Amperometric Titration of Silver as Xanthate and Its Determination in Presence of Lead

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Electrometric determination of silver by As_2O_3 was studied by dead stop end point procedure by Lambert and Walker.[1] Kalvoda and Zyka[2] developed an amperometric procedure for the element with potassium ferrocyanide using a base solution of 1 M potassium nitrate and an applied potential of −0.3V. Songina[3] titrated silver by potassium iodide at a rotating platinum electrode. Amperometric determination of silver by thiourea has been reported recently.[4,5]

Potassium ethyl xanthate is widely used as an extraction reagent for the detection of various metal ions.[6,7] Gravimetric[8,9] and a few electroanalytical methods[10,11] are also known using xanthate as a reagent. No attempt has, however, been made to use this reagent for amperometric titrations of metal ions. This communication deals with the use of xanthate as a precipitating agent in the amperometric determination of silver and its estimation in presence of lead. Two methods have been developed for the amperometric titrations. The first is based on the measurement of the anodic current of excess titrating agent after the end point. The second utilizes the decrease in height of the reduction wave of the uncombined metal ion during the course of the titration. A combination of these two methods is used for the determination of the constitents of a mixed solution of the two metal ions.

Solutions. Standard solutions of silver and lead were obtained from E. Merck reagents. Stock solution of 0.05 M xanthate was prepared and stored in a dark bottle.

Ammonium tartrate - potassium nitrate buffer was prepared from pure reagents.

The pH of the solution was measured with a line operated Beckmann Zeromatic pH meter.

Apparatus. A simple form of an amperometric unit with rotating platinum electrode described by Kolthoff[12] was used.

Experimental

Preliminary experiments were carried out to study appropriate conditions for the quantitative precipitation of silver in a base solution ammonium tartrate - potassium nitrate in a pH range 7 to 9 and the following procedure was evolved. An aliquot of silver solution was taken in a 100 m*l* pyrex beaker, to which sufficient buffer was added to maintain an overall concentration of 0.05 M. The pH of the solution was adjusted to 9 by adding aqueous ammonia. A potential of +0.2 V *vs.* SCE was applied, the galvanometer reading was noted initially and after each addition of the titrant. After the whole of the silver was removed as xanthate, excess reagent gave the diffusion current of its own resulting in a regular rise in the current. The plot of the volume of xanthate against galvanometer reading

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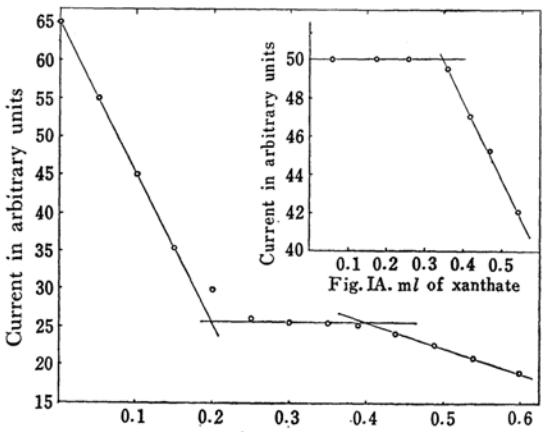

Fig. 1. Typical amperometric titration curves.
Fig. 1 A Titration curve of silver with xanthate.
Fig. 1 B Titration curve for a mixture of silver and lead.

TABLE 1. DETERMINATION OF SILVER AS XANTHATE

S. No.	Amount of Ag^+ taken, mg	Amount of Ag^+ found, mg	% error
1	0.10832	0.1091	+0.7
2	0.2708	0.2700	−0.3
3	0.5416	0.5400	−0.3
4	1.0832	1.0900	+0.7
5	1.3540	1.3500	−0.3
6	1.8956	1.8900	−0.3
7	2.1664	2.1500	−0.8

gave a curve shown in Fig. 1A. The results are given in Table 1.

Silver and Lead. Earlier results from these laboratories reported the determination of lead as xanthate.[13] Since the half wave potential of lead (−0.5 V) is more negative than that of silver (>0) at pH 8, the latter can be determined cathodically, while the lead end point is determined anodically. An attempt was therefore made to estimate silver and lead in a mixed solution.

13) G. S. Deshmukh and K. Saraswathi, *Indian J. Chem.*, **3**, 489 (1965).

Aliquots of lead and silver were taken in 100 m*l* pyrex beaker containing about 5 m*l* of ammonium tartrate and 5 m*l* of potassium nitrate (each 0.25 M approx.). The pH of the solution was adjusted to 8 with ammonia and the contents were diluted to 25 m*l* and the titration was performed with xanthate. The current was noted at +0.05 V. As the addition of xanthate continued, the diffusion current of silver reduced gradually and became steady. With further addition of the titrant lead started getting precipitated. After the whole of the lead was removed excess of the reagent gave the anodic diffusion current of its own. The intersection of the line of the residual current with reaction line and with excess reagent-line are the end points of silver and lead respectively (Fig. IB). The results of these titrations are given in Table 2.

TABLE 2. DETERMINATION OF SILVER AND LEAD

S. No.	Amount taken in mg		Amount found in mg		% error	
	Ag(I)	Pb(II)	Ag(I)	Pb(II)	Ag(I)	Pb(II)
1	0.2708	3.150	0.2700	3.143	−0.3	−0.2
2	0.5416	2.10	0.5400	2.083	−0.3	−0.8
3	0.5416	1.050	0.5534	1.044	+2.0	−0.6
4	1.0832	0.525	1.0800	0.5247	−0.16	−0.06
5	1.0832	1.050	1.0800	1.044	−0.16	−0.6
6	1.3540	0.315	1.3500	0.3500	−0.3	+0.5
7	2.1664	2.100	2.168	2.100	+0.09	—

Summary

A new procedure for the amperometric titration of silver with potassium ethyl xanthate at +0.2 V *vs.* SCE in ammonium tartrate-potassium nitrate buffer (adjusted to pH 9 with ammonia) has been described. A rotating platinum microelectrode was used. Details are given for the determination of silver in a mixture of silver and lead. The accuracy of the procedure is comparable with that obtained with classical methods.

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