Properties and Application of Poly(acrylphenylamidrazone-phenylhydrazide) Chelating Fiber for Enrichment–Separation of Trace Gold and Ruthenium from Solution Samples

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ABSTRACT: An ICP-OES method using a new poly(acrylphenylamidrazone-phenylhydrazide) chelating fiber to enrich and separate trace Au(III) and Ru(III) ions from solution samples is established. The results show that 50–500 ng/mL of Au or Ru ions can be enriched quantitatively by 0.1 g of the fiber at pH 4, with recoveries > 96%. The ions can be desorbed quantitatively with 10 mL of 4 M HCl and 3.0% $CS(NH_2)_2$ solution from the fiber column, with recoveries > 97%, and 200–1000-fold excesses of Cu(II), Zn(II), Ca(II), Mg(II), Mn(II), Cr(III), Fe(III), Ba(II), and Al(III) caused little interference in the determination of these ions by ICP–OES. The chelating fiber can be reused eight times, and the recoveries are all > 95%. The relative standard deviations for enrichment and determination of 50 ng/mL of Au and Ru are in the range 1.8–1.9% (1.9% for Au and 1.8% for Ru). The recoveries of trace Au and Ru ions added to real waste water and alloy samples are 96–98%. The concentration of each ion found in the alloy samples was in good agreement with that provided by the plant. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2656–2660, 2001

Key words: poly(acrylphenylamidrazone-phenylhydrazide) chelating fiber; enrichment–separation; gold; ruthenium; ICP–OES

INTRODUCTION

There are several examples of determinations of trace metals with preconcentration from solution sample containing trace amounts of noble metals with macroporous resins, that have a large adsorption capacity for noble metals.[1–5] However, because of the long soaking time used, the flow rates of the enriched elements are slow. A chelating fiber synthesized from polyacrylonitrile fiber has been used to rapidly and conveniently concentrate many elements, including the noble metals from different samples.[6–11] However, when the fiber was treated with a strong acid and then eluted with a large volume of water, the fiber swelled, resulting in problems with reusage. In the last few years, a new chelating fiber based on polyacrylonitrile fiber has been synthesized and used to enrich and separate rare trace metal ions with satisfactory results.[12–14]

In this paper, the chelating functional groups were grafted to a synthesized fiber; for example, polyacrylonitrile fiber. The synthesis is convenient, quick, and economical; moreover, it needs only one reaction step. This paper describes the synthesis and structure of the chelating fiber. Inductively coupled plasma–optical emission spec-
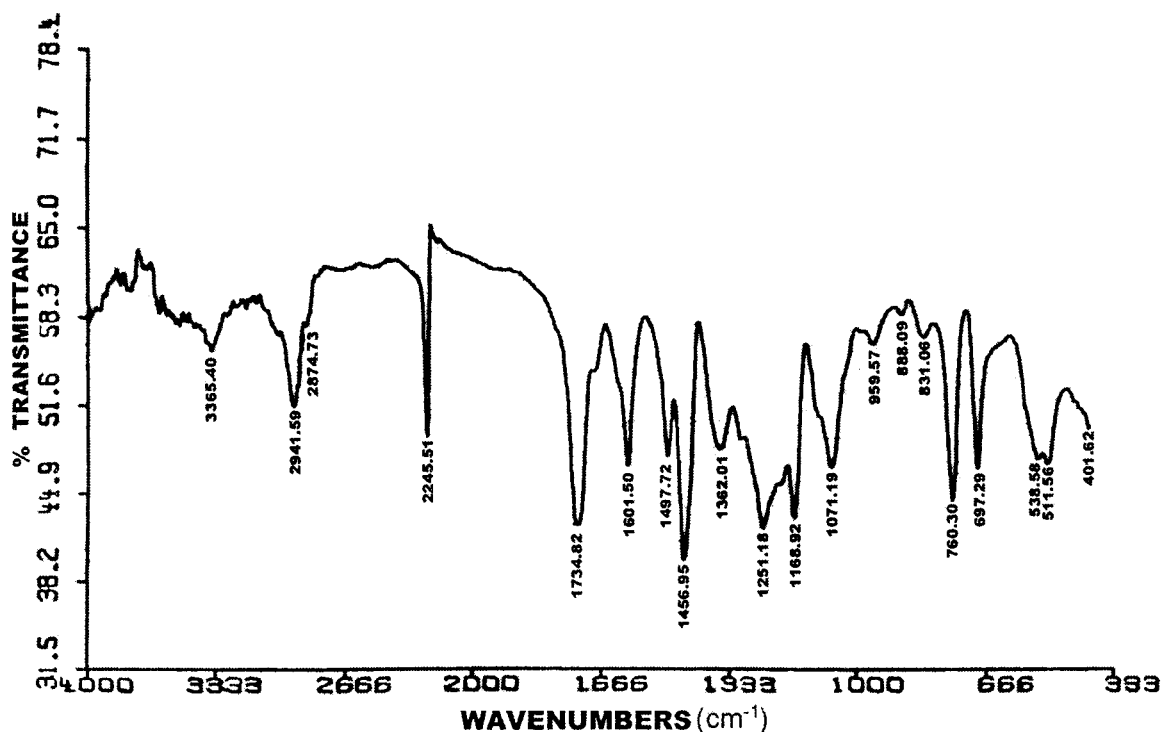
Figure 1   IR spectrum of the synthesized chelating fiber.

trometry (ICP–OES) is used to determine the efficiency with which Au(III) and Ru(III) ions are enriched onto and desorbed from the fiber column. The enrichment acidity, flow rate, desorption acidity, elution rate, adsorbing capacity, reuse performance, and interference by other ions are discussed. The analytical precision and accuracy of the method were tested with satisfactory results. This method is quick, convenient, precise, and accurate, and the chelating fiber is inexpensive.

EXPERIMENTAL

Instruments and Apparatus

An ICP/6500 inductively coupled plasma spectrometer (Perkin-Elmer), a model 360 FTIR spectrometer (Nicolet), a model 1106 elemental analyzer (Carlo Erba), a PHs-10c digital pH meter (Xiaoshan, China), and a three-necked flask for synthesizing the chelating fiber were used. For the adsorbing column, 0.15 g of chelating fiber was loaded into a glass tube (10 cm long × 0.4 cm i.d.; 0.15 cm i.d. at the lower end).

Reagents and Standard

Reagents of spectral and analytical purity and distilled water were used for all experiments. The 1

mg/mL stock solutions of Au(III) or Ru(III) each were made up from $HAuCl_4 \cdot H_2O$ and $(NH_4)_2$-$Ru(H_2O)Cl_5$ in 1 M hydrochloric acid. The mixed standard solution was prepared by diluting the stock solutions to result in Au(III) and Ru(III) concentrations of 50 μg/mL in 1 M HCl.

Synthesis of Chelating Fiber

The polyacrylonitrile fiber (containing 93% ploy-acrylonitrile, 5.7% methyl acrylate, and 1.3% itaconic acid) was from Lanzhou Chemical Fiber Factory (Lanzhou, China). Phenylhydrazine and distilled water (1 : 10 : 10) were mixed into a three-necked flask and refluxed for 9-h at 100°C (with stirring with an electromagnetic stirrer) until the color of the fiber changed to deep yellow. After washing with distilled water until neutral, the fiber was dried under an infrared (IR) lamp. The nitrogen content of the fiber determined by elemental analyzer was 24.2% after reaction and 23.2% before reaction. The existence of the chelating functional groups and the structure of the chelating fiber was verified by the IR spectrum (Figure 1). According to the literature,[15,16] the peaks in Figure 1 can be assigned as follows: γ/cm^{-1} 3365.4 (γ NH or γ OH), 2941.6 and 2874.7 (γ CH$_2$ and γ CH), 1734.8 (γ C=O), 1601.5 and 1497.7 (γ C=C of ⬡), 1456.9 (δ_SCH$_2$), 1251.2

($\delta_W CH_2$), 1168.9 (γ C—N and δ O=C—N), 1071.2 (δ C—N and γ N=C—N), 959.6 (δ N=C—N), 888.1 (δ_τNH), 831.0 (γ N—C=O), 760.3 and 697.2 9 (γ C—H of ⬡), and 538.6 (δ_τ C=O). And the peak of 2245.5 (γ C≡N) show that a part of C≡N remains in the fiber (where γ is a stretching vibration; δ is a bending vibration; δ_s is a scissor vibration; δ_w is a wagging vibration; and δ_τ is a twisting vibration). Based on the peak identities, the synthesis process of the chelating fiber may be briefly expressed as shown in Scheme 1.
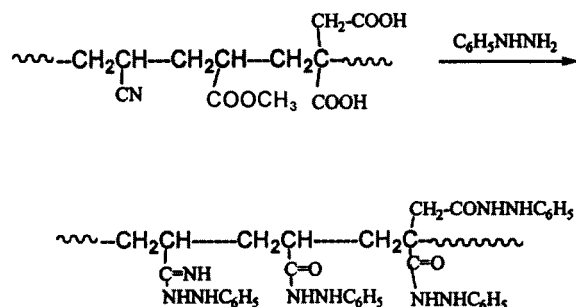
Analytical Procedure

The standard stock solutions of mixed ions or the real solution samples with different matrices (with Ca, Mg, Ba, Fe, and Al in the waste water sample and with Cu, Zn, Mn, Fe, and Mg in alloy sample) were prepared in high-purity cleaned vessels (100–1000 mL). The solutions were adjusted to the desired pH and passed through the adsorbing columns at a flow rate of 2 mL/min. After desorbing the analytes from the columns with 10 mL of 4 M HCl + 3.0% $CS(NH_2)_2$ at 2 mL/min of velocity, trace Au and Ru ions in the eluate were detected by the ICP/6500 spectrometer according to standard conditions (forward power, 1100 w; viewing height, 8 mm; Ar plasma gas flow, 14.0 L/min; Ar auxiliary gas flow, 0.7 L/min; Ar nebulizer gas flow, 1.0 L/min; solution uptake rate, 1.0 mL/min; wavelengths, Au,

Table I   Effect of pH on Analyte Enrichment

Ion (ng/mL)	Recovery (%)						
	pH 1	2	3	4	5	6	7
Au (50)	49	91	100	100	100	100	100
Ru (50)	6	18	88	97	98	100	100

Table II   Effect of Flow Rate on Analyte Enrichment

Ion (ng/mL)	Recovery (%)						8.0 (mL/min)
	0.5	1.0	2.0	3.0	4.0	6.0	
Au (50)	100	100	99	97	90	88	86
Ru (50)	100	99	98	95	94	91	90

242.795 nm and Ru, 240.272 nm; integration time, 10 s each).

RESULTS AND DISCUSSION

Effect of Acidity on Enrichment Recovery

Seven aliquots of 1 mL of mixed standard solutions containing 50 μg of Au(III) and Ru(III) ions were pipetted and diluted to 1000 mL with distilled water. Following the analytical procedure, the solutions were enriched by the fiber columns at pH 1–7 and then analyzed. The results in Table I show that the recoveries of trace Au and Ru ions after enrichment by the fiber columns at pH 4–7 were in the range 97–100%. Considering other factors, pH 4 was selected for further work.

In addition, the experiments showed that the chelating fiber cannot adsorbed 1000-fold excesses of K, Na, Ca, Mg, Ba, Co, Y, La, Mn, Ni, Cu, and Cd ions. Excesses of 100-fold of Cr(III), Pb(II), Hg(II), and Be(II) were only adsorbed 60% for Cr, 25% for Pb, 50% for Hg, and 30% for Be at pH 4–7. Bi(III), In(III), V(V), Ga(III), Ti(IV), and Sn(IV) could be adsorbed by the fiber columns to > 90% at pH 5–7, but they did not interfere with trace Au(III) and Ru(III) ions enrichment and determination at pH 4. For noble metals, Pt, Rh, and Ir were hardly adsorbed and Pd was enriched

Table III   Influence of Eluting Acidity on Analyte Desorption from the Fiber Column (in 10 mL HCl)

Ion (ng/mL)	Recovery (%)					6 M (HCl)
	1 M	2 M	3 M	4 M	5 M	
Au (50)	41	50	55	60	52	51
Ru (50)	50	59	61	66	64	61

Table IV Influence of Eluting Concentration of $CS(NH_2)_2$ on Analyte Desorption from the Fiber Column (in 10 mL 4 M HCl)

Ion (ng/mL)	Recovery (%)				
	0.5%	1.0%	1.5%	2.0%	3.0% $(CS(NH_2)_2)$
Au (50)	63	76	83	95	98
Ru (50)	72	79	89	97	99

between 20 and 50% at pH 1–7; so they did not interfere with Au and Ru analysis.

Effect of Flow Rate on Enrichment Recovery

According to the procedure just described, the flow rates through the fiber columns were controlled in the range 0.5–8.0 mL/min. The results in Table II show that trace Au and Ru ions can be quantitatively enriched by the fiber columns at 0.5–3.0 mL/min flow rates with recoveries > 95%. Therefore, 2.0 mL/min was selected as the flow rate for further work.

Influence of Elution Acidity and Concentration of $CS(NH_2)_2$

After trace Au and Ru ions had been enriched by the fiber columns at pH 4.0 at the 2 mL/min flow rate, the columns were eluted with only 10 mL of 1–6 M HCl or with 10 mL of 4 M HCl + 0.5–3.0% $CS(NH_2)_2$ solutions. The results in Tables III and IV show that trace Au and Ru ions cannot be desorbed quantitatively with only 10 mL of 1–6 M HCl, but can be desorbed with 10 mL of 4 M HCl + 3.0% $CS(NH_2)_2$ solution, with recoveries > 97%.

Adsorption Capacity

Two portions of the chelating fiber (0.1 g) were placed in two conical flasks, and 5 mL of 1 mg/mL

stock solutions of Au(III) or Ru(III) were added to the each flask and diluted to 100 mL. The acidity of each solution was adjusted to pH 4.0, and the flasks were shaken on a mechanical shaker. The concentration of ions in each solution was measured by ICP–OES for various intervals of time until equilibrium was reached. The static adsorption capacities of the fiber were calculated as 14.1 mg/g for Au and 15.9 mg/g for Ru. The dynamic adsorbing capacities through column adsorption were 10.9 mg/g for Au and 12.7 mg/g for Ru.

Stability and Reusability

The chelating fiber stored for ~ 1 year was eluted with 10 mL of 4 M HCl + 3.0% $CS(NH_2)_2$ and washed with (1 + 10) ammonia water and then with distilled water to neutrality. This fiber was then used for enrichment and determination of trace Au and Ru ions following the analytical procedure up to eight times. The results show that the fiber still possessed a good enrichment ability for trace Au and Ru ions, with recoveries > 95%. This fiber can resist strong acid and be reused well.

Interference of Other Ions

Different interfering ions were added to 1000 mL of the diluted mixed standard solutions and then enriched and determinated according to the analytical procedure. The results in Table V shows that 200- to 1000-fold excesses of Fe, Al, Ca, Cu, Mn, Zn, Mg, and Ba ions caused little interference with the enrichment and determination of trace Au and Ru ions. This result is because the fiber scarcely adsorbs the foreign ions at pH 4.0.

Analytical Precision and Accuracy

Following the described procedure, 10 portions of diluted mixed standard solutions containing 50 ng/mL of Au and Ru ions were enriched and analyzed. The results show that the recoveries of

Table V Inference of Other Ions on the Recovery of Au and Ru Ions

Ion (50 ng/mL)	Recovery (%)							
	Fe(III) (10)[a]	Al(III) (10)	Ca(II) (50)	Mg(II) (20)	Mn(II) (10)	Cu(II) (30)	Zn(II) (20)	Ba(II) (30)
Au	93	94	96	97	95	94	96	98
Ru	97	92	91	92	94	94	93	93

[a] Concentrations (ng/mL) given in parentheses.

Table VI   Analytical Results for Real Aqueous Solution Samples[a]

	Waste Water					Alloy Sample Solution				
Ion	Found (ng/mL)	Added (ng/mL)	Sum (ng/mL)	Recov. (%)	ETAAS (ng/mL)	Found (ng/mL)	Added (ng/mL)	Sum (ng/mL)	Recov. (%)	Provided (ng/mL)
Au	1.59 ± 0.2	5.0	6.40 ± 0.5	96.2	1.60	60.00 ± 1.2	50.0	108.65 ± 1.0	97.3	60.73
Ru	6.05 ± 0.4	5.0	10.96 ± 0.9	98.2	6.15	43.78 ± 2.0	50.0	92.0 ± 0.8	97.6	44.69

[a] Matrix compositions for waste water solution are Ca, Mg, Ba, Fe, and Al, and for alloy sample solution are Cu, Zn, Mn, Fe, and Mg.

trace Au and Ru ions were in the range 96–99%. The relative standard deviations (RSDs) were 1.8% for Au and 1.9% for Ru ions. Moreover, the accuracy of the combined ICP procedure was checked by analyzing real solution samples using the standard addition method for calibration. The results listed in Table VI show that recoveries of trace Au and Ru ions are $> 96\%$ and that contents of Au and Ru in the samples detected by the method are basically in agreement with the analytical value provided by the plants, with relative errors $< 2.1\%$. In addition, the enrichment and determination of trace Au and Ru ions in other aqueous solution samples by the described method provides satisfactory results as long as the pH is in the range 4–7.

CONCLUSION

The synthesized poly(acrylphenylamidrazone-phenylhydrazide) chelating fiber can quickly and conveniently be used for preconcentration and separation of trace Au and Ru ions from real solution samples containing many matrix elements. This procedure combined with ICP–OES has been proved to be efficient and feasible for the determination of trace Au and Ru ions in some real samples. It offers satisfactory detection limits with sufficient precision and accuracy, and the chelating fiber can be efficiently reused.

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