# Determination of Rhodamine B in Food Using Ionic Liquid–Coated Multiwalled Carbon Nanotube–Based Ultrasound-Assisted Dispersive Solid-Phase Microextraction Followed by High-Performance Liquid Chromatography

Xu Xu[1] · Minhui Zhang[1] · Lingling Wang[1] · Shuming Zhang[1] · Mingyang Liu[1] ·
Na Long[1] · Xinyu Qi[1] · Zizheng Cui[1] · Lei Zhang[1]

**Abstract** A modified Quick, Easy, Cheap, Effective, Rugged, and Safe method based on ultrasound-assisted dispersive solid-phase microextraction (dSPME) was developed for the determination of rhodamine B (RhB) in food samples. In this study, ionic liquid–coated multiwalled carbon nanotube (IL-MWCNT) was first used as dSPME material for the preconcentration of analyte. Several experimental parameters, including the type of ILs, the *ratios* of MWCNTs and ILs, amount of sorbent, extraction time, pH and ionic strength of sample solution, and desorption conditions, were evaluated. Under optimal experimental conditions, good linearity was observed in the range of 1.0–100.0 ng/mL with the correlation coefficient of 0.9978. The present method was applied to the analysis of different beverage and chili oil samples, and the recoveries of RhB obtained were in the range of 85.1–96.0 %. The results showed that the proposed method was a rapid, convenient, and feasible method for the determination of RhB in food samples.

✉ Lei Zhang
zhanglei63@126.com

[1] College of Chemistry, Liaoning University, 66 Chongshan Middle Road, Shenyang 110036, People's Republic of China

## Introduction

In recent years, food security issue has become the focus of threatening human survival. Rhodamine B (RhB), a synthetic dye, has been used for fluorescent labeling and food coloring due to its intense pink color (Nguyen and Francis 2003; Longmire et al. 2008). Synthetic dyes have several advantages compared with natural dyes, such as more colorfastness, greater stability, and lower production cost (Ma et al. 2006; Yoshioka and Ichihashi 2008; Long et al. 2011). However, because most synthetic dyes contain azoic groups and aromatic rings, they can result in allergy and asthmatic reactions, DNA damage, respiratory problem, thyroid tumors, chromosomal damage, hyperactivity, and abdominal pain when taken orally or absorbed by skin (Jain et al. 2007; Culzoni et al. 2009; Zhao et al. 2012). Now the use of synthetic dyes in foodstuffs is strictly controlled in many countries. However, to get major commercial benefits, the illegal use of prohibited dyes in foodstuffs is an ongoing problem. RhB was detected in several spices from Vietnam and paprika and chimi churri from Argentina. In view of the hazardous nature and harmful effects of RhB, developing a rapid and sensitive method to detect the compound in food is necessary.

Sample preparation is one of the most important steps in the analysis of samples, especially the analysis of complex samples. Due to the very low concentration of RhB residue in the complex sample matrices, an effective pretreatment method of sample is of vital importance for determination of RhB. In the reported methods, liquid–liquid extraction (Long et al. 2011) and solid-phase extraction (SPE) (Soylak et al. 2011) are widely used as sample preparation step for RhB determination. However, they suffer from the disadvantages of being time-consuming and using large amount of toxic organic solvents. Nowadays, a large number of

microextraction methods, such as solid-phase microextraction (SPME) (Cabaroglu et al. 2005; Adomaviciute et al. 2008) and liquid-phase microextraction (Asensio-Ramos et al. 2011; Abadi et al. 2012), which are more sensitive, cost-effective, and environmentally friendly, have become popular. Since these techniques are surface-dependent processes, a dispersive microextraction technique was recently proposed by means of dispersion to improve the contact area between sample solution and extractants and further shorten the extraction time and decrease the extractant consumption (Tsai et al. 2009; Yang et al. 2011). Tsai et al. proposed the functionalized silica-based sorbents for the extraction of tetracyclines in water and milk samples by the dispersive solid-phase microextraction (dSPME) method (Tsai et al. 2009). In the dSPME process, it is much easier for the target analytes to interact fully with the adsorbents, so higher adsorption capacities could be obtained in comparison with those in the traditional SPE. Moreover, the dSPME method is simple, rapid, and cost-effective. Since its emergence, the sorbent plays key role in obtaining higher enrichment efficiency of analytes. Up to date, developing new sorbent materials as extractants should be expected. Recently, carbon nanotubes (CNTs) are known to possess a strong adsorption affinity for a wide variety of organic compounds. Also, their large adsorption surfaces make them excellent materials for SPE of metal ions (Soylak and Unsal 2009; Soylak and Murat 2012) and SPME of organic analytes (Lu et al. 2007; Adomaviciute et al. 2008). However, CNTs are very prone to aggregation, which limits their excellent properties, mainly the ability to adsorb several compounds on their surface. Over the past decade, a variety of strategies have been devised to improve their solubility and dispersibility, mainly in strong acids or volatile organic solvents. In recent years, ionic liquid (IL) have emerged as "green" alternatives to volatile organic solvents for this purpose (Zhang et al. 2005; Wei et al. 2007; Yang et al. 2010). They are able to disperse CNTs by themselves, affording readily processed gelatinous substances. For this reason, ILs provide an excellent way to increase the CNT dispersibility without the need for solid substances or organic solvents. Recently, IL-modified multiwalled carbon nanotubes (IL-MWCNTs) have been prepared (Park et al. 2006; Karousis et al. 2010). They have excellent solubility and dispersibility in water, and the ionic liquid on the surface of carbon nanotubes has anion exchange groups. Both of them could be a potential sorbent for simultaneous extraction of the analytes with different polarity. To the best to our knowledge, IL-MWCNTs have not extracted RhB from food samples.

In the present study, an effective and rapid ionic liquid–coated multiwalled carbon nanotube–based ultrasound-assisted dispersive solid-phase microextraction (IL-MWCNT-UA-dSPME) method was first applied for one-step extraction and preconcentration of trace levels of RhB in food samples. The aim of this work is to simplify the analytical step, reduce the consumption of toxic solvents, and improve the sensitivity. Several experimental conditions, the type of ILs, the ratios of ILs and MWCNTs, amount of sorbent, extraction time, the pH and ionic strength of solution, and desorption conditions, were studied and optimized. The performances of developed method were evaluated.

## Materials and Methods

### Materials and Reagents

RhB was obtained from Dr. Ehrenstorfer (Dr. Ehrenstorfer GmbH, Augsburg, Germany). Stock standard solution for the RhB at the concentration level of 1000 µg/mL was prepared in methanol and stored at 4 °C in the dark. The working solutions were obtained daily by diluting the stock solutions with methanol or pure water. Chromatographic grade methanol was purchased from Fisher (Fisher Co., Pittsburgh, PA, USA). Analytical grade hydrochloric acid (HCl), sodium hydroxide, sodium chloride, ethanol, acetonitrile, and acetone were purchased from Beijing Chemicals (Beijing Chemical Factory, Beijing, China). Pure water was obtained with a Milli-Q water system (Millipore, Billerica, MA, USA). All the solvents and solutions were passed through a 0.45-µm nylon filter before being used. 1-Butyl-3-methylimidazolium hexafluorophosphate ([C$_4$MIM][PF$_6$]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C$_6$MIM][PF$_6$]), and 1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$MIM][PF$_6$]) were purchased from Chengjie Chemicals (Chengjie Chemical Co., Ltd., Shanghai, China).

MWCNTs (length 10–30 mm; specific surface area >500 m$^2$ g$^{-1}$; outer diameter <8 nm; 95 % purity) were purchased from Chengdu Organic Chemicals (Chengdu Organic Chemicals Co., Ltd., Chengdu, China).

### Instruments

An Agilent 1100 HPLC (Agilent, Palo Alto, CA, USA) equipped with an automatic sampler and diode array detector was used for the chromatographic analysis. Chromatographic separation of target analytes was performed on a Zorbax SB-C18 column (150 mm×4.6 mm I.D., 5 µm) (Agilent, Palo Alto, CA, USA).

UV–vis-NIR Cary 5000 (VARIAN Co., US) was used to record the absorption spectra of RhB. A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions. A model TDL80-2B centrifugal machine (Shanghai Anting Scientific Instrument Co., China) was used for sample treatment. The functional groups of IL-MWCNT surface was detected by AVATAR 330 Fourier transform infrared (FTIR) spectroscopy (NICOLET Co., USA).

## Sample Preparation

### Beverages

The beverage samples, including wine (sample 1), grape juice (sample 2), and blueberry juice (sample 3), were purchased from a local supermarket (Shenyang, China). The spiked beverage sample was prepared by spiking the working solution into 25 mL of beverage sample. In order to reduce the viscosity of the sample and be convenient for experimental operation, beverage samples were diluted 1:1 with pure water. The resulting solution was referred to as sample solution, filtered through 0.45-μm filters, and then stored at 4 °C.

### Chili oil

Chili oil samples (sample 4–6) were purchased from a local supermarket. Five grams of the sample was weighted into a 50-mL centrifuge tube and then was spiked with the working solution of RhB and then extracted with 10 mL of methanol. The supernatant was collected and diluted to 50 mL with pure water. The resulting solution was referred to as sample solution, filtered through 0.45-μm filters, and then stored at 4 °C.

## Sorbent Preparation

One hundred milligrams of MWCNTs and 100 μL of IL were placed into a 50-mL beaker. To ensure the IL to be well distributed, a reasonable amount of methanol was added until the mixture can be completely immersed in methanol. Then, the mixture was dispersed thoroughly by ultrasonic assistance for 30 min and evaporated to dryness under a nitrogen flow.

## IL-MWCNT-UA-dSPME

An amount of 15 mg of sorbent, 7.5 %$w/v$ NaCl were added to 50 mL of spiked sample solution adjusted at pH 3 using 2 mol/L HCl. After performing the extraction by ultrasonic for 3 min at room temperature, the sorbent was collected using a centrifuge at 4000 rpm for 10 min. Then, the extracted analyte was ultrasonically desorbed with 3.0 mL of ethanol + 2 % HCl (2 mol/L) for 1 min, and the solid/liquid phases were separated by centrifuging at 4000 rpm for 5 min. The supernatant was collected and evaporated to dryness under a gentle $N_2$ stream. The residue was dissolved in 500 μL of methanol. The resulting solution was referred to as analytical solution, filtered through a 0.22-μm PTFE filter membrane, and stored at 4 °C for HPLC analysis.

## Chromatographic Conditions

The mobile phase was a mixture of methanol–water (75:25 $v/v$). The flow rate and column temperature were set at 1.0 mL/ min and 30 °C, respectively. The detection wavelength for RhB was set at 550 nm. The injection volume of sample solution was 20 μL.

## Results and Discussion

### Characterization of IL-MWCNTs

The morphology of IL-MWCNTs was characterized by TEM. Figure 1A, B showed the typical TEM image of MWCNTs and IL-MWCNTs, which were dispersed in deionized water by sonication, respectively. It could be seen that MWCNTs were highly entangled with the diameter of several tens of nanometers. As a comparison, MWCNTs were much unfolded and a little widened after being treated with IL, indicating that IL could untangle MWCNTs and increase the effective surface area of MWCNTs.

The evidence for the successful adsorption of [$C_4$MIM][$PF_6$] onto the surface of MWCNTs is provided by FTIR spectra. The infrared spectra of MWCNTs (a) and [$C_4$MIM][$PF_6$]-coated MWCNTs (b) are presented in Fig. 1. Many absorption signals were matched between the two spectra. However, the stretching vibration of C–H band at 2972 and 3140 cm$^{-1}$, and the vibration of N–H in imidazole ring at 1470 cm$^{-1}$ appeared in the spectrum of the [$C_4$MIM][$PF_6$]-coated MWCNTs, as shown in Fig. 1b, indicating that [$C_4$MIM][$PF_6$] was successfully coated on the surface of MWCNTs.

### Optimization of the Solvent Extraction Step

For the performances of dSPME methods, the first step is to extract analytes from the solid samples with the appropriate solvent which would not affect the dSPME method. In this study, methanol, ethanol, acetonitrile, and acetone were used to extract the RhB from the chili oil samples, and the best extraction performance was obtained with methanol. In addition, 10 mL of methanol was enough to extract RhB from the 5-g chili oil sample, and the recovery had no significant difference. Therefore, 10 mL of methanol was used as extraction solvent for chili oil samples.

### Optimization of IL-MWCNT-dSPME Conditions

The parameters that affect the extraction efficiency, including the type of ILs, the ratios of ILs and MWCNTs, amount of sorbent, extraction time, the pH and ionic strength of solution, and desorption conditions, were investigated. All the experiments were performed in

**Fig. 1** TEM images of MWCNTs (A) and IL-MWCNTs (B); FTIR spectra of (**a**) MWCNTs and (**b**) IL-MWCNTs
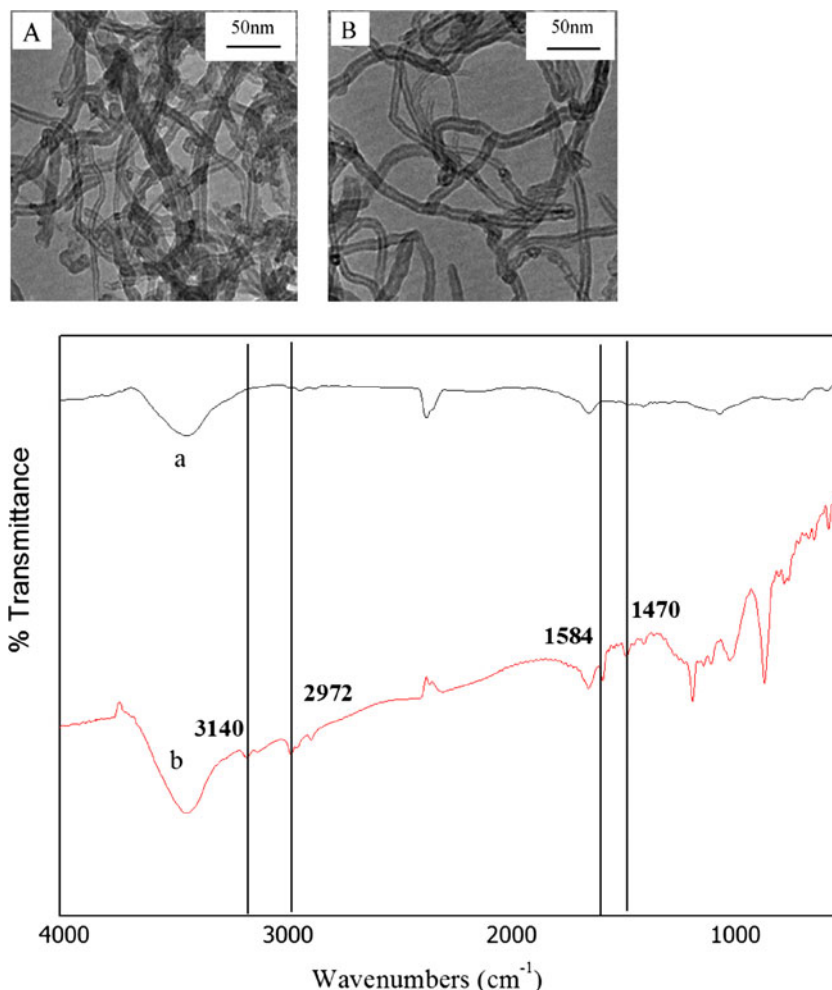


triplicate and the concentration of RhB in the spiked samples was 10.00 μg L$^{-1}$.

### Effect of the Type of ILs

The structures of ILs have significant influence on its physicochemical properties, which might greatly affect the recovery of the target analytes. In this work, three kinds of ILs, including [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$], and [C$_8$MIM][PF$_6$], were used as the extraction solvents, and the results are shown in Fig. 2a. It was observed that the recovery of the analyte obtained with [C$_8$MIM][PF$_6$] is significantly lower than that obtained with [C$_4$MIM][PF$_6$] and [C$_6$MIM][PF$_6$]. The reason maybe that the solubility of [C$_8$MIM][PF$_6$] in water is lower than that of [C$_4$MIM][PF$_6$] and [C$_6$MIM][PF$_6$]. Although the recovery obtained with [C$_4$MIM][PF$_6$] is comparable to those obtained with [C$_6$MIM][PF$_6$], increasing alkyl chain length can lead to increase of the solution viscosity, which may have negative effect on mass transfer. Therefore, [C$_4$MIM][PF$_6$] was selected as extraction solvent for further studies.

### Effect of the Ratios of ILs and MWCNTs

The volume of IL used in preconcentration procedure based on microextraction techniques was a crucial parameter for obtaining high performance and a high volume ratio of phases. The effect of the ratios of MWCNTs to IL, including 1:0, 1:0.5, 1:1, 1:2, 1:3, and 1:4, was tested. It is seen from Fig. 2b that the effect of the ratios on the recoveries is *significant*. When the mass ratio is 1:1, the recoveries of analyte are all *higher* than those obtained at the other mass ratio. Thus, the ratio of 1:1 was selected in this study.

### Effect of the amount of sorbent

The amount of the sorbent has a direct effect on the extraction of RhB. Different amounts of the sorbent ranging from 5 to 20 mg were applied to extract RhB from sample solution. The results indicated that 15 mg sorbent was enough for the extraction (Fig. 2c) with the recoveries ranging from 75.5 to 93.0 %. Further increasing the amount of the adsorbents gave
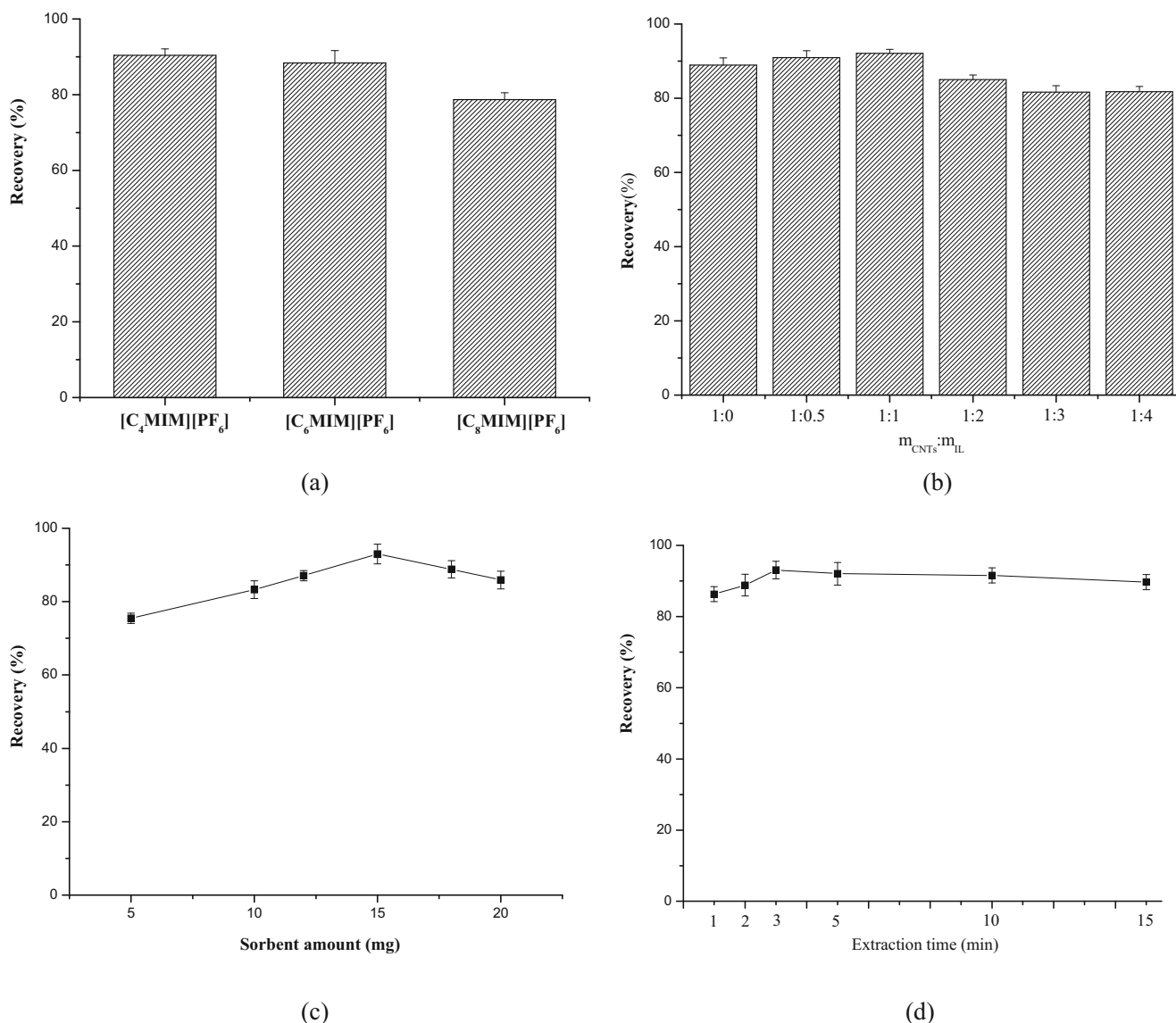
(a)

(b)

(c)

(d)

Fig. 2 The effect of the type of ILs (**a**), the *ratios* of ILs and MWCNTs (**b**), the amount of sorbent (**c**), and extraction time (**d**)

no significant improvement for the recoveries of RhB; therefore, 15 mg was selected as the amount of the adsorbents.

### Effect of Extraction Time

The extraction recovery is highly dependent on the mass transfer of analyte from sample solution to the sorbent. As a result, the effect of the extraction time from 1 to 15 min on the recoveries of RhB was investigated. The results indicated that the recoveries of RhB increased by extending the extraction time from 1 to 3 min, *until equilibrium was rapidly attained around* 3.0 min (Fig. 2d). The high surface area of IL-MWCNTs along with homogeneous distribution of the nanosorbent throughout the sample could be the possible reason for achieving such a fast extraction process. Moreover, the
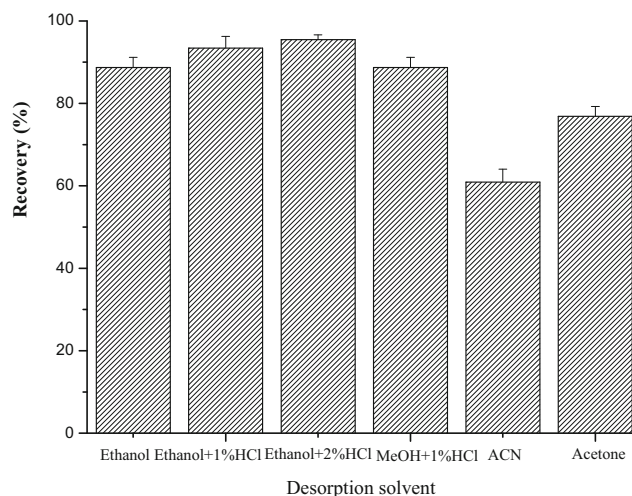


Fig. 3 Effect of desorption solvent

ultrasound can also increase the rate of mass transfer of analyte. This is a superior advantage over the conventional SPE and other microextraction techniques, which usually need more than 30–60 min to reach the equilibrium. Therefore, 3 min was chosen as the extraction time in this study.

## Effect of pH

Sample pH plays an important role in partitioning of the analytes especially those bearing ionizable polar groups. To evaluate the effect of sample pH in the present study, it was

**Fig. 4** The typical chromatograms of the blank (A) and spiked sample (B). (a) Wine, (b) chili oil. The concentrations of analyte are 2.0 μg/L in sample 1 and 10.0 μg/kg in sample 4
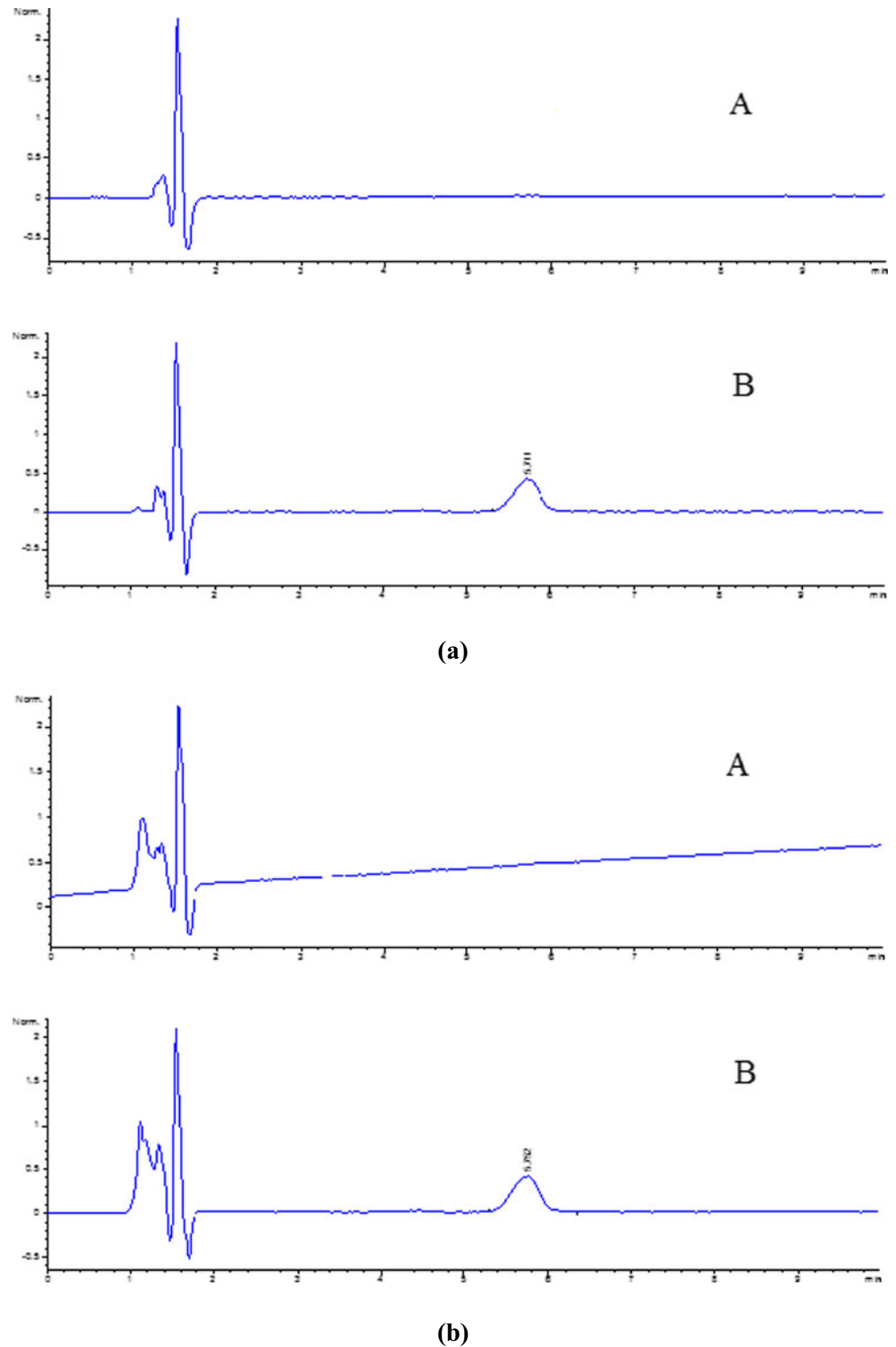


(a)



(b)

**Table 1** The intra- and inter-day precisions and recoveries of the assay (n=5).

| Sample | Added (ng/mL) | Intra-day | | Inter-day | |
|---|---|---|---|---|---|
| | | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) |
| Sample 1 | 2.0 | 94.8 | 3.1 | 91.5 | 4.7 |
| | 10.0 | 91.3 | 4.8 | 93.3 | 5.1 |
| | 20.0 | 95.0 | 2.7 | 96.0 | 6.0 |
| Sample 2 | 2.0 | 93.4 | 4.4 | 95.8 | 5.9 |
| | 10.0 | 90.9 | 1.7 | 93.0 | 4.2 |
| | 20.0 | 95.3 | 3.2 | 94.1 | 6.1 |
| Sample 3 | 2.0 | 92.5 | 4.6 | 94.2 | 4.8 |
| | 10.0 | 95.0 | 3.3 | 95.1 | 3.2 |
| | 20.0 | 93.7 | 2.9 | 93.4 | 5.9 |
| Sample 4 | 2.0 | 88.7 | 1.9 | 90.8 | 2.8 |
| | 10.0 | 90.4 | 3.4 | 89.5 | 4.7 |
| | 20.0 | 91.9 | 4.0 | 91.3 | 3.9 |
| Sample 5 | 2.0 | 87.5 | 4.7 | 93.6 | 5.0 |
| | 10.0 | 90.1 | 2.6 | 85.1 | 6.8 |
| | 20.0 | 92.0 | 3.0 | 90.0 | 4.3 |
| Sample 6 | 2.0 | 91.6 | 2.9 | 88.5 | 4.1 |
| | 10.0 | 88.7 | 3.5 | 93.0 | 2.9 |
| | 20.0 | 90.8 | 3.7 | 86.4 | 5.0 |

RSD relative standard deviation

varied from 2 to 11. The recovery of RhB increases slightly with the increase of pH values ranging from 2.0 to 3.0 and then decreases significantly with the increase of the pH values ranging from 3.0 to 11.0. This result may be related to the formation of different ionic species and the difference of UV absorption intensities of RhB at different pH values. On the one hand, the recovery of RhB is low in low pH medium, especially in strong acidic medium (Su et al. 2015). When pH value increases from 2.0 to 3.0, RhB is transformed from the cationic form into the zwitterionic form, which results in an increase in the recovery of RhB into ionic liquid. The attractive electrostatic interaction between $N^+$ group of ionic liquid and $COO^-$ group of the zwitterion is beneficial to the extraction of RhB into ionic liquid (Su et al. 2015). On the

other hand, the UV absorption band of RhB at approximately 550 nm was observed in acidic media, and the increase in the pH of the medium can result in the decrease in absorption intensity of the band (Soylak et al. 2011). Moreover, at high pH value, a small amount of RhB can be transformed into lactonic form, which can result in a low absorbance (Su et al. 2015). Based on the experimental results, the pH 3.0 was the best compromise.

### Effect of Ionic Strength

Addition of salt usually increases the ionic strength of the aqueous solution and would affect the solubility of organic solutes. This can be explained by the engagement of water

**Table 2** Comparison of the proposed method with other methods for the determination of RhB

| Method | Matrix | Recovery (%) | RSD (%) | Extraction time (min) | EF | LOD (ng/mL) | Reference |
|---|---|---|---|---|---|---|---|
| CPE-spectrophotometry | waste water | 96–103.5 | 0.87–2.4 | 30 | – | 1.3 | Pourreza et al. (2008) |
| MIPs-SPE-HPLC | waste water | 78.47–101.6 | 0.19–1.71 | 30 | – | 3.4 | Su et al. (2015) |
| SPE-spectrophotometry | soft drink, waste water and lipstick | 96–118 | 5.0 | – | 40 | 3.14 | Soylak et al. (2011) |
| DLLME | Tap water | 100–104.6 | 1.3 | – | 65.5 | 1.05 | Taziki et al. (2012) |
| This work | Beverage | 85.1–96.0 | 1.7–6.8 | 3 | 451 | 0.28 | Present study |

RSD relative standard deviation, EF enrichment factor, LOD limit of detection, CPE cloud point extraction, MIPs-SPE-HPLC magnetic molecularly imprinted polymers with HPLC, SPE solid-phase extraction

molecules in the hydration spheres around the ionic salt. These hydration spheres reduce the concentration of water available to dissolve solute molecules. This should, then, drive additional solutes into extracting medium. Considering these facts, the influence of salt addition was studied in the range of 0–10 % (w/v) of NaCl. Addition of salt up to 7.5 % (w/v) caused an increase in distribution constant of analyte between aqueous solution and sorbent and resulted in the increased extraction efficiency. Due to the enhancement in solution viscosity, a significant decrease in extraction efficiency of analyte was observed when the amount of salt exceeded 7.5 %w/v. Consequently, an amount of 7.5 %w/v NaCl was added to the extraction solution in further experiments.

**Desorption Conditions**

The desorption of RhB from the adsorbents was studied with different organic solvents, including ethanol, ethanol + 1 % HCl (2 mol/L), ethanol + 2 % HCl (2 mol/L), methanol + 1 % HCl (2 mol/L), acetonitrile, and acetone. As can be seen in Fig. 3, the best desorption performance was obtained with ethanol + 2 % HCl (2 mol/L). Therefore, ethanol + 2 % HCl (2 mol/L) is used as the desorption solvent.

Moreover, different volumes of desorption solvent ranging from 0.5 to 10 mL were also investigated and 3 mL of ethanol + 2 % HCl was enough to desorb RhB from the sorbent.

The effect of desorption time from 1 to 10 min was investigated. A desorption time of 1 min appeared to be sufficient for complete desorption. Finally, 1 min was selected as the optimum desorption time.

**Method Evaluation**

*Analytical Performances*

Under the optimal experimental conditions, a series of experiments were performed to obtain linear range, precision, the limit of detection (LOD) and quantification (LOQ), and enrichment factor (EF). The working curve was constructed by plotting the peak areas measured versus the concentrations of analyte in the spiked pure water samples. Good linearity was observed in the range of 1.0–100.0 ng/mL with the correlation coefficients (r) of 0.9978. The LOD and LOQ are determined based on the signal-to-noise ratio (S/N) of 3 and 10 and found to be 0.28 and 0.93 ng/mL, respectively. Under optimal conditions, EF (91) was obtained. To obtain EF, the standard curve was constructed by plotting the peak areas measured versus the analyte concentrations in the standard solution. The results indicate that the present method should be a feasible method in the determination of trace RhB.

*Analysis of Samples*

To evaluate the applicability of the proposed method, some real samples, including beverage samples (wine, grape juice, and blueberry juice) and chili oil samples, were analyzed. The typical chromatograms of the blank and spiked sample are shown in Fig. 4. As can be seen, no significant interference peaks were found at the retention time of RhB.

To evaluate precision and accuracy of the proposed method, the spiked samples were analyzed. Precision was evaluated by measuring intra-day and inter-day relative standard deviations (RSDs). The intra-day and inter-day precisions of the method were evaluated by analyzing the spiked draft beer samples at three concentrations levels on the same day and the 5 consecutive days, respectively. The results obtained are shown in Table 1, and the results indicate that the present method has good repeatability. RSDs and recoveries are in the range of 1.7–6.8 and 85.1–96.0 %, respectively. It can be considered that the present method provides acceptable recoveries for the determination of RhB in real samples.

**Comparison of IL-MWCNT-dSPME with Other Methods**

Some other methods reported in literature, such as cloud point extraction (CPE) with spectrophotometry (Pourreza et al. 2008), magnetic molecularly imprinted polymers with HPLC (MIPs-SPE-HPLC) (Su et al. 2015), SPE-spectrophotometry (Soylak et al. 2011), and DLLME with spectrophotometry (Rezaee et al. 2010; Taziki et al. 2012; Xiao et al. 2014), were compared with the proposed method, and the results are presented in Table 2. Compared with the reported methods, when the proposed method was applied, the LOD is lower, the extraction time is shorter, and the EF is higher, because ultrasound can obviously improve the analytical performance and extraction and preconcentration can be performed simultaneously. The results indicated that the proposed method was time-saving, convenient, sensitive, and suitable for determination of RhB in complex matrices, such as beverages and chili oil.

**Conclusion**

In this work, a simple and rapid method for analysis of RhB in beverage and chili oil samples has been developed based on ultrasound-assisted dispersive solid-phase microextraction coupled with HPLC determination. IL-MWCNTs were successfully used as adsorbent in dSPME for the extraction and preconcentration of RhB. The results demonstrated that the proposed method gives good recoveries and reproducibilities. The proposed method promises simplicity, less organic solvent consumption, and high sensitivity. Additional work is in progress on evaluating the performance of proposed method

for the determination of other food colorant residues in various matrices.

**Compliance with ethics standards**

**Ethical approval**  This article does not contain any studies with human or animal subjects.

**Informed consent**  Not applicable.

**Conflict of interest**  Xu Xu declares that he has no conflict of interest.
Minhui Zhang declares that he has no conflict of interest.
Lingling Wang declares that he has no conflict of interest.
Shuming Zhang declares that he has no conflict of interest.
Mingyang Liu declares that he has no conflict of interest.
Na Long declares that he has no conflict of interest.
Xinyu Qi declares that he has no conflict of interest.
Zizheng Cui declares that he has no conflict of interest.
Lei Zhang declares that he has no conflict of interest.

# References

Abadi MDM, Ashraf N, Chamsaz M, Shemirani F (2012) An overview of liquid phase microextraction approaches combined with UV–vis spectrophotometry. Talanta 99:1–12

Adomaviciute E, Jonusaite K, Barkauskas J, Vickackaite V (2008) Ingroove carbon nanotubes device for SPME of aromatic hydrocarbons. Chromatographia 67:599–605

Asensio-Ramos M, Ravelo-Pérez L, Ángel González-Curbelo M, Hernández-Borges J (2011) Liquid phase microextraction applications in food analysis. J Chromatogr A 1218:7415–7437

Cabaroglu T, Selli S, Kafkas E, Kurkcuoglu M, Canbas A, Baser KHC (2005) Determination of volatile compounds in sultaniye wine by solid-phase microextraction techniques. Chem Nat Compd 41:382–384

Culzoni M, Schenone A, Llamas N, Garrido M, Nezio M (2009) Fast chromatographic method for the determination of dyes in beverages by using high performance liquid chromatography-diode array detection data and second order algorithms. J Chromatogr A 1216:7063–7070

Jain R, Mathur M, Sikarwar S, Mittal A (2007) Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. J Environ Monit 85:956–964

Karousis N, Ichihashi T, Chen S, Shinohara H, Yudasaka M, Iijima S et al (2010) Imidazolium modified carbon nanohorns: switchable solubility and stabilization of metal nanoparticles. J Mater Chem 20:2959–2964

Long C, Mai Z, Yang X, Zhu B, Xu X (2011) A new liquid-liquid extraction method for determination of 6 azo-dyes in chilli poducts by high-performance liquid chromatography. Food Chem 126:1324–1329

Longmire MR, Ogawa M, Hama Y, Kosaka N, Regino CAS, Choyke PL et al (2008) Determination of optimal rhodamine fluorophore for in vivo optical imaging. Bioconjug Chem 19:1735–1742

Lu J, Liu J, Wei Y, Jiang K, Fan S, Liu J et al (2007) Preparation of single-walled carbon nanotube fiber coating for solid-phase microextraction of organochlorine pesticides in lake water and wastewater. J Sep Sci 30:2138–2143

Ma M, Luo X, Chen B, Su S, Yao S (2006) Simultaneous determination of water-soluble and fat-soluble synthetic colorants in foodstuff by high-performance liquid chromatography-diode array detection-electrospray mass spectrometry. J Chromatogr A 1103:170–176

Nguyen T, Francis MB (2003) Practical synthetic route to functionalized rhodamine dyes. Org Lett 5:3245–3248

Park MJ, Lee JK, Lee BS, Lee YW, Choi IS, Lee SG (2006) Covalent modification of multiwalled carbon nanotubes with imidazolium-based ionic liquids: effect of anions on solubility. Chem Mater 18:1546–1551

Pourreza N, Rastegarzadeh S, Larki A (2008) Micelle-mediated cloud point extraction and spectrophotometric determination of rhodamine B using Triton X-100. Talanta 77:733–736

Rezaee M, Yamini Y, Faraji M (2010) Evolution of dispersive liquid-liquid microextraction method. J Chromatogr A 1217:2342–2357

Soylak M, Murat I (2012) Determination of copper, cobalt, lead, and iron in table salt by faas after separation using violuric acid and multiwalled carbon nanotubes. Food Anal Methods 5:1003–1009

Soylak M, Unsal YE (2009) Simultaneous enrichment-separation of metal ions from environmental samples by solid-phase extraction using double-walled carbon nanotubes. J AOAC Int 92:1219–1224

Soylak M, Unsal YE, Yilmaz E, Tuzen M (2011) Determination of Rhodamine B in soft drink, waste water and lipstick samples after solid phase extraction. Food Chem Toxicol 49:1796–1799

Su X, Li X, Li J, Liu M, Lei F (2015) Synthesis and characterization of core-shell magnetic molecularly imprinted polymers for solid-phase extract ion and determination of Rhodamine B in food. Food Chem 171:292–297

Taziki M, Shemirani F, Majidi B (2012) Robust ionic liquid against high concentration of salt for preconcentration and determination of rhodamine B. Sep Purif Technol 97:216–220

Tsai WH, Huang TC, Huang JJ, Hsue YH, Chuang HY (2009) Dispersive solid-phase microextraction method for sample extraction in the analysis of four tetracyclines in water and milk samples by high-performance liquid chromatography with diode-array detection. J Chromatogr A 1216:2263–2269

Wei D, Kvarnstrom C, Lindfors T, Ivaska A (2007) Electrochemical functionalization of single walled carbon nanotubes with polyaniline in ionic liquids. Electrochem Commun 9:206–210

Xiao N, Deng J, Huang K, Ju S, Hu C, Liang J (2014) Application of derivative and derivative ratio spectrophotometry to simultaneous trace determination of rhodamine B and rhodamine 6G after dispersive liquid-liquid microextraction. Spectrochim Acta A Mol Biomol Spectrosc 128:312–318

Yang Y, Qiu S, He C, He W, Yu L, Xie X (2010) Green chemical functionalization of multiwalled carbon nanotubes with poly(−caprolactone) in ionic liquids. Appl Surf Sci 257:1010–1014

Yang Z, Liu Y, Lu Y, Wu T, Zhou Z et al (2011) Dispersive suspended microextraction. Anal Chim Acta 706:268–274

Yoshioka N, Ichihashi K (2008) Determination of 40 synthetic food colors in drinks and candies by high-performance liquid chromatography using a short column with photodiode array detection. Talanta 74:1408–1413

Zhang Y, Shen Y, Li J, Niu L, Dong S et al (2005) Electrochemical functionalization of single-walled carbon nanotubes in large quantities at a room-temperature ionic liquid supported three-dimensional network electrode. Langmuir 21:4797–4800

Zhao S, Yin J, Zhang J, Ding X, Wu Y, Shao B (2012) Determination of 23 dyes in chili powder and paste by high-performance liquid chromatography-electrospray ionization tandem mass spectrometry. Food Anal Methods 5:1018–1026