

USING GAS CHROMATOGRAPHY-HIGH RESOLUTION TIME OF FLIGHT MASS SPECTROMETRY TO UNCOVER POLLUTANTS IGNORED BY TARGETED ANALYTICAL APPROACHES

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are environmental pollutants formed as by-products of industrial and thermal processes. The historical analysis of these compounds has been achieved with high resolution, targeted analysis for quantitation of PCDD/Fs, using magnetic sector instruments (1) (HRMS). Recent advances in technology have led to comprehensive time-of-flight (TOF) mass spectrometers that can provide for quantitation of dioxins through the mandated concentration range while simultaneously acquiring data on other contaminants in the samples.

Materials and Methods

Six samples were investigated in this study. The samples were prepared at Ministry of the Environment Laboratory Services, according to standard methods used for the preparation of samples for PCDD/F analysis by HRMS (2). Two different instruments were used to obtain the data, namely a magnetic sector high-resolution mass spectrometer (GC-HRMS) and a high-resolution Time-of-Flight mass spectrometer (GC-HRT), details as described in Table 1.

Table 1. System Configuration

Type	GC-HRMS	GC-HRT
GC Model	Agilent Technologies HP6890	Agilent Technologies 7890
MS Model	Waters Autospec	LECO Corporation Pegasus HRT
MS Technique	Magnetic Sector Single Ion Monitoring (SIM) with resolving power of 10 000	Folded Flight Path [®] with resolving power of ~30 000
Software	MassLynx	LECO ChromaTOF (ver 1.79)
Column Type	J& W Scientific DB-5	Restek Corporation Rtx-Dioxin2
Column Specification	40 m; 0.18 mm id; 18 μm	40 m; 0.18 mm id; 18 μm

US EPA Method 1613B (3) calibration and verification solutions (EPA-1613CVS), labelled calibration solutions (EPA-1613LCS), internal standard spiking solution (EPA-613ISS) and cleanup standard stock solution (EPA-1613CSS) were selected for spiking and calibration purposes. Solutions were purchased from Wellington Laboratories (Guelph, Canada) and contained the seventeen native and corresponding mass-labelled PCDD/F congeners in nonane. Experimental conditions used for the analysis of the samples are shown in Table 2.

Table 2. Experimental Conditions for Sample Analysis

Parameter	GC-HRMS	GC-HRT
Amount Injected (μl)	1	2
Inlet Temperature (°C)	280	280
Helium Flow (ml/min)	0.8	1
Column 1	DB-5 (40m x 0.18mm x 0.18μm)	Rtx-Dioxin 2 (40m x 0.18mm x 0.18μm)
Oven 1 (°C)	140 (1 min) to 200 (52/min) to 235 (2.9/min, 3 min) to 267 (3/min) to 310 (7/min) (Until OCDD elutes)	140 (1 min) to 200 (50/min) to 260 (3/min) to 280 (1/min) to 310 (6/min) (5 min)
Transfer Line (°C)	280	300
Ion Source (°C)	280	280

Start Mass (Da)	SIM	140
End Mass (Da)	SIM	520
Acquisition Rate (spectra/s)	50 ms per ion	3
Electron Energy (eV)	35	50

Results and Discussion

A limitation of the sector HRMS method lies in its targeted approach that provides accurate quantitation of PCDDs and PCDFs, but does not give information on the presence of other persistent organic pollutants (POPs) in the sample. In TOF mass spectrometry full range mass spectra for all components present in the sample are obtained (4), and provided the mandated detection limits can be met for target compounds using TOF, we should then have a method that can identify all components of the sample, while also being able to quantify the targeted PCDDs and PCDFs. The low level standard (CS1) which contains 2,3,7,8-TCDD and 2,3,7,8-TCDF at 0.5 pg/μl, was used to determine the LOD possible for the HRT.

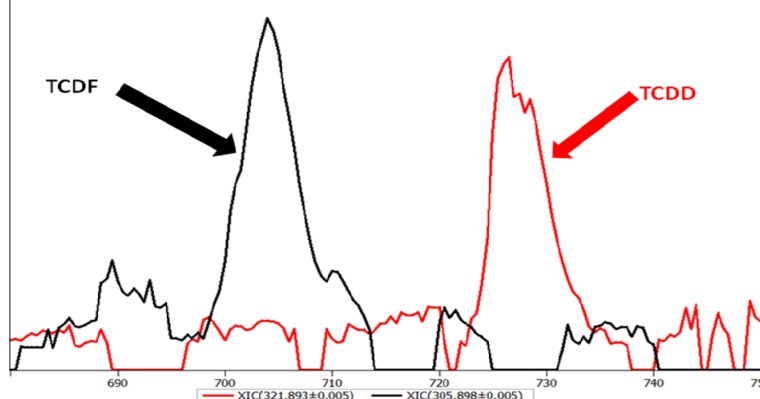


Figure 1. Extracted Ion Chromatogram for 2,3,7,8-TCDD and 2,3,7,8-TCDF at 0.5 pg/μl

This is demonstrated in Figure 1, which shows a plot of the ion at m/z 321.893 for TCDD and the ion at m/z 305.898 for TCDF, both at a concentration of 500 fg/μl (CS1 standard). The compounds are readily detected at the lowest level required by EPA method 1613B, CS1 at 500 fg/μl, providing assurance that the instrument has the sensitivity for low level dioxin determination.

The quantitative values for the six samples for the 17 PCDDs and PCDFs as mandated for analysis by EPA Method 1613B are shown in Table 3. When compared to one another, the results from the two high-resolution systems are generally in excellent agreement, showing that the high resolution TOF is capable of achieving the requirements for dioxin quantification according to EPA Method 1613B.

Table 3. Quantitative Results for Sample Analysis.

	GC-HRT	GC-HRMS	GC-HRT	GC-HRMS	GC-HRT	GC-HRMS	GC-HRT	GC-HRMS	GC-HRT	GC-HRMS	GC-HRT	GC-HRMS
	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
2378-TCDF	3.5	3.7	20	26	48	46	52	59	40	50	12	18
2378-TCDD	3.0	2.6	28	32	55	69	3.2	3.9	ND	0.7	15	20
12378-PCDF	2.7	1.7	21	18	22	14	120	140	35	40	16	19
23478-PCDF	4.5	5.6	21	19	143	180	39	55	24	31	17	17
12378-PCDD	1.4	1.1	2.8	2.8	10	3.0	5.1	4.7	ND	1.9	5.2	2.5
123678-HxCDF	2.2	5.4	76	85	220	240	280	330	97	120	71	73
123478-HxCDF	1.7	1.7	32	35	37	21	189	210	35	48	30	28
123789-HxCDF	ND	1.5	23	17	42	14	8.9	28	23	20	7.2	14

123478-HxCDD	ND	0.8	10	3.7	17	5.2	5.1	4.1	ND	2.9	5.8	2.9
123678-HxCDD	3.1	1.7	13	9.3	18	14	13	9.9	ND	5.8	10	8.3
123789-HxCDD	ND	1.6	14	6.0	28	8.6	20	8.1	14	3.9	12	5.2
234678-HxCDF	ND	0.6	8	2.3	14	1.5	86	50	17	4.7	6.7	2.7
1234678-HpCDF	12	15	290	300	620	990	710	1000	290	420	180	250
1234678-HpCDD	33	24	170	160	236	230	65	70	71	75	120	130
1234789-HpCDF	ND	1.5	55	47	51	17	380	470	72	79	30	38
OCDF	19	24	2300	2600	970	1100	6400	5200	1100	1200	1800	1800
OCDD	140	170	1200	1900	790	1300	170	220	370	550	1100	1500

Targeted dioxin analysis, as with the GC-HRMS sector system used in the SIM mode, cannot provide a comprehensive picture of all compounds present in the samples. Only the targeted PCDDs and PCDFs are detected, and additional POPs in the samples are ignored. Using the GC-HRT system permits numerous other POPs to be located and identified in the chromatograms. For example, in Sample 2 we can locate a compound with an accurate mass measured as 359.89648 that can be used to determine the formula for C₁₆H₈Br₂ with a mass accuracy of -0.55 ppm. Library searching of the spectrum allows the compound to be identified as 2, 7-Dibromopyrene. Numerous other POPs, which would not have been detected in SIM data, are shown in Table 4. These compounds are a random selection among many that were detected. A full picture of the sample is only possible when a comprehensive analysis is performed. An important part of the identification of unknown compounds is the measurement of accurate mass (Mass Acc.) and the determination of isotope abundance. As an example, one of the important POPs identified in Sample 6 is the brominated flame retardant tetrabromodiphenylether (TBDE) with a chemical formula C₁₂H₆Br₄O, and a molecular mass of 481.71455 Da.

Table 4. Some POPs Detected during Sample Analysis.

Sample	Compound	Similarity	Mass Acc. (ppm)	Sample	Compound	Similarity	Mass Acc. (ppm)
1	2,4,4',6- Tetrachlorobiphenyl	516	2.20	1	7H-Benz[de]anthracen-7-one	816	-0.66
2	Perylene	832	-0.71	2	2,5,4'-Trichloroterphenyl	608	-1.74
2	1,6,8-Trichloropyrene	702	0.29	2	Benz[a]anthracene	942	-0.22
2	9,10-Dichloroanthracene	958	-0.11				
3	3,3',4,4'-Tetrachlorobiphenyl	854	-0.15	4	Benzo[e]pyrene	824	0.23
5	Coronene	860	-0.16	5	2,3,3',4,4'-Pentachlorobiphenyl	769	0.51
5	2,2',4,4'-Tetrachlorobiphenyl	750	1.57	5			
6	2,3',4,4',6-Pentachlorobiphenyl	664	0.84	6	Benzyl butyl phthalate	927	-0.41
6	2,3,3',4,4',5-Hexachlorobiphenyl	853	1.82	6	Tetrabromodiphenylether	653	0.62

The measured molecular ion was 481.71496 Da, with a mass accuracy of 0.62 ppm, thus leading to a confident confirmation of identity. Measurement of the relative isotopic abundance in the molecular ion cluster is also an important confirmation of molecular formula. For tetrabromodiphenylether a comparison of measured and theoretical isotope abundance is shown in Table 5.

Table 5: Ion Abundance Ratios for Tetrabromodiphenylether

Ion(Da)	Height	Measured	Calculated	Difference (%)
		Relative Abundance	Relative Abundance	
481.71	19	21.3	17.3	23.1
483.71	67	75.3	67.8	11.1
485.71	89	100.0	100	-
487.71	58	65.2	65.8	-0.9

489.71	14.5	16.3	16.5	1.2
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These values, coupled with the excellent mass accuracy obtained on the molecular ion, provide strong confirmatory evidence of the proposed identification. GC-HRMS analysis of samples known to contain PCDDs and PCDFs cannot locate and identify other priority POPs that may be present in the samples in the same run. Time of flight systems have the sensitivity to achieve low detection levels mandated by regulatory authorities, and in addition, provide the flexibility to identify and quantify numerous other priority pollutants in the same analytical run.

References

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