Separation of Gold (III) as Its Ion-pair Complex with 18-Crown-6 from Hydrochloric Acid Media by Means of Solvent Extraction

Cristina T. CAMAGONG and Takaharu HONJO[†]

Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa-shi, Ishikawa, 920-1192, Japan

A new solvent extraction technique for the separation of gold(III) at trace amounts from hydrochloric acid media was developed based on the formation of an ion-association complex of tetrachloro gold anion, $AuCl_4^-$ with 18-crown-6 (18C6) oxonium cation in 1,2-dichloroethane. The effect of various factors (crown ether, acid concentration, solvent, shaking time, stripping reagent etc.) on the extraction and separation of gold(III) was investigated. Quantitative extraction was achieved using 0.05 mol dm^{-3} 18C6 in 1,2-dichloroethane at 4 mol dm^{-3} HCl within 5 min. Back-extraction was carried out by 5-min shaking with 0.1 mol dm^{-3} $Na_2S_2O_3$ in 0.2 mol dm^{-3} NH_3, followed by FAAS determination. Interference studies revealed excellent tolerance of the method to foreign ions. The method's high selectivity was demonstrated by a spike recovery of >96% for gold(III) and by the negligible extraction of silver(I). Using first-class silver reagents, the quantitative recovery of traces of gold(III) was achieved up to a 20-fold preconcentration factor.

Gold and silver are commonly found associated with each other. Several methods for gold analysis, however, possessed limited tolerance for the co-existence of silver and *vice versa*. In an analysis of gold in ores by flow injection on-line sorbent extraction preconcentration technique,[1] the presence of >2.5 μ g cm^{-3} silver interfered significantly with the determination. In another study,[2] the use of methylethylketone/ chloroform (MEK/CHCl$_3$) system was found limited by the incorporation of silver in the gold extract. On the other hand, the presence of gold at more than 10 g dm^{-3} considerably suppressed silver's signal in Electrothermal-AAS[3] and no improvement was made even after gold matrix reduction through addition of various organic reductants. Hence, a method development for separating gold and silver prior to analysis is considered necessary.

Several methods have poor selectivity as shown in the limited separation of gold and silver. One study[4] uses thiosulfate and ammonia aqueous media extracted by a primary amine-amine oxide mixture, giving only a separation factor ($\alpha_{Au/Ag}$) of 15. In addition, the use of an expensive amine oxide was found impractical. Sastre *et al.*[5] on the other hand, extracted gold from aqueous cyanide media by LIX 179 in the presence of silver. The maximum separation factor obtained is 9, which is much lower than the primary amine-amine oxide procedure and moreover, the equilibrium pH (9.8)

is basic which can promote metal hydrolysis. Burmaa *et al.*[6] studied the preference of dibutyl sulfide and selenide for gold in concentrated HCl solutions and of dibutyl selenide and telluride for silver in concentrated HNO$_3$ solutions. A review[7] cited the potential of these extractants, but no investigation was reported on the actual separation of gold and silver from a common acid solution.

Solvent extraction techniques are considered invaluable tools for the separation purposes of precious metals.[7] At present, our research group has done several studies on the use of crown ethers for the separation of different metals found adjacent to each other in the periodic table by solvent extraction techniques. The synergistic action of thenoyltrifluoroacetone and dibenzo-18-crown-6 (DB18C6) was found successful in the separation of cadmium and zinc[8] in solution, as well as for lanthanum and barium.[9] Separation of the precious metals such as platinum,[10] palladium,[11] rhodium[12] and iridium[13] from each other was also made possible through the formation of ion-association complexes with cationic dicyclo-18-crown-6 (DC18C6).

Previous studies[14,15] on the use of crown ethers for gold extraction were also found, however, none of which reported any practical application. In this work, the potential of 18C6 crown ether for the extraction and separation of gold from silver was investigated. The applicability of the proposed method for the isolation, preconcentration and determination of traces of gold was examined by spike recovery studies using first-class silver reagents.

[†] To whom correspondence should be addressed

E-mail: honjo@kenroku.kanazawa-u.ac.jp

Experimental

Apparatus

A Hitachi Polarized Zeeman Type Atomic Absorption/ Flame Emission Spectrophotometer, model Z-6100, a Taiyo Recipro Shaker, model SR-II and a Tomy Seiko Swing Type Centrifuge, model CD-50R, were used.

Reagents

Standard solutions were prepared by dilution of a 1,000 μ g cm^{-3} gold(III) stock solution (f = 1.003) in 1.0 mol dm^{-3} hydrochloric acid (CICA-Merck, Japan) to the working range. 18C6 (99% purity) was purchased from Acros Organics, USA. All aqueous solutions were prepared using distilled-deionized water (Nanopure system, Barnstead Ltd. USA). All other chemicals were of guaranteed grade and were used without further purification.

Procedure

Solvent Extraction. A sample aliquot (5 cm^3) of 4 mol dm^{-3} hydrochloric acid solution containing gold (0.5 – 10 μ g cm^{-3}) was placed into a 30-cm^3 glass-stoppered centrifuge tube. A 5 cm^3 of 1,2-dichloroethane solution containing 0.05 mol dm^{-3} 18C6 was added to the centrifuge tube, and the mixture was shaken on a shaking machine for 5 min. Phase separation was carried out by centrifugation at 2,000 rpm for 10 min. The organic phase was collected by pipetting into another centrifuge tube for back-extraction.

Back-extraction. The gold-loaded organic phase (5 cm^3) was shaken with 5 cm^3 of 0.10 mol dm^{-3} Na$_2$S$_2$O$_3$ in 0.10 mol dm^{-3} NH$_3$. The amount of gold stripped from the organic phase was determined by Flame-AAS at 242.8 nm under instrument`s optimum settings.

Results and Discussion

Effect of crown ether

The selectivity of the crown ether for the separation of gold and silver was highly considered in the optimization. The crown ethers investigated were DC18C6, 18C6 and DB18C6. The extraction behavior of gold and silver was examined at 1-12 mol dm^{-3} hydrochloric acid solutions using 0.05 mol dm^{-3} concentration of the crown ether in 1,2 -dichloroethane using a 5 - min shaking time. A 1:1 phase volume ratio was adopted. Among the investigated crown ethers, 18C6 gave excellent selectivity (Fig. 1) for the tetrachloro gold anion, AuCl$_4^-$, which is readily extracted in the organic phase while silver remains in solution. The formation of unextractable silver chloro complexes, AgCl$_n^{(n-1)-}$, accounts for silver`s negligible extraction at high hydrochloric acid concentrations. Moreover, Fig. 1 also shows that at $\geq$ 2 mol dm$^{-3}$ acid solutions, the high selectivity of 18C6 also resulted in gold`s quantitative extraction. For subsequent experiments, a 4 mol dm^{-3} concentration of hydrochloric acid was used.

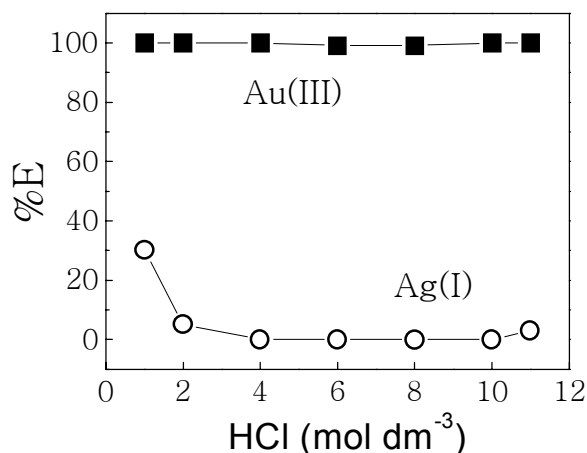Fig. 1 Effect of hydrochloric acid on the extraction of gold (IV) ($\blacksquare$) and silver (I) ($\bigcirc$) by 0.05 mol dm^{-3} 18C6 in 1,2-dichloroethane.

Selection of back-extracting agent

Various stripping reagents were studied using an organic phase solution of 0.05 mol dm^{-3} 18C6 in 1,2- dichloroethane loaded with 10 μ g cm^{-3} gold. A 1:1 phase volume was maintained. The stripping solutions investigated were: 11.0 mol dm^{-3} HCl + 0.05 mol dm^{-3} KSCN, 1.0 mol dm^{-3} NH$_3$-NH$_4$Cl,[11] 0.10 mol dm^{-3} NaOH,[16] 0.30 mol dm^{-3} thiourea,[5] 0.10 mol dm^{-3} Na$_2$S$_2$O$_3$[4] and 0.10 mol dm^{-3} Na$_2$S$_2$O$_3$ in 0.10 mol dm^{-3} NH$_3$.[4] Back-extraction using 0.10 mol dm^{-3} Na$_2$S$_2$O$_3$ in 0.10 mol dm^{-3} NH$_3$ was able to recover gold quantitatively from the loaded organic phase after a 30-min shaking time.

Effect of solvent

Different organic solvents were investigated for the optimum extraction of gold with 18C6 from 4 mol dm^{-3} hydrochloric acid solution. The examined solvents were as follows: chloroform, o-dichlorobenzene, nitrobenzene, 1,2-dichloroethane, cyclohexane, toluene and benzene. It was found that the extractability of gold was quantitative as the ion pair complex with protonated 18C6 in chloroform, 1,2- dichloroethane and o- dichlorobenzene. 1,2- dichloroethane was selected, because it is cheaper than o-dichlorobenzene and does not drip easily from the pipette tips in contrast to chloroform.

Effect of shaking time and phase volume ratio

The optimum shaking time was ascertained by measuring the recovery of gold after 15 sec – 45 min shaking periods, as shown in Table 1. It was found that the method gave rapid attainment of extraction equilibrium for gold in either forward or backward extraction within 3 min. A 5-min shaking time was taken as optimum for both procedures to ensure complete recovery.

The volume ratio of the aqueous phase to the organic phase was varied during gold extraction, and the preconcentration factor was determined. For a single extraction, it was found that the quantitative recovery of gold was attainable up to 20- fold (Vaq/Vorg = 10:0.5).

Table 1 Effect of shaking time on gold extraction

Time	Recovery, %	
	Forward extraction	Backward extraction
15 sec	90	61
3 min	100	98
5 min	98	101
10 min	97	100
15 min	98	99
30 min	100	97
45 min	99	100

HCl: 4 mol dm^{-3}; 18C6: 0.05 mol dm^{-3}; Solvent: 1,2-Dichloroethane

Composition of extracted species

Using the slope analysis method, the composition of the extracted species on the extraction of gold with 18C6 in 1,2- dichloroethane was investigated at a fixed hydrochloric acid concentration of 4 mol dm^{-3}. The plot of log D vs log $[18C6]_{org}$ gave a straight line with a slope of 1.01 as shown in Fig. 2, and the result is consistent with a previous research made by Koshima *et al.*[15] This suggests that under highly acidic conditions, the tetrachloro gold anion, $AuCl_4^-$, is extracted as an ion- association complex with the stable 18C6 oxonium cation. This result explains the inextractability of gold under basic conditions, where the formation of 18C6 oxonium cation is impossible. The resulting ion-association product, $[H_3O \cdot 18C6]^+[AuCl_4]^-$, indicates a metal to crown ether ratio of 1:1.
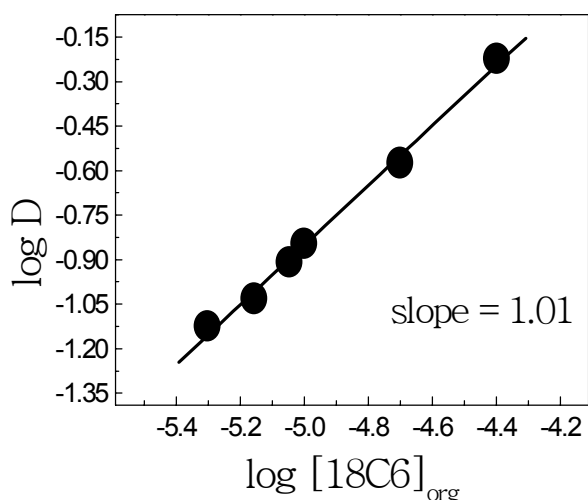

Fig. 2 Effect of varying the concentration of 18C6 on the distribution ratio of gold in 1,2-dichloroethane at 4mol dm^{-3} HCl.

Effect of foreign ions

The interference due to the presence of foreign ions in the extraction and determination of gold was investigated, and the method's tolerance limit for each foreign ion was identified. Under optimum conditions, various concentrations of the foreign ion were spiked individually in 1 μ g cm^{-3} gold solution before extraction. The recovery data are summarized in Table 2. It was observed that the method gave excellent tolerance for foreign ions. Although iridium[13] at 4 mol dm^{-3} hydrochloric acid solution initially reduced gold's recovery to about 50%, the use of back-washing technique was able to relieve this interference.

Table 2 Effect of foreign ions on gold extraction

Foreign ion	Tolerance limit (times that of gold)	Recovery of Gold, %
Na^+	300	103
K^+	300	100
Li^+	> 500	96
Rb^+	> 500	97
Mg^{2+}	400	98
Ca^{2+}	> 500	96
Cu^{2+}	300	100
Fe^{3+}	> 400	96 (ppt)
Zn^{2+}	300	96
Cd^{2+}	> 400	100
Mn^{2+}	> 400	101
Pb^{2+}	> 500	96
Ni^{2+}	400	98
Co^{2+}	> 500	95
NO_3^-	> 500	101
SO_4^{2-}	> 500	97
SCN^-	400	98
Pd^{2+}	> 400	102
Rh^{3+}	> 400	95
Pt^{4+}	200	98
Ru^{3+}	200	102
Ir^{4+}	> 200	99[a]

HCl: 4 mol dm^{-3}; 18C6: 0.05 mol dm^{-3}; Solvent: 1,2-Dichloroethane; Shaking time: 5 min
a: After back-washing

Analytical performance

A linear calibration curve (r^2=0.9999) was obtained in the range of 0–10 μ g cm^{-3} Au in 0.5 mol dm^{-3} hydrochloric acid after measurements of peak area of absorption using FAAS at 242.8 nm. The detection limit (average of blank value plus three times its standard deviation) was 0.25 ng cm^{-3}. The proposed method (Fig.3) was applied to the separation of gold and silver using spike recovery studies and the results are summarized in Table 3. The precision was good (standard deviations < 6%). A back-washing step was necessary for the complete separation of gold and silver, otherwise, 2-6% silver can be found in the gold extract. In all cases, gold was quantitatively extracted by the proposed method.
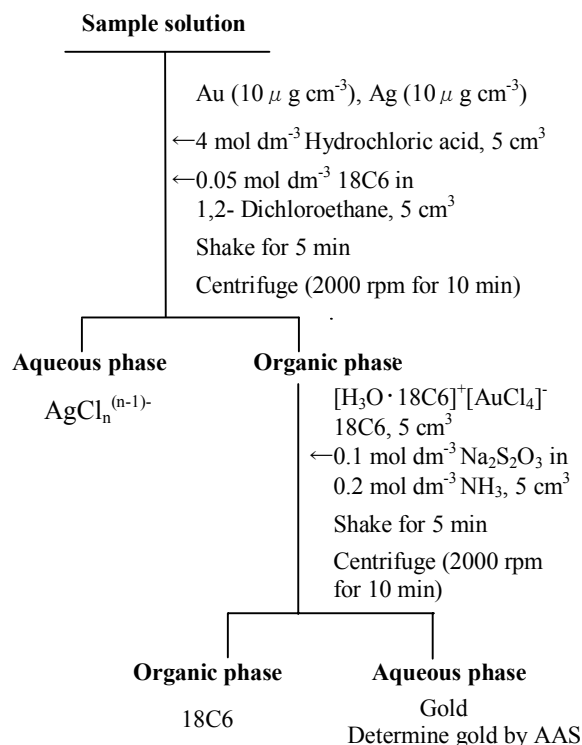
Sample solution

Au (10 μ g cm^{-3}), Ag (10 μ g cm^{-3})

←4 mol dm^{-3} Hydrochloric acid, 5 cm^3

←0.05 mol dm^{-3} 18C6 in
1,2- Dichloroethane, 5 cm^3

Shake for 5 min

Centrifuge (2000 rpm for 10 min)

Aqueous phase   **Organic phase**

AgCl$_n^{(n-1)-}$

[H$_3$O·18C6]$^+$[AuCl$_4$]$^-$
18C6, 5 cm^3

←0.1 mol dm^{-3} Na$_2$S$_2$O$_3$ in
0.2 mol dm^{-3} NH$_3$, 5 cm^3

Shake for 5 min

Centrifuge (2000 rpm
for 10 min)

Organic phase   **Aqueous phase**

18C6   Gold
Determine gold by AAS

Fig. 3 Analytical scheme for the determination of gold traces in hydrochloric acid media

It is also important to mention that the 4 mol dm^{-3} concentration of hydrochloric acid adopted limits the presence of silver in solution to a maximum of 100 μg cm^{-3} due to the observed precipitation (AgCl) at higher levels. On the basis of gold`s extraction behavior in Fig. 1, this limitation can be relieved by using more concentrated hydrochloric acid solutions.

Gold preconcentration

The potential of the method for gold preconcentration was also investigated. For this purpose, AgNO$_3$ (99.8% purity) and Ag$_2$SO$_4$ (90% purity) first-class reagents were spiked with 0.05 – 1.0 μg cm^{-3} gold and the results are given in Table 4. Their gold content was under detection limit (0.25 ng cm^{-3}) after 20 times preconcentration. The observed quantitative recovery (>96%) on the other hand, shows the capability of the method to preconcentrate trace levels of gold in silver matrices up to 20-fold.

Based on the results by ion-association complex formation, the proposed method was found to give excellent selectivity for gold extraction over silver and perform 20-fold preconcentration. The use of a more sensitive AAS instrument therefore, combined with the method`s high tolerance for co-existing foreign ions, can lead to better performance which can be applied in the determination of very low levels of gold such as that found in natural waters.[17]

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Table 3 Separation of gold and silver

Metal added, μ g cm^{-3}		Metal found, μ g cm$^{-3\ a}$		Recovery, %	
Au	Ag	Au	Ag	Au	Ag
1	1	1.01 ±0.01	0.04 ±0.01	101	4
10	1	10.03 ±0.15	0.06 ±0.01	100	6
100	1	95.67 ±1.53	0.02 ±0.01	96	2
1	1	0.99 ±0.04	0^b	99	0
1	10	1.00 ±0.01	0^b	100	0
1	100	1.01 ±0.02	0.029 ±0.005^b	101	0.03

HCl: 4 mol dm^{-3}; 18C6: 0.05 mol dm^{-3}; Solvent: 1,2-Dichloroethane; Shaking time: 5 min
a: Mean value of 3 determinations   b: After back-washing

Table 4 Trace enrichment of gold in silver samples

Sample, 100 μ g cm^{-3}	Precon- centration factor	Gold Added, μ g cm^{-3}	Gold Found μ g cm$^{-3\ a}$	Recovery, %
AgNO$_3$	1	1	0.96 ±0.02	96
	10	0.1	1.02 ±0.04	102
Ag$_2$SO$_4$	20	0.05	1.04 ±0.06	104

HCl: 4 mol dm^{-3}; 18C6: 0.05 mol dm^{-3}; Solvent: 1,2-Dichloroethane; Shaking time: 5 min
a: Mean value of 3 determinations