Microwave assisted extraction for the determination of PAHs, PAEs and OCPs in soils.

1.Introduction

With rapid economic, agricultural and industrial development, the organic pollutants as polycyclic aromatic hydrocarbons (PAHs), phthalates (PAEs) and organochlorine pesticides (OCPs) accumulating in soil turns to a major concern in recent years. The accumulations of organic pollutants not only affect the ecological system, but also increase the risk of human health. Conventionally, soxhlet extractor is used to extract organic pollutants from solid matrix. However, the shortcomings of Soxhlet extraction as time-consuming, solvent consuming are obvious.

To date, microwave assisted extraction (MAE) may currently be considered as a real alternative to conventional solvent extraction method. The main advantages of MAE are the reduction of extraction time and the reduction of solvent quantities. The whole extraction process needs less than 20 min and the solvent consumption is reduced to less than 30 mL. The method validation was performed in terms of recovery, repeatability, linearity and limit of quantification.

2.Instrumentation

The extractions were carried out with Topex+, with 60mL PTFE vessel (working pressure 20 atm, working temperature 200℃) made by PreeKem scientific instruments Co., Ltd. A rotary evaporator (EYELAN N-1100) was used for solvent evaporation and the determination of organic pollutants was carried out on GC-MS (Shimadazu QP-2010, Agilent 7890B-5977A).

Reagents

Acetone (chromatographic grade)

n-Hexane (chromatographic grade)

Anhydrous sodium sulfate (GR)

3.Analytical procedures

1. Sample extraction

Weighed 5 g dried soil samples into the vessel. Added 5 g Na_2SO_4 and spiked a certain amount of standard into the samples. Then added 25 mL extraction solvent (acetone: n-hexane = 1:1). Sealed the vessels, and homogenous the solvent with samples. After that, placed the vessels into the

microwave oven and programmed as follow.

Table1. Program of microwave extraction

steps	Program setting	
	Temperature (℃)	Holding time (min)
1	80	5
2	110	5
3	115	20

Took the vessels out of microwave when the temperature was fall below 60℃. After cooling to room temperature, filtered the samples and dried.

2. Filter and concentration

Filtered the sample with sand core funnel covered a thin layer of Na_2SO_4.Rinsed the funnel with hexane and transferred the samples to the steam bottle. Then, concentrated the sample to 1 mL, and diluted to 2 mL with hexane.

3. GC-MS test

The analysis was performed on GC-MS (Shimadazu, QP-2010). The carrier gas was helium at a constant flow rate of 1ml/min. The capillary column was HP-5MS. The program condition for PAHs, PAEs and OCPs were listed as follow.

Inlet temperature: 250℃

Injection volume:1.0 μL

Split ratio:10:1

Interface temperature: 300 ℃

GC oven program: 40℃ for 5min, rise the temperature from 40℃ to 310 ℃ at the rate of 10.0 ℃/min, hold the temperature at 310 ℃ for 3.5 min.

Carrier gas: Helium

Flow rate of carrier gas: 1.0mL/min

4.Results

Category	Compound name	CAS	Added volume (1ug/mL)	Recovery% ±RSD%	Added volume (1ug/mL)	Recovery% ±RSD%	reported recovery%
PAHs	Naphthanlene	91-20-3	1 mL	78±8	5 mL	85±7	67±28
	Acenaphthene	83-32-9	1 mL	84±10	5 mL	90±5	70±34
	Phenanthrene	85-01-8	1 mL	88±12	5 mL	97±6	100±40
	Anthracene	120-12-7	1 mL	93±11	5 mL	99±5	83±18
	Pyrene	129-00-0	1 mL	94±13	5 mL	99±6	97±20
	Benzo(a)anthracene	56-55-3	1 mL	60±17	5 mL	62±13	97±24
	Chrysene	218-01-9	1 mL	60±15	5 mL	91±6	88±34
	Benzo(b)fluoranthene	205-99-2	1 mL	93±10	5 mL	100±6	95±36
	Benzo(k)fluoranthene	207-08-9	1 mL	51±14	5 mL	61±11	94±20
	Benzo(a)pyrene	50-32-8	1 mL	90±11	5 mL	96±6	75±30
	Indeno(1,2,3-c,d)pyrene	193-39-5	1 mL	70±16	5 mL	98±7	92±40
	2-Chloronaphthalene	91-58-7	1 mL	98±16	5 mL	96±10	68±22
PAEs	Dimethyl phthalate	131-11-3	1 mL	86±10	5 mL	90±5	78±28
	Bis(2-ethylhexyl)phthalate	117-81-7	1 mL	91±12	5 mL	101±7	97±68
	Di-n-octyl phthalate	117-84-0	1 mL	65±11	5 mL	75±10	101±36
	Diethyl phthalate	84-66-2	1 mL	53±15	5 mL	66±10	86±36
OCPs	2,2'-dichlorodiethylether	111-44-4	1 mL	73±8	5 mL	74±11	65±30
	1,3-dichlorobenzen	541-73-1	1 mL	61±6	5 mL	76±10	60±36
	1,4-dichlorobenzen	106-46-7	1 mL	62±6	5 mL	74±9	58±36
	1,2-dichlorobenzene	95-50-1	1 mL	65±5	5 mL	76±10	59±34
	dichloroisopropyl ether	108-60-1	1 mL	77±9	5 mL	81±9	64±26
	1,2,4-trichlorobenzene	204-428-0	1 mL	81±9	5 mL	85±8	63±28

hexachlorobutadiene	87-68-3	1 mL	81±9	5 mL	85±7	49±16
Hexachlorocyclopentadiene	77-47-4	1 mL	77±9	5 mL	86±7	63±14
4-chlorophenylphenylether	7005-72-3	1 mL	88±12	5 mL	97±5	78±12
Hexachlorobenzene	118-74-1	1 mL	86±11	5 mL	95±5	78±34

5. Conclusions

The analysis of spiked soil samples shows good recovery and repeatability results in PAHs, PEAs and OCPs. This is a proof for analytically accurate preparation step of microwave assisted extraction. Comparing to soxhlet extraction method, MAE shows similar recovery results but with less time and solvent consumption in the sample preparation process. Therefore, MAE meets the modern needs of efficient, eco-friendly analysis.