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The Amperometric Determination of Thallium(III) and Silver(I) with Ascorbic Acid Using Two Polarized Indicator Electrodes

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Amperometric determinations of thallium(III) and silver(I) with ascorbic acid have been carried out with two polarized electrodes at 100 mV. and 50 mV. respectively. A simple method for the successive determination of thallium(III) and silver(I) has been developed. At an acidity of 0.1 to 1.0 N with respect to sulphuric acid, only thallium(III) is reduced; silver (I) remains unaffected. After the completion of the reaction with thallium(III), the pH of the solution is adjusted to 6.5 to 7.0 and the silver(I) is titrated with ascorbic acid.

In recent studies in this laboratory, it has been shown that the amperometric method using two polarized electrodes (biamperometric titration) can be applied with success to the successive determination of cerium and iron,(1) iron and vanadium(2) and a number of other elements.(3,4)

This paper will report the results of the biamperometric titration of thallium(III) and silver(I)

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(1) D. Singh, A. Varma and V. S. Agarwala, *Z. analyt. Chem.*, **183**, 172 (1961).

(2) D. Singh and A. Varma, *J. Sci. Res., B. H. U.*, **11**, 127 (1960—61).

(3) D. Singh and A. Varma, ibid., **11**, 202 (1960—61).

(4) D. Singh and A. Varma, ibid., **12**, 320 (1961—62).

separately and also together in a mixture, with a standard ascorbic acid solution used as the titrant.

Of the various methods employed to determine thallium(III), a few gravimetric and volumetric methods are important. The most useful titrimetric method was developed by Hollens and Spencer,5) who reduced thallium(III) ion with iodide and titrated the liberated iodine with thiosulphate or arsenite. Smith6) determined thallium(III) gravimetrically by precipitating it with tetraphenyl arsonium chloride in the presence of a considerable amount of hydrochloric acid. Busev et al.7) estimated thallium(III) by complexometric titration, and Berka and Busev8) determined it potentiometrically. Majumdar and Bhatnagar9) used the same method to determine thallium(III) with chromium(II).

Experimental and Results

A thallium(III) sulphate solution was prepared by dissolving thallium(III) oxide in 20.0 N sulphuric acid, and then making up the volume in a 100-ml. standard flask with distilled water; the solution was standardized iodimetrically. A stock solution of silver nitrate (A. R.) was prepared and standardized as usual. A weighed quantity of ascorbic acid, sold for medical purposes, was dissolved in water, and then a few milliliters of 25% formic acid was added as a stabilizer. The ascorbic acid solutions to be used were obtained by the accurate dilution of a more concentrated stock solution, which was standardized every day before use against a standard potassium iodate solution. All the other chemicals used were of C. P. grade.

Amperometric titrations at a constant voltage with two platinum electrodes were carried out with a circuit similar to those described by Foulk and Bawden10) and Stone and Scholten.11) The titration vessel was a 100 ml. beaker, covered with a tight-fitting rubber stopper provided with holes for the platinum electrodes, an inlet and an outlet for nitrogen, and a burette; a constant voltage of 50 mV. or 100 mV. was applied between the platinum electrodes, and the variations in the current were measured by a sensitive-mirror galvanometer with a lamp and scale arrangement. The galvanometer was shunted by a variable resistance so as to obtain the desired deflexions on the scale. The solution was uniformly stirred during the titration by a magnetic stirrer. The titration mixture, usually 20 ml. in the desired medium, was taken into the titration cell, and then the titrant was added from a 2.0-ml. semi-microburette with 0.01-ml. divisions. Equivalence points were obtained graphically by the plot of the galvanometer deflexion against the volume of the titrant added. A few typical titration curves are shown in Figs. 1 and 2. A large number of experiments were carried out, and each determination was repeated several times in order to obtain good and satisfactory results. The results of the determinations of thallium(III) and silver(I) are summarized in Tables I and II respectively.

TABLE I. DETERMINATION OF THALLIUM(III) AT 100 mV.
Volume of the titration mixture: 20 ml.
Medium: 0.1 to 1.0 N sulphuric acid

Determinations made	Amount of Tl(III) mg.		Experimental error %	
	Taken	Found	Average	Maximum
2	11.1725	11.140	−0.09	−0.25
2	4.469	4.474	+0.11	+0.11
3	2.2345	2.230	−0.18	−0.34
5	0.7918	0.7995	+1.00	+2.00
4	0.3959	0.3919	±0.00	−1.01
5	0.1980	0.1970	+0.09	+1.10
6	0.0792	0.0839	+2.22	+5.0

TABLE II. DETERMINATION OF SILVER(I) AT 50 mV.
Volume of the titration mixture: 20 ml.
Medium: pH: 6.5—7.0

Determinations made	Amount of Ag(I) mg.		Experimental error %	
	Taken	Found	Average	Maximum
2	25.80	25.84	+0.03	+0.15
3	9.98	9.99	+0.02	+0.11
4	5.12	5.13	+0.07	+0.35
6	1.259	1.266	+0.09	+0.4
9	1.079	1.085	+0.55	+3.1
5	0.5395	0.5340	−1.00	−2.1
4	0.2158	0.2114	−2.00	−4.2

The successive determinations of thallium(III) and silver(I) present together in test solutions were carried out, taking special care to maintain the acidity of the solution. Into a 0.1 N to 1.0 N medium with respect to sulphuric acid, ascorbic acid is an excellent reducing agent for thallium(III); silver(I) is, however, not reduced in this medium. Tervalent thallium has thus been successfully titrated with two polarized electrodes at an applied voltage of 100 mV. After the completion of the reduction of thallium(III), as established by a fall in the galvanometer deflexion to a constant value, a 6.0 N ammonia solution was added drop by drop until the pH of the solution became 6.5 to 7.0. The mixture was then titrated again at 100 mV. against

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5) W. R. A. Hollens and J. F. Spencer, *Analyst*, **60**, 673 (1935).

6) Wm. T. Smith, Jr., *Anal. Chem.*, **20**, 937 (1948).

7) A. I. Busev, L. L. Talipova and V. M. Ivanov, *Zh. Vses. Khim. Obschestva im D. I. Mendeleeva*, **6**, 598 (1961).

8) A. Berka and A. I. Busev, *Anal. Chim. Acta*, **27**, 493 (1962).

9) R. Majumbar and M. L. Bhatnagar, ibid., **25**, 203 (1961).

10) C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, **48**, 2045 (1926).

11) K. G. Stone and H. G. Scholton, *Anal. Chem.*, **24**, 671 (1952).

the standard ascorbic acid until the galvanometer deflexion approached a constant value.

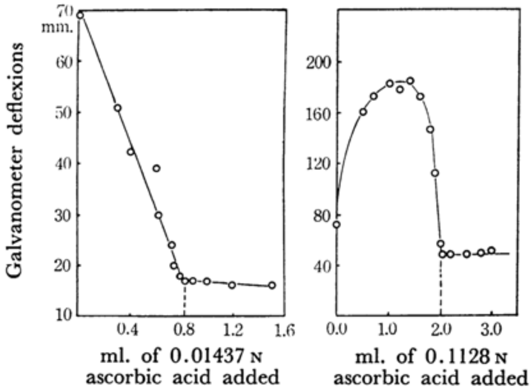

Fig. 1. Amperometric titrations of (a) 2.289 mg. of thallium(III) and (b) 25.84 mg. of silver(I) with two polarized electrodes.

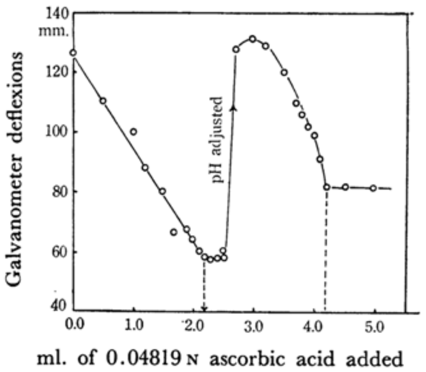

Fig. 2. Amperometric titrations of 6.027 mg. thallium(III) and 3.038 mg. silver(I) present together in solution with two polarized electrodes.

Table III. Determination of thallium(III) and silver(I) present together in solution at 100 mV.

Volume of the titration mixture: 20 ml.

Amount of Tl(III), mg.			Amount of Ag(I), mg.		
Taken	Found	Difference	Taken	Found	Difference
12.054	12.08	+0.026	6.18	6.20	+0.02
6.04	6.027	−0.013	3.09	3.067	−0.023
5.608	5.615	+0.007	2.162	2.133	−0.029
1.120	1.088	−0.032	1.081	1.078	−0.003
0.415	0.4535	+0.038	0.432	0.464	+0.032

The graphical method was employed to determine the equivalence point of these estimations, as is shown in Fig. 2; the results of the successive determinations of thallium(III) and silver(I) in various mixtures are presented in Table III.

Discussion

The normal oxidation-reduction potential of the $\text{Tl}^{3+}/\text{Tl}^{+}$ system is $E_0=1.21$ V., while that of $\text{Ag}^{+}/\text{Ag}^{0}$ couple is $E_0=0.7991$ V. As the normal redox potential of ascorbic acid is 0.40 V. at $[\text{H}^{+}]=1$, it can be used for the quantitative determination of thallium(III) in 0.1 N to 1.0 N sulphuric acid in the presence of univalent silver, since the latter is reduced only at pH 6.5 to 7.0.

In the present investigation reversible $\text{Tl}^{3+}/\text{Tl}^{+}$, $\text{Ag}^{+}/\text{Ag}^{0}$ couples are titrated by an irreversible system, with an appreciable current flowing through the cell before the end point. In the determination of thallium(III), the current is the greatest at the very beginning of the titration, since there is a considerable quantity of thallium(III) ions in the the sample taken for estimation. The concentration of the thallium(III) ions diminishes with the addition of the titrant, and thus there is a rapid decrease in the galvanometer deflexion; on the other hand, as the concentration of Ag^{+} diminishes, the galvanometer deflexion reaches a maximum when the titration has proceeded by 50%, and then falls on the further addition of ascorbic acid; this is in essential agreement with the earlier findings.[1-3,11] At the equivalence point and thereafter in both cases, no thallium(III) or silver(I) ions are left in the solution, and the limiting current for the couples, $\text{Tl}^{3+}/\text{Tl}^{+}$ or $\text{Ag}^{+}/\text{Ag}^{0}$, is virtually zero. Although both components of the ascorbic acid/dehydroascorbic acid system are present in the solution, practically no current flows through the titration cell since the couple is irreversible. The current will, therefore, attain a constant value depending upon the resistance of the circuit, and the curves have the shape shown in Figs. 1 and 2.

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