

CONTROLLED POTENTIAL COULOMETRIC DETERMINATION OF TIN

ALLEN J. BARD*

Department of Chemistry, Harvard University, Cambridge, Mass. (U.S.A.)

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Although tin has been determined several times by controlled potential gravimetric procedures^{1,2} a coulometric determination has not been previously reported. The known polarography of tin indicates that coulometric analysis should be feasible in halide media. Reduction of tin(IV) takes place stepwise, to the metal, on a mercury cathode, and coulometric analysis at both reduction stages was undertaken.

EXPERIMENTAL TECHNIQUE

Apparatus

The electrolysis cell (100-ml capacity and with mercury cathode of 16.7 cm² area) was the same as that described by LINGANE³. Tall-form electrolysis beakers were employed when gold cathodes were used. A constant speed mechanical stirrer was used, with stirring blades adjusted to keep the mercury-solution interface in rapid but smooth motion. Oxygen was excluded by passing a stream of nitrogen through the solution, prior to, and during electrolysis.

The anode was a platinum electrode (1 cm²) isolated from the test solution by enclosure in a glass tube with a sintered glass bottom. The anolyte (2 M sulfuric acid) was maintained at a higher level than the solution in the cathode chamber.

A potentiostat³ was used to maintain automatically the potential of the cathode at a constant value in reference to a saturated calomel electrode. The quantity of electricity consumed was measured with a hydrogen-nitrogen gas coulometer⁴. A more convenient coulometer which may be employed is the d.c. motor integrator⁵. Current measurements were made with a calibrated multi-ammeter in series with the cathode.

Procedure

The supporting electrolyte (3 M sodium bromide, 0.3 N hydrochloric acid) alone was placed in the cell, dissolved air was removed with purified nitrogen and the solution was subjected to a preliminary electrolysis with the potential of the cathode at -0.80 V vs. S.C.E., to remove traces of reducible impurities. This pre-electrolysis was continued until a small, constant, residual current was observed. The potentiostat was then set to maintain the potential of the cathode at the value used in the determination (-0.40 V vs. S.C.E. for reduction of tin(IV) to tin(II), -0.70 V vs. S.C.E. for reduction of tin(II) to the metal), the sample solution was added, and the

* Present address: University of Texas, Austin 12, Texas (U.S.A.)

electrolysis was allowed to proceed under automatic control until the current decreased to a constant, minimal value. The total quantity of electricity passed, the electrolysis duration, and the final current were noted.

Correction for the quantity of electricity associated with the background current was applied by assuming the final electrolysis current was constant throughout the electrolysis.

When a tin amalgam electrode was used, a similar procedure was followed, except that the tin solution, entirely in the stannic form, was stirred with the amalgam several minutes before electrolysis to reduce the tin(IV) to tin(II). The results were calculated as in the previous case, taking into account that twice as much tin was electrolyzed as was introduced. Tin amalgam was prepared by shaking an excess of pure granulated tin (20 to 40 mesh) with mercury, under dilute hydrochloric acid, until a saturated amalgam was obtained.

RESULTS AND DISCUSSION

The investigation of the electrogeneration of stannous tin as a coulometric titrant⁶ showed that reduction of stannic tin takes place with 100% current efficiency at a gold electrode in solutions containing a high concentration of bromide ion. This generation of tin(II) for coulometric titration was performed with a large and constant stannic tin concentration (0.2 M) at a small electrode. Controlled potential reduction of tin(IV) involves much smaller tin concentrations (0.03 M) and relatively large electrodes. These conditions have the effect of increasing the residual current relative to the stannic ion reduction current, causing the reduction to proceed at decreased current efficiency, and necessitating large residual current corrections. In Table I are shown some typical results for the reduction of stannic to stannous tin at gold electrodes.

The current decay during controlled potential electrolysis usually follows the expression³:

$$i = i_0 10^{-kt} \quad (1)$$

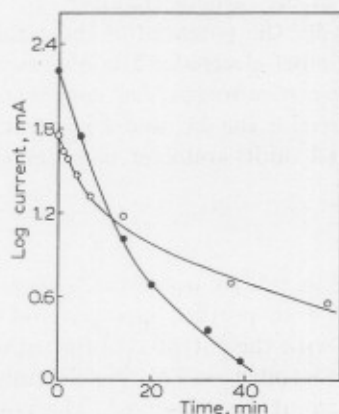


Fig. 1. Typical log current-time curves for the controlled potential electrolysis of tin(IV) at a gold electrode (ca. 72 cm²) in 3 M sodium bromide and 0.4 N hydrochloric acid. About 55.9 mg of stannic tin was reduced at a potential of -0.40 V vs. S.C.E.

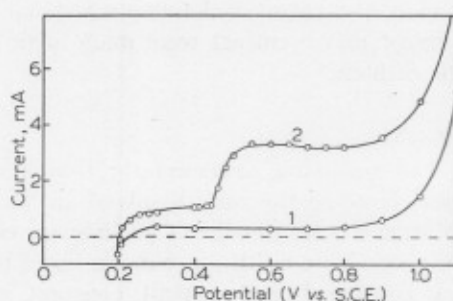


Fig. 2. Current-potential curves for the reduction of tin(IV) on a stirred mercury pool (ca. 16.7 cm²). (1) 3.2 M sodium bromide and 0.2 N hydrochloric acid alone. (2) supporting electrolyte containing 0.002 M stannic chloride.

where i is the current at time t , i_0 is the initial current, and k is a constant, whose magnitude depends upon the stirring rate, electrode area, solution volume and temperature. Typical log current *vs.* time curves for the reduction of tin(IV) at a gold cathode are shown in Fig. 1. The initial slope of these curves was used to calculate the k values quoted in Table I. From this k , predicted by the initial slope, (0.061 min^{-1}), the reaction would be predicted to be 99.9% complete in about 50 min. It is evident that the electrolysis does not follow equation (1) however, since the curves deviate significantly from linearity. The decrease of slope of the curves, which occurs after more than 80% of the reduction is complete, is primarily responsible for the long electrolysis durations.

TABLE I

COULOMETRIC DETERMINATION OF TIN ON GOLD ELECTRODES

The solution was 2–3 *M* in sodium bromide and 0.3–0.6 *N* in hydrochloric acid. Control potential $-0.40 \text{ V vs. S.C.E. (55.91 mg Sn taken)}$

Trial	Volume (ml)	Initial current (mA)	Final residual current (mA)	Electrolysis duration (h)	Amount Sn found (mg)	k (in min^{-1}) $\times 10^2$
1 ^a	60	11	0.4 ^c	13.8	56.18	0.2
2 ^a	25	18	0.8 ^c	12.1	60.06	0.4
3 ^b	100	165	2.2	2	64.33	7.8
4 ^b	100	80	0.5	8.3	54.06	6.1
5 ^b	100	145	0.3	12	55.84	7.2
6 ^b	115	56	1.0	8	54.71	6.3
7 ^b	83	22	1.0	9	48.24	4.6
				mean = 56.20 ± 3.7^1		
				% error = 0.5%		

^a 14.7 cm² flat gold electrode.

^b 72 cm² gold-plated platinum gauze, cylindrical, electrode.

^c Background current corrections made on the basis of the *pre*-electrolysis residual current (0.064 mA). Correction on the basis of *post*electrolysis current would yield very low results.

Deviation of log current *vs.* time curves from linearity has been shown⁷ to be caused by kinetic complications of the electrode reactions, such as secondary or competing chemical reactions. The curvature of the curves in this case might be caused by some constant reoxidation of stannous ion at the gold electrode (an example of case IIc, Ref.⁷), which would also give rise to a larger residual current during and following the electrolysis than before it⁸. Correction by assuming a constant background current, equal to the post-electrolysis current, would lead to over-correction for the background current, and negative errors. Assumption of constant background current equal to pre-electrolysis current causes undercorrection and positive errors.

Another possible kinetic complication might be the presence of two tin complexes in sluggish equilibrium with each other; the reduction at the given electrode potential proceeding through only one of the forms. After most of the easily reducible form has reacted, the rate of the electrode reaction will be governed by the slow, equilibration, step. This would lead to a decrease in the slope of the log current–time curves and anomalously long and varying electrolysis durations.

Therefore, although a coulometric determination of tin based upon the reduction of stannic to stannous tin at a gold electrode is possible, the results obtained are neither very precise, nor very accurate. A large degree of uncertainty is introduced by the background current corrections, which often amounted to 20% of the total coulombs consumed, because of the long electrolysis durations.

Electrolysis of tin(IV) on a mercury cathode offers the advantages of lower residual currents, shorter electrolysis durations by the use of smaller solution volumes and efficient stirring, and the possibility of carrying out a second reduction step, that of stannous ion to tin (amalgam). A current-potential curve for the reduction of tin(IV) at a large mercury pool electrode is shown in Fig. 2. This curve is quite similar to polarograms of tin(IV) taken with a d.m.e.⁹. Since mercury reduces stannic tin in a bromide medium, the first wave corresponds to the reduction of a mercury species (e.g. HgBr_4^{-2}) rather than tin(IV).

Electrolysis of tin(IV) solutions on a mercury cathode were performed by electrolysis at both -0.40 and -0.70 V vs. S.C.E., and typical results of this two-step reduction are shown in Table II. Although the first reduction step is 2.4% incomplete,

TABLE II

COULOMETRIC DETERMINATION OF TIN ON MERCURY CATHODE

The solution was 3 M in sodium bromide and 0.3 N in hydrochloric acid, with a volume of 30 ml (46.02 mg tin taken)

Control potential (V vs. S.C.E.)	Initial current (mA)	Residual current (mA)	Electrolysis duration (hr)	Amount Sn found (mg)
-0.40	50	0.25	3.5	45.15
-0.70	205	0.35	2.1	46.09
-0.40	88	0.25	2.5	45.31
-0.70	240	0.35	2.0	46.33
-0.40	74	0.35	2.5	44.29
-0.70	190	0.55	2.5	45.85
mean = step 1: 44.92 ± 0.42				
% error = -2.4%				
step 2: 46.09 ± 0.24				
% error = $+0.15\%$				

the second reduction, to tin amalgam, is complete and accurate. The stannic tin is reduced directly by the mercury and the first electrolysis at least partially involves reduction of a mercury species. Apparently some mercury species (e.g. Hg_2Br_2) is present which remains unreduced, even at a potential of -0.70 V vs. S.C.E. The second reduction step, stannous ion to tin amalgam, is rapid and quantitative, and therefore has greater analytical applicability.

To eliminate the time-consuming primary reduction step, a tin-amalgam cathode was employed. An investigation in this laboratory has shown¹⁰ that tin-amalgam completely reduces tin(IV) to tin(II), producing an equivalent quantity of tin(II), in a bromide medium. Of course in the presence of other substances which are reduced by tin-amalgam a mercury cathode must be used. Typical results in Table III demonstrate that 20 to 50 mg of tin in a volume of 30 ml can be determined with an average

TABLE III
COULOMETRIC DETERMINATION OF TIN ON TIN-AMALGAM CATHODE

Electrode potential = -0.70 V vs. S.C.E.
The solution was 3.3 M sodium bromide and 0.2 N hydrochloric acid, with a volume of 30 ml

Initial current (mA)	Residual current (mA)	Electrolysis duration (hours)	Amount Sn taken (mg)	Amount Sn found (mg)
300	0.08	3.5	23.01	23.31
190	0.15	2.3	23.01	23.16
210	0.15	2.2	23.01	22.71
			mean = 23.06 ± 0.23 , error = 0.21%	
465	0.30	1.0	53.57	54.49
465	0.35	1.0	53.57	53.67
430	0.70	2.0	53.57	52.98
			mean = 53.71 ± 0.52 , error = 0.26%	

error of somewhat less than 0.3% , with an electrolysis duration of about 2 hours, with this method. The results show an average deviation of about 1% , mainly because of the uncertainty in the background current corrections.

CONCLUSION

Since tin(IV) is reduced to stannous tin at potentials of -0.3 to -0.4 V vs. S.C.E., it will interfere during the controlled potential determination of copper and antimony, unless it is complexed (e.g. with tartrate¹). The reduction of tin(II) at potentials of -0.50 to -0.70 V vs. S.C.E. proceeds with 100% current efficiency at a mercury cathode, and may be determined coulometrically in the absence of metals not reduced at these potentials. Pre-reduction at -0.40 V will eliminate interference of copper, antimony and bismuth in this determination. Lead, which is reduced at about -0.50 V, will interfere. Finally, by electrolysis at -0.60 to -0.70 V vs. S.C.E., tin may be removed prior to the determination of such metals as nickel and zinc.

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SUMMARY

The controlled potential coulometric determination of tin in a bromide medium is described. Although the reduction of tin(IV) to tin(II) suffers from complications, and is analytically unsuitable, reduction of stannous tin at a mercury, or tin-amalgam electrode forms the basis of a successful analytical method.

RÉSUMÉ

Une méthode coulométrique, à potentiel contrôlé, est décrite pour le dosage de l'étain, en milieu bromhydrique. La réduction de l'étain(II) à une électrode de mercure ou d'étain amalgamé est tout à fait satisfaisante.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode mit kontrolliertem Potential zur Bestimmung von Zinn in bromwasserstoffsaurer Lösung. Als Grundlage der Methode dient die Reduktion von Zinn(II) an einer Quecksilber- oder Zinnamalgam Elektrode.

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