Poster Reprint

ASMS 2022
Poster number TP153

Simplifying Persistent Issues with Dioxins Analysis in the Environment using GC/MS/MS

Joel Ferrer[1], Tarun Anumol[2], Dale Walker[3], Luis Cuadra-Rodriguez[1], Doug King[1], Nick B Harden[1], Alex Graettinger[2], Anastasia Andrianova[2], Bruce Quimby[2]

[1]Agilent Technologies, Santa Clara, CA

[2]Agilent Technologies, Wilmington, DE

[3]Agilent Technologies, Cedar Creek, TX

Introduction

U.S. EPA Method 1613B has been one of the primary methods used in the analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in wastewater, soils, sludges, and other matrices.

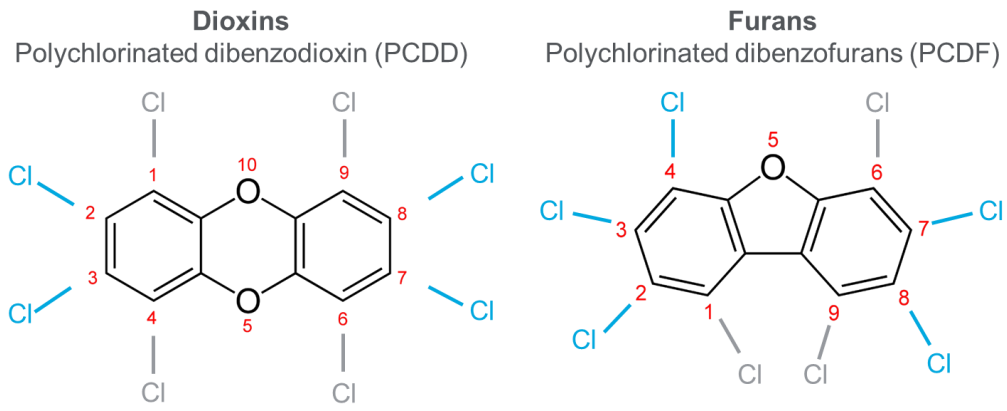

Figure 1. General chemical structure of PCDDs and PCDFs.

These compounds have more than 200 congeners, and seventeen of them are highly toxic and of interest in trace analysis.

Historically, these analyses have been performed using magnetic sector high resolution GC/MS. In 2021, the U.S. EPA evaluated an alternate test protocol (ATP) for analysis of Dioxins and Furans and determined the method was substantially similar to EPA 1613B and will recommend it be included in list of approved methods in 40 CFR Part 136.[1] The key upgrade to this method is that the GC/TQ could be considered an alternative technology for the analysis of dioxins and Furans.

This work describes the development of methodology and mechanism to meet regulatory guidance.

Figure 2. Agilent 8890B/7010B GC/TQ with the Agilent Reference Compound Introduction Valve (RCIV)

Experimental

Sample Preparation

The sample preparation and cleanup for this method is identical to U.S. EPA 1613B and was performed on real-world sample extracts in varying matrices (aqueous, solids, biosolids, and tissues) (Figure 3).[2] It is a performance-based cleanup thus sample preparation may vary based on efficiencies of interferences removed from the sample extract to increase signal to noise during analysis.

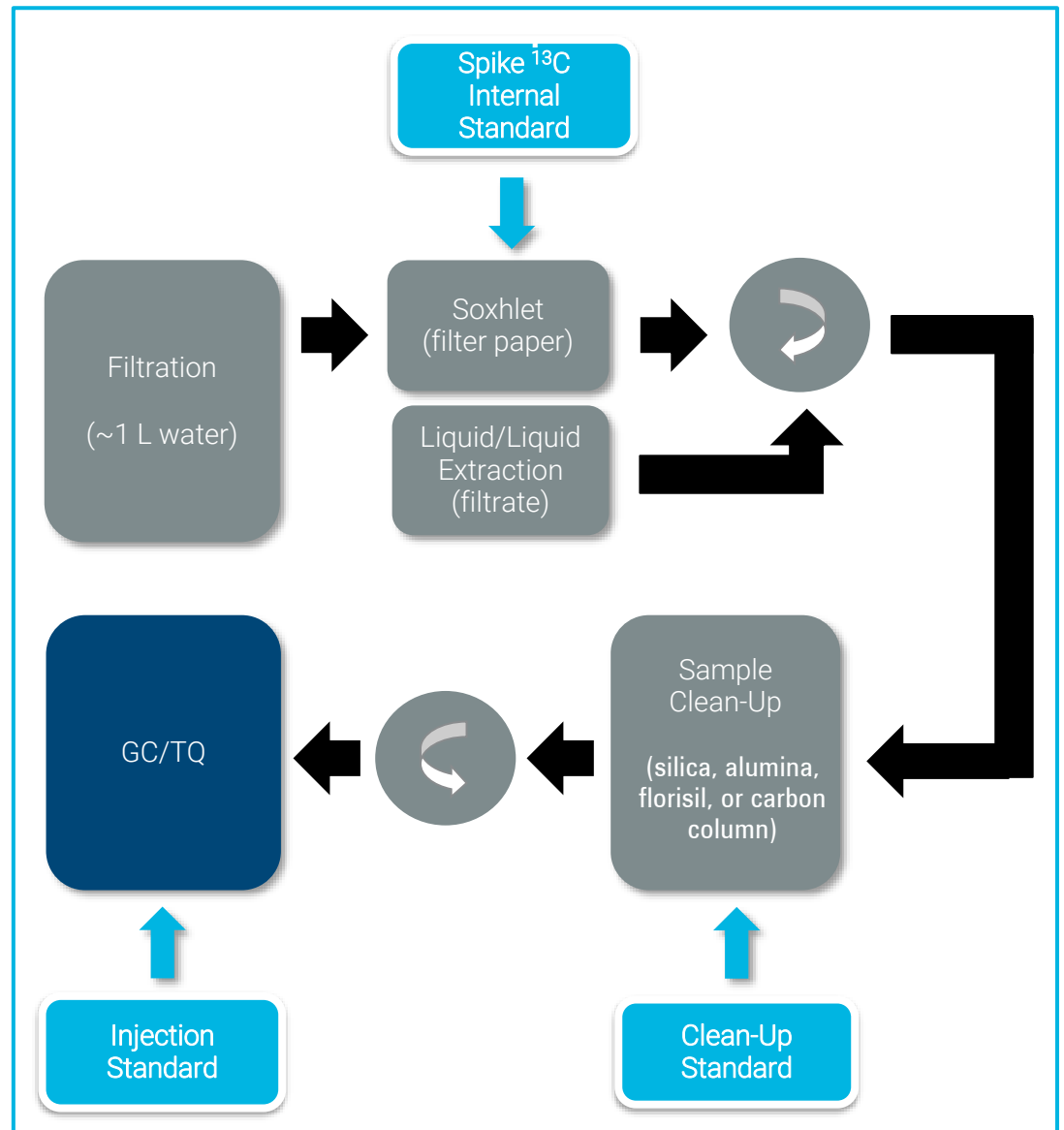

Figure 3. EPA 1613B sample preparation protocol.

System Configuration

The Agilent 7010B GC/TQ was coupled to an 8890 GC equipped with splitless inlet using a 60 m x 0.25 mm x 0.10 µm, (5%-Phenyl)-methylpolysiloxane column. A splitless, double taper, deactivated liner was used, and 1.0 µL of sample was injected. The GC/TQ was equipped with the Agilent Reference Compound Introduction Valve (RCIV) to infuse a low, optimized flow of perfluorotributylamine (PFTBA) into the source to monitor for changes in ion transmission and efficiency where the on and off states are controlled in the software.

Chromatography Performance

The GC/TQ analysis provided excellent chromatographic resolution and detection of the target PCDDs/PCDFs (Figure 4A). EPA 1613B requires the 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 4B does not exceed 25% of the 2,3,7,8-TCDD peak height "y."

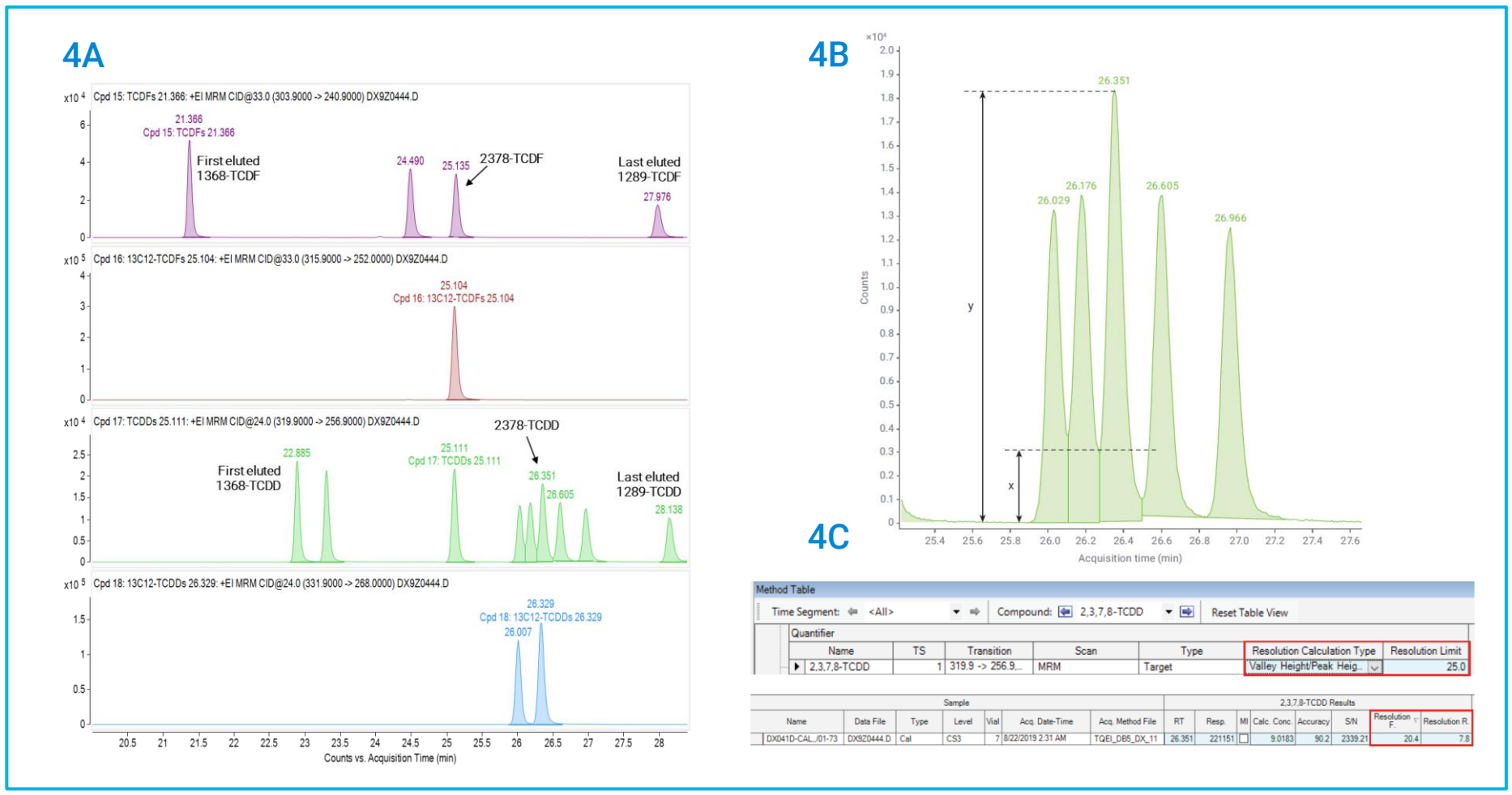

Figure 4. (4A) MRM chromatograms for TCDFs, labeled TCDF ISTD, TCDDs, and labeled TCDD ISTD. (4B) 2,3,7,8-TCDD and its close eluters. (4C) Top: Method setup for resolution check in MassHunter Quantitative Analysis. Bottom: Front and rear valley height/peak height resolution calculated for 2,3,7,8-TCDD and its closest eluting isomers.

Reference Compound Stability

A small but constant flow of the reference compound, PFTBA, required by the 1613B ATP was introduced into the GC/TQ via the RCIV (Figure 5). Changes in the PFTBA signal intensity provides a reliable metric for the GC/TQ performance and stability during the PCDDs and PCDFs analysis. The valve provides an optimized flow of PFTBA where control is fully integrated into the software, so no user manipulation is required.

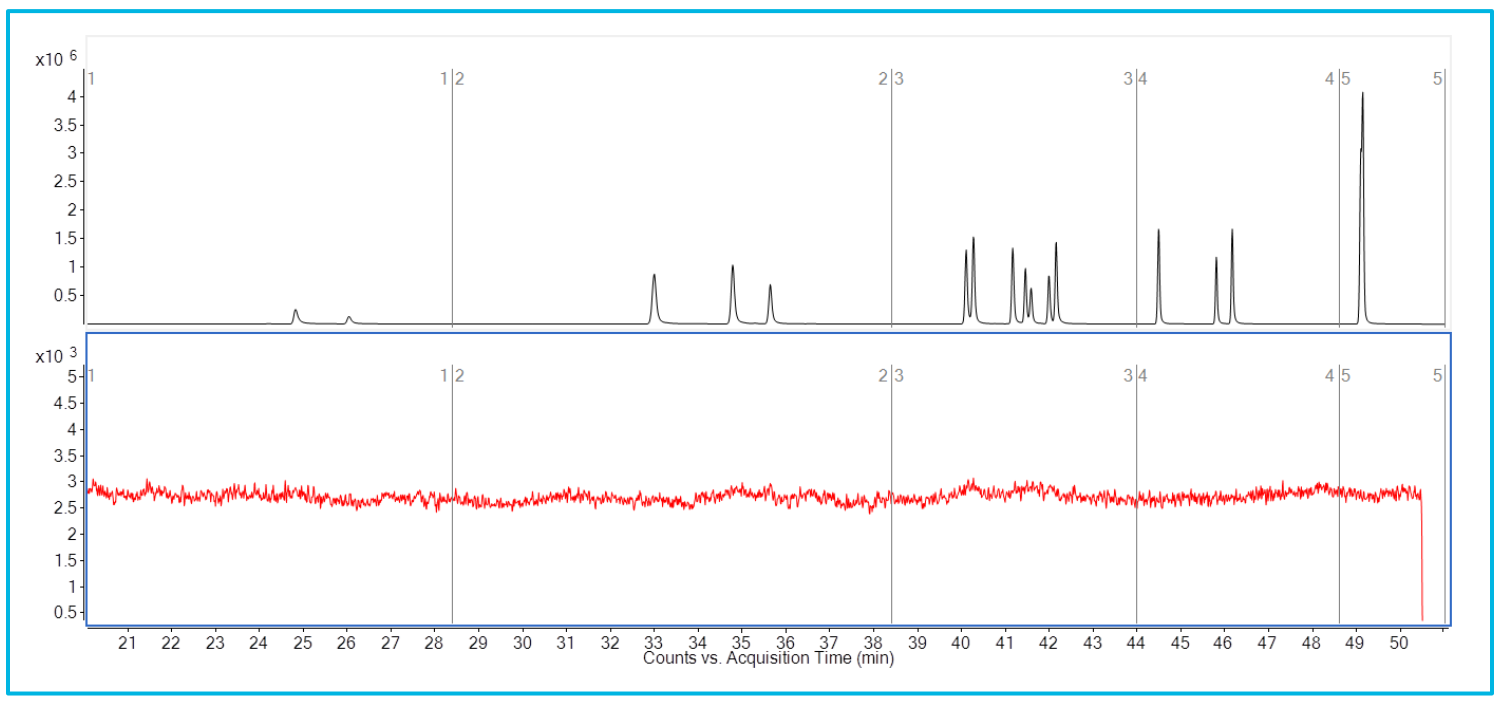

Figure 5. Stability of PFTBA response over the entire analytical run.

Results and Discussion

Performance and Recovery

Aqueous, solid, and tissue matrices were run and the mean % recovery and % RSD was calculated in Table 1 below. Results were compared and determined to meet Method 1613B Initial Performance and Recovery specifications.

The MDL results for the aqueous, solid, and tissue samples are shown in Table 2. The results obtained using the 7010B GC/TQ met and exceeded Method 1613B MRLs.

Figure 6 shows the comparison of the total PCDD and PCDF concentrations determined using GC/TQ and GC/HRMS. The results for the two technologies were comparable.

	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

Table 1. Concentration, mean % recovery (n = 4), and % RSD for spiked clean matrix.

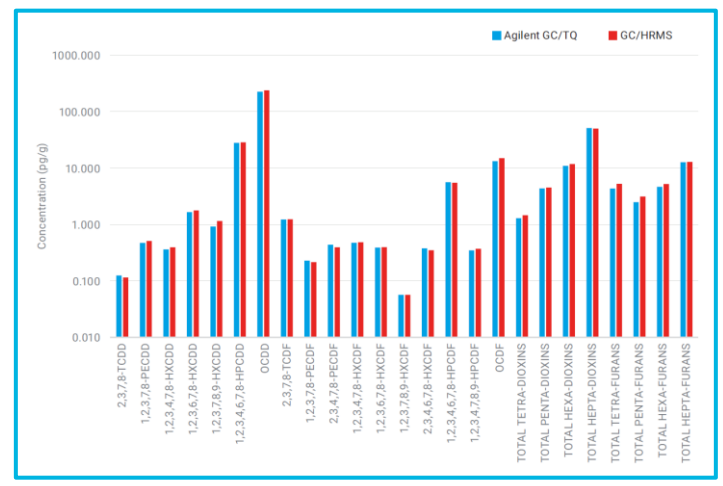

Figure 6. Comparison of total PCDD/PCDF for a real-world biosolids sample determined by GC/TQ (blue bars) and GC/HRMS (red bars).

Compound	Aqueous MDL and (MRL) in pg/L	Solid MDL and (MRL) in pg/g	Tissue 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)

Table 2. GC/TQ MDL results with comparison to Method 1613B MRLs.

Conclusions

GC/TQ provides many of the specificity and sensitivity advantages of HRMS

With the acceptance of triple quadrupole GC/MS as an equivalent technology for the analysis of regulated dioxins and furans, the advantages of 7010 series GC/TQ include:

- Lower cost and complexity compared to GC/HRMS.
- Increased versatility and robustness to lower laboratory costs and increase operational efficiency.
- High data quality for real world samples in complex matrices.

References

[1]US EPA. Methods for Measurement of 2,3,7,8-substituted tetra through octa-chlorinated dibenzo-p-dioxins and dibenzofurans in Wastewater. March 2021. https://epa.gov/.

[2]US EPA. Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, September 1994. https://nepis.epa. gov/.

[3]C. Hamilton, X. Xie, T. Anumol, A. Andrianova, D. Walker. An Alternate Testing Protocol for EPA 1613B using Agilent Triple Quadrupole GC/MS. *Agilent Technologies application note,* publication number 5994-3029EN, 2022.

https://explore.agilent.com/asms

This information is subject to change without notice.

DE35210494

© Agilent Technologies, Inc. 2022

Published in USA, May 20, 2022

Agilent

Trusted Answers