# Analytical Methods

## PAPER

# Ion pair based dispersive liquid–liquid microextraction for the preconcentration of ultra-trace levels of bismuth(III) and its determination by electrothermal atomic absorption spectroscopy

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A simple, selective and efficient ion pair based dispersive liquid–liquid microextraction method was used for the preconcentration of ultra-trace levels of Bi(III) prior to its determination by electrothermal atomic absorption spectrometry. This method is based on the complexation of Bi(III) with thiocyanate anion to form the anionic complexes, $Bi(SCN)_6^{3-}$ and $Bi(SCN)_4^-$. A cationic surfactant, cetylpyridinium chloride (CPC), was used as a counter ion. The resulting ion pair complexes were extracted into fine droplets of carbon tetrachloride by rapid injection of a mixture of acetone (as the disperser solvent) and carbon tetrachloride (as the extraction solvent) into the sample solution. Important parameters affecting the extraction efficiency, including sample pH, thiocyanate and CPC concentrations, and type and volume of the extraction and disperser solvents, were examined and optimized. Under the optimum conditions, the calibration graph was linear in the range of $0.3-8\ \mu g\ L^{-1}$ Bi (III) with a correlation coefficient of 0.9979. The relative standard deviation (RSD, %) based on eight replicate analyses of $2\ \mu g\ L^{-1}$ Bi(III) was 4.8%, and the detection limit (DL) of Bi(III) was $0.07\ \mu g\ L^{-1}$. The proposed method was validated by the analysis of a certified reference material and the spike method. The obtained results were in very good agreement with the certified values. The proposed method was successfully applied for the determination of ultra-trace levels of Bi(III) in different water and human serum samples.

## 1. Introduction

In recent years, environmental pollution by heavy metals has received considerable attention.[1,2] Bismuth (Bi) is a heavy metal with relatively wide applications in different fields such as the cosmetic industry,[3] medicine[4] and preparation of semiconductors.[5] It is used in the cosmetic industry as a pigment in eye shadows, hair sprays and nail polishes. Moreover, in the field of medicine, it is an ingredient used in few pharmaceutical compounds for the treatment of diarrhea, syphilis and eye infections.[3,4] As the use of bismuth has increased, it has spread in the environment, and the chance of exposure of organisms to bismuth has increased. Bismuth is slightly toxic and can affect the kidney and liver; therefore, analyzing and monitoring the content of bismuth in environmental samples is of great significance.[6] A variety of techniques have been developed for the determination of bismuth in different samples. These include UV-vis spectrophotometry,[7,8] atomic absorption spectrometry,[9,10] inductively coupled plasma mass spectrometry[11]

and inductively-coupled plasma optical emission spectrometry.[12] Among the abovementioned techniques, atomic absorption spectrometry is most often used because of its availability and simplicity. However, the direct determination of trace metals in real samples containing complex matrices or very low concentrations of analytes is difficult. In order to achieve this goal, separation and preconcentration procedures for sample preparation are necessary.[13]

Dispersive liquid–liquid microextraction (DLLME)[14,15] is a preconcentration technique, which has the advantages of simplicity, rapidity and use of highly reduced amounts of organic solvents. In this method, a mixture of disperser solvent and extraction solvent is rapidly injected into the sample solution, causing the formation of fine droplets of extraction solvent. Owing to the considerably large surface area between the extraction solvent and the aqueous sample, an equilibrium state is achieved quickly.

Spectrophotometry investigation of bismuth thiocyanate complexes has been performed by Kingery and Hume.[16] They have reported that different positively and negatively charged Bi–thiocyanate complexes were formed at different concentrations of thiocyanate anion. Based on the reported results, at a certain concentration of thiocyanate anion, the negatively

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charged Bi–thiocyanate complexes, $Bi(SCN)_6^{3-}$ and $Bi(SCN)_4^-$, are predominant. In this study, we used thiocyanate anion at a critical concentration to produce negatively charged Bi–thiocyanate complexes followed by the addition of cetylpyridinium chloride (CPC) as a positive counter ion to form hydrophobic ion pair complexes. The resulting ion pair complexes were extracted into fine droplets of extraction solvent by DLLME and quantitatively determined by electrothermal atomic absorption spectrometry (ETAAS). Different parameters affecting the extraction efficiency were extensively investigated and optimum conditions were selected.

## 2. Experimental

### 2.1. Instrumentation

A Nov AA 400, Analytik Jena graphite furnace atomic absorption spectrometer equipped with a deuterium lamp as a background correction system was used for the determination of bismuth in the extraction solvent. Pyrolytically coated graphite tubes with the L'Vov platform were used. A bismuth hollow cathode lamp at 223.1 nm was employed as the radiation source and measurements were carried out in peak area mode using a spectral bandwidth of 0.5 nm. Argon of 99.99% purity was used as the inert gas and its flow rate was maintained at 300 mL $min^{-1}$ during all stages except for the atomization, wherein the flow was stopped. The instrumental parameters are given in Table 1. The pH values in the aqueous phase were measured with a Metrohm 827 pH lab (Switzerland) glass-electrode pH meter. Phase separation was assisted using a Centurion Scientific Centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany).

### 2.2. Reagents and solutions

Bismuth standard solution (1000 mg $L^{-1}$) was prepared from bismuth(III) nitrate penta-hydrate (Sigma-Aldrich, USA) in deionized water (Barnstead, Nanopure Diamond purification system). The working standard solution was prepared daily by stepwise dilution from the standard stock solution with deionized water. A solution of 2.0 mol $L^{-1}$ thiocyanate anion was prepared from potassium thiocyanate (Merck, Darmstadt, Germany) in deionized water. Carbon tetrachloride, chloroform and dichloromethane as extraction solvents and ethanol, acetonitrile, acetone and methanol as disperser solvents were purchased from Merck (Darmstadt, Germany). A solution of

$10^{-2}$ mol $L^{-1}$ of cetylpyridinium chloride (CPC) (Merck, Darmstadt, Germany) was prepared in deionized water and used as the positive counter ion.

### 2.3. Preparation of real samples

**2.3.1. Water samples.** Different water samples, including tap (obtained from Mashhad, Iran), river (Kashaf Rood, Mashhad, Iran), mineral and spring (Nowchah, Mashhad, Iran) waters, were collected from their local sources and filtered through a No. 42 Whatman® paper to remove any suspended particles; the samples were then acidified with dilute nitric acid and stored in glass bottles at 5 °C. For the analysis of Bi content in real samples, six milliliters of each sample solution were transferred into the sample vial and analyzed according to the microextraction procedure.

**2.3.2. Serum samples.** The human serum samples (sample no. 1, 2 and 3) were collected from the Iranian Blood Transfusion Organization (Mashhad, Iran). Each sample (2.0 mL) was acidified with 30% (w/v) trichloroacetic acid solution to precipitate the proteins.[17] The mixture was then stirred in a vortex for 5 min and centrifuged for 15 min. The supernatant was decanted and filtered through a 0.22 μm membrane and diluted to 10 mL with deionized water. For the analysis of Bi(III) content in the serum samples, 2.5 mL of each sample was analyzed according to the method in Section 2.4.

### 2.4. Microextraction procedure

10 mL of sample solution containing 2 μg $L^{-1}$ Bi(III), 0.80 mol $L^{-1}$ $SCN^-$ and $1.5 \times 10^{-4}$ mol $L^{-1}$ CPC was adjusted at pH 2 with diluted nitric acid and transferred into a conical bottom glass centrifuged tube. 750 μL of acetone containing 60 μL of carbon tetrachloride was rapidly injected into the sample solution. A cloudy solution (water, acetone and carbon tetrachloride) formed in the test tube. In this step, hydrophobic ion pair based complexes of bismuth were extracted into fine droplets of carbon tetrachloride. The mixture was then centrifuged for 7 min at 3000 rpm; by this method, the dispersed fine droplets of carbon tetrachloride were sedimented at the bottom of the test tube. The volume of the sedimented phase was determined using a 100 μL micro-syringe and was about 40.0 μL. 25 μL of the sedimented phase was removed by a syringe and diluted to 50 μL with ethanol. Finally, 20 μL of this solution was injected into the electrothermal atomizer by an auto-sampler to obtain the analytical signal.

## 3. Results and discussion

### 3.1. Optimization of graphite furnace conditions

In order to obtain high extraction efficiency for the ETAAS measurement of Bi in the extraction solvent, the optimization of important parameters, including pyrolysis and atomization temperature in the graphite furnace, was studied. As the matrix of the extraction solvent is carbon tetrachloride and ethanol, it can be easily removed at 130 °C. The influence of pyrolysis temperature on Bi absorbance was studied in the range of 400–800 °C. The optimal pyrolysis temperature was observed at

Table 1  Instrumental parameters and temperature program for bismuth analysis

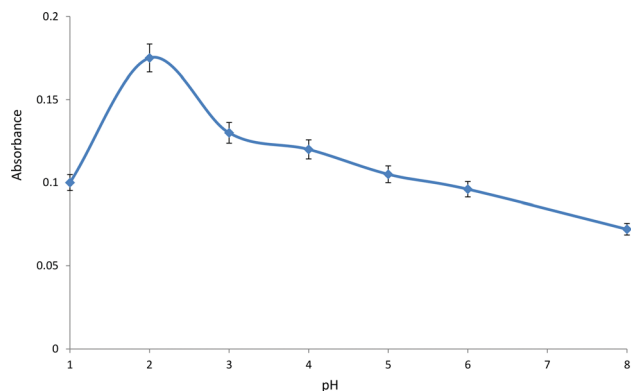| Step | Temp. (°C) | Ramp time (s) | Hold time (s) | Argon flow rate (mL $min^{-1}$) |
| --- | --- | --- | --- | --- |
| Drying 1 | 90 | 5 | 10 | 300 |
| Drying 2 | 130 | 3 | 15 | 300 |
| Ashing | 600 | 15 | 20 | 300 |
| Atomization | 2000 | 0 | 3 | 0 |
| Cleaning | 2400 | 2 | 3 | 300 |

Fig. 1 Effect of pH on the absorbance of Bi(III). Conditions: 2 μg L$^{-1}$ Bi(III), 0.80 mol L$^{-1}$ [SCN$^-$], $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC and 750 μL of acetone containing 60 μL CCl$_4$.



Fig. 3 Effect of CPC concentration on the absorbance of Bi(III). Conditions: 2 μg L$^{-1}$ Bi(III), pH 2, 0.80 mol L$^{-1}$ [SCN$^-$] and 750 μL of acetone containing 60 μL CCl$_4$.

550–650 °C, with a hold time of 20 s. Therefore, 600 °C was selected as the optimum pyrolysis temperature. The effect of atomization temperature on Bi absorbance was studied within the interval of 1600–2100 °C. The maximum signal was observed at 2000 °C, with a hold time of 3 s. Finally, a temperature of 2400 °C and a hold time of 3 s were chosen for the cleaning step. No matrix modifier was found to be useful for the enhancement of the sensitivity toward Bi. Therefore, all analyses were performed without the addition of matrix modifier.

### 3.2. Effect of pH

The effect of pH on the absorbance of Bi(III) was studied in the range of 1–8. The results presented in Fig. 1 show that the absorbance reached its maximum value at pH 2 and then decreased gradually at higher pH values. Based on the results, bismuth ion paired complex is stable in acidic conditions and its stability is reduced at higher pH values. Therefore, pH 2 was selected as the optimum value.

### 3.3. Effect of thiocyanate anion concentration

Thiocyanate anion has an important effect on the formation of negatively charged Bi(SCN)$_6$$^{3-}$ and Bi(SCN)$_4$$^-$ complexes.[16] To study the effect of thiocyanate concentration on the extraction

efficiency of Bi(III), its concentration was studied in the range of 0.2–1.4 mol L$^{-1}$. The results are shown in Fig. 2. Based on the results, the absorbance increased gradually as the thiocyanate concentration increased to 0.75 mol L$^{-1}$ and it remained constant afterwards. Therefore, a concentration of 0.80 mol L$^{-1}$ thiocyanate anion was selected as the optimum value.

### 3.4. Effect of CPC concentration

A cationic surfactant, cetyl pyridinium chloride (CPC), was used as a counter ion due to its ability to form ion pairs with the Bi(SCN)$_6$$^{3-}$ and Bi(SCN)$_4$$^-$ complexes. Different concentrations of CPC were used in the concentration range from $5.0 \times 10^{-5}$ to $2.0 \times 10^{-4}$ mol L$^{-1}$. As can be seen in Fig. 3, an increase in the extraction recovery of the ion pair occurred when the CPC concentration was increased up to $1.30 \times 10^{-4}$ mol L$^{-1}$, and the absorbance remained constant at higher CPC concentrations. Therefore, a concentration of $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC was selected as the optimum value.

### 3.5. Effect of type of extraction solvent

In order to obtain high extraction efficiency, the selection of the type of extraction solvent and disperser solvent must be optimized in a DLLME system. The effect of different extraction solvents, including carbon tetrachloride, chloroform and dichloromethane, were investigated. 750 μL of acetone containing different volumes of carbon tetrachloride,
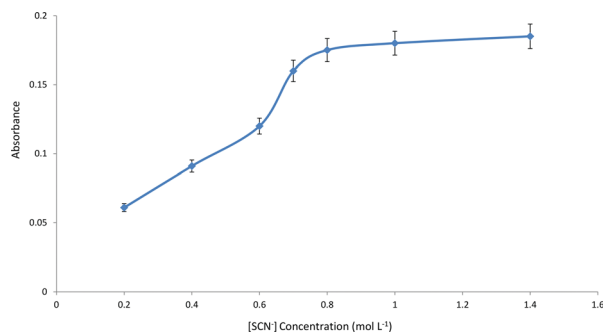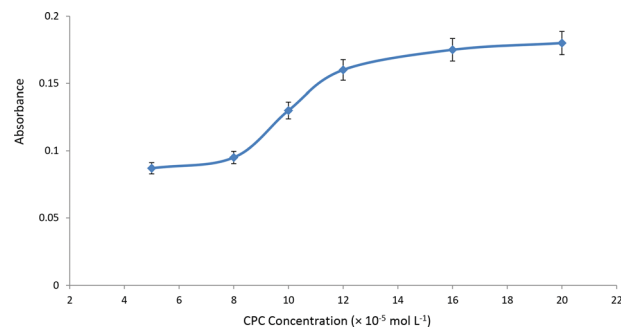


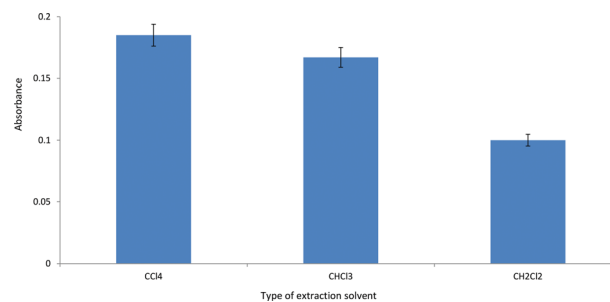Fig. 2 Effect of thiocyanate concentration on the absorbance of Bi(III). Conditions: 2 μg L$^{-1}$ Bi(III), pH 2, $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC and 750 μL of acetone containing 60 μL CCl$_4$.



Fig. 4 Effect of the type of extraction solvent on the absorbance of Bi(III). Conditions: 2 μg L$^{-1}$ Bi(III), pH 2, 0.80 mol L$^{-1}$ [SCN$^-$], $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC.
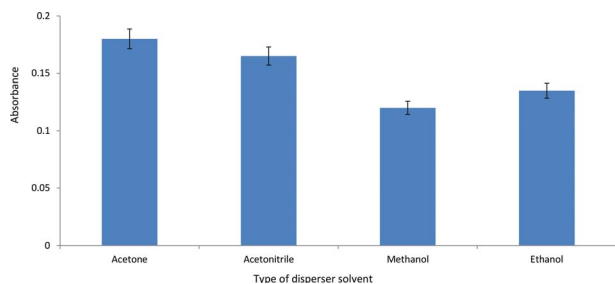
Fig. 5 Effect of the type of disperser solvent on the absorbance of Bi(III). Conditions: 2 µg L$^{-1}$ Bi(III), pH 2, 0.80 mol L$^{-1}$ [SCN$^-$], $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC.

dichloromethane and chloroform were injected into the sample solution to obtain 40 µL of sedimented extraction solvent. As shown in Fig. 4, carbon tetrachloride has the highest extraction efficiency; therefore, it was selected as the optimum extraction solvent.

### 3.6. Effect of volume of extraction solvent

To study the effect of extraction solvent volume on the absorbance of Bi(III), different volumes of carbon tetrachloride in the range of 50–150 µL were examined. The results (data not shown) show that 60 µL of carbon tetrachloride provides maximum extraction efficiency for the determination of Bi(III). Therefore, 60 µL of carbon tetrachloride was selected as the optimum volume.

Table 2  The effect of interfering ions on the absorbance of 2 µg L$^{-1}$ Bi(III)

| Interfering ions | Added as | Concentration (µg L$^{-1}$) | Recovery, % |
|---|---|---|---|
| Na$^+$ | NaNO$_3$ | 200 000 | 98.1 |
| Zn$^{2+}$ | Zn(NO$_3$)$_2$ | 500 | 96.9 |
| Cu$^{2+}$ | Cu(NO$_3$)$_2 \cdot$5H$_2$O | 500 | 96.7 |
| Mn$^{2+}$ | Mn(NO$_3$)$_2 \cdot$H$_2$O | 500 | 98.6 |
| Ni$^{2+}$ | Ni(NO$_3$)$_2$ | 500 | 99.0 |
| Pb$^{2+}$ | Pb(NO$_3$)$_2$ | 500 | 98.9 |
| Cd$^{2+}$ | Cd(NO$_3$)$_2 \cdot$H$_2$O | 500 | 98.9 |
| Fe$^{3+}$ | Fe(SO$_4$)$_2 \cdot$NH$_4 \cdot$12H$_2$O | 400 | 96.5 |
| Al$^{3+}$ | Al(NO$_3$)$_3 \cdot$9H$_2$O | 400 | 96.7 |
| Co$^{2+}$ | Co(NO$_3$)$_2 \cdot$6H$_2$O | 200 | 97.1 |
| SO$_4{}^{2-}$ | K$_2$SO$_4$ | 100 000 | 98.5 |
| Cl$^-$ | KCl | 100 000 | 100 |

### 3.7. Effect of type of disperser solvent

The selection of a disperser solvent is limited to solvents such as methanol, acetonitrile, ethanol and acetone, which are miscible with both water and extraction solvents. To study the effect of the type of disperser solvent on the absorbance of Bi(III), 750 µL of different disperser solvents, containing 60 µL of carbon tetrachloride for acetone and acetonitrile and 70 µL of carbon tetrachloride for ethanol and methanol, were injected into the sample solution to obtain 40 µL of sedimented extraction solvent. The results in Fig. 5 show that acetone has the
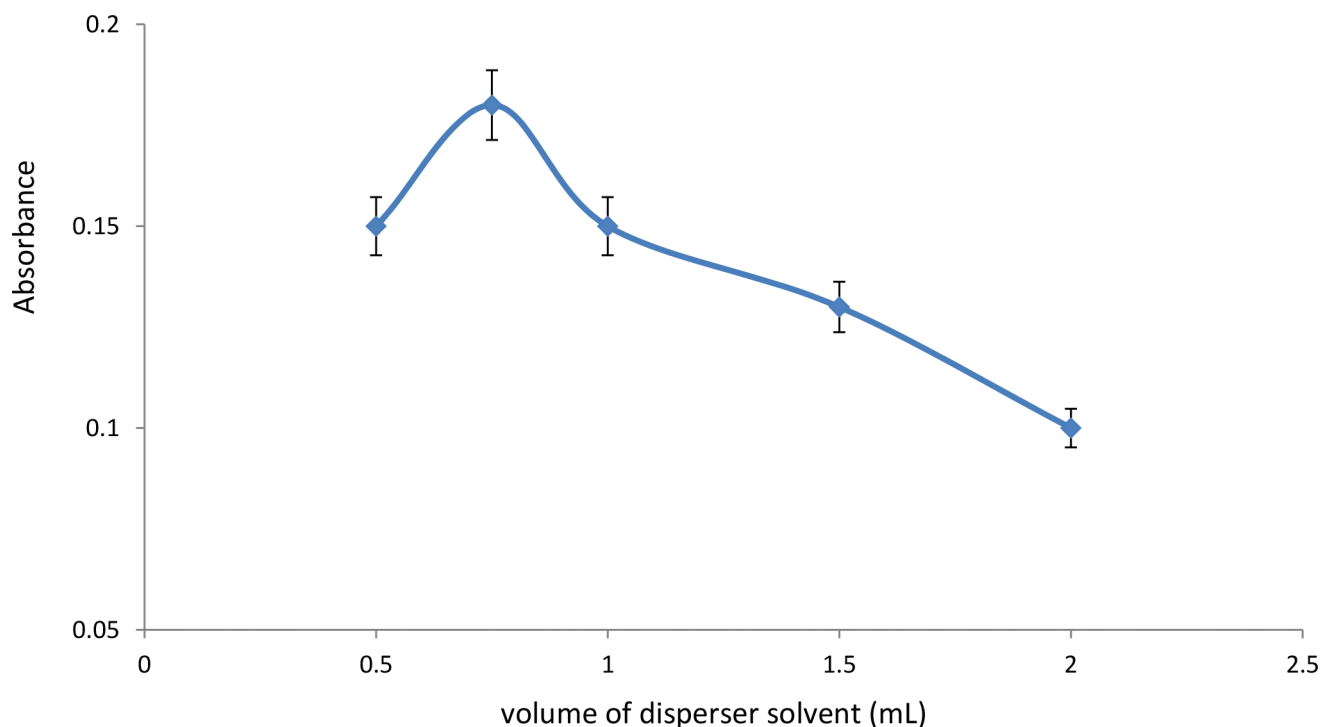


Fig. 6 Effect of the volume of disperser solvent on the absorbance of Bi(III). Conditions: 2 µg L$^{-1}$ Bi(III), pH 2, 0.80 mol L$^{-1}$ [SCN$^-$], $1.50 \times 10^{-4}$ mol L$^{-1}$ CPC.

**Table 3** Analysis of real samples for the determination of Bi(III). Results (mean ± standard deviation based on three replicate analyses)

| Sample | Added (µg L⁻¹) | Founded (µg L⁻¹) | Recovery (%) |
|---|---|---|---|
| Tap water[a] | — | 0.69 ± 0.03 | — |
| | 0.80 | 1.50 ± 0.08 | 100.7 |
| | 2.00 | 2.67 ± 0.11 | 99.2 |
| Spring water[b] | — | 1.1 ± 0.06 | — |
| | 0.80 | 2.01 ± 0.10 | 105.8 |
| | 2.00 | 3.25 ± 0.15 | 104.8 |
| Mineral water | — | ND[d] | — |
| | 0.80 | 0.86 ± 0.04 | 107.5 |
| | 2.00 | 2.11 ± 0.14 | 105.5 |
| River water[c] | — | 2.80 ± 0.15 | — |
| | 1.00 | 3.75 ± 0.17 | 98.7 |
| | 2.00 | 4.65 ± 0.20 | 96.9 |
| Sample no. 1 | — | ND | — |
| | 4.00 | 4.18 ± 0.17 | 104.5 |
| Sample no. 2 | — | ND | — |
| | 4.00 | 4.06 ± 0.16 | 101.5 |
| Sample no. 3 | — | 7.00 ± 0.41 | — |
| | 6.00 | 12.9 ± 0.55 | 99.2 |

[a] Obtained from Mashhad, Iran. [b] Nowchah, Mashhad, Iran. [c] Kashaf Rood, Mashhad, Iran. [d] Not detected.

maximum extraction efficiency for the microextraction of Bi(III); therefore, it was selected as the optimum disperser solvent.

### 3.8. Effect of volume of disperser solvent

To study the effect of the volume of disperser solvent on the absorbance of Bi(III), different volumes of disperser solvent in the range of 0.5–2 mL containing 60 µL of carbon tetrachloride were examined. The results are shown in Fig. 6. According to the results, the absorbance increases when the acetone volume is increased to 750 µL and decreases when the acetone volume is increased further. It seems that at low volumes of acetone, the cloudy state is not formed well and, therefore, the absorbance decreases; at high volumes of acetone, the solubility of the Bi(III) ion pair complex in water increases and thus the extraction efficiency decreases. Therefore, 750 µL of acetone was selected as the optimum value.

### 3.9. Effect of centrifuge conditions

The effect of the centrifugation rate on the absorbance of Bi(III) was studied in the range of 2000–3500 rpm with a constant

centrifuge time of 10 min. The results show that a 3000 rpm centrifuge rate is an optimal value for the separation of two immiscible phases. Moreover, the effect of centrifugation time on the absorbance of Bi(III) was studied in the range of 1–10 min with a constant centrifuge rate of 3000 rpm. The results (data not shown) show that 7 min centrifugation time is an optimal centrifuge time. Therefore, 7 min centrifugation time at 3000 rpm was selected as the optimum value.

### 3.10. Effect of interfering ions

The effect of different cations and anions on the recovery of Bi(III) was investigated to check the selectivity of the proposed method. An ion was considered to be interfering when it caused a variation in the absorbance of the analyte greater than ±5%. The recoveries of Bi(III) determined in various amounts of matrix ions are given in Table 2. As the results show, there is no interference from the coexisting ions in different real samples for the determination of Bi(III).

### 3.11. Analytical figures of merit

Under the optimum conditions, the calibration curve was linear in the range of 0.3–8 µg L⁻¹ Bi(III) with a correlation coefficient of 0.9979. The calibration equation after the preconcentration step was $A = 0.0246 + 0.0678C$, where $A$ is the analytical signal measured as absorbance and $C$ is the concentration of Bi(III) in µg L⁻¹. Moreover, the equation of the calibration curve without the preconcentration step was $A = 0.012 + 0.0005C$ within a dynamic range from 50 to 200 µg L⁻¹ Bi(III). The relative standard deviation (RSD, %) based on the eight replicate analysis of 2 µg L⁻¹ Bi(III) was 4.8%. The limit of detection (LOD) based on $3S_b/m$ (where $S_b$ is the standard deviation for six replicate analysis of the blank signals and $m$ is the slope of the calibration curve after extraction) was calculated to be 0.07 µg L⁻¹. The preconcentration factor (PF), calculated as the ratio between the volumes of the aqueous phase and the final volume of the extraction phase, was 125. The enhancement factor as calculated by the slope ratio of the calibration curves for Bi determination with and without ion paired based-DLLME was 136.

### 3.12. Analysis of real samples

In order to assess the applicability of the proposed method, different water and human serum samples were analyzed according to the microextraction procedure. The results are

**Table 4** Comparison of ion pair based DLLME with other reported methods for the determination of Bi(III)

| Method | Linear range (µg L⁻¹) | LOD (µg L⁻¹) | RSD (%) | PF | Ref. |
|---|---|---|---|---|---|
| DLLME-UV-vis | 5–400 | 1.6 | 1.14–2.66 | 62.5 | 7 |
| CPE-FAAS | — | 4.0 | 4.2 | — | 10 |
| UA-DLLME-W-coil ET-AAS | 2–30 | 0.2 | 4.7 | — | 18 |
| DLLME-flow injection inductively coupled plasma mass spectrometry | 0.01–1 | 0.0047 | 2.6–6.7 | — | 11 |
| DLLME-FAAS | 30–1700 | 3.0 | 1.5 | 28.6 | 9 |
| Ion paired DLLME-ETAAS | 0.3–8 | 0.07 | 4.8 | 125 | Present work |

shown in Table 3. In order to check the validity of the proposed method, spike methods were also performed on the samples. As shown in Table 3, the recovery values were in the range of 96–107%. The results show that the procedure is reliable for the determination of ultra-trace levels of Bi(III) in water and human serum samples. The accuracy of the method was validated by the analysis of CRM-TMDW (drinking water) certified reference material (http://www.highpuritystandards.com/store/home.php?cat=44). The observed value of the analysis of CRM was $9.73 \pm 0.58$ μg L$^{-1}$ (mean $\pm$ standard deviation based on three replicate analysis), which is in very good agreement with the certified value of 10 μg L$^{-1}$ Bi(III).

### 3.13. Comparison to other methods

A comparison of the proposed method with other reported preconcentration methods for the determination of Bi(III) is given in Table 4. As can be seen, the linear range, LOD and preconcentration factor (PF) of the proposed method are better or comparable to those of other reported methods. The simplicity of operation, rapidity, high sensitivity, low cost and high preconcentration factor are the few advantages of the proposed method.

## 4. Conclusions

An efficient, simple and sensitive ion paired based dispersive liquid–liquid microextraction method was used for the pre-concentration of ultra-trace levels of Bi(III) followed by its determination by ETAAS. This method is based on the complexation of Bi(III) with thiocyanate anion (SCN$^-$) to form negatively charged Bi(SCN)$_6^{3-}$ and Bi(SCN)$_4^-$. Cetyl pyridinium chloride (CPC) was used as a counter ion to form hydrophobic ion pair complexes, which are extractable into fine droplets of carbon tetrachloride by DLLME. The proposed method was successfully applied for the determination of trace levels of Bi(III) in different water and human serum samples.

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