High Performance Mass Spectrometry of Persistent Organic Pollutants: What Else Is In My Dioxin Sample?

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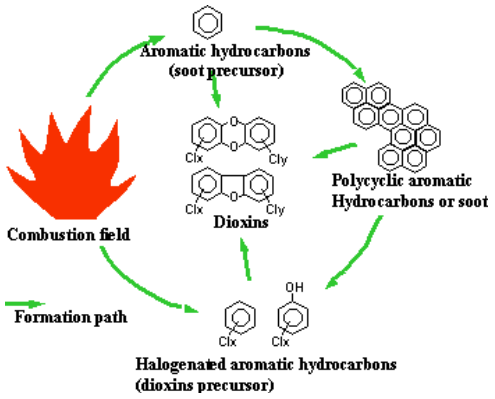
1. Introduction

Dioxin analysis in a regulated fashion requires conformity to the specifications of EPA Method 1613b[1]. Currently, laboratories performing EPA method 1613b utilize magnetic sector instruments which employ a targeted analysis strategy for these types of samples. This note describes the use of high resolution time-of-flight (HRT) mass spectrometry for a comprehensive analysis of environmental samples. Aside from dioxins, environmental samples may contain other classes of persistent organic pollutants (POPs) which may include polyaromatic hydrocarbons (PAHs), halogenated PAHs, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and new hazardous compounds resulting from industry attempts to stay ahead of regulation. Although not specifically controlled for through methods, these compounds can also be toxic and may be present at higher levels than the target dioxins.



Here, samples destined for analysis for dioxin content are analyzed in a comprehensive fashion using the Pegasus GC-HRT. The objective is to uncover what other POPs are present.

2. Results

Analysis of the provided fly ash sample produced the analytical ion chromatogram (AIC) shown in Figure 1 with 76 dioxins detected.

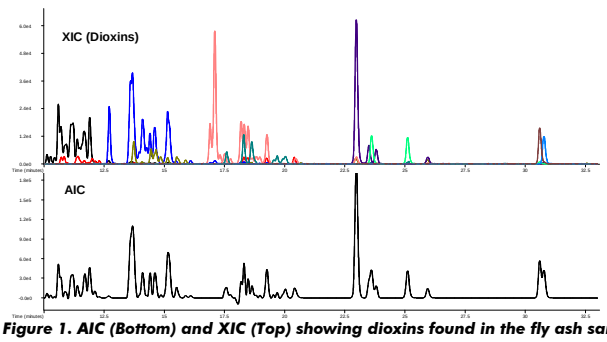


Figure 1. AIC (Bottom) and XIC (Top) showing dioxins found in the fly ash sample.

Table 1. 76 dioxins found in the fly ash sample.

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
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

Besides PCDDs and PCDFs, other oxygenated hetereocycles, PAHs, and halogenated PAHs were identified in the sample. Mass accuracy of 1.2 ppm or better was achieved for these untargeted analytes, and all spectral similarities were above 800 out of 1000.

PAHs were found at higher abundances than the dioxins and furans (Figure 2). Figure 3 shows mass spectral data for benzo[ghi]fluoranthene, and triphenylene. Spectral similarity values for these PAHs ranged from 896/1000 to 951/1000. Table 2 lists the formulas, RDBE and mass accuracy values for selected PAHs found in the sample.

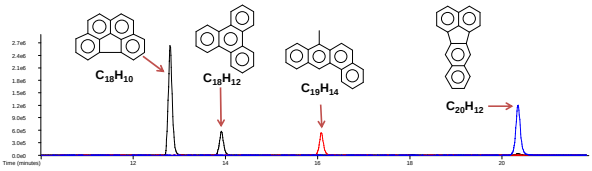


Figure 2. XIC showing select PAHs in fly ash sample.

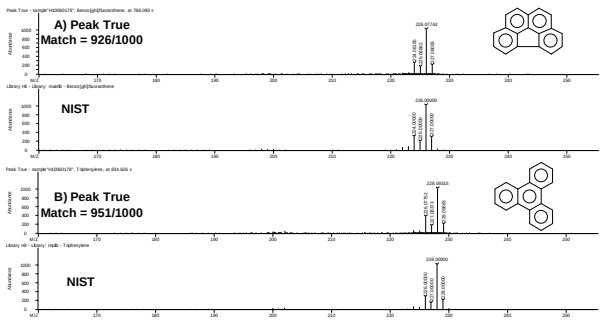


Figure 3. Peak True and NIST mass spectra for benzo[ghi]fluoranthene (A) and Triphenylene (B).

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Table 2. PAHs in fly ash 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

Other classes of compounds in the sample included halogenated PAHs and oxygen containing heterocycles (Figure 4). Mass accuracy values for the chlorinated and heterocyclic compounds ranged from -0.21 to 0.35 ppm (Table 3).

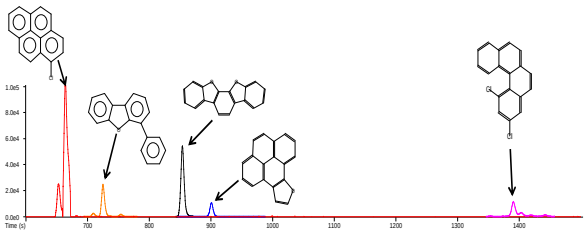

Figure 4. XIC showing chlorinated and heterocyclic compounds in fly ash sample.

Table 3. Chlorinated PAHs and heterocyclic compounds in fly ash sample.

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

3. Conclusion

The ability of comprehensive, high resolution time-of-flight mass spectrometry to detect and provide for identification of analytes in samples destined for dioxin analysis has been clearly demonstrated. A system capable of adhering to the performance criteria specified in EPA 1613b[1] while not being constrained by the targeted nature of analyses on magnetic sector instruments provides opportunities for more rigorous acquisition of information on analytes. It also allows for the retrospective, high-integrity analysis of data should new analytes become of interest. In addition to 76 dioxins detected in the sample, analytes belonging to other classes of compounds were confidently identified.

4. References

[1]Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, US Environmental Protection Agency.

5. Samples

A prepared fly ash sample with polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and several other classes of POPs was obtained from the EPA in Taiwan. Standard solutions containing 2,3,7,8-tetrachlorodibenzofuran (TCDF) and 2,3,7,8-tetrachlorodibenzodioxin (TCDD) were obtained commercially.

6. Experimental

Operational settings used for the GC-HRT

GC:	Agilent 7890
Column Type:	Restek Rxi-5Sil MS (30 m, 0.25 mm ID, 0.25 mm 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:	LECO Pegasus® GC-HRT
Source Temperature:	250°C
EI:	40 eV
Mass Range:	160 - 510 m/z
	High Resolution Mode

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