Separation/enrichment of Nickel( II ) using Potassium Bromide-PAN-Phenolphthalein System

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Abstract. Separation/enrichment of nickel( II ) using potassium bromide-PAN-phenolphthalein system is reported. Various factors affecting the separation/enrichment of nickel( II ) are studied, the separation/enrichment of nickel( II ) mechanism is deduced. The results show that by controlling pH 6.0, the chelate precipitate of Ni( II )-PAN formed from nickel( II ) and PAN could be adsorbed on the surface of microcrystalline phenolphthalein to form liquid-solid phases with a clear interface under the best conditions, while Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ are not adsorbed in this condition. So, the separation of Ni²⁺ form these metal ions is achieved. The method for the separation/enrichment of trace nickel is established. This method was applied to the quantitative separation/enrichment of trace Ni²⁺ in synthetic water, and the results are satisfactory.

1. Introduction
Nickel is an essential microelement of human body. Nickel deficiency can cause diabetes, anaemia, uremia, kidney failure and so on. On the contrary, excessive intake of nickel can cause poisoning etc. Therefore, it is of great importance and significance to separate/enrich and determinate trace nickel in environment. So far, extraction separation¹-⁵, HPLC separation⁶, ion exchange⁷, flotation separation⁸ have been used to separate/enrich Ni( II ).

The paper presents the separation/enrichment of nickel( II ) using potassium bromide-PAN-phenolphthalein system. Various affecting factors of the separation/enrichment of nickel( II ) are studied, the optimum separation/enrichment conditions are obtained, and the separation/enrichment of nickel( II ) mechanism is deduced. The results display that in existence of 0.50g KBr, when the 0.002mol/L PAN solution is 1.50 mL and 0.03% phenolphthalein solution is 1.00mL, the chelate precipitate of Ni( II )-PAN formed from nickel( II ) and PAN could be adsorbed on the surface of microcrystalline phenolphthalein to form liquid-solid phases with a clear interface by controlling pH 6.0. While Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ are not adsorbed in the same condition. So, the separation of Ni²⁺ form these metal ions is achieved. The method for the separation/enrichment of trace nickel( II ) is established. This method is used to the separation/enrichment of trace Ni²⁺ in synthetic water, and the enrichment yields are 95.8% - 106.7%.
2. Experimental

2.1 Equipment and reagents

A model 722S spectrophotometer (Shanghai No.3 Analysis Equipment Plant) is used. 1-(2-pyridylazo)-2-naphthol (PAN) ethanol solution: 0.002 mol/L. Phenolphthalein (PP) ethanol solution: 5%. Borax solution: 0.1 mol·L⁻¹. 4-(2-pyridylazo) resorcinol (PAR) ethanol solution: 1.0×10⁻³ mol·L⁻¹. Ni²⁺ standard solution: 1.000 g·L⁻¹. Ni²⁺ work solution: 50.0 µg·mL⁻¹, is prepared by appropriately diluting the Ni²⁺ standard solution (1.000 g·L⁻¹). The standard solution of other metal ions: 1.000 g·L⁻¹. The buffer solutions of different pH was prepared as reference 9.

2.2 Method

50µg Ni²⁺, 1.50 mL 0.002 mol·L⁻¹ PAN ethanol solution, 1.00 mL 0.03% PP ethanol solution and 4.00 mL pH 6.0 buffer solution are added into a 25 mL ground color comparison tube. 0.50 g KBr is added after the mixed solution is diluted to 10.00 mL with bidistilled water, then the mixed solution is shaken adequately and placed for a moment. 1.00 mL colature, 1.5 mL PAR ethanol solution and 3.0 mL borax solution are added into another 25 mL ground color comparison tube. The mixed solution is diluted to 25.00 mL and the absorbances are measured at 494 nm against the reagent blank prepared in the same way. The amounts of Ni²⁺ remained in the solution is calculated and the enrichment yield of Ni²⁺(E/%) is calculated.

Photometric analysis of other metal ions was referring the reference 10.

3. Results and discussion

3.1. Effect of PAN ethanol solution dosage

50µg Ni²⁺, 1.00 mL 0.03% phenolphthalein ethanol solution are applied to the proposed method, the effect of 0.002 mol·L⁻¹ PAN ethanol solution dosage on the enrichment yield of Ni²⁺ is shown in figure 1. We can see from figure 1 that the enrichment yield of Ni²⁺ is zero when PAN ethanol solution dosage is zero. With the increase of PAN ethanol solution dosage, the enrichment yield of Ni²⁺ increase. When PAN ethanol solution dosage is 1.50 mL or more, the enrichment yield of Ni²⁺ is 100%. Hence, 1.50 mL 0.002 mol·L⁻¹ PAN ethanol solution dosage is chosen.

3.2. Effect of Phenolphthalein ethanol solution dosage

According to the experimental method, 50µg Ni²⁺, 1.50 mL 0.002 mol·L⁻¹ PAN ethanol solution are added, the effect of 0.03% phenolphthalein ethanol solution dosage on the enrichment yield of Ni²⁺ is researched (figure 2). The enrichment yield of Ni²⁺ is 47.1% when 0.03% phenolphthalein ethanol solution dosage is zero. This is because there is a small amount of Ni(II)-PAN chelate precipitate formed. We can directly observed the produce of small precipitate in experiment. The enrichment yield of Ni²⁺ increase with the increase of phenolphthalein ethanol solution dosage. The enrichment yield of Ni²⁺ reaches 100% when the dosage of phenolphthalein ethanol solution dosage is 1.00 mL ~ 1.40 mL. So, 1.00 mL 0.03% phenolphthalein ethanol solution is selected.
3.3. Separation/enrichment mechanism

Based on the results above, when Ni\(^{2+}\), PAN and phenolphthalein simultaneously existed in the solution, Ni\(^{2+}\) can be completely enriched. Therefore, the enrichment mechanism of Ni\(^{2+}\) is as follows:

(1) When Ni\(^{2+}\) and PAN are added, phenolphthalein is not added, a part of Ni\(^{2+}\) can directly react with PAN to form the Ni\(^{2+}\)-PAN complex precipitate.

\[
\text{Ni}^{2+} + \text{PAN} \rightarrow \text{Ni}^{2+}\text{-PAN}\downarrow \\
\text{(Water phase)} \quad \text{(MPP phase)}
\]

(2) When Ni\(^{2+}\), PAN and phenolphthalein are added, Ni\(^{2+}\) can react with PAN to form the Ni\(^{2+}\)-PAN complex precipitate. The complex precipitate can be adsorbed on the surface of microcrystalline phenolphthalein (MPP). So, Ni\(^{2+}\) can be completely enriched.

\[
\text{Ni}^{2+} + \text{PAN} \rightarrow \text{Ni}^{2+}\text{-PAN}\downarrow \\
\text{(Water phase)} \quad \text{(MPP phase)}
\]

3.4. Effect of various salts

50 µg Ni\(^{2+}\), 1.50 mL 0.002 mol·L\(^{-1}\) PAN ethanol solution and 1.00 mL 0.03% phenolphthalein ethanol solution are added, the effects of various salts (NaCl, KNO\(_3\), (NH\(_4\))\(_2\)SO\(_4\) and NaBr) on liquid-solid parvafacies situation and the enrichment yield of Ni\(^{2+}\) are investigated. The results are shown in Table 1.

| Salt       | The mass of salt/g | The enrichment yield of Ni\(^{2+}\)/% | Liquid-solid parvafacies situation and effect                                      |
|------------|-------------------|-------------------------------------|----------------------------------------------------------------------------------|
| NaCl       | 0.5               | 81.3                                | Liquid-solid parvafacies can be achieved,                                        |
|            | 1.0               | 90.0                                | Liquid-solid interface clear, parvafacies velocity                               |
|            | 1.5               | 96.4                                | Liquid-solid interface clear, parvafacies velocity, effect is better.             |
|            | 0.5               | 100.0                               | Liquid-solid parvafacies can be achieved,                                        |
| KBr        | 1.0               | 100.0                               | Liquid-solid interface clear, parvafacies velocity                               |
|            | 1.5               | 100.0                               | Liquid-solid interface clear, parvafacies velocity, effect is best.              |
|            | 0.5               | 100.0                               | Liquid-solid parvafacies can be achieved,                                        |
| KNO\(_3\)  | 1.0               | 100.0                               | Liquid-solid interface clear, parvafacies velocity                               |
|            | 1.5               | 100.0                               | Liquid-solid interface clear, parvafacies velocity, effect is better.             |
|            | 0.5               | 86.1                                | Liquid-solid parvafacies can be achieved,                                        |
| (NH\(_4\))\(_2\)SO\(_4\) | 1.0               | 95.7                                | Liquid-solid interface clearer, parvafacies velocity                             |
1.5 98.2 is slow and parafacies effect is poor.

We can see from the Table 1 that liquid-solid parafacies can be achieved when NaCl, KNO₃, (NH₄)₂SO₄ and KBr exist in the solution, respectively. NaCl and (NH₄)₂SO₄ decrease enrichment yield of Ni²⁺ in a certain extent, besides parafacies effect is worst when (NH₄)₂SO₄ exists in the solution. The enrichment yields of Ni²⁺ are not affected when KNO₃ and KBr exist in the solution alone. In addition, liquid-solid interface is clear, parafacies velocity is fast and the effect is best when KBr exists in the solution. SO, 0.5 g NaBr is chosen.

3.5. Effect of pH

50µg metal ion, 1.50mL 0.002 mol·L⁻¹ PAN ethanol solution and 1.00mL 0.03% phenolphthalein ethanol solution are added, the effects of pH on the enrichment yield of different metal ions are shown in Table 2.

Table 2. The enrichment yield of other metal ions in different pH solution

| metal ion | pH 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 |
|-----------|--------|-----|-----|-----|-----|-----|-----|
| Ni²⁺      | 13.9%  | 100%| 100%| 100%| 100%| 100%| 100%|
| Mn²⁺      | 33.8%  | 0.0%| 0.0%| 0.0%| 0.0%| 0.0%| 29.0%|
| Zn²⁺      | 56.1%  | 20.0%| 30.9%| 25.3%| 22.2%| 9.2%| 30.5%|
| Al³⁺      | 4.4%   | 0.0%| 0.0%| 3.2%| 13.5%| 0.0%| 17.3%|
| Cu²⁺      | 0.0%   | 6.9%| 7.0%| 2.3%| 8.7%| 0.0%| 12.7%|
| Cd²⁺      | 10.4%  | 4.0%| 6.3%| 0.0%| 6.8%| 5.6%| 15.9%|

Table 2 show that at pH 2.0~7.0, the enrichment yield of Ni²⁺ maintain 100%. At pH 2.0~6.0, the enrichment yields of Mn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ are zero or lower. At pH 6.0, the enrichment yield of Zn²⁺ is lower. Hence, Ni²⁺ can be separated from Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ by controlling pH=6.0.

3.6. Separation of Ni (II) in binary systems

1.50mL 0.002 mol·L⁻¹ PAN ethanol solution and 1.00mL 0.03% phenolphthalein ethanol solution are added, the separation experiments are carried out between Ni²⁺ and Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ in synthesized samples of binary system at pH 6.0. The results are shown in Table 3.

Table 3. The separation results of binary-mixed ions (pH 6.0)

| Mixed ions | Dosage of metal ions(µg) | Content of metal ions in water phase (µg) | Enrichment yield(E/%) |
|------------|--------------------------|------------------------------------------|-----------------------|
| Ni²⁺-Mn²⁺  | 50.0 300.0 0.2 328.3 Ni  | 99.6 99.6 -2.8 Me                        |
| Ni²⁺-Zn²⁺  | 50.0 200.0 0.2 216.6 Ni  | 99.6 96.4 -3.2 Me                        |
| Ni²⁺-Al³⁺  | 50.0 300.0 0.2 388.6 Ni  | 99.6 99.8 -9.2 Me                        |
| Ni²⁺-Cu²⁺  | 50.0 300.0 0.2 520.1 Ni  | 100.0 100.0 -4.0 Me                      |
| Ni²⁺-Cd²⁺  | 50.0 200.0 0.2 218.7 Ni  | 99.6 99.6 -9.4 Me                        |

Me represents other other ions except Ni²⁺.
3.7. Separation of Ni (II) in polybasic systems

1.50mL 0.002 mol·L⁻¹ PAN ethanol solution and 1.00mL 0.03% phenolphthalein ethanol solution are added, the separations of Ni²⁺ from Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺ in synthesized samples of polybasic system are studied at pH 6.0 (Table 4).

| Number of the synthesized samples | 1    | 2    | 3    | 4    | 5    |
|-----------------------------------|------|------|------|------|------|
| Dosage of Ni²⁺ (µg)               | 50.0 | 100.0| 150.0| 200.0| 300.0|
| Dosage of Me (µg )                | 100.0| 200.0| 200.0| 300.0| 400.0|
| Ni²⁺ find in solid phase (µg)     | 47.9 | 106.7| 148.8| 200.5| 294.3|
| Enrichment yield of Ni²⁺ (E/%)    | 95.8 | 106.7| 99.2 | 100.3| 98.1 |

Me represent Mn²⁺, Zn²⁺, Al³⁺, Cu²⁺ and Cd²⁺.

4. Conclusion

In this paper, the separation/enrichment of nickel(II) using potassium bromide-PAN-phenolphthalein system is reported. This method is used to the separation/enrichment of trace Ni²⁺ in synthetic water, and the enrichment yields are 95.8% - 106.7%. It is clear that this research is of great foreground of application and certain practical value to establish a new method for separation/enrichment of trace nickel (II).

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