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A new supramolecular based liquid solid microextraction method for preconcentration and determination of trace bismuth in human blood serum and hair samples by electrothermal atomic absorption spectrometry

Hadi Kahe · **Mahmoud Chamsaz**

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Abstract A simple and reliable supramolecule-aggregated liquid solid microextraction method is described for preconcentration and determination of trace amounts of bismuth in water as well as human blood serum and hair samples. Catanionic microstructures of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) surfactants, dissolved in deionized water/propanol, are used as a green solvent to extract bismuth (III)-diethyldithiocarbamate complexes by dispersive microextraction methodology. The extracted solid phase is easily removed and dissolved in 50 μL propanol for subsequent measurement by electrothermal atomic absorption spectrometry (ET-AAS). The procedure benefits the merits of supramolecule aggregates' properties and dispersive microextraction technique using water as the main component of disperser solvent, leading to direct interaction with analyte. Phase separation behavior of extraction solvent and different parameters influencing the extraction efficiency of bismuth ion such as salt concentration, pH, centrifugation time, amount of chelating agent, SDS:CTAB mole ratio, and solvent amounts were thoroughly optimized. Under the optimal experimental conditions, the calibration curve was linear in the range of 0.3–6 μg L^{-1} Bi (III) with a limit of detection (LOD) of 0.16 μg L^{-1} ($S/N = 3$). The relative standard deviations (RSD) of determination were obtained to be 5.1 and 6.2 % for 1 and 3 μg L^{-1} of Bi (III), respectively. The developed method was successfully applied as a sensitive and accurate technique for determination of bismuth ion in human blood serum, hair samples, and a certified reference material.

Keywords Supramolecule aggregates · Cetyltrimethylammonium bromide (CTAB) · Sodium dodecyl sulfate (SDS) · Bismuth · Microextraction · Graphite furnace atomic absorption spectrometry

Introduction

In recent years, heavy metals' pollution in environment has received considerable attention (Panhwar et al. 2016; Panhwar et al. 2015). Bismuth compounds have been widely used in different fields such as cosmetics (Maile et al. 2005), semiconductors, alloys and metallurgical additives (Pistofidis et al. 2007; Cadore and Baccan 1997), and medicine (Sox and Olson 1989). In cosmetic industry, bismuth is used as a pigment in eye shadows, hair sprays, and nail polishes. It has been associated with medicine for more than two centuries, and some of the bismuth colloidal salts, including subcitrate and subgallate, have important applications in various pharmaceutical preparations and are employed as peptic ulcer treatment, antibacterial, anti-HIV, and radio-therapeutic agents (Sox and Olson 1989; Rastegarzadeh et al. 2014; Burguera et al. 2001; H. Sun et al. 1997). Although absorption of bismuth in human organism is generally low, this element is known to be

H. Kahe · M. Chamsaz (✉)
Department of Chemistry, Faculty of sciences, Ferdowsi University of Mashhad, Mashhad, Iran
e-mail: chamsaz@ferdowsi.um.ac.ir

toxic, and a number of hazardous effects such as nephrotoxicity, neurotoxicity, kidney damage, and nephropathy have been reported due to the use of bismuth-containing pharmaceuticals (Pamphlett et al. 2000; Tzanavaras et al. 2004).

The wide usage of bismuth and its spreading out in the environment, and due to the potential hazards caused by bismuth exposure to organisms, there is a great effort for strict monitoring of bismuth in environmental samples. A variety of analytical techniques, including UV-Vis spectrophotometry (Rastegarzadeh et al. 2014), flame atomic absorption spectrometry (Wen et al. 2012), electrothermal atomic absorption spectrometry (Ivanova et al. 1997; Yamini et al. 2002), inductivity-coupled plasma mass spectrometry (X. Jia et al. 2010), inductivity-coupled plasma atomic emission spectrometry (Moyano et al. 1999), and voltammetry (Guo et al. 2005), have been extensively employed for determination of bismuth compounds in different samples. Among these techniques, electrothermal atomic absorption spectrometry is widely used because of its availability and sensitivity. However, due to low concentrations of bismuth in real samples and their complex matrixes, direct determination of bismuth is seldom carried out, and a sample preparation step to isolate and concentrate the analyte is often necessary.

Dispersive liquid liquid microextraction (DLLME) (Rezaee et al. 2006) is one of the wildly employed preconcentration techniques due to its simplicity, rapidity, low-cost, and high enrichment factor and has been successfully applied for preconcentration of various organic and inorganic compounds in different samples (Rivas et al. 2009). Supramolecular solvents have unique properties making them very attractive to replace the toxic organic solvents in microextraction methods like DLLME (Jafarvand and Shemirani 2011). The possibly of performing different interactions such as hydrogen bond, ionic, π-cation, and dipole–dipole between analytes and hydrophilic or hydrophobic parts of surfactants in these solvents will enable them to extract various compounds with different polarities (Yilmaz and Soylak 2014; Ballesteros-Gómez et al. 2010).

At critical aggregation concentration (cac), it will be favorable for surfactants to interact and associate with each other (Steed et al. 2007) to form a variety of microstructures. Israelachvili et al. (1976) have introduced a parameter named packing factor (g), $g = V / a_0 \times l$, related to the volume of the hydrophobic chain (V), the cross-sectional area of the head group (a_0), and the chain length of surfactants (l) to predict the morphology of the aggregates. In a mixture of two oppositely charged surfactants known as catanionic systems, they can form a pseudo double-tailed zwitterionic surfactant, which has a smaller effective size in its head groups and an extended volume in its hydrophobic part of each former surfactants. As a result, various types of supramolecular microstructures such as lamellar or multilayer phases, vesicles, precipitates, and rodlike micelles with higher surface activity than each of the pure surfactant microstructures can be formed (Ballesteros-Gómez et al. 2010).

Our group had formerly developed a new method named supramolecule-aggregated based liquid solid microextraction (Kahe et al. 2016), and the aim of this study was to apply the procedure for preconcentration of bismuth (III) using catanionic microstructure aggregates of sodium dodecyl sulfate (SDS) and cetyltrimethy lammonium bromide (CTAB) surfactants as a novel green solvent. Various solutions of CTAB and SDS surfactants at different mole ratios were prepared in propanol-water, followed by injection in saline solutions of bismuth (III) in the presence of sodium diethyldithiocarbamate (NaDDTC) as chelating reagent. The resulting complex, Bi-(DDTC)$_3$, was extracted into microstructure aggregates of SDS/CTAB and was quantitatively determined by electrothermal atomic absorption spectrometry (ET-AAS). Various effective parameters on the extraction efficiency were exactly investigated to obtain optimum conditions, and finally, the proposed method was successfully applied for determination of Bi (III) in some real samples.

Experimental

Instrumentation

All measurements were carried out with an Analytik Jena electrothermal atomic absorption spectrometer model novAA 400p, equipped with a deuterium lamp as a background correction system, an MPE 60 autosampler, and bismuth hallow cathode lamp at 223.1 nm operated at 8 mA with a monochromator spectral band pass of 0.5 nm. All results were obtained in peak area mode using pyrolytically coated graphite tubes with L'Vov platform and argon purity of 99.996 % as the carrier gas. A Metrohm, 632 pH-meter with a glass-combined electrode and a Centurion Scientific centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany) were employed for pH adjustment and solvent phase separation, respectively.

Reagents and solutions

All chemicals were of analytical reagent grade, and deionized water was used throughout to prepare all aqueous solutions. A stock solution of 1000 mg L^{-1} bismuth (III) was prepared by dissolving appropriate amounts of bismuth nitrate penta-hydrate (Sigma-Aldrich, USA) in 10 % (*v*/*v*) nitric acid solution, and working standard solutions were prepared daily by successive dilutions of this stock solution in 0.5 % (*v*/*v*) nitric acid solution. Cetyltrimethylammonium bromide (CTAB, 99 %) and sodium dodecyl sulfate (SDS, 98 %) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Sodium diethyldithiocarbamate (NaDDTC) ≥97 %, ammonia solution 25 % (NH_3), propanol (99.7 %), ammonium nitrate (NH_4NO_3) ≥98 %, supra-pure nitric acid (HNO_3) 65 %, and hydrogen peroxide (H_2O_2) 30 %, ammonium di-hydrogen phosphate ($NH_4H_2PO_4$) ≥98 %, and palladium (Pd) 99.99 % were provided from Merck (Darmstadt, Germany). A 2 % *w*/*v* aqueous solution of NaDDTC was used as reagent solution, and a 0.2 % *w*/*v* solution of Pd and a 1 % *w*/*v* solution of $NH_4H_2PO_4$ were employed as matrix modifier. Standard solutions of 0.5 mol L^{-1} HNO_3 and NH_3 were used for pH adjustment.

Preparation of real sample

Human blood serum The serum sample was collected from the Blood Transfusion Organization (Mashhad, Iran). One gram of each sample was weighed in a 100-mL beaker followed by addition of 10 mL concentrated HNO_3 and 3 mL H_2O_2. The content of the beaker was heated on a hot plate at 150 °C until completely dissolved. The beaker was then left to cool down to room temperature, and its content was filtered by ashless filter papers in 50-mL volumetric flask and diluted to volume by 12 % NH_4NO_3 solution; after, pH adjustment was analyzed according to the proposed method.

Hair sample Hair sample in 0.5- to 1-cm lengths was, successively, washed with deionized water, acetone, and deionized water (Aydin et al. 2015; Fayazi et al. 2011) and was dried in an oven at 100 °C; 0.1 g of the sample was placed in a 50-mL beaker followed by addition of 6 mL concentrated HNO_3 and 2 mL concentrated H_2O_2. The content of the beaker was then prepared like human blood serum sample and analyzed according to the described procedure.

Microextraction method

Ten milliliters of Bi (III) sample solutions containing 12 % *w*/*v* NH_3NO_3 at pH 3 was transferred into a 15-mL centrifuge tube followed by addition of 200 μL chelating agent and 200 μL of the extraction solvent using a 1.00-mL syringe. The solution was gently shaken for a few seconds, and a cloudy solution of immiscible SDS/CTAB aggregates containing the extracted bismuth complex was started to separate from the solution on top of the aqueous phase. The solution was centrifuged for 5 min to accelerate the phase separation of the extraction solvent as a white flexible solid layer. The lower aqueous phase was taken out using a 10-mL syringe, and the solid layer was dissolved in 50 μL propanol. Twenty microliters of the extraction phase was injected into the graphite atomizer to obtain the analytical signal.

Results and discussion

Optimization of graphite furnace temperature program

In order to achieve maximum analytical signal of the extracted bismuth, it was necessary to optimize the temperature program of graphite furnace. As it was mentioned in previous study (Kahe et al. 2016), the matrix of the extraction solvent, SDS/CTAB microstructures, is not volatile, it cannot be removed in the drying step, and hence, three pyrolysis steps were needed to remove it in presence of 5 μL of the Pd and $NH_4H_2PO_4$ solutions, as matrix modifier. The influence of temperature in third step of pyrolysis on Bi absorbance was also studied, and the best result was observed at 700 °C with a hold time of 10 s. Moreover, no improvement on Bi absorbance was recognized at temperatures higher than 2200 °C, and it was chosen as the atomization temperature with a hold time of 5 s. In addition; a pre auto zero step before the auto zero was included to provide enough time for removing the ashes products

Table 1 The atomizer temperature program used for determining bismuth content

Steps	Temperature (°C)	Ramp (°C/s)	Hold time (s)	Gas flow
Drying	110	5	10	Max
Pyrolysis 1	250	20	20	Max
Pyrolysis 2	350	20	20	Max
Pyrolysis 3	700	20	10	Max
Pre auto zero	100	–	10	Max
Auto zero (AZ)	100	0	6	Stop
Atomization	2200	2000	5	Stop
Clean out	2450	500	4	Max

at lower temperatures with no reduction in the bismuth signal (Table 1).

Preparation of extraction solvent

It has been known that the co-existence of SDS, an anionic surfactant, and CTAB, a cationic one, in water will result in the formation of an insoluble sediment by strong attraction of their organic parts with opposite charges (Salkar et al. 1998). Although the sediment was also formed in all mixtures of the amphiphiles with a total concentration of 100 mM, it can be easily dissolved in the presence of appropriate amounts of water miscible solvents such as propanol (Kahe et al. 2016). The amount of propanol for dissolving the sediment was studied in the range of 1:1 to 1:20 of SDS:CTAB mole ratios. Obviously, more sediment is produced in mole ratios nearer to 1:1, which will increase the required propanol as shown in Fig. 1. These solutions are stable at least for 3 weeks.

Extraction solvent phase separation manner

The applicability of SDS/CTAB mixture as a green extraction solvent for preconcentration of Bi (III) complex as well as the phase separation manner of the surfactant aggregates has been thoroughly investigated.

It has been understood that inorganic salts can screen and naturalize the excess charges on the surface of supramolecule aggregates (Vlachy et al. 2008). This will force the microstructures to integrate together for the formation of an immiscible phase, which can be separated after centrifugation for a few minutes. It was found that, when a few hundred microliters of the prepared solutions was injected into a saline solutions containing enough concentration of NH_4NO_3, the SDS/CTAB macromolecules would start to associate and form a cloudy solution (Kahe et al. 2016). The separation phase phenomenon will just occur when the mole ratio of CTAB is more than SDS, in the range of 1:2 to 1:20, and it was not noticed at other mole ratios. The times

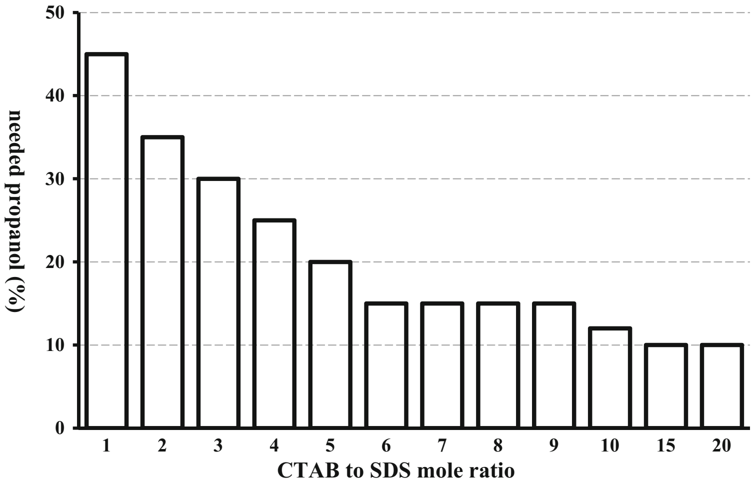


Fig. 1 The needed percentage of propanol in water to obtain a stable solution of SDS and CTAB mixture at different mole ratios with a total concentration of 100 mM

Table 2 The phase separation manner of 200 μL of the solution after injection in 10 mL of aqueous solution in different percentage of NH_4NO_3

SDS:CTAB mole ratio	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8	1:9	1:10	1:15	1:20
Salt percentage (*W/V* %)	Required centrifugation times (min)											
8	No	20–30			10						No	
10	No	7–10			5					10	15	No
12	No	7		5							10	20
15–30	No	5										10

No: Without any phase separation or with no stable separated phase

given in Table 2 are referred to conditions for achieving a transparent aqueous phase along with a separated flexible solid layer on top of it.

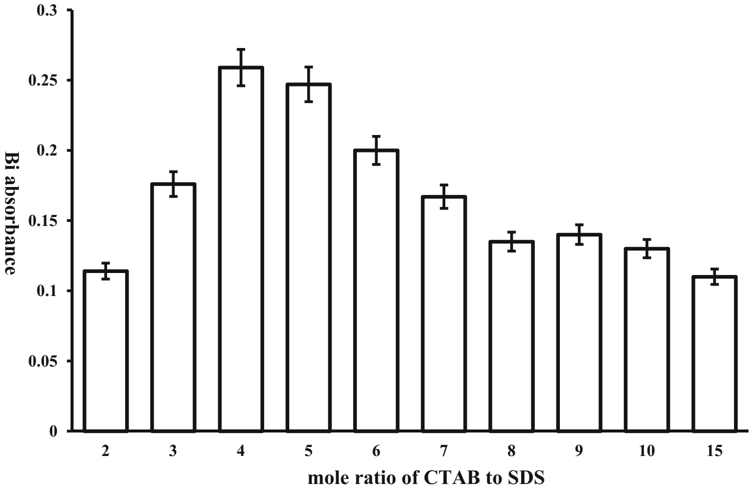
The designed microextraction method benefits noticeable advantages compared with coacervative techniques employed separately for SDS and CTAB as extraction solvents. SDS as an anionic surfactant shows a phase separation phenomenon in the presence of high concentration of hydrochloric acid (about 4 mol L^{-1}) just after several minutes of stirring and centrifugation (G. Jia et al. 2007; Casero et al. 1999), and no phase separation can occur even at high ionic strengths (2.0 M) or temperature (90 °C). This procedure is much harder for CTAB, where it happens in saturated sodium chloride solution in the presence of exactly a few microliters of a cosurfactant, e.g., 1-octanol which its presence is very vital (Jin et al. 1999; Crick and Conte 2000). However, the suggested methodology offers an easier process to achieve phase separation using both surfactants, and it was implemented for preconcentration of Bi (III)-DDTC complex for the following studies.

The mole ratio of SDS/CTAB in extraction solvent

It is clear (Table 2) that the phase separation manner of the extraction solvent depends significantly on the mole ratio of CTAB to SDS and especially, at lower percentages of inorganic salt; more centrifugation time is required. Therefore, to study the effect of mole ratio, the aqueous solutions containing 15 % NH_4NO_3 was examined to obtain phase separation in the same centrifugation time. As shown in Fig. 2, maximum absorbance was observed in the SDS:CTAB mole ratio of 1:4, which was selected for other experiments.

Water was the major component for dissolving the SDS/CTAB microstructures, and a solution of 25 % propanol in water was enough to prepare a stable

Fig. 2 Effect of SDS/CTAB mole ratio. Conditions: Bi (III) concentration, 3.0 μg L^{-1}; centrifugation time, 5 min; NH_4NO_3 percentage, 15 %; extraction solvent volume, 200 μL; pH 3; and NaDDTC value, 400 μg L^{-1}. Experiments were performed in triplicates ($n = 3$)



extraction solvent solution. As a result, the Bi (III) complex can be in direct contact with SDS/CTAB microstructures, and hence, the microextraction efficiency is improved.

Effect of the inorganic salt amount and centrifugation time

As demonstrated in Table 2, the centrifugation time and salt percentage have complementary effects, and more centrifugation time is needed using solutions with lower salt percentage. The results (not shown) confirmed that at higher centrifugation times, no significant difference was noticed. However, to achieve a faster microextraction procedure, 12 % (*w*/*v*) of NH_3NO_3 was used for subsequent testes.

Effect of extraction solvent volume

In order to obtain best extraction efficiency, the effect of extraction solvent volumes on Bi absorbance was examined in the range of 200–500 μL, and as shown in Fig. 3, the highest signal was achieved using 200 μL extraction solvent. The enrichment factor and detection sensitivity were decreased at higher volumes, and lower amounts than 200 μL was led to no phase separation. Hence, 200 μL extraction solvent was employed for subsequent tests.

Effect of pH

In heavy metals extraction, pH has a great effect on extraction efficiencies. The effect of pH was studied in range of 1 to 8, and the results are presented in Fig. 4, indicating that by increasing the pH up to 3, the bismuth absorbance was substantially improved. However, at higher pHs, the absorbance was gradually decreased, and hence, pH 3 was selected for further experiments.

Effect of ligand concentration

Diethyldithiocarbamate forms a stable neutral complex with bismuth (III) (Bi $(DDTC)_3$) (Cheng et al. 1955; Ishak et al. 2014), which can be extracted into the extraction solvent. Therefore, the presence of NaDDTC at appropriate concentration is important for high extraction efficiency. The influence of the ligand concentration on Bi absorbance was studied in the range of 2.34×10^{-4}–5.84×10^{-3} mol L^{-1}, and it was found that the signals increased gradually by increasing the diethyldithiocarbamate to 2.34×10^{-3} mol L^{-1} and it remained constant up to 3.35×10^{-3} mol L^{-1}. However, NaDDTC could be competitively co-extracted into the microstructure aggregates of SDS and CTAB at higher concentrations and remarkably decreased the bismuth absorbance. Therefore, 2.34×10^{-3} mol L^{-1} (400 μg L^{-1}) of the ligand was chosen for further experiments.

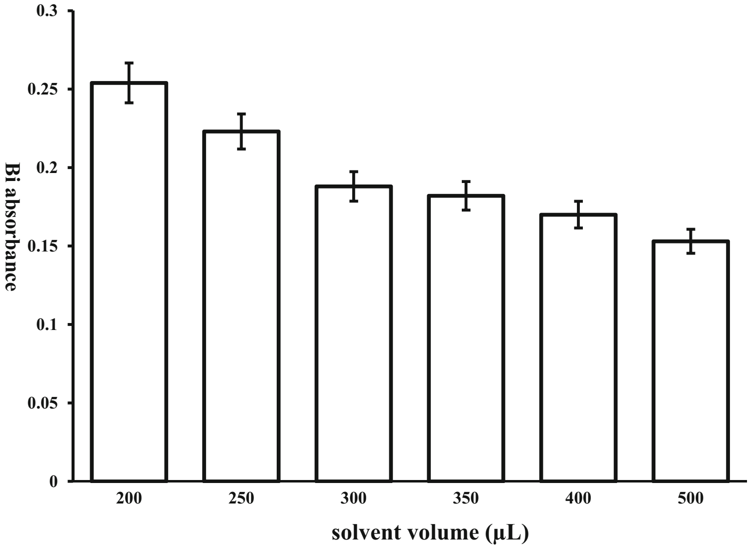


Fig. 3 Effect of solvent extraction volume. Conditions: Bi (III) concentration, 3.0 μg L^{-1}; SDS/CTAB mole ratio, 1:4; NH_4NO_3 percentage, 12 % *w*/*v*; centrifugation time, 5 min; pH 3; and NaDDTC value, 400 μg L^{-1}. Experiments were performed in triplicates (*n* = 3)

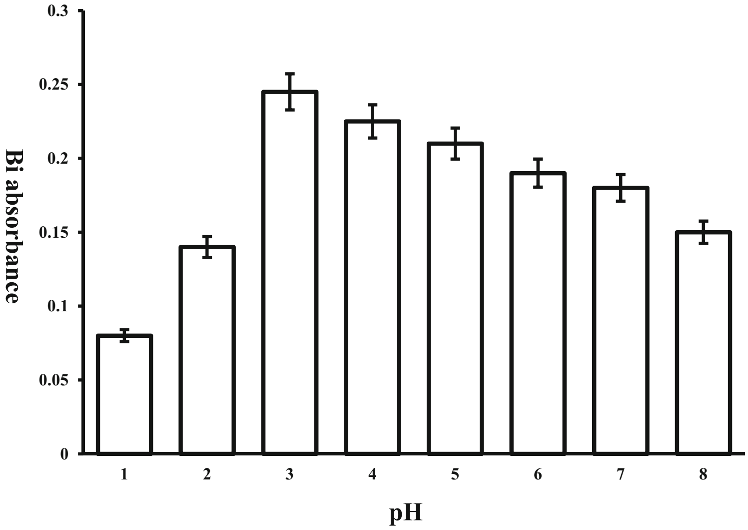


Fig. 4 Effect of solvent extraction volume. Conditions: Bi (III) concentration, 3.0 μg L^{-1}; SDS:CTAB mole ratio, 1:4; NH_4NO_3 percentage, 12 % *w*/*v*; extraction solvent volume, 200 μL; centrifugation time, 5 min; and NaDDTC value, 400 μg L^{-1}. Experiments were performed in triplicates (*n* = 3)

Interference studies

Sodium diethyldithiocarbamate is one of the most widely applied chelating agents, and it forms complexes with other heavy metal ions as well as bismuth, which can be competitively co-extracted into the extraction solvent. To evaluate the selectivity of the proposed method, the effect of various coexisting heavy metals on Bi absorbance was studied. An ion was considered to interfere when it caused an error in the absorbance of bismuth greater than ±5 %. The presented results in Table 3 demonstrate that the major heavy metal ions studied have no obvious interferences at 100-fold concentration with the target analyte, confirming the selectivity of the proposed method.

Table 3 Effect of interfering ions for the determination of Bi (III) (3 μg L^{-1})

Interfering ions	Interference/metal ratio	Recovery (%)
Fe^{+2}	100	102.5
Fe^{+3}	100	96.3
Co^{+2}	150	102.9
Cu^{+2}	100	97.4
As^{+3}	100	98.1
Pb^{+2}	200	103.8
Cd^{+2}	100	97.3
Mn^{+2}	100	97.6
Zn^{+2}	100	102.9
Sn^{+2}	100	97.7
Ni^{+2}	100	104.2
Hg^{+2}	300	103.2
Tl^{+3}	100	104.1

Analytical features of the method

Under the optimized experimental conditions, analytical characteristics of the proposed method were investigated. The calibration curve was linear in the range 0.3–6.0 μg L^{-1} bismuth with a correlation coefficient of 0.996. The regression equation of the calibration graph was $A = 0.0885\ C + 0.1138$ with a limit of detection (LOD) and enhancement factor of 0.16 μg L^{-1} (S/*N* = 3) and 47.5, respectively. At the optimized conditions, the relative standard deviations (RSD) for five replicate measurements of 1 and 3 μg L^{-1} bismuth were obtained 6.2 and 5.1 % respectively, which confirm the precision of the developed method.

Analysis of real sample

To evaluate the accuracy of the proposed method a CRM-TMDW (drinking water), certified reference material (http://www.highpuritystandards.com/store/home.php? cat=44) with a certified value of 10.0 μg L^{-1} Bi (III) was tested. Since the concentration value in CRM was higher than the upper limit of the linear range, a tenfold dilution was implemented prior to analysis, and its bismuth content was determined to be 10.4 ± 0.8 μg L^{-1}, which will agree well with the certified value.

Table 4 Determination of bismuth ion in real samples; results (mean ± standard deviation based on three replicated analyses)

Sample	Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Hair	0	–	–
	500	455.01 ± 38.01	91.0
	1500	1394.85 ± 133.91	92.9
Blood serum no 1	0	158.91 ± 12.52	–
	50	211.56 ± 16.63	105.3
	100	254.11 ± 22.30	95.2
Blood serum no 2	0	97.23 ± 8.52	
	50	146.22 ± 13.12	97.98
	100	193.41 ± 18.19	98.18

Moreover, to demonstrate the applicability of method, human hair and serum samples were analyzed for their Bi contents after preparation as mentioned before. The recovery tests were also carried out by spiking the samples with different bismuth concentrations. The dilution factors were 50 and 500 for human serum and hair samples, respectively, which were considered in calculations. As shown in Table 4, the results confirm the validity of the suggested method for determination of bismuth in these real samples.

Comparing the developed method with other methods

A comparison between the analytical performance of the suggested microextraction method and other techniques for measurement of Bi (III) ion is shown in Table 5. The procedure has an acceptable linear range with a reasonable precision and LOD compared with other methods.

This methodology introduces a green solvent as an excellent alternative to the use of toxic organic solvents employed in DLLME (Rastegarzadeh et al. 2014; Wen et al. 2014; Vakilzadeh et al. 2015). Moreover, the requirement of high sample volume for preconcentration used in SPE-FAAS (Pourreza and Sheikhnajdi 2012) is not necessary although flame atomic absorption spectrometry is easier than ET-AAS. As a simple technique, it can be implemented at room temperature without any control tools as used in CPE (M. Sun and Wu 2011), and the combination of this technique with ET-AAS provides a less expensive technique for bismuth measurement compared to ICP-OES.

Conclusion

Applying this methodology, supramolecule aggregates of SDS and CTAB were used as a green and safe solvent instead of toxic organic ones, in combination with dispersive microextraction technique to preconcentrate and determine bismuth in saline media, human blood serum, and hair samples.

Water is the main component of solvent for preparing SDS/CTAB solutions, which can provide nearly a direct interaction between analytes and the extraction solvent and higher extraction efficiency. Moreover, the solvent has same phase separation behavior at all pH values, and this applicability is an excellent attribute for this method. On the other hand, like all supramolecular solvents, SDS/CTAB aggregates have both hydrophilic and hydrophobic sites, which could interact with a wide variety of compounds, and we recommend the supramolecule aggregate dispersive microextraction method (SA-DME) as a simple, fast, and cheap technique for

Table 5 Comparison of the suggested method with others for determination of cadmium

Method	Sample volume (mL)	LOD (μg L^{-1})	RSD (%)	Dynamic range (μg L^{-1})	Ref
UA-DLLME-ET-AAS	10	0.2	4.7	2–30	(Wen et al. 2014)
DLLME-UV-Vis	10	1.6	1.14–2.66	5–400	(Rastegarzadeh et al. 2014)
IP-DLLME-ET-AAS	10	0.07	4.8	0.3–8	(Vakilzadeh et al. 2015)
SPE-FAAS	500	2.3	2.3	4–300	(Pourreza and Sheikhnajdi 2012)
CPE-FI-ICP-OES	25	0.12	2.3	Up to 50	(Sun and Wu 2011)
SA-DME	10	0.158	5.1–6.2	0.3–6	This work

preconcentration of various organic and inorganic compounds in real samples.

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Compliance with ethical standards

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Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent Not applicable.

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