11.0
19	Uridine monophosphate**	$C_9H_{13}N_2O_9P$	40.9	323.0301	323.0274	-2.7	-8.4
20	Hypoxanthine (HPX)**	$C_5H_4N_4O$	45.4	135.0311	135.0301	-1.0	-7.4
21	Phosphocreatine**	$C_4H_{10}N_3O_5P$	53.4	210.0276	210.0274	-0.2	-1.0
22	Alanine (Ala)**	$C_3H_7NO_2$	53.6	88.0405	88.0393	-1.2	-13.6
23	Guanidinopropanoate**	$C_4H_9N_3O_2$	53.9	130.0613	130.0611	-0.2	-1.5
24	Glucose phosphate**	$C_6H_{13}O_9P$	62.0	259.0234	259.0214	-2.0	-7.7

Note: Asterisk (*) signifies identification based on migration-time comparison to chemical standards. Double asterisk (**) denotes identification by tandem mass spectrometry experiments on related standards or comparison to data available in Metlin (hppt://metlin.scripps.edu), MzCloud (hppt://mzcloud.org), or HMDB (hppt://hmdb.ca). Dagger (†) indicates that tandem mass spectrum agrees with molecular fragmentation predicted in Mass Frontier 7.0 (Thermo Fisher). Double dagger (‡) indicates mass-match in Metlin. R1 indicates previous metabolite identification based on reference[1] and R2 indicates identification based on reference[2].

Table S4. Selected molecular features detected by anionic analysis of a single V1 cell.

Identifier	*m/z*	t_m (min)
1	204.0888	17.5
2	214.0492	19.1
3	124.0068	19.1
4	173.1060	22.7
5	136.9618	26.8
6	308.0950	29.2
7	254.1767	29.5
8	257.1761	29.7
9	243.0813	32.4
10	216.0885	32.9
11	186.1146	33.2
12	190.0551	35.2
13	181.0517	36.5
14	149.0470	40.5
15	176.9354	40.9
16	117.0565	44.4

References

1. R. M. Onjiko, S. E. Morris, S. A. Moody and P. Nemes, *Analyst*, 2016, **141**, 3648-3656.
2. R. M. Onjiko, E. P. Portero, S. A. Moody and P. Nemes, *Anal. Chem.*, 2017, **89**, 7069-7076.