

GC-HRMS

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

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Keywords

Brominated dioxins, halogens,
GC-HRMS, PTV injection

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 GC-HRMS instrument method for the analysis of brominated dioxins and furans.



Analytical setup

All measurements are performed using Thermo Scientific™ DFS™ magnetic sector GC-HRMS including TriPlus™ RSH Series Autosampler and TRACE™ 1610 GC equipped with 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).

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 perfluorokerosine (PFK) is used as a reference gas.

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

A.	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

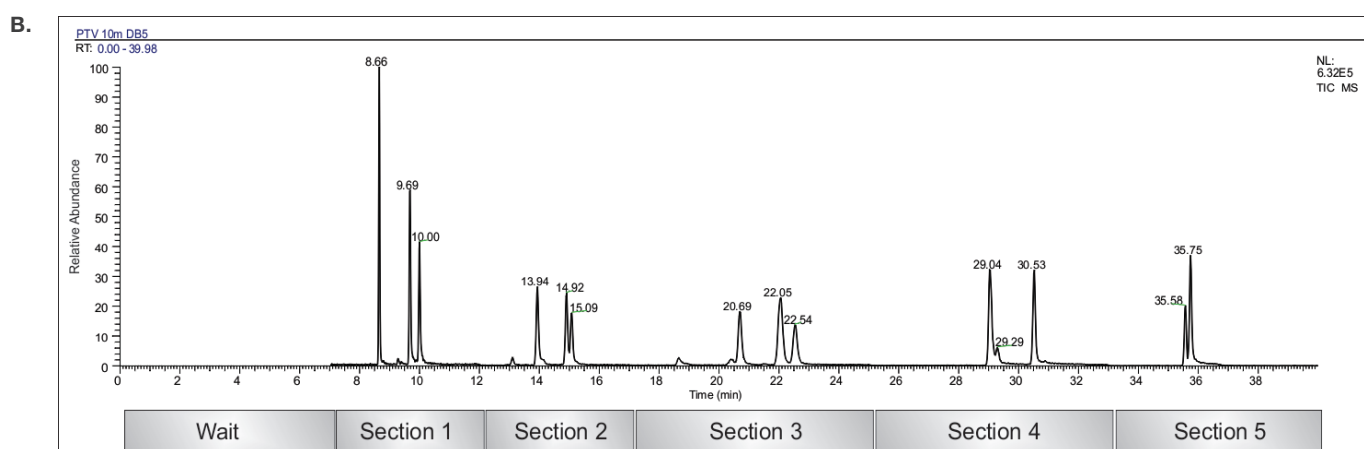


Figure 1. A) Multi-ion detection (MID) parameters for DFS Magnetic Sector GC-HRMS, B) MID section from tetra- to octa-bromo dibenzodioxin/furan.

Typically, the most intense isotope ion of the component is used for the Quantification mass and the second intense ion is used as Ratio mass. In case of coeluting or other distributions on the mass trace of a selected ion, other ions can also be selected and used as Quantification or Ratio mass.

For the native tetra-bromo dibenzofuran, the ion $C_{12}H_4^{79}Br^{81}Br_3O$ mass 485.69288 m/z (64.85%) was used as Ratio ion due to elevated noise caused by PFK on the mass trace of ion $C_{12}H_4^{79}Br_3^{81}BrO_2$ mass 481.69700 m/z (68.53%). For the same reason also ion $^{13}C_{12}H_4^{79}Br^{81}Br_3O$ mass 497.73313 m/z (64.85%) was used as Ratio ion for the $^{13}C_{12}$ labeled internal standard of tetra-bromo dibenzofuran instead of ion $^{13}C_{12}H_4^{79}Br_3^{81}BrO_2$ mass 493.73720 m/z (68.53%).

Table 1: MID Section 1 parameter (Start: 7 min, End: 12 min, Measure: 5 min, Cycle: 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 C ₁₂ -TBrCDF	QM 100%
497.73313	5	17	¹³ C ₁₂ -TBrCDF	RM 64.85%
497.69190	1	89	TBrCDD	RM 68.53%
499.68980	1	89	TBrCDD	QM 100%
509.73210	5	17	¹³ C ₁₂ -TBrCDD	RM 68.53%
511.73010	5	17	¹³ C ₁₂ -TBrCDD	QM 100%
516.96910	10	8	PFK	Calimass

For native hexa-bromo dibenzodioxin, the ion C₁₂H₂⁷⁹Br₂⁸¹Br₄O₂ 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 C₁₂H₂⁷⁹Br₄⁸¹Br₂O₂ mass 667.55110 m/z (77.10%).

Table 3: MID Section3 parameter (Start: 17 min, End: 25 min, Measure: 8 min, Cycle: 1.20 s).

Mass (m/z)	Int.	Time (ms)	Compound	Comment
630.9595	10	21	PFK	Lockmass
639.51590	1	214	HxBrCDF	QM 100%
641.51390	1	214	HxBrCDF	RM 64.85%
651.55620	5	42	¹³ C ₁₂ -HxBrCDF	QM 100%
653.55420	5	42	¹³ C ₁₂ -HxBrCDF	RM 64.85%
657.50880	1	214	HxBrCDD	RM 68.53%
659.50677	1	214	HxBrCDD	QM 100%
667.55110	5	42	¹³ C ₁₂ -HxBrCDD	RM 68.53%
669.54910	5	42	¹³ C ₁₂ -HxBrCDD	QM 100%
680.95630	10	21	PFK	Calimass

Table 5: MID Section 5 parameter (Start: 33 min, End: 40 min, Measure: 7 min, Cycle: 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 C ₁₂ -OBrcDF	RM 82.24%
811.37310	5	31	¹³ C ₁₂ -OBrcDF	QM 100%
813.32980	1	156	OBrcDD	RM 82.24%
815.32780	1	156	OBrcDD	QM 100%
825.37010	5	31	¹³ C ₁₂ -OBrcDD	RM 82.24%
827.36810	5	31	¹³ C ₁₂ -OBrcDD	QM 100%
842.94680	10	15	PFK	Calimass

Table 2: MID Section 2 parameter (Start: 12 min, End: 17 min, Measure: 5 min, Cycle: 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 C ₁₂ -PeBrCDF	QM 100%
575.64360	5	35	¹³ C ₁₂ -PeBrCDF	RM 97.28%
577.60040	1	175	PeBrCDD	QM 100%
579.59830	1	175	PeBrCDD	RM 97.28%
589.64060	5	35	¹³ C ₁₂ -PeBrCDD	QM 100%
591.63860	5	35	¹³ C ₁₂ -PeBrCDD	RM 97.28%
592.96270	10	17	PFK	Calimass

Table 4: MID Section 4 parameter (Start: 25 min, End: 33 min, Measure: 8 min, Cycle: 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 C ₁₂ -HpBrCDF	QM 100%
733.46260	5	35	¹³ C ₁₂ -HpBrCDF	RM 97.28%
735.41930	1	175	HpBrCDD	QM 100%
737.41730	1	175	HpBrCDD	RM 97.28%
747.45960	5	35	¹³ C ₁₂ -HpBrCDD	QM 100%
749.45750	5	35	¹³ C ₁₂ -HpBrCDD	RM 97.28%
780.94990	10	17	PFK	Calimass

Gas chromatograph and autosampler

All experiments were carried out using a 5% Diphenyl / 95% Dimethylpolysiloxan GC column. Detailed analytical setup for the TriPlus RSH SMART Autosampler, the iConnect PTV injector module and the TRACE 1610 GC is listed in Table 6.

Table 6: Gas chromatographer and autosampler analytical setup.

TriPlus RSH Autosampler parameters		iConnect PTV injector module parameters	
Injection mode	Basic	PTV mode	Splitless
Rapid mode	disabled	Temperature enable	On
Syringe volume	10 µL	Temperature	150 °C
Needle length	57 mm	Split flow	70 mL/min
Sample volume	2 µL	Splitless time	2 min
Plunger strokes	3	Purge flow	5 mL/min
Air and filling mode	Custom	Constant septum purge	On
Air volume	3 µL	Carrier mode	Constant Flow
Filling volume	2 µL	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 µL/sec	Carrier gas saver time	5 min
Delay after plunger strokes	1 s	Cyrogenics enable	Off
Viscosity delay	0 s	Use evaporation phase	No
TRACE 1610 GC parameters		Use cleaning phase	Yes
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 °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 (Figure 2 and 3) 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.

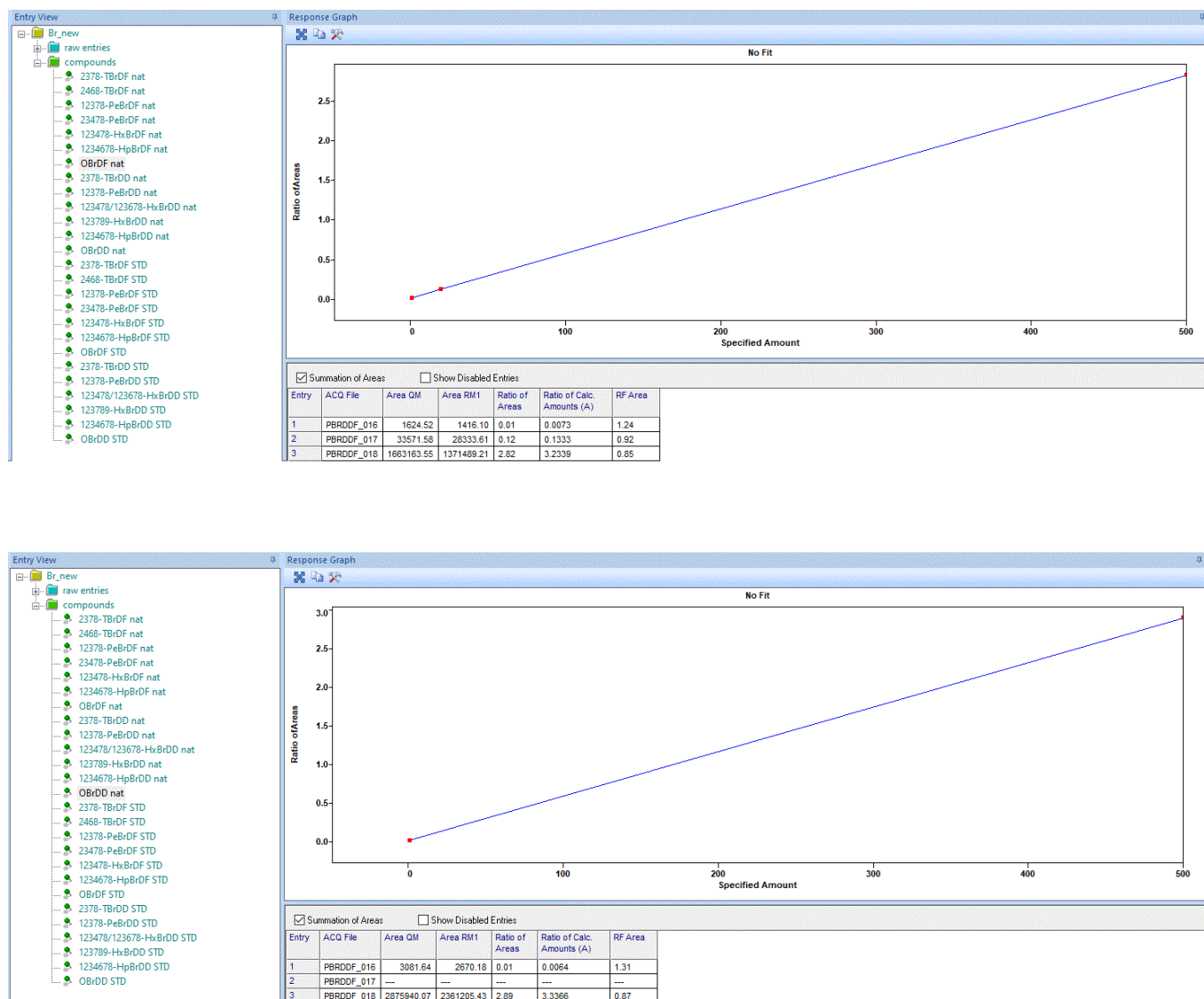


Figure 2: Calibration curve for A) octabromo-dibenzofuran and B) octabromo-dibenzodioxin.

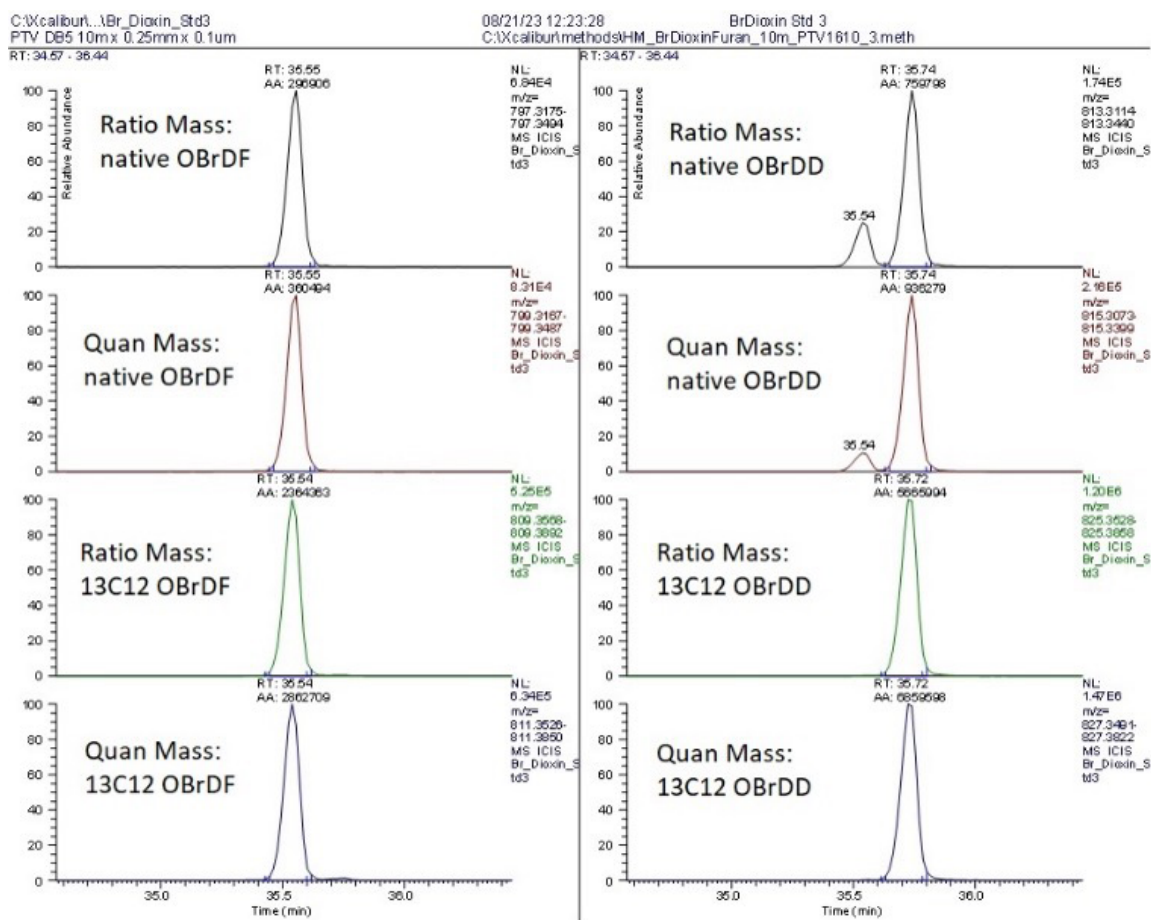


Figure 3: Chromatogram of octabromo-dibenzofuran (left) and octabromo-dibenzodioxin (right).

Conclusions

We report an optimized Programmed Temperature Vaporizing Injector method for the analysis of brominated dioxins. This method is clearly preferable to a Split/Spitless Injector method as thermally labile compounds such as octabromo-dibenzodioxin and the octabromo-dibenzofuran might decompose already during the injection process. The PTV method reduces the thermal stress on the analytes and is applicable for application in routine analysis of challenging compounds such as brominated dioxins and furans.

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