Defining and Detecting Complex Peak Relationships in Mass Spectral Data: The mz.unity Algorithm

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SUPPLEMENT S1. DESCRIPTION OF THE COMBINATORIAL SEARCH PROBLEM FOR COMPLEX PEAK RELATIONSHIPS.

Let O be the set of all observed <m,z>. Let M be a user supplied set of <m,z>. Find multisets R and S that satisfy:

$$R, S \subset O \cup M$$

$$R, S \not\subset M$$

$$R \cap S = \emptyset$$

$$\sum_{x \in R} x_m - \sum_{x \in S} x_m < \delta$$

$$\sum_{x \in R} x_z - \sum_{x \in S} x_z = 0$$

$$\delta = \frac{\varepsilon}{1E6} * \sum_{x \in R, S \cap O} \frac{x_m}{|x_z|}$$

Given a set of <m,z> pairs where m and z are positive or negative real numbers, find two sub-multisets whose summed mass is within error δ and whose summed charge is equal. Exclude pairs of multisets which share a member.

In broader terms, we have found a set of mass and charge transformations (corresponding to deprotonation, adduction, etc.) which convert a detected <m,z> value to a second <m, z> value. Thus this search ensures that the transformations of each <m,z> as described by members of each multiset results in an equal mass and charge.

SUPPLEMENT S2. FEATURES FROM NEGATIVE MODE INCLUDED IN THE COMPOSITE SPECTRUM

mz	maxo	source	mz	maxo	source
-146.046	2.76E+09	Psn	-400.134	1216220	psn
-128.035	3.52E+08	Psn	-188.002	1182428	psn
-102.056	3.12E+08	Psn	-665.11	1176081	psn
-147.049	1.64E+08	Psn	-542.059	1156010	psn
-662.102	1.37E+08	Psn	-189.088	1126616	psn
-231.098	1.15E+08	psn	-246.118	1123492	psn
-132.03	58812040	psn	-540.039	1110298	psn
-331.055	44957360	psn	-269.054	1099994	psn
-809.155	35751240	psn	-848.114	1090830	psn
-663.105	32867860	psn	-335.055	952685.8	psn
-540.054	31911818	psn	-206.012	938092.4	psn
-348.087	30048056	psn	-301.065	923233.9	psn
-293.099	29273104	psn	-516.063	921326.4	psn
-315.081	28147298	psn	-894.207	886170.4	psn
-148.05	24049586	psn	-500.09	873459.1	psn
-129.038	20168718	psn	-232.096	835217.1	psn
-103.059	15625474	psn	-345.178	834453.8	psn
-147.043	12138567	psn	-450.11	815158.2	psn
-283.068	11558971	psn	-456.246	809889.1	psn
-232.102	11044240	psn	-994.657	808162.4	psn
-245.114	10539088	psn	-881.311	808151.8	psn
-810.158	9959694	psn	-572.344	790534.1	psn
-664.108	6937656	psn	-134.034	789540.4	psn
-541.057	5288482	psn	-100.04	785416.2	psn
-662.603	5039852	psn	-187.109	781978.1	psn
-332.058	4757833	psn	-115.003	758465.8	psn
-306.077	4592574	psn	-456.166	758344.9	psn
-758.09	4585383	psn	-832.14	720119.6	psn
-88.0403	4487963	psn	-333.059	683614.1	psn
-168.028	3955738	psn	-875.176	680699.4	psn
-357.087	3907644	psn	-687.107	673873.8	psn
-129.019	3892937	psn	-337.063	672261.3	psn
-333.053	3772248	psn	-598.36	661826.6	psn
-294.102	3454026	psn			
-320.011	3302731	psn			
-847.11	3277035	psn			
-184.001	3091660	psn			
-349.09	3036758	psn			
-316.084	2891467	psn			
-133.033	2886159	psn			
-148.052	2825622	psn			
-811.16	2595229	psn			
-358.118	2563522	psn			
-228.049	2491125	psn			
-244.023	2471267	psn			
-146.025	2384161	psn			
-416.108	2370798	psn			
-993.655	2345890	psn			
-831.137	2325020	psn			
-760.078	2294203	psn			
-353.037	2244784	psn			
-130.039	2227558	psn			
-874.173	2207934	psn			
-146.104	2033520	psn			
-151.062	1948270	psn			
-378.152	1836020	psn			
-994.157	1833876	psn			
-317.039	1619828	psn			
-146.071	1601470	psn			
-146.02	1589578	psn			
-129.032	1572900	psn			
-244.119	1561877	psn			
-104.06	1533376	psn			
-103.053	1487027	psn			
-369.011	1482860	psn			
-744.105	1443245	psn			
-284.072	1440297	psn			
-149.053	1427846	psn			
-759.093	1331007	psn			
-350.083	1323925	psn			
-346.021	1306265	psn			
-233.103	1248925	psn			

-436.095	1239505	psn
-397.988	1222801	psn

SUPPLEMENT S3. FEATURES FROM POSITIVE MODE INCLUDED IN THE COMPOSITE SPECTRUM

mz	maxo	source									
148.06	1.81E+09	psp	170.0422	3883824	psp	465.3215	1884285	psp	173.0919	1058835	psp
130.0498	3.02E+08	psp	424.2588	3865671	psp	463.306	1875812	psp	425.2428	1038059	psp
233.2447	2.6E+08	psp	341.222	3865225	psp	230.1976	1848160	psp	196.1556	1034444	psp
664.1172	1.96E+08	psp	481.3163	3849028	psp	318.2982	1844858	psp	380.0776	1032436	psp
233.113	1.22E+08	psp	159.1603	3844951	psp	207.9982	1824690	psp	352.1902	1021926	psp
149.0633	91513336	psp	240.172	3813592	psp	438.2743	1823870	psp	246.2419	1021253	psp
102.0548	61472984	psp	243.2291	3693398	psp	308.1639	1808380	psp	393.2531	1016436	psp
123.0554	54190284	psp	261.276	3614619	psp	205.6433	1763577	psp	192.0241	1013983	psp
665.1202	50223776	psp	124.0587	3491213	psp	241.2133	1737384	psp	85.02834	1011348	psp
245.2447	48069948	psp	226.1565	3441997	psp	150.0665	1731420	psp	253.2133	1004417	psp
190.2025	28252376	psp	234.1538	3437938	psp	267.1369	1702268	psp	299.1636	1002699	psp
234.2479	26949514	psp	235.1617	3252422	psp	359.1025	1688196	psp	368.1851	1000992	psp
271.0688	21521252	psp	231.2293	3219105	psp	153.0405	1673078	psp	201.1903	991107.1	psp
276.2871	20748364	psp	383.2324	3199432	psp	346.1889	1665952	psp	289.2712	978187	psp
427.306	19735338	psp	702.0733	3124695	psp	483.2956	1661078	psp	350.1212	962097.6	psp
157.1447	18880884	psp	171.0762	3102233	psp	117.1263	1638529	psp	327.2175	961277.2	psp
257.2446	18655262	psp	248.1696	3073251	psp	369.2168	1625681	psp	234.1102	956079.1	psp
131.0531	17018116	psp	226.0376	2991801	psp	142.1339	1621513	psp	305.696	948127.1	psp
350.102	15073590	psp	283.132	2975036	psp	435.311	1610065	psp	260.6854	946392.5	psp
453.3216	15012519	psp	116.1184	2972269	psp	228.1819	1591366	psp	442.1668	945906.9	psp
247.1287	14912596	psp	493.3163	2965840	psp	232.1567	1547727	psp	323.215	943317.6	psp
150.0642	14645601	psp	269.2447	2952662	psp	432.1362	1543830	psp	422.2795	942465.8	psp
227.1644	13957159	psp	131.0338	2910072	psp	203.1866	1531236	psp	507.3319	936827.4	psp
191.1865	13730655	psp	103.0582	2891140	psp	273.0669	1513754	psp	225.1486	928799.9	psp
234.1163	12932350	psp	428.3099	2856149	psp	485.3112	1481398	psp	511.3267	928654.2	psp
265.0503	10756661	psp	451.306	2814969	psp	285.2398	1461184	psp	191.1024	925484.1	psp
666.1227	10674766	psp	477.3215	2653451	psp	222.1541	1426840	psp	996.1745	923613.8	psp
200.1869	10418991	psp	175.1553	2644349	psp	132.1131	1426403	psp	319.3297	923008.4	psp
295.1138	10269037	psp	686.0993	2641257	psp	667.1254	1425935	psp	412.2589	920321.3	psp
259.2604	8838102	psp	277.2905	2631271	psp	241.1616	1415203	psp	675.1086	918688	psp
304.1618	8177553	psp	450.2744	2600441	psp	440.2537	1412062	psp	289.2347	901264.7	psp
147.1604	7950535	psp	229.2137	2572000	psp	223.9721	1405962	psp	497.3113	896755.7	psp
214.2025	7811584	psp	234.2288	2559343	psp	304.2823	1398901	psp	176.0737	893954.2	psp
349.1181	7632175	psp	426.2745	2514821	psp	296.1167	1398888	psp	1014.651	888278.3	psp
314.2092	7174908	psp	379.2011	2492418	psp	271.224	1397299	psp	410.2432	887668.1	psp
434.2795	6942368	psp	99.0916	2480767	psp	235.2513	1393120	psp	427.2585	883956.6	psp
255.0949	6566525	psp	397.2115	2450742	psp	355.2012	1372936	psp	150.647	883463.1	psp
134.0447	6280206	psp	136.0618	2449351	psp	408.2639	1360118	psp	454.2693	877597.7	psp
251.0346	6058636	psp	191.2058	2432413	psp	158.1481	1357751	psp	495.2955	870804.2	psp
436.295	6045015	psp	601.3956	2407377	psp	496.3636	1350771	psp	256.1209	866752.1	psp
104.1181	5943378	psp	454.3255	2396598	psp	155.129	1348961	psp	489.3215	863220.1	psp
275.2555	5848210	psp	210.1713	2380743	psp	285.0829	1342086	psp	273.276	862540.6	psp
469.3164	5828522	psp	271.2604	2371772	psp	422.2432	1319220	psp	215.1024	861544.3	psp
261.2396	5793045	psp	495.3319	2369524	psp	353.2219	1308334	psp	392.2689	854450.4	psp
467.3007	5786659	psp	443.3009	2356544	psp	360.1324	1293417	psp	372.0838	849048	psp
234.242	5718033	psp	365.2218	2339415	psp	287.2555	1280357	psp	396.2639	846665.8	psp
410.2795	5668431	psp	323.0393	2321906	psp	335.7307	1272806	psp	267.0483	837923.8	psp
246.2481	5659415	psp	411.2635	2312104	psp	163.1552	1251915	psp	398.2431	837573.2	psp
149.0573	5610463	psp	233.1645	2304944	psp	333.0643	1236596	psp	703.077	835253.9	psp
202.2025	5554419	psp	455.3009	2298684	psp	235.1172	1228381	psp	440.29	828606.9	psp
288.2871	5536289	psp	326.1748	2271483	psp	192.19	1226547	psp	256.167	827247.1	psp
332.5624	5531230	psp	218.1975	2269794	psp	227.1979	1225753	psp	120.613	826322.6	psp
255.229	5406180	psp	258.2481	2242889	psp	129.1261	1218545	psp	151.0674	824307.5	psp
298.1796	5280998	psp	479.337	2236099	psp	310.1796	1211365	psp	342.1219	822430.4	psp
354.1695	5181576	psp	314.7111	2185420	psp	186.1713	1206633	psp	505.3164	815663.2	psp
269.1162	5132939	psp	594.4002	2179335	psp	436.2588	1201589	psp	286.1317	798008.8	psp
374.148	5068381	psp	388.1456	2168571	psp	143.1292	1200430	psp	556.3486	795780.7	psp
128.0707	5005582	psp	217.6432	2141469	psp	228.2184	1197925	psp	460.295	794064.2	psp
385.2481	4837042	psp	108.6127	2123574	psp	226.6486	1191097	psp	151.6549	793066.4	psp
384.2641	4743927	psp	272.0722	2101159	psp	131.0469	1184284	psp	239.1977	791010.1	psp
85.04767	4690118	psp	247.1618	2075201	psp	185.1761	1183860	psp	780.2363	789338.8	psp
218.6511	4430709	psp	138.6471	2071239	psp	183.1604	1172474	psp	1006.664	781422.4	psp
439.306	4337509	psp	388.0578	2069616	psp	483.332	1158942	psp	317.0835	781141.6	psp
320.1642	4316508	psp	132.0541	2067111	psp	153.0768	1157504	psp	242.1696	780253.4	psp
186.0162	4303773	psp	406.2483	2063521	psp	247.2239	1154023	psp	298.2719	780054.4	psp
322.1798	4289709	psp	468.2848	2022243	psp	995.6728	1127385	psp	148.0006	779222.2	psp
452.29	4236093	psp	351.1054	2003873	psp	285.0848	1110661	psp	406.1561	777100.1	psp
340.1903	4202912	psp	509.3111	1973029	psp	448.2951	1108775	psp	542.0681	770435.9	psp

239.1642	4089331	psp	226.2026	1969459	psp	351.2062	1105669	psp	121.6208	769528.5	psp
367.2375	4082911	psp	409.2954	1941976	psp	431.1876	1081482	psp	402.2345	767691.8	psp
198.1713	4067356	psp	100.0994	1925514	psp	395.2321	1076854	psp	418.2846	764103.7	psp
273.2396	4020422	psp	409.2477	1907389	psp	339.2062	1075096	psp	214.0916	763270.1	psp
216.2183	3967400	psp	322.207	1892691	psp	356.1375	1073961	psp	475.2136	759841.3	psp
248.2318	3908586	psp	248.1321	1892027	psp	269.1107	1062688	psp	304.0153	756906.7	psp
595.4037	753921.4	psp									
428.2903	752444.6	psp									
375.1518	751830	psp									
266.0537	749370.5	psp									
375.1989	749054.3	psp									
256.2324	740162.6	psp									
440.31	734644.9	psp									
335.2148	721214.6	psp									
352.0979	718792.9	psp									
411.2806	717596.1	psp									
687.1026	709065.9	psp									
341.1378	705273.1	psp									
152.1182	695237.9	psp									
411.2273	691263.7	psp									
148.0339	689500.3	psp									
264.1827	684786.1	psp									
203.206	678903.4	psp									
322.7088	663479.8	psp									
309.1479	649027.9	psp									
269.6907	638324.9	psp									
356.1851	623756.9	psp									
394.0932	618761.9	psp									
385.2679	615982.9	psp									
531.2981	614656.4	psp									
325.1431	606670.4	psp									
582.3642	606210.6	psp									
148.1637	593393	psp									
1015.153	591243.8	psp									
298.1513	589913.8	psp									
386.252	586079.9	psp									
314.1745	568435.3	psp									
271.1318	568325.4	psp									
481.2799	561573.8	psp									
238.1104	553831.4	psp									
404.1949	543094.6	psp									
189.1791	538244.8	psp									
235.245	531464.8	psp									
120.1133	530622.3	psp									
399.2272	530437.9	psp									
395.1958	520012.8	psp									
293.1164	515396.7	psp									
355.1735	509952.2	psp									
277.2846	505453.8	psp									
527.3216	500390	psp									
290.0722	491646	psp									
252.1722	487311.1	psp									
270.1196	474292.3	psp									
341.9714	469674.1	psp									
212.6328	468559.9	psp									

SUPPLEMENT S4. BACKGROUND PEAKS FROM POSTIVE MODE

85.07597, 86.05996, 86.07934, 87.05958, 87.09155, 88.02144, 88.07563, 89.07086, 89.10725, 90.05492, 91.05417, 92.03683, 93.12071, 94.06508, 95.0603, 96.08069, 96.99513, 97.07597, 98.07123, 98.08307, 98.98, 99.05523, 99.09154, 100.07561, 100.08836, 100.09939, 100.11199, 101.05966, 101.07089, 101.079, 101.10728, 102.09128, 102.10251, 103.08651, 104.01614, 104.07051, 104.11812, 104.99225, 105.10219, 105.12099, 107.07019, 108.61268, 109.11416, 111.01075, 111.05527, 111.09161, 111.11676, 112.08948, 112.09863, 113.07085, 113.10723, 114.09157, 114.10279, 114.11087, 114.61299, 115.0212, 115.09201, 115.10702, 116.07081, 116.11841, 117.00044, 117.06609, 117.10243, 117.12156, 117.12624, 118.03207, 118.06534, 118.08644, 118.09768, 118.13401, 119.01608, 119.08167, 120.0113, 120.06568, 120.11322, 120.61293, 121.01186, 121.62073, 122.00814, 122.07141, 123.09179, 123.12619, 124.08704, 125.03632, 125.07104, 125.10743, 125.12361, 126.10266, 127.08668, 127.10709, 128.08193, 128.09011, 128.11828, 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SUPPLEMENT S5. BACKGROUND PEAKS FROM NEGATIVE MODE

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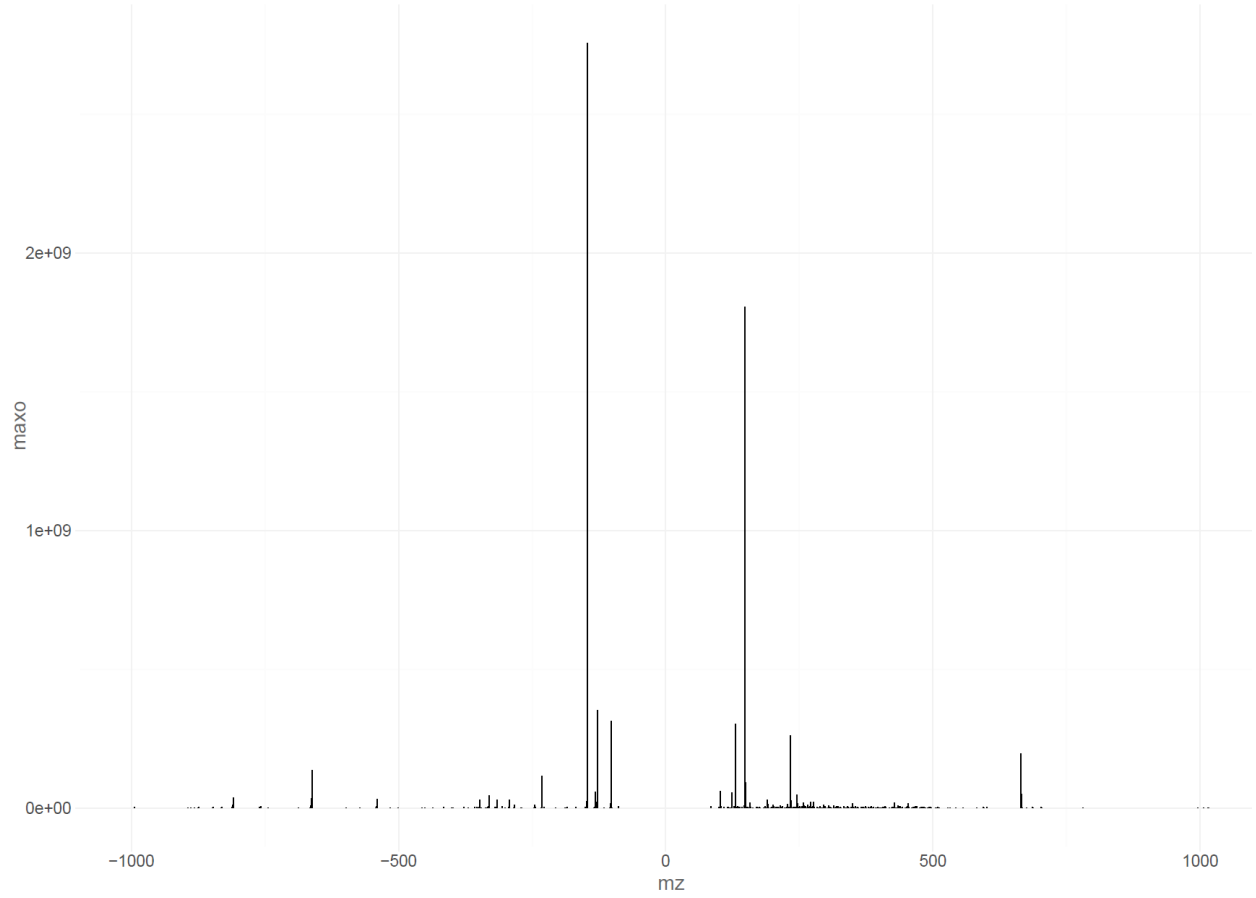
SUPPLEMENT S6. COMPOSITE SPECTRUM FROM 21-22 MINUTES OF A HILIC ANALYSIS OF E. COLI EXTRACT



SUPPLEMENT S7. LIST OF GRANULAR FORMULA USED

7.1 Isotopes: M.iso

	m	z	d
C12-13	1.003355	0	1
N14-15	0.997035	0	1
O16-18	2.004245	0	1
S32-33	0.999387	0	1
S32-34	1.995796	0	1
Cl35-37	1.99705	0	1
Br79-81	1.997953	0	1
Si28-29	0.999568	0	1
Si28-30	1.996843	0	1
K41-39	1.998119	0	1

7.2 Charge Carriers: M.z

	z	m	d
H+	1	1.007825	0
Na+	1	22.98977	0
K+	1	38.96371	0
Cl-	-1	34.96885	0
Br-	-1	78.91834	0

7.3 Neutral Formula: M.n

	z	m	d
-H2O	0	-18.0106	1
-CO2	0	-43.9898	1
-NH3	0	-17.0265	1
+HCOOH	0	46.00548	1
+CH3COOH	0	60.02113	1
+CF3COOH	0	113.9929	1
+CH3CN	0	41.02655	1
+CH3OH	0	32.02622	1
-CO	0	-27.9949	1
+H3PO4	0	97.9769	1
+SiO3H2	0	77.97732	1
+SiO4H4	0	95.98789	1
+SiC2H6O	0	74.01879	1

SUPPLEMENT S8. MZ.UNITY PARAMETERS USED FOR ANNOTATION OF THE COMPOSITE SPECTRUM

The code used to annotate this spectrum can be found online in the repository referenced in the main text. A summary of the annotation workflow is listed here.

8.1 Find peaks with isotope support for higher charge states

All peaks in the spectrum were searched with proposal charge $z = 2 * sign(m/z)$ and mass $m = abs(m/z) * 2$. Any isotopes found support the higher charge state assignment. Search was performed on peaks of both polarities.

- M = M.iso, ppm = 1, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(1))

8.2 Find peaks with isotope support for charge state z = 1

All peaks in the spectrum were searched with proposal charge $z = 1 * sign(m/z)$ and mass $m = abs(m/z) * 2$. Any isotopes found support the higher charge state. Search was performed on peaks of both polarities.

- M = M.iso, ppm = 1, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(1))

8.3 Annotate simple relationships

Peaks with a isotope support for charge state 2 were included along with all peaks for charge state 1. Search was performed on peaks of both polarities.

- Cross Polarity: M = M.z, ppm = 10, BM.limits = cbind(M.min = c(2), M.max = c(2), B.n = c(1)
- Single Charge Carriers: M = M.z, ppm = 2, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(1)
- Neutral losses and adducts: M = M.n, ppm = 2, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(1)

8.4 Annotate analyte-analyte mers and distal fragments

Peaks with a isotope support for charge state 2 were included along with all peaks for charge state 1. Search was performed sequentially first for negative and then for positive mode.

- M = M.z (only H^+), ppm = 2, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(2)

8.5 Annotate analyte-analyte mers and distal fragments across polarities

Peaks with a isotope support for charge state 2 were included along with all peaks for charge state 1. Search was performed on peaks of both polarities.

- M = M.z (only H^+), ppm = 2, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(2)

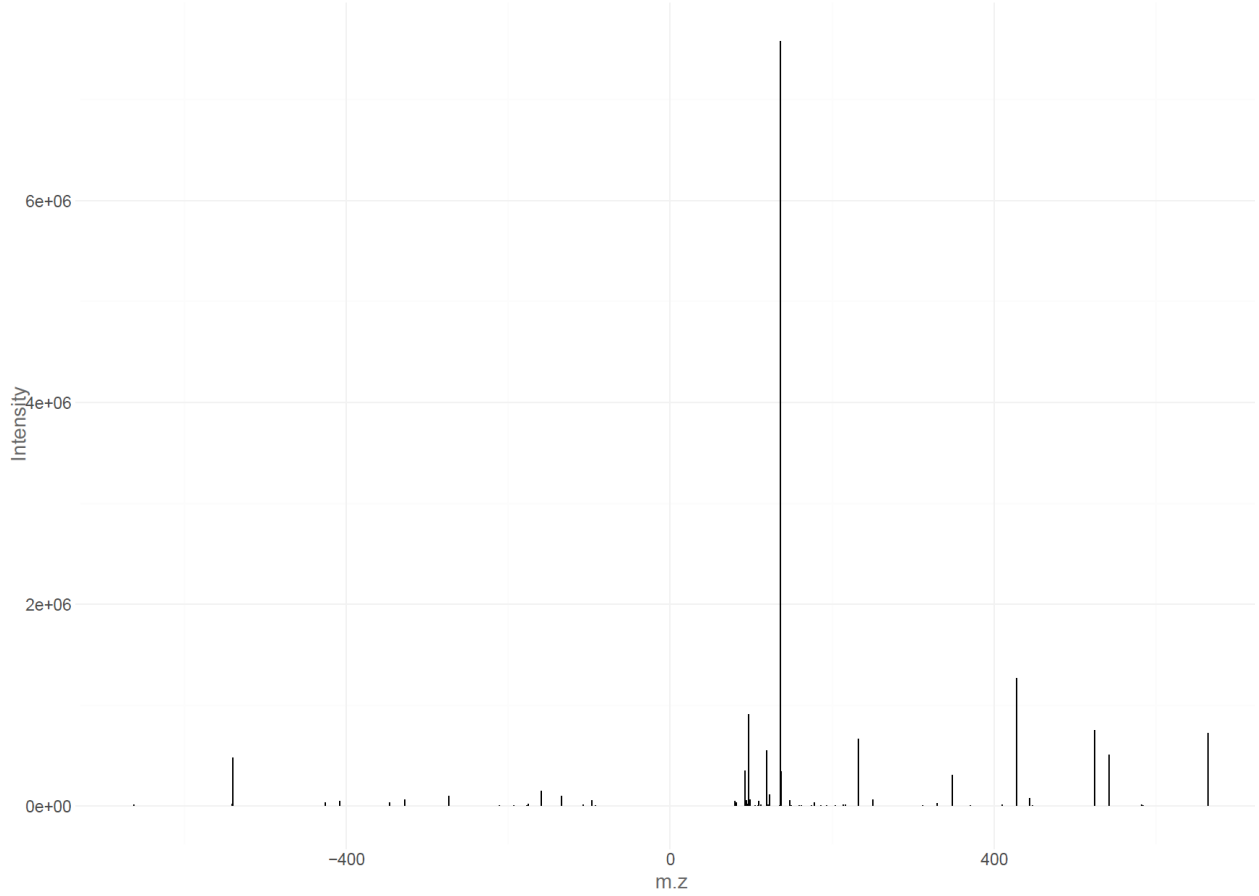
8.6 Annotate background mers

Peaks with a isotope support for charge state 2 were included along with all peaks for charge state 1. Features and mers were included in this search.

- M = M.z (only H^+), ppm = 2, BM.limits = cbind(M.min = c(1), M.max = c(1), B.n = c(2)

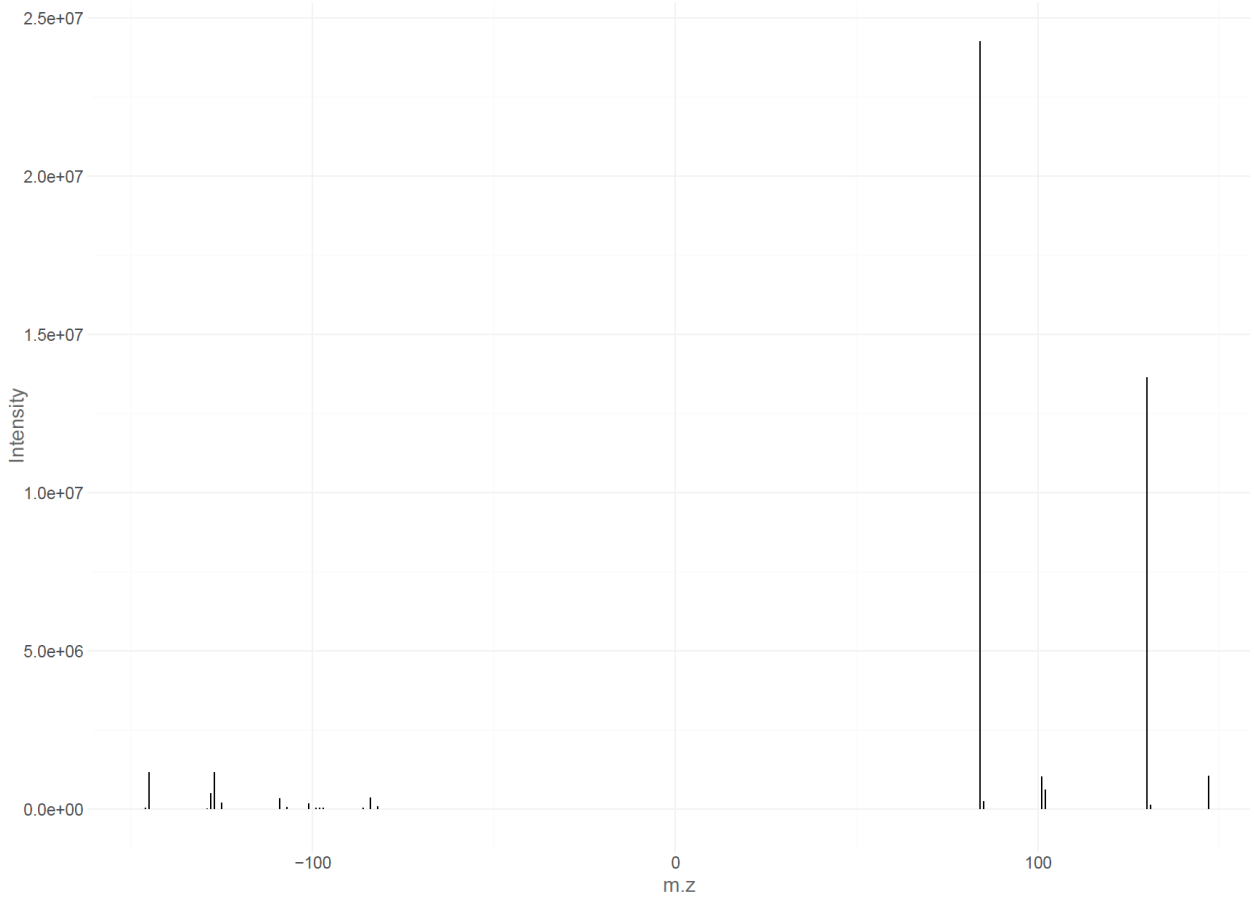
SUPPLEMENT S9. FRAGMENTATION SPECTRUM OF NAD

Spectra taken at collision energies 0, 10, 20, 40, 60, 90, and 120 were averaged from both positive and negative mode. The composite spectrum is shown below.



SUPPLEMENT S10. FRAGMENTATION SPECTRUM OF GLUTAMATE

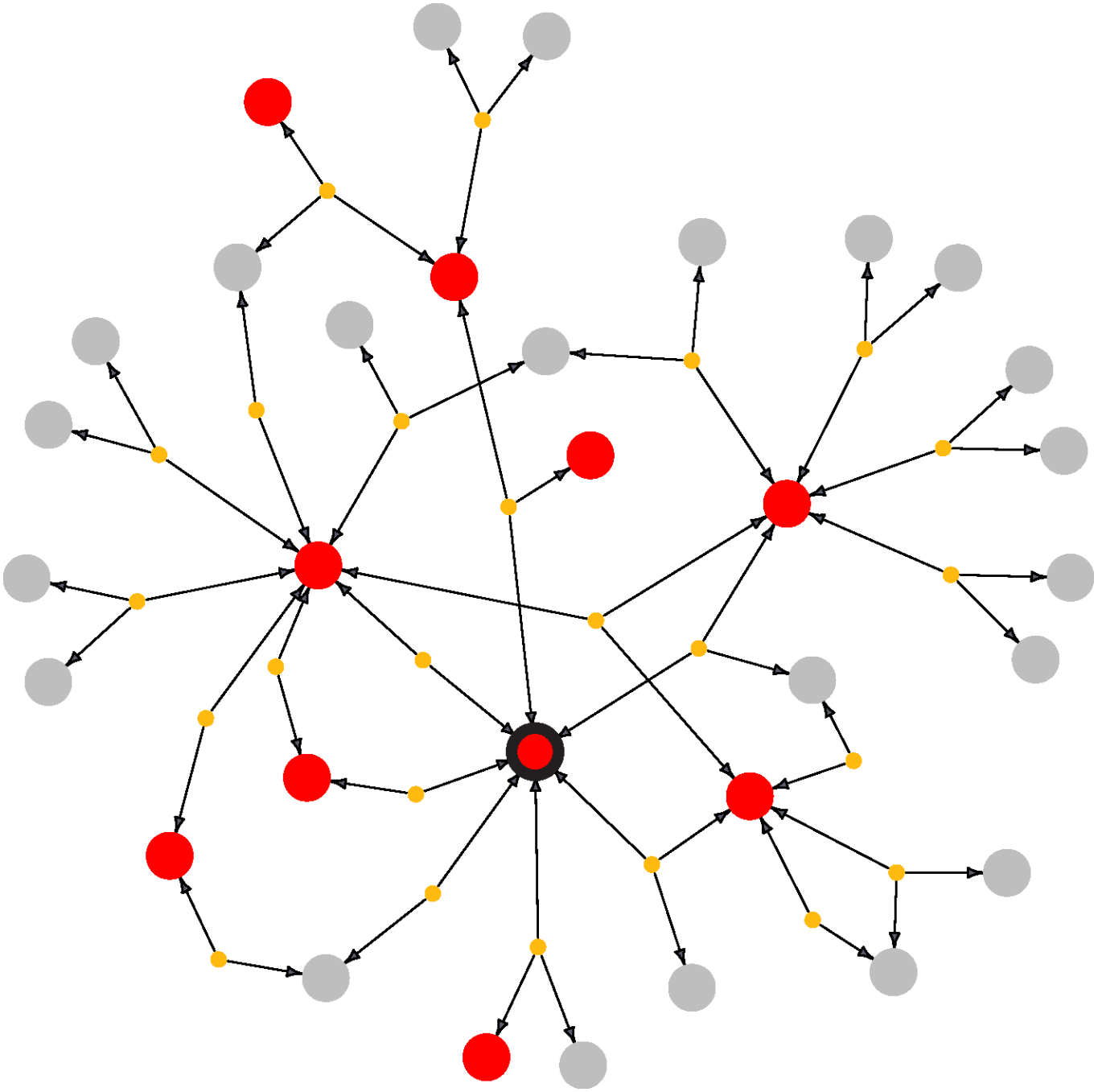
Spectra taken at collision energies 0, 10, 20, 40, 60, 90, and 120 were averaged from both positive and negative mode. The composite spectrum is shown below.



SUPPLEMENT S11. ANNOTATION OF 2-HYDROXYGLUTARATE METABOLIC PRODUCTS

2-Hydroxyglutarate (2HG) corresponds to the node with a thick black border. Large nodes are features. Small nodes are relationships. Red nodes were detected as enriched by $X^{13}CMS$. Grey nodes were not detected as enriched by $X^{13}CMS$.

Analysis by mz.unity revealed that all enriched features were transformations of 2HG. This indicates that 2HG is not significantly metabolized in colorectal cancer cells.[14]



(14) Gelman, S. J.; Mahieu, N. G.; Cho, K.; Llufrio, E. M.; Wencewicz, T. A.; Patti, G. J. *Cancer Metab.* **2015**, *3* (1), 1.

SUPPLEMENT S12. INTENSITITES, MASSES, AND RETENTION TIMES OF ADDUCTS

Maximum intensities from each chromatogram are inset. Retention times are in seconds. Masses from top to bottom and left to right: A, 146.0455, 168.0273, 184.0012; B, 146.0455, 662.1015, 809.1547; C, 146.0455, 98.0246, 436.0948.