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Utilization of a novel microwave-assisted homogeneous ionic liquid microextraction method for the determination of Sudan dyes in red wines

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ABSTRACT

A novel microwave-assisted homogeneous ionic liquid microextraction (MA-HILME) method was first developed for the extraction of Sudan dyes in red wines followed by detection using high-performance liquid chromatography. 1-dodecyl-3-methylimidazolium bromide ($[C_{12}MIM]Br$) was used as extractant in a microwave-assisted extraction (MAE) procedure, and then transferred into hydrophobic solid-state ionic liquid after adding ammonium hexafluorophosphate ($[NH_4][PF_6]$). The separation between liquid state sample and solid state extractant can be realized easily. Several experimental parameters, including type and amount of extraction solvent, microwave power and irradiation time, amount of ion-exchange reagent ($[NH_4][PF_6]$), pH of sample solution, and ionic strength, were evaluated. Under the optimum experimental conditions, the linearity for the determining of the analytes was in the range of 0.5–100 μg L^{-1}, with the correlation coefficients ranging from 0.9995 to 0.9999. The limits of detection for Sudan I, Sudan II, Sudan III, and Sudan IV were 0.19, 0.18, 0.24, and 0.16 μg L^{-1}, respectively. When the present method was applied to the determination of Sudan dyes in red wines, satisfactory recoveries were obtained in the range of 78.5–106.8%, and relative standard deviations were lower than 9.7%.

1. Introduction

Sudan dyes are a group of lipophilic azo dyes that are extensively used in oils, waxes, floor and shoe polishes, and printing inks [1,2]. They are classified as category 3 carcinogen by the International Agency for Research on Cancer (IARC) [3]. Now that Sudan dyes have been proven to be carcinogenic and mutagenic to humans [4,5], the use of Sudan dyes as additives in foodstuffs destined for human consumption is banned in most countries. However, Sudan dyes can still be found as additives in food due to their color-fastness, low cost and ready availability [6,7]. In order to protect the public health, a reliable, rapid, effective and high sensitive method for the determination of Sudan dyes in foods is demanded.

Until now, high-performance liquid chromatography (HPLC) coupled with different detectors including ultraviolet-visible (UV) detection [7], diode array detection (DAD) [8] and mass spectrometric (MS) detection [9] is the most extensively used technique for the determination of Sudan dyes in foodstuffs. Owing to the complexity of sample matrices and low levels of analytes, the analyte enrichment and sample cleanup are of vital importance prior to chromatographic analysis. Various sample preparation methods have been established for extraction and preconcentration of Sudan dyes from the matrix, such as ultrasonic-assisted extraction (UAE) [2], solid-phase extraction (SPE) [10], molecularly imprinted solid-phase extraction (MISPE) [11], cloud point extraction (CPE) [12], and stir bars microextraction [13]. Although each method has its advantages, most of those procedures suffer from several deficiencies, such as expenditure of time and organic solvent, tedious operation, or low enrichment factor. Therefore, a simple, rapid, economic, sensitive and environmental friendly method should be developed.

Lately, ionic liquids (ILs) have gained significant attention due to their unique physicochemical properties, such as negligible vapor pressure, good thermal and chemical stability, tunable viscosity and polarity, miscibility with water and organic solvents, and good solubility for various organic compounds and metal ions [14–16]. In addition, ILs can be readily adjusted according to the need for use. Therefore, novel "green" organic solvents have got wide application in analytical chemistry, especially in extraction and separation techniques, such as stationary phases for gas chromatography and mobile phase additives for liquid chromatography [17,18], liquid-phase microextraction (LPME) [19,20], solid-phase microextraction (SPME) [21], and aqueous two-phase systems extraction (ATPSE) [22]. Recently, a new mode of LPME termed homogeneous ionic liquid microextraction (HILME) has been developed [16,23–25]. This approach is based on utilizing a hydrophilic IL as extraction solvent, followed by addition of

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an ion-exchange reagent to promote a metathesis reaction, and so the hydrophilic IL is transformed to hydrophobic IL that settles down containing the preconcentrated analytes. HILME has superior advantages such as rapidity, low cost, high recovery and enrichment factor, environmental friendly, and this method has been widely applied for the extraction of organic pollutants in matrix samples [16,24,25]. In addition, considering ILs can efficiently absorb and transfer microwave energy, ILs as solvents and co-solvents are of promising potential in the MAE of organic compounds [14,26]. Compared with traditional extraction methods, IL-based MAE is a more efficient technique for sample pretreatment, which could improve extraction efficiency and decrease the extraction time.

In the present study, a novel MA-HILME method was first developed for the extraction and enrichment of Sudan dyes in red wines. In the novel MA-HILME technique, $[C_{12}MIM]Br$ was used as extractant in a MAE procedure. In the conventional HILME, the conventional hydrophilic IL, such as 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4MIM][BF_4]$) and 1-hexyl-3-methylimidazolium tetrafluoroborate ($[C_6MIM][BF_4]$) was used as extractant. Unlike the conventional HILME, the formed hydrophobic IL is in solid state after the addition of an ion-exchange reagent. In order to make the formed hydrophobic IL settle down completely the test tube was put into an ice bath for a few minutes. This new technique does not need special equipment, and the transfer of the solidified phase from aqueous phase can be carried out easily. Several experimental conditions were investigated and optimized. The present method was also applied to the analysis of real red wine samples.

2. Experimental

2.1. Chemicals and reagents

The standards of Sudan I–IV were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The purity of all the compounds was higher than 98%. The chemical structures of the compounds are shown in Fig. 1. Standard stock solution of each compound was prepared by dissolving each individual of Sudan dye in acetonitrile at a concentration level of 500 μg mL^{-1} and stored at 4 °C. The mixed working solutions were obtained by diluting the standard stock solutions with acetonitrile. Chromatographic grade acetonitrile was purchased from Fisher Corporation (Pittsburgh, PA, USA). Analytical grade hydrochloric acid, sodium hydroxide and sodium chloride were purchased from Beijing Chemical Factory (Beijing, China). Pure water was obtained with a Milli-Q water system (Millipore, Billerica, MA, USA). 1-ethy-3-methylimidazolium tetrafluoroborate ($[C_2MIM][BF_4]$), 1-dodecyl-3-methylimidazolium bromide ($[C_{12}MIM]Br$), N-butyl-N-methylpyrrolidinium tetrafluoroborate ($[C_4mpyrr][BF_4]$), and ammonium hexafluorophosphate ($[NH_4][PF_6]$) were obtained from Chengjie Chemical Co. Ltd. (Shanghai, China).

2.2. Instruments

The extraction was performed on a modified household microwave oven (SANYO, China) with a maximum microwave output power of 600 W. The microwave output power can be controlled with a continuously regulable transformer.

Chromatographic analysis was performed on a Shimadzu LC-20A HPLC system (Shimadzu, Kyoto, Japan) equipped with a binary high-pressure pump, a degasser, an SPD-20A ultraviolet detector, a heated column compartment, an injection valve and an LC workstation. The chromatographic separation of the analytes was carried out on an XDB-C18 column (150 mm × 4.6 mm I.D., 5 μm) (Agilent, Palo Alto, CA, USA).

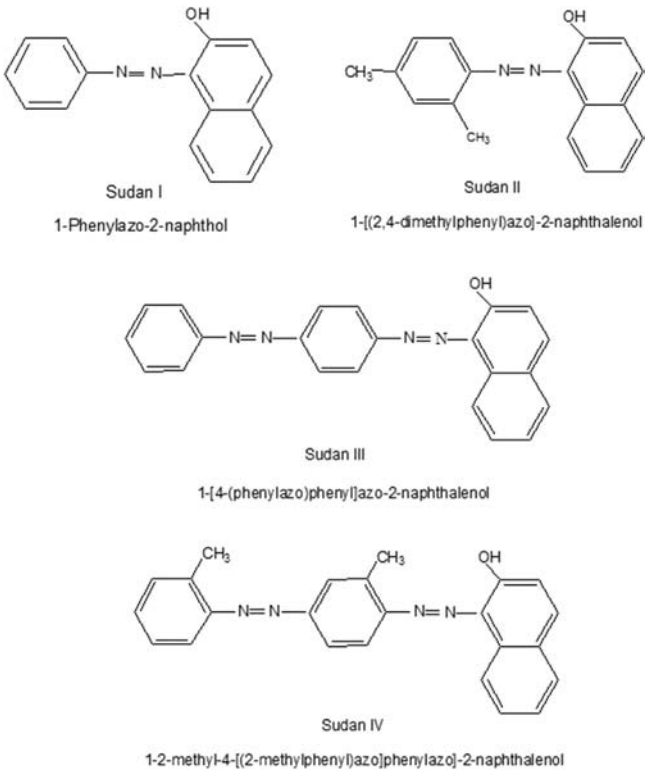

Fig. 1. Chemical structures of Sudan dyes.

A DELTA-320 acidity meter (Mettler-Toledo Instruments Co., Ltd, Shanghai, China) was used for pH measurement. The phase separation was performed on an LDZ4-1.2 centrifuge (Jingli centrifuge Co. Ltd, Beijing, China). A nitrogen gas blowing (DN-12A, Qiaofeng instrument Co. Ltd., Shanghai, China) was used to remove the remaining sample solution in the collected IL. All glassware and plasticware used in this work were washed with methanol and high pure water, and dried at 60 °C for at least 10 h.

2.3. Samples

In this study, six kinds of red wines were purchased randomly from local supermarkets in Changchun, China. The alcoholic degrees of the samples were between 12.0% and 14.5% (v/v) and all of them were brewed by glucose. All these real samples were filtered through 0.45 μm filters and then stored in brown glass containers at 4 °C before used.

The spiked samples were prepared by spiking the mixed stock solutions into red wine samples. Except for the experiments mentioned in Section 3.3, which were performed on all six samples, all other results were obtained with sample 1.

2.4. MA-HILME procedure

A total of 4 mL of the spiked sample, 0.20 g NaCl and 0.06 g $[C_{12}MIM]Br$ were placed into a 5 mL glass centrifuge tube. After $[C_{12}MIM]Br$ was dissolved completely, the sealed tube was immediately placed in the microwave oven and irradiated under the microwave power of 180 W for 90 s. The target analytes were extracted into the extraction solvent ($[C_{12}MIM]Br$) under microwave irradiation. After extraction, 0.0886 g $[NH_4][PF_6]$ was added. The test tube was thereafter put into an ice bath for 5 min, at this time a hydrophobic solid-state IL 1-dodecyl-3-methylimidazolium hexafluorophosphate ($[C_{12}MIM][PF_6]$) was formed containing the preconcentrated analytes. After centrifugation at 4000 rpm for 5 min, the IL was deposited at the bottom of the tube. The upper

aqueous phase was decanted completely, and the IL phase was purged under mild nitrogen stream at 40 °C to remove the remaining sample solution in the collected IL. Then, the IL was dissolved in 50 μL of acetonitrile. The resulting solution was referred as analytical solution, and filtered through 0.22 μm PTFE filter membrane before HPLC analysis. All experiments were performed in triplicate.

2.5. Chromatographic conditions

Isocratic elution was carried with acetonitrile as mobile phase at a flow rate of 0.3 mL min^{-1} [8]. The temperature of the column was kept at 35 °C. The injection volume of analytical solution was 20 μL. The monitoring wavelengths were 478 nm for Sudan I and Sudan II and 520 nm for Sudan III and Sudan IV.

3. Results and discussion

3.1. Optimization of the novel MA-HILME procedure

In order to obtain high extraction efficiency, the influence of experimental parameters, such as type and amount of extraction solvent, microwave power and irradiation time, amount of ion-exchange reagent ($[NH_4][PF_6]$), pH of sample solution, and ionic strength, was investigated. A preoptimization for the experimental parameters was performed and based on the preselected optimum parameters, the effects of different factors were studied again. When one parameter was changed, the other parameters were fixed at their optimized values. All experiments were performed in triplicate and the concentration of Sudan dyes in the spiked samples was 25 μg L^{-1}.

3.1.1. Effect of type of IL

The structures of ILs have significant influence on its physicochemical properties, which might greatly affect the extraction efficiency of the target analytes. In this study, three kinds of hydrophilic ILs, including $[C_2MIM][BF_4]$, $[C_{12}MIM]Br$ and $[C_4mpyrr][BF_4]$ were used as the extraction solvents, and $[NH_4][PF_6]$ was used as ion-exchange reagent. When $[C_2MIM][BF_4]$ was used, there was only very small amount of solid-state IL settled down at the bottom of the test tube after adding $[NH_4][PF_6]$ and centrifugation. The main reason may be due to the relatively high solubility of $[C_2MIM][PF_6]$ in water. The extraction efficiency of $[C_{12}MIM]Br$ and $[C_4mpyrr][BF_4]$ is shown in Fig. 2. The results indicated that the extraction recoveries obtained with $[C_{12}MIM]Br$ were much higher than those obtained with $[C_4mpyrr][BF_4]$. The reason may be that $[C_{12}MIM]Br$ is a kind of IL surfactant which is able to form micelles in aqueous solution and the IL micelles has good capacity to solubilize the target analytes [27]. Therefore, $[C_{12}MIM]Br$ was selected as extraction solvent for further studies.

3.1.2. Effect of amount of IL

The effect of amount of $[C_{12}MIM]Br$ on extraction recoveries was studied in the range of 0.02–0.10 g when the amount of $[NH_4][PF_6]$ was 0.0886 g. The recoveries of the target analytes increase with the increase in the amount of IL from 0.02 to 0.06 g, and almost unchanged when the amount increases from 0.06 to 0.10 g. When the amount of $[C_{12}MIM]Br$ was too small, the recoveries of Sudan dyes decreased since the amount of $[C_{12}MIM]Br$ was insufficient to extract the analytes and the resulting amount of $[C_{12}MIM][PF_6]$ decreased [28]. Hence, in further work, 0.06 g $[C_{12}MIM]Br$ was chosen.

3.1.3. Effect of microwave power and irradiation time

The temperature can affect the mass transfer rate of the analyte from aqueous solution into IL phase, thus affect the extraction efficiency. Because the temperature of the sample solution is strongly related to microwave irradiation power and time, the microwave power and irradiation time can affect the extraction recoveries. A series of experiments were designed for the optimization of microwave power when the irradiation time was 90 s. The recoveries of the target analytes increase from 60 to 180 W and slowly decrease thereafter. When the microwave power was too low, the diffusion rate of the analytes was low which resulted in relatively few amount of analytes transferring into the IL phase.

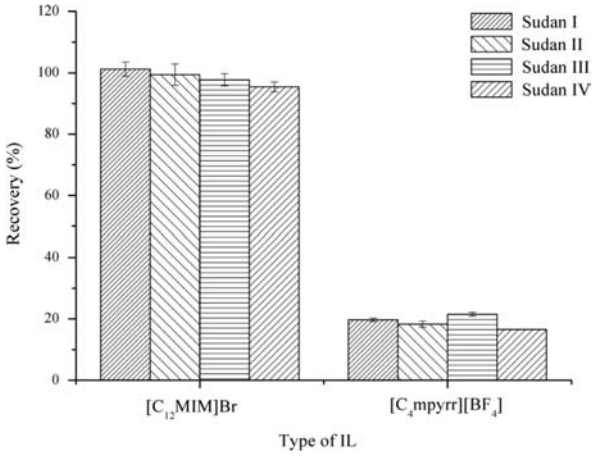

Fig. 2. Effect of type of ionic liquid. Amount of ionic liquid, 0.06 g; microwave power, 180 W; microwave irradiation time, 90 s; amount of $[NH_4][PF_6]$, 0.0886 g; NaCl concentration, 5%.

Table 1
t values between experimental parameter.

Experimental parameter	Parameter values	Analyte			
		Sudan I	Sudan II	Sudan III	Sudan IV
Amount of IL(g)	0.02	0.70	1.07	2.40	2.55
	0.04	4.35	3.80	7.34	7.02
	0.06	1.08	0.50	0.70	1.31
	0.08	1.93	2.00	0.07	
	0.10				
Microwave power (W)	60	15.07	9.52	8.69	8.54
	120	2.32	2.45	0.58	0.90
	180	2.97	5.77	0.54	1.70
	240	2.85	1.60	1.87	
	300				
Microwave irradiation time (s)	30	4.94	3.90	4.76	6.14
	45	1.47	1.98	2.38	0.79
	60	0.61	0.27	2.39	1.52
	75	3.48	5.03	5.09	2.46
	90	3.89	6.18	4.24	1.14
	105	2.70	4.16	6.89	
	120				
Amount of $[NH_4][PF_6]$ (g)	0.0295	5.46	2.60	4.72	3.64
	0.0590	3.21	2.11	3.01	4.04
	0.0886	0.68	0.03	0.65	0.16
	0.1181	1.09	1.50	1.77	1.97
	0.1476	1.55	1.33	0.71	
	0.1771				
NaCl concentration (w/v,%)	0	0.59	0.04	0.75	0.18
	1	0.15	0.06	0.25	1.67
	3	1.43	1.79	1.30	2.76
	5	3.98	2.77	2.67	4.26
	7	6.00	3.55	1.12	1.87
	10				

$T_{0.05,\ 4}$ =2.78.

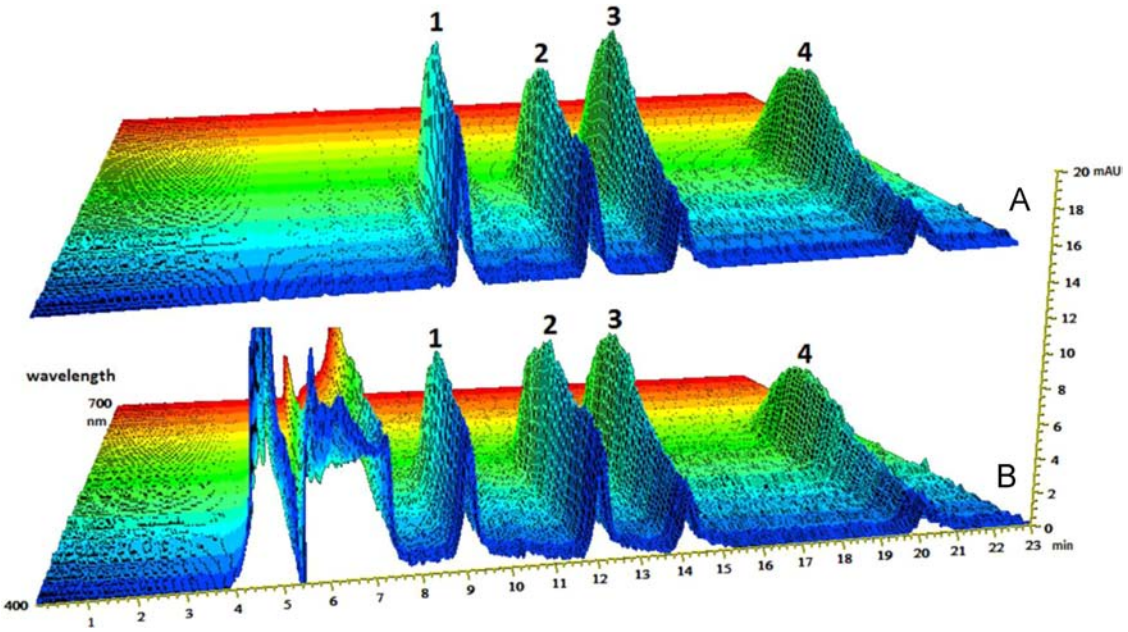

Fig. 3. Absorption spectra of the eluates from the standard solution (A) and spiked red wine sample (B). 1, Sudan I; 2, Sudan II; 3, Sudan III; 4, Sudan IV.

Table 2
Analytical performance.

Analyte	Regression equation[a] $A=(a\pm SD_a)+(b\pm SD_b)\,c$	Linear range (μg L^{-1})	Correlation coefficient (r)	Linearity[b]	Sy/x[c]	LOD (μg L^{-1})	LOQ (μg L^{-1})
Sudan I	$A=(2547.64\pm504.20)+(6201.21\pm11.03)\,c$	0.5–100	0.9998	0.9982	1006.13	0.19	0.64
Sudan II	$A=(2587.00\pm484.10)+(6787.90\pm11.83)\,c$	0.5–100	0.9998	0.9983	1054.77	0.18	0.59
Sudan III	$A=(2232.69\pm885.03)+(9326.37\pm22.99)\,c$	0.5–100	0.9995	0.9975	2169.38	0.24	0.79
Sudan IV	$A=(3322.32\pm375.18)+(101714.58\pm8.08)\,c$	0.5–100	0.9999	0.9999	672.58	0.16	0.53

[a] A is the peak area of Sudan dyes; c is the Sudan dyes concentration in μg L^{-1}; a is the intercept; b is the slope; SD_a and SD_b are standard deviations of intercept and slope, respectively.
[b] Linearity = SD_b/b.
[c] Standard deviation of residuals.

Table 3
The intra- and interday precisions and recoveries of the assay.

Analyte	Intra-day ($n=5$)		Inter-day ($n=5$)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sudan I	100.7	4.8	97.6	8.6
Sudan II	101.2	4.8	100.5	7.3
Sudan III	97.9	4.3	94.3	6.4
Sudan IV	95.5	4.2	94.0	6.4

Too high microwave power was not useful to increase the extraction recoveries. The reason may be due to the loss of Sudan dyes from volatilization. Based on the results, 180 W of microwave power was selected for the subsequent experiments.

The effect of microwave irradiation time was also studied. The recoveries of the target analytes increase with the increase of microwave irradiation time before 90 s, and then decrease thereafter. Thus, 90 s was chosen as the optimal extraction time.

3.1.4. *Effect of amount of $[NH_4][PF_6]$*

In this experiment, $[NH_4][PF_6]$ was used as ion-exchange reagent for the precipitation of the IL phase. The effect of amount

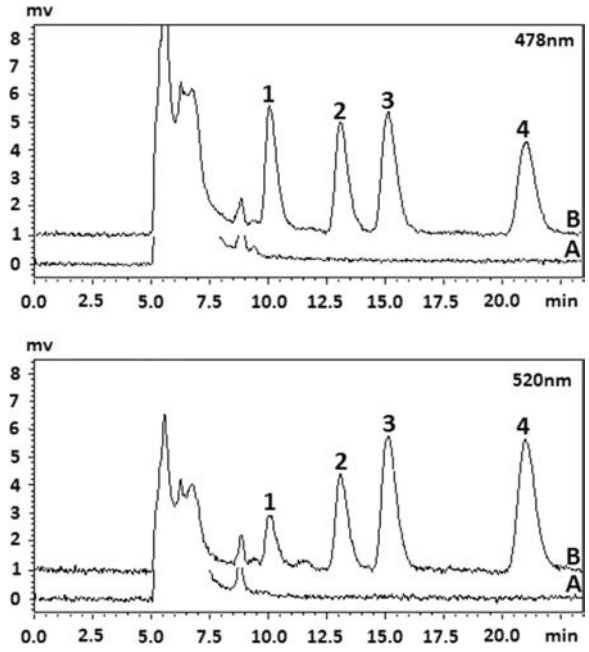

Fig. 4. Typical chromatograms for blank (A) and spiked (B) samples. The concentrations of analytes are 25 μg L^{-1}. 1, Sudan I; 2, Sudan II; 3, Sudan III; 4, Sudan IV.

of $[NH_4][PF_6]$ on the extraction recoveries was studied when the amount of $[C_{12}MIM]Br$ was 0.06 g. The results indicated that the recoveries of the target analytes increase with the increase in the amount of $[NH_4][PF_6]$ from 0.0295 to 0.0886 g, and the recoveries do not obviously change when the amount of $[NH_4][PF_6]$ ranging from 0.0886 to 0.1771 g. The reason may be due to the resulting amount of $[C_{12}MIM][PF_6]$ is unchanged. According to the results obtained, 0.0886 g of $[NH_4][PF_6]$ was used in this study. That is to say, the molar ration of $[C_{12}MIM]Br$ to $[NH_4][PF_6]$ was 1:3.

3.1.5. Effect of pH of sample solution

The pH of sample solution plays an important role in the extraction of organic compounds because the pH of solution determines the present state of the analytes. The influence of pH of sample solution in the range of 2.0–12.0 was investigated. The results indicated that the pH does not affect the recoveries of Sudan dyes obviously (except Sudan III and Sudan IV, pH 12.0). To simplify the experimental operation, the pH of sample solution was not adjusted.

3.1.6. Effect of ionic strength

To investigate the influence of ionic strength on the extraction efficiency, a series of experiments were performed by adding different amounts of NaCl (0–10%, w/v). The recoveries of the target analytes improve with the increase in NaCl concentration, reach the maximum at NaCl concentration of 5% and then decrease. The addition of salt into sample solution could reduce the solubility of the analytes and aid their partitioning into IL phase [14]. However, if too large amount of salt was added, Sudan dyes molecules may participate in electrostatic interactions with the salt ions in solution, thereby decreasing the transfer of Sudan dyes into extraction phase [29]. Furthermore, the viscosity of sample solution increased with the increase in ionic strength, which may make it more difficult for the target analyte molecules to diffuse into the IL phase [16]. Therefore, NaCl concentration of 5% was adopted in the following studies.

3.1.7. Statistical analysis

To evaluate the optimization of these experimental parameters, the student's *t*-test was applied [30], and the *t* values are listed in Table 1. The statistical analysis indicates that the differences between the optimal values and the nearest values for the experimental parameters are significant ($P < 0.05$). So, the selected optimal experimental parameters should be reasonable.

3.2. Method validation

The target analytes were identified by comparing their retention times and absorption spectra with those of the authentic standard analytes [31]. The spectral data for each chromatographic peak are helpful in the identification of species. The spiked sample and the standard solution of the analytes were analyzed using a 1100 series liquid chromatography (Agilent Technologies Inc., USA) equipped with photodiode-array detector (DAD) and the results are shown in Fig. 3.

3.2.1. Stability of standard stock solutions

Standard stock solution of each compound was prepared in acetonitrile at a concentration level of 500 μg mL^{-L} and stored at 4 °C for 1 day, 1 week, 2 weeks, 3 weeks, and 4 weeks. The mixed standard solution of 0.5 μg mL^{-1} was analyzed after dilution the standard stock solutions with acetonitrile. All experiments were performed in triplicate. The results indicated that there is no significant difference in the peak areas measured for each compound. The RSD values were in the range of 3.6–6.1% for all the analytes. It can be concluded that the standard stock solutions of Sudan dyes were stable for at least 4 weeks.

3.2.2. Limits of detection and quantification

Under the optimal experimental conditions, the working curves were constructed by plotting the peak areas measured versus the concentrations of analytes in the spiked samples. All experiments were performed in triplicate. The quality parameters of the straight line calibration curves [32] are listed in Table 2. The high values of the linearity and the correlation coefficient (*r*) of the

Table 4
Analytical results of real samples ($n=3$).

Analyte	Spiked concentration (μg L^{-1})	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sudan I	2	97.6	7.7	98.0	6.6	93.1	1.1	94.8	9.7	89.9	8.5	101.7	3.2
	40	92.1	2.3	82.6	1.1	91.7	4.1	89.5	5.2	93.7	6.5	97.5	1.9
Sudan II	2	97.9	2.0	97.6	2.7	96.3	4.3	98.1	8.5	92.3	7.6	88.6	8.3
	40	88.2	1.8	78.5	1.5	89.7	3.6	86.7	5.6	92.0	7.5	95.3	1.4
Sudan III	2	106.8	8.8	100.4	6.6	97.5	6.5	103.8	8.2	80.8	8.8	104.6	7.7
	40	89.0	1.6	81.9	1.1	88.5	3.4	82.9	4.8	85.2	6.4	89.8	3.3
Sudan IV	2	100.2	1.7	105.5	5.6	94.0	6.3	83.2	4.3	93.7	5.6	98.2	7.7
	40	88.3	1.6	79.3	4.5	86.6	4.1	81.0	4.4	80.8	5.3	88.1	1.4

Table 5
Test of correlation.

Analyte	*r*	*F*
Sudan I	−0.2676	0.1557
Sudan II	−0.3124	0.0479
Sudan III	−0.2757	0.1354
Sudan IV	−0.3033	0.0691

$F_{1,3}=10.13$.

regressing lines, small values of the standard deviation of residuals (Sy/x), the intercept (SD_a) and the slope (SD_b) indicated good linearity of the calibration graphs.

Limit of detection (LOD) and limit of quantification (LOQ) are considered as the minimum concentrations of analyte that can be confidently identified and quantified, respectively. The LODs and LOQs of the analytes were determined on the basis of a signal-to-noise (S/N) ratio of 3 and 10, and were in the range of 0.16–0.24 and 0.53–0.79 μg L^{-1} for all the analytes, respectively.

3.2.3. Precision and accuracy

The precision of the present method was evaluated by measuring intra- and interday relative standard deviations (RSDs) and the accuracy was evaluated by recovery test. The intra- and interday precisions were determined by assaying the spiked red wine samples at a concentration level of 25 μg L^{-1} in one day ($n=5$) and five consecutive days, respectively. The analytical results are presented in Table 3. The results show acceptable RSD values, ranging from 4.2 to 4.8% and from 6.4 to 8.6% for intra- and interday, respectively. Good recoveries were also obtained, which are in the range of 95.5–101.2 and 94.0–100.5% for intra- and interday, respectively.

3.2.4. Selectivity

The chromatograms of the extracts of blank samples and spiked sample are shown in Fig. 4. The concentration of Sudan dyes in the spiked samples was 25 μg L^{-1}. The results demonstrate that no interference peaks are observed at the retention positions of the target analytes in the chromatograms of blank red wine, which indicates that the selectivity of the present method is satisfactory. The approach used to measure selectivity was in agreement with the previously reported by Wang et al [28].

3.3. Application of the method

To demonstrate the practical applicability of the present method, the present method was applied to the analysis of six red wine samples. No Sudan dyes at detectable levels were found in these samples. The typical chromatograms of the blank and spiked red wine samples are shown in Fig. 4. As can be seen, no significant interference peaks are found at the retention positions of Sudan dyes. The Sudan dyes in the spiked samples were determined, and the results are listed in Table 4. The RSDs and recoveries are in the range of 1.1–9.7 and 78.5–106.8%, respectively. It can be considered that the present method provides good recoveries and acceptable precisions for the determination of Sudan dyes in real red wine samples.

In order to determine if there is a correlation between the recovery and concentration of the analytes, the relationship between the recovery and concentration was described as a linear regression equation [33]. The concentration levels of the spiked samples were 2, 25, 40, 50 and 100 μg L^{-1}. Based on the results, the linear correlation coefficients for the regression equations were obtained and listed in Table 5. To judge the correlation, F test was applied and the F values obtained also listed in Table 5. It can be seen from Table 5 that the recoveries should not be concentration-dependent because all the F values are lower than $F_{0.05(1,3)}$ value.

3.4. Comparison of MA-HILME with other methods

In order to evaluate the performances, the present method was compared with other methods reported in the literature, and the results are presented in Table 6. Compared with the reported methods, the present method has some advantages in the

Table 6
Comparison of the present method with other methods.

Method	Sample (amount)	Sample preparation	Material and reagent for extraction	Recovery (%)	LODs (μg L^{-1})	Ref.
Magnetic solid-phase extraction	Environmental water (75 mL)	Extraction (6 min)→magnetic separation→elution (3 min)→magnetic separation→evaporation→reconstitution→filtering	Fe_3O_4@SiO_2 microspheres, 4 mL acetonitrile	87.10–111.4	0.082–0.12	[34]
Magnetic solid-phase extraction	Red wine, juice, vinegar (100 mL)	Extraction (15 min)→magnetic separation →elution→magnetic separation→evaporation→reconstitution→filtering	Polystyrene-coated magnetic nanoparticles, 4 mL acetonitrile	76.2–92.7	0.0039–0.017	[35]
Liquid-liquid microextraction	Red wine, fruit juice (4 mL)	Liquid–liquid microextraction (10 min)→centrifugation (5 min)	50 μL $[C_6MIM][PF_6]$	80.12–108.28	0.428–1.454	[8]
Dispersive liquid-phase microextraction	Environmental water (10 mL)	Dispersive liquid-phase microextraction (20 min)→centrifugation (5 min)→low temperature (5 min)→separation→melting→reconstitution	100 μL 1-dodecanol	91.1–108.6	0.03	[36]
This method	Red wine (4 mL)	Microwave-assisted extraction (1.5 min)→adding $[NH_4][PF_6]$ into the solution→low temperature (5 min)→centrifugation (5 min)→nitrogen blow dryness→reconstitution→filtering	0.06 g $[C_{12}MIM]Br$	78.5–106.8	0.16–0.24	

expenditure of sample amount, extraction time and amount of organic solvent. Therefore, the novel MA-HILME-HPLC method is proposed for the simultaneous extraction and determination of Sudan dyes in red wines.

4. Conclusion

In this work, a novel analytical method, MA-HILME coupled with HPLC-UV, was successfully applied to the extraction of Sudan dyes from red wines. The procedure was based on utilizing a kind of hydrophilic IL ($[C_{12}MIM]Br$) as extraction solvent in a MAE procedure. Then, the hydrophilic IL containing the extracted analytes transferred into hydrophobic solid-state IL ($[C_{12}MIM][PF_6]$) via a simple methathesis reaction. Compared with conventional HILME, the transfer of the solidified phase from aqueous phase can be carried out easily. Another important feature of the developed preconcentration method is that it avoids the use of volatile and toxic organic solvent in the extraction procedure. The experimental results demonstrated that the present method would be a valuable alternative for the determination of Sudan dyes in red wine and would have surprising perspective in the routine analysis of banned dyes in other complex matrices.

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