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ORIGINAL

Liquid–Liquid Microextraction of Nitrophenols Using Supramolecular Solvent and Their Determination by HPLC with UV Detection

Qing Yang · Xiaoqing Chen · Xinyu Jiang

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Abstract A novel, efficient, and environmentally friendly method—supramolecular solvent liquid–liquid microextraction (SMS-LLME) combined with high-performance liquid chromatography (HPLC)—was first established for the determination of *p*-nitrophenol and *o*-nitrophenol in water samples. Several important parameters influencing extraction efficiency, such as the type and volume of extraction solvent, pH of sample, temperature, salt effect, extraction time, and stirring rate, were optimized in detail. Under the optimal conditions, the enrichment factor was 166 for *p*-nitrophenol and 160 for *o*-nitrophenol, and the limits of detection by HPLC were 0.26 and 0.58 μg L^{-1}, respectively. Excellent linearity with coefficients of correlation from 0.9996 to 0.9997 was observed in the concentration range of 2–1,000 μg L^{-1}. The ranges of intra- and interday precision ($n = 5$) at 100 μg L^{-1} of nitrophenols were 5.85–7.76 and 10.2–11.9 %, respectively. The SMS-LLME method was successfully applied for preconcentration of nitrophenols in environmental water samples.

Keywords High-performance liquid chromatography · Supramolecular solvent liquid–liquid microextraction · *p*-Nitrophenol · *o*-Nitrophenol · Water samples

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Q. Yang · X. Chen (✉) · X. Jiang (✉)
School of Chemistry and Chemical Engineering,
Central South University, Changsha 410083, China
e-mail: xqchen@csu.edu.cn

X. Jiang
e-mail: jiangxinyu@csu.edu.cn

Introduction

Nitrophenols are some of the most important contaminants present in the environment. They are used in various manufacturing processes for products such as pesticides, pharmaceuticals, plastics, azo dyes, pigments, wood preservatives, rubber chemicals, and explosives [1]. Because of their toxicity and carcinogenicity, some of them are included in the list of priority pollutants in many countries and are required to be determined. For instance, *p*-nitrophenol is one of the 129 organic pollutants listed by the United States Environmental Protection Agency (US-EPA) as carcinogens and perilous to human beings as well as the environment [2]. Furthermore, *p*-nitrophenol damages mitochondria and inhibits energy metabolism in human and animals [3]. Therefore, developing a simple, rapid, and environmentally friendly method for monitoring their presence in the environment is crucial.

In many analytical procedures, sample pretreatment is usually necessary for the determination of trace analytes in samples. Up to now, various pretreatment techniques have been developed to extract nitrophenols from aqueous samples, such as solid-phase extraction (SPE) [4, 5], solid-phase microextraction (SPME) [6, 7], single-drop microextraction (SDME) [8], and hollow-fiber liquid-phase microextraction (HF-LPME) [9]. However, SPE requires large volumes of toxic solvent, and the process is complicated and time consuming [10]. The primary advantages of SPME are its solvent-free nature and ability to be easily miniaturized [11]; unfortunately, the fibers used in SPME are relatively expensive, and the fused silica is fragile and easily broken [12, 13]. The shortcomings of SDME include instability and volatility of the extraction solvent [14]. Although HF-LPME is simple and consumes a small amount of organic solvent, long extraction times are often encountered [15].

Efforts have been made to overcome the limitations of the pretreatment techniques described above. Assadi et al. [16] developed a novel microextraction method, referred to as dispersive liquid–liquid microextraction (DLLME). The advantages of this method include low cost, high recovery, and short extraction time. DLLME has been applied for the determination of phenols, organophosphorus pesticides, and thiamine [17–19] in water samples. But in the DLLME method, the extraction solvents and dispersive solvents are usually toxic.

Supramolecular solvent [20–25] is a recent term referring to nano-structured liquids generated from amphiphiles through a sequential, self-assembly process occurring on two scales, molecular and nano. For the purpose of using less toxic extraction solvent, the tetrabutylammonium-induced liquid–liquid phase separation in vesicular solutions of alkyl carboxylic acids was recently described by Pérez-Bendito et al. [26]; this method presents a high potential for the extraction of bisphenols.

A new method applied in the present study, based on the principle of DLLME and supramolecular solvent mentioned previously, is supramolecular solvent liquid–liquid microextraction (SMS-LLME). To satisfy concerns about the environmental danger of waste solvent disposal, this technique uses low-toxicity supramolecular solvent (tetrabutylammonium-induced vesicles of decanoic acid). The supramolecular solvent has a lower density than water, and thus it is easily separated by centrifugation. After centrifugation, the supramolecular solvent can be easily transferred into a conical vial and used for HPLC analysis. Herein, the potential of SMS-LLME for the extraction of *p*-nitrophenol and *o*-nitrophenol in water samples followed by determination with HPLC was explored. The possible factors affecting extraction efficiency, such as type and volume of extraction solvent, salt effect, pH, temperature, stirring rate, and extraction time, were investigated and optimized.

Experimental

Chemicals and Reagents

All reagents used were of analytical grade. *p*-Nitrophenol (≥99.5 %) and *o*-nitrophenol (≥99.5 %) were purchased from Aladdin (www.aladdin-reagent.com). Decanoic acid was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and tetrabutylammonium hydroxide (Bu_4NOH, 25 %, w/v in water) was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Methanol (HPLC grade) was obtained from Tianjin Chemical Reagent Research Institute (Tianjin, China). The ultra-pure water was prepared by an MYQ subboiling distilling water purification system (Changsha, China).

Stock solutions of 1,000 mg L^{-1} nitrophenols were prepared by dissolving appropriate amounts of compounds in methanol, and then stored in a fridge at 4 °C. Working standard solutions were prepared weekly by diluting the stock standard solution with ultra-pure water to the required concentrations.

Apparatus

Chromatographic analysis was carried out on an Agilent 1260 HPLC system equipped with a manual injector and an SPD-10AV-UV detector. A Lichrospher C18 column (250 mm × 4.6 mm, 5 μm particle size; Hanbon Sci. & Tech.) was used, and all injections were performed automatically using a 20-μL sample loop. The operating conditions were as follows: mobile phase, isocratic elution of methanol/water (80:20, v/v); flow rate, 1.0 mL min^{-1}; column temperature, 25 °C; and detector wavelength, 290 nm.

Sample Solutions Preparation

Different water samples, including urban wastewater from downtown (Changsha, China), river water (Xiangjiang, China), and pond water (Central South University, China), were collected and the SMS-LLME method was applied to extract the nitrophenols. In order to remove any suspended material, each water sample was filtered through a 0.45-μm membrane. The pH of the samples was then adjusted at 6.0. For water samples containing a high concentration of calcium, the interference effect of calcium was removed by adding EDTA (2 mg L^{-1}) as a masking agent before extraction. Then the water samples were stored in amber glass bottles and maintained in the dark at 4 °C.

Supramolecular Solvent Preparation

Supramolecular solvent was prepared by mixing 5.15 g of decanoic acid and 15.6 mL of tetrabutylammonium hydroxide in 200 mL distilled water at pH 7. The mixture was stirred at 1,200 rpm for 10 min to dissolve the decanoic acid. Finally, phase separation was achieved by centrifugation of the mixture for 5 min at 4,000 rpm and the obtained supramolecular solvent was used for further experiments.

SMS-LLME Procedure

For SMS-LLME, 17.5 mL of aqueous solution (pH 6.0) containing 200 μg L^{-1} *p*-nitrophenol and *o*-nitrophenol was placed in an 18-mL vial and 100 μL of supramolecular solvent was added. The mixture was stirred with a 15 mm × 6 mm magnetic stirring bar for 30 min at 30 °C.

To control the temperature of the sample solution, a simple water bath placed on the heater-stirrer was used. Then, after centrifugation for 2 min at 4,000 rpm, the supramolecular solvent droplets floated on the surface of the aqueous solution (owing to their density being lower than that of water). The supramolecular solvent (volume 80 ± 5 μL) was subsequently transferred into the sample vial by a pipettor. Finally, 20 μL of the solvent was injected into the HPLC system for analysis.

Results and Discussion

Optimization of SMS-LLME

The general parameters expected to influence the extraction of nitrophenols by supramolecular solvent drops such as the composition of supramolecular solvent, pH, temperature, drop volume, stirring rate, ionic strength, and extraction time were investigated. To optimize the extraction conditions, the HPLC peak area of analytes was utilized to evaluate the extraction efficiency under different conditions. Triplicate extractions were performed for all experiments, and the average of these results was reported in figures or tables.

Composition of Supramolecular Solvent

The supramolecular solvent phase is produced from aqueous mixtures of protonated (DeA) and deprotonated (De^-) decanoic acid in the presence of tetrabutylammonium cation (Bu_4N^+). In an aqueous solution, DeA and De^- molecules assemble as small water-soluble vesicles. Addition of Bu_4N^+ to aqueous suspensions of these aggregates results in formation of larger vesicles made up of DeA and Bu_4NDe. The composition of the larger vesicles is a very important parameter which greatly influences its extraction capability. To study the effect of the composition of supramolecular solvent, the amount of $Bu_4N^+/DeA + De^-$ was varied between 0.1 and 1.0 (molar ratio) and the $DeA + De^-$ was kept constant at 0.15 mol L^{-1}. At 0.5 molar ratio, complete neutralization of De^- occurs, whereas at higher ratios, there is the possibility of cation–π interactions between the quaternary ammonium group of Bu_4N^+ non-bonded to De^- and the aromatic rings in the target analytes [27, 28]. Therefore, the molar ratio of 0.5 was selected.

Effect of Extraction Solvent Volume

To examine the effect of extraction solvent volume, solutions containing different volumes of supramolecular solvent (80, 90, 100, and 110 μL) were subjected to the same SMS-LLME procedure, while the volume of the sample solution was kept constant at 17.5 mL. As shown in Fig. 1, the peak areas of *p*-nitrophenol and *o*-nitrophenol increased as the volume of supramolecular solvent increased in the range of 80–100 μL, and then decreased as the volume of supramolecular solvent further increased owing to a dilution effect. Accordingly, 100 μL of supramolecular solvent was used as the extraction solvent in further experiments.

Effect of Temperature

Temperature affects both equilibrium and mass transfer in the SMS-LLME procedure. Therefore, the choice of a suitable extraction temperature is necessary. To study the effect of temperature, experiments were carried out by varying the temperature in the range of 20–60 °C. The experimental data are indicated in Fig. 2. The results showed that extraction efficiency increased when the temperature increased from 20 to 30 °C, probably because of the increase in mass transfer. The formation of air bubbles around the droplet when the temperature was near 60 °C resulted in dislodging of the drops to small bits; therefore the extraction efficiency was decreased. On the basis of these results, the temperature of the solution was adjusted at 30 °C in the subsequent experiments.

Effect of Extraction Time

The extraction time is defined as an interval from the injection of the supramolecular solvent to the start of centrifugation in the SMS-LLME procedure. In this study, the effect of extraction time on the extraction efficiency

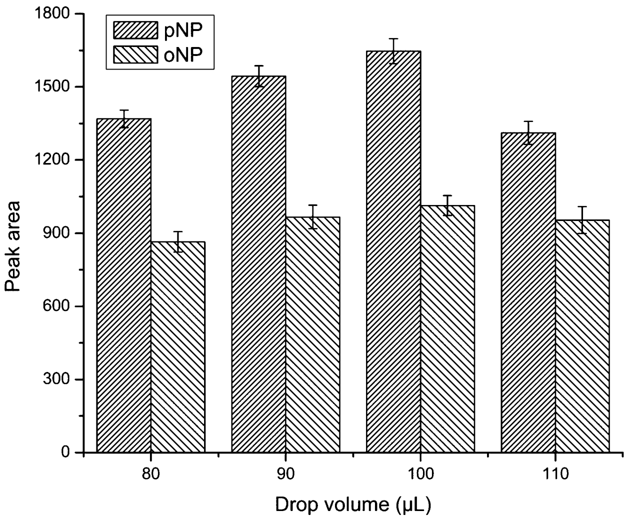

Fig. 1 Effect of supramolecular solvent volume on the SMS-LLME efficiency. Extraction conditions: sample solution, 17.5 mL of 200 μg L^{-1} of each nitrophenol; pH 6; stirring rate, 1,400 rpm; temperature, 30 °C; extraction time, 30 min

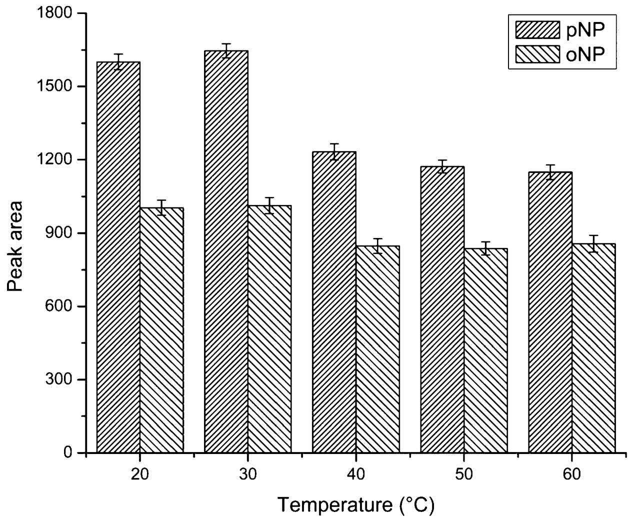

Fig. 2 Effect of temperature on the extraction efficiency of nitrophenols. Extraction conditions: sample solution, 17.5 mL of 200 μg L^{-1} of each nitrophenol; supramolecular solvent volume, 100 μL; pH 6; stirring rate, 1,400 rpm; extraction time, 30 min

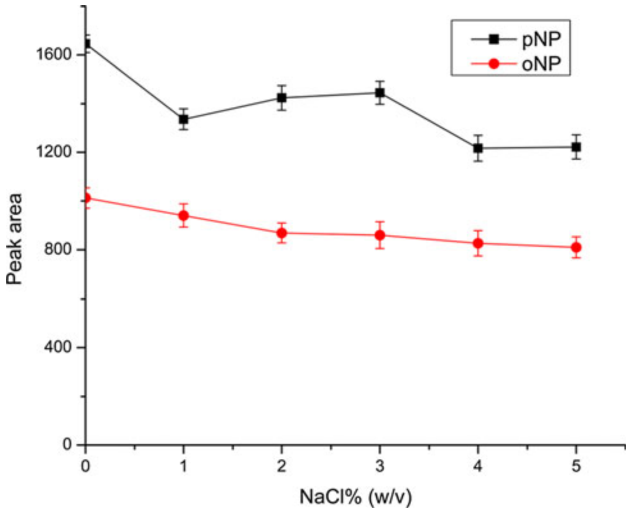

Fig. 3 Effect of salt addition on the SMS-LLME efficiency. Extraction conditions: sample solution, 17.5 mL of 200 μg L^{-1} of each nitrophenol; supramolecular solvent volume, 100 μL; pH 6; stirring rate, 1,400 rpm; temperature, 30 °C; extraction time, 30 min

was carried out by varying the extraction time from 10 to 50 min. The results indicated that the peak areas increased when the extraction time was increased from 10 to 30 min, and the equilibrium between the two phases was reached after 30 min. Therefore, the extraction time of 30 min was selected.

Effect of Ionic Strength

The addition of salt plays a vital role in conventional extraction processes because it can increase an aqueous solution's ionic strength, which decreases the solubility of the analytes in the sample solution as well as improves the extraction efficiency. To study the influence of ionic strength on SMS-LLME performance, experiments were carried out by adding different amounts of NaCl (0–5 %, w/v). It was found that salt concentration had an opposite effect for the two kinds of compounds (Fig. 3). This is possibly because at higher concentrations of salt, the vesicular droplet becomes unstable owing to bubble formation. Hence, no salt was added in the subsequent experiments.

Effect of pH

In most cases, the pH of samples can influence the state of analytes in aqueous solution, especially for a weak acid or weak alkali. As weak acid substances, nitrophenols exist in two forms in solution, a molecular state and an ionic state. The effect of sample pH was investigated in the range of 3–9 by adding appropriate amounts of sodium hydroxide or hydrochloric acid to water samples. The results showed that the maximal peak areas were acquired at pH 6. It seems that both neutral and ionized nitrophenols were efficiently extracted by the coacervates at this pH. On the basis of these results, pH 6.0 was selected for further studies.

Effect of Stirring Rate

Stirring the aqueous solution during the extraction makes a stable cloudy solution and accelerates the mass transfer of analytes from the aqueous solution to the extracting phase. The effect of stirring rate in the range of 1,000–1,800 rpm on the extraction efficiency of nitrophenols was studied. As can be seen in Fig. 4, peak areas increased by increasing the stirring rate up to 1,400 rpm, and then decreased as the stirring rate further increased. This is possibly because at higher stirring rate the vesicular droplet size decreases, so the collected solvent volume decreased and thus resulted in a decrease of extraction efficiency. Thus, all the extraction experiments were performed at 1,400 rpm stirring rate.

Quantitative Analysis

To evaluate the proposed SMS-LLME method, quantitative parameters of the method were investigated under the optimized conditions. The results are summarized in Table 1. Excellent linearity was observed in the concentration range of 2–1,000 μg L^{-1} for *p*-nitrophenol and *o*-nitrophenol with coefficients of correlation 0.9996 and 0.9997. The preconcentration factors (PFs) for the nitrophenols were calculated as the ratio of the final nitrophenols concentration in the supramolecular solvent phase and

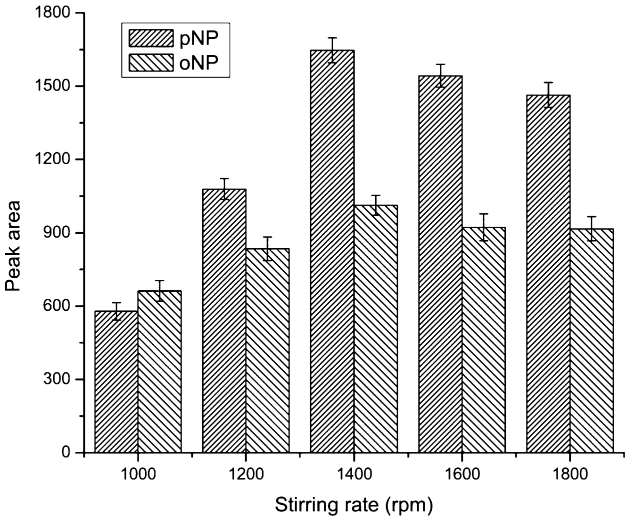

Fig. 4 Effect of stirring rate on the SMS-LLME efficiency. Extraction conditions: sample solution, 17.5 mL of 200 μg L^{-1} of each nitrophenol; supramolecular solvent volume, 100 μL; pH 6; temperature, 30 °C; extraction time, 30 min

Table 1 SMS-LLME performance and validation data

Analyte	Linearity		LOD (μg L^{-1})	Precision (RSD %, $n = 5$)		PF
	LDR (μg L^{-1})	R^2		Intraday	Interday	
pNP	2–1,000	0.9997	0.26	7.76	11.9	166
oNP	2–1,000	0.9996	0.58	5.85	10.2	160

the initial concentration of nitrophenols within the sample solution. The obtained PFs were high and varied between 160 and 166, and the chromatogram to prove the high preconcentraction efficiency is shown in Fig. 5. The limits of detection (LODs) for the nitrophenols based on a signal to noise ratio (S/N) of 3 varied in the range of 0.26–0.58 μg L^{-1}. Intraday precision was assessed by five determinations in 1 day, and the relative standard deviations (RSDs) were 5.85 and 7.76 %, respectively. The interday RSDs at five different days were in the range of 10.2–11.9 %. These excellent results confirmed that the proposed method has high sensitivity and stability, and may facilitate the analysis of nitrophenols at trace level.

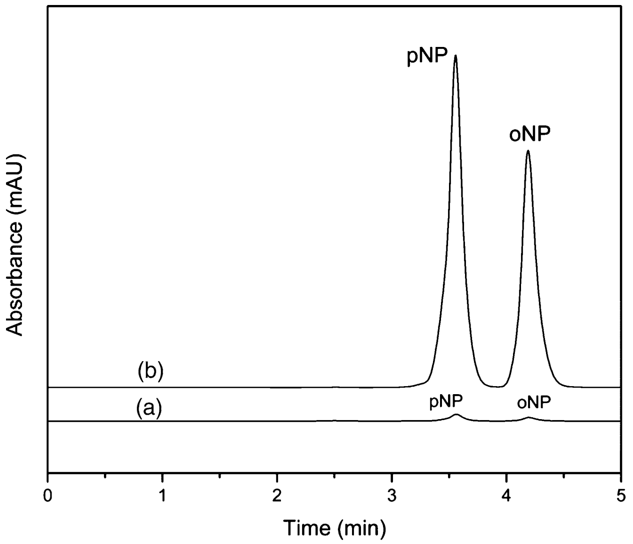

Fig. 5 HPLC chromatograms of the aqueous solution containing 200 μg L^{-1} nitrophenols *a* before SMS-LLME and *b* after SMS-LLME

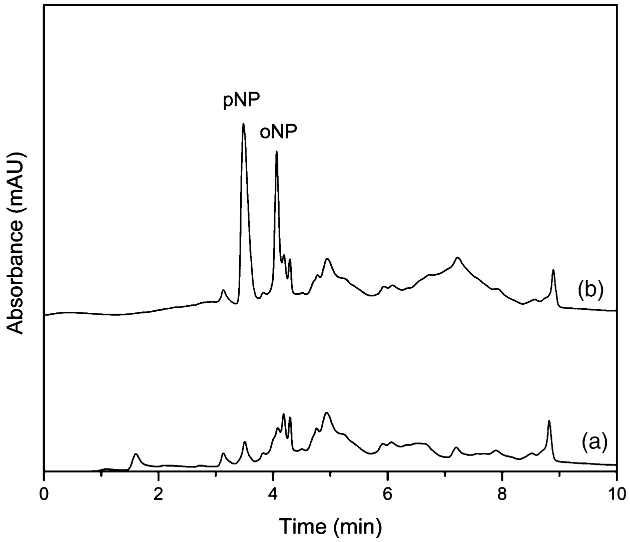

Fig. 6 HPLC chromatograms of the *a* non-spiked and *b* spiked river water (100 μg L^{-1} of the target analytes) analyzed with SMS-LLME

Analysis of Natural Water Samples

The practical applicability of the proposed method was evaluated by extracting nitrophenols from water samples of different sources including pond, river, and urban wastewater. The results showed that nitrophenol residues were below the detectable level in all samples. These water samples were then spiked with standards of the two nitrophenols at different levels to assess the matrix effect. The chromatograms of river water for blank and spiking at the concentration level 100 μg L^{-1} of nitrophenols are shown in Fig. 6. The relative recoveries (RR) for the two nitrophenols in pond, river, and urban wastewater were in the ranges of 90.6–98.2 and 92.2–97.3 %, respectively (Table 2), indicating that the proposed method is feasible for the determination of nitrophenols in water samples.

Comparison of SMS-LLME with Other Methods

Extraction and determination of nitrophenols in water samples by the proposed method were compared with those

Table 2 Determination of nitrophenols in water samples

Analyte	River water			Pond water			Urban wastewater		
	Conc. (μg L^{-1})	RR (%)	RSD (%)	Conc. (μg L^{-1})	RR (%)	RSD (%)	Conc. (μg L^{-1})	RR (%)	RSD (%)
pNP	<LOD	90.6	9.4	<LOD	94.3	11.4	<LOD	98.2	10.7
oNP	<LOD	92.2	8.9	<LOD	93.0	7.2	<LOD	97.3	6.5

Table 3 Comparison of SMS-LLME with other methods for the determination of nitrophenols

Analyte	Method	Extraction solvent	Linear range (μg L^{-1})	LOD (μg L^{-1})	RSD (%)	References
pNP	SPE-HPLC	–	5–1,000	1.1	4.8	[29]
pNP	SPME-HPLC	Methanol	100–2,500	18	9.8–13.2	[30]
pNP-oNP	HF-LPME-CE	1-Octanol	50–300	10–40	1.25–2.32	[9]
oNP	SDME-HPLC	[C$_4$MIM] [PF$_6$]	0.5–100	0.5	5.4–8.9	[8]
pNP-oNP	SMS-LLME	Supramolecular solvent	2–1,000	0.26–0.58	5.85–7.76	Proposed method

of other methods and the results are shown in Table 3. As shown, the advantages of the method described here over the other methods include (a) instead of volatile organic solvent, supramolecular solvent is used as the extraction solvent, which is safer and more environmentally friendly; (b) the linear range is wider; and (c) lower LODs in comparison with other methods. In conclusion, SMS-LLME presents a simple, fast, and environmentally friendly technique with low sample consumption that can be used for the preconcentration of nitrophenols from aqueous samples.

Conclusion

In this study, a novel, simple, and sensitive SMS-LLME technique coupled with HPLC was developed for the determination of nitrophenols in water samples. This method is attractive owing to its simplicity, sensitivity, analytical precision, low consumption of organic solvent, low cost, and short sample preparation time. The supramolecular solvents made up of tetrabutylammonium-induced vesicles of decanoic acid are proposed as valuable extraction solvents in this microextraction. To the best of our knowledge, this is the first time that the SMS-LLME was applied for the determination of *p*-nitrophenol and *o*-nitrophenol in real water samples with wide linearities, good precisions, and satisfactory relative recoveries. This technique possesses a great potential in the rapid preconcentration and analysis of other nitrophenol compounds in the environmental samples.

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