Determination of PCDD/Fs in Environmental Samples using Accelerated Solvent Extraction (ASE) and GC-MS/MS

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Key Words

Dioxins, furans, PCDD, PCDF, environmental, fly ash, sediments, complex matrix, accelerated solvent extraction, isotope dilution, pressurized solvent extraction

Introduction

The measurement of PCDD/Fs in the environment is a widespread activity carried out by many regulatory agencies globally. The chronic toxicity of these compounds to humans and wildlife at extremely low concentrations requires that the techniques used in determination must be both sensitive and selective enough to allow high confidence results. This is especially true when measuring background levels in environmental matrices, such as soil and sediment or byproducts from waste incineration processes. Traditionally high resolution magnetic sector GC-MS (GC-HRMS) instrumentation has delivered the required analytical performance and has become the gold standard technique. In recent years, there has been more interest in GC triple-quadrupole instrumentation for this purpose, especially in the area of food safety control.[1,2] For this area and environmental analysis, it is necessary to deliver data that performs in the range of HRMS systems, which requires especially sensitive triple-quadrupole systems. It is also necessary to incorporate data-processing software specifically designed to handle the complex calculations associated with dioxins analysis.

This application note describes the use of the Thermo Scientific™ TSQ Quantum™ XLS Ultra GC-MS/MS as applied to the analysis of PCDDs/PCDFs in sediments, soils, bottom, and fly ash (as incineration by-products) at the levels of interest and the level of agreement with "gold standard" analysis using GC-HRMS.

During this study, instrumental LOQs using GC-MS/MS were calculated in the low fg/μL concentration ranges. This, along with further analytical performance, is discussed alongside GC-HRMS; especially the degree of agreement between the techniques in some routine sample batches.

Materials and Methods

Extraction and Cleanup

The standard spiking protocols, extraction, and cleanup process for all sediment and soil samples were performed using an ISO17025 accredited in-house variation of EPA 1613B3. For incinerator ash samples, an in-house method based upon EN 19484 was applied.

For both of these methods, accelerated solvent extraction was used as the preferred technique for extraction after initial sample processing. This is routinely used in the laboratory to reduce solvent consumption, allow for automation, and to generate efficient sample extractions within the performance limits required.

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Accelerated Solvent Extraction Methods

ASE cells were loaded with a base layer of copper filings then a layer of rinsed Ottawa sand (previously ashed at 450 °C) after which 5 g of sample for soils/sediments (1 g for fly ash). Finally, another layer of sand was added to fill the cell and then extracted (Figure 1).
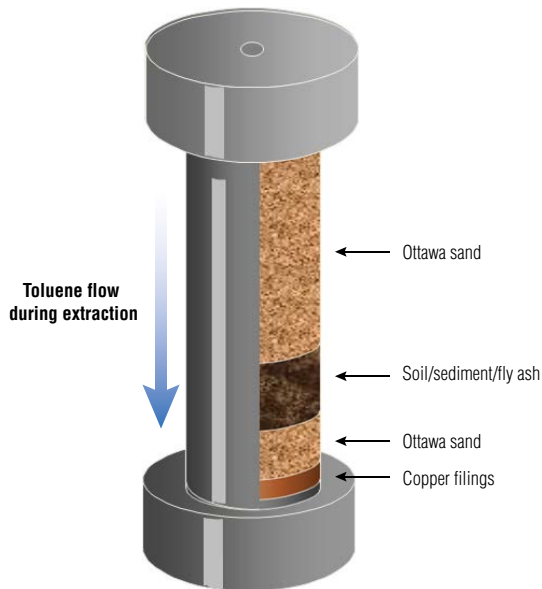
Extraction Solvent:	Toluene
Extraction Pressure:	1500 psi
Oven Temperature:	175 ˚C
Heating Time:	8 minutes
Static Time:	5 minutes
Flush:	60 % Cell volume
Purge:	N_2 240 Seconds

Figure 1. Cell schematic and method conditions for the extraction of PCDD/Fs from soil, sediment, and fly ash samples.

GC-MS Measurement & Data Processing

The GC-MS/MS measurements were performed using a Thermo Scientific™ TRACE™ GC Ultra coupled to a TSQ Quantum XLS Ultra GC-MS/MS system with quantitation performed using Thermo Scientific TargetQuan 3 software. Tables 1 and 2 show the instrument parameters used.

Table 1. GC and injector conditions.

Split/Splitless Injector (PCDD/Fs)	
Injection Temperature	260 °C
Liner	Splitless straight liner (Siltek) 3 × 8 × 105 mm (PN 453T2121)
Injected Volume	2 µL (toluene)
Splitless Time	1.5 min
Surge Pressure	22 psi (1 min)

GC Program	
GC Column	TraceGOLD TG-5SilMS 60m × 0.25mm × 0.25um (PN 26096-1540)
GC Column Flow	1.2 mL/min constant
Initial Temperature	120 °C
Rate 1	18 °C/min to 200 °C (10 min)
Rate 2	4 °C/min to 290 °C
Final Temperature	290 °C for 15 min

Table 2. Mass spectrometer parameters.

Parameters	
Source Temperature	250 °C
Ionization	EI
Electron Energy	40 eV
Emission Current	50 µA
Q2 Gas Pressure (Argon)	1.5 mTorr
Collision Energy	22 eV
Q1 Peak Width FWHM	0.7 Da
Q3 Peak Width FWHM	0.7 Da

The collision cell (Q2) gas pressure and collision energy were optimized for PCDD/F measurement at 22 eV. The monitored selected reaction monitoring (SRM) transitions as well as the MS conditions are given below in Table 3.

Table 3. Target congener groups SRM transitions.

Compound Name	Abrev.	Formula	Nominal Mass	Exact Mass	Presursor Ion m/z	Product Ion m/z	Collision Energy [ev]
Tetrachloro-dibenzodioxin	TCDD	$C_{12}H_4O_2Cl_4$	320	319.8965	319.90	256.93	22
					321.89	258.93	22
Pentachloro-dibenzodioxin	PeCDD	$C_{12}H_3O_2Cl_5$	354	353.8576	355.85	292.89	22
					357.85	294.89	22
Hexachloro-dibenzodioxin	HeCDD	$C_{12}H_2O_2Cl_6$	388	387.8186	387.82	324.86	22
					389.82	326.85	22
Heptachloro-dibenzodioxin	HpCDD	$C_{12}H_1O_2Cl_7$	422	421.7796	423.78	360.81	22
					425.77	362.81	22
Octachloro-dibenzodioxin	OCDD	$C_{12}O_2Cl_8$	456	455.7407	457.74	394.77	22
					459.74	396.77	22
Tetrachloro-[$^{13}C_{12}$]dibenzodioxin	TCDD	$^{13}C_{12}H^4O_2Cl_4$	332	331.9368	331.94	267.97	22
					333.93	269.97	22
Pentachloro-[$^{13}C_{12}$]dibenzodioxin	PeCDD	$^{13}C_{12}H_3O_2Cl_5$	366	365.8978	367.90	303.93	22
					369.89	305.89	22
Hexachloro-[$^{13}C_{12}$]dibenzodioxin	HeCDD	$^{13}C_{12}H_2O_2C_{l6}$	400	399.8589	399.86	335.89	22
					401.86	337.89	22
Heptachloro-[$^{13}C_{12}$]dibenzodioxin	HpCDD	$^{13}C_{12}H_1O_2Cl_7$	434	433.8199	435.82	371.85	22
					437.81	373.85	22
Octachloro-[$^{13}C_{12}$]dibenzodioxin	OCDD	$^{13}C_{12}O_2Cl_8$	468	467.7809	469.78	405.81	22
					471.78	407.81	22
Tetrachloro-dibenzofuran	TCDF	$C_{12}H_4OCl_4$	304	303.9016	303.90	240.94	22
					305.90	242.94	22
Pentachloro-dibenzofuran	PeCDF	$C_{12}H_3OCl_5$	338	337.8627	339.86	276.90	22
					341.86	278.89	22
Hexachloro-dibenzofuran	HeCDF	$C_{12}H_2OCl_6$	372	371.8237	371.82	308.86	22
					373.82	310.86	22
Heptachloro-dibenzofuran	HpCDF	$C_{12}H_1OCl_7$	406	405.7847	407.78	344.82	22
					409.78	346.82	22
Octachloro-dibenzofuran	OCDF	$C_{12}OCl_8$	440	439.7457	441.76	378.80	22
					443.76	380.79	22
Tetrachloro-[$^{13}C_{12}$]dibenzofuran	TCDF	$^{13}C_{12}H_4OCl_4$	316	315.9419	315.94	251.97	22
					317.94	253.97	22
Pentachloro-[$^{13}C_{12}$]dibenzofuran	PeCDF	$^{13}C_{12}H_3OCl_5$	350	349.9029	351.90	287.93	22
					353.90	289.93	22
Hexachloro-[$^{13}C_{12}$]dibenzofuran	HeCDF	$^{13}C_{12}H_2OCl_6$	384	383.8639	383.86	319.90	22
					385.86	321.89	22
Heptachloro-[$^{13}C_{12}$]dibenzofuran	HpCDF	$^{13}C_{12}H_1OCl_7$	418	417.8250	419.82	355.86	22
					421.82	357.85	22
Octachloro-[$^{13}C_{12}$]dibenzofuran	OCDF	$^{13}C_{12}OCl_8$	452	451.7860	453.78	389.82	22
					455.78	391.81	22

Results and Discussion

Sensitivity for PCDD/F Analysis

The prerequisites for a technique to be applicable to low level PCDD/F determinations is sensitivity and selectivity. The concentration levels where these substances are required to be measured often exceed the performance capability of bench-top GC-MS systems. In order to test the sensitivity of the TSQ Quantum XLS Ultra for this application, a serial dilution of commonly used EPA 1613B CS1 standard was performed, and increasingly low levels were injected onto the system. The limit of detection (LOD) was then calculated using statistical methods. Figure 2 shows the lowest level CS1 dilution (x10 – vial concentrations given in Table 4) used for this study. Quantitative SRM ions are clearly detected along with the confirmatory SRM ions for all PCDD/Fs tested within the QC ion ratio criteria. Precision studies at this level enabled an LOD to be calculated for the methodology. Table 4 gives the precision data obtained and calculated LOD at 99 % confidence limits. The LOD obtained from the TSQ Quantum XLS Ultra was found at a level that is highly applicable for environmental dioxins analysis in a range of sample types.

Table 4. Instrumental LOD (pg/µL) given to 2 d.p. (99% confidence) and precision data (n=10) for PCDD/Fs from GC-MS/MS analysis of a ten times diluted EPA 1613 CS1.

|	Concentration pg/µL	RSD %	LOD (99) pg/µL
2,3,7,8 TCDF	0.05	6.2	0.01
2,3,7,8 TCDD	0.05	11.1	0.01
1,2,3,7,8 PeCDF	0.25	6.0	0.03
2,3,4,7,8-PeCDF	0.25	4.6	0.03
1,2,3,7,8 PeCDD	0.25	9.2	0.05
1,2,3,4,7,8-HxCDF	0.25	7.7	0.04
1,2,3,6,7,8-HxCDF	0.25	4.7	0.03
2,3,4,6,7,8-HxCDF	0.25	4.1	0.02
1,2,3,4,7,8-HxCDD	0.25	7.7	0.04
1,2,3,6,7,8-HxCDD	0.25	6.1	0.03
1,2,3,7,8,9-HxCDD	0.25	5.0	0.03
1,2,3,7,8,9-HxCDF	0.25	4.9	0.03
1,2,3,4,6,7,8-HpCDF	0.25	5.2	0.03
1,2,3,4,6,7,8-HpCDD	0.25	6.8	0.04
1,2,3,4,7,8,9-HpCDF	0.25	5.7	0.03
OCDD	0.5	7.9	0.09
OCDF	0.5	4.8	0.05
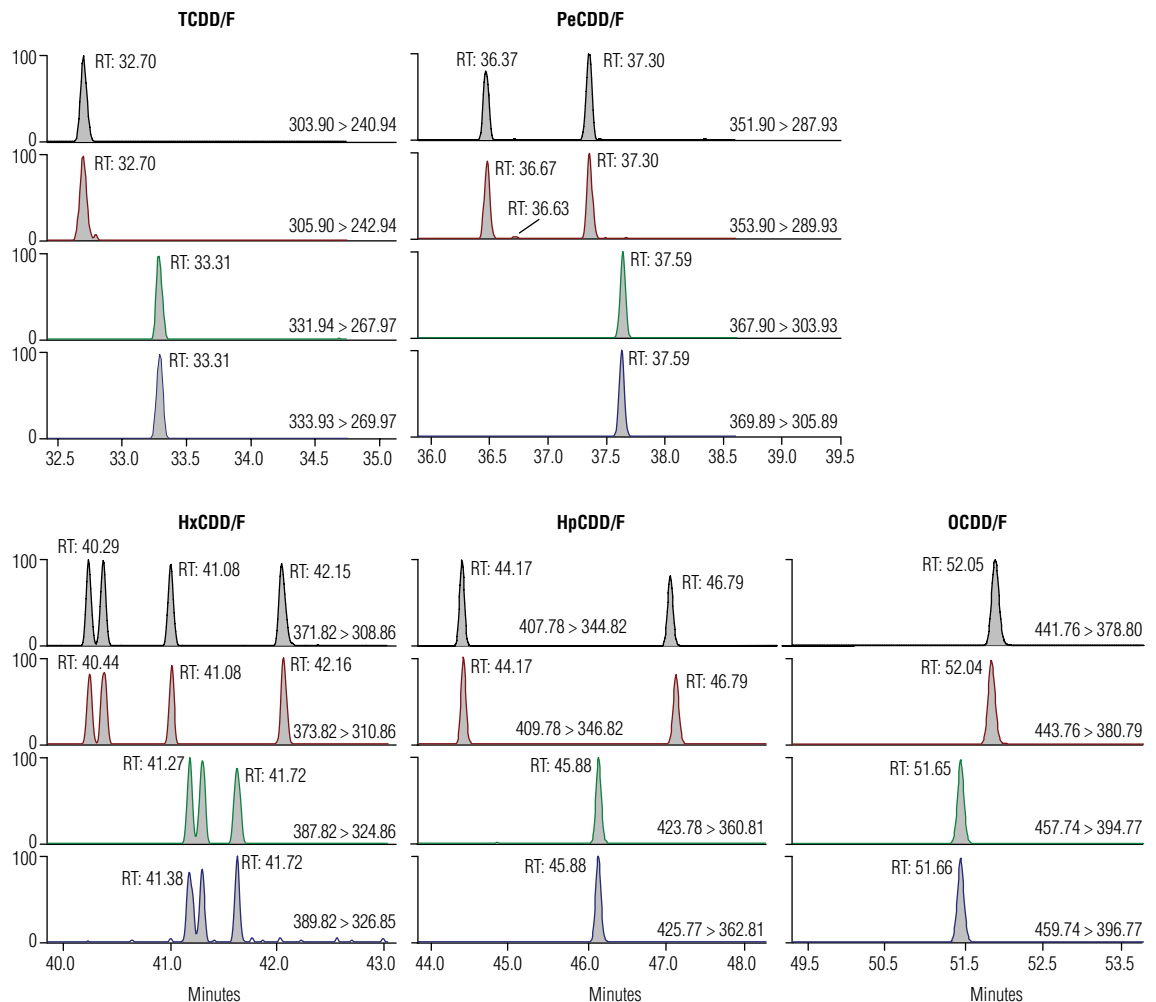
Figure 2. SRM chromatograms of PCDD/Fs after injection of a 10x diluted EPA1613B CS1 standard. (TCDD/F 0.05 pg/µL, PeCDD/F thru HpCDD/F 0.25 pg/µL, OCDD/F 0.5 pg/µL)

Quality Control in Routine Sample Batches

To evaluate the quantitative performance of the TSQ Quantum XLS Ultra when applied to analytical quality control samples, data was taken and compared with that obtained on currently implemented GC-HRMS systems (see Figure 3). These quality control samples included certified reference materials (CRMs) for sediments SETOC 738 and CRM 490 incinerator fly ash. These were all processed through the entire method procedure which included accelerated sample extraction. All of the compound recovery QC criteria specified in EPA 1613 and EN1948 were satisfied. This gave confidence that the extraction yielded high recoveries throughout the study.

CRM 490 is a highly contaminated incinerator fly ash. This type of sample and level of contamination allows for a great opportunity for interference to occur. The MS/MS system measured consistently higher concentrations for TCDD/F and some penta and hexa furans. This was indeed closer to the true CRM consensus value, so the QC check passed.

SETOC 738 is a sediment CRM sample that is much lower level CRM and had good agreement in the calculated concentrations between the GC-MS/MS and HRMS data.

The GC-MS/MS data on these three types of QC sample all fell within acceptable performance limits for the current methodology suggesting that the selectivity and quantitative performance of the technique is applicable for reporting PCDD/F data in the routine environmental lab.
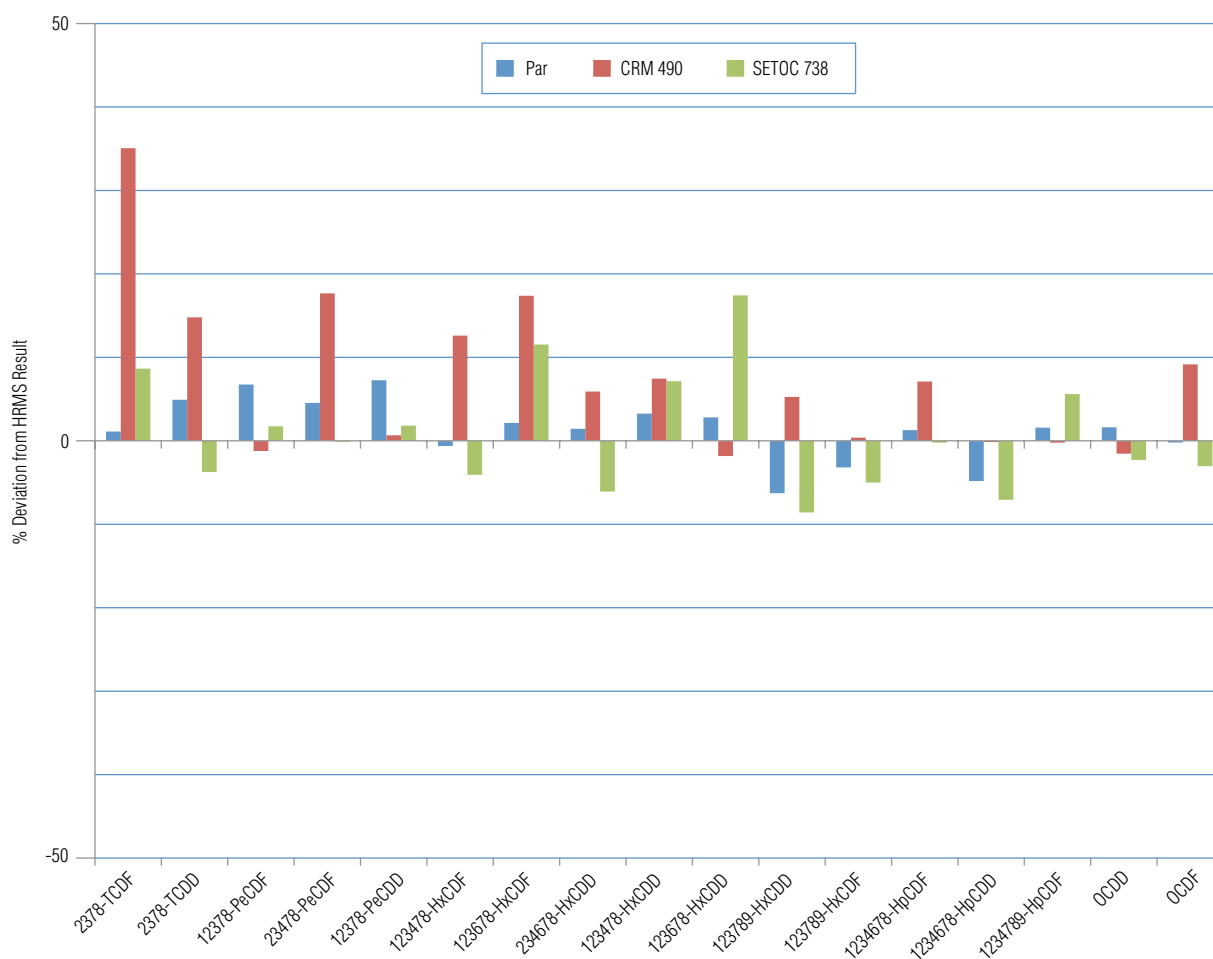

Figure 3. Mean GC-MS/MS results for routine laboratory QC samples for the in-house PCDD/Fs method over 3 routine batches of samples. This is plotted as difference to result obtained on the GC-HRMS system.The QCs include a precision and recovery standard (PAR), Incinerator fly ash certified reference material (CRM 490) and a sediment certified reference material (SETOC 738).

Routine Samples

The QC performance was reflected in the real sample batches with generally very good agreement in results between the GC-MS/MS and GC-HRMS approach. Larger deviations in calculated value were reported for incinerator fly ash samples, particularly for the lower chlorinated PCDFs. These differences are thought to arise from selectivity differences in the two techniques. The GC-MS/MS result remained valid within the quality control criteria specified within the methodology. SRM chromatograms for TCDDs in three different routine environmental sample types are given in Figure 4. These include both quantifying and confirming SRM transitions. The selective detection of the highly significant 2,3,7,8-TCDD congener was achievable in all samples.

Calculated concentrations for each congener are given in Table 5 for both the GC-MS/MS and GC-HRMS analyses for routine soil, sediment, and a matrix QC sample. Again, these show a good level of agreement in the calculated result. For the soil samples, the TSQ Quantum XLS Ultra showed confirmed detections of PCDD/Fs for the low concentration samples when no result was reported from GC-HRMS. This was due to the lower performance of the GC-HRMS system used in this study and not directly related the more sensitive systems available today.
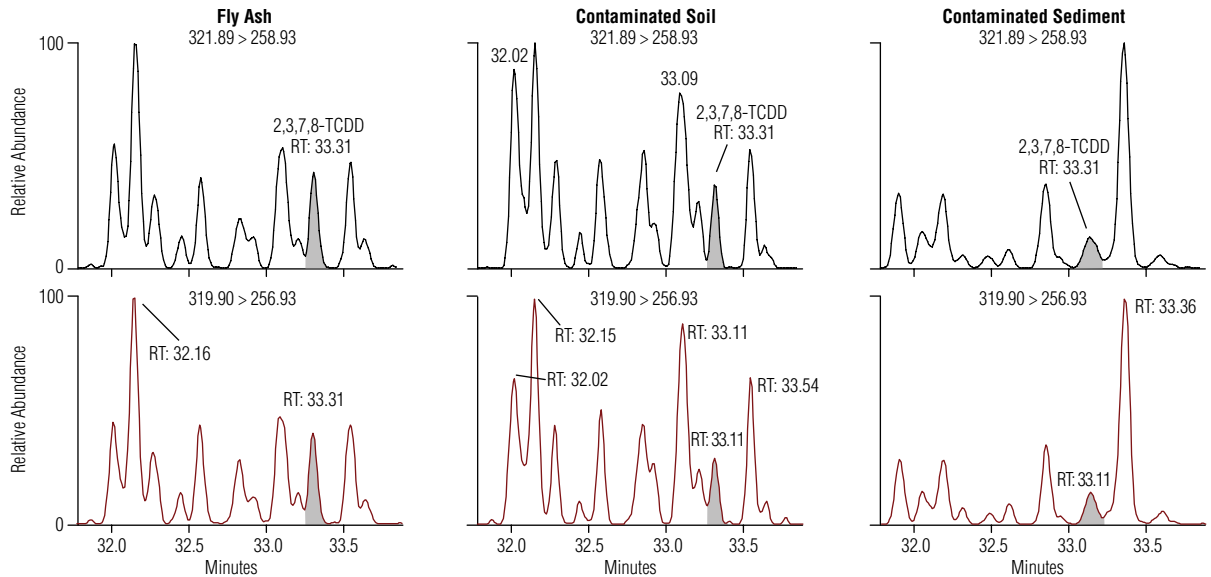

Figure 4. TCDD SRM chromatograms for three different sample types typically analyzed in the environmental laboratory.
Left: Fly ash (2,3,7,8-TCDD 31.4 ng/kg), Center: Contaminated soil (2,3,7,8-TCDD 1.85 ng/kg), Right: Contaminated sediment (2,3,7,8-TCDD 17.9 ng/kg).

Table 5. Calculated concentrations of TCDD/F congeners in soil and sediment samples run on both GC-MS/MS and GC-HRMS. (ND=not detected)

	Soil		Sediment 1		Sediment 2		SETOC 738 (CRM	
	GC-MS/MS ng/kg	GC-HRMS ng/kg	GC-MS/MS ng/kg	GC-HRMS ng/kg	GC-MS/MS ng/kg	GC-HRMS ng/kg	GC-MS/MS ng/kg	GC-HRMS ng/kg
2,3,7,8 TCDF	0.992	1.23	16.0	10.4	2.15	1.51	17.9	17.1
2,3,7,8 TCDD	ND	ND	1.85	2.29	2.03	5.10	23.1	23.9
1,2,3,7,8 PeCDF	1.26	<1.79	25.4	25.4	4.90	4.52	7.36	6.76
2,3,4,7, 8 PeCDF	1.57	1.96	41.5	44.2	10.7	9.29	47.8	45.4
1,2,3,7,8, PeCDD	0.436	ND	5.49	5.71	9.14	7.95	7.26	6.91
1,2,3,4,7,8,-HxCDF	1.89	1.89	56.1	57.3	64.8	71.9	43.8	45.1
1,2,3,6,7,8,-HxCDF	1.81	2.14	64.8	55.0	223	197	15.1	14.7
2,3,4,6,7,8,-HxCDF	2.53	2.83	86.9	91.5	9.47	11.5	20.2	18.4
1,2,3,4,7,8,-HxCDD	0.271	ND	5.38	6.34	15.0	10.9	10.4	8.62
1,2,3,6,7,8,-HxCDD	0.382	0.905	8.33	8.58	17.6	16.7	28.1	20.1
1,2,3,7,8,9-HxCDD	0.469	ND	6.62	6.97	17.5	14.0	21.4	22.4
1,2,3,7,8,9-HxCDF	0.932	ND	25.8	31.4	15.2	13.4	4.65	5.40
1,2,3,4,6,7,8-HpCDF	12.9	14.2	464	473	5.05	4.58	214	202
1,2,3,4,6,7,8-HpCDD	4.80	5.78	63.4	62.2	18.3	16.6	416	433
1,2,3,4,7,8,9-HpCDF	1.90	3.07	48.8	48.8	68.3	54.4	15.1	15.4
OCDD	24.7	23.8	153	191	6.38	5.38	3020	3030
OCDF	258	291	475	554	47.7	39.5	290	316

Conclusion

- The TSQ Quantum XLS Ultra GC-MS/MS is a highly sensitive and selective system applicable to dioxins and furans analysis in a range of environmental sample types and generates results that perform within current in-house QC criteria.

- Some differences arise in the calculated concentration between the GC-MS/MS and GC-HRMS analysis. These are thought to be related to the differences in the selectivity mechanism of each system.

- GC-MS/MS applied to PCDD/Fs still allows for full isotope dilution quantitation as currently used by GC-HRMS systems. TargetQuan 3 software can be used with the TSQ Quantum XLS Ultra to provide the specific calculations required.

- The Thermo Scientific™ Dionex™ ASE™ Accelerated Solvent Extractor system allows for unattended, efficient extractions from all samples and enabled recoveries well within QC criteria.

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