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Amperometric Determination of Silver(I) with Hydrazine Sulfide and Its Estimation in Presence of Lead(II)

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Synopsis. Silver(I) has been estimated by an amperometric method using hydrazine sulfide as titrant. The titration is carried out in ammonium tartrate–ammonia supporting electrolyte (pH$\approx$9). Further, this method is extended to determine silver(I) in presence of lead(II). Under these conditions lead(II) reacts only after all silver(I) has been precipitated. The accuracy of the procedure is comparable with that obtained in classical method.

One of the oldest procedure for the determination of silver was carried out by Lamber and Walker[1)] using dead stop end point method. Potassium hexacyanoferrate(II)[2)] has been used for the determination of silver at an applied potential of +0.4 V. Songina[3)] titrated silver with potassium iodide at rotating platinum electrode. Thiourea[4,5)] has been successfully used for estimation of silver. Deshmukh and Garde[6)] determined silver using potassium thiocarbonate. Ethyl xanthate[7)] was used to determine silver alone and in presence of lead. Many complexing agents like diphosphorus pentasulfide,[8)] thiosemicarbazide,[9)] and 8 quinolinethiol[10)] have been successfully used to determine silver. Recently ethyltrithiocarbonate[11)] has been reported as titrant for silver.

In the present investigation a new amperometric method for determination of silver(I) has been developed using hydrazine sulfide as titrant. The procedure is further applied for quantitative estimation of silver(I) in presence of lead(II). Preliminary studies of the polarogram characteristics of hydrazine sulfide at dropping mercury electrode revealed a well developed anodic wave in pH range 8 to 9.5 in ammonium tartrate–ammonia buffer. It was considered useful for titration of metals giving precipitates. Furthermore the anodic current of hydrazine sulfide and cathodic current of metal ions can be employed for simultaneous determination of binary mixture of silver and lead.

Experimental and Results

Solutions. Stock solutions of silver(I) and lead(II) were prepared from AnalaR grade samples. These stock solutions were standardized by classical methods.[12)] The lower concentrations were then obtained by successive dilution of these stock solutions. The standard solution of hydrazine sulfide was prepared by dissolving an accurately weighed quantity of pure recrystallised sulfur in hydrazine hydrate and was protected from atmospheric contact with a layer of petroleum ether. The solution was found to be quite stable under these conditions.[13)]

Ammonium tartrate solution (0.1 M (1 M=1 mol dm^{-3})) was prepared from pure sample and its pH was adjusted to 9 by concentrated ammonia.

Table 1. Amperometric determination of Ag^I with hydrazine sulfide

Supporting electrolyte: 0.1 M ammonium tartrate+ammonia (pH$\approx$9).

Potential applied: +0.2 V *versus* SCE.

Observation No.	Amount of Ag^I (mg)		Error
	Taken	Found	%
1	0.539	0.535	−0.74
2	0.8071	0.8011	−0.98
3	1.0788	1.0785	−0.04
4	1.3485	1.3478	−0.34
5	1.618	1.618	—
6	2.157	2.165	+0.37

A simple form of an amperometric titration unit with rotating platinum micro electrode described by Kolthoff[14)] was used.

Determination of Silver(I). Preliminary experiments were carried out to study appropriate conditions for quantitative precipitation of silver in base solution of ammonium tartrate–ammonia in pH range 8 to 9.5 and following procedure was followed.

An aliquots of silver(I) solution was placed in Pyrex beaker containing 25 ml of ammonium tartrate–ammonia buffer (pH$\approx$9). The titration was carried out at an applied potential of +0.2 V *versus* SCE. The calibrated 2 ml microburette was used for delivery of titrant. The galvanometer reading was noted initially and after each addition of titrant. The diffusion current remained constant till the whole of silver was precipitated. After the end point hydrazine sulfide gave the diffusion current of its own, resulting the regular rise in the current. The plot of volume of hydrazine sulfide added against galvanometer reading gave reverse 'L' shaped curve. The results are given in Table 1.

Determination of Silver(I) and Lead(II). Earlier results from this laboratory reported determination of lead with hydrazine sulfide.[13)] Since the half wave potential of lead(II) (−0.54 V) is more negative than that of silver(I) (>O) at pH 9, the latter can be determined cathodically while lead(II) end point can be determined anodically. An attempt was, therefore, made to estimate silver(I) and lead(II) in mixed solution. The applied potential, which was chosen, was such that lead(II) was not reduced at this potential but reagent has anodic diffusion current.

Aliquots of silver(I) and lead(II) were taken in 100 ml Pyrex beaker containing 25 ml ammonium tartrate – ammonia buffer (pH$\approx$9). The titration was performed with hydrazine sulfide. The current was noted at −0.2 V *versus* SCE. With the addition of hydrazine sulfide to mixture, diffusion current of silver (I) reduced gradually and became steady. When all

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silver was precipitated with further addition of titrant, lead started getting precipitated. After all lead(II) was precipitated excess of reagent gave anodic diffusion current of its own. A typical titration curve is shown in Fig. 1. The first intersection gives the amount of silver(I) while second intersection gives the amount of lead(II). The results are returned in Table 2.

Besides simplicity, accuracy and time economy a significant advantage offered by the present method is the use of pure elemental sulfur directly as primary standard for preparing the solution of the titrant.

Table 2. Determination of Ag^I and Pb^{II} with hydrazine sulfide

Supporting electrolyte: 0.1 M ammonium tartrate + ammonia (pH≈9).
Potential applied: −0.2 V *versus* SCE.

Observation	Amount taken (mg)		Amount found (mg)		Error/%	
	Ag^I	Pb^{II}	Ag^I	Pb^{II}	Ag^I	Pb^{II}
1	0.539	1.036	0.535	1.038	−0.74	+0.19
2	0.8091	2.590	0.8084	2.586	−0.08	−0.15
3	1.6182	4.144	1.5982	4.140	−0.61	−0.096
4	2.1576	1.036	2.1497	1.038	−0.36	+0.19
5	2.1576	3.108	2.165	3.105	+0.37	−0.09
6	1.0788	3.108	1.0788	3.084	—	−0.77

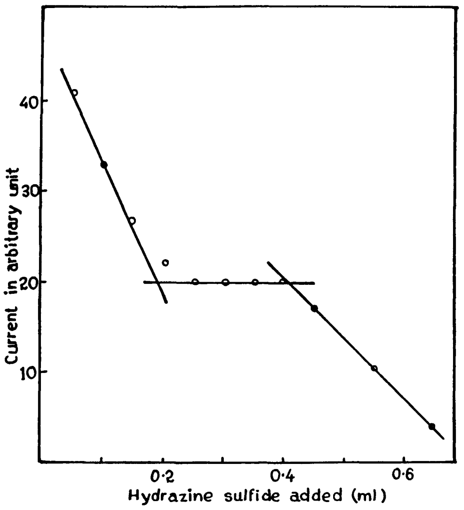

Fig. 1. A typical amperometric titration curve for mixture of Ag^+ and Pb^{II} in tartrate buffer at −0.2 V *versus* SCE.

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