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Extraction of Ultra Trace Amounts Bismuth in Water Samples Using Cloud Point Extraction with 2-Amino-Cyclopentene-1-Dithiocarboxylic Acid

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Abstract: A new approach for a cloud point extraction-electrothermal atomic absorption spectrometric method was used for determining bismuth. The aqueous analyte was acidified with sulfuric acid (pH 3.0–3.5). Triton X-114 was added as a surfactant and 2-amino-cyclopentene-1-dithiocarboxylic acid was used as a complexing agent. After phase separation at 50 °C based on the cloud point separation of the mixture, the surfactant-rich phasen was diluted using tetrahydrofuran (THF). Twenty microliters (20 µL) of the enriched solution and 10 µl of 0.1% (w/v) Pd $(NO_3)_2$ as chemical modifier were dispersed into the graphite tube and the analyte was determined by electrothermal atomic absorption spectrometry. After optimizing extraction conditions and instrumental parameters, a preconcentration factor of 195 was obtained for a sample of only 10 mL. The detection limit was 0.04 ng ml^{-1} and the analytical curve was linear for the concentration range of 0.04–0.70 ng mL^{-1}. Relative standard deviations were <5%. The method was successfully applied for the extraction and determination of bismuth in water samples.

Keywords: Cloud point extraction; Bismuth; Electrothermal atomic absorption spectrometry; 2-amino-cyclopentene-1-dithiocarboxylic acid; Tap water.

INTRODUCTION

Bismuth has been associated with medicine for more than 200 years. The element was first introduced in a pharmaceutical used in the treatment of syphilis (Bertholf *et al.*., 1985). Presently, bismuth is used in the cosmetics industry for the preparation of creams and hair dyes, while some of its colloidal salts (subcitrate and subgallate), due to their antiseptic, astringent and diuretic properties, have important applications in pharmaceutical preparations and are employed as anti-ulcer, antibacterial, anti-HIV and radiotherapeutic agents (Burguera *et al.*., 2001).

When cloud point extraction is used for the extraction of metal chelates, flame atomic absorption spectrometry (FAAS) is by far the most frequently used technique for analyte detection. Although FAAS provides fast throughput, techniques of higher sensitivity would improve considerably detection limits for several analytes. In this sense, electro thermal atomic absorption spectrometry is an efficient alternative, particularly because the organic matrix, consisting of the surfactant and residual organic substances from the digested material, can be eliminated during the gradual increase in temperature prior to the atomization of the analyte.

The aim of this work is to introduce a reliable method for determination of bismuth in tap water samples by electrothermal atomic absorption spectrometry after preconcentration by the cloud point extraction technique. Preconcentration of a 10 mL sample solution allowed an enrichment factor approaching 195, which compared favorably with

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other CPE methodologies (Garrido *et al.* 2004, Manzoori *et al.* 2003).

EXPERIMENTAL

Apparatus

The experiments were performed using a Shimadzu atomic absorption spectrometer (AA 6800G) with a graphite furnace atomizer (GFA-6500), and an autosampler (ASC-6100). A bismuth hollow cathode lamp (Hamamatsu Photonics, L233 Series), operated at a current of 10mA and a wavelength of 223.1 nm with a spectral band- pass of 0.5 nm was used. Pyrolytic graphite-coated graphite tubes (P/N 206-69984-02) were purchased from Shimadzu. The sample injection volume was 20 µL in all experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table 1. Argon 99.995% purchased from Roham Gas Co. (Tehran, Iran) was used as sheath gas. A thermostated bath (Fison, model HAKKE-N_3) maintained at the desired temperature was used for cloud point preconcentration experiments and phase separation was assisted using a centrifuge.

Table 1: Instrumental parameters for bismuth determination [a]

Stage	Temperature(˚C)	Time(s)	Argone gas flow (ml min^{-1})	
			Ramp	Hold
60	5	20	250	
90	5	10	250	
120	10	10	250	
1150	10	15	500	
2000	-	3	0	
2200	-	2	500	

[a] $Pd(NO_3)_2$ as a modifier was used and the integration time was 3 s.

Reagents

Analytical-grade reagents and deionized doubly distilled water were used. The nonionic surfactant Triton X-114 (Sigma) was used without further purification. Stock solution of bismuth was prepared from Merck Titrasol standard solutions ($Bi\ (NO_3)_3$) in 5% HNO_3. Working standard solutions were obtained by appropriate dilution of the stock standard solution.

A solution of 5×10^{-4} M 2-amino-cyclopentene-1-dithiocarboxylic acid (Merck) was prepared by dissolving appropriate amounts of this reagent in THF (Merck). Sulfuric acid (Merck) was purchased and used in order to adjust pH. A 0.1% (w/v) chemical modifier solution was prepared by diluting palladium stock solution (10 g L^{-1}, Merck). The materials and vessels used for trace analysis were kept in a chromic acid mixture (saturated $K_2Cr_2O_7$ in concentrated H_2SO_4) for at least 1 h and were subsequently rinsed four times with deionized doubly distilled water before use.

Cloud point preconcentration procedure

For the cloud point preconcentration, 10 ml aliquots of the sample or analyte standard (0.04–0.70 ng mL^{-1}), Triton X-114 (0.05% (w/v), 2-amino-cyclopentene-1-dithiocarboxylic acid (5×10^{-6} M) and sulfuric acid (pH 3.0–3.5), were kept in a thermostated bath at 50 ˚C for 5 min. Separation of the aqueous and surfactant-rich phases was accomplished by centrifugation for 10 min at 3500 rpm. After cooling in an ice–NaCl mixture (5 min), the surfactant-rich phase became viscous. The aqueous supernatant phase was then separated completely by a 5-ml syringe centered in the tube. To decrease the viscosity of the surfactant-rich phase and facilitate sample handling, 50µL of THF was added and 20 µL of the final solution plus 10µL of $Pd(NO_3)_2$ (0.1% (w/v)) as chemical modifier was injected to the graphite furnace by autosampler.

RESULTS AND DISCUSSIONS

Optimization of the furnace conditions

To reduce interferences and to increase accuracy, the use of a chemical modifier has become indispensable for stabilization of volatile elements during the pretreatment step. The main purpose of using a modifier or a modifier mixture in ET-AAS was to stabilize relatively volatile elements so that higher permissible pyrolysis temperatures can be used to efficiently volatilize the matrix components in a sample prior to atomization of the analyte (He *et al.* 1996; Wei-Ming *et al.* 1997; Acar *et al.* 1997; Shan, *et al.* 1995; Imai *et al.* 1996; Havezov *et al.* 1995; Moghimi *et al.* 2007; Moghimi *et al.* 2008). By using higher pyrolysis temperatures, less interference were encountered in the atomization step (He *et al..*, 1996). In these experiments we used Pd (10 µg) as a modifier. When Pd was not added, the loss of bismuth was observed at pyrolysis temperatures higher than 450 °C. The influence of the palladium on the background level and atomic signal was of utmost importance. Addition of a 0.1% (w/v) $Pd(NO_3)_2$ solution, allowed increasing the pyrolysis temperature to 1150 °C with considerable background reduction without losses of bismuth (Fig. 1).

The atomic signals were enhanced by 35% when Pd injected volume was increased from 5 to 10 µL. For aliquots larger than 10 µL, the signals were not further improved. The modifier volume was thus chosen as 10 µL.

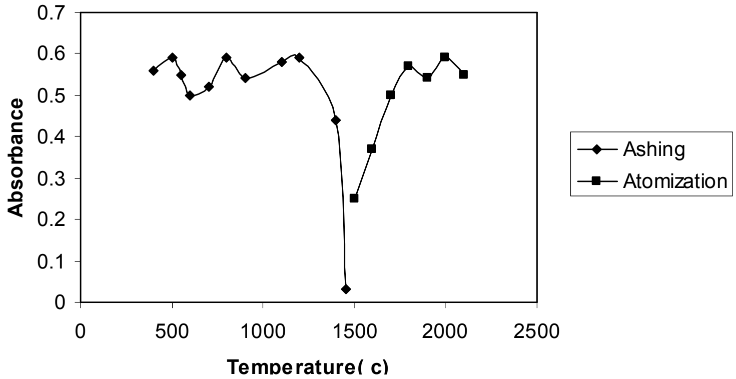

Fig. 1. Pyrolysis and atomization temperature curves after preconcentration. Initial bismuth concentration is 0.5 ng mL^{-1}

The Effect of pH

CPE of bismuth was performed in solutions of pH ranging from 0.5 to 9.5. Separation of metal ions by cloud point method involves the prior formation of a complex with suf- ficient hydrophobicity to be extracted in to the small volume of surfactant-rich phase. Extraction recovery depends on the pH at which complex formation occurs.

Fig. 2 shows the effect of pH on the extraction of bismuth complex. It was found that in the pH range 2.5–6.0, extraction was quantitative. Extraction recovery of bismuth decreased at 6 < pH < 2.5 because its complex was decomposed at pH values smaller than 2.5. In subsequent experiments a pH of 3.0–3.5 was chosen because lead, thallium and cadmium dithizonates were unstable in slightly acidic medium (3.0–3.5); further, the optimum condition for the selective extraction of a soft acid like bismuth by 2-amino-cyclopentene-1-dithiocarboxylic acid was attained in acidic conditions.

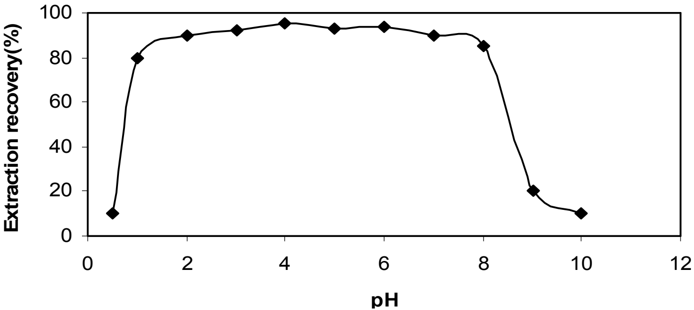

Fig. 2. Effect of pH on the extraction recovery of bismuth Applied condition is of 0.5 ng mL^{-1} Bi, 5 × 10^{-6} M2-amino-cyclopentene-1-dithiocarboxylic acid, 0.05% (w/v) Triton X-114 and 1% THF.

The effect of 2-amino-cyclopentene-1-dithiocarboxylic acid concentration

The extraction recovery as a function of the 2-amino-cyclopentene-1-dithiocarboxylic acid concentration is shown in Fig. 3. For this study, 10mL of a solution containing 0.5 ng ml^{-1} bismuth in 0.05% (w/v) Triton X-114 with various amounts of 2-amino-cyclopentene-1-dithiocarboxylic acid was subjected to the cloud point preconcentration process. At this stated concentration of bismuth, ~100% extraction was achieved for a 2-amino-cyclopentene-1-dithiocarboxylic acid concentration of 0.8 × 10^{-6} M. A concentration of 5 × 10^{-6} M 2-amino-cyclopentene-1-dithiocarboxylic acid was chosen for subsequent experiments.

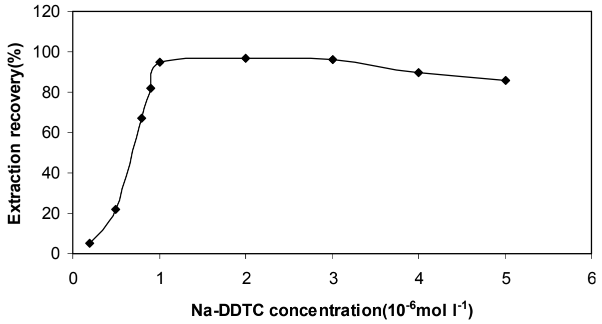

Fig. 3. Effect of 2-amino-cyclopentene-1-dithiocarboxylic acid concentration on the extraction recovery of bismuth utilized condition is of 0.5 ng mL^{-1} Bi, 0.05% (w/v) Triton X-114, 1% THF, pH 3.0–3.5.

The effect of triton X-114 concentration

A successful cloud point extraction should be able to maximize the extraction efficiency through minimizing the phase volume ratio ($V_{\mathrm{org}}/V_{\mathrm{aqueous}}$), so as to improve the preconcentration factor. Triton X-114 was chosen as the nonionic surfactant due to its low cloud point temperature and high density, which facilitates phase separation by centrifugation. Fig. 4 highlights the effect of the surfactant concentration in the range of 0.04–0.25% (w/v) on the extraction efficiency. Triton X-114 was found to quantitatively extract the Bi-DDTC complex from the aqueous sample at surfactant concentrations above 0.05%, using a single step extraction procedure. Using more than 0.05% of surfactant, the analytical sensitivity decreased due to dilution of the sample by additional surfactant solution. Applied condition is of 0.5 ng mL^{-1} Bi, 5 × 10^{-6} M 2-amino-cyclopentene-1-dithiocarboxylic acid, 1% THF, pH 3.0–3.5

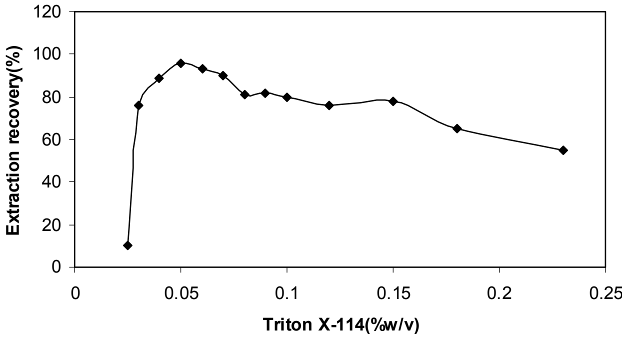

Fig. 4. Extraction recovery of the bismuth as a function of Triton X-114 concentration

Selection of the dilution agent for the surfactant-rich phase

High viscosity of the surfactant-rich phase (~20 cP) was drastically decreased using diluting agents. Different solvents such as methanol, ethanol and acidic solutions of methanol and ethanol were tried. None of these solvents could dissolve the extracted phase completely. However, THF dissolved the surfactant-rich phase and the extracted materials (complex of bismuth and excess of 2-amino-cyclopentene-1-dithiocarboxylic acid) completely and the best results were obtained with these diluents.

The effect of THF concentration

Fig. 5 shows the effect of THF concentration on extraction efficiency. It was found that the extraction efficiency decreased at THF concentrations >3% due to dissolution of the surfactant phase and a decrease in the volume of this phase. Hence, a relatively concentrated solution (5×10^{-4} M) of 2-amino-cyclopentene-1-dithiocarboxylic acid was used in THF.

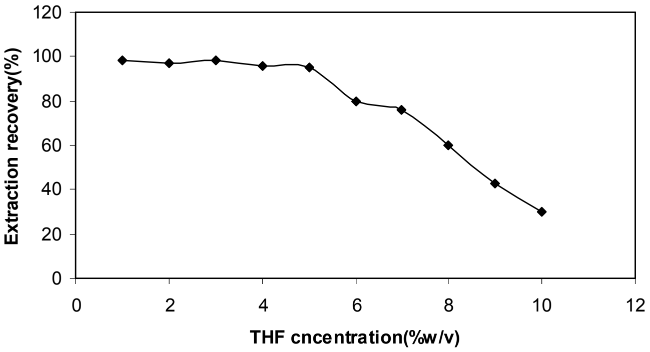

Fig. 5. Effect of THF concentration on the extraction recovery of bismuth utilized condition is of 0.5 ng mL^{-1} Bi, 5×10^{-6} M 2-amino-cyclopentene-1-dithiocarboxylic acid , 0.05% (w/v) Triton X-114, pH 3.0–3.5.

The effect of equilibration temperature and time

The equilibration temperature above the cloud point and the incubation time were also optimized. The shortest incubation time and the lowest possible equilibration temperature are desired. The results, illustrated in Fig. 6 show excellent recoveries for equilibration temperature from 40 to 60 °C.

Higher temperature led to the decomposition of 2-amino-cyclopentene-1-dithiocarboxylic acid and the reduction of extraction yield. A temperature of 50°C was hence used in all experiments. The dependence of extraction efficiency upon incubation time was studied in the range of 5–20 min. An incubation time of 5 min was sufficient for quantitative extraction.

Interferences

Bismuth (III) ions produced an orange–brown complex with 2-amino-cyclopentene-1-dithiocarboxylic acid, $Bi(HD_2)_3$, which was stable over the pH range 2.5–6.0. 2-amino-cyclopentene-1-dithiocarboxylic acid is known to be highly selective for bismuth at pH 3.0–3.5 (Marczenko 1985). Just lead, thallium and cadmium can be co-extracted with bismuth but their dithizonates are unstable in slightly acidic medium (pH 3.0–3.5). The noble metals (Pt, Pd, Au, Ag, and Hg) and copper are quantitatively extracted with 2-amino-cyclopentene-1-dithiocarboxylic acid at pH 0.5–1.0. The results of the interference study are shown in Table 2; it was seen that bismuth recovery was essentially quantitative in the presence of foreign cautions. Therefore these ions produced no interference in the extraction of bismuth.

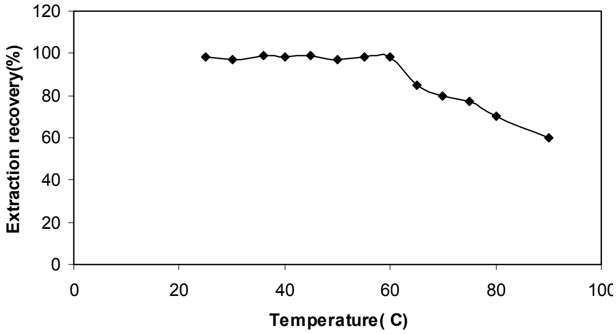

Fig. 6. Effect of equilibration temperature on the extraction recovery of bismuth applied condition is of 0.5 ng mL^{-1} Bi, 5×10^{-6} M 2-amino-cyclopentene-1-dithiocarboxylic acid, 0.05% (w/v) Triton X-114, 1% THF, pH 3.0–3.5.

Table 2: Effect of foreign ions on the preconcentration and determination of bismuth (0.3 ng mL^{-1})

Ion	Ion/Bi ratio	Extraction recovery (%)
Tl^{3+}	1100	96.5
Cd^{2+}	1000	96.4
Pt^{4+}	1100	99.1
Pd^{2+}	1000	97.1
Au^{3+}	1100	98.3
Ag^{+}	1100	99.5
Hg^{2+}	1000	93.7
Cu^{2+}	1100	97.9
Sn^{2+}	1100	95.0
Zn^{2+}	1000	96.6
Pb^{2+}	1000	95.5
Cd^{2+}	900	96.3
Mg^{2+}	1250	95.7
Ca^{2+}	1200	97.0
Al^{3+}	1000	96.5
PO_4^{3-}	1000	94.4
NO^{3-}	1100	95.5
ClO_4^{-}	1100	96.6
Cl^{-}	1100	95.7
I^{-}	550	97.3

Characteristics of the method

A calibration curve was constructed by preconcentration of 10 ml of sample standard solutions with Triton X-114. Table 3 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for bismuth was linear from 0.05 to 0.70 ng mL^{-1}.

The enhancement factor of about 195 was obtained by preconcentration a 10ml of sample. The limit of detection was calculated to be 0.04 ng ml^{-1}(S/N = 3). If samples with volumes larger than 20 μl were injected into graphite furnace, sensitivity can be increased but in all experiments we injected 20µl of analyte, because, otherwise sample may spread to the low-temperature areas of the furnace, or may overflow to the filler port that results in decreased accuracy.

ANALYSIS OF REAL SAMPLES

In order to validate the proposed methodology, the developed procedure was applied to the determination of bismuth in tap water, and some waste water samples. Various water samples were also analyzed (Table 4) in all cases the spike recoveries were excellent, showing no matrix interferences.

Table 3: Analytical characteristics of the method

	Bi with CPE	Bi without CPE
Concentration rang (ng mL^{-1})	0.04-0.70	4-110
Slope	0.756	0.0038
Intercept	0.018	0.004
Correlation coefficient(R)	0.9993	0.9994
R.S.D.(%) (n= 5)[a]	4.0	4.7
LOD(ng ml^{-1})[b]	0.04	1.5
Enhancement factor[c]	195	-

[a] Bismuth concentration was 0.3 ng mL−1 for which the R.S.D. was obtained.
[b] Determined as three times of the standard deviation of the blank signal.
[c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Table 4**:** Determination of Bi in real samples (results of recoveries of spiked samples).

Sample	Added	Found[a]	ICP- AES	Recovery(%)
Bi(ng mL^{-1})	-	0.165±0.01	0.171	-
Tap water[b]	0.3	0.458±0.03	0.462	99.1
Bi(ng mL^{-1})	-	0.102±0.03	0.100	-
Rain water[c]	0.3	0.399±0.04	0.404	98.9

[a] Mean of three experiments ± standard deviation.
[b] From drinking water system of Saveh, Iran.
[c] From Rain water of Varamin, Iran.

CONCLUSIONS

We have proposed the use of cloud point extraction as an alternative method for the preconcentration of Bi as a prior step to its determination by ET-AAS. The method allowed the determination of ultra low levels of Bi by ET-AAS.

The methodology offered a simple, rapid, sensitive, low cost, good extraction efficiency and lower toxicity than those using organic solvents. Environmental pollution was limited to a small amount of surfactant. The method gave a low limit of detection and good R.S.D.

Compared with other methods, interference from other cations was minor. The proposed method can be applied for the determination of bismuth in tap water.

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