

Decoding Synthetic Pathways of Chemical Warfare Precursors: Advanced Impurity Profiling of Methylphosphonothioic Dichloride Using GC×GC-TOFMS-Chemometrics Hybrid Platforms

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General

The solvents used in this experiment are all commercially available. P_2S_5 , $AlCl_3$, and the solvent toluene, were obtained from Macklin.

Methylphosphonothioic dichloride synthesized samples were analyzed by a comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometer (GC×GC-TOFMS, Guangzhou Hexin Instrument Co., Ltd., GGT 0620). The sample injection was performed on a fully automatic multi-functional injection platform (CTC PAL RTC). The mass spectrometry (MS) detector voltage was -1750 V; the ionization energy was 70 eV; the MS acquisition mass range was 40 – 500 amu, the MS data acquisition rate was $10\,000$ spectra/s, and the solvent delay was 3 min. And ^{31}P NMR spectra were recorded in $CDCl_3$ at ambient temperature on a Bruker 121.5 MHz.

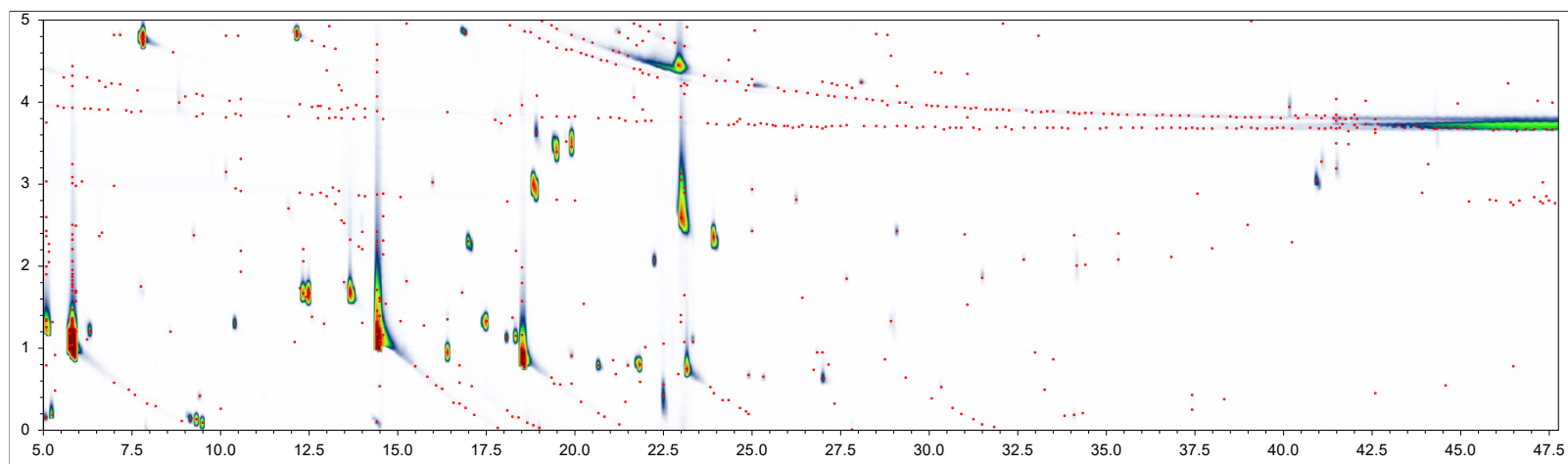


Figure 1 The two-dimensional chromatogram of GCxGC-TOFMS for sample a-1

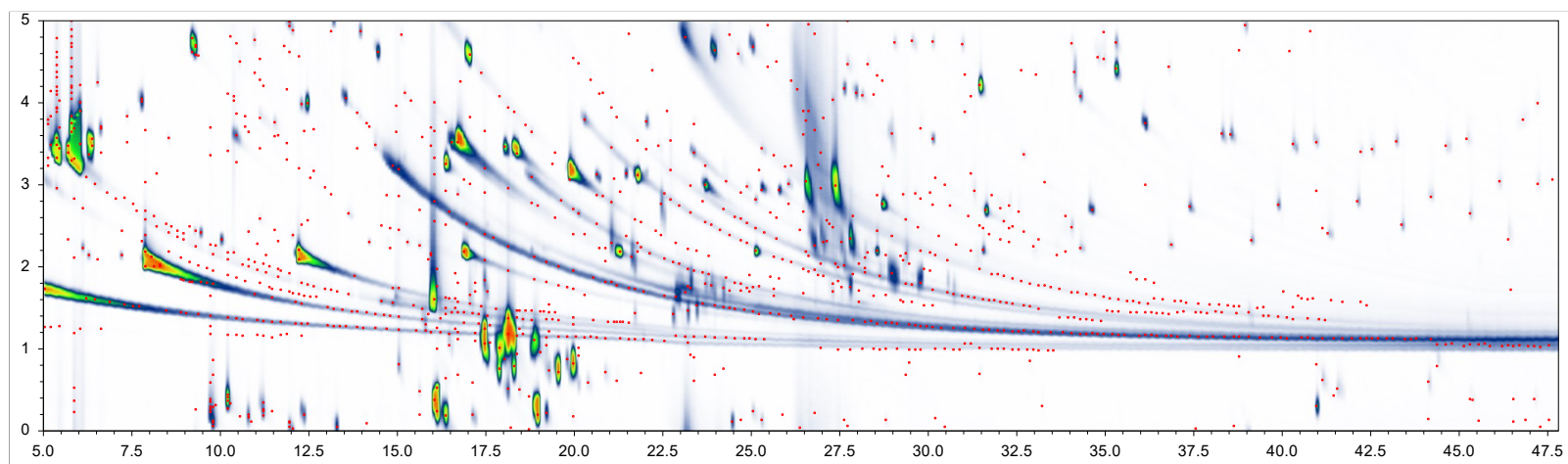


Figure 2 The two-dimensional chromatogram of GCxGC-TOFMS for sample a-2

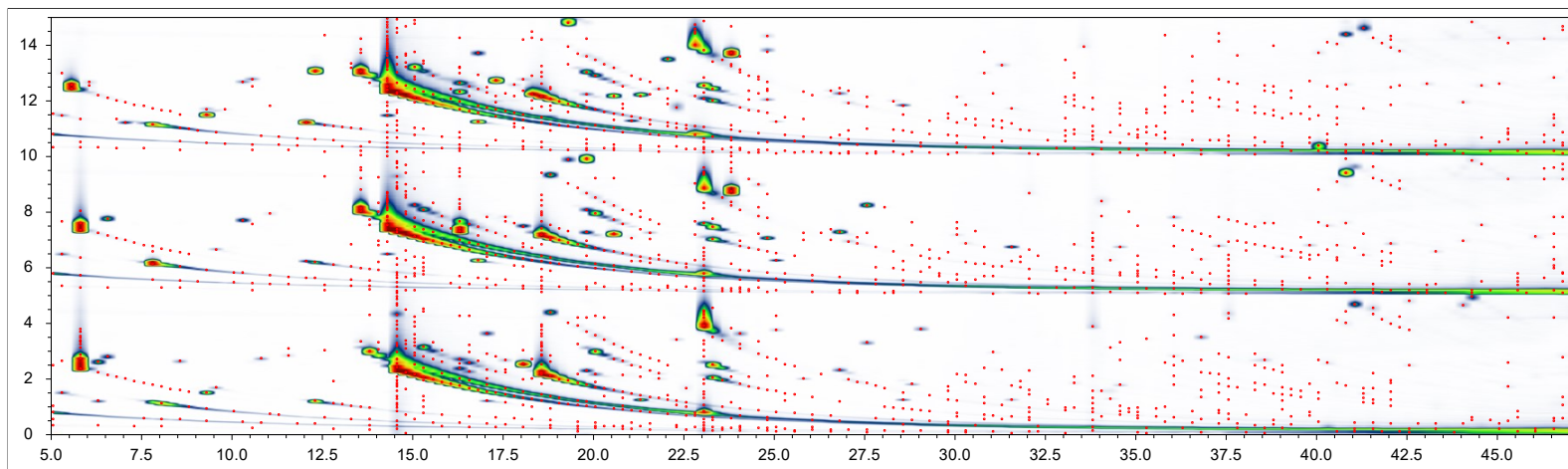


Figure 3 The two-dimensional chromatogram of GC×GC-TOFMS for sample a-3

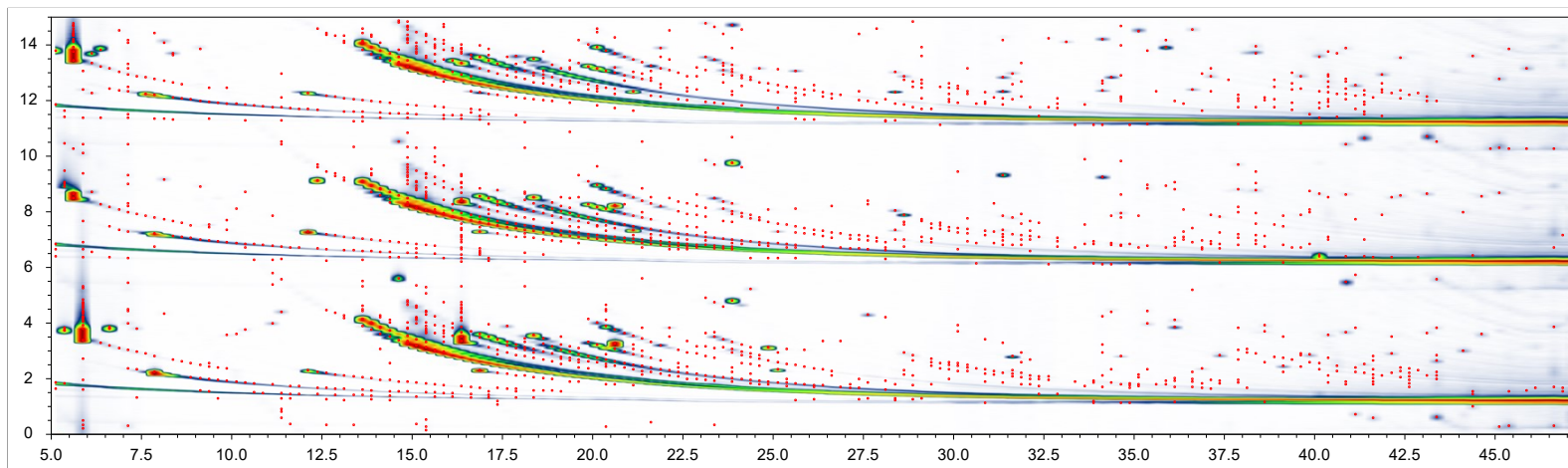


Figure 4 The two-dimensional chromatogram of GC×GC-TOFMS for sample b-1

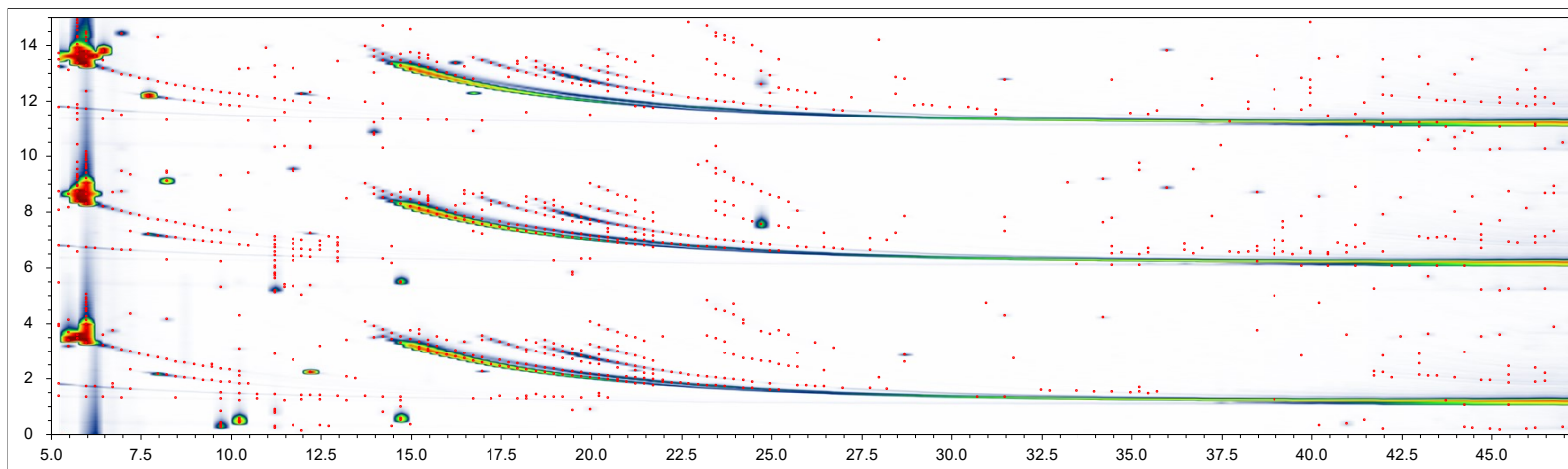


Figure 5 The two-dimensional chromatogram of GCxGC-TOFMS for sample b-2

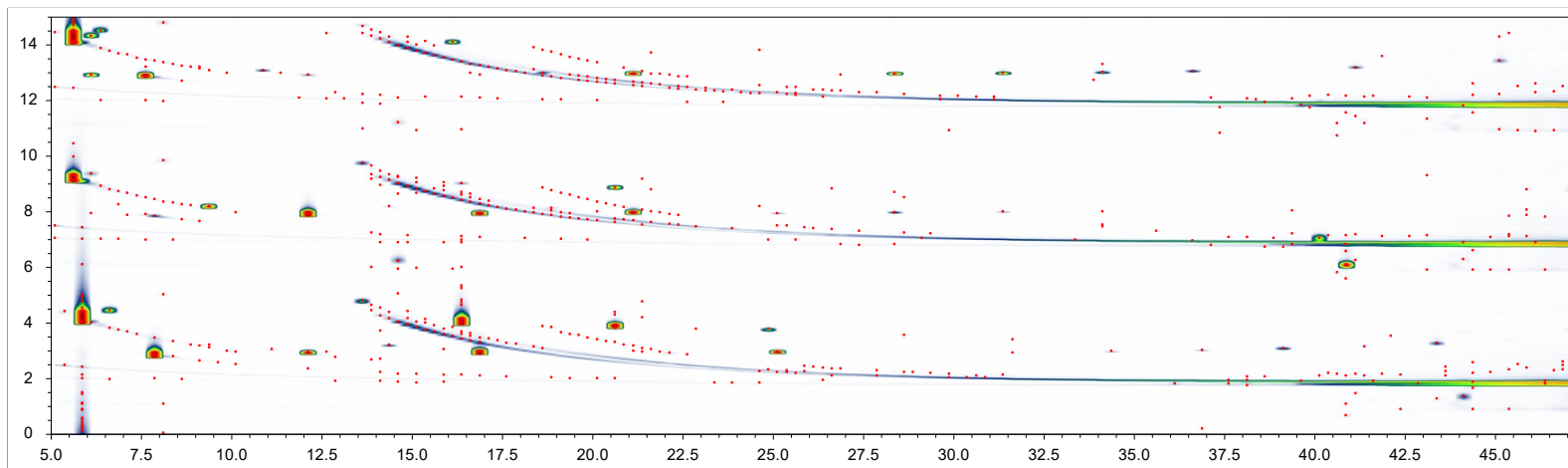


Figure 6 The two-dimensional chromatogram of GCxGC-TOFMS for sample b-3

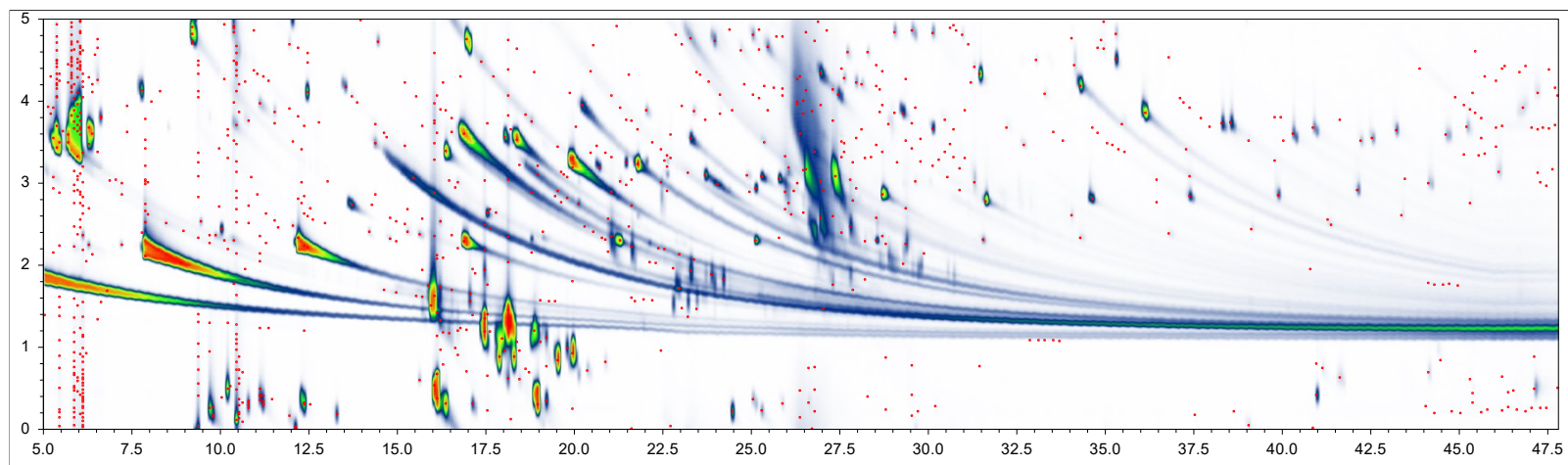


Figure 7 The two-dimensional chromatogram of GC×GC-TOFMS for sample test a-1

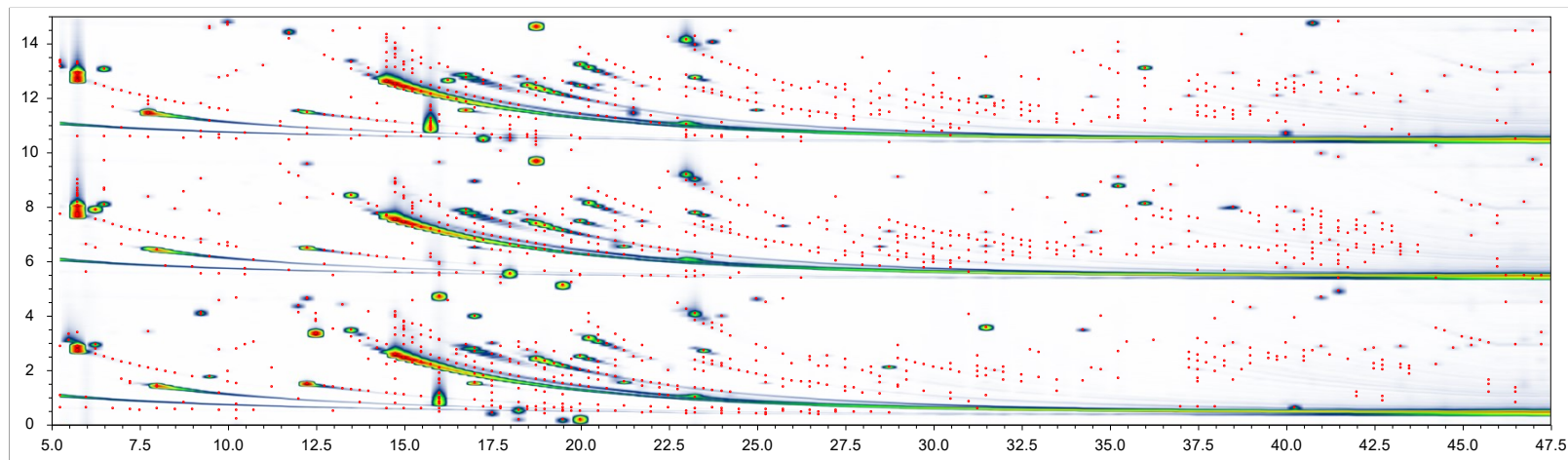


Figure 8 The two-dimensional chromatogram of GC×GC-TOFMS for sample test a-2

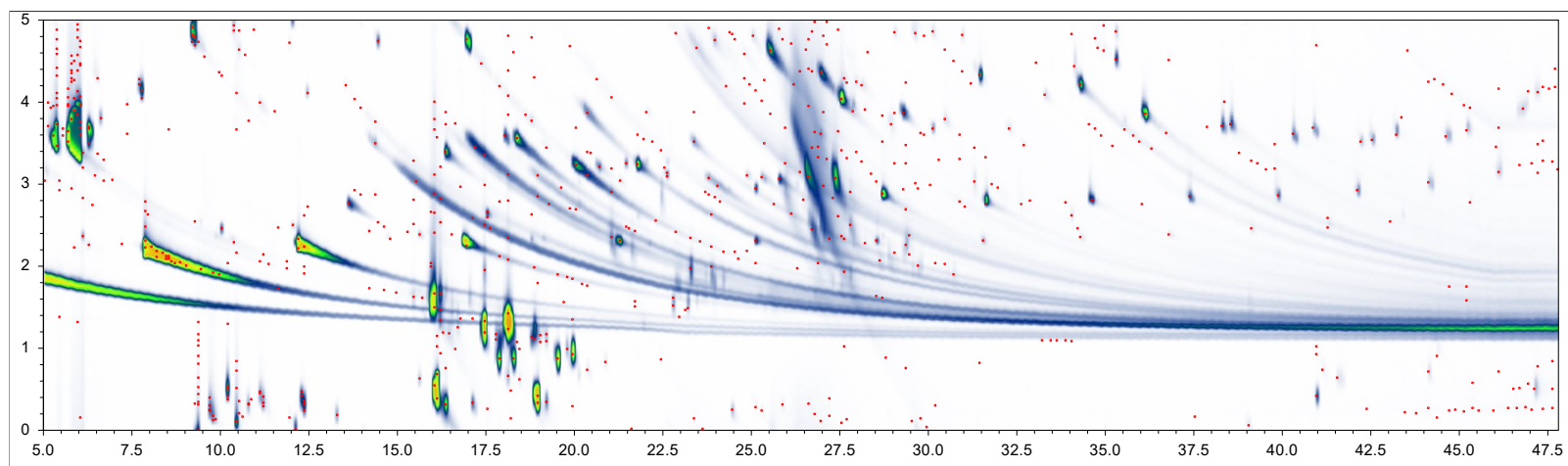


Figure 9 The two-dimensional chromatogram of GC×GC-TOFMS for sample test a-3

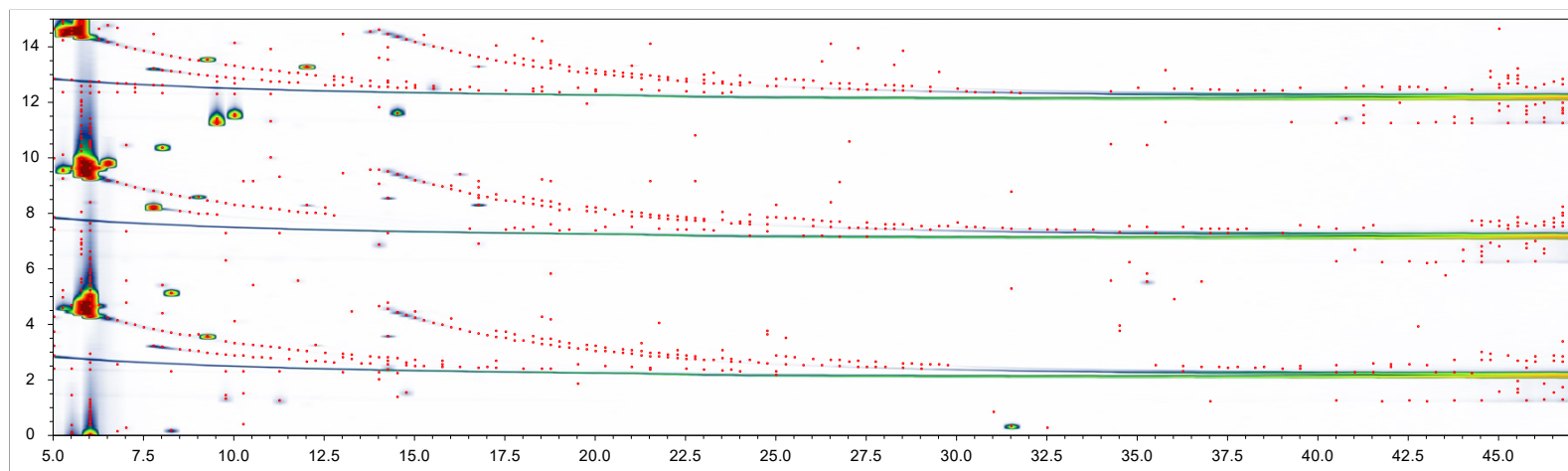


Figure 10 The two-dimensional chromatogram of GC×GC-TOFMS for sample test b-1

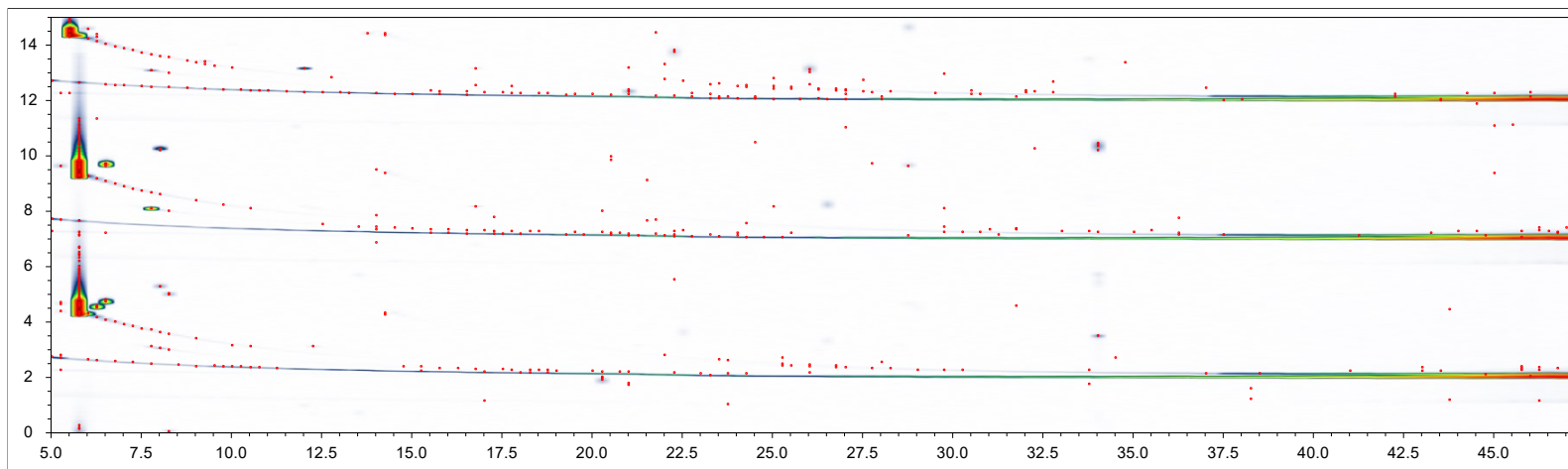


Figure 11 The two-dimensional chromatogram of GCxGC-TOFMS for sample test b-2

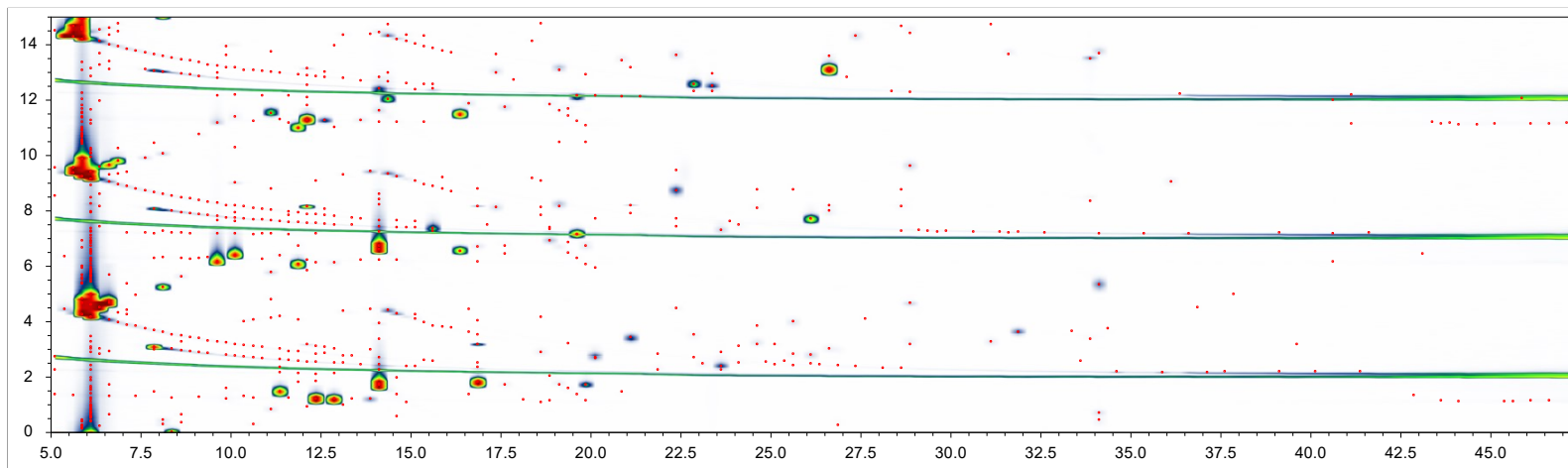


Figure 12 The two-dimensional chromatogram of GCxGC-TOFMS for sample test b-3

Table 1 Data matrix constructed by extracting peak areas from sample mass spectra

Sample	1	2	3	4	5	6	7	8	9	10
a-1	0	0	0	0	0	830.721	0	0	0	0
a-2	18.983	29.048	18.414	17.011	122.985	1775.086	24.395	30.448	55.598	74.285
a-3	32.58	29.654	22.746	78.209	78.587	0	36.84	19.649	22.334	6013.194
b-1	13.752	17.509	0	0	0	0	16.187	0	0	0
b-2	10.557	20.674	0	0	0	0	23.779	0	0	0
b-3	0	0	0	0	0	0	0	0	0	0
test-a-1	0	0	0	0	0	0	0	0	0	32254.166
test-a-2	0	0	0	0	0	0	0	0	0	57970.265
test-a-3	0	0	0	0	0	0	0	0	0	70744.124
test-b-1	0	25.924	0	0	0	0	0	0	0	0
test-b-2	0	13.993	0	0	0	0	41.985	0	0	0
test-b-3	0	0	0	0	0	0	33.037	0	0	0

Sample	11	12	13	14	15	16	17	18	19	20
a-1	180.129	0	0	1317.31	450.246	3904.131	100.386	0	0	180.129
a-2	226.311	25.563	67.335	394.049	1314.251	3319.763	110.026	15.548	127.146	226.311
a-3	537.418	24.302	101.758	955.791	496.39	2834.725	0	59.665	73.647	537.418
b-1	0	58.728	169.256	0	328.388	5359.578	0	0	70.05	0
b-2	0	33.685	16.834	0	416.142	29080.052	0	0	22.195	0

b-3	0	0	9.627	0	0	146.669	0	0	29.63	0
test-a-1	180.129	0	0	1317.31	450.246	0	0	0	0	180.129
test-a-2	226.311	0	0	394.049	1314.251	0	186.969	0	0	226.311
test-a-3	537.418	0	0	955.791	496.39	0	111.808	0	0	537.418
test-b-1	0	43.663	56.85	0	328.388	4288.879	0	0	55.459	0
test-b-2	0	38.573	18.288	0	416.142	0	0	0	34.49	0
test-b-3	0	0	0	0	0	2243.622	0	0	0	0

Sample	21	22	23	24	25	26	27	28	29	30
a-1	98.909	71.527	2575.754	13159.444	46.922	16.284	462.428	0	3197.373	0
a-2	0	54.158	6036.157	7913.185	18.662	54.836	0	0	4496.362	1629.568
a-3	912.451	94.597	5265.587	9123.289	0	59.444	518.033	0	0	507.39
b-1	0	13.333	0	0	0	0	0	42.936	0	25.616
b-2	0	93.722	0	0	0	0	0	27.139	0	77.259
b-3	0	50.876	0	0	0	0	0	0	0	35.695
test-a-1	18527.259	0	2575.754	13159.444	0	0	13050.898	0	0	117.442
test-a-2	11381.699	0	6036.157	7913.185	0	0	30321.389	0	0	189.473
test-a-3	8479.367	0	5265.587	9123.289	0	0	31273.279	0	0	0
test-b-1	0	19.89	0	0	0	0	0	0	0	515.868
test-b-2	0	0	0	0	0	0	0	0	0	95.273
test-b-3	0	18.96	0	0	0	0	0	0	0	73.5

Sample	31	32	33	34	35	36	37	38	39	40
a-1	0	0	181.582	38.363	77.1	0	46.425	2877.829	492.537	0
a-2	0	143.607	0	79.783	73.076	0	70.799	8286.467	323.159	210.814
a-3	0	106.518	160.421	0	31.959	0	0	1142.617	926.205	265.968
b-1	57.951	0	0	162.687	0	419.987	0	0	0	0
b-2	0	0	0	123.567	0	0	0	0	0	0
b-3	17.931	0	0	0	0	81.701	0	0	0	0
test-a-1	0	0	0	0	0	0	0	0	1815.534	0
test-a-2	0	0	0	0	0		0	0	764.506	0
test-a-3	0	0	0	0	0		0	0	12273.325	0
test-b-1	0	0	0	0	0	0	0	0	0	0
test-b-2	14.971	0	0	0	0	0	0	0	0	0
test-b-3	27.411	0	0	0	0	0	0	0	0	0

Sample	41	42	43	44	45	46	47	48	49	50
a-1	0	0	0	0	0	0	0	185.135	34.244	241.909
a-2	474.555	44.555	2.467	16.569	0	0	415.171	129.397	89.275	185.857
a-3	114.45	24.678	19.731	8.012	0	0	44.335	0	0	131.226
b-1	135.476	0	0	0	63.791	0	84.923	0	0	0
b-2	230.647	0	15.969	0	0	19.781	0	0	0	0

b-3	0	0	33.566	0	26.848	5.105	26.703	0	0	0
test-a-1	694.943	0	0	0	0	0	0	0	0	1365.785
test-a-2	222.956	0	0	0	0	0	0	0	0	1195.453
test-a-3	0	0	0	0	0	0	0	0	0	0
test-b-1	0	0	0	0	0	0	0	0	0	175.496
test-b-2	0	0	0	0	64.687	0	40.917	0	0	38.454
test-b-3	0	0	0	0	16.015	0	38.535	0	0	73.045

Sample	51	52	53	54	55	56	57	58
a-1	0	0		0	0	0	0	0
a-2	189.21	0	24.998	0	0	0	20796.451	0
a-3	177.921	0	73.808	0	0	0	0	0
b-1	0	15.697	0	0	0	190.238	0	7.903
b-2	0	9.803	0	6.842	8.473	9.302	28.605	2.925
b-3	0	0	0	9.675	6.22	0	2.147	0
test-a-1	0	0	0	0	0	0	0	335852.415
test-a-2	0	0	0	0	0	0	0	497.673
test-a-3	0	0	0	0	0	0	0	97269.146
test-b-1	0	0	0	0	0	0	90.359	0
test-b-2	0	0	0	0	0	0	6.338	0
test-b-3	0	0	0	0	0	0	0	0