

STUDY ON RAPID ANALYSIS OF PERSISTENT ORGANIC POLLUTANTS IN SOILS AND SEDIMENTS BY MICROWAVE-ASSISTED EXTRACTION

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Abstract

A method combined microwave-assisted extraction (MAE) and purification with the vacuum manifold was studied for rapid analysis of persistent organic pollutants (POPs) in soils and sediments. Three grams of sample was extracted with a mixed solvent composed of 6 mL of hexane, 2 mL of ethanol and 2 mL of water at a temperature of 120°C for 15 min. After extraction, the sample was directly applied to purification process without concentration and solvent substitution procedures. As a result of POPs spiked test, the recoveries of all compounds were over 80% and the relative standard deviations of replicate analysis were within 8.4%. Compared with the conventional Soxhlet extraction using soil and sediment samples, POPs concentration and the reproducibility by our MAE method were equivalent, the ratios of total concentration were in the range of 98-123%, and the relative standard deviations were within 20%. The total time required for the pretreatment process was only 2 h.

Introduction

Organochlorine pesticides such as DDT and hexachlorocyclohexane (HCH) are representative persistent organic pollutants. These compounds are accumulated in soils, sediments and living organisms because of their hydrophobicity and stability. In Japan, official methods of POPs analysis in soils are carried out in accordance with the methods published by Japan Environment Ministry^{1,2}. These methods can be performed with accuracy and precision, however they need long analysis time because of complicated analytical procedures. Therefore, we have difficulty dealing with a survey of soil pollution in an emergency. In this study, we have studied on the rapid analysis of POPs in soils and sediments by MAE. In our previous studies, we found that the extraction efficiency of dioxins increased with the addition of water and ethanol to the extraction solvent³. Furthermore, we confirmed that our MAE method could be performed without sample drying⁴. The main objective of this study is to develop the pretreatment process with rapidness and efficiency between extraction and refining procedure. Additionally, we compared the quantitative determination of POPs in soils and sediments between our MAE method and the conventional Soxhlet extraction.

Methods and Materials

Samples

The soil and sediment samples were collected from the farms, industrial sites, and bay area in Japan. All the samples were homogenized by hand mixing, sieved to < 2 mm, and then stored in a sample bottle at a room temperature until chemical analysis was performed. The water content of each sample was gravimetrically measured, after they had been dried at 105°C for 2 h.

Microwave assisted extraction

The experimental procedures of POPs standard spiked test and validation test were shown in Fig.1. The validation test using soil and sediment samples

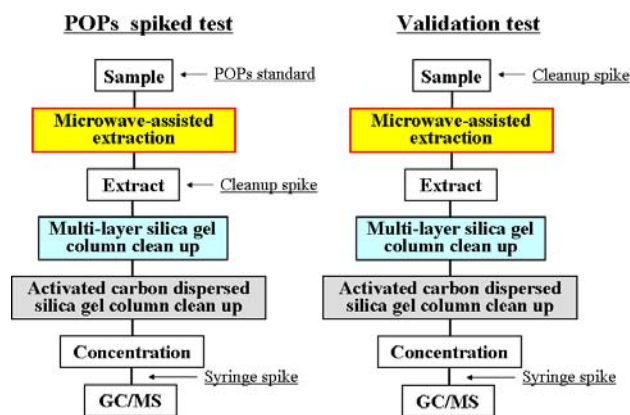


Fig.1 Analysis flow of POPs spiked test and validation test

was performed as follows. Three grams of each soil or sediment was weighed into quartz glass extraction cells (45 mL, Q-20; Milestone General, Italy). After the addition of an internal standard as a cleanup spike (2000 pg of ^{13}C -labeled POPs; Cambridge Isotope Laboratory Inc., USA) the sample was extracted with a mixed solvent composed of 6 mL of hexane, 2 mL of ethanol and 2 mL of water at a temperature of 120°C for 15 min using a microwave extraction system (ETHOS TC; Milestone General). After cooling, 5 mL of the extract from the hexane layer was transferred with a whole pipette to the multilayer silica gel column (Fig.2). The extract was refined with the multilayer silica gel and the activated carbon dispersed silica gel column. The refined solution was finally concentrated to 50 μl by nitrogen flow following the addition of an internal standard as a syringe spike (500 pg of ^{13}C -labeled 4,4'-DiCB and 2,3',4',5-TetraCB). The total time required for these analytical procedures was approximately 2 h.

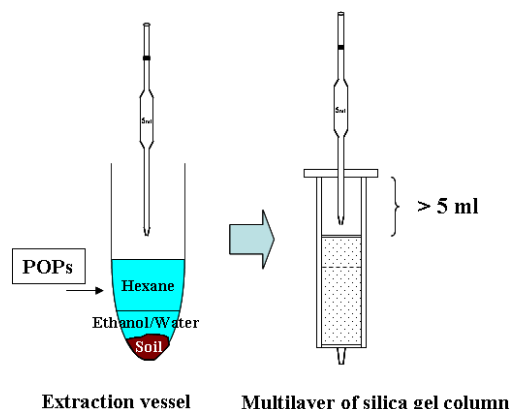


Fig.2 Simple operation of transferring hexane extract on a refining column after MAE

Soxhlet extraction

Five grams of each soil or sediment was weighed into quartz glass extraction thimble, followed by 4000 pg of an internal standard as a cleanup spike was added. Soxhlet extraction was performed with 400 mL of acetone/hexane (1:1) for 7 h. After extraction, the extract was concentrated and performed solvent replacement with hexane, then adjusted to 10 mL. Five mL of extract was refined with the multilayer of silica gel and the activated carbon dispersed silica gel. After the treated sample was concentrated to approximately 2 mL, the refined solution was finally concentrated to 50 μl by nitrogen flow following the addition of an internal standard as a syringe spike.

Analysis

The identification and quantification of POPs were performed by high-resolution gas chromatography coupled with a quadrupole mass spectrometric detector (HRGC/QMSD) (Agilent 6890/5973N, DB-5MS capillary column (30 m \times 0.25 mm i.d.; J&W Scientific, USA) were used for the separation of POPs. The column oven temperature of the DB-5MS was programmed at a rate of $30^\circ\text{C min}^{-1}$ from an initial temperature of 130°C (2 min hold) to a temperature of 170°C (1 min hold), then at a rate of 5°C min^{-1} to a final temperature of 300°C (3 min hold). The injector temperature was retained at 250°C and each sample (2 μl) was injected in the splitless mode. Analysis was performed using EI ionization and selected ion monitoring mode.

Results and Discussion

Recoveries of spiked POPs

Experiments of POPs spiked test were performed three times, respectively. The results were shown in Fig.3. The recoveries were calculated by this formula (Recoveries [%] = detectable amount of POPs [pg] \times 6/5 [mL] / injection amount of those [pg] \times 100). The average recoveries of POPs from test soil were in the range of 75-102%, and the relative standard deviations were within 8.4%.

In the previous studies on extraction of DDT by MAE, Gfrerer indicated that an extraction

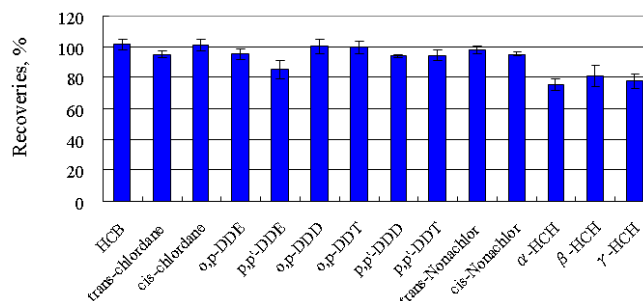


Fig.3 Recoveries of POPs in spiked soil A by MAE with a solvent of hexane 6 mL, ethanol 2 mL and water 2 mL (average + standard deviation, n=3)

temperature should not exceed 120°C to avoid DDT break down⁵. However, the recoveries of o,p-DDT and p,p'-DDT in this experiment were about 100%, a degradation of DDT was no found even though the maximum temperature of our MAE method was 120°C. These results showed that the simplified pretreatment process of our MAE method was effective.

Comparisons of POPs concentration between our MAE method and Soxhelt extraction

We compared the quantitative determination of POPs in real samples between our MAE method and the conventional Soxhlet as a validation test. First of all, comparisons of the POPs concentration in soil A between our MAE method and the conventional Soxhlet extraction were shown in Table 1. The ratio was calculated by this formula (Ratio [%] = concentration of POPs by our MAE method / that by the conventional Soxhlet extraction ×100). The average concentration and reproducibility were based on the repeated analysis (n = 3). The concentration and reproducibility obtained by our MAE method corresponded to those of the conventional method. The ratios of POPs concentration were 101%-131%, the relative standard deviations of replicate analysis by our MAE method and the conventional method were in the range of 2.1-16%, 2.3-21% respectively.

Table 1 Comparisons of POPs concentration in soil A between MAE and Soxhlet method (n = 3)

Compounds	MAE		Soxhlet		Ratio (%)
	Concentration (pg/g dry.wt.)	R.S.D. (%)	Concentration (pg/g dry.wt.)	R.S.D. (%)	
HCB	161	11	125	12	129
trans-Chlordane	126	8.5	112	11	112
cis-Chlordane	184	10	148	6.2	124
o,p-DDE	-	-	-	-	-
p,p'-DDE	1165	2.9	1045	12	111
o,p-DDD	110	10	85	15	129
o,p-DDT	298	2.1	227	8.5	131
p,p'-DDD	201	12	199	2.3	101
p,p'-DDT	2124	8.2	1671	15	127
trans-Nonachlor	537	7.6	438	3.8	122
cis-Nonachlor	266	10	216	15	123
α-HCH	7316	13	6048	19	121
β-HCH	3590	16	2977	17	121
γ-HCH	19094	13	15589	21	122

Following that, we performed the additional validation test using soil B-D, sediment A and B with different contaminated levels (300–95000 pg/g) and pollution patterns. Comparisons of the POPs concentration obtained by our MAE method and the conventional Soxhlet extraction were shown in Fig.4 including data of soil A.

The ratios of total POPs concentration in soil A-D, sediment A and B were 122%, 98%, 110%, 113%, 119% and 123%, respectively. The concentrations obtained by our MAE method were generally comparable to those by the

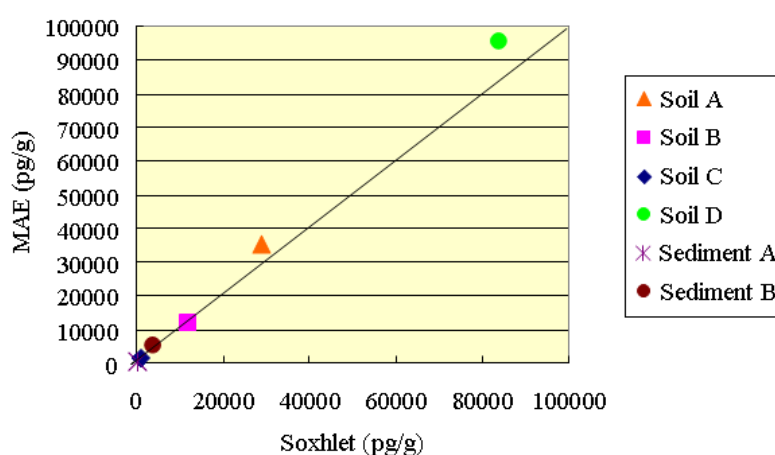


Fig.4 Comparisons of POPs concentration in soil A-D and sediment A,B between MAE and Soxhlet method (n = 1)

conventional Soxhlet extraction, although some interference peaks were detected near by targeted compounds in the chromatogram obtained by both methods. In addition, water content of samples did not influence the quantitative determination of POPs. These results showed that the quantitative determination of POPs by our MAE method was equivalent to that determined by the conventional method.

The total time required for the pretreatment process from sample treatment to purification procedures was approximately 2 h. Our MAE method can reduce drastically not only analysis time and analytical procedures but also organic solvent consumption compared to Soxhlet extraction. Additionally, the most advantage of MAE is that lots of samples can be extracted simultaneously. In this study, we developed the simple pretreatment process using the combination of MAE and purification with the vacuum manifold. This indicates that we can perform the rapid analysis of POPs in soils and sediments. Furthermore, it is considered to deal with a survey of soil pollution in an emergency.

Acknowledgment

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