GC-MS Analysis of Polychlorinated Biphenyl Congeners Using a New Capillary GC Column

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Abstract

- The analysis of polychlorinated biphenyls (PCB's) by GC can be a very challenging analysis. Numerous researchers have demonstrated various separations on the common commercially available GC stationary phases, but all of these have had limitations when it comes to the separation of all 209 possible PCB congeners. While it may be argued that the complete separation of all 209 possible congeners is not necessary, separation of the environmentally significant and the toxic congeners is important.
- The separation requirements for the analysis of PCB congeners differ considerably depending on the type of detector used. Separation needs when using a mass spectrometer are different then when using standard GC detectors.
- This presentation will discuss the separation needs for PCB congeners when using a mass spectrometer, and demonstrate an improved separation of PCB congeners, using a new capillary stationary phase developed for this purpose.

Experiment

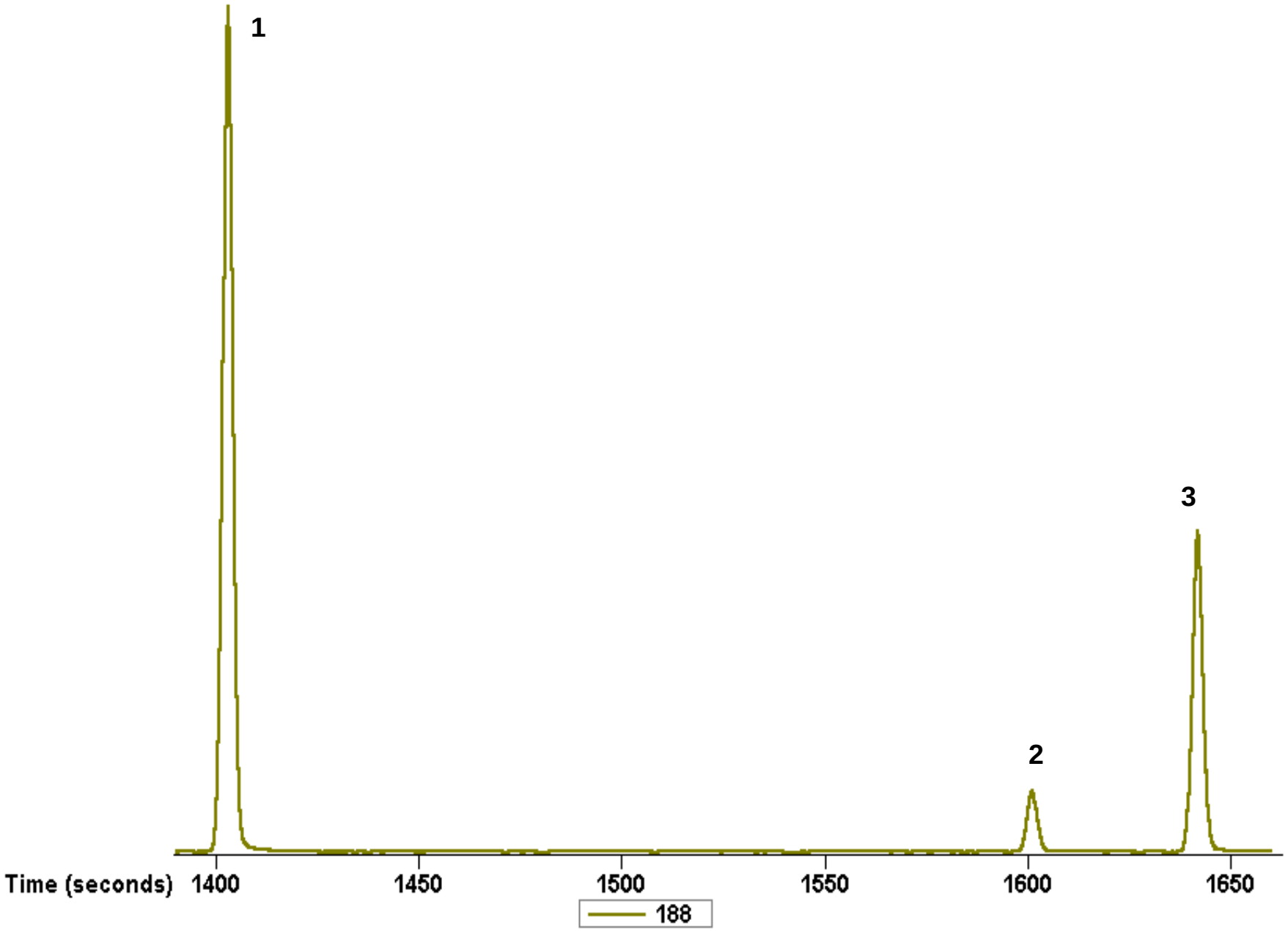
- Determine retention times for all 209 PCBs on a new low-bleed capillary column
  - AccuStandard 9 mixtures
  - Hexachlorobenzene for relative retention times
- Analyze mix of Aroclors 1221:1242:1254:1262
  - 1:2:2:2 ratio
  - Show chromatogram with congeners labeled
- GC-MS results obtained using a time-of-flight mass spectrometer to allow for possible spectral deconvolution

GC-TOFMS Conditions

- Gas Chromatography
  - One microliter splitless 250°C, 60 sec valve
  - 60 m x 0.18 mm x 0.18 µm Restek Rtx-PCB column
    - Constant flow helium, 1.5 mL/minute
    - 70°C (1 min), 50°/min to 120°, 3°/min to 360° (1 min)
- Mass Spectrometry LECO Pegasus III
  - Source temperature: 225°C
  - Electron ionization: 70 eV
  - Stored mass range: 120 to 520 u
  - Acquisition rate: 5 spectra/sec

Aroclor Mix Chromatogram

- Overlaid ion chromatograms are plotted
  - For example, hexachlorobiphenyl is 360
  - Peaks are labeled with congener numbers
    - Text size and format is only for space and not meant to indicate anything about PCBs, except:
    - European indicator congeners are in red
- Chromatograms are not to one scale
  - Each panel is adjusted so most of the PCB peaks can be seen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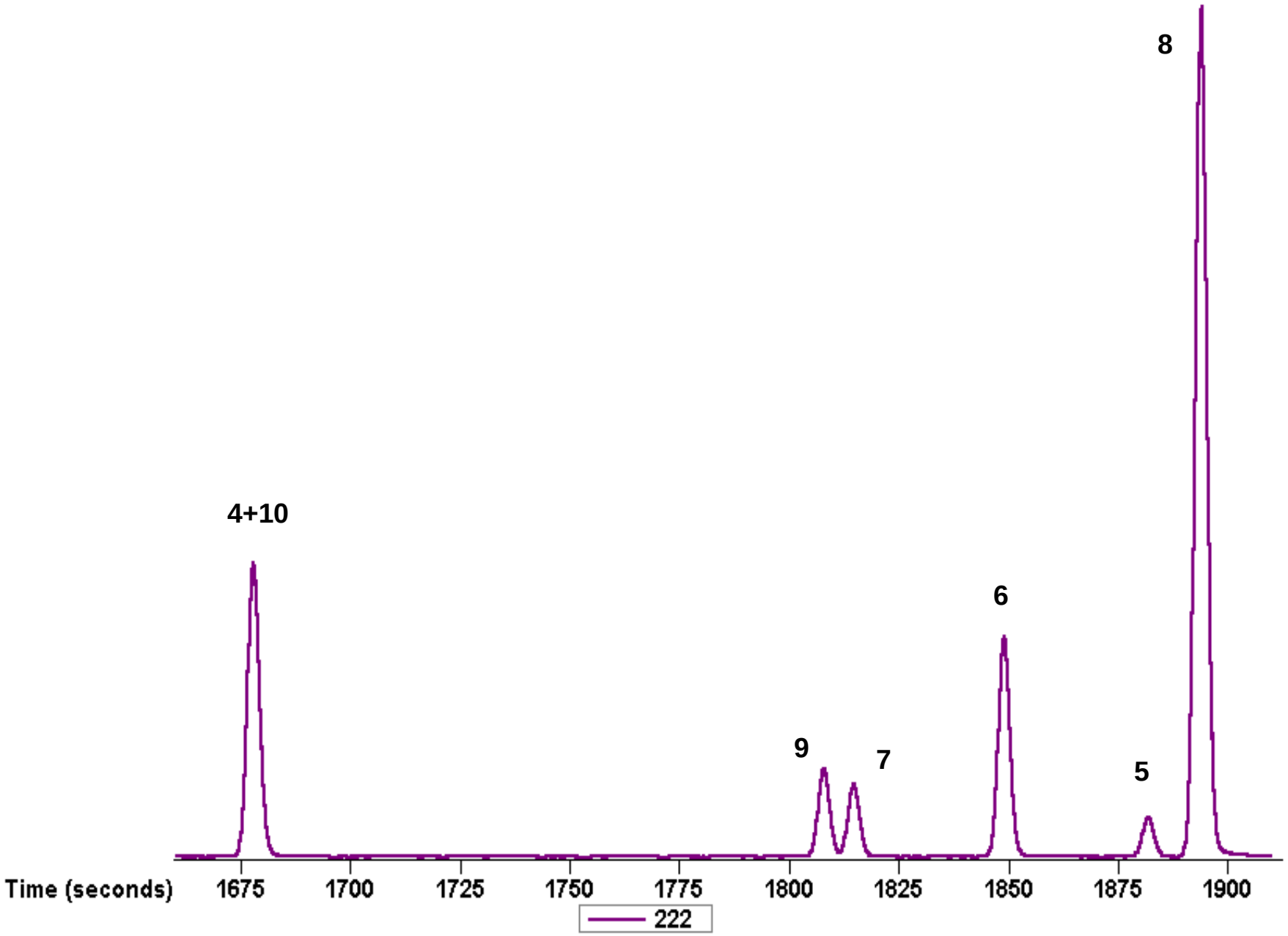
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1825
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1875
1900
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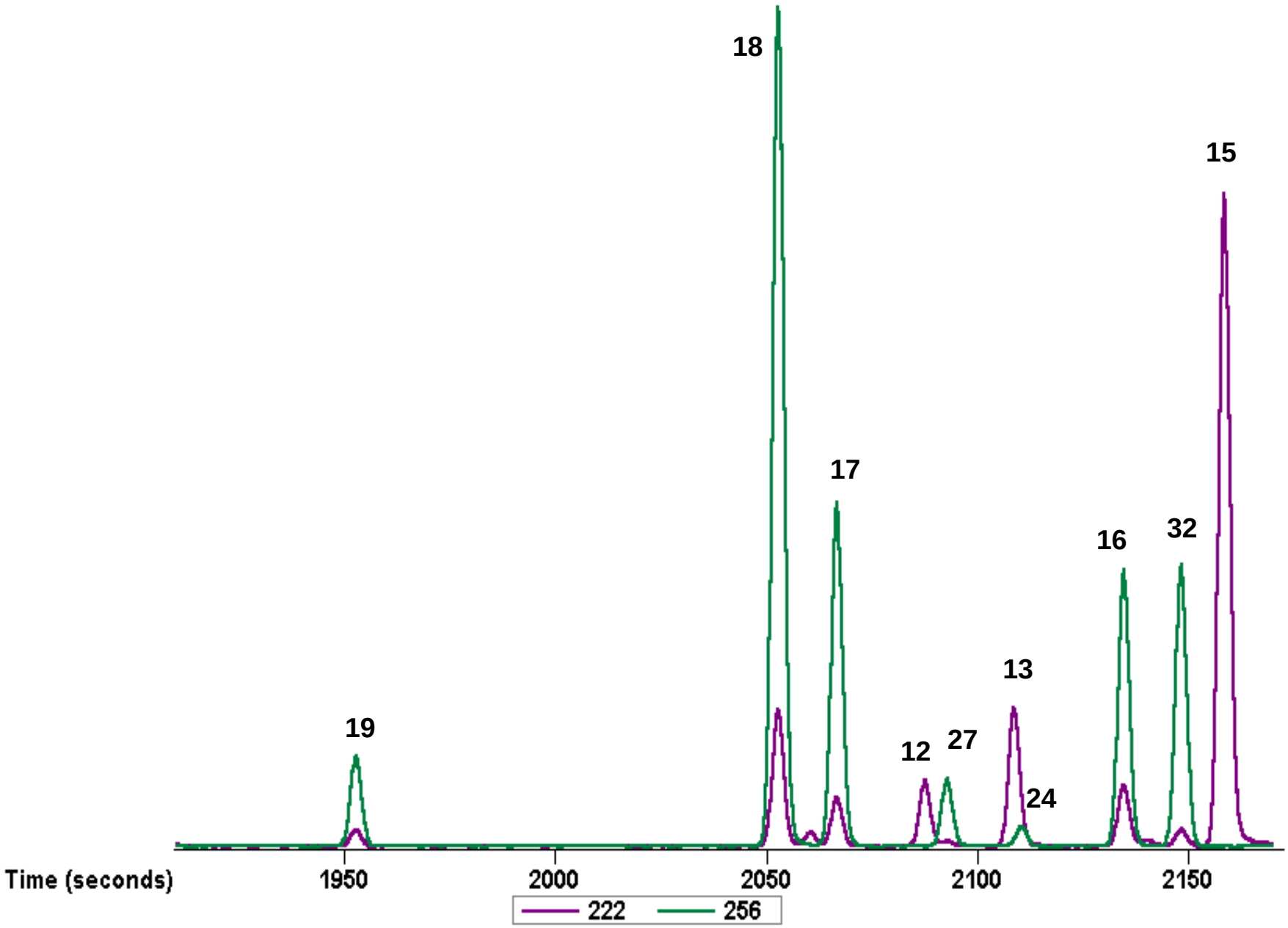
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Time (seconds)
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2100
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222
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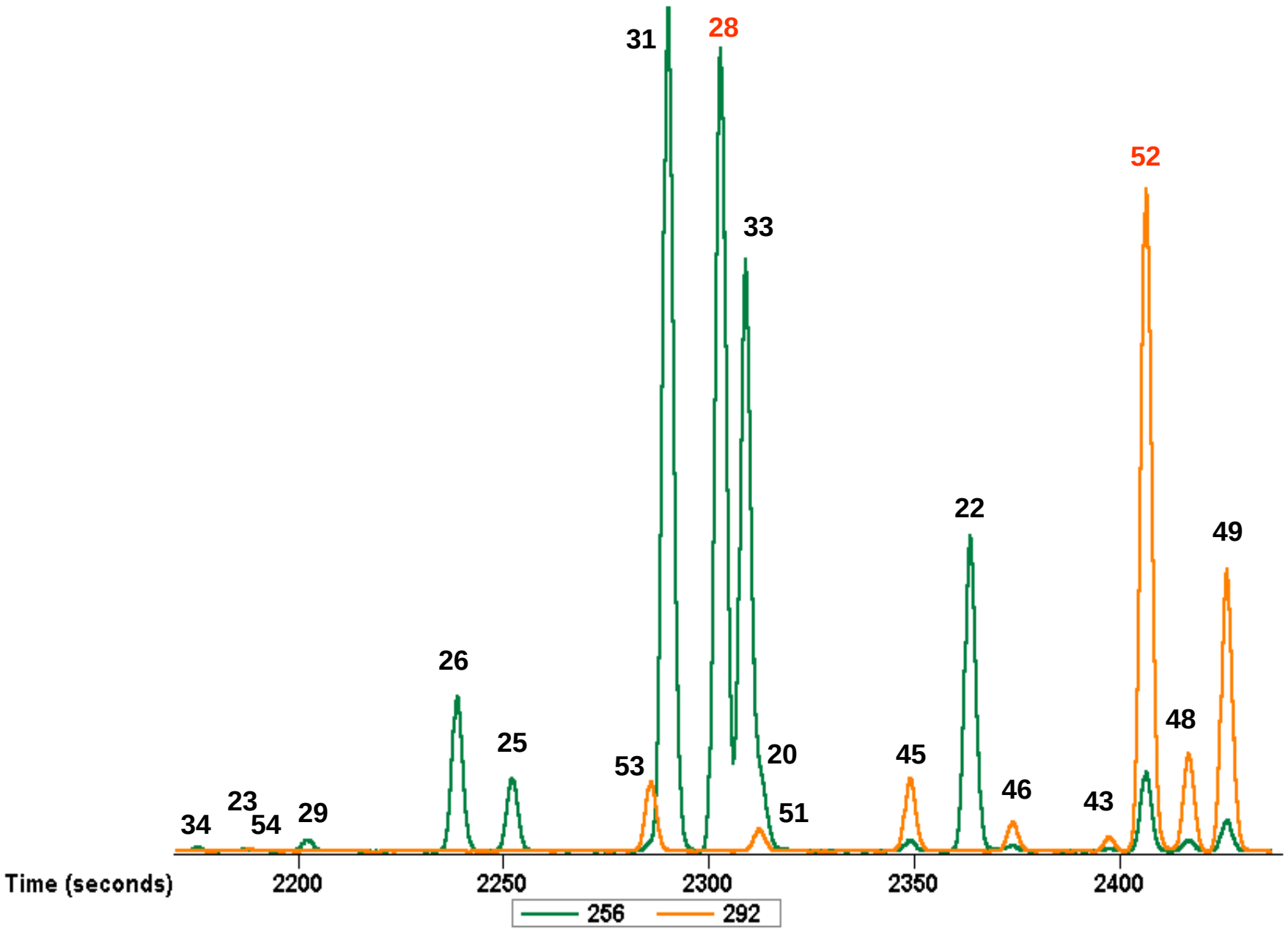
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26
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Time (seconds)
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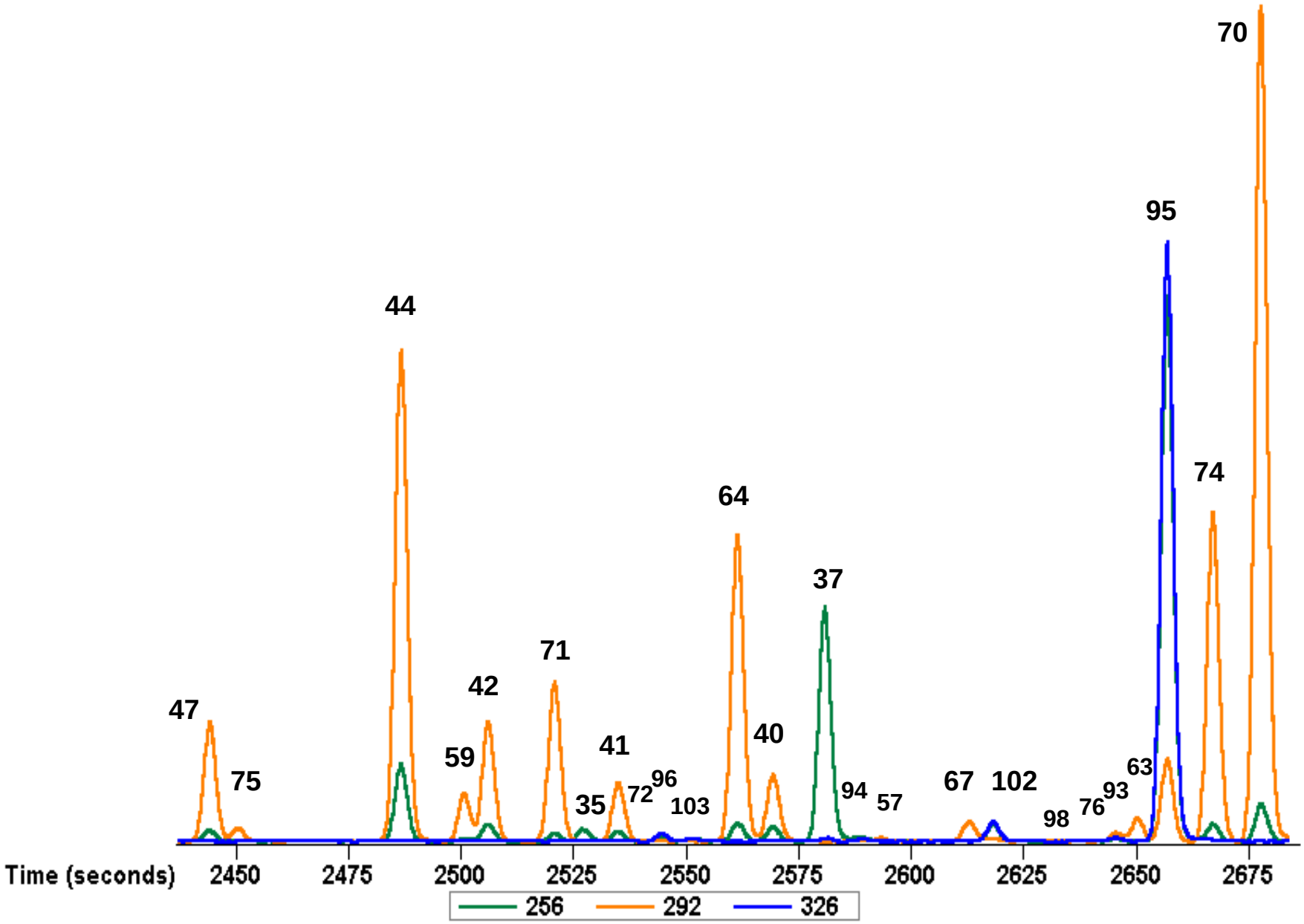
2250
2300
2350
2400
256
292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37
71
42
47
41
59
40
75
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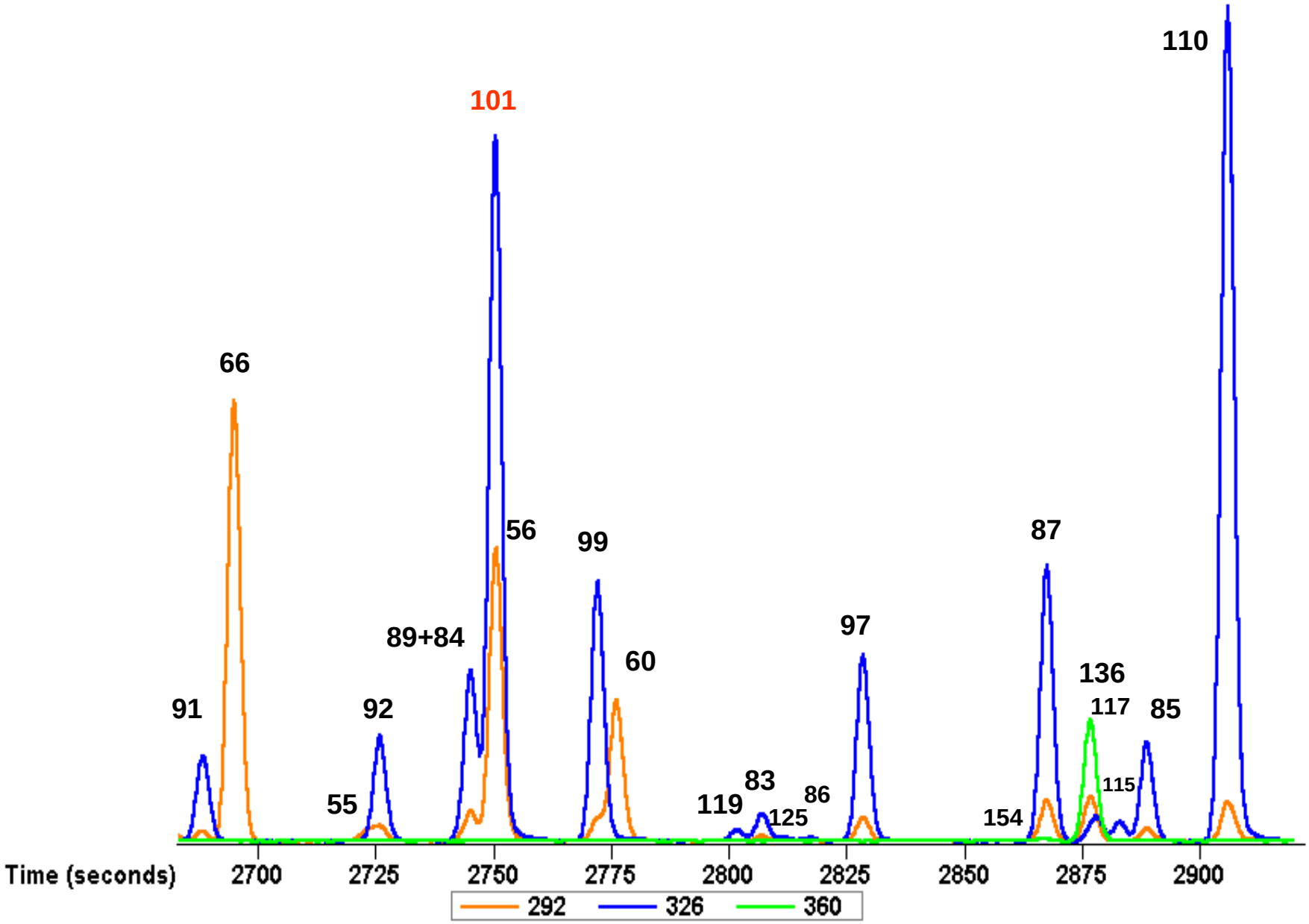
72
96
103
94
57
67
102
98
76
93
63
Time (seconds)
2450
2475
2500
2525
2550
2575
2600
2625
2650
2675
256
292
326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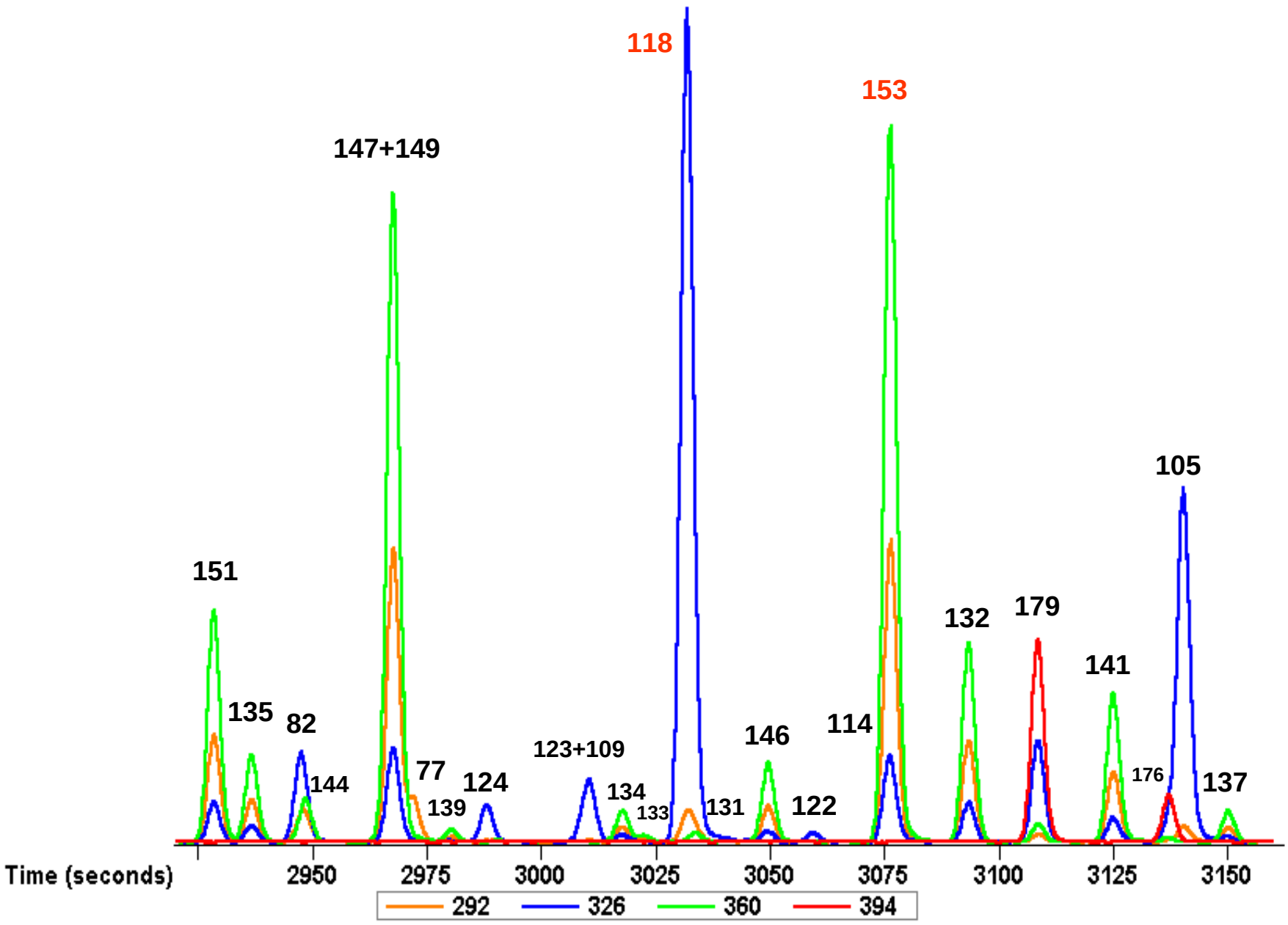
101
66
56
99
87
89+84
97
60
136
91
92
117
85
55
83
115
119
86
125
154
Time (seconds)
2700
2725
2750
2775
2800
2825
2850
2875
2900
292
326
360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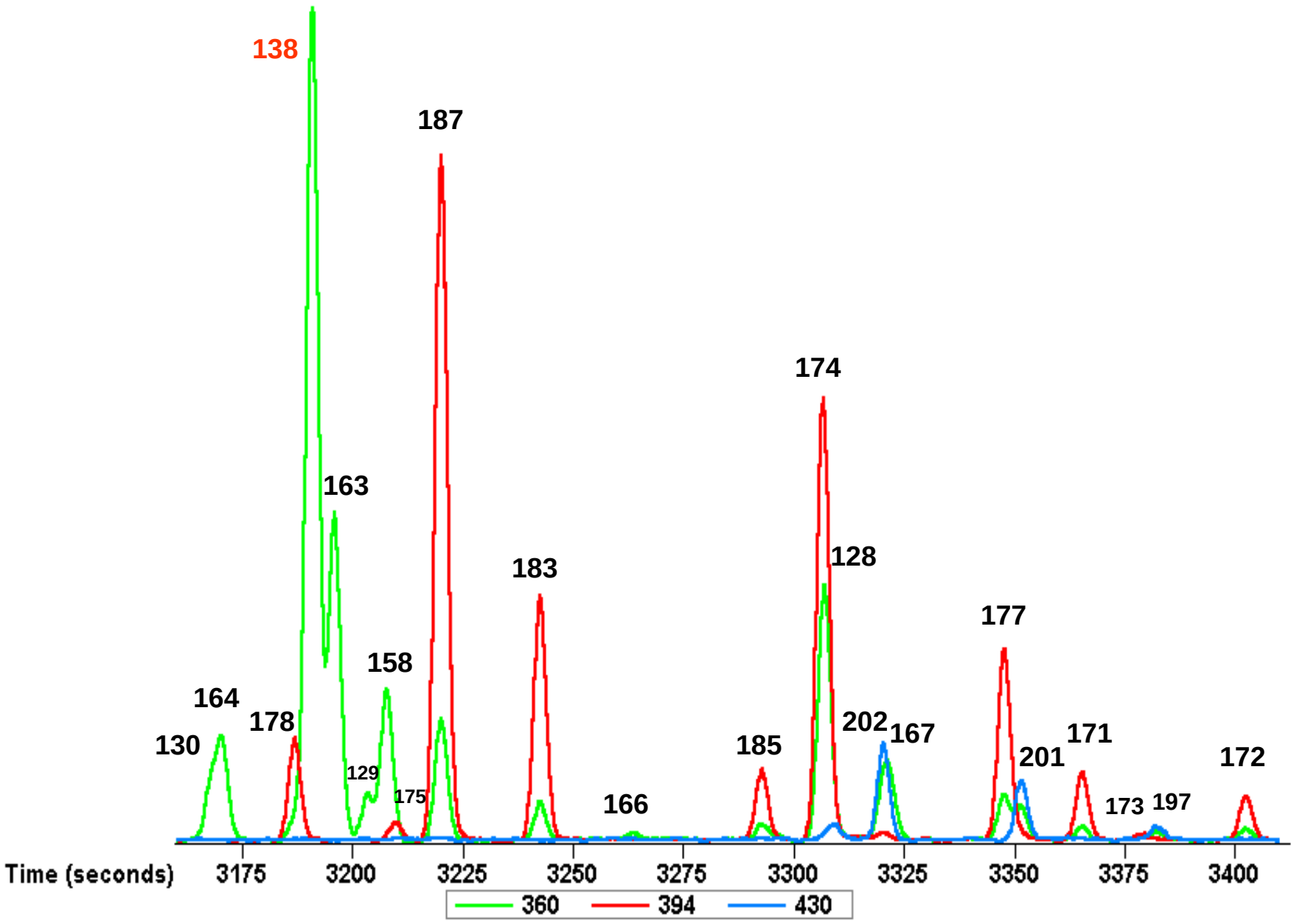
153
147+149
105
151
135
82
144
77
139
124
123+109
134
133
131
146
122
114
132
179
141
176
137
Time (seconds)
2950
2975
3000
3025
3050
3075
3100
3125
3150
292
326
360
394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174
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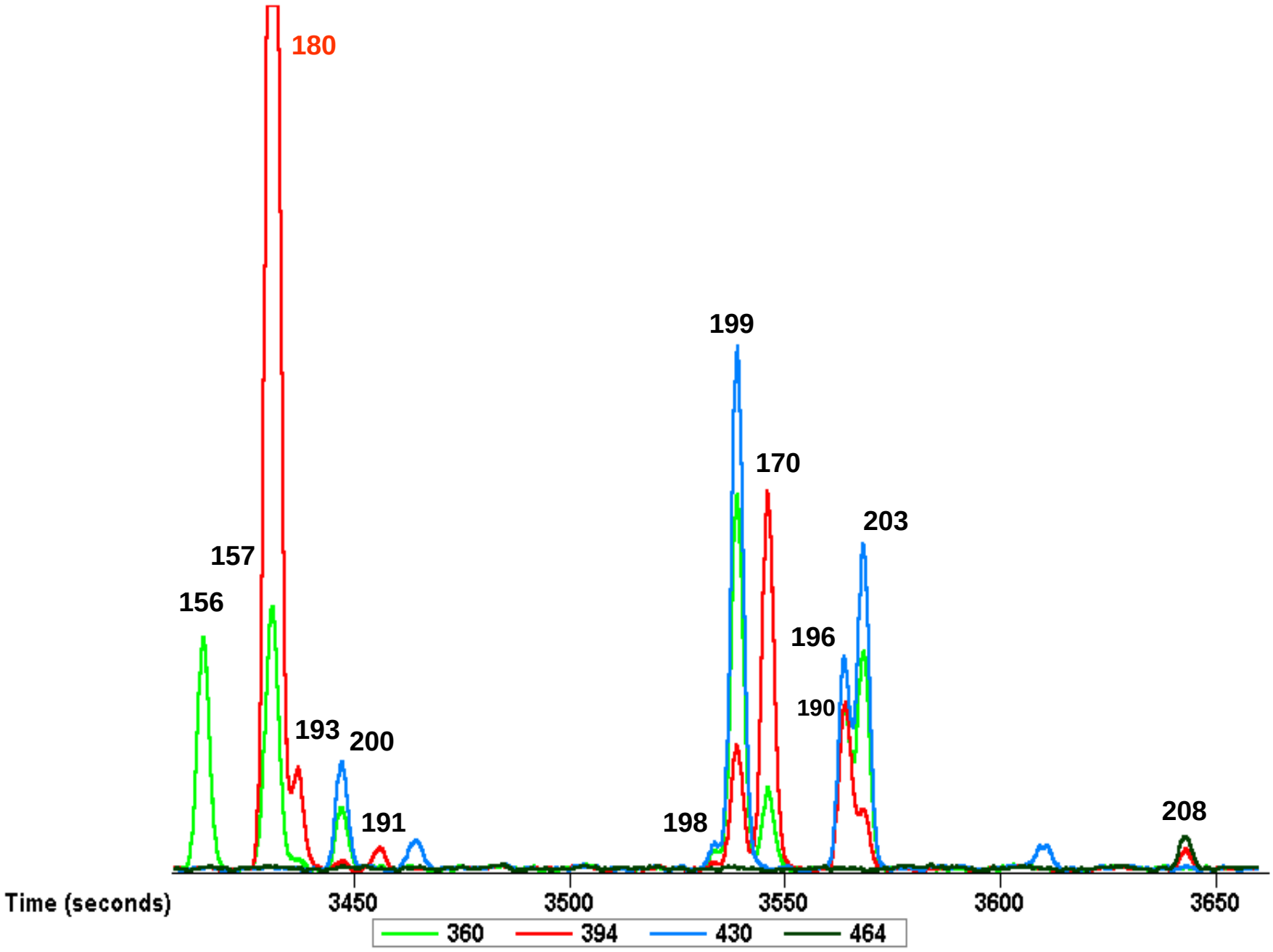
177
164
178
130
202
167
171
185
201
172
129
175
166
173
197
Time (seconds)
3175
3200
3225
3250
3275
3300
3325
3350
3375
3400
360
394
430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191
198
208
Time (seconds)
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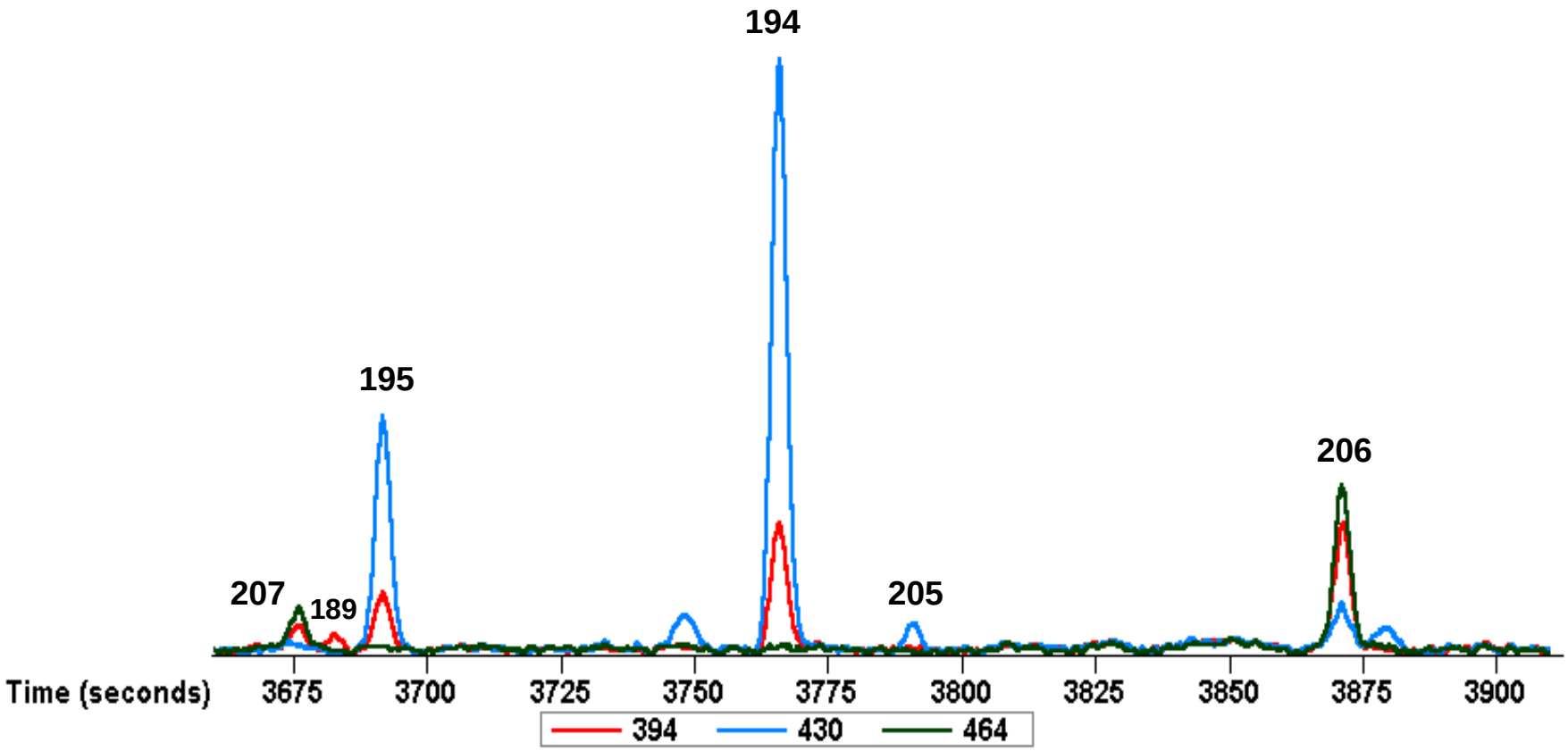
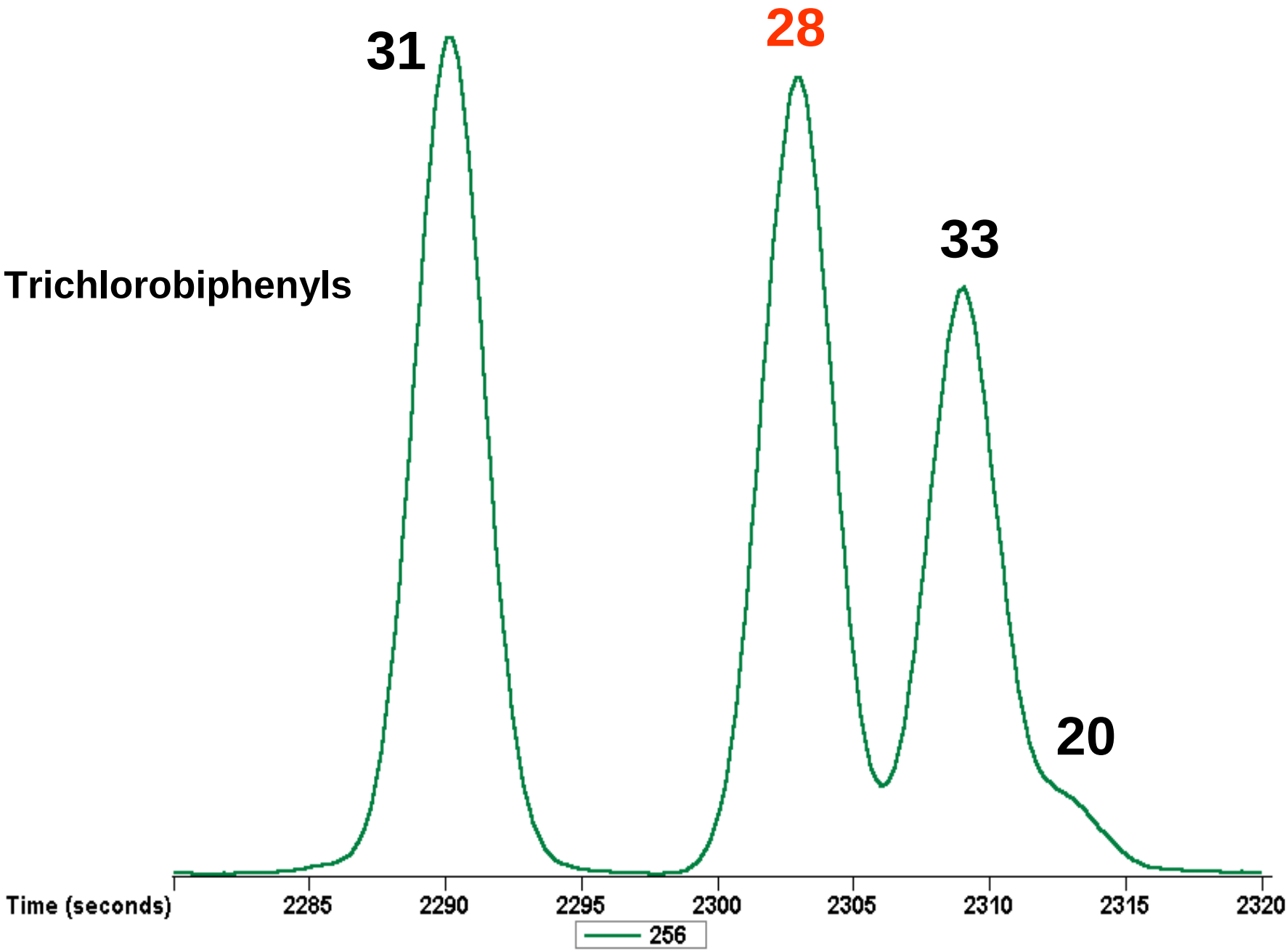
3500
3550
3600
3650
360
394
430
464


194
195
206
207
189
205
Time (seconds)
3675
3700
3725
3750
3775
3800
3825
3850
3875
3900
394
430
464

Important Congener Separations

- European indicator PCBs
- May coelute on 5% phenyl methylsilicone and other column phases


Trichlorobiphenyls
31
28
33
20
Time (seconds)
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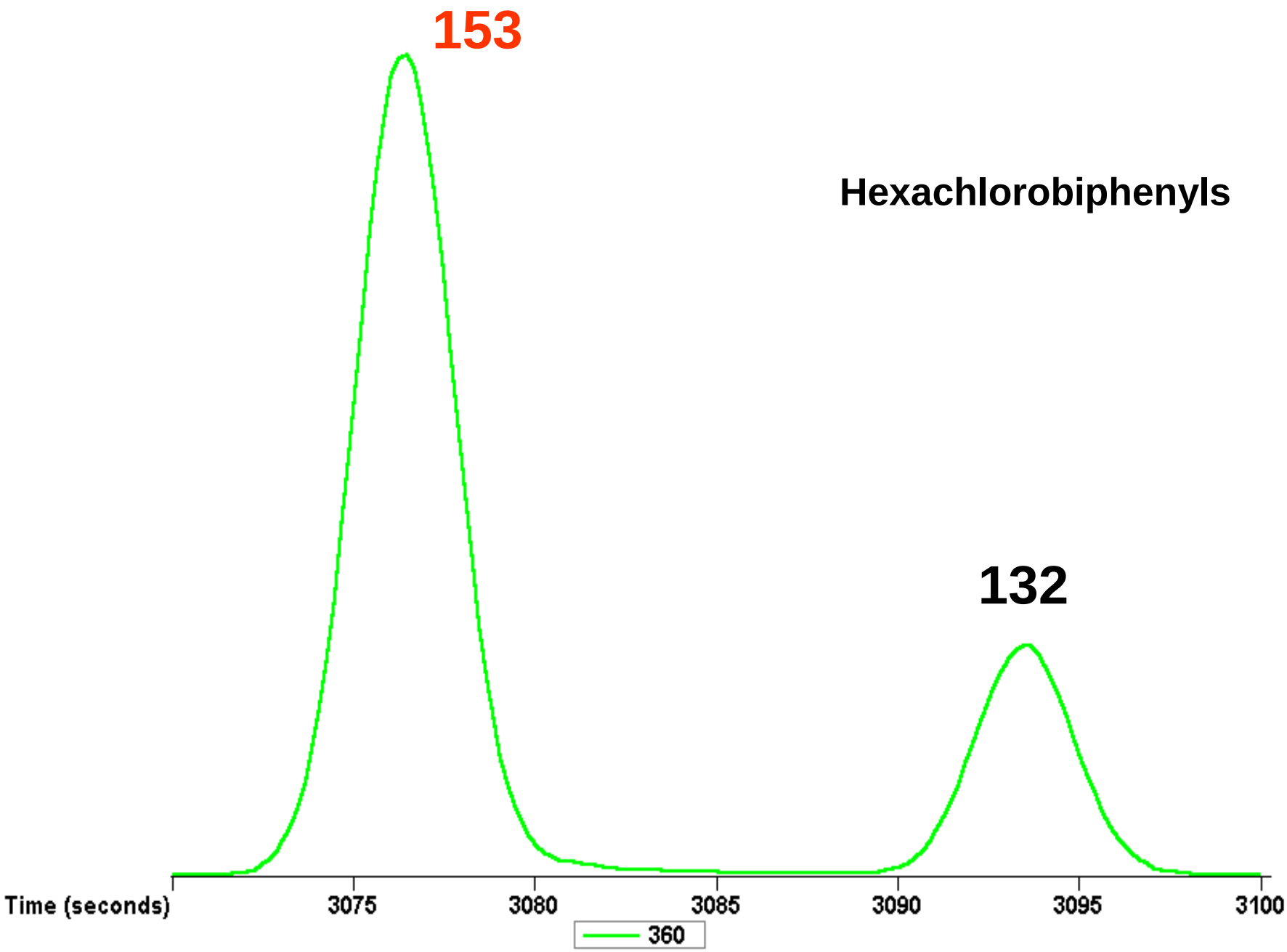
2290
2295
2300
2305
2310
2315
2320
256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Hexachlorobiphenyls
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Time (seconds)
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3080
3085
3090
3095
3100
360

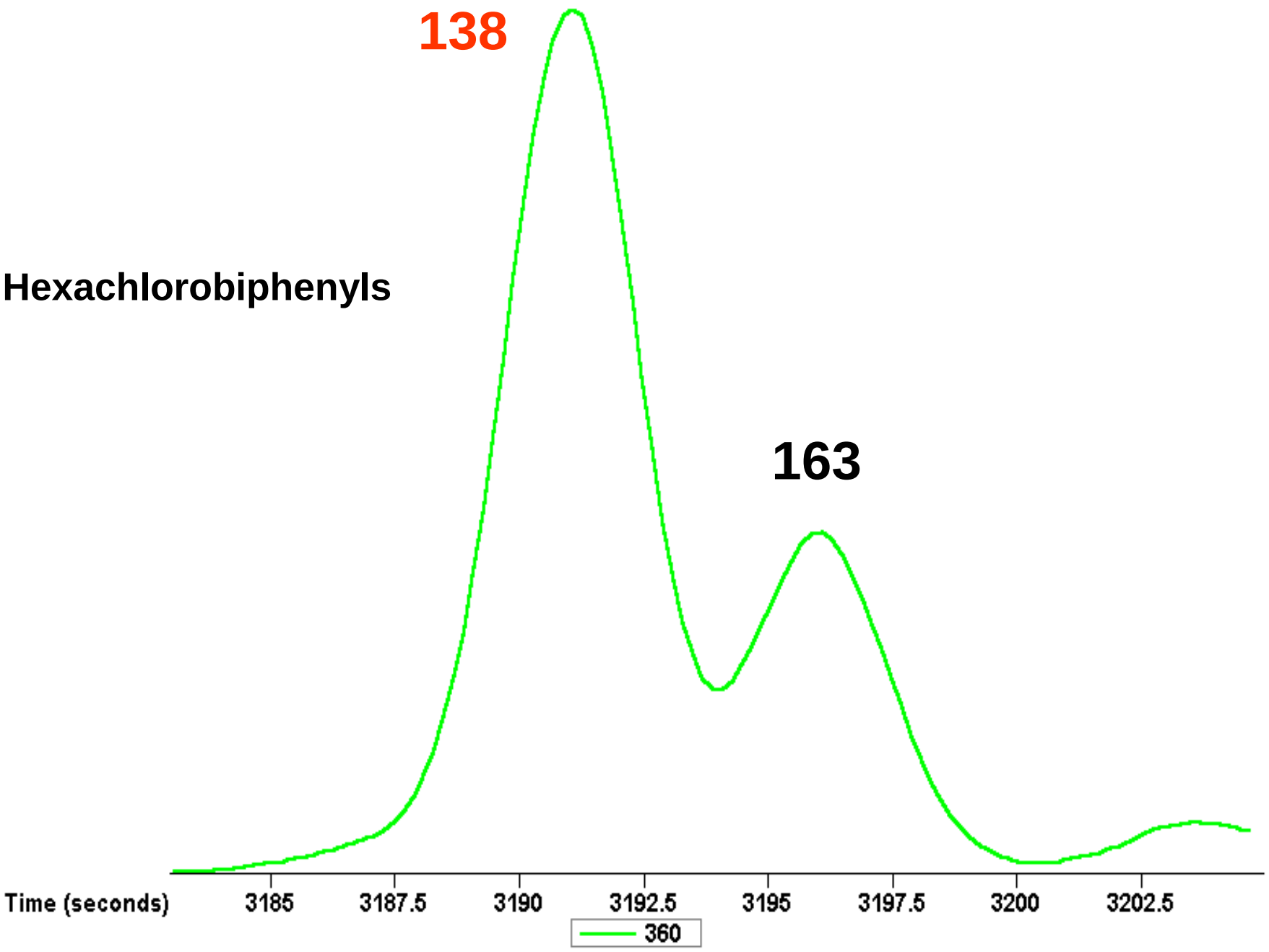
138
Hexachlorobiphenyls
163
Time (seconds)
3185
3187.5
3190
3192.5
3195
3197.5
3200
3202.5
360

Table Key

- Congener classification according to their significance in Aroclors 1242, 1254, or 1260
  - **<u>Bold Underline</u>**: Congener > 1.0 Wt%
  - **Bold**: Congener 0.05 to 1.0 Wt%
  - *Italics*: Trace or undetected congener
- Congener naming according to Guitart et al. by chlorine positions
  - 107: 234-35
  - 108: 2346-3
  - 109: 235-34
  - 199: 2345-2356
  - 200: 23456-236
  - 201: 2346-2356
- RRT is relative retention time
- Coelutions of significance where MS won't help are

PCB#	Cl#	RT (sec)	RT (min)	RRT
1	1	1403.3	23.39	0.7206
2	1	1601.3	26.69	0.8222
3	1	1642.1	27.37	0.8432
4	2	1678.1	27.97	0.8617
10	2	1679.7	28.00	0.8625
9	2	1808.3	30.14	0.9285
7	2	1815.3	30.26	0.9321
6	2	1849.3	30.82	0.9496
5	2	1882.3	31.37	0.9665
8	2	1894.3	31.57	0.9727
19	3	1953.3	32.55	1.0030
14	2	1963.3	32.72	1.0079
30	3	1993.5	33.22	1.0236
18	3	2053.3	34.22	1.0543
11	2	2061.1	34.35	1.0582
17	3	2067.3	34.46	1.0615
12	2	2088.1	34.80	1.0721
27	3	2093.3	34.89	1.0748
13	2	2109.3	35.15	1.0829
24	3	2110.9	35.18	1.0839

PCB#	Cl#	RT (sec)	RT (min)	RRT
16	3	2135.1	35.58	1.0963
32	3	2148.7	35.81	1.1033
15	2	2158.9	35.98	1.1084
34	3	2176.1	36.27	1.1173
23	3	2187.3	36.45	1.1234
54	4	2188.9	36.48	1.1237
29	3	2202.7	36.71	1.1309
50	4	2237.1	37.28	1.1486
26	3	2239.3	37.32	1.1498
25	3	2252.7	37.54	1.1567
53	4	2286.5	38.11	1.1738
31	3	2290.7	38.18	1.1762
28	3	2303.5	38.39	1.1828
33	3	2309.5	38.49	1.1858
51	4	2312.9	38.55	1.1874
21	3	2312.7	38.54	1.1874
20	3	2313.3	38.56	1.1877
45	4	2349.5	39.16	1.2064
22	3	2364.3	39.40	1.2140
73	4	2374.3	39.57	1.2189

PCB#	Cl#	RT (sec)	RT (min)	RRT
46	4	2374.5	39.58	1.2193
69	4	2391.5	39.86	1.2279
43	4	2397.7	39.96	1.2312
36	3	2398.9	39.98	1.2317
52	4	2406.9	40.11	1.2359
48	4	2417.3	40.29	1.2412
49	4	2426.5	40.44	1.2458
104	5	2440.3	40.67	1.2529
47	4	2444.7	40.75	1.2552
65	4	2448.5	40.81	1.2571
75	4	2451.3	40.85	1.2584
62	4	2450.7	40.84	1.2586
39	3	2452.9	40.88	1.2598
38	3	2461.3	41.02	1.2637
44	4	2487.3	41.45	1.2772
59	4	2501.3	41.69	1.2842
42	4	2506.7	41.78	1.2870
71	4	2521.5	42.02	1.2947
35	3	2527.9	42.13	1.2978
41	4	2535.7	42.26	1.3020

PCB#	Cl#	RT (sec)	RT (min)	RRT
72	4	2542.1	42.37	1.3052
96	5	2545.1	42.42	1.3067
103	5	2552.3	42.54	1.3105
68	4	2560.5	42.67	1.3150
64	4	2561.9	42.70	1.3153
40	4	2569.9	42.83	1.3195
37	3	2581.3	43.02	1.3254
100	5	2581.9	43.03	1.3255
94	5	2589.1	43.15	1.3297
57	4	2594.1	43.23	1.3319
67	4	2613.5	43.56	1.3420
58	4	2614.7	43.58	1.3426
102	5	2618.9	43.65	1.3446
61	4	2635.9	43.93	1.3533
98	5	2637.9	43.96	1.3544
93	5	2646.1	44.10	1.3586
76	4	2646.1	44.10	1.3587
63	4	2650.9	44.18	1.3610
121	5	2653.9	44.23	1.3630
95	5	2657.5	44.29	1.3646

PCB#	Cl#	RT (sec)	RT (min)	RRT
88	5	2658.9	44.31	1.3656
74	4	2667.9	44.46	1.3699
155	6	2675.7	44.59	1.3742
70	4	2678.3	44.64	1.3752
91	5	2688.7	44.81	1.3805
66	4	2695.7	44.93	1.3842
80	4	2709.7	45.16	1.3917
55	4	2723.3	45.39	1.3984
92	5	2726.5	45.44	1.3999
89	5	2743.7	45.73	1.4087
84	5	2745.9	45.77	1.4100
101	5	2750.9	45.85	1.4124
90	5	2751.5	45.86	1.4125
56	4	2751.5	45.86	1.4128
113	5	2757.3	45.95	1.4157
99	5	2772.9	46.21	1.4238
150	5	2776.1	46.27	1.4258
60	4	2776.7	46.28	1.4258
152	6	2798.9	46.65	1.4370
119	5	2802.3	46.71	1.4388

PCB#	Cl#	RT (sec)	RT (min)	RRT
83	5	2807.5	46.79	1.4416
125	5	2811.3	46.85	1.4438
112	5	2812.1	46.87	1.4440
86	5	2817.7	46.96	1.4467
108	5	2821.5	47.02	1.4488
145	6	2825.9	47.10	1.4509
97	5	2828.9	47.15	1.4524
148	6	2835.5	47.26	1.4563
79	4	2841.9	47.36	1.4591
116	5	2855.5	47.59	1.4665
154	6	2867.7	47.79	1.4722
87	5	2868.3	47.80	1.4728
78	4	2870.3	47.84	1.4737
111	5	2871.1	47.85	1.4746
136	6	2877.3	47.96	1.4773
117	5	2878.9	47.98	1.4780
115	5	2883.5	48.06	1.4806
85	5	2889.1	48.15	1.4833
120	5	2895.7	48.26	1.4869
110	5	2906.7	48.44	1.4925

PCB#	Cl#	RT (sec)	RT (min)	RRT
81	4	2927.7	48.79	1.5030
151	6	2929.1	48.82	1.5039
135	6	2937.3	48.96	1.5082
82	5	2948.3	49.14	1.5139
144	6	2949.1	49.15	1.5142
147	6	2966.3	49.44	1.5231
149	6	2968.3	49.47	1.5241
77	4	2972.3	49.54	1.5261
140	6	2980.3	49.67	1.5306
139	6	2981.3	49.69	1.5307
124	5	2988.9	49.81	1.5344
143	6	2990.5	49.84	1.5359
107	5	3005.3	50.09	1.5430
123	5	3009.5	50.16	1.5452
109	5	3011.3	50.19	1.5462
188	7	3011.5	50.19	1.5467
134	6	3018.5	50.31	1.5498
106	5	3018.9	50.31	1.5500
133	6	3023.1	50.38	1.5521
142	6	3027.5	50.46	1.5549

PCB#	Cl#	RT (sec)	RT (min)	RRT
118	5	3032.5	50.54	1.5570
131	6	3034.3	50.57	1.5580
184	7	3040.7	50.68	1.5612
165	6	3044.1	50.73	1.5628
146	6	3050.3	50.84	1.5663
122	5	3060.1	51.00	1.5710
161	6	3060.3	51.00	1.5712
168	6	3072.5	51.21	1.5780
114	5	3076.1	51.27	1.5794
153	6	3077.1	51.28	1.5800
132	6	3094.1	51.57	1.5887
179	7	3109.3	51.82	1.5966
141	6	3125.7	52.10	1.6050
176	7	3137.5	52.29	1.6109
105	5	3140.9	52.35	1.6126
137	6	3150.7	52.51	1.6177
186	7	3157.1	52.62	1.6211
127	5	3157.7	52.63	1.6212
130	6	3168.7	52.81	1.6267
164	6	3171.1	52.85	1.6283

PCB#	Cl#	RT (sec)	RT (min)	RRT
178	7	3187.7	53.13	1.6368
138	6	3191.7	53.19	1.6389
163	6	3196.7	53.28	1.6411
160	6	3198.9	53.31	1.6429
129	6	3203.9	53.40	1.6450
158	6	3208.5	53.48	1.6473
182	7	3209.7	53.49	1.6480
175	7	3210.5	53.51	1.6482
187	7	3221.1	53.68	1.6540
183	7	3243.3	54.06	1.6654
166	6	3264.1	54.40	1.6759
159	6	3277.3	54.62	1.6828
126	5	3290.3	54.84	1.6893
185	7	3293.3	54.89	1.6909
162	6	3295.9	54.93	1.6927
128	6	3307.9	55.13	1.6984
174	7	3307.7	55.13	1.6984
202	8	3321.1	55.35	1.7050
167	6	3322.7	55.38	1.7060
181	7	3328.9	55.48	1.7091

PCB#	Cl#	RT (sec)	RT (min)	RRT
177	7	3348.5	55.81	1.7194
201	8	3352.3	55.87	1.7210
204	8	3353.9	55.90	1.7220
171	7	3366.1	56.10	1.7284
173	7	3379.7	56.33	1.7354
197	8	3383.1	56.39	1.7371
172	7	3403.1	56.72	1.7474
192	7	3414.7	56.91	1.7534
156	6	3415.3	56.92	1.7535
157	6	3430.1	57.17	1.7611
180	7	3432.1	57.20	1.7623
193	7	3437.5	57.29	1.7651
200	8	3447.7	57.46	1.7700
191	7	3456.5	57.61	1.7747
198	8	3534.3	58.90	1.8148
199	8	3539.9	59.00	1.8177
170	7	3546.9	59.12	1.8212
190	7	3564.7	59.41	1.8302
196	8	3564.7	59.41	1.8304
203	8	3569.3	59.49	1.8328

PCB#	Cl#	RT (sec)	RT (min)	RRT
169	6	3583.5	59.72	1.8399
208	9	3643.7	60.73	1.8708
207	9	3676.5	61.28	1.8876
189	7	3683.3	61.39	1.8911
195	8	3692.9	61.55	1.8962
194	8	3766.9	62.78	1.9342
205	8	3791.5	63.19	1.9468
206	9	3872.3	64.54	1.9884
209	10	3952.9	65.88	2.0295

Conclusions

- Greater than 140 Aroclor PCBs can be determined with the new column and mass spectrometry
- The seven European indicator PCBs can be determined individually
- Spectral deconvolution available with TOFMS allows qualitative identification for coeluting PCBs