Application Note

An Alternate Testing Protocol for EPA 1613B using Agilent Triple Quadrupole GC/MS

Determination of 2,3,7,8-substituted tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans

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Abstract

This study provides data used to create an alternate testing protocol for the U.S. Environmental Protection Agency (EPA) to use for Agilent 7010B Triple Quadrupole GC/MS analysis of tetra- through octa-dioxins and furans that is equivalent to EPA Method 1613B. EPA Method 1613B is used for the determination of the 17 toxic tetra- through octa-chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs) in aqueous, solid, and tissue matrices by isotope dilution gas chromatography/high-resolution mass spectrometry (GC/HRMS) using magnetic sector instruments. Traditionally used for dioxins analysis because of their high sensitivity, GC/HRMS instruments are expensive to maintain, require a highly specialized skill set to operate, and are being phased out by manufacturers.

However, current GC/MS/MS (GC/TQ) technology provides many of the specificity and sensitivity advantages of HRMS for the analysis of regulated dioxins and furans, without the cost and complexity, and with added versatility and robustness. This application note describes a method developed in collaboration with SGS AXYS Analytical Services Ltd., SGS AXYS Method 16130, that uses the Agilent 7890B gas chromatograph coupled with an Agilent 7010B Triple Quadrupole GC/MS and Agilent Reference Compound Introduction Valve. Performance factors investigated included sensitivity, linearity, method detection limits (MDLs), recovery, and results compared to reference material. The GC/TQ results met the QA/QC and performance specifications described in Method 1613B for the analysis of polychlorinated dioxins and furans (PCDDs/PCDFs) in environmental matrices with the ability to monitor for any changes in ion transmission or efficiency. Overall, the GC/TQ method produced accurate data for real-world sample matrices, offering a lower cost, more efficient alternative to GC/HRMS.

Introduction

Dioxins are pollutants of concern due to the adverse effects of trace-level chronic exposure, persistence in the environment, and bio-accumulation in the food chain.1 For this reason, they are monitored by environmental agencies worldwide.

The U.S. Environmental Protection Agency (EPA) has promulgated Method 1613B for the determination of the 17 toxic 2,3,7,8-substituted tetra- through octa-chlorinated CDDs/CDFs in aqueous, solid, and tissue matrices by isotope dilution gas chromatography/high-resolution mass spectrometry (GC/HRMS) using magnetic sector instruments. As originally written, Method 1613B requires a high mass resolution of ≥10,000, which can only be achieved using GC/HRMS. Traditionally, magnetic sector MS instruments have been used for this analysis due to lack of better alternatives. However, magnetic sector MS instruments are expensive to maintain and require a highly specialized skill set to operate. In addition, with suppliers discontinuing or phasing out manufacture of magnetic sector GC/HRMS instruments, an alternate technique that provides data of the same quality, with easier and more robust operation, is required.

MS/MS technology offers many of the specificity and sensitivity advantages of HRMS methods without the need for high mass resolution, or the cost and complexity of HRMS instruments. Approval of a method that uses GC/MS/MS (GC/TQ) for determination of dioxins and furans has the potential to lower laboratory costs. Developed in collaboration with SGS AXYS ANALYTICAL SERVICES LTD, this application note describes a GC/TQ method using an Agilent 7890B gas chromatograph coupled with an Agilent 7010B Triple Quadrupole GC/MS that meets the QA/QC and performance specifications in Method 1613B for the analysis of polychlorinated dioxins and furans (PCDDs/PCDFs) in environmental matrices. The method--SGS AXYS Method 16130--is approved by the US EPA as an alternate testing protocol for analyzing the Dioxins in EPA 1613B. Performance factors investigated in this application note included sensitivity, linearity, method detection limits (MDLs), recovery, and results for reference materials.

The EPA has reviewed the SGS AXYS Method 16130 using the 7010B Triple Quadrupole GC/MS and supporting validation data submitted by SGS AXYS, and has determined that it meets requirements as an alternate testing protocol for measurement of 2,3,7,8-substituted tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) in wastewater with performance similar to the methods listed in 40 CFR Part 136. Though the EPA has not yet promulgated the method or published it in the CFR at the time of this publication, on a facility-by-facility basis laboratories may seek approval from their regional authority to use the method in measuring PCDDs/PCDFs in wastewater in per the Clean Water Act (CWA) program.

Experimental

Sample preparation and extraction
Sample cleanup is required to maintain the MS instrument in good condition, and to avoid mass fluctuations and changes in ionization efficiency due to background matrix. For this application note, analyses were performed using real-world sample extracts from four matrices (aqueous, solids, biosolids, and tissues) that had been archived at SGS AXYS Analytical Services after preparation and extraction per EPA Method 1613B.1 In this procedure, stable isotope-labeled analogs of 15 of the 2,3,7,8-substituted CDDs/CDFs are spiked prior to extraction. After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. After cleanup, the extract is concentrated to near dryness. Immediately prior to injection into the GC for GC/TQ analysis, internal standards were added to each extract.

GC/TQ analysis and instrumentation

GC/TQ analysis was carried out with a 7890B gas chromatograph coupled with a 7010B Triple Quadrupole GC/MS. The 7890B gas chromatograph was equipped with a 60 meter Agilent DB-5 column (part number 122-5061). All GC/HRMS data used for comparison were also collected using a DB-5 column operated under similar conditions. The 7010B Triple quadrupole GC/MS was operated in the MRM mode and equipped with a high-efficiency EI source (HES). The GC/TQ parameters are provided in Table 1.

The GC/TQ system was tuned to Agilent specifications using perfluorotributylamine (PFTBA) and the default HES tune. The method stipulates that the system is ready to operate as long as the vendor-specified tune criteria are met. Method 1613B requires a mass resolution check every 12 hours. The analogous parameter when using MS/MS is a mass calibration and tuning check. Every 12 hours the mass calibration was monitored by measuring the amount of peak drift from the expected masses for PFTBA. If the peak apex had shifted more than 0.3 amu from the expected value, then the instrument was recalibrated.

The need for lock mass monitoring of the GC/HRMS system for Method 1613B was replaced by use of a stability reference compound in the GC/TQ method. A small but constant amount of PFTBA, the reference compound used for tuning and mass calibration, was introduced using the Agilent Reference Compound Introduction Valve (RCIV).

The MRM transition 414.0 & 264.0 was monitored throughout the run. The RCIV is controlled through Agilent MassHunter software and provides an optimized flow of PFTBA to monitor for any changes in the ionization efficiency and ion transmission through changes in the reference compound signal intensity.

Two transitions were monitored for each of the native PCDD/PCDF analytes and their corresponding 13C-labeled analogues. Two masses from the molecular ion cluster were used as the transition precursors, each with its own product ion (loss of neutral $CO^{35}Cl$).

MRM delivers a unique product ion that can be monitored and quantified in a complicated matrix, providing the selectivity needed for PCDD/PCDF analysis. The triple-stage selection process for ions reaching the detector results in low noise and thus a high signal-to-noise ratio (S/N) and good sensitivity and selectivity for analytes.

The primary and secondary transitions for each analyte and labeled compound are listed in Table 2. Agilent MassHunter software was used for data acquisition, analysis, and reporting.

Table 1. GC/TQ parameters.

Parameter	Value
	Gas Chromatograph
Model	Agilent 7890B gas chromatograph
Column	Agilent DB-5, 60 m × 0.25 mm, 0.1 µm (p/n 122-5061)
Column Pneumatics	Constant flow, He carrier gas
Injector Mode	Splitless
Injector Liner	Inlet liner, splitless, double taper, deactivated (p/n 5181-3315)
Injection Volume	1.0 µL
Injector Temperature	290 °C
Flow Rate	0.93 mL/min
Temperature Program	90 °C for 2 min, 22 °C/min to 200 °C, 1 °C/min to 215 °C, hold 10 min, 5.2 °C/min to 300 °C, hold 2.7 min
Total Run Time	51.05 min
Equilibration Time	0.1 min
	Mass Spectrometer
Model	Agilent 7010B Triple Quadrupole GC/MS
Reference Compound Controller	Agilent Reference Compound Introduction Valve (p/n G7050A)
Ionization Mode	EI, 70 eV
Acquisition Mode	MRM
Filament Current	100 µA
Collision Gas	N_2 at 1.5 mL/min
Quench Gas	He at 2.25 mL/min
GC Interface Temperature	290 °C
Ion Source Temperature	290 °C
Quadrupole 1 Temperature	150 °C
Quadrupole 2 Temperature	150 °C

Table 2. MRM transitions.

Analytes	Primary MRM Transition *(m/z)*	Collision Energy (CE)	Secondary MRM Transition (*m/z*)	CE	Surrogate
2,3,7,8-TCDD	319.9 & 256.9	24	321.9 & 258.9	24	$^{13}C_{12}$-2,3,7,8-TCDD
1,3,6,8-TCDD	319.9 & 256.9	24	321.9 & 258.9	24	^{13}C12-2,3,7,8-TCDD
1,3,7,9-TCDD	319.9 & 256.9	24	321.9 & 258.9	24	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	355.9 & 292.9	25	353.9 & 290.9	25	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	389.8 & 326.9	25	391.8 & 328.9	25	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	389.8 & 326.9	25	391.8 & 328.9	25	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	389.8 & 3269	25	391.8 & 328.9	25	Mean of $^{13}C_{12}$-1,2,3,6,7,8/1,2,3,4,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	423.8 & 360.8	25	425.8 & 362.8	25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	457.7 & 394.8	26	459.7 & 396.8	26	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	303.9 & 240.9	33	305.9 & 242.9	33	$^{13}C_{12}$-2,3,7,8 -TCDF
1,2,7,8-TCDF	303.9 & 240.9	33	305.9 & 242.9	33	$^{13}C_{12}$-2,3,7,8 -TCDF
1,2,3,7,8-PeCDF	339.9 & 276.9	35	337.9 & 274.9	35	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	339.9 & 276.9	35	337.9 & 274.9	35	$^{13}C_{12}$-2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	373.8 & 310.9	35	375.8 & 312.9	35	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	373.8 & 310.9	35	375.8 & 312.9	35	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF

Table 2. MRM transitions (continued)

Analytes	Primary MRM Transition (*m/z*)	Collision Energy (CE)	Secondary MRM Transition (*m/z*)	CE	Surrogate
2,3,4,6,7,8-HxCDF	373.8 & 310.9	35	375.8 & 312.9	35	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	373.8 & 310.9	35	375.8 & 312.9	35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	407.8 & 344.8	36	409.8 & 346.8	36	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	407.8 & 344.8	36	409.8 & 346.8	36	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF
OCDF	441.7 & 378.8	35	443.7 & 380.8	35	$^{13}C_{12}$-OCDD
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	327.9 & 262.9	33	—		$^{13}C_{12}$-1,2,3,4-TCDD
Labeled Surrogates					**Recovery Calculated Using**
$^{13}C_{12}$-2,3,7,8-TCDD	331.9 & 268.0	24	333.9 & 270.0	24	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	367.9 & 303.9	25	365.9 & 301.9	25	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	401.9 & 337.9	25	403.9 & 339.9	25	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	401.9 & 337.9	25	403.9 & 339.9	25	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	435.8 & 371.9	25	437.8 & 373.9	25	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	469.8 & 405.8	26	471.8 & 407.8	26	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8 -TCDF	315.9 & 252.0	33	317.9 & 254.0	33	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	351.9 & 287.9	35	349.9 & 285.9	35	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	351.9 & 287.9	35	349.9 & 285.9	35	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	385.9 & 321.9	35	387.9 & 323.9	35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	385.9 & 321.9	35	387.9 & 323.9	35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	385.9 & 321.9	35	387.9> 323.9	35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	385.9 & 321.9	35	387.9 & 323.9	35	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	419.8 & 355.9	36	421.8 & 357.9	36	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	419.8 & 355.9	36	421.8 & 357.9	36	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	331.9 & 268.0	24	333.9 & 270.0	24	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	401.9 & 337.9	25	403.9 & 339.9	25	
Cl-DPE Transitions					
Descriptor			**Type**	**Substance**	
1	375.8 & 305.9	30	M+2	HxCDPE	
2	409.8 & 339.9	25	M+2	HpCDPE	
3	445.8 & 373.8	30	M+4	OCDPE	
4	479.7 & 407.8	30	M+4	NCDPE	
5	513.7 & 443.7	30	M+4	DCDPE	

As with the GC/HRMS Method 1613B, individual PCDD/PCDFs were identified by comparing the GC retention time and MRM transition product ion ratio (primary/secondary transition, Table 3), with the corresponding retention time of the authentic standard and the theoretical transition product ion ratio.

Though not used here, Agilent's-patented retention time locking (RTL) technology could be used for this application. RTL provides the same retention times on one Agilent GC/MS system to those on another like system with the same nominal column. It also enables a single GC to have the same retention time after the column is trimmed for maintenance.

Shown in Table 3, the QC limits (±15% of theoretical) of Method 1613B were applied to the MS/MS data. The non-2,3,7,8 substituted isomers and congeners were identified when retention times and ion-abundance ratios were within predefined limits.

Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDF was achieved using GC columns that resolve these isomers from the other tetra-isomers.

Table 3. Theoretical product ion ratios and ratio QC limits.

Species Monitored	MRM Transition Precursor *m/z* (Primary/Secondary)	MRM Transition Product* Ion Theoretical Ratio‡	QC Limit**	
			Lower	Upper
Cl_4CDD†	(M+2)/M	0.96	0.82	1.10
Cl_4CDF	(M+2)/M	0.96	0.82	1.10
Cl_5CDD	M/(M+2)	0.78	0.66	0.90
Cl_5CDF	M/(M+2)	0.78	0.66	0.90
Cl_6CDD	(M+4)/(M+2)	0.64	0.54	0.74
Cl_6CDF	(M+4)/(M+2)	0.64	0.54	0.74
Cl_7CDD	(M+4)/(M+2)	0.80	0.68	0.92
Cl_7CDF	(M+4)/(M+2)	0.80	0.68	0.92
Cl_8CDD	(M+4)/(M+2)	0.96	0.82	1.10
Cl_8CDF	(M+4)/(M+2)	0.96	0.82	1.10

** Product ions are due to loss of [CO35Cl].*
*** QC limits represent ±15% windows around the theoretical MRM transition product ion ratios.*
† Does not apply to 37Cl4 -2,3,7,8-TCDD (cleanup standard).
‡ Transition product ion ratios are calculated as secondary ion/primary ion.

Method evaluation samples analyzed

Calibration was performed using a six-point calibration series of solutions covering the working concentration range. The operational range was 0.1 to 200 ng/mL for 2,3,7,8-TCDD and 2,3,7,8-TCDF; 1 to 2,000 ng/mL for OCDD and OCDF; and 0.5 to 1,000 ng/mL for all other dioxins and furans in the method. In addition to target (native) PCDDs/PCDFs, the calibration solutions also contained a suite of labeled surrogates (at 100 ng/mL except for $^{13}C_{12}$-OCDD at 200 ng/mL) and recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD at 100 ng/mL).

Following the procedure in Method 1613B, at least three initial calibrations were used to determine linearity of the GC/TQ instrument response.

Three method detection level (MDL) experiments were run (one each of spiked aqueous, solids, and tissues), per 40 CFR 136.3, Appendix B, Revision 2, on the GC/TQ instrument and compared to the Method 1613B minimum required levels (MRLs).

Extracts of nine real-world samples each from four matrices (aqueous, solids, biosolids, and tissues) were run by GC/TQ and compared to GC/HRMS results for PCDDs/PCDFs previously obtained for the same extracts. The samples were selected to be representative of different wastewater producers and environmental situations.

Four replicates of each of spiked reference (clean) materials (reagent water, Ottawa sand, and vegetable oil) were analyzed to produce an Initial Performance and Recovery (IPR) dataset to determine method recovery. Results were compared to Method 1613B recovery specifications.

A solids standard reference material (NIST 1944) and a tissue certified reference material (EDF 2525) were analyzed to determine the accuracy of the GC/TQ method. No aqueous reference samples were available. Results were compared to the certified values. In addition to the NIST and EDF samples, tissue and sediment/soil proficiency testing samples provided by Sigma-Aldrich RTC were also analyzed by GC/HRMS and GC/TQ.

Batch QC (blanks and ongoing precision and recovery samples) accompanying each of the extracts were also run. Blanks from method detection limit (MDL), recovery, and sample batches were run and compared to Method 1613B criteria.

Results and discussion

Chromatography performance and sensitivity

The GC/TQ analysis provided good chromatographic separation and detection of the target PCDDs/PCDFs as shown for TCDFs and TCDDs in Figure 1A, and for HxCDDs in Figure 1B.

Method 1613B calls for calculation of the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers. The height of the valley between the isomers most closely eluting to the 2,3,7,8-TCDD labeled "x" in Figure 2 does not exceed 25% of the 2,3,7,8-TCDD peak height "y." This parameter can be set as an outlier in the MassHunter Quantitative Analysis method as shown in Figure 3A. If the valley exceeds 25%, the analytical conditions need to be adjusted or the analysis repeated using a different GC column. Figure 3B demonstrates that the front and rear valley height/peak height resolution values were 20.4 and 7.8, respectively, and did not exceed the 25% threshold.

The 7010B Triple Quadrupole GC/MS system showed good sensitivity and S/N for PCDD/PCDFs. The GC/TQ system also provided very good reproducibility at low-level spikes, allowing for low-level quantitation, which is critically important because the EPA lowest Concentration Minimum Reporting Level (LCMRL) takes into account both sensitivity and reproducibility in its calculations. The system provided at least 10:1 S/N requirements for all compounds at the calibration standard level 1 (CS1)-level as required by EPA, and generally exceeded that with requirement with low RSDs.

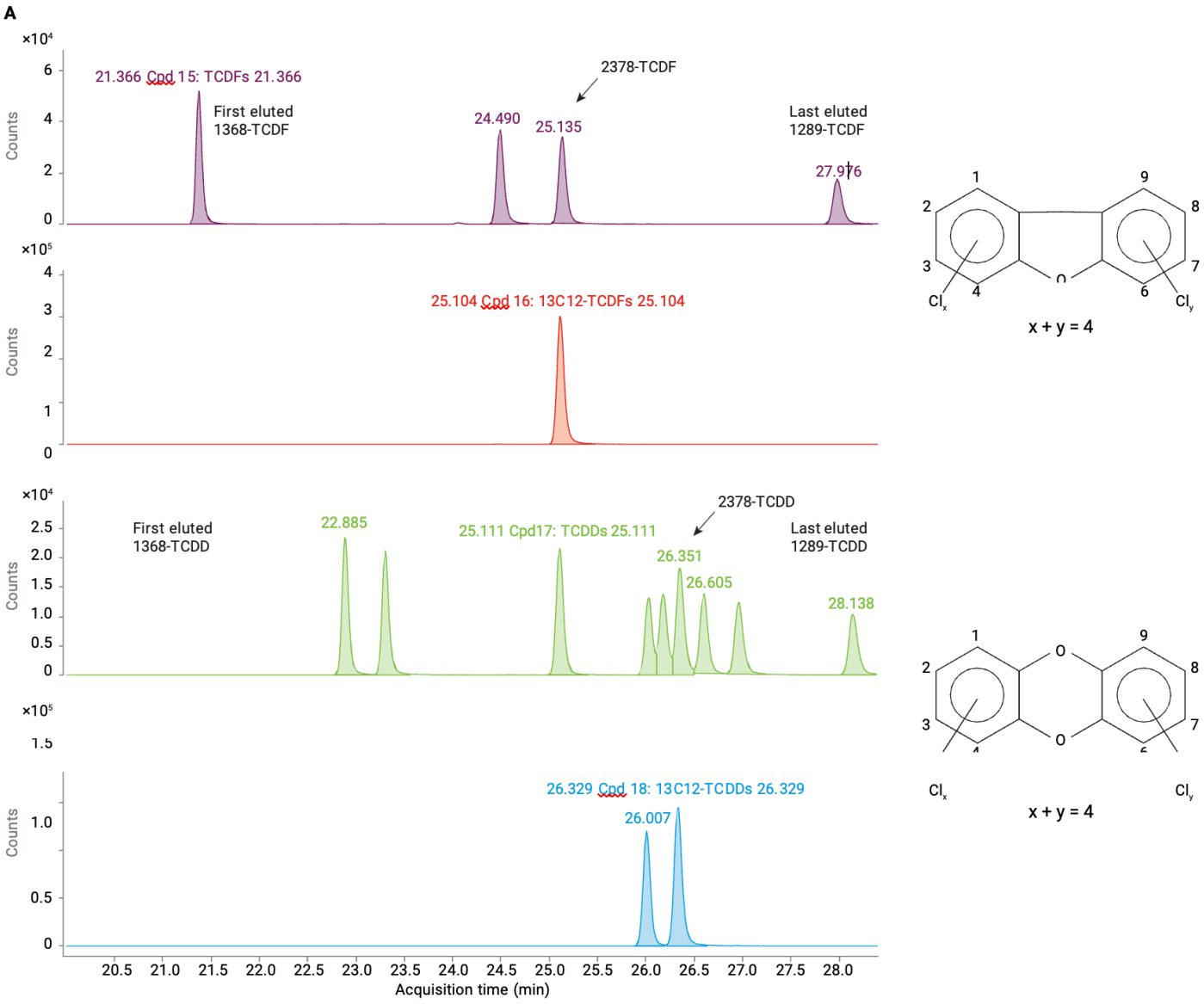

Figure 1A. MRM chromatograms for tetrachlorinated dibenzofurans (TCDFs), labeled TCDF ISTD, tetrachlorinated dibenzodioxins (TCDDs), and labeled TCDD ISTD.

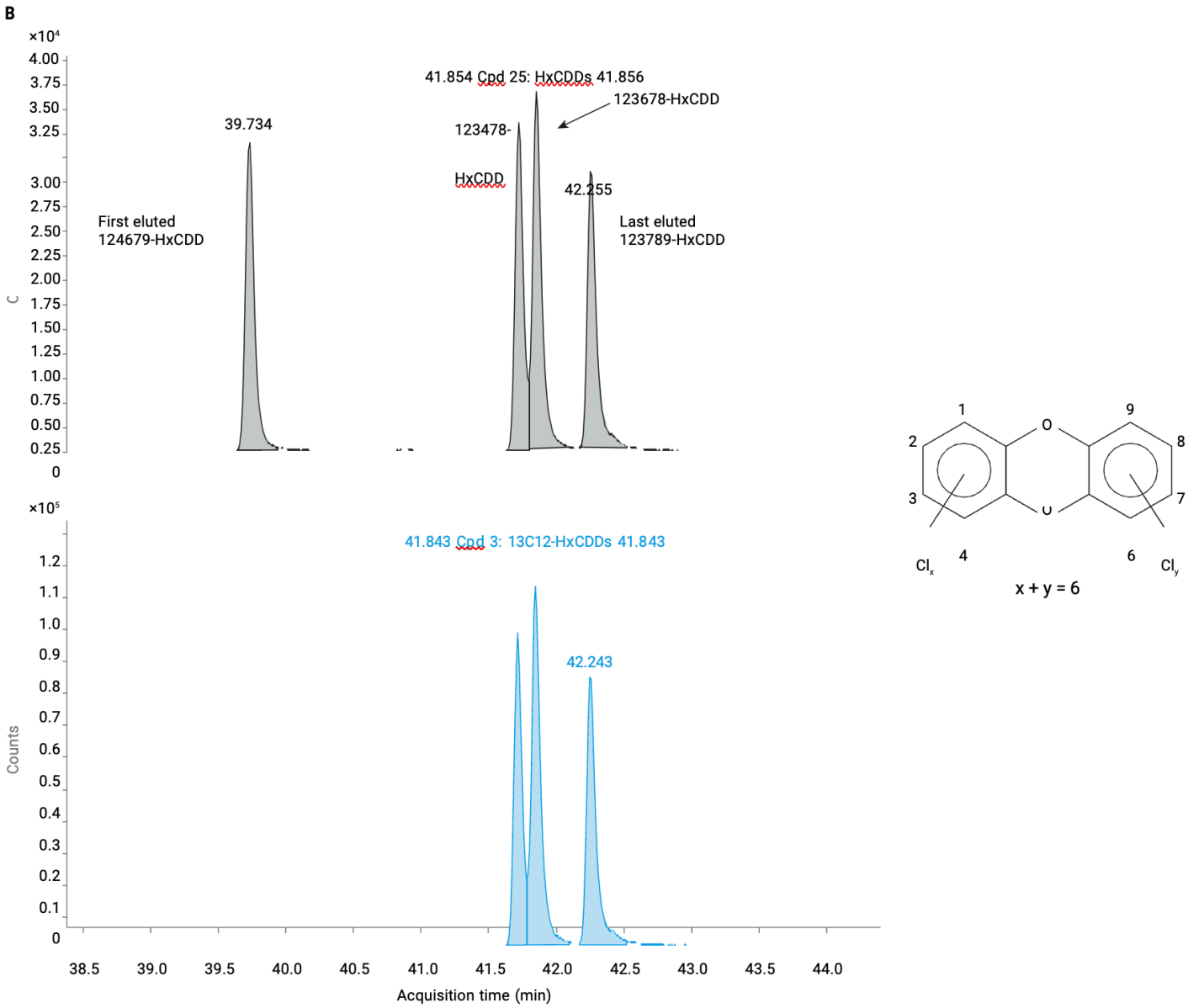

Figure 1B. Hexachlorinated dibenzodioxins HxCDDs and the corresponding ISTD.

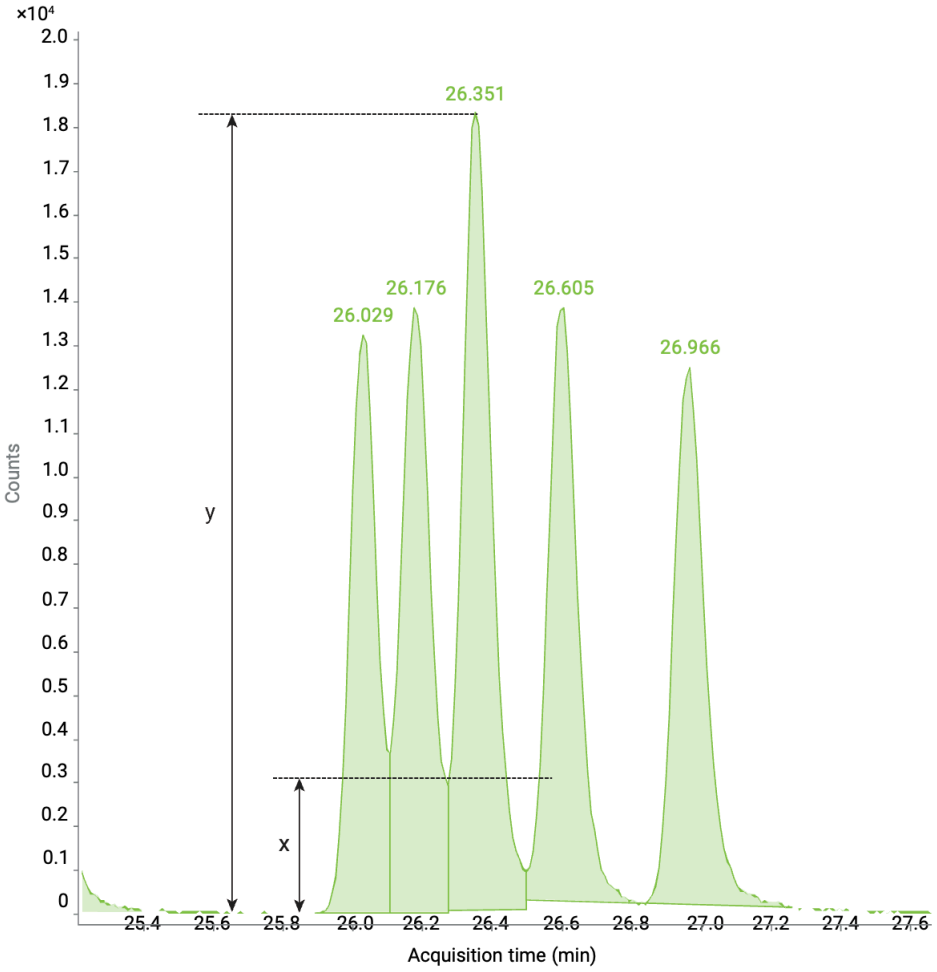

Figure 2. 2,3,7,8-TCDD and its close eluters.

A

Method Table

Time Segment: <All> Compound: 2,3,7,8-TCDD Reset Table View

Quantifier

Name	TS	Transition	Scan	Type	Resolution Calculation Type	Resolution Limit
2,3,7,8-TCDD	1	319.9 -> 256.9,...	MRM	Target	Valley Height/Peak Heig...	25.0

B

Sample							2,3,7,8-TCDD Results							
Name	Data File	Type	Level	Vial	Acq. Date-Time	Acq. Method File	RT	Resp.	MI	Calc. Conc.	Accuracy	S/N	Resolution F.	Resolution R.
DX041D-CAL../01-73	DX9ZD444.D	Cal	CS3	7	8/22/2019 2:31 AM	TQEI_DB5_DX_11	26.351	221151		9.0183	90.2	2339.21	20.4	7.8

Figure 3. (A) Method setup for resolution check in MassHunter Quantitative Analysis; (B) front and rear valley height/peak height resolution calculated for 2,3,7,8-TCDD and its closest eluting isomers.

The 7010B triple quadrupole GC/MS is equipped with a high-efficiency EI source that produces up to 20 times more ions and maximizes ion transfer into the quadrupole mass analyzer, allowing significantly more sensitivity while still maintaining robustness.

Linearity, MDLs, total PCDD/PCDF

The GC/TQ system showed good linearity over the Method 1613B calibration range and met Method 1613B specifications. Linearity values expressed in terms of % RSDs of response factors for the target analytes across the calibration range were less than 20% and ranged from 2.2 to 15.4%. The 20% RSD limit does not apply to the labeled compounds, which are quantified by internal standard, not by isotope dilution. The %RSD of the PCDD/PCDF response factors for the five sets (days) of initial calibrations for the GC/TQ system are shown in Table 4. The results underscored the excellent dynamic range of the 7010B triple quadrupole GC/MS system.

The GC/TQ MDL results for the aqueous (1 L), solid (10 g), and tissue (10 g) samples are shown in Table 5. The results obtained using the 7010B triple quadrupole GC/MS system far surpassed Method 1613B MRLs.

Total PCDD and PCDF concentrations from the real-world sample extracts were reported by MassHunter software for each level of chlorination by summing the concentration of the individual peaks meeting quantification criteria (peak shape, S/N, and product ion ratio) in the appropriate retention time window. Figure 4 shows the comparison of the total PCDD and PCDF concentrations determined using GC/HRMS and GC/TQ. The results for the two technologies were comparable.

Table 4. %RSDs of the PCDD/PCDF response factors for the five days of initial calibrations.

Date Acquired	19-AUG-19	21-AUG-19	06-JAN-20	07-JAN-20	08-JAN-20
Data File ID	DX9Z0415-A1	DX9Z0444-A1	DX9Z0830-A1	DX9Z0837-A1	DX9Z0853-A1
Name	RRF %RSD	RRF %RSD	RRF %RSD	RRF %RSD	RRF %RSD
2,3,7,8-TCDF	4.0	3.0	4.4	2.7	2.4
1,2,3,7,8-PeCDF	3.7	2.8	3.4	2.9	2.7
2,3,4,7,8-PeCDF	3.8	3.5	4.1	3.9	4.3
1,2,3,4,7,8-HxCDF	3.1	4.5	4.4	2.3	5.6
1,2,3,6,7,8-HxCDF	3.0	3.5	5.3	3.6	8.1
2,3,4,6,7,8-HxCDF	3.0	3.9	6.2	4.5	1.3
1,2,3,7,8,9-HxCDF	4.6	5.4	6.7	2.7	6.0
1,2,3,4,6,7,8-HpCDF	3.2	4.3	3.7	4.8	4.3
1,2,3,4,7,8,9-HpCDF	4.6	4.7	4.6	5.8	4.0
OCDF	7.1	10.2	9.0	7.0	6.3
2,3,7,8-TCDD	2.9	4.8	6.3	5.6	7.3
1,2,3,7,8-PeCDD	4.6	4.6	2.2	2.3	3.9
1,2,3,4,7,8-HxCDD	4.3	4.0	2.3	2.3	3.1
1,2,3,6,7,8-HxCDD	5.4	5.3	5.2	2.6	5.3
1,2,3,7,8,9-HxCDD	5.3	3.4	6.8	3.6	4.7
1,2,3,4,6,7,8-HpCDD	2.6	3.9	8.4	4.3	4.9
OCDD	3.6	3.6	5.7	4.5	4.8
^{13}C-2,3,7,8-TCDF	6.1	5.4	6.9	8.0	7.8
^{13}C-1,2,3,7,8-PeCDF	15.2	17.6	21.7	22.4	23.5
^{13}C-2,3,4,7,8-PeCDF	17.5	19.9	25.0	26.3	26.1
^{13}C-1,2,3,4,7,8-HxCDF	3.1	3.0	4.5	4.4	2.5
^{13}C-1,2,3,6,7,8-HxCDF	2.2	4.8	5.8	3.7	1.7
^{13}C-2,3,4,6,7,8-HxCDF	2.4	2.5	4.4	4.6	1.8
^{13}C-1,2,3,7,8,9-HxCDF	4.1	3.6	2.9	4.1	3.3
^{13}C-1,2,3,4,6,7,8-HpCDF	3.4	3.8	4.4	8.3	3.0
^{13}C-1,2,3,4,7,8,9-HpCDF	4.3	3.2	3.4	10.2	5.0
^{13}C-2,3,7,8-TCDD	8.4	10.3	11.5	13.2	13.2
^{13}C-1,2,3,7,8-PeCDD	16.7	19.7	24.7	25.9	25.3
^{13}C-1,2,3,4,7,8-HxCDD	2.1	3.2	3.8	3.3	2.4
^{13}C-1,2,3,6,7,8-HxCDD	2.8	3.4	2.8	4.0	3.2
^{13}C-1,2,3,4,6,7,8-HpCDD	4.8	5.3	4.3	9.0	5.5
^{13}C-OCDD	7.5	5.6	7.0	9.0	6.9
^{13}C-1,2,3,4-TCDD	17.6	8.6	15.0	11.4	13.6
^{13}C-1,2,3,7,8,9-HxCDD	36.2	31.6	38.3	38.4	27.5
^{37}Cl-2,3,7,8-TCDD	9.7	11.9	11.4	15.8	14.3

Recoveries

Three sets of spiked clean matrix one each of aqueous (1 L), solids (10 g) and tissues (10 g) were run and the mean percent recovery (n = 4) and percent RSD calculated (Figure 6). Results were compared and determined to conform to Method 1613B IPR specifications.

Proficiency, SRM, and CRM results The evaluation report from Sigma-Aldrich RTC, Inc. concluded that both GC/HRMS and GC/TQ results obtained from the proficiency tests were acceptable and met study criteria and with an overall score of 100%. These results indicate the accuracy of PCDD/PCDF data from the 7010B Triple Quadrupole GC/MS analysis of the environmental matrices. The results of the GC/TQ analysis of the solids SRM (NIST 1944) and tissue CRM (EDF 2525) also demonstrated the accuracy of the GC/TQ method.

Table 5. GC/TQ MDL results with comparison to Method 1613B MRLs.

Compound	Aqueous	Solid	Tissue
	MDL and (MRL) in pg/L	MDL and (MRL) in pg/g	MDL and (MRL) in pg/g
2,3,7,8-TCDD	1.1 (10)	0.029 (1)	0.057 (0.5)
1,2,3,7,8-PeCDD	1.39 (50)	0.037 (5)	0.051 (2.5)
1,2,3,4,7,8-HxCDD	1.05 (50)	0.042 (5)	0.061 (2.5)
1,2,3,6,7,8-HxCDD	1.08 (50)	0.045 (5)	0.033 (2.5)
1,2,3,7,8,9-HxCDD	1.78 (50)	0.064 (5)	0.067 (2.5)
1,2,3,4,6,7,8-HpCDD	1.19 (50)	0.070 (5)	0.032 (2.5)
OCDD	9.4 (100)	0.311 (10)	0.085 (5)
2,3,7,8-TCDF	0.56 (10)	0.60 (1)	0.056 (0.5)
1,2,3,7,8-PeCDF	1.0 (50)	0.037 (5)	0.046 (2.5)
2,3,4,7,8-PeCDF	1.25 (50)	0.039 (5)	0.033 (2.5)
1,2,3,4,7,8-HxCDF	0.89 (50)	0.032 (5)	0.029 (2.5)
1,2,3,6,7,8-HxCDF	1.11 (50)	0.031 (5)	0.046 (2.5)
1,2,3,7,8,9-HxCDF	1.22 (50)	0.048 (5)	0.084 (2.5)
2,3,4,6,7,8-HxCDF	1.26 (50)	0.026 (5)	0.034 (2.5)
1,2,3,4,6,7,8-HpCDF	0.92 (50)	0.255 (5)	0.064 (2.5)
1,2,3,4,7,8,9-HpCDF	1.35 (50)	0.028 (5)	0.043 (2.5)
OCDF	2.81 (100)	0.365 (10)	0.113 (5)

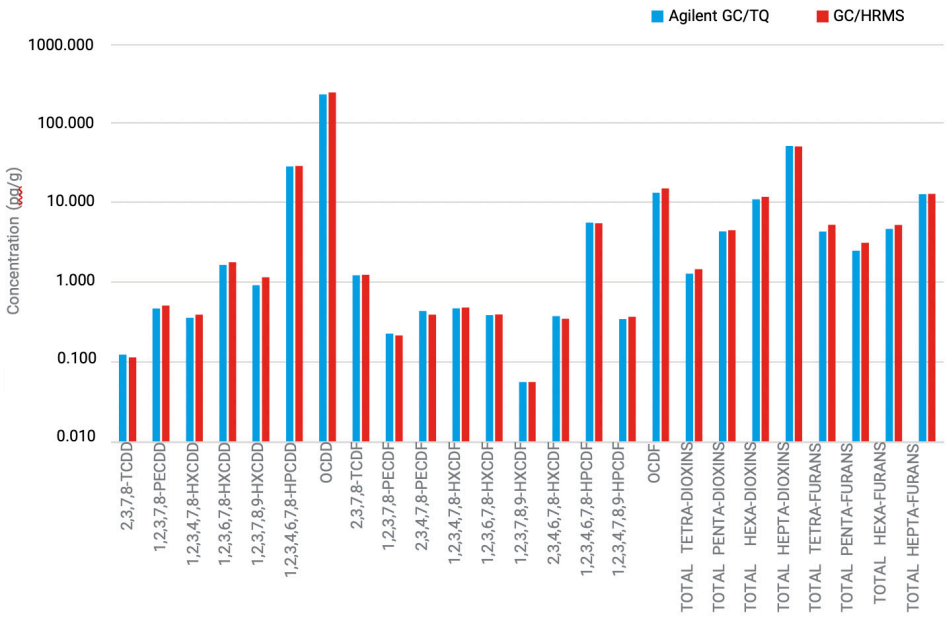

Figure 4. Comparison of total PCDD/PCDF for a real-world biosolids sample determined by GC/TQ (blue bars) and GC/HRMS (red bars).

Table 6. Fortified concentration, mean percent recovery (n = 4), and percent RSD for spiked clean matrix.

	Aqueous			Solids			Tissues		
	Total Conc. (pg/L)	Mean % Recovery	RSD (%)	Total Conc. (pg/L)	Mean % Recovery	RSD (%)	Total Conc. (pg/g)	Mean % Recovery	RSD (%)
2,3,7,8-TCDD	200	99	2	20	102	2	20	102	1
1,2,3,7,8-PECDD	1,000	98	2	100	99	2	100	100	1
1,2,3,4,7,8-HXCDD	1,000	97	2	100	99	1	100	99	1
1,2,3,6,7,8-HXCDD	1,000	96	3	100	98	3	100	98	2
1,2,3,7,8,9-HXCDD	1,000	103	4	100	109	3	100	118	12
1,2,3,4,6,7,8-HPCDD	1,000	98	2	100	100	2	100	98	1
OCDD	2,000	98	2	200	100	2	200	99	1
2,3,7,8-TCDF	200	99	2	20	101	2	20	101	1
1,2,3,7,8-PECDF	1,000	97	2	100	100	2	100	100	1
2,3,4,7,8-PECDF	1,000	97	2	100	99	2	100	99	1
1,2,3,4,7,8-HXCDF	1,000	95	2	100	98	1	100	97	1
1,2,3,6,7,8-HXCDF	1,000	98	4	100	102	2	100	98	2
1,2,3,7,8,9-HXCDF	1,000	102	3	100	103	2	100	102	1
2,3,4,6,7,8-HXCDF	1,000	97	3	100	99	2	100	98	1
1,2,3,4,6,7,8-HPCDF	1,000	107	3	100	108	2	100	109	6
1,2,3,4,7,8,9-HPCDF	1,000	98	3	100	100	2	100	100	1
OCDF	2,000	92	2	200	97	2	200	94	3
^{13}C-2,3,7,8-TCDD	2,000	70	8	200	58	12	200	73	4
^{13}C-1,2,3,7,8-PECDD	2,000	74	9	200	62	15	200	78	5
^{13}C-1,2,3,4,7,8-HXCDD	2,000	81	4	200	64	10	200	71	9
^{13}C-1,2,3,6,7,8-HXCDD	2,000	79	5	200	61	9	200	70	9
^{13}C-1,2,3,4,6,7,8- HPCDD	2,000	87	5	200	69	12	200	74	9
^{13}C-OCDD	4,000	76	5	400	60	14	400	63	9
^{13}C-2,3,7,8-TCDF	2,000	67	7	200	53	11	200	65	3
^{13}C-1,2,3,7,8-PECDF	2,000	68	9	200	57	14	200	71	5
^{13}C-2,3,4,7,8-PECDF	2,000	69	9	200	57	15	200	74	4
^{13}C-1,2,3,4,7,8-HXCDF	2,000	77	5	200	63	9	200	66	10
^{13}C-1,2,3,6,7,8-HXCDF	2,000	78	6	200	61	9	200	68	8
^{13}C-1,2,3,7,8,9-HXCDF	2,000	75	4	200	60	12	200	73	8
^{13}C-2,3,4,6,7,8-HXCDF	2,000	79	5	200	62	10	200	70	9
^{13}C-1,2,3,4,6,7,8- HPCDF	2,000	77	6	200	62	9	200	66	9
^{13}C-1,2,3,4,7,8,9- HPCDF	2,000	83	5	200	67	12	200	71	12
^{37}Cl-2,3,7,8-TCDD	200	73	6	20	69	7	20	79	3

Note about potential interferences

In this study, the analysis of 36 real-world samples of four sample matrices showed no interferences, and chromatography and quantified results for GC/TQ were equivalent to GC/HRMS.

In addition, concentrated standards of PAH, alkylated PAH and chlorinated pesticides showed no response when analyzed by the GC/TQ method.

However, because there is incomplete chromatographic separation of the chlorinated diphenyl ethers (CDPEs) from PCDFs, a characteristic *m/z* for each chlorinated diphenyl ether must be monitored. If detected at the retention time of any PCDFs, additional cleanup must be performed per Method 1613B. The GC/HRMS requirement to monitor CDPEs and perform additional cleanup when detected remains when using the GC/TQ method.

In addition, although there are small mass differences (about 6 amu) between some PCBs and some PCDD/PCDFs at the same level of chlorination, the DB-5 column provides complete chromatographic separation of these compounds. However as with GC/HRMS, interferences from fragments of higher homolog PCBs are possible. It is recommended that extract cleanup procedures include a step to remove PCBs from sample extracts.

Conclusion

GC/TQ technology provides many of the specificity and sensitivity advantages of HRMS for the analysis of regulated dioxins and furans without the cost and complexity of HRMS instruments, with added versatility and robustness. Approval of GC/TQ technology for determination of dioxins and furans as an alternative testing protocol to Method 1316B has the potential to significantly lower laboratory costs and increase operational efficiency.

This application note described and evaluated the GC/TQ SGS AXYS Method 16130 using the Agilent 7890B gas chromatograph coupled with an Agilent 7010B Triple Quadrupole GC/MS. The method will eventually be added into the Federal Register. The results obtained were determined to meet the QA/QC and performance specifications in Method 1613B for the analysis of PCDDs/PCDFs in environmental matrices. Performance factors investigated included sensitivity, linearity, MDLs, recovery, and results compared to reference material. The results of the performance tests demonstrated that GC/TQ using 7010B Triple Quadrupole GC/MS provides data of the same quality for real world samples representing complex matrices.

References

1. US EPA. Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, September 1994. https://nepis.epa.gov/ (accessed December 1, 2020)

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