

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

m/z	t_m (min)	m/z	t_m (min)	m/z	t_m (min)
173.1027	11.3	343.8039	20.3	261.1350	29.6
145.0957	13.9	168.0413	20.5	257.1761	29.7
213.1135	14.4	126.0041	20.7	270.1717	29.7
211.0593	14.9	150.0570	20.8	364.1125	29.8
195.0857	15.0	164.0006	20.8	304.1518	29.8
145.0605	15.1	166.0519	20.8	348.1424	29.8
180.0331	15.8	114.9363	21.2	225.1499	29.8
194.0430	16.3	160.0599	21.7	264.1585	29.8
179.0555	16.4	173.1060	22.7	280.1324	29.8
185.9915	16.5	154.0614	23.2	293.1781	29.9
199.9901	16.5	112.9854	24.7	244.1559	30.3
242.0362	16.5	132.0286	24.8	211.1346	30.5
273.1059	16.5	331.5562	25.8	258.1714	30.9
172.0222	16.8	291.9683	25.8	294.1393	31.0
314.8748	17.3	152.0108	26.5	328.0466	31.2
204.0888	17.5	242.1145	26.6	214.1457	31.2
130.0613	17.6	78.9598	26.7	105.0191	31.3
170.0429	17.6	182.0581	26.7	209.1554	31.3
186.0166	17.7	96.9695	26.8	227.1269	31.4
192.0509	17.7	136.9618	26.8	245.0436	31.7
188.0169	17.9	156.9821	27.2	250.1466	31.7
183.0162	18.0	144.9751	27.3	363.0204	31.8
229.0413	18.0	238.9463	27.5	122.9933	31.8
223.0096	18.1	387.1692	27.9	199.1714	31.9
315.9317	18.2	140.0115	28.2	150.0415	31.9
116.0725	18.2	253.2161	28.4	233.1551	31.9
153.0272	18.3	180.0036	28.5	302.0854	31.9
190.0351	18.3	195.9774	28.5	218.1044	32.0
140.0112	18.5	299.9044	28.5	240.0860	32.0
169.0002	18.5	161.9930	28.6	262.0677	32.0
193.0701	18.5	201.9858	28.7	280.0777	32.0
131.0461	18.6	288.1824	28.8	324.0685	32.0
249.0243	18.6	272.1873	29.0	362.0244	32.0
138.0555	18.8	308.0998	29.2	274.0617	32.1
100.0410	19.0	256.1923	29.2	278.0417	32.1
214.0492	19.1	237.0919	29.3	340.0410	32.1
124.0068	19.1	254.1767	29.5	346.0513	32.1
400.1150	19.9	312.0709	29.6	146.0832	32.1

<i>m/z</i>	<i>t_m</i> (min)	<i>m/z</i>	<i>t_m</i> (min)	<i>m/z</i>	<i>t_m</i> (min)
200.1303	32.2	179.0751	39.3	290.9664	49.7
349.0044	32.2	182.0472	39.7	171.0125	50.5
243.0813	32.4	138.9780	39.8	213.9731	50.8
185.1554	32.6	199.0001	39.9	234.1102	50.9
144.0310	32.8	176.9354	40.0	173.0040	51.0
275.1325	32.8	296.9767	40.1	121.0305	51.1
216.0885	32.9	131.0724	40.2	210.0276	53.4
125.0981	33.2	146.0472	40.4	232.0090	53.4
186.1146	33.2	149.0470	40.5	112.0511	53.5
221.0824	33.3	362.0071	40.9	120.9804	53.5
321.0455	33.4	380.0180	40.9	88.0405	53.6
172.1431	33.5	176.9372	40.9	102.9703	53.6
217.9959	33.8	323.0301	40.9	166.9735	53.6
251.0712	34.0	282.0396	40.9	271.9400	53.6
236.0980	34.1	272.9581	41.0	285.9386	53.6
285.0446	34.1	132.0420	41.0	192.0174	53.7
149.1341	34.3	213.0235	41.0	247.9830	53.7
172.0999	34.5	267.5315	42.4	269.9646	53.7
175.0229	34.5	282.0214	43.0	130.0613	53.9
157.2450	34.8	111.0211	43.1	103.0760	55.2
159.1295	34.9	241.0127	43.1	192.9881	55.3
190.0551	35.2	283.0236	43.1	208.9613	55.3
177.0928	35.6	117.0565	44.4	248.9531	55.5
248.0784	35.6	229.0107	44.5	135.0131	57.3
127.0265	36.0	231.0182	45.3	105.0205	57.8
143.1086	36.5	207.0131	45.4	115.0761	60.8
181.0517	36.5	135.0311	45.4	100.9857	61.3
193.0913	37.1	197.0312	45.4	188.9389	61.3
171.0057	38.2	298.9435	46.3	200.9415	61.3
289.0316	38.3	271.4403	47.3	225.1867	61.3
322.0462	38.4	110.0358	47.4	239.2023	61.4
290.0891	38.5	131.0727	47.7	259.0234	62.0
129.0930	38.5	150.0176	47.7	130.0617	66.1
134.0482	38.7	128.0364	47.8		
165.0414	38.7	119.0360	48.0		

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

ID	Metabolite	Formula	Time (min)	m/z measured	m/z theoretical	$\Delta m/z$ (mDa)	$\Delta m/z$ (ppm)
31	Creatine (CR) ^{*,**,R1}	C ₄ H ₉ N ₃ O ₂	25.6	132.0779	132.0768	-1.1	-8.7
32	Pro-Val (PV) ^{**,R2}	C ₁₀ H ₁₈ N ₂ O ₃	25.8	215.1378	215.1390	1.2	5.7
33	Alanine (Ala) ^{*,R1}	C ₃ H ₇ NO ₂	27.4	90.0548	90.0550	0.2	1.7
34	Argininosuccinate (ASA) ^{**}	C ₁₀ H ₁₈ N ₄ O ₆	28.5	291.1292	291.1299	0.7	2.4
35	Valine (Val) ^{*,**,R1}	C ₅ H ₁₁ NO ₂	30.5	118.0864	118.0863	-0.1	-1.2
36	Serine (Ser) ^{*,**,R1}	C ₃ H ₇ NO ₃	30.6	106.0498	106.0499	0.1	0.7
37	Isoleucine ^{*,‡,R1}	C ₆ H ₁₃ NO ₂	30.7	132.1023	132.1019	-0.4	-3.0
38	Leucine ^{*,‡,R1}	C ₆ H ₁₃ NO ₂	31.0	132.1023	132.1019	-0.4	-3.0
39	Asparagine (Asn) ^{**}	C ₄ H ₈ N ₂ O ₃	32.1	133.0610	133.0608	-0.2	-1.7
40	Threonine (Thr) ^{*,**,R1}	C ₄ H ₉ NO ₃	32.1	120.0654	120.0655	0.1	1.0
41	Tryptophan (Trp) ^{*,**,R1}	C ₁₁ H ₁₂ N ₂ O ₂	32.6	205.0967	205.0972	0.5	2.2
42	Methionine (Met) ^{*,**,R1}	C ₅ H ₁₁ NO ₂ S	32.7	150.0588	150.0583	-0.5	-3.2
43	Glutamine (Gln) ^{**}	C ₅ H ₁₀ N ₂ O ₃	32.8	147.0769	147.0764	-0.5	-3.3
44	2-Aminoadate ^{**,R2}	C ₆ H ₁₁ NO ₄	32.9	162.0767	162.0761	-0.6	-3.8
45	Acetylhomoserine ^{†,R2}	C ₆ H ₁₁ NO ₄	32.9	162.0767	162.0761	-0.6	-3.8
46	Citrulline (Cit) ^{**,R1}	C ₆ H ₁₃ N ₃ O ₃	33.1	176.1027	176.1030	0.3	1.5
47	Homocitrulline ^{**,R1}	C ₇ H ₁₅ N ₃ O ₃	33.2	190.1178	190.1186	0.8	4.3
48	Glutamic acid (Glu) ^{**}	C ₅ H ₉ NO ₄	33.2	148.0610	148.0604	-0.6	-3.8
49	Phenylalanine (Phe) ^{**,R1}	C ₉ H ₁₁ NO ₂	33.7	166.0867	166.0863	-0.4	-2.7
50	Acetyllysine ^{†,R2}	C ₈ H ₁₆ N ₂ O ₃	34.0	189.1219	189.1234	1.5	7.8
51	Tyrosine (Tyr) ^{*,**,R1}	C ₉ H ₁₁ NO ₃	34.1	182.0813	182.0812	-0.1	-0.7
52	Hypoxanthine (HPX) ^{**}	C ₅ H ₄ N ₄ O	34.3	137.0461	137.0458	-0.3	-2.3
53	Proline (Pro) ^{*,**,R1}	C ₅ H ₉ NO ₂	34.6	116.0707	116.0706	-0.1	-0.8
54	Ser-Val (SV) ^{†,R2}	C ₈ H ₁₆ N ₂ O ₄	34.9	205.1181	205.1183	0.2	0.9
55	Cysteine ^{*,**,R2}	C ₃ H ₇ NO ₂ S	35.8	122.0269	122.0270	0.1	1.0
56	Aspartic acid ^{*,**}	C ₄ H ₇ NO ₄	36.0	134.0451	134.0448	-0.3	-2.4
57	Glycine betaine (GB) ^{*,‡,R1}	C ₅ H ₁₁ NO ₂	36.6	118.0864	118.0863	-0.1	-1.2
58	Glutathione, oxidized (GSSG) ^{**,R1}	C ₂₀ H ₃₂ N ₆ O ₁₂ S ₂	37.2	307.0826	307.0833	0.7	2.1
59	Hydroxyproline (Hyp) ^{**}	C ₅ H ₉ NO ₃	38.3	132.0660	132.0655	-0.5	-3.6
60	Glutathione (GSH) ^{*,**,R1}	C ₁₀ H ₁₇ N ₃ O ₆ S	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)	<i>m/z</i> measured	<i>m/z</i> theoretical	$\Delta m/z$ (mDa)	$\Delta m/z$ (ppm)
<u>1</u>	Arginine (Arg)**	C ₆ H ₁₄ N ₄ O ₂	11.3	173.1027	173.1033	0.6	3.5
<u>2</u>	Lysine (Lys)**	C ₆ H ₁₄ N ₂ O ₂	13.9	145.0958	145.0971	1.3	9.2
<u>3</u>	Glutamine (Gln)**	C ₅ H ₁₀ N ₂ O ₃	15.1	145.0605	145.0608	0.3	2.3
<u>4</u>	Glucose**	C ₆ H ₁₂ O ₆	16.4	179.0555	179.0550	-0.5	-2.8
<u>5</u>	Asparagine (Asn)**	C ₄ H ₈ N ₂ O ₃	17.3	131.0461	131.0451	-1.0	-7.6
<u>6</u>	Creatine (CR)**	C ₄ H ₉ N ₃ O ₂	17.6	130.0613	130.0609	-0.4	-3.1
<u>7</u>	Phenethoxybenzamid - oxopentanoic acid**	C ₁₉ H ₁₉ N ₃ O ₇	19.9	400.1150	400.1139	-1.1	-2.8
<u>8</u>	Phosphorylcholine**	C ₄ H ₁₂ NO ₄ P	20.5	168.0413	168.042	0.7	4.3
<u>9</u>	Pyridoxal**	C ₈ H ₉ NO ₃	20.8	166.0519	166.0498	-2.1	-12.6
<u>10</u>	Aspartic acid (Asp)**	C ₄ H ₇ NO ₄	24.8	132.0287	132.0291	0.4	3.3
<u>11</u>	Phosphoylethanolamine**	C ₂ H ₈ NO ₄ P	28.2	140.0115	140.0107	-0.8	-5.7
<u>12</u>	Glyceric acid**	C ₃ H ₆ O ₄	31.3	105.0191	105.0182	-0.9	-8.6
<u>13</u>	Guanine**	C ₅ H ₅ N ₅ O	31.9	150.0415	150.041	-0.5	-3.3
<u>14</u>	Pantothenic acid**	C ₉ H ₁₇ NO ₅	32.0	218.1044	218.1023	-2.1	-9.6
<u>15</u>	Cytidine phosphate (CMP)**	C ₉ H ₁₄ N ₃ O ₈ P	38.4	322.0462	322.0434	-2.8	-8.7
<u>16</u>	Adenine**	C ₅ H ₅ N ₅	38.7	134.0482	134.0461	-2.1	-15.7
<u>17</u>	Pyridoxic acid (PHOS)**	C ₈ H ₉ NO ₄	39.7	182.0472	182.0447	-2.5	-13.7
<u>18</u>	Glutamate (Glu)**	C ₅ H ₉ NO ₄	40.4	146.0472	146.0456	-1.6	-11.0
<u>19</u>	Uridine monophosphate**	C ₉ H ₁₃ N ₂ O ₉ P	40.9	323.0301	323.0274	-2.7	-8.4
<u>20</u>	Hypoxanthine (HPX)**	C ₅ H ₄ N ₄ O	45.4	135.0311	135.0301	-1.0	-7.4
<u>21</u>	Phosphocreatine**	C ₄ H ₁₀ N ₃ O ₅ P	53.4	210.0276	210.0274	-0.2	-1.0
<u>22</u>	Alanine (Ala)**	C ₃ H ₇ NO ₂	53.6	88.0405	88.0393	-1.2	-13.6
<u>23</u>	Guanidinopropanoate**	C ₄ H ₉ N ₃ O ₂	53.9	130.0613	130.0611	-0.2	-1.5
<u>24</u>	Glucose phosphate**	C ₆ H ₁₃ O ₉ P	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 (<http://metlin.scripps.edu>), MzCloud (<http://mzcloud.org>), or HMDB (<http://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 reference¹ and R2 indicates identification based on reference².

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

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