

Analysis of Dioxins and PCBs

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Regulated PCBs

BZ_1992	IUPAC_NAME	BTAG_ECO	NOAA_SUM	CSL Dx / Planar PCBs	MC_HIPRIO	MC_2PRIO	ION_1	ION_2	ION_RATIO	WHO TEF 98	WHO TEF 05	Coelute_DB5
28	2,4,4'-Trichlorobiphenyl	TRUE	TRUE		FALSE	FALSE	255.9613	257.9586	1.03			31
52	2,2',5,5'-Tetrachlorobiphenyl	TRUE	TRUE		FALSE	TRUE	289.9224	291.9194	0.78			
77	3,3',4,4'-Tetrachlorobiphenyl	TRUE	TRUE	TRUE	TRUE	FALSE	289.9224	291.9194	0.78	0.0001	0.0001	110
81	3,4,4',5-Tetrachlorobiphenyl	TRUE	FALSE	TRUE	FALSE	TRUE	289.9224	291.9194	0.78	0.0001	0.0003	
101	2,2',4,5,5'-Pentachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	325.8804	327.8774	1.55			84,90
105	2,3,3',4,4'-Pentachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	325.8804	327.8774	1.55	0.0001	0.00003	132,153
114	2,3,4,4',5-Pentachlorobiphenyl	TRUE	FALSE		FALSE	TRUE	325.8804	327.8774	1.55	0.0005	0.00003	
118	2,3',4,4',5-Pentachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	325.8804	327.8774	1.55	0.0001	0.00003	149
123	2,3',4,4',5'-Pentachlorobiphenyl	TRUE	FALSE		FALSE	TRUE	325.8804	327.8774	1.55	0.0001	0.00003	149
126	3,3',4,4',5-Pentachlorobiphenyl	TRUE	TRUE	TRUE	TRUE	FALSE	325.8804	327.8774	1.55	0.1	0.1	
138	2,2',3,4,4',5'-Hexachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	359.8415	361.8395	1.24			160,163
153	2,2',4,4',5,5'-Hexachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	359.8415	361.8395	1.24			132,105
156	2,3,3',4,4',5-Hexachlorobiphenyl	TRUE	FALSE		TRUE	FALSE	359.8415	361.8395	1.24	0.0005	0.00003	171,202
157	2,3,3',4,4',5'-Hexachlorobiphenyl	TRUE	FALSE		FALSE	TRUE	359.8415	361.8395	1.24	0.0005	0.00003	
167	2,3',4,4',5,5'-Hexachlorobiphenyl	TRUE	FALSE		FALSE	TRUE	359.8415	361.8395	1.24	0.00001	0.00003	128,162
169	3,3',4,4',5,5'-Hexachlorobiphenyl	TRUE	TRUE	TRUE	TRUE	FALSE	359.8415	361.8395	1.24	0.01	0.03	
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	TRUE	TRUE		TRUE	FALSE	393.8025	395.7995	1.04			
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	TRUE	FALSE		FALSE	TRUE	393.8025	395.7995	1.04	0.0001	0.00003	

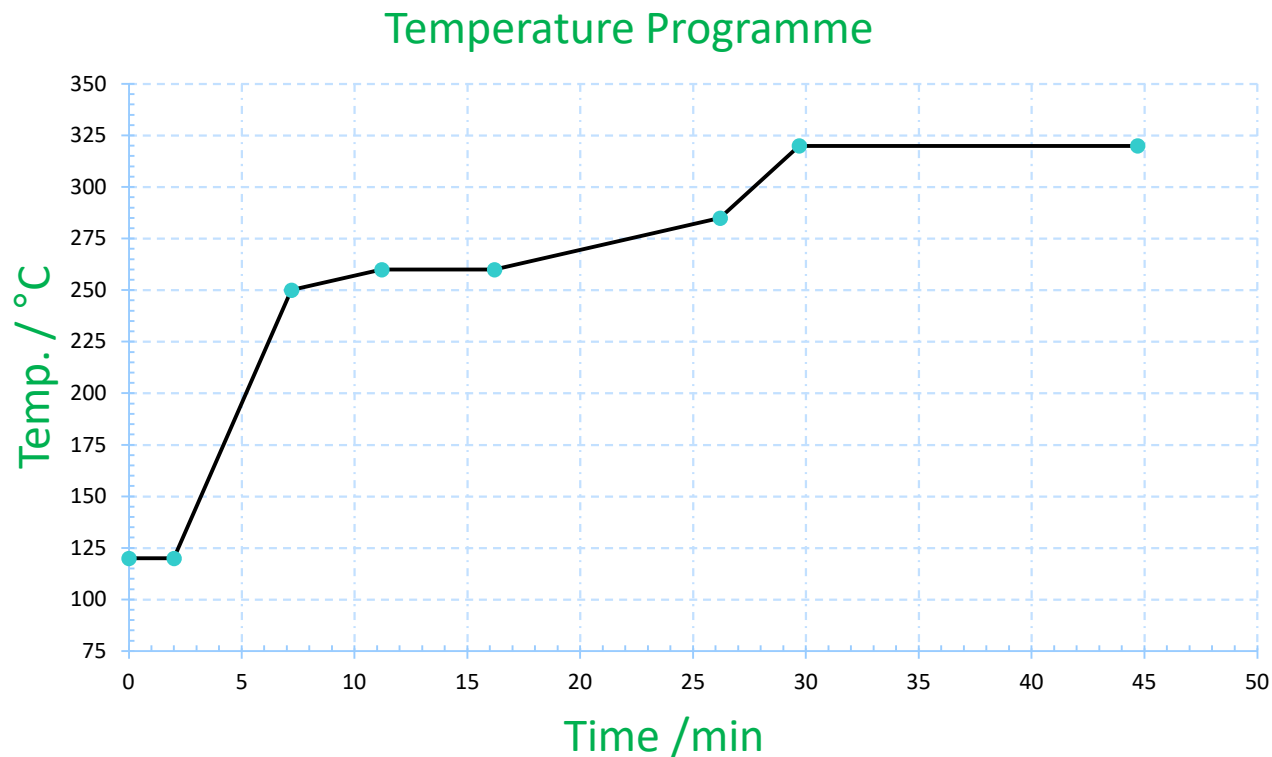
Separation usually performed on DB-5 column

Alternative GC phases: TG-Dioxin, HT-8, XLB



Oven Programme for TG-Dioxin Column

- 60 m column, 0.25 mm x 0.25 μm film
- Same programme for PCBs or dioxins



PCBs – ions monitored from Isotope clusters

	No. of C	No. of H	Total Cl	No. of		Exact mass	Theoretical intensity	Relative intensity	¹³ C ₁₂ surrogates		
				³⁵ Cl	³⁷ Cl						
PCB40 to PCB81	12	6	4	4	0	289.9224M	95.83	0.782	301.9626		
	12	6	4	3	1	291.9194M+2	122.52	1.000	303.9597	0.782	
	12	6	4	2	2	293.9165M+4	58.74	0.479	305.9567		
	291.988	12	6	4	1	3	295.9135M+6	9.39	0.077	307.9538	
	12	6	4	0	4	297.9106M+8	1.00	0.008			

	No. of C	No. of H	Total Cl	No. of		Exact mass	Theoretical intensity	Relative intensity	¹³ C ₁₂ surrogates		
				³⁵ Cl	³⁷ Cl						
PCB82 to PCB127	12	5	5	5	0	323.8834M	299.85	0.626	335.9236		
	12	5	5	4	1	325.8804M+2	479.17	1.000	337.9207	1.564	
	12	5	5	3	2	327.8775M+4	306.30	0.639	339.9177		
	326.433	12	5	5	2	3	329.8745M+6	97.90	0.204	341.9148	
	12	5	5	1	4	331.8716M+8	15.64	0.033			
	12	5	5	0	5	333.8686M+10	1.00	0.002			



Isotope clusters – Patterns of intensity

												Degree of Halogenation	No. of Peaks in cluster
											1	0	1
									1	1	1	1	2
							1	2	1	1	2	3	
					1	3	3	1	1	1	3	4	
				1	4	6	4	1	1	1	4	5	
			1	5	10	10	5	1	1	1	5	6	
		1	6	15	20	15	6	1	1	1	6	7	
	1	7	21	35	35	21	7	1	1	1	7	8	
	1	8	28	56	70	56	28	8	1	1	8	9	
	1	9	36	84	126	126	84	36	9	1	9	10	
1	10	45	120	210	252	210	120	45	10	1	10	11	

Relative peak intensities



Monitored Ions

- Dioxins and PCBs by HRMS
 - Select M^+ and $[M+2]^+$ peaks, or $[M+2]^+$ and $[M+4]^+$
- Dioxins and PCBs by MS/MS (EI)
 - Dioxins – Loss of COCl from parent ion / $[M+2]^+$
 - PCBs – Loss of Cl_2 from parent ion / $[M+2]^+$



Monitored Ions – PCDD/Fs

Congener	Precursor ion	Product ion	Collision
			Energy
TetraCDF	303.9	240.9	33
TetraCDF	305.9	242.9	33
13C12-TetraCDF	315.9	251.9	33
13C12-TetraCDF	317.9	253.9	33
TetraCDD	319.9	256.9	24
TetraCDD	321.9	258.9	24
13C12-TetraCDD	331.9	267.9	24
13C12-TetraCDD	333.9	269.9	24
PentaCDF	337.9	274.9	35
PentaCDF	339.9	276.9	35
13C12-PentaCDF	349.9	285.9	35
13C12-PentaCDF	351.9	287.9	35
PentaCDD	353.9	290.9	25
PentaCDD	355.9	292.9	25
13C12-PentaCDD	365.9	301.9	25
13C12-PentaCDD	367.9	303.9	25
HexaCDF	373.8	310.9	35
HexaCDF	375.8	312.9	35
13C12-HexaCDF	385.8	321.9	35
13C12-HexaCDF	387.8	323.9	35

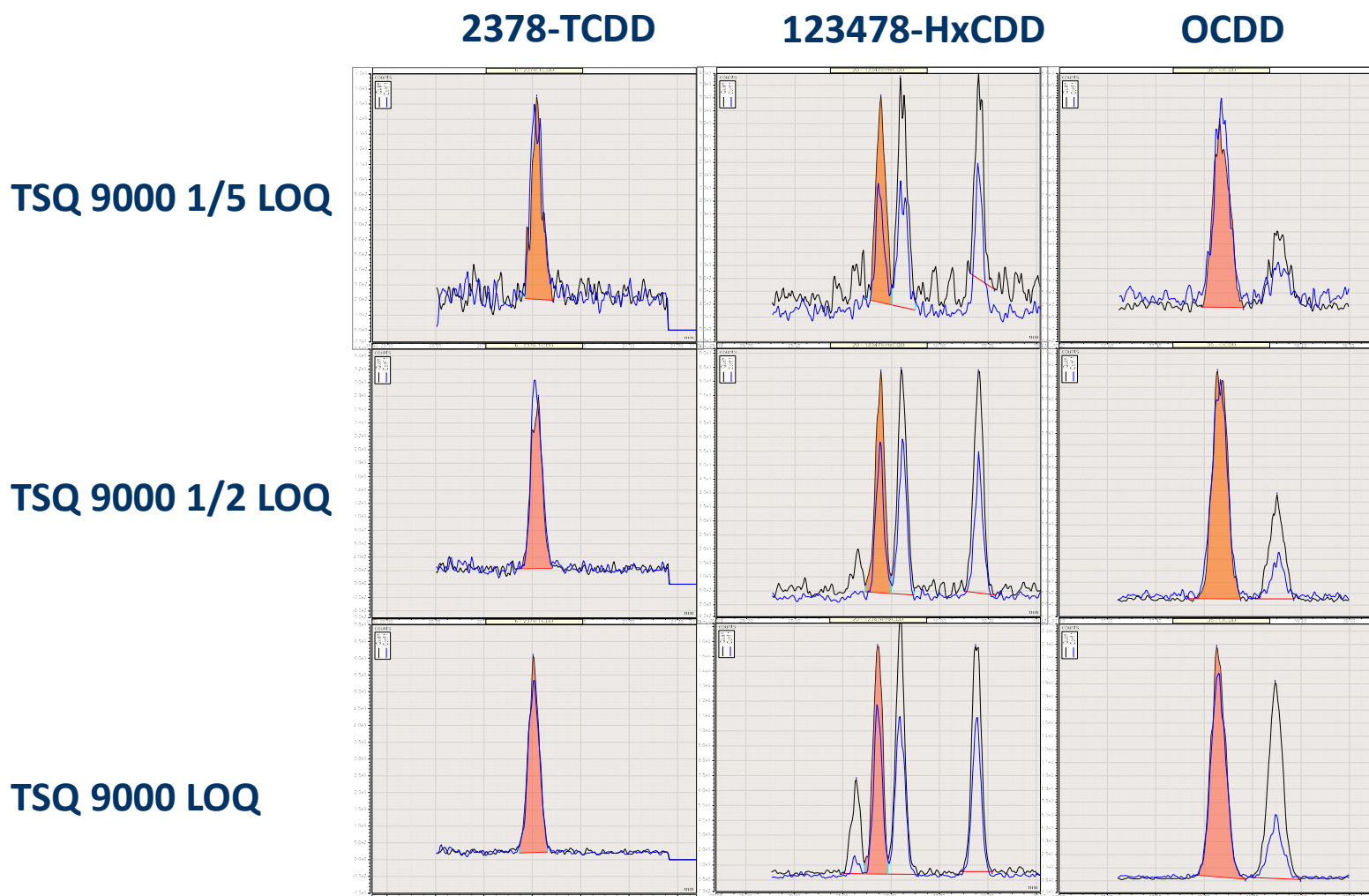


Monitored Ions – PCDD/Fs

Congener	Precursor ion	Product ion	Collision Energy
HexaCDD	389.8	326.9	25
HexaCDD	391.8	328.9	25
13C12-HexaCDD	401.8	337.8	25
13C12-HexaCDD	403.8	339.8	25
HeptaCDF	407.8	344.8	36
HeptaCDF	409.8	346.8	36
13C12-HeptaCDF	419.8	355.8	36
13C12-HeptaCDF	421.8	357.8	36
HeptaCDD	423.8	360.8	25
HeptaCDD	425.8	362.8	25
13C12-HeptaCDD	435.8	371.8	25
13C12-HeptaCDD	437.8	373.8	25
OctaCDF	441.7	378.8	35
OctaCDF	443.7	380.8	35
13C12-OctaCDF	453.7	389.8	35
13C12-OctaCDF	455.7	391.8	35
OctaCDD	457.7	394.8	26
OctaCDD	459.7	396.8	26
13C12-OctaCDD	469.7	405.8	26
13C12-OctaCDD	471.7	407.8	26



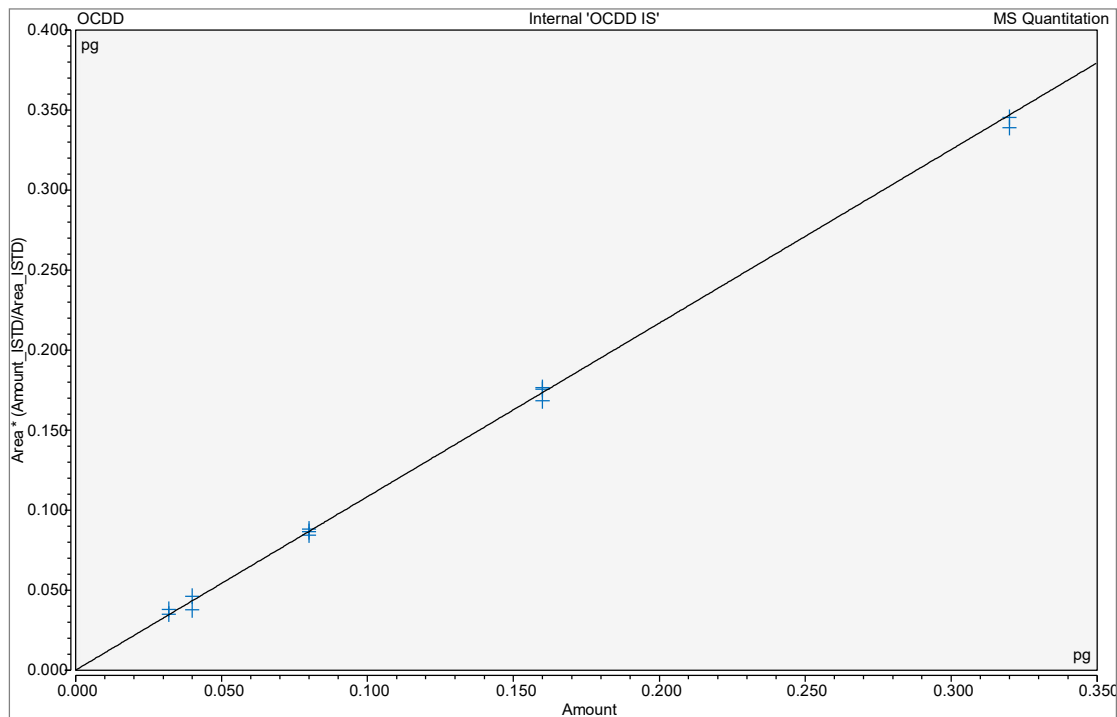
LOQs – GC-MS/MS, 2 μ L injection



No data smoothing applied, ion ratios and RRFs within $\pm 15\%$ of calibration average



Calibration: OCDD (MS/MS)



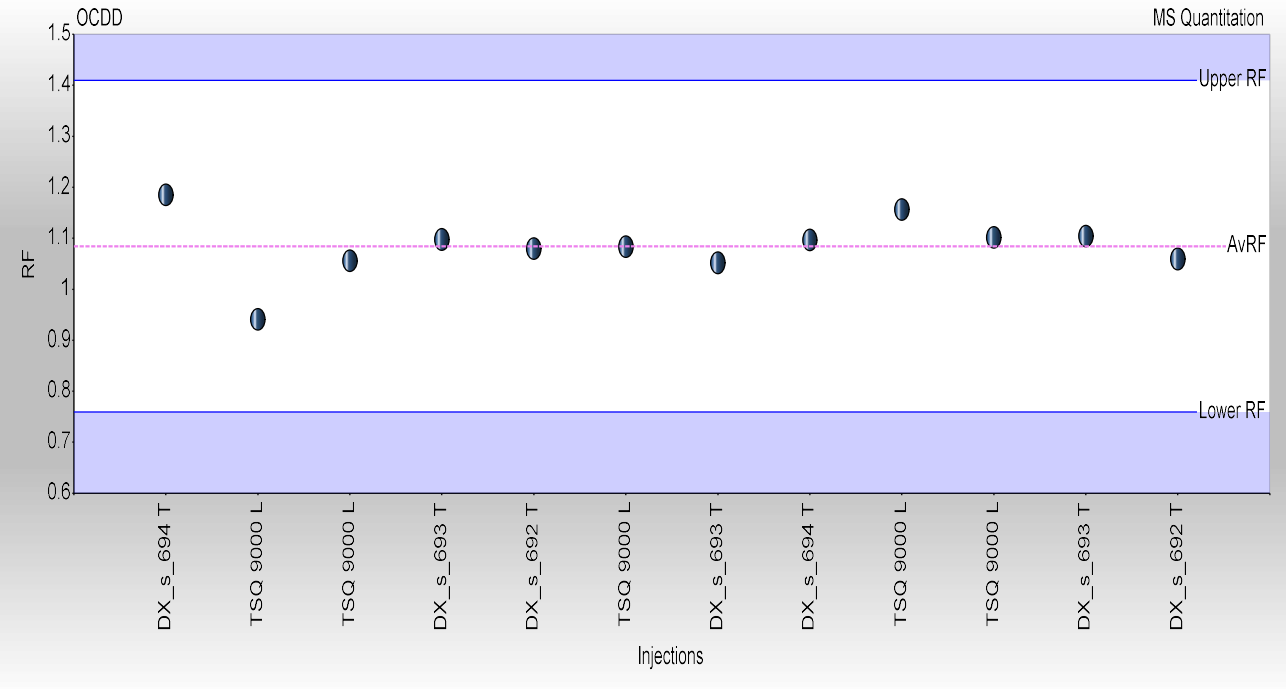
Ave RF = 1.084

R² = 0.999

Residual % RSD = 5.5%



Calibration: OCDD – RRF stability (MS/MS)



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