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การพัฒนาเทคนิคเฮชสเปซโซลิดเฟสไมโครเอ๊กแทรกชั่นให้รวดเร็วและง่าย เพื่อวิเคราะห์ปริมาณสารฆ่าแมลงกลุ่มออร์กาโนคลอรีนในตะกอนดิน โดยเทคนิคแก๊สโครมาโทกราฟี

Rapid and Simple Headspace Solid-Phase Microextraction for the Determination of Trace Organochlorine Pesticides in Sediment by Gas Chromatography

Amornrat Wongklom[1]

บทคัดย่อ

ในงานนี้ได้พัฒนาวิธีการสกัดและวิเคราะห์ปริมาณสารฆ่าแมลงกลุ่มออร์กาโนคลอรีน 5 ชนิด (เฮปตาคลอร์ ออลดริน 4,4-ดีดีอี 2,4-ดีดีที และ 4,4-ดีดีที) ในตะกอนดินด้วยเทคนิคเฮดสเปซโซลิดเฟสไมโครเอ๊กแทรกชันร่วมกับเทคนิคแก๊สโครมาโทกราฟีให้เป็นวิธีที่รวดเร็วและง่ายในการวิเคราะห์ โดยศึกษาปัจจัยที่มีผลต่อกระบวนการสกัด ได้แก่ ชนิดของไฟเบอร์ อุณหภูมิและเวลาการสกัด การเติมตัวทำละลายมีขั้วและเกลือ กระบวนการสกัดทำได้โดยสกัดตะกอนดินหนัก 0.5 กรัมที่แขวนลอยในน้ำ 1 มิลลิลิตร สกัดสารบริเวณเหนือตัวอย่างด้วยไฟเบอร์ชนิด โพลีไดเมทิลไซล็อกเซนหนา 100 ไมโครเมตร ควบคุมอุณหภูมิที่ 70 องศาเซลเซียส เป็นเวลา 60 นาที กวนตัวอย่างตลอดช่วงการสกัด และวิเคราะห์ปริมาณสารฆ่าแมลงกลุ่มออร์กาโนคลอรีนด้วยเทคนิคแก๊สโครมาโทรกราฟีร่วมกับเครื่องตรวจวัดชนิดจับอิเล็คตรอนโดยใช้สภาวะเหมาะสม จากการศึกษาผลของการเติมตัวทำละลายมีขั้วและเกลือพบว่าให้ประสิทธิภาพการสกัดแตกต่างกันโดยสาร 4,4-ดีดีอี 2,4-ดีดีที และ 4,4-ดีดีที จะมีสัญญาณการวิเคราะห์สูงเมื่อเติมตัวทำละลายมีขั้วแต่สัญญาณของสารเฮปตาคลอร์และออลดรินจะลดลงเล็กน้อย และเมื่อเติมเกลือโซเดียมคลอไรด์จะให้สัญญาณการวิเคราะห์ต่ำที่สุด จากนั้นเก็บตัวอย่างตะกอนดินระหว่างเดือนพฤศจิกายน 2553 ถึง เดือนสิงหาคม 2554 จาก 6 สถานีเริ่มต้นจากอำเภอท่าตูม จังหวัดสุรินทร์ จนถึงอำเภอโขงเจียม จังหวัดอุบลราชธานี (ระยะทางประมาณ 350 กิโลเมตร) จากการวิเคราะห์ปริมาณ พบว่าตรวจพบสารฆ่าแมลงในทุกสถานีมีปริมาณอยู่ระหว่าง 2.20 ถึง 521 พิโคกรัม/กรัมของน้ำหนักตะกอนดินแห้ง ซึ่งปริมาณมีค่าไม่เกินเกณฑ์มาตรฐานคุณภาพดินกำหนดโดยกรมควบคุมมลพิษ

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ABSTRACT

Rapid and simple headspace solid-phase microextraction (HS-SPME) technique with gas chromatography was developed for extraction and determination of 5-organochlorine pesticides (OPCs; heptachlor, aldrin, 4,4-DDE, 2,4-DDT, 4,4-DDT) in sediment. The parameters affecting the extraction process such as fiber type, extraction temperature and time, and the addition of hydrophilic solvents and salt were studied. For HS-SPME, the suspension of 0.5-g sediment in 1-mL of water was extracted in the headspace using 100-µm PDMS fiber with extraction temperature of 70°C for 60 min, stirred during extraction. The OCPs was determined by GC-ECD with the optimum condition. The addition of hydrophilic solvents and sodium chloride had different effects on the extraction of OCPs. Higher responses of OCPs (4,4-DDE, 2,4-DDT, 4,4-DDT) were obtained when hydrophilic solvent was added to the sediment while heptachlor and aldrin slightly decreased and the response for adding the salt was the lowest. Sediment samples were collected from November 2010 to September 2011 from 6 stations starting from Amphoe Tatoom, Surin province to Amphoe Khongchiam, Ubon Ratchathani province (about 350 km). OCPs were found in all stations and quantities were in the range of 2.20 to 521 pg/g-dw of sediment. The quantities found were not over the values established by the Pollution Control Department for the soil quality.

คำสำคัญ: สารฆ่าแมลงกลุ่มออร์กาโนคลอรีน ตะกอนดิน เทคนิคแก๊สโครมาโทกราฟี
Keywords: Organochlorine pesticides, Sediment, Gas chromatography

Introduction

Organochlorine pesticides (OCPs) have been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. Despite the ban and restriction on the usage of OCPs in developed countries during the 1970s and 1980s, some developing countries are still using them for agricultural and public purposes because of the low cost and versatility in controlling various insects (Fatoki and Awofolu, 2003). In Thailand, the use of OCPs started from 1949 to 1990s. In particular, DDT was the first pesticide that had been used for malaria control in the country since 1949 and had been banned in Thailand during 1980s to 2004 (Keithmaleestti et al., 2009). OCPs have been extensively used in past decades against vegetal pests and vector borne diseases, and have highly contaminated the soil and sediment environments. Several OCPs including HCHs, aldrin, endosulfan, and DDTs have been promulgated as POPs or

endocrine disrupting chemicals (Chang and Doong, 2006). Sediment is one of the principal reservoirs of environmental pesticides, representing a source from which residues can be released to the atmosphere, groundwater and living organisms. Thus, it is important to monitor and analyse OCPs residues in sediments that serve as the primary sink for a majority of pesticides used in agriculture.

A number of conventional methods have been proposed for isolation, separation and analysis of OCPs in sediment samples such as ultrasonic solvent extraction, accelerate solvent extraction, microwave extraction and others. Analytical procedures are usually comprised of three steps: extraction, clean-up and analysis with drawbacks including time and solvent consumption. However, these procedures are usually expensive and labor-and time-consuming because typical environmental samples cannot be directly analyzed by the chromatographic techniques. In addition, large amounts of sample volumes are usually needed because of the low concentrations of OCP residues in sediments (Chang and Doong, 2006).

The present study is to investigate the applicability of HS-SPME combined with gas chromatography (GC) and electron capture detection (ECD) to the determination of OCPs in sediment samples. Several advantages such as cheap, solvent free, using whole sample for analysis, and easy to automate can be pointed out in relation to this technique when compared to the conventional method (Kataoka et al., 2000). The SPME device is commercially available and consists of two major components: the syringe assembly and fiber assembly. The syringe serves as a holder for the fiber assembly which is comprised of a needle that protects a small-diameter fused-silica fiber that has been coated with a liquid polymeric stationary phase. During sampling the coated fiber is directly exposed to the headspace above the sample, allowing absorption of the analyte according to their affinity toward the fiber coating. The analytes are thermally desorbed from the fiber in the hot injector of a gas chromatograph and are subsequently analyzed (Magdic and Pawliszyn, 1996). Also, a study on pesticides analysis by SPME was carried out. Results of the analysis showed that SPME was an accurate and fast method for sample preparation and analysis in aqueous solutions such as BTEX (Ezquerro et al., 2004) in water. In addition, headspace solid–phase microextraction (HS-SPME) has been used to determine the pesticide in soils, sediments, water, whole human blood, fruits and vegetables (Bouaid et al., 2001; Magdic and Pawliszyn, 1996), and polychlorinated biphenyls in soils and sediments (Montes et al., 2006). To enhance the desorption

efficiency of pollutions from environmental matrix and to increase the extraction efficiency of SPME, fiber has been developed for the determination of OCPs in soils and sediments (Doong and Liao, 2001; Chang and Doong, 2006; Alvarez et al., 2008). The use of surfactant to enhance the extraction of OCPs in sediments has been reported. However, the determination of OCPs in soil and sediment samples by HS-SPME has received only limited attention and still remains unclear. The aim of this study was to optimize extraction efficiency of HS-SPME for 5 selected OCPs from river sediments. Five OCPs, two different classes, cyclodiene (aldrin, heptachlor) and diphenyl aliphatic (4,4-DDE, 2,4-DDT, 4,4-DDT) pesticides, were selected as the model compounds because the residues of these compounds are most often detected in sediment environments. The HS-SPME procedure was optimized with variables involving SPME fiber selection, extraction temperature and time, and the addition of hydrophilic solvents and salt. The OCPs were identified and quantified by GC-ECD.

Materials and Methods

Materials

The OCPs standard obtained from AccuStandard, Inc., New Haven, USA. Four kinds of SPME fibers, a 100-μm poly (dimethylsiloxane) (PDMS) fiber, 75-μm carboxen (CAR) - PDMS, 85-μm polyacrylate (PA) and 65-μm PDMS-divinylbenzene (DVB) fiber and solid-phase microextraction system were purchased from Supelco Co., Inc. (Supelco, Bellefonte, PA,USA). All chemicals and solvents were analytical reagent grade, purchased from Sigma Chemical Co. Deionized water was obtained from a Milli-Q water purification system. All glasswares and 15-mL amber vials capped with PTFE-coated septa were well-cleaned with detergent, then sequentially rinsed with distilled water and hexane, respectively.

Study area and Sampling

The Moon river is one of the polluted rivers in Thailand because of large amounts of industrial wastewater and sewages discharged from a traditional agricultural production area in northeastern Thailand. The river has long historically been contaminated with heavy metals, other volatile and semivolatile organic compounds. The sampling sites were selected to the distribution of OCPs concentrations in sediments from the Moon river. The sediment samples were collected for six times from November 2010 to September 2011 from 6 stations including 1) Amphoe Tatoom, Surin province, 2) Amphoe Rasisalai, Sisaket province, 3) Amphoe Yangchumnoi, Sisaket province, 4) Amphoe Warinchamrab, Ubonratchathani province, 5) Amphoe Tansoom, Ubonratchathani province,and

6)Amphoe Khongchiam, Ubonratchathani province. The 0-20 cm of the surface sediments were sampled using a stainless steel grab sampler. Immediately after collection, sediments were preserved at 0-4°C in order to avoid degradation.

Solid-phase microextraction procedures

Sediments were dried and sieved with a sieve (20-mesh, 63 µm pore size) to remove coarse particles and debris. Samples from the Moon river were prepared by spiking appropriate amounts of the diluted working solution (2µg/L) to sediments to get the final OCPs concentration of 40.0 pg/g-dw. Sediment samples were waited to evaporate the solvent. The HS-SPME extractions were performed by placing approximately 0.5-g of spiked samples and 1-mL of deionized water into 15-mL amber vials capped with PTFE-coated septa. Magnetic stirring with a 8-mm long teflon coated stir bar was used to agitate the slurry. The HS-SPME experiment was conducted by immersing the fiber in the headspace of the sample. OCPs sorbed on the stationary phase of the fibers into the extraction temperature and time as 70°C and 60 min, respectively. After extraction, the fiber was desorbed into the liner of the GC injector port at 270°C for 5 min. Possible carryover was removed by keeping the fiber in the injector for a period of time with the splitless mode. Reinserting the fiber into the injector after the run showed no obvious carryover (Wongklom and Intaraprasert, 2011).

Analytical procedures

A Varian Star 3600 CX gas chromatograph (GC) equipped with an electron capture detector (ECD) was used to determine the OCPs concentrations in sediments. The GC injector was operated in a splitless at 270°C. The temperature of ECD was 280°C. A 15-m DB-1 capillary column (0.25 mm inner diameter, 0.25µm film thickness (F&W Scientific, Folsom, CA) was used for separating the OCPs and was held at 100°C for 2 min, increased to 180°C at a rate of 10°C/min, held for 4 min, and finally ramped to 280°C at a rate of 10°C/min, held for 6 min. The carrier gas was nitrogen at a flow rate of 1.5 mL/min. Nitrogen gas was used as the make-up gase at flow rate of 28 mL/min.

The linearity of the method was tested by extracting six spiked sediment sample with increasing concentrations over a range between 4.00 and 400 pg/g-dw. The accuracy was estimated by means of recovery experiments, analyzing sediment sample (n=5) spiked at 10.0 pg/g–dw. The limit of detection (LOD) was estimated as the analyte concentration that produced a peak signal of three times the background noise from the chromatogram at the lowest fortification level tested.

Results and Discussion

Optimization of HS-SPME

An effective HS-SPME procedure for the determination of OCPs concentrations in sediments, SPME fiber type, extraction temperature and time, and the addition of hydrophillic solvents and salt were optimized.

The sensitivity of each fiber is different depending on the molecular mass and polarity of the analytes to be extracted (Lambropoulou and Albanis, 2001). The commercially available SPME fibers (100-µm PDMS, 75-µm CAR-PDMS, 85-µm PA, 65-µm PDMS-DVB fiber were compared for determinating 5-OCPs. Figure 1 shows a low adsorption efficiency of the CAR-PDMS fiber was observed for the extraction of 2,4-DDT and 4,4-DDT. The 100-µm PDMS fiber obtained high efficiency for all OCPs. Doong and Liao (2001) reported that the 100-µm PDMS and 65-µm PDMS-DVB fiber showed good extraction efficiency for 18-OCPs. The OCPs are typically considered as hydrophobic organic compounds. The log values of octanol-water partition coefficients (K_{ow}) range from 2.70 (heptachlor) to 6.91 (4,4-DDT) and the water solubilities at 25°C were from 0.025 (4,4-DDT) to 0.12 mg/L (DDE). Therefore, these analytes would be expected to partition readily into a more non-polar fiber coating rather than a polar fiber such PA, CAR-PDMS, PDMS-DVB fiber. The 100-µm PDMS fiber showed the best extraction efficiency for all OCPs. Therefore, the 100-µm PDMS fiber was selected for further optimization experiments.

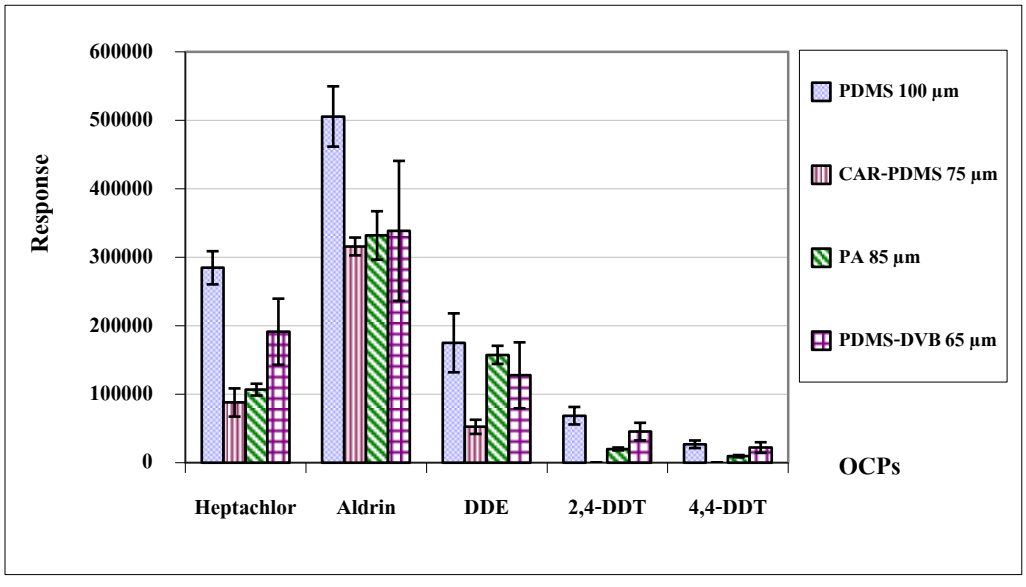

Figure 1. Effect of available SPME fiber ,extraction temperature and time were 70°C and 30 min, respectively

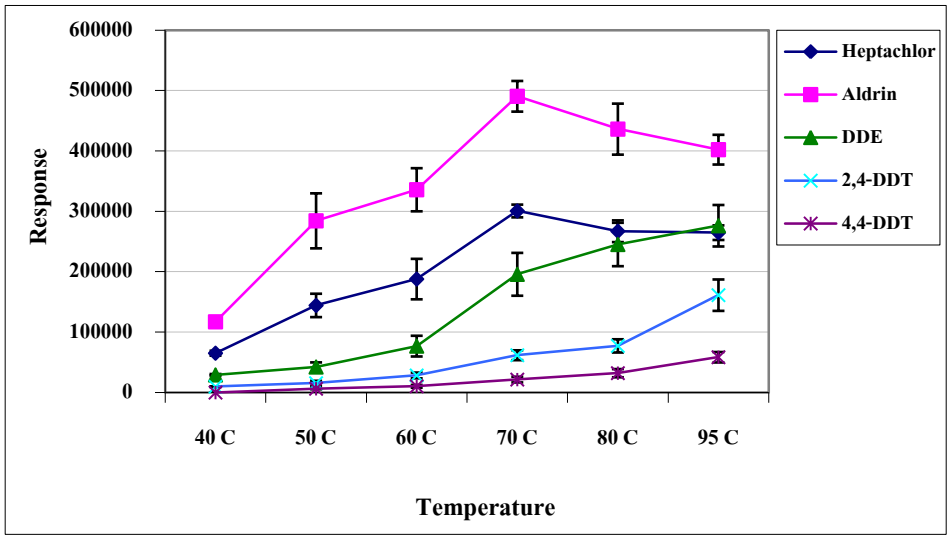

Figure 2. Effect of extraction temperature, using 100-µm PDMS fiber and extraction time was 30 min

The increase in extraction temperature increased the extraction efficiency of OCPs, due to the decrease in the partition coefficient (K_p) between OCPs and sediment particles but the increased temperature significantly enhanced the mass transfer and diffusion rates of OCPs from solid phase to aqueous solution, and then to gaseous phase (Chang and Doong, 2006). The change in extraction temperature was determined in the range of 40–95°C. Figure 2 shows the increased temperature tend to higher amount of OCPs existed in the gas phase. The response of all OCPs became obvious when the temperature was higher than 60°C but the response of aldrin and heptachlor decreased when the temperature was higher than 70°C, due to the adsorption of analyte by the fiber is an exothermic process, a high temperature could decrease the SPME distribution coefficients of analyte (Doong and Liao, 2001; Chang and Doong, 2006). Thus, an extraction temperature of 70°C was selected for further experiments.

Since the HS-SPME technique is an equilibrium process of the analyte between the vapor phase and fiber coating, the extraction time required to reach the equilibrium between the fiber stationary phase and the sediment sample was determined. When analytes have low Henry's constant values, low concentrations at the vapor pressure are expected, thus translated on a small concentration gradient and so there is a subsequent and longer periods to reach the equilibrium needed. Also analytes with high molecular mass are expected to need longer equilibrium times, due to their

lower diffusion coefficient (Lambropoulou and Albanis, 2001). The extraction time was determined in the range of 15 to 120 min. Figure 3 shows the using long time for HS-SPME procedure obtained good efficiency for extraction of OCPs, but the responses of heptachlor and aldrin decreased after 60 min and increased in higher than 120 min. The results showed that the equilibrium is compound-dependent and can vary significantly between the different compounds. The short equilibrium time for heptachlor, aldrin (60 min) may be due to the high vapor pressure at 70°C and the long equilibrium time for 4,4-DDE, 2,4-DDT and 4,4-DDT (120 min) due to the low vapor pressure at 70°C, the low water solubilities and high K_{ow} values. The higher response was observed when long equilibrium time was for all OCPs (120 min). However, the extraction time of 120 min was so long for HS-SPME procedures to extract the OCPs, thus an extraction time of 60 min was selected to perform the sample analysis.

The effect of the addition of hydrophilic solvents and sodium chloride to the samples was studied. Figure 4 shows no increase of the response was observed after the addition of NaCl. It corresponded to a study by Alvarez et al. (2008) who reported the addition of sodium chloride was a significant variable only for a few pesticides, better responses were registered working at the low level (0%NaCl), thus the addition of NaCl did not promote “salting-out” effect in the soil sample. The addition of salt to aqueous samples is frequently used to enhance the sensitivity of headspace analysis of polar compound; for non-polar compounds this effect is expected to be insignificant (Llompart et al., 1999). The addition of hydrophilic solvents (methanol, acetonitrile) response increased, such as heptachlor, aldrin and 4,4-DDE. The increase in sensitivity of polar metabolites with the addition of hydrophilic solvents due to the displacement of the analytes from the active site in the sediment (Doong and Liao, 2001; Chang and Doong, 2006). However, these added solvents would also decrease the response of certain OCPs, like 2,4-DDT and 4,4-DDT. Ezquerro et al. (2004) reported that the addition of water to the soil sample causes higher extraction yields and a significant increase in the chromatographic signal. Moreover, water displaces the analytes from the active sites in the soil; they are desorbed from the soil into the solvent for salvation, and then they migrate to the headspace. Therefore, addition of 1-mL of water into the 0.5-g sediment was selected for further determination.

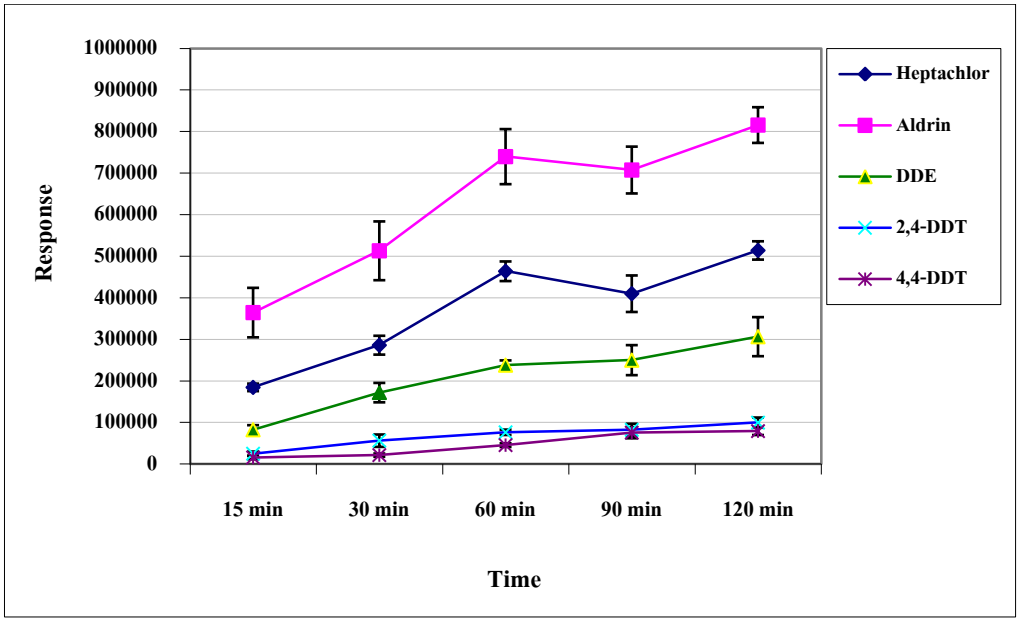

Figure 3. Effect of extraction time, using 100-µm PDMS fiber and extraction temperature was 70°C

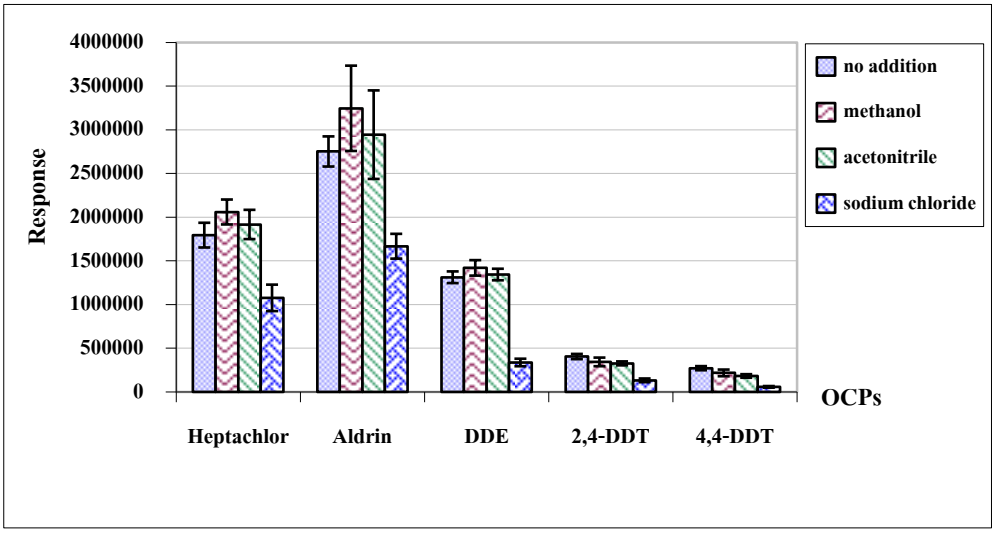

Figure 4. Effect of addition of hydrophilic solvents and sodium chloride, using 100-µm PDMS fiber, extraction temperature and time were 70°C and 60 min, respectively and addition of water into sediment 0.5g

Analytical performance of HS-SPME-GC-ECD

Table 1 shows the analytical performance of HS-SPME-GC-ECD; the linearity, accuracy, precision and limits of detection (LODs) of OCPs using the developed HS-SPME procedure. The linearity of the HS-SPME method was tested by extracting the OCPs in the gas phase. The applied concentrations were in the range of 4.00 to 400 pg/g–dry weight of sediment. The HS-SPME procedure showed a good linear behavior in the tested range, with correlation coefficients ranging between 0.997 to 0.999. The precision of the method was determined by performing five consecutive extractions with concentration of 10.0 pg/g-dw. The relative standard deviation (%RSDs) was lower than 10% which were in the range from 2.37% (4,4-DDT) to 7.31% (2,4-DDT). The limits of detection (LODs) was lower 10.0 pg/g level for sediment sample analysis. The recovery of the method was determined by performing five consecutive extractions with concentration of 10.0 pg/g-dw. These correspond to the recoveries of 80.02 to 91.16%. The recoveries obtained in this study are comparable with the recovery values reported by Doong and Liao (68 to 127%), Chang and Doong (71 to 121%), Alvarez et al. (61 to 125%) and Lambropoulou and Albanis (74 to 91%). Therefore, the developed HS-SPME procedure is suitable for the determination of the multi-residue analysis of the OCPs in sediment. This analytical procedure is also evaluated by its high accuracy which was also carried out by using a gas chromatograph with an electron capture detector.

Real sediment samples determination

Sediments from the Moon river were determined by using the developed method. Sediment samples were collected from 6 stations starting from Amphoe Tatoom, Surin province to Amphoe Khongchiam, Ubonratchathani province. These studies found the contamination of all OCPs in all collected stations from the Moon river from November 2010 to September 2011. The contamination of heptachlor, aldrin, 4,4-DDE, 2,4-DDT, 4,4-DDT was in the range of 2.20-521 pg/g, 6.00-9.70 pg/g, 2.70-21.4 pg/g, 4.50-7.90 pg/g and 4.00-6.60 pg/g-dw, respectively. The mean quantity of OCPs obtained by using HS-SPME-GC-ECD was in the range of 2.20 to 521 pg/g-dw. The quantity of OCPs found in sediment samples was not over the standard of the soil quality standard by the Pollution Control Department (total OCPs were not over 690 ng/g for soil).

Table 1. Analytical performance for determination of some OCPs in sediment samples by HS-SPME-GC-ECD

OCPs	Linear range (pg/g)	Linearity (6 level)	Precision (%RSD, n=5)	Mean Recovery (%R)	LOD (pg/g)
Heptachlor	4.00 – 400	0.998	4.71	84.16	2.00
Aldrin	4.00 – 400	0.997	7.16	80.02	2.00
4,4-DDE	4.00 – 400	0.998	3.95	84.18	2.00
2,4-DDT	4.00 – 400	0.998	7.31	89.60	4.00
4,4-DDT	4.00 – 400	0.999	2.37	91.16	4.00

Conclusions

In this study, the HS-SPME-GC-ECD technique has been developed to effectively determine the concentration of OCPs in sediment samples. The developed HS-SPME-GC-ECD exhibits a rapid and simple technique and a good analytical performance for the determination of OCPs in ng/g level of the sample. Concentration of OCPs has been successfully measured in surface sediment in the Moon river, Thailand. The concentration of OCP residues ranged from 2.20 to 521 pg/g-dw. The quantity of 5-OCPs found in sediment was not over the standard of the soil quality standard by the Pollution Control Department. The OCP levels found in the Moon river could be regarded as the guideline for OCP residues in northeastern Thailand. Their detectable levels in sediment indicate that they can persist in agricultural fields for a long time.

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