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**The Analysis of all 209 PCB Congeners on
the SPB™-Octyl and MDN™-5S
Capillary Columns**

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Abstract

In the current realm of environmental analysis, the determination of individual PCB congeners, rather than Aroclor mixtures as a whole, is becoming increasingly important. Research studies have linked certain PCB congeners to potential toxic effects in the body. Specifically, those that lack chlorine substituents in the ortho position (coplanar) act similarly *in vivo* to polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs.) Current methodologies recommend the use of two columns to separate the entire list of 209 congeners. In the work presented, congeners are separated using a combination of 30m x 0.25mm ID x 0.25 μ m SPB-Octyl and MDN-5S columns.

Congeners are divided between five separate standard mixtures analyzed by GC/MS individually, and then as a composite. Extracted ion chromatograms of the base peak in the spectrum from each degree of chlorination are examined in individual mixes and peak identities are assigned. This information is used to assign peak identities later in the composite runs. Chromatograms are presented showing the identification of the peaks on each column along with a table summarizing the elution order and retention times. The work shows that the SPB-Octyl resolves all coplanar congeners with the exception of IUPAC #'s 156 and 157. Congeners 156 and 157 are resolved on the MDN-5S.

Introduction

Of the 209 existing PCB congeners, 12 have been identified by the World Health Organization (WHO) as having dioxin-like toxicity. These congeners, often referred to as “coplanar” have had their toxicity relative to 2,3,7,8-TCDD described in terms of “toxic equivalency factors” (TEFs.) These TEFs are often used in matters of risk assessment and regulatory control. These congeners are also described as targets for analysis in the recently issued United States Environmental Protection Agency (USEPA) Method 1668A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS.

To analyze for these 12 congeners by GC/MS, it is necessary that they be resolved from congeners which are of the same degree of chlorination. The 30m x 0.25mm ID, 0.25 μ m SPB-Octyl and MDN-5S can be used in a multidimensional analysis to resolve these 12 congeners. The toxic congeners of interest are: 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189. The following information will show that the SPB-Octyl has the ability to resolve all of these congeners with the exception of 156 and 157. It will also demonstrate that the MDN-5S can resolve 11 of the 12 toxic congeners, including 156 and 157.

Run Conditions

The run conditions used for both columns:

Column Dimensions: 30m x 0.25mm ID, 0.25 μ m

Oven: 75°C, hold 2 min., 15°C/min. to 150°C,
2.5°C/min. to 290°C, no hold

Flow: He, 37cm/sec, set at 200°C

Injector Temp.: 270°C

MSD Interface Temp.: 280°C

Detector: HP™ 5972 MSD, scan range 100-550 amu,
1.7 scans/sec

Injection: 25-75ppm in hexane, 0.5 μ L splitless,
splitter open after 2 minutes

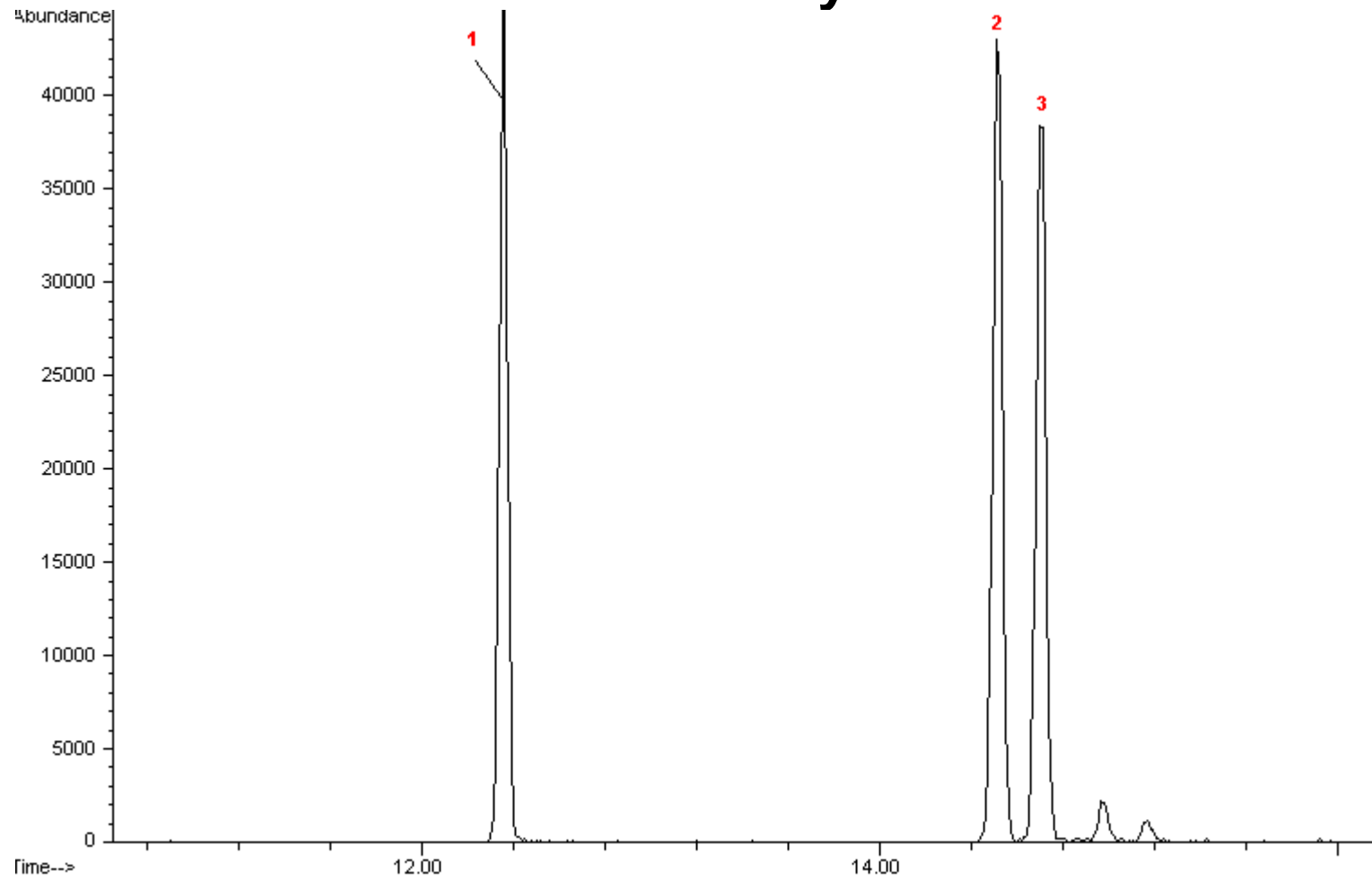
The following mass to charge ratios were used to extract ion chromatograms from the composite runs of all 209 congeners:

| | |
|----------------|--------------------|
| m/z=188 | monochloro |
| m/z=222 | dichloro |
| m/z=256 | trichloro |
| m/z=290 | tetrachloro |
| m/z=326 | pentachloro |
| m/z=360 | hexachloro |
| m/z=394 | heptachloro |
| m/z=428 | octachloro |
| m/z=462 | nonachloro |
| m/z=496 | decachloro |

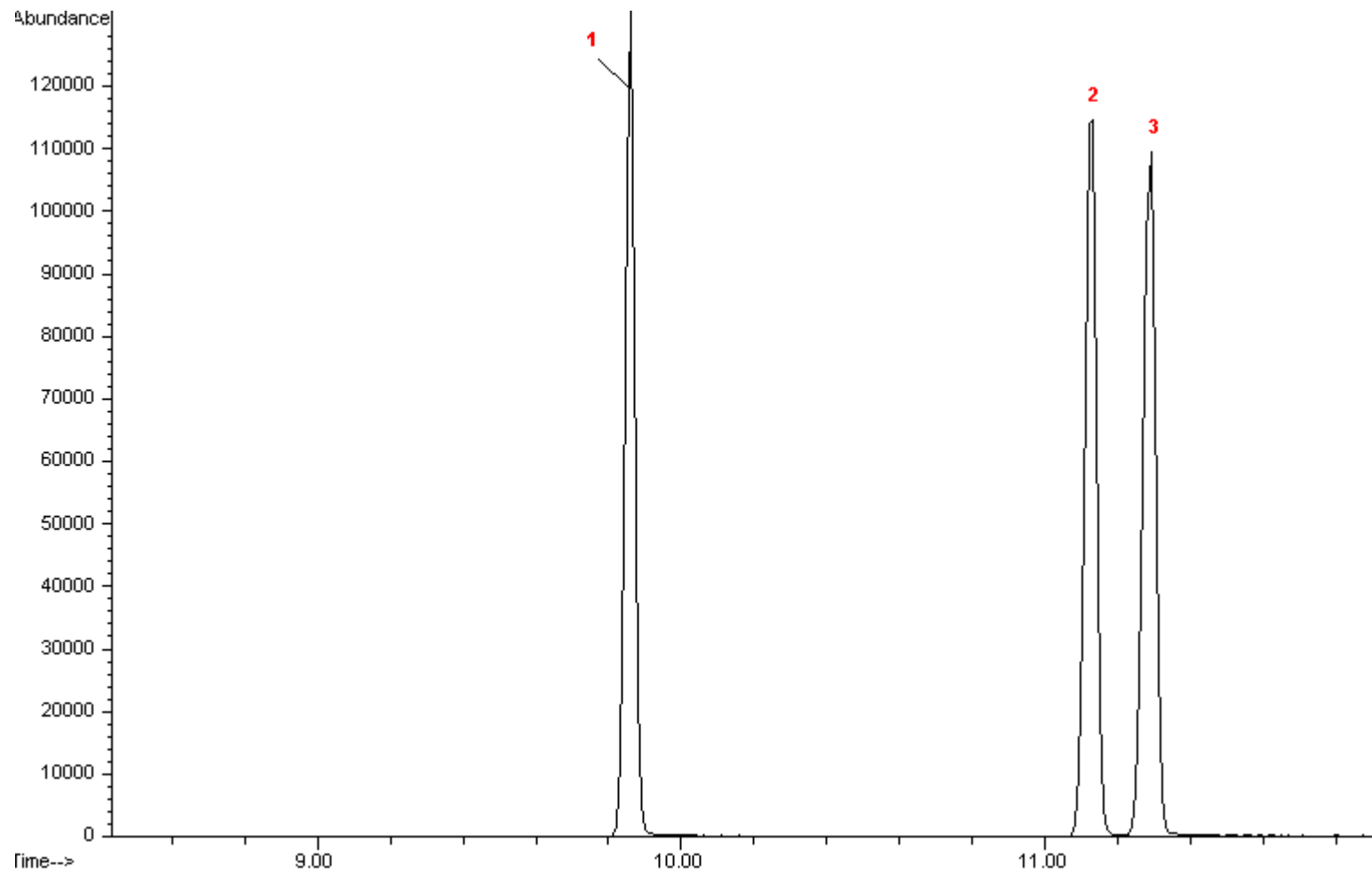
The SPB-Octyl resolved 11 of the 12 toxic congeners, the one coelution being 156 and 157. These congeners have equal TEF values, and are sometimes reported together. The peak visible next to 169 in the extracted ion chromatogram of the hexachloro congeners is a mass contribution from 198 and 199 (both octachlorinated congeners.) Congener 169 would be totally mass resolved from these two congeners on an MSD with higher mass resolution capability. Of the remaining 197 congeners, 140 were resolved.

The MDN-5S resolved 11 of the 12 toxic congeners (including 156 and 157.) It did not resolve 123, which coelutes with another pentachlorinated congener (109.) This is a coelution which would interfere with an accurate analysis for 123. Of the remaining 197 congeners, 120 were resolved.

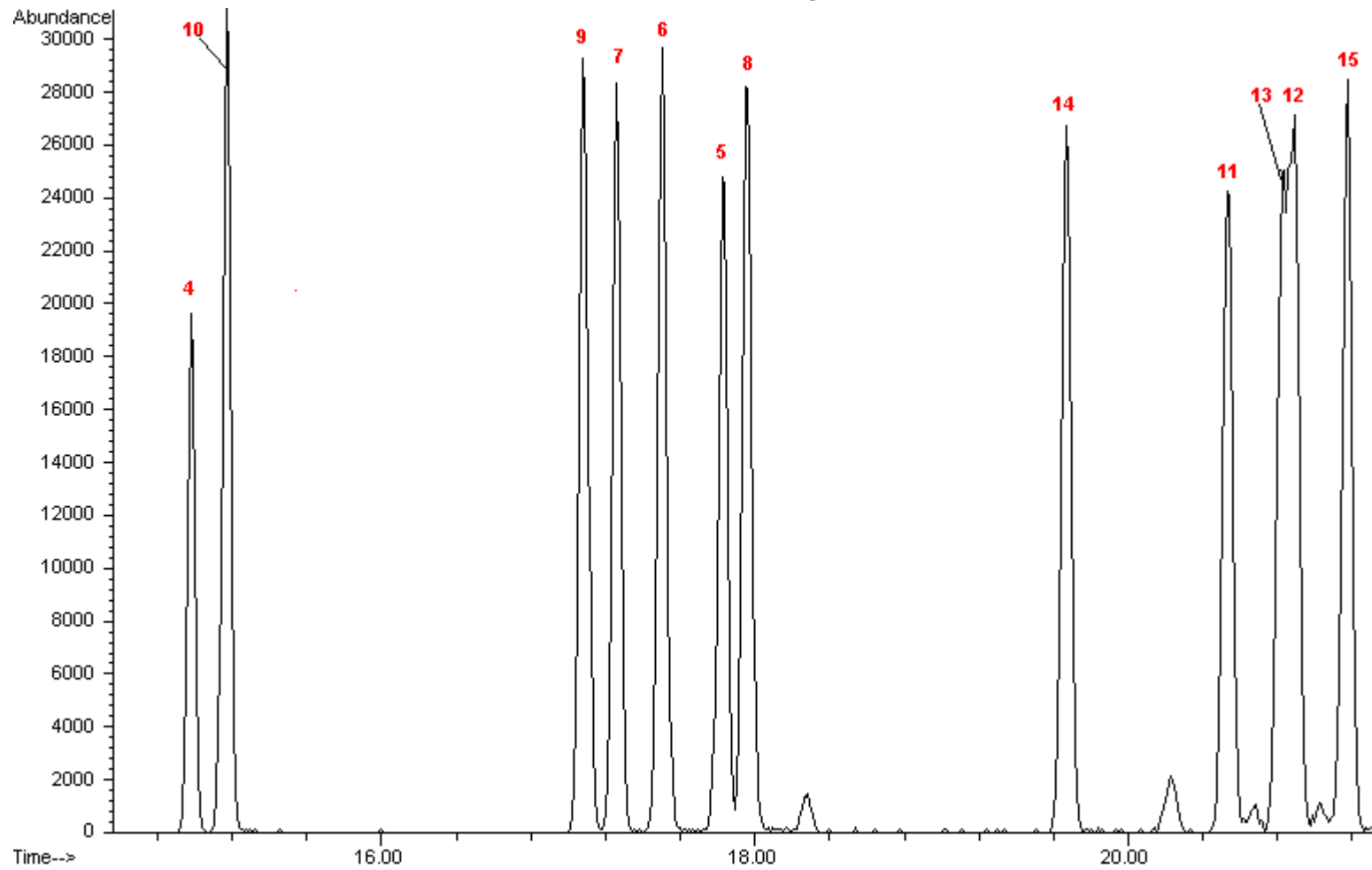
Monochloro, m/z=188 SPB-Octyl



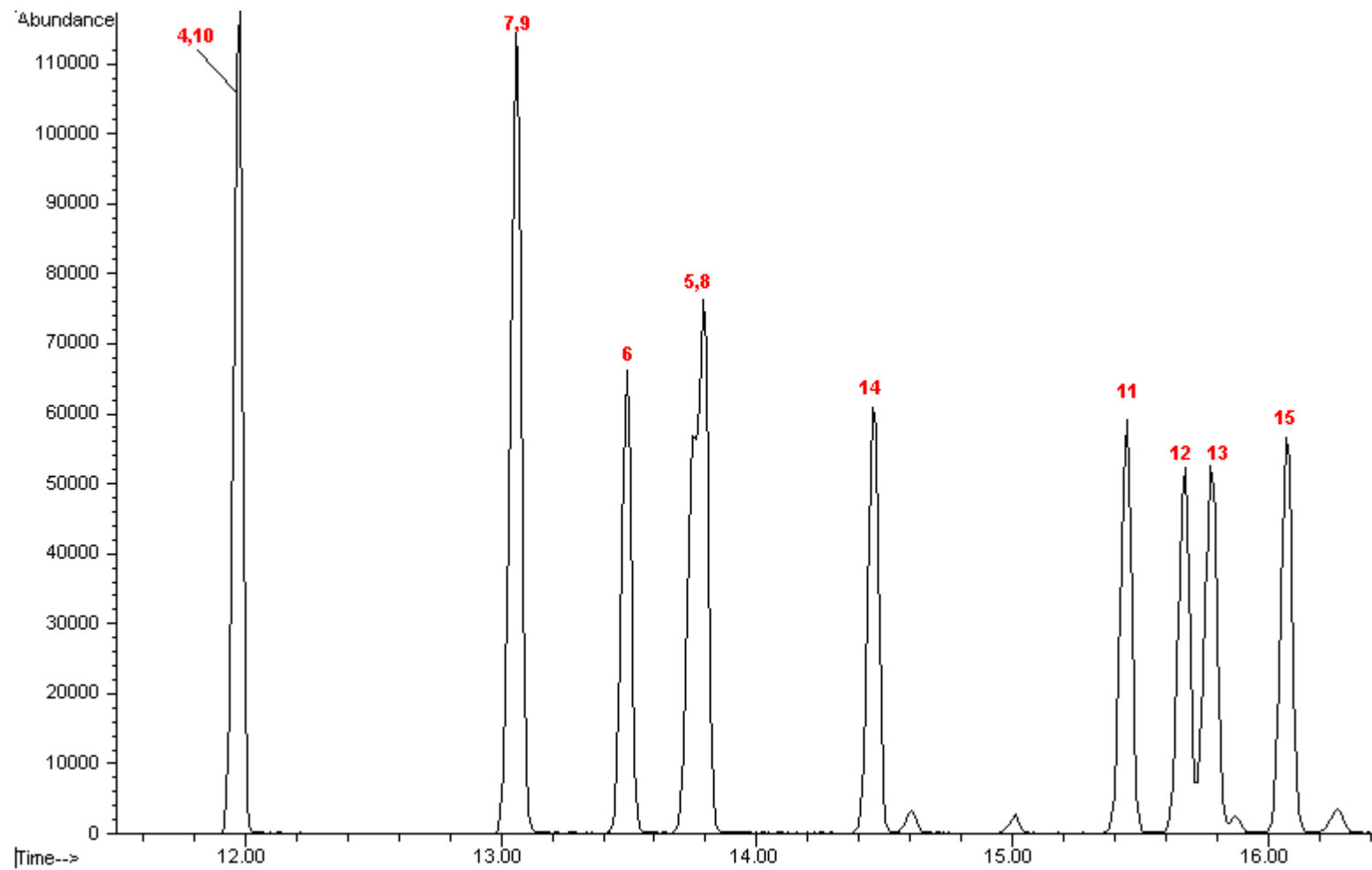
Monochloro, m/z=188 MDN-5S



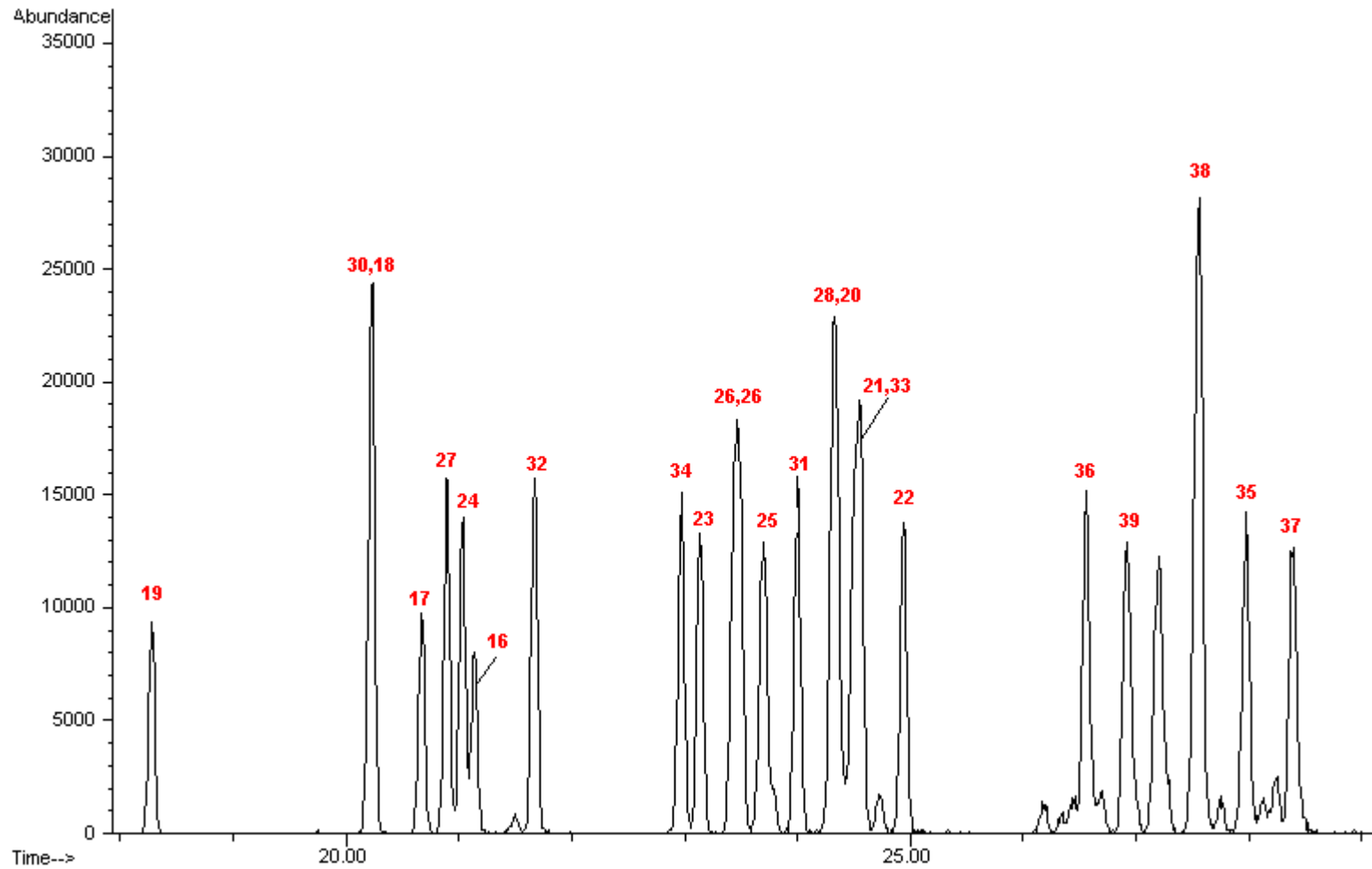
Dichloro, m/z=222 SPB-Octyl



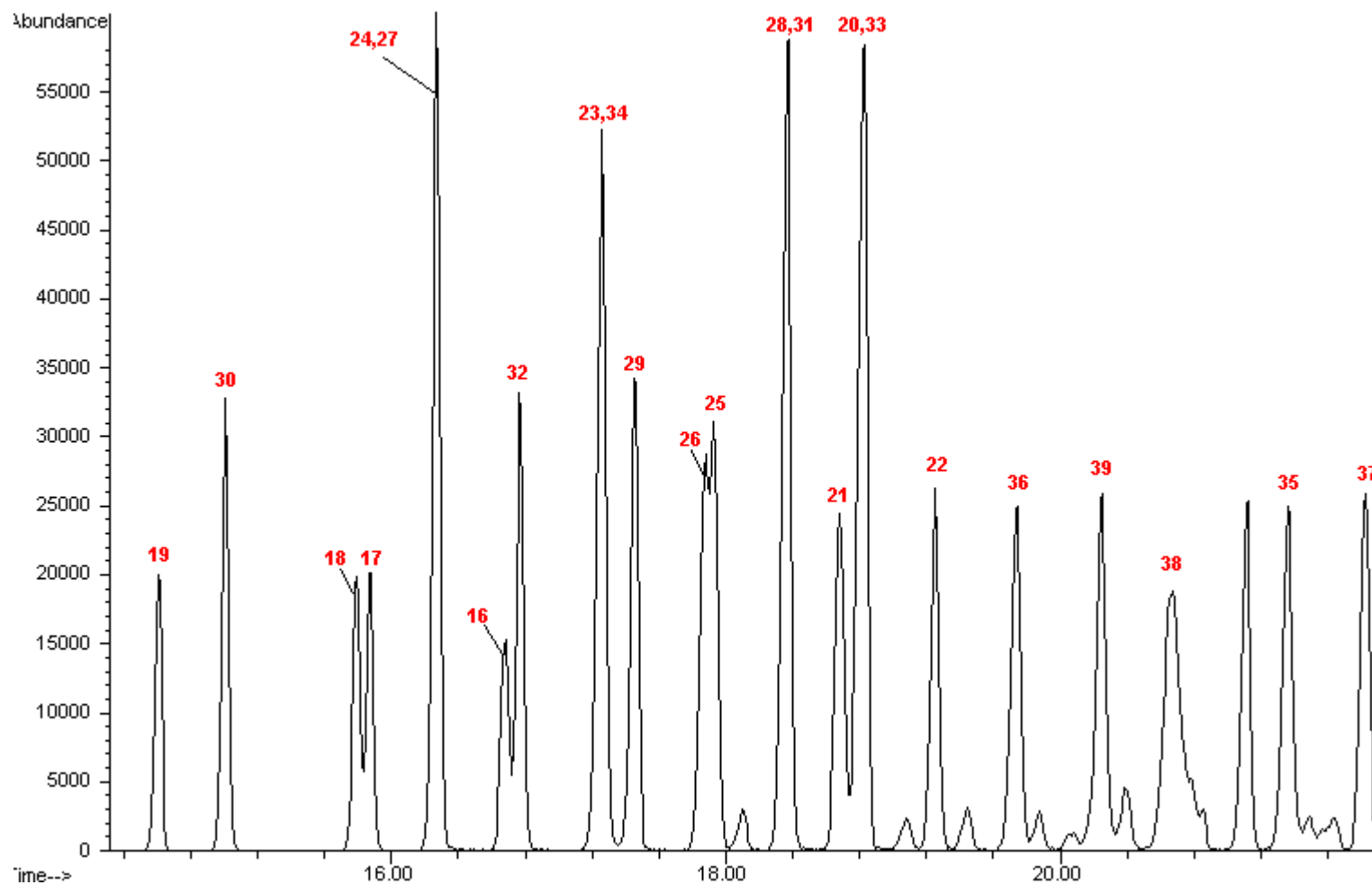
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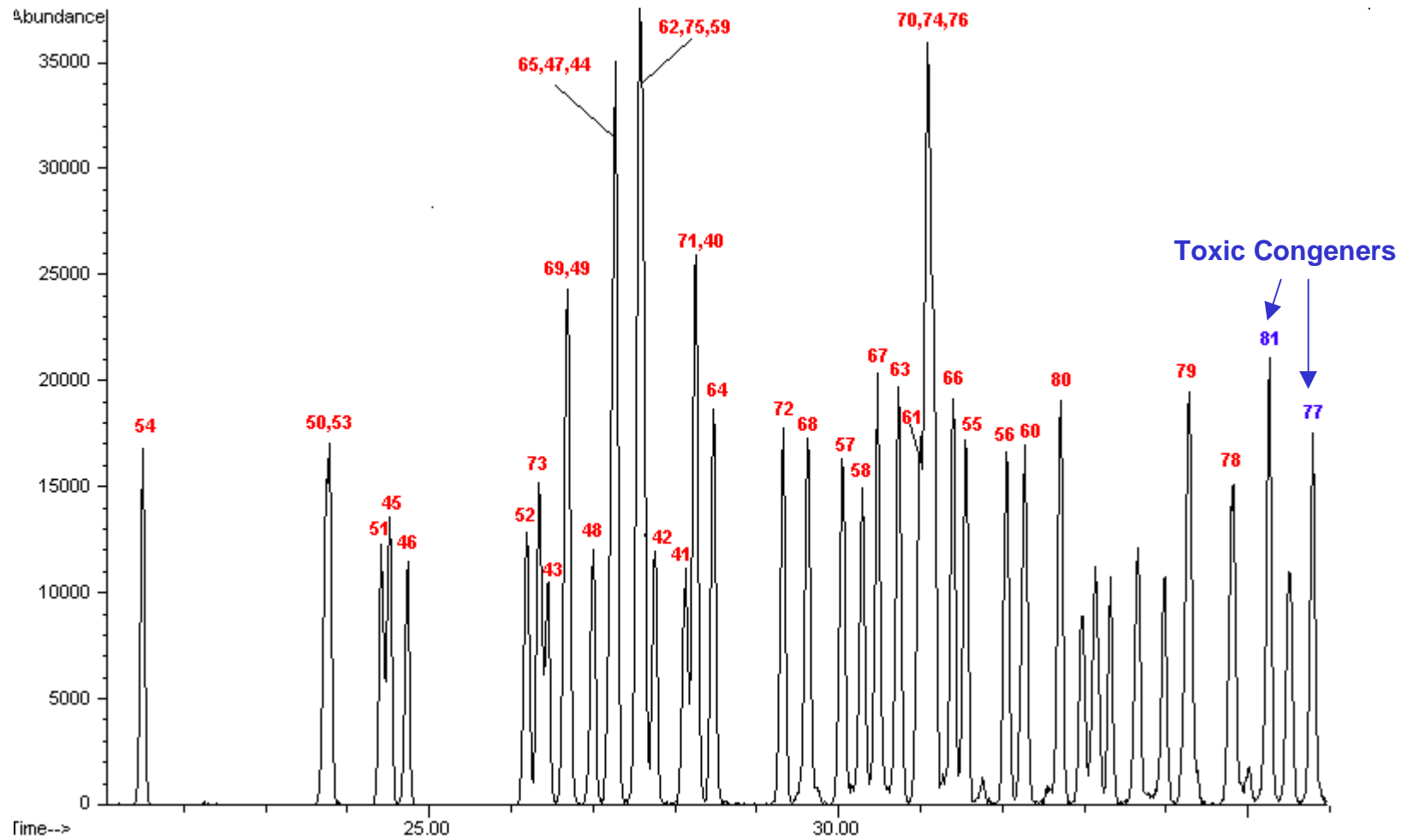
Trichloro, m/z=256 SPB-Octyl



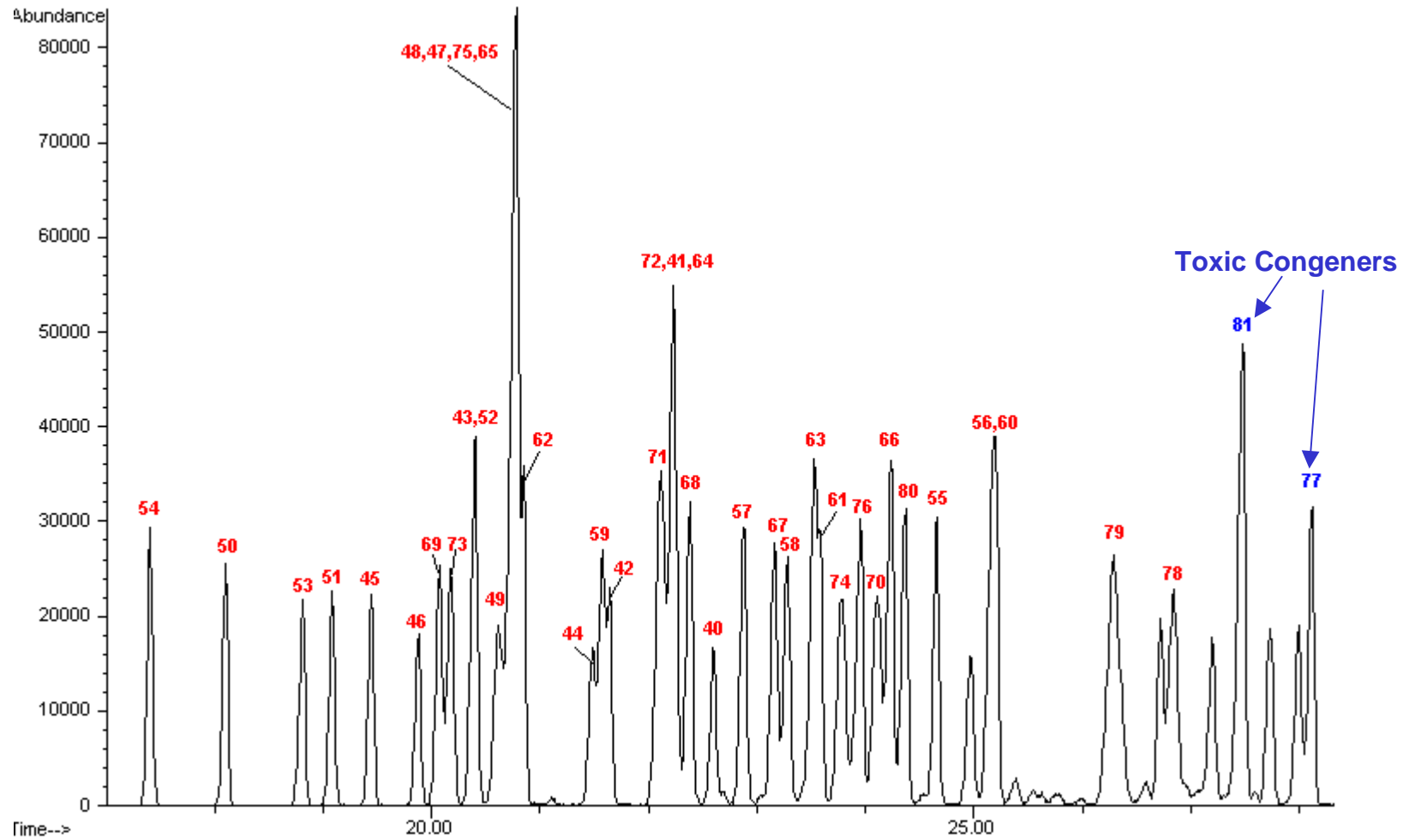
Trichloro, m/z=256 MDN-5S



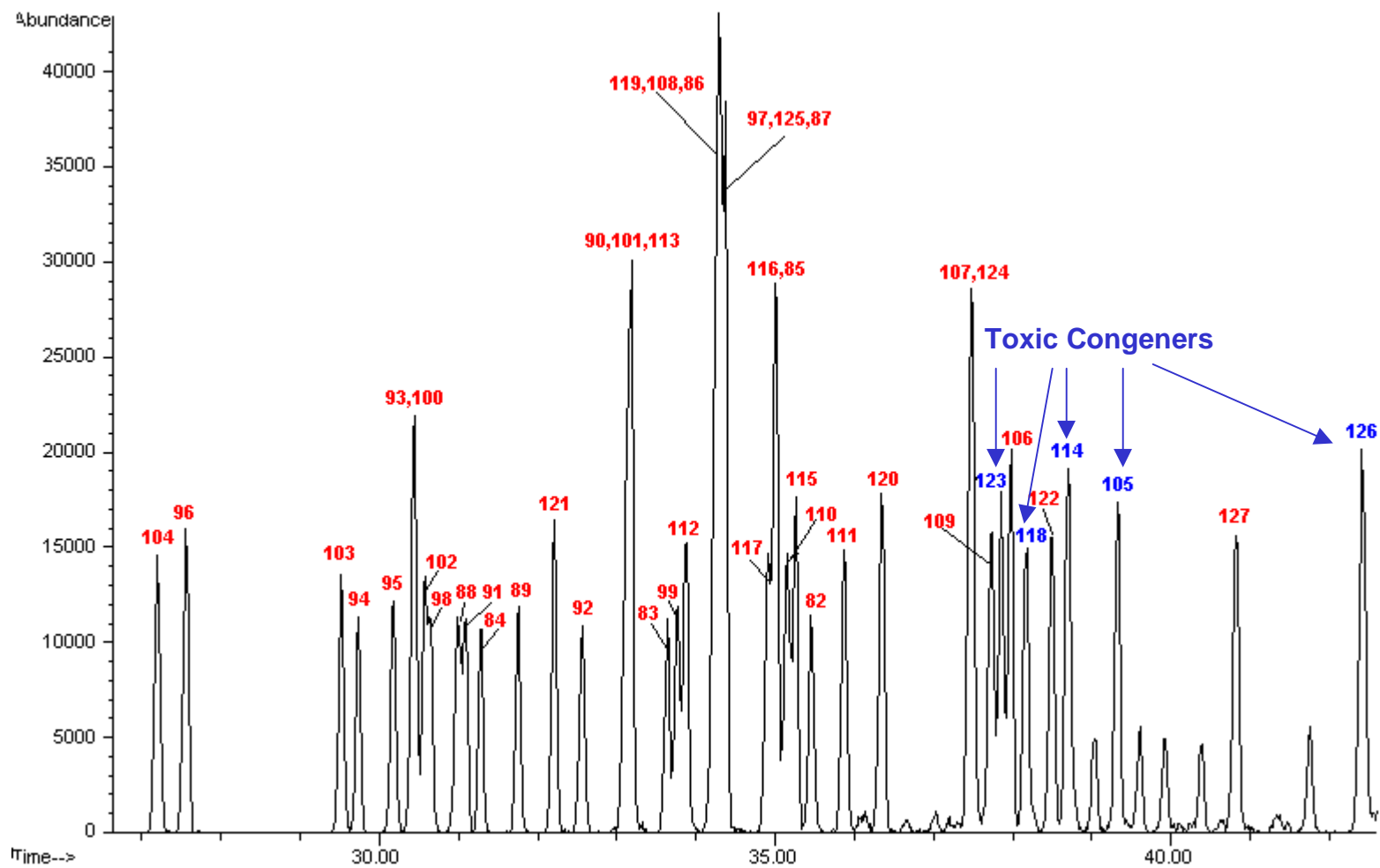
Tetrachloro, m/z=290 SPB-Octyl



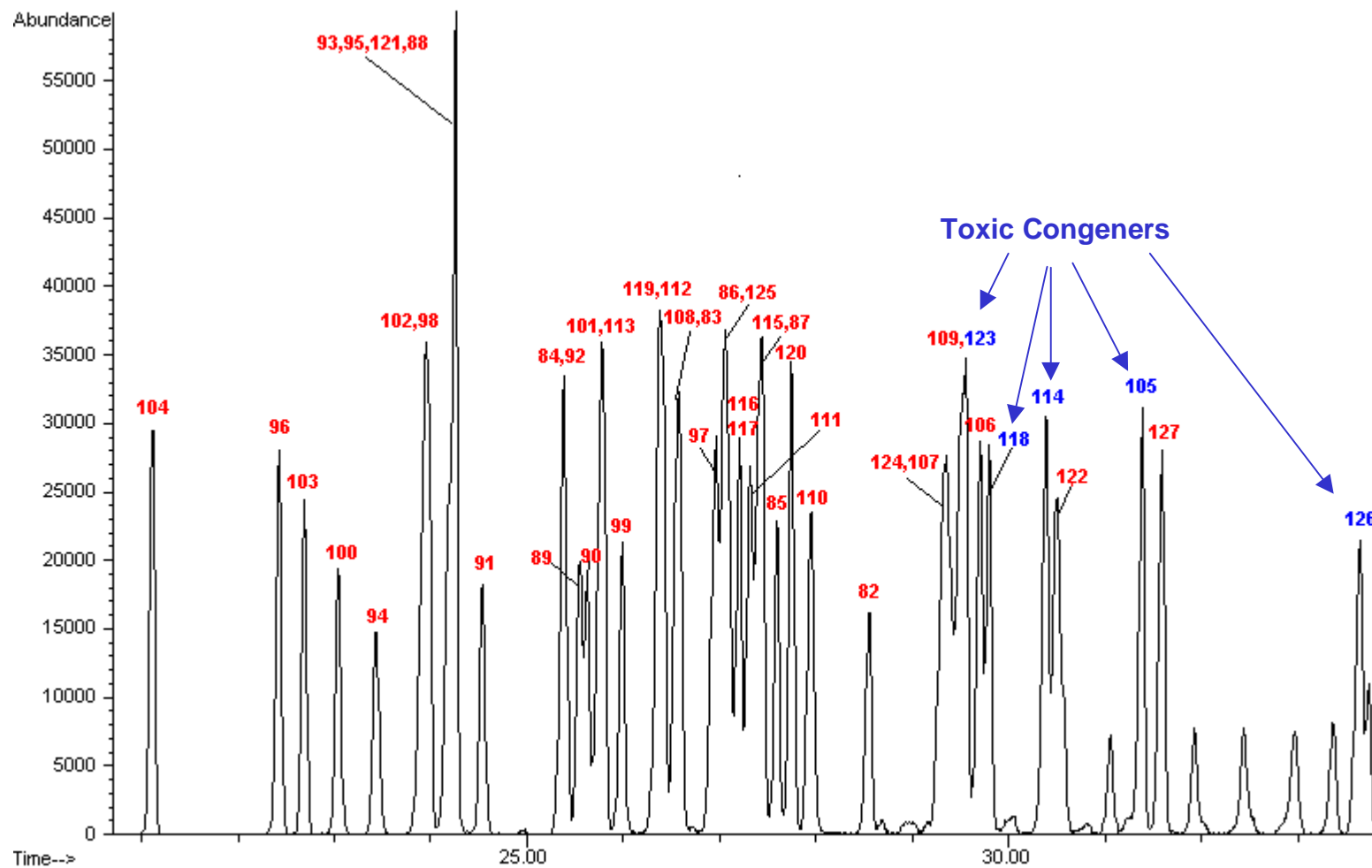
Tetrachloro, m/z=290 MDN-5S



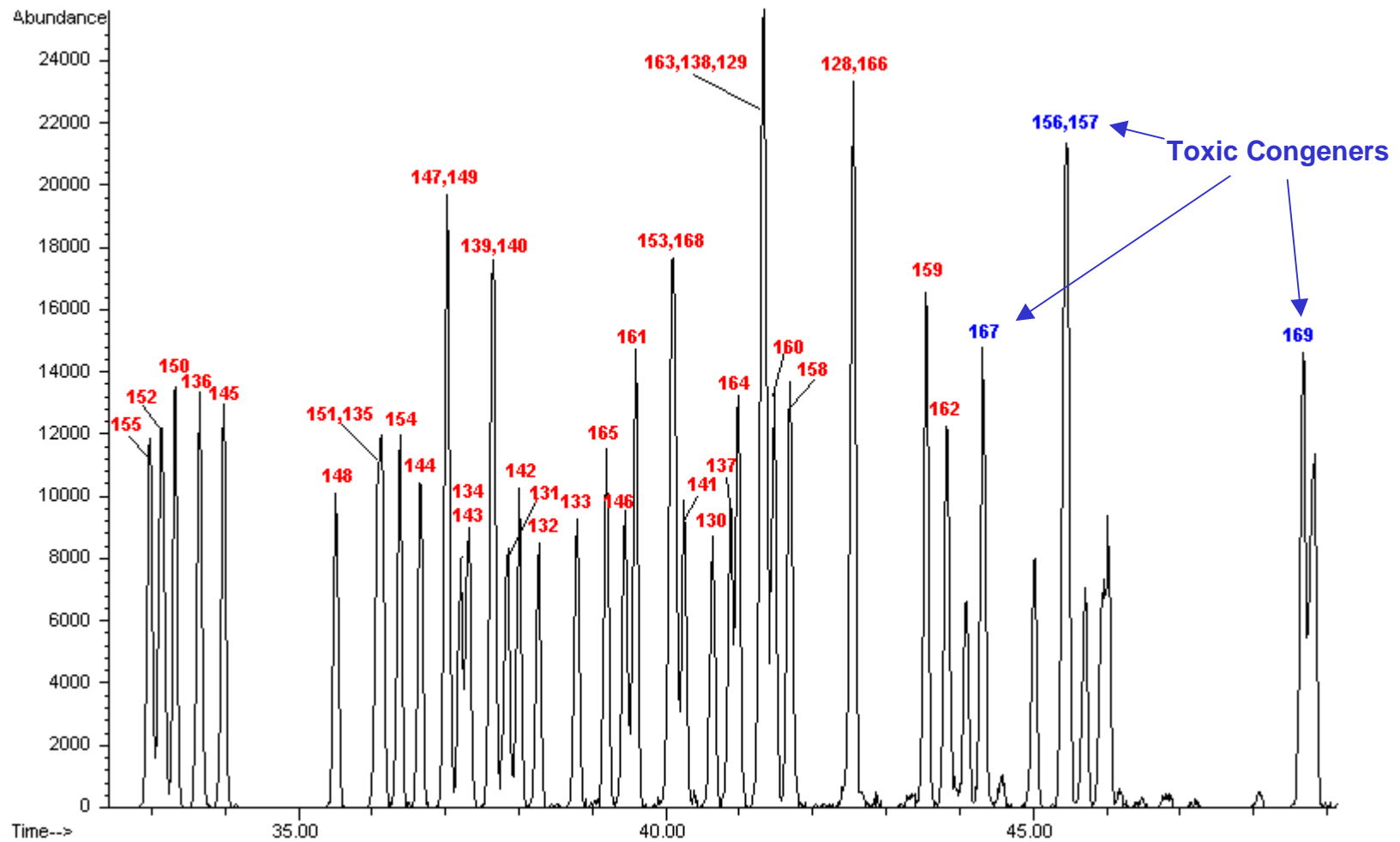
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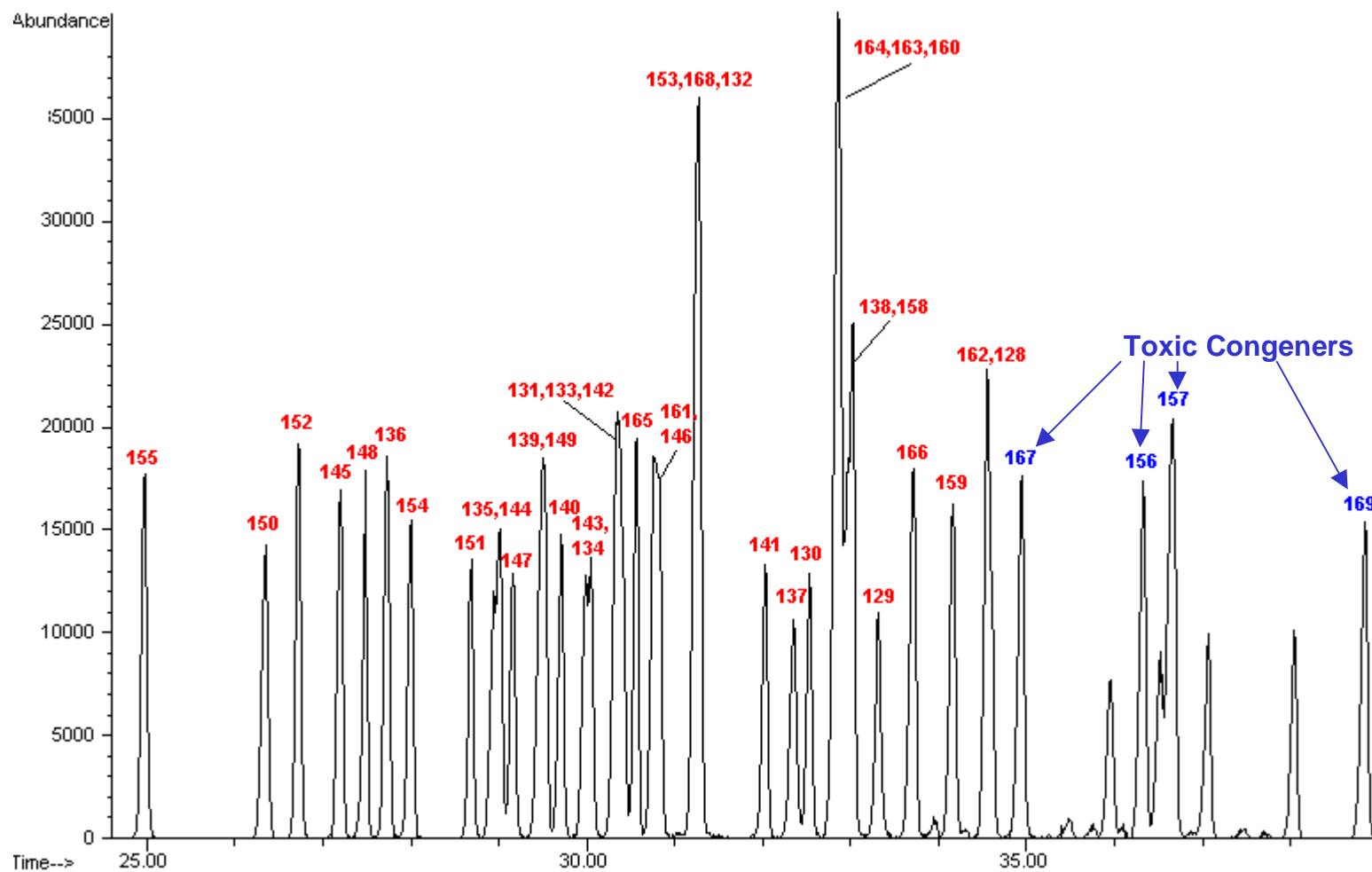
Pentachloro, m/z=326 MDN-5S



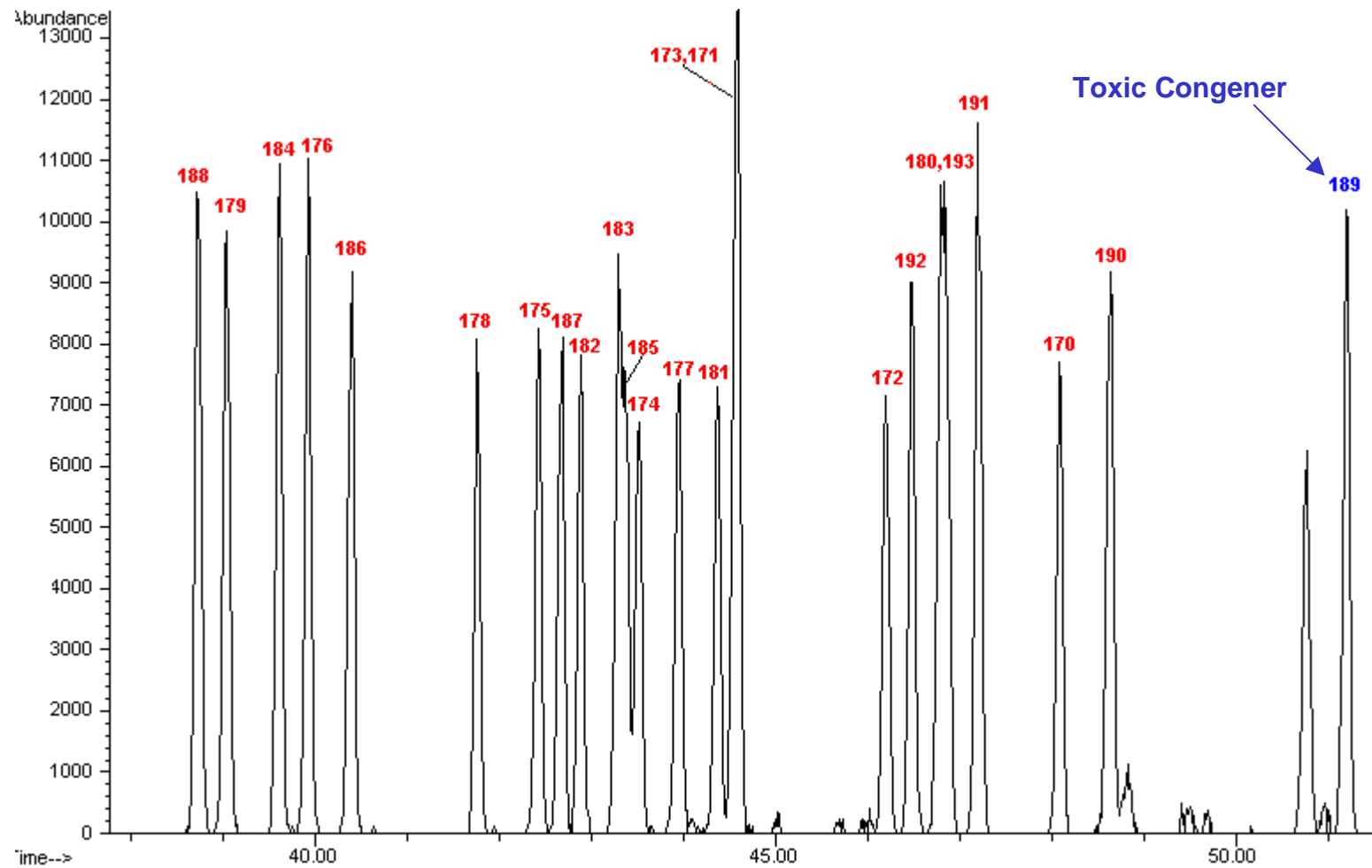
Hexachloro, m/z=360 SPB-Octyl



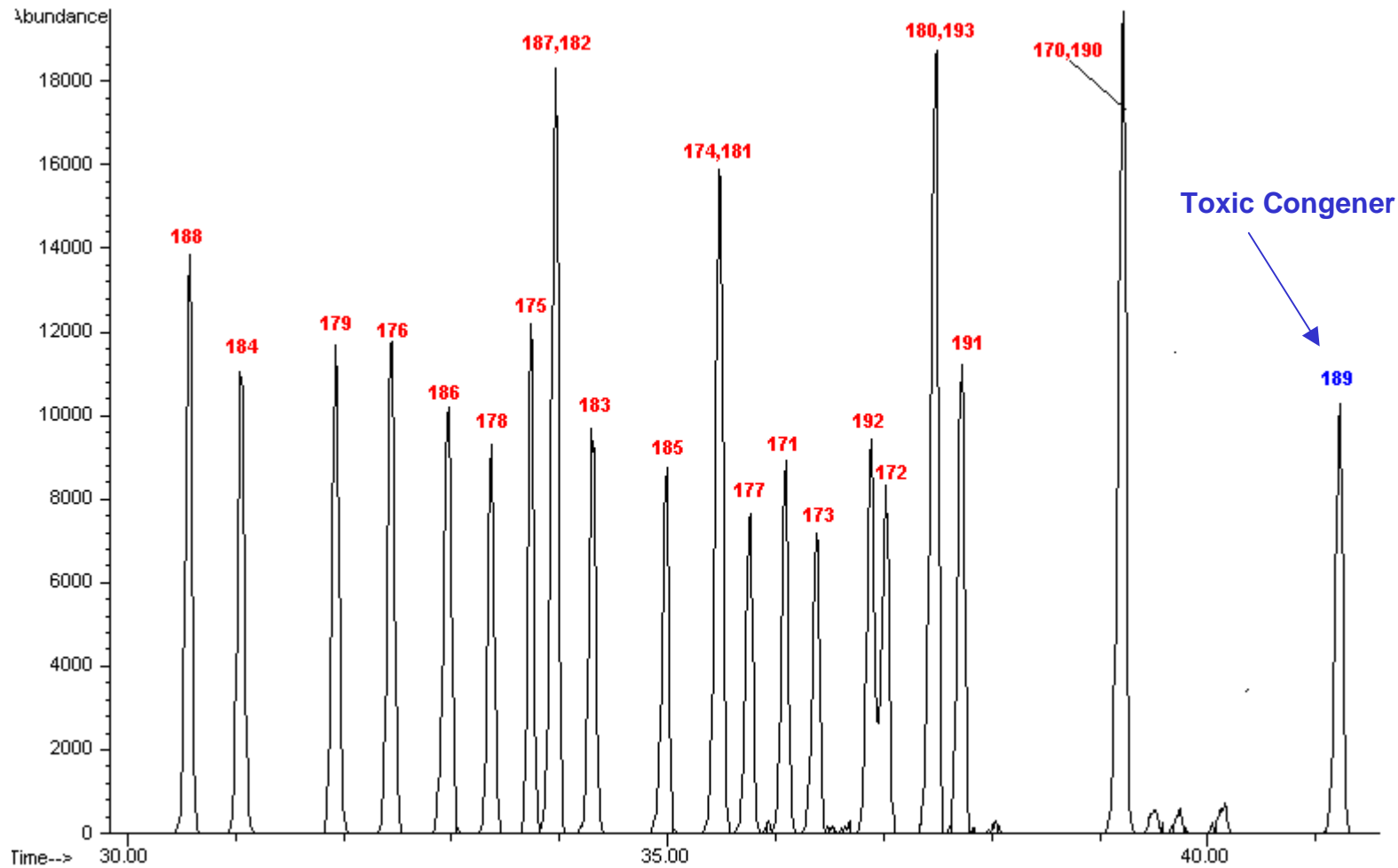
Hexachloro, m/z=360 MDN-5S



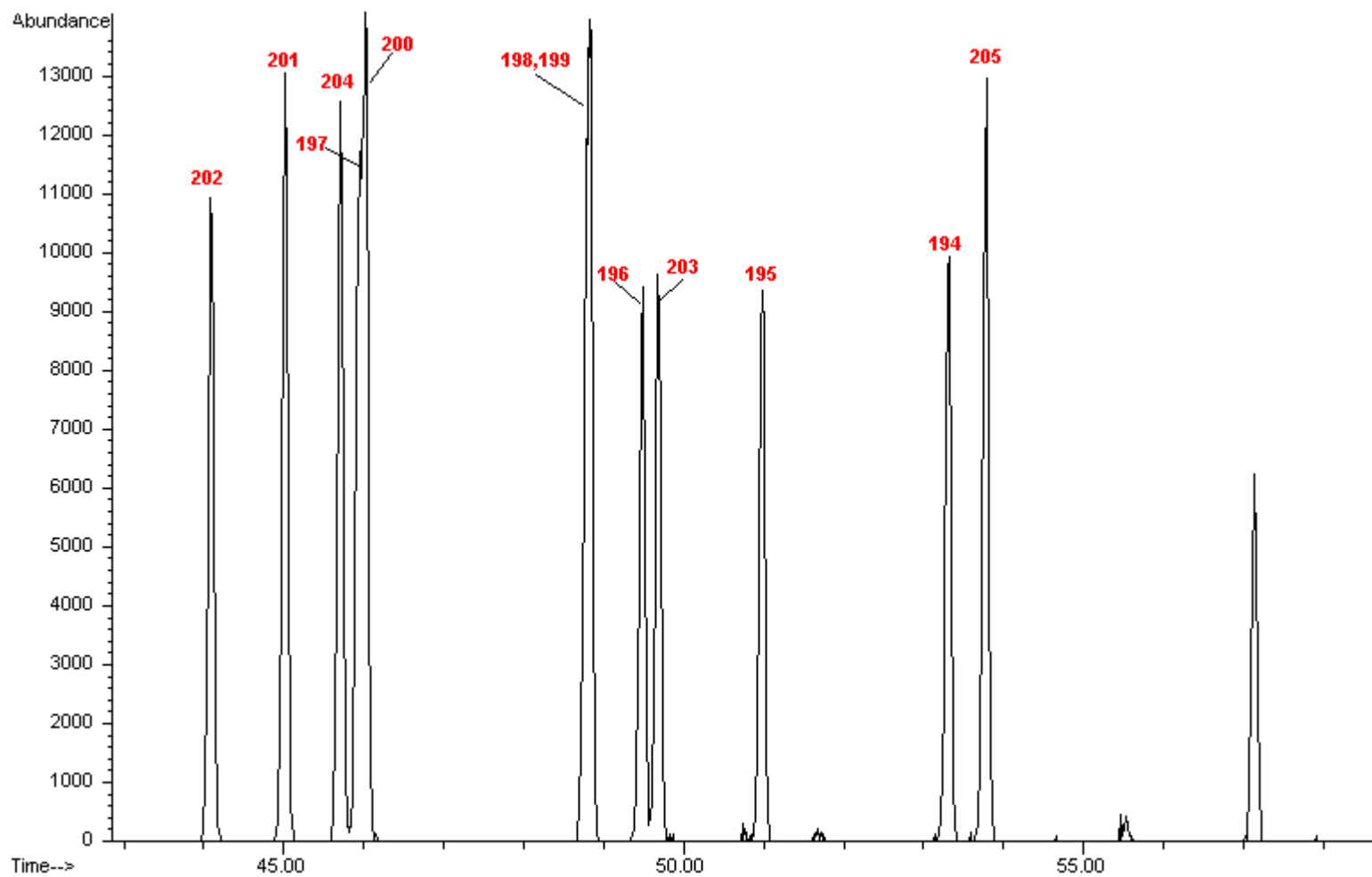
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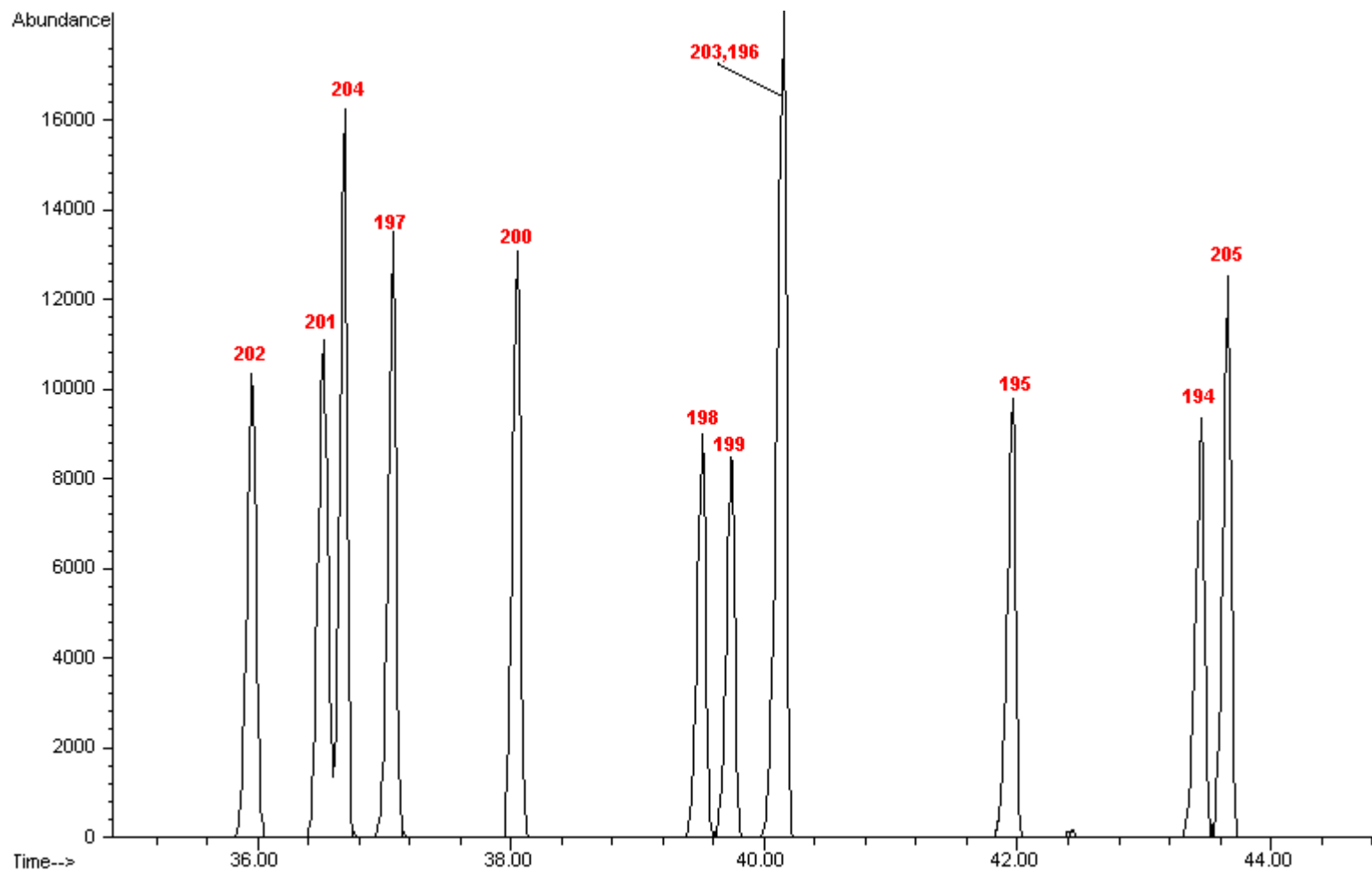
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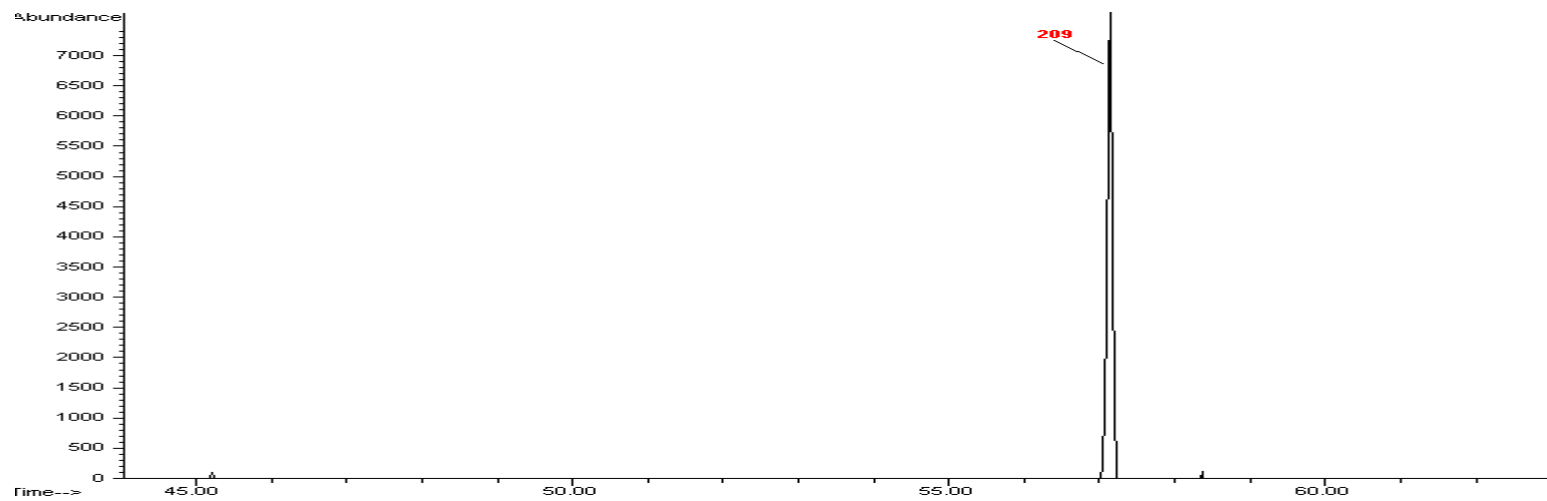
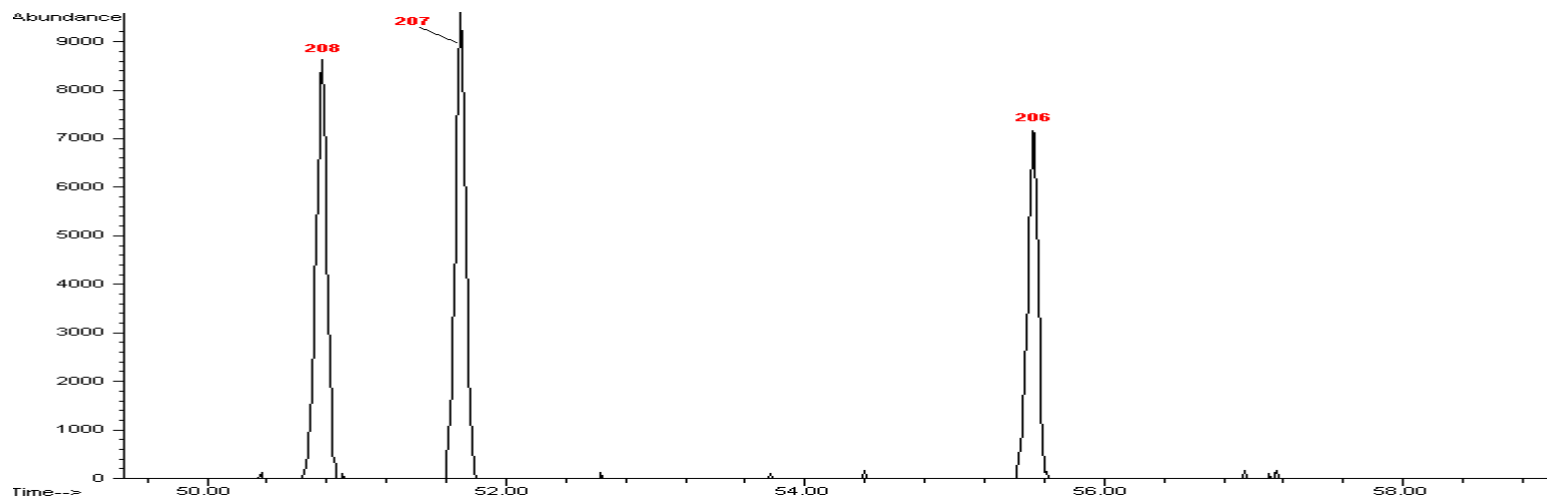
Octachloro, m/z=428 SPB-Octyl



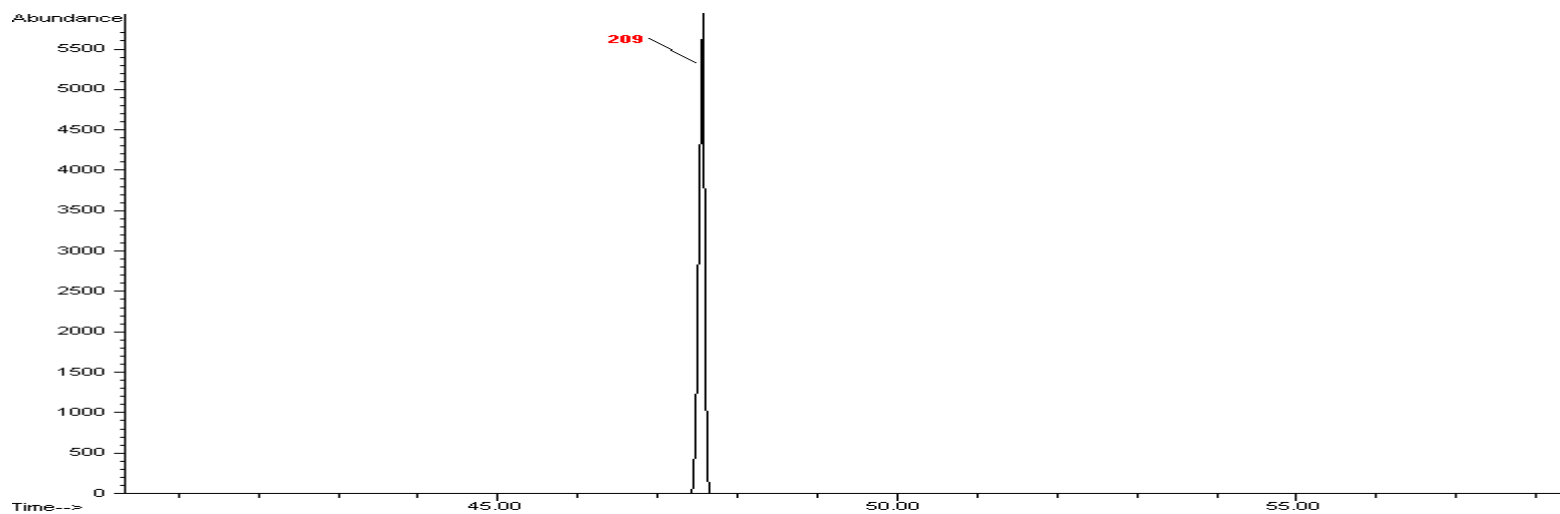
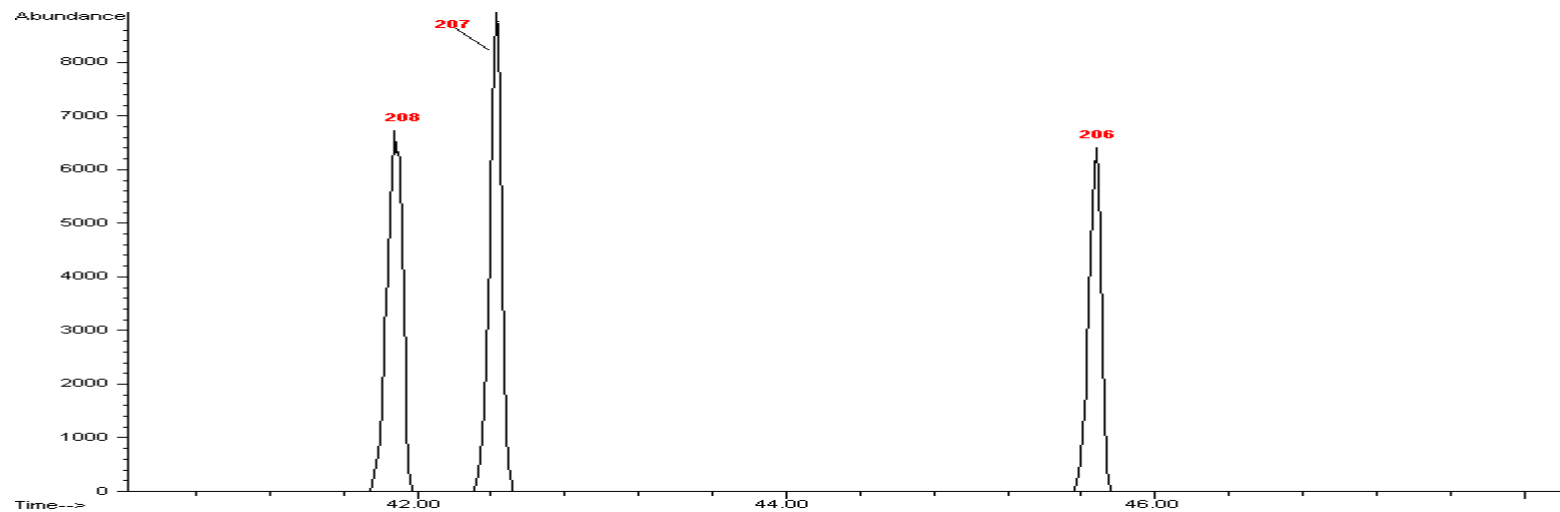
Octachloro, m/z=428 MDN-5S



Nona & Decachloro, m/z=462 & 496 SPB-Octyl



Nona & Decachloro, m/z=462 & 496 MDN-5S



The retention times of the congeners on the SPB-Octyl and MDN-5S have been listed in Tables 1 and 2. The toxic congeners of interest have been indicated with a “*”.

When using mass spectral detection, the two columns together can resolve all 12 of the toxic congeners and approximately 171 of the remaining 197 congeners.

Table 1: Retention Times of PCB Congeners on the SPB-Octyl

| No. | RT | No. | RT | No. | RT | No. | RT | No. | RT | No. | RT |
|------------------------------------|-------|-----------------|-------|-------------------|-------|----------------|-------|--------------------|-------|----------------|-------|
| Mono | | 21,33 | 24.55 | 70,74,76 | 31.09 | 117 | 34.93 | 131 | 37.85 | 183 | 43.30 |
| 1 | 12.36 | 22 | 24.95 | 66 | 31.40 | 116,85 | 35.01 | 142 | 38.01 | 185 | 43.35 |
| 2 | 14.51 | 36 | 26.56 | 55 | 31.55 | 110 | 35.15 | 132 | 38.27 | 174 | 43.52 |
| 3 | 14.70 | 39 | 26.92 | 56 | 32.06 | 115 | 35.27 | 133 | 38.79 | 177 | 43.95 |
| Di | | 38 | 27.56 | 60 | 32.27 | 82 | 35.46 | 165 | 39.19 | 181 | 44.36 |
| 4 | 14.98 | 35 | 27.98 | 80 | 32.71 | 111 | 35.88 | 146 | 39.44 | 173,171 | 44.59 |
| 10 | 15.17 | 37 | 28.40 | 79 | 34.28 | 120 | 36.35 | 161 | 39.60 | 172 | 46.20 |
| 9 | 17.08 | Tetra | | 78 | 34.82 | 107,124 | 37.48 | 153,168 | 40.11 | 192 | 46.49 |
| 7 | 17.26 | 54 | 21.50 | 81* | 35.27 | 109 | 37.74 | 141 | 40.25 | 180,193 | 46.80 |
| 6 | 17.51 | 50,53 | 23.78 | 77* | 35.79 | 123* | 37.86 | 130 | 40.64 | 191 | 47.20 |
| 5 | 17.82 | 51 | 24.42 | Penta | | 106 | 37.98 | 137 | 40.89 | 170 | 48.09 |
| 8 | 17.95 | 45 | 24.51 | 104 | 27.27 | 118* | 38.18 | 164 | 40.99 | 190 | 48.64 |
| 14 | 19.67 | 46 | 24.74 | 96 | 27.57 | 122 | 38.50 | 163,138,129 | 41.33 | 189* | 51.20 |
| 11 | 20.53 | 52 | 26.19 | 103 | 29.53 | 114* | 38.71 | 160 | 41.48 | Octa | |
| 13 | 20.84 | 73 | 26.35 | 94 | 29.74 | 105* | 39.33 | 158 | 41.69 | 202 | 44.10 |
| 12 | 20.89 | 43 | 26.45 | 95 | 30.18 | 127 | 40.83 | 128,166 | 42.56 | 201 | 45.02 |
| 15 | 21.18 | 69,49 | 26.70 | 93,100 | 30.44 | 126* | 42.42 | 159 | 43.55 | 204 | 45.71 |
| Tri | | 48 | 27.00 | 102 | 30.58 | Hexa | | 162 | 43.83 | 197 | 45.96 |
| 19 | 18.28 | 65,47,44 | 27.28 | 98 | 30.64 | 155 | 32.98 | 167* | 44.32 | 200 | 46.03 |
| 30,18 | 20.23 | 62,75,59 | 27.58 | 88 | 31.00 | 152 | 33.13 | 156*,157* | 45.46 | 198,199 | 48.83 |
| 17 | 20.68 | 42 | 27.76 | 91 | 31.09 | 150 | 33.33 | 169* | 48.66 | 196 | 49.49 |
| 27 | 20.90 | 41 | 28.13 | 84 | 31.29 | 136 | 33.66 | Hepta | | 203 | 49.68 |
| 24 | 21.04 | 71,40 | 28.26 | 89 | 31.77 | 145 | 33.98 | 188 | 38.72 | 195 | 50.99 |
| 16 | 21.14 | 64 | 28.48 | 121 | 32.22 | 148 | 35.51 | 179 | 39.03 | 194 | 53.32 |
| 32 | 21.68 | 72 | 29.32 | 92 | 32.56 | 151,135 | 36.13 | 184 | 39.61 | 205 | 53.79 |
| 34 | 22.97 | 68 | 29.63 | 90,101,113 | 33.19 | 154 | 36.38 | 176 | 39.93 | Nona | |
| 23 | 23.14 | 57 | 30.05 | 83 | 33.64 | 144 | 36.66 | 186 | 40.39 | 208 | 50.77 |
| 29,26 | 23.47 | 58 | 30.30 | 99 | 33.77 | 147,149 | 37.03 | 178 | 41.75 | 207 | 51.70 |
| 25 | 23.70 | 67 | 30.48 | 112 | 33.88 | 134 | 37.21 | 175 | 42.42 | 206 | 55.53 |
| 31 | 24.01 | 63 | 30.73 | 119,108,86 | 34.29 | 143 | 37.32 | 187 | 42.68 | Deca | |
| 28,20 | 24.33 | 61 | 31.01 | 97,125,87 | 34.37 | 139,140 | 37.65 | 182 | 42.89 | 209 | 57.15 |
| *Toxic congener of interest | | | | | | | | | | | |

Table 2: Retention Times of PCB Congeners on the MDN-5S

| No. | RT | No. | RT | No. | RT | No. | RT | No. | RT | No. | RT |
|--------------|-------|--------------------|-------|---------------------|-------|-----------------|-------|--------------------|-------|----------------|-------|
| Mono | | 22 | 19.26 | 63,61 | 23.54 | 86,125 | 27.06 | 139,149 | 29.51 | 187,182 | 33.97 |
| 1 | 9.86 | 36 | 19.74 | 74 | 23.79 | 116,117 | 27.21 | 140 | 29.71 | 183 | 34.31 |
| 2 | 11.13 | 39 | 20.25 | 76 | 23.96 | 111 | 27.32 | 143 | 30.00 | 185 | 34.99 |
| 3 | 11.29 | 38 | 20.68 | 70 | 24.11 | 115,87 | 27.44 | 134 | 30.05 | 174,181 | 35.49 |
| Di | | 35 | 21.37 | 66 | 24.24 | 85 | 27.60 | 131,133,142 | 30.36 | 177 | 35.76 |
| 4,10 | 11.98 | 37 | 21.83 | 80 | 24.37 | 120 | 27.75 | 165 | 30.57 | 171 | 36.10 |
| 7,9 | 13.07 | Tetra | | 55 | 24.66 | 110 | 27.95 | 161,146 | 30.77 | 173 | 36.38 |
| 6 | 13.50 | 54 | 17.41 | 56,60 | 25.20 | 82 | 28.56 | 153,168,132 | 31.27 | 192 | 36.89 |
| 5,8 | 13.80 | 50 | 18.11 | 79 | 26.29 | 124,107 | 29.36 | 141 | 32.03 | 172 | 37.02 |
| 14 | 14.46 | 53 | 18.82 | 78 | 26.84 | 109,123* | 29.56 | 137 | 32.36 | 180,193 | 37.49 |
| 11 | 15.45 | 51 | 19.09 | 81* | 27.48 | 106 | 29.71 | 130 | 32.54 | 191 | 37.73 |
| 12 | 15.68 | 45 | 19.45 | 77* | 28.12 | 118* | 29.80 | 164,163,160 | 32.87 | 170,190 | 39.22 |
| 13 | 15.78 | 46 | 19.88 | Penta | | 114* | 30.39 | 138,158 | 33.03 | 189* | 41.22 |
| 15 | 16.08 | 69 | 20.08 | 104 | 21.12 | 122 | 30.50 | 129 | 33.32 | Octa | |
| Tri | | 73 | 20.18 | 96 | 22.44 | 105* | 31.39 | 166 | 33.72 | 202 | 35.96 |
| 19 | 14.61 | 43,52 | 20.41 | 103 | 22.70 | 127 | 31.60 | 159 | 34.17 | 201 | 36.52 |
| 30 | 15.01 | 49 | 20.62 | 100 | 23.05 | 126* | 33.65 | 162,128 | 34.56 | 204 | 36.69 |
| 18 | 15.80 | 48,47,75,65 | 20.78 | 94 | 23.44 | Hexa | | 167* | 34.95 | 197 | 37.07 |
| 17 | 15.88 | 62 | 20.85 | 102,98 | 23.96 | 155 | 24.98 | 156* | 36.34 | 200 | 38.06 |
| 24,27 | 16.28 | 44 | 21.49 | 93,95,121,88 | 24.26 | 150 | 26.35 | 157* | 36.66 | 198 | 39.52 |
| 16 | 16.69 | 59 | 21.58 | 91 | 24.54 | 152 | 26.73 | 169* | 38.85 | 199 | 39.75 |
| 32 | 16.77 | 42 | 21.65 | 84,92 | 25.39 | 145 | 27.21 | Hepta | | 203,196 | 40.16 |
| 23,34 | 17.27 | 71 | 22.12 | 89 | 25.55 | 148 | 27.49 | 188 | 30.58 | 195 | 41.97 |
| 29 | 17.46 | 72,41,64 | 22.23 | 90 | 25.63 | 136 | 27.73 | 184 | 31.06 | 194 | 43.46 |
| 26 | 17.88 | 68 | 22.39 | 101,113 | 25.79 | 154 | 28.00 | 179 | 31.93 | 205 | 43.67 |
| 25 | 17.93 | 40 | 22.60 | 99 | 25.99 | 151 | 28.69 | 176 | 32.45 | Nona | |
| 28,31 | 18.37 | 57 | 22.88 | 119,112 | 26.39 | 135 | 28.95 | 186 | 32.97 | 208 | 41.88 |
| 21 | 18.68 | 67 | 23.17 | 108,83 | 26.58 | 144 | 29.02 | 178 | 33.37 | 207 | 42.44 |
| 20,33 | 18.83 | 58 | 23.29 | 97 | 26.97 | 147 | 29.16 | 175 | 33.74 | 206 | 45.69 |
| | | | | | | | | | | Deca | |
| | | | | | | | | | | 209 | 47.58 |

*Toxic congener of interest

Conclusion

If used together, the 30m x 0.25mm ID, 0.25 μ m SPB-Octyl and MDN-5S can resolve all 12 PCB congeners listed as toxic by the World Health Organization, and designated in USEPA Method 1668A. When used with mass spectral detection, the two columns together can resolve approximately 183 of the 209 PCB congeners.

References

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