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Application of an imidazoline group-containing chelating fiber for the determination of trace noble metals in superhigh-temperature alloys

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Abstract An imidazoline group-containing chelating fiber was prepared by means of the reaction of nitrile groups with ethylenediamine in an hydrazine-modified polyacrylonitrile fiber. The adsorption properties of the chelating fiber for Au(III), Pd(II), Pt(IV), Ir(IV), Os(IV), Rh(III) and Ru(IV) ions, such as binding capacity, distribution coefficient, sorptive rate and quantitative elution of Au(III), Pd(II) and Pt(IV) ions were investigated. The imidazoline group-containing chelating fiber possessed high binding capacities and good adsorption kinetic properties, exhibited high affinity for noble metals in 0.1–1.0 mol/L HCl and could be efficiently re-used. After the separation of trace Au(III), Pd(II) and Pt(IV) ions from a matrix using the chelating fiber, these ions could be determined by ICP-AES with satisfactory results, and the relative standard deviation for Au(III), Pd(II) and Pt(IV) ions was less than 6%.

Introduction

Noble metals are a class of trace elements which are components in superhigh-temperature alloys [1]. But their trace levels and the coexistence of noble metals with other metal ions result in difficult extraction, separation and determination for these ions.

Many separation and preconcentration techniques including fire assay [2], coprecipitation [3], solvent extraction [4, 5] and ion-exchange or sorption [6, 7] have been proposed for the determination of noble metals in various environmental samples. The adsorption method on chelat-

ing resins has a high adsorption capacity for noble metals [8–11], but a slow sorption rate. Recently, fibrous sorbents, which exhibit good kinetic properties with larger surface areas than gel-structure granular ion-exchangers and porous copolymers which can be used in the forms of filaments, belt and non-woven material, has drawn the attention of researchers. Many ion exchange chelating fibers containing 2-mercaptobenzothiazole [6], thioureido [12], thioamide [13, 14], benzimidazole [15, 16], amidoxime [17] have been used to preconcentrate noble metals. Resins containing imidazoline groups for the extraction of noble metals have been described [18, 19].

In this study, we developed a new chelating fiber with imidazoline groups bound to the polyacrylonitrile fiber for the separation and determination of noble metals from matrix components. The sorption properties of the chelating fiber for noble metals were investigated in detail. The material recommended was applied to the preseparation and determination of trace noble metals in superhigh-temperature alloys.

Experimental

Instruments and reagents. Spectroflame ICP Argon-plasma emission spectrometer (ICP-AES) was used for the determination of all metal ions. The selected analytical wavelengths were: Au 265.595 and 242.795 nm, Pd 340.458 nm, Pt 265.945, 306.471 and 177.700 nm, Ir 224.268 nm, Os 228.226 nm, Rh 343.489 nm, and Ru 267.876 nm. The optimum instrumental parameters were: Forward power 1200 W, Reflected power < 5, Coolant gas flow rate 16 L/min, Auxiliary gas flow rate 0.3 L/min, Nebulizer gas flow rate 0.8 L/min, Nebulizer gas pressure $2.38 \cdot 10^5$ pa, Sample uptake rate 1.5 mL/min. A HZQ-C air-bath shaker was employed to shake the solution.

Standard solutions of noble metals (1000 mg/L) were provided by the Research Institute of Noble Metals, Academia Sinica. All other chemicals were of analytical grade or better. Deionized water was used throughout.

The superhigh-temperature alloy was obtained from Central Iron and Steel Research Institute and its composition is given in Table 1. The polyacrylonitrile fiber (diameter < 10 μ m) was purchased from a Chinese Chemical Factory, Beijing.

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Table 1 Composition (%) of the superhigh-temperature alloy sample

	Elements												
	Ni	Fe	Cr	Nb	Mo	Ti	Al	Co	Cu	B	C	Si	Mn
Components (%)	52.5–53.5	18–19	18–19	5.0–5.2	3.0	1.0	0.50	< 0.1	0.018	0.003	0.34	0.12	0.02

Synthesis of the imidazoline group-containing chelating fiber. 25 g of polyacrylonitrile fiber and 1000 mL of hydrazine hydrate was reacted in a 1.25 L flat-flange reaction vessel for 2–2.5 h at 90–94 °C, then suction-filtered, washed with ethanol and dried at 55–60 °C overnight [20]. A mixture of 800 mL ethylenediamine and 1 g sulfur flour in a flat-flange reaction vessel was heated to 90 °C, and 20 g of the dry hydrazine-modified fiber was added. After heating for 7 h at 95–98 °C, the reaction system was cooled, suction-filtered, washed with 50–60 °C deionized water and dried at 50–60 °C overnight. The uptake of the imidazoline group in the chelating fiber was verified by infrared spectroscopy analysis [21].

Binding capacity. A batch technique was applied to determine the binding capacity of the chelating fiber. Triplicate samples (0.10 g each) of the chelating fiber were equilibrated by shaking for 24 h in 10 mL of 0.01 mol/L solution of individual metal salts containing 0.10 mol/L HCl at 25 °C. The residual concentration of metal ions was analyzed by ICP-AES. The distribution coefficients (D) were also determined by a similar method.

Adsorptive rate of precious metals. Batch experiments were performed to investigate the adsorption rate of the chelating fiber for noble metals. A mixture of 50 mL of 0.5 mol/L HCl and 0.5 mol/L NaCl containing 1 mg of Au(III), Pd(II) and Pt(IV), 0.5 mg of Ru(IV), Rh(III), Os(IV) and Ir(IV) ions was immediately added to 0.40 g of the fiber samples, which were previously transferred into 1000 mL flasks. After a time interval, 0.5 mL aliquots of the tested solutions were collected, centrifuged and decanted to separate any remaining fiber. The metal ion concentrations in solution were determined by ICP-AES. The amounts of added ions did not exceed the saturation adsorption capacity of the chelating fiber for these metal ions.

Preparation and adsorption procedure of the fiber column. The chelating fiber was soaked in 0.1 mol/L HCl overnight before use. Dry 0.40 g of the chelating fiber suspended in water was slurry-packed into a glass column (15 cm long, inner diameter 0.7 cm) rinsed with deionized water. The bed height of the chelating fiber column was 4 cm.

A 10 mL volume of 10 mg/L either Au(III), Pd(II) or Pt(IV) ion in 0.5 mol/L HCl was passed through the adsorption columns at flow rates of 1–5 mL/min. After the passage of the solutions, the columns were rinsed twice with 10 mL of 0.5 mol/L HCl. The concentrations of metal ions in effluents were determined by ICP-AES.

Preparation and determination of real sample. 1–2 g of superhigh-temperature alloy samples were placed in a 500 mL beaker, and 50 mL of *aqua regia* was added. Then, the beaker was heated at 150 °C until the sample was completely dissolved. After the excess of HCl and HNO₃ was evaporated, 20 mL of 6 mol/L HCl and an amount of 20 µg or 10 µg of Au(III), Pd(II), and Pt(IV) ions were added to the beaker, then the mixed solution was diluted to a vol-

ume of 500 mL. In this case, the sample solution contained 0.1–0.5 mol/L HCl.

The prepared sample solution was passed through the fiber-filled column using a peristaltic pump at a flow rate of 2 mL/min. After washing with 50 mL of 0.1 mol/L HCl, the Au(III), Pd(II), and Pt(IV) ions adsorbed in the column were eluted with 10 mL of 1.0 mol/L HCl and 5% thiourea, as well as 10 mL of 2 mol/L HClO₄ and 5% thiourea at a flow rate of 2 mL/min. The eluted ions were determined by ICP-AES.

Results and discussion

Binding capacity

The chelating fiber capacities for noble metals and other ions are reported in Table 2. The results show that the imidazoline group-containing chelating fiber exhibits high adsorption capacities for noble metals in comparison with those of the other ions. The specific capacities for noble metal ions decrease in the following sequence: Au(III) > Pd(II) > Os(IV) ≈ Ir(IV) > Pt(IV) > Rh(III) > Ru(IV) and the adsorption capacities for Fe(III), Co(II), Ni(II), Cr(III), Mn(II), Cu(II) and Al(III) ions are low.

Distribution coefficients(D)

To evaluate the affinity of fibrous sorbent, the D values for the metal ions between the chelating fiber and the liquid phase are summarized in Table 3. It is evident that Au(III), Pd(II), Pt(IV), Os(IV), Ru(IV), Ir(IV) and Rh(III) ions are strongly adsorbed by the chelating fiber even at high concentration of HCl; whereas, the D values of the other metal ions are remarkably low in a wide concentration range of HCl. The results show that the newly developed chelating fiber has excellent selective sorption properties for precious metal ions and provides a possibility for the separation of noble metals from matrix components.

Sorption rates

The adsorption rate curves of mixed noble metal ions are shown in Fig. 1. As can be seen, after 5 min treatment

Table 2 Specific capacity of the imidazoline group-containing chelating fiber for metal ions in 0.1 mol/L HCl

Unit	Metal ions													
	Au(III)	Pd(II)	Pt(IV)	Ir(IV)	Os(IV)	Rh(III)	Ru(IV)	Ni(II)	Co(II)	Cr(III)	Mn(II)	Fe(III)	Cu(II)	Al(III)
mg/g	724.0	180.8	184.3	195.9	194.9	89.8	69.1	0.0	0.88	1.52	3.55	0.44	3.02	0.05
mmol/g	3.68	1.70	0.94	1.02	1.03	0.87	0.68	0.0	0.015	0.029	0.065	0.008	0.048	0.002

Table 3 Distribution coefficients (mL/g) of metal ions between the chelating fiber and aqueous phase in various concentration

Metal ions	Concentration of HCl (mol/L)				
	0.1	0.5	1.0	2.0	4.0
Au(III)	3.68×10^4	3.29×10^4	2.90×10^4	1.88×10^3	3.98×10^2
Pd(II)	6.58×10^4	3.99×10^4	9.80×10^3	1.36×10^3	2.63×10^2
Pt(IV)	3.64×10^4	8.01×10^3	1.80×10^3	3.64×10^2	2.31×10^2
Ir(IV)	2.36×10^4	1.24×10^4	6.28×10^3	3.25×10^3	6.39×10^2
Os(IV)	3.01×10^4	3.21×10^3	1.43×10^3	6.19×10^2	4.07×10^2
Rh(III)	4.95×10^2	5.78×10^2	6.25×10^2	1.17×10^2	1.18×10^2
Ru(IV)	6.80×10^2	2.67×10^2	1.65×10^2	1.46×10^2	1.51×10^2
Ni(II)	0.85	1.64	0.0	0.25	0.94
Co(II)	1.36	0.17	0.08	0.25	1.18
Cr(III)	2.57	0.81	1.35	1.63	1.53
Mn(II)	1.51	0.20	0.20	0.40	0.0
Fe(III)	1.66	0.29	0.0	0.10	1.96
Cu(II)	17.1	11.28	10.85	8.87	9.70
Al(III)	2.13	1.43	2.99	2.70	2.74

Fig. 1 Simultaneous sorption of noble metal ions by the imidazole group-containing chelating fiber

time, an extraction percentage of 90% or greater yields for Pd(II), Pt(IV), Os(IV) and Ir(IV) ions is obtained, while the adsorption percentages of Au(III), Ru(IV) and Rh(III) are below 85%. After stirring for 24 h, the extraction yields of Au(III), Ru(IV) and Rh(III) ions reach 99, 67 and 85%, respectively. This phenomenon is mainly explained by the competitive adsorption among noble metal ions, in which the modified chelating fiber has a higher affinity for Au(III), Pd(II), Pt(IV), Os(IV) and Ir(IV) ions than for Ru(IV) and Rh(III).

In addition, the effect of different flow rates on the adsorption efficiency was tested at flow rates from 1 to 5 mL/min. The results show that Au(III), Pd(II) and Pt(IV) ions can be concentrated quantitatively at flow rate less than 5 mL/min.

Selection of conditions for column desorption

After a mixture containing 100 μ g of Au(III), Pd(II) and Pt(IV) ions passed through the fiber column, the sorbed noble metals were immediately eluted with an eluant containing different concentrations of HCl and 5% thiourea.

The results are shown in Table 4. The Au(III) and Pd(II) ions can be quantitatively desorbed with a mixture of 20 mL of 0.5–2 mol/L HCl and 5% thiourea at a flow rate of 3 mL/min with recoveries of 98–102%. This result is attributed to the formation of the complex of Au(III) and Pd(II) ions with thiourea [22]. The recovery of Pt(IV) is only 56–57%. To elute Pt(IV) ion from the fiber column, a mixed solution of 2 mol/L HClO_4 and 5% thiourea as eluant was tested for the desorption of Pt(IV) ion, and a recovery of 98% can be achieved.

Effect of interfering ions

A mixture, containing matrix ions 300 mg/L of Fe(III), 500 mg/L of Ni(II), 5 mg/L of Cu(II), Co(II) and Al(III), 200 mg/L of Cr(III), 10 mg/L of Ti(IV) and Mo(VI) as well as 20 μ g/L of Au(III), Pd(II) and Pt(IV) ions was used as experimental sample. The results demonstrate that the presence of large amounts of other ions has no significant effect on the quantitative recovery of Au(III), Pd(II) and Pt(IV) ions. Owing to the lower concentrations in the real sample, other precious and heavy metals (e.g. Ru(IV), Rh(III), Os(IV), Ir(IV), Ag(I), Cd(II), Hg(II), Bi(III) and Tl(I)) were not studied in this experiment.

Reusability of the chelating fiber

After the dry chelating fiber had been stored at room temperature for about 2 years, trace amounts of Au(III),

Table 4 Effect of HCl concentration on recovery (%) using 20 mL of a mixture of various concentration of HCl and 5% thiourea as eluent

Noble metals	Concentration of HCl (mol/L) + 5% thiourea			
	0.5	1.0	2.0	4.0
Au(III)	97.8	101.1	100.2	98.8
Pd(II)	98.6	98.4	101.5	90.7
Pt(IV)	57.8	56.8	56.6	57.5

Table 5 Analysis results ($\mu\text{g}/500\text{ mL}$) and recovery (%) of noble metals in the superhigh-temperature alloy^a

Metals	One gram super alloy							Two grams super alloy						
	Added	Found				Average	Recovery	Added	Found				Average	Recovery
Au(III)	20.0	19.8	20.8	19.4	19.5	19.9	99.4	10.0	9.99	9.89	9.84	9.52	9.85	98.5
		19.6	19.9	20.3	20.1				9.72	10.2	9.77	9.87		
Pd(II)	20.0	19.1	19.5	19.5	18.9	19.4	96.9	10.0	9.82	9.98	9.69	10.3	9.95	99.5
		19.6	19.1	19.5	19.7				9.79	9.80	9.91	10.4		
Pt(IV)	20.0	19.9	18.7	19.5	19.0	19.2	96.0	10.0	9.43	9.55	9.42	9.76	9.59	95.9
		19.4	19.0	19.1	18.9				10.1	9.58	9.82	9.03		

^a Eight measurements of each sample, the RSD was less than 6%

Pd(II) and Pt(IV) ions in solution were passed through the chelating fiber column, then they were eluted subsequently with a mixture of 1 mol/L HCl and 5% thiourea as well as 1 mol/L HClO_4 and 5% thiourea. The column was washed with deionized water until neutrality. The chelating fiber column was repeatedly used ten times according to the above procedure. The results show that quantitative extraction and recovery (> 96%) were achieved. Moreover, a swelling of the chelating fiber is not observed after tenfold use.

Analysis of Au(III), Pd(II) and Pt(IV) ions in superhigh-temperature alloy

Because a certified alloy sample containing trace noble metals is not available, the accuracy of the proposed method for the determination of trace Au(III), Pd(II) and Pt(IV) ions in superhigh-temperature alloy was assessed by adding trace noble metals to the alloy sample before matrix separation and preconcentration. The recoveries of three noble metal ions are given in Table 5, showing sufficiently high recoveries (> 95%), high reliability and validity of this method. The developed method is recommended to determine trace Au(III), Pd(II) and Pt(IV) ions contained 0.002–0.0005% in super alloy samples with the relative standard deviation less than 6%.

Conclusion

The imidazoline group-containing chelating fiber is simply prepared by means of two steps chemical reaction. The imidazoline group of the fiber exhibits high affinity for noble metals compared with other metal ions in 0.1–1.0 mol/L HCl. The chelating adsorption technique using the newly developed imidazoline group-containing chelating fiber column provides an effective separation and preconcentration procedure for the determination of trace noble metals in a superhigh-temperature alloy. In 0.1–1.0 mol/L HCl medium, trace amounts of Au(III), Pd(II) and Pt(IV) ions can be separated from other metal ions. The combination of this pre separation technique with sample analysis by ICP-AES provides a standard

method for the determination of trace noble metals in superhigh-temperature alloy.

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