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

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***Abstract*—A novel method for the separation/enrichment of trace Bi3+ using microcrystalline thymolphthalein loaded with diacetydioxime was established. The effects of different parameters on the enrichment yield of Bi3+ have been investigated. The possible enrichment mechanism of Bi3+ was discussed. The results showed that under the optimum conditions, in diacetydioxime (DMG)-thymolphthalein (TP) system, the chelate settlement of [Bi(DMG)2] which formed by Bi3+ and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, and the liquid-solid phases were formed with clear interface, while Cd2+,Zn2+ and Mn2+ could not be adsorbed. The quantitative separation of Bi3+ from those metal ions was achieved. A new method for the separation enrichment of trace Bi3+ was established. The proposed method has been successfully applied to the quantitative separation of trace Bi3+ in the samles of synthetic water, and the enrichment yield was 94.4%~100.9%.**

Keywords-Bismuth (III) aration enrichment; Diacetydioxime; 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 Bi3+ in environment is usually very low, separation and enrichment must be carried out before measurement. There are many other methods to separate and enrich Bi(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 diacetydioxime. Controling pH 9.0, when the dosage of 0.010 mol·L^{-1} DMG solution and 0.020 mol·L^{-1} TP solution all was 2.00 mL, chelate settlement of $[Bi(DMG)_2]$ 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 samles 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 system13, 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.

Diacetydioxime (DMG) solution: 0.010 mol•L^{-1}. Thymolphthalein (TP) ethanol solution: 0.020 mol•L-1.1.0×10^{-3} mol•L^{-1} of 2-(5-bromo-2-pyridylazo)-5-diethy-laminophenol (5-Br-PADAP) ethanol solution was prepared by dissolving 0.1746 g 5-Br-PADAP in 500 mL ethanol. Cetyl trim ethyl ammonium bromide (CTMAB) solution: 0.01 mol•L^{-1}. A stock of standard solution of Bi^{3+}:1.000 g•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

50μg of Bi^{3+},a given amounts of 0.010 mol•L^{-1} diacetydioxime (DMG) solution and 0.020 mol•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 1.0×10-3 mol•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 Bi^{3+} 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 Bi^{3+} was investigated. The results show that the enrichment yield of Bi^{3+} is 58.3% in the absence of TP. It is probable that a part of Bi^{3+} 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 Bi^{3+} increase with the increase of thymolphthalein dosage. When the dosage of thymolphthalein is up to 1.50 mL or more, the enrichment yield of Bi^{3+} was 100%.It is probable that DMG adsorbed onto microcrystalline thymolphthalein (TP) has higher concentration and can react with Bi^{3+} 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 Bi^{3+} was investigated. The results show that with the increase of DMG dosage, the enrichment yield of Bi^{3+} increase. For the reason that Bi^{3+} 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 Bi^{3+}. When the dosage of DMG was 1.50 mL, Bi^{3+} can be completely retained on the surface of microcrystalline TP. The enrichment yield of Bi^{3+} 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 of Bi^{3+}

Based on the results above, it could be concluded that only in the simultaneous presence of Bi^{3+}, DMG and TP, can Bi^{3+} be completed enriched. Therefore, when Bi^{3+}, DMG and TP simultaneous existed in the solution, it seems reasonable that the enrichment mechanism of Bi^{3+} is as follows:

1) When the solution includes DMG but not TP, a part of Bi^{3+} can directly react with DMG to form the chelate settlement of $Bi(DMG)_2$, which leads to a part of Bi^{3+} be enriched.

$$Bi^{3+} + 2DMFG \rightarrow Bt\left(G_2\right)\downarrow$$

2) When Bi^{3+}, DMG and TP simultaneous 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 Bi^{3+} 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.

$$\underset{(\text{Water phase})}{Bi\left(DMG\right)_2\downarrow} \rightarrow \underset{(\text{MTP phase})}{Bi\left(DMG\right)_2\downarrow}$$

$$\underset{(\text{Water phase})}{Bi^{3+}} + \underset{(\text{MTP phase})}{2DMG} \rightarrow \underset{(\text{MTP phase})}{Bi\left(DMG\right)_2^{-}}$$

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 Bi^{3+} was not affected by pH, or the enrichment yield of Bi^{3+} remained 100%. While the enrichment yield of Cd^{2+}, Zn^{2+} and Mn^{2+} were lesser at pH9.0.Therefore, Bi^{3+} can be separated from Cd^{2+}, Zn^{2+} and Mn^{2+} 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)		Content of metal ions in water phase (μg)		Enrichment yield (E/%)	
	Bi	Me	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 Bi^{3+}

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 Bi3+ (μg)	100.0	200.0	300.0	400.0	500.0
Dosage of Cd2+,Zn2+ and Mn2+ (μg)	100.0	100.0	150.0	200.0	200.0
Bi3+ found in solid phase (μg)	100.9	200.6	302.8	377.6	504.2
Enrichment yield of Bi3+ (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 diacetydioxime was reported. By controlling pH 9.0, when the dosage of 0.020 $mol \cdot L^{-1}$ thymolphthalein solution was 2.00 mL and 0.010 $mol \cdot L^{-1}$ diacetydioxime solution was 2.00mL respectively, the chelate settlement of $[Bi(DMG)_2]$ 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.

REFERENCES

[1] Anant P. Argekar and Ashok K. Shetty. Extraction and spectrophotometric determination of bismuth (III) with Cyanex 301.Analyst, 1995, 120, 1819-1822.

[2] Yadvendra K. Agrawal and Vinay J. Bhatt.Extraction and spectrophotometric determination of bismuth (III) with N-m-tolyl-p-chlorobenzohydroxamic acid and xylenol orange. Analyst, 1984, 109, 1287-1289.

[3] G. B. Kolekara, T. N. Lokhandea, P. N. Bhosalea, et al.. Extraction, Separation and Spectrophotometric Determination of Bismuth(III) Using 1(4' romophenyl) 4,4,6-Trimethyl (1H,4H)-Pyrimidine-2-Thiol.Anal. Lett, 1998, 31(13):2241-2254.

[4] A. Alonso, M. J. Almendral, M. D. Báez, et al. Determination of bismuth in pharmaceutical products using liquid-liquid extraction in a flow injection system. Anal. Chim. Acta, 2000, 408(1-2): 129-133.

[5] Kazimierz W, Katarzyna W and Edith M.C.U. Application of Internal Standard for Micro Extraction-Spectrophotometric Determination of Bismuth in Pharmaceutical Formulations. Microchim. Acta, 2000, 135(1-2):87-90.

[6] D. Thorburn Burnsa, N. Chimpaleea and M. Harriott. Flow-injection extraction spectrophotometric determination of bismuth as tetraiodobismuthate(III) with the tetramethylenebis(triphenylphosphonium) cation. Anal. Chim. Acta, 89,225: 9-453.

[7] Li, Q.M., Ouyang, R.Z., Zhu, G.F., et al. Proconcentration by Microcrystalline Phenolphthalein for Determining Trace Molybdenum(VII)ter by GFAAS. Chem.Res. Chinese U.2005, 21(5), 622-625.

[8] Wen, X.-R., Tu, C.-Q. Study on spectrophotometric method for determination of bismuth after flotation separation using microcrystalline adsorption system. J.Chin. Chem. Soc, 2012, 59(2), 213-218.

[9] Taher, M.A., Puri, B.K. Differential pulse polarographic determination of trace amount of bismuth in various complex samples after preconcentration of its 1-(2-Pyridylazo)-2-naphthol complex by column and microcrystalline naphthalene methods. Electroanalysis,1999,11 (12), 899-904.

[10] Ishida, K., Puri, B.K., Satake, M., Mehra, M.C. Determination of bismuth by flame atomic-absorption spectrophotometry after separation by adsorption of its 2-mercaptobenzothiazole complex on microcrystalline naphthalene. Talanta, 1985,32 (3), 207-208.

[11] Burns, D.T., Tungkananuruk, N., Thuwasin, S. Spectrophotometric determination of bismuth after extraction of tetrabutylammonium tetraiodobismuthate(III) with microcrystalline benzophenone. Anal. Chim. Acta, 2000,419 (1), 41-44.

[12] Thorburn Burns, D., Chimpalee, D. Spectrophotometric determination of bismuth after extraction of 1-naphthylmethyltriphenylphosphonium tetraiodobismuthate(III) with microcrystalline benzophenone. (1992) Anal. Chim. Acta, 1992,256 (1), 87-90.

[13] Li,Q.M.,Zhao,X.H., Guan,X., et al. A novel method of the separation/preconcentration and determination of trace molybdenum(VI) in water samples using microcrystalline triphenylmethane loaded with salicyl fluorone. Anal. Chim. Acta, 2006, 562, 44- 0.'

[14] Chang,W.-B.;Li,K.-A.Brief Handbook of Analytical Chemistry; Beijing University Press: Beijing,1981;262.

[15] Pan,J.-M.; Chen,Y.-S.; Yan,H.-T. Chromogenic Agent and Its Application in Metallurgical Analysis; Shanghai Scientific and Technical Publisher: Shanghai, 1981,116.