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Determination of Microamounts of Palladium(II) by Extraction Method without Usual Organic Solvents

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Abstract. The favorable distribution equilibrium of the complex of Pd(II)-5-Cl-PADAB between the two phases of PEG2000-$(NH_4)_2SO_4$-H_2O extraction system was investigated. The extraction efficiency (%E), distribution coefficient and concentration factors are studied. Spectrophotometric characteristics of the complex in such a system are stable. This method was used to determine micro-amounts of palladium(II) in secondary alloys of Ni. This method of extraction overcomes many disadvantages of methods using usual organic reagents as solvents. It is a convenient, rapid, economical way.

Key words: extraction, water soluble polymer PEG2000, microamounts of palladium, spectrophotometric determination.

Liquid–liquid extraction with conventional organic substances as solvents usually has good selectivity, and has been widely used. However, the use of organic solvent provides obstacles to applications of extraction methods in analytical laboratories and in technology. Environmental concerns with such organic reagents include their flammable, explosive, volatile, and toxic nature, when conventional extraction methods are used to extract complexes or organic substances with multiple charges, the extraction efficiency (%E) is not always favorable. It is of practical interest to study a new type of extraction system to solve these problems.

Aqueous solutions of the water soluble polymer Polyethylene Glycol 2000 (PEG2000) can be separated into two phases in the presence of some inorganic salts [1–2]. Li Buhai et al. investigated conditions for the phase separation of PEG2000 and established some extraction methods by taking advantage of this phenomenon [3–6].

In this paper, we selected the reagent 4-(5-Cl-pyridylazo)-1,3-diaminobenzene (5-Cl-PADAB), which has been used as a spectrophotometric reagent to determine Co(II), Pd(II) and other ions, as the extracting reagent and established a method to extract and determine microamounts of palladium(II) in secondary alloys of Ni. This method is based on the phase separation of 16% PEG2000 aqueous solutions in the

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presence of $(NH_4)_2SO_4$. The results of this study show that this method is feasible to separate and determine microamounts of Pd(II) in complex alloys.

Large amount of Ni(II), Cu(II) and other metal ions present in such alloys do not interfere with the determination of Pd(II) after this extraction process. The extraction method overcomes the above-mentioned drawbacks because the PEG2000-$(NH_4)_2SO_4$-H_2O solvent system is inflammable, nonvolatile, and nontoxic. Low price and ability to recycle PEG2000 make it an economical procedure. Environmental pollution is reduced.

The water soluble polymer PEG2000 is a kind of non-ionic surfactant. Its water solubility arises from hydrogen bonds between oxygen of ether bonds in PEG2000 molecule with water. Higher temperature and some electrolytes like aminium salts can destroy this hydrogen bond and phase separation occurs. The method can be compared with a cloud point extraction which is also based on non-ionic surfactant separation into two phases above the cloud point temperature [8–12]. The two phases of the extraction system described here are more stable, and are not like the two phases of cloud point extraction which are easily affected by a temperature change resulting in decreased %E. Those differences make the PEG2000-$(NH_4)_2SO_4$-H_2O extraction method more convenient and more rapid.

Experimental

Apparatus and Reagents

A Model 721A spectrophotometer (Analytical Equipment Factory, Sichuan) was used for photometric measurements.

A 40.0% (W/V) aqueous solution of PEG2000 was prepared by dissolving 100.0 grams of solid of PEG2000 in 250 ml distilled water. A 0.040% 5-Cl-PADAB alcohol solution was used as extractant and 40% ammonium sulfate was prepared for washing the test tube.

A stock 1.000 mg/ml solution of palladium(II) was prepared. A 10.0 μg/ml Pd(II) solution was prepared by diluting 1.00 ml of this stock solution to 100.0 ml using distilled water.

A 2.3% solution of sodium citrate with pH 2.2 was used as buffer solution.

All reagents were of analytical grade.

Sample Treatment

About 5 g of secondary alloy of Ni was dissolved in 50 ml aqua regia, then the solution was evaporated to nearly dry, followed by addition of 10 ml of 6 mol/l HCl, and evaporated again. These steps were repeated two or three times. 5 ml of 1.0 mol/l HCl was added to dissolve the solid and the solution was transferred into a 100-ml volumetric flask and diluted to volume with 1.0 mol/l HCl. The appropriate volume was taken in a 25 ml tube for the determination of Pd(II).

Procedure

1.0 ml of the 1.00 μg/ml solution of Pd(II), 4.0 ml 40% solution of PEG2000 [3] was added into a 25 ml tube fitted with a stopper, the acidity of the solution adjusted with about 1.0 ml sodium citrate solution and appropriate amount of HCl solution, given 0.2 ml 0.040% 5-Cl-PADAB alcohol solution then, the solution was diluted to 10.0 ml with distilled water and mixed well. The tube was placed in a water bath at 80.0 °C for 6 minutes, then removed and cooled to room temperature under running water.

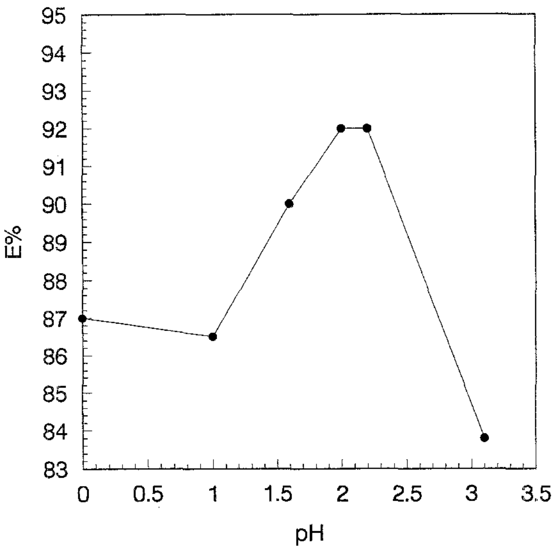

Fig. 1. Effect of pH on E% of Pd(II)-5-Cl-PADAB complex $C_{PEG2000} = 16\%$, $C_{5\text{-Cl-PADAB}} = 3.25 \times 10^{-5}$ mol/l, $C_{(NH_4)_2SO_4} = 36\%$, [Pd(II)]: 10.0 µg/10.0 ml

3.6 g solid of $(NH_4)_2SO_4$ was added to the solution and the mixture was shaken for 3 minutes. The mixture was transferred into a separatory funnel, the tube was washed two or three times with 1–2 ml of 40.0% $(NH_4)_2SO_4$ solution, and the washing solutions were combined with the mixture solution. The solution separated into two phases after 5 minutes. The upper phase was PEG2000 phase and the lower phase was water phase. The water phase was discarded and the PEG2000 phase was transferred carefully into a 10.0 ml volumetric flask. The separatory funnel was washed two or three times with distilled water and the washing solutions combined with the PEG2000 phase. The solution was adjusted to pH 1.0 with hydrogen chloride and diluted to volume, then shaken carefully. The absorbance of Pd(II)-5-Cl-PADAB was measured at 576 nm with 1 cm cell [7], and the %E was calculated.

Results and Discussion

Extraction Conditions

Effect of acidity. It was shown in Fig. 1 that as the pH was changed from 1.9 to 2.3, the %E of the Pd(II)-5-Cl-PADAB complex in the presence of PEG2000 achieved a maximum value. In addition, the experiments indicated that when the pH is higher than 2.4 or lower than 1.8, the %E decreased, probably because the Pd(II)-5-Cl-PADAB complex was not stable at high pH and the separation of phase was unfavorable at low pH. So pH 2.2 was chosen for further work. The volume of the two phase were stable at that pH value. Figure 1 also shows that the efficiency of extraction (%E) is over 90%.

Effect of $(NH_4)_2SO_4$ concentration. It was shown that as the concentration of $(NH_4)_2SO_4$ was changed from 35 to 37%, a solution of 16% PEG2000 separated into two phases and the %E of the Pd(II)-5-Cl-PADAB complex achieved a maximum value and then decreased (Fig. 2). With the concentration of $(NH_4)_2SO_4$ increased, the PEG2000 separated out and %E was therefore increased. After the PEG2000 was completely separated out, the salt-effect of the excess $(NH_4)_2SO_4$ decreased the stability of the complex and hence decreased %E.

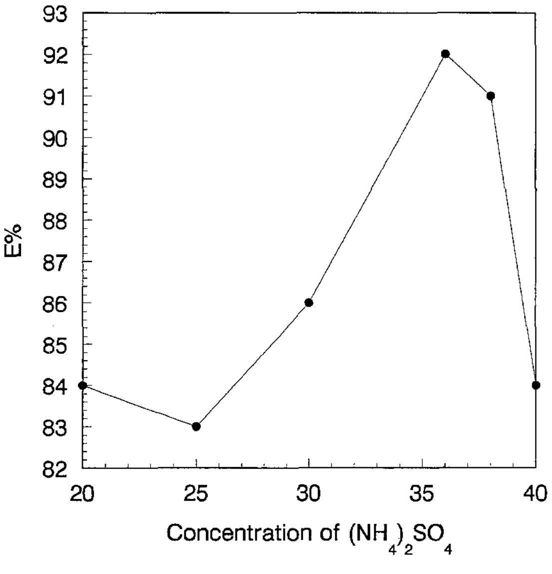

Fig. 2. Effect of $(NH_4)_2SO_4$ concentration on E% of Pd(II)-5-Cl-PADAB complex. pH 2.2, other conditions as same as Fig. 1

Effect of amounts of 0.040% 5-Cl-PADAB solution. It was shown from experimental results that as the amount of the 0.040% 5-Cl-PADAB solution was changed from 0.010 to 0.10 ml, the %E of the Pd(II)5-Cl-PADAB complex increased. However, when the amount of 0.040% 5-Cl-PADAB solution was more than 0.10 ml, the %E reached maximum value with good repeatability. A 0.20 ml volume of 0.040% 5-Cl-PADAB solution was chosen for further work.

Degree of concentration. In the standard procedure and optimum conditions, the total volume of two phases was over 10.0 ml, and the ratio of two phases ($V_{PEG2000}/V_{water}$) was 0.25. The concentration factor was 3.8. The maximum extraction efficiency (%E) reached 92.0%, and distribution coefficient was 46.

Effect of coexisting ions on determination of Pd(II). The effect of twenty-six ions was investigated to determine their behaviour with 5-Cl-PADAB in the presence of under the optimum conditions used above. The tolerance limit produces a 5% error in the determination of 10.0 μg palladium(II) per 10.0 ml. The tolerance limits of various ions are presented in Table. 1. The results indicated most ions didn't interfere in the determination of palladium(II). It is worth mentioning that large amount of Ni(II) will exist in the water phase in the form of precipitate after phase separation. And it is easy to separate this precipitate from the PEG 2000 phase by draining out the lower water phase.

Spectrophotometric Determination

Absorption spectra. Figure 3 shows the absorption spectra of Pd(II) and the 5-Cl-PADAB complex formed in the absence (curve 1) and presence (curve 2) of PEG2000 and those of the corresponding reagent blanks (curve 3 and curve 4, respectively). Their maximum absorption wavelengths were 570 and 576 nm, respectively.

Table 1. Effect of other ions (10.0 μg/10 ml)

Ion	Tolerance limit (μg)	Ion	Tolerance limit (μg)
Tl(III)	1000	As(V)	100
Mn(II)	1000	Cd(II)	5000
Ni(II)[a]	40000	Ga(III)	120
Cu(II)[a]	20000	Se(IV)	100
Ti(IV)	200	Th(IV)	300
In(III)	2000	Sc(III)	200
Co(II)	50	Zn(II)	1000
Be(II)	1000	Os(IV)	200
Mg(II)	1000	Ir(III)	20
Zr(IV)	200	Pt(IV)	450
Fe(III)	5000	Ru(III)	500
Pd(II)	100	Rh(III)	100
Au(III)	30	Te(IV)	200

[a] Masked by sodium citrate.

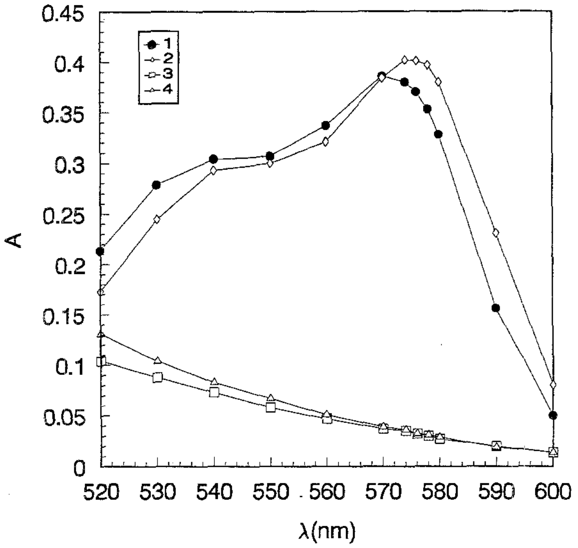

Fig. 3. Absorption spectra of Pd(II)-5-Cl-PADAB complex in the presence and absence PEG2000. *1* Pd(II)-5-Cl-PADAB complex in absence of PEG2000 vs. reagent blank; *2* Pd(II)-5-Cl-PADAB complex in presence of PEG2000, vs. reagent blank; *3* reagent blank in the absence of PEG2000, vs. distilled water; *4* reagent blank in presence of PEG2000, vs. distilled water; [Pd(II)]: 7.0 μg/10.0 ml, pH 2.2

Figure 3 also indicated their maximum absorption wavelengths were not significantly different. Tiny differences between two absorption maxima come from the formation of micelles of PEG2000 around the complex. In this work, the absorbance of the complex in the presence of PEG2000 was measured at 576 nm with a 1-cm cell, and the %E was calculated.

Stability of Pd(II)-5-Cl-PADAB complex. Experimental results indicated that once the Pd(II)-5-Cl-PADAB complex was completely formed and extracted into PEG2000 phase, it remained stable at least for 12 hours.

Table 2. Content[a] of every component of standard samples (μg/g)

No.	Content					
1	Au	144	Ru	32.4	Ni	66.92%
	Pd	189	Rh	37.3	Cu	14.04%
	Pt	306	Ir	29.0	Fe	8.41%
	Os	22.4				
2	Au	130	Ru	29.6	Ni	65.17%
	Pd	161	Rh	37.9	Cu	14.64%
	Pt	300	Ir	27.7	Fe	8.03%
	Os	22.4				

[a] Determined by atomic absorption.

Calibration curve. Under the optimum conditions for the formation and extraction of Pd(II)-5-Cl-PADAB complex, the Lambert-Beer Law was obeyed from 0.50 to 10.0 μg/10 ml (Pd(II). Morever, the following calibration equation could be obtained from the measurement.

$$A = 0.057C + 0.0054,$$

where C represented Pd(II) μg/ml. The correlation coefficient was found to be 0.9998.

Applications

The method described in this work was successfully applied to the determination of Pd in secondary alloys of Ni. The composition of this alloy is complex and is shown in Table 2 by atomic absorption. It shows that there are large amounts of Ni, Cu, Fe and microamounts of various precious metals in the sample. It is not convenient to separate and determine Pd in such complex samples by usual extraction methods. But this sample can be determined directly after only a single separation by the extraction system described in this paper. The results for determination of Pd(II) are listed in Table 3. The relative errors are 2σ. We find that there were no significant

Table 3. Analysis of secondary alloy of Ni sample

No.	Pd content in samples[a] (μg/g)	Determined content[b] (μg/g)	Relative error (%)	Pd added (μg)	Recovery Pd (%)
1	189	187	−1.0	1.00	98.0
				1.50	97.3
				2.00	96.3
				1.00	100.0
2	161	165	2.4	1.00	100.0
				1.50	102.1
				2.00	103.5

[a] Standard samples; [b] n = 7.

differences between the Pd(II) content obtained by the extraction method and by atomic absorption. This extraction method is a feasible way to separate and determine Pd(II).

Conclusion

The commercially available reagent 5-Cl-PADAB has been applied in determining Co(II), Pd(II) and others for a long time. The predominant reason for applying it here, however, is not to expand its applications, but to use it as extracting reagent and spectrophotometric reagent to separate and determine microamounts of Pd(II) existed in complex samples. It is demonstrated here that this extracting reagent performs well for separating microamounts of Pd(II) in this extraction method. This extraction method using a PEG2000-$(NH_4)_2SO_4$-H_2O phase separation system can be used to substitute for those expensive, toxic, dangerous extraction systems which use conventional organic solvents, PEG2000 can be used repeatedly if recovered, and these are the most beneficial characteristics of this extraction method.

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