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Evaluation of expanded graphite as on-line solid-phase extraction sorbent for high performance liquid chromatographic determination of trace levels of DDTs in water samples

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Abstract

Dichlorodiphenyltrichloroethane (DDT) and its metabolites are a typical kind of persistent organic pollutants (POPs). Development of a simple, cost-effective and sensitive methodology to monitor DDTs concentrations in water environment is of particular significance for understanding the fate and behavior of these pollutants. In this paper, a method on the basis of solid-phase extraction (SPE) using expanded graphite (EG) as sorbent coupled on-line with high performance liquid chromatography (HPLC) was developed for the determination of trace levels of *p*,*p*′-DDD (2,2-bis(4-chlorophenyl)-1,1-dichloroethane), *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE (2,2-bis(4-chlorophenyl)-1,1-dichloroethene) in water. The analytes in water were preconcentrated onto the SPE column packed with expanded graphite, and subsequently eluted with methanol–water (90:10) mixed solvent. HPLC with a photodiode array detector was used for their separation and detection. The developed on-line solid-phase extraction protocol for HPLC permits the current HPLC separation and the next preconcentration proceeded in parallel, and thus allows one determination within 8 min. The precision (R.S.D.) for 10 replicate injections of a mixture of 1 $\mu g\,l^{-1}$ of each analyte was 3.2–6.2% for the peak area measurement. The detection limits (S/N = 3) for preconcentrating 50 ml of sample solution ranged from 10 to 25 $ng\,l^{-1}$ at a sample throughput of 7.5 samples h^{-1}. The enhancement factors were about 700. The method was applied to the determination of trace *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE in local lake, river and tap water samples.
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Keywords: Solid-phase extraction; High performance liquid chromatography; Expanded graphite; DDTs

1. Introduction

Dichlorodiphenyltrichloroethane (DDT) was employed extensively from the early 1950s for control of soil-dwelling insects and for control of vector against diseases such as malaria and typhus until the production ban commenced in 1974 [1]. DDT and its metabolites are highly persistent in the environment [2], and are the archetypes of fat soluble, nonbiodegradable and bioaccumulating compounds [3]. They are paradigmatic endocrine disruptor, and may cause serious environmental and health problems in animals and humans. Because of their stability and persistence in the environment, they are frequently referred to as the persistent organic pollutants (POPs) [4] and listed on the United Nations Stockholm Convention [5]. Even after being banned, DDTs are still produced and used in many developing countries for malarial control, because of the resurgence of malarial in many such countries and the costs and failures of alternative methods [6].

The environmental contamination by DDTs is spread all over the world, especially the DDTs are transported to the Arctic and are then subjected to biological mechanisms that lead to the high-level contamination for certain species. In the transport process, marine and/or lake play an important role as a sink of pollutants. Rain also influences the transport and precipitation process a great deal. Therefore, it is important to monitor DDTs concentrations in water environment for understanding the fate and behavior of these pollutants [7].

One of the primary goals in water analyses for pesticides is to reach determination limits of about 0.1 $\mu g\,l^{-1}$ for individual pesticides and 0.5 $\mu g\,l^{-1}$ for total concentrations in order

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to meet the requirements of the European Union (EU) Drinking Water Directives and those of the US National Pesticide Survey [8–10]. These levels call for methods with very low detection limits. DDTs are usually determined by gas chromatographic (GC) techniques with mass spectrometric (MS) or electron capture detection (ECD) [1–4,7,8,11–13]. High performance liquid chromatography (HPLC) with MS detection has also been used for this purpose [10]. However, determination of (ultra)trace levels of DDTs in relatively unpolluted water samples requires a suitable preconcentration technique [10]. The most common choices are solid-phase extraction (SPE) and liquid–liquid extraction (LLE). LLE followed by concentration through evaporation to dryness and dissolution of the residue in a low volume of organic solvent may result in serious losses of analytes [10]. Compared to LLE, SPE method can prevent the formation of emulsions and reduce the amount of solvent for the extraction [7,14–16].

Expanded graphite (EG) is a highly porous worm-like and very light material with typical apparent densities of 0.002–0.01 g cm^{-3}, and is a material of growing importance because of numerous actual and potential applications [17,18]. The absorbing spaces of EG can be divided into two types. One is the wrapping absorption space (WAS) constructed by EG stacking on each other; the second is the pores in each EG worm-like segment [19]. EG is a good sorbent due to the network pore structure [20], weak polarity [21], hydrophobic and lipophilic nature with extremely high selective sorption capacity to large organic compounds with weak polarity from water [22]. EG has been used to remove heavy oil floating on water [23,24], organic compounds [25], and pesticides [20] for environmental protection, but no work, to our knowledge, has been reported on the use of EG as on-line SPE sorbent for HPLC determination of trace POPs in environmental materials.

The aim of this work was to develop a simple, cost-effective and sensitive method for the determination of *p*,*p*′-DDD (2,2-bis(4-chlorophenyl)-1,1-dichloroethane), *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE (2,2-bis(4-chlorophenyl)-1,1-dichloroethene) at low μg l^{-1} levels in water without the need for time-consuming sample treatment by on-line coupling SPE preconcentration using EG as sorbent to HPLC. The design of the on-line SPE preconcentration system for HPLC, and the potential factors affecting the SPE and subsequent HPLC separation of the analytes were described and discussed in detail. The developed method was applied to determination of trace *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE in local water samples.

2. Experimental

2.1. Apparatus

The chromatographic system consists of a model 600 HPLC pump and a Waters 2996 Photodiode Array Detector (Waters, Milford, MA, USA). All separations were achieved on an analytical reversed-phase column (ZORBAX SB-C18 5 μm, 4.6 mm i.d. × 15 cm long, Agilent, Palo Alto, USA) at a mobile flow rate of 1.0 ml min^{-1} under isocratic conditions at room temperature. The Empower Software was used to acquire and process spectral and chromatographic data. The photodiode array detector was operated between 210 and 400 nm.

A model FIA-3100 flow injection system (Vital Instruments Co. Ltd, Beijing, China) was used for solid-phase extraction preconcentration. Tygon pump tubes were used for delivering the sample solution. Small-bore (0.5 mm i.d.) PTFE tubings were adapted for all connections with shortest possible length to minimize the dead volume.

The scanning electron micrograph (SEM) micrographs of the EG were obtained from a model S-700 Scanning electron microscopy (Shimadzu, Kyoto, Japan). A model ASAP 2010 Specific surface area and pore size distribution analyzer (Shimadzu, Kyoto, Japan) was used for calculating the specific surface area and pore diameter of EG.

2.2. Materials and reagents

All reagents were of the highest available purity and at least of analytical grade. Doubly deionized water (DDW, 18 MΩ cm^{-1}) obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO, USA) was used throughout.

Working solutions of *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE were prepared from a mixture standard stock solution containing 50 mg l^{-1} *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE, respectively (National Research Center for Certified Reference Materials, Beijing, China) by stepwise dilution with DDW just before use.

The expanded graphite used as sorbent was prepared as described previously [26]. It is worm-like with an average pore diameter of ∼100 nm and a specific surface area of 36.0 $\text{m}^2\ \text{g}^{-1}$. The scanning electron micrograph of the EG was shown in Fig. 1. A precolumn (1.5 cm × 4 mm i.d.) dry-packed with 10 mg of the EG was used for the solid-phase extraction preconcentration of DDTs in water. Before measurements, the SPE column was conditioned by flushing with mobile phase.

Best chromatographic resolution for the separation of *p*,*p*′-DDD, *p*,*p*′-DDT, *o*,*p*′-DDT and *p*,*p*′-DDE was obtained with a mixture of methanol (Concord Technology Co. Ltd., Tianjin, China) and water (90:10). The mobile phase was filtered through 0.45-μm filter prior to use. High purity helium was used for degassing the mobile phase.

2.3. Measurement of the breakthrough volumes and dynamic capacity

The following procedure was employed to measure the breakthrough volumes and dynamic capacity of the EG. A 50 μg l^{-1} of DDTs solution was pumped at a flow rate of 8 ml min^{-1} through the SPE column packed with 10 mg of the EG until the concentration of the DDTs in the effluent was the same as in the influent. Successively fractions of 10 ml effluent portions were collected, in which the concentrations of the DDTs were measured by HPLC. The dynamic capacity was calculated according to Wang and Barnes [27].

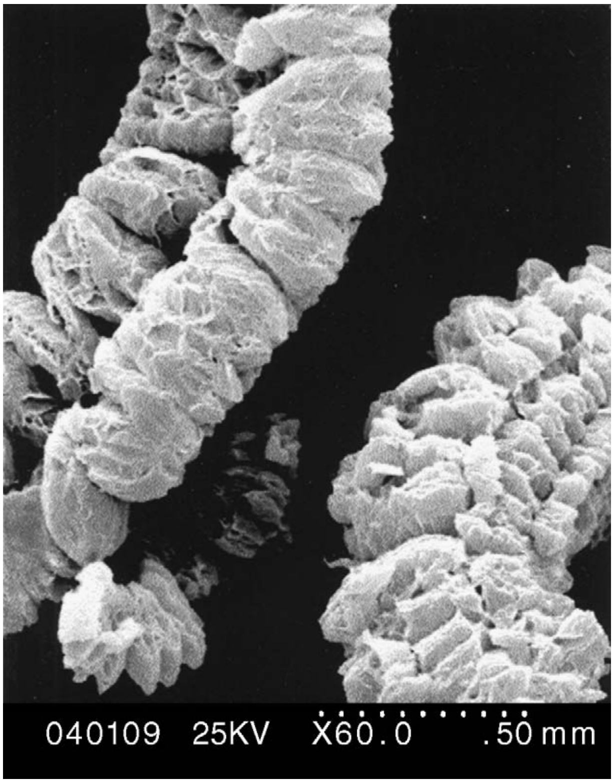

Fig. 1. SEM micrographs of EG.

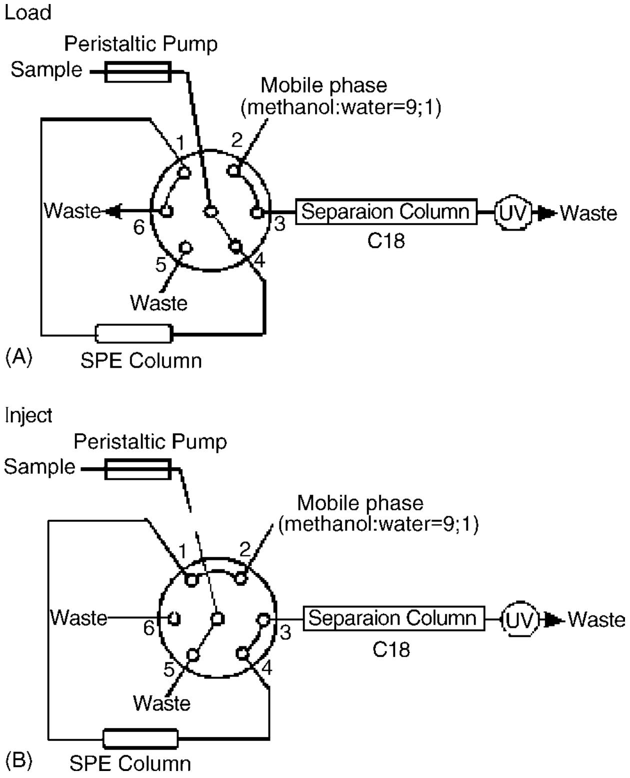

Fig. 2. Schematic diagram of the on-line solid-phase extraction preconcentration coupled with HPLC-DAD. HPLC injector valve position: (A) load; (B) inject.

2.4. Samples

River water, lake water and tap water were collected locally. The samples were filtered through 0.45-μm Supor filters, stored in precleaned glass bottles, which were thoroughly washed with detergents, water, methanol, and doubly deionized water, and dried before use, and analyzed immediately after sampling. As the pH of the water samples ranged from 7.6 to 8.5, all water samples were adjusted to pH 5.00–5.60 with a HAc–NaAc Buffer to avoid degradation of some of the DDTs under alkaline conditions and to insure the efficient solid-phase extraction of the analytes by the EG sorbent.

2.5. Procedures for the on-line SPE preconcentration and HPLC separation

A schematic diagram for the on-line SPE method coupled to HPLC for determination of trace levels of DDT in water is shown in Fig. 2. First, the sample solution was introduced onto the precolumn packed with the EG at a flow rate of 8 ml min^{-1} for 375 s while the HPLC injector valve was in the load position so that the DDTs were preconcentrated by the EG-packed precolumn and the unwanted water went to waste (W) (Fig. 2(A)). Second, the analytes adsorbed on the precolumn were eluted in the backflush mode by the HPLC mobile phase at a flow rate of 1.0 ml min^{-1} into the chromatographic separation column for 1.5 min by switching HPLC valve from “load” to “inject” position (Fig. 2(B)). As such, the sample band in the precolumn was compressed into a narrow band before entering the analytical column and the band broaden effect was reduced [28]. Third, the HPLC injector valve was turned to the “load” position for next sample preconcentration while the analytes were separated in the chromatographic separation column to improve sample throughput. In this way, a complete cycle of the on-line SPE preconcentration and HPLC separation of the DDTs lasted 8 min. Chromatograms were recorded and stored on the hard disk of the computer. The peak areas were calculated at their respective maximum absorbance wavelength (245 nm for *p,p′*-DDE, 231 nm for *p,p′*-DDD, 237 nm for *p,p′*-DDT, and 235 nm for *o,p′*-DDT) and used for data evaluation.

3. Results and discussion

3.1. Breakthrough volumes and dynamic capacity

Breakthrough volume is important in SPE because it represents the sample volume that can be preconcentrated without loss of analytes during the loading of sample. Breakthrough volumes were calculated at $C_e/C_i = 0.01$, where C_e is the analyte concentration in the effluent and C_i is the analytes concentration in the influent. The breakthrough volume for *p,p′*-DDD, *p,p′*-DDT *o,p′*-DDT and *p,p′*-DDE at 50 μg l^{-1} was 80, 70, 100 and 100 ml, respectively. The dynamic capacity describes the operational characteristics of a sorbent in the column operation mode. The total dynamic capacity of the EG for the four DDTs at a sample loading flow rate of 8 ml min^{-1} was 2.8 mg g^{-1}.

Table 1
Characteristic data of the developed on-line solid-phase extraction preconcentration for HPLC determination of trace levels of DDTs under the optimal conditions

	p,p′-DDD	*p,p*′-DDT	*o,p*′-DDT	*p,p*′-DDE
Enhancement factors[a]	687	747	759	690
Detection limits (S/N = 3) (ng l^{-1})	10	17	24	25
Peak area precision[b] (n = 10) (%, R.S.D.)	6.1	3.5	6.2	3.2
Linear concentration range of the calibration graph (μg l^{-1})	0.05–20	0.05–20	0.05–20	0.05–20
Retention efficiency (%)	71	74	78	72
Sample consumption (ml)	50			

[a] Compared with direct injection of 20 μl sample solution.
[b] Using a mixture of 1 μg l^{-1} of each DDTs.

3.2. Factors affecting the on-line SPE preconcentration of DDTs

The effect of sample pH on the adsorption of DDTs was studied in the pH range of 3.0–7.0, and the results showed that the maximum chromatographic peak areas of *p,p*′-DDE, *p,p*′-DDD, *p,p*′-DDT and *o,p*′-DDT were obtained in the pH range of 4.5–5.7, 3.0–6.0, 3.0–5.7 and 3.0–5.7, respectively. Out of these optimum pH ranges, the chromatographic peak areas of *p,p*′-DDE, *p,p*′-DDD, *p,p*′-DDT and *o,p*′-DDT decreased. These results show that the four DDTs can be effectively adsorbed by the EG-packed column in the pH range of 4.5–5.7.

The influence of sample loading flow rate on the sorption preconcentration of DDTs was investigated with 10 μg l^{-1} DDTs for 60-s preconcentration. It was found that the chromatographic peak areas of *p,p*′-DDE, *p,p*′-DDD, *p,p*′-DDT and *o,p*′-DDT increased linearly as the sample flow rate increased from 1.4 to 9.2 ml min^{-1}. The effect of sample loading time on the adsorption of DDTs was investigated with 10 μg l^{-1} DDTs at a sample flow rate of 8 ml min^{-1}. The chromatographic peak areas of *p,p*′-DDE, *p,p*′-DDD, *p,p*′-DDT and *o,p*′-DDT increased almost linearly as the sample loading time increased up to at least 420 s.

Based on the above results, we selected the following conditions for the on-line solid-phase extraction preconcentration of DDTs: the sample loading time = 375 s, sample loading flow rate = 8 ml min^{-1}, sample pH 5.0–5.6.

3.3. Desorption of the adsorbed DDTs from the EG-packed column

For simplicity, the optimum HPLC mobile phase (MeOH:H_2O = 90:10) was used for the desorption of the adsorbed DDTs from the EG-packed column. The time required for quantitative desorption of the adsorbed DDTs when the HPLC injector valve was in the “inject” position was evaluated in order to determine when the HPLC injector valve should turn to the “load” position for next on-line solid-phase extraction during the HPLC separation of the analytes this cycle. It was found that the chromatographic peak areas of the DDTs increased remarkably as the desorption time increased from 0.5 to 1.0 min, then leveled off in the range of 1.0–8.0 min. Accordingly, 1.5-min desorption was selected to ensure the complete stripping of the adsorbed DDTs from the EG-packed column. Once the adsorbed DDTs was quantitatively stripped from the EG-packed column, the HPLC injector valve turned to the “load” position for next preconcentration so that the current HPLC separation and the next preconcentration proceeded in parallel.

3.4. HPLC separation

The composition of the mobile phase was optimized to obtain baseline separation of the four DDTs as short as possible. Various ratios of MeOH:H_2O (i.e. MeOH:H_2O = 100:0; 95:5; 90:10; 85:15) were tested as the mobile phase for this purpose. When the pure methanol was used, the four DDTs cannot be baseline separated. With the decrease of the methanol content, the resolution became better while the separation time became longer. The four DDTs could be baseline separated within 8 min with the mobile phase of MeOH:H_2O = 90:10. However, the use of MeOH:H_2O = 85:15 as mobile phase required 16 min for a baseline separation of the four DDTs. On the basis of the above results, we selected MeOH:H_2O = 90:10 as the mobile phase for HPLC separation of the four DDTs.

Table 2
Comparison of the developed method with a few published methods for determination of DDTs in terms of detection limits and the time needed for one determination

Technique used	Sample preteatment	Time required for one determination	Detection limits (ng l^{-1})			
			p,p′-DDD	*p,p*′-DDT	*o,p*′-DDT	*p,p*′-DDE
EG-SPE/HPLC-PAD (this work)	On-line SPE	8 min	10	17	24	25
HPLC-UV [29]	–	–	–	20000	–	20000
Activated carbon filter filtration (ACFF)-GC-MS [7]	Off-line collection of analytes in 3 l water with activated carbon filter	>48 h	0.02	0.07	–	0.02
LLE-GC-ECD [3]	Off-line solvent extraction of analytes in 1 l water followed by column chromatographic clean-up	–	13.4	18.9	6	–

Table 3
Analytical results for the DDTs in water samples

Sample	Spike of each analyte ($\mu g\,l^{-1}$)	Concentration found (mean $\pm\,\sigma$, $n=3$) ($\mu g\,l^{-1}$)			
		p,p′-DDD	*p,p′*-DDT	*o,p′*-DDT	*p,p′*-DDE
Lake water 1	0	0.17 ± 0.07	nd[a]	0.10 ± 0.01	0.18 ± 0.03
	1	1.22 ± 0.08	0.98 ± 0.03	1.03 ± 0.02	1.13 ± 0.01
Lake water 2	0	nd	nd	nd	nd
	1	0.97 ± 0.06	0.93 ± 0.03	0.91 ± 0.04	0.92 ± 0.05
River water 1	0	nd	nd	nd	nd
	1	0.97 ± 0.06	0.93 ± 0.06	0.97 ± 0.08	0.99 ± 0.08
River water 2	0	nd	nd	nd	nd
	1	0.94 ± 0.06	1.08 ± 0.09	0.95 ± 0.06	1.03 ± 0.06
Tap water	0	nd	nd	nd	nd
	1	0.95 ± 0.06	0.94 ± 0.06	0.89 ± 0.03	1.09 ± 0.09

[a] Not detected.

3.5. *Analytical figures of merit*

The analytical characteristic data of the developed on-line solid-phase extraction preconcentration method coupled with HPLC for the determination of DDTs were summarized in Table 1. The precision (R.S.D.) for 10 replicate injections of a mixture of 1 $\mu g\,l^{-1}$ of each analyte was 3.2–6.2% for the peak area measurement. With the consumption of 50 ml sample solution, the enhancement factor defined as the ratio of the sensitivity obtained by on-line SPE-HPLC to that obtained by conventional HPLC with direct injection of 20 μl solution ranged from 687 to 759. The linear concentration ranges were from 0.05 to 20 $\mu g\,l^{-1}$ for *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDT, and *p,p′*-DDE. The detection limits (S/N = 3) of *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDT and *p,p′*-DDE were 10, 17, 24 and 25 $ng\,l^{-1}$, respectively. The retention efficiency of the EG-packed SPE column for the four DDTs was 71–78%.

A comparison of the developed method with a few published techniques for the determination of DDTs was made in terms of detection limits and the time required for one determination. As shown in Table 2, the detection limits achieved by the developed method were at the same order with those obtained by GC-ECD [3], and three order lower than those achieved by a conventional HPLC-UV method [29]. Although the developed method gave three order higher detection limits than the activated carbon filter filtration (ACFF)-GC-MS [7], the time required for one determination by the later method was at least 48 h, 360 times of that by the present method. Moreover, one disadvantage of the ACFF-GC-MS technique is that this technique is difficult for successful on-line preconcentration.

To evaluate the usefulness of the developed method, five local environmental water samples were collected, and analyzed for trace levels of DDT by the developed method. A standard addition calibration protocol was employed for quantification. The recoveries were estimated by comparing the increased peak area of the chromatographic peak of each analyte due to spiking to that of the chromatographic peak of each analyte in standard solution with the same concentration as spiking. Typical chromatograms of a real water sample and spiked water samples are shown in Fig. 3. The analytical results obtained by the developed method were given in Table 3. The recoveries of 0.1 and 1 $\mu g\,l^{-1}$ of *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDT and *p,p′*-DDE spiked in these water samples were 84–110 and 89–109%, respectively. The concentrations of the four DDTs in these water samples were found to be up to 0.18 $\mu g\,l^{-1}$.

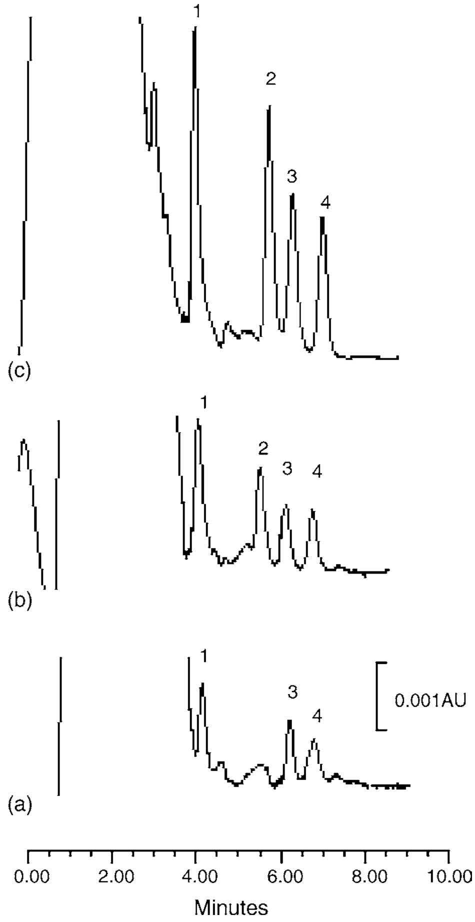

Fig. 3. Chromatograms of (a) a lake water sample; (b) a lake water sample spiked with 0.1 $\mu g\,l^{-1}$ *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDT and *p,p′*-DDE; (c) a lake water sample spiked with 1 $\mu g\,l^{-1}$ of *p,p′*-DDD, *p,p′*-DDT, *o,p′*-DDT and *p,p′*-DDE each.

4. Conclusions

The results in this work have demonstrated the feasibility of the expanded graphite as sorbent for on-line SPE preconcentration method coupled with HPLC for the determination of trace levels of DDT in environmental water samples. The developed method is simple, sensitive and cost-effective. The expanded graphite possesses great potential for its application in the field of POPs analytical chemistry due to its good adsorption properties and low cost.

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