COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN

TITRATION OF +3 GOLD AND +5 VANADIUM

ALLEN J. BARD AND JAMES J. LINGANE

Department of Chemistry, Harvard University, Cambridge 38, Mass., U.S.A.

In a recent study[1] in this laboratory the conditions under which +2 tin can be electrogenerated with 100% current efficiency have been determined. Iodine and bromine can be titrated successfully by use of either a gold or platinum generator electrode provided a concentrated (3 to $4M$) bromide solution of stannic chloride is used as supporting electrolyte. The titration of iodine serves for the determination of substances which oxidize iodide ion to iodine (coulometric iodometry) and the bromine titration can be employed for the determination of those organic compounds that undergo bromination or oxidation by bromine.

The present study extends the applications of coulometric titration with +2 tin to the determination of +3 gold and +5 vanadium. Although these elements can be titrated iodometrically, the direct titrations are more selective and subject to fewer interferences.

A coulometric titration of +3 gold to the elemental state in a hydrochloric acid medium with electrogenerated chlorocuprous ion, using potentiometric e.p. indication, has been described by LINGANE[2]. The titration with +2 tin was performed using potentiometric, amperometric, and spectrophotometric end-points.

The titration of +5 vanadium has been performed previously with several coulometric reductants. With chlorocuprous ion[3], or ferrous ion[4], reduction of vanadium proceeds to the +4 state, while titanous ion[5] causes reduction to +3 vanadium. With +2 tin the titration of +5 vanadium proceeds to the +4 state, and the e.p. can be recognized potentiometrically.

EXPERIMENTAL

The titration cell, apparatus, and conditions for 100% current efficiency have been described previously[1]. Amperometric and potentiometric e.p. detection followed the usual practice[6].

Absorption curves were recorded with a Cary Recording Spectrophotometer, Model 11 (Applied Physics Corp., Pasadena, Calif.). Spectrophotometric titrations were performed in a 180 ml tall form beaker held in a modified cell-holder of a Beckman DU Spectrophotometer. The generator electrode and the auxiliary electrode chamber were introduced into the cell through a stopper, from above, in such a manner as to be out of the light path. The solution was stirred by means of a magnetic stirrer beneath the cell compartment.

The optimum supporting electrolyte is 3 to $4M$ sodium bromide, $0.3N$ hydrochloric acid, and $0.2M$ stannic chloride. As discussed in a previous paper[1], with this electrolyte current efficiency for reduction of +4 tin remains at 99.5 to 99.9% with generating current densities of 10 to 84 mA/cm² at a gold generator cathode.

PERFORMANCE DATA

Titration of gold

The general characteristics of the potentiometric titration curve of +3 gold are

shown by the automatically recorded curve in Fig. 1. The main inflection occurs after the equivalence point chiefly because the reaction is somewhat slow near the e.p. When the titration is performed manually, with 1 to 2 min waiting periods between each generation increment, the inflection coincides with the e.p.
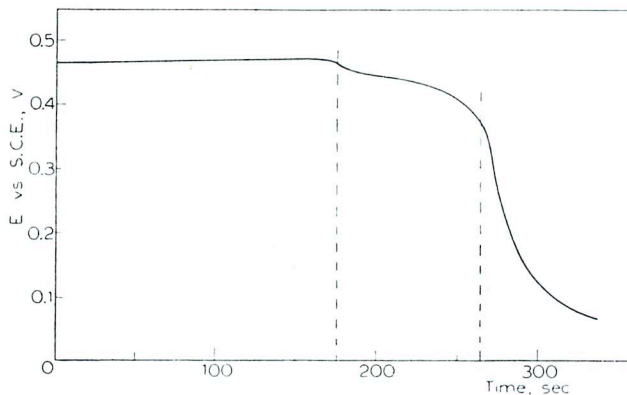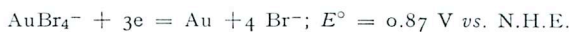

Fig. 1. Titration of 5.58 mg of +3 gold in 70 ml of 4M sodium bromide, 0.2M stannic chloride, and 0.3N hydrochloric acid, with a generating current of 31.1 mA. The potential of a gold indicator electrode during the titration was recorded automatically with a recording potentiometer.

It is evident from the first small inflection that the reduction of $AuBr_4^-$ proceeds stepwise, first to $AuBr_2^-$ and finally to the metal. Just as in the titration of +3 gold with chloro cuprous ion in chloride medium[2], the potential of the gold indicator electrode increases slightly, but definitely, during the first two thirds of the titration. This anomaly, which persists even in manual titrations with several min waiting at each point, results from the fact that a gold electrode is very slow in acquiring its equilibrium potential in a solution containing a mixture of +3 and +1 gold. The increase in potential is considerably smaller than was previously observed[2] in chloride medium, which suggests that the $AuBr_4^-/AuBr_2^-$ couple behaves somewhat more reversibly than does the $AuCl_4^-/AuCl_2^-$ couple. This same anomalous increase in potential has also been observed by ERDEY AND RADY[7] in their recent study of the titration of +3 gold with ascorbic acid in the ordinary volumetric manner.

During the last third of the titration the potential stabilizes rapidly and its value corresponds closely to the value expected from the standard potential of the $AuBr_2^-/$ Au couple.

Accurate measurements of the standard potentials of the three gold couples in bromide media do not appear to have been made at 25°. However, from the measurements of GRUBE et al.[8] at 60°

$$AuBr_2^- + e = Au + 2Br^-; \quad E° = 0.96 \text{ V } vs. \text{ N.H.E.}$$

$$AuBr_4^- + 3e = Au + 4 Br^-; \quad E° = 0.87 \text{ V } vs. \text{ N.H.E.}$$

$$AuBr_4^- + 2e = AuBr_2^- + 2Br^-; \quad E° = 0.82 \text{ V } vs. \text{ N.H.E.}$$

References p. 587

VOL. **20** (1959)   COULOMETRIC TITRATION OF Au AND V   583

From these values, we have for the disproportionation equilibrium at 60°

$$3AuBr_2^- = 3Au + AuBr_4^- + 2Br^-$$
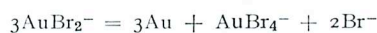
$$K = \frac{(AuBr_4^-)(Br^-)^2}{(AuBr_2^-)^3} = 54000$$

From the magnitude and form of this equilibrium constant it is clear, with a large total concentration of $AuBr_2^-$ and $AuBr_4^-$, and a relatively small concentration of bromide ion, that $+1$ gold is unstable. However, under the diametrically opposite conditions of the present study (very small total concentration of gold and very large bromide ion concentration) the balance of the disproportionation equilibrium should be far to the left. The observed stepwise reduction of the $+3$ gold is consistent with this prediction.

The titration can also be followed amperometrically by observing the current between two identical, small gold electrodes (1 cm² each is suitable) across which a constant voltage of the order of 100 to 200 mV is impressed. Fig. 2 shows a typical amperometric titration curve. The anode is depolarized throughout the titration by the reaction $Au + 2Br^- = AuBr_2^- + e$, and the cathode, at which the reaction is initially $AuBr_4^- + 2e = AuBr_2^- + 2Br^-$ and finally $AuBr_2^- + e = Au + 2Br^-$, actually functions as the indicator electrode. The indicator current decreases continuously up to the e.p. in tune with the decreasing concentrations of $AuBr_4^-$ and $AuBr_2^-$. The irreversible behaviour of the stannic–stannous couple causes the indicator current to remain very small beyond the e.p. There is some semblance of an increase in slope at the two-thirds point, which suggests that the overpotential required for
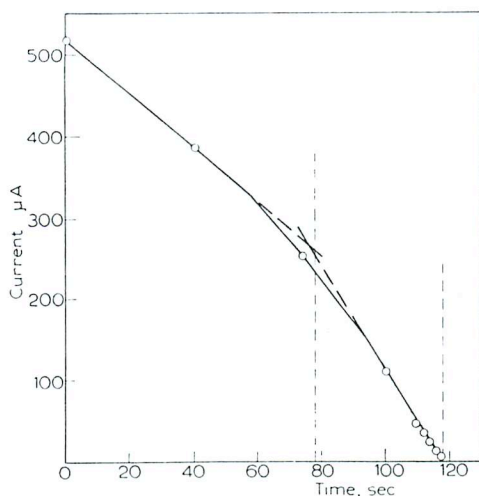

Fig. 2. Amperometric titration of 5.27 mg of $+3$ gold in 70 ml of $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.3N$ hydrochloric acid, with a generating current of 64.9 mA. A constant voltage of 150 mV was impressed across the two indentical gold indicator electrodes (area 1 cm² each).
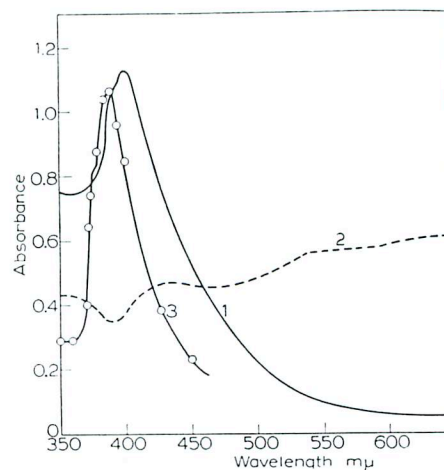

Fig. 3. Absorption spectra during the titration of 100 ml of 0.346 mM $+3$ gold in $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.25M$ hydrochloric acid. (1) Original solution. (2) Solution titrated past the two-thirds point, containing $AuBr_2^-$ and colloidal gold. (3) 0.402 mM $+2$ tin alone. Curves 1 and 2 were recorded with a 1-cm light path, but a 10-cm light path was used for curve 3.

References p. 587

the reduction of $AuBr_2^-$ is smaller than that for the reduction of $AuBr_4^-$, but obviously this e.p. is too indistinct for practical use.

During the titration of $AuBr_4^-$ with +2 tin, the solution, initially colored orange-yellow, changes to colorless when the titration is two-thirds complete, and then to various shades of purple as colloidal gold is formed. These color changes suggested the possibility of following the titration spectrophotometrically.

Fig. 3 shows spectrophotometric absorption curves taken during a titration of +3 gold with electrogenerated +2 tin. The absorption peak of $AuBr_4^-$ at 400 mμ has an extinction coefficient of 3,270 l/mole cm. TURKEVICH et al.[9] found that colloidal gold sols, in the presence of aurous gold, show a broad absorption band throughout the visible region, rising to a maximum at about 700 mμ. Curve 2 corresponds to this description. From curve 3 it is seen that $SnBr_4^{-2}$ has an absorption peak at about 388 mμ (depending slightly upon the tin concentration) with an extinction coefficient of only 268 l/mole cm. The stannic bromide complex absorbs only in the region of 300 to 360 mμ with a maximum at about 320 mμ.

The spectrophotometric titration of +3 gold was performed by setting the Beckman DU spectrophotometer at a wave-length of 400 mμ, the slit width at 0.15 mm, and the absorbance at 0.00 with the cell removed from the holder. The use of air as reference (zero absorbance) is convenient, since only the change in absorbance rather than its absolute value is needed for titration purposes.

A typical spectrophotometric titration curve is shown in Fig. 4. The absorbance readings were independent of the stirring rate, and became stable within 1 min. After the e.p. (reduction of +3 to +1 gold) the readings took about 15 min to become fairly steady, because the gold sol was undergoing particle size (and absorption) fluctuations. In contradistinction to potentiometric and amperometric detection, spectrophotometric detection reveals only the first e.p. and the second is inaccessible.

Table I summarizes data obtained in 37 titrations using potentiometric, amperometric, and spectrophotometric e.p. detection. In each case the supporting electrolyte was pre-titrated to the e.p. before the gold sample was added. With either potentiometric or amperometric detection 0.5 to 23 mg of gold is titratable with an average error of ca. $\pm$ 0.3%. Spectrophotometric titration was both less precise and less accurate (average error ca. + 2%).

TABLE I

COULOMETRIC TITRATION OF +3 GOLD

Supporting electrolyte was 4M sodium bromide, 0.2M stannic chloride, and 0.3N hydrochloric acid, and the volume was 70 to 110 ml. The area of the gold generator cathode was 1 cm^2, except with the 22.62 mg sample, in which case it was 4 cm^2.

Gold taken mg	No. of trials	Current mA mg	Gold found (average) mg	Average deviation mg	End-point detection
5.271	5	63.90	5.259	$\pm$0.015	
5.271	4	32.14	5.276	$\pm$0.018	Potent.
1.055	3	9.971	1.055	$\pm$0.001	
22.62	4	100.75	22.76	$\pm$0.04	
5.271	7	65.00	5.266	$\pm$0.012	Amp.
5.271	6	34.10	5.272	$\pm$0.009	
5.271	3	9.961	5.271	$\pm$0.007	
5.271	4	60.75	5.370	$\pm$0.069	Spectro.
5.271	1	33.36	5.267	—	

References p. 587

, but obvious-

olored orange-
e, and then to
nges suggested

a titration of
r₁⁻ at 400 mμ
.⁹ found that
sorption band
Curve 2 corre-
an absorption
n) with an ex-
mplex absorbs
.

ing the Beck-
h at 0.15 mm,
The use of air
m absorbance

he absorbance
within 1 min.
15 min to be-
d absorption)
ric detection,
s inaccessible.
tric, ampero-
pporting elec-
l. With either
table with an
ss precise and

.N hydrochloric
s 1 cm², except

End-point detection

Potent.

Amp.

Spectro.

We have not investigated interference by other metals. However, of the elements commonly associated with gold, we would not expect interference from lead, silver or mercury. Quite possibly platinum may interfere as it does in the titration with chloro cuprous ion in chloride medium[2].
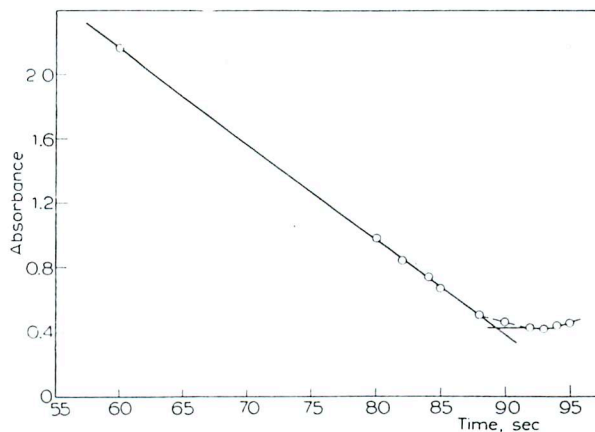

Fig. 4. Spectrophotometric titration of 5.27 mg of +3 gold in 100 ml of $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.3N$ hydrochloric acid, with a generating current of 60.7 mA. Absorbance was measured against air at 400 mμ. The end-point corresponds to reduction of the +3 gold to the +1 state.

Titration of +5 vanadium

The titration of +5 vanadium to the +4 state was performed with the same supporting electrolyte used for the titration of gold, using potentiometric e.p. detection. Amperometric e.p. detection is not suitable because in acidic bromide medium the V^{+5}–V^{+4} couple behaves irreversibly, and since the stannic–stannous couple also functions irreversibly there is no clear definition of an end-point.

The titration can also be followed spectrophotometrically by measuring the change in absorbance at 390 mμ. At this wave length +5 vanadium and +2 tin both absorb strongly, whereas +4 vanadium and +4 tin do not. Hence the titration curve is V-shaped with the e.p. at minimum absorbance.

In the acidic bromide medium used ($4M$ sodium bromide, $0.25N$ hydrochloric acid, and $0.2M$ stannic chloride) the formal potential of the V^{+5}/V^{+4} couple is $+0.63$ V *vs.* S.C.E. ($+0.87$ V *vs.* N.H.E.). This is large enough, in the presence of a high concentration of bromide ion, so that some of the +5 vanadium is reduced by bromide ion when the sample is added to the supporting electrolyte. Because the bromine formed is partly lost by volatilization in the nitrogen stream used to remove dissolved air, this reaction causes a negative error.

For example, when eight 2.739-mg samples of +5 vanadium were titrated one after the other in the same batch of supporting electrolyte the errors in percent were *seriatim* —7.9, —5.1, —2.1, +0.3, 0.0, —0.4, —0.4, and —0.5. The negative error, initially quite large, disappeared after three samples were added and titrated. The reason for this effect is that +4 vanadium accumulates in the solution during the

References p. 587

successive titrations, and after about three samples have been titrated (*i.e.*, when the concentration ratio of +5 to +4 vanadium becomes 1/3 or smaller) the potential of the V^{+5}/V^{+4} couple is decreased sufficiently so that +5 vanadium no longer oxidizes bromide ion.

The obvious way to prevent this error in the first place is to add to the supporting electrolyte sufficient +4 vanadium (as vanadyl sulfate) so that the potential of the V^{+5}/V^{+4} couple is kept below the value at which bromide ion is oxidized. This was done in all subsequent titrations. In addition the supporting electrolyte (con-

TABLE II

COULOMETRIC TITRATION OF +5 VANADIUM

The supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride, $0.25N$ hydrochloric acid, and $0.004M$ vanadyl sulfate, and the volume was *ca.* 70 ml. Dissolved air was removed with nitrogen. The area of the gold generator cathode was 1 cm^2. Potentiometric e.p. detection was employed.

Vanadium taken mg	No. of trials	Current mA	Vanadium found (average) mg	Average deviation mg
2.739	5	34.56	2.738	±0.002
2.739	5	34.46	2.738	±0.007
5.467	3	67.08	5.472	±0.010
5.467	4	68.50	5.461	±0.004
0.5462	7	10.48	0.5458[a]	±0.0046

[a] In these trials +2 tin was generated beyond the e.p. and the excess was back titrated with electrogenerated bromine using a 1-cm^2 platinum anode.

taining +4 vanadium) was pre-titrated to the e.p. before the sample of +5 vanadium was added.

Results obtained in 24 titrations of 0.5 to 5.5 mg quantities of +5 vanadium are summarized in Table II. The average deviation is seen to be *ca.* ±0.2% with the larger samples and ±0.8% with the 0.5 mg samples.

SUMMARY

Methods are described for the titration of +3 gold and +5 vanadium with electrogenerated +2 tin in an acidic bromide medium. Quantities of gold from 1 to 23 mg are titratable with an average error of *ca.* +0.3%, using either potentiometric or amperometric e.p. detection. Spectrophotometric detection can also be used but is somewhat less precise, Using potentiometric detection 0.5 to mg of +5 vanadium is titratable to the +4 state with an average error of ±0.2%.

RÉSUMÉ

On décrit des méthodes pour le titrage coulométrique de l'or(III) et du vanadium (V) au moyen de l'étain(II), en solution acide, en présence de bromure, avec détection potentiométrique, ampérométrique ou photométrique du point final.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur coulometrischen Titration von Gold-(III) und Vanadium-

(V) mit Hilfe von Zinn-(II) in bromidhaltiger, saurer Lösung. Der Endpunkt kann potentiometrisch, amperometrisch oder photometrisch bestimmt werden.

REFERENCES

1 A. J. BARD AND J. J. LINGANE, *Anal. Chim. Acta*, 20 (1959) 463.
2 J. J. LINGANE, *Anal. Chim. Acta*, 19 (1958) 394.
3 D. J. MEIER, R. J. MEYERS AND E. H. SWIFT, *J. Am. Chem. Soc.*, 71 (1949) 2340.
4 W. OELSEN AND P. GÖBBELS, *Stahl u. Eisen*, 69 (1949) 33.
5 J. J. LINGANE AND J. H. KENNEDY, *Anal. Chim. Acta*, 15 (1956) 465.
6 J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, 1958.
7 L. ERDEY AND G. RADY, *Talanta*, 1 (1958) 159.
8 G. GRUBE, T. MORITA, J. HELFER AND M. BÄRMANN, *Z. Elektrochem.*, 38 (1932) 117.
9 J. TURKEVICH, G. GARTON AND P. C. STEVENSON, *J. Colloid Sci.*, (1954) Sup. 1, 26.