AMPEROMETRIC DETERMINATION OF SILVER AND LEAD WITH N-METHYLANILINE CARBODITHIOATE AS TITRANT

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Silver is closely associated with lead in nature and also in some alloys. The cupellation procedure in the metallurgy of silver is mainly meant for its separation from lead. Therefore, estimation of the two metals in a mixture by a suitable technique is of considerable analytical importance.

Various methods for the amperometric titration of silver [1-3] and lead [4-6] are known in literature. In the present investigation, they have been estimated separately as well as in a mixture using N-methylaniline carbodithioate as titrant. N-methyl aniline carbodithioate produces a well defined diffusion controlled anodic wave in 6.5-11.0 pH range. This is useful for the titrations of metals precipitating as carbodithioates. A combined use of the cathodic current of metal ions and the anodic current of carbodithioate can be employed for the simultaneous determination in binary mixtures.

A solution of 0.1 M ammonium tartrate + 0.1 M potassium nitrate in the pH range (7-10) was found to be a good medium for the titration of silver and lead and gave quantitative reproducible results. In an ammonical tartrate solution (pH=9),lead reacts only after all the silver has been precipitated. Since the half wave potential of lead is considerably more negative than silver, the latter may be determined cathodically, while lead is determined anodically. Titrations of silver and lead with carbodithioate using different concentrations of these cations revealed that these cations formed 1:1 and 1:2 complex with carbodithioate respectively.

EXPERIMENTAL

Reagents

N-methylaniline carbodithioate was prepared by the method of Macrotrigiano[7]. Stock solution of it was prepared by dissolving a calculated amount in distilled water and standardized against a standard solution of mercuric nitrate using diphenyl carbazone as the internal indicator. Solutions of supporting electrolytes were prepared by dissolving A.R. grade potassium nitrate, ammonium tartrate in distilled water. Stock solutions of silver and lead were prepared from silver nitrate, and lead nitrate. Silver nitrate was standardized by Volhard's method, while lead nitrate with EDTA solutions . Dilute ammonia solution was used for pH adjustments.

Instruments

The titrations were performed by using a manual Toshniwal polarograph. An Elico pH meter was used for pH measurements.

Procedure

Determination of Silver: An aliquot of silver solution was taken and a requisite volume of ammonium tartrate and potassium nitrate buffer (pH = 9.5) was added to maintain the overall ionic strength at 0.1M. Nitrogen was passed slowly through the solution for 15 minutes. Titration was carried out using a rotating platinum microelectrode at a potential of + 0.1 V. The diffusion current remained constant till the whole of silver was precipitated. After the end point, current increased with the addition of titrant solution. The plot of volume of carbodithioate added vs the diffusion current gave a reverse L-shaped curve.

Determination of lead: Lead solution was taken in a beaker containing 25 ml solution of ammonium tartrate and potassium nitrate to keep their concentration at 0.05M and 0.1M respectively in 25 ml of the final solution. The pH of the medium was adjusted to 8.6. Nitrogen was passed slowly through the

TABLE 1

DETERMINATION OF Ag(I) AND Pb(II) WITH N-METHYLANILINE CARBODITHIOATE

Curve	Amount of Ag(I) mg		Standard deviation %	Amount of Pb(II) mg		Standard deviation (%)
	Taken	Found		Taken	Found	
A	0.054	0.054	0.21	0.103	0.103	0.22
B	0.216	0.218	0.46	0.207	0.207	0.25
C	0.432	0.434	0.37	0.311	0.309	0.43
D	0.539	0.538	0.35	0.466	0.465	0.25
E	0.809	0.809	0.53	0.622	0.620	0.28
F	1.077	1.073	0.49	0.725	0.728	0.45

* Average of six replicate determinations.

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solution for 15 minutes. A potential of -0.2 V vs SCE was applied to the dropping mercury electrode. The current reading was recorded initially as well as after each small addition of standard carbodithioate solution. The volume of titrant added was plotted against current readings. The results of these titrations are given in Table-1.

Silver and Lead

Into a 50 ml beaker, introduced 2.5 ml of a solution (0.1 M in ammonium tartrate + potassium nitrate, pH 9.5). Measured the residual current of the air-free solution at -0.2V vs SCE using a dme and then added a mixture of silver and lead. While bubbling nitrogen through the solution, titrated with carbodithioate solution at the same applied potential. The intersections of the line of residual current with the reaction line and with the excess reagent line are the end points for silver and for the sum of silver and lead respectively (Fig 1). The results of these titrations are given in Table-2. The system can be titrated successfully by this method in the range of 5:1 or 1.5 Ag/Pb.

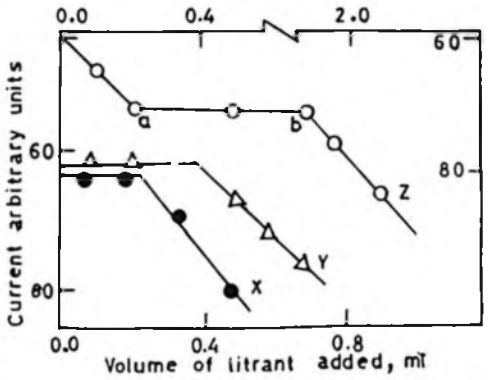


Fig 1. Typical Titration curve using N-Methyl-aniline Carbodithioate as titrant
Graph X - metal determined Ag; potential +0.1 V pH 9.5
Graph Y - metal determined Pb; potential -0.2 V pH 8.6
Graph Z - Mixture of Ag and Pb; potential set -0.2 V
Initial cathodic current due to silver
Final anodic current due to titrant
a) End point of Ag b) End point of Pb

Intefering Ions

In the titration of silver and lead, it was found that the results were not effected by large excess of As(III), Sb(III), Ba(III), Mg(II), In(III), Th(IV), W(VI), and Zr(IV). The interference due to Tl(I), Co(III), Ni(II), and Cu(II) can be eliminated by simultaneous determination. Cd(II) and Zn(II) could be eliminated by masking with sodium cyanide solution.

TABLE 2

SIMULTANEOUS DETERMINATION OF SILVER AND LEAD.
BASE ELECTROLYTE:
0.1M AMMONIUM TARTARATE +0.1M POTASSIUM NITRATE
N-METHYLANILINE CARBODITHIOATE = 0.01 M
pH = 9.5 APPLIED POTENTIAL = -0.2V vs SCE.
INDICATOR ELECTRODE = D.M.E.

Curve	Amount taken (mg)		Amount found* (mg)		Relative standard deviation (%)
	Ag	Pb	Ag	Pb	
A	0.216	1.347	0.217	1.345	0.80
B	0.432	1.243	0.435	1.244	0.63
C	0.648	1.139	0.647	1.137	0.96
D	1.080	0.725	1.060	0.727	0.64
E	1.296	0.622	1.294	0.624	0.59
F	1.620	0.518	1.619	0.519	0.82

* Average of six determinations.

REFERENCES

1. V.A. Pavlichenko, L.M. Tkacheva, and Yu. I. Usatenko, *Zavod. Lab.*, 43 (1977), 1303.

2. A.M. Gevorgyan, Sh. T. Talipov, V.A. Khadeev, E.V. Molodozhan, and V.S. Kostylev, *Deposited Doc. VINITI*, upp (1975), 2035; *Chem. Abst.* 87, (1977) 177075a

3. O.P. Agarwal, Jagmohan and Rajani, J. *Electrochem. Soc. India*, 32(3) (1983), 229-230.

4. D. Mukhamedzhanova, Sh. T. Talipov, and V.A. Khadeev, *Uzb. Khim. Zh.* 14, (1970) 8.

5. L.T. Chernomorchenko, A.S. Grzhegorzhevskii and G.A. Butenko, *Zavod, Lab.*, 42 (1976), 401.

6. G.S. Deshmukh, A.G. Kulkarni and S.N. Joshi, *Indian J. Chem. Sect. A.* 21A (7) (1982) 755.

7. G.M. Macrotrigiano, G.C. Pellacani, C. Preti, G. Tosi, *Bull. Chem. Soc. Japan*, V. 48 (1975) 1018.

8. A.I. Vogel *A Textbook of Quantitative Inorganic Analysis*, Longmans, 4th ed. (1978), pp. 338, 342.