

CLOUD POINT EXTRACTION AND SPECTRO- PHOTOMETRIC DETERMINATION OF As(III) USING BRILLIANT BLACK BN AS AN EXTRACTION AGENT IN WATER SAMPLES

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ABSTRACT. Cloud point methodology was successfully used for the extraction of trace amounts of arsenic (III) as a prior step to their determination by spectrophotometry. For the proposed method, Brilliant Black BN (BBB), trioctylamine (TOA), Triton X-114, and NaCl were applied as chelating, sensitizing agent, extraction and co-extraction agents, respectively. A linear calibration curve in the range of 8-1000 $\mu\text{g L}^{-1}$ of Brilliant Black BN (BBB) was acquired. Under the optimized conditions, the limit of detection (LOD) was 2.4 $\mu\text{g L}^{-1}$ and the relative standard deviation (RSD) for 2.4, 100 and 400 $\mu\text{g L}^{-1}$ were 1.26, 2.05 and 1.18, respectively ($n = 11$). The application of the work is determination of arsenic (III) quantities in the various samples by spectrophotometric method. In addition, in this work TOA plays the same role of cationic surfactant and as a novel ion pairing reagent that was innovatively used instead of common cationic surfactants such as cetyltrimethylammonium bromide (CTAB).

Keywords: *Cloud point extraction; Brilliant Black BN (BBB); trioctylamine (TOA); water samples; Spectrophotometry, As(III)*

INTRODUCTION

Arsenic (As) is widely distributed in the environment, water, soils, sediments and rocks in its different forms (As(III), As(V) and organic species) [1]. Occupational exposure and arsenic poisoning may occur in persons working in industries involving the use of inorganic arsenic and its compounds, such as wood preservation, glass production, nonferrous metal alloys, and electronic semiconductor manufacturing. Inorganic arsenic is also found in coke oven emissions associated with the smelter industry [2]. It was ranked as the No. 1 of

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hazardous element and has serious effects on plants, animals and human health [3]. Millions of people worldwide are exposed to arsenic in their drinking water and ingested arsenic is an established cause of bladder, lung, and skin cancer. In addition to cancer, arsenic in water has also been associated with cardiovascular disease, skin lesions, diabetes, reproductive disorders, cognitive deficits in children and other health effects [4]. The linkage between arsenic contamination in water, arsenic concentration and accumulation in various biological samples, and oxidative DNA damage, has been proved [5]. Exposing to arsenic induces increases in DNA double strand breaks in both cell lines [6]. Because of the importance of this issue, a lot of researchers have done studies regarding measuring of Arsenic by various methods [7]. Also there are some works previously reported regarding determination of arsenic by spectrophotometric methods in the literature [13-16].

Cloud point extraction (CPE) is an outstanding alternative to conventional solvent extraction method because it produces high extraction efficiencies and pre-concentration factors, by using inexpensive and non-toxic reagents [3].

In the last decade, the increase of attention and interest upon the use of aqueous micellar solution has been found in field of separation science [17]. The cloud point extraction (CPE) technique has also been applied as a procedure for determination and removal of dyes and pigments as well as analyzing metals. [18,19]. In the present work, we applied CPE for the determination of arsenic (III) quantities in the various samples by BBB as the ligand which has made the work as a novel method.

RESULTS AND DISCUSSION

In this study, As (III) ion interacted with Brilliant Black BN, an anionic dye, which led to the formation of (As-Brilliant Black BN) complex. This complex was extracted by mixed-micelle mediated extraction through the ion pairing reagent (TOA) and non-ionic (Triton-X114) surfactants. The absorption spectra of As-BBB-TOA complexation showed a maximum absorption band at 616 nm. To obtain the maximum absorbance and sensitivity, we need to optimize various conditions which can affect the extraction. Hence, the effects of various operating conditions have been investigated and the optimum concentrations have been established for CPE.

In the present work, in order to study As (III) ion, a procedure is adopted which As (III) was used in the presence of BBB ion as a chelating agent. The interaction between arsenic and BBB that has four anionic sites to interaction with target metals led to the formation of $[\text{As-BBB}]^{1-}$ anionic complex. With regard to the fact that, hydrophobic ion-associated complexes could be more

efficiently extracted into surfactant-rich phase than ionic ion-associated complexes, small amount of ion pairing reagent (TOA) also as the sensitizing agent and a cationic auxiliary ligand was added. The addition of ion pairing reagent (sensitizing agent) improves the selectivity and sensitivity of the metal determinations. So, TOA⁺ as sensitivity enhancement agent was added, producing a neutral and stable ion-pair complex (ternary ion-association system), [As-BBB-TOA]. Most importantly, a colored ligand such as BBB takes the solution to visible area and as a matter of fact, in spectrophotometric method, the study of visible absorption area would be the most convenient and accurate type of detection because numerous solvents and reagents used in CPE and liquid-liquid extraction (LLE) have adsorption spectra in UV area which interfere in the determination of the goal analytes. After that, we used TOA as the ion pairing reagent, cationic surfactant, sensitizing agent and a cationic auxiliary ligand. ion pairing reagent can interact with dye and/or the metal-dye complex as an individual molecule or aggregates. With regard to the fact that, hydrophobic ion-associated complexes could be more efficiently extracted into surfactant-rich phase than ionic ion-associated complexes, small amount of ion pairing reagent (TOA) was added. The addition of sensitizing agent improves the selectivity and sensitivity of the metal determinations. In the last step, NaCl was used as the electrolyte to increase the efficient extraction.

Effect of pH

pH is an important analytical parameter that significantly influence the formation of metal-ligand complex. Therefore, in order to acquire the favorable preconcentration efficiencies, the pH values were studied in the ranges of 1.0–8.0. For this range we studied the various values of Na₂HPO₄ with acid citric to make the buffer to reach the desired pH.

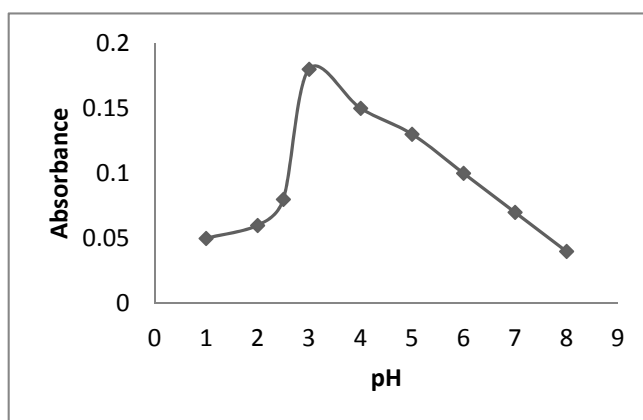


Figure 1. The concentration effect of pH on CPE

Thus the highest absorbance was obtained at pH 3. It is shown in Fig. 1. Probably, at lower pH values the rate of complex formation is low and at higher pH values the complex decomposes. Hereby, pH 3 was selected for the further experiments by 1.5 mL of *Mcllvaine's buffer* solution.

Effect of Brilliant Black BN dye concentration

For studying the effect of Brilliant Black BN on extraction of Arsenic ($50 \mu\text{g L}^{-1}$), a solution containing Arsenic and various amounts of Brilliant Black BN was provided. The extraction efficiency was the highest when $1.33 \times 10^{-5} \text{ mol L}^{-1}$ (2ml) of Brilliant Black BN was applied. Thus, it was chosen for subsequent experiment. As it is observable in Fig. 2, at higher concentrations the absorbance declined, because the excessive Brilliant Black BN could be co-extracted into the surfactant rich phase, thus decreased the extraction efficiency of target complex.

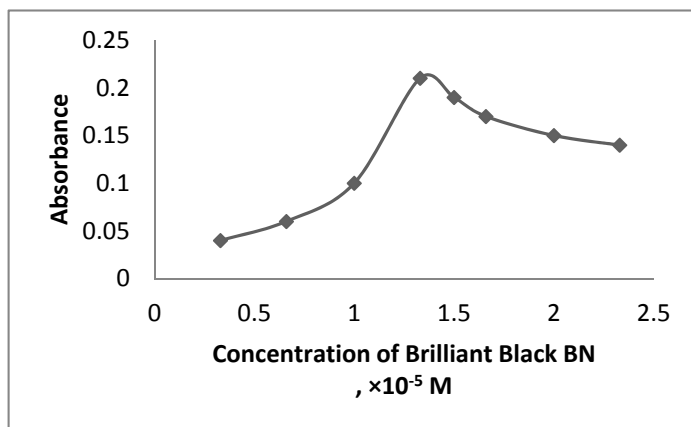


Figure 2. The concentration effect of Brilliant Black BN on CPE

Effect of ion pairing reagent concentration

With regard to the fact that, hydrophobic ion-associated complexes could be more efficiently extracted into surfactant-rich phase than ionic ion-associated complexes, small amount of TOA^+ was added in the presence of $50 \mu\text{g L}^{-1}$ of arsenic.

Amines lead to aminium salts in the presence of acids like HCl, HBr and HI due to protonation.



The result was the formation of [As-(BBB)-TOA] hydrophobic complex. Also, in order to improve the sensitivity and selectivity as well as increasing the efficiency of CPE, initially, three amines such trioctylamine (TOA), triethylamin (TEA) and tripropylamine (TPA) were considered and investigated in the range of 0.05-0.4% v/v. The best extraction yield was obtained in presence of TOA. Therefore, to the use of TOA was decided for further studies. The effect of TOA concentration, used as sensitive improving auxiliary ligand, on the extraction yield of As(III) was studied in range of 0.05-0.4% v/v. The effect of concentration of TOA as well as TEA and TPA on extraction yield is shown in Fig. 3. The extraction yield gradually increased by increasing TOA concentration up to 0.2% v/v, and quickly declined at higher concentrations. This is probably because of an increase in the blank absorbance and decrease the absorbance of ternary ion association also, excessive presence of TOA⁺ in the solution can act as a competitor for As(III) in complexation with BBB. As a result, the 0.2% v/v TOA solution was selected as the optimal ion pairing reagent concentration.

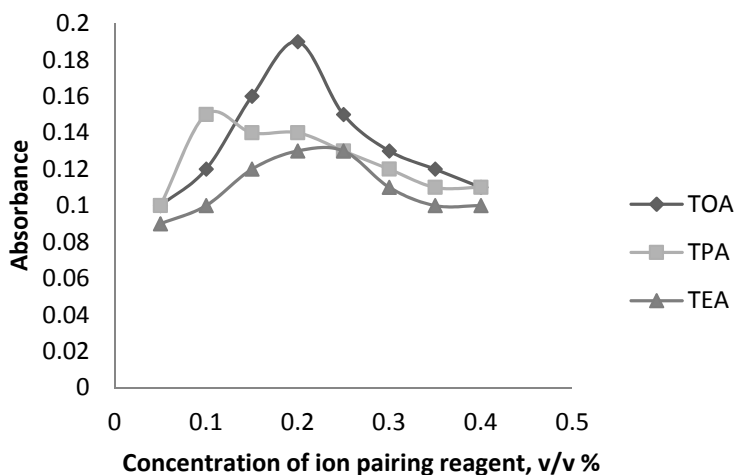


Figure 3. The concentration effect of ion pairing reagent on CPE

Effect of non-ionic surfactants

Optimization of this parameter was carried out in order to accomplish a minimum desirable surfactant concentration with maximum extraction efficiency. Some non-ionic surfactants including Triton X-114, Triton X-100 and Triton X-45 (0.1-0.45% (v/v)) were applied to CPE. Among them Triton X-114 was selected due to its higher extraction efficiency. Triton X-114 was chosen as

a surfactant due to its low cloud point temperature and high density of surfactant-rich phase, this facilitates phase separation by centrifugation. So, for further studies it was chosen. With increasing the surfactant concentration up to 0.3% (v/v) the signal increased. Thus, it was used as optimum concentration. At lower concentrations, the extraction efficiency of the complexes is low, probably because of an inadequacy in the assemblies to entrap the hydrophobic complex quantitatively. The preconcentration was decreased at higher concentrations due to increase in the volume of the surfactant-rich phase. Therefore, the measured absorbance as a result of sensitivity is decreased. The results are shown in Fig. 4.

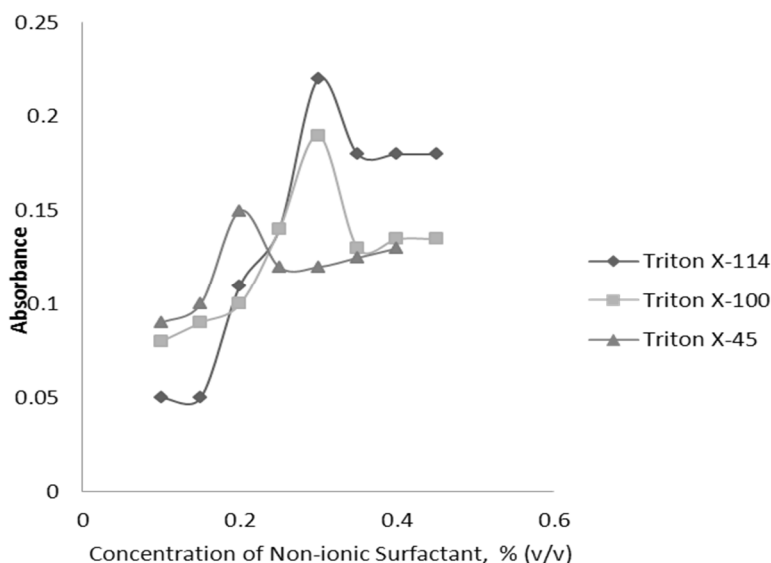


Figure 4. The concentration effect of Non-ionic Surfactant on CPE

Effect of ionic salt concentration

To investigate the influence of electrolyte concentration on the extraction efficiency, 0.1 mol L⁻¹ NaCl and KCl were surveyed to solution in various amounts as the co-extraction agents. NaCl showed a more increase on the absorbance of solution. Thus, it was chosen for the further studies. It increased the extraction efficiency of arsenic up to 1.0×10⁻² mol L⁻¹ and was chosen to next studies. The salting-out ability of the cations follows the Hofmeister series (Na⁺ > K⁺) and can be related to the ions from Gibbs' free energy of hydration. (Fig. 5)

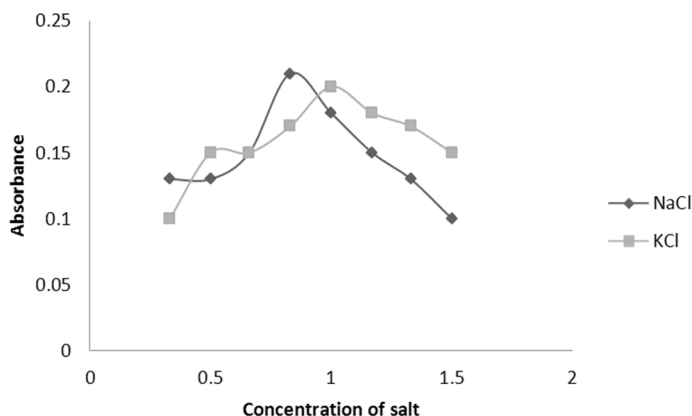


Figure 5. The concentration effect of salt on CPE

Effect of incubation time and centrifuge time and rate

For investigation of effective preconcentration and easy phase separation, the centrifugation time, equilibration temperature and incubation time were optimized. The results demonstrated that centrifuging for 5 min at 3500 rpm leading to the highest extraction of As(III). Additionally, the influence of time on the extraction of As(III) was surveyed in the time range of 5-20 min which the maximum absorbance was acquired 10 min. The influence of equilibration temperature in the range of 20-60 °C was investigated. It was established that 45 °C is sufficient for the quantitative analysis.

Analytical performance

Analytical characteristic data of the proposed CPE for As(III) was studied. In the range of 8 to 1000 $\mu\text{g L}^{-1}$ the calibration curve for arsenic was linear. The limit of detection (LOD) was 2.4 $\mu\text{g L}^{-1}$ and was calculated according to $3 S_{\text{blank}} / s$, where S_{blank} was obtained from the standard deviation for 10 replicate measurements of a blank solution, and s is the slope of the calibration graph. The regression equation was acquired by the least square method is $A = 2.19 \times 10^{-3} C_{\text{As}} + 1.75 \times 10^{-2}$ for 8-1000 $\mu\text{g L}^{-1}$ of As(III) with a correlation coefficient of 0.998 ($n = 10$), where A is the absorbance and C_{As} shows the concentration of As(III) in $\mu\text{g L}^{-1}$. The relative standard deviation (RSD) at 2.4 and 100 and 400 $\mu\text{g L}^{-1}$ were 1.26, 2.05 and 1.18, respectively ($n = 11$). The preconcentration factor was 21.4.

Interference studies

The validity of the method was assessed by investigating the effect of various foreign ions which are likely to interfere in the determination.

Usually coexisting ions may influence on objective determination of As(III) by CPE. To verify this assumption, solutions containing $100 \mu\text{g L}^{-1}$ of As(III) were taken with different amounts of foreign ions and recommended procedure was followed. The results were summarized in Table 1.

Table 1. The effect of other species on the determination of $100 \mu\text{g L}^{-1}$ of As(III)

Foreign ions	Tolerance limit ($\mu\text{g mL}^{-1}$)
Cl ⁻ , Na ⁺ , K ⁺ , NH ₄ ⁺ , NO ₃ ⁻	1000
Cu ²⁺ , Pb ²⁺ , Li ⁺ , Ca ²⁺	800
Ag ⁺ , HCO ₃ ⁻ , Cd ²⁺	500
Br ⁻ , HPO ₄ ²⁻	250
Ni ²⁺ , Sn ²⁺ , Co ²⁺	100
Al ³⁺ , Fe ³⁺ , Cr ⁶⁺ , Sb ³⁺	50

APPLICATION

The proposed method was employed for the determination of As(III) in various water samples. Five replicates determinations were carried out and the obtained results (Table 2) were satisfactory. The high percentage recovery was confirmed the accuracy, precision and the independence of the procedure from the matrix interference.

Table 2. Determination of Arsenic in different Water samples and recovery tests

Sample	As (III) added ($\mu\text{g L}^{-1}$)	As (III) Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)
River water ^b	-	61.17 ± 0.12	-	2.1
	50	110.58 ± 0.16	99.47	1.6
	100	159.15 ± 0.080	98.75	2.9
River water ^c	-	14.96 ± 0.51	-	1.1
	50	62.76 ± 0.17	96.61	3.0
	100	112.50 ± 0.11	97.86	2.5
Tap water	-	8.21 ± 0.16	-	2.1
	50	58.14 ± 0.10	99.88	2.1
	100	110.51 ± 0.19	102.12	2.3
Well water	-	20.15 ± 0.03	-	2.1
	50	71.81 ± 0.17	102.37	1.7
	100	118.60 ± 0.04	98.81	1.8
Spring water	-	22.17 ± 0.09	-	2.0
	50	70.84 ± 0.18	98.16	2.5
	100	121.15 ± 0.04	99.16	3.0

^a $\bar{x} \pm ts\sqrt{n}$ at 95% confidence (n = 5)

^b zayande rood river, Esfahan (located in an industrial area)

^c beshar river-tang-e-sorkh village branch (located in a nonindustrial area)

EXPERIMENTAL

Apparatus

Absorption spectra and absorbance measurements were made by a Shimadzu UV-1800, UV-Vis spectrophotometer using 1 cm quartz cells (1.0 mL). A Metrohm digital pH meter (model 691) with a combined glass electrode was applied to measure pH values. A Hettich universal 320 centrifuge was used to hasten the phase separation.

Standard solutions and reagents

The non-ionic surfactant Triton X-114 (3%, v/v) (Sigma-Aldrich, Steinheim, Germany) was used without further purification. Stock standard solution of Arsenic was prepared from the 1000 mg L⁻¹ As(III) standard by dissolving appropriate amount of As₂O₃ (Merck, Darmstadt, Germany) in 3 M NaOH and pH 7.0 with 5 M HCl solution. The 1.0×10⁻⁴ mol L⁻¹ of Brilliant Black BN (Merck, Germany), solution was obtained by dissolving 0.0086 g of it in 100 ml water. A 3% v/v stock solution of trioctylamine (TOA) (Sigma-Aldrich) was attained by diluting 3.0 mL of the reagent to 100 mL water containing 1 mL of HCl (0.1 mol L⁻¹) in a volumetric flask. The McIlvaine's buffer solution was provided by 4.11 ml of 0.2 M Na₂HPO₄ in 15.89 ml of 0.1 M citric acid. Stock solution of NaCl (1.0×10⁻¹) was prepared by dissolving 0.584 gr of it in distilled water and diluting to 100 mL in a flask.

Procedure

An aliquot of the solution containing As(III) (in the range of 8-1000 µg L⁻¹), 2 mL of Brilliant Black BN (1.0×10⁻⁴ mol L⁻¹), 1.5 mL of 3% (v/v) of Triton X-114, 1 mL of 3% TOA, 1.75 mL of 0.1 mol L⁻¹ of NaCl and 1.5 mL of *McIlvaine's buffer* (pH =3) was transferred into a 15 mL tube, and equilibrated at 45 °C in a thermostat bath for 10 min. The separation into two phases was accelerated by centrifuging at 3500 rpm for 5 min. The contents of tubes were cooled in an ice-bath for 6 minutes, the surfactant-rich phase became viscous, and the upper aqueous phase was decanted. The surfactant-rich phase of this procedure was dissolved and diluted to 0.7 mL with the methanol and transferred into a quartz cell. The absorbance spectrum of the solution was measured at the 616 nm. A blank solution that was prepared in the same way except that distilled water was used instead of As(III) was also submitted to the same course of action and its spectrum was measured.

Sample preparation

Different water samples were preconcentrated. All the collected samples were spiked with a suitable amount of standard solution of As(III). All the aforementioned samples were filtered through a 0.44 μ m membrane to remove the suspended and floated particles. Standard addition method was applied so as to calculate recovery values and check accuracy of results.

CONCLUSION

The proposed work was found to be very simple, direct, very selective and sensitive. The limit of detection of the proposed method seems to be satisfactory. The possible interference of some important ions was investigated and no important interference was encountered. The Simplicity in operation, good precision, being economical, low extraction time and the lack of the toxic solvents presence in the method are from other benefits of the work. The proposed method formed hydrophobic ion-associated complex, and the hydrophobic complexes are more extractable by Triton X-114 than the non hydrophobic complexes. Spectrophotometry of such colored ternary complexes probably provides the most sensitive, relatively simple and fast approach to trace metal analysis. This reason is extendable to contrast among the ligandless extractions and those have one or more ligands. In addition, the percentage recoveries were higher than 96% confirming the accuracy. Considering the achieved results, the arsenic quantities, in water samples of the river located in industrial area is considerably higher than the nonindustrial one. And well water and spring water (as unpurified samples) have more quantities of arsenic as compared to tap water (as purified sample). This method gives reasonably good detection limit, wide linearity and also good standard deviations.

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