Comparative PCDD/F Analysis with GC-HRMS, GC-HRTOFMS and GCxGC-TOFMS
Discovery of Compounds Not Found in Environmental Analysis Guided by EPA 1613B

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Introduction

Globally, chlorinated dioxins and furans are analysed by expensive gas chromatography – high resolution mass spectrometry (GC-HRMS) using EPA Methods such as 8290A or 1613B, or local methodology based on these

To achieve the sensitivity required by regulatory methods, the HRMS approach uses selected ion monitoring (SIM)

This is a target molecule technique, and requires a list of the selected analytes before running the analysis to set up the experimental parameters

Only the targeted compounds are located – all other information about the sample is forfeited

Using high res systems to do SIM is also expensive and requires a high degree of operator sophistication

Time of Flight (TOF) mass spectrometers do not use SIM. All analyses provide full range mass spectra for all the analytes in the sample

This is an important advantage, and provided the mandated sensitivities can be obtained using TOF, we should then have a method which can locate and identify all components of the sample, while also being able to quantify targeted PCDDs and PCDFs, all in one run

This applies both to the Pegasus 4D (GCxGC-TOFMS) and to the Pegasus HRT (High Resolution TOFMS)

Determine if GCXGC-TOFMS and GC-HRT has the *sensitivity* to calibrate 2378-TCDD and 2378-TCDF down to 0.5 pg/µl as required by EPA Method 1613, and to analyse samples at this level

Determine if GCXGC-TOFMS and GC-HRT can provide the *selectivity* necessary to measure 17 dioxins and furans (from Method 1613, assigned due to their toxicity) in a variety of sample matrices

Determine if the techniques can identify other POP components present in real world samples, which are not located by the target approach

Run the relevant ^{13}C labelled standard set for 1613B

Use these results to obtain response factors for the PCDD/Fs

Run the sample set and calculate quantitative values for the PCDD/Fs

Data mine the samples for other POPs which may be present in the samples

Methods

- Air-dry samples
- Addition of labelled standards
- Soxhlet extraction
- Column clean-up
  - Acid-base-$AgNO_3$ Si
  - Alumina
  - Carbon
- Conc to 20µL
- GC-HRMS
  - EI at lower eV
  - 10,000 Resolution
  - SIM
- GC-HRT LECO Pegasus HRT
- GCxGC-TOFMS LECO Pegasus 4D

Analysis Conditions GC-HRMS

Inlet 280°C

Constant Flow He at 0.8 ml/min

40m x 0.18mm x 0.18µm DB-5

140°C (1min), 52°C/min to 200°C, 2.9°C/min to 235°C (3 min), 3°C/min to 267°C (3 min), 7°C/min to 310°C (Hold until OCDD elutes)

Transfer Line 280°C

HRMS, EI+, SIM, 35 eV

Analysis Conditions GC-HRT

Inlet 280°C

Corrected Constant Flow He at 1 mL/min

40m x 0.18mm x 0.18µm Rtx-Dioxin2 Arylene backbone-modified siloxane column selective for coplanars

140°C (1min), 50°C/min to 200°C, 3°C/min to 260°C, 1°C/min to 280°C, 6°C/min to 310°C (5 min)

Transfer Line 300°C

HRT, EI+, 140 to 520 u, 3 spectra/s, 50 eV

Analysis Conditions GCxGC-TOFMS

40m x 0.18mm x 0.18µm Rtx-Dioxin2 Arylene backbone-modified siloxane column selective for coplanars

120°C (2min), 20°C/min to 200°C, 5°C/min to 320°C (3 min)

1.0m x 0.15mm x 0.15µm Rxi-17Sil MS 50% phenyl (silarylene) / 50% methyl type siloxane

+ 5°C offset from primary column

Corrected Constant Flow He at 1.4 mL/min (Speed optimized flow)

Thermal modulation, 2.0 sec (Hot time 0.70 sec, Cool time 0.30 sec)

TOFMS, EI+, 45 to 750 u, 100 spectra/s

Quantitative Results

Sample 1	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	3.5	3.0	2.7	4.5	1.46	2.2	1.7	ND	ND
GC-HRMS	3.7	2.6	1.7	5.6	1.1	5.4	1.7	1.5	0.81
GCxGC-TOFMS	ND	ND	ND	ND	ND	11	ND	ND	ND
GCxGC-TOFMS (x5)	3.5	5.6	6.6	12	ND	9.8	5.7	6.5	ND

Sample 1	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	3.1	ND	ND	12	33	ND	19	150
GC-HRMS	1.7	1.6	0.60	15	24	1.5	24	170
GCxGC-TOFMS	ND	ND	ND	ND	31	16	ND	160
GCxGC-TOFMS (x5)	6.3	ND	ND	ND	31	16	31	170

Sample 2	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	20	28	21	21	2.8	76	32	23	10
GC-HRMS	26	32	18	19	2.8	85	35	17	3.7
GCxGC-TOFMS	22	48	18	20	ND	90	40	32	ND

Sample 2	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	13	14	7.9	280	170	55	2400	1200
GC-HRMS	9.3	6.0	2.3	300	160	47	2600	1900
GCxGC-TOFMS	ND	ND	ND	410	230	120	2400	1500

Sample 3	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	48	55	22	140	10	220	37	42	17
GC-HRMS	46	69	14	180	3.1	240	21	14	5.2
GCxGC-TOFMS	40	73	32	150	21	210	46	41	18

Sample 3	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	18	28	13	620	240	51	980	790
GC-HRMS	14	8.6	1.5	990	230	17	1100	1300
GCxGC-TOFMS	41	32	36	950	210	58	980	990

Sample 4	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	52	3.2	120	39	5.1	280	190	8.9	5.1
GC-HRMS	59	3.9	140	55	4.7	330	210	28	4.1
GCxGC-TOFMS	48	5.8	130	36	14	210	210	75	23

Sample 4	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	13	20	86	710	65	380	6500	170
GC-HRMS	9.9	8.1	50	1000	70	470	5200	220
GCxGC-TOFMS	14	18	100	1000	66	460	5100	190

Sample 5	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	40	ND	35	24	ND	97	35	23	ND
GC-HRMS	50	0.65	40	31	1.9	120	48	20	2.9
GCxGC-TOFMS	43	ND	43	30	ND	120	47	29	ND

Sample 5	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	ND	14	17	290	71	72	1100	370
GC-HRMS	5.8	3.9	4.7	420	75	79	1200	550
GCxGC-TOFMS	10	15	38	400	78	90	1200	480

Sample 6	2378-TCDF	2378-TCDD	12378-PCDF	23478-PCDF	12378-PCDD	123678-HxCDF	123478-HxCDF	123789-HxCDF	123478-HxCDD
GC-HRT	12	15	16	17	5.2	71	30	7.2	5.8
GC-HRMS	18	20	19	17	2.5	73	28	14	2.9
GCxGC-TOFMS	15	21	21	18	ND	59	28	17	7.8

Sample 6	123678-HxCDD	123789-HxCDD	234678-HxCDF	1234678-HpCDF	1234678-HpCDD	1234789-HpCDF	OCDF	OCDD
GC-HRT	10	12	6.7	180	120	30	1800	1100
GC-HRMS	8.3	5.2	2.7	250	130	38	1800	1500
GCxGC-TOFMS	10	ND	15	220	110	31	1900	1400

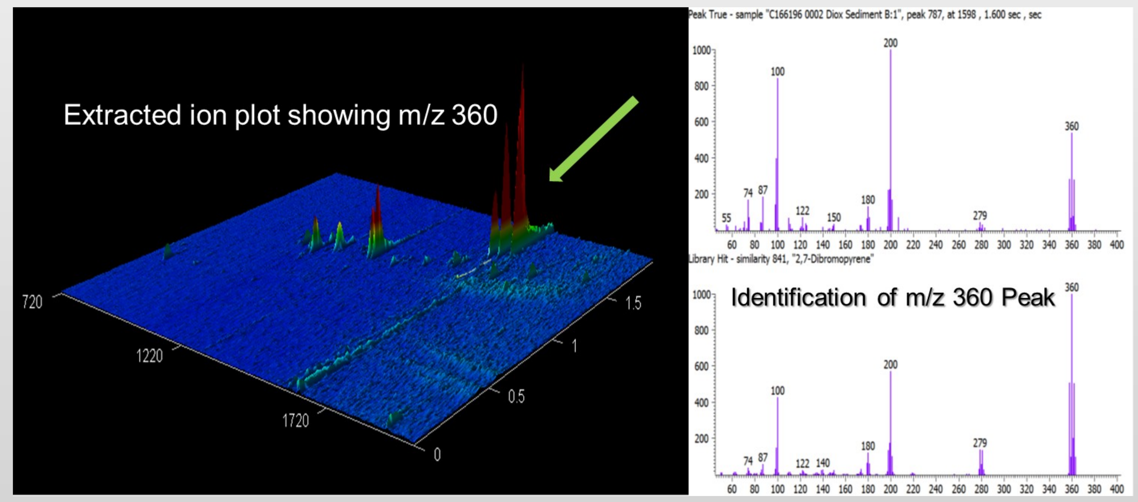
Comprehensive Sample Evaluation

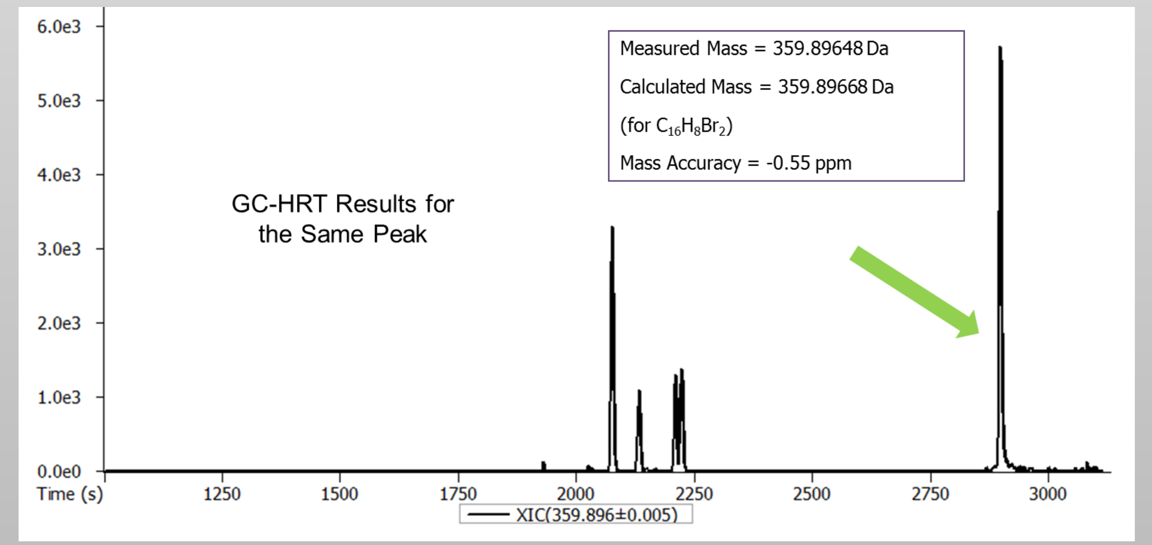
As mentioned previously, with SIM (& also MS/MS) analyses only the targeted compounds are located – all other information about the sample is forfeited

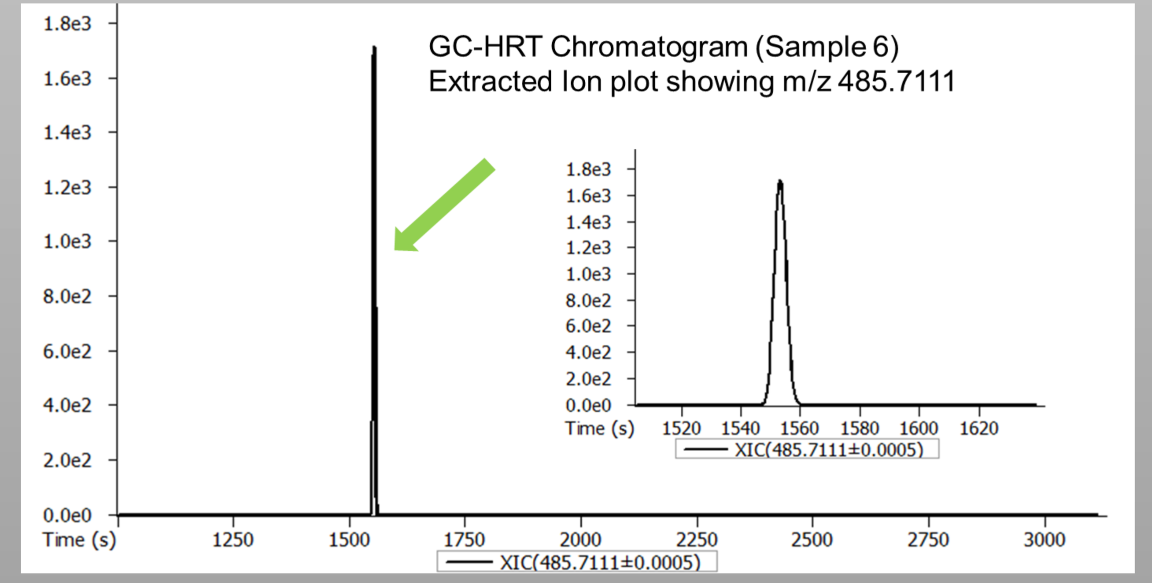
TOF mass spectrometers do not use SIM. All analyses provide full range mass spectra for all the analytes in the sample

We should then be able to locate and identify all components of the sample, while also being able to quantify targeted PCDDs and PCDFs, all in one run

Lets look at the samples above and see if additional POPs can be located, which have not been seen in the GC-HRMS method







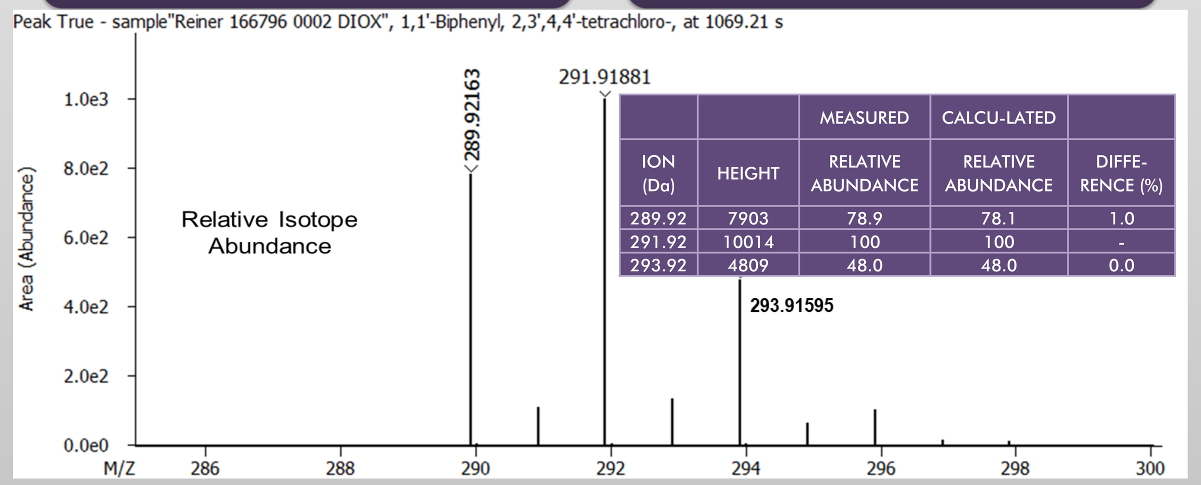
Other Compounds in the Samples

Sample	Compound	Similarity	Mass Accuracy (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	1,6,8-Trichloropyrene	702	0.29
2	2,5,4′-Trichloroterphenyl	608	-1.74
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	2,2′,4,4′-Tetrachlorobiphenyl	750	1.57
5	2,3,3′,4,4′-Pentachlorobiphenyl	769	0.51
6	2,3′,4,4′,6-Pentachlorobiphenyl	664	0.84
6	2,3,3′,4,4′,5-Hexachlorobiphenyl	853	1.82
6	Benzyl butyl phthalate	927	-0.41
6	Tetrabromodiphenylether	653	0.62

Relative Isotope Abundances

For compounds with pronounced molecular ion clusters (arising from the presence of Cl or Br in the molecule) measurement of relative isotopic abundance is an important confirmation of molecular formula

In general, differences of up to 30% are considered acceptable when working with POPs at low levels



Conclusions

GC-HRMS or GC-MS/MS analysis of PCDD/Fs requires a targeted approach
- Not able to locate other POPs in the samples

TOF technology, using either GCxGC or HRT, provides an alternative approach capable of:
- Achieving the levels mandated for analysis by regulatory authorities
- Locating and identifying other priority pollutants present in the sample in the same analytical run

GCxGC-TOFMS system, select the correct choice of the column combination
- Permits good separation of PCDD/Fs from matrix interference (and other POPs)

Mass accuracy for PCDD/Fs and other POPs present in the samples is excellent
- (usually < 1ppm) that allows confident formula assignment

Isotope ratio measurement for the molecular ion cluster is an additional confirmation of formula assignment
- The results obtained with the HRT are in good agreement with the theoretical values