Determination of Polychlorinated Dibenzo-p-dioxins and Furans (PCDD/Fs) in Environmental Samples and Incinerator Ash Using Accelerated Solvent Extraction with High Sensitivity GC-MS/MS

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Overview

Purpose: To demonstrate a total workflow solution for extraction of dioxins and furans from environmental samples.

Methods: Extraction of dioxins and furans was automated by using the Thermo Scientific™ Dionex™ 350 Accelerated Solvent Extractor. Analysis was performed using the Thermo Scientific™ TSQ Quantum XLS Ultra™ GC-MS/MS system.

Results: Use of the Dionex 350 ASE system and TSQ Quantum XLS Ultra GC-MS/MS yields an efficient workflow solution for extraction and analysis of dioxins and furans from a range of environmental samples.

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 poster describes the use of the Dionex ASE 350 system and the TSQ Quantum XLS Ultra GC-MS/MS as applied to the extraction and 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. 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.

Methods

Extraction and Clean Up

The standard spiking protocols, extraction, and cleanup process for all sediment and soil samples were performed using an ISO17025 accredited in-house variation of U.S. EPA Method 1613B.[3] For incinerator ash samples, an in-house method based upon EN 19484 was applied. For both of these methods, the Dionex ASE 350 system (Figure 1) was used for the 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.

Thermo Scientific™ Dionex™ 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 2). The extraction method conditions are specified in Table 1.
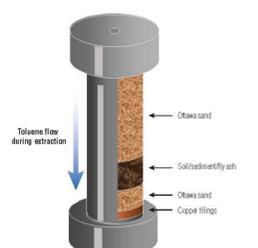

Figure 1: Dionex ASE 350 system

Figure 2: Extraction Cell Schematic

Table 1: Accelerated Solvent Extraction Method Conditions

Oven Temperature	175 °C
Pressure	1500 psi
Oven Heat up Time	8 minutes
Static Time	5 minutes
Static Cycles	1
Rinse Volume	60%
Nitrogen Purge Time	240 seconds
Extraction Solvent	Toluene

GC-MS Measurement and Data Processing

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

Table 2: GC Conditions

Injection Temperature	260 °C
Liner	Splitless straight liner (3 x 8 x 105 mm)
Injected Volume	2 μL (toluene)
Splitless Time	1.5 minutes
Surge Pressure	22 psi (1 minute)
Analytical Column	Thermo Scientific™ TraceGOLD TG-5 SILMS Guard GC Columns (60 m x 0/25 mm x 0.25 μm)
GC Column Flow	1.2 mL/min constant
Initial Temperature	120 °C
Rate 1	18 °C/min to 200 °C/min (10 min)
Rate 2	4 °C/min to 290 °C/min
Final Temperature	290 °C/min

Table 3: Mass Spec Parameters

Source Temperature	250 °C
Ionization	EII
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

Table 2 and 3: Instrument parameters used.

Results

Sensitivity for PCDD/F Analysis

The prerequisites for a technique to be applicable to low level PCDD/F determinations are 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 U.S. EPA Method 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 3 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.
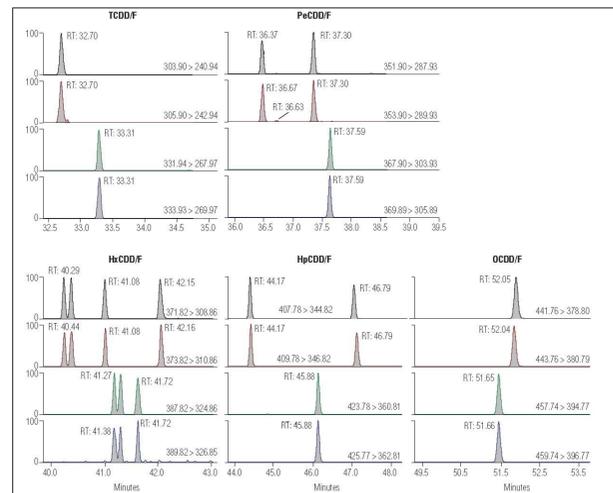

Figure 3: SRM chromatograms of PCDD/Fs after injection of a 10x diluted U.S. EPA 1613 CS1 standard (TCDD/F 0.05 pg/μL, PeCDD/F through HpCDD/F 0.25 pg/μL, OCDD/F 0.5 pg/μL).

Table 4: Instrumental LOD (pg/μL) and Precision Data (n=10)

Compound	Concentration (pg/μL)	RSD %	LOD (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-HxCDF	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

Table 4: Concentrations, precision data obtained and calculated LOD at 99% confidence limits.

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 4). 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 U.S. 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.
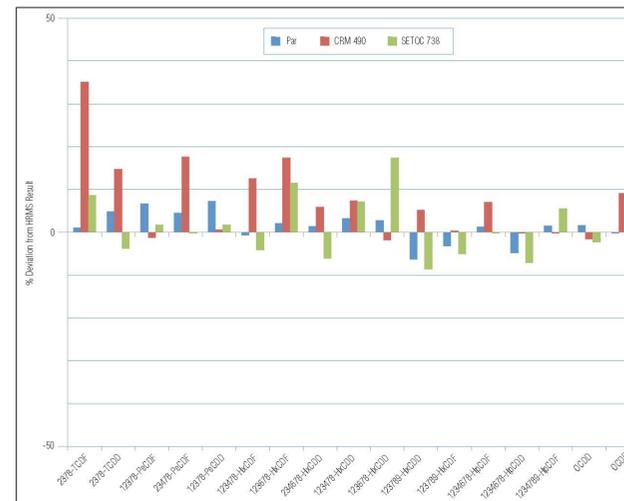

Figure 4: Mean GC-MS/MS Routine Laboratory QC Samples.

Figure 5: TSQ Quantum XLS Ultra GC-MS/MS System.

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 6. 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.
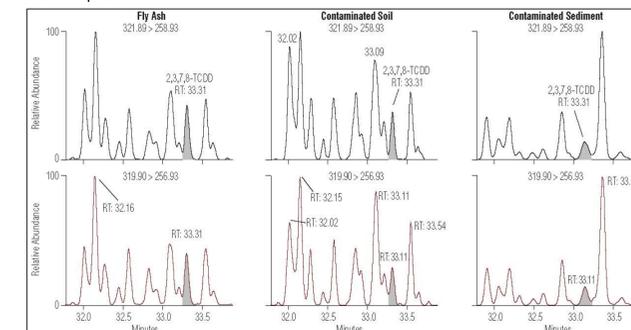

Figure 6: SRM Chromatograms for Three Different Sample Types.

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.

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

- The Dionex ASE 350 system allows for unattended, efficient extractions from all samples and enabled recoveries well within QC criteria.

References

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