

Supercritical Fluid Extraction of Soil Samples for the Analysis of PCDDs and PCDFs Using Isotope Dilution Quantitation

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Abstract

Off-line supercritical fluid extraction (SFE) and classical Soxhlet extraction techniques were extensively compared using unfortified soil samples. When using ^{15}C -labelled 2,3,7,8-substituted PCDD/PCDFs as surrogates, SFE extractions were found to give lower recoveries. However, the SFE data were comparable to the Soxhlet data when the analytes were quantitated using isotope dilution. No appreciable differences in detection limits were observed.

Introduction

Supercritical fluid extraction (SFE) is growing in popularity as a viable alternative to solvent-based Soxhlet extraction for the analysis of a large number of organic pollutants. Much of the work to date on the supercritical fluid extraction of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been conducted using fly ash samples¹⁻⁶⁾ or artificially fortified (spiked) samples⁷⁾; some of these efforts have been reviewed recently⁸⁾.

When evaluating any analytical methodology, it is desirable to study a wide range of concentrations, typical of levels found in real world samples. The high amounts of PCDDs and PCDFs present in most fly ash samples often permit the extract to be analyzed directly without further clean-up^{1,2)}. This represents an ideal case, which is not characteristic of matrices contaminated at ultra-trace levels. In the current study, we have evaluated a single set of off-line SFE conditions for the extraction of PCDDs and PCDFs in two unfortified soil samples. Analytes were quantitated by isotope dilution using gas chromatography/high resolution mass spectrometry (GC/HRMS) or tandem mass spectrometry (GC/MS/MS).

Experimental

A sediment sample (EC-2) containing high ppt levels of PCDDs and PCDFs was obtained from the National Water Research Institute (867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario, L7R 4A6). A low-level sediment sample (HS-2) was obtained from the National Research Council Institute for Marine Biosciences (1411 Oxford Street, Halifax, Nova Scotia, B3H 3Z1). Both samples are being investigated as potential standard reference materials and

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were used as received.

All supercritical fluid extractions were performed dynamically using a Dionex SFE Model 723 (SFE-703 extractor and an SFE-703M co-solvent addition module). The carbon dioxide was modified with pesticide grade acetone at a 15% molar volume. Extraction cells were 24 ml in volume and fitted with 0.5 μm frits. Linear restrictors (500 ml/min of gas flow) heated to 175C were used. Samples were extracted at 120C at a pressure of 450 atm for 60 minutes. Typical flows of gaseous CO_2 ranged from 550 - 850 ml/min. The sample extracts were collected in 25 ml vials containing 15 ml of pesticide grade hexane which had been cooled to 5C for at least 15 minutes before starting the extraction.

Sample extracts were analyzed by GC/MS/MS (Varian 3400 GC, Finnigan MAT TSQ 70 triple quadrupole mass spectrometer, and an ICIS II data system) or GC/HRMS (Hewlett-Packard 5890 Series II GC, VG Autospec at 10,000 resolution, and an OPUS data system). All samples were chromatographed using a 60m x 0.25 mm i.d. x 0.25 μm film thickness J&W DB-5 fused silica capillary column.

Standard PCDD/PCDF mixtures were prepared from stock solutions obtained from either Cambridge Isotope Laboratories, Inc. or Wellington Laboratories. The internal quantitation standard contained 15 $^{13}\text{C}_{12}$ 2,3,7,8-substituted PCDDs and PCDFs (see Table 1 for specific congeners). Following extraction, the samples were spiked with a clean-up standard ($^{37}\text{Cl}_4$ -2,3,7,8- T_4CDD) in order to differentiate between losses occurring at the extraction and clean-up stages. Prior to injection, the samples were reconstituted with a recovery standard solution containing $^{13}\text{C}_{12}$ -1,2,3,4- T_4CDD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9- H_6CDD at 100 $\mu\text{g}/\mu\text{L}$ in nonane.

Sample extracts were cleaned-up using a dual stage open column chromatography procedure consisting of modified silica and alumina stationary phases. Samples were further cleaned-up using an automated HPLC carbon-based method to remove diphenylether interferences. Complete details of the analytical procedure are available elsewhere⁹.

Results and Discussion

A comparison of average results (in ppt) for the Soxhlet and supercritical fluid extraction of a high-level soil sample is presented in Table 1. With the exception of 1,2,3,7,8,9- H_6CDF , the Soxhlet data show a high degree of precision. When a single outlying data point from the 10 Soxhlet replicates is removed from the data set (based on Dixon's Q test), the RSD for 1,2,3,7,8,9- H_6CDF becomes 14%. For the Soxhlet data, surrogate recoveries ranged from 68 to 85%, with an average clean-up standard recovery of 54%.

The supercritical fluid extraction data for EC-2 also show a high degree of precision. The 23% RSD obtained for the total T_4CDF value was likely biased by a single SFE replicate for which substantial losses during the sample clean-up were experienced (clean-up standard recovery of only 22%). The ^{13}C -labelled surrogate recoveries for the SFE data range from 42 to 64%, and an average clean-up standard recovery of 46% was observed.

Despite lower surrogate recoveries, the SFE data compare favourably with the Soxhlet extractions (Table 1). For example, the 2,3,7,8- T_4CDD was quantitated at 270 ppt in each case, yet the SFE surrogate recovery was only 42% versus 68% for the Soxhlet extraction. Similarly, the 2,3,7,8- T_4CDF was found at 100 ppt, with recoveries differing by over 30% (68%

for Soxhlet versus 38% for SFE). These observations suggest that isotope dilution quantitation is valid for PCDDs and PCDFs under the current SFE conditions.

**TABLE 1: Average EC-2 Soil Values (ppt)
Comparison of Soxhlet versus Supercritical Fluid Extraction**

Group Totals	Soxhlet Extraction (n=10)			Supercritical Fluid Extraction (n=5)		
	Value	% RSD	Isomers	Value	% RSD	Isomers
Total T ₄ CDD	430	9.7	8	430	5.5	7
Total P ₅ CDD	300	3.7	11	290	10	10
Total H ₆ CDD	720	5.8	7	770	1.7	7
Total H ₇ CDD	1300	7.0	2	1500	9.8	2
Total O ₈ CDD	4000	6.2	1	5000	3.5	1
Total T ₄ CDF	620	12	17	570	23	14
Total P ₅ CDF	820	9.4	14	830	5.3	12
Total H ₆ CDF	1900	5.7	12	1800	4.9	10
Total H ₇ CDF	3800	8.2	4	4220	2.0	4
Total O ₈ CDF	7800	8.3	1	7900	1.9	1
2,3,7,8-substituted isomers	Value	% RSD	% Recovery*	Value	% RSD	% Recovery*
2,3,7,8-T ₄ CDD	270	9.1	68	270	4.1	42
1,2,3,7,8-P ₅ CDD	24	12	74	24	2.2	48
1,2,3,4,7,8-H ₆ CDD	23	8.3	76	24	4.2	59
1,2,3,6,7,8-H ₆ CDD	83	3.6	78	90	2.1	59
1,2,3,7,8,9-H ₆ CDD	60	6.2	77	64	2.0	59
1,2,3,4,6,7,8-H ₇ CDD	720	6.7	81	800	4.3	61
2,3,7,8-T ₄ CDF**	100	7.3	68	100	0.9	38
1,2,3,7,8-P ₅ CDF	39	14	74	40	3.7	46
2,3,4,7,8-P ₅ CDF	62	5.5	79	63	2.8	49
1,2,3,4,7,8-H ₆ CDF	740	5.3	81	770	2.3	60
1,2,3,6,7,8-H ₆ CDF	120	6.2	81	130	0.0	58
2,3,4,6,7,8-H ₆ CDF	45	9.0	82	44	3.5	60
1,2,3,7,8,9-H ₆ CDF	4.9	31	84	4.1	5.4	62
1,2,3,4,6,7,8-H ₇ CDF	2600	6.7	85	2700	2.0	64
1,2,3,4,7,8,9-H ₇ CDF	160	5.5	83	170	2.7	61

Values are corrected for recovery of ¹³C- labelled surrogates.

* Refers to recovery of corresponding ¹³C-labelled surrogate.

** Maximum possible concentration due to potential chromatographic overlap.

**TABLE 2: Average HS-2 Soil Values (ppt)
Comparison of Soxhlet versus Supercritical Fluid Extraction**

Group Totals	Soxhlet Extraction (n=4)			Supercritical Fluid Extraction (n=5)		
	Value	% RSD	Isomers	Value	% RSD	Isomers
Total T ₄ CDD	3.9	14	2	4.3	28	2
Total P ₃ CDD	17	7.8	6	16	22	6
Total H ₆ CDD	510	5.6	8	570	6.9	7
Total H ₇ CDD	4700	8.3	2	5300	6.6	2
Total O ₈ CDD	6500	4.2	1	7500	6.9	1
Total T ₄ CDF	39	11	13	26	16	7
Total P ₃ CDF	33	13	8	33	12	7
Total H ₆ CDF	89	3.2	6	94	6.3	6
Total H ₇ CDF	293	3.3	4	340	5.5	4
Total O ₈ CDF	300	3.8	1	280	6.2	1
2,3,7,8-substituted isomers	Value	% RSD	% Recovery*	Value	% RSD	% Recovery*
2,3,7,8-T ₄ CDD	ND(1)		62	ND(1)		48
1,2,3,7,8-P ₃ CDD	1.6	4.6	69	ND(1)		55
1,2,3,4,7,8-H ₆ CDD	4.5	4.8	74	6.0	27	61
1,2,3,6,7,8-H ₆ CDD	19	4.3	75	24	12	59
1,2,3,7,8,9-H ₆ CDD	24	4.3	74	27	13	62
1,2,3,4,6,7,8-H ₇ CDD	1200	8.1	80	1300	8.5	64
2,3,7,8-T ₄ CDF**	8.5	11	62	8.9	6.7	41
1,2,3,7,8-P ₃ CDF	1.9	17	68	2.4	17	49
2,3,4,7,8-P ₃ CDF	3.7	7.9	71	4.3	16	53
1,2,3,4,7,8-H ₆ CDF	17	7.3	79	20	6.6	58
1,2,3,6,7,8-H ₆ CDF	3.7	5.6	80	4.7	24	56
2,3,4,6,7,8-H ₆ CDF	3.7	18	81	4.4	31	58
1,2,3,7,8,9-H ₆ CDF	ND(1)		83	ND(1)		62
1,2,3,4,6,7,8-H ₇ CDF	91	1.6	83	110	4.1	58
1,2,3,4,7,8,9-H ₇ CDF	5.2	6.7	84	7.5	34	58

ND=not detected. Detection limit, in ppt, given in brackets. Values not used for statistical calculations.

Values are corrected for recovery of ¹³C- labelled surrogates.

* Refers to recovery of corresponding ¹³C-labelled surrogate.

** Maximum possible concentration due to potential chromatographic overlap.

Similar correspondence is once again observed for the low-level data (Table 2). Even as values approach the method detection limit of 1 ppt, the two data sets remain comparable. Surrogate recoveries range from 62 to 80% for the Soxhlet data and 41 to 62% for the SFE data. The clean-up losses were similar (56% for Soxhlet and 52% for SFE).

Conclusions

When analytes are adsorbed to the matrix, as is the case with spiked samples, extraction may be accomplished using mild conditions. Such conditions may not be sufficient for the removal of native PCDD/PCDF, which are physically entrapped (absorbed) in the matrix. This distinction is of great significance when using isotope dilution techniques, as was pointed out in a recent review⁸. We conclude that this recovery related issue is not of concern for the samples, spiking levels, and extraction procedures employed herein.

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