Preconcentration and separation of trace Pd(II) and Pt(IV) with silica gel bonded by aminopropyl-benzoylazo-4-(2-pyridylazo)-resorcinol

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This paper reports a simple and highly selective method for preconcentrating and separating of trace Pd(II) and Pt(IV) with silica gel bonded by aminopropyl-benzoylazo-4-(2-pyridylazo)-resorcinol (ABPR·SG). ABPR·SG is stable in solution from 6 mol/L HCl to pH 7.0 and in common organic solvents. The maximum adsorptive capacity of Pd(II) on ABPR·SG is 362 μmol/g. After preconcentration and separation by using ABPR·SG column, Pd(II) and Pt(IV) of μg/L level in artificial water samples can be measured reliably by common spectrophotometry. The maximum concentration factors of Pd(II) and Pt(IV) on ABPR·SG column are 143 and 125 respectively. The chromatographic column packed with ABPR·SG can be reused. The method is simple and efficient.

Keywords Preconcentration, separation, ABPR·SG, spectrophotometry

Introduction

Preconcentration and separation methods for modern analytical chemistry are very important. Silica gel used as solid support for chelating groups shows faster metal ion-exchange kinetics and the better mechanical strength than most of chelating resins, so silica gel modified by chelating reagents for preconcentrating and separating metal ions have gained growing interest in recent years.[1-9] In the study, the metal ions were usually determinated by atomic adsorption spectrometry or inductively coupled plasma atomic emission spectrometry. The apparatus used was more expensive, and the method was not very simple.

A few modified silica gels have been prepared and used in our laboratory with some chelating for preconcentration and separation of some trace metal ions.[10-14] They can greatly improve the adsorbability of silica gel and the selectivity for metal ions. In this paper, a new silica gel bonded by aminopropyl-benzoylazo-4-(2-pyridylazo)-resorcinol (ABPR·SG) was prepared. The study indicated that ABPR·SG was stable in strongly acidic solutions and common organic solutions. Pd(II) and Pt(IV) of μg/L level in artificial water samples can be preconcentrated by ABPR·SG column rapidly, then determined by common spectrophotometry conveniently.

Experimental

Reagents and apparatus

Standard solutions of 1.000 mg/mL of each metal ion were prepared by dissolving pure metals or corresponding metal salts in nitric acid, hydrochloric acid, hydrofluoric acid or sulphuric acid according to their characteristics. All working solutions were obtained by dilution with deionized water to 10 μg/mL.

For buffer solutions we used the following: Britton-Robison (BR) buffer solutions (0.1 mol/L, pH 1.0—10.0),[15] sodium acetate (1.0 mol/L, pH 5.0), sodium borate (0.4 mol/L, pH 8.0,9.5).

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The silica gel (SG, 60—80 mesh, 10 μm) was made in Haiyang Chemical Factory, Qingdao City, China. (Aminopropyl)triethyl-oxysilicane (KH550) was obtained from Gai County, China. It was distilled at 2000 Pa and the fraction was collected between 109 and 112℃.

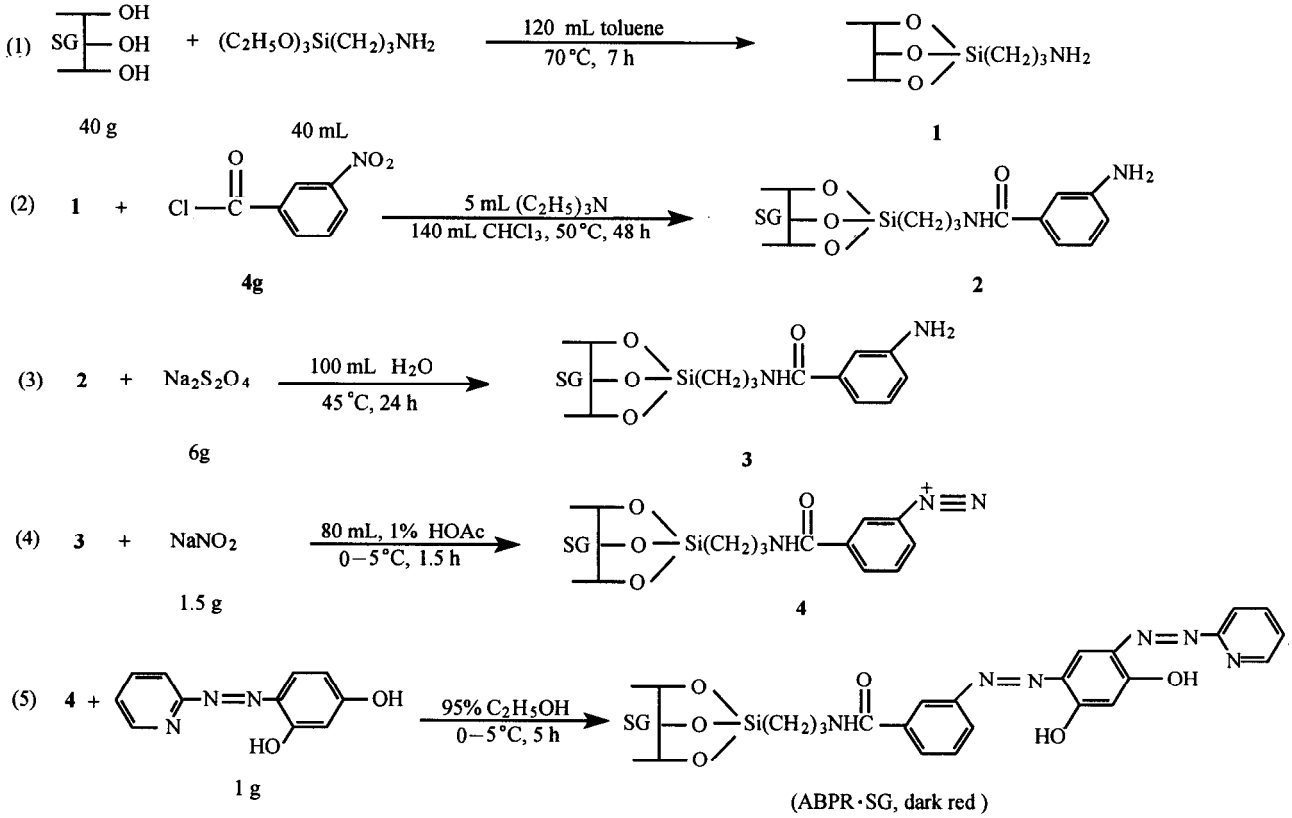
A glass tube (200 mm × 10 mm i.d.) was used as a chromatographic column and washed with 95% ethanol + hydrochloric acid (1 + 1), EDTA aqueous solution, HNO_3 (1 + 1), and deionized water successively.

All chemicals used here were of analytical grade.

A Shimadzu UV-120-02 spectrophotometer (Japan), a Model 821 pH meter (Zhongshan University, China), and a Nicolet FTIR 7199B infrared spectrophotometer (USA) were used during the study.

Preparation of ABPR·SG

Silica gel was immersed in hydrochloric (1 + 1) for two days and then washed with deionized water until no chloride appeared in the washings. The cleaned silica gel was dried at 110℃ for one day. The procedures of synthesizing ABPR·SG can be indicated by the following reactions:



Batch experiments

In several 50 mL glass-stoppered Erlenmeyer flasks, 0.1 g of ABPR·SG, a suitable amount of metal ion and buffer solution were added. These mixtures in the Erlenmeyer flasks were shaken mechanically at room temperature for a certain period of time. After standing, the unextracted metal ion in the solution phase was measured by spectrophotometry. This method was used to study the effects of pH and shaking time on the retention of metal ions on ABPR·SG, and to measure the maximum adsorption capacity of Pd(II) on ABPR·SG.

Column experiments

Certain ABPR·SG soaked in buffer solution was

packed in glass column. The solution containing metal ion was adjusted to a suitable pH and percolated through the column at certain flow rate. Then the metal ion retained on the column was eluted with suitable eluant at lower flow rate and determined spectrophotometrically.

Measurement of the amount of metal ions

The amount of metal ion was measured by spectrophotometry.[13]

Results and discussion

Infrared spectral analysis for ABPR·SG *and* SG

ABPR·SG (with 10 μm SG) was synthesized according to the above-mentioned procedures. 1 mg of ABPR·SG or SG was ground with 100 mg of KBr into powder and pressed to tablet respectively. The spectra of ABPR·SG and SG were recorded on an infrared spectrophotometer (Fig.1). ν(cm^{-1}): 3600—3200(O—H, N—H); 3170, 3074 (Ar—H); 2891(C—H); 1645 (C=O); 1546(N—H); 1274(N—H, C—N). There is a great difference between the spectra of ABPR·SG and SG. It can be proved that the synthetic product is ABPR·SG.

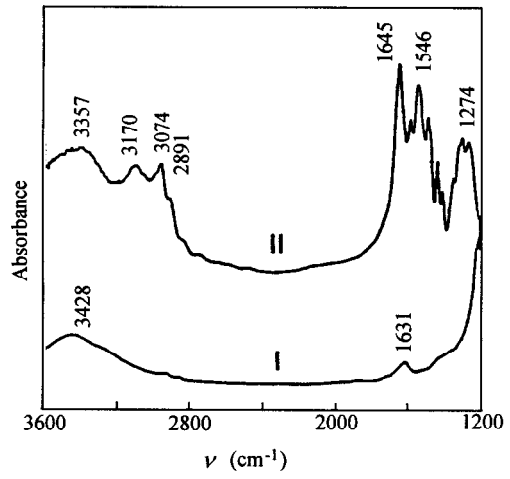


Fig. 1 Infrared spectra: I. SG; II. ABPR·SG (SG as blank).

Stability of ABPR·SG

A few common organic solvents (ethanol, acetone, chloroform) and different aqueous solutions between 6 mol/L HCl and pH 7.0 with 0.2 g of ABPR·SG were shaken for 30 min, respectively. The supernatants were colorless. It is obvious that ABPR·SG is stable in the range of 6 mol/L HCl to pH 7.0 and in common organic solvents. The behaviors strongly support that the ligand is chemically bonded to silica gel and not simply adsorbed on the surface. When ABPR·SG was kept in common glass desiccator for one year, the results of experiments could still be repeated.

Effect of pH *on the adsorption of metal ions*

The adsorptivity of metal ions on ABPR·SG in different buffer solutions was examined by batch method. It is obvious from Fig. 2 that the metal ions investigated show a considerable variation of percentage retention with changes in pH. Pd(II) and Pt(IV) can be adsorbed on ABPR·SG with 95—100% retention when the acidity is greater than pH 1.0, but common transition metal and the other metal ions can be retained on ABPR·SG in weak acid or neutral solution, which is indicative of the higher selectivity towards Pd(II) and Pt(IV). We can also know from Fig. 1 most of metal ions will not interfere with the extraction of Pd(II) or Pt(IV) if the solutions are controlled at pH 1.0. Therefore, pH 1.0 was chosen for separating Pd(II) or Pt(IV) from the others as following study.

Effect of shaking time on retention of Pd(II) *or* Pt(IV)

The solutions containing 50 μg/15 mL Pd(II) or Pt(IV) and 0.1 g of ABPR·SG were shaken. It is notable from Fig. 3 that Pd(II) is rapidly extracted after only 5 min of shaking, corresponding to about 100% extraction of the Pd(II) present in the solution. But a maximum value of Pt(IV) on ABPR·SG is reached after 30 min.

Maximum adsorption of Pd(II) *on* ABPR·SG

At pH 1.0, changing the concentration of Pd(II), the adsorption capacity of Pd(II) on ABPR·SG was different. Maximum adsorption capacity on ABPR·SG is 362 μmol/g for Pd(II) (Fig. 4). It is satisfactory for the analyzing trace elements.

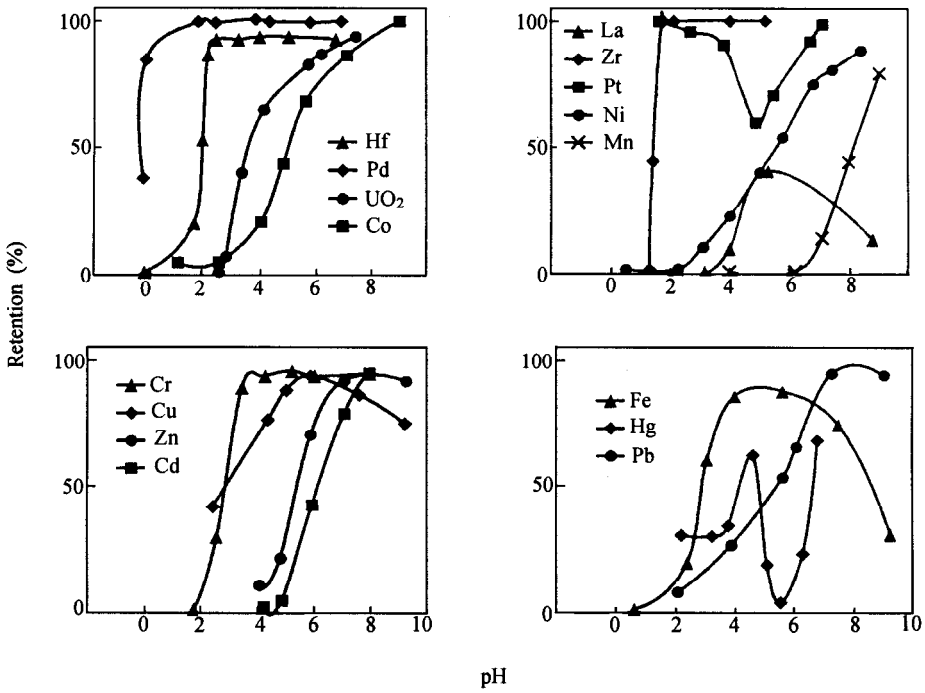


Fig. 2 Effect of pH on the adsorption of metal ions (0.1 g of ABPR·SC, 50 μg/15 mL metal ions, shaking time 30 min).

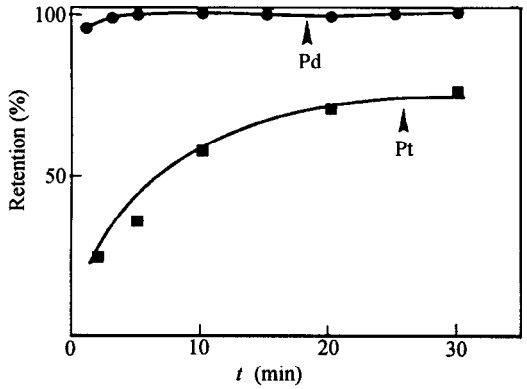


Fig. 3 Effect of shaking time on retention of Pd(II) and Pt(IV): 0.1 g of ABPR·SG, 50 μg/15 mL metal ions at pH 1.0 solution.

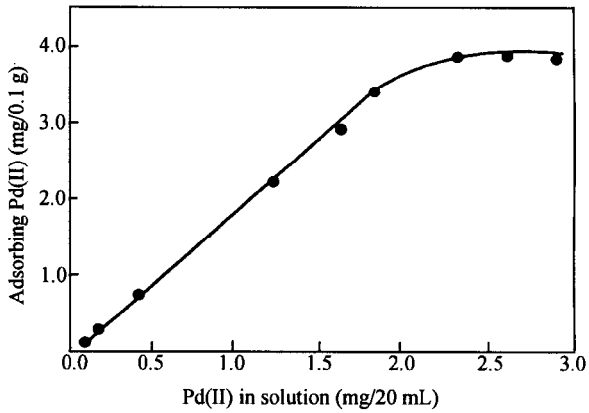


Fig. 4 Maximum adsorption of Pd(II) on ABPR·SG.

Elution curves of Pd(II) *and* Pt(IV)

4.5 g of ABPR·SG was immersed in pH 1.0 solution and packed in a glass column. The height of packing material was 6 cm in this column. 50 mL of solution containing Pd(II) or Pt(IV) (20 μg, at pH 1.0) was passed through the column with 2 mL/min flow rate, then Pd(II) or Pt(IV) was eluted by solution of 0.03 mol/L thiourea in 0.1 mol/L HCl with 0.2 mL/min flow rate. The elution curves of Pd(II) and Pt(IV) are shown in Fig. 5. When the eluants were collected from 2.0 to 9.0 mL and from 2.5 to 10.5 mL for Pd(II) and Pt(IV) respectively, both the recoveries of Pd(II) and Pt(IV) were 100%.

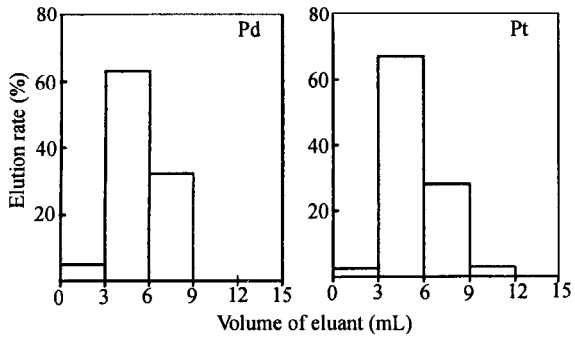


Fig. 5 Elution curves of Pd(II) and Pt(IV).

Preconcentration and recoveries of Pd(II) *and* Pt(IV)

According to the conditions of elution curves of Pd(II) and Pt(IV), 20 μg of Pd(II) or Pt(IV) in different volumes was made up and passed through ABPR·SG column, then Pd(II) or Pt(IV) preconcentrated on column was eluted and determined as above. The maximum concentration factors of Pd(II) and Pt(IV) in Table 1 are 286 and 250, respectively.

Table 1 Preconcentration and recoveries of Pd(II) and Pt(IV)

Solution volume	Recovery (%)		Concentration factor	
(mL)	Pd(II)	Pt(IV)	Pd(II)	Pt(IV)
50	97	100	7	6
200	97	97	29	25
1000	95	95	143	125
2000	97	93	286	250

Effect of flow rate on the recoveries of Pd(II) *and* Pt(IV)

The same solutions (50 μg/1000 mL Pd(II) or Pt(IV) at pH 1.0) were percolated through ABPR·SG column with different flow rates. The recoveries of Pd(II) and Pt(IV) are satisfied (Table 2) when eluting rates are lower than 11.0 and 4.8 mL/min, respectively, because the adsorptive equilibration is reached faster between Pd(II) and ABPR·SG than between Pt(IV) and ABPR·SG (Fig. 3).

Table 2 Effect of flow rate on the recoveries of Pd(II) and Pt(IV)

Pd(II)	Flow rate (mL/min)	3.0	3.8	6.5	7.5	9.4	11.0
	Recovery (%)	95	97	100	95	100	99
Pt(IV)	Flow rate (mL/min)	4.0	4.8	11.0			
	Recovery (%)	99	95	89			

Preconcentration and determination of Pd(II) *and* Pt(IV) *in the artificial water sample*

The artificial water sample (1 L, at pH 1.0), containing 20 μg of Pd(II) or Pt(IV), and Pb(II), Cr(III), Ni(II), UO_2(II), Zn(II), Zr(IV), Hf(IV), La(III) (the amount of each ion is 200 μg), 20 μg of Hg(II) and 20 μg of Cu(II), was passed through ABPR·SG column, and then preconcentrated Pd(II) or Pt(IV) was eluted. The recoveries of Pd(II) and Pt(IV) are 100% and 99% respectively, and the concentration factors are 143, 125 for Pd(II) and Pt(IV).

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