Synthesis of Polyacrylaminothiourea Chelating Fiber and Properties of Concentration and Separation of Trace Noble Metal Ions from Samples

GONG, Bo-Lin*,a,b(龚波林)   WANG, Yana(王彦)   SUN, Yan-Pub(孙彦璞)
Zhao, Jian-Guoa(赵建国)

a Institute of Modern Separation Science, Northwest University, Xi'an, Shannxi 710069, China
b Department of Chemistry, Ningxia University, Yinchuan, Ningxia 750021, China

A novel polyacrylaminothiourea chelating fiber was synthesized simply and rapidly from nitrilon (an acrylonitrile-based synthetic fiber), which was applied to preconcentrate and separate of trace amount of Au(III), Pt(IV), Pd(IV) and Ir(IV) ions from solution of samples. The analyzed ions can be quantitatively concentrated by the fiber up to a flow rate of 20.0 mL/min at pH 2, and can also be desorbed with 15 mL of 4 mol/L HCl + 3% thiourea from the fiber column with recoveries of 96.5%—100%. The chelating fiber can be reused for ten times, the recoveries of these ions are still over 92%, and hundred to thousand times of excess of Fe(III), Al(III), Ca(II), Mg(II), Ni(II), Mn(II), Cu(II), Zn(II), and Cd(II) cause no interference on the determination of the analyzed ions by inductively-coupled plasma atomic emission spectrometry (ICP-AES). The static saturation adsorption capacities of the fiber for the analytes are in the range of 1.15—2.80 mmol/g. The relative standard deviations for the determination of 20.0 ng/mL each of Au(III), Pt(IV), Pd(IV) and Ir(IV) are in the range of 0.7%—3.0%. The recoveries for test from standard additions to real solution samples are between 96% and 100%. The concentration of each ion in powder sample detected by the method is in good agreement with the certified value.

Keywords   concentration, separation, polyacrylacylaminothiourea chelating fiber, gold, platinum, palladium, iridium

Introduction

The preconcentration and separation trace of noble metals by means of macroporous resins[1-6] or chelating fibers[7-9] have been reported. However, the majority of macroporous resins suffer from a slow rate of uptake of metal ions. Typically, the chelating fibers have low capacities and desorption of noble metals from the fibers is usually difficult. Furthermore, the synthesis of the chelating resins or fibers usually takes a long time and the synthetic process is complicated. In this paper, a new polyacrylacylaminothiourea chelating fiber was synthesized rapidly by a one-step reaction of nitrilon with aqueous aminothiourea (thiosemicarbazide). The structure of the chelating fiber was analyzed by using Fourier transform infrared spectroscopy (FT-IR).[10-11] The properties of the chelating fiber for the preconcentration and separation of trace of Au(III), Pt(IV), Pd(IV) and Ir(IV) ions from aqueous solution sample, as measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES), were studied in detail. Good precision and the accuracy of the proposed method could be achieved by analysis of a real aqueous sample and a powder sample with satisfactory results.

Experimental

Instruments and apparatus

An ICP/6500 inductively-coupled plasma spectrom-

eter (Perkin-Elmer), a model 170-sx Fourier transform IR spectrometer (Nicolet), a Model 1106 Elemental Analyzer (Carlo Erba), and a Model pHs-3A digital pH meter (Analysis Instrument Factory at Beijing, China) were used. The adsorption column is a glass tube (15 cm length, 0.5 cm i.d. and 0.2 cm i.d. at the lower end) containing 0.1 g of polyacrylacylaminothiourea chelating fiber in high-purity water over night, and a small pad of adsorbent cotton-wool has been placed beforehand.

Reagents and standards

Nitrilon (Lanzhou Chemical Factory) was cut with scissors, washed with ethanol and distilled water, and dried under an infrared drying lamp. Reagents of spectral and analytical grade were used for all experiments. The stock solutions of 1.00 mg/mL of the four analyzed ions were prepared by dissolving spectroscopically pure $HAuCl_4 \cdot 4H_2O$, $(NH_4)_2PtCl_6$, $(NH_4)_2PdCl_6$ and $(NH_4)_2$-IrCl$_6$(Shanghai Reagent Factory) respectively in dilute 1.0 mol/L HCl. They were diluted and mixed to give stock standard solutions of 20.0 μg/mL for each of Au, Pt, Pd and Ir in 1.0 mol/L HCl, and the standard solutions were used for all experiments.

Synthesis and characterization of the chelating fiber

A 30 g portion of dried nitrilon (containing 93% acrylonitrile, 5.7% methyl acrylate and 1.3% itaconic acid) and 150 g of 45% aminothiourea (thiosemicarbazide) aqueous solution were placed in a three-necked flask. The mixture was adjusted to pH 8—9 with a NaOH solution, and refluxed for 12 h at 85—95 ℃ with slow stirring. The product was washed with distilled water until neutral and dried under IR irradiation. Thus, a golden-colored polyacrylacylaminothiourea chelating fiber was obtained. Its nitrogen content determined by the Kjeldahl-Gunning method is 29.5%. The synthetic reaction can be briefly expressed by Eq. (1).
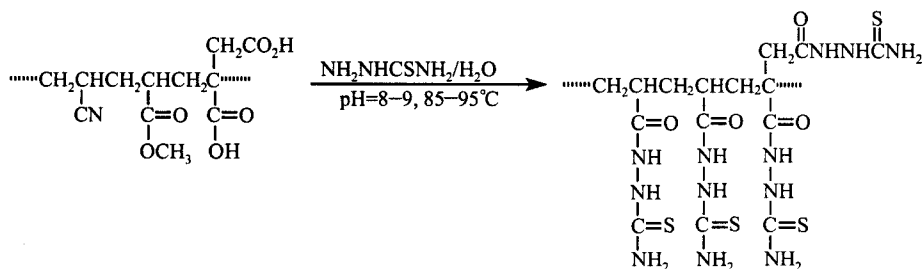
According to the references,[10-12] the IR spectrum of the polyacrylacylaminothiourea chelating fiber can be assigned as follows: 3452.7 and 3340.5 cm^{-1}(ν_{N-H_2} and ν_{N-H}), 2945.9 and 2878.1 cm^{-1} (ν_{C-H} of CH_2 and CH), 1748.1 cm^{-1} ($\nu_{C=O}$), 1224.6 cm^{-1} ($\nu_{C=S}$), 1635.2 cm^{-1} ($\delta_{s NH_2}$), 1419.3 cm^{-1} ($\delta_{s CH_2}$), 1372.1 cm^{-1} (ν_{C-N} of S = C—NH), 1142.4 cm^{-1} (ν_{C-N} of CH_2NH_2), 1054.9 cm^{-1}(δ_{C-N}), 829.6 cm^{-1}(δ_{NH_2}), 778.2 cm^{-1} $\delta_{P CH_2}$), 679.6 cm^{-1} $\delta_{w NH_2}$).

(ν, stretching vibration; δ, bending vibration; δ_s, scissoring vibration; δ_P, rocking vibration, δ_w, wagging vibration). The IR spectrum of chelating fiber presents the N—H and C = S characteristic vibrational adsorption bands (3342.2 and 1224.6 cm^{-1}). A comparison between the IR spectrum of the chelating fiber with that of nitrilon shows that the 2250.5 cm^{-1} of CN vibrational adsorption band disappeares. These observations demonstrate that the analytical functional groups have been attached to the fiber.

Analytical procedure

The mixed standard solutions of Au, Pt, Pd and Ir or real sample solutions were pipetted into beakers (100—1000 mL). The solutions were adjusted to pH 2 with aqueous ammonia and dilute HCl solution and passed through the adsorbing column at a flow rate of 20.0 mL/min. The analytes were desorbed from the columns with 15 mL of 4 mol/L HCl + 3% $CS(NH_2)_2$ solution (70 ℃) at a flow rate of 5.0 mL/min. Subsequently, the ions in the 15 mL of eluate were determined by the ICP spectrometer. Spectrometer conditions

were as follows: forward power, 1100 W; viewing height, 15 mm; Ar plasma gas flow rate, 15 L/min; Ar nebulizer gas flow rate 1.0 L/min; Ar auxiliary gas flow rate, 0.7 L/min; wavelengths: Au, 242.795 nm; Pt, 214.423 nm; Pd, 248.892 nm; Ir, 224.268 nm.

Results and discussion

Effect of acidity on adsorption

Mixed stock standard solutions containing 20.0 ng/mL for each of Au, Pt, Pd and Ir ions were concentrated by means of the column procedure described in the range of 10^{-5}—2 mol/L HCl. The results (Fig. 1) show that trace Au and Ir at 1.0—10^{-5} mol/L; Pt at 10^{-1}—10^{-5} mol/L and Pd at 10^{-2}—10^{-3} mol/L can be enriched quantitatively by the fiber with recoveries over 95% and the recoveries of all elements were higher than 97% at 10^{-2} mol/L. In order to determine these elements simultaneously, pH 2 was selected as the enrichment acidity.
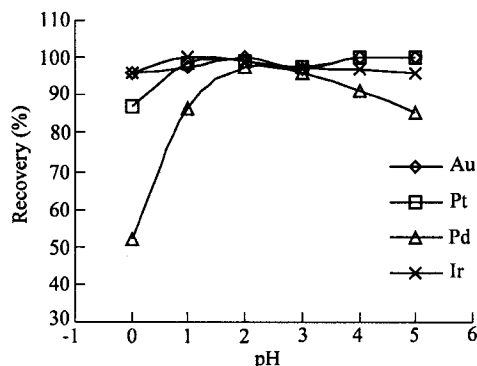

Fig. 1 Effect of pH on preconcentration of noble metals recovery.

In addition, at pH 3, K, Na, Ca, Mg, Ni(II), Cu(II), Co(II), Mn(II), Ga(III) and As(III) were not adsorbed by the fiber column, La(III), Hg(II), Cd (II) and Pb(II) were adsorbed only by 15%—45%, and Ru(III) and Rh(III) were enriched by 60%—70%. Because the fiber adsorbs Au, Pt, Pd and Ir ions more strongly, and their enrichments were not influenced by those other ions either.

Effect of flow rate on enrichment

When the recommended procedure was used, the

flow rate for preconcentration of the analytes on fiber column at pH 2.0 varies between 5.0 mL/min and 35.0 mL/min. The results given in Fig. 2 show that Au, Pt, Pd and Ir ions can be enriched quantitatively at flow rate below 25.0 mL/min with recoveries above 94%. A 20.0 mL/min flow rate was selected for preconcentration velocity.
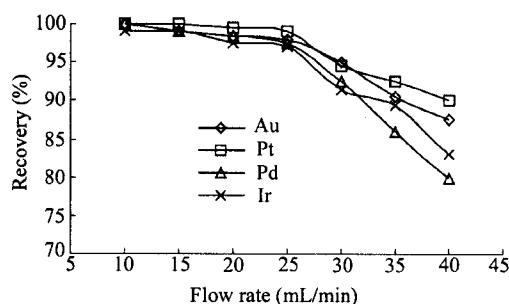

Fig. 2 Effect of flow rate on enrichment recovery.

Influence of desorption acidity

After the trace of Au, Pt, Pd and Ir were enriched on the fiber column following the above procedure, each column was eluted with 15 mL of 2—7 mol/L HCl + 3% CS(NH$_2$)$_2$ solution at 70 ℃. The results in Fig. 3 show that these elements can be desorbed with 15 mL of 4 mol/L HCl + 3% CS(NH$_2$)$_2$ solution from columns with recoveries above 96%. However, it was also observed that when the concentration of the eluent was higher than 4 mol/L HCl or the concentration of CS (NH$_2$)$_2$ was higher than 3%, the ICP-AES results gradually decreased. This occurs because the nebulization rates are reduced relatively to the standard solutions.
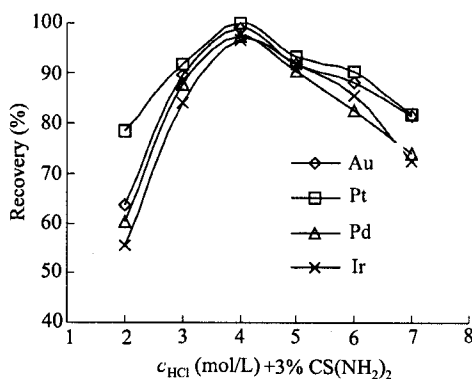

Fig. 3 Influence of desorption acidity on recovery.

Influence of desorption flow rate

After the trace of Au, Pt, Pd and Ir ions had been enriched by the fiber as described in the preceding sections, the influence of the flow rate on desorption of the analytes from the columns with 15 mL of 4 mol/L HCl + 3% CS(NH₂)₂ was investigated. The results in Fig. 4 show that desorption recoveries of Au, Pt, Pd and Ir were higher than 97% for the flow rate at 5.0 mL/min. A 5.0 mL/min flow rate was selected for the eluent flow rate.
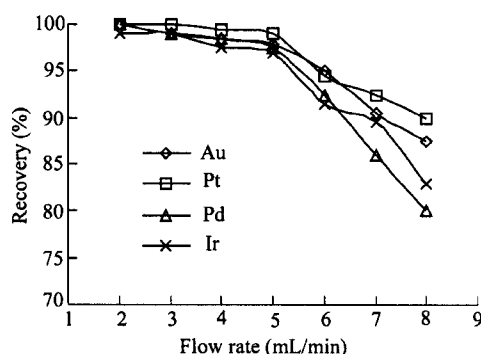

Fig. 4 Influence of desorption flow rate on recovery.

Static saturation adsorption capacity and reuse property

A 0.1 g portion of the fiber was placed in each of the four conical flasks. A stock solution of each of Au, Pt, Pd and Ir ions was added to each flask and diluted to an equal volume of 100 mL. The acidity of each solu-

tion was adjusted to pH 2, and the vessels were shaken in a mechanical vibrator. The concentrations of the above ions in solution were measured at regular intervals of 10 min by ICP-AES until an equilibrium was reached. Thus, the saturated adsorption capacity of the fiber was calculated, which was 2.80 mmol/g for Au (III), 1.75 mmol/g for Pt(IV), 1.56 mmol/g for Pd (IV) and 1.15 mmol/g for Ir(IV), respectively.

When the fiber was used successively for 10 times as described above for the enrichment of Au, Pt, Pd and Ir ions and desorbed from the fiber each time with 15 mL of 4 mol/L HCl + 3% CS(NH₂)₂, the adsorption efficiency was still higher than 92%. The chelating fiber after being used for 10 times did not display obvious swelling effect.

Interference of other ions

Different potential interfering ions were added to dilute analytes standards. The analytes were preconcentrated and determined as described above. The results summarized in Table 1 show that hundred to thousand times of excesses of these ions cause little interference in the recoveries of the analytes. Various other concomitant precious and heavy metals (*e. g.* Os, Ag, Ru, Rh, Cd, Hg, Bi and Tl) did not interfere with the analytes because either their concentrations in real samples were very low or the rates at which they were adsorbed by the fiber were much lower than the adsorption rates of the analytes.

Table 1 Interference of other ions on analyte recoveries

Ions[a]	Recovery[b] (%)								
	Ca(II)	Mg(II)	Fe(III)[c]	Al(III)[c]	Zn(II)	Cu(II)	Mn(II)	Ni(II)	Cd(II)
Au	98.5	99.0	96.5	95.0	98.5	98.5	100	98.0	96.0
Pt	99.4	99.0	95.5	96.0	98.5	98.5	99.0	100	97.8
Pd	100	100	96.0	94.5	97.5	96.0	95.5	100	95.0
Ir	98.0	97.5	95.5	97.0	100	98.5	98.0	97.0	96.0

[a] Concentration of Au(III), Pt(IV), Pd(IV) and Ir(IV) was 50 ng/mL each. [b] Interfering ions concentrations (μg·mL⁻¹) are: Ca(II), 50; Mg(II), 50; Fe(III), 50; Al(III), 50; Zn(II), 50; Cu(II), 50; Mn(II), 30; Ni(II), 30; Cd(II), 30. [c] Al(III) was masked with 0.1 g citric acid and Fe(III) was masked with 0.1 g of hydroxylamine hydrochloride (NH₂OH·HCl).

Analytical precision and accuracy

Under the selected conditions, the recoveries of traces of 20.0 ng/mL for each of Au, Pt, Pd and Ir in 1000 mL of solutions, enriched and determined succes-

sively seven times, were in the range of 97%—100%. The relative standard deviation (R. S. D) was between 0.7% and 2.6%.

The accuracy of the combined preconcentration ICP procedure was checked by analysing real aqueous and

powder samples obtained from a non-ferrous metal smelter using the standard addition method. The results in Table 2 show that the recoveries of Au(III), Pt(IV), Pd(IV) and Ir(IV) ions added to the sample were in the range of 97%—99%, Ds were in the range of 2.1%—3.0%. To evaluate the accuracy of the method, a 0.1000 g portion of a powdered non-ferrous metal sample (containing Zn, Ni, Cu, Cd, Mn, Fe, Al, Ca and Mg etc. matrix elements) from a smelter was weighed and put into a Ni crucible to which 0.3 g of Na_2CO_3 and 1.0 g Na_2O_2 were added. The crucible was heated in a furnace for 7 min at 750 ℃, then cooled to room tem-

perature. The melted sample in the crucible was leached with 30 mL of boiling distilled water into a beaker, to which 30 mL of 12 mol/L HCl was then added with stirring, and heated for 30 min until the solution becomes transparent. The solution was diluted to 1000 mL with distilled water and was adjusted to pH 2 with aqueous ammonia. Then 10 mL of this solution was analyzed according to the analytical procedure and the results are given in Table 3. It can be seen that the results are in good agreement with the values specified (the results obtained by the smelter laboratory using high-temperature electrothermal atomic absorption spectrometry).

Table 2   Analytical results of a real sample with non-ferrous metal matrix[a]

Element	Concentration (ng/mL)			Recovery (%)	R.S.D (%)
	Found ($n = 5$)	Added	Total ($n = 5$)		
Au	30.5 ± 0.5	50.0	80.0 ± 0.8	99.0	3.0
Pt	115.0 ± 2.0	50.0	164.0 ± 2.5	98.0	2.1
Pd	49.0 ± 1.0	50.0	98.0 ± 1.6	98.0	2.5
Ir	45.0 ± 0.7	50.0	93.5 ± 1.2	97.0	2.7

[a] 0.1 g citric acid and 0.1 g $NH_2OH \cdot HCl$ were added.

Table 3   Analytical results of digested powder sample solution diluted in 1000 times

Element	Specified value[a] ($\mu g/mL$)	Found[b] ($\mu g/mL$)	R.S.D (%)
Au	0.320	0.318	3.2
Pt	0.650	0.640	2.3
Pd	0.380	0.375	2.7
Ir	0.330	0.327	3.0

[a] Results obtained by the smelter laboratory using high-temperature electrothermal atomic adsorption spectrometry; [b] Average of five determinations.

Conclusion

A new polyacrylacylaminothiourea chelating fiber shows a high adsorption selectivity for Au(III), Pt(IV), Pd(IV) and Ir(IV) ions, and the adsorbed ions can be readily desorbed from the fiber column by a 15 mL of 4 mol/L HCl + 3% thiourea solution. The fiber also presents the advantage of lower interference, higher adsorption capacity, better reuse ability and higher chemical mechanical stability than those reported.[1-9] Furthermore, the synthesis of the fiber is simple and economical. Preconcentration by this fiber combined with ICP-AES can be applied to the determination of trace Au(III), Pt(IV), Pd(IV) and Ir(IV) ions in real solution samples

and powder samples with satisfactory results.

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