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Development of an inexpensive and sensitive method for the determination of low quantity of arsenic species in water samples by CPE–FAAS

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ABSTRACT

The simple and rapid preconcentration technique using cloud point extraction (CPE) was applied for the determination of As(V) and total inorganic arsenic (As(V) plus As(III)) in water samples by means of FAAS. As(V) has formed an ion-pairing complex with Pyronine B in the presence of cetyl pyridinium chloride (CPC) at pH 8.0 and extracted into the non-ionic surfactant Triton X-114, after centrifugation the surfactant-rich phase was separated and diluted with 1.0 mol L^{-1} HNO_3 in methanol. The proposed method is very versatile and economic because it exclusively used conventional FAAS. After optimization of the CPE conditions, a preconcentration factor of 120, the detection and quantification limits of 1.67 and 5.06 μg L^{-1} with a correlation coefficient of 0.9978 were obtained from the calibration curve constructed in the range of 5.0–2200 μg L^{-1}. The relative standard deviation, RSD as a measure of precision was less than 4.1% and the recoveries were in the range of 98.2–102.4%, 97.4–101.2% and 97.8–101.1% for As(V), As(III) and total As, respectively. The method was validated by the analysis of standard reference materials, TMDA-53.3 and NIST 1643e and applied to the determination of As(III) and As(V) in some real samples including natural drinking water and tap water samples with satisfactory results. The results obtained (34.70 ± 1.08 μg L^{-1} and 60.25 ± 1.07 μg L^{-1}) were in good agreement with the certified values (34.20 ± 1.38 μg L^{-1} and 60.45 ± 1.78 μg L^{-1}).

1. Introduction

Arsenic is well known to be poisonous to organisms; however, the toxic effect of As is highly dependent on its chemical forms [1–3]. As is a ubiquitous element in the environment originating from natural sources (geologic formations, geothermal activity and volcanic activity) as well as human activities [4–6]. Major anthropogenic sources of As include wood preservatives (chromated copper arsenate), agricultural uses (monosodium methane arsonate as pesticide and disodium methane arsonate as herbicide), industrial uses (a range of arsenicals in electrophotography, catalysts, pyrotechnics, antifouling paints, pharmaceutical substances), mining and smelting. Due to its natural and anthropogenic occurrence, the entire population is exposed to (low levels) As through food, water and air. The majority of As speciation studies have targeted both plants and fauna of marine origin, as they are known to accumulate As to relatively high levels compared to other food sources. Fish and seafood are known to contribute to the majority of ingested As (75%) although it generally only constitutes a small percentage (2%) of the daily dietary intake [7–12].

It has been reported that the same metal ion may possess different toxicity in its different oxidation states, which are responsible for their different physico-chemical and biological activities. This indicates that it is very important to be able to measure inorganic As species in water sensitively and reliably. Although the above mentioned risks do not distinguish between the toxic effects of the inorganic As species arsenite As(III) and arsenate As(V) individually. It is important to note that the toxicity of As(III) is greater than the toxicity of As(V) [13,14].

The term speciation analysis has often been used to indicate the analytical activity of identifying chemical species and measuring their distribution. Sometimes, it is used to indicate that a method gives more information on the form in which the element is present than other more commonly applied techniques (e.g., measuring distinct organomercury compounds as opposed to a total mercury determination). Thus, in order to obtain the information on toxicity and biotransformation of elements in aquatic and biological systems, the speciation of metal ions is of great importance [15–18].

Since the concentrations of As species in water and real samples are very low, sensitive analytical techniques are required such as high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC–ICP-MS) [19–22], inductively coupled plasma mass spectrometry (ICP-MS) [23,24], colorometric [25], inductively coupled plasma atomic emission spectrometry (ICP-AES) [26,27], hydride generation

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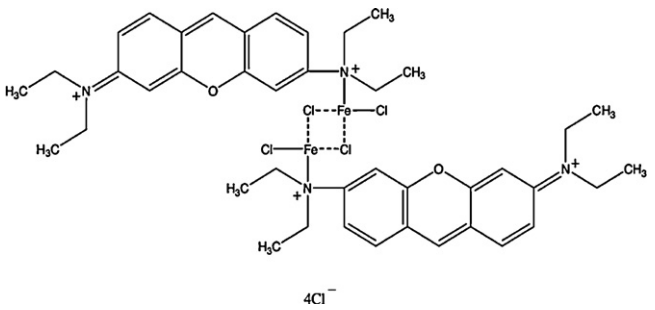

Fig. 1. The open molecular structure of Pyronine B.

and atomic fluorescence spectrometry (HG-AFS) [28,29], electrothermal atomic absorption spectrometry (ET-AAS) [30,31] and hydride generation atomic absorption spectrometry(HGAAS) [32].

Analytical techniques such as graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) can only determine total amount of As. For the determination of inorganic As species in natural waters, where the concentration of As is usually found at trace levels, preliminary species separation and preconcentration is required before detection. For the speciation of As(III) and As(V), the separation and preconcentration methods reported in the literature are usually based on hydride generation [33,34], liquid–liquid extraction (LLE) [35], solid phase extraction (SPE) [36–40] and coprecipitation [41,42] etc. However, some disadvantages limit their applications such as time-consuming, unsatisfactory enrichment factors, using toxic organic solvents and forming secondary wastes. Cloud point extraction (CPE) [43–45] is fairly a versatile method for the separation and preconcentration of metal ions having considerable properties such as simplicity, cheapness, fast, selectivity and sensitivity.

In the present work, a CPE method based on the ion-pairing complex formation of As(V) with Pyronine B [(3,6-bis(diethylamino)-xanthylium chloride, ferric chloride complex); Fig. 1] in the presence of CPC using Triton X-114 as extracting nonionic surfactant agent was proposed for the separation and preconcentration of As(V) at pH 8.0 prior to its determination by FAAS. The proposed method is a combination of CPE and FAAS as a detection tool for As species. The method is very versatile and economic because it exclusively used conventional FAAS which is available in almost every laboratory. It is first time, analysis of As species was performed by using CPE–FAAS method in this study. It may be a useful analytical tool as an alternative to expensive and time consuming techniques such as ICP-MS, ICP-AES, and HG-AFS.

2. Experimental

2.1. Instrumentation

An atomic absorption spectrometer (Shimadzu AAS-6300) equipped with an As hollow cathode lamp and an air–acetylene flame atomizer was used for As determinations. The wavelength, lamp current and spectral bandwidth were 197.2 nm (the most sensitive line according to manufacture firm, Hamamatsu, Japan), 10 mA and 0.2 nm, respectively. The pH measurements were carried out with a pH meter (Selecta 2001 pH-meter). A centrifuge (Hettich Universal) was used to accelerate and facilitate the phase separation process. A thermostatic water-bath (Nüve 120) was used in CPE procedures.

2.2. Reagents and standard solutions

All chemicals used were of analytical reagent grade. Deionized water (18.2 MΩ) was used in all experiments. For the preparation of 100 ml pH 8.0 borate buffer solution, 50 mL of 0.05 mol L^{-1} tri sodium tetra borate (Merck, Darmstadt, Germany) and 44 mL of 0.1 mol L^{-} HCl (Merck) solutions were mixed. Stock solutions of 1000 mg L^{-1} As(V) and As(III) were prepared from Na_2HAsO_4 and As_2O_3 (Merck). The solution of Triton X-114 (Sigma, St. Louis, MO, USA) was prepared by dissolving it in water. The stock chelating ligand solution (4.7×10^{-4} mol L^{-1} Pyronine B) was prepared by dissolving an appropriate amount of Pyronine B (Sigma) in water. The ionic surfactant solutions (3.0×10^{-3} mol L^{-1}) cetyl pyridium chloride (CPC), cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) were prepared by dissolving an appropriate amount of chemicals (Sigma) in water. All of the vessels and pipettes used for trace analysis were kept in 10% (w/v) HNO_3 for at least 24 h and subsequently washed four times with water.

2.3. The general procedure

An aliquot of the sample or standard solution containing As(V) in the range of 5–2200 μg L^{-1}, 0.2 mL of 5.0% (v/v) Triton X-114, 0.8 mL of 3.0×10^{-3} mol L^{-1} Pyronine B, 1.5 mL of 20% (w/v) NaCl solution, 1.0 mL of 3.0×10^{-3} mol L^{-1} CPC and 2.0 mL of buffer solution was mixed in a flask of 50 mL and kept in a thermostatic water-bath at 50 °C for 10 min. A centrifuge was used to accelerate phase separation at 3500 rpm for 5 min. Then, the mixture was cooled in a refrigerator for 30 min in order to increase the viscosity of the surfactant-rich phase and facilitate the removal of the aqueous phase. After that, the aqueous phase was easily separated from surfactant-rich phase with decantation. 1.0 mL of 1.0 mol L^{-1} HNO_3 in methanol solution was added to the surfactant-rich phase to reduce its viscosity before determination of As by FAAS. Finally, the As concentrations were determined by calibration curve obtained by FAAS or using standard additions approach.

2.4. As(V)/As(III) speciation procedure

The speciation procedure was applied to model solutions and natural water samples for oxidation of As(III) to As(V) in below. In this procedure, 3×10^{-4} mol L^{-1} of $KMnO_4$ solution containing 0.3 mol L^{-1} HCl was used as an oxidizing agent. After the oxidation of As(III) to As(V), pH of solution was adjusted to 7.0 using 2.0 mol L^{-1} NaOH and then, the presented method was applied for the determination of the total As. The amounts of As were determined by flame atomic absorption spectrometry. The amount of As(III) is calculated by difference of total As and As(V) concentrations.

3. Results and discussion

3.1. Effect of pH and concentration of buffer

In CPE method, pH plays a unique role on metal complex formation and subsequent extraction procedures. The effect of pH on the CPE efficiency of As(V) was studied in the range of pH 1.0–11.0 and the results were shown in Fig. 2. It could be seen that the highest analytical signal for As(V) was obtained in the pH 8.0. In low pH values, the extraction efficiency is very low due to be slow of complex formation rate. In the range of 8–11, the cause of decrease in extraction efficiency may be degradation of ion pairing complex due to precipitation of ferric ions taking place in planar structure of ligand as $Fe(OH)_3$. At pH 8.0 As is in the form of $HAsO_4^{2-}$ due

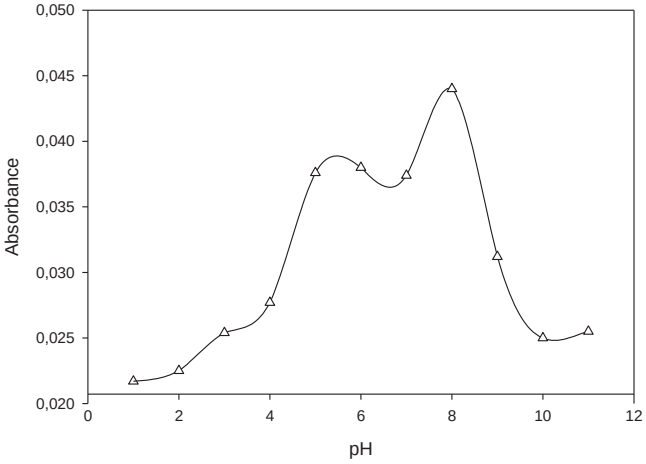

Fig. 2. Effect of pH on cloud point extraction.

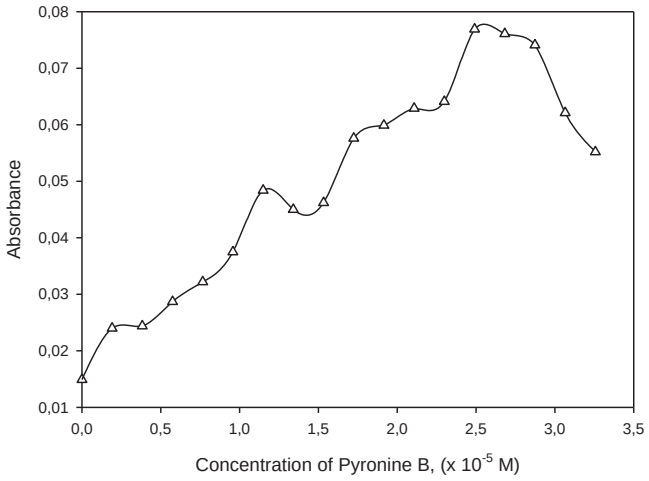

Fig. 4. Effect of Pyronine B concentration on CPE.

to be 2.24, 6.96 and 11.5 of its pK_a values, respectively whereas pK_a values of ligand are 6.9 and 10.1 [46]. Ligand is a highly stabile basic dye having a dimeric planar structure covalently bonded onto nitrogen atom of each monomer with bridged dimeric Fe(III) chloride ion [47].

After the optimum pH was selected, the concentration of buffer solution as a function of volume of buffer solution at a fixed concentration was also studied in the range of 0–7 mL. As can be seen in Fig. 3, the maximum analytical signal was achieved by using 2.0 mL buffer solution in final volume of 50.0 mL.

3.2. Effect of amount of complexing agent

The effect of the concentration of Pyronine B on analytical signal intensity of As(V) was investigated in the range of $(0–3.25) \times 10^{-5}$ mol L^{-1} and the results were illustrated in Fig. 4. The signal intensity of As(V) strongly depended on the amount of Pyronine B. With the increase in concentration of Pyronine B, the signal intensity initially increased, and maximum signal intensity was achieved after the concentration of the Pyronine B approached to 2.5×10^{-5} mol L^{-1} and then gradually decreased due to degradation of ligand. Therefore, a concentration of 2.5×10^{-5} mol L^{-1} was selected as optimal value in this work.

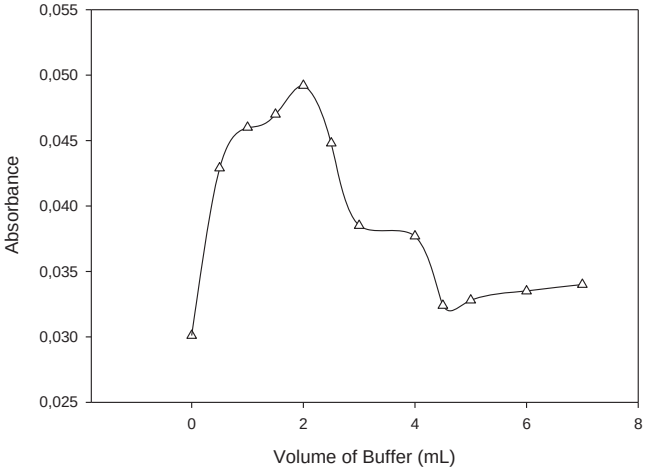

Fig. 3. Effect of buffer volume (in 50 mL) on CPE.

3.3. Effect of ionic surfactant amount

The variations of analytical signal as a function of concentration of ionic surfactants, CPC, CTAB, and SDS, which are chosen as auxiliary ligand, were presented in Fig. 5. The dependence of CPE to auxiliary ligand concentration was examined in the range of $(0.1–1.8) \times 10^{-5}$ mol L^{-1}. The best efficiency of extraction was obtained in the presence of CPC. As it can be seen, the extraction of As(V) increases up to CPC concentration of 1.0×10^{-5} mol L^{-1}, and gradually decreases in higher concentrations. Therefore, an auxiliary ligand concentration of 1.0×10^{-5} mol L^{-1} of CPC was selected as the optimum condition for the subsequent studies.

3.4. Effect of nonionic surfactant amount

In the preliminary experiments, it is observed that the addition of the nonionic surfactants such as Triton X-100 and Ponpe 7.5 to ternary complex system of As(V)–Pyronine B–CPC and heating the solution provides a successful extraction. This clearly shows that the ternary complex of As(V)–Pyronine B–CPC can be extracted by CPE method. Therefore, the effect of Ponpe 7.5 and the Triton X-114 concentration on the analytical response of 500 μg L^{-1} of As(V) were investigated in the range of 0.00–0.20% (v/v). As can be seen from Fig. 6, the measured absorbance reached a maximum value at concentrations of 0.05% (v/v) of Triton X-114. Therefore,

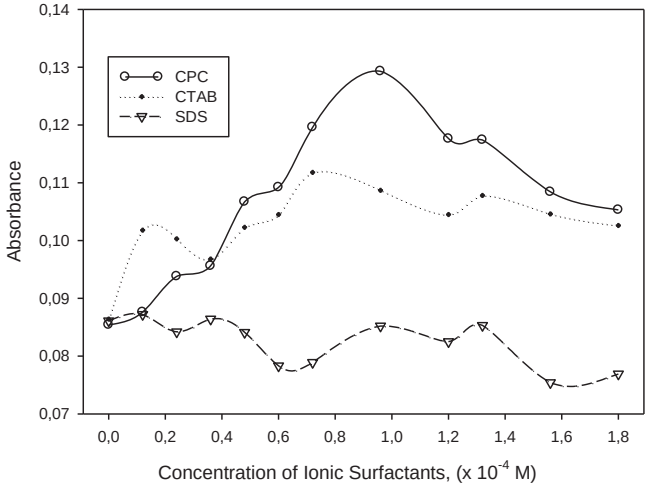

Fig. 5. Effect of ionic surfactant concentration on CPE.

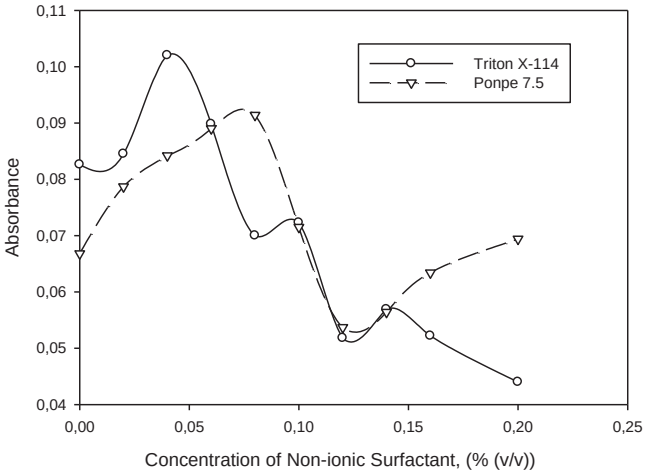

Fig. 6. Effect of nonionic surfactant concentration on CPE.

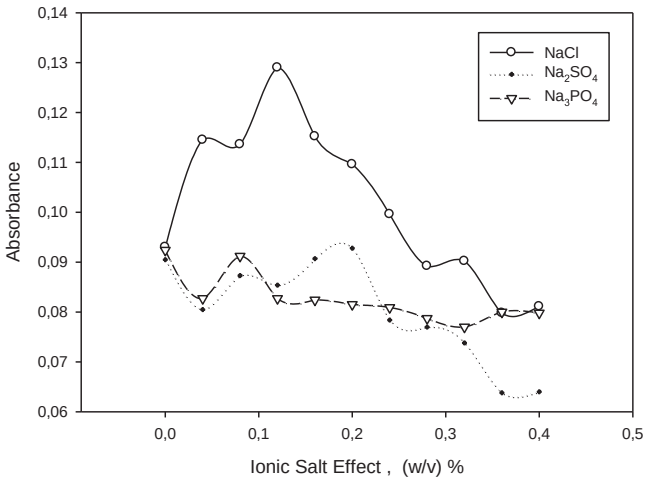

Fig. 7. Effect of ionic salt concentration on CPE.

Triton X-114 due to give a higher absorbance at equal-molar concentration according to Ponpe 7.5 was selected as suitable nonionic surfactant and its optimum amounts of nonionic surfactant with a concentration of 0.05% (v/v) for subsequent studies.

3.5. Effect of equilibration temperature and incubation time

Optimal temperature and incubation time for CPE experimental were optimized to achieve an easy and efficient phase separation and preconcentration. It was desirable to employ the shortest equilibration time and the lowest possible incubation temperature. The dependences of extraction efficiency upon equilibration temperature and time were studied with a range of 30–70 °C and 5–30 min, respectively. The results showed that an equilibration temperature of 50 °C and a time of 10 min were adequate to achieve quantitative extraction.

3.6. Effect of ionic strength

The presence of inorganic electrolytes decreases the cloud point temperature due to dehydration of the poly(oxyethylene) chains. Additionally, inorganic salts enhance the hydrophobic interactions among the surfactant aggregates and the analytes, thus favouring their extraction from the aqueous to the micellar phase.

The influence of ionic strength was examined by studying the response for various ionic salts such as NaCl, Na_2SO_4, and Na_3PO_4 in the range 0–0.4% (w/v). As it is seen in Fig. 7, the analytical signal increases with the concentration of NaCl up to 0.12 (w/v) and then gradually decreased. In the presence of Na_2SO_4 and Na_3PO_4 electrolytes, the analytical signal was very low and rapidly decreased with increasing salt concentration especially in the range of 0.2–0.4% (w/v). Therefore, NaCl was selected as the best suitable ionic salt for further studies because the absorbance reached to a maximum value at a concentration of 0.12% (w/v) in the presence of only NaCl.

3.7. Optimization of oxidation of As(III) to As(V) procedure

Different types of oxidizing agents for oxidation of As(III) to As(V) have various advantages and drawbacks. Potassium permanganate was selected as a more convenient and reliable oxidant, which allowed rapid and complete oxidation of As(III) to As(V) at room temperature without any interfering of excess amount of permanganate in the As determination step. Even at higher concentrations an efficient oxidation with permanganate was succeeded. Percentage oxidation was obtained by comparing the analytical signals of the identical concentration of As(V) and that of As(III) with adding of the oxidizing agent at known concentrations, which is obtained with cloud point extraction procedure after atomic spectroscopic detection. It has been found that permanganate concentration of 0.0003 mol L^{-1} is enough for complete oxidation of As(III) to As(V) as shown in Fig. 8.

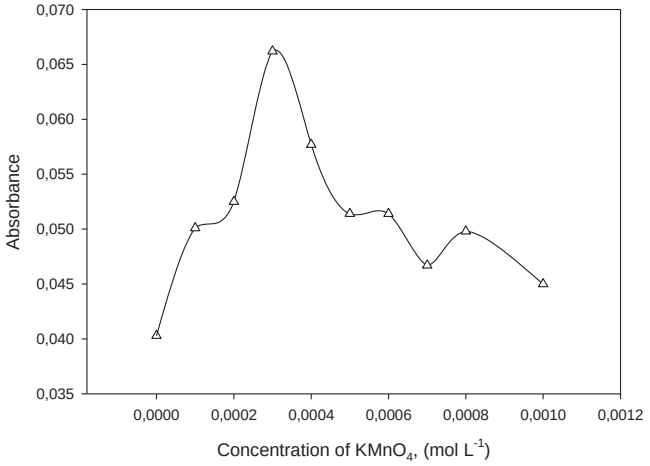

Fig. 8. Effect of concentration of permanganate on oxidation efficiency of As(III) to As(V).

The developed CPE–FAAS method was used for speciation of the inorganic As species after oxidation of As(III) to As(V) using a permanganate solution. For this purpose, the changing concentrations of As (III) in the range of 50–1000 μg L^{-1} in the presence of the fixed As(V) concentration of 25.0 μg L^{-1} were spiked into the solution media. After oxidation with permanganate, total speciation analysis was also made by using FAAS based on preconcentration with CPE under optimum experimental conditions. The concentration of As(III) was calculated by the difference between total As and As(V). The REs and RSDs for three replicate measurements of 50.0, 250.0, 500.0, 750.0 and 1000.0 μg L^{-1} of As(III) in the presence of 50.0 μg L^{-1} of As(V) were between 0.6–4.3% and 0.071–2.53%, respectively. The recovery experiments of the speciation procedure were carried out by the analysis of samples spiked with known amounts of As(III) at fixed As(V) concentration of 25.0 μg L^{-1}. The results are presented in Table 1. The results indicated that the recoveries were reasonable for trace analysis, ranging from 95.70% to 100.94%.

Table 1
The results of As speciation by means of FAAS based upon pre-concentration with cloud point extraction in the mixtures containing As(V) and As(III) at the known concentration ratios after pre-reducing procedure.

Sample or sample mixture	Ratio	Added As(III) ($\mu g\,L^{-1}$)	Total As(V) + As (III) ($\mu g\,L^{-1}$)	Found As(III) ($\mu g\,L^{-1}$)[a]	% RE	% RSD	% Recovery
–	–	25	24.85 ± 0.05	24.85 ± 0.05	−0.60	0.18	99.40
50 $\mu g\,L^{-1}$ As(V)	1:1	50	97.85 ± 0.08	47.85 ± 0.07	−4.30	2.53	95.70
	1:5	250	302.35 ± 0.06	252.35 ± 0.06	+0.94	0.36	100.94
	1:10	500	564.15 ± 0.05	514.15 ± 0.06	+2.83	0.18	102.83
	1:15	750	799.18 ± 0.05	749.18 ± 0.04	−0.11	0.093	99.89
	1:20	1000	1054.20 ± 0.04	1004.20 ± 0.04	0.42	0.071	100.42

[a] The average value plus standard deviation of three replicate measurements after pre-oxidation with permanganate.

Table 2
Tolerance limits of interfering foreign ions for determination of 500 $\mu g\,L^{-1}$ As(V) under the optimized conditions.

Co-existing ions	Foreign ion to analyte ratio
K^+, Na^+ and NH_4^+	1000
Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}	750
NO_2^-, NO_3^-, HPO_4^{2-}, PO_4^{3-}, HCO_3^- and CO_3^{2-}	500
Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Ba^{2+}	350
Cd^{2+}, Sr^{2+}, Ca^{2+}, Mn^{2+} and Sn^{4+}	300
Co^{2+}, Ni^{2+} and Cu^{2+}	200
Fe^{3+}	100
Fe^{2+} and Cr^{3+}	50

3.8. Effect of interference ions

In view of the high selectivity provided by FAAS, the interferences studied were those related to the extraction step, *i.e.* the co-existing metal ions and the cations that may react with As(V) in the form of $HAsO_4^{2-}$, as well as the cations and anions that may react with metal binder and redox active Pyronine B in cationic form and reduce the extraction efficiency. Under the optimized for CPE, interference studies were carried out by individually spiking gradually increased amounts of foreign interfering ions into the test standard solution containing As(V) at 500 $\mu g\,L^{-1}$ before subjected to the CPE, and a deviation greater than ±5.0% from the signals observed in absence of any foreign ions was used as the criterion of interference occurring. Table 2 depicts the tolerance limits of the diverse ions, *i.e.* interferent-to-analyte ratios in which the relative error was less than ±5.0%. As can be seen, Fe^{2+} and Cr^{3+} ions partly interfere at a ratio of 50. The results showed that excess amounts of common cations and anions do not interfere on the determination of trace quantities of As species. The interference superiority of the method especially against phosphate, PO_4^{3-} and HPO_4^{2-} may be due to high selectivity tendency of ligand into As(V) present in form of $HAsO_4^{2-}$ at pH 8.0.

3.9. Characteristics of the proposed method

Analytical characteristic data of the proposed CPE–FAAS for As(V) were as follows. The RSDs as a measure of precision for 10 replicate determinations of 5.0 $\mu g\,L^{-1}$ of As(V) was 2.1%. The preconcentration factor, which is defined as the concentration ratio of analyte in the final diluted surfactant-rich extract ready for FAAS determination and in the initial solution was 120 for As(V). The calibration graph was obtained by preconcentration of 50 mL of sample under the optimum experimental conditions. The linear range was from 5 to 2200 $\mu g\,L^{-1}$ for As(V). The calibration function was $A = 0.0116 + 7.0 \times 10^{-5} C$ ($N = 6$) with a correlation coefficient 0.9978, where C was the concentration of As(V) in $\mu g\,L^{-1}$. The detection and quantification limits, calculated according to $3S_0/s$ and $10S_0/s(3\sigma)$, where S_0 was obtained from the standard deviation for 10 replicate measurements of a blank solution, and s is the slope of the calibration graph, were 1.67 and 5.06 $\mu g\,L^{-1}$ respectively.

3.10. Application of real samples—evaluation of the proposed method

The accuracy and validity of the proposed method were examined by determining the As species in water samples. The proposed method has directly been applied for the determination of As(V) and As (III) in both tap and commercial drinking water. Additionally, the recovery experiments of different amount of As species were carried out by using calibration curve method, and the results are shown in Table 3. The results indicated that the recoveries are quantitatively at reasonable levels for trace As analysis, ranging from 98.0 to 104.0%.

In order to establish the validity of the proposed procedure, the method has been applied for the determination of the content of total As in water standard reference materials (TMDA 53.3 and NIST-1643e). Suitable aliquot of the sample (20 mL) was diluted to a final volume of 50 mL with water and other reagents used in optimization step prior to analysis. The determined values (34.70 ± 1.08 $\mu g\,L^{-1}$ and 60.25 ± 1.07 $\mu g\,L^{-1}$ for five

Table 3
Speciation of As(III), As(V) and total As in water samples[a] (sample volume of 40 mL, $n = 4$).

Samples	Added ($\mu g\,L^{-1}$)		Found ($\mu g\,L^{-1}$)			% Recovery[d]			% REs		% RSDs	
	As(III)	As(V)	As(III)	As(V)	Total As	As(III)	As(V)	Total As	As(III)	As(V)	As(III)	As(V)
Tap water	–	–	17.8 ± 0.2	10.1 ± 0.2	27.9 ± 0.4	–	–	–	–	–	3.1	4.1
	50.0	50.0	66.9 ± 0.1	59.7 ± 0.3	76.6 ± 0.3	98.7	99.3	98.3	−1.8	−0.7	3.5	3.5
	100.0	100.0	118.3 ± 0.1	109.1 ± 0.1	127.4 ± 0.1	100.4	99.1	99.6	+0.4	−0.9	2.9	3.6
Commercial	–	–	–	–	–	–	–	–	–	–	–	–
drinking	50.0	50.0	49.3 ± 0.3	50.8 ± 0.2	100.1 ± 0.1	98.6	101.6	101.1	−1.4	+1.6	3.2	2.9
water[b]	100.0	100.0	101.2 ± 0.1	99.8 ± 0.2	201.0 ± 0.1	101.2	99.8	100.5	+1.2	−0.2	3.0	3.0
Commercial	–	–	–	–	–	–	–	–	–	–	–	–
drinking	50.0	50.0	48.7 ± 0.4	49.1 ± 0.3	97.8 ± 0.4	97.4	98.2	97.8	−2.6	−1.8	3.0	3.4
water[c]	100.0	100.0	99.1 ± 0.2	102.4 ± 0.1	201.5 ± 0.1	99.1	102.4	100.7	−0.9	+2.4	2.8	2.9

[a] Average of three samples ± standard deviation.
[b] It was bought from a local market (Niksar water, Tokat).
[c] It was bought from a local market (Pınar water, Sivas).
[d] The % recovery calculated as: % Recovery = $C_{\text{after spiking}}/C_{\text{initial}} + C_{\text{spiked}} \times 100$.

Table 4
The analytical results for total As determination in the environmental water reference materials (sample volume of 20 mL, $n = 5$).

Samples	Certified value ($\mu g\,L^{-1}$)	Added ($\mu g\,L^{-1}$)	Found* ($\mu g\,L^{-1}$)	% RSD	% Recovery
TMDA 53.3 a trace element fortified calibration standard**	34.20 ± 1.38	–	34.70 ± 1.08[a] (34.32 ± 1.05)[b]	3.11	101.5
		10.00	44.83 ± 1.32	2.94	101.4
		25.00	59.85 ± 1.24	2.07	101.1
		50.00	84.85 ± 1.18	1.39	100.7
NIST-1643e simulated fresh water-trace elements***	60.45 ± 1.78	–	60.25 ± 1.07[a] (60.38 ± 1.02)[b]	1.77	99.7
		10.00	70.65 ± 1.36	1.92	102.3
		25.00	84.75 ± 1.25	1.47	99.2
		50.00	110.35 ± 1.15	1.04	99.9

[a] The average value plus standard deviation found by using directly calibration curve method under the optimized reagent conditions.
[b] The average value plus standard deviation found by using standard addition curve method under the optimized reagent conditions.
* The average value plus standard deviation for five replicate measurements at probability level of 0.05.
** Statistical student's t-test and F-variance test results: $t_{experimental} = 0.451$ and $F_{4,4}$: 1.63, $t_{theoretical} = 2.57$ and $F_{4,4}$: 6.39 at 95% confidence limit ($n = 5$).
*** Statistical student's t-test and F-variance test results: $t_{experimental} = 0.152$ and $F_{4,4}$: 2.77, $t_{theoretical} = 2.57$ and $F_{4,4}$: 6.39 at 95% confidence limit ($n = 5$).

Table 5
Comparison of the proposed method with some methods published in literature.

Species	Chelating agent	The detection method	Experimental system	Linear range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	Enrichment factor	% RSD	Ref.
As(III)	Ammonium pyrolidine dithiocarbamate	ET-AAS	CPE Triton X-114	0.1-20	0.04	36	3.0	[48]
As(III)	Br-PADAP	UV–vis	Spectrophometry	100–2000	14.0	Not defined	5.0	[49]
As(III), As(V)	Ammonium pyrolidine dithiocarbamate	ET-AAS	Liquid–liquid microextraction	Not defined	0.01	115	2.4	[50]
As(III), total As	Ammonium pyrolidine dithiocarbamate	ET-AAS	CPE Triton X-114	0.5–20.0 0.2–20	0.02 0.066	40	2.3	[51]
As(III)	Ethylenediamine-N,N′-diacetic-N,N′ dipropionic acid	UV–vis	Kinetic spectrophometry	50–200	20.0	Not defined	7.6	[52]
As(III) As(V)	No ligant	HG-AAS	Biosorption	Not defined	0.011	35	7.0	[53]
As(III), As(V)	Molybdate	ET-AAS	CPE Triton X-114	0.02–0.35	0.01	52.5	5.0	[54]
As(III) As(V)	Ammonium pyrolidine dithiocarbamate	GF-AAS	Liquid–liquid microextraction	0.1–10	0.036	45	3.1	[55]
As(III), As(V)	Pyronine B	FAAS	CPE Triton X-114	5.0–2200	1.67	120	2.1	Presented method

replicate measurements) by using calibration curve method are in good agreement with the certified values ($34.20 \pm 1.38\ \mu g\,L^{-1}$ and $60.45 \pm 1.78\ \mu g\,L^{-1}$) while the results found by using standard addition curve method are $34.32 \pm 1.05\ \mu g\,L^{-1}$ and $60.38 \pm 1.02\ \mu g\,L^{-1}$, respectively. To check the accuracy of the method, spiking was performed in five replicate at three concentration levels (10, 25 and 50 $\mu g\,L^{-1}$) of As^{5+}, for both certified standard reference water samples separately (Table 4). The accuracy of total As was also monitored and checked by using recovery tests based on both calibration curve method and standard addition curve method for possible matrix effect (Table 4). The obtained results quantitatively showed sufficient recoveries with RSDs changing in the range of % 1.04–3.11 for total As (>99.2%).

4. Conclusions

In the present study, Pyronine B as chelating ligand was firstly used for As determination in this method. To date, APDC (ammonium pyrolidine dithiocarbamate) was generally used for this purpose. Pyronine B forms a stable ternary complex with As(V) ions in the presence of CPC at pH 8.0. Furthermore, the linear range of the presented method is wider than those of the methods exists in literature. The obtained enrichment factor is the best value according to the literature. The detection limit of the method is superior to those of preconcentration techniques used for As analyses. Table 5 compares the characteristic data of the present method with those reported in literature. All methods mentioned in literature for determination of As species by means of CPE use very expensive instruments such as ET-AAS, HG-AAS, and ICP-MS. As for the presented method, it exclusively uses conventional FAAS. It has not been observed a method for As determination by using CPE/FAAS system in literature until the present time.

The CPE separation, preconcentration and speciation procedure described above facilitates a selective preconcentration of As(V) in the presence of As(III) from very dilute solutions. Furthermore, the permanganate oxidation of As(III) to As(V) allows the determination of total inorganic As. The concentration of As(III) in the samples could be calculated by the difference in concentration between As(V) and the total As. The proposed method has advantages of wide linear range, low detection limit, high selectivity, good reproducibility, adequate accuracy, quantitative recovery, relatively high preconcentration factor. With 50 mL sample volume, one sample can be analyzed in approximately 50 min. The recommended procedure can be successfully applied to speciation, preconcentration and determination of inorganic As in a wide range of natural water samples.

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