ATOMIC-ABSORPTION DETERMINATION OF PALLADIUM IN COPPER ANODE SLIME AFTER SELECTIVE SEPARATION BY SYNERGISTIC EXTRACTION

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Abstract - A synergistic extraction system has been reported in a previous paper for the selective extraction of Pd from solution also containing Pt with quinolin-8-ol and tributylphosphite in CHCl_3 [1]. This method was applied to a synthetic sample solution, the composition of which was similar to that of anode slime obtained from an electrolytic copper refinery. The results indicated that trace amounts of approximately 5×10^{-4} M Pd could be separated from similar concentrations of Pt. Under the conditions employed, Cu was extracted only to a negligible extent. In the present work, the method was applied to a real sample of copper anode slime which had the following composition; Pd, 0.36; Pt, 0.27; Pb, 0.16; Ag, 0.075; Cu, 0.019; Rh, 0.013 and trace amounts of Ir and Au (total mass, 0.90 g). The Pd in CHCl_3 phase was found to be quantitatively back-extractable within 5 minutes by shaking with dilute HCl solution containing 0.5 M thiourea. Details of the extraction procedure including the back-extraction process for the separation of Pd as well as the analytical results of Pd contents in sample, as determined by atomic-absorption spectrophotometry, are described in this paper.

Key words palladium, selective extraction, copper slime

INTRODUCTION

In a previous paper we have reported a new method of synergistic extraction which has been developed for the selective separation of Pd from Pt[1]. The method was based on the extraction of Pd with chloroform containing 8-hydroxy quinoline (HQ) and tributylphosphite (TBPI). When a solution containing both Pd and Pt (5×10^{-4} M each) was extracted using the proposed method, the separation of Pd from Pt was in the ratio of 2000:1. The proposed method was applied to a synthetic sample solution which contained various elements in amounts similar to those expected in solutions of anode slime obtained from an electrolytic copper refinery. The mixture had the following composition : Ag, 0.076; Cu, 0.19; Bi, 0.076; Se, 0.053; Zn, 0.038; Pd, 0.053; Pt, 0.097; and Pb, 0.18g(total mass, 0.76g). The results also indicated that trace amounts of Pd (ca. 5×10^{-4} M) could be separated effectively from equal amounts of Pt.

In the present work, the proposed method was developed as a selective preconcentration method, which was applicable to a real sample of copper anode slime. The Pd in chloroform phase was found to be quantitatively back extractable within 5 minutes by shaking with dilute hydrochloric solution containing 0.5 M thiourea. After back-extraction, the Pd in aqueous phase was determined by atomic absorption spectrophotometry. The separation of Pd from Pt and also from various coexisting elements contained in copper anode slime were found to be satisfactory.

EXPERIMENTAL

Chemicals All the chemical reagents were prepared as described previously[1]. Prior to extraction the oxidation states of Pd(II) and Pt(IV) in HCl were confirmed by visible absorption spectra[2]. The solid sample of copper anode slime had the following composition; Pd, 0.36; Pt, 0.27; Pb, 0.16; Ag, 0.075; Cu, 0.019; Rh, 0.013g; trace amounts of Ir and Au (total mass, 0.90g). It was treated as follows:

Extraction, back-extraction and determination of Pd To a beaker containing the slime sample was added aqua regia and the solution was heated on a hot-plate to near-dryness. Concentrated HCl was then added and the contents of the beaker were evaporated to dryness; the treatment with concentrated HCl was repeated twice more after which the dry mass was dissolved in 5×10^{-3} M HCl and the grey residue was filtered through two sheets of filter-paper (Whatman No.1). The concentrations of Pd and Pt were determined by atomic absorption spectrometry (339 nm for Pd, 265 nm for Pt). A 10-mL volume of the sample solution (5×10^{-3} M HCl) was extracted with an equal volume of CHCl_3 containing 5×10^{-4} M HQ plus 1×10^{-3} M TBPI. The Pd in CHCl_3 phase was back-extracted into aqueous phase by shaking with dilute HCl solution containing 0.5 M thiourea. As expected, the results indicated that trace amounts of Pd (ca. 5×10^{-4} M) could be determined quantitatively by atomic absorption spectrometry after effective separation that employed selective synergistic extraction as well as back-extraction using thiourea.

RESULTS AND DISCUSSION

Extraction The sample solution was extracted with CHCl_3 containing HQ plus TBPI. The distribution coefficients of various elements contained in the anode slime were obtained as shown in Table 1. The metal concentration in the aqueous phase was determined by atomic absorption spectrometry, while the metal concentration in the organic phase was calculated from the difference between the metal content in the aqueous phase before and after extraction. The separation ratio is defined as $D(\text{Pd})/D(\text{Pt})$, where $D(\text{Pd})$ and $D(\text{Pt})$ are the distribution coefficients of each metal between the aqueous and organic phases.

TABLE 1. Distribution coefficients of various elements contained in anode slime

Extractant	Distribution coefficient					
	Pd	Pt	Cu	Rh	Ir	Au
HQ (5×10^{-4} M)	0.545	0.016	0.11	0.22	<d.l.	<d.l.
TBPI (1×10^{-3} M)	1.43	0.055	0.098	0.10	<d.l.	<d.l.
HQ + TBPI (5×10^{-4} M) (1×10^{-3} M)	40.1	0.041	0.11	0.079	<d.l.	<d.l.

d.l. = detection limit

Back-extraction of Pd with thiourea A 10-mL volume of chloroform containing Pd (ca. 5×10^{-4} M), which had been previously extracted into CHCl_3 phase with 5×10^{-4} M HQ plus 1×10^{-3} M TBPI, was back-extracted by shaking with an equal volume of HCl solution containing various concentrations of thiourea. The back-extraction efficiencies of Pd are shown in Table 2.

TABLE 2 Back-extraction efficiencies of Pd from CHCl_3 phase into aqueous phase with thiourea. Shaking time = 15 min. Shaking speed = 120 r.p.m.

Back-extractant	Recovery ratio of Pd
2.0 M HCl containing 0.2 M thiourea	81 %
1.0 M HCl containing 0.2 M thiourea	90 %
0.5 M HCl containing 0.2 M thiourea	97 %
0.5 M HCl containing 0.1 M thiourea	67 %
0.5 M HCl containing 0.2 M thiourea	97 %
0.5 M HCl containing 0.5 M thiourea	100 %

As shown in Table 2, trace amounts of Pd (ca. 5×10^{-4} M) in CHCl_3 phase could be quantitatively back-extracted into the aqueous phase by shaking with 0.5 M HCl containing 0.5 M thiourea within 15 min. In order to minimize the shaking time, further extractions were made, which indicated that 5 min. shaking was adequate for back-extraction of Pd as shown in Table 3.

TABLE 3. Back-extraction efficiencies of Pd at various shaking times.
Back-extractant = 0.5 M HCl containing 0.5 M thiourea.
Shaking speed = 120 r.p.m.

Shaking time (min) :	1	2	3	4	5
Recovery ratio of Pd (%):	81	87	95	97	100

The back-extraction of Pd by shaking with 0.5 M HCl containing 0.5 M thiourea for 5 min. is seen to be satisfactory. The quantitative recovery of Pd by the proposed back-extraction method was further confirmed in the case of a real sample of copper anode slime, as follows: The slime sample was treated with aqua regia and concentrated HCl as described above. The concentration of Pd in the filtrate, obtained as above, was determined by the ICP-AES method. An aliquot of the filtrate was extracted with CHCl_3 containing HQ plus TBPI. The Pd extracted into CHCl_3 phase was back-extracted by the proposed method with thiourea. After back-extraction, the Pd in aqueous phase was determined by atomic absorption spectrometry. The Pd concentration in the solution of slime sample as determined by the ICP-AES agreed well with that determined by atomic absorption spectrometry after back-extraction. This indicates the quantitative recovery of Pd by the proposed method of back-extraction.

In the initial stage of the present work, back-extraction of Pd was attempted using various methods which included pH variation of aqueous phase, shaking with concentrated acids or bases etc., however, none of them showed quantitative recovery of Pd. Thiourea is widely used in analytical chemistry, in particular solvent extraction of the platinum group metals[3,4]. Accordingly, thiourea was tried specifically for the back-extraction of Pd for the present work. Fortunately the results showed excellent recovery.

Pd complexes after back-extraction with thiourea In order to study the nature of the Pd complex formed in the back-extraction, a spectrophotometric absorption spectrum was obtained following the method described by Shlenskaya et al[3]. A portion of aqueous solution containing Pd was extracted with CHCl_3 containing HQ plus TBPI, after which the CHCl_3 phase was shaken with

HCl containing various concentration of thiourea, as described above. The absorption spectra of the aqueous phase were recorded as shown in Fig. 1, which agrees well with the similar spectra reported previously[3].

Fig. 1. Absorption spectra of thiourea complexes of Pd(II) in chloride media obtained after back-extraction with thiourea. Pd(II) concentration in CHCl_3 phase = ca. 5×10^{-4} M. Back-extraction systems : [Thm]/[Pd(II)] : 1) 1:1, 2) 2:1, 3) 3:1, 4) 5:1, 5) 1,000:1. After back-extraction, aqueous phase was diluted with 0.5 M HCl to the following ratio, respectively : 1) 1:10, 2) 1:20, 3) 1:30, 4) 1:50, 5) 1:10,000.

They showed that Pd formed the mixed complexes with thiourea in chloride media in the following manner, indicating gradual replacement of chloride ions by thiourea(Thm).

In our previous work, in an attempt to investigate the composition of the extracted species via NMR spectroscopy and thermogravimetry, the species was postulated to be $\text{Pd} \cdot \text{Q} \cdot \text{TBPI} \cdot \text{Cl}$ [1]. It is certainly noteworthy that judging from the similarity of two absorption spectra, the Pd species formed in the back-extraction by the present method now appear to be the mixed complexes of $\text{PdCl}_{4-n}(\text{Thm})_n^{2-n}$ as shown by Shlenskaya [3].

Further work The proposed method is currently being applied in our Laboratory in order to determine Pd in various samples of copper anode slime, and the results will be published elsewhere.

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