

Microwave-Assisted Solvent Extraction of a Sediment Reference Material for the Polychlorinated Biphenyls Analysis

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Introduction

Polychlorinated biphenyls (PCBs) are serious and ubiquitous environmental organic pollutants which were widely used as transformer dielectric fluids, plasticisers and flame retardants, etc., in industry. Although the production of PCBs has been curtailed, the disposal, dump leaching and accidental spillage of the millions of pounds of these persistent products still cause environmental problems in air, water, and biological samples.

The applications of microwave energy to assist solvent extraction of toxic organics pollutants from various solids samples has been evaluated by a number laboratories in past few years¹⁻⁹. Ganzler *et al*¹ were the first to report the use of microwave radiation extraction method on solid matrices in the presence of polar organic solvents. The method has also been extended to the extractions of essential oils and natural products from different biological materials¹⁰⁻¹². This method is able to save solvent consumption volume and energy as well as to reduce waste and extraction period drastically which have made this technique a very attractive alternative to the conventional method - Soxhlet extraction.

As part of a series of studies, this report describes the results of microwave-assisted solvent extraction for the determination of polychlorinated biphenyls in sediment reference materials.

Experimental

Sample Materials

Sample used for this study were Hamilton Harbour sediment reference material EC-1¹³ prepared by the National Water Research Institute, Environment Canada. Sample size used for the extraction was 0.5 grams.

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Microwave-Assisted Solvent Extraction and Cleanup Procedures

The extractions were performed in a CEM MES-1000 equipped with a temperature control device and safety features including a solvent sensing alarm, pressure relief device and explosion protective shield. The samples were spiked with $^{13}\text{C}_{12}$ -PCB surrogates solution, prepared by the Analysis and Air Quality Division¹⁴, Environmental technology Centre, inside a 100-mL Teflon vessels before adding extraction solvents. The extraction conditions and solvents used are listed in Table 1. The extracts were then dried over sodium sulphate anhydrous, rotor evaporated, and acid/base column cleanup¹⁴. The PCBs fraction eluted from the column was blowdown with nitrogen to less than 350 uL and spiked with internal standards 50 uL each of hexachlorobenzene (HCB), PCB-83, and PCB-101*.

GC/ECD Analysis

The instrument consisted of a Hewlett Packard 5890II gas chromatograph equipped with a splitless injector, electron capture detector, and a 30 meter DB-5 column (30m x 0.25 mm i.d.). The GC oven temperature program was 90°C for 0.5 min, temperature-ramped to 200°C at 15 °C /min and held for 5 min, then to 285 °C at 5 °C /min and held for 10 min. Detector temperature was kept at 320 °C. The instrument was equipped with Hewlett Packard 7673A autoinjector and data was processed and recorded on an HP Vetra ES micro-computer. The working calibration standards were mixtures of 1:1:1 Aroclors 1242, 1254, and 1260 in benzene at the concentrations of 5.0, 2.0, 1.0, 0.2, and 0.04 ng/uL.

GC/MS Analysis¹⁵

The Hewlett Packard 5890II GC was equipped with on column injector and DB-5 column(30m x 0.25 mm i.d.) and a 10 m x 0.5 mm deactivated fused silica precolumn. The analytical column was inserted directly into the mass spectrometer. The injector temperature was 280 °C. The GC was set at a constant pressure of 10 psi. After an injection of 2uL sample, the GC oven temperature program started at 90 °C with a 2 min hold, 90 °C to 180 °C at 15 °C/min no hold, 180 °C to 240 °C at 3 °C/min, no hold, 240 to 285 °C at 10 °C/min with 15 min hold. A Hewlett Packard 5972 MSD was operated at 70 eV electron energy with a source temperature of 180 °C. Data was collected using a HP G1034C MS ChemStation software. A window defining standard was used to determine the range of retention times for each homologue group. A calibration standard was used to determine ion ratios and response factors¹⁵. To be identified as a PCB, the extracted ion peak would have to fall within the predefined homologue time frame, have a parent as well as two daughter ion peaks, and have a proper ratio of parent to daughter ion.

Results and Discussion

Two types of extraction solvent mixtures, i.e. hexane/acetone and cyclohexane/water, were used for this study. Hexane and cyclohexane are relatively nonpolar organic solvents which do not absorb significant amount of microwave irradiation under 2450 MHz. In order to increase the sample temperature to achieve set point temperature within reasonable time frame, solvent with higher dielectric constant is essential to be added to the sample so as to assist the conversion of microwave energy to heat. The microwave extraction conditions used for the study are listed in Table 1.

The multiple analysis results of PCBs in EC-1 extracted by Soxhlet and Ultrasonic Methods reported by Lee and *et. al.*¹³ are listed in Table 2 for the comparison purpose. The results from extraction conditions 1 (Table 3) and 3 (Table 4) were comparable to the previous reported data. Sediment extracted under condition 2 (Table 3) and 4 (Table 4) showed relative low recoveries which might be due to the lower extraction temperature. It also indicated that the standard deviation obtained from extraction solvent of hexane/acetone was superior to that of cyclohexane/water mixture.

Samples extracted under condition 1 were repeated by GC/MS analyses (Table 5) which provided correspondent results as reported data¹³ for each homologue group. The microwave-assisted method gives comparable extraction efficiencies and precision for the determination of PCBs in sediment. The real benefits in replacing the Soxhlet and other time-consuming methods with the microwave method are that we can reduce the extraction time from 20 hours to 10-20 minutes (excluding the time required for evaporation and cleanup) and solvent quantity reduced to 20 ml per sample. In view of advantages of this study and previous results^{7,8}, the development of this methodologies in applying microwave radiation to assist solvent extraction of pollutants from environmental sample matrices is warranted.

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References

- (1) Granzler K.; Salgó, A.; and Valdó, K., *J. Chromatogr.* 1986, 371, 299-301.
- (2) Lopez-Avila, V.; Young, R. and Beckert, W.F., *Anal. Chem.*, 1994, 66, 1097-1106.
- (3) Lopez-Avila, V.; Young, R.; Benedicto, J.; Ho, P.; Kim, R. and Beckert, W.F., *Anal. Chem.*, 1995, 67, 2096-2102.
- (4) Paré, J.R.J.; Belanger, J.M.R. and Stafford, S.S., *Trends Anal. Chem.*, 1994, 13, 176-184.
- (5) Jassie, L.B.; Hays, M.J. and Wise, S.A., *Proceedings of 1994 Pittsburgh Conference*, Chicago, IL.
- (6) Onuska, K.I. and Terry, K.A., *High Resol. Chromatogr.*, 1995, 18, 417-421.
- (7) Lao, R.C.; Shu, Y.Y.; Holmes, J. and Chiu, C., *Microchemical.*, 1996, 53, 99-108.
- (8) Lao, R.C.; Shu, Y.Y.; Chiu, C.H.; Lanoy, M.; Holmes, J.; Turle, R.; Belanger, M.R. and Paré, J.R.J. the 89th Annual Meeting and Exhibition of the Air & Waste Management Association, Nashville, Tennessee, 1996, Paper No. 96-FA150.06.
- (9) Chee, K. K.; Wong, M. K. and Lee, H. K., *J. Chromatography A*, 1996, 723, 259-271.
- (10) Young, J. C., *J. Agri. Food Chem.*, 1995, 2904-2910.
- (11) Paré, J.R.J., U.S. Patents No. 5,338,557, 5,377,426, 5,458,897 and 5,519,947; various international counterparts.
- (12) Chen, S. S. and Spiro, M., *J. Microwave Power and Electromagnetic Energy*, 1994, 29, 231-241.
- (13) Lee, H.-B. and Chau, A. S. Y., *Analyst*, 1987, 112, 37-40.

Dioxin '97, Indianapolis, Indiana, USA

- (14) Analysis and Methods Division, Environmental Technology Centre, Environment Canada, Reference Method EPS 1/RM/3, 1990.
- (15) Shu, Y. Y.; Dowdall, J. E.; Chiu, C. and Lao, R. C. Intern. J. Environ. Anal. Chem., 1995, 60, 185-194.

Table 1. Extraction Conditions

	Condition 1	Condition 2	Condition 3	Condition 4
Solvents and Ratios	Cyclohexane: Acetone = 1:1	Cyclohexane: Acetone = 1:1	Cyclohexane: Water = 3:1	Cyclohexane: Water = 3:1
Volume	20 mL			
Extraction Periods	10 min			
Microwave Power	500 W			
Temperature	100 °C	70 °C	100 °C	70 °C

Table 2. Results of Multiple Analysis for Total PCBs in EC-1¹³.

Extraction Methods	Ultrasonic	Soxhlet
Number of Analyses	97	72
Range (ug/g)	1.85-2.15	1.88-2.17
Average	2.02	1.97
Standard Deviation	0.07	0.08

Table 3. GC/ECD Results of PCBs Analyses from Microwave-Assisted Solvent Extraction with 1:1 Hexane to Acetone Ratio.

Extraction Conditions	1 (n=6)	2 (n=6)
Average ug/g	1.91	1.78
Relative Standard Deviation %	4.3	7.5

ANALYSIS

Table 4. GC/ECD Results of PCBs Analyses from Microwave-Assisted Solvent Extraction with 3:1 Cyclohexane to Water Ratio.

Extraction Conditions	3	4
Average ug/g	1.85	1.57
Relative Standard Deviation %	10.4	12.6

Table 5. Comparison the Results between Microwave-Assisted Solvent Extraction and Reported Method¹³ for the PCBs in EC-1.

Homologue	Reported Data		MASE (Extracted by Condition 1)	
	Average(ng/g) n=6	Standard Deviation	Average(ng/g) n=6	Standard Deviation
Cl ₁ -PCB	-	-	-	-
Cl ₂ -PCB	-	-	-	-
Cl ₃ -PCB	184	12	210	9
Cl ₄ -PCB	453	24	553	29
Cl ₅ -PCB	688	33	595	23
Cl ₆ -PCB	280	21	313	15
Cl ₇ -PCB	161	6.7	189	9
Cl ₈ -PCB	98	7.6	55	8
Cl ₉ -PCB	-	-	-	-
Cl ₁₀ -PCB	-	-	-	-
Total Concentration	1864		1915	