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Technical Notes

Development and Application of Porous Membrane-Protected Carbon Nanotube Micro-Solid-Phase Extraction Combined with Gas Chromatography/Mass Spectrometry

Chanbasha Basheer,† Anass Ali Alnedhary,‡ B. S. Madhava Rao,‡ Suresh Valliyaveettil,*,† and Hian Kee Lee*,†

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, and Department of Chemistry, Pune University, Pune 411007, India

A novel, multiwalled carbon nanotube (MWCNT)-supported micro-solid-phase extraction (μ-SPE) procedure has been developed. A 6-mg sample of MWCNTs was packed inside a (2 cm × 1.5 cm) sheet of porous polypropylene membrane whose edges were heat-sealed to secure the contents. The μ-SPE device, which was wetted with dichloromethane, was then placed in a stirred sewage sludge sample solution to extract organophosporous pesticides, used here as model compounds. Tumbling of the extraction device within the sample solution facilitated extraction, and the porous membrane acted as a filter to exclude the extraction of extraneous materials. After extraction, analytes were desorbed in hexane and analyzed using gas chromatography/mass spectrometry. Since the porous membrane afforded protection of the MWCNTs, no further cleanup of the extract was required. The π−π electrostatic interaction with the analytes and the large surface area of MWCNTs facilitated the adsorption of analytes, with good selectivity and reproducibility. Under the optimized extraction conditions, the method showed good linearity in the range of 0.1−50 μg/L, repeatability of the extractions (RSD 2−8%, $n = 4$), and low limits of detection (1−7 pg/g). No analyte carryover effect was observed, and each μ-SPE device could be used for up to 30 extractions. Comparison was made with hollow fiber protected solid-phase microextraction and headspace solid-phase microextraction; μ-SPE was demonstrated to be a fast, accurate, and cost-effective pretreatment method for sewage sludge samples.

Organophosphorus pesticides (OPPs) are persistent contaminants that are highly soluble in water.[1,2] Contamination of organic pollutants including OPPs is a common environmental problem. To determine these compounds at ultratrace levels, suitable enrichment procedures are needed. Liquid−liquid extraction (LLE) and solid-phase extraction (SPE) are well-established procedures for concentrating analytes in aqueous samples.[3] However, they are time-consuming and require moderate to large amounts of high-purity organic solvents that are potentially toxic and expensive. Recently, solvent-minimized, membrane-based extraction techniques have been developed for the extraction of OPPs. These include liquid-phase microextraction (LPME).[4] Similarly, polymer-based microextraction techniques such as solid-phase microextraction (SPME)[5,6] and stir bar sorptive extraction (SBSE)[7] have been reported for the extraction of OPPs. For analyzing complex and dirty samples, samples were usually precleaned before direct extraction by these procedures. Alternatively, headspace extractions have been recommended for both SPME[8] and SBSE.[9] Hollow fiber membrane-protected SPME (HFM-SPME) has been reported for the direct extraction of analytes from complex samples.[10] However, it is not suitable for extracting higher molecular weight compounds.[11] The use of SPME is often associated with carryover problems. For example, Hawthorne et al.[12] reported a severe carryover of polychlorinated biphenyls, up to 20% on the SPME fiber and incomplete desorption

* To whom correspondence should be addressed. E-mail: chmleehk@nus.edu.sg; chmsv@nus.edu.sg. Tel.: +65-6516-2995. Fax: +65−6779−1691.

† National University of Singapore.

‡ Pune University.

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of analytes in the GC. Porous membrane-based LPME has been shown to have good sample cleanup and analyte-enrichment properties.[13] However, solvents available for extracting polar compounds (OPPs are moderately polar compounds) in LPME are limited.[14,15] Carbon nanotubes have unique electronic, mechanical, and chemical properties and have attracted attention in recent years.[16−20] Based on the carbon layers of the wall of the nanotubes, these materials may be classified as single-walled carbon nanotubes (CNTs)[17] or multiwalled (MW)CNTs.[18,19] Recently, MWCNTs have been used to remove dioxin from air.[21] Cai and co-workers[22,23] and Li et al.[24] explored the potential of MWCNT as SPE packing material for the extraction of alkylphenols, phthalates, and volatile organic compounds.

Here, we report a novel approach in which MWCNTs are used to extract OPPs from environmental samples. MWCNTs were packed within a porous polypropylene membrane sheet and used for OPP extraction from sewage sludge samples. Like SPE, this extraction procedure involves analyte adsorption followed by solvent desorption but on a much smaller scale. We term it micro-SPE (μ-SPE). The performance of the proposed method was evaluated by comparing with the results of HFM-SPME and headspace (HS)-SPME.

EXPERIMENTAL SECTION

Reagents and Materials. OPPs were bought from Aldrich (Milwaukee, WI). HPLC-grade organic solvents were purchased from Merck (Darmstadt, Germany). Ultrapure water was prepared with a Mill-Q (Millipore, Bedford, MA) water purification system. Stock solutions (0.1 mg/mL of each OPP) were prepared in methanol. Q3/2 Accurel 2E HF (R/P) polypropylene (PP) sheet (157-μm thickness, 0.2 −μm pore size) and Q3/2 hollow fiber membrane (600-μm internal diameter, 200-μm wall thickness, and 0.2-μm pore size) were purchased from Membrana GmbH (Wuppertal, Germany). The SPME fiber (PDMS, 100-μm thickness) and holder used were purchased from Supelco (Bellefonte, PA). MWCNTs were obtained from Honeywell Private Limited (Singapore).

GC/MS. Sample analyses were carried out using a Shimadzu (Tokyo, Japan) QP2010 GC/MS system equipped with a Shimadzu AOC-20i autosampler and a DB-5 (J & W Scientific, Folsom, CA) fused-silica capillary column (30 m × 0.32 mm internal diameter (i.d.) 0.25-μm film thickness). Helium (purity 99.9999%) was used as the carrier gas at a flow rate of 1.5 mL/min and a split ratio of 20. Samples (5 μL) were injected in splitless mode with an injection time of 2 min. The injection temperature was set at 250 °C and the interface temperature kept at 280 °C. The GC/MS temperature program used was as follows: initial temperature 60 °C, held for 2 min, then increased by 30 °C/min to 250 °C, 30 °C/min to 280 °C, and held for 2 min. For SPME, fibers were desorbed over 3 min. OPP standards and samples were analyzed in selective ion monitoring mode with a detector voltage of 1.5 kV. A specific ion was selected for each analyte, and the most abundant ion was selected as the quantitative ion, while two other ions were used for the confirmation of identities of individual analytes.

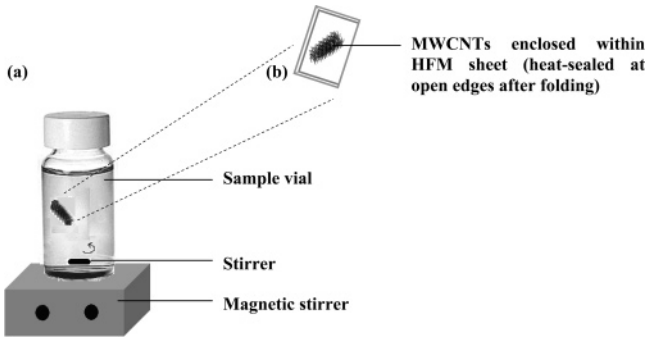

Figure 1. Schematics of (a) μ-SPE system (b) enlarged image of extraction device.

Sewage Sample Preparation. Sewage sludge samples were collected from a sewage treatment plant and stored in glass bottles precleaned with acetone. The bottles were covered with aluminum foil, transported under cooled conditions to the laboratory, and stored in the dark at −20 °C until analysis. Sludge samples (50 mg/mL) were filtered and analyzed for total organic carbon (TOC). The TOC values varied from 28 to 34 g/kg, and pH varied between 6.5 and 7.3. Blank analysis of sewage sludge using μ-SPE showed no contamination of OPPs. Therefore, the samples were used for method evaluation. Samples were not extracted immediately after spiking. A portion of the sewage sludge sample (100 mL) was spiked with standard OPPs. The sample pH and sodium chloride concentration were adjusted and then carefully homogenized. The sample was allowed to stand overnight before being extracted.

Preparation of μ-SPE Device. The μ-SPE device consists of MWCNTs enclosed within a PP sheet membrane envelope. To prepare the latter, the longer edge of a PP sheet was folded over to a width of ∼2.2 cm. The edge of the flap was then heat-sealed to the main sheet. The foldover section was then trimmed off from the main membrane sheet. The former was then cut (at ∼1.5-cm intervals) into individual rectangular pieces (2 cm × 1.5 cm). One of the two open ends of each piece was then heat-sealed. A glass Pasteur pipet and a glass funnel were used to introduce MWCNTS (6 mg) into the resulting membrane envelope via the remaining open end, which it was then heat-sealed to secure the contents (Figure 1).

Carbon Nanotube Micro-Solid-Phase Extraction. Each μ-SPE device was cleaned by ultrasonication in acetone for 10 min and then stored in the same solvent until use. For extraction, the μ-SPE device was placed in a sewage sludge sample that was stirred at ∼105 rad/s (1000 rpm; 1 rpm = 0.1047 rad/s). The device tumbled freely in the sample during extraction. After extraction (30 min), the device was removed, rinsed in the ultrapure water, dried with lint free tissue, and placed in a 100-μL autosample vial. The analytes were desorbed by ultrasonication

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in hexane (100 μL), and 5 μL of the extract was used for GC/MS analysis. The μ-SPE device could be reused after rinsing with the same solvent.

Hollow Fiber Membrane-Protected Solid-Phase Microextraction. Performing SPME by direct immersion of the fiber in sewage sludge is difficult owing to the complexity of the sample and gives unsatisfactory results. Cellulose or PP membranes have been used to protect the SPME fiber.[10,11] To compare with the performance of μ-SPE, HFM-protected SPME was used to process the sewage sludge samples as described previously.[10,11] Briefly, the SPME fiber assembly was inserted into a 7-cm-long HFM (one end sealed by flame) so that the membrane enclosed both the stainless steel tubing and the PDMS−DVB-coated fiber. For extraction, a long-neck, 10-mL vial was filled with 5 mL of the sewage sludge sample containing sodium chloride (5%, w/v). The pH was adjusted to 8. The HFM-protected SPME fiber was exposed to the sample for 40 min at 60 °C for extraction equilibrium to be attained. The sample was stirred vigorously (105 rad/s) during the extraction. These were optimized conditions. After extraction, the HFM was discarded. The metallic tubing of the SPME fiber holder and the fiber were gently wiped with soft tissue to remove water droplets. No interference from water was observed, and thermal desorption of the analytes was achieved as normal by inserting the SPME fiber into the GC injection port (held at 250°C) for 3 min. All desorptions were performed in the splitless mode. Each fiber was reused for up to ~30 analyses.

Headspace Solid-Phase Microextraction. As a further comparison, sewage sludge samples were also processed by HS-SPME. These experiments were performed using a manual SPME device with the same type of fiber as described above.[25] A 10-mL vial was filled with a 5-mL sludge sample. Extraction was carried out by exposing the fiber in the headspace of the sewage sludge stirred at 105 rad/s for 40 min at 90 °C. These were optimized conditions. After extraction, thermal desorption was performed as usual in the GC injector at 250 °C for 3 min.

Figure 2 shows the chromatograms of extracts after μ-SPE, HFM-SPME, and HS-SPME of sewage samples spiked at 5 μg/L individual OPPs. All three procedures gave comparatively clean chromatograms.

Amount of Analyte Extracted and Extraction Efficiency. As in SPME, the amount of analyte extracted and the extraction efficiency of μ-SPE depend on the interactions between the analytes and MWCNTs, which include $\pi-\pi$, electrostatic and hydrophobic interactions. The amount of analyte extracted and the extraction efficiency of SPME may be evaluated by the following equation[27]

$$n_A = FA = (m/A_d)A \quad (1)$$

The amount of analyte extracted n_A can be easily obtained from experimental measurements with the above expression. n_A is the amount (mass) of analyte extracted by SPME, F is the detector response factor, which can be calculated by comparing the amount of analyte (m) injected to the area counts (A_d) obtained by liquid injection, A is the response obtained by SPME.

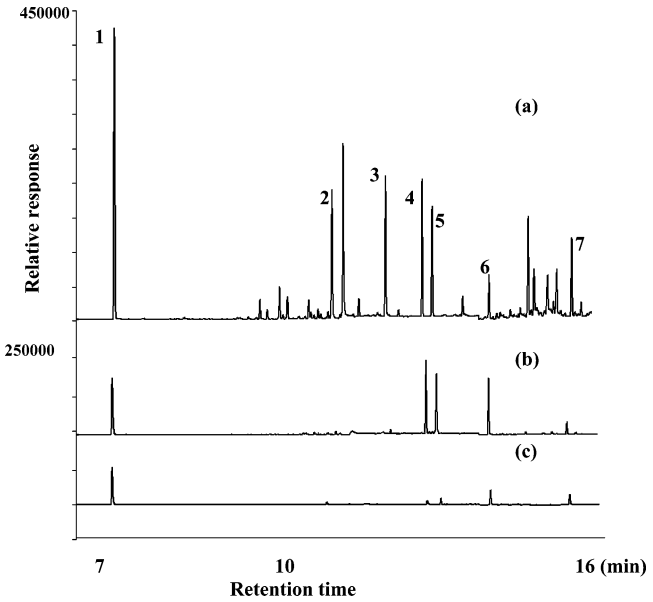

Figure 2. GC/MS chromatograms of spiked sewage sludge extracts after (a) μ-SPE, (b) HFM-SPME, and (c) HS-SPME. Each sludge sample was spiked with 5 μg/L of each OPP. Peaks: (1) triethylphosphorothioate, (2) thionazin, (3) sulfotep, (4) phorate, (5) disulfoton, (6) methyl parathion, and (7) ethyl parathion. GC/MS conditions are given in the text.

Since, in μ-SPE, analytes were desorbed with an organic solvent, the volume of desorption solvent V_d and volume of solvent injected (V_i) into the GC/MS were used to calculate the response factor F.

$$n_A = FA = (m/A_d)AV_d/V_i \quad (2)$$

The percentage extraction efficiency (E) was calculated as follows

$$\% E = n_{A/}C_i \quad (3)$$

where C_i is the initial concentration. The respective extraction efficiencies of μ-SPE, HFM-SPME, and HS−SPME were calculated and are listed in Table 1. As can be seen, the OPPs were extracted more efficiently than in the other two SPME procedures. This may be due to higher surface area afforded by the MWCNTs (131.7 m^2/g) and $\pi-\pi$ electrostatic interactions with target analytes.[22]

RESULTS AND DISCUSSION

To evaluate μ-SPE, consideration was given to such factors as sample size, extraction time and desorption time, desorption solvents, pH, and ionic strength that influence extraction efficiency. In preliminary experiments, SPME with the PDMS-, PA-, and PDMS−DVB-coated fibers were evaluated for OPP extraction. The PDMS−DVB fiber gave the most satisfactory results and was therefore used for further experiments.

Extraction Time. μ-SPE involves dynamic partitioning of the OPPs between the MWCNTs and the sample solution. The extraction efficiency depends on the mass transfer of analyte from the sample solution to the MWCNTs. Since mass transfer is a time-dependent process, the effect of extraction time was exam-

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Table 1. Extraction Efficiency of μ-SPE, HFM-SPME, and HS-SPME of OPPs from Sewage Sludge Samples

	amount of analyte extracted (ng)[a]			extraction efficiency (%)[b]		
	μ-SPE	HFM-SPME	HS-SPME	μ-SPE	HFM-SPME	HS-SPME
triethylphosphorothioate	269	5	3	67	1	0.8
thionazin	181	0.5	0.3	45	0.1	0.1
sulfotep	411	8	7	103	2	2
phorate	363	9	8	91	2	2
disulfoton	369	7	4	92	2	1
methyl parathion	146	0.2	0.1	37	0.1	0.1
ethyl parathion	219	0.7	0.5	55	0.2	0.1

[a] 20 (μ-SPE) and 5 mL (SPME) of sewage sludge samples were extracted. Amount of analyte extracted (n_A) as in eq 2. [b] The percentages of extracted amounts of analytes by the respective extraction procedures (%E) as calculated by eq 3.

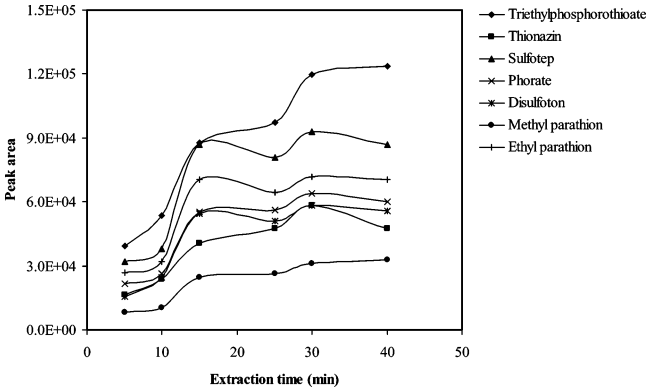

Figure 3. μ-SPE extraction time profile of seven OPPs in sewage sludge. Concentration, 5 μg/L of each analyte.

ined in this study. The sample was continuously stirred at room temperature (25°C) with a magnetic stirrer to facilitate the mass-transfer process and to decrease the time required for equilibrium to be established. The stirring speed was fixed at 105 rad/s. The adsorption profile of the OPPs in sludge sample on the μ-SPE was determined by extracting the analytes for 10−40 min. The highest extraction was achieved at 30 min (Figure 3), and after more than 30 min, no considerable improvement in peak area response was observed. In fact, for some analytes extraction decreased beyond 30 min. This result is often observed in similar extraction work. Therefore, 30 min was chosen as optimum extraction time. For both HFM-SPME and HS-SPME, 40-min, extractions gave optimum results (as shown above).

Organic Solvent Conditioning and Extraction Temperature. The MWCNTs and PP membrane are hydrophobic in nature, and low wettability was observed when μ-SPE devices were directly exposed to a sewage solution. Slow extraction rates and low extraction efficiencies were obtained. To address these issues, the wettability of the extraction device needed to be enhanced. A more favorable extraction temperature was also required. In previous reports, the wettability of MWCNTs, used as an SPE adsorbent, was improved by conditioning with organic solvents.[22] In the present case, the device was conditioned with organic solvents (the μ-SPE device was immersed in various solvents such as methanol, acetone, hexane, dichloromethane, and toluene for ~1 min and was then ultrasonicated for 2 min in ultrapure water).

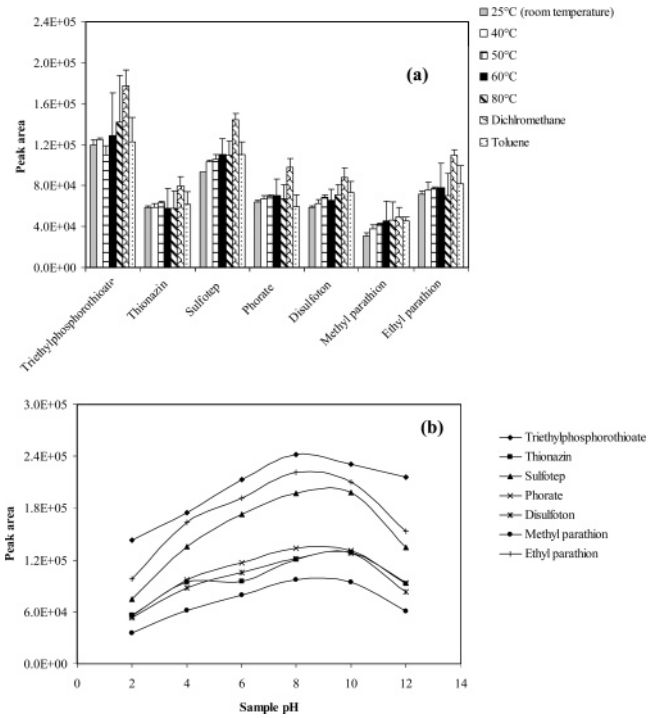

Figure 4. Effect of extraction temperature and solvent conditioning on μ-SPE (a) and influence of sample pH (b).

In this conditioning procedure, only trace amounts of organic solvents were retained by the MWCNTs and the polypropylene membrane. These solvents were easily evaporated during extraction (almost most of the solvent evaporated within 20 min of extraction).

Results showed that wetting with polar solvents such as acetone and methanol gave poorer efficiencies than that with nonpolar solvents such as dichloromethane (DCM) and toluene. Results are shown in Figure 4a.

We also evaluated the extraction efficiency of μ-SPE at different extraction temperatures. The extraction temperatures from 25 to 80 °C were studied; extraction efficiency increased with increase in temperature. Figure 4a shows the influence of extraction temperature and solvent wetting on μ-SPE. The solvent used for conditioning has little influence on extraction. During extraction, trace amounts of organic solvent may be retained on the pores of the porous membrane/MWCNT. The trapped organic solvent was acting as a carrier to enhance the extraction recovery. Similar phenomena have been reported in liquid-phase microextraction techniques.[28,29] Experiments conducted without any MWCNTs, but only the PP envelop, did not extract any analytes. From this, we concluded that only the MWCNTs could extract the OPPs, not the solvent or the envelope alone

Recently, Yudasaka et al.[30] reported a simple nanoextraction mechanism by carbon nanotubes (CNTs) and organic solvent. Organic solvents such as toluene and ethanol were tested to trap the C_{60} as a guest molecule. If the solvent has strong affinity for

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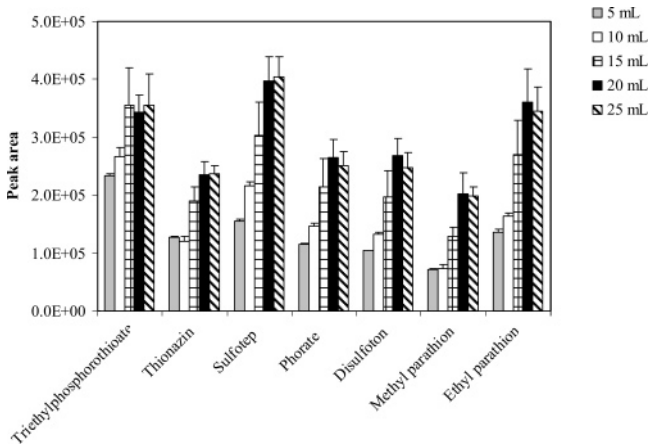

Figure 5. Effect of sample volume of OPPs on μ-SPE.

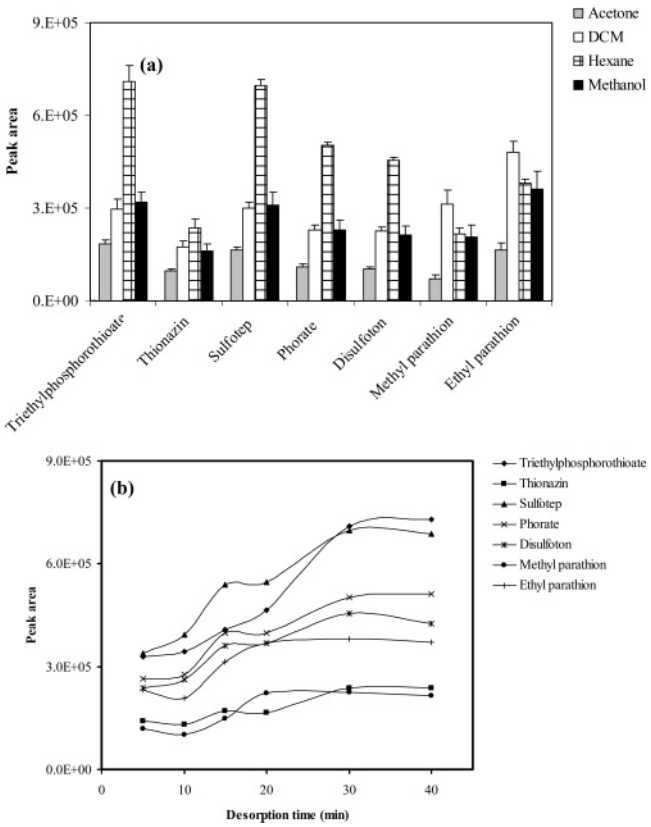

Figure 6. Effect of desorption solvent (a) and desorption time (b) on μ-SPE.

the guest molecule and CNTs, this nanoextraction does not work. If the solvent has weak interaction with the guest molecule and CNTs, nanoextraction is favored. In our case, the trace amount of DCM may have weak interaction with either CNTs or OPPs. Therefore, the extraction efficiency is higher after conditioning with DCM. μ-SPE with DCM wetting at room temperature (25 °C) gave better results than at higher temperatures.

In HFM-SPME and HS-SPME, the influence of extraction temperature was investigated between 25 and 90 °C for HFM-SPME and 40−100 °C for HS-SPME. Results show that 60 and 80 °C are the optimum temperatures for HFM-SPME and HS-SPME, respectively.

Salt and Sample pH. The salting-out effect has been used universally in SPME and LLE. Generally, addition of salt can decrease the solubility of analytes in the aqueous sample and enhances their partitioning into the adsorbent.[31,32] The influence of sodium chloride addition (from 5 to 30% (w/v)) was investigated. Both μ-SPE and HFM-SPME gave better response with 5% (w/v) salt in the sample solution, and 20% was optimum for HS-SPME.

The effect of sample pH in the range of 2−12 was also investigated. The change in extraction efficiency of μ-SPE with varying pH is shown in Figure 4b. OPP extraction increased from pH 2 to 8 and then decreased thereafter. At highly basic conditions (pH >10), extraction efficiencies of μ-SPE were low. This could be due to hydrolysis of OPPs at alkaline conditions.[33] Thus, the sample pH was adjusted to 8 for subsequent experiments. Similar trends were observed for both HFM-SPME and HS-SPME

Sample Volume. The effect of sample sizes (5−25 mL) on extraction was studied. Figure 5 shows the influence of sample volume on μ-SPE. Lower sample volumes gave poor analyte enrichment. The latter was at its maximum when 20 mL of sample was used. Above 20 mL, the extraction efficiency of μ-SPE decreased except for triethylphosphorothioate and sulfotep. As we mentioned earlier, the μ-SPE procedure is an equilibrium procedure. The amount of analyte that can be extracted depends on the partition coefficient of the analyte between the sample and the MWCNTs. This type of observation is common in many microextraction procedures.[34,35] This could be due to the possible saturation of the MWCNT capacity for a large sample volume, or a longer extraction time is needed for a >20-mL sample to reach equilibrium; 20 mL was therefore selected as sample volume for further optimization of μ-SPE.

We also studied the optimum sample volumes for HFM-SPME and HS-SPME. A volume of 5 mL appears to be most favored for both procedures; the peak areas were decreased by up to 20% when a 20-mL solution was used in place of a 5-mL sample.

Desorption Time and Desorption Solvents. As in the case of SPE and SBSE,[36−39] in μ-SPE, analytes were desorbed using an organic solvent from the MWCNTs after extraction. The analytes considered here are relatively hydrophobic and may not be easily desorbed. Thus, a suitable organic solvent was needed for this process. Both the PP membrane and MWCNTs are insoluble in most common organic solvents such as acetone, hexane, dichloromethane, and methanol; these solvents were therefore investigated. Figure 6a shows the influence of desorption solvent on μ-SPE performance. The more polar solvents (acetone and

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Table 2. Quantitative Data Comparison: Linearity, Repeatability (% RSD, $n = 4$), and Limits of Detection (S/N = 3) of OPPs

	μ-SPE[a]			HFM-SPME[b]			HS-SPME[c]		
	corr coeff (r)	RSDs (%)	LODs (pg/g)	corr coeff (r)	RSDs (%)	LODs (pg/g)	corr coeff (r)	RSDs (%)	LODs (pg/g)
triethylphosphorothioate	0.9979	8	2	0.9989	9	10	0.9863	3	22
thionazin	0.9991	4	3	0.9881	10	55	0.9920	13	93
sulfotep	0.9990	6	1	0.9974	2	14	0.9976	5	21
phorate	0.9995	2	3	0.9977	3	13	0.9974	6	29
disulfoton	0.9990	5	5	0.9951	4	40	0.9981	7	61
methyl parathion	0.9987	5	7	0.9837	13	67	0.9834	14	85
ethyl parathion	0.9992	3	4	0.9704	11	40	0.9975	9	70

Linearity ranges: [a]0.1−50, [b]2.5−50, and [c]5−50 μg/L. Precision were calculated at 5 μg/L spiked solutions.

methanol) gave poorer desorption than the other, relatively nonpolar solvents. The effect of desorption time over the range of 5−40 min was investigated. Figure 6b shows that all the OPPs were desorbed almost completely within 30 min of ultrasonication. Desorption was incomplete when shorter times were used as expected. Above 30 min, no considerable increase in desorption efficiency was observed. After the first desorption, the extraction device was further desorbed in order to test carryover effects. No analytes were detected in the second desorption, and no observable damage to the device was observed for up to 30 analyses. Additionally, the extraction efficiency was not compromised when the device was used repeatedly. The device was generally robust with only the consideration of its longevity being dependent on the durability of the protective PP membrane envelope.

Owing to their high cost, SPME fibers are designed to be reusable. For this reason, the carryover effects were also monitored. For five successive analyses, a desorbed fiber was tested for indication of carryover by reinserting it immediately into the GC injector. Desorption temperature was varied between 220 and 250 °C, with the latter giving complete desorption with no carryover with a 3-min desorption time.

Quantitative Calibration and Reproducibility. Under the optimized conditions, calibration curves were constructed for μ-SPE, HFM-SPME, and HS-SPME. The results shown in Table 2 indicate good linearity with correlation coefficients for μ-SPE (>0.997 (0.1−50 μg/L)), HFM-SPME (>0.984 (2.5−50 μg/L)), and HS-SPME (>0.983 (5−50 μg/L)) The reproducibility was determined by four repeated extractions of a 5 μg/L OPP spiked sewage sludge sample. The relative standard deviations (RSD, $n = 4$) were between 2 and 8% for μ-SPE, 3−13% for HFM-SPME, and 6−14% for HS−SPME. The limits of detection (LODs) were calculated at a signal-to-noise ratio of 3. The LODs for μ-SPE (1−7 pg/g) were better than those for HFM-SPME (10−64 pg/g) and HS-SPME (21−93 pg/g). This is ascribed to the more efficient adsorption of OPPs by MWCNTs and the greater capacity of these materials.

CONCLUSIONS

In this report, a multiwalled carbon nanotube-based microextraction technique was developed. The feasibility of the procedure, termed μ-SPE, was tested by using it to extract organophosporous pesticides from sludge samples. The limits of detection were in the sub-parts-per-billion ranges (1−7 pg/g) and precision was ≤8%; in comparison, for the SPME methods considered here, hollow fiber membrane protected-SPME and headspace-SPME, the values were LOD 10−67 pg/g, precision ≤13%, and LOD 21−93 pg/g, precision ≤14%, respectively. No analyte carryover was observed after repeated desorptions. Potentially, this newly developed microextraction technique can be used to extract complex matrixes, such as biological fluids, sewage sludge, and sludge samples, while preventing coextraction of extraneous materials. One drawback is that it is not easily automated. The method has several other benefits, however. It is robust and durable and a single device can be used for 30 extractions. The μ-SPE device is easy to prepare in-house at reasonable cost.

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