

PRECONCENTRATION OF GOLD (III), PALLADIUM (II) AND RUTHENIUM(III) WITH DITHIO-CARBAMATE-CHITIN

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Abstract - Dithiocarbamate-chitin (DTC-chitin) has been synthesized and used for concentration of gold (III), palladium (II) and ruthenium (III) from an acidic solution. The former two metals were quantitatively retained on the polymer from 6 M hydrochloric acid even at a high flow rate (15 ml min⁻¹), in contrast to only 80% retention for ruthenium in a narrow pH range, 3.0-4.5. Gold retained on the polymer could be eluted with 1 M nitric acid containing 5% thiourea, while palladium with 1.6-fold diluted inverse aqua regia.

Key words dithiocarbamate-chitin, preconcentration, gold, palladium, ruthenium

Dithiocarbamate-chitin (DTC-chitin) has been synthesized and used for preconcentration of silver, cobalt, cadmium, copper and nickel at a pH above 2.5, and iron in a narrow pH range, 4.0-6.5[1]. The derivatives of chitin were thought to mostly keep their original structure and contain DTC-chitosan fraction in their frame, so DTC-chitin had no tendency to gelatinize in an acidic medium unlike the analogous derivatives prepared from chitosan by the method reported by Muzzarelli et al.[2]. Since the concentration levels of noble metals in natural waters are extremely low, their distribution in seawater and inland waters have not been revealed to date. Therefore, preconcentration is essential for their precise determination from natural water samples. This paper describes the adsorption behavior of DTC-chitin for gold(III), palladium (II) and ruthenium(III), and application to the analysis of gold in several geochemical samples.

EXPERIMENTAL

Apparatus A Hitachi Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for determination of gold and palladium. A Shimadzu UV-160 spectrophotometer was used for ruthenium analysis. A Toyo Kagaku SF-160K fraction collector and a Horiba F-12 pH meter were used.

Reagents Chitin powder (Nakarai Chemicals), carbon disulfide, 2-propanol (Ishizu Chemicals), 10% tetramethylammonium hydroxide in methanol (Tokyo Kasei) and thiourea (Kanto Chemicals) of analytical reagent grade were used without further purification. Standard stock solutions (1 mg ml⁻¹) of gold and palladium were prepared by dissolving each metal in aqua regia, followed by evaporating and dissolving in 1 M (mol dm⁻³) hydrochloric acid and diluted to desired volume. A stock solution of ruthenium (1 mg ml⁻¹) was prepared by dissolving ruthenium(III) chloride in 1 M hydrochloric acid and standardized by gravimetry after reducing to ruthenium metal by using magnesium metal.

Preparation of DTC-chitin About 10 g of chitin powder (80-100 mesh) was put into an Erlenmeyer flask. Then, 150 ml of 2-propanol, 10 ml of carbon disulfide and 2 ml of 10% tetramethylammonium hydroxide in methanol were added to the flask. The flask was covered with a small petri dish, and then was allowed to stand in a dark place at room temperature for 2 d with continuous stirring by a magnetic stirrer. After the contents were filtered through a glass filter the polymer was washed with deionized water and then 2-propanol and dried at 60°C under reduced pressure for 24 h.

Procedure **Batch experiments:** A 20-ml portion of each metal solution (10 µg ml⁻¹) adjusted to the required pH value and 0.3 g of DTC-chitin were put into a 50-ml glass-stoppered centrifuge tube. The contents were shaken at 300 strokes min⁻¹ for 10 min at room temperature. After shaking, the

contents were filtered through a dry sheet of Toyo No. 5A filter paper. The metal concentration was measured by flame atomic absorption spectrometry (FAAS) for gold and palladium, while by extraction/spectrophotometry of a tropolone complex for ruthenium, and the percent retention was calculated. At the same time the pH of the filtrate was measured. The same experiments were carried out by using untreated chitin. Column experiments: A glass column (i.d. 10 mm) was filled with 0.3 g of the DTC-chitin. A given volume of the sample solution containing each metal ion adjusted to a suitable pH and then percolated through the column at various flow rates by using a peristaltic pump. The effluent was collected by a fraction collector and the metal concentration was measured as described above.

RESULTS AND DISCUSSION

Effect of acid concentration on the retention of each metal ion The

retention of each metal ion from aqueous solution at various acidities was examined by the batch method using 10-ppm metal solution. The results obtained from hydrochloric acid solution are illustrated in Fig. 1 (a)-(c). Gold (III) and palladium(II) were quantitatively retained in the range of 6 M hydrochloric acid to pH 9.0, while ruthenium (III) was retained only 80% in a narrow pH range, 3.0-4.5, but not retained at pH below 0. However, in the experiments using ^{106}Ru in trace levels only 40% was retained at pH above 4.0. The difference between both results may be attributed to the formation of ruthenium(III) hydroxide which precipitates at pH 3.2-3.5 in ppm levels.

Retention capacities of gold (III) and palladium (II) on DTC-chitin and untreated chitin Gold and palladium ions were also retained on untreated chitin at pH 2.5-5.0, and higher than 3.0, respectively. In the previous paper [1], the retention with untreated chitin was attributed to metal hydroxide formation, since the same results were obtained by a batch method for cobalt(II) under the same conditions without chitin. However, in the present study, it was found that gold and palladium ions were retained on the chitin at much lower pH than those for their

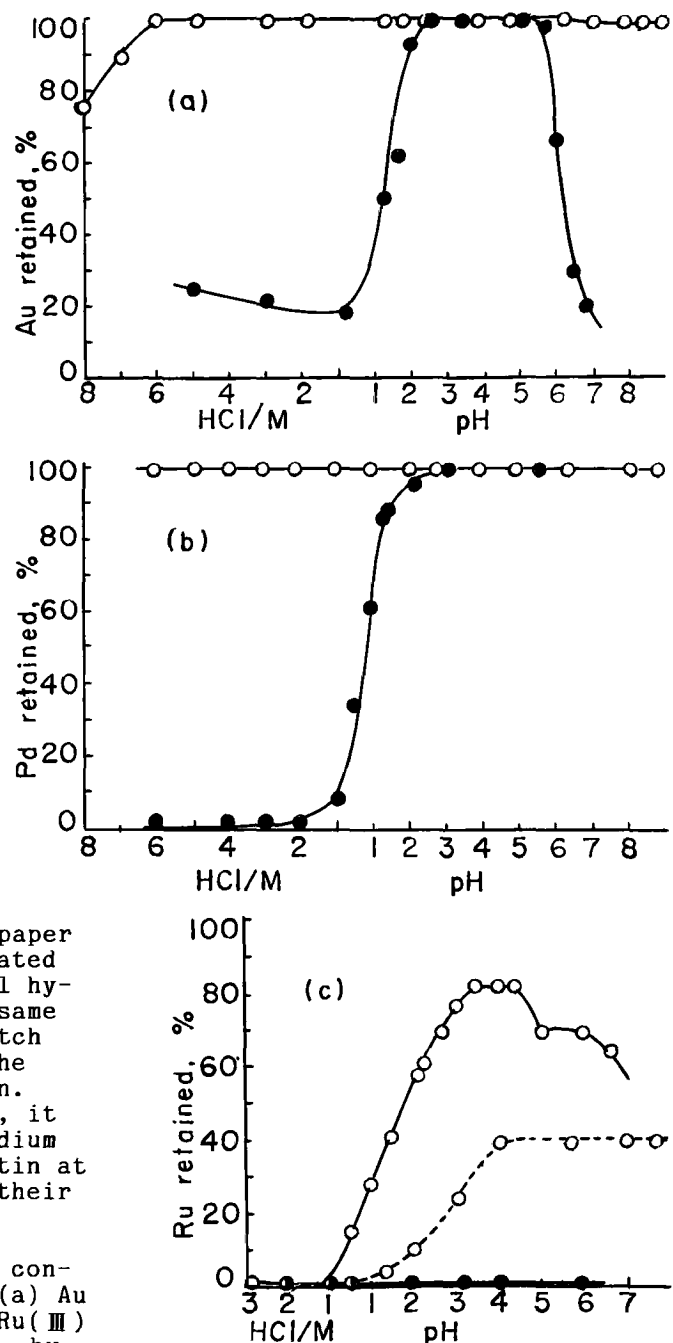


Fig. 1 Effect of pH and acid concentration on retention of (a) Au (III), (b) Pd(II) and (c) Ru(III) —10 ppm and ----trace level, by (○) DTC-chitin and (●) chitin

hydroxide formation, 11 and >9.0, respectively. Specially in the case of gold(III), the retention decreased at pH above 5.5 at which hydroxide formation started. Therefore, the retention of metal ions with untreated chitin should be attributed to the complex formation between a metal ion and amino group in the chain of chitosan which may originally exist in the chitin powder used. Then, the sorption capacities of chitin and DTC-chitin for palladium(II) were determined by a breakthrough method using a column packed with 0.3 g of each polymer and a 10-ppm palladium solution. The results are shown in Table 1, together with the capacity for gold(III). Because of the incomplete retention, the

sorption capacity for ruthenium(III) was not measured. Palladium(II) was not retained on the untreated chitin from 2 M hydrochloric acid solution. By assuming that all the amino groups in chitin powder are saturated with palladium ion forming 1:1 complex, the amount of the amino group which exist in the chitin

should be about $130 \mu\text{mol g}^{-1}$. This value agreed very closely with that obtained by DTC-chitin at pH 4.0. On the other hand, from 2 M hydrochloric acid solution, palladium retained on DTC-chitin amounted to $99 \mu\text{mol g}^{-1}$ which agreed with amounts of DTC group introduced in the DTC-chitin ($100 \mu\text{mol g}^{-1}$) determined by tin(II)-strong phosphoric acid reduction method[1,3]. These facts indicate that the original chitin contained ca. 0.2% amino group and 77% of the amino group was converted to DTC-group which reacted with palladium(II) ion to form 1:1 complex. Thus, at pH 4.0, not only DTC-group but the remained amino group in DTC-chitin may react with the metal ion, while in 2 M hydrochloric acid solution only DTC-group can form a DTC-palladium complex. From these results, a possibility is suggested that a DTC-chitin containing desired amounts of DTC-group may be easily prepared by using a chitin a part of which has been converted to chitosan by the deacetylation of chitin.

Effect of shaking time and flow rate on the retention of each metal ion

The retention of each metal from a 5 ppm solution at pH 1.0, 1.0 and 4.0 for gold, palladium and ruthenium, respectively, was examined after various shaking times. The results showed that more than 99% of gold and palladium was sorbed within 1 min and 30 s, respectively, while ruthenium required 5 min for the maximum retention. Moreover, palladium(II) could be quickly sorbed on the DTC-chitin column, since the sorption capacities determined at various flow rates such as, 1, 10 and 15 ml min⁻¹, were almost equal. On the other hand, the sorption capacity for gold(III) decreased with increase of flow rate from $64 \mu\text{mol g}^{-1}$ at 1.0 ml min⁻¹ to $54 \mu\text{mol g}^{-1}$ at 12 ml min⁻¹. However, when

the metal concentration is much lower and the sample volume is larger, the recovery of metal was almost quantitative as shown in Table 2. As can be seen from Table 2, the both metals spiked to a filtered seawater adjusted to pH 2.0 were also completely recovered. After passing the sample solution at flow rate of 15 ml min⁻¹, the retained metal was eluted with 1 M nitric acid containing 5% thiourea for gold and 1.6-fold diluted inverse aqua regia for palladium. Each effluent was submitted to FAAS measurement. Slightly low recovery obtained for palladium may be

attributed to incomplete elution of the metal as described below.

Elution of metals from the DTC-chitin column As can be seen from Fig. 1, gold and palladium retained on the polymer are not expected to be eluted with a simple acid. Among various kinds of eluants examined such as, aqueous solution of thiourea and nitric acid containing thiourea varying the concentration ratio, 1 M nitric acid containing 5% thiourea was found to quantitatively elute gold but not palladium. A 5% aqueous solution of

TABLE 1. Sorption capacity of chitin and DTC-chitin

Ion	Sorption capacity/mg g ⁻¹ ($\mu\text{mol g}^{-1}$)			
	Chitin	[pH]	DTC-chitin	[pH]
Au(III)	—		12.6 (64)	[4.0]
Pd(II)	14 (132)	[4.0]	13.5 (127)	[4.0]
Pd(II)	—		10.5 (99)	[2M-HCl]

TABLE 2. Recoveries of gold(III) and palladium(II) on DTC-chitin column*

Ion	Concn./ ng ml ⁻¹	Sample vol./ml	Recovery ^b %
Au(III)	1.0	8000	102 ± 1
	5.0	2000	99 ± 1
	5.0	2000	101 ± 1
	10.0	2000	101 ± 1
Pd(II)	5.0	2000	95 ± 2
	5.0	2000	96 ± 2
	10.0	2000	96 ± 2

* Flow rate: 15 ml min⁻¹

^b Values are averages of three runs.
Metal spiked to filtered seawater

thiourea could elute about 85% of gold. On the other hand, palladium was not effectively eluted with any acids and chelating agents, probably according to high stability of its DTC complex. As the results of examination, 1.6-fold diluted inverse aqua regia was found to be most adequate for complete elution of the element. The results are shown in Fig. 2 (a) and (b). As can be seen from the figures, gold can be completely eluted with 10 ml of 1 M nitric acid containing 5% thiourea. Palladium can be eluted with 20 ml of 1.6-fold diluted inverse aqua regia, but further dilution of the reagent is not recommended.

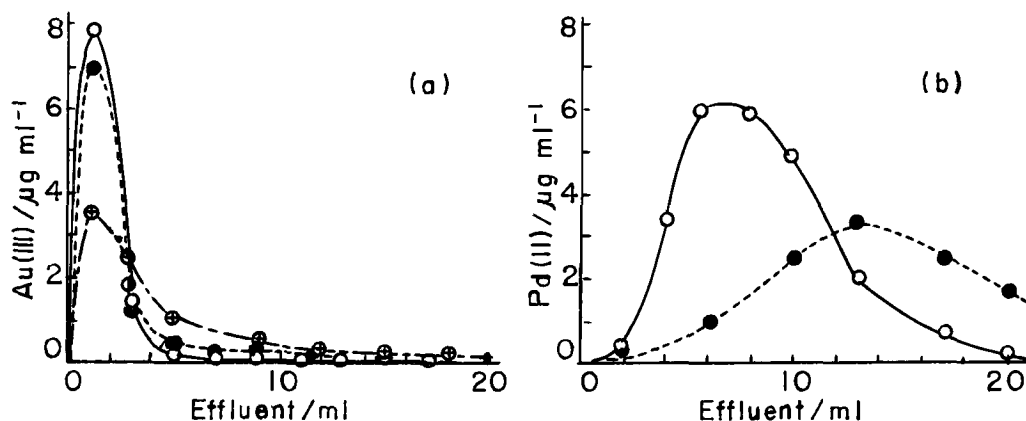


Fig. 2 Elution of metals retained on a DTC-chitin column. (a) Au(III): (○) 1 M HNO₃ (5% thiourea). (●) 0.2 M HNO₃ (5% thiourea). (⊕) 5% thiourea aqueous solution. (b) Pd(II): (○) 1.6-fold diluted inverse aqua regia. (●) 2.0-fold diluted inverse aqua regia.

Effect of diverse ions and ligands on the retention of gold(III) and palladium(II)

Some metal ions which may react with DTC at pH lower than 2.0, such as bismuth(III), copper(II), silver(I) and tin(IV) and some ligands were investigated for their effect on the preconcentration process. A 100 ml of each sample of gold and palladium (0.1 µg ml⁻¹) along with one of the other substances was passed through the column. As shown in Table 3, tested ions and ligands gave no effect on the retention of gold and palladium.

Analysis of geochemical samples for gold The present method was applied to a river sediment and a gold ore samples. The sediment was collected from Hodatsu-river, near Mt. Hodatsu, Ishikawa Pref., and the ore sample had been collected at Kanehira mine, Ishikawa Pref. The sample was pulverized to 100 mesh with an agate mortar and heated with aqua regia in a PTFE vial. The solution was filtered and diluted with deionized water, then processed as described above. The results are shown in Table 4.

TABLE 3. Effect of diverse ions and ligands on the retention of gold(III) and palladium(II)

Ion or ligand	concn./ µg ml ⁻¹	Recovery, %	
		Au(III)	Pd(II)
Ag(I)	10	100	100
Au(III)	10	---	100
Bi(III)	10	99	99
Cu(II)	10	100	99
	50	100	99
Pd(II)	10	100	---
Sn(IV)	10	99	98
SCN ⁻	0.01M	100	99
	0.1 M	100	100
S ₂ O ₃ ²⁻	0.01M	100	100
	0.1 M	100	100

TABLE 4. Analysis of gold in river sediment and ore mineral

Sample	Weight taken/g	Au contents/ ng g ⁻¹
Sediment	200	15 ± 0.5
Gold ore	11	290 ± 10

Values are averages of three runs.

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