Simultaneous Extraction of PAHs and PCBs from Environmental Samples Using Accelerated Solvent Extraction

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Overview

Purpose: Demonstrate the fast and simultaneous extraction of Polyaromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in soil and mussel tissue using a single method.

Methods: Sample preparation using the Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor system with Gas Chromatograph (GC) with Electron-Capture Detector (ECD) and Gas Chromatograph with Mass Spectrometer (GC-MS).

Results: The data presented here show that accelerated solvent extraction can be used for simultaneous extraction of these persistent organic pollutants (POPs) in two environmentally relevant matrices. The recovery ranges for all compounds were within 83-114% with low % RSD that indicate excellent reproducibility. This work demonstrates that accelerated solvent extraction can be used with GC-ECD and GC-MS to improve the productivity of the overall analytical workflow.

Introduction

Accelerated solvent extraction is an established technique used for the extraction of solid and semisolid sample matrices using common solvents. Typical accelerated solvent extraction parameters include elevated temperature and pressure, which enhance the kinetics of the extraction process. This, in turn, results in extraction efficiencies that are equivalent to or greater than those achieved with a Soxhlet extractor, but in a fraction of the time while consuming much less solvent. Accelerated solvent extraction has been approved for use in U.S. EPA Method 3545A for the extraction of PCBs, organochlorine pesticides (OCPs), base/neutral/acid (BNA) compounds, organophosphorus pesticides (OPPs), herbicides, dioxins and is in compliance with U.S. EPA SW-846. Traditional extraction methods, such as Soxhlet and sonication, typically take hours and produce large amounts of organic solvent waste. Accelerated solvent extraction reduces solvent consumption and automates sample preparation.

PAHs and PCBs are considered toxic and carcinogenic, and are classified as persistent organic pollutants (POPs). Typically, PAHs and PCBs are extracted with separate methods using different solvent combinations. The purpose of this study is to report on the development of a single extraction method for PAHs and PCBs from mussel tissue and soil using accelerated solvent extraction.

Methods

Sample Preparation Equipment and Standards

- Dionex ASE 350 Accelerated Solvent Extractor system, equipped with 66-mL Stainless Steel Extraction Cell Kit
- Glass Fiber Filters
- Collection Bottles, 250 mL
- GC-ECD
- GC-MS
- Capillary Column 40 m x 0.18 mm i.d., d_f = 0.18 µm
- 5% Diphenyl Capillary Column 30 m x 0.25 mm i.d., d_f = 0.5 µm
- Nitrogen Evaporator (or equivalent)
- Semi-Volatile Internal Standard Mix
- 8270 Calibration Mix
- 8270 Base/Neutrals Surrogate Mix
- Aroclor 1254 Mix
- 2, 4, 5, 6-Tetrachloro-m-xylene (surrogate)
- Decachlorobiphenyl (Internal Standard)

Sample Information

New Zealand green-lipped mussels were purchased from a local grocery store and stored in a refrigerator at 4 °C until extraction.

Contaminated soil used in this study was certified reference material (CRM911-50G) for Aroclor 1254-Loam, purchased from Resource Technology Corporation (Laramie, Wyoming, USA).

Analysis of Extracts

GC-MS and GC-ECD were used to separate and identify PAHs and PCBs, respectively.

GC-MS Conditions	
Column:	5% Diphenyl Capillary Column 30 m x 0.25 mm i.d.,d_f = 0.5 µm
Injection Port Temperature:	280 °C
Injection Mode:	Splitless
Column Flow Rate:	1.4 (mL/min) constant flow
Oven Temperature:	50 °C (hold for 1 min) to 320 °C at 6 °C/min (hold for 10 mins)

GC-ECD Conditions	
Column:	Capillary Column 40 m x 0.18 mm i.d.,d_f = 0.18 µm
Injection Port Temperature:	250 °C
Injection Mode:	Splitless
Purge Time:	1.00 min
Makeup Gas:	Nitrogen
Column Flow Rate:	1.5 (mL/min) constant flow
Oven Temperature:	100 °C (hold for 1 min) to 200 °C at 30 °C/min to 320 °C at 2 °C/min (hold for 2 min)

The study consists of two parts:

1. Extraction of PAHs and PCBs from spiked mussel tissue at two different temperatures (see Table 1); and
2. Extraction of PAHs and PCBs from soil as per standard reference materials (SRMs) provided by Resources Technology Corporation

TABLE 1. Accelerated solvent extraction conditions.

	Method 1	Method 2
System Pressure	10 MPa (1500 psi)	10 MPa (1500 psi)
Oven Temperature	125 °C	100 °C
Sample Size	5 g	5 g
Oven Heatup Time	6 min	5 min
Static Time	6 min	4 min
Static Cycles	4	5
Rinse Volume	40 mLs (60% of extraction cell volume)	40 mLs (60% of extraction cell volume)
Solvent	Dichloromethane	Dichloromethane
Nitrogen Purge	300 s	300 s
Extraction Time	30 min	25 min
Cell Size	66 mLs	66 mLs

Results

The purpose of this work was to develop a single extraction method for both PAHs and PCBs. As shown in Tables 2 and 3, the percent recoveries for all compounds with both accelerated solvent extraction methods are within acceptable EPA recovery limits. While the results from accelerated solvent extraction Method 1 were very good, matrix interferences due to coextractable compounds were evident in the chromatograms (see Figure 1). These interferences necessitate frequent injection port cleanings. When the conditions of accelerated solvent extraction Method 2 were employed, the amount of co-extractables in the extracts was negligible (see Figure 2). However, as shown in Table 3, the recoveries for some of the higher molecular weight compounds (Benzo(a)pyrene, Benzo(ghi)perylene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd) pyrene and Aroclor 1254) were reduced, compared to the higher extraction temperature of Method 1.

TABLE 2. Data for mussel and soil samples by Method 1.

PAH Recoveries – Mussel (N = 6)				PAH Recoveries – Soil (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**	**Compound**	**% Recovery**	**SD**	**% RSD**
Nitrobenzene-d5**	83.3	0.54	13.05	Nitrobenzene-d5**	94.6	0.81	17.20
2-Fluorobiphenyl**	95.1	0.43	9.13	2-Fluorobiphenyl**	101.2	0.25	4.87
p-Terphenyl-d4**	91.4	0.27	5.92	p-Terphenyl-d4**	102.1	0.10	1.94
Naphthalene	89.1	0.28	6.33	Naphthalene	79.0	0.47	6.29
Acenaphthylene	101.2	0.30	5.91	Acenaphthylene	76.3	0.21	5.44
Acenaphthene	98.3	0.28	5.65	Acenaphthene	102.9	0.33	6.40
Fluorene	107.5	0.46	8.65	Fluorene	80.3	0.21	5.31
Phenanthrene	104.6	0.30	5.70	Phenanthrene	114.8	0.37	6.39
Anthracene	100.1	0.29	5.77	Anthracene	91.4	0.51	11.19
Fluoranthene	97.1	0.30	6.24	Fluoranthene	103.6	0.12	2.23
Pyrene	88.9	0.24	5.31	Pyrene	97.4	0.14	2.90
Benzo(a)anthracene	85.4	0.21	4.85	Benzo(a)anthracene	99.0	0.17	3.35
Chrysene	95.5	0.27	5.66	Chrysene	91.2	0.09	1.90
Benzo(b)fluoranthene	91.7	0.31	6.72	Benzo(b)fluoranthene	96.3	0.14	2.82
Benzo(k)fluoranthene	88.3	0.20	4.43	Benzo(k)fluoranthene	92.8	0.13	2.70
Benzo(a)pyrene	89.9	0.28	6.29	Benzo(a)pyrene	83.0	0.23	5.52
Benzo(ghi)perylene	94.1	0.31	6.60	Benzo(ghi)perylene	82.4	0.13	3.22
Dibenzo(a,h)anthracene	92.3	0.28	6.06	Dibenzo(a,h)anthracene	78.9	0.15	3.68
Indeno(1,2,3-cd) pyrene	91.1	0.31	6.72	Indeno(1,2,3-cd) pyrene	84.6	0.11	2.65
PCB Recoveries – Mussel (N = 6)				**PCB Recoveries – Soil (N = 6)**			
Compound	**% Recovery**	**SD**	**% RSD**	**Compound**	**% Recovery**	**SD**	**% RSD**
2,4,5,6-tetrachloro-m-xylene**	93.1	0.48	5.21	2,4,5,6-tetrachloro-m-xylene**	86.7	1.2	4.72
Aroclor 1254	95.9	0.06	3.26	Aroclor 1254	101.6	0.19	3.15

**Surrogate Spike

TABLE 3. Data for mussel samples extracted by Method 2.

PAH Recoveries - Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
Nitrobenzene-d5**	84.8	0.11	12.46
2-Fluorobiphenyl**	112.3	0.06	5.12
p-Terphenyl-d4**	105.8	0.10	9.09
Naphthalene	72.5	0.08	10.85
Acenaphthylene	82.3	0.09	10.50
Acenaphthene	81.2	0.07	9.20
Fluorene	79.5	0.06	7.41
Phenanthrene	95.3	0.06	6.49
Anthracene	85.2	0.07	8.01
Fluoranthene	90.8	0.08	8.43
Pyrene	86.2	0.07	7.82
Benzo(a)anthracene	84.7	0.09	10.48
Chrysene	114.0	0.11	9.99
Benzo(b)fluoranthene	89.2	0.07	7.97
Benzo(k)fluoranthene	84.7	0.05	5.33
Benzo(a)pyrene	77.7	0.08	10.39
Benzo(ghi)perylene	87.5	0.14	16.46
Dibenzo(a,h)anthracene	77.7	0.08	10.85
Indeno(1,2,3-cd) pyrene	83.5	0.07	7.97
PCB Recoveries – Mussel (N = 6)			
Compound	**% Recovery**	**SD**	**% RSD**
2,4,5,6-tetrachloro-m-xylene**	94.67	3.75	3.96
Aroclor 1254	85.68	1.87	2.18

**Surrogate Spike

FIGURE 1. GC-MS analysis of mussel sample extracted by Method 1.

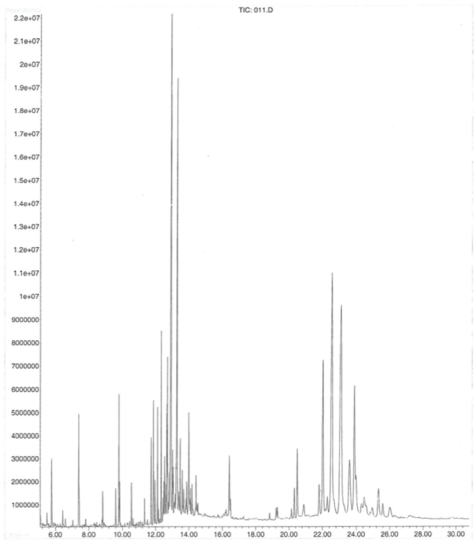
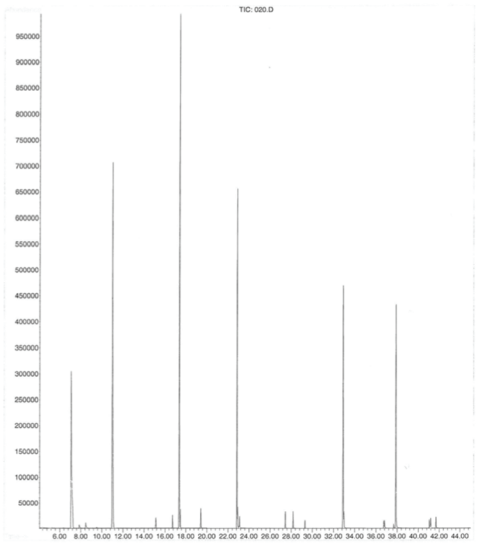


FIGURE 2. GC-MS analysis of mussel sample extracted by Method 2.



In-Cell Cleanup

One of the steps that can be combined is the introduction of an adsorbent into the extraction cell. Without the in-cell cleanup, Gel Permeation Chromatography (GPC) would need to be done, thus adding an hour or more to the analysis process. This will, in turn, necessitate cleaning the injection port more frequently.

For soil and tissue extracts, GPC is a very good method for removing sulfur and lipids, but the initial setup can be very expensive. The processing time per sample is between 30 to 70 minutes. For these reasons, alumina was added to the extraction cells. No further cleanup was required for the accelerated solvent extracts (Alumina, Acidic, 60-325 Mesh, Fisher Chemical). Using selective accelerated solvent extraction conditions coupled with in-cell cleanup (alumina), extracts can be produced that are free of matrix interferences. These sample extracts can be analyzed without time-consuming cleanup steps.

Conclusion

- Accelerated solvent extraction provides rapid processing, up to 24 samples can be processed sequentially at 20 minutes per sample
- The extraction of PAHs and PCBs can be combined into one method in environmentally relevant matrices with excellent percent recoveries.
- GPC cleanup can be eliminated in this combined extraction method by adding acidic alumina to the extraction cells.

For more information, refer to recent Thermo Scientific Application Note 1025.

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