# AMPEROMETRIC DETERMINATION OF SILVER, MERCURY AND LEAD USING THIOXANTHATE

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Ethylthioxanthate has been used for the amperometric titration of Ag & Hg (II). The titrations are carried out in ammonium tartrate + potassium nitrate solution (PH = 9.0) using a rotating platinum electrode (1000 rpm) as an indicator electrode. Various foreign ions like Mo (VI), V(V), Th (IV), Zr (IV), Au (III), As (III), Sb (III), In (III), Te (VI), La (III), U (VI), Cr (III), Ca, Ba, Mg, Al & Mn do not cause any interference. Accurate results have been obtained for the estimation of Ag & Hg (II) in the presence of Pb using a d.m.e. operated at -0.2V vs S. C. E.

Various methods for the amperometric titration of silver [1–3] and mercury [4–6] are known in literature. In the present investigation a new amperometric method for the determination of silver and mercury has been developed using ethylthioxanthate as titrant. The procedure has further been applied to the quantitative estimation of these cations in the presence of lead. Ethylthioxanthate produces a well defined diffusion controlled anodic wave in 6.5–11 0 pH range in various supporting electrolytes[7]. This was considered to be useful for the titrations of metals precipitating as thioxanthates. Furthermore, the combined use of the cathodic current of metal-ions and the anodic current of thioxanthate can be employed for the simultaneous determination of binary mixtures. Earlier results from these laboratories reported the determination of lead as thioxanthate.[8] A solution of 0.05-0.15 M ammonium tartrate + potassium nitrate in the pH range (7–10) was found to be a good medium for the titration of silver and mercury and gave quantitative reproducible results. In an ammoniacal tartrate solution (pH = 9) lead reacts only after all the silver or mercury has been precipitated. Since the half wave potential of lead is considerably more negative than that of silver or mercury, the latter may be determined cathodically, while lead is determined anodically. Titrations of silver and mercury with thioxanthate using different concentrations of these cations revealed that these cations formed a 1:1 and 1:2 complex with thioxanthate respectively.

**Experimental:** Stock solutions of silver, mercury and lead were prepared from silver nitrate, mercuric nitrate and lead nitrate (E. Merk). Silver nitrate was standardized by Volhards' Method, while mercuric nitrate and lead nitrate was standardized with thiocyanate and EDTA solutions respectively. Sodium salt of ethylthioxanthate was prepared according to Atuki and Takada.[9] A fresh solution of 0.01M thioxanthate was prepared. Potassium nitrate and ammonium tartrate solutions were prepared from pure samples. Dilute ammonia solution was used for pH adjustments.

**Determination of Silver** : An aliquot of silver solution (0.10–1.0 mg) was taken and a requisite volume of ammonium tartrate and potassium nitrate buffer (pH 9.5) was added so as to maintain the overall concentration at 0.1 M. Using a rotating platinum microelectrode, titration was carried out at a potential of +0.1 V vs SCE. The diffusion current remained constant till the whole of silver was precipitated. After the end point, current increased with the addition of thioxanthate solution. The plot of volume of thioxanthate added versus the diffusion current gave a reverse L– shaped curve.

**Determination of Mercury :** Mercury solution (0. 15–1.1 mg) was taken in a beaker, containing an appropriate volume of 0. 1M ammonium tartrate + potassium nitrate. pH was adjusted to 9, and the titration was performed using the r.p.e. operated at +0.15 V vs SCE. After each addition of the titrant, the reading was noted when the current became steady. The results of these titrations are given in Table–1.

**Silver and Lead** : Into a 50 ml beaker, introduced 25 ml of a solution (0 1 M in ammoniumtartrate + potasium nitrate, pH 9.5). Measured the residual current of the air free solution at –0.2 V vs SCE using a d.m.e and then added a mixture of 0.04 to 0.2 mM of silver and lead. While bubling nitrogen through the solution, titrated with the thioxanthate 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. The results of these titrations are given in Table II. The standard deviation is less than 0.004 for both metals.

**Mercury and Lead** : Aliquots of mercury and lead solutions were taken in a beaker containing ammoniacal solution of potassium nitrate + ammonium tartrate (overall 0.1 M, pH 9). The current was noted at-0.2V and the titration with thioxanthate was carried out at this potential. The results are given in table III.

**Interfering Ions** : In the titration of silver and mercury it was found that the results were not affected by large excess of Mo (VI), V(V), Th (IV), Zr (IV), Te (VI), La (III), U (VI), Cr (III), Mn (II), Ca, Ba, Mg, Al, Au (III), As (III), Sb (III), and In (III). Pd (II), Bi (III), Co (II), Ni (II), Tl (I) and Cd interfered with the titration. (Table IV)

The data recorded in Table I, II & III are reproducible and within the limits of experimental errors. The average percentage recovery for silver and mercury is 99.64 and 99.36 respectively while standard deviations for the three determinations of silver and mercury have been given in the Tables. The method is also applicable to the determination of mg quantities of these cations and is comparable with other classical procedures in so far as its simplicity and precision are concerned.

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**TABLE-1 Determination of Ag (I) and Hg (II) with Ethylthioxanthate**

| Amount of Ag (I), mg. | | Standard Deviation | Amount of Hg (II), mg | | Standard Deviation |
|---|---|---|---|---|---|
| Taken | Found | | Taken | Found | |
| 0.1080 | 0.1069 | 0.0032 | 0.1504 | 0.1494 | 0.0010 |
| | 0.1073 | | | 0.1515 | |
| | 0.1075 | | | 0.1517 | |
| 0.1620 | 0.1620 | 0.0039 | 0.2507 | 0.2507 | 0.0010 |
| | 0.1610 | | | 0.2498 | |
| | 0.1608 | | | 0.2499 | |
| 0.2700 | 0.2689 | 0.0010 | 0.5015 | 0.5035 | 0 0010 |
| | 0.2704 | | | 0.5015 | |
| | 0.2687 | | | 0.5024 | |
| 0.5400 | 0.5413 | 0.0007 | 0.7522 | 0.7562 | 0.0021 |
| | 0.5390 | | | 0.7518 | |
| | 0.5410 | | | 0.7490 | |
| 0.8100 | 0.8154 | 0.0027 | 1.0030 | 1.0130 | 0.0035 |
| | 0.8130 | | | 1.0122 | |
| | 0.8100 | | | 1.0086 | |
| 1.0800 | 1.0850 | 0.0011 | 1.1033 | 1.1052 | 0.0023 |
| | 1.0782 | | | 1.1083 | |
| | 1.0835 | | | 1.1096 | |

**TABLE II Determination of Silver and Lead in a Mixture**

| Amount taken, (mg) | | Amount found, (mg) | | Standard Deviation | |
|---|---|---|---|---|---|
| Ag (I) | Pb (II) | Ag (I) | Pb (II) | Ag (I) | Pb (II) |
| 0.1620 | 0.8806 | 0.1631 | 0.8805 | 0.0006 | 0.0010 |
| | | 0.1625 | 0.8791 | | |
| | | 0.1620 | 0.8820 | | |

| | | | | | |
|---|---|---|---|---|---|
| 0.2160 | 1.0360 | 0.2171 | 1·0360 | 0.0010 | 0.0020 |
| | | 0.2162 | 1.0348 | | |
| | | 0.2182 | 1.0387 | | |
| 0.2700 | 0.7770 | 0.2689 | 0.7780 | 0.0010 | 0.0020 |
| | | 0.2700 | 0.7765 | | |
| | | 0.2712 | 0.7800 | | |
| 0.5400 | 0.5180 | 0.5346 | 0.5232 | 0.0030 | 0.0014 |
| | | 0.5378 | 0.5205 | | |
| | | 0.5400 | 0.5186 | | |
| 0.6480 | 0.6216 | 0.6426 | 0.6273 | 0.0020 | 0.0010 |
| | | 0.6440 | 0.6296 | | |
| | | 0.6462 | 0.6280 | | |
| 1.0800 | 0.2072 | 1.0750 | 0.2062 | 0.0047 | 0.0009 |
| | | 1.0800 | 0.2078 | | |
| | | 1.0845 | 0.2078 | | |

**TABLE III Determination of Mercury and Lead in a Mixture**

| Amount taken, (mg) | | Amount found, (mg) | | Standard Deviation | |
|---|---|---|---|---|---|
| Hg (II) | Pb (II) | Hg (II) | Pb (II) | Hg (II) | Pb (II) |
| 0.1504 | 1.0360 | 0.1520 | 1.0344 | 0.0010 | 0 0040 |
| | | 0.1518 | 1.0382 | | |
| | | 0.1520 | 1.0302 | | |
| 0.2507 | 0.7770 | 0.2457 | 0.7822 | 0.0010 | 0.0020 |
| | | 0.2468 | 0.7800 | | |
| | | 0.2478 | 0.7789 | | |
| 0.4012 | 0.6216 | 0.4062 | 0.6164 | 0.0036 | 0.0008 |
| | | 0.4059 | 0.6180 | | |
| | | 0.3998 | 0.6171 | | |
| 0.5015 | 0.5180 | 0.4965 | 0.5232 | 0.0019 | 0.0025 |
| | | 0.5002 | 0.5248 | | |
| | | 0.4978 | 0.5200 | | |
| 0.6519 | 0.4144 | 0.6500 | 0.4185 | 0.0053 | 0.0012 |
| | | 0.6482 | 0.4190 | | |
| | | 0.6579 | 0.4198 | | |
| 0.7522 | 0.3108 | 0.7532 | 0.3098 | 0.0019 | 0.0010 |
| | | 0.7528 | 0.3081 | | |
| | | 0.7497 | 0.3102 | | |
| 1.0030 | 0.2072 | 1.0080 | 0.2151 | 0.0024 | 0.0009 |
| | | 1.0072 | 0.2142 | | |
| | | 1.0035 | 0.2132 | | |

TABLE IV. EFFECT OF FOREIGN IONS

| Foreign ion added | Concentration | Amount of Ag(I) (mg) Taken | Found | Recovery % |
|---|---|---|---|---|
| Sb (III) | 2.5 mM | 0.5400 | 0.5389 | 99 80 |
| As (III) | 2.5 mM | 0.5400 | 0.5380 | 99.63 |
| In (III) | 2.5 mM | 0.5400 | 0.5376 | 99.55 |
| Mo (VI) | 2.5 mM | 0.5400 | 0.5312 | 98.37 |
| V (V) | 2 5 mM | 0 5400 | 0.5400 | 100.00 |
| Th (IV) | 2.5 mM | 0.5400 | 0.5392 | 99.85 |
| Te (VI) | 2.5 mM | 0.5400 | 0.5386 | 99.74 |
| La (III) | 2.5 mM | 0.5400 | 0.5400 | 100.00 |
| Au (III) | 2.5 mM | 0.5400 | 0.5375 | 99.53 |
| U (VI ) | 2.5 mM | 0.5400 | 0.5400 | 100.00 |
| Zr (IV) | 2.5 mM | 0.5400 | 0.5378 | 99.61 |

Average percent recovery = 99.64

| | | Amount of Hg (II), (mg) Taken | Found | |
|---|---|---|---|---|
| Sb (III) | 2.5 mM | 0.5015 | 0.4991 | 99.42 |
| As (III) | 2.5 mM | 0.5015 | 0 4950 | 98.72 |
| In (III) | 2.5 mM | 0.5015 | 0.4981 | 99.32 |
| Mo (VI) | 2.5 mM | 0 5015 | 0.5015 | 100.00 |
| V (V) | 2.5 mM | 0.5015 | 0 4960 | 98.90 |
| Th (IV) | 2.5 mM | 0.5015 | 0.5000 | 99.70 |
| Te (VI) | 2.5 mM | 0.5015 | 0.5010 | 99.90 |
| La (III) | 2.5 mM | 0 5015 | 0.4981 | 99.32 |
| Au (III) | 2.5 mM | 0.5015 | 0.4958 | 98.86 |
| U (VI) | 2.5 mM | 0.5015 | 0.4982 | 99.34 |
| Zr (IV) | 2.5 mM | 0.5015 | 0.4989 | 99.48 |

Average percent recovery = 99.36

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