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Selective Ion Flotation Separation and Concentration of Ultra Trace Amounts of Bismuth Using Arsenazo III and Its Determination by Inductively Coupled Plasma-Atomic Emission Spectrometry

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A rapid, selective, and highly sensitive froth flotation method for the separation and enrichment of ultra trace amounts of bismuth is developed. The bismuth-Arsenazo III complex is concentrated from 1000 mL of aqueous solution into the scum in the presence of cetyltrimethylammonium bromide (CTAB) as a cationic surfactant. The proposed procedure of pre-concentration is applied prior to the determination of bismuth using inductively coupled plasma–atomic emission spectrometry (ICP-AES). Effects of Arsenazo III concentration, pH, CTAB concentration, and foreign ions have been studied. The proposed method possesses a pre-concentration factor of 500 and a detection limit of 0.28 ng mL^{-1}.

Keywords Arsenazo III; bismuth; froth-flotation; ICP-AES determination

INTRODUCTION

Bismuth is one of the least abundant elements (0.1 ppm or less) in the earth's crust. This element has been widely used in industry and medicine in recent years. In the industry part, bismuth and its compounds are used in the preparation and recycling of uranium nuclear fuels, in semiconductors, cosmetic preparations, alloys, and metallurgical additives (1,2). In the medication part, for nearly 150 years, low doses of bismuth compounds have been excellent remedies against gastric disorders, especially for colitis, diarrhea, and peptic ulcers. They were and still are used for burn bandage dressings, antiseptic powders, salves, or ointments and in the treatment of venereal diseases (3). Therefore, in parallel with increasing the uses of bismuth in each of the mentioned parts, it has spread in the environment and thus it is important to determine bismuth at ultra trace levels in environmental and biological samples.

The determination of extremely low concentrations of bismuth in different samples requires powerful techniques and only few techniques have sufficient sensitivity. Inductively coupled plasma mass spectrometry (ICP-MS) has been used for direct determination of low concentrations of bismuth (4,5). However, a simple method such as ICP-AES is generally insensitive for the determination of bismuth (6) in environmental and biological samples at low ng mL^{-1} levels and requires a pre-concentration step for extending the detection limit.

The flotation separation techniques, possessing the advantages of rapidity, simplicity, and high pre-concentration factor over most of other pre-concentration methods (7,8), have been widely used to separate and concentrate trace elements from aqueous systems (9–23). A survey of the literature shows that the application of flotation techniques have been reviewed by Alfassi and Wai (8), and Caballero et al. (15). The precipitate flotation separation with hydrated iron(III) oxide (12) and thionalide (17) have been used for the pre-concentration of trace amounts of bismuth in water. However, to the best of our knowledge, the ion flotation of low ng mL^{-1} levels of bismuth from aqueous samples using Arsenazo III has not been reported previously.

This paper describes the first application of the ion flotation separation technique using Arsenazo III for the enrichment of ultra trace amounts of bismuth in aqueous systems. The Bi-Arsenazo III-CTAB ion adduct (insoluble ion pair) is readily separated from the mother liquor, and dissolved in nitric acid solution for ICP-AES. The influences of several factors including Arsenazo III concentration, pH of test solution, CTAB concentration, and foreign ions on the recovery were studied, and the optimum experimental conditions are presented.

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EXPERIMENTAL

Reagents

Reagent grade cetyltrimethylammonium bromide (CTAB,) and Arsenazo III (2,2′-[1,8-dihydroxy-3,6-disulfo-2,7-naphthylenebis(azo)]-dibenzenearsonic acid) were of the highest purity available (>99% purity) from Aldrich and used as received. The nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification. Stock solutions of bismuth (1.0 mg mL^{-1}) were prepared by dissolving 2.3210 g of bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$ (AnalaR, BDH), in 100 mL of nitric acid (1 + 3) and diluting to 1000 mL with distilled water. Doubly distilled deionized water was used throughout. Bismuth sub nitrate powder (Sepidaj Pharmaceutical Co., Tehran, Iran) and bismuth sub citrate tablets (Arya Pharmaceutical Co., Tehran, Iran) were used as received.

Apparatus

The flotation cell used (Fig. 1) was made by joining a sintered glass (porosity No. 4) funnel to a cylindrical glass tube of 4-cm inner diameter and 105-cm length. The scum or foam layer was collected with a sampling bottle. A non-oil compressor was used for bubbling.

The metal ion determinations were carried out with a simultaneous inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The ICP conditions are given in Table 1. The pH of the solutions are determined and adjusted using a model 620 Metrohm pH meter equipped with a combined glass-calomel electrode.

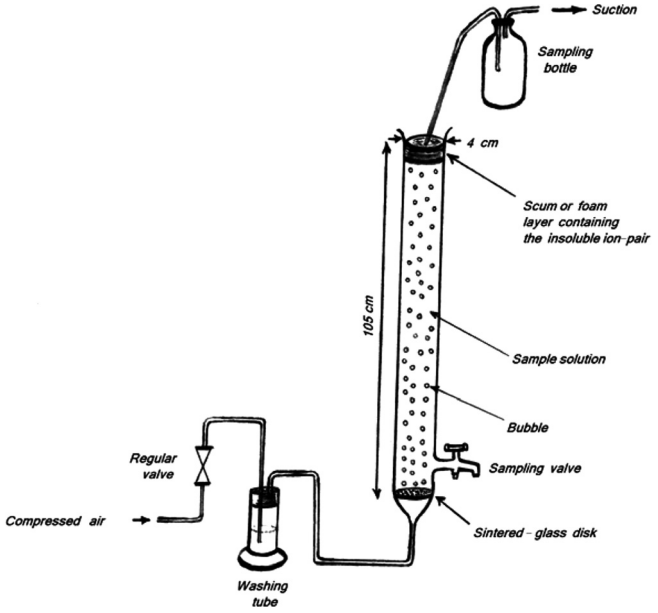

FIG. 1. Schematic diagram of flotation system.

TABLE 1
Instrumental and operating conditions ICP-AES measurements

Parameter	Type or amount
Frequency generator/MHz	40
Plasma viewing mode	Radial
Viewing height/mm	8
Injector i.d./mm	2.5
Optical mount	Echelle grating + cross-dispersion
Grating line number/mm^{-1}	95
Focal length/cm	40
Detector	CCD
Nebulizer	Concentric
Spray chamber	Cyclonic
RF power/kW	1.2
Plasma gas flow rate/l m^{-1}	13.5
Auxilary gas flow rate/L m^{-1}	0.75
Nebulizer pressure/KPa	200
Rinse time/s	10
Selected emission line/nm	Bi(223.061)

Procedure

All the flotation experiments were carried out at ambient temperature using the cell shown in Fig. 1. In a typical experiment, the sample solution containing 0.150 mg of bismuth ion was transferred into a 1000 mL beaker. After adding 5 mL of saturated KNO_3 solution (to adjust the ionic strength), 15 mL of 0.1 wt% of Arsenazo III solution, 2 mL of 1 wt% of CTAB solution in 95% ethanol, and 50 mL of 1 M acetate buffer of pH 4.0, and stirring for 20 min, the mixture was diluted to 1000 mL with water. The sample solution was then transferred into the flotation cell. An air stream (50 mL min^{-1}) was passed into the solution for several minutes, until the solution became colorless or pale pink (ultimate flotation test). The resulting foam layer containing the insoluble ion pair was sucked into the sampling bottle. The foam in the sampling bottle was dissolved in three 5-mL portions of hot concentrated nitric acid and 2 mL 30% w/w hydrogen peroxide. The solution was then evaporated to near dryness. The residue was dissolved in 1 mL of concentrated nitric acid and 1 mL of water. The resulting 2-mL solution was analyzed by inductively coupled plasma-atomic emission spectrometry for bismuth. If a residual solution (underneath the foam) in a flotation cell should also be analyzed, it could be collected through the sampling valve (Fig. 1), otherwise it might be discarded.

Digestion of Bismuth-Containing Pharmaceuticals

Bismuth Sub Nitrate Powder

A portion (0.14 g) of this medicine was dissolved in 10 mL of concentrated HNO_3 and evaporated to dryness. The residue was dissolved and diluted to 1000 mL with

1 M HNO_3. Then an appropriate volume was taken from the solution and analyzed for determination of bismuth, using the recommended procedure.

Bismuth Sub Citrate Tablets

One tablet (0.42 g) was dissolved in a mixture of 10 mL of concentrated HNO_3 and 2 mL of concentrated $HClO_4$. The mixture was heated to near dryness. The residue was dissolved in distilled water and filtered with filter paper (Whatman No. 1). The filtrate was diluted to 1000 mL with 1 M HNO_3. Then an appropriate volume was taken from solution and analyzed for determination of bismuth by the recommended procedure.

RESULTS AND DISCUSSION

Bismuth(III) is well known to form a negatively charged purple-red stable 2:1 (ligand-to-metal) complex with Arsenazo III, which strongly absorbs light at a wavelength of 615 nm (24,25). In the presence of a cationic surfactant such as CTAB, the Bi-Arsenazo III complex will form an ion-paired adduct, which is more or less insoluble in water, via the formation of a well-flocculated precipitate. Thus, in this work, we examined the use of Arsenazo III as a very promising reagent in the development of the rapid froth flotation method for the selective separation and enrichment of ultra trace amounts of Bi(III) ions from aqueous samples.

In the course of the optimization processes, the effectiveness of metal ion extraction from the solution was evaluated from the ultimate collected foam and, in some cases, it was rechecked by downstream experiments using the equation $\%R = 100\ (C^0_{Bi} - C_{Bi})/C_{Bi}$, where C^0_{Bi} and C_{Bi} are the bismuth concentrations in aqueous phase before and after flotation, respectively.

Influence of Medium pH on Flotation Efficiency

The pH of solution is considered to affect the floatability on two aspects,

1. the complex formation and
2. the reaction with a surfactant.

However, since CTAB keeps up its positive character in acidic, neutral, and alkaline media (26), the reaction between the complexed ions and the surfactant does not significantly gets influenced by the pH of solution.

To investigate the influence of the pH on the formation of Bi(III)-Arsenazo III complex and, hence, on the flotation efficiency of the system, the effect of varying pH of the sample solution from 0.0 to12.0 on the floatability of 7.2×10^{-7} M of Bi(III) was studied in the presence of 15 mL of 0.1 wt% of Arsenazo III solution, 5 mL of saturated KNO_3 solution, and 2 mL of 1 wt% of CTAB solution in 95% ethanol (Fig. 2).

From the results shown in Fig. 2, it is obvious that the maximum flotation efficiency (>98%) is attained in a pH range of 2.0–10.0. However, the Bi(III) recovery is sharply decreased at lower pH values (<2). The previous colorimetric studies have demonstrated that Bi(III)-Arsenazo III complex can be formed at a relatively more acidic range of pHs (24,25); thus, the decreased flotation recovery at pH < 2 is most probably due to the diminished stability of the surface foam layer supporting the insoluble ion pair at this relatively narrow pH range. On the other hand, at pH values >10.0, the efficiency of the method is also decreased due to possible hydrolysis of Bi(III) ion to an anionic species BiO_2^- (27). Thus, in all further experiments, a pH of 4.0 was used for the flotation studies.

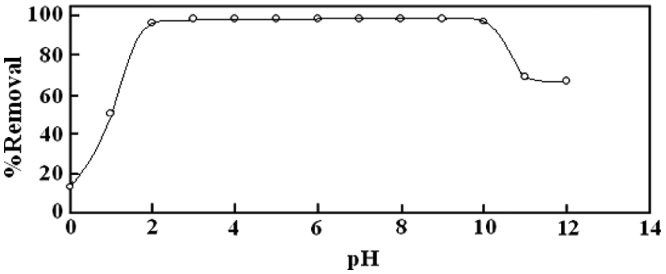

FIG. 2. Influence of pH of test solution on the recovery of Bi(III) ion. The experimental conditions are given in the text.

Effect of Arsenazo III Concentration on Flotation Efficiency

As the relative amount of complexing agent is expected to largely affect the flotation separation processes (22,23,28,29), the influence of Arsenazo III concentration on the floatability of bismuth was investigated. Figure 3 shows the results of the effect of the amount of 0.1 wt% Arsenazo III on the floatability of 7.2×10^{-7} M of Bi(III) at pH 4.0 in the presence of 5 mL of saturated KNO_3 solution and 2 mL of 1 wt% of CTAB solution. As is obvious, while the bismuth recovery is negligible in the absence of Arsenazo III, the flotation efficiency increased with increasing reagent concentration, and recoveries larger than 98% were obtained with >10 mL of 0.1 wt% of Arsenazo III solution. Thus, for subsequent work, 15 mL of 0.1 wt% of the reagent solution was used.

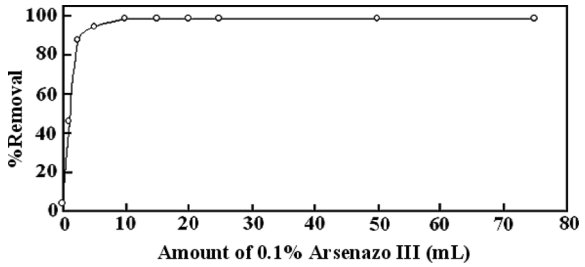

FIG. 3. Influence of amount of 0.1% Arsenazo III solution on the recovery of Bi(III) ion. The experimental conditions are given in the text.

It is worth mentioning that the presence of excess amounts of the reagent revealed no adverse effect on the flotation process. This is an advantageous point, as the procedure could thus be applied to the analysis of bismuth in real samples.

Effect of CTAB Concentration on Flotation Efficiency

In ion flotation techniques a trace metal ion or its charged complex ion forms a water insoluble hydrophobic bulky ion paired adduct with a suitable surfactant of the opposite charge at the surface of inert gas bubbles, which then can ascend to the top of the solution. The quantity of the surfactant should be a little greater than the required stoichiometric amount, but too excessive amounts are undesirable (30). This is because the gas bubbles are surrounded with excess surfactant. Especially, if the surfactant exceeds the critical micelle concentration (CMC), the charged complex ions become hydrophilic again owing to their adsorption at the surface of the micelle (7). The bubble size is also getting smaller with augmenting the surfactant concentration, which results in the formation of a creamier foam (19).

Thus, due to the negative charge of the Bi-Arsenazo III complex, CTAB as a suitable cationic surfactant was chosen to facilitate the flotation process. To study the influence of surfactant concentration, an increasing amount of a 1 wt% ethanolic solution of CTAB from 0.2 to 8.0 mL was added to 7.2×10^{-7} M of Bi(III) at pH 4.0 in the presence of 5 mL of saturated KNO_3 solution and 15 mL of 0.1 wt% of Arsenazo III solution and the results are shown in Fig. 4. As seen, while only 62% bismuth recovery is achieved in the absence of the surfactant, the flotation efficiency increases rapidly with the increasing volume of CTAB solution from 0.2 to 1.0 mL; in the presence of 1.0 to 8.0 mL of the surfactant solution, the flotation of Bi(III) ion remains more or less quantitative. Therefore, 2.0 mL of 1 wt% of CTAB solution in 95% ethanol was selected for further studies. It is worth mentioning that, even in the presence of 8.0 mL of CTAB solution, the surfactant critical micelle concentration is not reached and, therefore, the curve in Fig. 4 attains a plateau without any subsequent decrease in the floatability of the system.

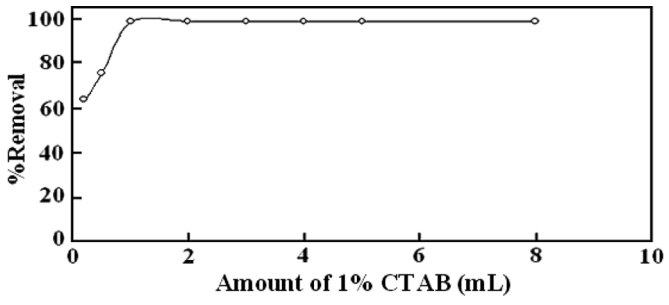

FIG. 4. Influence of amount of 1% CTAB solution in 95% ethanol on the recovery of Bi(III) ion. The experimental conditions are given in the text.

TABLE 2
Tolerance ratio of foreign ions for determination of 7.2×10^{-7} M of Bi(III) ion

Ion	Tolerance ratio
K^+, Na^+, Li^+, Cs^+, Ca^{2+}, Mg^{2+}	1000[a]
Sr^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Sb^{3+}, Ce^{3+}, Ni^{2+}	
Ba^{2+}, Sn^{2+}, Pb^{2+}, Mn^{2+}	700
Al^{3+}	200
Fe^{3+}	1
Fe^{3+}[b]	100

[a]Maximum limit tested.
[b]In the presence of 0.05 M ascorbic acid, as reducing agent.

Effect of Diverse Ions on Bismuth Recovery

The effect of a variety of alkali, alkaline earth, transition, and heavy metal ions on the recovery of Bi(III) was investigated. An ion was considered to be an interferent when it caused an error greater than ±5% in determination of bismuth by the proposed method. The results, presented in Table 2, indicate that most of the investigated ions did not interfere in the pre-concentration and the determination of Bi(III) even when their concentrations were in 200- to 1000-fold excess over Bi(III). As is seen, among all cations tested, only Fe^{3+} ions show a serious

TABLE 3
Determination of Bi(III) ion concentrations in different water samples

	Bi(III)/ng mL^{-1}			
Water sample	Added	Found	% Recovery	RSD%
Tap water (Tehran)	None	N.D.[a]		
	50.0	49.2	98.4	3.5
Well water (Tehran)	None	N.D.		
	50.0	48.0	96.0	3.1
Spring water (Damavand)	None	N.D.		
	50.0	49.0	98.0	2.4

[a]Not detected.

TABLE 4
Determination of bismuth in pharmaceutical samples

Sample	Declared bismuth content	Bismuth found by calibration method	Bismuth found by standard additions method
Bismuth sub nitrate Power/ $mg\,g^{-1}$	714.0	713.9 (3.1)[a]	714.0 (3.2)
Bismuth sub citrate Tablet/mg $tablet^{-1}$	107.6	105.8 (3.2)	105.9 (3.3)

[a]Values in parentheses are SDs for three replicate measurements.

interfering effect on the recovery of bismuth ions. However, the quantitative recovery of bismuth in the presence of significant amounts of Fe^{3+} ions was achieved by the iron reduction in the presence of 0.05 M ascorbic acid in the aqueous phase, as a suitable reducing agent (tolerance ratio of 100).

Preconcentration Factor and Detection Limit

The pre-concentration factor of the proposed flotation method is 500 with recoveries of greater than 98%. To determine the standard deviation of the method, 10 blanks were floated by the recommended procedure and then the concentration of bismuth ion was determined by ICP-AES. The detection limit of the method (DL) was estimated as three times the standard deviation (S_b) of the blank. The value of DL for bismuth was found to be $0.28\,ng\,mL^{-1}$.

APPLICATIONS

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of Bi(III) in natural water and pharmaceutical samples.

Recovery Yields of Bismuth in Natural Water Samples

The developed flotation procedure was applied to the determination and recovery of Bi(III) in several natural water samples and the results are summarized in Table 3. As seen, the recoveries of spiked known additions to different water samples lay within the range 96.0–98.5%.

Analysis of Pharmaceutical Samples

The proposed flotation procedure was successfully applied to the determination of bismuth in two bismuth-containing pharmaceutical preparations and the results are given in Table 4. As is obvious, there are satisfactory agreements between the results obtained by the proposed method and declared bismuth contents of the drugs.

CONCLUSIONS

The presented flotation technique enables ultra trace amounts of bismuth to be rapidly (at the most 15 min) and selectively separated from a relatively large volume of sample solution with Arsenazo III at pH 4.0 in the presence of CTAB, using simple apparatus and procedure and small amounts of reagents. The usefulness of this technique has been proved by a number of examples in analysis of natural waters and pharmaceutical preparations. The detection limit of the proposed method is $0.28\,ng\,mL^{-1}$. A comparison with the previously published pre-concentration and determination methods for Bi(III) ion using co-precipitation (31), solvent extraction (32,33), cloud point extraction (34,35), solid phase extraction (36–39), and precipitate flotation (12,17) clearly revealed that the proposed method is not only among the most sensitive ones, but also is superior over most of them in terms of simplicity, selectivity, and the pre-concentration factor.

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