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Microwave Assisted Extraction of Polychlorinated Biphenyls from Environmental Samples

Milestone Application Report ETHOS X - PCBs - EPA 3546 Method

Polychlorinated Biphenyls (PCBs) are toxic and persistent molecules covered by the Stockholm Convention and several governments require their analysis in environmental samples. Microwave assisted solvent extraction is a well-established sample preparation technique applied in several official methods. Milestone ETHOS X equipped with fastEX-24 eT rotor and disposable glass vial, was used in this study to prove its efficacy in the extraction of PCBs compare to the Soxhlet extraction.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of organic pollutants consisting of 209 congeners having biphenyl as the core structural unit and a variable number of chlorine substituents.

PCBs were extensively utilized in industries in open (as additives to glues, dyes, and construction materials) and in closed systems (coolants and lubricants in transformers, dielectric fluids in capacitors, hydraulic fluids and heat-transfer media). Given their resistance to degradation, PCBs have long persistency in the environment and they tend to bio-accumulate in the food chain. PCBs are found in all the environmental matrices, around the world, since they are transported across international boundaries far from their sources, even to regions where they have never been used or produced. Since their toxicity and persistence, PCBs are one of the twelve POPs (Persistent Organic Pollutants) covered by the Stockholm Convention.[1]

EPA 3546[2] outlines the procedure for extracting water insoluble or slightly water-soluble organic compounds from soils, clays, sediments, sludges, and solid wastes.

EPA 3546 is a specific method for Microwave Assisted Solvent Extraction (MASE), a well-established sample preparation technique that enables extractions with reduced solvent volume and time. This application note represents a guideline for the extraction of the priority polychlorinated biphenyls from both standard reference materials and spiked materials using the official method EPA 3546. The efficiency of MASE was compared in this study with a conventional Soxhlet extraction.

Table 1 - Labelled Internal Standard Solution

Analyte	
^{13}C -PCB 4	^{13}C -PCB 118
^{13}C -PCB 37	^{13}C -PCB 126
^{13}C -PCB 81	^{13}C -PCB 169
^{13}C -PCB 77	^{13}C -PCB 156
^{13}C -PCB 123	^{13}C -PCB 189
^{13}C -PCB 105	

EXPERIMENTAL

Equipment

- Milestone ETHOS X
- fastEX-24 eT rotor [3]
- 100-mL disposable glass vials
- SFS-24 (Simultaneous Filtration System)
- GC-HRMS

Figure 1 – Milestone ETHOS X with fastex-24 eT (left) and SFS-24 filtration system (right).

Standard and Reagents

Standards, surrogates and internal standard were purchased by Sigma Aldrich. Grade solvent pesticide were used. Sodium sulfate anhydrous, silica gel (activated for at least 16 h at 130°C) and glass wool or paper filter were used in the clean-up procedure.

According to the analytical method EPA 8270e,[4] internal surrogates and standards were used.

Table 2 - PCBs Stock solution

Analyte	CAS No	Analyte	CAS No
PCB 8	34883-43-7	**PCB 128**	38380-07-3
PCB 18	37680-65-2	**PCB 138**	35065-28-2
PCB 28	7012-37-5	**PCB 149**	38380-04-0
PCB 44	41464-39-5	**PCB 153**	35065-27-1
PCB 52	35693-99-3	**PCB 156**	38380-08-4
PCB 101	37680-73-2	**PCB 170**	35065-30-6
PCB 105	32598-14-4	**PCB 180**	35065-29-3
PCB 118	31508-00-6	**PCB 187**	52663-68-0
PCB 126	57465-28-8		

Samples

The sandy loam soil LGC6115 and harbor sediment BCR 536 standard reference materials were used for the determination of PCBs. For PCBs not included in the certified materials a spiking stock solution on blank soil was used.

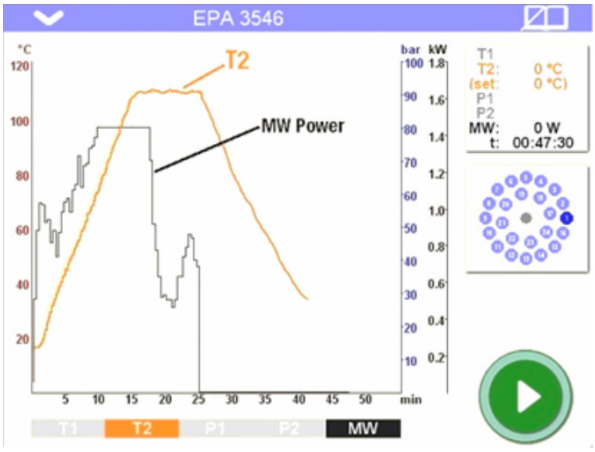

Figure 2 - Microwave run profile.

Sample Preparation

The samples were collected and stored in accordance with the requirements of EPA 3546.

Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composited samples. Grind or otherwise reduce the particle size of the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole.

Ground samples, wet or dried, were weighed directly into the 100 mL disposable glass vials of the fastEX- 24 eT rotor. 30 mL of acetone-hexane (1:1) was used as extraction mixture. An aliquot of the internal standard solution was added to the samples just prior to solvent addition then the glass vials were closed (automatic capping tool available).

Extraction process and clean up

According to the moisture content, the proper built-in method was selected.

Table 3 - Microwave Program

Step	Time (min)	Power (W)	Temperature (°C)
1	15	up to 1600	110
2	10	up to 1600	110

After the extraction, samples were filtered with milestone SFS-24 simultaneous filtration system using sodium sulfate anhydrous. The vials were rinsed with additional solvent aliquots. SFS-24 allows to filter 24 samples simultaneously with different types of filters available. Extracts and rinse solution were collected together. The extract was subsequently concentrated with nitrogen flow. If purification is not required, concentrate directly until 0.5 mL and add the appropriate surrogate standard solution to achieve the surrogate standard concentration. If purification is necessary, concentrate the extract directly until 2 mL. Purify the solution according to the method (EPA 3620, 3630, 3660, 3665). Finally, the extracts obtained by ETHOS X were concentrated for analysis.

Analitical conditions

A GC-HRMS System equipped with a split-splitless injector, autosampler and mass detector were used. Sample injection volume was 1 µL. A HT8-PCB - 60 m x 0.25 mm ID (SGE) was used for the analyses. The injector was maintained at 260 °C and the transfer line at 280 °C. A five steps ramp oven program was used.

Table 4 – GC oven program

Rate (°C/min)	Temperature (°C)	Plateaus (min)
20	100	1
30	180	0.5
2	260	0.5
5	300	2.9
10	310	10.5

Helium was used as the carrier gas.

RESULTS AND DISCUSSION

Results from extractions of sandy loam soil LGC6115 and harbor sediment BCR 536 standard reference materials are shown in Tables 5 and 6.

Recovery for all compounds is in the range 70-120% of the certified standard reference material.

Table 5 - PCBs recovery from Fresh Harbor Sediment BCR 536 (1 g) (n=4)

PCB Congener	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
PCB 28	44	42.46	96.5	5.5
PCB 52	38	30.83	81.1	8.9
PCB 101	44	43.03	97.8	5.6
PCB 105	3.5	3.27	93.5	4.5
PCB 118	27.5	22.82	83.0	3.0
PCB 128	5.4	4.38	81.1	1.6
PCB 138	27	26.27	97.3	1.6
PCB 149	49	46.26	94.4	0.5
PCB 153	50	48.09	96.2	0.6
PCB 156	3	2.32	77.3	1.4
PCB 170	13.4	12.56	93.7	3.6
PCB 180	22.4	23.60	105.3	2.9

Table 6 - PCBs recovery from Sandy loam soil LGC6115 (1 g) (n=4)

PCB Congener	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
PCB 101	93	74	79.6	1.8
PCB 118	116	86	74.1	4.9
PCB 138	16	14	87.5	0.2

Table 6 - PCBs recovery from Sandy loam soil LGC6115 (1 g) (n=4) (continuation)

PCB Congener	Certified value (mg/kg)	Ethos X (mg/kg)	Recovery (%)	RSD (%)
PCB 153	19	17	89.5	3.2
PCB 180	9.6	10	104.2	2.6

A specific test was performed to compare Microwave extraction efficiency with the most used traditional technique, the Soxhlet extraction. For this purpose, a solid waste was used (Table 7).

Table 7 – Recovery of PCBs from solid waste sample (1 g) – Ethos X compared to Soxhlet (n=4)

Analyte	Soxhlet (mg/kg)	Ethos X (Recovery % of Soxhlet)	RSD (%)
PCB 28	4.09	88.1	5.2
PCB 52	3.70	88.5	4.8
PCB 101	3.18	72.7	2.6
PCB 105	1.22	90.1	6.4
PCB 118	2.68	79.0	2.0
PCB 126	0.16	118.1	4.2
PCB 128	0.55	82.9	3.4
PCB 138	1.79	80.5	8.3
PCB 153	1.46	90.2	6.1
PCB 170	0.41	78.8	2.2
PCB 180	0.36	81.3	7.7
PCB 187	0.35	100.2	5.3

Additionally, a PCBs mixture was spiked to a blank soil in order to test the performance of the fastEX24 eT on a wider list of compounds (Table 8).

Table 8 - PCBs recovery from Spike solution (n=4)

Analyte	Spike (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
PCB 8	20	15.9	79.5	6.4
PCB 18	20	22.5	112.5	4.3
PCB 28	20	15.07	75.4	5.7
PCB 44	20	22.3	111.5	3.3
PCB 52	20	21.7	108.5	4.1
PCB 101	20	21.36	106.8	6.4

Table 8 - PCBs recovery from Spike solution (n=4) (continuation)

Analyte	Spike (µg/kg)	Ethos X (µg/kg)	Recovery (%)	RSD (%)
PCB 118	20	18.61	93.1	2.8
PCB 128	20	18.39	91.9	3.2
PCB 138	20	21.96	109.8	5.3
PCB 153	20	15.8	79	4.0
PCB 170	20	23.07	115.3	3.5
PCB 180	20	22.77	113.8	1.9
PCB 187	20	22.67	113.4	2.3

CONCLUSION

The results demonstrate the efficiency of the ETHOS X with fastEX-24 eT rotor for the PCBs extraction. Extraction efficiencies were good, proved by high recovery rate. The comparison between Soxhlet extraction and MAE demonstrates the efficacy of microwave extraction.

The fastEX-24 eT enables simultaneous solvent extraction of up to 24 samples in only 40 minutes (cooling step included). This in turns means that is able to extract over 200 samples in 8-hour workday. Contamination, memory effects, and cleaning are completely eliminated due to the use of cheap disposable glass vials. The use of contactless temperature control ensures high reproducibility and full recovery of the target analytes for full compliance with Official Methods.

Thanks to the unique design, fastEX-24 eT is easily applied also on difficult samples such as solid wastes and plastics.

ETHOS X provides extracts with the lowest solvent usage and significant time compared to all the other extraction technique.

The ETHOS X with all its unique features fully addresses the need of environmental laboratories in terms of productivity, ease of use, running costs, and extraction quality.

REFERENCES

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4. EPA 8270 E – Semivolatile organic compound GC-MS https://www.epa.gov/esam/epa-method-8270e-sw-846-semivolatile-organic-compounds-gas-chromatographymass-spectrometry-gc

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