

Separation/enrichment of trace Zinc using potassium bromide-dimethylglyoxime-thymolphthalein system

Changqing Tu¹ and Xinrong Wen

College of Chemistry and Environment, Jiaying University, Meizhou, Guangdong 514015, China.

¹ tcq@jyu.edu.cn

Abstract. A new method for the separation enrichment of trace Zn^{2+} using microcrystalline thymolphthalein as an adsorbent was established. The separation enrichment behaviour of Zn^{2+} and the conditions for the separation quantitatively of Zn^{2+} with other metal ions were investigated. The possible separation enrichment mechanism of Zn^{2+} was discussed in detail. The results showed that by controlling pH 10.0, in KBr-diacetyldioxime(DMG)-thymolphthalein(TP) system, chelate settlement of $\text{Zn}(\text{DMG})_2$ which formed by Zn^{2+} and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, and the liquid-solid phases were formed with clear interface, while Cu^{2+} , Bi^{3+} , Al^{3+} , Hg^{2+} could not be adsorbed. The quantitative separation of Zn^{2+} from those metal ions was achieved. The proposed method has been successfully applied to the quantitative separation of trace Zn^{2+} in synthetic water samples with enrichment yield of 93.5%~99.3%.

1. Introduction

Zinc is one of the essential microelements for humans, and it is an important element of maintaining normal growth and development and metabolism. Zinc deficiency or Zinc excess harm to the human body. Therefore, it is of great importance to determinate trace Zinc in environmental samples. Separation and enrichment step is necessary before determining, Zn^{2+} due to the low concentration of Zn^{2+} in environmental samples. Up to now, there are many methods to separate and enrich Zn^{2+} , such as solid-phase extraction,[1-2] solid-liquid extraction,[3] liquid-liquid extraction,[4] cloud point preconcentration,[5] column separation,[6-7], ion-exchange separation,[8] etc.

In this paper, a new method for the separation enrichment of trace Zn^{2+} using microcrystalline thymolphthalein as an adsorbent was reported. By controlling pH 10.0, in KBr-diacetyldioxime(DMG)-thymolphthalein(TP) system, chelate settlement of $\text{Zn}(\text{DMG})_2$ which formed by Zn^{2+} and DMG was quantitatively adsorbed on the surface of microcrystalline thymolphthalein, while Cu^{2+} , Bi^{3+} , Al^{3+} , Hg^{2+} could not be adsorbed. The quantitative separation of Zn^{2+} from those metal ions was achieved. A new method for the separation enrichment of trace Zn^{2+} was established, and it has been successfully applied to the quantitative separation of trace Zn^{2+} in synthetic water samples with satisfactory results. Zn^{2+} and Hg^{2+} always cannot be separated easily because of similar properties, but Zn^{2+} and Hg^{2+} could be separated perfectly by using this method.



2. Experiment

2.1. Apparatus and reagents

A model 722S spectrophotometer was used for photometric measurements. Diacetyldioxime (DMG) ethanol solution: $2.0 \text{ g}\cdot\text{L}^{-1}$. Thymolphthalein (TP) solution: 3%. Zn^{2+} standard solution of Zn^{2+} : $50 \text{ mg}\cdot\text{mL}^{-1}$, was prepared by appropriately diluting the stock standard solution of Zn^{2+} ($1.000 \text{ g}\cdot\text{L}^{-1}$). Standard solution of other metal ions was prepared by appropriately diluting the stock standard solution ($1.000 \text{ g}\cdot\text{L}^{-1}$). 4-(2-pyridylazo) resorcinol (PAR) ethanol solution: $1.0\times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. Borax solution: $0.1 \text{ mol}\cdot\text{L}^{-1}$. Buffer solutions of different pH were prepared as references [9].

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

2.2. Method

$50 \mu\text{g}$ of Zn^{2+} , a given amount of $2.0 \text{ g}\cdot\text{L}^{-1}$ DMG solution, 3% TP solution and pH=10.0 buffer solution were added into a 25 mL ground color comparison tube, and dilute the mixture to 10.00 mL with bidistilled water. 1.0 g KBr was added and shaken adequately and they were kept still for a moment. 1.5 mL PAR ethanol solution and 3.0 mL borax solution was transferred into another 25 mL ground color comparison tube, then 1.00 mL of filtrate was added. The solution was diluted to the mark and the absorbance was measured at 494 nm against the reagent blank prepared in the same way. The amount of Zn^{2+} remained in the solution was calculated. The enrichment yield of Zn^{2+} (E/%) was calculated according to the determination results. The determination of other metal ions was referring the reference [10].

3. Results and discussions

3.1. Effect of TP dosage

$50 \mu\text{g}$ of Zn^{2+} , 1.50 mL of $2.0 \text{ g}\cdot\text{L}^{-1}$ DMG solution, 4.50 mL of pH=10.0 buffer solution were applied to the proposed method, the effect of 3% TP dosage on the enrichment yield of Zn^{2+} was studied, the results were shown in Figure 1. The results show that the enrichment yield of Zn^{2+} is 48.6% in the absence of TP. It is probable that the partially Zn^{2+} can directly react with DMG to form the chelate precipitate of $\text{Zn}(\text{DMG})_2$. It is consistent with the phenomenon of precipitate which can be directly observed without TP in experiment.

The enrichment yield of Zn^{2+} increases with the increase of TP dosage. It is probable that DMG adsorbed onto microcrystalline thymolphthalein has higher concentration and can react with Zn^{2+} left in the solution to form the chelate precipitate of $\text{Zn}(\text{DMG})_2$, and the chelate can be adsorbed on the surface of microcrystalline TP. This indicates that microcrystalline thymolphthalein loaded with DMG can perfectly adsorb trace Zn^{2+} in solution, and the concentration of Zn^{2+} decreases to zero. When the dosage of TP is up to 3.00 mL or more, the enrichment yield of Zn^{2+} was 100%. So, 3.00 mL of DDBAB was used.

3.2. Effect of DMG dosage

The effect of DMG dosage on the enrichment yield of Zn^{2+} was shown in Figure 2. The amount of DMG is regarded as an important affecting factor on the enrichment yield of Zn^{2+} . The enrichment yield of Zn^{2+} was 54.4% without DMG in the solution. It is likely that Zn^{2+} can be absorbed directly on the surface of microcrystalline TP at pH=10.0. With the increase of DMG dosage, the enrichment yield of Zn^{2+} increased. For the reason that Zn^{2+} can react with DMG to form the water-insoluble chelate of $\text{Zn}(\text{DMG})_2$, and the chelate can be adsorbed on the surface of microcrystalline TP. The amount of $\text{Zn}(\text{DMG})_2$ increases when the solution includes more DMG. It leads to the increase of enrichment yield of Zn^{2+} . When the dosage of DMG was 0.25 mL , Zn^{2+} can be completely retained on the surface of microcrystalline TP. It indicates that $\text{Zn}(\text{DMG})_2$ can be quantitatively retained on the surface of microcrystalline TP. The enrichment yield of Zn^{2+} maintained 100% with further increasing the dosage of DMG. Hence, 0.30 mL of DMG was chosen for all further studies.

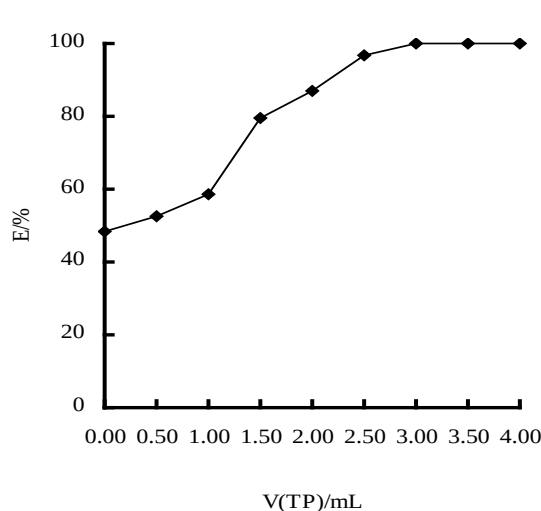


Figure 1. Effect of TP dosage on the enrichment yield of Zn^{2+}

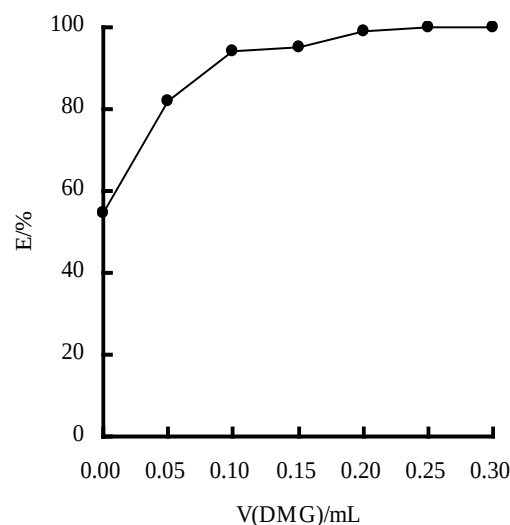


Figure 2. Effect of DMG dosage on the enrichment yield of Zn^{2+}

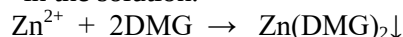
3.3. Effect of pH=10.0 buffer solution dosage

With the increase of pH=10.0 buffer solution dosage, the enrichment yield of Zn^{2+} increased. When the dosage of pH=10.0 buffer solution was 4.00 mL, the enrichment yield of Zn^{2+} was 100%. The enrichment yield of Zn^{2+} maintained 100% with further increasing the the dosage of pH=10.0 buffer solution. Hence, 4.00 mL of pH=10.0 buffer solution was chosen.

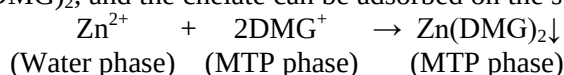
3.4. Enrichment mechanism of Zn^{2+}

Based on the results above, it could be concluded that Zn^{2+} could not be completed enriched when the solution includes TP but not DMG, nor when the solution includes DMG but not TP. Only in the simultaneous presence of DMG and TP in the solution, can Zn^{2+} be completed enriched. So, the enrichment mechanism of Zn^{2+} is as follows:

(1) When the solution includes DMG but not thymolphthalein, partially Zn^{2+} can directly react with DMG to form the chelate precipitate of $Zn(DMG)_2$, which leads to the decrease of the concentration of Zn^{2+} in the solution.



(2) When the solution includes both DMG and thymolphthalein at pH 10.0, DMG adsorbed onto microcrystalline thymolphthalein reacts with Zn^{2+} left in the solution to form the chelate precipitate of $Zn(DMG)_2$, and the chelate can be adsorbed on the surface of microcrystalline thymolphthalein (MTP).



3.5. Effect of various salts

The effects of various salts including NaCl, NaNO₃, (NH₄)₂SO₄ and KBr on liquid-solid divarication and the flotation yield of Zn^{2+} were investigated. The results showed that liquid-solid divarication could be realized at the presence of each of four salts above. NaCl decreased the enrichment yield of Zn^{2+} in a certain extent. The presence of KBr could speed up liquid-solid divarication and made the interface more clear between two phases, and consequently Zn^{2+} could be separated quickly and completely. When 1.0g of KBr was added, it could make liquid-solid phase separation perfectly. Therefore, 1.0 g KBr was chosen in the further studies.

3.6. The enrichment yield of different metal ions

When Zn^{2+} dosage was 50 μg , the dosage of TP, DMG and pH=10.0 buffer solution was 3.00 mL, 0.30, 4.00 mL respectively, the enrichment yield of Zn^{2+} was 100%. Under the same conditions, the enrichment yield of Cu^{2+} , Bi^{3+} , Al^{3+} and Hg^{2+} was 5.2%, 7.8%, 6.6%, 4.5% respectively. Therefore, Zn^{2+} can be separated from Cu^{2+} , Bi^{3+} , Al^{3+} and Hg^{2+} .

3.7. Separation enrichment experiments

Under the optimum conditions, the separations of Zn^{2+} from Cu^{2+} , Bi^{3+} , Al^{3+} and Hg^{2+} in synthesized samples of binary and polybasic system were studied. The results were shown in Table 1 and Table 2.

Table 1. The separation results of binary-mixed ions

Mixed ions	Dosage of metal ions(μg)		Content of metal ions in water phase (μg)		Enrichment yield(E/%)	
	Zn	Me	Zn	Me	Zn	Me
Zn^{2+} - Cu^{2+}	50	100	0.1	93.7	99.8	6.3
	50	200	0.2	193.2	99.6	3.4
	50	300	0.2	295.5	99.6	1.5
Zn^{2+} - Bi^{3+}	50	100	0.1	93.9	99.8	6.1
	50	200	0	188.9	100	5.6
	50	300	0.2	296.6	99.6	1.1
Zn^{2+} - Hg^{2+}	50	100	0.1	92.4	99.8	7.6
	50	200	0.2	198.3	99.6	0.9
	50	300	0.1	309.7	99.8	-3.2
Zn^{2+} - Al^{3+}	50	100	0.1	92.4	99.8	7.6
	50	200	0	190.3	99.6	4.9
	50	300	0.1	303.9	99.8	-1.3

Me represents other metal ions except Zn^{2+} .

Table 2. Separation results of Zn^{2+} from polybasic-mixed ions

Number of the synthesized samples	1	2	3
Dosage of Zn^{2+} (μg)	100.0	200.0	400.0
Dosage of Me (μg)	200.0	300.0	500.0
Zn^{2+} found in solid phase (μg)	95.0	198.6	373.9
Enrichment yield of Zn^{2+} (E/%)	95.0	99.3	93.5

Me represents Cu^{2+} , Bi^{3+} , Al^{3+} and Hg^{2+} .

4. Conclusion

In this paper, separation/enrichment of trace Zn^{2+} using potassium bromide-dimethylglyoxime-thymolphthalein system was studied. This method has been successfully used for the separation/enrichment of trace Zn^{2+} in the samples of synthetic water with satisfactory results. The recoveries were 93.5%~99.3%. This study had certain practical significance on establishing a new methods of separation/enrichment of trace Zn^{2+} .

Acknowledgement

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