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Determination of triazine herbicides using membrane-protected carbon nanotubes solid phase membrane tip extraction prior to micro-liquid chromatography

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ABSTRACT

A novel microextraction technique termed solid phase membrane tip extraction (SPMTE) was developed. Selected triazine herbicides were employed as model compounds to evaluate the extraction performance and multiwall carbon nanotubes (MWCNTs) were used as the adsorbent enclosed in SPMTE device. The SPMTE procedure was performed in semi-automated dynamic mode and several important extraction parameters were comprehensively optimized. Under the optimum extraction conditions, the method showed good linearity in the range of 1–100 μg/L, acceptable reproducibility (RSD 6–8%, $n = 5$), low limits of detection (0.2–0.5 μg/L), and satisfactory relative recoveries (95–101%). The SPMTE device could be regenerated and reused up to 15 analyses with no analyte carry-over effects observed. Comparison was made with commercially available solid phase extraction-molecular imprinted polymer cartridge (SPE-MIP) for triazine herbicides as the reference method. The new developed method showed comparable or even better results against reference method and is a simple, feasible, and cost effective microextraction technique.

1. Introduction

Triazine herbicides are well-known herbicides that are usually applied to soil and absorbed by the roots of seedling weeds. Triazine and its degradation products are highly toxic and are usually reportedly present in waters, soils and organisms due to their high persistency [1]. The extractions of triazine herbicides from various sample matrices have been carried out largely by liquid–liquid extraction (LLE) [2,3], solid phase extraction (SPE) [4,5], solid phase microextraction (SPME) [6–8], and liquid phase microextraction (LPME) [9,10] in conjunction with chromatographic and electrophoretic analytical methods. Although LLE is an easy and simple sample handling technique, it is considered to be a time-consuming and multistage operation technique. The common benefits of SPE relative to LLE are reduced analysis time and total organic solvent consumption and waste disposal. Recently, molecular imprinted polymer SPE cartridges for triazine herbicides (developed by MIP Technologies AB as SupelMIP SPE—Triazine 10) are commercially available which claim a recovery of 80–90% for most of the triazine herbicides [11]. Recently, miniaturization has become an important trend in the development of sample preparation techniques. SPME is well-known as a rugged, sensitive and solvent-free extraction method. A range of different fiber coatings are commercially available for various applications. Micro-solid phase extraction (μ-SPE) that utilizes sorbent held in polypropylene membrane envelope as extraction medium was reported by Lee and co-workers [12]. Carbon nanotubes (CNTs) have attracted great attention in recent years due to their unique physical and chemical properties. Numerous research studies based on the use of CNTs as adsorbent in analytical procedures were reported in recent years. Long and Yang [13] reported that multiwall carbon nanotubes (MWCNTs) have very strong adsorption to dioxin and thus are expected to be ideal sorbent for dioxin removal. In addition, the potential of MWCNT as adsorbent in solid phase extraction was explored by several research groups in extracting alkylphenol, phthalates, organophosphorus pesticides, volatile organic compounds [14–17]. Drugs such as antibiotics, anxiolytics and anti-inflammatories or antidepressants have also been extracted using MWCNTs as SPE sorbents [18–24]. The applicability of MWCNTs in extracting selected triazine herbicides was also reported [25–27]. The overall procedures were time-consuming and required large sample volume in order to achieve desired detection sensitivity.

In this study, a novel extraction method, solid phase membrane tip extraction (SPMTE), involving the use of tiny cone-shaped membrane tip protected MWCNTs was evaluated for the extraction of selected triazine herbicides in river water samples. The method was optimized for the selection of conditioning solvent, extraction time, pH, salting-out effect, sample volume, desorption solvent and

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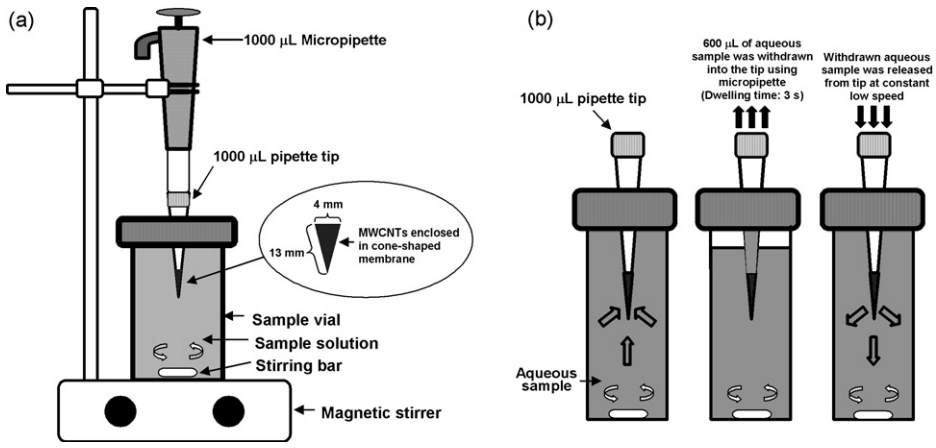

Fig. 1. Schematics of (a) the SPMTE setup and (b) expanded view of dynamic SPMTE.

desorption time. The method was performed in semi-automated dynamic mode to increase the overall extraction efficiency. Finally, comparison of this new method with a method using commercially available SPE-molecular imprinted polymer cartridge was also performed.

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade or better. Triazine herbicides (simazine, cyanazine, atrazine, and propazine) were purchased from Fluka, Switzerland. Methidathion was obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade organic solvents were purchased from J.T. Baker (USA). Double-distilled deionized water of at least 18 MΩ was purified by Nano ultrapure water system (Barnstead, USA). Stock standard solutions (1000 μg/mL) of the analytes were prepared in acetonitrile and were stored in the freezer at about −18 °C. Working standard solutions of lower concentration were prepared by dilution with acetonitrile. Q3/2 Accurel 2E HF (R/P) polypropylene sheet (157 μm thickness, 0.2 μm pore size) was purchased from Membrana (Wuppertal, Germany). MWCNTs were obtained from Sun Nanotech (Jiangxi, China). SupelMIP SPE-Triazine 10 SPE cartridges were obtained from Supelco (PA, USA).

2.2. Micro-LC analysis

The micro-LC systems consisted of a conventional micro-LC system coupled with a column oven of a Perkin Elmer Autosystem Gas Chromatography (USA). Micro-LC separations were carried out on a 3 μm Diamondbond C-18 120 Å micro-LC column (10 cm × 1000 μm I.D.) (ZirChrom Separation, USA) using a Jasco Micro 21PU-01 capillary LC pump (Kyoto, Japan) for mobile phase delivery. A Rheodyne 7725 micro-volume injection valve (Cotati, USA) fitted with a 0.5 μL internal loop was used for sample introduction. Analyte peaks were detected using a Jasco UV-2075 Plus UV-Vis detector (Kyoto, Japan) equipped with micro-flow-cell and were recorded on a Powerchrome data recording system (eDAQ, Australia). Separations of prepared mixture were carried using mobile phase acetonitrile–water (30:70) (v/v) at column temperature of 80 °C. The flow rate was fixed at 70 μL/min. The prepared mixture was injected onto the column in triplicate. UV detection of analytes was at 220 nm.

2.3. River water samples

River water samples were collected from Skudai River, Johor, Malaysia in Teflon bottles pre-cleaned with acetone. The bottles were covered with aluminum foil and stored in the dark at −4 °C until analysis. Blank analysis of river water using SPMTE and SPE-MIP showed no contamination of triazine herbicides. Hence, the samples were used for method evaluation. The river water sample was spiked with triazine herbicides standard and sample pH was adjusted and then carefully homogenized. The spiked sample was allowed to stand overnight before extraction.

2.4. Preparation of SPMTE device

The SPMTE device consisted of MWCNTs enclosed within a home-made cone-shaped polypropylene (PP) membrane attached to 1000 μL capacity pipette tip. A PP sheet membrane was cut into an equilateral triangle with each side of approximately 15 mm. The edge of the membrane was folded to form a scalene triangle shape with sides of 15, 13 and 7.5 mm. The edge of the longest flap was then heat-sealed using a portable impulse heat sealer with seal width of 0.5 mm. A glass Pasteur pipette was used to introduce MWCNTs (3 mg) into the cone-shaped membrane via the remaining open end, which it was then heat-sealed to secure the adsorbents. Each cone-shaped membrane-protected MWCNTs with sides of approximately 13 mm and width of 4 mm was cleaned by ultrasonication in acetone for 10 min and then stored in the same solvent until use. The tip-end (∼7 mm length) of a commercially available 1000 μL pipette tip was cut-off. The tip-end was slight compressed and the cone-shaped membrane was inserted into the modified tip and fully fitted the tip-end prior to extraction. The SPMTE device was exposed to the sample during the extraction as shown in Fig. 1a.

2.5. Solid phase membrane tip extraction

The solid phase membrane tip was placed in the river water sample that was stirred at 1000 rpm. At 5 min interval of the extraction, a dynamic extraction procedure was performed (Fig. 1b). A 600 μL of aqueous sample was withdrawn manually into the tip at rate of approximately 30 μL/s using a digital micropipette (Nichiryo, Japan). After a dwelling time of approximately 3 s, the withdrawn aqueous sample was released from the tip back into the sample vial at same speed. This procedure was repeated 5 times and the micropipette was detached from the tip. The dynamic extraction procedure was repeated at every 5 min interval until the end of extraction. (The number of dynamic extraction procedure was per-

formed depending on total extraction time.) After extraction, the cone-shaped membrane was removed, rinsed in ultra-pure water, dried with lint-free tissue and placed in a 500 μL safe-lock tube. Desorption volume of 100 μL was used as this was the minimum amount that allowed the SPMTE device to be fully immersed in the solvent. The analytes were desorbed by ultrasonication in acetonitrile (100 μL) and 0.5 μL was injected into the micro-LC.

2.6. Solid phase extraction using molecularly imprinted polymers (SPE-MIP)

Commercially available SupelMIP SPE-Triazine 10 SPE cartridge (Supelco, USA) was used as reference method to evaluate our developed method. The extraction procedures were certified and provided by the manufacturer (MIP Technologies AB, PA, USA). The cartridge was equilibrated by 1 mL methanol; 1 mL ultra-pure water; 1 mL 2 mM ammonium dihydrogen phosphate at pH 3 and allowed to dry during conditioning. River water was acidified to pH 4 with 0.1 M hydrochloric acid and spiked with standard solution. Spiked river water sample (15 mL) was loaded into the cartridge at a flow rate of 0.5 mL/min. After the sample loading, the cartridge was washed with 1 mL of 0.1 M HCl; 1 mL of ultra-pure water and vacuum was applied through cartridge for 20 min to remove residual moisture, followed by 1.5 mL of dichloromethane and vacuum was applied through cartridge for 5 min. The analytes were eluted with 3× 1 mL of methanol. The extract was evaporated and reconstituted with 100 μL of acetonitrile prior to micro-LC analysis. The same procedure was performed on blank river water sample.

2.7. Extraction efficiency and relative recovery

The extraction mechanism of SPMTE is similar to those of SPME and SBSE which generally depend on the interactions between analytes and MWCNTs such as π–π, electrostatic and hydrophobic interactions [12]. The amount of analyte extracted by SPMTE can be evaluated by the following equation [28]:

$$n_A = FA = \left(\frac{m}{A_d}\right) A \left(\frac{V_d}{V_i}\right) \quad (1)$$

where n_A is the amount (mass) of analyte extracted by SPMTE, F is the detector response factor, which can be calculated based on the amount of analyte (m) injected to the area counts (A_d) obtained by liquid injection, and A is the response obtained by SPMTE. The SPMTE device was desorbed in organic solvent prior to analysis. Hence, the volume of desorption solvent (V_d) and volume of solvent injected (V_i) into the micro-LC were used to calculate the response factor F.

The percentage extraction efficiency (E) was calculated as follows:

$$\%E = \left(\frac{n_A}{C_i}\right) \times 100 \quad (2)$$

where C_i is the initial amount (mass) of analyte.

3. Results and discussion

3.1. Optimization of SPMTE

3.1.1. Organic solvent conditioning and extraction time

The type of organic solvent used to immobilize the pores of the membrane and increase the wettability of the SPMTE device is a critical factor since MWCNTs and polypropylene membrane are hydrophobic in nature. The selection of organic solvent to enhance the wettability of extraction device was performed using methanol, acetonitrile, isopropanol, acetone, and dichloromethane. The SPMTE device was immersed in respective solvents for 2 min and was then rinsed with ultra-pure water. It was found that conditioning of SPMTE device with acetonitrile gave highest extraction efficiency.

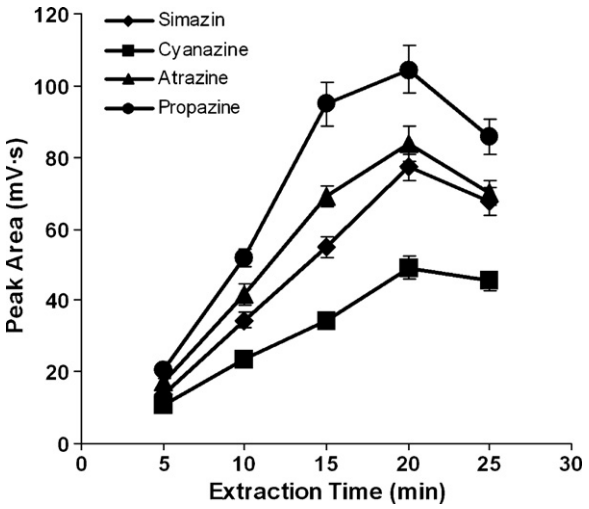

Fig. 2. SPMTE extraction-time profile of triazine herbicides in river water. Extraction conditions: 5 μg/L of spiked solution; desorption time: 15 min; desorption solvent: 100 μL of acetonitrile; sample volume: 15 mL; no adjustment of sample pH and salt. (Error bars represent standard deviation of results n = 5.)

Mass-transfer is a time-dependent process and equilibrium is attained only after certain period of time. For method optimization, it is therefore important to establish the extraction-time profiles of target compounds so as to configure the time after which equilibrium is attained in practice. Extractions were first performed to compare static SPMTE with dynamic SPMTE procedure. The sample solution was continuously stirred at room temperature (25 °C) at 1000 rpm. Dynamic SPMTE demonstrated a greater performance with up to 2-fold reduction in extraction time required against the static SPMTE. The adsorption profile of the triazine herbicides in spiked river water sample on the dynamic SPMTE was determined by extracting the analytes for 5–25 min. The highest extraction was achieved at 20 min (Fig. 2). Slight decrease of peak area response was observed when longer exposure times (25 min) were applied. This might probably be due to the back-extraction of analytes from adsorbent into sample solution. Hence, 20 min was chosen as the optimum extraction time.

3.1.2. Salt and sample pH

Depending on the nature of the target analytes, addition of salt to the sample solution can decrease the solubility of the analytes and therefore enhance extraction because of the salting-out effect. In this study, the effect of salt on extraction efficiency was determined by adding sodium chloride at concentrations of 0, 1, 2.5, 5 and 10% (w/v) in spiked river water sample. The peak areas for triazine herbicides obtained highest values when 1% of sodium chloride was added to the samples. Further addition of sodium chloride did not result in an increase in extraction efficiency. Therefore, subsequent experiments were carried out with adding 1% (w/v) salt. Adjustment of the pH can enhance extraction, as dissociation equilibrium is affected together with the solubility of the acidic/basic target analytes. In the present study, the extractions were performed under different pH conditions ranging from pH 2 to 10 (Fig. 3). An increase of peak area response was observed when the pH was increased from 2 to 4 and the response remained constant or slight decreased across pH range of 4–10. The pKa values of all selected triazine herbicides were approximately 2.00. All the compounds could exist as molecules and could be easily extracted at pH 4 or greater. Therefore, pH 4 was selected for subsequent analyses.

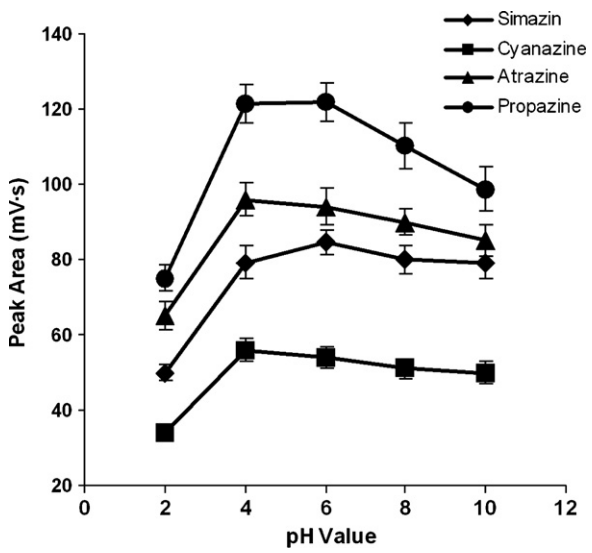

Fig. 3. Effect of sample pH on SPMTE. Extraction conditions: 5 μg/L of spiked solution; extraction time: 20 min; desorption time: 15 min; desorption solvent: 100 μL of acetonitrile; sample volume: 15 mL; salt 1%. (Error bars represent standard deviation of results $n = 5$.)

3.1.3. Desorption solvents, desorption time and sample volume

In SPMTE procedure, analytes were desorbed using an organic solvent from the MWCNTs after extraction. Organic solvents compatible with micro-LC such as methanol, acetonitrile, isopropanol and tetrahydrofuran were evaluated. Results showed that acetonitrile gave highest peak area response and sharper chromatographic target analyte peaks. A series of desorption times (ultrasonication) in the range of 5–30 min was investigated (Fig. 4a). Analyte peak area response obtained the highest values at desorption time of 15 min. No significant increase in peak area was observed when longer desorption times were applied. After the first desorption, the SPMTE device was further desorbed to be reused in the study of carry-over effects. No analytes were detected in consecutive desorption and the SPMTE devices were found to be reusable for up to 15 analyses. Device-to-device variation was also tested for selected triazine herbicides at optimum conditions and satisfactory RSDs of less than 10% were obtained. The sample volume is important in determining the loading capacity of SPMTE device as well as the overall time required by SPMTE to reach equilibrium. Five different sample volumes (5–25 mL) spiked at 5 μg/L were studied (Fig. 4b). Lower sample volume generally resulted in poorer peak area response. Highest extraction efficiency was observed when 15 mL sample volume was used. Slight decrease in peak area response was noted when larger sample volumes (20 and 25 mL) were applied in the extraction. This phenomenon might be due to the saturation of the MWCNTs (~3 mg) capacity for a large sample volume.

3.2. Method validation

To validate the applicability of the proposed SPMTE procedure, the linearity, limits of detection, and reproducibility for both SPMTE and SPE-MIP methods were investigated using the optimum extraction conditions and the results are listed in Table 1. As can be seen, good linearities were obtained for both SPMTE and SPE-MIP with correlation coefficients of >0.9975 (1.0–100 μg/L) and >0.9991 (0.5–100 μg/L), respectively. The limits of detection (LODs) were calculated at a signal-to-noise ratio of 3. The LODs and LOQs for SPMTE (0.2–0.5; 1.2–1.8 μg/L) were generally comparable

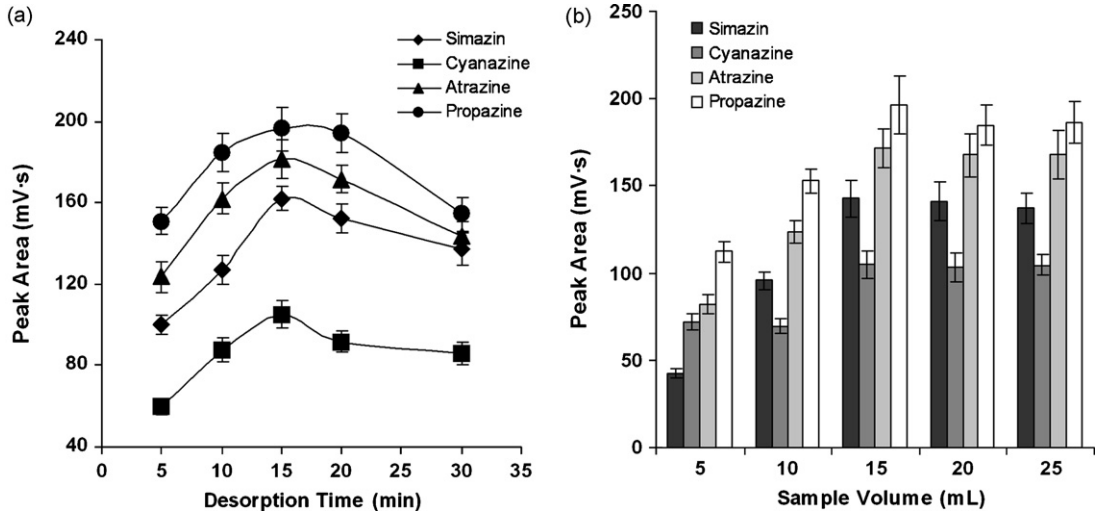

Fig. 4. Effect of desorption time (a) and sample volume (b) on SPMTE. Extraction conditions: 5 μg/L of spiked solution; extraction time: 20 min; desorption solvent: 100 μL of acetonitrile; salt 1%; sample pH 4. (Error bars represent standard deviation of results $n = 5$.)

Table 1
Quantitative data comparison: linearity, repeatability (% RSD, $n = 5$), and limits of detection of triazine herbicides.

	SPMTE				SPE-MIP			
	Corr. Coeff. (r)[a]	RSD (%)	LODs (μg/L)[b]	LOQs (μg/L)[c]	Corr. Coeff. (r)[a]	RSD (%)	LODs (μg/L)[b]	LOQs (μg/L)[c]
Simazine	0.9975	8.5	0.5	1.7	0.9999	6.8	0.2	1.0
Cyanazine	0.9999	6.3	0.2	1.2	0.9991	5.7	0.2	1.1
Atrazine	0.9997	5.7	0.2	1.5	0.9994	6.5	0.1	0.9
Propazine	0.9995	6.4	0.5	1.8	0.9994	5.2	0.3	1.3

[a] Linearity ranges: 1.0–100 μg/L (SPMTE) and 0.5–100 μg/L (SPE-MIP).
[b] LODs: S/N = 3.
[c] LOQs: (10 × standard deviation for the blank)/slope of calibration curve.

Table 2
Extraction efficiency of SPMTE and SPE-MIP of triazine herbicides from river water samples.

	Absolute extraction efficiency (%)		Relative recovery (%)[a] (% RSD, $n = 5$)	
	SPMTE	SPE-MIP	SPMTE	SPE-MIP
Simazine	64	86	98 (8)	85 (4)
Cyanazine	57	88	96 (8)	88 (6)
Atrazine	55	90	95 (6)	89 (5)
Propazine	71	83	101 (7)	87 (4)

[a] Percentage of relative peak area of the analytes in spiked river water and ultra-pure water sample extracts, with both samples spiked at 5 μg/L of triazine herbicides.

with those achieved by SPE-MIP (0.1–0.3; 0.9–1.3 μg/L). The reproducibility was determined by five repeated extractions of 10 μg/L triazine herbicides-spiked river water sample. The RSDs for SPMTE were generally acceptable (6–8%) even though extractions were performed using the same SPMTE device. Although lower RSDs (4–5%) were achieved by SPE-MIP, the extractions were performed using new cartridge for each extraction. The SPE-MIP cartridge was found to be reusable practically for a maximum of 3 spiked river water analyses. Furthermore, unlike SPMTE device, the SPE-MIP cartridge requires high quantity of organic solvent for rinsing and cleaning prior to subsequent extractions. In contrast, the small pore size of the membrane for SPMTE device functions as a cleanup filter that prevents large molecules and particles present in river water sample from interfering with the extraction while all sample matrices in river water sample are directly exposed to adsorbent which leads to low reproducibility of SPE-MIP cartridge. Fig. 5 shows chromatograms of extracts after dynamic SPMTE and SPE-MIP of blank river water samples and samples spiked with 10 μg/L of individual triazine herbicides. The clean chromatograms of blank river water samples extracts showed no contamination of triazine herbicides. All peaks in spiked river water extracts were well separated with good resolution.

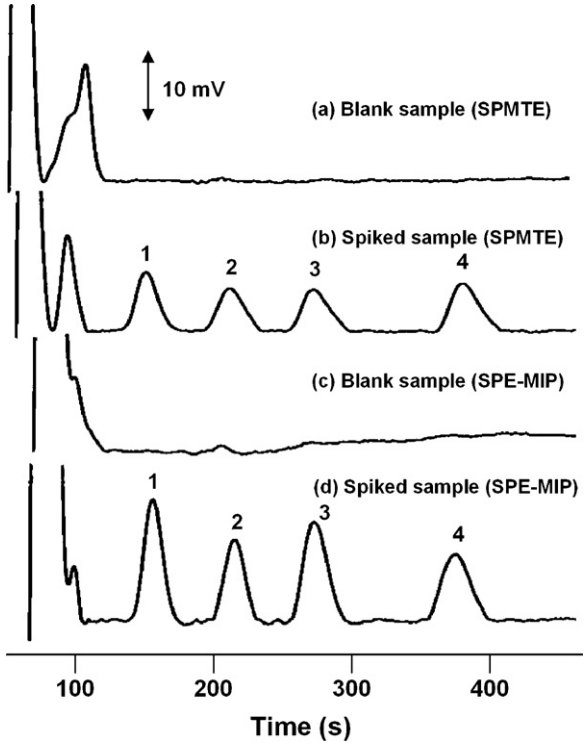

Fig. 5. Micro-LC chromatograms of river water extracts using optimum SPMTE and SPE-MIP procedure. (a) Blank sample—SPMTE; (b) sample spiked with 10 μg/L of each triazine herbicides—SPMTE; (c) blank sample—SPE-MIP; (d) sample spiked with 10 μg/L of each triazine herbicides—SPE-MIP. Peaks: (1) simazin, (2) cyanazine, (3) atrazine, and (4) propazine. Micro-LC conditions are as described in the text.

3.3. Analytical performance

Comprehensive extraction performance based on absolute extraction efficiency and relative recovery (percentage of peak area of the analytes in river water and ultra-pure water sample extracts, with both samples spiked at same level of triazine herbicides) were calculated and listed in Table 2. The absolute extraction recovery achieved by SPE-MIP was significantly higher (83–90%) than those obtained by SPMTE (55–71%). These results signify that SPMTE is a non-exhaustive extraction method and is generally based on phase-equilibrium between sample solution and the adsorbent. Similar to other microextraction methods, good accuracy of the results can be obtained easily with a spiked real sample calibration for analytical quantification [29]. The relative recovery was investigated to study the matrix effect towards the extraction efficiency of respective devices. The SPE-MIP gave relative recoveries in the range of 85–89% with RSD values between 4 and 6%. On the other hand, SPMTE achieved relative recoveries of 95–101% with RSD values in the range of 6–8%. These indicate that the matrix effects on SPMTE method are negligible thanks to the small pore-size membrane present as extraction barrier between sample matrixes and adsorbent in SPMTE device.

4. Conclusion

In the present article, a new miniaturized extraction method termed SPMTE was developed. The SPMTE performed in semi-automated dynamic mode showed excellent extraction efficiency in the extraction of selected triazine herbicides in river water samples. The comparison of SPMTE procedure with reference method SPE-MIP indicates that SPMTE is advantageous in terms of shorter extraction time, low solvent usage, cost effective, easy to use, and comparable LODs as well as method reproducibility. In the presence of the porous membrane as protection barrier, the technique could be used to extract complex matrices, such as biological fluids, sludge samples, etc. Future investigations will be focused on fully automated dynamic mode throughout the SPMTE procedure as well as the real-world environmental and biological sample analysis.

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