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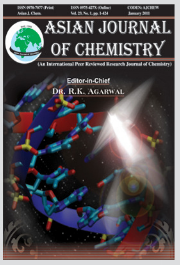

Determination of Bismuth with *p*-Acetylarsenazo by Spectrophotometry

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In 0.090 mol/L of nitric acid medium, *p*-acetylarsenazo and bismuth(III) form a 2:1 purple red complex. Its maximum absorption wavelength is located at 666 nm and the apparent molar absorptivity is $\varepsilon_{666\,nm} = 4.46 \times 10^4$ L mol^{-1} cm^{-1}. When the content of bismuth(III) is in the range of 0.50-4.5 μg/mL. The detection limit of the method is 0.13 μg/mL. The method has been successfully applied to the determination of bismuth in water sample.

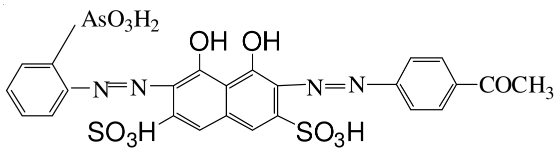
Key Words: *p*-Acetylarsenazo, Bismuth, Spectrophotometry.

INTRODUCTION

Bismuth is a rare heavy metal element and its content in the earth's crust is very low. Although the application of bismuth and its compounds is extensive, there is their bad aspect. From the view of toxicology, if the bismuth amount that exceeds the maximum limit that human body can endure is excessively exposed or if the amount of heavy metal bismuth human body accumulates exceeds a certain limit, influences on the health of human body must be brought. After bismuth goes into human body by bite and sup of people or by dryking water,it is able to accumulate in the brain part and kidney of human body and lurks for long until after the maximum load that human body can endure is exceeded and then pathological changes takes place. This can influence memory of human body and kidney function[1]. Thus, development of analytical method for the determination of bismuth has quite important significance.

For the determination of bismuth, mostly used method is EDTA titration method for macro- or semimicro- analysis[2]. In microanalysis of bismuth, the reported methods have square wave voltammetry (SWV)[3], inductively coupled plasma-atomic emission spectrometry (ICP-AES)[4,5], atomic absorption spectrometry (AAS)[6] and spectrophotometry[7-9], *etc*. For SWV, ICP-AES, AAS methods, the instrumentation price is high and the operation is complex. Comparatively, for the spectrophotometric determination of bismuth, the operation is simple and the cost is low. The sensitivity of determination of bismuth by thiourea-fluoride spectrophotometry[7] is low. The selectivity of determination of bismuth by sulfonazo-DBM method is poor[8]. Spectrophotometric method of the determination of bismuth using chlorophosphonazo(III) needs heating and the operation is not convenient[9]. Thus, development of a new method for the determination of bismuth still has an important significance.

p-Acetylarsenazo ($C_{24}H_{19}AsN_4O_{12}S_2$, abbreviated as ASA*p*A),whose structural formula is as follows:



was ever used in the determination of rare earths[10]. This paper studied the optimum experimental conditions of spectrophotometric determination of Bi(III) with ASA*p*A in nitric acid medium and the properties of the system, establishing a new method for the determination of bismuth. The method has been successfully applied to the analysis of water sample with satisfactory results.

EXPERIMENTAL

Preparation of bismuth(III) working solution: Bismuth metal was dissolved by using HNO_3 (ρ = 1.42 g/mL) to prepare 1.000 mg/mL of 1 mol/L nitric acid as bismuth standard stock solution. One mL was taken from the bismuth(III) standard stock solution, placed in a 100-mL calibrated flask and diluted to the mark by 0.5 mol/L of perchloric acid to obtain 10 μg/mL Bi(III) working solution. ASA*p*A solution: 0.1 % (w/v) aqueous solution. HNO_3 solution: 3 mol/L.

Unless otherwise stated all reagents were of analytical-reagent grade and distilled water was used throughout the study. Absorbances were measured on a A 722S spectrophotometer (Shanghai Linggunag Technique Co. Ltd., China) with 1 cm cells.

General procedure: In a 10 mL calibrated flask, add 20 µg Bi(III) working solution, 0.30 mL of 3 mol/L HNO_3 solution, 3.5 mL of 0.1 % (w/v) ASA*p*A solution and dilute to the mark with water. After standing for 2 min, measure the absorbance at 666 nm in a 1 cm cell against a reagent blank.

Procedure for the determination of bismuth in lake water sample: 1 L of lake water was accurately taken, placed in a beaker, evaporated on an electric cooker until it was concentrated to a small amount and a few drops of 6 mol/L HNO_3 were added. The contents were filtered and the filtrate was placed in a 25 mL calibrated flask, diluted to the mark with water. 2 mL of the above sample was taken and placed in a 10 mL calibrated flask and the remainder was the same as the general procedure for the determination of bismuth content. Then, bismuth content in the sample was calculated. The result of atomic absorption spectrometry was used as contrast result. The determined results are shown in Table-1.

RESULTS AND DISCUSSION

Absorption spectra: According to the general procedure the absorption spectra were drawn and the results are shown as Fig. 1. ASA*p*A and Bi^{3+} formed a violet-red complex and the maximum absorption wavelength of the complex is 666 nm. For the reagent blank at 560 nm its absorbance is the largest. The contrast of the method is 106 nm. In present studies, 666 nm was selected as the experimental measurement wavelength.

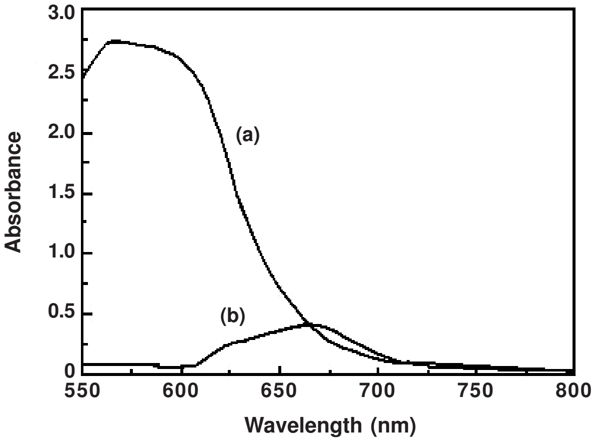


Fig. 1. Absorption spectra: (a) Reagent blank (water as reference); (b) ASA*p*A-Bi(III) complex (reagent blank as refernce). $[Bi^{3+}] = 9.6 \times 10^{-6}$ mol/L; [ASA*p*A] = 5.0×10^{-4} mol/L; $[HNO_3] = 0.090$ mol/L

Optimization of experimental variables

Effect of the amount of nitric acid: 0.1, 0.2, 0.3, 0.4, 0.5 mL of 3 mol/L nitric acid were, respectively taken and according to the general procedure the determinations were made to record their absorbances. The results showed that when the amount of nitric acid was in the range of 0.1-0.5 mL, the variation of absorbance was very small. At 0.3 mL, the absorbance was a maximum. Therefore, the optimum amount of nitric acid was selected to be 3 mL. At this time, the concentration of nitirc acid in the system was 0.090 mol/L.

Effect of the amount of ASA*p*A: 0, 1.0, 2.0, 3.0, 3.5, 4.0, 5.0 mL of 0.1 % (w/v) ASA*p*A were, respectively taken and according to the general procedure the determinations were made to record their absorbances. The experimental results showed that when the amount of ASA*p*A was in the range of 0-3.0 mL, the absorbance determined increased by degrees. Over the range of 3.0-4.0 mL, the absorbance was bigger and the variation was smaller. At 3.5 mL, the absorbance was maximum. Afterwards, over the range of 3.5-5.0 mL, the absorbance decreased. Thus, 3.5 mL of 0.1 % (w/v) ASA*p*A solution was selected.

Effect of the order of reagent addition: The experimental results showed that the order of reagent addition had not effect on the absorbance of this system. This (w/v) employed the order of Bi(III) + HNO_3 + ASA*p*A.

Complex composition and stability: By means of molar-ratio method and equimolar continuous variation method, the composition of the complex was determined to obtain the composition ratio of the complex as ASA*p*A: Bi(III) = 2:1.

When 2.0 µg/mL Bi(III) was determined at room temperature, the colour reaction reached stable after 2 min. Within 4 h, the absorbance variation was less than 5 % and the complex remained stable.

Analytical figures of merit-working curve, sensitivity, precision and accuracy: Under the optimum experimental conditions, the calibration curve was drawn for bismuth determination. The experimental results showed that Beer's law was obeyed over the concentration range of 0.50-4.5 µg/mL for Bi(III) and the linear regression equation was: $A = 0.1886C + 0.0436$ (C: µg/mL), with a correlation coefficient of $\gamma = 0.9946$. The apparent molar absorptivity of the method was calculated to be $\varepsilon_{666\,nm} = 4.46 \times 10^4$ L mol^{-1} cm^{-1}. According to the general procedure 11 parallel determinations of 2.00 µg/mL of Bi(III) were made and the average value determined was 2.03 µg/mL. The relative standard deviation of the determined results was 1.2 %. For the practical determination of bismuth in lake water sample, the determined results show (Table-1) that the method has good precision and accuracy. For 11 determination of reagent blank, the standard deviation obtained was 0.83 %. Based on $\rho = 3S/K$ (S = standard deviation of 11 parallel determination of reagent blank, K = slope

TABLE-1
ANALYTICAL RESULTS OF SAMPLE

Sample	Found (ng/g)	Average (ng/g)	RSD (%)	Added (µg/mL)	Recovered (µg/mL)	Recovery (%)	Atomic absorption spectrometry (ng/g)
Lake water	293.2, 287.9, 286.6, 293.9, 287.9, 291.9, 298.5, 295.9, 289.9, 296.5, 290.6	292.1	1.34	2.000	1.960	98.02	292.0

of working curve), the detection limit of the method was calculated to be 0.13 μg/mL.

Effect of coexisting substances: The effect of coexisting substances on the determination of 2.0 μg/mL Bi^{3+} was studied under the optimum conditions. A ± 5 % deviation from absorbance value for Bi^{3+} alone was considered as the criterion of the interference. The allowable amounts of coexisting substances (multiple in mass, m/m) are as follows: K^+, Na^+, NH_4^+, Cl^-, OAc^-, SiO_3^{2-}, SO_4^{2-}, PO_4^{3-} (1000); Hg^{2+}, F^-, Br^-, I^-, NO_2^-, $C_2O_4^{2-}$ (500); B^{3+}, Mn^{2+} (100); Cu^{2+}, Mn^{2+} (50); Co^{2+}, Ni^{2+} (25); Mg^{2+}, Cr^{3+} (20); Zn^{2+}, Pb^{2+} (10); Fe^{2+}, Sn^{2+}, Al^{3+}, Cr^{3+}, W^{6+}, Mo^{6+} (1); Ca^{2+} (0.2); Fe^{3+} (0.1); La^{3+}, Y^{3+} (0.01).

Analysis of lake water: Using the above-stated procedure, bismuth amount of the lake water was determined. The result shown in Table-1 is in good agreement with that of atomic absorption method. It can be seen that the analytical results of the lake water sample were satisfactory.

Conclusion

The paper established the optimum experimental conditions of spectrophotometric determination of Bi(III) with *p*-acetylarsenazo. The present method has been successfully applied to the analysis of the lake water sample. The linear range of bismuth(III) determined by present method was 0.50-4.50 μg/mL. The apparent molar absorptivity of the method was $\varepsilon_{666\ nm} = 4.46 \times 10^4$ L mol^{-1} cm^{-1} and detection limit was 0.13 μg/mL.

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