

COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN DETERMINATION OF IODINE, BROMINE, AND VARIOUS OXIDANTS VIA IODOMETRY

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Although the roster of coulometric titrations now includes many reactions of classical titrimetry¹, the use of electrogenerated +2 tin as a coulometric titrant has not previously been reported. We have found that in an acidic bromide medium +4 tin (probably SnBr_6^{-2}) is reduced to the +2 state (probably SnBr_4^{-2}) with 100% current efficiency at a gold cathode. The formal potential of the stannic-stannous couple in bromide medium is +0.27 V vs. N.H.E., a value sufficiently reducing so that (in principle) +2 tin should serve for the titration of divers oxidants.

In practice one encounters the inconvenience that the rate of reduction of most substances by +2 tin is relatively small, but this can be circumvented by either of two means. Firstly, an excess of +2 tin can be generated in the test solution, and, after a short waiting period, the polarity of the generating electrode is reversed from cathode to anode and the excess +2 tin is titrated by the bromine electrogenerated at the anode. The other expedient, applicable to the determination of substances capable of oxidizing iodide to iodine, is "coulometric iodometry". An excess of iodide ion is added to the test solution, and the liberated iodine is titrated with the electrogenerated +2 tin. The iodine-stannous reaction is rapid, and equivalence points can be detected accurately either potentiometrically or amperometrically.

ROWLEY AND SWIFT² determined iodine (and thus various oxidants *via* iodometry) by adding a measured excess of standard thiosulfate solution, and back titration of the excess thiosulfate with electrogenerated iodine. This method suffers from the disadvantage of requiring a standard thiosulfate solution, and is only semi-coulometric. Direct titration of iodine with electrogenerated +2 tin is simpler and more convenient.

EXPERIMENTAL

The coulometric titrations were performed in the usual manner¹. The titration cell, whose capacity was *ca.* 175 ml, is shown in Fig. 1. The auxiliary electrode is separated from the titration chamber by two sintered glass disks, so that interchamber transfer is effectively minimized. The test solution was stirred efficiently with a magnetic stirrer.

Because oxygen is reduced concomitantly with +4 tin at the cathode, elimination of dissolved air from the solution is necessary. By using a non-oxygen producing auxiliary electrode (*e.g.* a cadmium rod in 0.5M cadmium chloride), and passing nitrogen through all of the chambers, oxygen was effectively excluded.

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In most titrations of iodine, a gold generator cathode (1×1 cm) was employed. A platinum generator cathode (1×1 cm) was used in titrations of bromine, since bromine oxidizes gold in a bromide medium. Both bromine and iodine were generated at platinum anodes (1×1 cm).

The supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride and $0.2N$ hydrochloric acid. The solution was first deaerated, and then made $0.01M$ in respect to potassium iodide when iodometric determinations were to be performed. The sample of the oxidant to be titrated was then added. Nitrogen was passed only over the surface of the solution during the titration to avoid volatilization of the bromine or iodine.

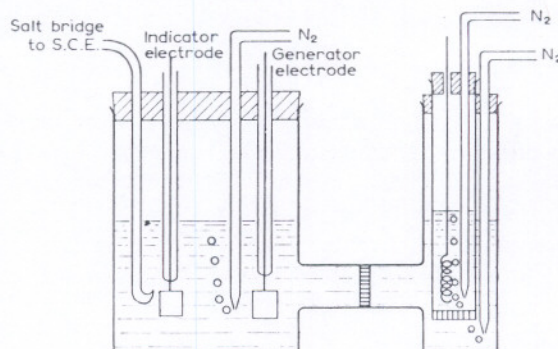


Fig. 1. Coulometric titration cell.

Potentiometric end-point detection with a platinum foil indicator electrode and saturated calomel reference electrode followed the usual practice. The amperometric detection system comprised two identical platinum electrodes (1×1 cm) across which 150 mV applied voltage was maintained. The indicator current was observed with a shunted galvanometer. Detailed discussions of both these end-point detection techniques as applied to coulometric titration are available in *Electroanalytical Chemistry*¹.

Current-efficiency for electrogeneration of +2 tin

The electrogeneration of +2 tin was studied only in bromide and chloride media, because it is known from polarographic data that +4 tin produces well delineated reduction waves only in these media. Current efficiencies for the reduction of stannic ion in various chloride and bromide media at gold and platinum cathodes were estimated from current-potential curves with and without stannic ion present¹. The same cell and conditions used for the coulometric titrations were employed.

These current-potential curves predicted current efficiencies closer to 100% with a gold cathode than with platinum, because gold has a higher hydrogen overvoltage. Although 100% current efficiency is not easily attainable in a chloride medium, a bromide medium (*ca.* $3M$) proved successful. The current efficiency is higher in bromide than in chloride medium because the bromostannate ion requires less over-

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potential for its reduction, and thus is reduced to the stannous state more in advance of hydrogen ion reduction, than the chloro-stannate ion.

A relatively large bromide ion concentration is necessary to maintain the major part of the +4 tin as SnBr_6^{-2} , and hydrogen ion also is essential to prevent its hydrolysis. With 0.2M stannic tin the bromide ion concentration must be at least 2.8M, and 3 to 4M is optimum. A range of hydrogen ion concentration from 0.15 to 0.4M is satisfactory. At lower acidities hydrolysis of SnBr_6^{-2} occurs, while at higher acidities hydrogen ion reduction concomitantly with reduction of SnBr_6^{-2} becomes significant.

The supporting electrolyte finally selected as optimum was 4M sodium bromide, 0.2M stannic chloride, and 0.2N hydrochloric acid. Bromide complexes stannic tin more strongly than chloride does, so the electrochemistry of this solution is characteristic of SnBr_6^{-2} .

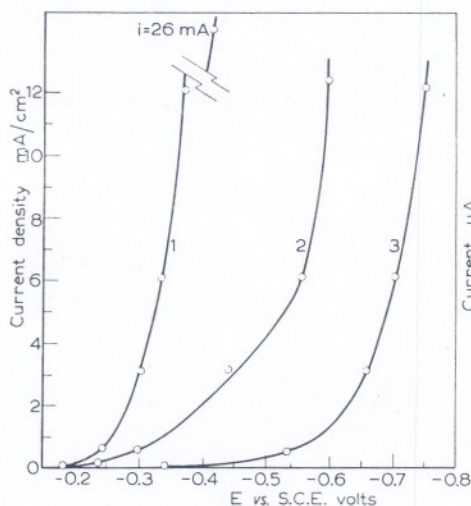


Fig. 2. Increase of hydrogen overpotential by tin oxide film on platinum cathode. In all cases the supporting electrolyte was air-free 3M sodium bromide and 0.4M perchloric acid, the area of the platinum cathode was 1.68 cm², and the solutions were stirred. (2) Supporting electrolyte alone with clean (unfilmed) platinum cathode. (3) Supporting electrolyte alone but cathode carried a film of hydrous stannic oxide. (1) 0.2M stannic chloride present.

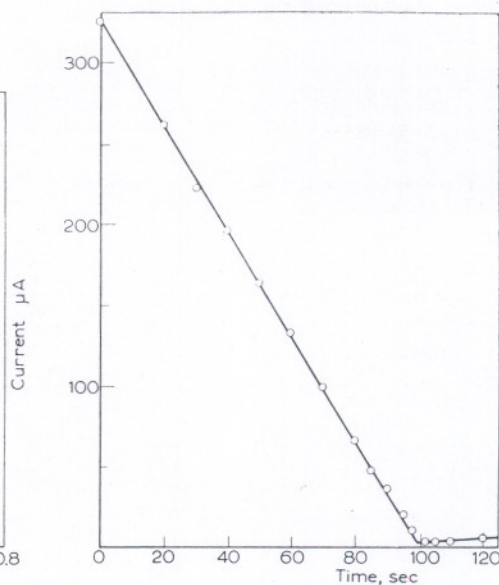


Fig. 3. Typical amperometric titration curve of 2.70 mg of iodine with electrogenerated +2 tin, using two 1 cm² platinum indicator electrodes subjected to an applied voltage of 150 mV.

With a freshly cleaned platinum cathode the current efficiency for reduction of SnBr_6^{-2} is considerably short of 100%. However, once the platinum cathode has been used it functions nearly as efficiently as gold. During the reduction of the +4 tin the platinum cathode acquires a film of stannic hydrous oxide, which increases the hydrogen overpotential by about 150 mV and thus greatly minimizes co-reduc-

tion of hydrogen ion. This beneficial phenomenon is demonstrated by the current-potential curves in Fig. 2, and it will be discussed in detail in a separate communication. The film of stannic hydrous oxide is not removed by even prolonged washing with water, nor by gentle wiping with filter paper, so that no special care is needed in handling the filmed electrode. The film can be removed with hot hydrochloric or hydrobromic acids or sodium hydroxide.

The current efficiencies predicted from the current-potential curves were verified by directly determining the amount of +2 tin produced under a particular set of conditions as follows. The +4 tin solution was electrolyzed at either a platinum or gold cathode with a known current for a measured time. The +2 tin produced was then back-titrated with electrogenerated iodine, employing an amperometric end-point as described in a following section. The average current efficiencies at current densities of 10 to 84 mA/cm² was for platinum 99.3 ± 0.2%, and for gold 99.7 ± 0.2%. With both electrodes the current efficiency decreased at current densities below 5 mA/cm².

TABLE I
COULOMETRIC TITRATION OF IODATE, IRON, AND CERIUM (IODOMETRICALLY) WITH
ELECTROGENERATED STANNOUS ION

The solution was 4M sodium bromide, 0.2N hydrochloric acid, 0.008M potassium iodide, and 0.2M stannic chloride, with a volume of ca. 50 ml. A gold generator cathode (1 × 1 cm) was used, except as noted

Substance titrated	No. of trials	Current (mA)	Taken (mg)	Found (mg)	Mean deviation (mg)	Av. error %	End-point
Iodate	3	10.10	0.7174	0.7173	0.0007	-0.05	Amp.
	3	22.78	1.794	1.795	0.001	+0.02	"
	3	22.90	1.891	1.894	0.005	+0.2	"
	3	22.89	1.891	1.892 ^a	0.005	+0.1	"
	3	33.11	3.587	3.592	0.007	+0.1	"
	1	22.98	1.891	1.897 ^b	—	+0.3	"
	1	22.86	1.891	1.889 ^c	—	-0.1	"
	5	10.10	0.3587	0.3595	0.0050	+0.2	Pot.
	3	10.00	0.7174	0.7180	0.0021	+0.05	"
	3	33.10	3.587	3.578	0.007	-0.3	"
	Iron (+3)	3	10.12	0.5640	0.5635	0.005	-0.10
3		22.78	2.820	2.804	0.012	-0.56	"
3		33.14	5.640	5.635	0.011	-0.10	"
Cerium (+4)	5	23.04	6.663	6.655	0.046	-0.13	"
	2	33.26	13.33	13.38	0.01	+0.35	"

^a Platinum electrode 0.7 × 1.8 cm used.

^b Solution made 0.06M in fluoride.

^c Solution made 0.10M in fluoride.

Titration performance data

Coulometric iodometry. Typical results of the iodometric determination of potassium iodate, +3 iron, and +4 cerium in Table I demonstrate that the titration is precise and accurate.

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The shape of the amperometric titration curve is shown in Fig. 3. The current remains small after the end-point because the stannic-stannous couple behaves quite irreversibly, and the applied voltage of 150 mV is smaller than the total cathodic and anodic overpotentials.

Using potentiometric end-point detection, the equivalence point potential is +0.28 V vs. S.C.E. The supporting electrolyte was pre-titrated to this potential before the sample was added.

TABLE II

COULOMETRIC TITRATION OF BROMINE WITH +2 TIN

Bromine was produced *in situ* by addition of potassium bromate solution to ca. 50 ml of 4M sodium bromide, 0.2M stannic chloride, and 0.2N hydrochloric acid. The generator electrode was platinum, 0.8 × 2.0 cm.

Current (mA)	Potassium bromate (mg)		% Error
	Taken	Found	
23.00	1.265	1.256	-0.7
		1.256	-0.7
		1.262	-0.2
		1.273	0.6
		1.280	1.2
		1.285	1.6
		1.265	0.0
		1.272	0.6
		1.268	0.2
			Av. 1.269 ± 8
22.82	1.274	1.271	-0.2
		1.281	0.6
		1.280	0.5
		Av. 1.277 ± 4	0.2
33.25	2.530	2.524	-0.2
33.15	2.547	2.544	-0.1
		2.552	0.2
		2.551	0.2
		Av. 2.549 ± 3	0.1
62.06	5.094	5.098	0.1

Direct titration of bromine. Typical results of the titration of bromine (generated *in situ* by the addition of potassium bromate) in Table II demonstrate that bromine may be determined with an average error of 0.2 to 0.3%. The amperometric end-point was similar to that obtained in the iodine titration.

The reaction tends to be slow near the end-point, but a titration can be completed in 5 min. When titrations were performed by successive additions of bromate samples to the supporting electrolyte, the first sample gave results about 0.001 milliequivalent low. Results with subsequent samples were close to the theoretical value. This negative error in the first titration was probably due to reducing impurities in the

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solution, and was eliminated by generating bromine at a platinum anode, stirring for 5 minutes, and titrating to the end-point with +2 tin, before the sample was added.

Titration using potentiometric end-point detection were somewhat slower, since the bromine-bromide couple establishes potentials sluggishly at platinum electrodes.

Direct and reverse titrations with the stannous-bromine and stannous-iodine systems

Because a bromide medium is used in generating +2 tin, the stannous-bromine couple (or by addition of a small amount of iodide, the stannous-iodine couple) can be employed *via* back titration in cases where direct titration is not feasible because of a too small reaction rate. By appropriate selection of polarity of the generator electrode in the test solution, bromine can be generated *via* anodic oxidation of bromide ion, or stannous tin can be generated by cathodic reduction of stannic ion. By generation of an excess of +2 tin and back-titration with either bromine or iodine, titration of dyes and other substances which are reduced only slowly by +2 tin is possible. Similarly +2 tin can be used as a back-titrant for slow oxidations, brominations or iodinations.

Typical results in Tables III and IV demonstrate that anodic and cathodic generation times coincide within a few parts per thousand at current densities of 5 to 84

TABLE III

DIRECT AND BACK TITRATIONS WITH THE STANNOUS-IODINE SYSTEM

The solution was 3.5M in sodium bromide, 0.2M in stannic chloride, 0.2N in hydrochloric acid, and 8 mM in potassium iodide. The volume was *ca.* 56 ml. The generator cathode was a gold electrode (1 × 1 cm), and the generator anode was of platinum (1 × 1 cm).

Current (mA)	Substance generated first	Iodine gener. time (sec)	Stannous gener. time (sec)
<i>Amperometric end-point</i>			
5.218	iodine	100.0	100.3
	stannous	99.1	100.0
9.975	iodine	100.0	100.3
	stannous	99.8	100.0
23.06	iodine	100.0	100.0
	stannous	99.4	100.1
41.08	iodine	100.0	100.1
	stannous	99.5	100.0
84.05	iodine	49.98	50.13
	stannous	49.86	49.93
<i>Potentiometric end-point</i>			
10.05	iodine	100.0	100.1
	stannous	99.7	100.0
20.54	iodine	100.0	100.0
	stannous	100.0	99.9
31.34	iodine	100.0	100.0
	stannous	100.0	100.0
86.01	iodine	50.01	50.13
	stannous	49.92	50.00

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TABLE IV

DIRECT AND BACK TITRATIONS WITH THE STANNOUS-BROMINE SYSTEM

The solution was 3.5*M* sodium bromide, 0.2*M* stannic chloride, and 0.2*N* hydrochloric acid. The volume was ca. 57 ml. The generator electrode was platinum (1 × 1 cm).

Current (mA)	Substance generated first	Bromine gener. time (sec)	Stannous gener. time (sec)
<i>Amperometric end-point</i>			
9.210	bromine	100.0	100.5
	stannous	99.6	100.0
30.88	bromine	100.0	99.8
	stannous	99.5	100.0
43.80	bromine	100.0	99.8
	stannous	99.6	100.0
73.79	bromine	50.00	49.97
	stannous	49.95	49.99
<i>Potentiometric end-point</i>			
9.982	bromine	100.0	100.9
	stannous	99.6	100.0
19.81	bromine	100.0	99.9
	stannous	99.8	100.0
31.16	bromine	100.0	99.6
	stannous	99.6	100.0
42.77	bromine	100.0	99.6
	stannous	99.8	100.0
81.66	bromine	50.01	49.89
	stannous	49.87	49.96

mA/cm². Amperometric and potentiometric end-point detection both were employed. The equivalence point potential of the bromine-stannous titration is +0.38 V vs. S.C.E.

Quinone (*p*-benzoquinone) was chosen as a model organic compound to be titrated with the stannous-bromine system. The curve obtained with a two-electrode amperometric indicating system is shown in Fig. 4 and is typical of the titration of a reversible couple with an irreversible one. The initial current is small, because oxidation of bromide at the indicator anode and reduction of quinone at the indicator cathode take place at potentials farther apart than the impressed voltage (150 mV). As the titration proceeds, the reaction at the indicator anode becomes the oxidation of hydroquinone, and since the quinone-hydroquinone couple is reversible, the indicator current increases. The current reaches a maximum about mid-way through the titration (with indicator electrodes of equal size) and then decreases as more quinone is reduced, the cathode becoming the indicator electrode. Since the stannic-stannous couple is irreversible, the current remains small after the equivalence point.

The fact that the stannous-quinone reaction is somewhat slow renders the direct

titration of quinone inconvenient, and a back-titration procedure is preferable. Excess +2 tin was generated, and then the excess was determined by back-titration with bromine.

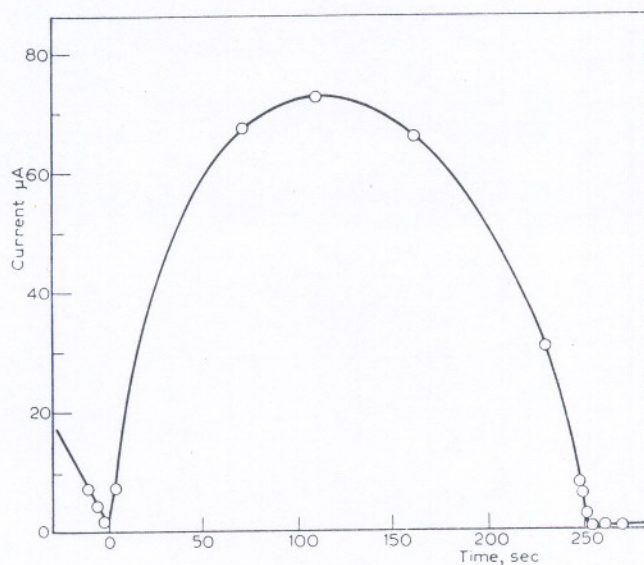


Fig. 4. Amperometric monitoring of coulometric titration of quinone with +2 tin (to the right) and of hydroquinone with bromine (to the left). 3.07 mg of quinone in *ca.* 50 ml of 3*M* sodium bromide, 0.2*N* hydrochloric acid, and 0.2*M* stannic chloride, with 22.8 mA generating current. The two platinum indicator electrodes were subjected to an applied voltage of 150 mV.

TABLE V

COULOMETRIC TITRATION OF QUINONE AND HYDROQUINONE WITH THE STANNOUS-BROMINE SYSTEM

The solution was 3*M* sodium bromide, 0.2*M* stannic chloride, and 0.2*N* hydrochloric acid with a volume of *ca.* 50 ml

Sample	Current (mA)	Quinone (or hydroquinone) taken (mg)	Quinone (or hydroquinone) found (mg)	% Error
<i>Quinone</i>				
1	33.24	6.138	6.108	-0.5
2	33.20		6.146	0.1
3	33.08		6.119	-0.3
4	33.20		6.124	-0.2
5	33.16		6.124	-0.2
			mean 6.124 ± 8	-0.2
<i>Hydroquinone</i>				
1	33.24	6.252	6.254	0.0
2	33.20		6.270	0.4
4	33.20		6.249	-0.1
5	33.16		6.265	0.2
			mean 6.259 ± 8	0.1

The oxidation of hydroquinone by bromine was studied in the same solution by continuation of the back-titration. In this titration the indicator current rises as quinone is produced, and then decreases to a minimum. Past the equivalence point the indicator current again rises because the bromine-bromide couple behaves quasi-reversibly. Bromine was generated slightly past the e.p., and then back-titrated with +2 tin. Bromine does not add to the quinone ring, even at a two-fold excess under these conditions.

In the potentiometric titration of quinone with +2 tin the expected titration curve was obtained, with the equivalence point potential at +0.25 V vs. S.C.E. However, the potentiometric titration of hydroquinone with bromine is unsatisfactory, because there is no distinct potential change at the end-point. Because even in the titration of quinone long times were required for the establishment of steady potentials, amperometric end-point detection is preferable in both cases.

Typical results in Table V demonstrate that quinone and hydroquinone can be titrated with the stannous-bromine system with an average error of about $\pm 0.2\%$.

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SUMMARY

The use of electrolytically generated +2 tin as a coulometric titrant has been studied. In a 3 to 4M sodium bromide and 0.2N hydrochloric acid solution, containing 0.2M stannic chloride, the generation of stannous ion is 100% efficient up to a current density of 80 mA/cm². With this medium iodine and bromine can be titrated coulometrically with errors of about $\pm 0.3\%$ or less. The titration is well suited for the iodometric determination of strong oxidants. Employing stannous ion and bromine for direct and reverse titrations, quinone and hydroquinone have been titrated.

RÉSUMÉ

On a étudié l'utilisation, pour les titrages coulométriques, de l'étain(II) électrolytiquement formé. On peut ainsi titrer l'iode et le brome et effectuer des dosages iodométriques d'oxydants forts.

ZUSAMMENFASSUNG

Es wird über coulometrische Titration mit Hilfe von elektrolytisch gebildetem Zinn-(II) berichtet. Beschrieben werden die Titrationen von Brom und Jod sowie die jodometrische Bestimmung starker Oxydationsmittel.

REFERENCES

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