

A New Alternative Test Procedure for the Determination of Dioxins & Furans by Method 1613b replacing GC-HRMS with GC-MS/MS

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August 2021

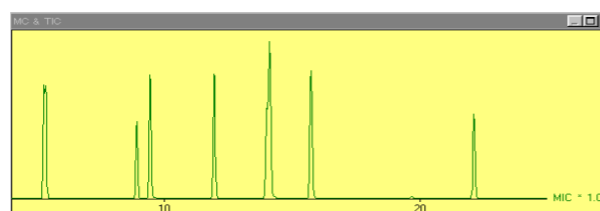
Brief introduction to the project goals: What will be changed?

| | Method 1613b | PAM1613 |
|---------------------------|----------------------------|---|
| Scope | | No change |
| Sampling and preservation | | No change |
| Matrices | Wastewater, solids, tissue | Wastewater, drinking water, solids, tissue, air |
| Extraction | | Same as method, air = CAA method |
| Detection | GC/HRMS | GC-MS/MS |
| QC criteria | HRMS specific | MS/MS specific |
| QC criteria | | No change |
| Reporting | | No change |

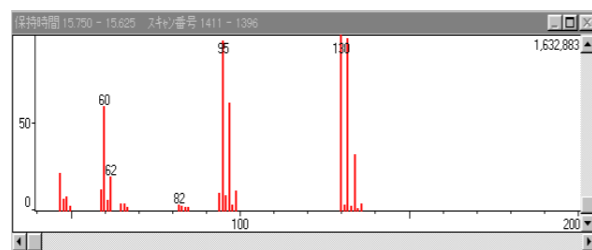
HRMS and MS/MS Instrument Operation

| | HRMS | MS/MS |
|-----------------------------|---|--|
| GC | Agilent | Shimadzu |
| Column | DB-5MS UI 60m x 0.25mm x 0.25 μ m | DB-5MS UI 60m x 0.25mm x 0.25 μ m |
| Injection port liner | 4 mm ID x 78.5 mm Volume ~ 800 μ L | 3.5 mm ID x 95 mm Volume ~ 800 μ L |
| Source Temperature | 280 °C | 230 °C |
| Detection resolution | 10,000 | Unit (0.6 FWHM) |
| Mass scan range | 339.86 – 409.80 | MRM transitions (ranging from 319.0 to 513.7) |
| Drift | Mass locking | Monitor PFTBA |

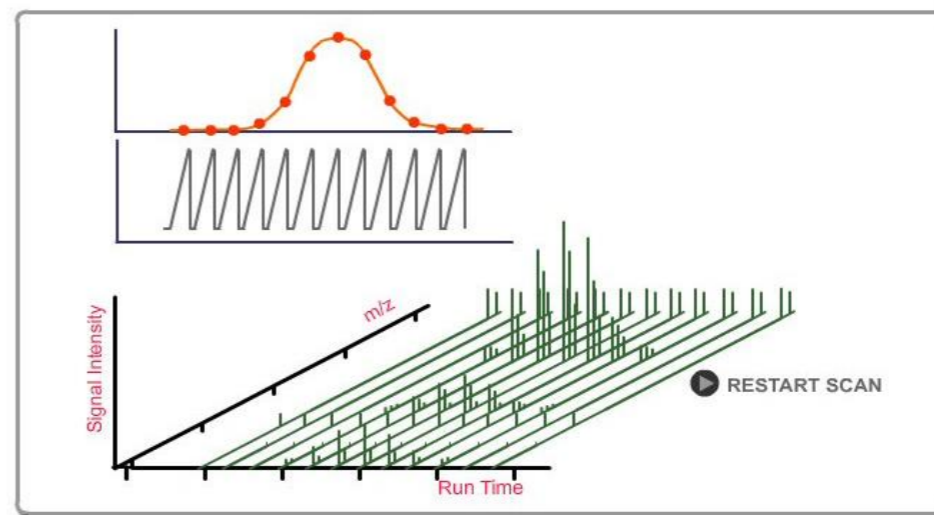
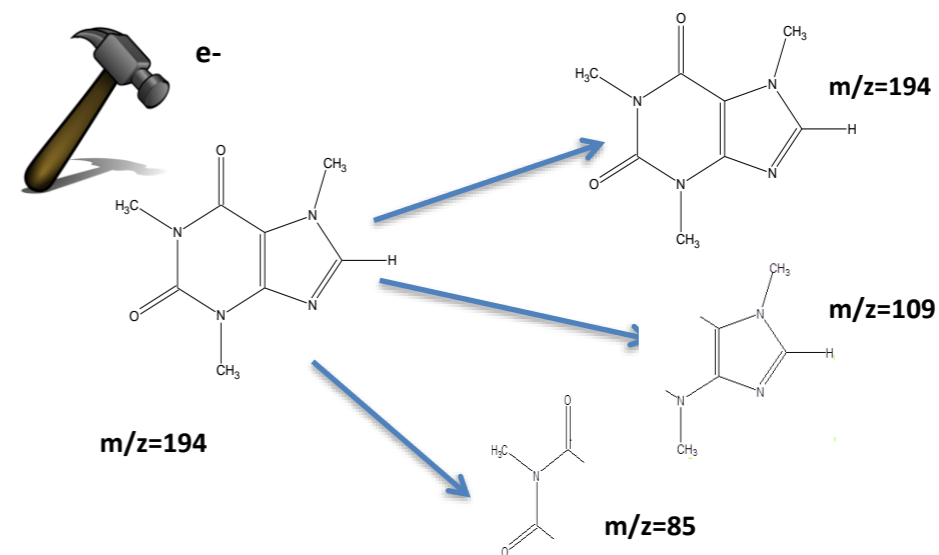
Brief explanation of GCMS and GC-MSMS.....



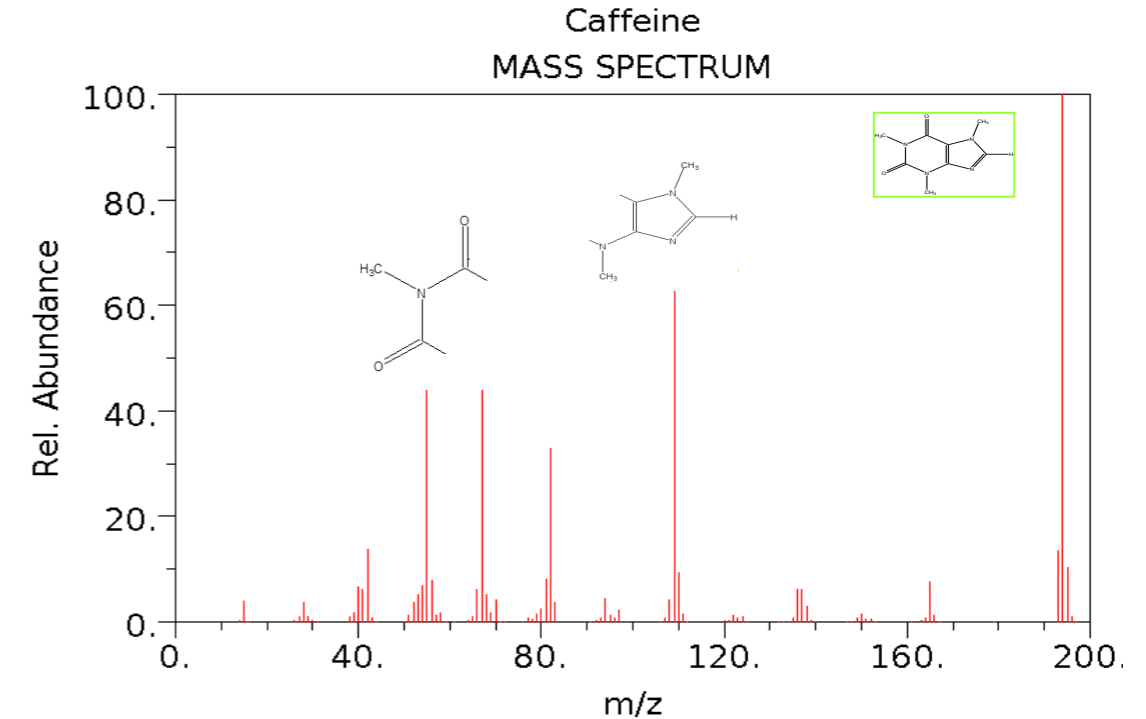
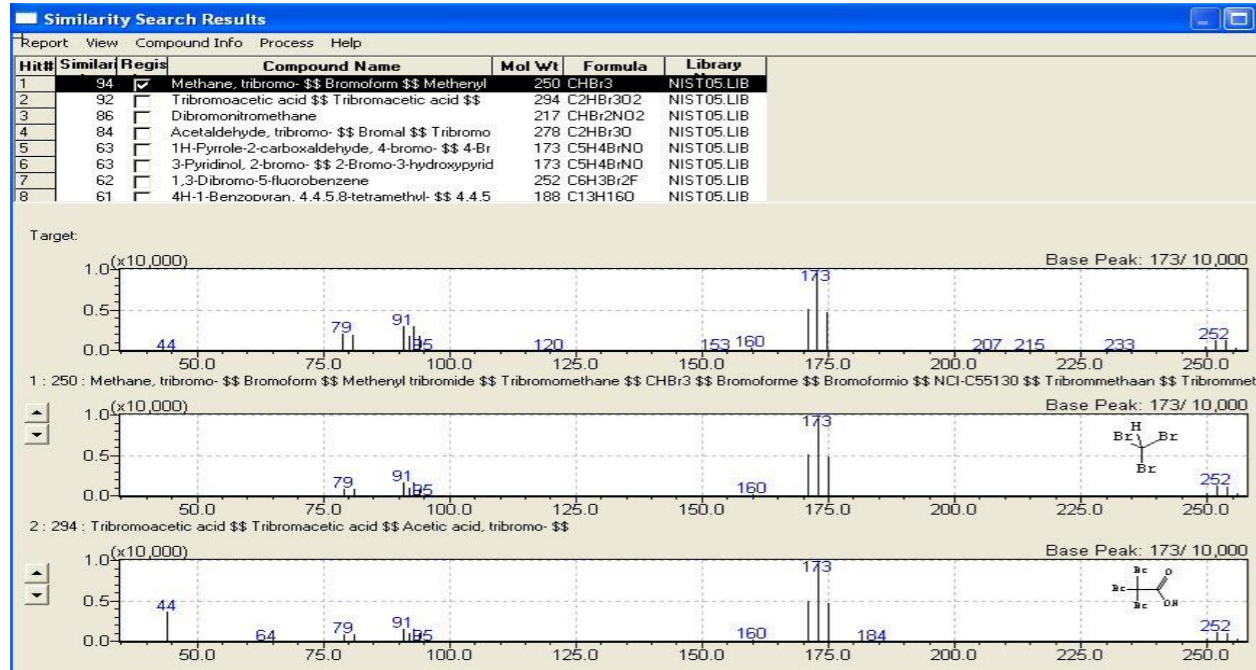
Gas Chromatograph: separation on a capillary column, identification by RT, and quantitation



Mass Spectrometer: positive identification by matching to a library

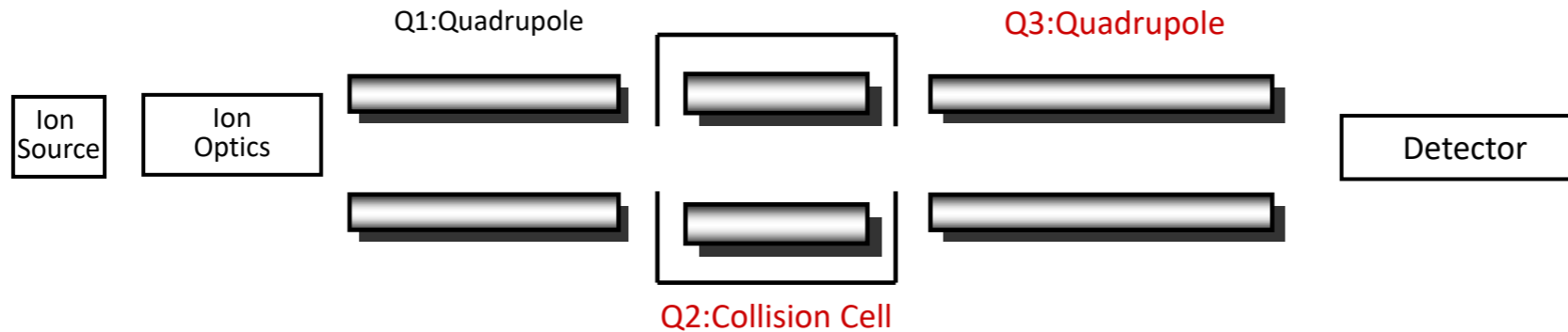
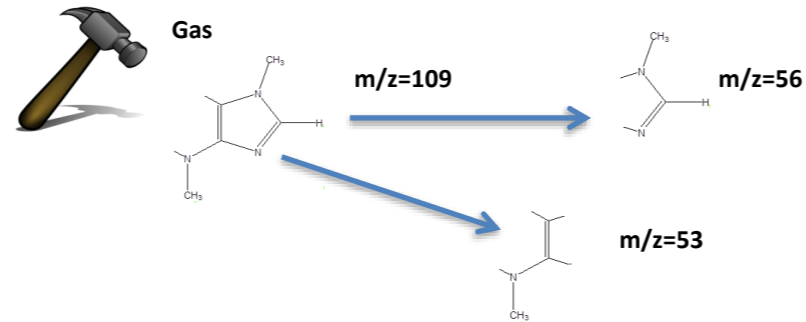
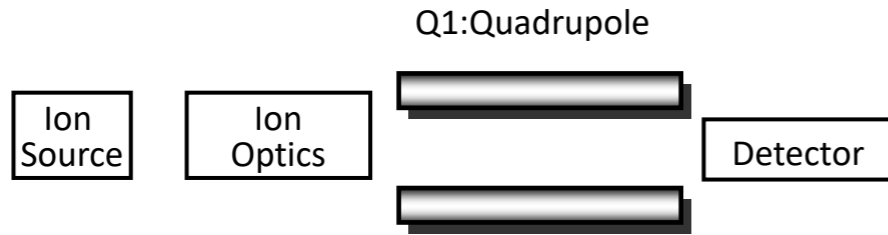


Detected Peaks - Confirmed for Positive Identification, with Mass Spectra Specific to Compound

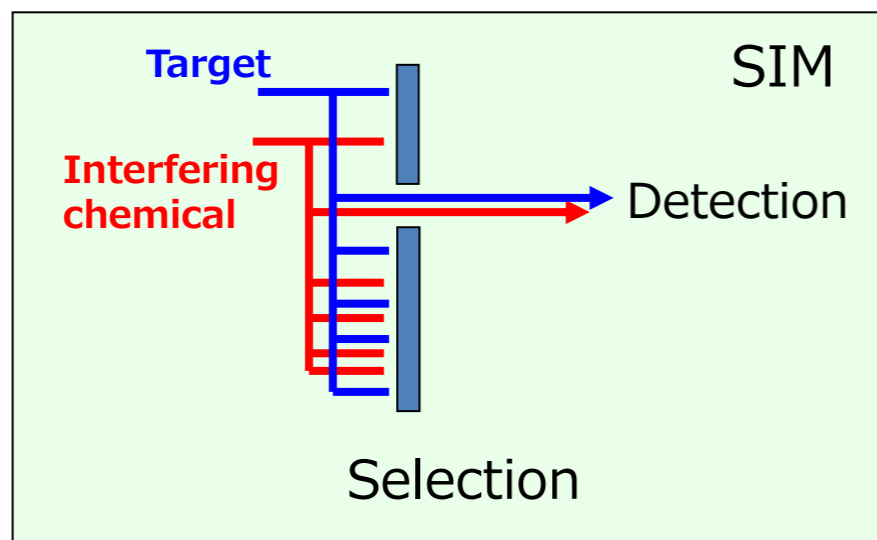
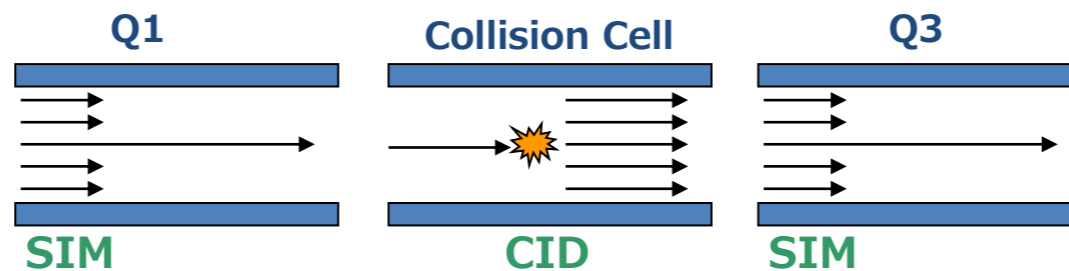


NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

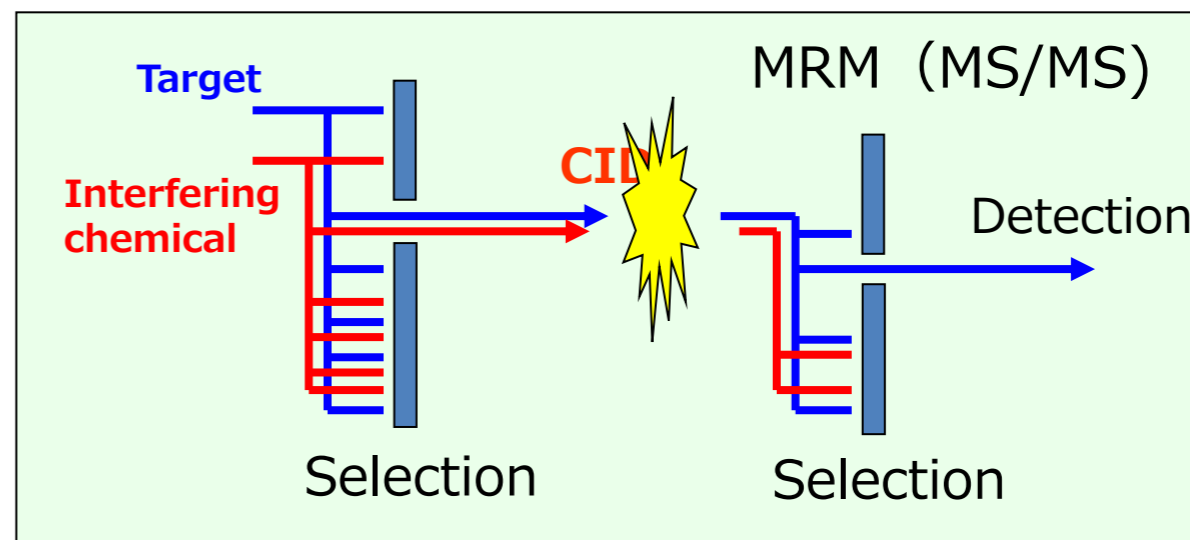
Triple Quadrupole - Adds a Collision Cell and Another Quadrupole



“SIM” the first fragment and “SIM” the second fragment for a very selective measurement with high S/N

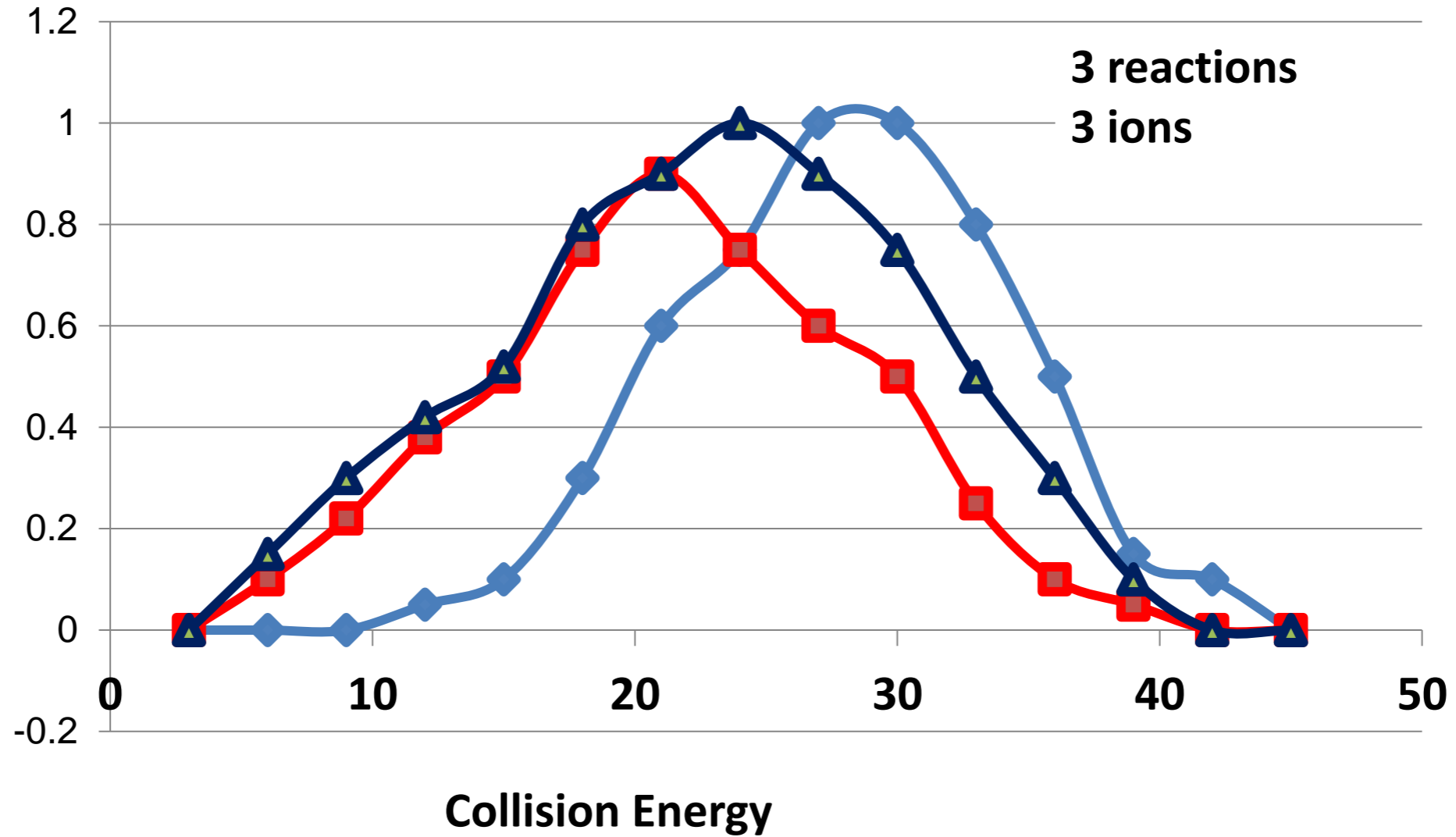


SIM reduces interference, but does not completely eliminate it

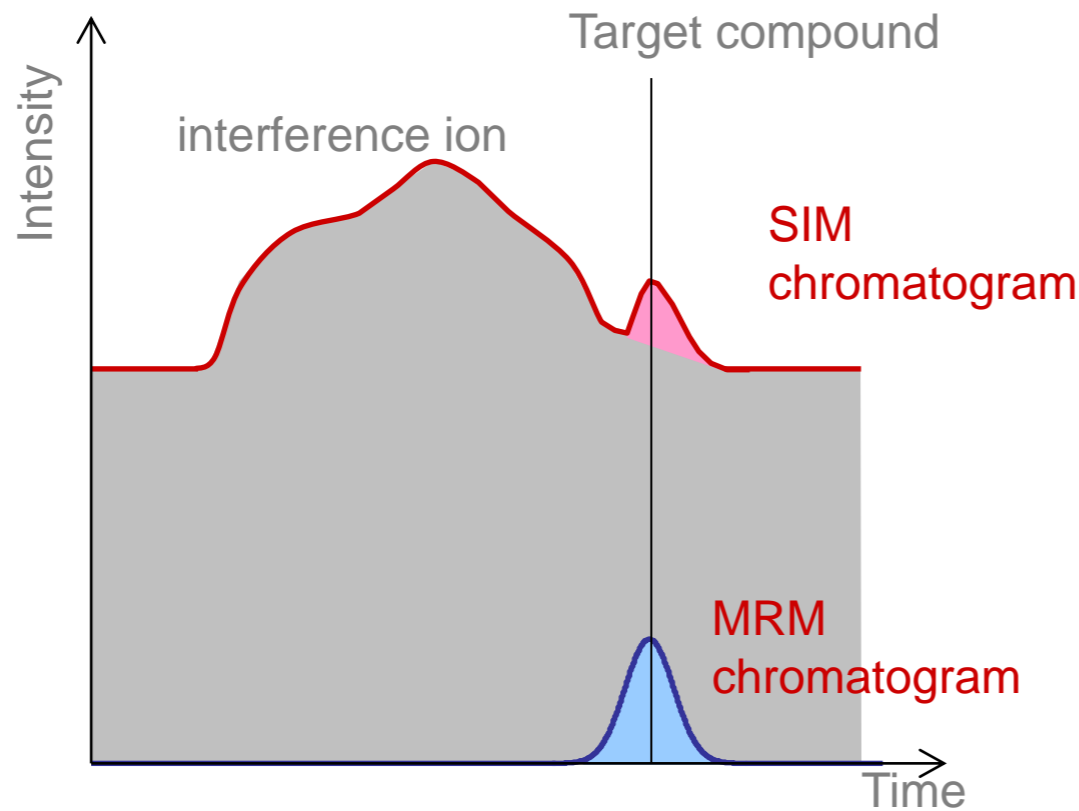


MRM eliminates remaining interference

Each MRM Transition is Optimized by Collision Energy for Maximum Sensitivity

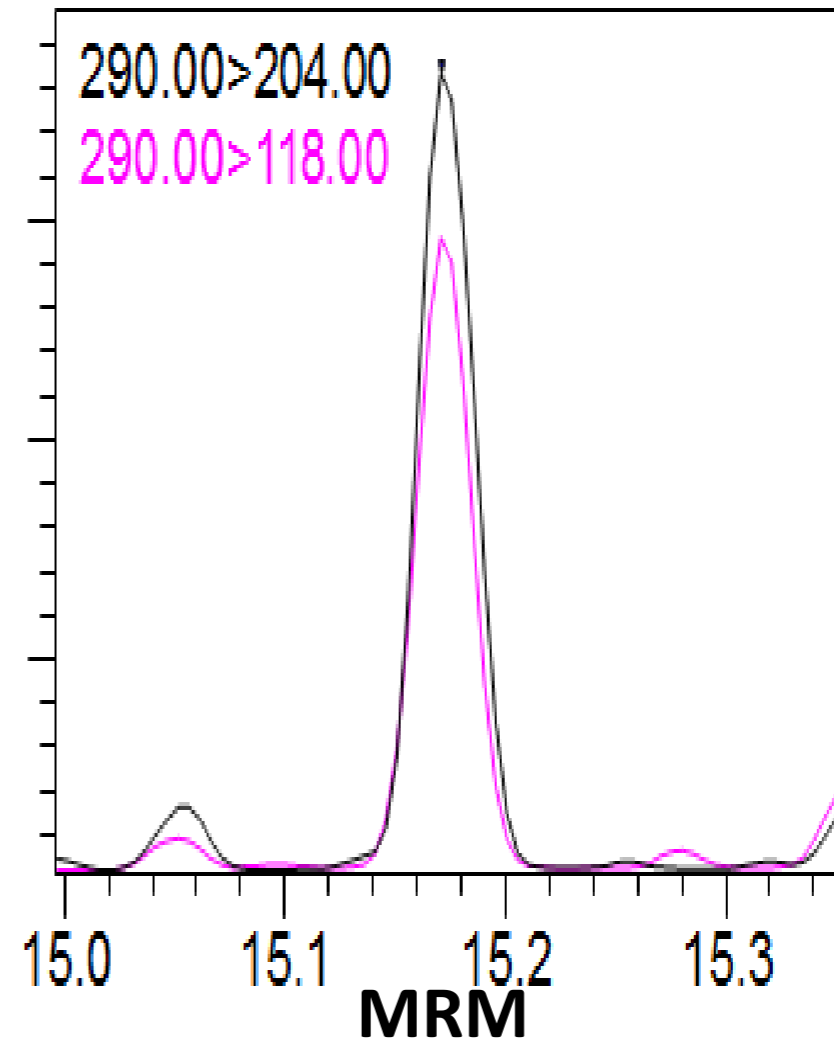
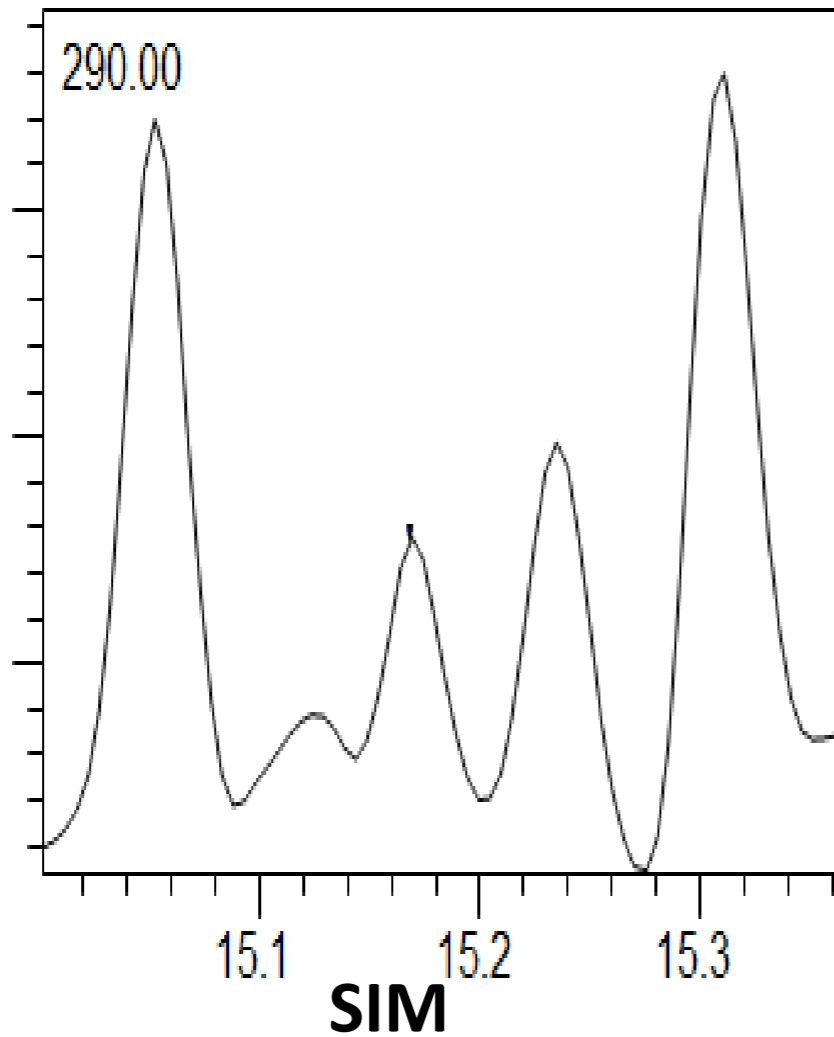


Triple Quad - Ideal for GCMS Analysis in Complex Matrices Where SIM is Problematic

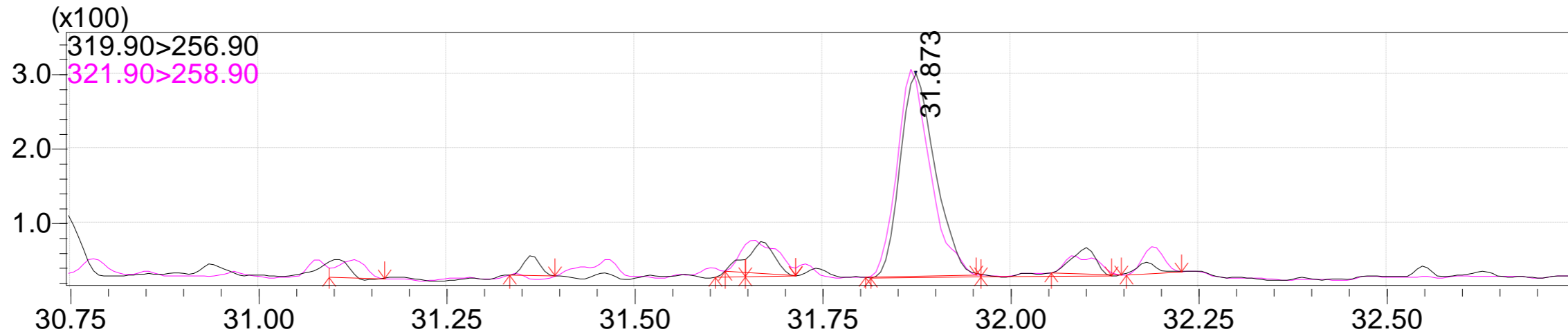


- S/N ratio is enhanced
- Extremely selective for quantitation
- 10x lower MDL than SIM
- Extended linear range

SIM and MRM Data Showing Better Detection and Selectivity by MRM



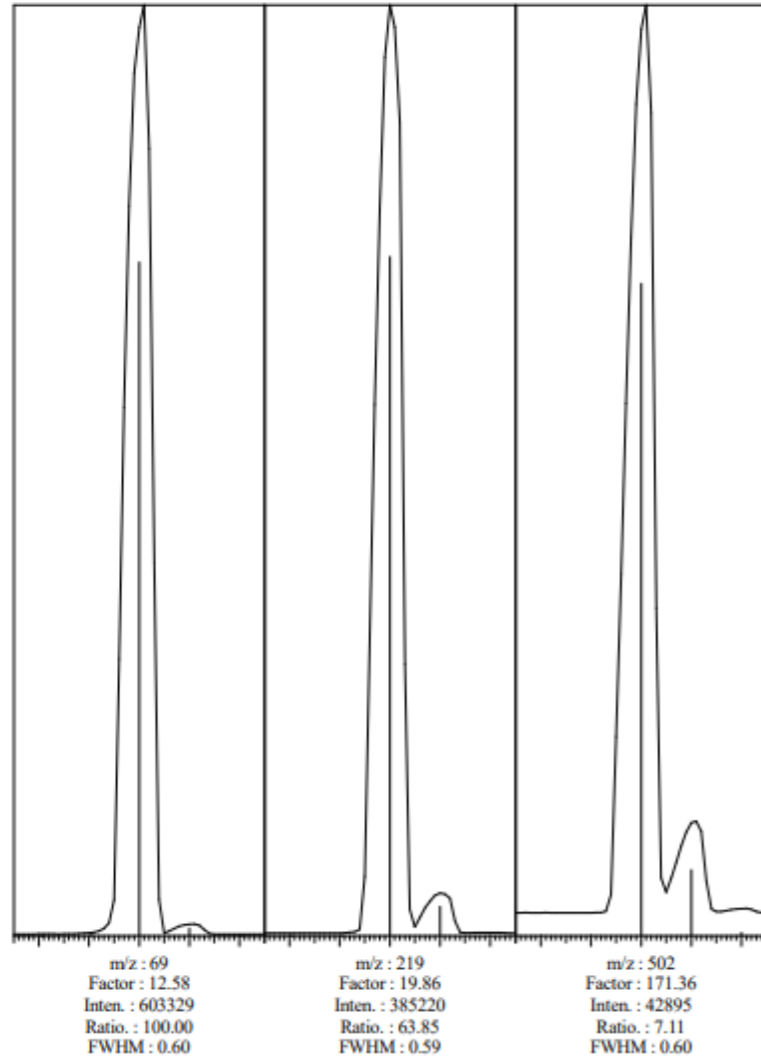
In this ATP, we are simply replacing the selectivity of high resolution with the selectivity of MRM



Low level MRM “trace” of 2,3,7,8 - TCDD in highly contaminated soil

Section 10.1.2.3: Tune parameters were adjusted to reflect at least 1 AMU unit resolution

Tuning Result



Not greater than 0.7 AMU FWHM in autotune

m/z 69

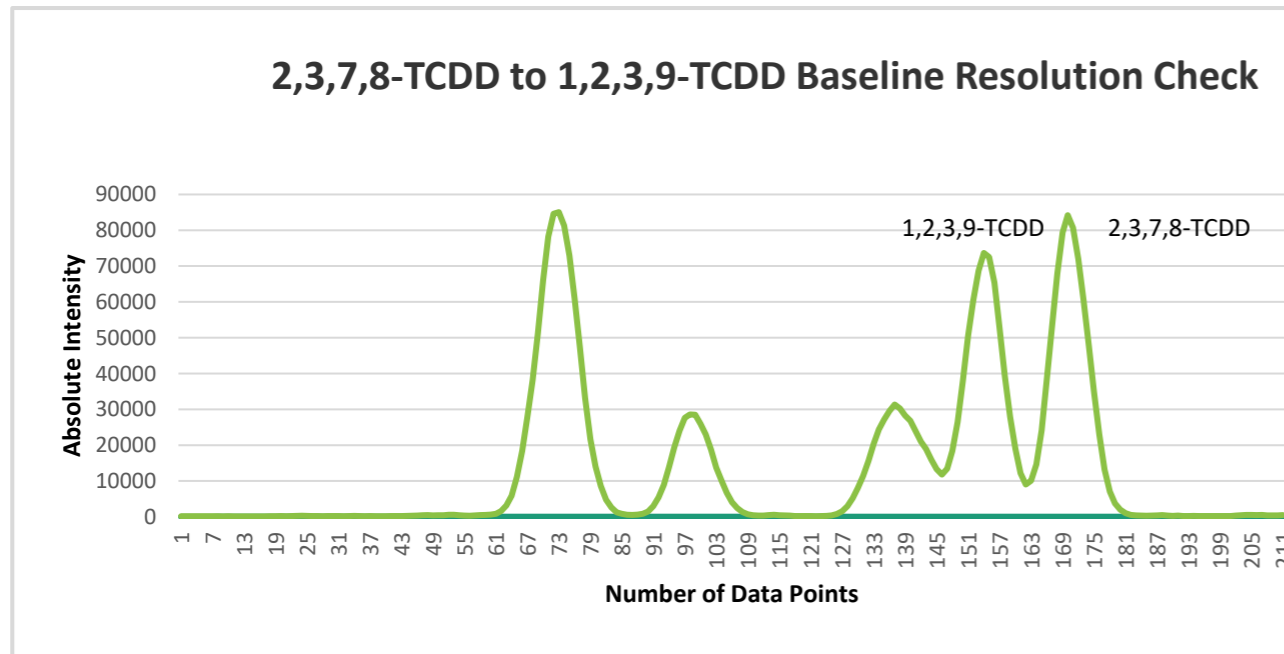
m/z 264

m/z 502

Drift no more than a 0.2 amu

The first step in the validation – Duplicate chromatography with the HRMS (to extent possible)

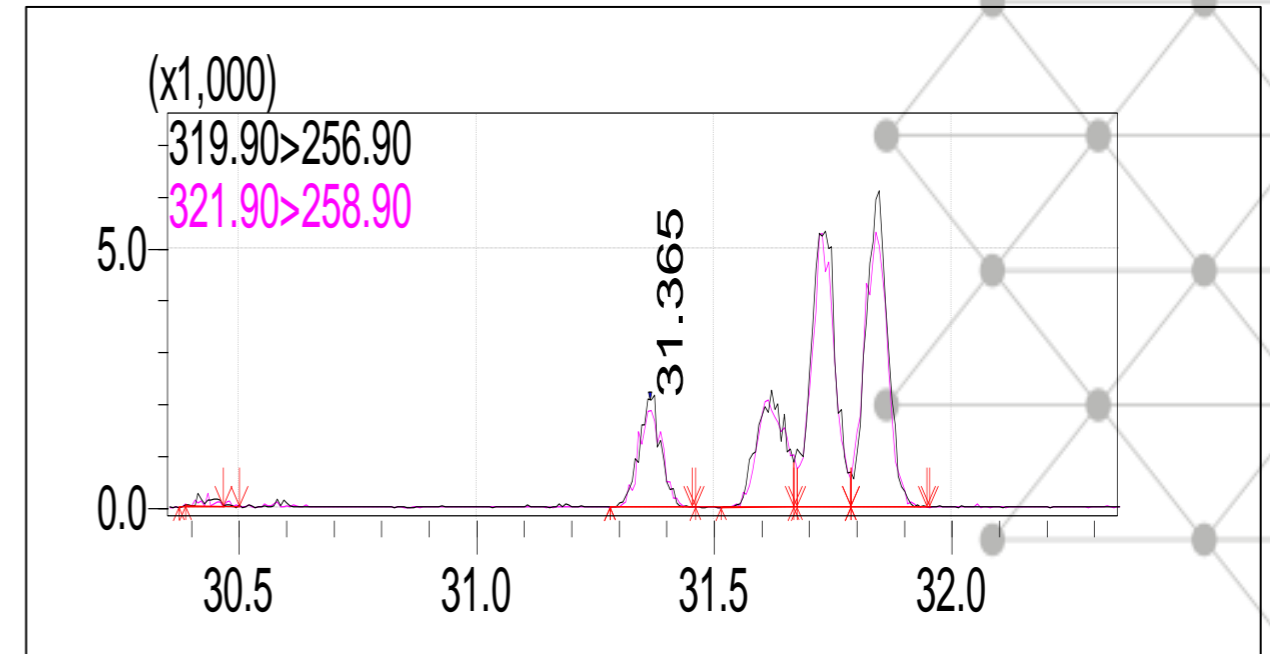
10.4.3 Isomer specificity



Resolution: **11%**

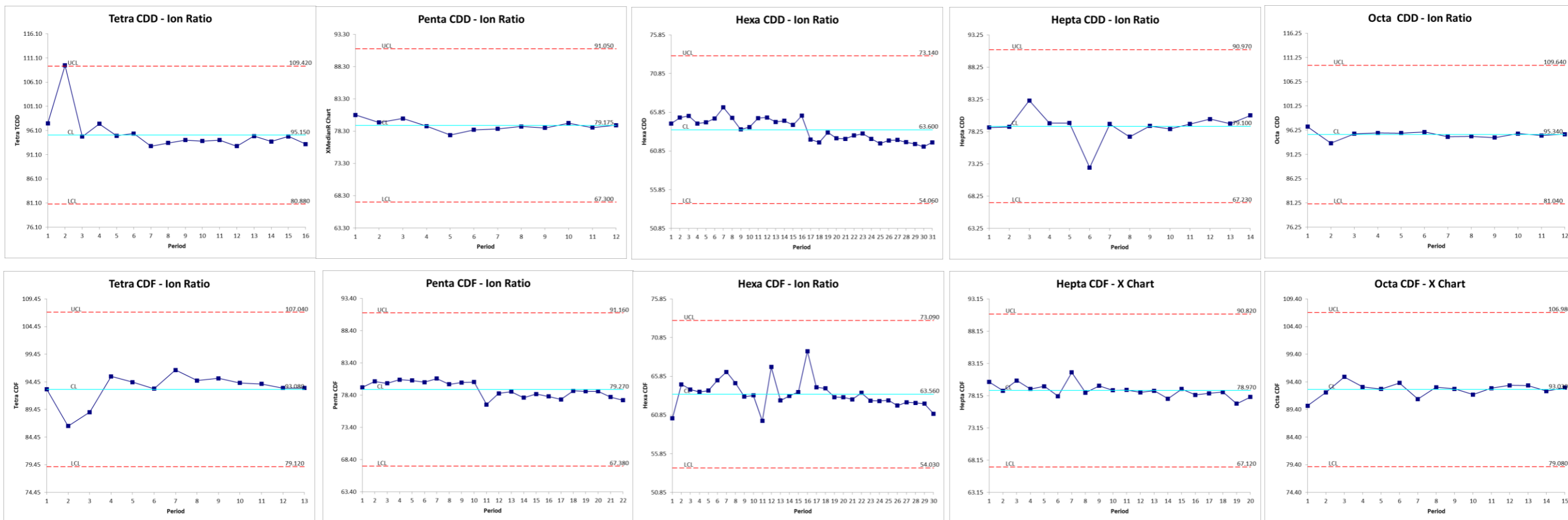
Limit = **25%**

10.2.4 Absolute Retention time



1,2,3,4 – TCDD absolute retention time > 25 minutes on DB-5 column (required)

Next, we verified MRM transitions (Table 8) & qualifier ion ratios were within theoretical values (Table 9)



Next: Verification that the CS1 standard (1 μ L injection) has a S/N of 10 or greater (10.2.3)

| Analyte | 5/10/2021 | 6/1/2021 | 6/2/2021 | 6/14/2021 | 6/24/2021 | 6/29/2021 | 7/8/2021 | 7/15/2021 |
|---|-----------|----------|----------|-----------|-----------|-----------|----------|-----------|
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin | 959 | 623 | 469 | 471 | 181 | 295 | 655 | 145 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin | 992 | 1869 | 4096 | 347 | 1511 | 1472 | 3335 | 689 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin | 228 | 187 | 169 | 95 | 126 | 122 | 144 | 155 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin | 235 | 193 | 185 | 92 | 137 | 122 | 156 | 109 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin | 226 | 176 | 173 | 92 | 132 | 119 | 147 | 98 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin | 777 | 2052 | 3147 | 197 | 797 | 987 | 2766 | 422 |
| Octachlorodibenzo-p-dioxin | 5033 | 5008 | 6028 | 515 | 1117 | 1428 | 5391 | 530 |
| 2,3,7,8-Tetrachlorodibenzofuran | 392 | 427 | 1146 | 58 | 378 | 357 | 1042 | 178 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 666 | 1276 | 1378 | 163 | 1618 | 1664 | 1196 | 785 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 709 | 796 | 1338 | 183 | 2102 | 681 | 1132 | 876 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 678 | 1597 | 2358 | 219 | 1593 | 1994 | 1971 | 818 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 644 | 1501 | 2163 | 194 | 1655 | 1751 | 1867 | 807 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 671 | 776 | 572 | 190 | 556 | 1461 | 490 | 599 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 548 | 679 | 484 | 142 | 616 | 1167 | 419 | 447 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 873 | 1373 | 1887 | 102 | 1381 | 1098 | 1702 | 616 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 671 | 614 | 1186 | 81 | 799 | 614 | 1029 | 531 |
| Octachlorodibenzofuran | 1201 | 1717 | 5861 | 222 | 1269 | 1455 | 5512 | 682 |

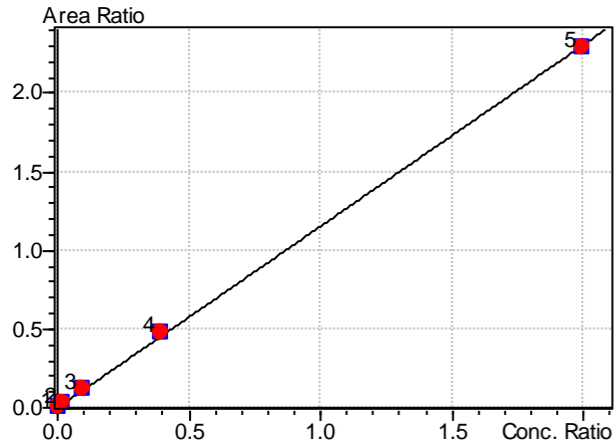
Calibrate Instrument for Fifteen 2,3,7,8 Target Analytes Using Isotope Dilution (Section 10.5)

2,3,7,8-Tetrachlorodibenzo-p-dioxin

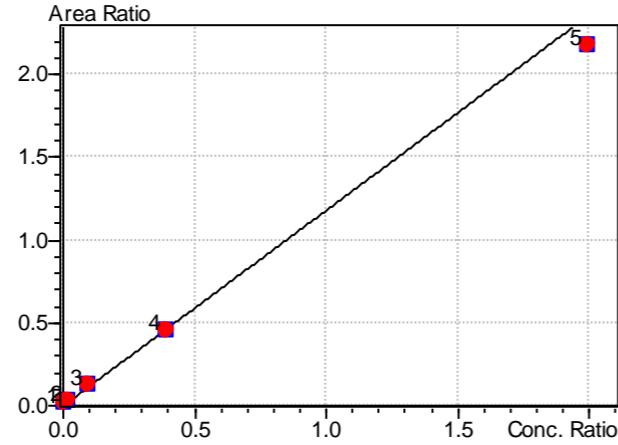
2,3,7,8-Tetrachlorodibenzofuran

1,2,3,7,8-Pentachlorodibenzo-p-dioxin

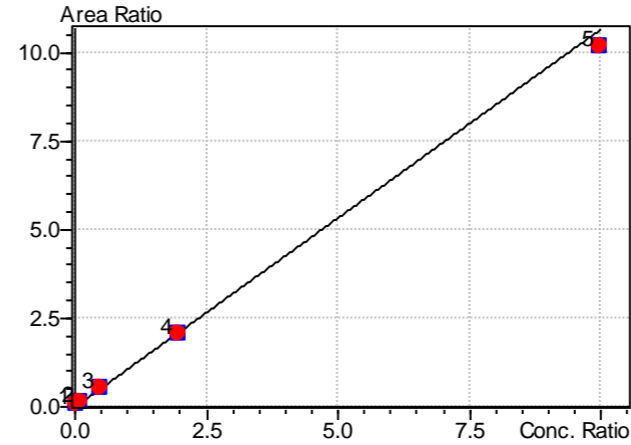
1,2,3,7,8-Pentachlorodibenzofuran



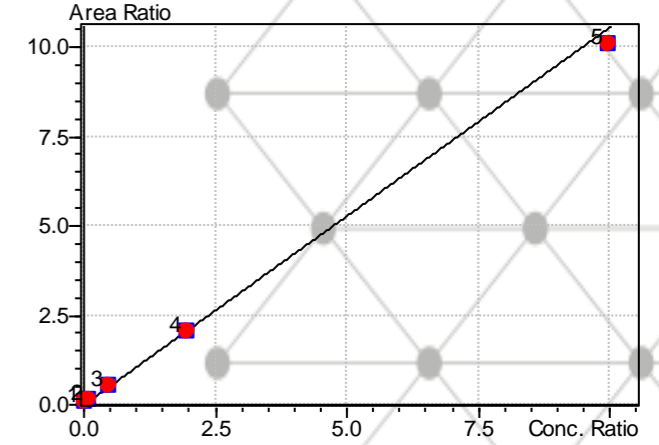
Mean RF : 1.154748
RF SD : 0.0723729
RF %RSD : 6.267419



Mean RF : 1.179659
RF SD : 0.0796125
RF %RSD : 6.748773



Mean RF : 1.066094
RF SD : 0.0578500
RF %RSD : 5.426357



Mean RF : 1.055942
RF SD : 0.0523577
RF %RSD : 4.958388

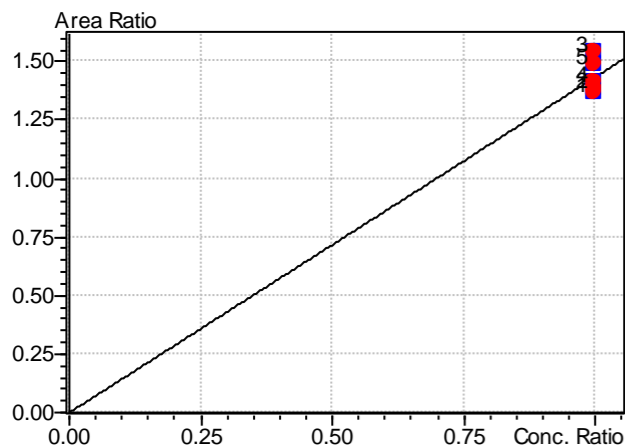
Instrument Calibration of Compounds Calculated by Internal Standard vs Isotope Dilution (per Sec 10.6 in 1613B)

2,3,7,8-Tetrachlorodibenzo-p-dioxin-13C12 (S)

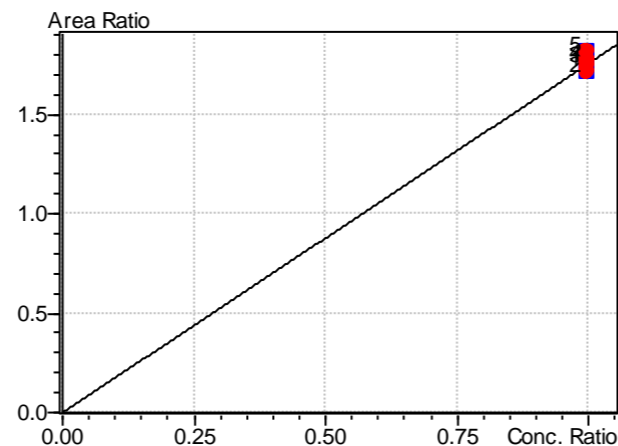
2,3,7,8-Tetrachlorodibenzofuran-13C12 (S)

1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin

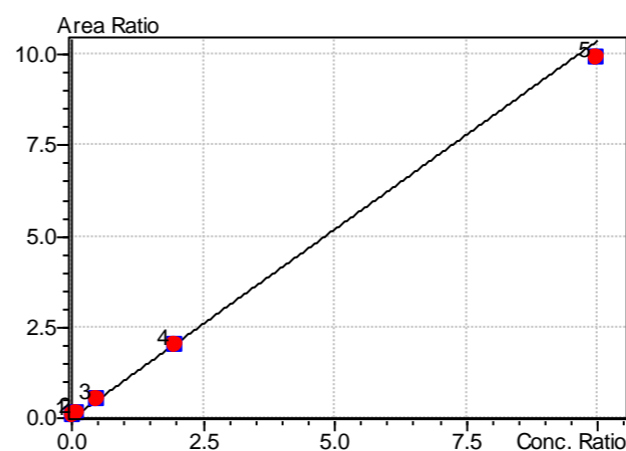
Octachlorodibenzofuran



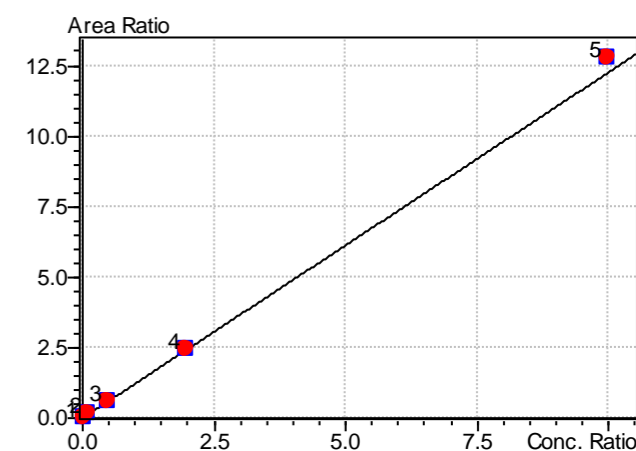
Mean RF : 1.434384
RF SD : 0.0721951
RF %RSD : 5.033180



Mean RF : 1.757166
RF SD : 0.0355826
RF %RSD : 2.024997



Mean RF : 1.039866
RF SD : 0.0648624
RF %RSD : 6.237573



Mean RF : 1.226142
RF SD : 0.0639670
RF %RSD : 5.216930

Repeatability of Target ICAL over ~ three months

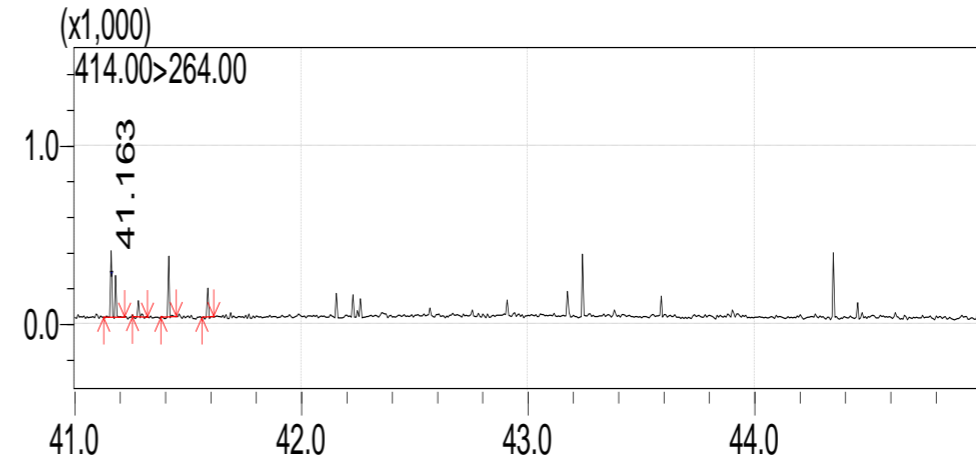
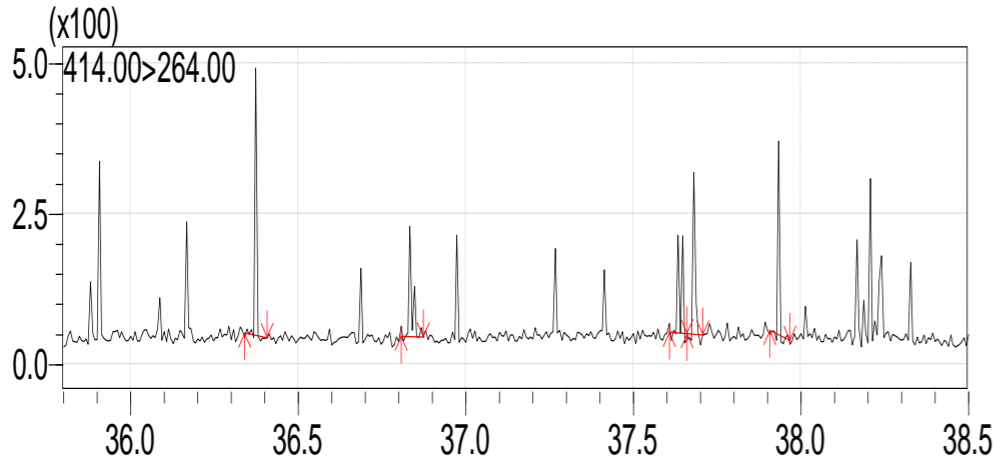
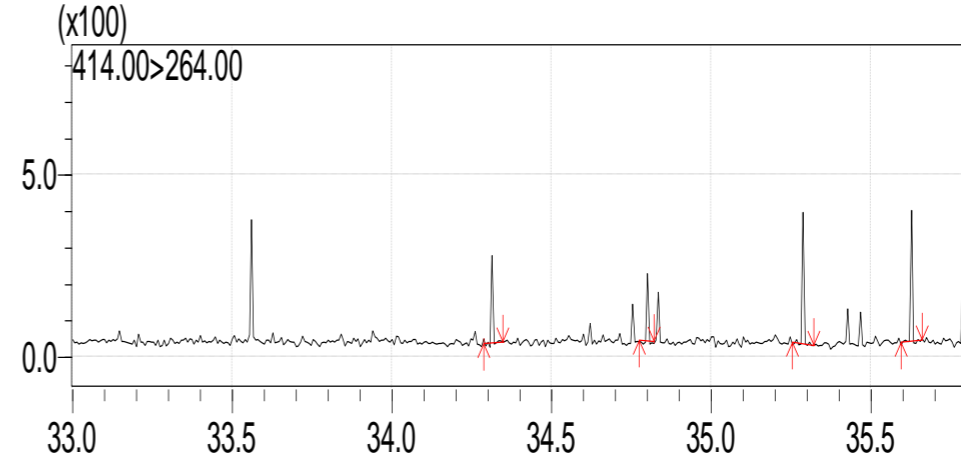
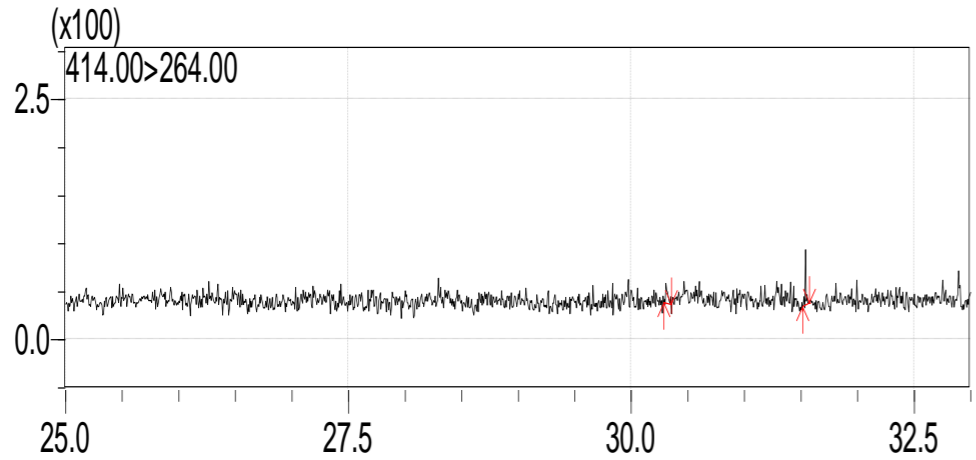
| Compound Name | 5/10/2021 | | 6/12/2021 | | 6/29/2021 | |
|---|-----------|----------|-----------|-----------|-----------|----------|
| | Mean RF | RF %RSD | Mean RF | RF %RSD | Mean RF | RF %RSD |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin | 1.179348 | 9.267654 | 1.159625 | 7.374795 | 1.169744 | 8.825416 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin | 1.041278 | 7.984401 | 1.004499 | 5.520641 | 1.052229 | 8.048561 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin | 1.052185 | 8.336673 | 1.006229 | 6.089719 | 1.046507 | 9.829302 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin | 1.05505 | 6.813428 | 1.001459 | 5.10416 | 1.096707 | 7.931747 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin | 1.087861 | 11.58138 | 0.997987 | 6.111245 | 1.051466 | 6.035913 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin | 1.112426 | 8.237804 | 1.07554 | 5.22895 | 1.113814 | 9.481065 |
| Octachlorodibenzo-p-dioxin | 1.237598 | 22.50152 | 1.203738 | 22.652314 | 1.042218 | 7.18232 |
| 2,3,7,8-Tetrachlorodibenzofuran | 1.158012 | 10.31181 | 1.112381 | 5.596462 | 1.10659 | 6.221342 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 1.033088 | 7.800385 | 0.998834 | 4.486977 | 1.03322 | 6.871412 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 1.11178 | 6.905324 | 1.071585 | 4.792594 | 1.119704 | 7.555176 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 1.059481 | 8.543972 | 1.002317 | 5.910157 | 1.076827 | 8.41047 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 1.01215 | 5.744571 | 0.991316 | 6.276268 | 1.05709 | 8.953919 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 1.18842 | 14.93938 | 1.157542 | 6.231949 | 1.253174 | 8.97111 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 0.860941 | 5.566722 | 0.84456 | 5.130754 | 0.893158 | 7.947057 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 1.101583 | 7.801756 | 1.054935 | 3.302767 | 1.08034 | 7.458126 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 1.078697 | 11.71977 | 1.02199 | 6.880244 | 1.040864 | 7.635429 |
| Octachlorodibenzofuran | 1.081007 | 6.752986 | 1.057972 | 11.769038 | 1.220162 | 7.104081 |

Repeatability of Surrogate ICAL over ~ three months

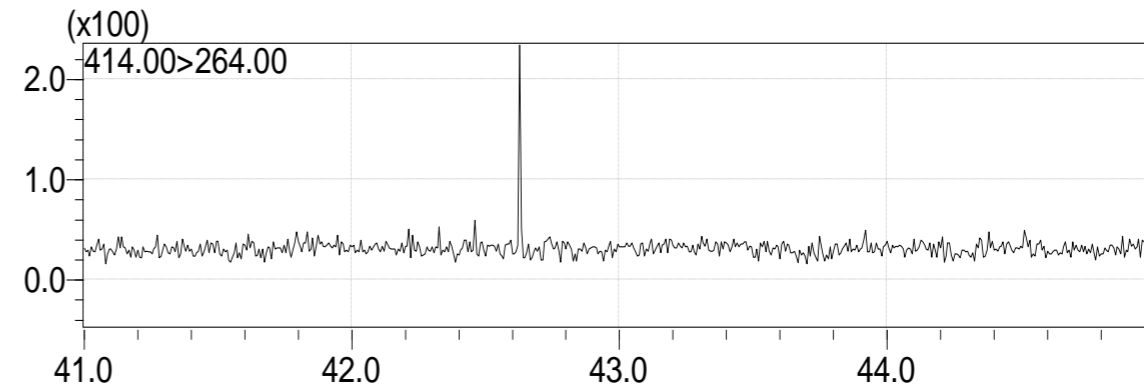
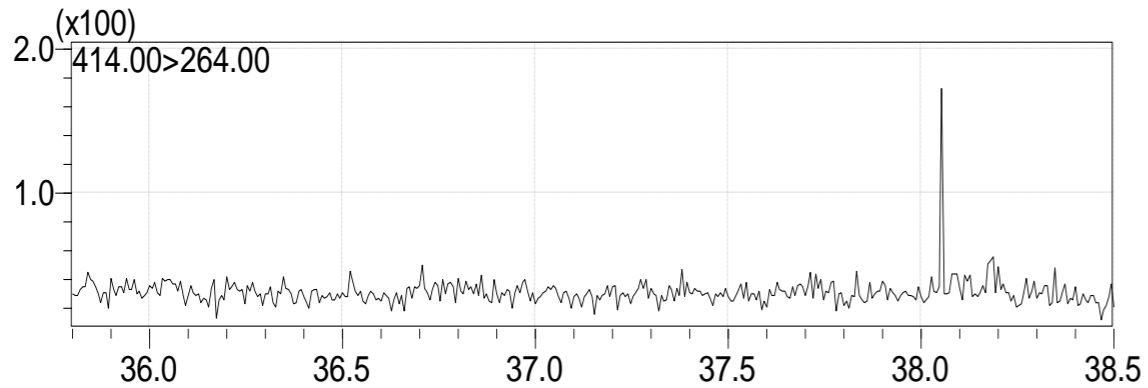
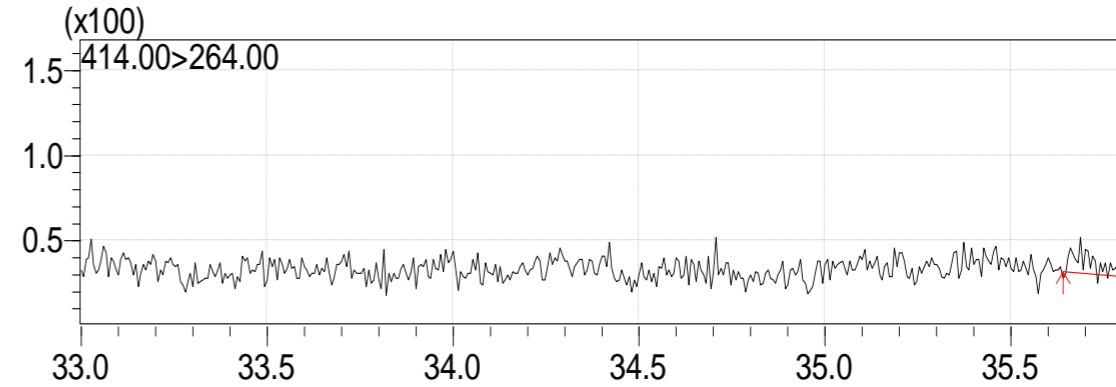
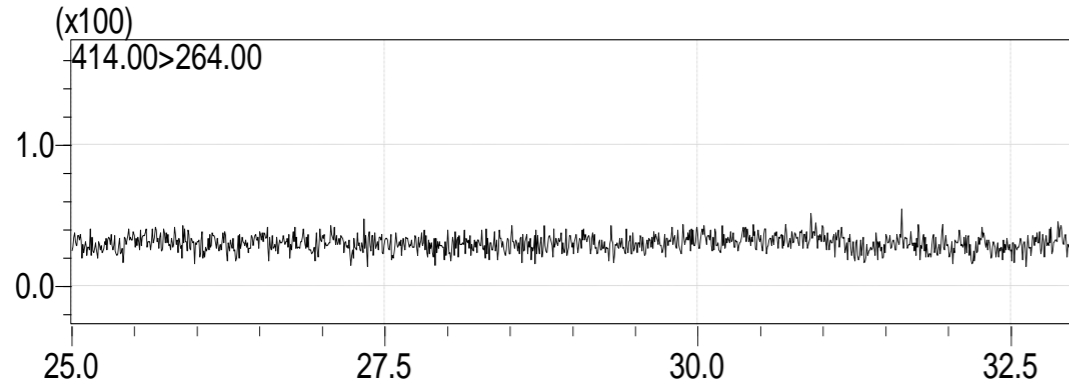
| Compound Name | 5/10/2021 | | 6/12/2021 | | 6/29/2021 | |
|---|-----------|----------|-----------|----------|-----------|----------|
| | Mean RF | RF %RSD | Mean RF | RF %RSD | Mean RF | RF %RSD |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-13C12 (S) | 1.47086 | 1.685002 | 1.419643 | 1.268207 | 1.433139 | 5.098128 |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-37Cl4 * | 3.535532 | 9.139408 | 3.22633 | 5.309459 | 3.483264 | 10.52561 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin-13C12 (S) | 1.380991 | 5.622272 | 1.318395 | 3.667073 | 1.202359 | 2.843046 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 0.980491 | 4.202868 | 0.944708 | 1.775542 | 0.984945 | 3.036991 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 0.911365 | 3.620442 | 0.941063 | 1.6085 | 0.947313 | 2.343127 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin-13C12 (S) | 0.794038 | 2.357297 | 0.809551 | 2.068466 | 0.773139 | 2.021059 |
| Octachlorodibenzo-p-dioxin-13C12 (S) | 0.624091 | 3.632486 | 0.632046 | 5.080355 | 0.581543 | 3.716926 |
| 2,3,7,8-Tetrachlorodibenzofuran-13C12 (S) | 1.787497 | 1.276091 | 1.75273 | 1.622427 | 1.786612 | 1.681549 |
| 1,2,3,7,8-Pentachlorodibenzofuran-13C12 (S) | 1.730429 | 2.938881 | 1.678984 | 3.891992 | 1.509653 | 3.310403 |
| 2,3,4,7,8-Pentachlorodibenzofuran-13C12 (S) | 1.844474 | 4.649975 | 1.797223 | 4.15323 | 1.570551 | 2.668893 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran-13C12 (S) | 1.233442 | 2.280982 | 1.194707 | 2.281161 | 1.217693 | 1.753531 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 1.155494 | 3.868279 | 1.141301 | 2.497376 | 1.180354 | 2.282872 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 1.218267 | 1.324792 | 1.198561 | 1.490342 | 1.207497 | 1.205949 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran-13C12 (S) | 1.055359 | 3.11881 | 1.060354 | 1.934957 | 1.048848 | 3.093955 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran-13C12 (S) | 1.008051 | 6.73874 | 0.992382 | 8.027804 | 0.944264 | 2.538748 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran-13C12 (S) | 0.933166 | 4.688486 | 0.952988 | 3.641022 | 0.928067 | 2.426142 |

* Clean-up standard verification

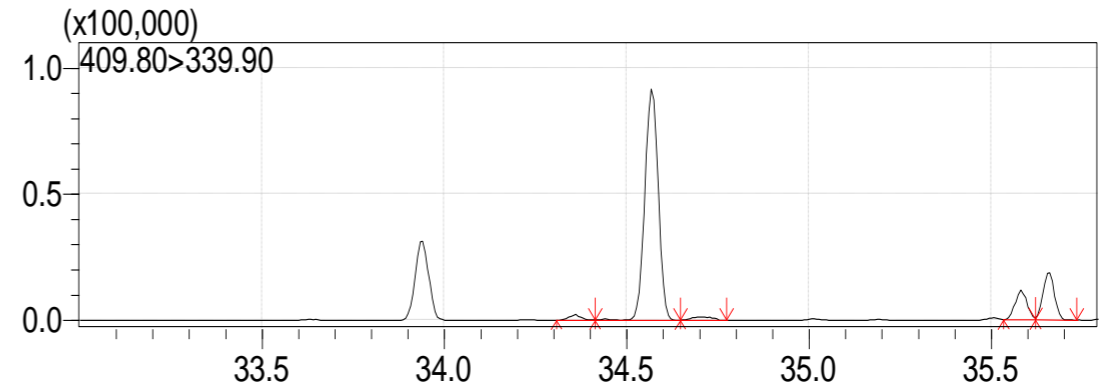
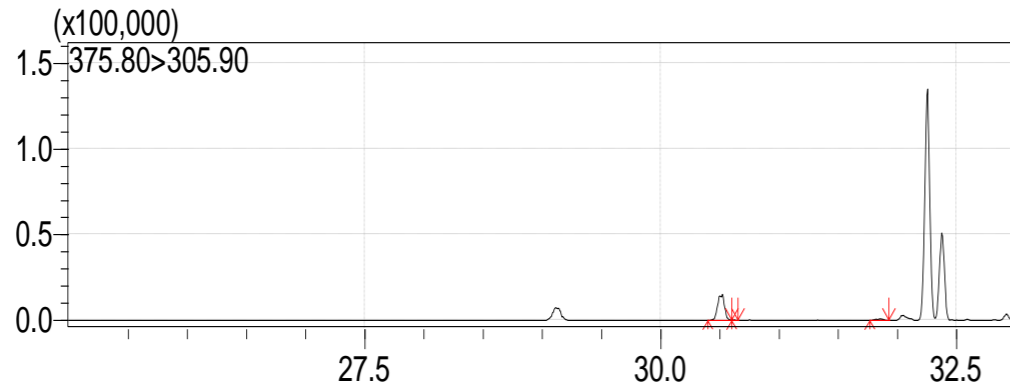
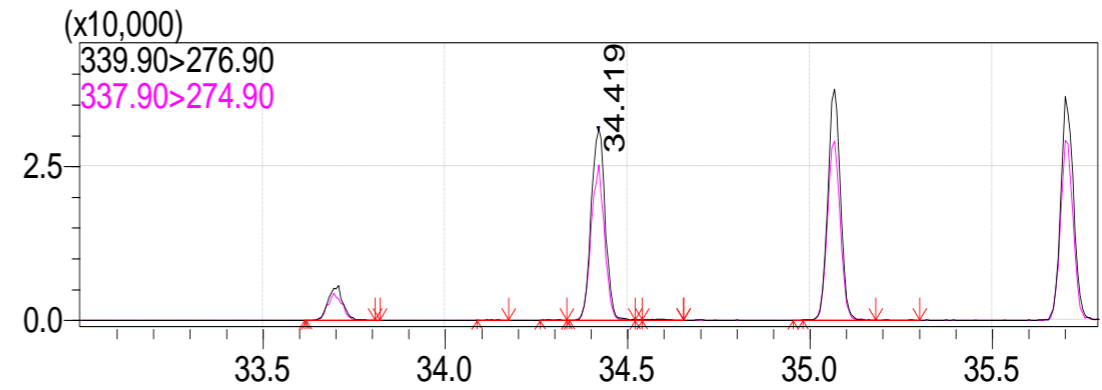
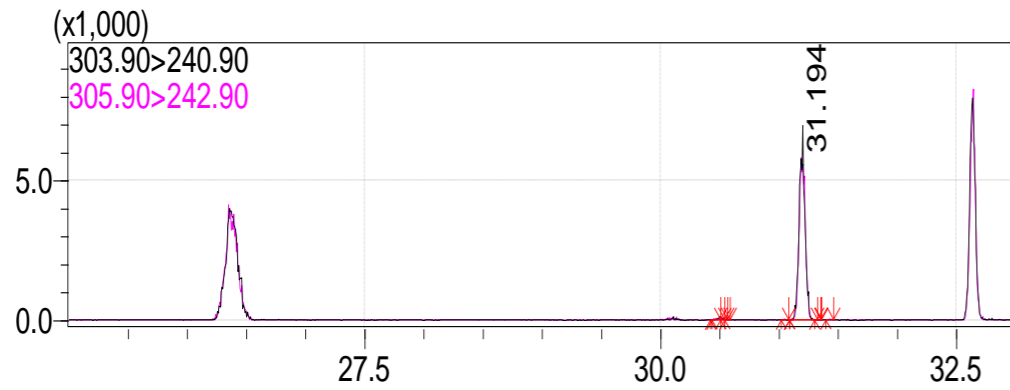
Effect of a Contaminated Soil Matrix on PFTBA (10.4.1.1)



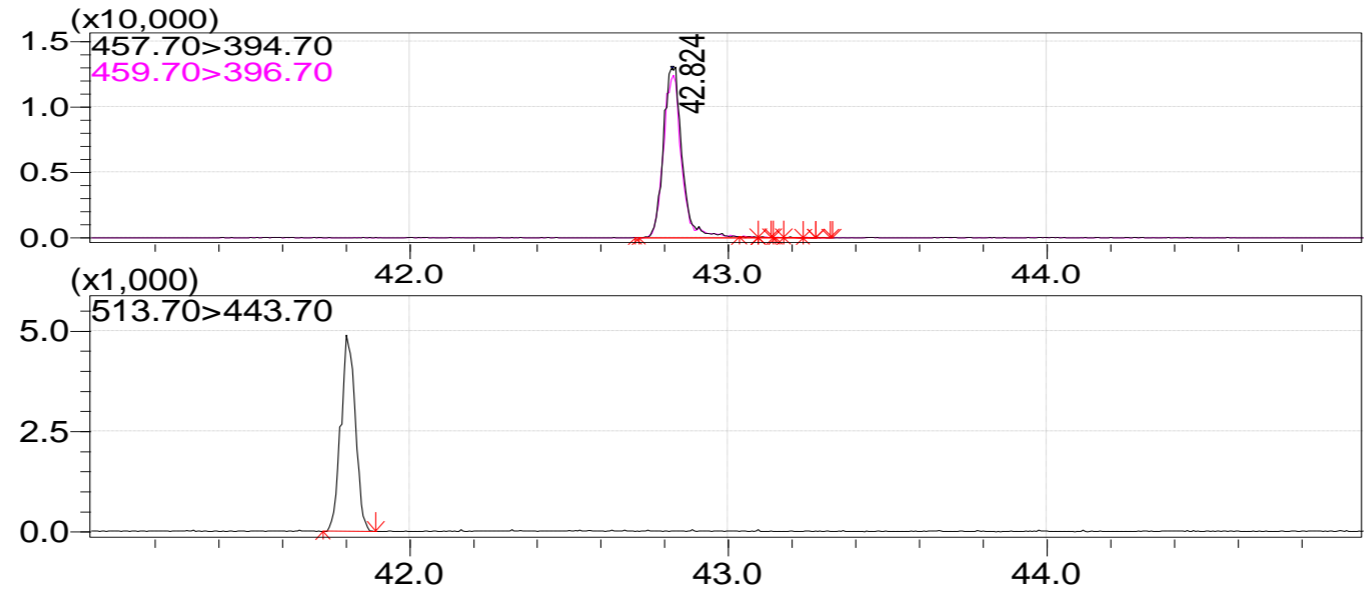
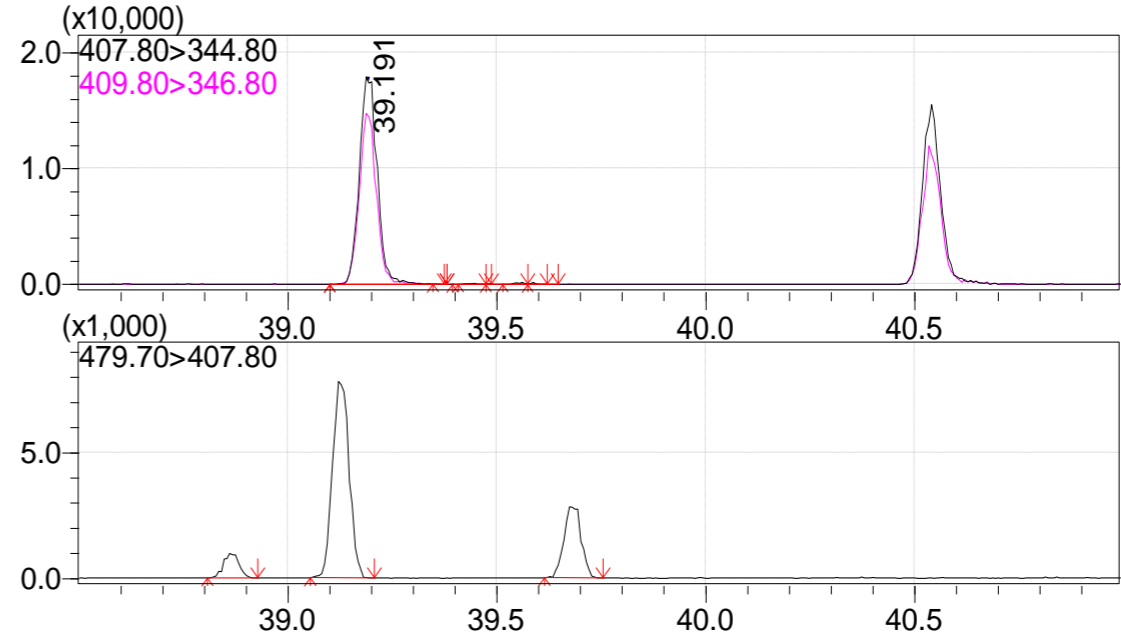
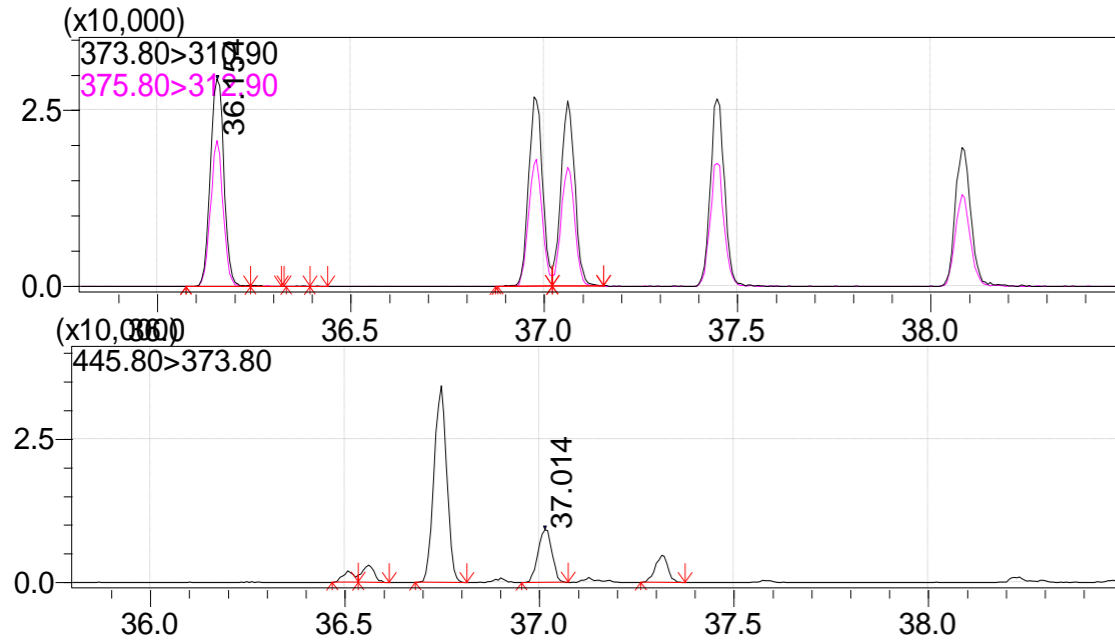
Effects of a Fish Tissue Matrix on PFTBA (10.4.1.1)



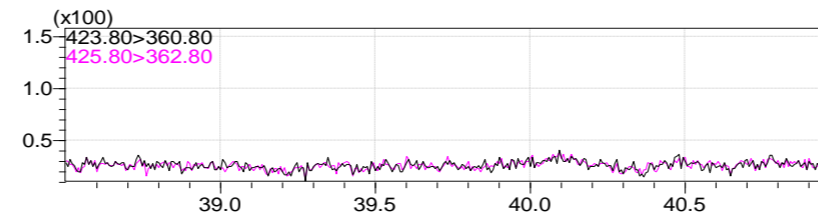
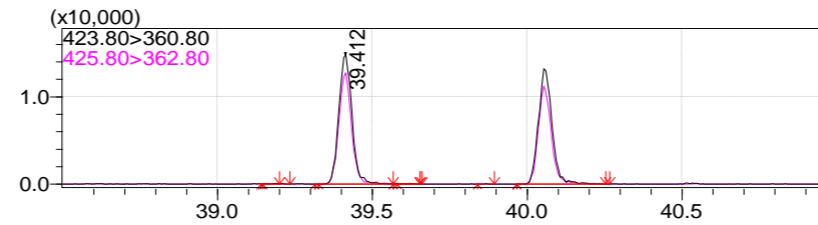
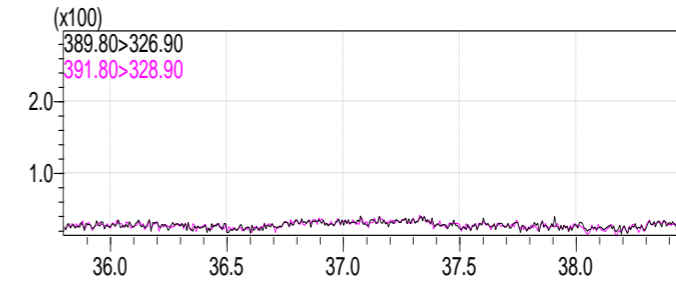
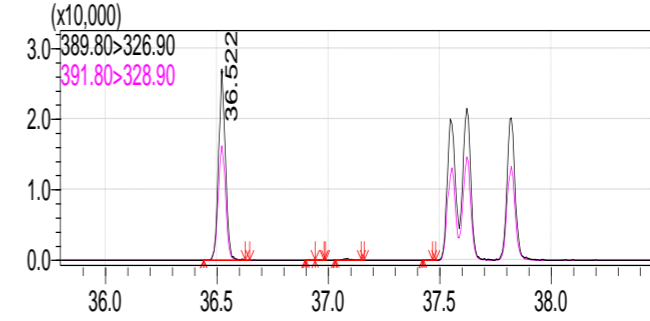
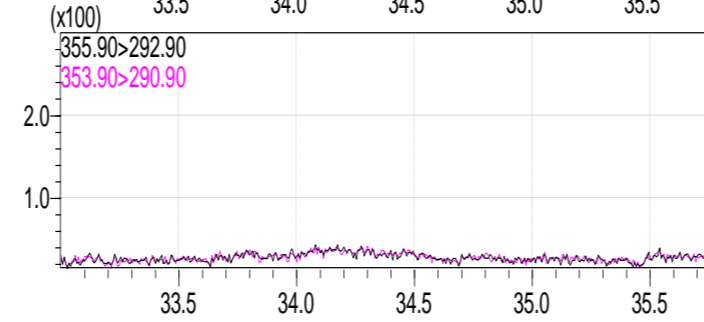
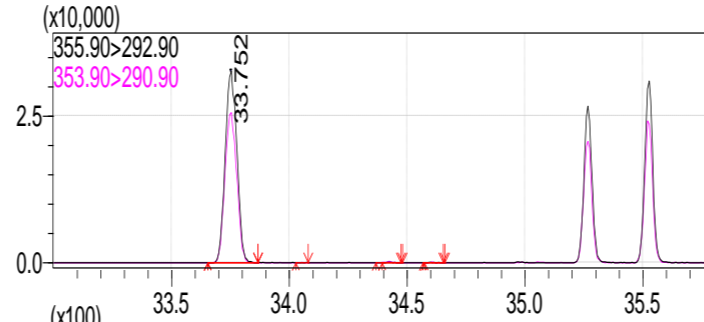
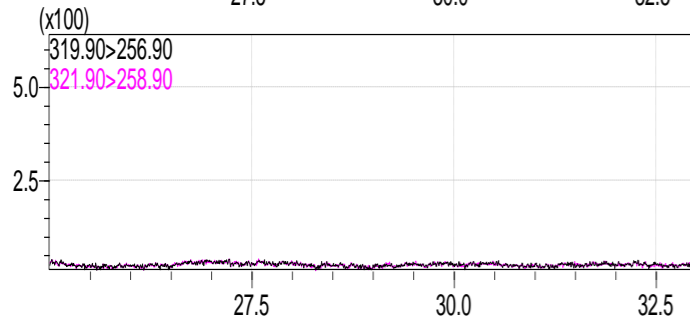
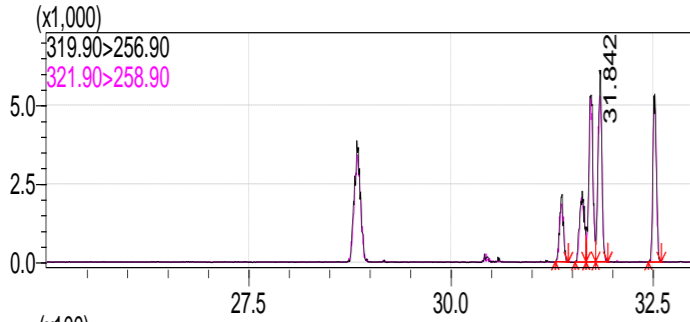
Potential for Ether Interference in tetra- and penta-furans in Tissue Samples (10.4.1.2)



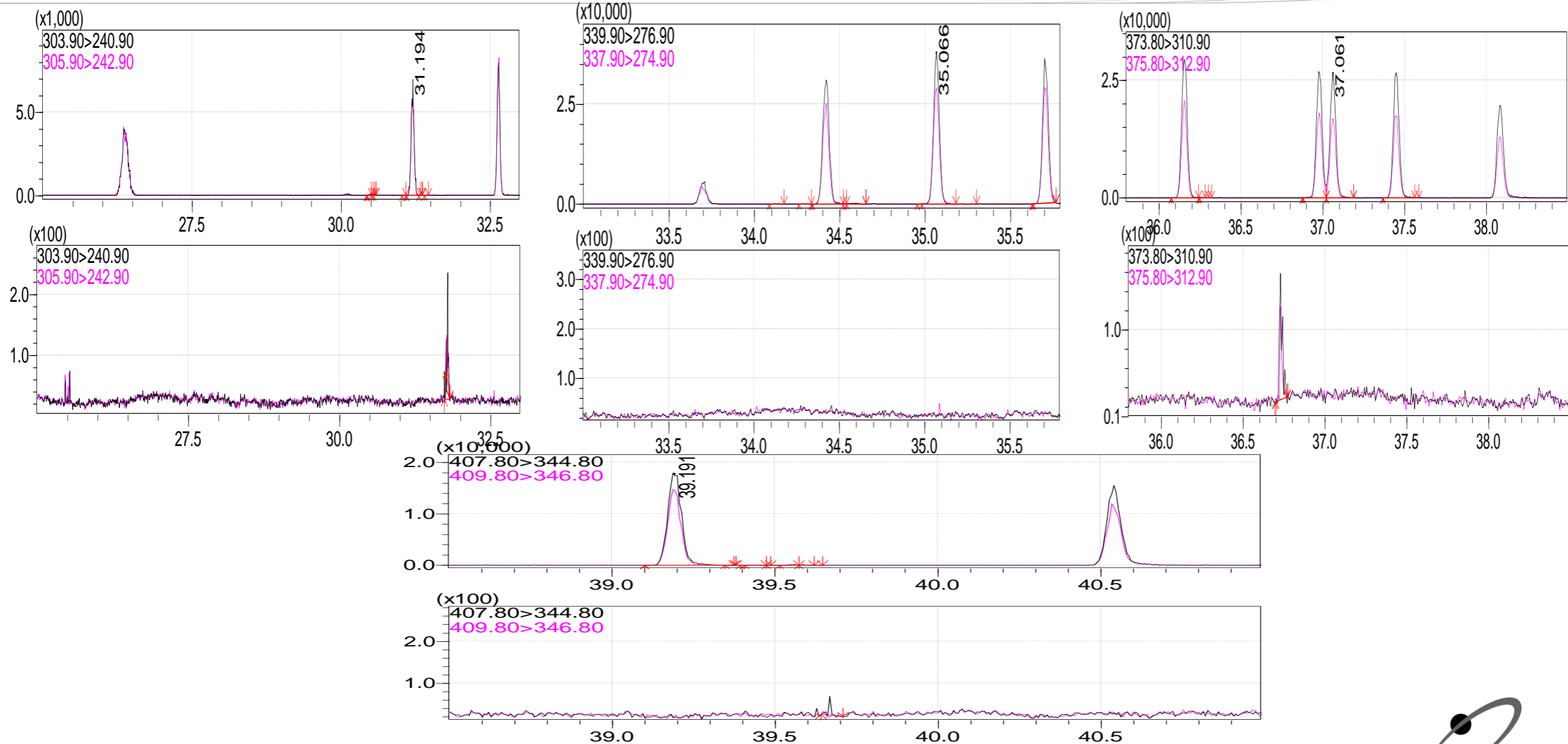
Monitoring for CDPE Interference for Hexa-, Hepta-, and Octa- Furans (10.4.1.2)



Verification – Absence of Interferences by PCBs on Dioxins (10.1.4.3)

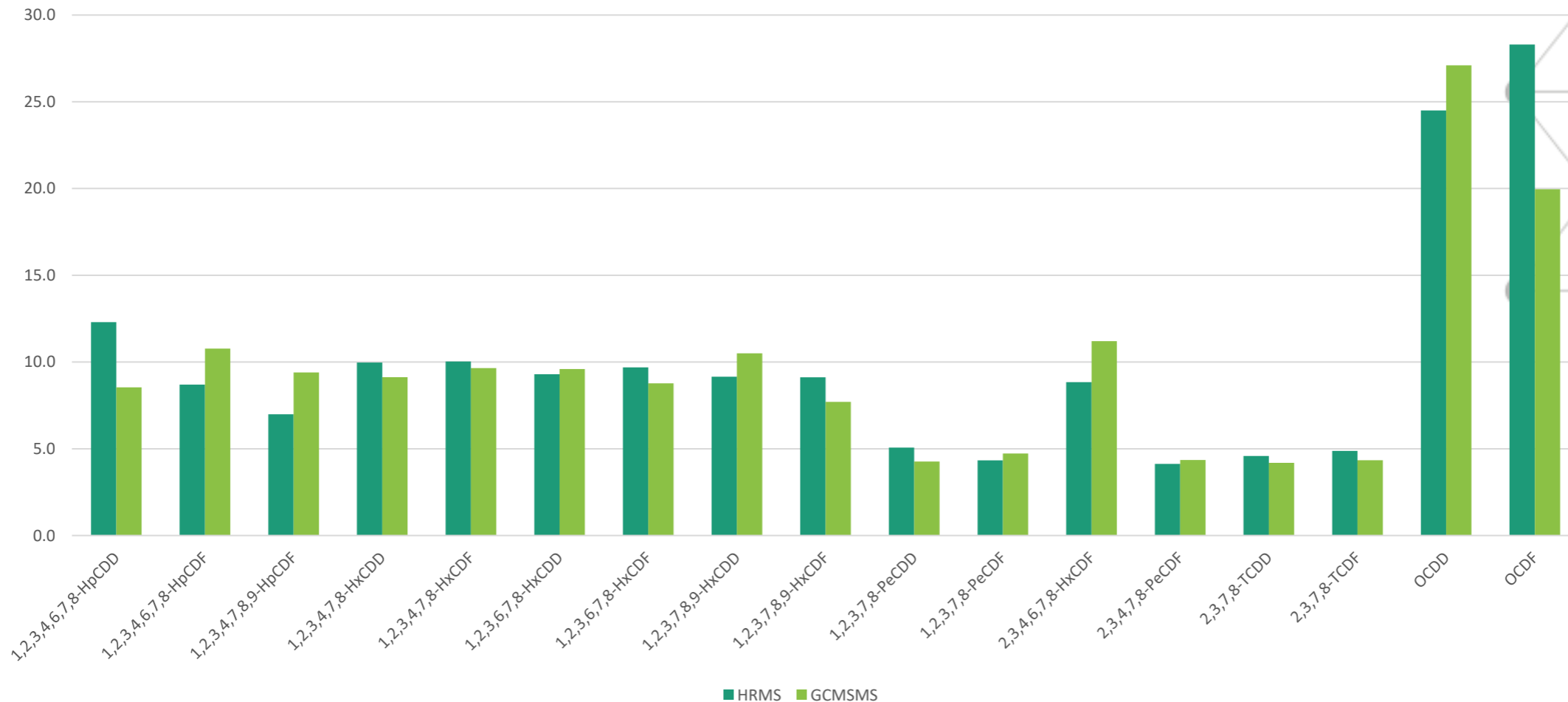


Verification of Absence of Interferences by PCBs on Furans (10.1.4.3)



Analysis of MRL Verification Extracts on HRMS and MS/MS Instruments (aqueous samples)

Comparison of MRL Extracts





Analysis of OPR (LCS) Over Several Months

| Analyte | LCS (7/8/2021) | LCS2 (7/9/2021) | LCS (6/16/2021) | LCS (7/12/2021) | LCS(6/17/2021) | IPR | | OPR | |
|---|----------------|-----------------|-----------------|-----------------|----------------|-----|------|-----|------|
| | | | | | | LCL | UCL | LCL | UCL |
| 2,3,7,8 TCDD | 11 | 9.7 | 10.3 | 10.7 | 10.4 | 8.3 | 12.9 | 6.7 | 15.8 |
| 2,3,7,8 -TCDF | 10 | 9.2 | 10.3 | 10.8 | 9.4 | 8.7 | 13.7 | 7.5 | 15.8 |
| 1,2,3,7,8 PeCDD | 46 | 42 | 43 | 49 | 42 | 38 | 66 | 35 | 71 |
| 1,2,3,7,8-PeCDF | 49 | 46 | 46 | 51 | 44 | 43 | 62 | 40 | 67 |
| 2,3,4,7,8-PeCDF | 49 | 43 | 46 | 53 | 43 | 36 | 75 | 34 | 80 |
| 1,2,3,4,7,8-HxCDD | 56 | 47 | 49 | 55 | 43 | 39 | 76 | 35 | 82 |
| 1,2,3,6,7,8-HxCDD | 52 | 54 | 49 | 52 | 54 | 42 | 62 | 38 | 67 |
| 1,2,3,7,8,9-HxCDD | 54 | 53 | 47 | 57 | 56 | 37 | 71 | 32 | 81 |
| 1,2,3,4,7,8_HxCDF | 52 | 47 | 49 | 54 | 47 | 41 | 59 | 36 | 67 |
| 1,2,3,6,7,8-HxCDF | 48 | 50 | 45 | 53 | 45 | 46 | 60 | 42 | 65 |
| 1,2,3,7,8,9-HxCDF | 38 | 48 | 39 | 52 | 36 | 42 | 61 | 39 | 65 |
| 2,3,4,6,7,8-HxCDF | 68 | 43 | 56 | 53 | 54 | 37 | 74 | 35 | 78 |
| 1,2,3,4,6,7,8-HpCDD | 46 | 43 | 44 | 49 | 42 | 38 | 65 | 35 | 70 |
| 1,2,3,4,6,7,8-HpCDF | 52 | 47 | 48 | 55 | 46 | 45 | 56 | 41 | 61 |
| 1,2,3,4,7,8,9-HpCDF | 52 | 48 | 49 | 54 | 44 | 43 | 63 | 39 | 69 |
| OCDD | 110 | 98 | 105 | 108 | 103 | 89 | 127 | 78 | 144 |
| OCDF | 110 | 97 | 97 | 110 | 89 | 74 | 146 | 63 | 170 |
| Surrogate Recovery | LCS (7/8/2021) | LCS2 (7/9/2021) | LCS (6/16/2021) | LCS (5/29/2021) | LCS(6/17/2021) | IPR | | OPR | |
| | | | | | | LCL | UCL | LCL | UCL |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-13C12 (S) | 70 | 78 | 62 | 63 | 43 | 28 | 134 | 20 | 175 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin-13C12 (S) | 87 | 135 | 88 | 70 | 26 | 27 | 184 | 21 | 227 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 79 | 83 | 73 | 68 | 64 | 29 | 147 | 21 | 193 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 74 | 74 | 70 | 67 | 46 | 34 | 122 | 25 | 163 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin-13C12 (S) | 74 | 83 | 79 | 70 | 70 | 34 | 129 | 26 | 166 |
| Octachlorodibenzo-p-dioxin-13C12 (S) | 57 | 127 | 132 | 113 | 142 | 41 | 276 | 26 | 397 |
| 2,3,7,8-Tetrachlorodibenzofuran-13C12 (S) | 72 | 77 | 61 | 66 | 57 | 31 | 113 | 22 | 152 |
| 1,2,3,7,8-Pentachlorodibenzofuran-13C12 (S) | 69 | 116 | 79 | 65 | 32 | 27 | 156 | 21 | 192 |
| 2,3,4,7,8-Pentachlorodibenzofuran-13C12 (S) | 74 | 126 | 87 | 64 | 30 | 16 | 279 | 13 | 328 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran-13C12 (S) | 75 | 88 | 70 | 68 | 65 | 27 | 152 | 19 | 202 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 79 | 86 | 75 | 60 | 66 | 30 | 122 | 21 | 159 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 77 | 88 | 74 | 70 | 65 | 24 | 157 | 22 | 176 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran-13C12 (S) | 105 | 85 | 54 | 70 | 27 | 29 | 136 | 17 | 205 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran-13C12 (S) | 73 | 84 | 76 | 68 | 68 | 32 | 110 | 21 | 158 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran-13C12 (S) | 68 | 77 | 73 | 66 | 64 | 28 | 141 | 20 | 186 |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-37Cl4 | 71 | 68 | 62 | 81 | 56 | 39 | 154 | 31 | 191 |

Results and Surrogate Recovery in 9 Contaminated Matrices

| Analyte | Matrix 1 | Matrix 2 | Matrix 3 | Matrix 4 | Matrix 5 | Matrix 6 | Matrix 7 | Matrix 8 | Matrix 9 | | |
|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----|-----|
| 2,3,7,8 TCDD | | | 0.3 | | | | | | | | |
| 2,3,7,8 -TCDF | 0.5 | 0.63 | 2.5 | | 0.22 | 0.28 | 0.99 | | | | |
| 1,2,3,7,8 PeCDD | | | 0.87 | | 0.24 | 0.32 | 1.7 | | 0.82 | | |
| 1,2,3,7,8-PeCDF | | | | | | | 0.6 | | 2.9 | | |
| 2,3,4,7,8-PeCDF | 0.88 | 1.2 | 2.5 | 0.3 | 0.7 | 0.61 | 1.2 | 0.81 | 2.7 | | |
| 1,2,3,4,7,8-HxCDD | 0.38 | | | 0.3 | 2.3 | | 3.9 | 0.47 | 0.72 | | |
| 1,2,3,6,7,8-HxCDD | 0.39 | 0.33 | 1.2 | 0.33 | 2.1 | 1.1 | | 0.5 | 1.3 | | |
| 1,2,3,7,8,9-HxCDD | 0.49 | 0.36 | 0.56 | | 1.3 | 0.79 | | 0.77 | 1.1 | | |
| 1,2,3,4,7,8_HxCDF | 0.86 | 1.7 | 5.4 | 0.38 | 1.3 | 1.2 | 1.8 | 1 | 4.7 | | |
| 1,2,3,6,7,8-HxCDF | 0.94 | 1.7 | 3.1 | 0.39 | 1.2 | 1.2 | 1.8 | | 2.6 | | |
| 1,2,3,7,8,9-HxCDF | 0.71 | 2.5 | 3.4 | 0.24 | 0.26 | 0.94 | | 0.82 | 2.2 | | |
| 2,3,4,6,7,8-HxCDF/F | 0.6 | 0.36 | 0.94 | 0.32 | 0.76 | 0.29 | | 0.31 | 1.4 | | |
| 1,2,3,4,6,7,8-HpCDD | 5.1 | 5.3 | 13 | 4.8 | 41 | 33 | 81 | 19 | 20 | | |
| 1,2,3,4,6,7,8-HpCDF | 4.7 | 12 | | 4.2 | 8.2 | | | 8.6 | 18 | | |
| 1,2,3,4,7,8,9-HpCDF | 0.27 | 0.63 | | | 1.2 | 0.74 | | | 0.62 | | |
| OCDD | 20 | 29 | 74 | 1100 | 760 | 240 | 360 | 130 | 100 | | |
| OCDF | 2 | 5.7 | 12 | 5.3 | 44 | | 16 | 5.7 | 15 | | |
| Surrogate Recovery | Matrix 1 | Matrix 2 | Matrix 3 | Matrix 4 | Matrix 5 | Matrix 6 | Matrix 7 | Matrix 8 | Matrix 9 | LCL | UCL |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-13C12 (S) | 61 | 71 | 57 | 75 | 50 | 73 | 62 | 47 | 68 | 20 | 175 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin-13C12 (S) | 69 | 78 | 84 | 106 | 57 | 79 | 88 | 46 | 89 | 21 | 227 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 68 | 73 | 63 | 88 | 48 | 63 | 54 | 54 | 69 | 21 | 193 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 65 | 76 | 66 | 79 | 51 | 63 | 57 | 50 | 66 | 25 | 163 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin-13C12 (S) | 65 | 70 | 61 | 81 | 47 | 62 | 75 | 50 | 74 | 26 | 166 |
| Octachlorodibenzo-p-dioxin-13C12 (S) | 56 | 50 | 40 | 2 | 0 | 35 | 32 | 35 | 52 | 26 | 397 |
| 2,3,7,8-Tetrachlorodibenzofuran-13C12 (S) | 64 | 69 | 59 | 76 | 53 | 60 | 53 | 48 | 72 | 22 | 152 |
| 1,2,3,7,8-Pentachlorodibenzofuran-13C12 (S) | 60 | 71 | 67 | 77 | 50 | 57 | 58 | 49 | 68 | 21 | 192 |
| 2,3,4,7,8-Pentachlorodibenzofuran-13C12 (S) | 61 | 69 | 74 | 83 | 54 | 61 | 73 | 48 | 67 | 13 | 328 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran-13C12 (S) | 65 | 74 | 58 | 82 | 47 | 62 | 54 | 54 | 67 | 19 | 202 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 69 | 72 | 60 | 83 | 51 | 62 | 58 | 52 | 67 | 21 | 159 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 68 | 75 | 63 | 84 | 52 | 64 | 57 | 53 | 71 | 22 | 176 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran-13C12 (S) | 127 | 77 | 75 | 139 | 92 | 59 | 62 | 98 | 117 | 17 | 205 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran-13C12 (S) | 64 | 70 | 61 | 81 | 47 | 61 | 75 | 49 | 74 | 21 | 158 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran-13C12 (S) | 63 | 65 | 55 | 78 | 9 | 55 | 47 | 46 | 52 | 20 | 186 |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-37Cl4 | 61 | 58 | 75 | 79 | 72 | 65 | 54 | 82 | 69 | 31 | 191 |

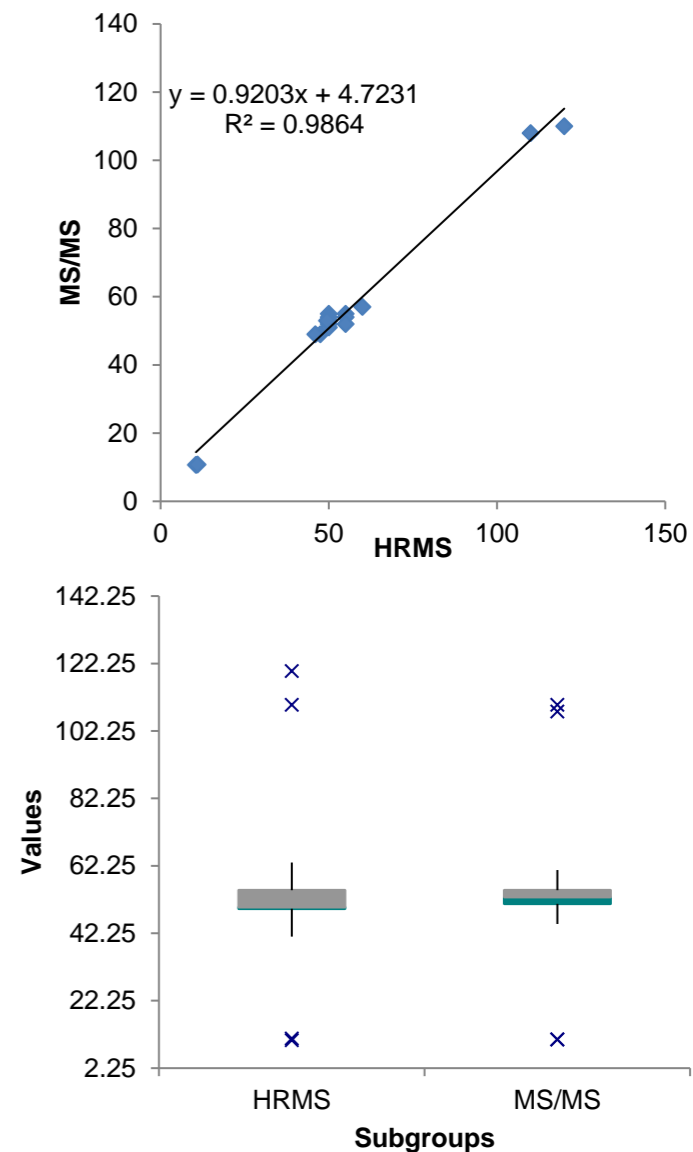
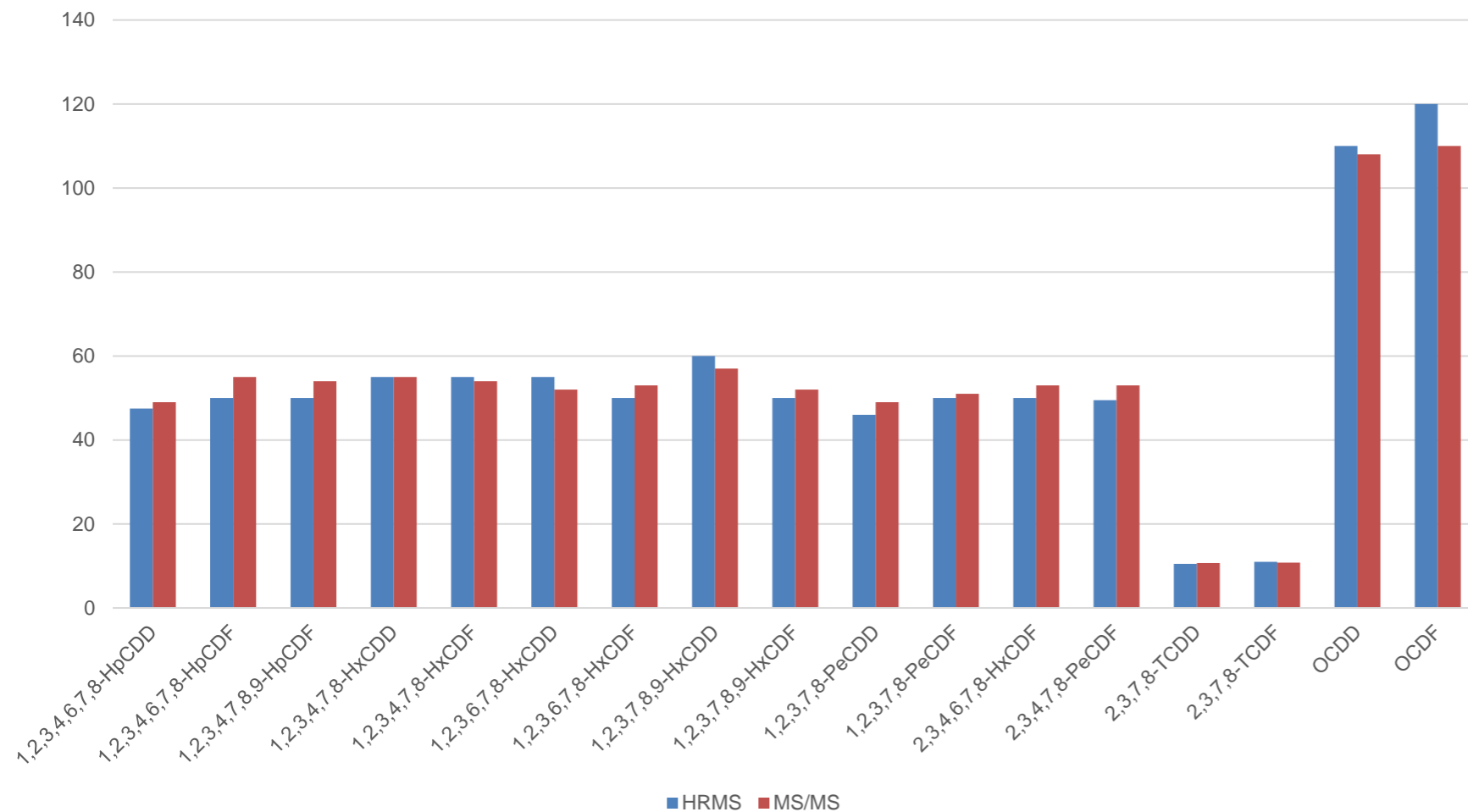


Matrix Spike and Matrix Spike Duplicate results – 2 sets

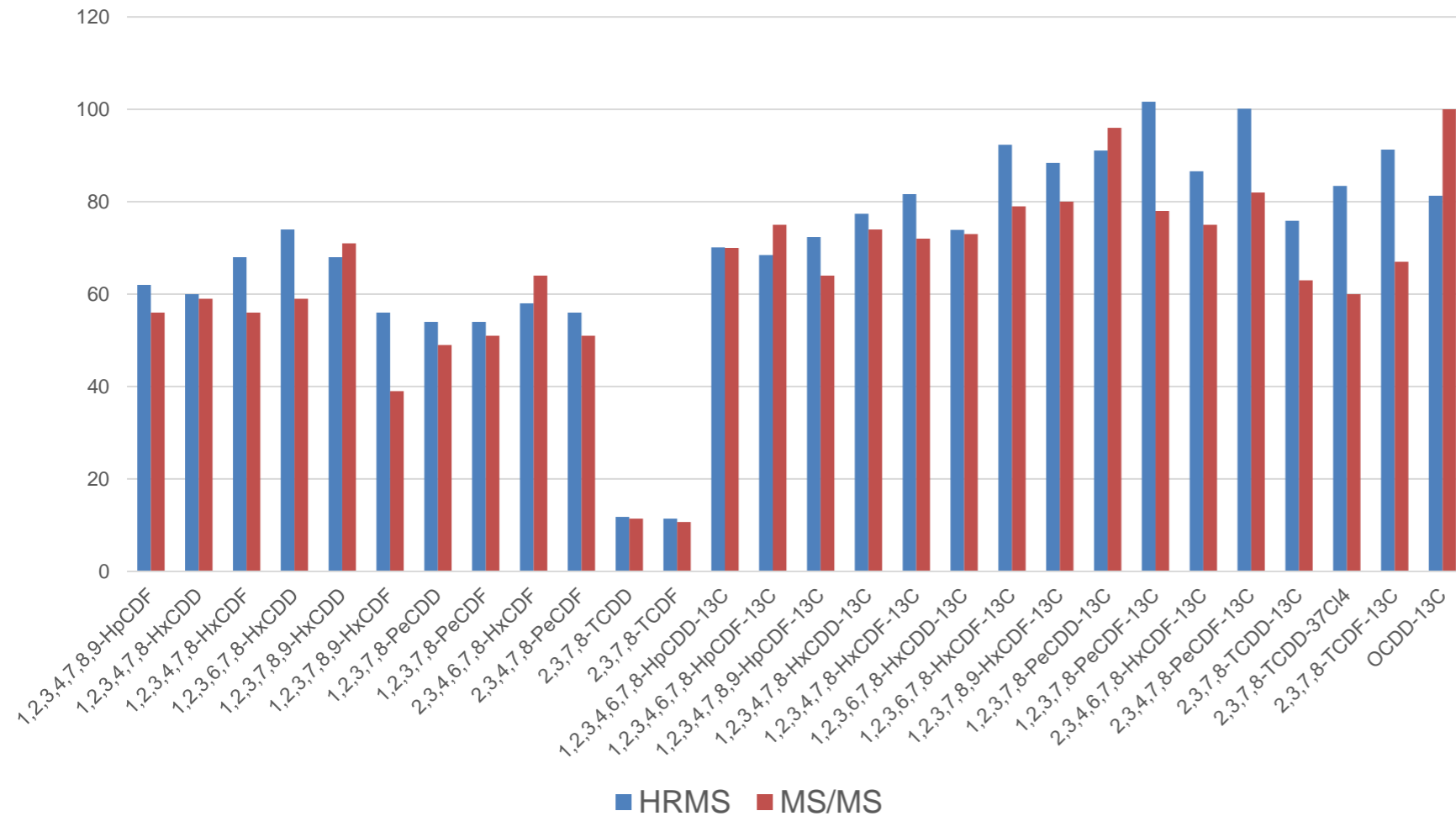
| Analyte | MS1 | MS1D | MS2 | MS2D | Blank | | |
|---|-----|------|-----|------|-------|-----|-----|
| 2,3,7,8 TCDD | 9.8 | 11 | 9.9 | 9.6 | | | |
| 2,3,7,8 -TCDF | 10 | 14 | 11 | 10 | | | |
| 1,2,3,7,8 PeCDD | 44 | 47 | 45 | 44 | | | |
| 1,2,3,7,8-PeCDF | 47 | 52 | 49 | 48 | | | |
| 2,3,4,7,8-PeCDF | 47 | 54 | 55 | 47 | | | |
| 1,2,3,4,7,8-HxCDD | 48 | 51 | 54 | 50 | | | |
| 1,2,3,6,7,8-HxCDD | 53 | 57 | 52 | 53 | | | |
| 1,2,3,7,8,9-HxCDD | 52 | 62 | 52 | 50 | | | |
| 1,2,3,4,7,8_HxCDF | 50 | 56 | 51 | 50 | | | |
| 1,2,3,6,7,8-HxCDF | 46 | 51 | 52 | 51 | | | |
| 1,2,3,7,8,9-HxCDF | 26 | 32 | 42 | 40 | | | |
| 2,3,4,6,7,8-HxCDF | 83 | 88 | 61 | 55 | | | |
| 1,2,3,4,6,7,8-HpCDD | 51 | 62 | 92 | 57 | | | |
| 1,2,3,4,6,7,8-HpCDF | 53 | 63 | 66 | 52 | | | |
| 1,2,3,4,7,8,9-HpCDF | 50 | 53 | 52 | 50 | | | |
| OCDD | 120 | 160 | 480 | 150 | | | |
| OCDF | 100 | 110 | 130 | 97 | | | |
| Surrogate Recovery | MS1 | MS1D | MS2 | MS2D | Blank | LCL | UCL |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-13C12 (S) | 60 | 64 | 57 | 67 | 60 | 20 | 175 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin-13C12 (S) | 65 | 73 | 85 | 101 | 70 | 21 | 227 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 65 | 73 | 59 | 70 | 68 | 21 | 193 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin-13C12 (S) | 58 | 64 | 61 | 66 | 66 | 25 | 163 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin-13C12 (S) | 61 | 73 | 60 | 67 | 68 | 26 | 166 |
| Octachlorodibenzo-p-dioxin-13C12 (S) | 51 | 54 | 47 | 45 | 57 | 26 | 397 |
| 2,3,7,8-Tetrachlorodibenzofuran-13C12 (S) | 63 | 66 | 58 | 69 | 63 | 22 | 152 |
| 1,2,3,7,8-Pentachlorodibenzofuran-13C12 (S) | 57 | 63 | 69 | 80 | 60 | 21 | 192 |
| 2,3,4,7,8-Pentachlorodibenzofuran-13C12 (S) | 59 | 66 | 71 | 83 | 65 | 13 | 328 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran-13C12 (S) | 64 | 68 | 59 | 66 | 66 | 19 | 202 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 66 | 71 | 61 | 67 | 69 | 21 | 159 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran-13C12 (S) | 65 | 70 | 60 | 69 | 69 | 22 | 176 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran-13C12 (S) | 120 | 123 | 76 | 82 | 123 | 17 | 205 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran-13C12 (S) | 61 | 73 | 60 | 67 | 68 | 21 | 158 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran-13C12 (S) | 59 | 69 | 64 | 59 | 65 | 20 | 186 |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin-37Cl4 | 54 | 63 | 45 | 63 | 68 | 31 | 191 |

Comparison of LCS Data Between the Two Instrument - Same extract...MS/MS data more precise.

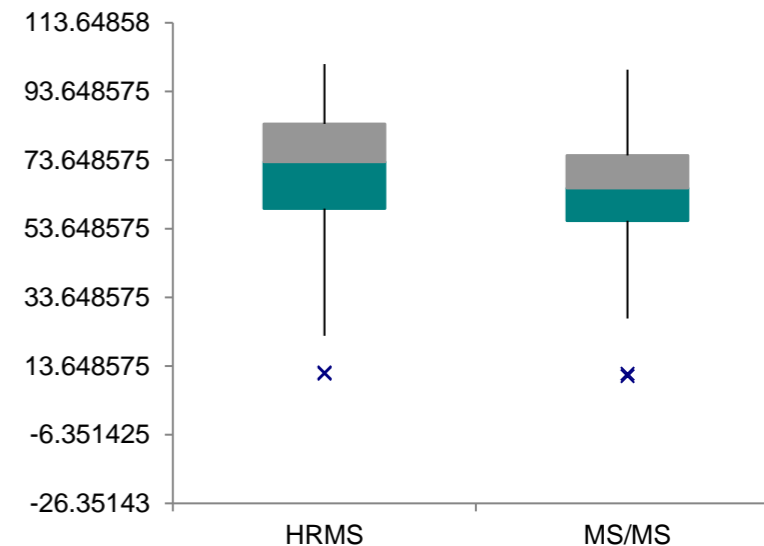
Comparison of HRMS and MS/MS results on an LCS



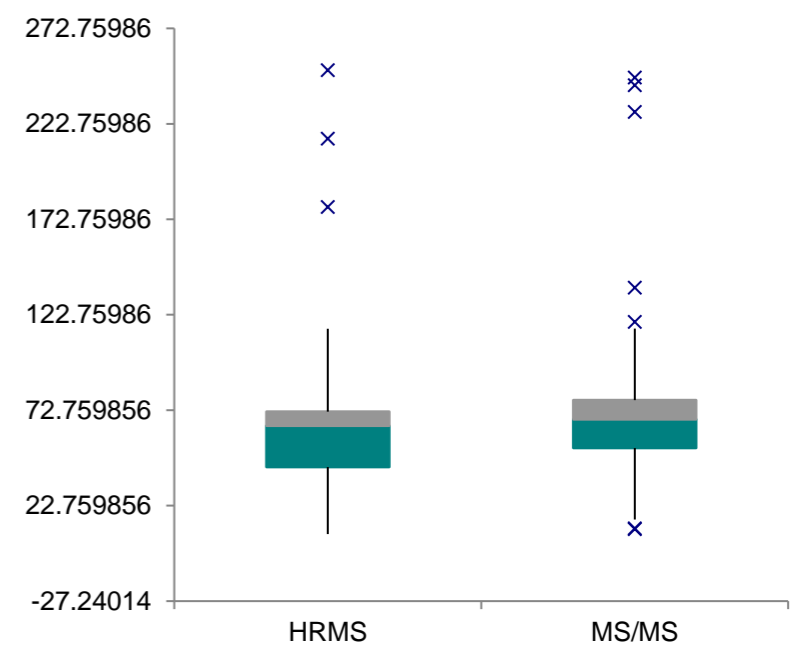
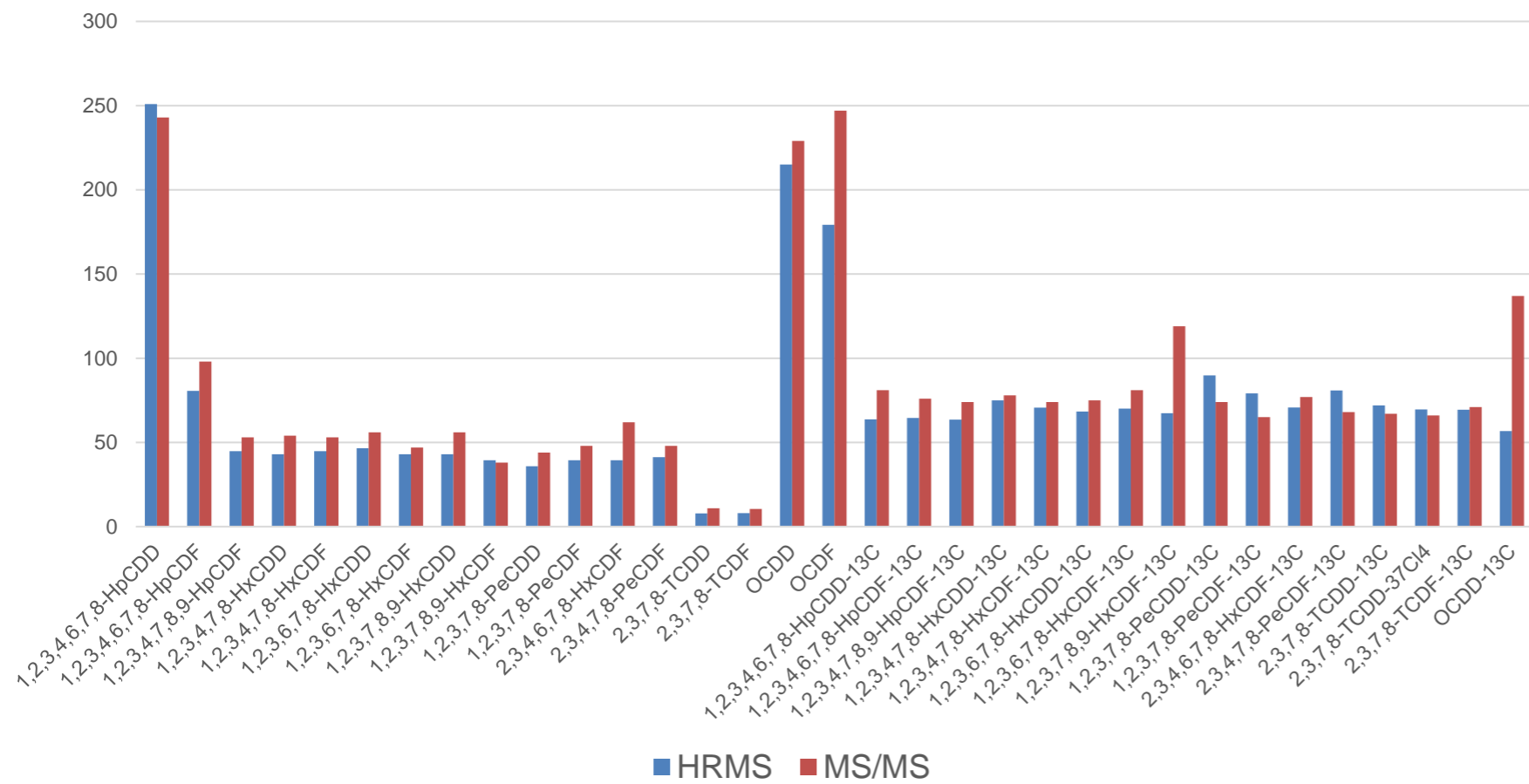
Comparison of Matrix Spike Data (solid sample) - MS/MS Data... More precise, slightly lower

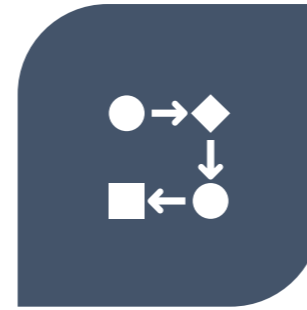


Flagged HRMS data excluded



Comparison of Matrix Spike Data (solid sample - MS/MS data...More precise, slightly higher





**DATA IS PRELIMINARY AND
WAITING FOR COMPLETE
VALIDATION (OF DATA).**



**THIS PRESENTATION
REPRESENTS PROGRESS TO
DATE**



**PRELIMINARY DATA SHOWS
MS/MS SUITABLE AS AN
ALTERNATIVE DETECTOR FOR
HRMS**

Summary and Conclusion

Thank You

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