

COULOMETRIC TITRATION OF COPPER(II) WITH ELECTRO-GENERATED CHROMIUM(II)

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(Received November 2nd, 1961)

Chromium(II) is one of the most powerful reductants used in titrimetric analysis¹. Because chromous ion reacts rapidly with oxygen, elaborate precautions are necessary in preparing and storing standard solutions for titrations. These circumstances suggest the application of coulometric electrogeneration of chromium(II) as a titrant.

Several early investigators in the field of coulometric titrations unsuccessfully attempted the electrogeneration of chromous ion². Generally either 100% current efficiency for the electroreduction of chromium(III) could not be attained, or the chromium(II) produced reduced hydrogen ion during the titration at a sufficiently rapid rate to cause sizeable errors. Recently two studies describing the coulometric titration of oxygen with chromous ion have been reported^{3,4}. The present study was undertaken to examine the current efficiency for the electrogeneration of chromium(II), and to apply this titrant to the determination of substances other than oxygen.

EXPERIMENTAL

Apparatus and reagents

The titration was performed in an H-cell with a 175-ml cathode (titration) chamber and a 50-ml anode chamber (Fig. 1). These two chambers were separated by a fine-porosity sintered glass disk and a saturated potassium chloride-agar plug. The anode was a cadmium rod enclosed in a glass tube with a sintered glass bottom. Nitrogen, passed through two tubes containing amalgamated zinc and 0.1 *M* chromous chloride in 1 *M* sulfuric acid, was bubbled through all chambers before and during the titration. These precautions were taken to prevent the diffusion of oxygen and products formed at the anode into the cathode chamber. A mercury pool cathode with an area of 19.6 cm² could be introduced and removed through a side-arm fitting on the titration cell. The anode chamber contained 5 *M* calcium chloride for chromic chloride supporting electrolytes, and 0.1 *M* potassium chloride for the chromic sulfate solutions. Stirring was accomplished with a magnetic stirrer; the stirrer bar resting on the mercury cathode.

A Sargent Coulometric Current Source, Model IV (E. H. Sargent, Chicago, Ill.) was employed. Potentiometric end-point detection, employing a mercury pool indicator electrode and a saturated calomel electrode with a fiber salt bridge, followed the usual practice. The functioning of the mercury pool indicator electrode was not affected by stirring rate, vibrations, etc.

Standard copper(II) and nickel(II) solutions were prepared by dissolving the pure metals in nitric acid and diluting to volume. The saturated calcium chloride solutions were filtered before use. All other reagents were used without further purification.

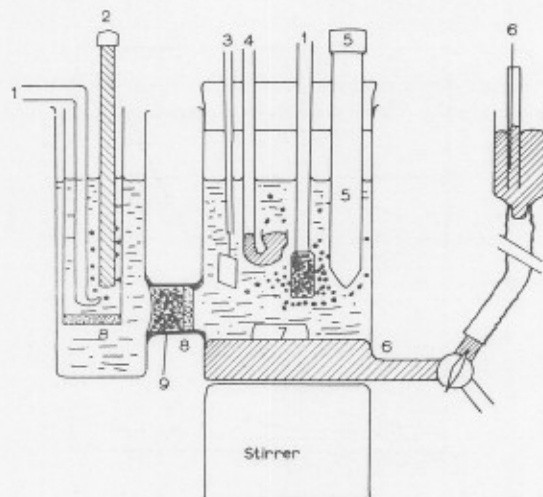


Fig. 1. Coulometric titration cell. 1, nitrogen inlets; 2, cadmium anode; 3, platinum indicator electrode (used only in preliminary experiments); 4, mercury pool indicator electrode; 5, saturated calomel electrode; 6, mercury pool cathode; 7, magnetic stirring bar; 8, fine porosity sintered glass disks; 9, agar-potassium chloride plug.

Procedure

Supporting electrolyte solution was freshly prepared and deaerated for about 15 min before use. The mercury pool was introduced and the solution was pre-titrated to the approximate end-point potential of the titration. The mercury pool was withdrawn and the sample solution was added and deaerated. Finally the mercury pool was reintroduced, and the sample titrated. This procedure effectively eliminated oxidation of mercury by any oxygen initially contained in the supporting electrolyte sample solutions, and allowed pre-reduction of impurities in the supporting electrolyte.

CURRENT EFFICIENCY FOR GENERATION OF CHROMIUM(II)

The current efficiency for the electroreduction of chromium(III) was determined from current-potential curves of solutions with and without chromic ion present⁵. Polarographic studies show that the reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is quite irreversible, but becomes more reversible with increasing concentrations of chloride ion. In saturated calcium chloride solutions the reduction of chromic chloride is polarographically reversible⁶.

Current-potential curves at a large mercury pool electrode for various concentrations of chromic chloride in saturated calcium chloride are shown in Fig. 2. These curves were obtained by recording the potential of the mercury pool electrode with time at a constant current density, and plotting the steady state potential (after about 30 sec) against current. The curves indicate that current efficiencies of greater than 99% should be obtainable for current densities of 5 to 9 mA/cm² (Table I). The

current efficiency determined by actual titration of the electrogenerated chromous ion with standard ceric sulfate or potassium dichromate solutions, however, appeared much lower. Attempts to use chromous ion, electrogenerated in a saturated calcium chloride solution, for the titration of copper(II) were also unsuccessful; the rate of the

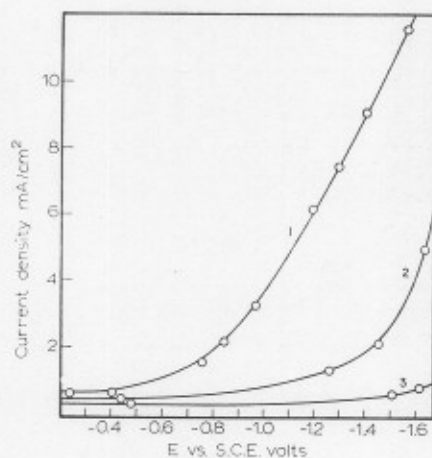


Fig. 2. Current-cathode potential curves for the reduction of chromium(III) chloride. The solution contained saturated calcium chloride and 1, 0.1 *M* chromic chloride; 2, 0.01 *M* chromic chloride; 3, supporting electrolyte alone.

TABLE I
PREDICTED CURRENT EFFICIENCIES FOR THE ELECTROREDUCTION OF CHROMIUM(III)

Current density mA/cm ²	Current efficiency %
<i>0.1 M chromic chloride</i> - <i>saturated calcium chloride</i>	
0.5	94
1.0	96
2.0	97
6.0	99.2
7.0	99.4
9.0	99.2
11.0	98.2
<i>0.1 M chromic sulfate</i> - <i>0.1 M potassium chloride</i>	
0.1	85
0.3	91
1.0	98
1.5	97
2.0	96
3.0	80

titration reaction appeared slow and large (15–20%) positive errors were obtained. The difference between the predicted and the apparent current efficiencies was attributed to some reduction of hydrogen ion by the chromous ion.

MEITES determined chromium by reduction to the chromous state (at about -1.1 V vs. S.C.E., apparently not at 100% current efficiency), and then controlled

potential coulometric reoxidation at -0.40 V vs. S.C.E., in 6 M hydrochloric acid⁷. Under these conditions, chromous ion apparently did not react very rapidly with hydrogen ion. Although the reaction of chromium(II) with hydrogen ion is generally a slow reaction, in the present study this reaction may have been either catalyzed by impurities in the calcium chloride (all brands of "reagent-grade" calcium chloride were found to contain sizeable amounts of impurities) or induced by the titration reactions.

Current-potential curves obtained in a chromic sulfate -0.1 M potassium chloride solution, the medium used by JAMES AND STEPHENS⁴, are shown in Fig. 3. Because of

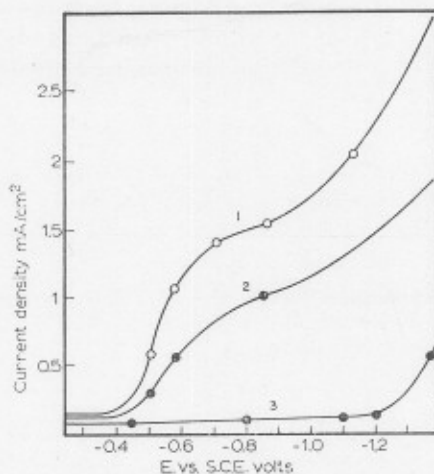


Fig. 3. Current-cathode potential curves for the reduction of chromium(III) sulfate. The mercury cathode had an area of 19.6 cm². The solution contained 0.1 M potassium chloride and 1, 0.1 M chromic sulfate; 2, 0.01 M chromic sulfate; 3, supporting electrolyte alone.

the slow rate of ligand exchange in chromium complexes, these curves are probably characteristic of chromium(III)-sulfate complexes. Under these conditions the current efficiency is largest (about 98%) at a current density of 1 mA/cm², and drops off sharply at both higher and lower current densities (Table I). The narrow range of effective current densities is caused by the low limiting current plateau for the reduction of the current-potential curves. Since JAMES AND STEPHENS obtained titration efficiencies of better than 99.5% for the determination of oxygen under these conditions, some direct electrode reduction of oxygen itself (rather than by reaction with chromous ion) must take place⁸. The overall reduction of oxygen may also occur by the oxidation of the mercury to mercurous chloride which is then cathodically reduced.

PERFORMANCE DATA

In chloride media, the titration of copper(II) proceeds in two steps, first to copper(I) and then to the metal⁹. A typical potentiometric titration curve for the titration of copper(II) with electrogenerated chromous ion, employing a mercury pool indicator electrode is shown in Fig. 4. The titration reaction was quite rapid initially, but establishment of steady indicator electrode potentials became slow toward the end-

point. At the chloride and reactant concentrations employed, the second titration step, copper(I) to the metal, was not readily obtained. The magnitude of the potential change at the equivalence point is quite small, and exact location of the end-point was often difficult. The size of the end-point potential change is larger when a platinum indicator electrode is employed⁹, but we preferred to keep platinum out of the titration cell for fear of catalyzing the reduction of hydrogen ion by chromous ion. Table II summarizes data for the titration of copper(II) with chromium(II) using

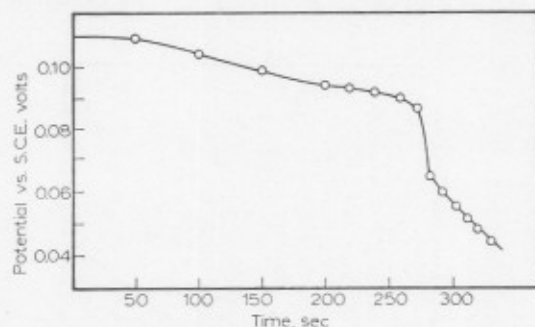


Fig. 4. Titration of 1.339 mg of copper(II) in 105 ml of 0.1 *M* chromic sulfate and 0.1 *M* potassium chloride at a 19.6 cm² mercury cathode at a current of 9.66 mA. The potential of a mercury pool indicator electrode was measured vs. a S.C.E. with a pH meter.

TABLE II
COULOMETRIC TITRATION OF COPPER(II)

Supporting electrolyte was 0.1 *M* chromic sulfate and 0.1 *M* potassium chloride, and the volume was about 110 ml. The area of the mercury generator cathode was 19.6 cm², and the current was 9.66 mA.

Copper taken (mg)	Copper found (mg)	Error (mg)
0.804	0.805	+0.001
0.804	0.795	-0.009
1.339	1.305	-0.034
1.339	1.313	-0.026
1.790	1.761	-0.029
1.790	1.750	-0.040
1.790	1.757	-0.033
2.280	2.226	-0.054
2.280	2.239	-0.041

potentiometric end-point detection. That the error is somewhat negative is suggestive of difficulty in locating, or in obtaining complete reduction of copper(II) at the end-point, rather than loss of high current efficiency or side reactions.

Several titrations of nickel(II) with electrogenerated chromium(II) were attempted. The reaction appeared slow and is probably not useful analytically. An interesting observation during the titration is that the only well-defined "break" in the potentiometric titration curve occurs at the completion of reduction of nickel(II) to nickel(I), rather than to the metal. Although nickel(I) has been reported in cyanide solutions, no evidence has been presented for its presence in a chloride medium.

Since the titrations were performed in the presence of nitrate ion (introduced in the standard solutions), one might wonder about its interference during titrations with chromous ion. Titrimetric methods for nitrate involving chromous solutions have been described¹⁰, but the reaction between nitrate and chromous ion is slow, and only proceeds faster at elevated temperatures and in the presence of a catalyst. Apparently the rate of this reaction, as compared to the rate of reduction of copper(II) with chromium(II), is sufficiently slow so as not to interfere in the titration, although the drifting of the indicator electrode potential sometimes noted after the equivalence point may be caused by the chromium(II)-nitrate reaction. The direct cathodic reduction of nitrate ion occurs at potentials more negative than that attained by the mercury cathode in these titrations¹¹. During other titrations with chromium(II), it might be advisable to eliminate nitrate ion from the titration medium.

CONCLUSION

Chromium(II) can be generated at close to 100% current efficiency by reduction of chromium(III). The present study indicates that reduction of chromic sulfate, rather than chromic chloride in concentrated chloride media, appears to be more useful, although other supporting electrolytes bear investigation. Since mercury itself is a good reducing agent in a chloride medium, oxidants with potentials above +0.25 V vs. N.H.E. may react with mercury. Direct titrations with chromium(II) are therefore limited to those oxidants with potentials between *ca.* +0.25 and -0.4 V vs. N.H.E. For many titrations in this range, electrogenerated titanium(III) or iron(II) ethylenediaminetetraacetate⁵ can also be used. The widest application of coulometric titrations with chromium(II) will probably be in the determination of oxygen.

SUMMARY

The current efficiency for the electrogeneration of chromium(II) for use as a coulometric titrant was studied for several supporting electrolytes. With a mercury cathode and a 0.1 M chromic sulfate-0.1 M potassium chloride medium, 0.8 to 2.8 mg of copper(II) in 110 ml of solution can be titrated using potentiometric end-point detection.

RÉSUMÉ

Description d'une méthode coulométrique pour le dosage du cuivre(II), au moyen de chrome(II), formé électrochimiquement. Divers électrolytes de base ont été examinés.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode zur Bestimmung von Kupfer-(II) mit elektrolytisch erzeugten Chrom-(II)-Lösung.

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