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Spectrophotometric detection of rhodamine B in tap water, lipstick, rouge, and nail polish samples after supramolecular solvent microextraction

Nebiye ÖZKANTAR[1], Mustafa SOYLAK[2], Mustafa TÜZEN[1,*]
[1]Department of Chemistry, Faculty of Science and Arts, Gaziosmanpaşa University, Tokat, Turkey
[2]Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey

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Abstract: A simple and sensitive supramolecular solvent-based dispersive liquid–liquid microextraction method was described for the separation/preconcentration and spectrophotometric detection of rhodamine B. The microextraction method, which was realized at ambient temperature for the detection of rhodamine B, was carried out by using supramolecular solvents such as tetrahydrofuran and decanoic acid. The method was based on analyses of rhodamine B by using UV-Vis spectrophotometry at 558 nm. The influences of some parameters such as pH, sample volume, eluent solutions, centrifugation time, and ultrasonic bath time were optimized. The effects of various matrix ions were also investigated. Moreover, the limit of detection and limit of quantification were calculated as 0.49 μg L^{-1} and 1.47 μg L^{-1}, respectively. The preconcentration factor was 30. The relative standard deviation was determined as 5.8% in 0.5 $\times$ 10^{-4} M rhodamine B. The procedure was validated by addition/recovery tests. The microextraction method was applied to determination of rhodamine B in tap water samples and cosmetic samples such as nail polish, rouge, and lipstick.

Key words: Preconcentration, rhodamine B, spectrophotometry, microextraction, cosmetic, water

1. Introduction

In industrial areas, dyes are used to color textiles, leather, paper, plastics, etc., and water is also consumed remarkably.[1] These dyes, which originate from industrial processes, enter the environment through waste water.[2] The presence of dyes in waste water is a major source of concern as it has negative effects on many areas of life. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons.[3] One of these dyes, rhodamine B, which appears red to violet, has a molecular weight of 479.02 g/mol and molecular formula of $C_{28}H_{31}ClN_2O_3$. It is commonly used as a tracer dye in water to determine the rate and direction of flow and transport. Rhodamine dyes are used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy, and ELISA.[4]

Due to its extensive pink color, rhodamine B has been widely used as a dye in many industrial applications, such as in the food, textile, drug, and cosmetic industries. Rhodamine B is used for coloring in many fields, such as in drugs, cosmetics, and textile products. It is also used as a tool for tracing water pollution. Its usage in industrial fields, which is a menace to human health, brings about toxicity for organisms living in water. It may cause long-term unhealthy effects in aquatic environments and it is harmful when it comes in contact with skin. On the other hand, rhodamine B may cause congenital diseases and cancer, which is the worst disease of our

*Correspondence: mustafa.tuzen@gop.edu.tr

age. Rhodamine B is a triphenylmethane dye. Due to the harmful effects of rhodamine B, many countries have prohibited it from using in food samples. Because of its harmful effects, rhodamine B, which exists in many samples such as waste water, is supposed to be removed with separation-enrichment and analysis methods. This requirement leads to the developing of many analytical methods.

Sample preparation is one of the most important steps in the analysis of rhodamine B with a UV-Vis spectrophotometer. Due to the very low concentrations of rhodamine B that can be found in environmental samples, cosmetics, and food samples and on account of its matrix effects, a number of effective separation and enrichment methods have been improved for the determination of rhodamine B.[5−7] Some of these methods are adsorption, cloud point extraction, and liquid–liquid extraction. These methods have some disadvantages such as causing considerable amounts of chemical solvent losses and usage, having a small preconcentration factor, and requiring many processes. Therefore, microextraction methods such as dispersive liquid–liquid microextraction, supramolecular solvent-based microextraction, and single drop microextraction have become popular. In this study, a supramolecular solvent-based microextraction process has been developed for the process of separation and enrichment of rhodamine B that exists at trace levels in various samples. This method is a well-defined supramolecular solvent system based on the merging of two or more components. As a result of this combination, the processing of polar and nonpolar solvent systems consists of two parts, which are nano and molecular in size.[8−13]

Analysis of dyes has been performed by fluorescence spectrometry, mass spectrometry, phosphorescence spectrometry, and UV-Vis spectrometry. UV-Vis spectrometry is very important and has been used substantially for determination of dyes due to its simple usage and being cheaper than other approaches. Most of the studies based on the determination of dye were performed using UV-Vis spectrometry.[14−21]

The aim of this study was to develop a simple and rapid supramolecular solvent-based microextraction method for separation/enrichment and analysis of rhodamine B in real samples by using UV-Vis spectrometry. The analysis of rhodamine B by UV-Vis spectrometry was carried out at a wavelength of 558 nm. The analytical parameters for quantitative extraction were optimized.

2. Results and discussion

2.1. Effect of pH

The transformation of rhodamine B from liquid phase to extraction phase depends on the pH value. Model solutions were prepared at different pH values (1.0–6.0) with the help of buffer solution in order to determine the optimum pH range for the quantitative extraction of rhodamine B. For this purpose, model solutions were prepared between the values of 1 and 6. Later, the microextraction method was applied to the specimens by UV-Vis spectrophotometer. All results obtained at pH 3.0 were quantitative and the highest recovery was obtained at pH 3.0 (Figure 1). The optimum sample solution pH was chosen as 3.0 and the subsequent work was continued at pH 3.0.

2.2. Effect of supramolecular solvent type and amount

When microextraction studies from preliminary methods are examined, the types and quantities of the components rank among the most important parameters. Different organic solvents, which include tetrahydrofuran (THF) with 1-decanol, undecanol, and decanoic acid, are tested with the intent of optimization of the method. While recovering rhodamine B, the effects of nonmolecular, water-immiscible, and micelle-forming organic solvents were identified. For this, THF-decanoic acid, THF-undecanol, and THF-1-decanol solvents were used.

The results of organic solvent type parameter selection were 99%, 79%, and 86%, respectively. The supramolecular solvent-based microextraction method with decanoic acid was chosen since recovery values of 95% or more were obtained. For this parameter, the amount of supramolecular solvents, which were chosen to obtain the best recovery value, were investigated after the solvent selection.

Extraction solvents containing different amounts of decanoic acid (50–200 mg) were prepared to determine the optimal decanoic acid amount that should be present in the supramolecular solvent. The optimum amount of decanoic acid was selected as 150 mg (Figure 2).

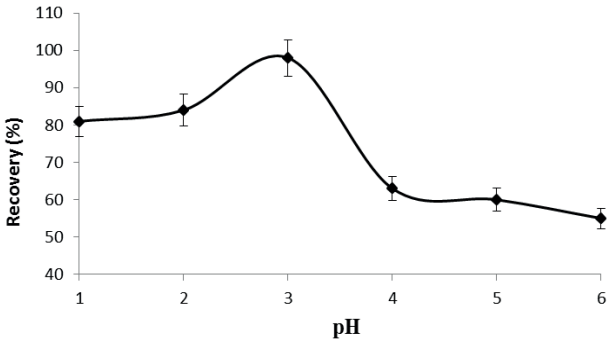

Figure 1. Effects of pH on the recoveries of rhodamine B (N = 3).

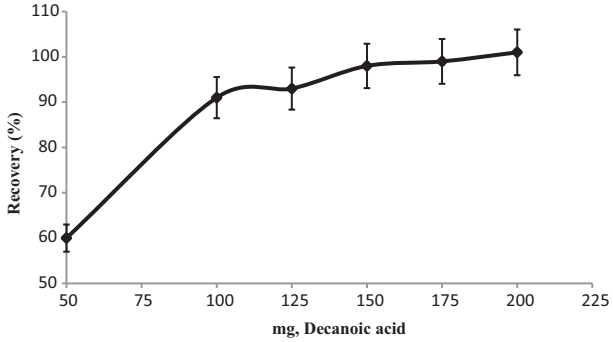

Figure 2. Effects of decanoic acid amount on the recoveries of rhodamine B (N = 3).

In addition, the influence of THF volume, which should be present in the supramolecular solvent, was studied for the recovery of the rhodamine B. For this, 150 mg of decanoic acid and supramolecular solvents containing THF with increasing volumes were prepared. Quantitative recovery values were obtained when the volume of THF was between 550 μL and 600 μL. Optimum THF volume was selected as 600 μL. The volume of THF was kept constant at 0.6 mL (Figure 3).

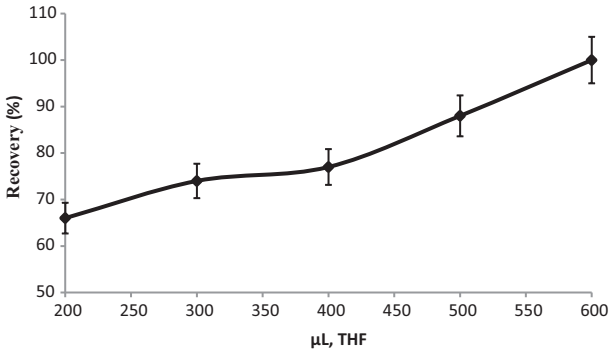

Figure 3. Effects of THF volume on the recoveries of rhodamine B (N = 3).

As a result, further experiments were carried out using 150 mg of decanoic acid and 0.6 mL of THF, followed by separation-enrichment by microextraction with supramolecular solvent.

2.3. Effects of centrifugation time and ultrasonic bath time

After extraction solvent was injected into the model solution platform, mixtures were sonicated between 1 and 5 min in order to provide the formation of the micelle with the help of ultrasonic vibration. As the sonication time increased, more clouding occurred in the mixtures. This indicates that extraction drops whose dimensions

are nano or molecular dissolve more in the solution platform. In addition to this observation, concordantly, the highest and quantitative recovery values were obtained in 5 min. A centrifuge operation was applied to mixtures at 4000 rpm between 5 and 20 min to separate the supramolecular extraction phase from the water phase. In the end, a notable phase separation and quantitative results were observed with 10 min for the centrifuge operation.

2.4. Effect of sample volume

Samples in volumes of 10 to 40 mL were prepared so as to investigate the effects of sample volume of the recovery of rhodamine B under the optimum conditions. While obtaining quantitative recovery values for the sample of 30 mL, recovery values started decreasing in the samples of over 30 mL. In this manner, the preconcentration factor was calculated as 30 owing to the fact that the last volume was 1000 μL.

2.5. Matrix effects

Alkaline metals, earth alkaline metals, dyes, and some anions with a concentration above the tolerance level bring about the matrix effect in the determination of rhodamine B. That is why, once the developed method is applied, evaluating the matrix effect of foreign ions is one of the most important parameters. The tolerance concentrations of each of the foreign ions and dyes mentioned above were investigated and the recovery values were calculated. The results are shown in Table 1.

Table 1. Influences of some foreign ions on the recoveries of rhodamine B (sample volume: 10 mL, final volume: 1 mL, N = 3).

Foreign ions	Added as	Concentration (mg L^{-1})	Recovery (%)
K^+	KCl	2000	96 ± 4*
Mg^{2+}	$MgCl_2$	1000	95 ± 3
Ca^{2+}	$CaCl_2$	1000	96 ± 3
SO_4^{2-}	Na_2SO_4	2500	95 ± 3
Na^+	NaCl	2000	100 ± 1
Pb^{2+}	$Pb(NO_3)_2$	100	97 ± 2
Cu^{2+}	$Cu(NO_3)_2$	50	98 ± 3
Zn^{2+}	$Zn(NO_3)_2$	50	98 ± 1
Chromotrope FB	Chromotrope FB	100	96 ± 5
Sudan I	Sudan I	1	100 ± 2
Sudan Orange G	Sudan Orange G	1	101 ± 3
Chicago Sky Blue 6B	Chicago Sky Blue 6B	100	97 ± 5
Brilliant Black BN	Brilliant Black BN	20	97 ± 1

*Mean ± standard deviation.

2.6. Analytical performance

Addition/recovery experiments were carried out to prove the validity of the applied supramolecular solvent-based microextraction method. With the known concentration, the recovery value of the added concentration was calculated by adding the sample solution of rhodamine B. The results are shown in Table 2.

Table 2. Tests of addition/recovery in the experiments for rhodamine B (sample volume: 10 mL, final volume: 1 mL, N = 3).

Samples	Added (μg / mL)	Found (μg / mL)	Recovery (%)
Tap water	0.0	N. D.*	-
	2.4	2.36 ± 0.02*	98
	4.8	4.75 ± 0.03	98
	7.2	7.23 ± 0.05	100
	9.6	9.67 ± 0.02	101
Lipstick	0.0	1.12 ± 0.02	-
	2.4	3.50 ± 0.02	99
	7.2	8.25 ± 0.10	99
Rouge	0.0	1.49 ± 0.005	-
	4.8	6.47 ± 0.10	104
	7.2	8.72 ± 0.20	100
Nail polish	0.0	0.03 ± 0.01	-
	2.4	2.47 ± 0.04	102
	4.8	4.84 ±0.05	100

*Mean ± standard deviation, N. D.: not detected.

Limit of detection, limit of quantification, relative standard deviation, and enrichment factors were calculated to evaluate the analytical performance of the developed supramolecular solvent-based microextraction method. The results of analytical performance studies are indicated in Table 3. The regression equation was A = 0.140C + 0.0012. The linear range was calculated as 1.5–70 μg L^{-1}.

Table 3. Validation parameters for rhodamine B analysis.

Limit of detection (LOD) (μg L^{-1})	0.49
Limit of quantification (LOQ) (μg L^{-1})	1.47
Relative standard deviation (RSD) (%)	5.8
Correlation coefficient (r^2)	0.9997
Preconcentration factor	30
Linear range	1.5–70 μg L^{-1}

2.7. Analysis of real samples

The method developed for addition/recovery was applied to cosmetic materials such as lipstick, rouge, and nail polish and to water samples. Before applying the developed microextraction method, 0.5 g of the lipstick, rouge, and nail polish samples was weighed and taken out with a scoop and 10 mL of ethyl alcohol was added to the shaker for about 2 h to dissolve the dye phase. Five parallel tubes were then prepared to apply the developed microextraction method and 0.0–9.6 μg/mL of rhodamine B was added to these sample solutions and the developed microextraction method was applied. Finally, analyte concentrations in the final volume were analyzed with a UV-Vis spectrophotometer.

In addition, the method developed for this study was applied to tap water samples. Blank samples were also analyzed. The validation of the method was checked by the addition-recovery tests. The results are shown in Table 2.

2.8. Comparison with existing methods

The proposed supramolecular solvent-based microextraction procedure for rhodamine B was compared with other methods from a literature survey. According to the literature reviews, this study has good efficiency compared to other studies related to rhodamine B because of the large surface area between the analyte and microextraction solvent. In comparison with other techniques for rhodamine B removal, the present study takes place in a short extraction time and at room temperature. Higher recovery values were obtained in this study compared to other studies and these values were attained within a shorter period and in lower concentrations by using rhodamine B and organic solvents.[22] A low detection limit was found in this study compared to some literature values, as shown in Table 4.

Table 4. Comparison between the proposed method and other procedures from the reported literature for rhodamine B determination.

Preconcentration method	Analysis method	RSD* (%)	LOD	PF*	Samples	Ref.
Ionic liquid aqueous two-phase systems coupled	UV-Vis spectrophotometer	3.8	3.2 ng L^{-1}	-	Soft drink	4
Solid phase extraction	UV-Vis spectrophotometer	5	3.14 μg L^{-1}	40	Soft drink, waste water, and lipstick samples	5
Dispersive liquid–liquid microextraction	UV-Vis spectrophotometer	4	2.1 μg L^{-1}	-	Environmental and food, cosmetics, and water samples	20
Solid phase extraction	High-performance liquid chromatography	-	3.6 μg L^{-1}	-	Red wine and river water samples	21
Ultrasound-assisted DSPE	HPLC-DAD	< 6.8	0.28 μg L^{-1}	91	Wine, grape juice, blueberry juice, and chili oil	22
microextraction	UV-Vis spectrophotometer	5.8	0.49 μg L^{-1}	30	Cosmetics and water samples	This work

*RSD: Relative standard deviation; PF: preconcentration factor.

2.9. Conclusions

A supramolecular solvent-based dispersive liquid–liquid microextraction method for determination of trace amounts of rhodamine B was established using a UV-Vis spectrophotometer. In our study, in low quantities organic solvents such as 600 μL of THF and 150 mg of decanoic acid were used to form the supramoleculer solvent phase. Therefore, it can be said that this study is environmentally friendly and cost-efficient and has almost no negative effects on health. This method was applied in a simple manner without spending much time and very efficient results were obtained by using only one extraction method. Moreover, the selectivity of the method is good; there is no interaction effect in the presence of matrix ions. Owing to such advantages, the method is practical and reliable for determining rhodamine B in environmental water samples and cosmetics. At the same time, the developed supramolecular microextraction method can be implemented not only for detection of organic types but also for separation and enrichment studies of inorganic types such as trace elements.

3. Experimental

3.1. Apparatus

A Hitachi 150-20 UV-Vis spectrometer was used in order to measure absorbance values of rhodamine B. A PHS-3C pH meter (Nel pH-900, Ankara, Turkey) was utilized with a combined glass electrode to determine pH values. The distilled water was obtained with the help of the Millipore Milli-Q system (18 MΩ cm^{-1} resistivity, Millipore, Bedford, MA, USA). An ALC PK 120 model centrifuge (Buckinghamshire, UK) was used.

3.2. Chemicals and reagents

All reagents and chemicals were utilized in analytical purity. A standard rhodamine B 1×10^{-3} M stock solution was prepared in ethanol (Sigma-Aldrich Co., Milwaukee, WI, USA). The solution was diluted to 1×10^{-4} M in order to form a calibration curve. Moreover, standard solutions with increasing concentrations were prepared from this solution, which was diluted before. Values of pH were adjusted by adding buffer solutions within the range of 1 to 6 pH. All chemicals and analytical grade solutions were prepared in deionized water.

3.3. Supramolecular solvent-based microextraction procedure

The sample solution of rhodamine B was taken in a 50-mL centrifuge tube, and then 2 mL of acetate buffer solution was added to adjust the sample pH to 3 by using diluted NaOH and HCl solutions. After pH regulation, 600 μL of THF and 150 mg of decanoic acid were added to the rhodamine B sample solution to form the supramolecular solvent. After these steps, the sample solution of rhodamine B was sonicated for 5 min and a cloudy solution was obtained. This solution was centrifuged at 4000 rpm for 10 min. At the end of the centrifugation, the solvent phases were completely separated from the aqueous phase and formed a solvent solution in the upper phase. The lower water phase was eliminated with an injector. After the liquid phase was taken from the solution, the volume of the remaining phase was between 200 and 300 μL. The supramolecular solvent (about 200–300 μL) was completed to 1000 μL with ethanol. Finally, the developed microextraction method as applied to the final solution was measured by UV-Vis spectrophotometer at 558 nm (Figure 4).

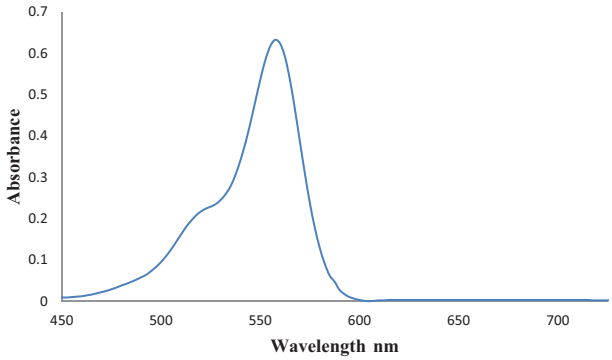

Figure 4. UV-Vis spectrum of rhodamine B.

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References

1. Ravi, K.; Deebika, B.; Balu, K. *J. Hazard. Mater.* **2005***, 122*, 75-83.
2. Hema, M.; Arivoli, S. *Arab. J. Chem.* **2007**, *2*, 43-51.
3. Metivier-Pignon, H.; Faur-Brasquet, C.; Cloirec, P. L. *Sep. Purif. Technol.* **2003**, *31*, 3-11.
4. Wu, J.; Fu, H.; Zhu, X. *Sci. Res.* **2014**, *2*, 17-25.
5. Soylak, M.; Unsal, Y. E.; Yilmaz, E.; Tuzen, M. *Food Chem. Toxicol.* **2011**, *49*, 1796-1799.
6. Pourreza, N.; Rastegarzadeh, S.; Larki, A. *Talanta* **2008**, *77*, 733-736.
7. Sleiman, M.; Vildozo, D. L.; Ferronato, C.; Chovelon, J. M. *Appl. Catal. B Environ.* **2007**, *77*, 1-11.
8. Wang, S.; Xu, Z.; Fang, G.; Duan, Z.; Zhang, Y.; Chen, S. *J. Agric. Food Chem.* **2007**, *55*, 3869-3876.
9. Jaina, R.; Mathura, M.; Sikarwara, S.; Mittal, A. *J. Environ. Manage.* **2007**, *85*, 956-964.
10. Soylak, M.; Unsal, Y. E.; Tuzen, M. *Food Chem. Toxicol.* **2011**, *49*, 1183-1187.
11. Ping, Q.; Tao, Z.; Zejun, W.; Xiaoyan, L.; Xuewu, Z. *Food Chem.* **2011**, *125*, 1462-1467.
12. Dinc, E.; Baydan, E.; Kanbur M.; Onur, F. *Talanta* **2002**, *58*, 579-594.
13. An, L.; Deng, J.; Zhou, L.; Li, H.; Chen, F.; Wang, H. U; Liu, Y. *J. Hazard. Mater.* **2010**, *175*, 883-888.
14. Sohrabi, M. R.; Ghavami, M. *J. Hazard. Mater.* **2008**, *153*, 1235-1239.
15. Watanabe, T.; Takizawa, T.; Honda, K. *J. Phys. Chem.* **1977**, *81*, 1845-1851.
16. Qu, P.; Zhao, J.; Shen, T.; Hidaka, H. *J. Mol. Catal.* **1997**, *120*, 235-245.
17. Alothman, A. Z.; Habila, M. A.; Yilmaz, E.; Al-Harbi, N. M.; Soylak, M. *Int. J. Environ. An. Ch.* **2015**, *95*, 1311-1320.
18. Aydin, F.; Yilmaz, E.; Soylak, M. *RSC Adv.* **2015**, *5*, 94879-94886.
19. Yigit, S.; Tuzen, M.; Soylak, M.; Dogan, M. *Int. J. Environ. An. Ch.* **2016**, *96*, 568-575.
20. Unsal, Y. E.; Soylak, M.; Tuzen, M. *Desalin. Water Treat.* **2015**, *55*, 2103-2108.
21. Wu, Z. L.; Liu, Q.; Chen, X. Q.; Yu, J. G. *J. Separ. Sci.* **2015**, *38*, 3404-3411.
22. Xu, X.; Zhang, M.; Wang, L.; Zhang, S.; Liu, M.; Long, N.; Qi, X.; Cui, Z.; Zhang, L. *Food Anal. Methods* **2016**, *9*, 1696-1705.