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SYNTHESIS OF FUNCTIONAL RESINS CONTAINING HETEROCYCLIC RINGS AND THEIR SORPTION PROPERTIES FOR NOBLE-METAL IONS

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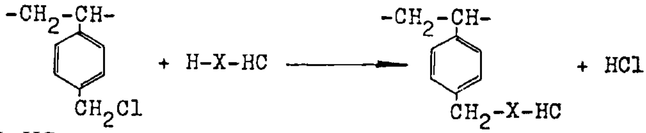
ABSTRACT

Five kinds of functional resins, 2-aminopyridine resin (2-APR), 3-APR, 4-APR, 2-hydroxypyridine resin (2-HPR), and 2-thiolbenzothiazole resin (2-TBTR), were synthesized. The functional group capacities of the resins were 3.0-4.2 mmol/g resin. The sorption capacities of 4-APR, 3-APR, and 2-APR for Au(III) and Pt(IV) were 3.12-3.22 mmol Au(III)/g APR and 1.27-1.60 mmol Pt(IV)/g APR. The molar complex ratios, Au(III)/NH–C_5H_4N and Pt(IV)/NH–C_5H_4N were 0.84-0.97 and 0.34-0.48, respectively. Selective sorption of 4-APR for various coexistent metal ions over a wide acidity range (1-5 *N* HCl) was in the following order: Pt(IV) > Au(III) > Cd^{2+} > Zn^{2+} > Pd(II) > Mn^{2+}, Cu^{2+}, Fe^{3+}. The Au(III) adsorbed on APR can be quantitatively eluted with 2% aqueous thiourea. The regenerated APR can be reused without apparent decrease in the sorption capacity for Au(III). The separation of Au(III) and Cu^{2+} was studied preliminarily. The excellent properties show that APR may be used in the gold industry. The sorption capacities of 2-HPR for Au(III) is 0.99 mmol Au(III)/g 2-HPR. That of 2-TBTR for Au(III) is less than that of APR. 2-HPR is stable below 100°C, while 4-APR and 2-APR are stable below 80°C in air.

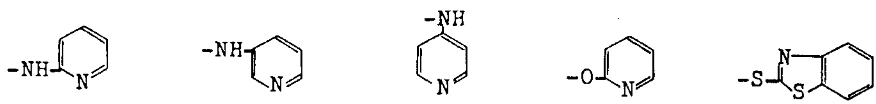
INTRODUCTION

A series of new functional resins bearing dithiocarbamate groups and its oxidation products [1]; cyclic sulfite, cyclic carbonate [2]; amino (β-hydroxyl)-formate, amino (β-hydroxyl)sulfite [3]; 4-(2-pyridylazo)resorcinol [4]; natural humic acid [5]; and ellagitannic acid [6] have been reported recently by the author and his coworkers. The sorption properties of the above-mentioned functional resins for many kinds of heavy-metal, noble-metal, and rare-metal ions have been determined. Some of these resins are useful in separation and recovery of useful metal ions, separation of heavy metal ions from wastewater, preconcentration, and determination of trace metal ions in natural water.

In the present work five kinds of new functional resins bearing a heterocyclic ring have been synthesized according to the following reaction:



where –X–HC:



Aminopyridine resins (APR) have high sorption capacities for Au(III). The Au(III) adsorbed on 4-APR can be quantitatively eluted with 2% aqueous thiourea. The regenerated 4-APR can be reused without apparently decreased sorption capacity for Au(III). These excellent properties of APR may introduce its use in the gold industry. The sorption properties of 2-hydroxypyridine resin (2-HPR) and 2-thiobenzothiazole resin (2-TBTR) have been also determined.

EXPERIMENTAL

1. Materials

Macroporous chloromethylated polystyrene beads: Degree of crosslinking 6% (divinylbenzene), chlorine content 21.66%, specific surface area 13.0 m^2/g.

4-Aminopyridine: Prepared according to the literature [7, 8], white powder, mp 155-157°C, purity > 98%, elemental analysis: C 63.27%, H 6.59%, N 28.67% (calculated: C 63.80%, H 6.43%, N 29.77%), NMR δ (ppm) 6.52, 8.02 (literature values 6.50, 8.03 [9]).

3-Aminopyridine: L.R., purity 98%. 2-Aminopyridine: Purity 98%. 2-Hydroxypyridine: Purity 97%, mp 90-92°C. 2-Thiolbenzothiazole: C.P., mp 177-179°C. 1,4-Dioxane: A.R., purified before use.

2. Synthesis of Aminopyridine Resins

Three kinds of APR were synthesized according to Ref. 9 under optimum conditions.

3. Synthesis of 2-Hydroxypyridine Resin and 2-Thiolbenzothiazole Resin

After swelling in 15 mL purified 1,4-dioxane, 1.0 g (6.11 mmol Cl) macroporous chloromethylated polystyrene beads was treated with 18.33 mmol (heterocyclic compound/Cl molar ratio 3) 2-hydroxypyridine or 2-thiolbenzothiazole and with (or without) 18.33 mmol metallic sodium, at 60°C, for 15 h with stirring. The resins were washed thoroughly with deionized water to pH 6 and then with acetone. Then the resins were dried at 50°C under vacuum. The elemental analysis and IR spectra of the resin were determined.

4. Sorption Properties

The concentration of metal ions was measured by UV-VIS photometer and AAS (atomic absorption spectrometer).

RESULTS AND DISCUSSION

1. Functional Group Conversion and Functional Group Capacities of APR

The influence of solvents on the conversion of functional groups of 4-APR (63.7% in 1,4-dioxane, 61.7% in toluene) is very small. Because 1,4-dioxane is easily soluble in water, we selected 1,4-dioxane as the solvent. The synthesis of 4-APR was investigated under the following conditions: molar ratio of reagents ($NH_2/Cl = 0.25\text{-}5.0$), reaction temperature (50-100°C), reaction time (3-25 h), 1,4-dioxane as the solvent.

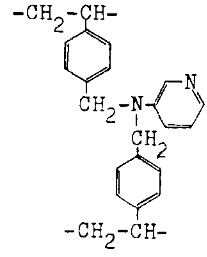
Under the optimum synthesis condition for 4-APR, three kinds of APR were synthesized [9]. The percentage of functional group conversion and the functional group capacities of APR are listed in Table 1.

The data listed in Table 1 show that 3-APR has the highest additional crosslinking, as shown in the following probable structure, because it has the lowest residual chlorine and nitrogen content of the three kinds of APR. Although 2-APR has the highest functional group, it has the lowest sorption

TABLE 1. Functional Group Conversion and Functional Group Capacity of APR

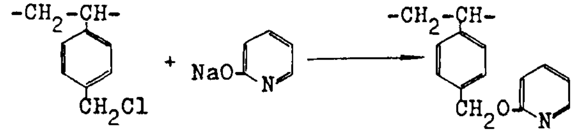
	Elementary analysis			
Resin	N, %	Residue, Cl, %	Functional group conversion, %	Functional group capacity, mmol $-NH-C_5H_5N$/g
4-APR	9.32	4.22	67.4	3.33
3-APR	9.03	1.26	64.8	3.22
2-APR	10.40	3.28	77.3	3.71

capacity for Au(III), as listed in Table 2. These phenomena may be explained by the steric hindrance of APR and the different basicities of low molecular weight model aminopyridines.



2. Factors Which Affect the Dehydrochlorination and the Quality of 2-HPR and 2-TBTR

(1) 2-HPR



2-HPR

The conversion of functional groups of 2-HPR reaches 91.0% (N = 5.87%, residue Cl = 2.73%, 4.19 mmol $O-C_5H_4N$/g 2-HPR) when chloromethylated polystyrene reacts with 2-hydroxypyridine in the presence of metallic sodium

TABLE 2. Sorption Capacities, Complex Ratios, Sorption Rates, and Distribution Coefficients of APR for Au(III) and Pt(IV)

	Sorption capacity		Complex ratio		$T_{1/2}$		K_d	
Resin	Au(III), mmol Au(III)/g	Pt(IV),[a] mmol Pt(IV)/g	Au(III) (Au/FG)	Pt(IV) (Pt/FG)	Au(III), h	Pt(IV), h	Au(III), mL/g	Pt(IV), mL/g
4-APR	3.22,[b] (30°C)	1.60	0.97	0.48	0.3	0.7	1380	1480
3-APR	3.23,[c] (34°C)	1.53	1.00	0.48	1.5	1.7	1170	1174
2-APR	3.12,[c] (34°C)	1.27	0.84	0.34	1.7	1.5	1102	657

[a]Determination conditions same as for Fig. 3.

[b]Determination conditions same as for Fig. 2.

[c]3-APR 99.6 mg, 0.1 *N* HCl 25 mL; 2-APR 102.1 mg, 1 *N* HCl 25 mL; 4.45 mg Au(III)/mL solution 20.0 mL, individually, at 34°C, shaking for 24 h.

(Williamson reaction), but the conversion is only 0.59% (N = 0.05%, Cl = 10.1%) in the absence of metallic sodium.

(2) 2-TBTR

In the presence of metallic sodium, the synthesis of 2-thiobenzothiazole resin (2-TBTR) is quite successful, the conversion reaching 82.3%. The functional group capacities of 2-TBTR calculated from nitrogen and sulfur content (N 4.25%, S 19.3%, residue Cl 4.76%) are 3.03 and 3.01 mmol $-S-C_7H_4NS$/g, respectively.

3. Selective Sorption of Various Metal Ions on 4-APR and 2-HPR and Influence of Acidity on Sorption Properties

Determination of the selective sorption of functional resins for various metal ions is very important because it can provide information for the separation and preconcentration of various metal ions.

The factors which affect the selective sorption are very complex, such as the character of the functional resin, the affinity of the resin for metal ions, the stability constants of the complex ions, pH or acidity of the medium, etc.

The selective sorption on 4-APR for various ions over a wide acidity range (1-6 *N* HCl) in the presence of equal weights of Au(III), Pt(IV), Pd(II), Zn^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, or Fe^{3+} is shown in Fig. 1.

Under the experimental condition, the selective sorption on 4-APR of various metal ions over a wide acidity range (1-6 *N* HCl) is in the following order: Pt(IV) > Au(III) > Cd^{2+} > Zn^{2+} > Pd(II) > Mn^{2+}, Cu^{2+}, Fe^{3+}. Under the same experimental condition, the sorption of 2-HPR for Au(III) and Pt(IV) over a wide acidity range (1-6 *N* HCl) is higher, but for Mn^{2+}, Cu^{2+}, and Fe^{3+} it is very low.

The influence of acidity on the sorption of resins for noble metal ions is evident. Under the same experimental conditions, the sorption on 4-APR and 3-APR of Au(III) is higher than 95% over a wide acidity range (4-5 *N* HCl), and reaches 100% in 1 *N* HCl. The sorption of Au(III) on 2-APR is lower than on 4-APR.

The optimum acidities of the sorption of 2-HPR and 2-TBTR for Au(III) are 3-6 *N* HCl and 6 *N* HCl, respectively. Under high acidity conditions, 2-HPR adsorbs $AuCl_4^-$ readily, but this is probably due to the formation of the pyridinum and oxonium salts of 2-HPR.

In the presence of both Pt(IV) and Pd(II) in 0.1, 1, 3, and 6 *N* HCl solutions, 2-HPR has the highest sorption of Pt(IV) and Pd(II) in 1 *N* HCl solution.

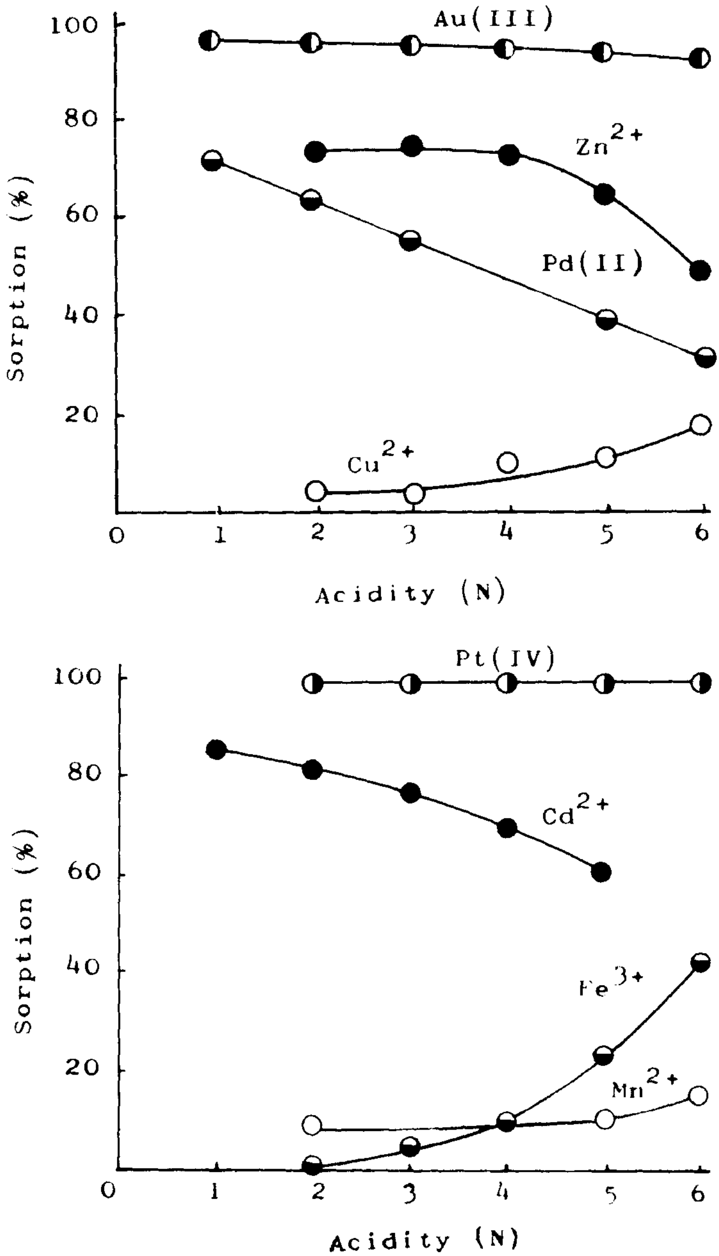


FIG. 1. Sorption of 4-APR for various ions at different acidities. Various metal ions 1.0 mg, 4-APR 100 mg, total volume of solution 25 mL.

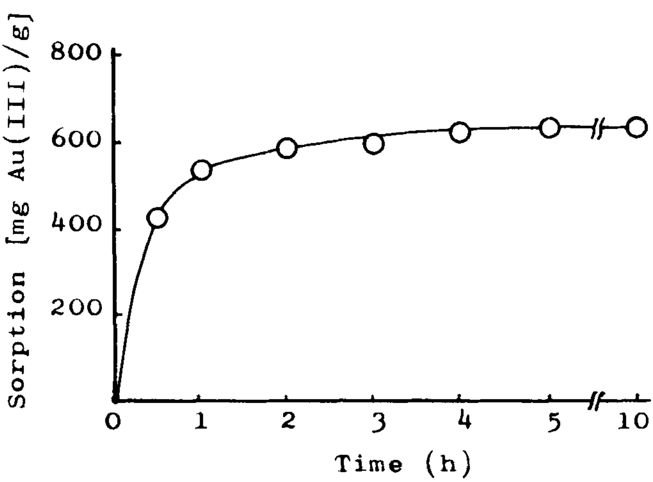


FIG. 2. Sorption of 4-APR for Au(III). Au(III) 86.4 mg, 0.1 *N* HCl, total volume of solution 25 mL, 4-APR 100 mg, 30°C, shaking.

4. Sorption Rates ($T_{1/2}$), Sorption Capacities, Distribution Coefficients K_d, Complex Ratio of the Resins for Noble Metal Ions

(1) APR

The half-time $T_{1/2}$, the sorption capacity, and K_d are very important quantitative measures of the sorption abilities of the resins for metal ions. These data for the three kinds of APR with Au(III) and Pt(IV) are shown in Figs. 2 and 3 and listed in Table 2.

The sorption capacities of APR for Au(III) are high, 615-635 mg Au(III)/g APR. The complexing ratio, Au(III)/$-NH-C_5H_4N$ (Au/FG), of 4-APR and 3-APR for Au(III) reaches 1, meaning that 1 $AuCl_4^-$ ion can be just complexed by 1 $-NH-C_5H_4N$ group.

The sorption capacities of the three kinds of aminopyridine resins for Pt(IV) are 247.1-311.2 mg Pt(IV)/g APR or 1.27-1.60 mmol Pt(IV)/g APR. The complex ratio, Pt(IV)/functional group $-NH-C_5H_4N$ (Pt/FG), of 4-APR and 3-APR for Pt(IV) reaches 0.48, i.e., one $PtCl_6^{2-}$ ion must be complexed by 2 $-NH-C_5H_4N$ groups. On the other hand, under the same conditions, the complex ratios of 2-APR for Au(III) and Pt(IV) are only 0.84 and 0.34, respectively, probably due to the steric hindrance of 2-APR and the lower basicity of the 2-aminopyridinyl group.

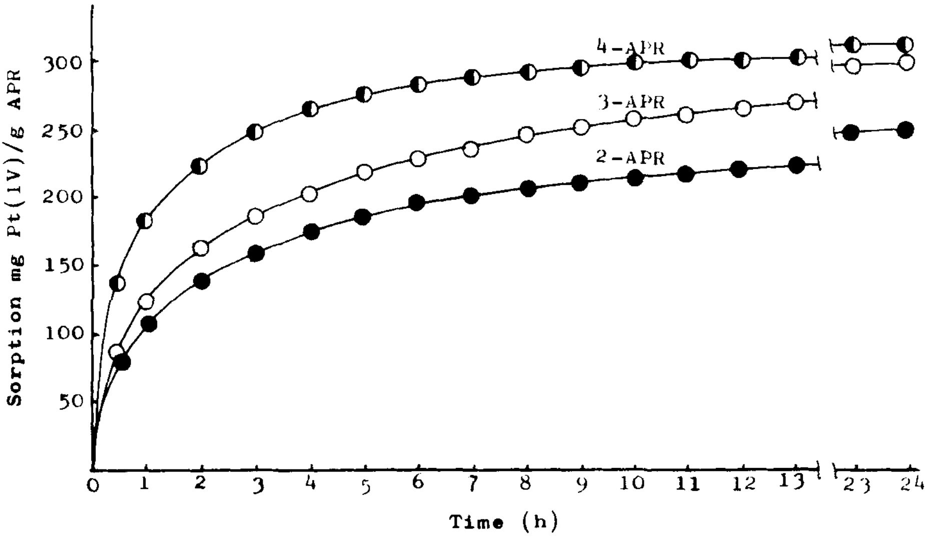


FIG. 3. Sorption of APR for Pt(IV). 4-APR: 96.7 mg, pH 2 buffer solution 25 mL. 3-APR: 95.5 mg, 2 N HCl 25 mL. 2-APR: 99.1 mg, pH 1 buffer solution 25 mL. For all determinations: 3.82 mg Pt(IV)/mL solution 10 mL, 35°C, shaking.

We use $T_{1/2}$ to represent the sorption rate. $T_{1/2}$ is the time required to reach half of the equilibrium sorption capacity. The order of $T_{1/2}$ for Au(III) on the three kinds of APR is 4-APR $\ll$ 3-APR $<$ 2-APR, while it is 4-APR $\ll$ 2-APR $<$ 3-APR for Pt(IV).

Adsorbability of a metal ion on a resin can be expressed in term of the distribution coefficient K_d, which is defined as [10]

$$K_d = \frac{\text{amount of metal ion on the resin}}{\text{amount of metal ion in solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of resin (g)}} .$$

The conditions in Table 2 are also useful to determine K_d. After shaking for 24 h, the aqueous solution is separated from the resin, and then the residual amounts of the metal ions are determined. Then K_d can be calculated (Table 2).

The order of distribution coefficients for the three kinds of APR for Au(III) and Pt(IV) are identical: 4-APR $>$ 3-APR $>$ 2-APR.

When equal weights of Pt(IV) and Pd(II) are fed to a given amount of 4-APR (or 2-APR or 2-HPR), the molar ratio of Pt(IV)/Pd(II) in the initial solution is 0.55, but for 4-APR, 2-APR, and 2-HPR it is 1.11, 1.31, and 1.45, respectively.

4-APR has the best overall sorption properties, probably due to the lowest steric hindrance of the 4-aminopyridine group and the highest equilibrium constant (K_1) of protonation of 4-aminopyridine (4-AP $K_1 = 10^{9.18}$, 2-AP $K_1 = 10^{6.71}$, 3-AP $K_1 = 10^{6.03}$ at 25°C) [11].

(2) 2-HPR

The sorption capacity of 2-HPR for Au(III) at 30°C is 196 mg Au(III) (1.00 mmol)/g 2-HPR. The complex ratio Au(III)/$-O-C_5H_4N$ is 0.237. The sorption half-time ($T_{1/2}$) of 2-HPR for Au(III) is 0.8 h. The distribution coefficient K_d of 2-HPR with Au(III) is 681 mL/g.

5. Elution of Au(III) Adsorbed on 4-APR

The Au(III) adsorbed on 4-APR can be eluted quantitatively with 2% aqueous thiourea by the dynamic method, and it reaches 99%. After the eluted 4-APR is washed thoroughly with deionized water to free it from thiourea, the Au(III) adsorbed on the regenerated 4-APR can also be 100% eluted with 2% aqueous thiourea, as shown in Fig. 4.

The IR spectrum of the regenerated resin is exactly the same as that of 4-APR. The regenerated 4-APR (S < 1%, N 9.40%), compared with the original 4-APR (S 0%, N 9.32%), contains a small amount of sulfur and slightly increased N content probably due to incomplete washing out of thiourea. The sorption rate curve of the regenerated 4-APR for Au(III) is very similar to that of 4-APR, as shown in Fig. 2. The sorption capacity of the regenerated 4-APR for Au(III) is slightly lower than that of 4-APR (about 4.7%). Accordingly, the 4-APR can be regenerated very well and reused for the sorption for Au(III).

6. Separation of Au(III) and Cu^{2+}

2-HPR and 2-TBTR have poor sorption for Cu^{2+} over the wide acidity range of 1-6 N HCl. In general, the resins containing pyridyl groups, such as polysytrene beads bearing $-NH-CH_2-C_5H_4N$ groups, usually have good sorption ability for Cu^{2+}, but the sorption on 2-HPR, which also contains pyridyl groups, of Cu^{2+} is only 4.5%. The sorption on 2-TBTR of Cu^{2+} is also only 4.5%.

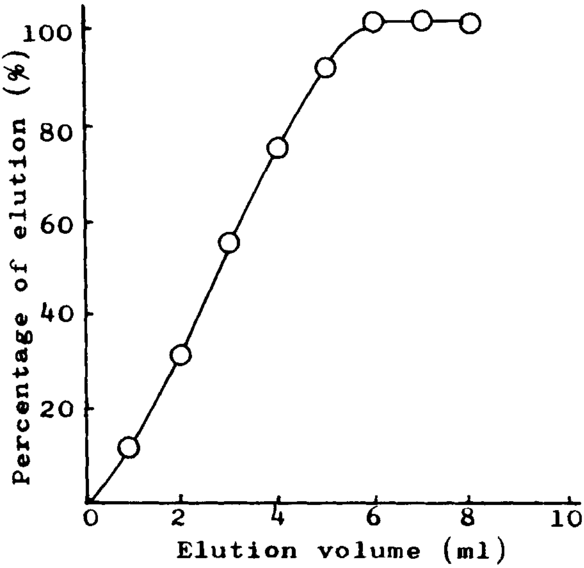


FIG. 4. Elution of Au(III) adsorbed on regenerated 4-APR. Adsorbed Au(III) 14 mg, resin bed 10 mm diameter X 15 mm, eluent 2% aqueous thiourea, flow rate 1 mL/min, room temperature.

The separation of Au(III) and Cu^{2+} was studied preliminarily by using the 4-APR batch process. The data listed in Table 3 show that Au(III) can be quantitatively adsorbed by 4-APR, and Au(III) adsorbed on 4-APR can also be eluted quantitatively by a 2% aqueous solution of thiourea.

In the presence of Au(III), the sorption of 4-APR for Cu^{2+} is only 28.6% (Table 3), and the Cu^{2+} adsorbed on 4-APR can only be partially eluted (43.4%). Therefore, Au(III) and Cu^{2+} may be separated by 4-APR.

TABLE 3. Separation of Au(III) and Cu^{2+} by 4-APR[a]

Ion	Ion content in initial solution, mg	Ion content adsorbed on 4-APR, mg	Ion content in 10 mL eluant, mg
Au(III)	4.65	4.59	4.60
Cu^{2+}	23.99	6.85	2.97

[a]1.0 g 4-APR, column diameter 10 mm, 20 mL solution containing 4.65 mg Au(III) and 23.99 mg Cu^{2+}, 2% aqueous thiourea as eluant.

Thermal weight loss curves of the resins show that 2-HPR is stable up to 100°C, while 4-APR and 2-APR are stable up to 80°C in air.

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