

Separation of gold (3) and silver (1) as their ion-pair complexes with crown ethers by solvent extraction

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学位論文要旨

Abstract

A new solvent extraction method was developed for the separation of gold and silver in hydrochloric acid, HCl, and/ or potassium thiocyanate, KSCN, media using ion-pair complex formation with crown ethers in 1,2 dichloroethane. At ≥ 2 mol/L HCl, the tetrachloro gold anion, AuCl_4^- , forms an ion-pair complex with 18-crown-6 (18C6) oxonium cation, $[\text{18C6} \cdot \text{H}_3\text{O}]^+$, in 1,2-dichloroethane. Silver chloro complexes, $\text{AgCl}_n^{(n-1)}$, were unextractable under these conditions. Among the investigated crown ethers, the use of 18C6 resulted best in both the quantitative extraction of gold and its complete separation from silver. Back-extraction was carried-out by the use of 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ in 0.2 mol/L NH_3 , followed by flame atomic absorption spectrometry (FAAS) for determination.

The addition of 0.05 mol/L KSCN to 1.0 mol/L HCl enabled the succeeding extraction of silver with dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane. Both 18C6 and DC18C6 in chloroform extracts silver quantitatively in nitrate media, but the use of 1,2-dichloroethane extends the high extraction efficiency of DC18C6 to the 1 mol/L HCl region. Silver thiocyanate complex, $\text{Ag}(\text{SCN})_2^-$, was extracted as an ion-pair with the potassium DC18C6 cation, $[\text{DC18C6} \cdot \text{K}]^+$, in 1,2-dichloroethane. Stripping of the extracted silver was

achieved by use of 3 mol/L KSCN and was subsequently determined by FAAS. The optimum condition for silver extraction was also found favorable for the extraction of gold, platinum and palladium. Exploiting the extractability differences of these noble metals with 18-membered crown ethers at different HCl and/or KSCN media was instrumental to the separation of silver.

Introduction

Both rare and highly valuable, gold and silver are commonly found associated with each other in various materials. Traditional methods for their separation involve a series of dissolution, precipitation and redissolution processes. The number of repeating cycles depends on the target purity. The development of a highly selective analytical procedure for the separation of gold and silver evidently poses a challenging research.

Continuous efforts were devoted to studies on crown ether-mediated separation of metal ions based on the macrocycle's excellent selectivity for metals and its ability to transfer these inorganic substances across boundaries of immiscible phases. Exploiting the differences between the extractability of metals from sample matrices with various crown ethers can be used in the development of a separation procedure such as that based on ion-pair complex formation; phase transfer of metal analytes as complex anions, extracted as counter ions to the captured cation in the macrocycle's cavity. In hydrochloric acid and/or potassium thiocyanate media, the neutral ion-association product consists of a macrocyclic cation and an extractable anionic metal chloro complex, MCl_n^{x-} , or an extractable anionic metal thiocyanate complex, $M(SCN)_n^{x-}$.

The main objective of this study is to develop a separation procedure for gold and silver using ion-pair complex formation with crown ethers. The subsequent extraction, back-extraction and determination procedures will also be established. Conditions that result in the best separation and in the quantitative recovery of gold and silver are taken as optimum.

Experimental procedure

Solvent extraction Equal volumes (5 mL) of an aqueous solution of 4mol/L hydrochloric acid containing 0.5-10 μ g/mL each of gold and silver and a 1,2- dichloroethane solution of 0.05 mol/L 18C6 were placed into a 30-mL glass-stoppered centrifuge tube. The mixture was shaken for 5 min (by shaking machine) and phase separation was carried out by centrifugation at 2,000

rpm for at least 5 min. The gold-loaded organic phase was collected for back-extraction. The remaining aqueous phase was diluted 4-folds followed by addition of 0.05 mol/L KSCN. This was then shaken for 5 min with a 1,2-dichloroethane solution of 0.05 mol/L DC18C6 for the extraction of silver. After phase separation, the silver-loaded organic phase was collected.

Back-extraction procedure The gold and silver-loaded organic phase was next shaken with 5 mL each of 0.10 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ in 0.10 mol/L NH_3 and 3 mol/L KSCN, respectively. The amount of gold and silver stripped from the organic phase was determined by Flame-AAS.

Results and discussion

Effect of crown ether

The crown ethers examined were DC18C6, 18C6, DB18C6 and 15C5. Extractions in hydrochloric acid media using 0.05 mol/L 18C6 in 1,2-dichloroethane resulted best in the separation and quantitative extraction of gold from its solution with silver as shown in Fig. 1. The addition of 0.05 mol/L KSCN to the silver solution in 1.0 mol/L HCl subsequently extracts silver by 0.05 mol/L DC18C6 in 1,2-dichloroethane (Fig. 2).

Effect of solvent

Among the different organic solvents investigated, the use of 1,2-dichloroethane resulted in the best separation and quantitative extraction of gold. Although a chloroform solution of 18C6 or DC18C6 can extract silver quantitatively in nitrate media, only the use of a 1,2-dichloroethane solution of DC18C6 extracts silver in the 1.0 mol/L HCl region (Fig. 2).

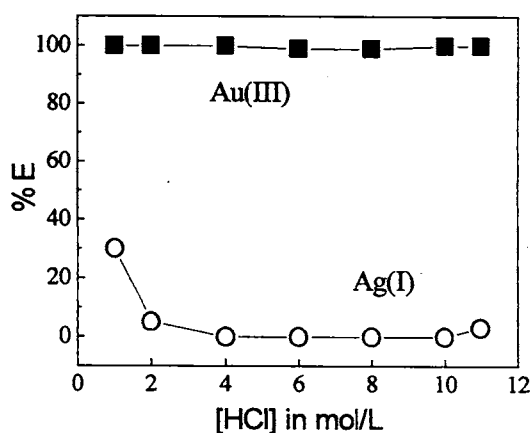


Fig. 1. Effect of increasing the hydrochloric acid concentration on the extraction of gold (■) and silver (○) by 0.05 mol/L 18C6 in 1,2-dichloroethane

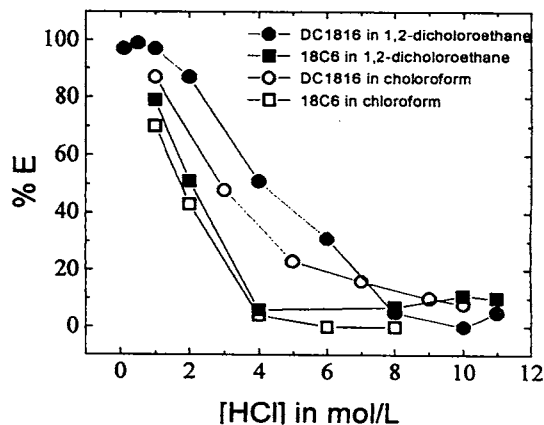


Fig. 2. Extraction of silver using 18C6 and DC18C6 in chloroform and 1,2-dichloroethane with increasing hydrochloric acid concentration

Effect of shaking time

For the forward and backward extraction of gold and silver, a short 5 min-shaking time was found sufficient for their separation and individual quantitative extraction. This indicates that under the ion-pair complex formation mechanism, the extraction equilibrium of the metal analytes is rapidly achieved in the proposed method.

Preconcentration factor

The preconcentration factor was determined by increasing the phase volume ratio (V_{aq}/V_{org}). The quantitative recovery of gold was attainable up to 20-fold in a single extraction. For a minimum recovery of 90 % silver, the corresponding preconcentration factor for 0.1, 0.5 and 1 mol/L HCl composition of the sample were 60-, 30- and 5-fold, respectively.

Composition of extracted species

Inspection of the slopes derived from the plots of log [crown ether] vs log of distribution ratio was used in the determination. Gold was extracted from 4 mol/L HCl with various 18C6 concentrations in 1,2-dichloroethane. Similarly, various solutions of DC18C6 in 1,2-dichloroethane extract silver from 0.05 mol/L KSCN in 1 mol/L HCl. For both metals, a 1:1 metal-to-crown ether ratio was derived from the slope analysis data which indicates a composition of $[18C6 \cdot H_3O]^+ AuCl_4^-$ for the extracted species of gold and a composition of $[DC18C6 \cdot K]^+ Ag(SCN)_2^-$ for silver.

Interference studies

Interference studies were conducted by adding various amounts of foreign ions to a 1 μ g/mL gold or silver solution before extraction. The proposed method was found to have excellent tolerance for the examined foreign ions. Back-washing easily removed iridium interference on gold extraction. On the other hand, the optimum condition for silver extraction was also found favorable for the extraction of gold, platinum and palladium. Exploiting the extractability differences of these noble metals with 18-membered crown ethers at different hydrochloric acid and/or potassium thiocyanate media was instrumental to the separation of silver.

Separation of gold and silver

The high efficiency of the developed method for the separation of gold and silver can be seen in the spike recovery results shown in Table 1. A back-washing step was necessary for their complete separation. The proposed extraction procedure was applied to the determination of traces of gold and silver in a selection of chemical reagents.

Conclusion

The selectivity of the proposed method for the separation of gold and silver was very good. It can therefore be used in the production of highly purified materials by extracting trace gold or silver

impurity. The efficiency of ion-pair complex formation for the separation of the noble metals also indicates its suitability for the separation of future combination of metals.

Table 1 Separation of gold and silver

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

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

学位論文審査結果の要旨

本学位論文に関し、平成14年7月18日に第1回学位論文審査委員会を開催し、口頭発表と面接審査を行った。さらに、7月30日に第2回審査会を開催し、口頭発表の後に協議した結果、以下のように判定した。

本論文は、18-クラウン-6 (18C6) の1, 2-ジクロロエタン溶液を用いて金(Ⅲ)と銀(Ⅰ)を含む塩酸媒体から金(Ⅲ)だけを、またジシクロヘキシル-18-クラウン-6 (DC18C6) の1, 2-ジクロロエタン溶液を用いてチオシアン酸カリウムを含む塩酸媒体から銀(Ⅰ)をイオン対錯体として定量的に抽出分離する新しい方法を創案したもので研究成果は以下の通りである。

- 1) 金(Ⅲ)は0.05mol/L 18C6の1, 2-ジクロロエタン溶液により4mol/L塩酸から5分以内にヒドロオキソニウムイオンを内包したクラウンエーテルの陽イオン($18C6 \cdot H_3O^+$)と $AuCl_4^-$ の陰イオンとの1:1のイオン対錯体として定量的に抽出できる。このとき、銀(Ⅰ)も2~6%抽出されるが、溶媒相洗浄により完全に除去できた。金(Ⅲ)のストリッピングは、0.1mol/L $Na_2S_2O_3$ の存在下で0.2mol/Lアンモニアにより5分以内に達成できた。その後、金(Ⅲ)をフレイム原子吸光法で定量したが、21種の共存イオンの妨害もなく、検出限界は0.25ng/mL、スパイク回収は>96%で20倍濃縮も可能であった。また、高純度の銀塩試薬中の微量の金を分離定量できた。
- 2) 銀(Ⅰ)は0.05mol/L DC18C6の1, 2-ジクロロエタン溶液により、0.05mol/Lチオシアン酸カリウム存在下で1.0mol/L塩酸から5分以内に、カリウムイオンを内包したクラウンエーテルの陽イオン($DC18C6 \cdot K^+$)と $Ag(SCN)_2^-$ の陰イオンとの1:1のイオン対錯体として定量的に抽出できる。抽出された銀(Ⅰ)のストリッピングは3.0mol/Lのチオシアン酸カリウム溶液により5分以内に達成できた。その後、銀(Ⅰ)をフレイム原子吸光法で定量したが、22種の共存イオンの妨害もなく、検出限界は13 μ g/mL、スパイク回収は96%で、酸濃度を下げる(0.1mol/L)と60倍濃縮も可能であった。また、高純度の金、白金及びパラジウム塩中の微量の銀を分離定量できた。

以上のように、本論文は、クラウンエーテルがヒドロオキソニウムイオン又はカリウムイオンを内包した陽イオンとなり、金(Ⅲ)の塩化物及び銀(Ⅰ)のチオシアン化物の陰イオンをイオン対錯体として抽出する新奇な抽出挙動を見出し、抽出機構も調べ、金(Ⅲ)及び銀(Ⅰ)イオンの選択的な抽出分離法を開発したもので、博士論文に値するものと判定した。