

Study on Separation/enrichment of Bismuth Using Microcrystalline Thymolphthalein Loaded with Diacetyldioxime

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Abstract—A novel method for the separation/enrichment of trace Bi^{3+} using microcrystalline thymolphthalein loaded with diacetyldioxime was established. The effects of different parameters on the enrichment yield of Bi^{3+} have been investigated. The possible enrichment mechanism of Bi^{3+} was discussed. The results showed that under the optimum conditions, in diacetyldioxime (DMG)-thymolphthalein (TP) system, the chelate settlement of $[\text{Bi}(\text{DMG})_2]$ which formed by Bi^{3+} and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, and the liquid-solid phases were formed with clear interface, while Cd^{2+} , Zn^{2+} and Mn^{2+} could not be adsorbed. The quantitative separation of Bi^{3+} from those metal ions was achieved. A new method for the separation enrichment of trace Bi^{3+} was established. The proposed method has been successfully applied to the quantitative separation of trace Bi^{3+} in the samples of synthetic water, and the enrichment yield was 94.4%~100.9%.

Keywords—Bismuth (III) aration enrichment; Diacetyldioxime; Microcrystalline thymolphthalein

I. INTRODUCTION

Bismuth is a kind of widely used metal in the form of oxides, carbonates and sulfides in nature; it is a non-essential element for human and belongs to the toxic metal. Consequently, it is of great importance and significance to separate and determinate trace Bismuth in environmental samples. Since the content of Bi^{3+} in environment is usually very low, separation and enrichment must be carried out before measurement. There are many other methods to separate and enrich $\text{Bi}(\text{III})$, chxtraction [1-3], liquid-quid extraction [4], micro extraction [5], flow-injection extraction [6] and so on. The techniques for the enrichment/separation and determination of metal ions using microcrystalline adsorption system have been reported [7-8] in recent year.

In this paper we have studied the separation/enrichment of trace Bi^{3+} using microcrystalline thymolphthalein loaded with diacetyldioxime. Controlling pH 9.0, when the dosage of $0.010 \text{ mol} \cdot \text{L}^{-1}$ DMG solution and $0.020 \text{ mol} \cdot \text{L}^{-1}$ TP solution all was 2.00 mL, chelate settlement of $[\text{Bi}(\text{DMG})_2]$ which formed by Bi^{3+} and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, while Cd^{2+} , Zn^{2+} and Mn^{2+} could not be adsorbed. The quantitative separation of Bi^{3+} from those metal ions was achieved. The proposed method has been successfully applied to the quantitative separation of trace Bi^{3+} in the samples of

synthetic water, and the enrichment yield was 94.4%~100.9%.

Compared this method with the separation/enrichment and determination of trace bismuth using microcrystalline naphthalene system [9-10], microcrystalline benzophenone system [11-12], microcrystalline triphenylmethane system [13], the environmental pollution caused by naphthalene, benzophenone, triphenylmethane and organic reagent can be eliminated, and the harm to operators in experiment can be avoided.

II. EXPERIMENTAL

A. Equipment and Reagents

A model 723S spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd) was used for photometric measurements. A model UV-2401 UV-visible spectrophotometer (The Shimadzu Corporation, Japan) was used for scanning the absorption spectrum.

Diacetyldioxime (DMG) solution: $0.010 \text{ mol} \cdot \text{L}^{-1}$. Thymolphthalein (TP) ethanol solution: $0.020 \text{ mol} \cdot \text{L}^{-1}$. $1.10 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) ethanol solution was prepared by dissolving 0.1746 g 5-Br-PADAP in 500 mL ethanol. Cetyl trimethyl ammonium bromide (CTMAB) solution: $0.01 \text{ mol} \cdot \text{L}^{-1}$. A stock of standard solution of Bi^{3+} : $1.000 \text{ g} \cdot \text{L}^{-1}$. A working standard solution was prepared by appropriately diluting the stock standard solution. Standard solution of other metal ions was prepared by appropriately diluting the stock standard solution. Buffer solutions of different pH was prepared as references [14].

All reagents were of analytical reagent grade. Bidistilled water was used throughout.

B. Method

$50 \mu\text{g}$ of Bi^{3+} , a given amounts of $0.010 \text{ mol} \cdot \text{L}^{-1}$ diacetyldioxime (DMG) solution and $0.020 \text{ mol} \cdot \text{L}^{-1}$ thymolphthalein (TP) solution were added into a 25 mL ground color comparison tube. Then adjust the pH with pH 9.0 buffer solutions and dilute the mixture to 10.00 mL with bidistilled water. Shaken adequately and they were kept still for a moment. 1.00 mL of water sample in the lower layer was transferred into another 25 mL ground color comparison tube, and 1.5 mL of $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol

(5-Br-PADAP) ethanol solution and 1.0 mL of 0.01 mol·L⁻¹ CTMAB solution were added. The solution was diluted to the mark and the absorbance was measured at 555 nm against the reagent blank prepared in the same way. The amount of Bi³⁺ remained in the solution was calculated. The enrichment yield of Bi³⁺ (E/%) was calculated according to the determination results. Photometric analysis of other metal ions was referring the reference [15].

The determination of the content of trace Bi³⁺ in microcrystalline adsorption solid phase is as follows: the precipitation by filtration was dissolved in ethanol, and then was transferred into a 25 mL ground color comparison tube and diluted the mixture to 10.00 mL with bidistilled water, shaken adequately and they were kept still for a moment, and the content of Bi³⁺ was determined in the same method above.

III. RESULTS AND DISCUSSION

A. Effect of Thymolphthalein Dosage

50 µg of Bi³⁺ and 2.00 mL of 0.010 mol·L⁻¹ DMG solution were applied to the proposed method. The effect of TP dosage on the enrichment yield of Bi³⁺ was investigated. The results show that the enrichment yield of Bi³⁺ is 58.3% in the absence of TP. It is probable that a part of Bi³⁺ can directly react with DMG to form the chelate settlement of Bi(DMG)₂. It is consistent with the phenomenon of precipitate which can be directly observed without TP in experiment.

The enrichment yield of Bi³⁺ increase with the increase of thymolphthalein dosage. When the dosage of thymolphthalein is up to 1.50 mL or more, the enrichment yield of Bi³⁺ was 100%. It is probable that DMG adsorbed onto microcrystalline thymolphthalein (TP) has higher concentration and can react with Bi³⁺ left in the solution to form the chelate precipitate of Bi(DMG)₂ and can be adsorbed on the surface of microcrystalline TP. Therefore, 2.00 mL of TP was selected.

B. Effect of DMG Dosage

The effect of DMG dosage on the enrichment yield of Bi³⁺ was investigated. The results show that with the increase of DMG dosage, the enrichment yield of Bi³⁺ increase. For the reason that Bi³⁺ can react with DMG to form the water-insoluble chelate of Bi(DMG)₂, and it can be adsorbed on the surface of microcrystalline TP. The amount of Bi(DMG)₂ increases when the solution includes more DMG. It leads to the increase of enrichment yield of Bi³⁺. When the dosage of DMG was 1.50 mL, Bi³⁺ can be completely retained on the surface of microcrystalline TP. The enrichment yield of Bi³⁺ maintained 100% with further increasing the dosage of DMG. Hence, 2.00 mL of DMG was chosen for all further studies.

C. Enrichment Mechanism of Bi³⁺

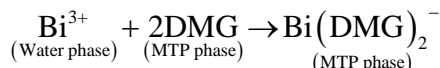
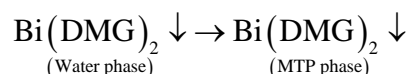
Based on the results above, it could be concluded that only in the simultaneous presence of Bi³⁺, DMG and TP, can Bi³⁺ be completely enriched. Therefore, when Bi³⁺, DMG and

TP simultaneously existed in the solution, it seems reasonable that the enrichment mechanism of Bi³⁺ is as follows:

1) When the solution includes DMG but not TP, a part of Bi³⁺ can directly react with DMG to form the chelate settlement of Bi(DMG)₂, which leads to a part of Bi³⁺ be enriched.



2) When Bi³⁺, DMG and TP simultaneously existed in the solution, the chelate settlement of Bi(DMG)₂ in water phase was adsorbed on the surface of microcrystalline TP, meanwhile DMG adsorbed onto microcrystalline TP reacts with Bi³⁺ left in the solution to form the chelate settlement of Bi(DMG)₂, and it can be adsorbed on the surface of microcrystalline TP(MTP) also.



D. Effect of pH

Under the optimum conditions, the effects of pH on the enrichment yield of different metal ions were investigated. The experimental results showed that in the pH range 7.0~10.0, the enrichment yield of Bi³⁺ was not affected by pH, or the enrichment yield of Bi³⁺ remained 100%. While the enrichment yield of Cd²⁺, Zn²⁺ and Mn²⁺ were lesser at pH9.0. Therefore, Bi³⁺ can be separated from Cd²⁺, Zn²⁺ and Mn²⁺ in the solution at pH9.0.

TABLE I. THE SEPARATION RESULTS OF BINARY-MIXED IONS (pH=9.0)

Mixed ions	Dosage of metal ions(µg)	of	Content of metal ions in water phase (µg)		Enrichment yield (E/%)	
			Bi	Me	Bi	Me
Bi ³⁺ -Cd ²⁺	50	200	0	190.4	100	4.8
	50	400	0.2	385.4	99.6	3.7
	50	500	0.1	505.4	99.8	-1.1
Bi ³⁺ -Zn ²⁺	50	200	0.1	205.1	99.8	-2.6
	50	400	0	395.3	100	1.2
	50	500	0.1	511.8	99.8	-2.4
Bi ³⁺ -Mn ²⁺	50	200	0.3	196.7	99.4	1.7
	50	400	0.2	407.2	99.6	-1.8
	50	500	0.1	513.1	99.8	-2.6

Me represents other other ions except Bi³⁺

E. Separation Experiments

Under the chosen conditions, the separations of Bi^{3+} from Cd^{2+} , Zn^{2+} and Mn^{2+} in synthesized samples of binary and polybasic system were studied respectively at pH9.0. The results are shown in Table 1 and Table 2.

TABLE II. THE SEPARATION RESULTS OF Bi^{3+} FROM POLYBASIC-MIXED IONS (pH=9.0)

Number of the synthesized samples	1	2	3	4	5
Dosage of Bi^{3+} (μg)	100. 0	200. 0	300. 0	400. 0	500. 0
Dosage of Cd^{2+} , Zn^{2+} and Mn^{2+} (μg)	100. 0	100. 0	150. 0	200. 0	200. 0
Bi^{3+} found in solid phase (μg)	100. 9	200. 6	302. 8	377. 6	504. 2
Enrichment yield of Bi^{3+} (E/%)	100. 9	100. 3	100. 9	94.4	100. 8

IV. CONCLUSION

In this paper, a novel method for the separation/enrichment of trace Bi^{3+} using microcrystalline thymolphthalein loaded with diacetyldioxime was reported. By controlling pH 9.0, when the dosage of 0.020 mol L^{-1} thymolphthalein solution was 2.00 mL and 0.010 mol L^{-1} diacetyldioxime solution was 2.00mL respectively, the chelate settlement of $[\text{Bi}(\text{DMG})_2]$ which formed by Bi^{3+} and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, and the liquid-solid phases were formed with clear interface, while Cd^{2+} , Zn^{2+} and Mn^{2+} could not be adsorbed. The quantitative separation of Bi^{3+} from those metal ions was achieved. The proposed method has been successfully applied to the quantitative separation of trace Bi^{3+} in the samples of synthetic water, and the enrichment yield was 94.4%~100.9%. It was obvious that this study had certain practical significance and foreground of application on establishing new methods of separation/enrichment of trace bismuth.

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