Application Note

The Analysis of Chlorinated Dioxins using Automated Pressurized Liquid Extraction, Multicolumn Cleanup and Concentration

Introduction

Polychlorinated Dioxins and Difurans are among the most toxic organic compounds, of which 17 contain the 2,3,7,8 configuration of chlorination and are measured in TEQ. Analytically, dioxins represent sample prep challenges due to the low detection level requirements. Having efficient extraction procedures and ultra clean extracts is a necessity for GC/HRMS analysis of these compounds.

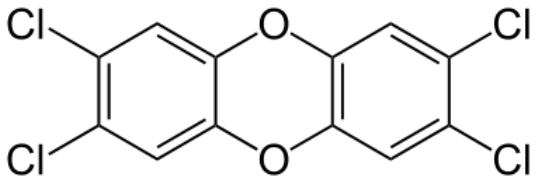


Figure #1, 2,3,7,8-TCDD structure

Traditional dioxin/difuran extraction procedures require 24 hour soxlet extraction, and a wide array of manual sorbent clean up procedures, each with their own evaporation step. This results in extensive manual prep hours, high levels of potential error, and increased potential for background or cross contamination of samples. By utilizing the FMS total prep process, extraction and clean-up processes are automated into a high efficiency process capable of delivering same day analysis of these samples. The following procedure details the sample prep procedures for implementing the TRP process on soil and sediment samples.

Instrumentation

- FMS, Inc. PLE®
- FMS, Inc. Power Prep®
- FMS, Inc. SuperVap® Concentrator
- FMS, Inc. 200ml direct to vial concentrator tubes
- FMS, Inc. 200ml concentrator tubes (1ml termination)
- Thermo Trace Ultra GC with DFS HRMS

Consumables

- FMS, Inc. High Capacity Acidic Silica columns
- FMS, Inc. Classical Silver Nitrate ABN columns
- FMS, Inc. Basic Alumina columns
- FMS, Inc. Carbon columns
- Fisher Optima* Toluene
- Fisher Optima* ETAC
- Fisher Optima* n-Hexane
- EMD Omni* Benzene
- Fisher Optima* Methylene Chloride
- Agilent Hydromatrix©
- Ottawa Sand
- NIST 1944 RM; River Sediment
- Cambridge Isotopes EDF-9999, EPA 1613 calibration Standards
- Cambridge Isotopes EDF-8999, EPA 1613 Labeled Surrogate
- Cambridge Isotopes EDF-5999, EPA 1613 Recovery Standard
- Cambridge Isotopes EDF-6999, Labeled Clean-up Standard
- Cambridge Isotopes EDF-7999, EPA 1613 PAR
- RTC SPE016-10G PT soil Sample

Procedure

- Sample amounts are measured in grams (20 grams Ottawa Sand for IPR)
- Samples are spiked with EPA 1613 labeled surrogates
- Samples are mixed with Hydromatrix (baked at 500 ºC).
- Samples are transferred to 40 ml extraction cells
- Cells are capped and loaded onto the PLE

PLE Pressurized Liquid Extraction

1. Cells filled with Hexane:DCM (50:50)
2. Cells pressurized to 1500PSI
3. Cells heated to 120 degrees C for 20 minutes
4. Cells cooled to ambient temperature
5. Cells flushed with 20mls solvent
6. Cells purged with N2 and extract discharged to SuperVap Concentrator..

FMS
Fluid Management Systems

Procedure (Cont.)

SuperVap

1. Preheat temp: 20 minutes at 60 °C
2. Evap mode w/Sensor temp: 60 °C
3. Nitrogen Pressure: 10 PSI

Power Prep

1. Columns conditioned
2. Load sample extract(s)
3. Silica columns eluted onto Alumnina column with Hexane
4. Alumina column eluted onto carbon column with DCM:Hexane
5. Carbon column rinsed with ETAC:Benzene
6. Carbon column back eluted with Toluene
7. Toluene elute collected in direct to GC vial tubes in Super Vap concentrator

SuperVap

1. Preheat temp: 20 minutes at 60 °C
2. Evap mode w/Sensor temp: 60 °C
3. Nitrogen Pressure: 10 PSI

Results

Table #1. Mean recoveries and deviations for labeled compounds; IPR, NIST 1944 and PT.

Compound	Mean Rec.	STD DEV
2,3,7,8-TCDD	94%	7.1%
1,2,3,7,8-PeCDD	97%	8.1%
1,2,3,4,7,8-HxCDD	93%	7.3%
1,2,3,6,7,8-HxCDD	93%	7.0%
1,2,3,4,6,7,8-HpCDD	92%	7.3%
OCDD	85%	7.5%
2,3,7,8-TCDF	97%	6.8%
1,2,3,7,8-PeCDF	93%	7.3%
2,3,4,7,8-PeCDF	94%	7.4%
1,2,3,4,7,8-HxCDF	92%	6.8%
1,2,3,6,7,8-HxCDF	93%	6.8%
2,3,4,6,7,8-HxCDF	93%	6.8%
1,2,3,7,8,9-HxCDF	90%	7.4%
1,2,3,4,6,7,8-HpCDF	90%	6.8%
1,2,3,4,7,8,9-HpCDF	82%	7.8%

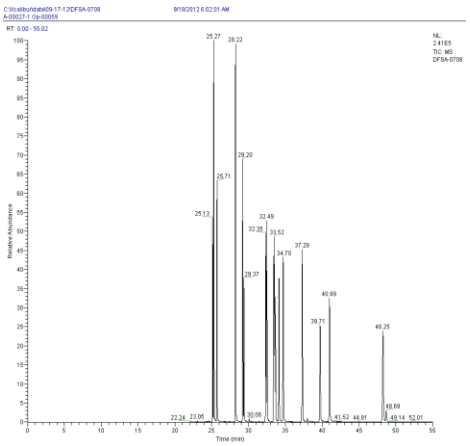
Results

Table #2. Results of NIST 1944 analysis (pg/g)

Compound	Calc. Conc.	Cert Value
2,3,7,8-TCDD	120.19	133
1,2,3,7,8-PeCDD	20.13	19
1,2,3,4,7,8-HxCDD	21.44	26
1,2,3,6,7,8-HxCDD	52.35	56
1,2,3,7,8,9-HxCDD	35.04	53
1,2,3,4,6,7,8-HpCDD	744.78	800
OCDD	5015.97	5800
2,3,7,8-TCDF	33.07	39
1,2,3,7,8-PeCDF	38.13	45
2,3,4,7,8-PeCDF	39.39	45
1,2,3,4,7,8-HxCDF	179.73	220
1,2,3,6,7,8-HxCDF	81.94	90
2,3,4,6,7,8-HxCDF	52.06	54
1,2,3,7,8,9-HxCDF	16.56	19
1,2,3,4,6,7,8-HpCDF	972.81	1000
1,2,3,4,7,8,9-HpCDF	39.2	40
OCDF	1164.8	1000

Table #3. Results of PT analysis (pg/g)

Compound	Calc. Conc.	Cert Value
2,3,7,8-TCDD	327.56	357
1,2,3,7,8-PeCDD	81.36	88.2
1,2,3,4,7,8-HxCDD	631.73	688
1,2,3,6,7,8-HxCDD	206.31	207
1,2,3,7,8,9-HxCDD	238.57	265
1,2,3,4,6,7,8-HpCDD	431.88	454
OCDD	572.86	437
2,3,7,8-TCDF	410.50	415
1,2,3,7,8-PeCDF	738.69	860
2,3,4,7,8-PeCDF	318.57	340
1,2,3,4,7,8-HxCDF	271.27	263
1,2,3,6,7,8-HxCDF	243.46	282
2,3,4,6,7,8-HxCDF	151.49	172
1,2,3,7,8,9-HxCDF	558.10	626
1,2,3,4,6,7,8-HpCDF	192.23	190
1,2,3,4,7,8,9-HpCDF	479.34	507
OCDF	253.94	322



TIC for PT sample

Total Rapid Prep System for Extraction Cleanup and Concentration

Conclusions

The results of the IPR replicates demonstrate the excellent precision and accuracy of the TRP system in a clean sample matrix. The accurate quantitation of both the NIST 1944 and blind RTC PT study display both the PLE's ability to extract analytes from difficult matrices, and the Power Prep's capacity to not only clean extracts for trace level detection, but fractionate out high concentrations of non-dioxin/difuran analytes. The usage of the silver nitrate ABN silica columns completely removed extracted sulfur from the NIST 1944 reference sample, an otherwise troublesome contaminant.

The result of implementing the TRP system proves to be a highly efficient, automated process delivering both precision and reproducibility in a single day of sample prep.

For more information contact FMS:
FMS, Inc.
580 Pleasant Street
Watertown, MA 02472
Phone: (617) 393-2396
Fax: (617) 393-0194
Email: onlineinfo@fms-inc.com
Web site: www.fms-inc.com

FMS
Fluid Management Systems