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Quantitative Determination of Dioxins in Drinking Water by Isotope Dilution using Triple Quadrupole GC-MS/MS

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Introduction

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), generally termed as dioxins, are persistent organic pollutants. Their stabilities have been accumulating to environmental problems. In addition to the gas chromatograph coupled with high resolution mass spectrometry (GC-HRMS) system, EU regulation 589/2014 has included the use of tandem mass-spectrometry (GC-MS/MS) system as a confirmatory method for determination of dioxins in feed and food[1]. This motivates the use of the inexpensive and user-friendly GC-MS/MS system to identify and quantify dioxins. In this study, we report a method developed with the cost-effective triple quadrupole GC-MS/MS system for high sensitivity detection and quantification of dioxins in water samples, as a proposed alternative to the EPA method 1613 with a change of detector.

Experimental

Calibration standards, native and ^{13}C-labelled compound spiking solutions of seventeen dioxin congeners were purchased directly from Cambridge Isotope Laboratory and used for method development and performance evaluation. The calibration standards were ready for direct injection.
Three water samples: local tap water, bottled mineral water and swimming pool water, with visibly absent particles were used in this study. Sample preparation was done according to EPA method 1613, using liquid-liquid extraction with a concentration factor of 50,000. Cleanup was not required for these relatively clean samples[2].
A triple quadrupole GC-MS/MS, GCMS-TQ8040 (Shimadzu Corporation, Japan), was employed in this study. The analytical conditions are described in Table 1.

Results and Discussion

Method Development

Excellent GC separation for all 17 dioxin congeners, including the critical hexa-isomer region, was achieved (Fig.1). The peak-to-peak overlap is minimal (<1% overlap).

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Table 1: GC-MS/MS analytical conditions of GCMS-8040 for dioxins analysis.

GC conditions	
Autosampler	: AOC-20i
Column	: SH-Rxi-5Sil MS 60m x 0.25mm ID x 0.25um df
Injection Condition	: 285°C, splitless mode
Injection Volume	: 2µL
Gas Flow Condition	: He, constant linear velocity mode Linear velocity 29.4cm/s Purge flow 5mL/min
Oven Temp. Program	: 150°C (1min) → 20°C/min to 220°C → 2°C/min to 260°C (3min) → 5°C/min to 320°C (8.5min)
MS/MS parameters	
Ion Source Temp.	: 230°C
Interface Temp.	: 280°C
Ionization Mode	: EI, 70eV
Q1 Resolution	: 0.9amu
Q3 Resolution	: 0.9amu
Solvent Cut Time	: 16min
MRM Transitions	: Optimized
Collision Energy	: Optimized
Detector Voltage	: Programmed
Min Dwell Time	: 25ms

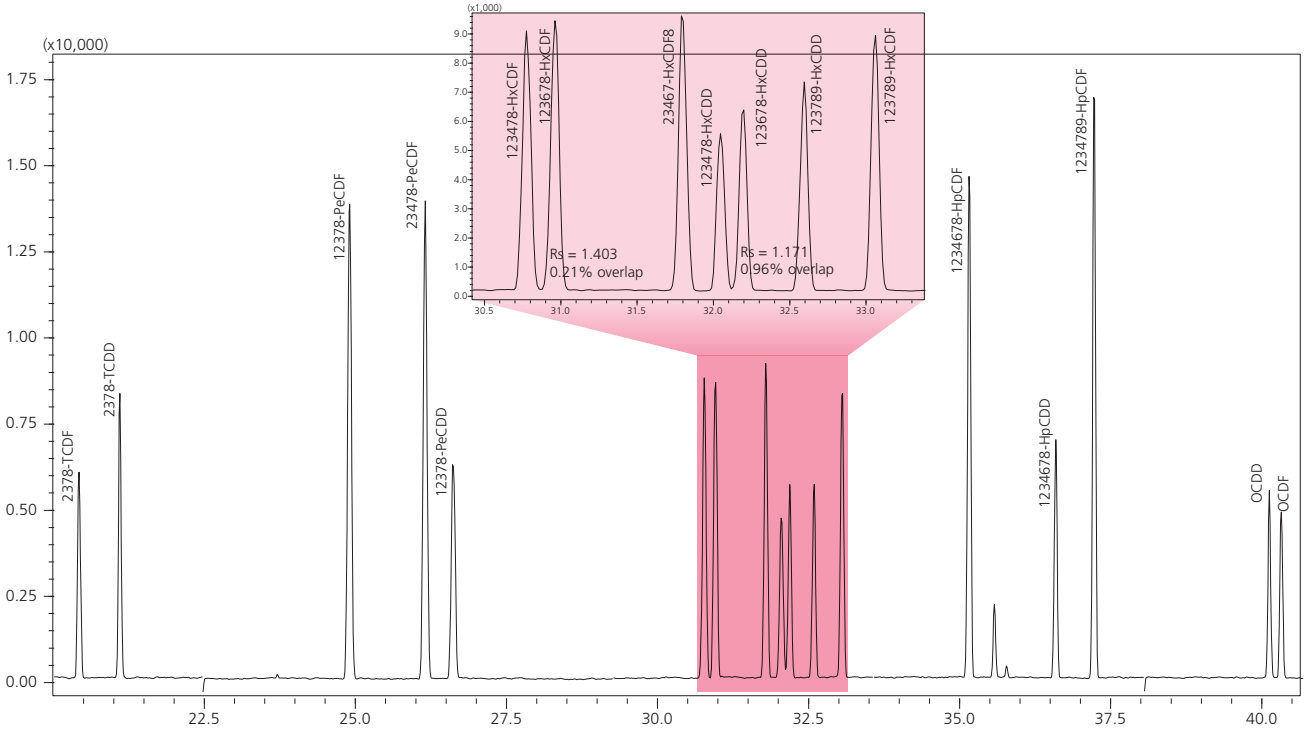

Figure 1: TIC of 17 congeners at 0.05 ng/mL TCDD (CS0.1 level), with hexa-dioxin region highlighted.

The instrument parameters used were based on previous work[3,4]. In this study, a time program for the detector voltage was included. The sensitivity of the instrument was intentionally enhanced by increasing detector voltage for the region where the more toxic dioxin congeners elute. The voltage was then reduced near the end of the analysis.

System and Laboratory Performance

The workflow of method validation is summarized in Figure 2. Calibration curves of seven concentration levels for each congener were established, as illustrated in Table 2. The repeatability at each level was found to be less than 10 % RSD (n=7). All seventeen congeners were calibrated with excellent linearity (R^2>0.999). Calibration curves of three most toxic congeners are shown in Figure 3.
Before each sample batch, a VER (calibration verification) standard with concentration of CS3 was injected to validate the calibration curve (results in Table 3). This was followed by an ongoing precision and recovery (OPR) analysis. The OPR was spiked to VER concentration in reagent water, and was used to check system performance. Recovery checks (REC) were conducted for all spiked samples to ensure good method performance. The method blank analysis was then performed to ensure no contamination and carryover. The results for OPR and method blank (with REC) are shown in Table 5.

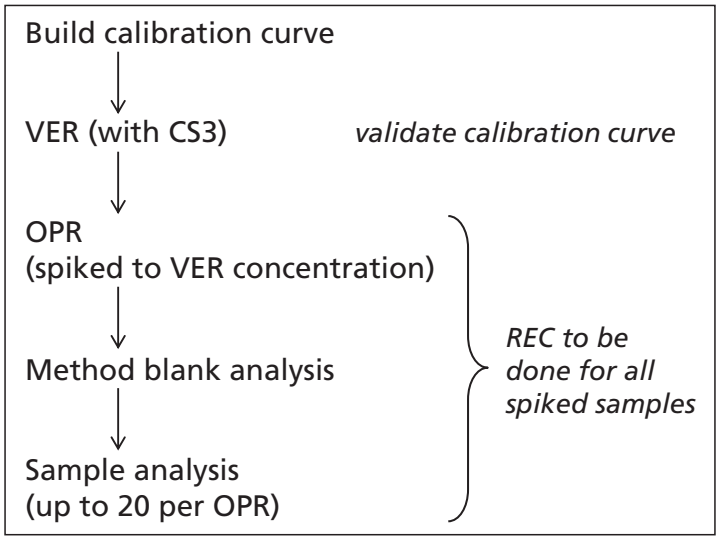

Figure 2: Method validation workflow.

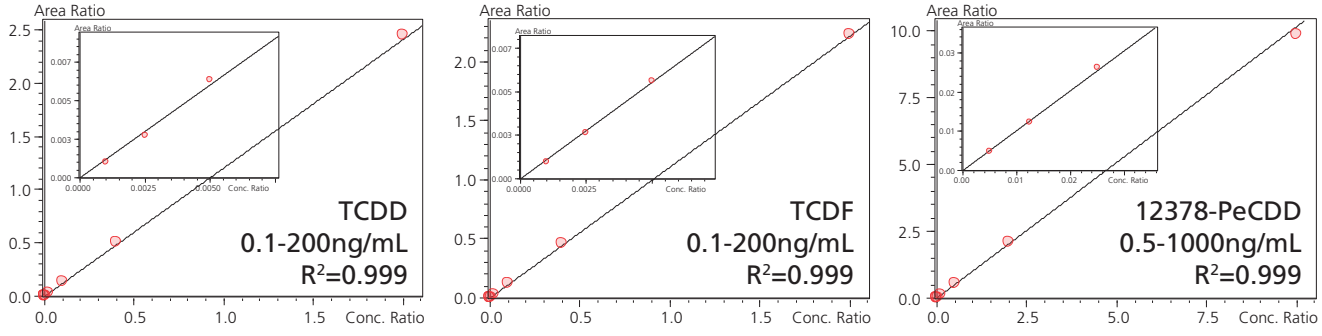

Figure 3: Representative calibration curves with the lowest calibration levels in each insert.

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Table 2: Calibration curve information using isotope diluted internal standard method and repeatability at each level (n=7) for 17 dioxin congeners (all with $R^2 > 0.999$).

Dioxin Congener*	Calibration Range (ng/mL)						
	CS0.2 (RSD)	CS0.5 (RSD)	CS1 (RSD)	CS2 (RSD)	CS3 (RSD)	CS4 (RSD)	CS5 (RSD)
2378-TCDD	0.1 (9.9)	0.25 (5.1)	0.5 (3.4)	2 (4.2)	10 (1.3)	40 (1.4)	200 (2.6)
12378-PeCDD	0.5 (2.5)	1.25 (2.1)	2.5 (3.4)	10 (3.3)	50 (2.4)	200 (1.8)	1000 (1.5)
123478-HxCDD	0.5 (7.9)	1.25 (2.0)	2.5 (3.8)	10 (2.3)	50 (1.5)	200 (2.2)	1000 (0.9)
123678-HxCDD	0.5 (2.3)	1.25 (3.9)	2.5 (2.6)	10 (0.9)	50 (1.2)	200 (2.3)	1000 (2.9)
123789-HxCDD	0.5 (8.6)	1.25 (3.1)	2.5 (1.8)	10 (2.4)	50 (1.3)	200 (3.2)	1000 (2.4)
1234678-HpCDD	0.5 (4.5)	1.25 (5.1)	2.5 (3.7)	10 (2.7)	50 (1.2)	200 (2.3)	1000 (2.9)
OCDD	1 (4.4)	2.5 (4.5)	5 (4.2)	20 (2.2)	100 (2.5)	400 (1.9)	2000 (1.3)
2378-TCDF	0.1 (8.7)	0.25 (5.2)	0.5 (5.0)	2 (2.6)	10 (2.1)	40 (1.2)	200 (1.8)
12378-PeCDF	0.5 (6.0)	1.25 (4.1)	2.5 (4.8)	10 (1.9)	50 (0.7)	200 (2.5)	1000 (2.1)
23478-PeCDF	0.5 (3.8)	1.25 (2.6)	2.5 (3.2)	10 (3.2)	50 (1.4)	200 (2.6)	1000 (2.0)
123478-HxCDF	0.5 (5.3)	1.25 (4.0)	2.5 (3.7)	10 (2.7)	50 (1.3)	200 (2.7)	1000 (1.5)
123678-HxCDF	0.5 (3.9)	1.25 (3.5)	2.5 (4.6)	10 (2.5)	50 (1.2)	200 (1.6)	1000 (2.0)
234678-HxCDF	0.5 (5.6)	1.25 (5.0)	2.5 (5.0)	10 (2.1)	50 (1.2)	200 (3.0)	1000 (2.2)
123789-HxCDF	0.5 (7.6)	1.25 (2.0)	2.5 (3.9)	10 (2.8)	50 (2.8)	200 (2.3)	1000 (3.0)
1234678-HpCDF	0.5 (4.6)	1.25 (2.6)	2.5 (4.4)	10 (3.5)	50 (0.7)	200 (2.8)	1000 (1.7)
1234789-HpCDF	0.5 (4.8)	1.25 (3.2)	2.5 (3.5)	10 (2.6)	50 (2.1)	200 (2.6)	1000 (2.9)
OCDF	1 (3.5)	2.5 (3.2)	5 (1.9)	20 (2.7)	100 (2.3)	400 (2.4)	2000 (1.8)

*Abbreviations: "T" = tetra; "Pe" = penta; "Hx" = hexa; "Hp" = hepta; "O" = octa; "CDD" = chlorodibenzodioxin; "CDF" = chlorodibenzofuran; TCDD/F = 2378-TeCDD/F

Table 3: VER analysis test criteria and results.

Name	Test Conc. (ng/mL)	VER (ng/mL)	
		Criteria	Result
2378-TCDD	10	7.8-12.9	10.0
12378-PeCDD	50	39-65	47.8
123478-HxCDD	50	39-64	49.3
123678-HxCDD	50	39-64	48.9
123789-HxCDD	50	41-61	49.1
1234678-HpCDD	50	43-58	48.6
OCDD	100	79-126	81.6
2378-TCDF	10	8.4-12.0	10.0
12378-PeCDF	50	41-60	47.8
23478-PeCDF	50	41-61	48.4
123478-HxCDF	50	45-56	48.2
123678-HxCDF	50	44-57	48.6
234678-HxCDF	50	45-56	48.3
123789-HxCDF	50	44-57	48.0
1234678-HpCDF	50	45-55	47.2
1234789-HpCDF	50	43-58	45.5
OCDF	100	63-159	89.5

Method Detection Limit (MDL)

As TCDD was calibrated to 0.1 ng/mL, the MDL was first estimated to be 10 times lower. Seven extracts fortified at 0.05 ng/mL were then analysed to obtain the MDL. The results (in ng/mL) are found in Table 4. For seven replicates and six degrees of freedom, the Student's t-value is 3.143, and the MDL is calculated as follows[5]:

$$MDL_{in\ extract} = s.d. \times t = 0.0041 \times 3.143 = 0.013 ng/mL$$

The equivalent amount in water sample is:

$$MDL_{in\ sample} = \frac{MDL_{extract} \times V_{extract}}{V_{sample}} = \frac{0.013 ng/mL \times 20 \mu L}{1L} = 0.26 pg/L$$

The MDL is verified by a five-point check[6]:

1. Spike Level (MDLx10 > spike)	: (0.013*10)ng/mL= 0.13ng/mL	[passed, spike = 0.05ng/mL]
2. Spike Level (MDL < spike)	: MDL = 0.013ng/mL	[passed, spike = 0.05ng/mL]
3. MDL < Required Minimum Level (ML)	: MDL = 0.26pg/L	[passed, ML = 10pg/L]
4. S/N Estimate (mean/s.d.)	: 0.0309/0.0041 = 7.54	[passed, S/N is 3-10]
5. Average %Recovery	: 61.7%	[passed, %Rec is 25-164]

Sample Analysis

Three water samples were analysed using the established method. The minimum levels to report in sample are 10 pg/L for TCDD/F (0.5 ng/mL in extract), 50 pg/L for Pe-, Hx-, Hp-CDD/F, and 100 pg/L for OCDD/F. All three samples used in this study passed the REC criteria, and they do not contain any dioxins congeners above the minimum reporting levels (ML). The results (with REC) are listed in Table 5.

Table 4: MDL results in (ng/mL).

Sample#	Results	%Rec
sample 1	0.032	64%
sample 2	0.034	68%
sample 3	0.034	68%
sample 4	0.024	48%
sample 5	0.027	54%
sample 6	0.030	60%
sample 7	0.035	70%
mean	**0.0309**	**61.7%**
s.d.	**0.0041**	

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Table 5: Test criteria and results for OPR analysis, method blank and water sample analyses.
Results below Minimum Level are denoted as "< ML".

Name	Test Conc. (ng/mL)	OPR (ng/mL)		Conc. (ng/mL)			
		Criteria	Result	Method Blank	Sample 1†	Sample 2†	Sample 3†
2378-TCDD	10	6.7-15.8	10.0	< ML	< ML	< ML	< ML
12378-PeCDD	50	35-71	44.5	< ML	< ML	< ML	< ML
123478-HxCDD	50	35-82	48.5	< ML	< ML	< ML	< ML
123678-HxCDD	50	38-67	48.8	< ML	< ML	< ML	< ML
123789-HxCDD	50	32-81	38.3	< ML	< ML	< ML	< ML
1234678-HpCDD	50	35-70	44.8	< ML	< ML	< ML	< ML
OCDD	100	78-144	91.0	< ML	< ML	< ML	< ML
2378-TeCDF	10	7.5-15.8	9.8	< ML	< ML	< ML	< ML
12378-PeCDF	50	40-67	43.3	< ML	< ML	< ML	< ML
23478-PeCDF	50	34-80	45.1	< ML	< ML	< ML	< ML
123478-HxCDF	50	36-67	47.9	< ML	< ML	< ML	< ML
123678-HxCDF	50	42-65	48.4	< ML	< ML	< ML	< ML
234678-HxCDF	50	39-65	47.7	< ML	< ML	< ML	< ML
123789-HxCDF	50	35-78	46.0	< ML	< ML	< ML	< ML
1234678-HpCDF	50	41-61	40.6	< ML	< ML	< ML	< ML
1234789-HpCDF	50	39-69	41.6	< ML	< ML	< ML	< ML
OCDF	100	63-170	85.9	< ML	< ML	< ML	< ML
^{13}C-1234-TCDD	100	IS	100	100	100	100	100
^{13}C-2378-TCDD	100	25-164	83.5	63.7	76.4	68.0	66.3
^{13}C-12378-PeCDD	100	25-181	86.7	65.4	77.3	69.7	70.5
^{13}C-123478-HxCDD	100	32-141	80.7	63.5	74.2	71.8	68.8
^{13}C-123678-HxCDD	100	28-130	80.8	62.7	73.8	70.9	70.8
^{13}C-123789-HxCDD	100	IS	100	100	100	100	100
^{13}C-1234678-HpCDD	100	23-140	80.3	60.5	74.9	74.2	77.4
^{13}C-OCDD	200	34-313	148.9	108.4	143.7	143.8	148.7
^{13}C-2378-TeCDF	100	24-169	81.7	68.3	74.6	68.3	66.5
^{13}C-12378-PeCDF	100	24-185	84.8	67.2	73.9	67.9	69.7
^{13}C-23478-PeCDF	100	21-178	85.0	67.2	76.3	68.2	69.4
^{13}C-123478-HxCDF	100	26-152	79.4	62.4	70.7	67.9	68.1
^{13}C-123678-HxCDF	100	26-123	78.7	63.4	71.4	67.8	68.0
^{13}C-234678-HxCDF	100	29-147	79.6	64.4	72.0	67.1	64.7
^{13}C-123789-HxCDF	100	28-136	76.7	62.4	69.6	69.6	68.4
^{13}C-1234678-HpCDF	100	28-143	80.5	64.7	74.5	75.4	75.2
^{13}C-1234789-HpCDF	100	26-138	79.4	63.9	75.4	73.2	74.2

†Sample 1 is local tap water, sample 2 is mineral water purchased locally, sample 3 is swimming pool water.

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Conclusions

A GC-MS/MS method has been developed, optimized and validated with EPA 1613 criteria. Calibration was done on 7 levels (all RSD<10%, n=7) with excellent linearity (R^2>0.999). Good system and laboratory performance was illustrated and the MDL of TCDD was determined to be 0.26 pg/L using this method. Analyses were performed on three water samples, and the developed method was shown to be a valid alternative for EPA 1613.

References

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