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Dispersive liquid–liquid microextraction–spectrophotometry combination for determination of rhodamine B in food, water, and environmental samples

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ABSTRACT

A new dispersive liquid–liquid microextraction procedure combined with UV–visible spectrophotometry is described for sensitive and selective determination of rhodamine B. Various analytical parameters such as pH, extraction and dispersive solvents type and volume, sample volumes, and extraction time were optimized. Matrix effects of concomitants were also examined. Preconcentration factor was found to be 330. Detection limit was calculated as 2.1 μg L^{-1}. The relative standard deviation was found to be 4%. The validation of the developed procedure was checked by the addition/recovery tests. The procedure was successfully performed to the determination of trace levels of rhodamine B in drug, ink, food, cosmetic product, and waste waters.

Keywords: Microextraction; Spectrophotometry; Rhodamine B; Drug; Cosmetic; Food; Waste water

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1. Introduction

Toxic and cancerous effects of rhodamine dyes are generally known. They are soluble in water and organic solvents [1]. Rhodamine causes irritation to the skin, eyes, and respiratory tract [2–4]. The presence of carcinogenic dye like rhodamine B in textile and cosmetic waste water affects the quality of water to consumers. Rhodamine B is used to dye various textile products [2,5–10].

Various analytical methods have been used for the detection of dyes such as differential pulse polarography, voltammetry, liquid chromatography–chemiluminescence, and micellar electrokinetic capillary chromatography [11,12]. UV–visible spectrophotometer is one of the most reliable technique for the detection of rhodamine dyes, because it is simple and has a lower cost than other instruments. Due to low concentrations of rhodamine dyes in environmental samples and matrix interferences, there is a necessity for the enrichment and separation procedures [13,14].

Several techniques have been applied for the separation and enrichment of organic and inorganic pollutants including adsorption, dispersive liquid–liquid extraction, micellar extraction, etc. [15–19]. Dispersive liquid–liquid microextraction (DLLME) [20] is based on a ternary component solvent system like homogeneous solvent extraction techniques [21–23]. The principal advantages of the method are the low cost of common solvents, the use of simple equipment, high

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recoveries, and enrichment factors. According to our literature survey, until now, DLLME procedure is not used for separation and preconcentration of rhodamine B in drug, ink, food, cosmetic product, and waste waters.

The aim of this work is to combine DLLME with UV–visible spectrophotometry and propose a new technique for separation, preconcentration and determination of trace amounts of rhodamine B in real samples.

2. Experimental

2.1. Instrument

A Hitachi 150–20 spectrophotometer with quartz micro cell, a path length of 10 mm, and a volume of 700 µL was used for absorbance measurements. pH values were measured with a PHS-3C pH meter (model Nel pH-900 Nel Company, Ankara, Turkey) supplied with a combined glass electrode. ALC PK 120 model centrifuge (Buckinghamshire, England) was used. The ultra pure water was prepared using a water purification system (Millipore Milli-Q system 18 MΩ cm^{-1} resistivity, Millipore, Bedford, MA, USA).

2.2. Solutions and reagents

All chemicals used were of analytical reagent grade (Merck, Darmstadt, Germany) and purchased from Sigma-Aldrich (Milwaukee, WI, USA). Rhodamine B was purchased from Sigma-Aldrich Co (Milwaukee, WI, USA). An amount of 1×10^{-3} mol L^{-1} stock solution of rhodamine B was prepared in ethanol and stored at 4°C in the dark. A calibration curve was established using the standard solutions by dilution from stock solutions. The pH values were adjusted by addition of phosphate buffer solutions ($H_2PO_4^-/H_3PO_4$), acetate buffer solutions (CH_3COO^-/CH_3COOH), and ammonium buffer solutions (NH_4^+/NH_3).

2.3. Analytical procedure

A 25 mL sample solution containing 2×10^{-6} M of rhodamine B at pH 4 was placed in a 50 mL conical tube. The pH of model solution was adjusted to 4.0 by using acetate buffer solutions. After 300 µL of chloroform and 1,000 µL of ethanol were added into the model solution, a cloudy solution was formed in the tube. The magnetic stirrer was turned on and the mixture was centrifuged at 3,500 rpm for 6 min. Then 50 µL of sediment phase was diluted with ethanol to 150 µL. Rhodamine B in solution was determined by UV–visible spectrophotometer at 556 nm.

2.4. Applications

The developed method was applied to drug, ink, food, cosmetic product, and different industrial waste water samples according to the procedure given in literature [7]. The pH of the samples was adjusted to 4 by acetate buffer solutions. Then the preconcentration procedure, as given above, was applied to all the samples. Blank samples were also analyzed. Rhodamine B in the samples was determined by UV–visible spectrophotometer at 556 nm. The validation of the developed method was checked by the standard addition method.

3. Results and discussion

3.1. Effect of the pH

The effects of pH on the recoveries of rhodamine B on the presented system was studied at the pH range of 2–10. The results are demonstrated in Fig. 1. pH adjustments of the solutions were done by the addition of related buffer. The recovery of rhodamine B was found quantitative in the pH range of 2.0–5.0. Accordingly, pH 4 was selected for further work and real sample analysis.

3.2. Disperser solvent

Ethanol was chosen for the subsequent experiments due to its less toxicity and the higher solubility for rhodamine B. The effect of the volume of ethanol on the extraction efficiency was also examined (Fig. 2). In order to optimize ethanol volume, various experiments were performed using different volumes of ethanol (0.1–2.5 mL) containing 2×10^{-6} M of rhodamine B and 300 µL of chloroform, respectively. At low volume, ethanol could not disperse chloroform properly

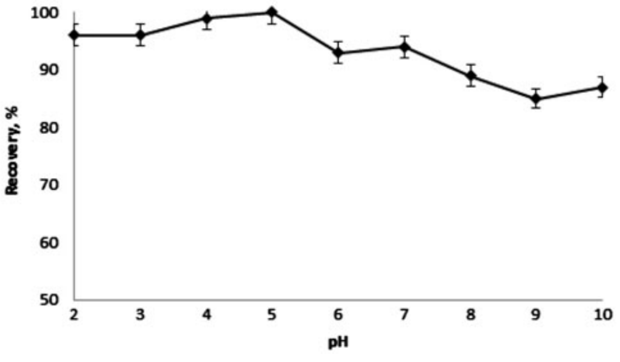

Fig. 1. Influences of pH on the recoveries of rhodamine B ($N = 3$).

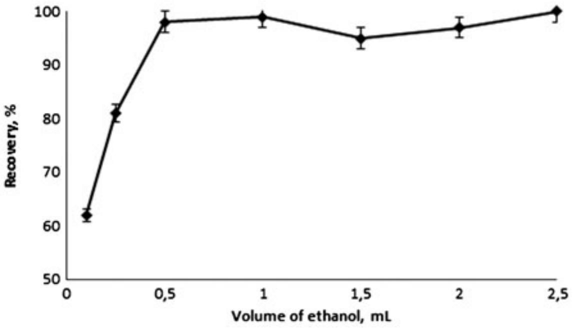

Fig. 2. Effects of ethanol volume on the recoveries of rhodamine B ($N = 3$).

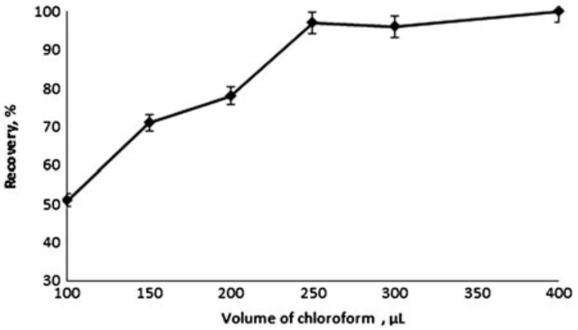

Fig. 3. Effects chloroform volume on the recoveries of rhodamine B ($N = 3$).

and cloudy solution was not formed completely. The recovery values of rhodamine B were quantitative at the volume of ethanol 0.5–2.5 mL. 1.0 mL ethanol was chosen for subsequent work and real sample analysis.

3.3. Extraction solvent

Chloroform was chosen as the extraction solvent for the presented system. In order to examine the effect of the extraction solvent volume, solutions containing different volume of chloroform (50–400 µL) were subjected to the same DLLME methods. The results are shown in Fig. 3. The recovery values of rhodamine B were obtained quantitative in the range of 250–400 µL of extraction solvent volume. Thereby, 300 µL of chloroform was used as extraction solvent in the further experiments.

3.4. Effect amount of NaCl

Sodium chloride was used to examine the effect of ionic strength on the extraction efficiency. For investigating the effect of the ionic strength on the DLLME

Table 1
Influences of some foreign ions on the recoveries of rhodamine B ($N = 3$)

Concomitant	Added as	Concentration (µg mL^{-1})	Recovery (%)
Na^+	NaCl	8,000	94 ± 1
SO_4^{2-}	Na_2SO_4	1,250	93 ± 2
K^+	KNO_3	2,000	94 ± 2
Mg^{2+}	$Mg(NO_3)_2$	2,500	95 ± 3
NO_3^-	KNO_3	2,500	92 ± 1
Cl^-	NaCl	12,500	96 ± 2
I^-	NaI	500	94 ± 1
F^-	NaF	500	96 ± 2
Ca^{2+}	$CaCl_2$	20,000	94 ± 2
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	30	93 ± 2
Cr^{3+}	$Cr(NO_3)_3$	30	99 ± 3
Cr^{6+}	K_2CrO_4	40	98 ± 1
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	40	96 ± 2
Fe^{2+}	$Fe(NO_3)_2$	25	99 ± 2
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	40	98 ± 1
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	40	101 ± 1
Mn^{2+}	$MnSO_4$	35	100 ± 2
Pb^{2+}	$Pb(NO_3)_2$	30	94 ± 3
Zn^{2+}	$Zn(NO_3)_2$	20	99 ± 1
Sunset yellow		3	100 ± 1
Allura red		2	99 ± 1
Sudan orange G		4	100 ± 2
Tatrazine		4	98 ± 1

performance, several experiments were applied by adding different amounts of NaCl from 0.0 to 10.0% (w/v). The maximum extraction efficiency was achieved in that containing 0.5–2.0% (w/v) amount of NaCl. Above this concentration range, the cloudy solution formation was unsatisfactory. Therefore, 1.0% (w/v) NaCl was used in all subsequent study.

3.5. Effects of centrifugation speed and time

The effects of centrifugation speed on the recoveries of rhodamine B, on the proposed method of DLLME, were examined in the speed range of 500–4,000 rpm with the constant experimental conditions. Quantitative recoveries (95%) were obtained in the range of 3,000–4,000 rpm.

The effects of centrifugation time on the recoveries were also investigated in the range of 1–10 min. The recoveries of rhodamine B on the recommended method of DLLME were higher than 95% in the range of 4–10 min. 3,500 rpm for 5 min was selected as centrifugation speed and time for further study.

3.6. Sample volume

The sample volume is a key factor to obtain high preconcentration factor [24–28]. The effects of sample volume on the quantitative extraction efficiencies of rhodamine B were examined in the range of 10–50 mL. The recoveries of rhodamine B were quantitative (95%) with 50 mL. A preconcentration factor of 330 can be achieved when using 50 mL of the sample volume and 150 μL of final volume.

3.7. Effect of foreign ions

In instrumental detection of the analytes at trace levels the effects of matrix components should be investigated [29–36]. Spectrophotometric detection of rhodamine B using DLLME showed the selectivity of the developed technique. The found results are summarized in Table 1. Under optimized parameters, model solutions of 2×10^{-6} M rhodamine B containing the added foreign ions were treated adequately to the development technique. The tolerance limit is described as some azo dyes, heavy metals, cations, and anions concentrations causing a relative error smaller than 5%.

3.8. Analytical figures of merit

The analytical characteristics data of the recommended method of DLLME were achieved under the optimum experimental parameters. The calibration graph was linear in range of 0.1–3.0 μg mL^{-1} with a correlation coefficient (r^2) of 0.9997. The regression

Table 2
Tests of addition/recovery in the experiments for rhodamine B (Sample volume: 50 mL, $N = 3$)

Samples	Added (μg)	Found (μg)	Recovery (%)
Waste water from food industry	0	BDL	
	0.25	0.24 ± 0.01	98
	0.5	0.48 ± 0.02	96
	1.0	0.97 ± 0.03	97
Drug 1	0	4.8 ± 0.2	
	0.5	5.3 ± 0.3	100
	1.0	5.81 ± 0.3	101
	2.0	6.76 ± 0.5	98
Waste water from textile industry	0	13.2 ± 0.4	
	1.0	14.1 ± 0.7	91
	2.0	14.9 ± 0.7	89
	4.0	16.8 ± 0.8	91
Kizilirmak river water	0	BDL	
	0.25	0.25 ± 0.02	100
	0.5	0.49 ± 0.02	99
	1.0	0.95 ± 0.06	95
Fruit juice	0	BDL	
	0.25	0.23 ± 0.02	94
	0.5	0.45 ± 0.04	91
	1.0	0.93 ± 0.04	93

Note: BDL—Below the detection limit.

Table 3
Application of the method to the determination of rhodamine B in real samples ($N = 3$)

Samples	Concentration, $\mu g\ g^{-1}$
Drug 1	4.8 ± 0.2
Drug 2	BDL
Drug 3	BDL
Candy 1	BDL
Candy 2	BDL
Lipstick 1	12.1 ± 1.1
Lipstick 2	32.9 ± 2.1
Nail polish	18.9 ± 1.7
Rouge	12.3 ± 0.9
Ink 1	BDL
Ink 2	35.2 ± 2.4
	Concentration, $\mu g\ L^{-1}$
Antifreeze	10.7 ± 0.6
Fruit juice	BDL
Soft drink 1	BDL
Waste water from metal industry	BDL
Waste water from textile industry	13.2 ± 0.4

Note: BDL—Below the detection limit.

equation was $A = 0.2779C + 0.0037$. The limit of detection, defined as the concentration equivalent to 3 times the standard deviation ($n = 11$) of the reagent blank [7] was found as $2.1\ \mu g\ L^{-1}$. The relative standard deviation for ten-replicate measurement of 2×10^{-6} M rhodamine B was 4%. The method was repeated 10 times for rhodamine B. It was found that the recovery of rhodamine B was 98 ± 2 at 95% confidence level.

3.9. Applications

We have studied applicability of proposed DLLME method for the determination of rhodamine B in environmental water samples. The recommended preconcentration method was carried out to the determination of rhodamine B by standard addition tests. The validation of the procedure was checked by addition-recovery tests. The resulting data are demonstrated in Table 2. As it could be seen, the recoveries of rhodamine B for spiked samples were in the range of 95–100%. The development method was applied to drug, ink, food, cosmetic product, and different industrial waste water samples (Table 3).

4. Conclusions

A DLLME method for determination of trace amounts of rhodamine B using UV–visible spectrophotometry was established. The advantages of this method are low cost, minimum use of toxic organic solvent, enhancement of sensitivity, simple, rapid, and environmental friendly. The diverse ions effects with the developed procedure were reasonably tolerable. Our results are comparable with literature values with respect to both detection limit and preconcentration factor [5,7,10]. Low detection limit and high preconcentration factor were found in this study.

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