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Determination of formaldehyde in beverages using microwave-assisted derivatization and ionic liquid-based dispersive liquid–liquid microextraction followed by high-performance liquid chromatography

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ABSTRACT

A simple method based on simultaneous microwave-assisted derivatization and ionic liquid-based dispersive liquid–liquid microextraction (IL-based DLLME) is proposed for the derivatization, extraction and preconcentration of formaldehyde in beverage samples prior to the determination by high-performance liquid chromatography (HPLC). Formaldehyde was in situ derivatized with 2,4-dinitrophenylhydrazine (DNPH) and simultaneously extracted and preconcentrated by using microwave-assisted derivatization and IL-based DLLME in a single step. Several experimental parameters, including type and volume of extraction solvent, type and volume of disperser, microwave power and irradiation time, volume of DNPH, pH of sample solution, and ionic strength were evaluated. When the microwave power was 120 W, formaldehyde could be derivatized and extracted simultaneously only within 90 s. Under optimal experimental conditions, good linearity was observed in the range of 0.5–50 ng/mL with the correlation coefficient of 0.9965, and the limit of detection was 0.12 ng/mL. The proposed method was applied to the analysis of different beverage samples, and the recoveries of formaldehyde obtained were in the range of 84.9–95.1% with the relative standard deviations lower than 8.4%. The results showed that the proposed method was a rapid, convenient and feasible method for the determination of formaldehyde in beverage samples.

1. Introduction

Carbonyl compounds are widely found in food products. They can originate from raw materials, alcoholic fermentation [1] or a wide range of chemical reactions, such as lipid oxidation, Maillard reactions, Strecker degradation and aldol condensation [2]. Formaldehyde is a most widespread carbonyl compound coming from combustion and oxidation of hydrocarbons. In recent years, formaldehyde receives a great deal of attention, owing to its widespread use in food products and possible carcinogenic properties [3,4]. Formaldehyde is usually used as antiseptic in many foods such as beverage, meat, mushroom, bean curd, vermicelli, and hydrated food to keep them pleasant [5–7], but poses a threat to human health. An acceptable daily intake of 0.2 mg/kg body weight has been set by the US Environmental Protection Agency for formaldehyde [8]. A rapid, simple and sensitive method for the determination of formaldehyde in beverages is required.

A variety of methods have been developed for the determination of formaldehyde, such as spectrophotometry [9–12], fluorometry [13,14], capillary electrophoresis (CE) [15], high-performance liquid chromatography (HPLC) [16–20], gas chromatography–mass spectrometry (GC–MS) [21–23] and HPLC–MS [24]. Most spectrophotometric methods were developed based on reaction of formaldehyde with various reagents to form colored derivatives. In recent years, HPLC is broadly applied to the separation of formaldehyde from possible interferents and improvement of the detection limit [17,18]. Formaldehyde can react with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone before HPLC analysis [18–20]. Therefore, the determination of formaldehyde by HPLC requires a derivatization step which generally is tedious, time consuming and can lead to the loss of analytes. In order to surmount these disadvantages, the in situ derivatization should be satisfactory. It is possible to include the derivatization in the extraction process of the analytes.

Sample preparation is an important step in the analytical process when trace analytes are determined [25]. Owing to the complexity of sample matrices, the relatively low concentrations of formaldehyde in beverages, high reactivity due to the polar carbonyl group, and the presence of more abundant esters and alcohols, sample cleanup and enrichment were necessary to improve sensitivity. In recent years, microextraction techniques have gained interest in the analytical chemistry. The solid-phase

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microextraction (SPME) coupled with on-fiber derivatization or after aqueous phase derivatization provides a simple and solventless sample preparation and has been used for extracting formaldehyde from food samples [21–23]. However, SPME is time-consuming and the fiber is expensive and easily destroyed during the derivatization process. Compared with the SPME derivatization, liquid phase microextraction (LPME) derivatization has the benefits of both cost-effectiveness and convenience, and has been applied for the determination of formaldehyde in food matrices [19]. However, LPME coupled with in situ derivatization still has some drawbacks such as instability of the microdrop, operational difficulty and bubble formation during the extraction. Recently, dispersive liquid–liquid microextraction (DLLME) has emerged as an attractive alternative for sample preparation, which eliminates all the problems described above [26]. In this method, a mixture of extraction solvent and disperser is rapidly injected into an aqueous sample, resulting in the formation of a cloudy solution. The DLLME is very convenient to operate and extraction could be completed in a few seconds. In this technique, it is considerably important to select an extraction solvent with higher density than water, high extraction capability and good chromatographic behavior. Chlorobenzene, carbon tetrachloride, tetrachloroethylene and dichloromethane were used as extraction solvents in DLLME, but the solvents are toxic and environment-unfriendly. DLLME coupled with in situ derivatization has been applied previously for the analysis of aldehydes in cosmetic and blood samples using carbon tetrachloride as extraction solvent [27,28].

Ionic liquids (ILs), which have unique properties such as negligible vapor pressure, miscibility with water and organic solvents, good solubility for organic and inorganic compounds, high thermal stability and environmental benignity, have been used as extraction solvents instead of organic solvents in analytical chemistry [29,30]. The ILs have been used as extraction solvents in DLLME [31–36]. To the best of our knowledge, IL-based DLLME has not been applied for the extraction of formaldehyde from beverages samples. Additionally, considering the central molecules of ILs are the combination of the organic cations and various anions [37], they can efficiently absorb and transfer microwave energy. The studies using ILs as solvents in the microwave-assisted extraction (MAE) of organic compounds have been reported [38–41]. Compared with conventional extraction methods, IL-based MAE is an more efficient procedure for sample pretreatment, which could improve extraction efficiency and save time.

In the present study, simultaneous microwave-assisted derivatization and ionic liquid-based dispersive liquid–liquid microextraction (IL-based DLLME) was first applied for the one-step derivatization and extraction of formaldehyde in beverage 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 were studied and optimized. The performances of developed method were evaluated.

2. Experimental

2.1. Chemicals and reagents

Guaranteed grade formaldehyde (100 μg/mL) was used as standard solution and purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). DNPH was purchased from Beijing Chemical Co. (Beijing, China) and recrystallized twice in acetonitrile solution. 200 μg/mL DNPH solution was prepared by dissolving the reagent in acetonitrile. Chromatographic grade acetonitrile was purchased from Fisher Corporation (Pittsburgh, PA, USA). 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 used. 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$), and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) were purchased from Chengjie Chemical Co., Ltd. (Shanghai, China).

2.2. Instruments

A household microwave oven (SANYO, China) modified in the laboratory with a maximum microwave output power of 600 W was used for the simultaneous microwave-assisted derivatization and IL-based DLLME. The microwave energy can be continuously transmitted to the reactor, and the microwave output power can be controlled with a continuously regulating transformer.

A Shimadzu LC-20A HPLC system (Shimadzu, Kyoto, Japan) equipped with a SPD-20A ultraviolet detector was used. Chromatographic separation was performed on a XDB-C18 column (150 mm × 4.6 mm I.D., 5 μm) (Agilent, Palo Alto, CA, USA).

2.3. Beverage samples

Beverage samples, including draft beer, cola, apple juice, orange juice and peach juice were purchased from a local supermarket (Changchun, China). In order to reduce the viscosity of the sample and be convenient for experimental operation, beverage samples were diluted 1:1 with pure water. Then the samples were adjusted with formic acid to a pH of 3 and filtered through 0.45 μm filters. The resulting solutions were referred to as sample solutions.

2.4. Simultaneous microwave-assisted derivatization and IL-based DLLME

5 mL of sample solution was placed in a 10 mL glass centrifuge tube and then a mixture of 0.4 mL acetonitrile (disperser), 70 μL IL (extraction solvent) and 40 μL DNPH (derivatization reagent) were injected rapidly into the sample solution with a syringe and mixed up by shaking with hands. The resulting cloudy solution was immediately placed in the microwave oven and irradiated under the microwave power of 120 W for 90 s. In this step, formaldehyde was derivatized with DNPH and extracted into the fine droplet of IL. Then the solution was centrifuged at 4000 rpm for 10 min. The upper aqueous phase was removed, and the IL phase was dissolved in 100 μL acetonitrile. The resulting solution was referred to as analytical solution, filtered through a 0.22 μm PTFE filter membrane and stored for HPLC analysis.

2.5. Chromatographic conditions

The mobile phase was a mixture of acetonitrile–water (60:40, v/v). The flow rate and column temperature were set at 1.0 mL/min and 30 °C, respectively. The detection wavelength for the formaldehyde–DNPH derivative was set at 352 nm. The injection volume of sample solution was 20 μL.

3. Results and discussion

3.1. Optimization of simultaneous microwave-assisted derivatization and IL-based DLLME

The efficiency of the simultaneous microwave-assisted derivatization and IL-based DLLME can be affected by several parameters, including type and volume of extraction solvent, type and volume of disperser, microwave power and irradiation time, volume of DNPH, pH of sample solution as well as ionic strength. The spiked samples were prepared by spiking the standard solution in the pure water

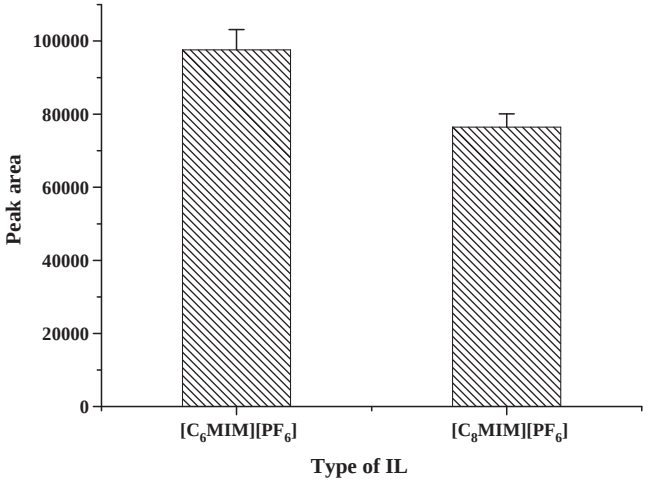

Fig. 1. Effect of type of IL on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

and used in the experiments for optimization. All the experiments were performed in triplicate. The concentration of formaldehyde in the spiked samples was 10 ng/mL.

3.1.1. Type and volume of extraction solvent

In order to achieve good extraction efficiency of the target compound, the effects of type and volume of the extraction solvent were studied. In this study, $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, and $[C_8MIM][PF_6]$ were used as extraction solvents. The solubilities of three ILs in water are 18.8, 7.5, and 2.0 g/L, and the viscosities are 450, 585, and 710 mPa s at 25 °C, respectively [34]. It was observed that when $[C_4MIM][PF_6]$ was used as the extraction solvent, the sample solution was always transparent and no IL phase appeared at the bottom of the tube after centrifugation. The reason may be that the solubility of $[C_4MIM][PF_6]$ in water is higher than those of $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$. As shown in Fig. 1, the peak area obtained with $[C_6MIM][PF_6]$ is larger than that obtained with $[C_8MIM][PF_6]$. Therefore, $[C_6MIM][PF_6]$ was selected as extraction solvent for further studies.

The volume of $[C_6MIM][PF_6]$ was also studied in the range of 40–90 μL. As shown in Fig. 2, the largest peak area of formaldehyde derivative was achieved when 70 μL of $[C_6MIM][PF_6]$ was used. When too small volume of $[C_6MIM][PF_6]$ was used, the peak area of formaldehyde derivative decreased since the amount of $[C_6MIM][PF_6]$ was insufficient to extract the analyte. However, too large volume of $[C_6MIM][PF_6]$ can lead to a decrease in the peak area of the analyte because the increase of the IL phase volume could result in the decrease of the analyte concentration in IL phase. Thus, 70 μL of $[C_6MIM][PF_6]$ was used in the subsequent experiments.

3.1.2. Type and volume of disperser

The disperser should be miscible with both IL and water. In this experiment, acetonitrile, methanol, and acetone were selected as dispersers. The effect of the dispersers on the extraction efficiency of formaldehyde derivative was studied, and the results are shown in Fig. 3. It can be seen that the highest extraction efficiency is obtained when acetonitrile is used as the disperser. Therefore, acetonitrile was chosen as the disperser in the following experiments.

The volume of disperser can directly affect the solubility of IL in aqueous phase and the volume of IL phase, which can affect the extraction efficiency of formaldehyde derivatives. As shown in Fig. 4, the peak area of formaldehyde derivative increases firstly

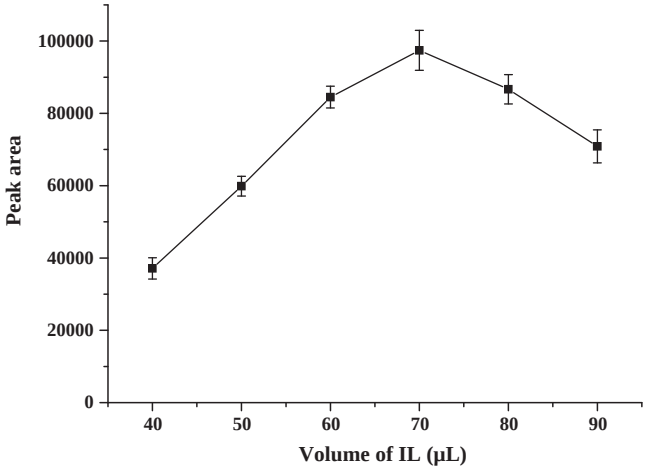

Fig. 2. Effect of the volume of IL on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

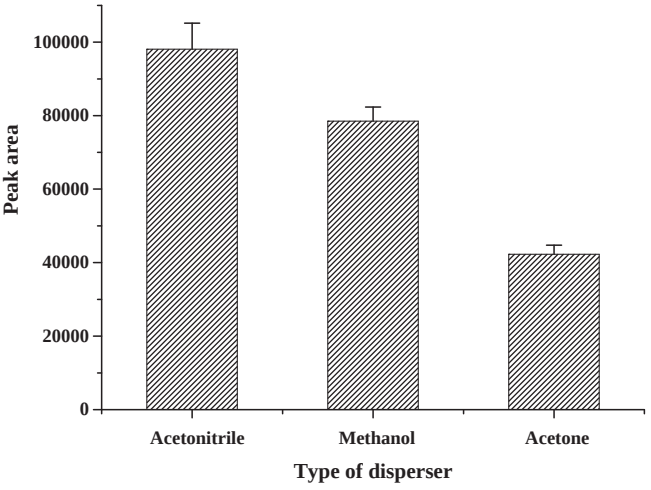

Fig. 3. Effect of type of disperser on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

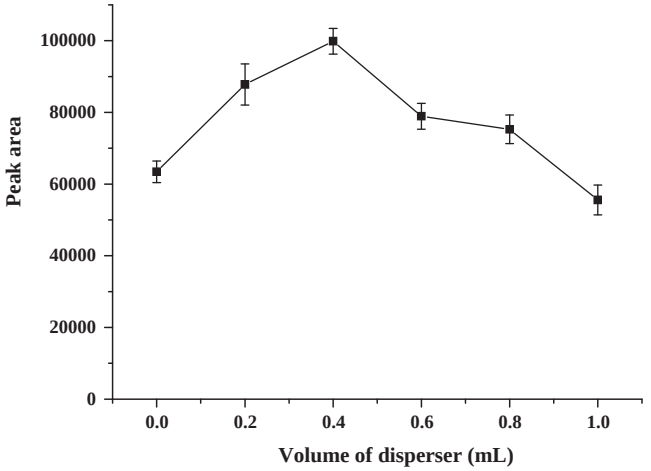

Fig. 4. Effect of the volume of disperser on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

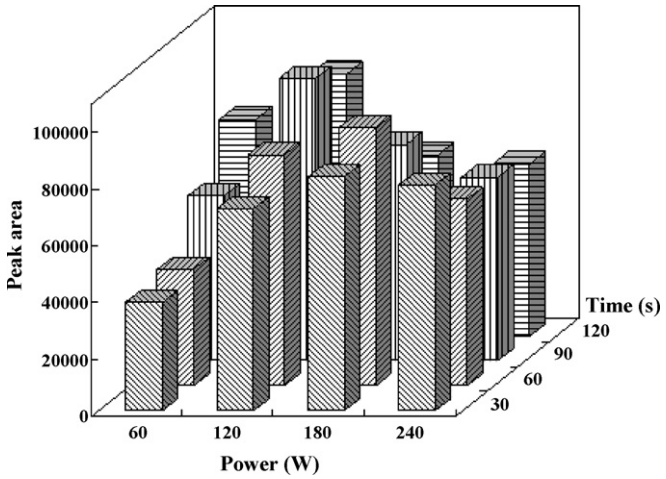

Fig. 5. Effect of microwave power and irradiation time on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; derivatization reagent volume, 40 μL; pH of sample solution, 3.

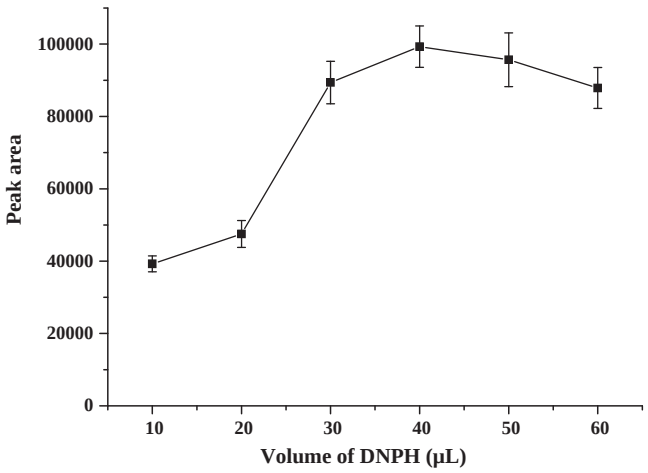

Fig. 6. Effect of derivatization reagent volume on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; pH of sample solution, 3.

and then decreases with the increase of the volume of acetonitrile. When the volume of acetonitrile was too small, the cloudy solution was not formed well and the extraction efficiency of formaldehyde derivative was low. However, when the volume of acetonitrile was too large, the solubility of IL in aqueous solution increased and the extraction efficiency of formaldehyde derivative decreased. Therefore, 0.4 mL acetonitrile was selected in the further experiments.

3.1.3. Effect of microwave irradiation power and time

The temperature can affect the mass transfer rate of analyte and the derivazation reaction rate. The microwave irradiation power and time will affect the extraction and derivatization efficiency of formaldehyde because the temperature of sample solution is strongly related to the microwave irradiation power and time. Therefore, the effect of microwave irradiation power and time was studied. As shown in Fig. 5, the peak area of formaldehyde derivative is the highest when the microwave irradiation power is 120 W and irradiation time is 90 s. The increase of microwave irradiation power and time can result in the decrease of the viscosity of IL, increase of both the rate of derivatization reaction and the rate of mass transfer of analyte. On the other hand, the increase of microwave irradiation power and time can cause the increase of solubility of IL in the sample solution and the decrease of IL phase volume, which can result in the decrease of the extraction efficiency of formaldehyde derivative. Therefore, microwave irradiation power and time selected were 120 W and 90 s, respectively.

3.1.4. Effect of derivatization reagent volume

In the determination of formaldehyde, the often used derivatization reagent is DNPH, which reacted with formaldehyde to form the corresponding hydrazone [18–20]. In order to investigate the influence of DNPH volume on derivatization efficiency was studied and the results are shown in Fig. 6. It can be seen that the peak area of formaldehyde derivative increases with the increase of DNPH volume in the range of 10–40 μL, and slightly decrease with the increase of DNPH volume in the range of 40–60 μL. Therefore, 40 μL of DNPH was selected in the following experiments.

3.1.5. Effect of pH value of sample solution

The derivatization reaction of formaldehyde with DNPH should be in acid medium. In addition, the pH of sample solution plays an important role in the extraction of organic compounds because the pH value of the solution determines the present state of analytes. On the other hand, when the pH value was too low, the emulsive phenomenon did not occur, and the volume of IL phase was sharply reduced. Therefore, formic acid was added in the sample solution to adjust the pH of sample solution. The results are shown in Fig. 7. It can be seen that the peak area of formaldehyde derivative is the largest when pH value is 3, which is in agreement with the result previously reported for aldehyde derivatization [28]. Accordingly, pH 3 was chosen in the following experiments.

3.1.6. Effect of ionic strength

The increase of ionic strength can improve the extraction efficiency due to salting out effect when the traditional organic solvent was used as extraction solvent. Generally, NaCl was used to reduce the solubility of analytes in the aqueous sample and enhance their partitioning into the adsorbent or organic phase. However, the addition of NaCl had different effects when ILs were used as the extraction solvents. The solubility of the ILs in water increases in the presence of NaCl [42,43]. When the concentration of NaCl is too high, the ion exchange between IL and chloride occurs, which can make $[C_6MIM][Cl]$ soluble in water, leading to the decrease of the amount of IL phase and the poor extraction performance

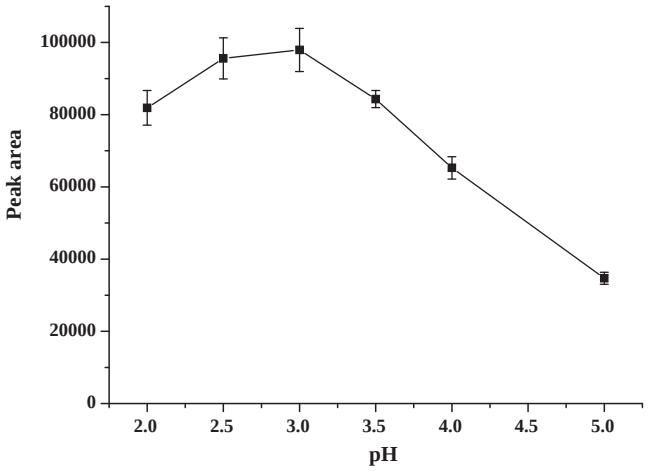

Fig. 7. Effect of sample pH on derivatization and extraction efficiency of formaldehyde in sample. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL.

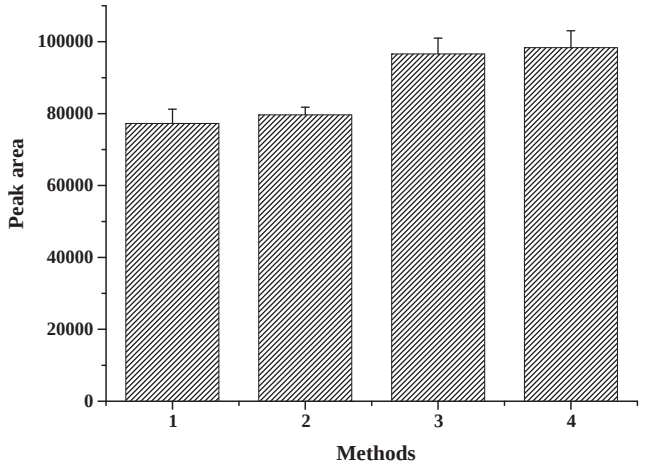

Fig. 8. Effect of microwave irradiation on derivatization and extraction. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; DLLME time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

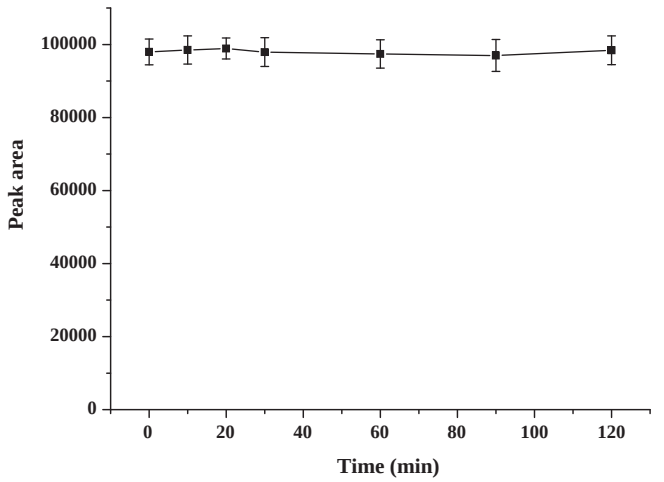

Fig. 9. Stability of derivative. Spiked concentration, 10 ng/mL; extraction solvent ($[C_6MIM][PF_6]$) volume, 70 μL; disperser (acetonitrile) volume, 0.4 mL; microwave power, 120 W; microwave irradiation time, 90 s; derivatization reagent volume, 40 μL; pH of sample solution, 3.

[44]. On basis of these results, NaCl was not used in the subsequent experiments.

3.2. Effect of microwave irradiation

Four methods, including microwave-assisted derivatization (120 W, 90 s) prior to DLLME (Method 1), water-bath derivatization (15 min, 60 °C) prior to DLLME (Method 2) [20], microwave-assisted derivatization prior to microwave-assisted DLLME (Method 3), and simultaneous microwave-assisted derivatization and DLLME (Method 4), were performed to study the effects of the microwave irradiation on the derivatization and extraction and the results obtained are shown in Fig. 8. There is no significant difference between the results obtained by Method 1 and Method 2. The derivatization time for microwave-assisted derivatization (90 s) is much shorter than that for water-bath derivatization (15 min), because the microwave irradiation can promote the derivatization reaction. The comparison of results obtained by Method 1 with that obtained by Method 3 can shows the effect of microwave irradiation on DLLME. As shown in Fig. 8, the peak area of formaldehyde derivative obtained by Method 3 was higher than that obtained by Method 1. The reason may be that ILs have high viscosity at low temperature, which results in the low mass transfer rate of analyte in ILs. Microwave irradiation results in the increase of the temperature, the decrease of the viscosity of the ILs and therefore, the increase of the mass transfer rates of analyte. The experimental results indicate that the microwave irradiation can promote both the derivatization reaction and mass transter of the analyte. The same results were obtained by Methods 3 and 4, which indicated that the derivatization and extraction can be performed separately or simultaneously. However, to save time, simultaneous derivatization and extraction was selected.

3.3. Method evaluation

3.3.1. Analytical performances

Under the optimal conditions, the proposed method was evaluated. Pure water samples spiked at different concentrations of formaldehyde (0.5–50 ng/mL) were used. For each concentration level, three replicate analyses were performed. The relationship between the analyte concentration (c) and measured peak area (A) was expressed as regression equation: $A = 2723.1 + 10108.5c$. The relationship exhibited good linearity with correlation coefficient (r) of 0.9965. The limit of detection (LOD) was determined based on the signal to noise (S/N) ratio of 3 and found to be 0.12 ng/mL. Precision was evaluated by measuring intra-day and inter-day relative standard deviations (RSDs). The intra-day and inter-day precision of the method were evaluated by analyzing the spiked draft beer samples at three concentrations levels (2, 5 and 20 ng/mL) on the same day and the five consecutive days, respectively. The results obtained are shown in Table 1. The intra- and inter-day precision are in the range of 3.5–5.4% and 4.2–8.1%, respectively.

3.3.2. Stability of derivative

The stability of derivative was assessed by analyzing water sample containing the formaldehyde at the concentration of 10 ng/mL. When derivatization and extraction were finished, the analytical solutions stood for 0 min, 10 min, 20 min, 30 min, 60 min, 90 min, and 120 min, respectively, and then were analyzed. The results are shown in Fig. 9. It was found that the derivative was stable under room temperature for 120 min.

3.3.3. Analysis of samples

To evaluate the applicability of the proposed method, some real samples, including draft beer, cola, fruit (apple, orange and peach) juice were analyzed. In order to reduce the viscosity, the beverages

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

Added (ng/mL)	Intra-day			Inter-day		
	Found (ng/mL)	Recovery (%)	RSD (%)	Found (ng/mL)	Recovery (%)	RSD (%)
2.0	1.8	89.5	5.4	1.8	89.5	5.9
5.0	4.6	91.2	3.5	4.4	88.0	8.1
20.0	18.1	90.4	4.7	18.2	90.8	4.2

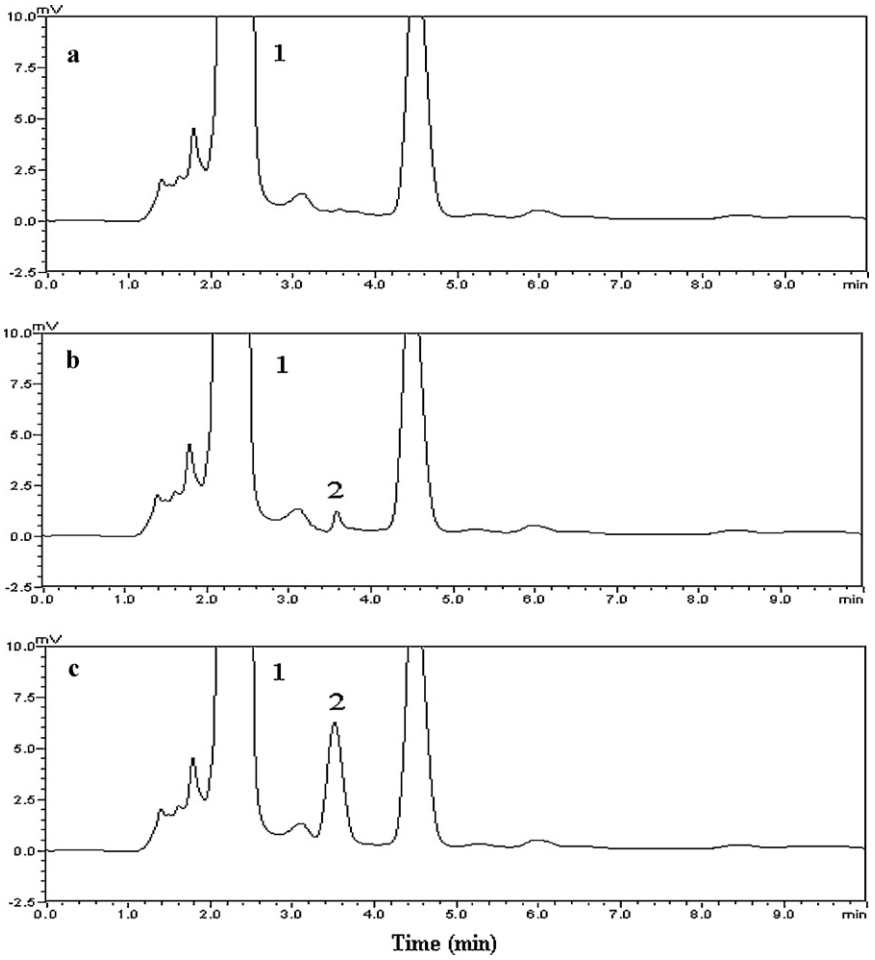

Fig. 10. Typical chromatograms for blank (a), spiked at 1.0 ng/mL (b) and spiked at 20 ng/mL (c) beer sample obtained at wavelength 352 nm. (1) DNPH and (2) DNPH–HCHO derivative.

samples were diluted 1:1 with pure water prior to their analysis. The typical chromatograms of the blank and spiked draft beer sample are shown in Fig. 10. As can be seen, no significant interference peaks are found at the retention time of formaldehyde. To evaluate precision and accuracy of the proposed method, the spiked samples were analyzed and the analytical results are shown in Table 2. The relative standard deviations (RSDs) and recoveries are in the range of 3.4–8.4% and 85.4–95.1%, respectively. It can be considered that the present method provides acceptable recoveries for the determination of formaldehyde in real beverage samples.

3.3.4. Comparison of microwave-assisted derivatization and IL-based DLLME with other methods

Some other methods reported in literature, such as colorimetric-solid phase extraction (C-SPE) [9], flow injection analysis with spectrophotometric detection (FIA-SPD) [10], FIA with

Table 2
Formaldehyde content and the spiked recoveries in different beverages.

Sample	Content[a] (ng/mL)	Added (ng/mL)	Found[a] (ng/mL)	Recovery (%)	RSD (%)
Draft beer	0.0	2.0	1.8 ± 0.1	89.5	5.4
		5.0	4.6 ± 0.2	91.2	3.5
		20.0	18.1 ± 0.8	90.4	4.7
Cola	7.6 ± 0.5	2.0	9.4 ± 0.7	87.5	7.8
		5.0	12.1 ± 1.0	90.1	8.4
		20.0	26.1 ± 1.2	92.3	4.7
Apple juice	15.4 ± 1.2	2.0	17.2 ± 0.6	90.4	3.6
		5.0	19.8 ± 0.9	87.5	4.8
		20.0	34.4 ± 2.4	95.1	7.1
Orange juice	1.8 ± 0.1	2.0	3.5 ± 0.2	85.4	6.5
		5.0	6.2 ± 0.2	88.9	3.4
		20.0	19.2 ± 1.4	87.1	7.4
Peach juice	6.5 ± 0.5	2.0	8.4 ± 0.5	94.6	5.9
		5.0	10.7 ± 0.8	84.9	7.5
		20.0	24.6 ± 1.1	90.5	4.4

[a] Results expressed as mean ± SD, $n = 5$.

Table 3
Comparison of the proposed method with other methods for the determination of formaldehyde.

Method	Matrix	Extraction time (min)	LOD (ng/mL)	Reference
C-SPE	Drinking water	3	80	[9]
FIA-SPD	Beer	40	2.5	[10]
FIA-FD	Alcoholic beverages	–	3.1	[13]
mini-CE-ED	Wines, beer	60	9.1	[15]
HPLC-DAD	Spirits	20	24	[16]
The proposed method	Beverages	1.5	0.12	–

fluorimetric detection (FIA-FD) [13], miniaturised capillary electrophoresis with electrochemical detection (mini-CE-ED) [15], HPLC with diode-array detection (HPLC-DAD) [16], were compared with the proposed method, and the results are presented in Table 3. Compared with the reported methods, when the proposed method was applied, the LOD is lower and the extraction time is shorter because microwave irradiation can obviously improve the analytical performance and extraction, derivatization, and preconcentration can be performed simultaneously. The results indicated that the proposed method was timesaving, convenient, sensitive and suitable for determination of formaldehyde in complex matrices, such as beverages.

4. Conclusion

The simultaneous microwave-assisted derivatization and IL-based DLLME was established for the determination of trace amount of formaldehyde in beverage samples. When the microwave-assisted derivatization and the IL-based DLLME extraction were finished simultaneously in one step, the overall extraction time was shortened. The microwave irradiation was beneficial to transfer of the analyte from aqueous solution to IL phase and to accelerate the derivatization reaction. When IL was used as the extraction solvent the consumption of organic solvent can be reduced and the extraction time can be shortened. The experimental results indicate that the proposed method reveals an excellent prospect in the field of sample pretreatment of food and may be a useful guidance for determination other carbonyl compounds.

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