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Amperometric Titration of Lead with Potassium Dithiotrihydroxymethyl Aminomethane and Its Determination in Presence of Mercury and Silver

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Synopsis. Amperometric titration of lead with potassium dithiotrihydroxymethyl aminomethane at −0.2 V (*vs.* SCE) in ammoniacal ammonium tartrate–potassium nitrate base electrolyte (pH 8.0) has been carried out with a dropping mercury electrode. Lead has also been estimated in binary solutions with silver and mercury. The accuracy of the procedure is comparable to that obtained with classical methods.

Electrometric determination of lead by precipitating with sulphate ion was first introduced by Majer.[1] Later Kolthoff and Pan[2] titrated lead with dichromate amperometrically. Lead estimation with EDTA was carried out by Tanaka *et al.*[3] The use of mercaptobenzothiazole in the amperometric estimation of lead was reported by Cihalik *et al.*[4] Diethyldithiocarbamate[5] was also reported as a successful reagent in amperometric titration for lead.

Potassium dithiotrihydroxymethyl aminomethane has now been used as a precipitating agent in the amperometric determination of lead, which has also been estimated in presence of mercury and silver. This reagent with the structural formula, $(CH_2OH)_3$ C–NH–C(SK)=S, having two sulphur and one nitrogen which can act as donors, forms insoluble complexes with metal ions. Polarographic characteristics of this compound revealed an anodic wave at dropping mercury electrode extending over a wide span of potential (−0.7 V *vs.* SCE) in ammoniacal ammonium tartrate and potassium nitrate base electrolyte (pH 7.0—10.5). The diffusion current was found to be proportional to the concentration. 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 complete precipitation of lead. In the second procedure dealing with the analysis of binary mixtures, the applied potential was so chosen that one of the two components is reduced at that potential. This also being the oxidation potential of the titrant, the current readings include the cathodic current of the reducible ion as well as the anodic current of the reagent. With the addition of the reagent, the ion reducible at the applied potential is preferentially precipitated and the cathodic current is decreased. When whole of the metal ion is precipitated, the current is reduced to residual current value, and the second component starts getting precipitated. The current remained steady during this stage, and after the complete precipitation of the second cation the anodic current of the excess reagent begins to increase.

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Solutions. Stock solutions of various metal ions were prepared from E. Merck's guaranteed reagents and standardized by gravimetric procedures.[6] All other reagents used were of AnalaR variety. The preparation and standardization[7] of potassium dithiotrihydroxymethyl aminomethane were carried out as follows: 200 ml of saturated solution of trihydroxymethyl aminomethane was taken in a beaker and 5 g of KOH was added. The beaker was cooled in ice, and then 10 ml of carbon disulphide was added, and stirred thoroughly with magnetic stirrer for 16 hr. The excess carbon disulphide was then removed by thorough shaking with double distilled pure benzene and the liquid was separated using a separating funnel. It was then evaporated little by heating on water bath and cooled in ice. Highly hygroscopic crystalline solid was separated. An aqueous solution of the reagent was standardized with potassium ferricyanide in alkaline medium in presence of osmium tetroxide as catalyst by amperometric titration at a potential of +0.2 V (*vs.* SCE) using rotating platinum micro-electrode.

Apparatus. A Fisher Electropode in conjunction with dropping mercury electrode and saturated calomel electrode was used for the titration. The pH measurements were made with a line operated Beckmann Zeromatic pH meter.

Experimental

The appropriate operative conditions for quantitative estimation of lead were established by trial experiments and it was observed that reproducible results were obtained in a base electrolyte consisting of ammoniacal ammonium tartrate and potassium nitrate (overall concentration 0.05—0.25 M) and pH range 7.0—9.0. In the actual procedure an aliquot of lead solution was taken in a titration cell containing 0.1 M base electrolyte. The pH of the solution was adjusted to 8.0 by adding ammonia. Pure nitrogen was passed into the solution to remove oxygen. A potential of −0.2 V (*vs.* SCE) was applied, the galvanometer reading was noted initially and after each addition of the titrant. After complete precipitation of lead, excess reagent gave the anodic

TABLE 1. AMPEROMETRIC DETERMINATION OF LEAD WITH POTASSIUM DITHIOTRIHYDROXYMETHYL AMINOMETHANE

Amount (mg) of Pb^{2+}		% Error
Taken	Found	
0.5084	0.5083	−0.02
1.0170	1.0170	—
0.6355	0.6325	−0.47
2.2330	2.2330	—
2.9770	2.9840	+0.23

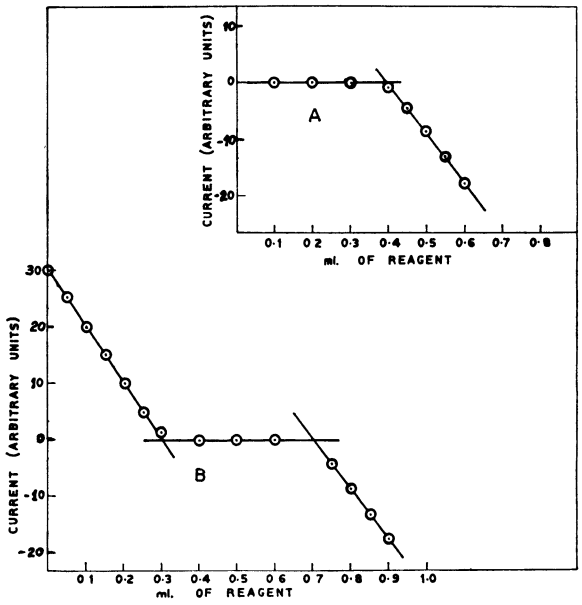

Fig. 1. Typical amperometric titration curves.

diffusion current of its own resulting in a regular rise in the current. The end point was located graphically (Fig. 1, Curve A). The results of estimations are given in Table 1.

For the determination of lead+silver and lead+mercury in a binary mixture, the titrations were carried out in ammoniacal ammonium tartrate and potassium nitrate base electrolyte of pH 8.0 at an applied potential of −0.2 V (*vs.* SCE). At this potential silver or mercury had its cathodic current while lead remained unreduced. During the titration the current decreased with the precipitation of silver or mercury and remained constant with the commencement of lead precipitation and increased with the anodic diffusion current of the excess reagent. The end points were located graphically (Fig. 1, Curve B), the first point of intersection gave the end point for silver or mercury and second point of intersection gave the end point for lead. The results of these titrations are given in Table 2.

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Table 2. Amperometric determination of the two components of binary mixtures with potassium dithiotrihydroxymethyl aminomethane

Mixture of Pb^{2+} and Ag^+					
Amount taken (mg)		Amount found (mg)		% Error	
Pb^{2+}	Ag^+	Pb^{2+}	Ag^+	Pb^{2+}	Ag^+
1.3460	0.8754	1.3510	0.8584	+0.37	−1.94
1.2430	1.1670	1.2430	1.1620	—	−0.42
1.6576	1.4590	1.6510	1.4470	−0.40	−0.82
2.0720	1.7508	2.0720	1.7508	—	—
1.4890	1.1670	1.4890	1.1570	—	−0.86
Mixture of Pb^{2+} and Hg^+					
Amount taken (mg)		Amount found (mg)		% Error	
Pb^{2+}	Hg^+	Pb^{2+}	Hg^+	Pb^{2+}	Hg^+
1.8650	1.7620	1.8320	1.7620	−0.16	—
2.0720	1.1740	2.0740	1.1730	+0.09	−0.08
3.1080	0.5872	3.1120	0.5851	+0.13	−0.35
4.1440	2.3490	4.1500	2.3460	+0.14	−0.13
1.6580	0.5872	1.6580	0.5851	—	−0.35

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