Optimized PTV method for analysis of brominated dioxins and furans using magnetic sector GC-HRMS

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Abstract

Purpose: The analysis of brominated Dioxins and Furans are known to be challenging due to their thermolability. Therefore, a robust method need optimized settings in each part of the analysis such as injection, oven and mass spectrometer. The use of a Programmed Temperature Vaporizing (PTV) Injector module is the best choice for this type of analysis.

Methods: Brominated Dioxin and Furan standards were measured using a GC-HRMS system equipped with a PTV Injector module following the concept of isotope dilution technique, analog to the EPA Method 1613 for Chlorinated Dioxins and Furans. All instrument parameters especially the injector parameter were optimized towards the best performance with the focus on the octa bromo Dioxin and Furan.

Results: In contrast of using a Split Spitless (SSL) injector for this type of analysis, a robust routine instrument method could only be achieved by using instant connected PTV injector module with optimized parameters.

Introduction

Dioxins are widespread environmental pollutants that can be found in air, products, soil residues and wastewater, allowing them to easily enter the food chain and become the main source of dioxin in humans. Considering their high toxicity, numerous studies are focused on dioxin research and quantitation, with polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) being the main targets. However, there are also other halogenated dioxins existing such as the polybrominated dibenzodioxins (PBrDD) and polybrominated dibenzofurans (PBrDF) or even mixed halogenated dioxins, and furans substituted with both chlorine and bromine. The knowledge of brominated dioxins in terms of occurrence, quantity and health risk is limited compared to chlorinated dioxins. One reason for this limitation are analytic challenges associated with the analysis of brominated dioxins. These compounds are known to be less stable compared to chlorinated dioxins, especially in terms of temperature, with octabromo-dibenzodioxin and the octabromo-dibenzofuran being extremely thermolabile. This challenge can be addressed by using Programmed Temperature Vaporizing (PTV) Injector instead of a standard Split/Spitless (SSL) Injector since PTV ensures a smooth transfer from the extract onto the analytical GC column, especially for the higher brominated dioxins/furans, and it reduces the thermal stress. Here we present an optimized workflow for the analysis of brominated dioxins and furans.

Materials and methods

All measurements are performed using Thermo Scientific™ DFS™ magnetic sector GC-HRMS including Thermo Scientific™ TriPlus™ RSH Autosampler and Thermo Scientific™ TRACE™ 1610 GC equipped with the Thermo Scientific™ iConnect™ PTV Injector Module. The instrument method was tested on Bromodioxin/Furan Calibration Standard Solution in nonane from Cambridge Isotope Laboratories Inc. (CS1 PN: EDF5407-1; CS3 PN: EDF5407-3 and CS5 PN: EDF5407-5). The data evaluation was done with Thermo Scientific™ TargetQuan Software.

Figure 1. DFS Magnetic Sector GC-HRMS coupled to two TRACE 1610 GCs.

Mass Spectrometer

DFS Magnetic Sector GC-HRMS is operated in Electron Impact (EI) ionization mode set to 47 eV with an emission current of 1 mA and a source temperature of 270 °C. Full acceleration voltage of the instrument is 5 kV. The resolution is set to 10.000 at 5 % height and high boiling perfluoro kerosine (PFK) is used as a reference gas.

All measurements are done in multi-ion detection (MID) mode and the acquisition time is divided into 5 segments, one for each bromination degree starting from tetra-bromo to octa-bromo (Figure 2 and Tables 1-6)

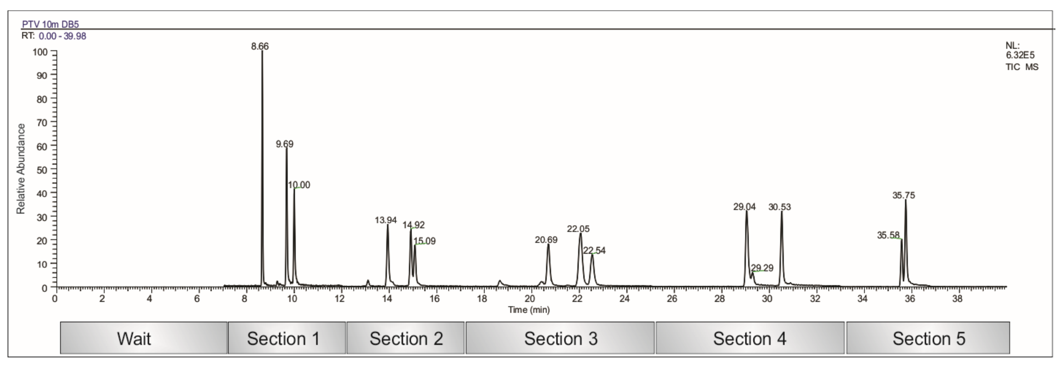

Figure 2. Chromatogram of Br-Dioxin / Furans divided by 5 Multi Ion Detection Segments.

Table 1. Global settings of the 5 Segment Multi Ion Detection.

Parameter	Value
Segments	5
Acquire time	40 [min]
MID mode	Lock
Data type	Centroid
Width 1st lock	0.2 [amu]
Sweep peak width	3
Offset	20 uV
Measure/Lock ratio	1
Magnetic delay	60 [ms]
Electric delay	8 [ms]

Table 2. MID Section 1, Tetra Bromo Dioxin/Furan, (Start: 7 min, End: 12 min, Cycle time: 0.55 s).

Mass (m/z)	Int.	Time [ms]	Compound	Comment
480.96910	10	8	PFK	Lockmass
483.69490	1	89	TBrCDF	QM 100%
485.69288	1	89	TBrCDF	RM 64.85%
495.73520	5	17	[13]C12-TBrCDF	QM 100%
497.73313	5	17	[13]C12-TBrCDF	RM 64.85%
497.69190	1	89	TBrCDD	RM 68.53%
499.68980	1	89	TBrCDD	QM 100%
509.73210	5	17	[13]C12-TBrCDD	RM 68.53%
511.73010	5	17	[13]C12-TBrCDD	QM 100%
516.96910	10	8	PFK	Calimass

Table 3. MID Section 2, Penta Bromo Dioxin/Furan, (Start: 12 min, End: 17 min, Cycle time: 1 s).

Mass (m/z)	Int.	Time (ms)	Compound	Comment
554.96590	10	17	PFK	Lockmass
561.60540	1	175	PeBrCDF	QM 100%
563.60340	1	175	PeBrCDF	RM 97.28%
573.64570	5	35	[13]C12-PeBrCDF	QM 100%
575.64360	5	35	[13]C12-PeBrCDF	RM 97.28%
577.60040	1	175	PeBrCDD	QM 100%
579.59830	1	175	PeBrCDD	RM 97.28%
589.64060	5	35	[13]C12-PeBrCDD	QM 100%
591.63860	5	35	[13]C12-PeBrCDD	RM 97.28%
592.96270	10	17	PFK	Calimass

Table 4. MID Section 3, Hexa Bromo Dioxin/Furan, (Start: 17 min, End: 25 min, Cycle time: 1.2 s).

Mass (m/z)	Int.	Time (ms)	Compound	Comment
630.9595	10	21	PFK	Lockmass
639.51590	1	214	HxBrCDF	RM 77.10%
641.51390	1	214	HxBrCDF	QM 100%
651.55620	5	42	[13]C12-HxBrCDF	RM 77.10%
653.55420	5	42	[13]C12-HxBrCDF	QM 100%
657.50880	1	214	HxBrCDD	QM 100%
659.50677	1	214	HxBrCDD	RM 72.96%
667.55110	5	42	[13]C12-HxBrCDD	RM 77.10%
669.54910	5	42	[13]C12-HxBrCDD	QM 100%

Table 5. MID Section 4, Hepta Bromo Dioxin/Furan, (Start: 25 min, End: 33 min, Cycle time: 1 s).

Mass (m/z)	Int.	Time (ms)	Compound	Comment
716.95630	10	17	PFK	Lockmass
719.42440	1	175	HpBrCDF	QM 100%
721.42240	1	175	HpBrCDF	RM 97.28%
731.46470	5	35	[13]C12-HpBrCDF	QM 100%
733.46260	5	35	[13]C12-HpBrCDF	RM 97.28%
735.41930	1	175	HpBrCDD	QM 100%
737.41730	1	175	HpBrCDD	RM 97.28%
747.45960	5	35	[13]C12-HpBrCDD	QM 100%
749.45750	5	35	[13]C12-HpBrCDD	RM 97.28%
780.94990	10	17	PFK	Calimass

Table 6. MID Section 5, Octa Bromo Dioxin/Furan, (Start: 33 min, End: 40 min, Cycle time: 0.9 s).

Mass (m/z)	Int.	Time (ms)	Compound	Comment
780.94990	10	15	PFK	Lockmass
797.33490	1	156	OBrCDF	RM 82.24%
799.33290	1	156	OBrCDF	QM 100%
809.37520	5	31	[13]C12-OBrCDF	RM 82.24%
811.37310	5	31	[13]C12-OBrCDF	QM 100%
813.32980	1	156	OBrCDD	RM 82.24%
815.32780	1	156	OBrCDD	QM 100%
825.37010	5	31	[13]C12-OBrCDD	RM 82.24%
827.36810	5	31	[13]C12-OBrCDD	QM 100%
842.94680	10	15	PFK	Calimass

For native hexa-bromo dibenzodioxin, the ion $C_{12}H_2{}^{79}Br_2{}^{81}Br_4O_2$ mass 659.50677 m/z (72.96%) was used as Ratio ion due to elevated noise caused by PFK on the mass trace of ion $C_{12}H_2{}^{79}Br_4{}^{81}Br_2O_2$ mass 667.55110 m/z (77.10%).

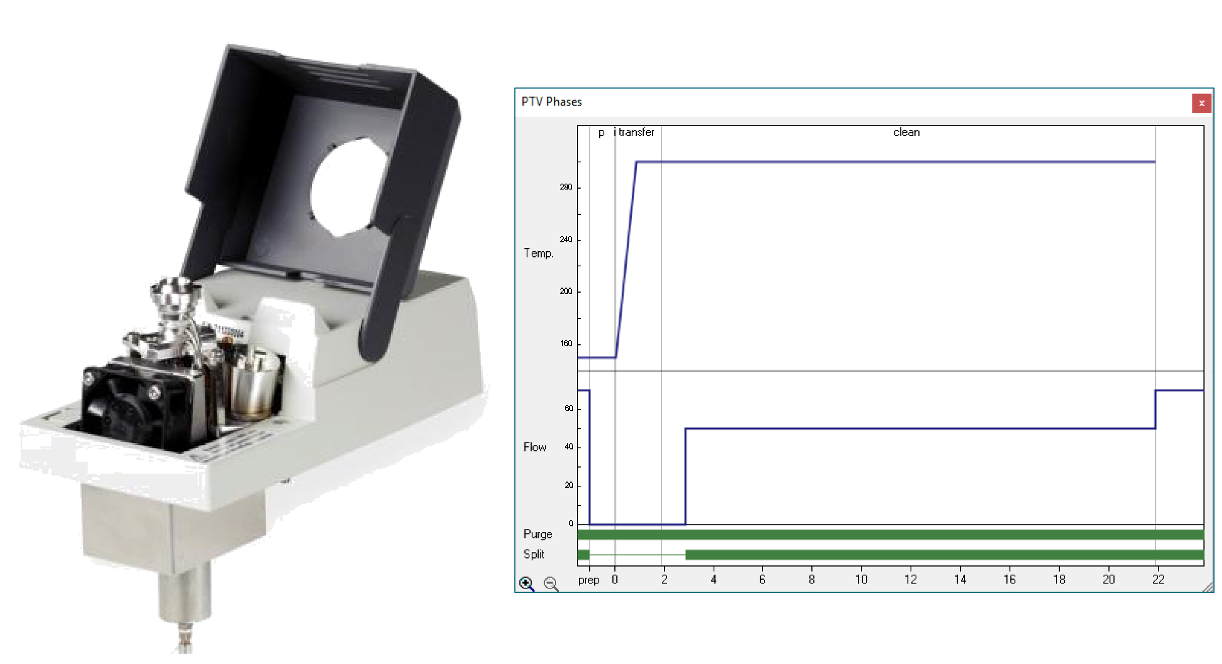

Figure 3. iConnect PTV Injector Module (left) and temperature, flow and valve status plot (right).

Gas chromatograph and autosampler

All experiments were carried out on using a 5% Diphenyl / 95% Dimethylpolysiloxan GC column. Detailed analytical setup for the TriPlus RSH Autosampler, the iConnect PTV injector module, and the TRACE 1610 GC is listed in Tables 7 and 8.

Table 7. Triplus RSH Autosampler and iConnect PTV injector module parameter.

TriPlus RSH Autosampler parameters		iConnect PTV injector module parameters	
Injection mode	Basic	**PTV mode**	Splitless
Rapid mode	disabled	**Temperature enable**	On
Syringe volume	10 mL	**Temperature**	150° C
Needle length	57 mm	**Split flow**	70 mL/min
Sample volume	2 mL	**Splitless time**	2 min
Plunger strokes	3	**Purge flow**	5 mL/min
Air and filling mode	Custom	**Constant septum purge**	On
Air volume	3 mL	**Carrier mode**	Constant Flow
Filling Volume	2 mL	**Carrier flow**	1.3 mL/min
Bottom sense	enabled	**Vacuum compensation**	On
Height from bottom	0.3 mm	**Carrier gas saver enable**	On
Sample type	Custom	**Carrier gas saver flow**	20 mL/min
Sample pullup speed	1 mL /sec	**Carrier gas saver time**	5 min
Delay after plunger strokes	1 s	**Cyrogenics enable**	Off
Viscosity delay	0 s	**Use evaporation phase**	No
		Use cleaning phase	Yes

Table 8. TRACE 1610 GC parameters.

TRACE 1610 GC parameters			
Maximum temperature	350 ° C	**Use ramped pressure**	No
Prep-run timeout	10 min	**Transfer temperature delay**	1 min
Equilibration time	0.50 min	**Injection time**	0.05 min
Ready delay	0 min	**Transfer rate**	3 ° C/s
Oven on/off	On	**Transfer temperature**	300 ° C
Cryogenics enable	Off	**Transfer time**	1 min
Initial temperature	120.0 ° C	**Cleaning rate**	14.5 ° C/s
Number of ramps	3	**Cleaning temperature**	300 ° C
Ramp 01 rate	20 ° C/min	**Cleaning time**	20 min
Ramp 01 final temperature	220 ° C		
Ramp 01 hold time	5 min		
Ramp 02 rate	3 ° C/min		
Ramp 02 final temperature	235 ° C		
Ramp 02 hold time	7 min		
Ramp 03 rate	4.6 ° C/min		
Ramp 03 final temperature	300 ° C		
Ramp 03 hold time	2 min		

Results

We demonstrate successful application of the PTV methodology for analysis of polybrominated dibenzo-furans and -dioxins. Especially the challenging octabromo-dibenzodioxin and the octabromo-dibenzofuran could be measured down to the CS1 Standard. The RF values for tetrabromo-dibenzofurans and hexabromo-dibenzodioxin could be improved by selecting Ratio masses with less chemical noise on the mass trace caused by PFK ions.

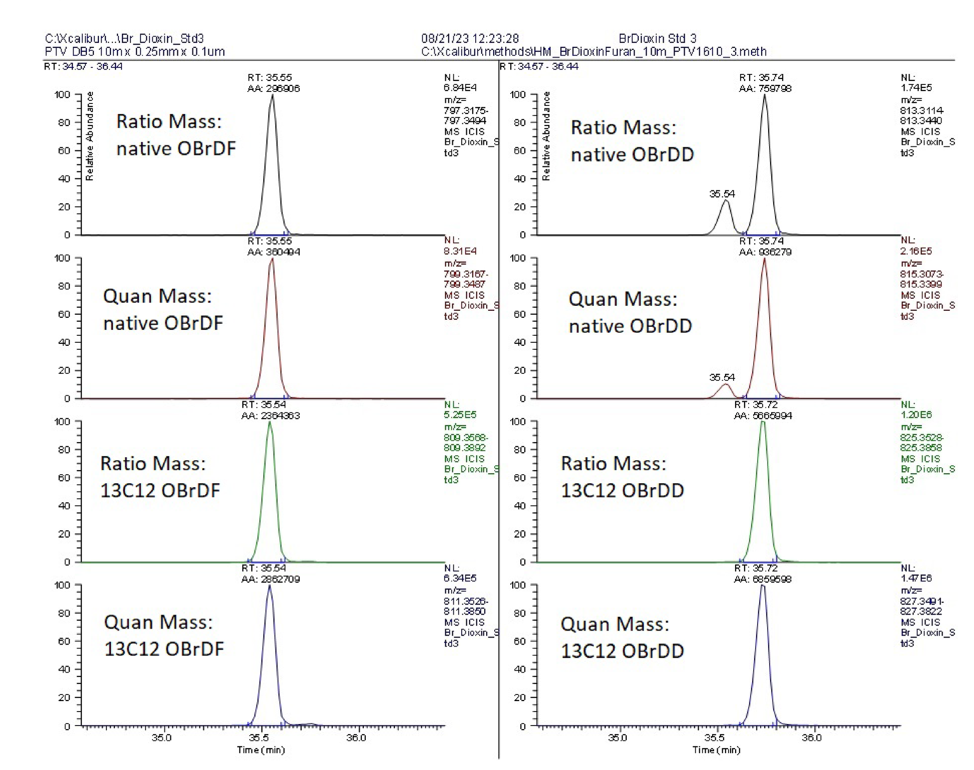

Figure 4. Chromatogram of native and $^{13}C_{12}$ labeled standard of Octa-Bromo Dioxin and Furan.

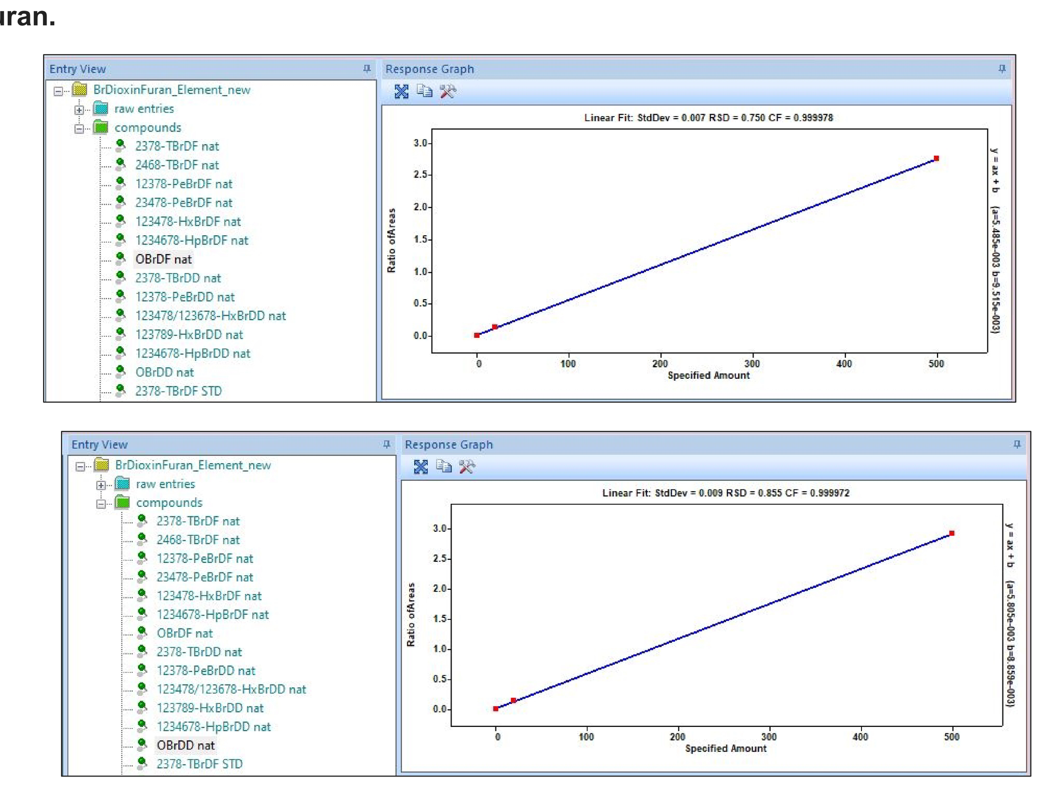

Figure 5. Response Graph of Octa-Bromo Dioxin and Furan with a linear Fit plot.

Conclusions

- A robust routine instrument method could be defined using Thermo Scientific DFS Magnetic Sector GC-HRMS in combination with an iConnect PTV injector module.
- Cross experiments using a Split Spitless (SSL) injector showed bad performance or no acceptable results at all with this type of injector.

References

1.US EPA Method 1613 revision B

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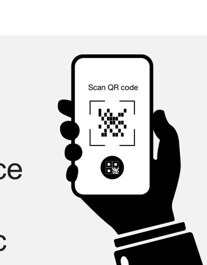

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