What Else Is In My Dioxin Sample? High Performance Time-Of-Flight Mass Spectral Analysis Of Environmental Samples

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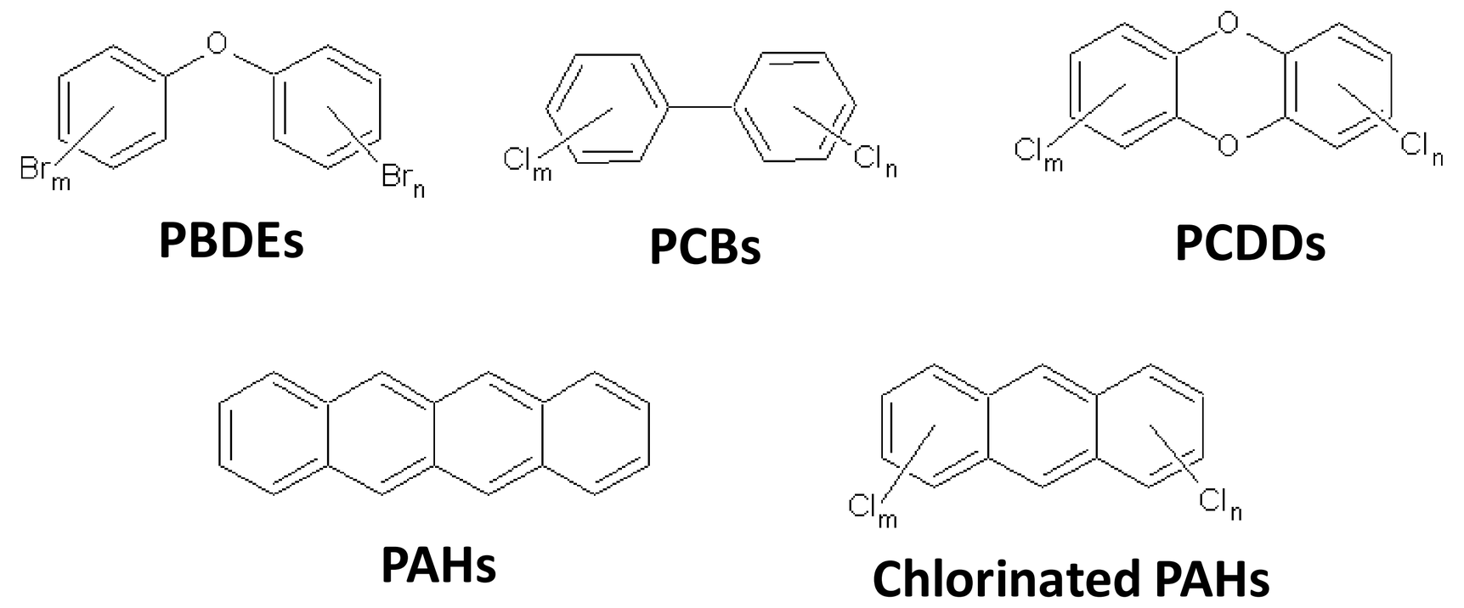
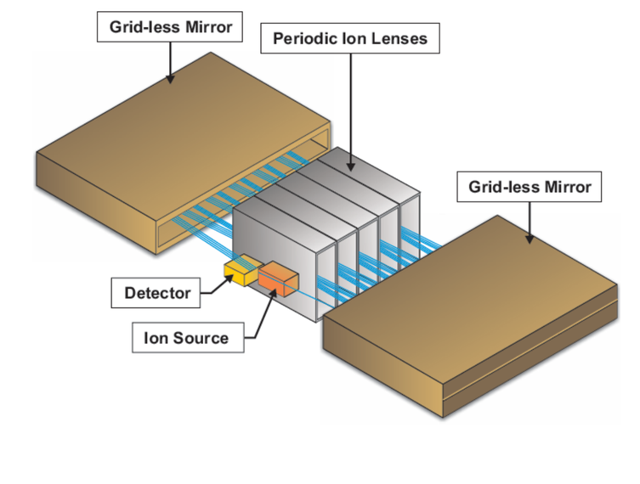
Introduction

Polychlorinated dibenzo-p-dioxins and furans are some of the most toxic materials known to man. They are relatively inert, fat soluble halogenated organic compounds that bioaccumulate in the environment. These persistent organic pollutants (POPs) have been linked to adverse cancer, reproductive and endocrine effects. In addition to dioxins, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), environmental samples may contain polyaromatic hydrocarbons (PAHs), halogenated PAHs, or numerous other industrial products and undiscovered hazardous compounds. These untargeted compounds may also be toxic and can be present in much higher concentrations than the target dioxins.



Persistent Organic Pollutants

High resolution TOFMS can be used for the comprehensive analysis of complex environmental samples. The advantages of high performance TOFMS for POP analysis are rapid acquisition of spectral data across a wide mass range with a minimum reduction in sensitivity, high resolving power to minimize interferences and high mass accuracy for robust elemental composition determinations. While other MS systems rely on selected ion monitoring to achieve the necessary detection limits for environmental studies, high resolution TOFMS can provide sensitivity while acquiring full mass range spectra allowing for identification of not only targeted compounds, but newly emerging environmental contaminants.



High Performance TOF MS (left) and its Folded Flight Path Mass Analyzer (Right)

Experimental

Standards and Samples:

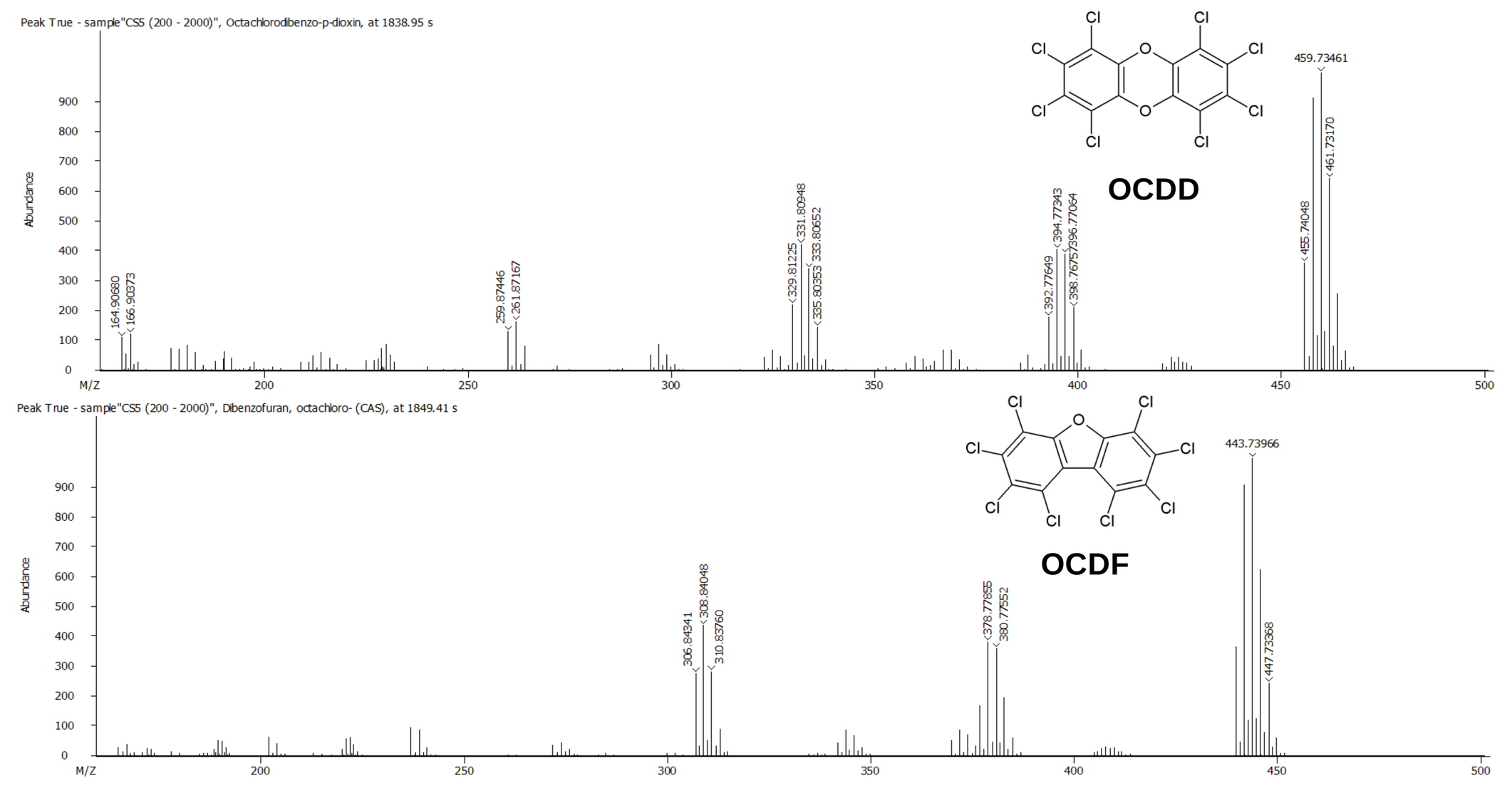
Calibration standards (CS1 – CS5) were purchased from Wellington Laboratories (Guelph, Canada). Sediment and fly ash samples containing both PCDDs and PCDFs, as well as several classes of POPs were obtained from the EPA in Taiwan.

Instrument Parameters:

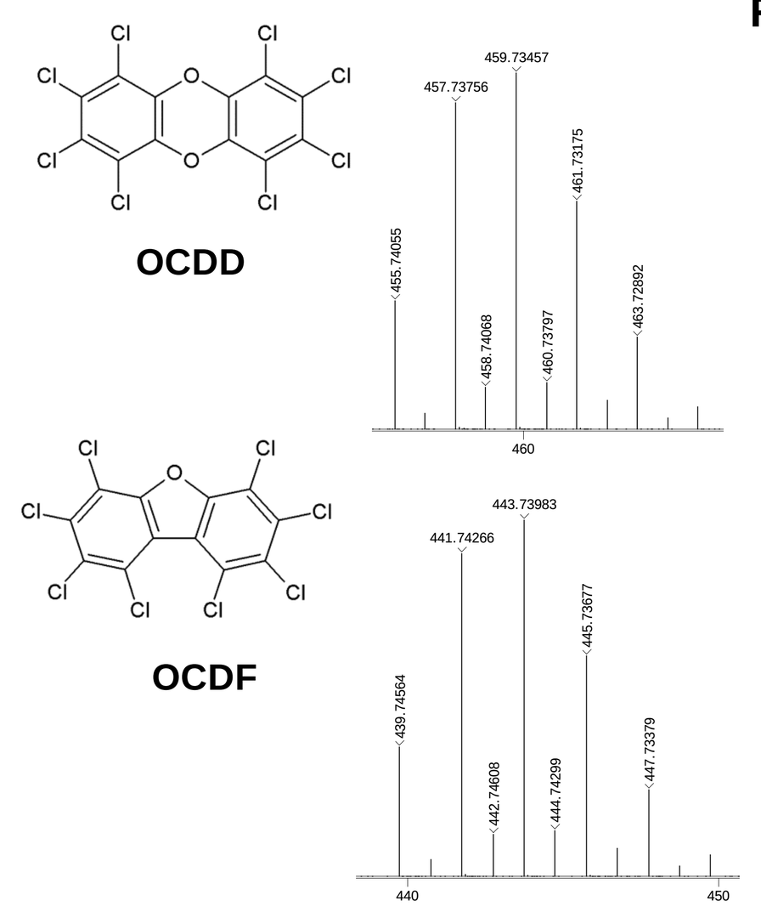
- GC: *Agilent 7890*
  - Column Type: Restek *Rxi*-5 (30 m, 0.25 mm ID, 0.25 μm *df*)
  - Inj. Temp.: 250°C
  - Injection: Splitless, 2 μL
  - Oven: 120°C (1)→220°C(20°C/min)→240°C(2.0°C/min)→ 250°C (1.0°C/min)→260°C(5.0°C/min)→265°C(1.0°C/min)
  - Carrier Gas: He, 1.0 mL/min constant flow
- MS: *Pegasus GC-HRT*
  - Source Temp.: 250 °C
  - EI: 40 eV
  - Mass Range: 160 - 510 m/z, High Resolution Mode

Representative Standard Data: CS5

Mass Spectra (OCDD, OCDF):



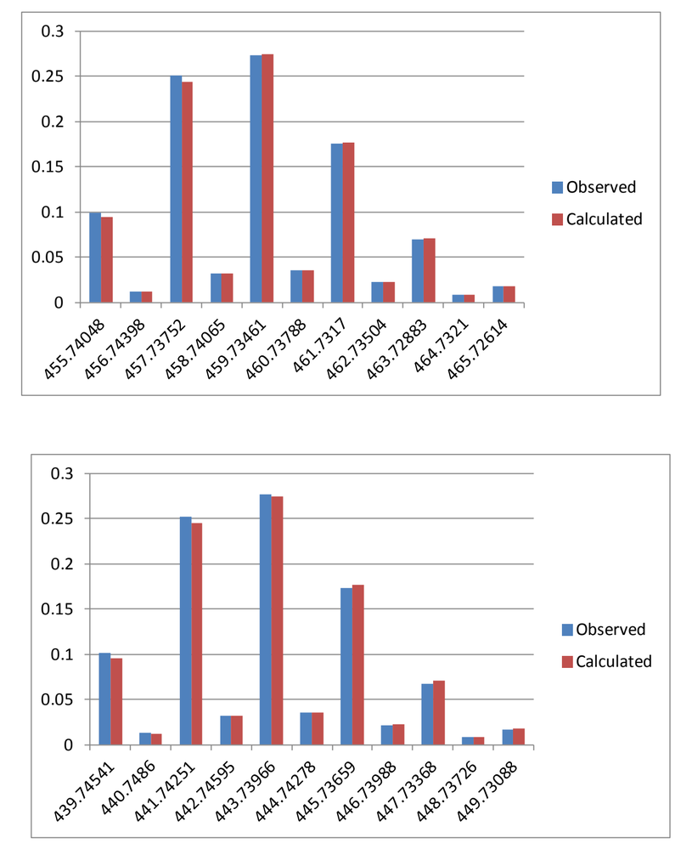
Relative Abundance Values (OCDD, OCDF)



Relative Abundance

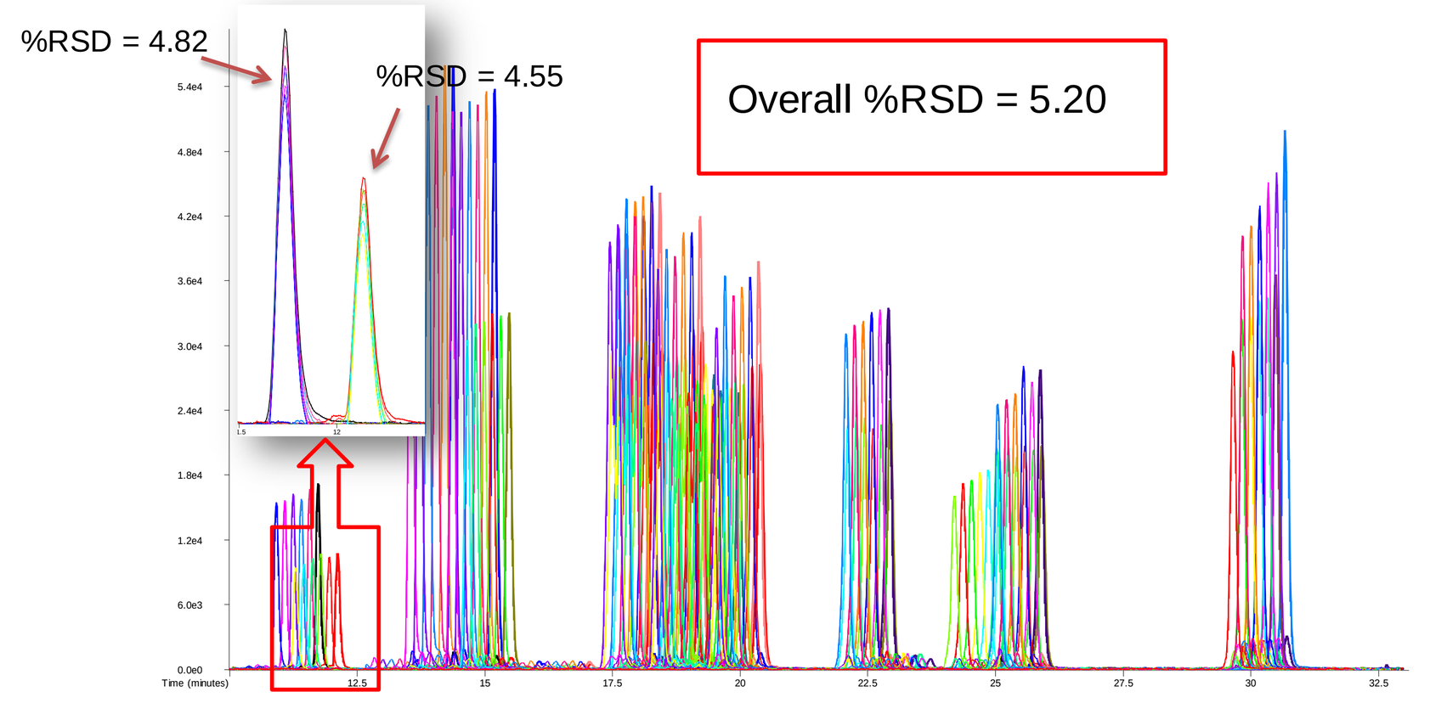
Mass	Observed	Calculated
455.74048	0.099	0.095
456.74398	0.012	0.012
457.73752	0.251	0.244
458.74065	0.032	0.032
459.73461	0.274	0.275
460.73788	0.036	0.036
461.73170	0.176	0.177
462.73504	0.022	0.023
463.72883	0.070	0.072
464.73210	0.009	0.009
465.72614	0.018	0.019

Mass	Observed	Calculated
439.74541	0.101	0.095
440.74860	0.013	0.012
441.74251	0.252	0.245
442.74595	0.033	0.032
443.73966	0.277	0.275
444.74278	0.035	0.036
445.73659	0.173	0.177
446.73988	0.022	0.023
447.73368	0.068	0.071
448.73726	0.009	0.009
449.73088	0.017	0.018



Data CS3 Standard

Extracted Ion Chromatograms (XICs) -- Five Replicate Injections:



Mass Accuracy Values: Native PCDF/Ds

Name	Formula	Calculated M+	Observed M+	Mass Accuracy (ppm)
TCDF N	C12H4OCl4	303.90108	303.90123	0.51
TCDD N	C12H4O2Cl4	319.89599	319.89556	-1.36
PCDF N	C12H3OCl5	337.86211	337.86202	-0.26
PCDF N	C12H3OCl5	337.86211	337.86183	-0.81
PCDD N	C12H3O2Cl5	353.85702	353.85716	0.41
HxCDF N	C12H2OCl6	371.82313	371.82306	-0.20
HxCDF N	C12H2OCl6	371.82313	371.82354	1.09
HxCDF N	C12H2OCl6	371.82313	371.82302	-0.30
HxCDD N	C12H2O2Cl6	387.81805	387.81810	0.14
HxCDD N	C12H2O2Cl6	387.81805	387.81817	0.32
HxCDD N	C12H2O2Cl6	387.81805	387.81830	0.65
HxCDF N	C12H2OCl6	371.82313	371.82348	0.94
HpCDF N	C12HOCl7	405.78416	405.78394	-0.55
HpCDD N	C12HO2Cl7	421.77908	421.77908	0.00
HpCDF N	C12HOCl7	405.78416	405.78421	0.13
OCDD N	C12O2Cl8	455.74010	455.74044	0.74
OCDF N	C12OCl8	439.74519	439.74450	-1.56

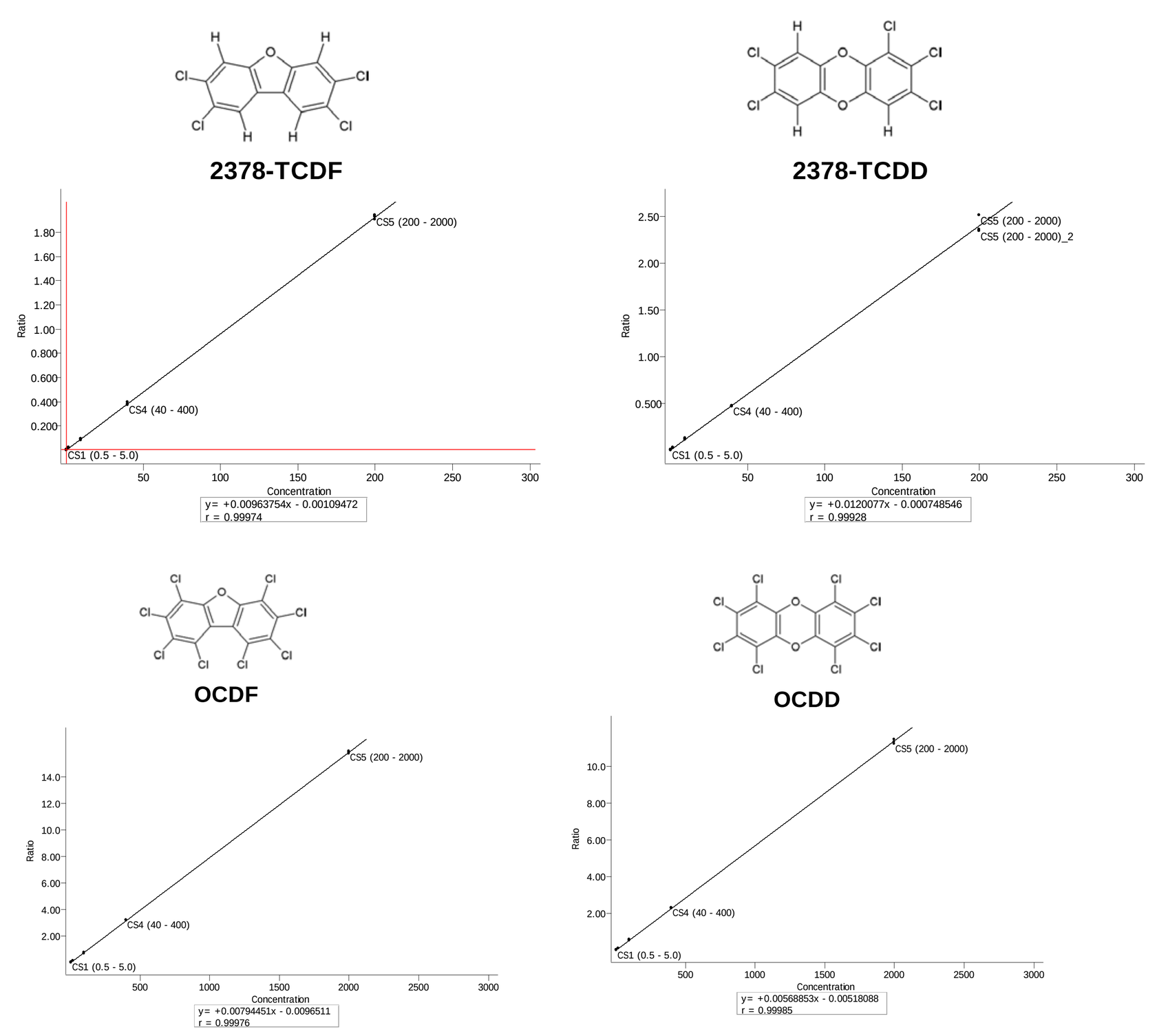
Ave. = 0.57 ppm

Mass Accuracy Values: Labeled PCDF/Ds

Labeled Compound	Calc M+	Obs M+	Mass Accuracy ppm		Calc M+2	Obs M+2	Mass Accuracy ppm
TCDF L	315.94134	315.94136	0.08		317.93839	317.93851	0.39
TCDD L	331.93625	331.93650	0.76		333.93330	333.93331	0.03
Labeled Compound	**Calc M+2**	**Obs M+2**	**Mass Accuracy ppm**		**Calc M+4**	**Obs M+4**	**Mass Accuracy ppm**
PCDF L	351.89941	351.89951	0.28		353.89646	353.89646	-0.01
PCDF L	351.89941	351.89943	0.05		353.89646	353.89653	0.19
PCDD L	367.89433	367.89474	1.12		369.89138	369.89154	0.44
HxCDF L	385.86044	385.86054	0.26		387.85749	387.85761	0.31
HxCDF L	385.86044	385.86034	-0.26		387.85749	387.85787	0.98
HxCDF L	385.86044	385.86057	0.34		387.85749	387.85732	-0.44
HxCDD L	401.85535	401.85543	0.19		403.85240	403.85215	-0.63
HxCDD L	401.85535	401.85558	0.56		403.85240	403.85259	0.46
HxCDD L	401.85535	401.85555	0.49		403.85240	403.85252	0.29
HxCDF L	385.86044	385.86034	-0.26		387.85749	387.85754	0.13
HpCDF L	419.82147	419.82138	-0.21		421.81852	421.81864	0.29
HpCDD L	435.81638	435.81667	0.66		437.81343	437.81322	-0.49
HpCDF L	419.82147	419.82162	0.36		421.81852	421.81878	0.62
OCDD L	469.77741	469.77746	0.11		471.77446	471.77413	-0.70

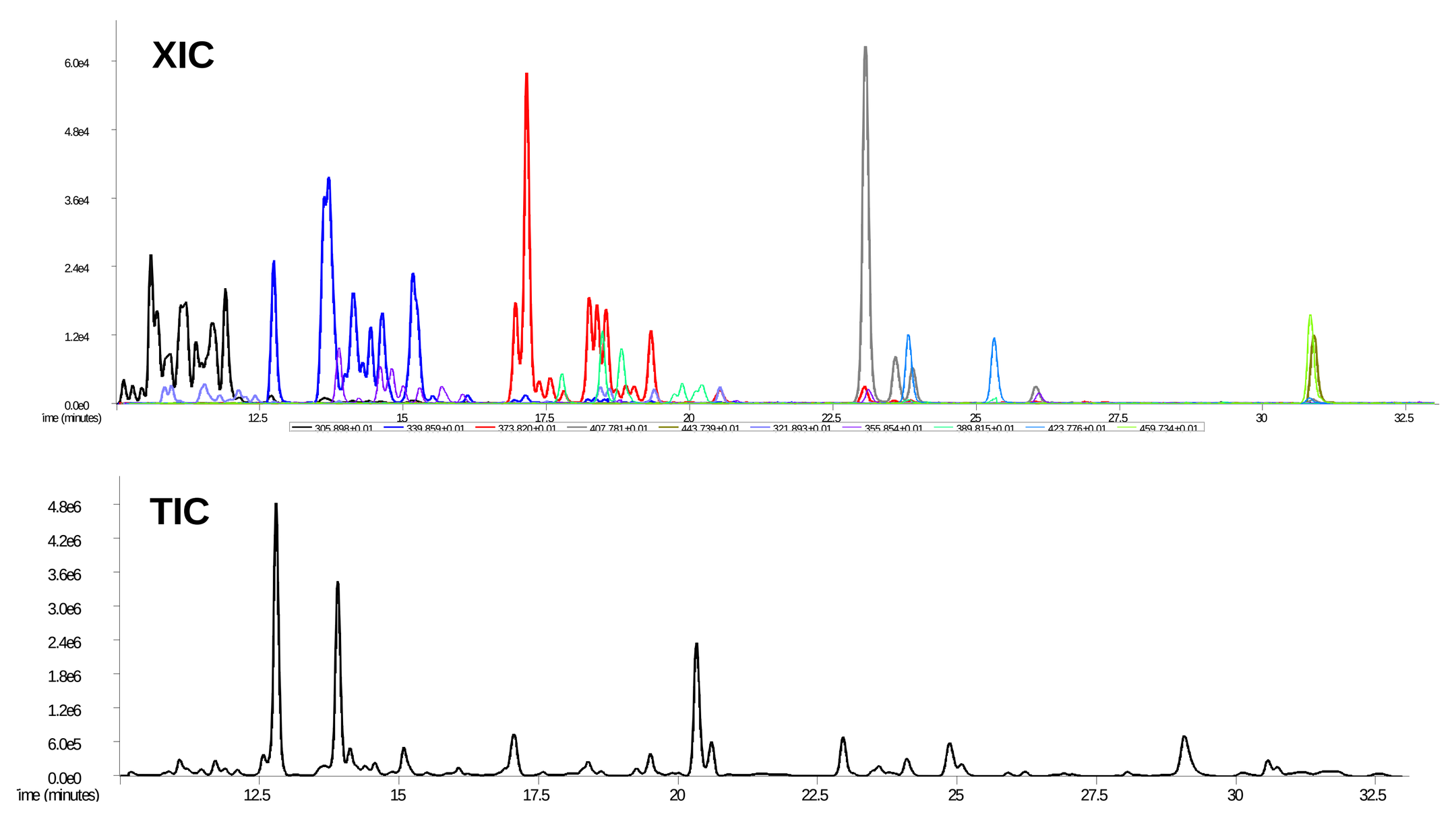
Ave. = 0.39 ppm

Calibration Results:



Results: Fly Ash

TIC and XIC for sample:

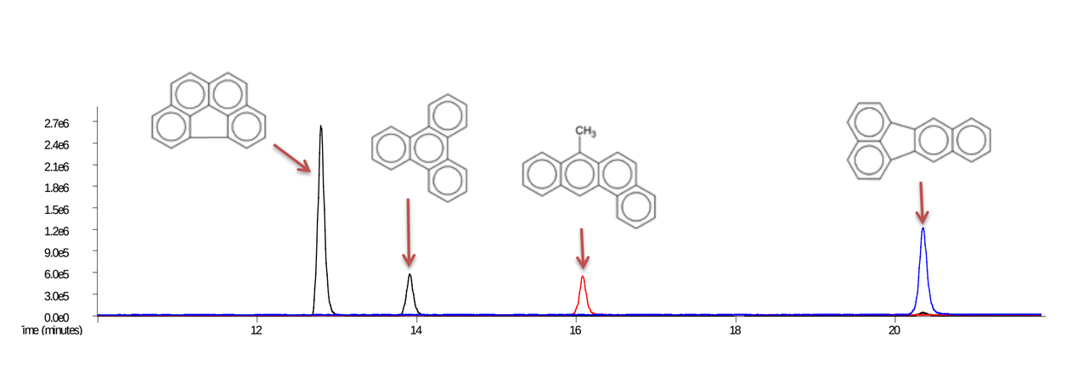


Target Analyte Finding -- 76 Dioxins:

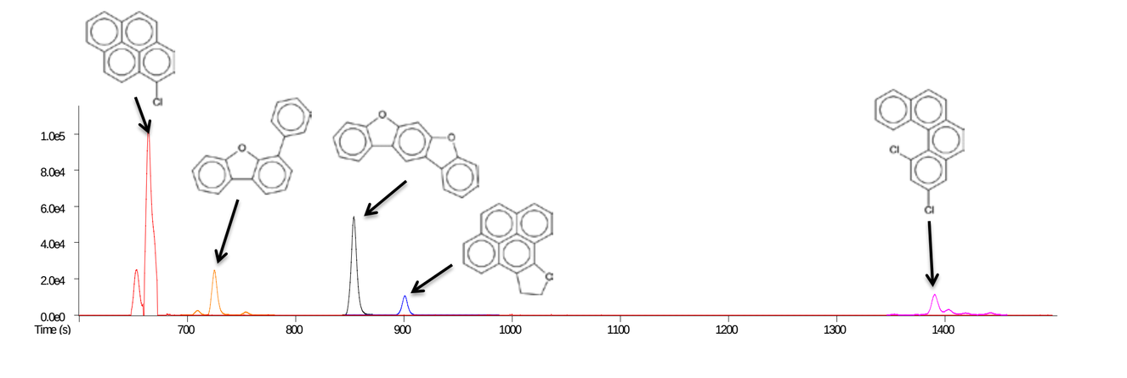
Peak #	Name	R.T. (s)	Quant S/N	Area	Height
1	TCDF N	607.5	231	45522	4629
2	TCDF N	617	148	27060	2969
3	TCDF N	626	70	9492	1397
4	TCDF N	636	1702	599207	34033
5	TCDD N	643	85	11796	1700
6	TCDD N	650.5	98	15172	1955
7	TCDF N	655	341	94019	6811
8	TCDF N	671	1193	503575	23865
9	TCDF N	683.5	419	87513	8375
10	TCDD N	684.5	245	93572	4901
11	TCDD N	700.5	71	15029	1425
12	2378-TCDF N	701	866	144124	8660
14	TCDD L	711	585	152418	11695
15	TCDF N	714	1325	335836	26508
16	TCDD N	720.5	146	58007	2916
18	TCDD N	738	67	16718	1349
19	TCDD N	757.5	25	7665	506
20	TCDF N	761.5	100	30673	1993
21	PCDF N	820	2894	1493648	57882
22	PCDD N	824	681	204802	13618
23	PCDD N	844.5	64	17905	1278
24	PCDF N	846	1062	326860	21248
25	PCDF N	856	54	5874	1076
27	12378-PCDF N	864.5	672	67004	6725
28	PCDD N	867	324	69690	6483
29	PCDF N	876.5	924	267925	18476
30	PCDD N	879.5	305	79188	6097
31	PCDD N	891.5	147	34660	2942
32	PCDD N	908.5	176	48501	3529
33	23478-PCDF N:2	909	2043	440715	20429

Peak #	Name	R.T. (s)	Quant S/N	Area	Height
35	PCDF N	929.5	55	11679	1105
37	12378-PCDD N	931.5	256	45608	2559
38	PCDD N	953.5	100	27712	1999
39	PCDF N	965.5	91	30171	1814
40	HxCDF N	1014	708	126499	14155
41	HxCDF N	1026	3895	1012971	77894
42	HxCDF N	1039.5	135	23815	2708
43	HxCDF N	1050.5	264	64894	5286
44	HxCDD N	1055.5	402	122722	8046
45	HxCDF N	1065	135	32685	2706
46	HxCDF N	1091	683	124227	13651
47	HxCDD N	1098	967	280421	19331
49	123478-HxCDF N	1099.5	533	45724	5334
51	123678-HxCDF N:2	1109	760	53517	7600
52	HxCDD N	1118	742	252883	14840
53	HxCDF N	1129.5	99	18045	1976
54	HxCDF N	1138.5	121	24994	2414
56	234678-HxCDF N:3	1156	1093	170249	10934
58	HxCDD N	1173	40	5640	798
60	HxCDD N	1181.5	162	36980	3234
62	HxCDD N	1202.005	240	107096	4809
64	123789-HxCDF N:4	1228	209	40141	2088
66	1234678-HpCDF N	1379	5629	935138	56293
67	HpCDF N	1410	667	208625	13330
68	HpCDD N	1417	1089	369451	21777
69	HpCDF N	1428	485	150041	9698
71	1234678-HpCDD N	1506.5	1038	185225	10384
73	1234789-HpCDF N:2	1557	264	46933	2637
75	OCDD N	1836	1410	251057	14097
76	OCDF N	1846.5	1091	190870	10906

What else is in my sample?

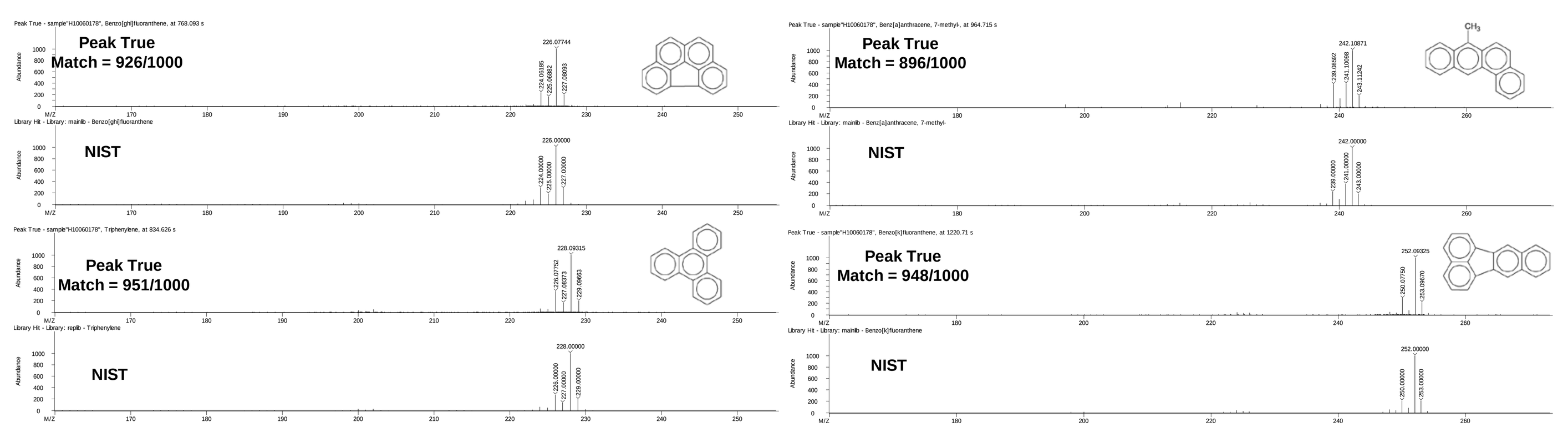


Name	Formula	RDBE	Mass Accuracy (ppm)
Benzo[ghi]fluoranthene	C18H10	14	-1.14
Triphenylene	C18H12	13	-0.89
Benz[a]anthracene, 7-methyl-	C19H14	13	-1.21
Benzo[k]fluoranthene	C20H12	15	-0.42



Name	Similarity	Formula	Mass Accuracy (ppm)
1-Chloropyrene	913	C16H9Cl	-0.21
4-Phenyldibenzofuran	879	C18H12O	0.35
Benzo[2,1-b:3,4-b']bisbenzofuran	891	C18H10O2	0.22
Pyreno[4,5-b]furan (CAS)	918	C18H10O	0.21
1,3-Dichlorobenzo[c]phenanthrene	821	C18H10Cl2	0.13

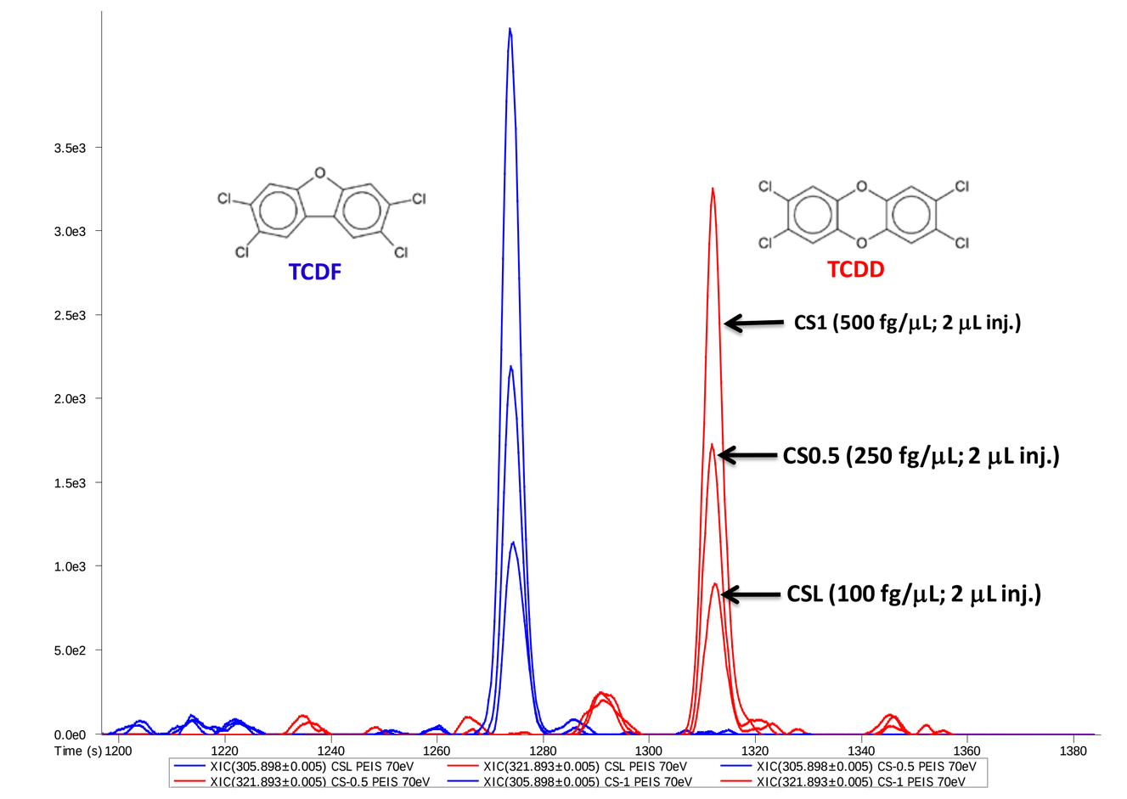
Mass Spectra: PAHs



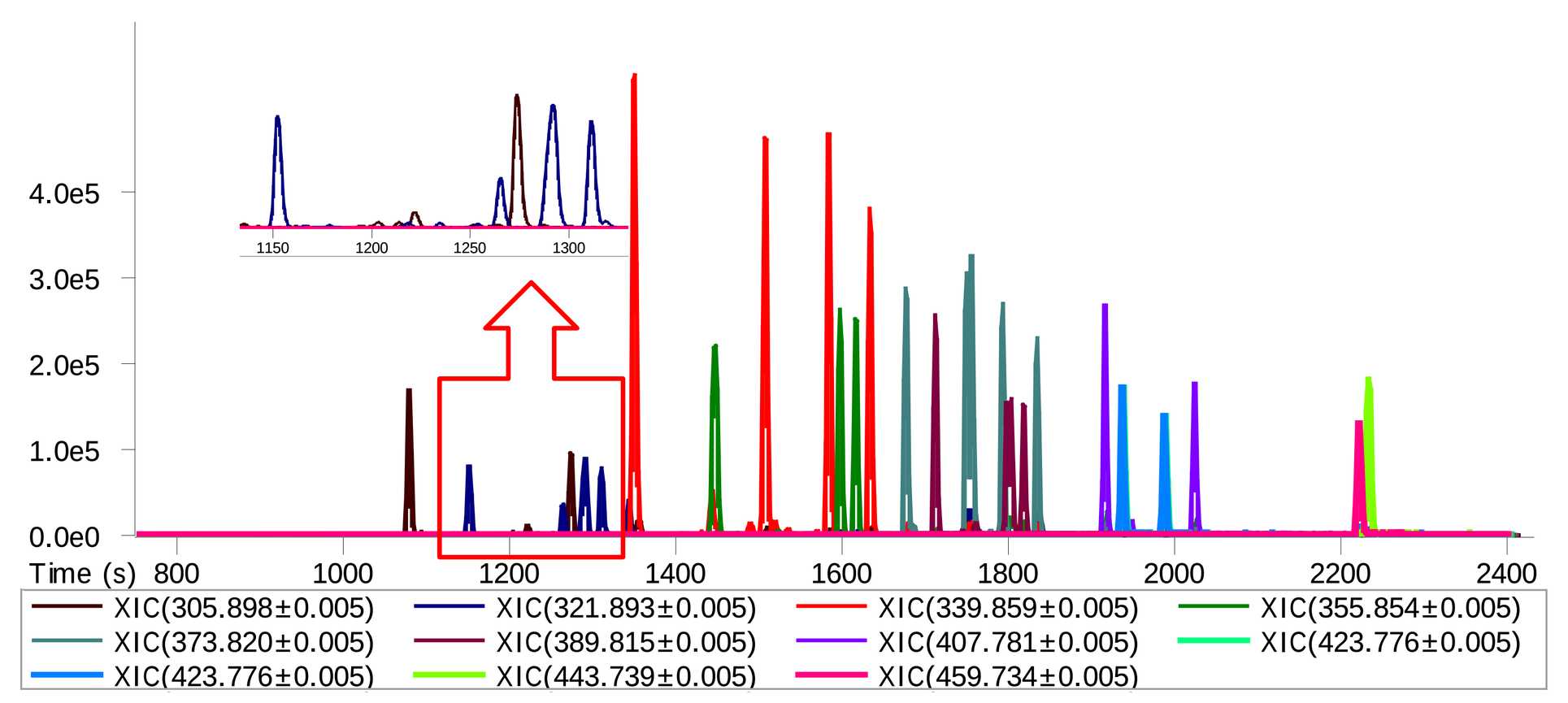
Current Work

Current work focuses on the use of a pulsed electron ionization source for sensitivity enhancement, and improving chromatographic resolution by using longer, thin film columns (e.g., Rtx-Dioxin-2, 40m x 0.18 mm x 0.18 μm).

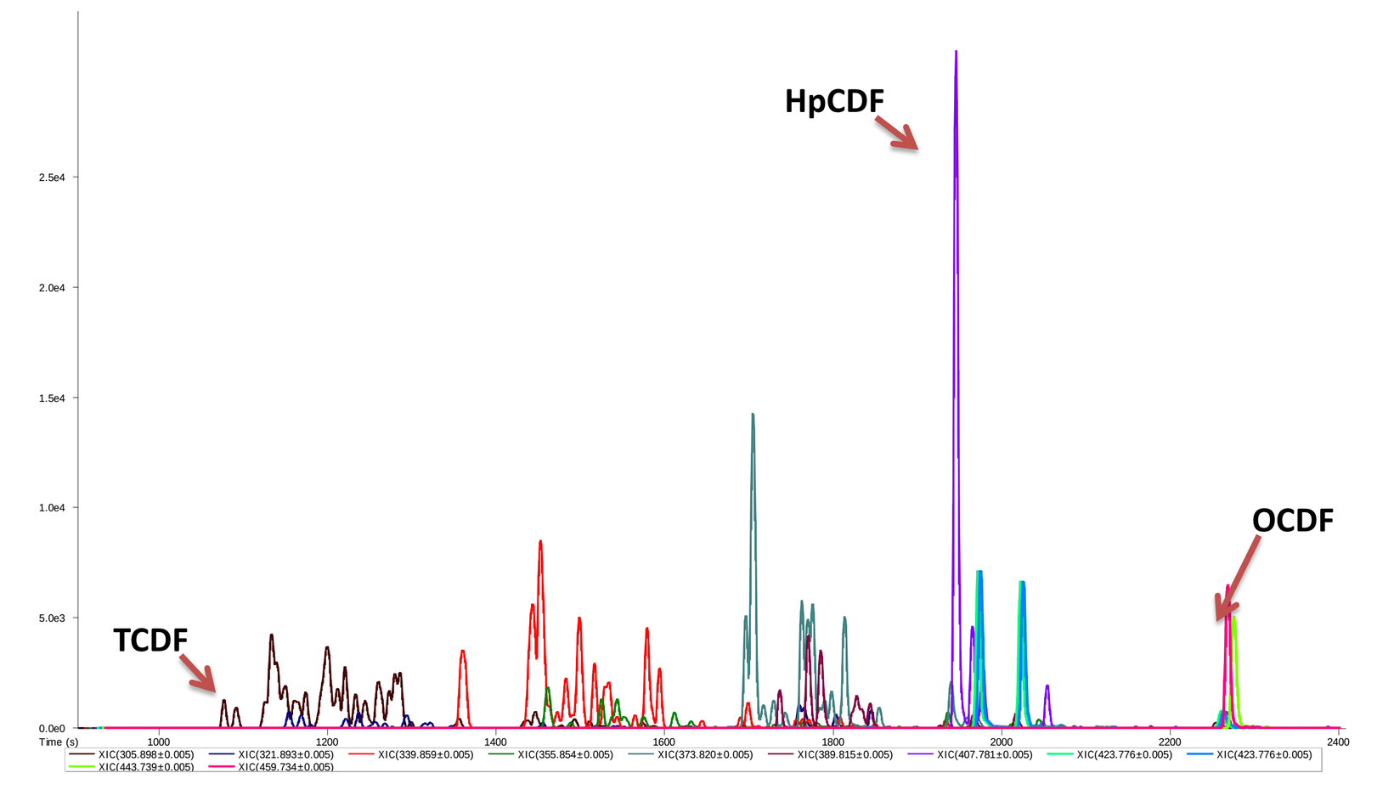
XIC 2378-TCDF and 2378-TCDD (CSL – CS1)



Chromatographic Resolution: CS3WT Verification Standard



XIC sediment sample – 110 Dioxins:



Compound	R.T. (s)	Area	Expected Ion m/z	Observed Ion m/z	Mass Accurac	Mass Delta(Da)
TCDF	1077	22675	303.90108	303.90072	-1.16	-0.00035
HpCDF	1924	955747	405.78416	405.78363	-1.30	-0.00053
OCDF	2244	194071	439.74519	439.74475	-0.98	-0.00043

Conclusion

High performance TOFMS provides a comprehensive profile of samples in a single acquisition. Its high resolving power and excellent mass accuracy values make it a practical choice for the analysis of complex environmental samples.