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Novel on-site sample preparation approach with a portable agitator using functional polymer-coated multi-fibers for the microextraction of organophosphorus pesticides in seawater

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ABSTRACT

A novel on-site sample preparation approach for the organophosphorus pesticides (OPPs) using functional polymer-coated fibers with a portable agitation device has been developed and demonstrated. In this approach, a handheld battery-operated electric toothbrush was used to provide agitation of the sample solution at the sampling site to facilitate extraction. A functional conjugated polymer (2-(9,9-*bis*(6-bromo-2-ethylhexyl)9-*H*-fluoren-2-yl)benzene-1,4-diamine) was coated on commercial Technora fibers (each strand consisted of 1000 filaments, each of diameter ca. 9.23 μm) which were then used for extraction. After extraction, the fibers were brought back to the laboratory in an icebox. The analytes were subsequently desorbed by organic solvent and the extract was analysed by gas chromatography–mass spectrometry. Six OPPs, triethylphosphorothiolate, thionazin, sulfotep, phorate, disulfoton and parathion were used as model compounds. Experimental parameters such as extraction time, desorption time, types of polymer fibers and fiber coatings as well the nature of desorption solvent were optimized in the laboratory prior to its on-site application of the procedure. Using optimum extraction conditions calibration curves were linear with correlation coefficient of 0.9748–0.9998 over the concentration range of 0.1–10 μg l^{-1}. The method detection limits (at a signal-to-noise ratio of 3) were in the range of 0.3–30.3 ng l^{-1}, which were lower than what could be achieved with solid-phase extraction performed at the laboratory. The proposed method was evaluated for the on-site extraction of OPPs in seawater samples.

1. Introduction

Organophosphorus (OP) compounds are among the most toxic substances commonly used as pesticides, insecticides and chemical warfare agents [1]. OPs cause irreversible phosphorylation of sterases in the central nervous system of insects and mammals and act as cholinesterase inhibitors [2]. Hence, there is an increasing demand for developing methods for the determination of such contaminants in the environment. Early detection of OP neurotoxins is important for protecting water resources, in the defence against terrorist activity, and for monitoring detoxification processes. Widespread use of organophosphorus pesticides (OPPs) for crop protection has also raised great concern due to their significant half-lives; they can persist in surface and ground water [3–6].

The European Union sets the maximum level of concentrations of 0.5 μg l^{-1} for the sum of all OPPs and a concentration of 0.1 μg l^{-1} for a single compound [7] in environmental water samples. Sensitive analytical approaches are required to detect OPPs at trace levels, and limits of detection of below 0.1 μg l^{-1} need to be achieved. The determination of trace level OPPs in seawater using conventional approaches requires multistep sample preparation. Additionally, in conventional methodologies, samples have to be transported to the laboratory for processing and analysis. Therefore, the availability of simple on-site extraction techniques would be desirable so that at least part of the analytical process could be conducted in the field.

The most frequently used on-site or field aqueous sampling techniques require large volumes of samples and specialized equipment for analysis [8]. The large volume sampling strategies employed in field studies are both labor-intensive and not useful for simultaneous sampling [9–15]. Recently, semi-permeable membrane devices and solid-phase microextraction (SPME) procedures have been shown to overcome many such drawbacks of large volume sampling [8,16–18]. In SPME, a single polymer-coated fiber is used for the extraction, and for on-site applications a time-weighted average sampling method is commonly used which requires longer extraction time [19].

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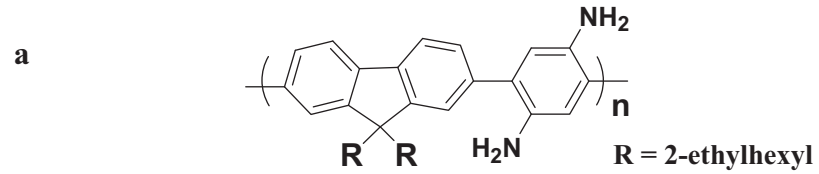

(2-(9,9-bis(6-bromo-2-ethylhexyl)9-*H*-fluoren-2-yl)benzene-1,4-diamine) (ACP)

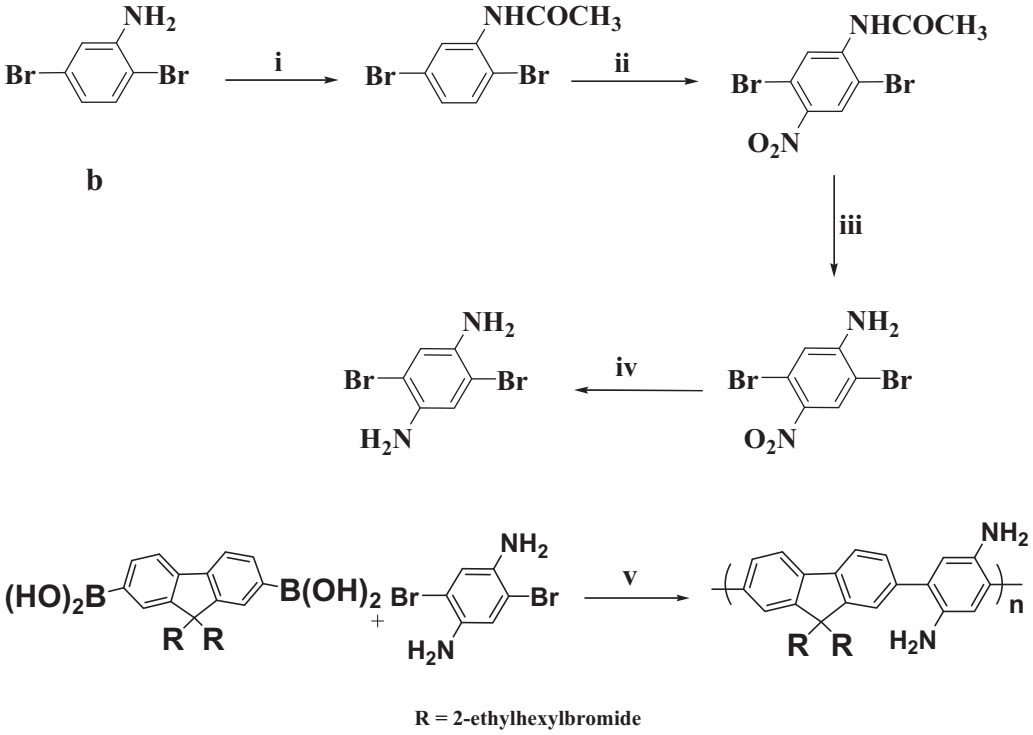

Fig. 1. Structures of polymer and reagents, and reaction scheme. (a) Structure of NNN (referred to as ACP) and (b) synthetic scheme for ACP (A1): (i) acetic anhydride, water, reflux, 4 h; (ii) conc. H_2SO_4, conc. HNO_3, 10 °C, 2 h; (iii) 1 M HCl, reflux 15 h; (iv) 6 M HCl, ethanol, Sn metal, 6 h and (v) K_2CO_3, THF, 3.0 mol% $Pd(PPh_3)_4$, CTAB, reflux, 4 days.

Recently [20], we developed a simple extraction technique using commercial Kevlar fibers (each strand of which consists of 1000 filaments) with high-performance liquid chromatography (HPLC)-fluorescence detection for the determination of trace PAHs in water samples. This was an alternative approach to the extraction device introduced by Jinno et al, in which a bundle of commercially available fibers such as Nomex, Kevlar, Technora and Zylon were packed into a needle and used for extracting a wide range of organic compounds [21].

We had also previously reported a simple and cost-effective technique of polymer-coated hollow fiber microextraction (PC-HFME) as an on-site sample preparation approach for seawater samples [22]. A disadvantage of on-site PC-HFME is the manual shaking (as an alternative to mechanical stirring, which was not available on-site) of the sample solution to facilitate extraction. In order to eliminate this labor-intensive step in on-site extraction in the present work, we investigated the use of a battery-operated electric toothbrush as a portable agitator during the extraction. As in the previous work [20], commercial fibers were used directly as extraction devices. Additionally, in the present case, in order to enhance extraction efficiency, a functional polymer (2-(9,9-*bis*(6-bromo-2-ethylhexyl)9-*H*-fluoren-2-yl)benzene-1,4-diamine), synthesized in our laboratory, was coated on the fibers, as in PC-HFME. After on-site extraction with the aid of the portable agitator, the coated fibers were placed in autosampler vials, which were sealed with paraffin film and stored in an ice-box, and subsequently transported to the laboratory for analyte desorption and gas chromatography–mass spectrometric (GC–MS) analysis The proposed method was used to determine OPPs in Singapore seawater samples.

2. Experimental

2.1. Standards and reagents

Spectrophotometric grade n-hexane was purchased from Acros Organics (Geel, Belgium). Ultrapure water was produced on a Nanopure water purification system (Barnstead, Dubuque, IA, USA). HPLC-grade acetone, methanol and tetrahydrofuran were purchased from Tedia (Fairfield, IN, USA). A stock standard solution of a mixture of OPPs in methylene chloride was obtained from Protocol (Metuchen, NJ, USA). Polymer fibers (Nomex, Kevlar, Technora and Zylon) were obtained as a gift from Professor Kiyokatsu Jinno (Toyohashi University of Technology, Japan). For this study a single fiber strand was used for extraction. The (conventional) ultrasonicator used for analyte desorption was brought from Soni-

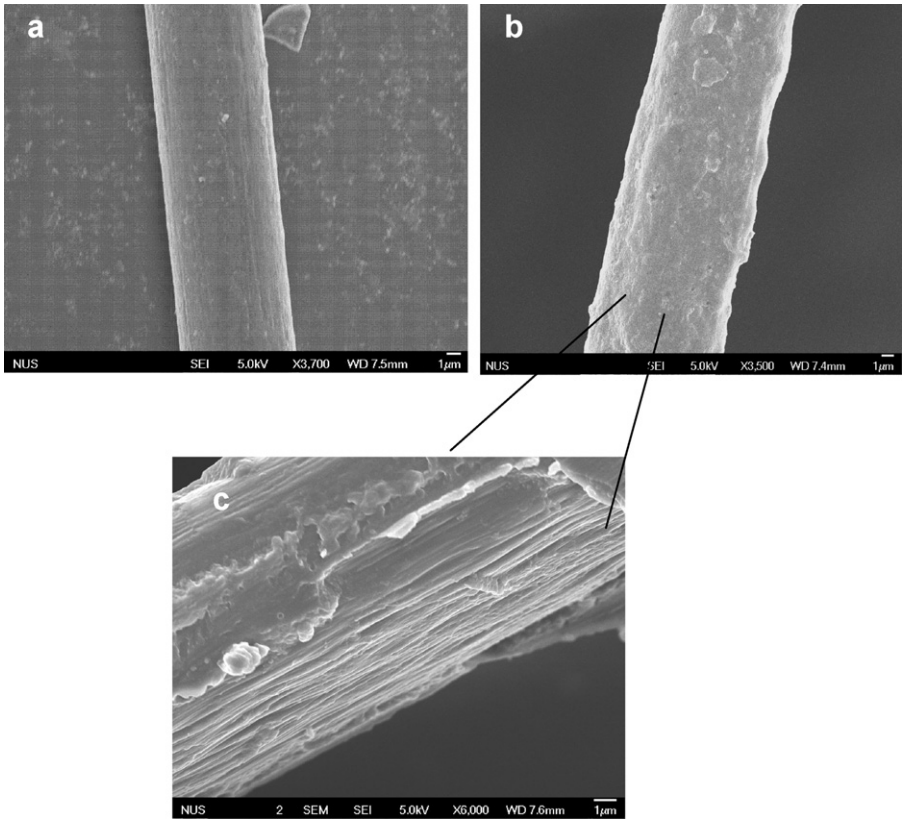

Fig. 2. Scanning electron micrographs of (a) a single filament (3700× magnification); (b) a filament with ACP coating (3500× magnification); and (c) magnified view (6000×) of a coated filament.

clean (Thebarton, Australia). The widely available battery-operated electric toothbrush, Oral-B CrossAction Power with a replaceable rotating power head (Procter and Gamble, Cincinnati, OH, USA), was purchased from a local store in Singapore and used as a portable agitator without any modification. The polydimethylsiloxane (PDMS) polymer comprising Slygard 184 silicone elastomer and curing agent was purchased from Dow Corning Corporation (Midland, MI, USA). A PDMS–divinyl benzene (DVB)-coated (65-μm thickness) fiber purchased from Supelco (Bellefonte, PA, USA) was used for SPME. A standard stock solution containing 10 μg ml^{-1} of each analyte was prepared in acetone. A working standard solution (0.5 μg ml^{-1} of each analyte) was used for low concentration spiking; for high concentration spiking, the stock solution was used. The structures of the organophosphorus pesticides have now been included in the Supplementary material.

2.2. Instrumentation

The OPPs were identified and quantified using a Shimadzu Model QP 2010 (Kyoto, Japan) gas chromatography–mass spectrometry (GC–MS) system with a splitless injection port equipped with a Shimadzu AOC-20i auto sampler. A 30 m × 0.25 mm i.d., film thickness 0.25 μm (J&W Scientific, Folsom, CA, USA) DB-5 fused silica capillary column was used for separations. Helium (purity

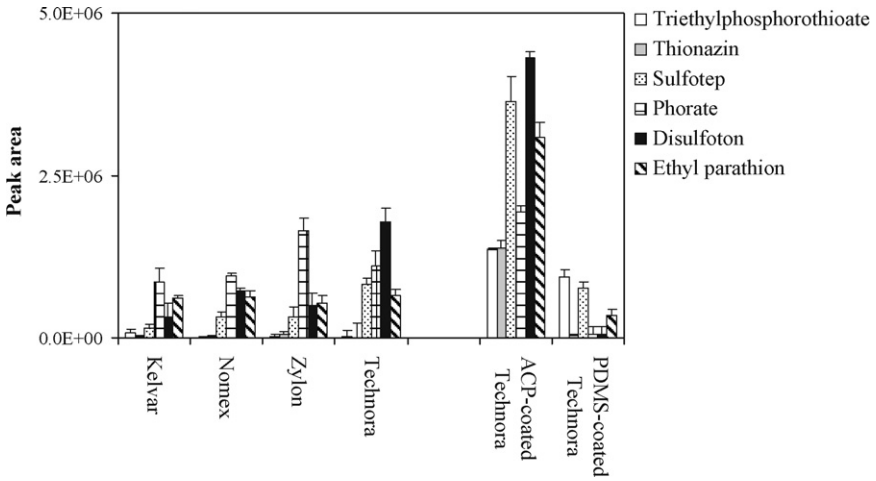

Fig. 3. Suitability of various fibers as sorbents for OPPs in spiked water samples. Samples were spiked at a level of 5 μg l^{-1} of each analyte. *Conditions*: Extraction time of 30 min at 105 rad s^{-1} conventional magnetic stirring, with 20-min desorption by ultrasonication using 100 μl of methanol.

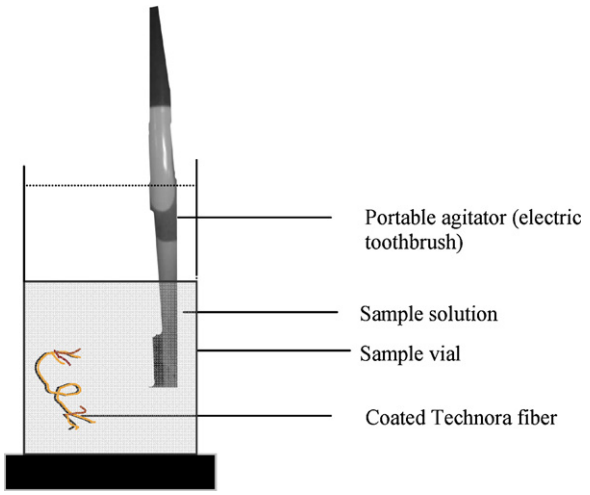

Fig. 4. Schematic of on-site extraction with portable agitator.

99.9999%) was used as carrier gas with a flow rate of 1.5 ml min^{-1}. The injection temperature was set at 250 °C, the interface temperature at 280 °C and the detection temperature at 280 °C. The GC temperature program was as follows: initial temperature 50 °C (held for 2 min), then an increase by 10 °C min^{-1} to 300 °C (held for 3 min). The OPP standards and the samples were analysed in selective ion monitoring mode at a detector voltage of 1.5 kV. The target ions used were molecular ions of the OPPs.

2.3. Synthesis of amine containing conjugated polymer

The polymer (2-(9,9-*bis*(6-bromo-2-ethylhexyl)9-*H*-fluoren-2-yl)benzene-1,4-diamine), hereafter referred to as amine-containing polymer (ACP) (Fig. 1a), was synthesized according to the synthetic scheme outlined in Fig. 1b. Monomer 2,5-dibromo-4-aminoaniline was synthesized as reported in the literature [23]. 2,5-Dibromoaniline was acetylated to obtain 2,5-dibromoacetanilide, which on nitration gave a mixture of 2,5-dibromo-4-nitroacetanilide and 3,6-dibromo-2-nitroacetanilide. The mixture was refluxed with hydrochloric acid to give 2,5-dibromo-4-nitroaniline and 3,6-dibromo-2-nitroaniline. This reaction mixture was washed with hexane to separate hexane-soluble 3,6-dibromo-2-nitroaniline and hexane-insoluble 2,5-dibromo-4-nitroaniline. 2,5-Dibromo-4-nitroaniline was then reduced with tin and hydrochloric acid to obtain 2,5-dibromo-4-aminoaniline in good yield (70%).

The polymerization reaction was carried out using Suzuki coupling with 5 mol% tetrakis (triphenylphosphine) palladium

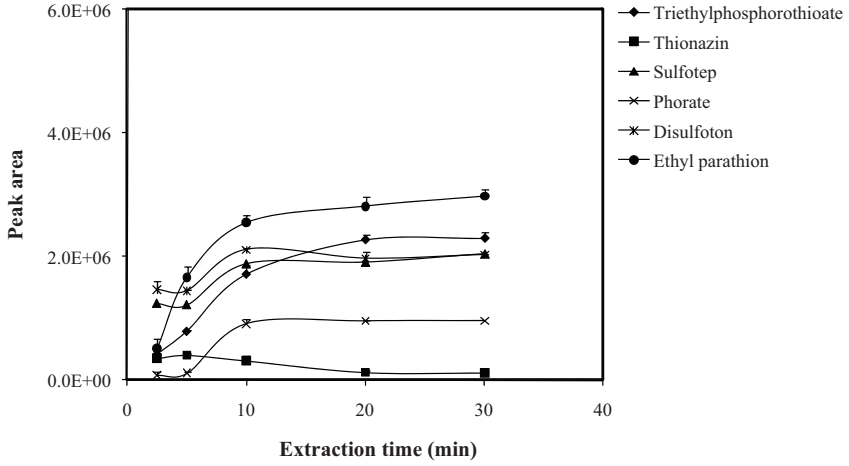

Fig. 5. Extraction time profile of OPPs using ACP-coated Technora fiber at 105 rad s^{-1}; extracts were desorbed for 20 min by ultrasonication using 100 μl of methanol.

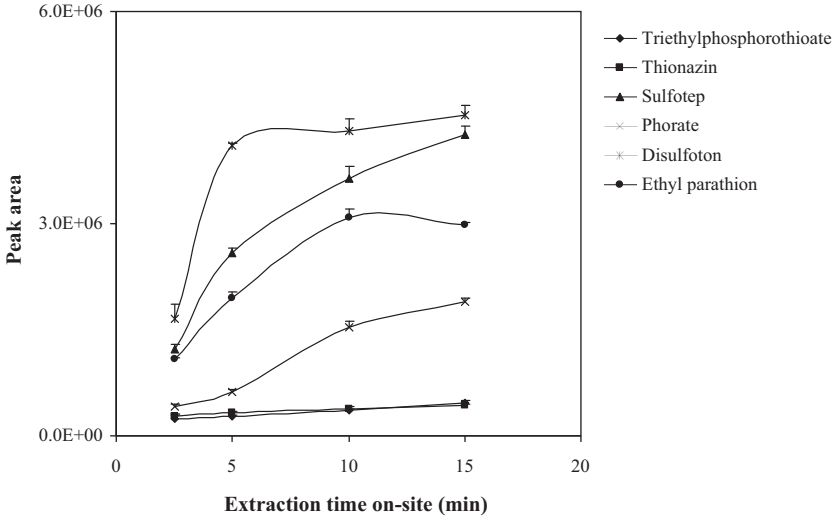

Fig. 6. Extraction time profile of OPPs using ACP-coated Technora fiber using portable agitator. Extracts were desorbed for 20 min by ultrasonication using 100 μl of methanol.

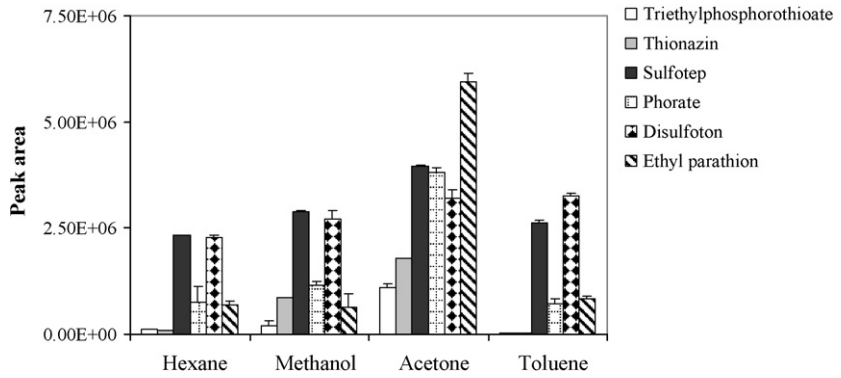

Fig. 7. Selection of desorption solvent. *Extraction conditions*: ACP-coated Technora fiber as a sorbent; extraction was performed for 10 min at 105 rad s^{-1} and then analytes were desorbed for 20 min by ultrasonication using 100 μl of solvent.

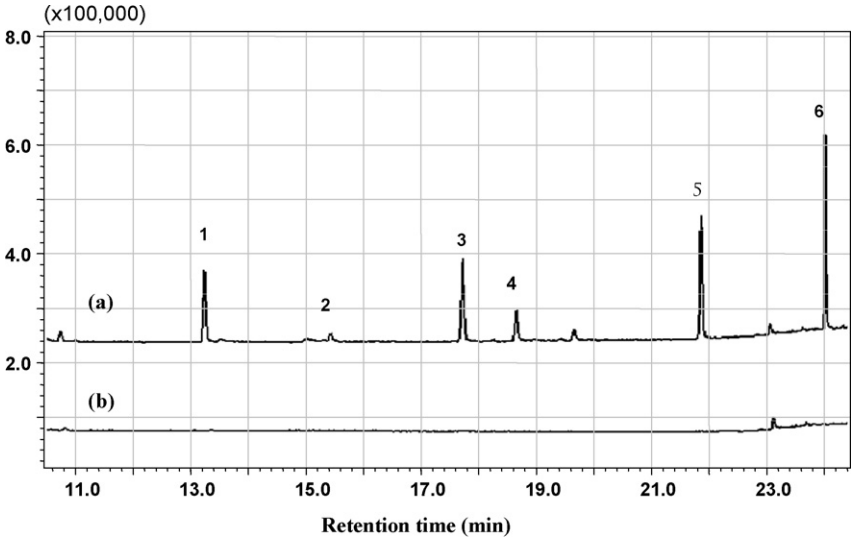

Fig. 8. Chromatograms of (a) spiked (1 μg l^{-1} of each analyte) water sample extract, and (b) blank seawater extract (sample from Labrador Park site) after onsite extraction. *Peak identifications*: (1) triethylphosphorothioate, (2) thionazin, (3) sulfotep, (4) phorate, (5) disulfoton and (6) ethyl parathion. *Conditions*: Extraction time of 10 min, with 10-min desorption by ultrasonication using 100 μl of acetone.

Table 1
Normalized recoveries of OPPs extracted without sample stirring and magnetic stirring at 105 rad s^{-1}.

	Normalized recoveries for extraction without stirring (n = 3) Extraction time (h)					Normalized recovery with magnetic stirring at 105 rad s^{-1} for 20 min
	0.5	1	6	12	24	
Triethylphosphorothioate	12	23	50	66	64	60
Thionazin	18	29	37	43	43	85
Sulfotep	41	40	52	46	54	43
Phorate	13	15	50	60	46	118
Disulfoton	42	42	61	51	58	51
Ethyl parathion	12	37	57	41	33	137

Normalized relative recoveries were calculated by comparing the recoveries of portable agitation mode (taken as 100%) over non-stirring mode and magnetic stirring respectively.

Table 2
Linearity range of calibration plots, limits of detection (LODs), precision (%RSDs) of onsite ACP-coated Technora fiber extraction with portable agitation and laboratory-based SPME.

	ACP-coated Technora fiber extraction				SPME			
	Linearity (μg l^{-1})	Correlation coefficient	%RSD	LOD (ng l^{-1})	Linearity (μg l^{-1})	Correlation coefficient	%RSD	LOD (ng l^{-1})
Triethylphosphorothioate	0.1–10	0.9778	7	4.1	0.5–50	0.966	4	16.6
Thionazin	0.1–10	0.9748	4	30.3	0.5–50	0.982	5	47.7
Sulfotep	0.1–10	0.9998	7	4.6	0.5–50	0.998	10	3.1
Phorate	0.1–10	0.9902	6	1.8	0.5–50	0.997	2	4.7
Disulfoton	0.1–10	0.9796	6	0.3	0.5–50	0.998	3	5.9
Ethyl parathion	0.1–10	0.9987	7	0.7	0.5–50	0.997	10	11.2

Table 3
Concentrations OPPs in Singapore seawater samples by onsite ACP-coated Technora fibers extraction with portable agitation.

	Concentrations of OPPs in Singapore seawater ($\mu g\,l^{-1}$) ($n=3$)					
	Changi Beach	East Coast Park	Labrador Park	Marina South	West Coast Park	Pasir Ris Park
Triethylphosphorothioate	0.12	0.04	nd[a]	0.11	0.06	nd
Thionazin	0.60	0.04	nd	0.53	0.04	nd
Sulfotep	0.25	0.04	nd	0.25	0.08	nd
Phorate	0.08	0.04	nd	0.09	0.04	nd
Disulfoton	0.01	nd	nd	0.01	nd	nd
Ethyl parathion	0.06	0.04	nd	0.07	0.04	nd

[a] nd, non-detected.

($Pd(PPh_3)_4$) as a catalyst (purchased from Sigma–Aldrich (St. Louis, MO, USA)) in a mixture (3:2, v/v) of aqueous (2 M) potassium carbonate and tetrahydrofuran under a nitrogen atmosphere at 75–80 °C for 72 h. After completion of the reaction, the polymer was precipitated from methanol. The resulting solid was washed with acetone and further purified by reprecipitation of chloroform solution of polymer with methanol.

2.4. Water sample collection

On-site extractions from sea water were carried at six coastal recreational areas in Singapore namely Changi Beach, East Coast Park, Labrador Park, Marina South, Pasir Ris Park and West Coast Park. At the same time sea water samples at the same locations were collected in 1 l glass bottles for laboratory extraction without any pre-treatment or filtration.

2.5. Extraction with ACP-coated Technora fiber

2.5.1. Laboratory extraction of OPPs

An ACP-coated Technora fiber was placed in a spiked sample solution (10 ml). The solution was continuously agitated at ca. 105 rad s^{-1} (1000 rpm; 1 rpm = 0.1047 rad s^{-1}) using a magnetic stirrer for 10 min. After extraction, the fibers were removed and dabbed dry with lint-free tissue. They were then placed inside a GC–MS autosampler vial (of 150-μl capacity). Acetone (100 μl) was added to the vial for solvent desorption via conventional ultrasonication for 20 min. After desorption, the fibers were removed from the vial, and the extract was directly analysed by GC–MS.

2.5.2. On-site extraction of OPPs

An ACP-coated Technora fiber was placed in 10 ml of seawater (pH and salinity were not adjusted). The portable agitator was applied to the sample for 5 min (see Fig. 4). After extraction, the fibers were placed in the autosampler vial. The latter was sealed, stored in an icebox and transported to the laboratory, where the analytes were solvent-desorbed ultrasonically as described above. At each site, the same procedure was carried out in triplicate. At the end of each extraction, the used fibers and portable agitator were conditioned with acetone for 10 min to eliminated matrix and carryover effects. Each fiber could be used for up to 60 extractions.

2.6. Comparison with SPME

Previously optimized SPME conditions [24] were utilized for comparative purposes. Briefly, the experimental conditions were: 10-mL seawater (adjusted to 10% (w/v) salt concentration with sodium chloride) was extracted by direct immersion of the PDMS–DVB fiber with stirring (at 105 rad s^{-1}). After extraction was performed for 30 min, the SPME fiber was desorbed in the injection-port of the GC–MS for 3 min at 250 °C. Sample blank experiments were carried out periodically to test carryover effects

3. Results and discussion

3.1. Preliminary extraction and polymer coatings

In initial studies, Nomex, Kevlar, Technora and Zylon fibers were cut and tied at the end (using the same fiber type) to prevent fraying, to obtain effective lengths of ~3 cm; these were used to extract the OPPs (Fig. 2). Among the fibers used Technora showed the highest extraction efficiency. In an attempt to further improve the performance of the Technora fiber, it was coated with PDMS. The fiber was dipped into the Slygard 184 silicone elastomer and curing agent (30:1 ratio) for 5 min after which it was removed and dried in the oven for 24 h at 100 °C. It was rinsed with methanol and stored until ready for use. Unfortunately, the PDMS-coated Technora fiber showed poorer extraction when compared to Technora itself although PDMS has been successfully used as sorbent for OPP extraction [24]. Nomex, Kevlar, Technora and Zylon were then separately coated with ACP (5 mg ml^{-1} solution for 24 h). The ACP-coated fibers were removed and air-dried for 1 h at 60 °C in the oven, then rinsed with acetone prior to use. ACP consists of phenylene with free amino groups on opposite sides (*para*-position) of the benzene ring. These amino groups (being a hydrogen bond donor) can conceivably be expected to have stronger interaction via hydrogen bonding with OPPs (which are hydrogen bond acceptors). The micrograph of the polymer-coated fibers confirms the uniform layer of polymer coating over the surface of the fiber

Table 4
Recoveries, %RSD of onsite microextraction and SPME ($n=3$).

	[a]Relative recoveries ($n=3$) from samples spiked at 1 $\mu g\,l^{-1}$			
	Onsite microextraction		SPME	
	Recovery (%)	%RSD	Recovery (%)	%RSD
Triethylphosphorothioate	103	6	89	4
Thionazin	93	2	74	10
Sulfotep	109	13	74	16
Phorate	93	4	83	13
Disulfoton	108	4	80	17
Ethyl parathion	90	4	63	9

[a] Relative recoveries = ratios of peak areas of analytes from extracts of spiked seawater and spiked ultrapure water, for on-site and SPME techniques respectively.

(Fig. 2). The ACP-coated Technora fiber showed higher extraction efficiency than the other coated fibers (Fig. 3). A series of preliminary blank extractions was also performed: (i) extraction of OPPs with toothbrush agitation (without ACP-coated Technora fiber) to determine if the toothbrush itself (holder or bristles) could extract any analytes; (ii) control extraction (without spiking and without the ACP-coated Technora fiber), and (ii) rinsing under ultrasonication of the toothbrush itself with acetone for 20 min to identify leached materials, if any, that might interfere with the OPP analysis. The results demonstrated that none of the OPPs were extracted by the toothbrush holder or bristles, and no materials at any significant or interfering amounts were observed to have leached out when the toothbrush was rinsed with acetone. These results also showed that there were no carry-over problems. Small amounts of plasticizers were leached out at the first and second rinsing, but none after the third rinsing, suggesting that the toothbrush should be subjected to this treatment before being used for experiments. In any case, with selective ion monitoring mode, none of the leached materials interfered with OPP extraction and determination (see Supplementary material for the relevant chromatograms which show no interferences) (Fig. 4).

Polymer fiber microextraction is essentially similar to SPME or stir-bar sportive extraction and is therefore an equilibrium-based process. The equilibrium time profile for the laboratory-based extraction was studied between the range of 5 and 25 min with magnetic stirring speed of 105 rad s^{-1}. The analytes, disulfoton, sulfotep and phorate, reached equilibrium after about an extraction time of 10 min (Fig. 5). The extraction of triethylphosphorothioate and ethylparathion continued to increase after 10 min. For thionazin, however, extraction showed a gradual decrease after 5 min. It is not clear why this is so at this time. Based on these observations; 10 min extraction time appeared to be a reasonable compromise. With experiments performed at the laboratory with the battery-operated portable agitator, the extraction time profile was evaluated between 2.5 and 30 min. The extraction performance increased with increasing time, with no attainment of equilibrium over this period (Fig. 6). Based on the data shown in Fig. 6, 5 min was considered as a reasonable extraction time.

Extraction was also carried out without any stirring from 0.5 to 24 h to compare with the case in which magnetic stirring (at 105 rad s^{-1}) for 20 min was applied. The samples were spiked at 1 $\mu g\,l^{-1}$ of each analyte and the experiments were conducted at the laboratory. Table 1 shows the normalized extraction recoveries with respect to portable agitation mode. As expected, the procedure without sample agitation gave poorer analyte extraction compared to that in which the portable agitator (the potential on-site approach) was used. Magnetic stirring allowed extraction equilibrium to be reached (and sooner as well), but with the portable agitation mode equilibrium would take far longer to be achieved, and thus non-equilibrium extraction was adopted. This, in all likelihood, accounted for the differences in extraction profiles of the various OPPs between the two agitation modes. Except for triethylphosphorothioate, sulfotep and disulfoton, the recoveries of other analytes and comparable extraction performance were obtained for magnetic stirring (conventional laboratory extraction) and the on-site approach (under non-equilibrium conditions). The results support the idea that this on-site extraction approach was a viable approach where an independent power supply and a magnetic stirrer are unavailable.

The most appropriate solvent for desorption should be able to dissolve the analytes well, but should have no effect on the ACP. All the fibers considered as well as the ACP were insoluble in hexane, acetone and methanol, which were therefore evaluated as the most suitable desorption solvent. Fig. 7 shows that acetone gave better responses for all the OPPs. Using acetone as the desorption solvent, various desorption times of between 5 and 20 min were investigated to select the most suitable time and a period of 10 min (with ultrasonication) was suitable. However, for some of the analytes, peak areas decreased at >10 min desorption (results not shown). It is conceivable that over a prolonged period, these analytes could readsorb on the coating. Another possible reason is analyte degradation. It is believed that further studies would be needed in order to investigate this issue further. Nevertheless, in respect of the possibility of readsorption, carryover was eliminated by ultrasonically cleaning the fiber in acetone for 10 min before it was used for the next extraction.

The effect of sample pH on the extraction efficiency was studied (at the laboratory). Acidic or basic pH was achieved by adding 6 M hydrochloric acid or 2 M sodium hydroxide respectively. The sample pH range of 2 and 12 was considered, and found to have no influence on the extraction efficiency up to pH 10, whereas, at highly basic conditions (pH >10), extraction efficiencies were low. This could be due to hydrolysis of OPPs at alkaline conditions [25]. The effect of ionic strength (addition of sodium chloride) on extraction efficiency from 3% to 30% (w/v) was investigated; no effect was observed. Hence, seawater sample pH (7.8–8.3) and salt concentrations were not adjusted before extraction.

3.2. Method evaluation

To evaluate the performance of the coated Technora fibers, linearity at five concentration levels of between 0.1 and 10 $\mu g\,l^{-1}$ in water was plotted using the on-site conditions obtained previously. For each level, triplicate analyses were performed. Good linearity was achieved with a correlation coefficient (r) of between 0.9748 and 0.9998 with relative standard deviation (RSD) of between 4% and 7%. The limits of detection (LODs) at (a signal-to-noise ratio of 3) in the range of 0.3–30.3 ng l^{-1} was obtained. A comparison of LODs obtained by this method with SPME is shown in Table 2; the present method gave very favourable performance. These results demonstrate the suitability of the technique for routine trace level determination of OPPs. Fig. 8 shows the chromatograms of OPPs-spiked water, and of a non-spiked genuine seawater sample, after extraction under the same conditions, indicating the good performance afforded by the present procedure.

3.3. Water sample analysis

To evaluate the practical applicability of the proposed microextraction approach, seawater samples were extracted on-site with agitation by the portable device. The concentrations of OPPs detected in the samples are shown in Table 3. To determine the extraction efficiency of the microextraction procedure and SPME, genuine seawater samples from Labrador Park (in which no OPPs were detected) were spiked at 1 $\mu g\,l^{-1}$ concentrations and relative recoveries (ratios of peak areas of analytes from extracts of spiked seawater, and spiked ultrapure water for on-site and SPME technique respectively) were calculated. The experiments were conducted in triplicate. The relative recoveries were calculated using standard addition (Table 4). The recoveries were between 93% and 109% for fiber extraction, and between 63% and 89% for SPME. The corresponding relative standard deviations (%RSDs) for fiber microextraction was <13% (n = 3) and for SPME, <16%. This clearly indicates that the proposed method compared favourably with the previously optimized SPME method [26]. However, the LODs of the fiber microextraction method were superior to the latter technique, indicating that on-site fiber microextraction of OPPs with a portable agitator is a feasible approach for environmental analysis.

4. Conclusion

Functional polymer-coated Technora fibers with a battery-operated electric toothbrush providing effective portable agitation during extraction were demonstrated to be a simple and sensitive method for on-site extraction of organophosphorus pesticides from seawater. The method required only small amounts of sample and solvent. After extraction, the polymer-coated fibers were conveniently transported back to the laboratory in an icebox for further processing. This on-site extraction approach was advantageous because only the fibers were brought back to the laboratory, the transportation of water samples being avoided, and no other sampling accessories or power supply were needed. The fibers could be used for 60 separate extractions and provided good recoveries, and were suitable for routine environmental monitoring.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.12.033.

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