THE CHROMIC-CHROMOUS COUPLE AS AN INTERMEDIATE IN COULOMETRIC ANALYSIS

By

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INTRODUCTION AND HISTORY

Coulometric analysis is a method of analysis which depends on the measurement of the quantity of electricity necessary to complete a chemical oxidation or reduction. The relationship between the amount of current passed and the quantity of material oxidized or reduced was first enunciated by Michael Faraday. The two laws which bear his name are:

(1) The mass of a substance involved in reaction at each electrode is directly proportional to the quantity of electricity passed through the solution.

(2) The masses of different substances produced during electrolysis are directly proportional to their equivalent weights.

It is on the foundation of these two laws that coulometric analysis rests.

Szebelledy and Somogyi (17) have pointed out that coulometric processes may be divided into two types:

(1) Those in which the desired reaction takes place directly at a suitable electrode.

(2) Those in which an intermediate half-cell reaction takes place at the electrode and the material produced by this reaction then reacts quantitatively with the substance being analyzed.

Further, the process may be divided as to oxidation or reduction, oxidation taking place at the anode or positive pole, and reduction taking place at the cathode or negative pole.

Coulometric analysis is generally considered to have had its origin with the two European workers, Szebelledy and Somogyi. In 1938, they reported that they were able to determine thiocyanate in solution by electrically generating bromine and then allowing the bromine to oxidize the thiocyanate (18). The excess bromine was titrated with a standard sodium thiosulfate solution using a starch-iodide indicator. Throughout the titration the potential was held constant and the amount of electricity passed was measured with a silver coulometer. Using this same method they also determined hydroxylamine (19) and hydrazine (20).

Szebelledy and Somogyi (21), (22) also determined hydrochloric and sulfuric acid by electrolyzing them in a cell consisting of a platinum cathode and a silver anode. Potassium chloride was added to the acid and the solution was electrolyzed to a bromo-cresol green end point.

Recently Lingane and Small (11) developed a method for the determination of the halides. In their method, the halide solution was placed in a cell containing a silver anode and a platinum cathode. By proper adjustment of the applied voltage, the potential of the anode remained constant and at a value such that the reaction $Ag + X^- \longrightarrow AgX + e$, where $\underline{X}^-$ denotes chloride, bromide or iodide ion, proceeded quantitatively. As the halide concentration decreased in the solution, the current dropped exponentially, and became virtually zero when the electrolysis was conpleted. The quantity of halide in the solution was found employing a coulometer to measure electricity used in the reaction. Faraday's laws were then used to calculate the amount of halide present. They report that the ions may be determined either singly or together, the iodide being deposited first, followed by the bromide and chloride.

In each of the above determinations the voltage was held constant while the current was allowed to decrease, the amount of electricity passed being measured by means of a coulometer. It should be noted that while the results obtained by this method are satisfactory, there is a considerable amount of trouble and time involved in the use of a coulometer. It would seem plausible that if a constant current could be used, the procedure would be simplified since a simple multiplication of current times time, in seconds, would give directly the number of coulombs of electricity passed during the electrolysis.

In 1948, Meyers and Swift (13) reported such an analysis. Instead of a constant voltage they used a constant current, with an appropriate timing device. In this method, bromine was generated at the anode and then allowed to oxidize arsenic (III). The end point was determined amperometrically. Later, Farrington and Swift (6), (14) showed that chlorine and iodine could also be used in the same type of analysis.

Seas, Nieman, and Swift (16) have used the constant current method to generate bromine which in turn was used to oxidize thiodiglycol. The end point was amperometric and was based on the fact that when a suitable potential was applied to an electrode in a solution containing bromide ions, the indicator cathode became polarized and current would flow only when there was a very small excess of free bromine in the solution.

Very recently, Furman, Cooke and Reilley (8) used a large platinum anode to generate ceric ions which then were allowed to oxidize ferrous ions. An electronic circuit supplied the current and its magnitude was determined by measuring the voltage drop across a standard resistor with a potentiometer. In their apparatus the anode and the cathode were separated, the cathode being placed in a cylinder with a porous bottom through which electrical contact could be made with the anolyte. The level of the catholyte was maintained above that of the rest of the solution so that diffusion of ceric or ferrous ions into the cathode would not occur.

It was mentioned earlier that the coulometric processes could be either anodic or cathodic. All of the constant current methods mentioned to this point have been anodic but coulometric analysis is not limited to this. Cooke and Furman (2) used a 10 square centimeter platinum cathode to generate ferrous ions from a ferric ammonium sulfate solution. The ferrous ions were then used to reduce chromate or ceric ions. The end point was determined potentiometrically and the method proved to be very satisfactory. Furman, Cooke and Reilley (7) also used electrically generated ferrous ions to determine metavanadate in the presence of large amounts of uranium.

Meier, Meyers, and Swift (12) determined chromates and vanadates by the electrical reduction of cupric copper to cuprous and the subsequent chemical oxidation back to cupric by reduction of the chromates and vanadates. A divided cell was used and the end point was determined amperometrically.

Carson and Ko (1) have used the coulometric method for determining organic acids in the presence of large amounts of mineral acids. It has been shown that the organic acids could be titrated directly by a standard alkali in a 70% isopropyl alcohol solution. The difficulty with this procedure was that such small amounts of alkali were required for the organic acid in comparison with that used for the mineral acid, that carbonate-free alkali had to be used to eliminate the high blanks that would result. In the coulometric procedure, the OH^- ion is generated at the cathode, used immediately, and thus the storage problems are eliminated.

This year, De Ford, Pitts and Johns (3) introduced a new innovation in the field of coulometric analysis. Heretofore, the intermediate reaction took place in the cell containing the substance to be determined. However, in this new method, which was used for the determination of acids and bases, the intermediate reaction took place externally and the product was then titrated into a cell containing the substance to be determined. In this procedure a sodium sulfate solution was allowed to flow through a Y-shaped tube. In one arm of the Y was the anode and in the other arm was the cathode, acid being formed at the anode and base at the cathode. Thus by using one solution, either acids or bases could be determined. They also pointed out that in this method there was no danger of impurities in the sample being oxidized or reduced at the electrode, and thus causing an error in the amount of current required for the oxidation or reduction of the substance in question. They (4) have also perfected an automatic instrument for use with this method.

In searching the literature, Mr. John Donahue (5) found that the strongest reducing couple which had been reported was the cupric-cuprous couple used by Meier, Meyers and Swift. This couple had been used for strong oxidizing agents such as chromates and vanadates. Also it was used for micro samples and at rather small currents. During the course of his research, Mr. Donahue showed that the stronger couple, the titanic-titanous couple, was suitable as an intermediate. In his work, Mr. Donahue used macro samples and considerably larger currents than are usually reported. The purpose of the larger currents was to facilitate the use of larger samples and to shorten the time required to complete a determination. A potentiometric end point was used, since, with currents greater than 10 milliamperes, an amperometric end point is obliterated by parasitic currents (3).

The student's proposal was to study

/ Since the titanic-titanous couple proved to be effective as an intermediate, it was decided to investigate a still stronger couple, the chromic-chromous couple.) Again macro samples, comparatively large currents and a potentiometric end point were to be used. The apparatus was modified somewhat, particularly the cell and the cathode, but otherwise the circuits, current source, etc., remained the same as those used by Donahue.

REAGENTS

All reagents used were C.P. or reagent grade. Solutions were prepared as follows:

Ferric Sulfate (0.5M solution). Approximately 28 grams of standarizing-quality iron wire were placed in a liter beaker together with 250 ml. of concentrated hydrochloric acid and 150 ml. of distilled water. The beaker was covered and warmed until all of the wire had gone into solution; then 65 ml. of concentrated nitric acid were added and the solution was evaporated to half its original volume. It was then cooled somewhat and 150 ml. of concentrated sulfuric acid added slowly. The solution was then evaporated until the white fumes of sulfur trioxide appeared. After cooling, it was diluted with 200 ml. of distilled water and allowed to stand until all the ferric sulfate had dissolved. The solution was then diluted to a final volume of 500 ml. after which it was stored in a brown, glass-stoppered bottle.

Sulfuric Acid (1N solution). To 500 ml. of water were added 55 ml. of concentrated acid. This was then made up to one liter.

Potassium Chrome Alum Solution. Enough of the salt was added to a quantity of water so that on standing several days there was still an excess in the bottom of the container. It was found, however, that this excess would dissolve over a 2 to 3 week period and thus a completely saturated solution was not obtained. For the most part, the results reported in this thesis were obtained using measured portions of one particular three gallon stock solution. The concentration of this solution was determined by measuring its density and reading the concentration from a graph prepared from data found in the literature (9). As a check on the validity of this data, three volumetric determinations were made, the values obtained being found to agree favorably with those read from the graph. The three gallon stock was found to contain 250 grams per liter and an additional one gallon supply prepared later contained 287 grams per liter.

Sodium Hydroxide (4N solution). Forty grams of sodium hydroxide pellets were dissolved in a minimum quantity of water and the solution, on cooling, was made up to 250 ml.

Chromic Sulfate Solution. Solutions of varying concentrations were prepared and used during the early part of the experimental work. The most concentrated solution used contained 143 grams of the salt in 250 ml. of solution.

Titanium Tetrachloride Solution. Following the procedure used by Donahue, (5) five hundred ml. of this solution were prepared by adding water to 200 ml. of pure $TiCl_4$ until hydrolysis ceased and then adding enough water to make the final volume 500 ml. This solution was stored in a one-liter glass-stoppered bottle.

Agar-Ammonium Nitrate Gel. A quantity of this material was prepared by adding 3 grams of agar to each 100 ml. of 1M ammonium nitrate solution and heating on a steam bath with stirring until all the agar had dissolved. It was found that the agar-ammonium nitrate solution should be neither less, nor much greater than 3% agar by weight. This gel was prepared and stored in a 250-ml. Erlenmeyer flask.

APPARATUS AND EXPERIMENTAL

The direct current source for this research was supplied by a bank of eight 6-volt lead storage batteries. These batteries were connected in series and supplied approximately 48 volts. The purpose of using this large number lies in the fact that by using a comparatively large voltage and correspondingly large external resistances, small changes in cell resistance would cause only negligible changes in the current. It was found that this arrangement gave a very satisfactory current though perhaps not as steady as might be obtained with an electronically controlled source. The batteries were connected to the electrolysis circuit by means of a D. P. D. T. switch S_1 (See Figure 1). This arrangement was used so that the batteries could be charged by a D. C. generator without removing the connections to the batteries.

The current was controlled by means of two 500 ohm, 50-watt variable resistors and one 10-ohm, 25-watt variable resistor (R_1, R_2 and R_3). These resistors were connected in series with each other and with the batteries. Switch S_4 provided for cutting the cell out of the circuit and replacing the cell with a variable resistor R_4 so that current could flow through the resistor without flowing through the electrolysis cell. The purpose of this resistor was to

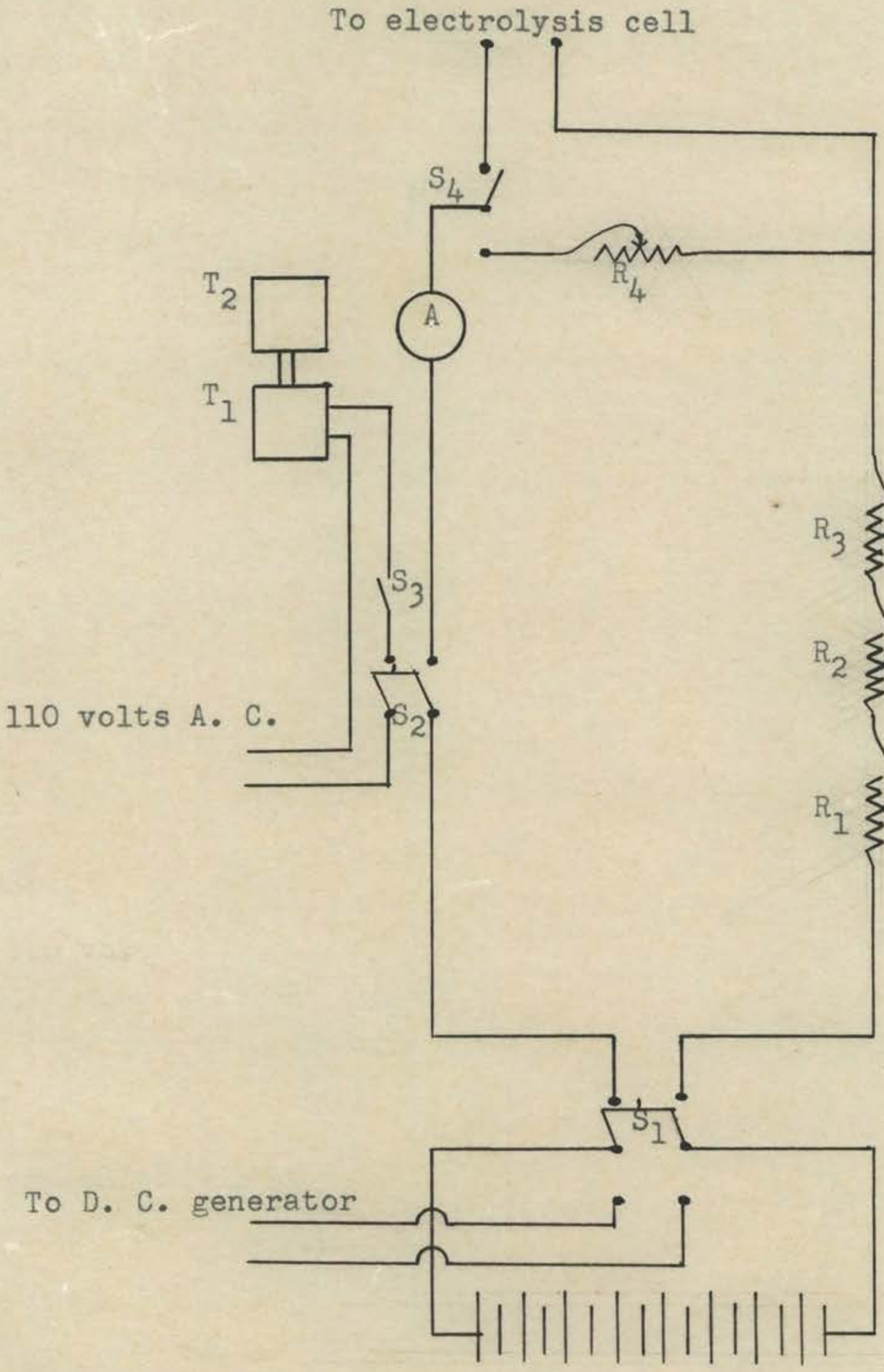
To electrolysis cell
S4
R4
T2
A
T1
S3
110 volts A. C.
S2
R3
R2
R1
S1
To D. C. generator

Figure 1

provide a "warm-up" circuit for the batteries so they could be allowed to attain a stable state before electrolysis was started. Thus when electrolysis was begun a steady current would be available.

The amount of current flowing was indicated by a Weston multi-range direct current milliammeter (Model No. 430) (A). It was necessary to tap the instrument several times during the course of a run to prevent "sticking" of the needle and insure a proper reading. The milliammeter was standarized by measuring the potential drop across a standard one-ohm resistor (Leeds and Northrup Co., Cat. No. 1006954) by means of a potentiometer. For readings of 0.1, 0.05 and 0.2 amps., the actual current flowing was found to be 0.1019, 0.0491 and 0.1910 amps., respectively.

For the early part of this research, a Gra Lab Universal Timer (T_1) was used. The timer was controlled by one side of a D. P. S. T. switch S_2 while the electrolysis circuit was controlled by the other half of this same switch. Consequently, when the circuit was closed, the timer and electrolysis started simultaneously. Switch S_3 was provided so that the electrolysis circuit could be closed without actuating the timer.

It was found after a time that the timer did not stop immediately after the current was shut off, but instead kept moving for a fraction of a second. A Precision Scientific Co. Timer (T_2) was then obtained and was connected into an outlet plug in the Gra Lab Timer. It was found that the Gra Lab Timer gained approximately one second for each four stops. It was used in conjunction with the Precision Timer, however, because the dial was marked in minutes while the Precision Timer, which was marked in seconds, was somewhat difficult to read. All times used in plots were obtained from the Precision Timer.

At the outset of the problem a cell similar to that described by Donahue was used, the only difference being that a mercury pool in the bottom of the beaker was substituted for the gold cathode. No runs were made with a gold electrode using the potassium chrom alum as it was felt the higher hydrogen overvoltage at a mercury surface would aid in preventing hydrogen evolution.

The electrolysis cell used by Mr. Donahue and also by us at the beginning of this problem consisted of a 150 ml. beaker which was covered with a plywood disk. This disk provided openings for the anode compartment, the indicator and reference electrodes, the cathode lead and a carbon dioxide tube. The mercury cathode covered the bottom of the cell and on top of the mercury was floated the stirring element of a magnetic stirrer. The anode compartment was a glass tube 20 mm. in diameter fitted at the bottom with a fritted glass disk of medium porosity. The anode was a platinum wire gauze anode taken from an ordinary set of electrodes used in electrodeposition.

how many [illegible]

After numerous runs it was decided that the stirring provided by the magnetic stirrer was insufficient and also that the mercury pool was too large. It was thought that if the size of the pool were reduced, the tendency for hydrogen to be evolved would be lessened due to the increase in current density and the consequent increase in hydrogen overvoltage. Consequently, a new "H"-type cell was made (See Figure 2). The cathode chamber was constructed from a 40 × 200 mm. test tube (A). Into the side of this tube was sealed a tube 60 mm. long (B) containing a 20 mm. fritted glass disk (C), of medium porosity, in its center. To the other end of this tube was sealed the anode chamber (D) made from a tube 25 × 80 mm. A 45-mm. piece of 6-mm. tubing (E) was sealed into the cathode chamber to provide an opening through which carbon dioxide or nitrogen could be passed. The cathode chamber was closed with a rubber stopper, through which openings were made for the stirrer (F), the side arm (G) of a saturated calomel half cell, and the indicator electrode (H) which was a short piece of platinum wire sealed into a piece of 7-mm. soft glass tubing. Contact with the mercury cathode (J), which was approximately 2.1 cm. in diameter, was made by a platinum wire (K) sealed through the bottom of the cathode chamber. The anode (L) was the same as described previously. The stirrer (F) was a glass propellor-type stirrer driven by a variable-speed stirring motor.

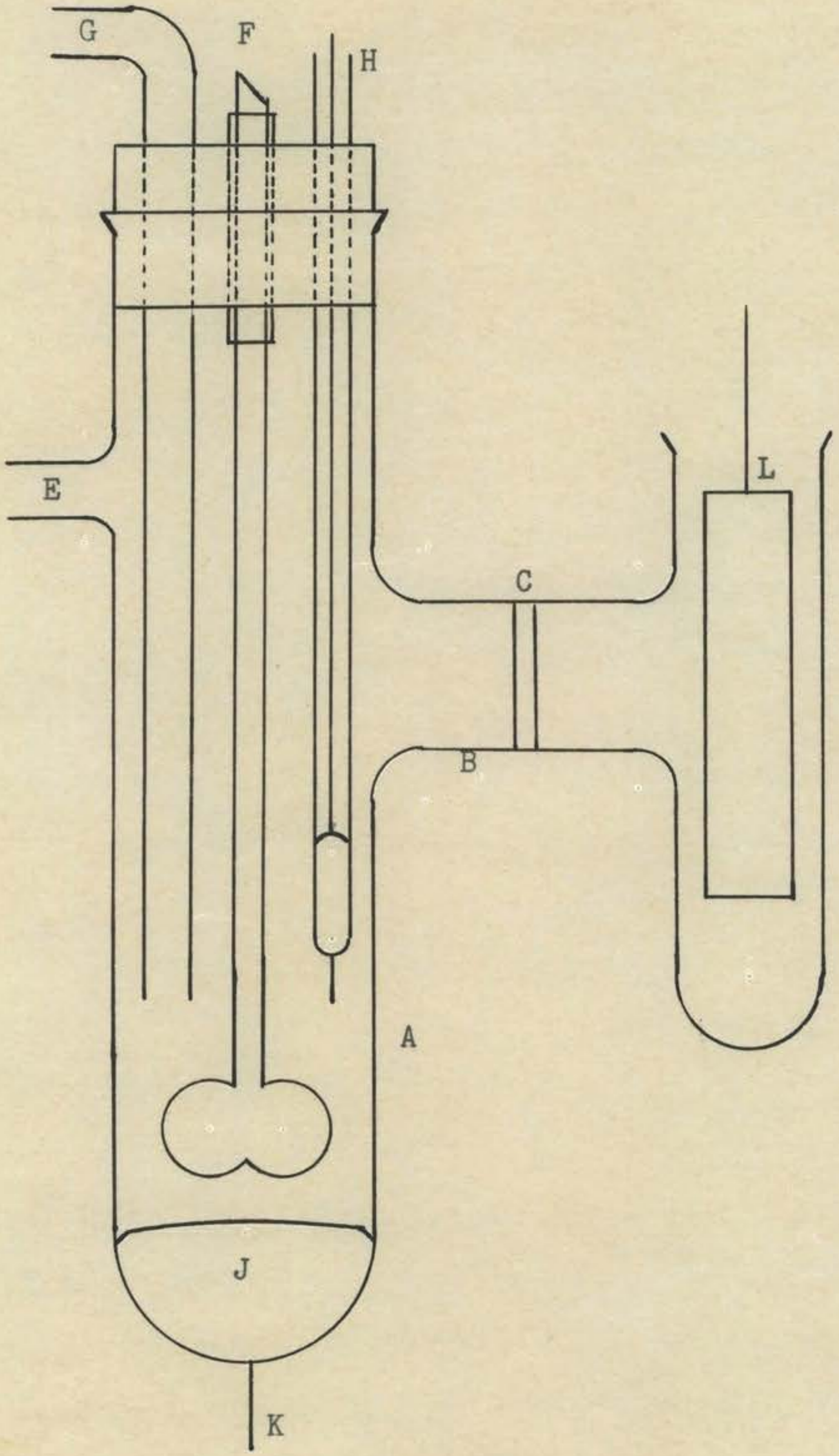

Figure 2

The potentiometer used was a self-contained unit consisting of working resistances, working battery, tap key, galvanometer, and a Central Scientific Co. Potentiometer (Cat. No. 83411) all incorporated into one box. The potentiometer was standardized against an Eppley cell. As mentioned above, a saturated calomel half cell and a platinum wire indicator electrode were used in conjunction with the potentiometer for determining end points.

At the beginning of this problem an attempt was made to use the mercury cathode with titanium tetrachloride as an intermediate. It was found, however, that as soon as the electrolysis circuit was closed, a large amount of precipitate was formed. On looking in a table of standard oxidation-reduction potentials (10), the following values were found:

$$Cr^{+2} \longrightarrow Cr^{+3} + e \qquad (.41 \text{ v.})$$

$$2\,Hg + 2Cl^{-} \longrightarrow Hg_2Cl_2 + 2e \qquad (-.2676 \text{ v.})$$

Since the concentration of chloride ion present in the solution was large compared to the concentration of ferric ion, it seemed probable, therefore, that the precipitate observed was mercurous chloride formed by the oxidation of mercury by either the titanic chloride, the ferric salt, or both. → analysis [illegible] to see For this reason experiments with the titanium compound were discontinued and those with chromium sulfate were started. In the first runs made, however, it was noted that a precipitate was still forming. Further checks indicated that this was probably due to chloride ion diffusing from the potassium chloride-agar salt bridge into the catholyte. To eliminate this, an agar-ammonium nitrate plug was substituted for the agar-potassium chloride plug used at that time, and this trouble immediately disappeared.

When experiments were begun using the chromic-chromous couple, a solution of potassium chrome alum was the first salt used as a source of chromic ions. Hydrogen evolution was at once encountered and it was thought for some time that these poor results were caused by an unfavorably low concentration of chromic ions provided by this solution. Since chromic sulfate is considerably more soluble than the potassium compound, a series of runs were made using this salt. The results obtained were no better than those with the potassium compound; consequently, since a large supply of the potassium chrome alum was available the use of chromic sulfate was discontinued. In light of later findings, namely that the pH of the solution must be controlled rather carefully, it is now thought that the chromic sulfate might be just as useful as the potassium compound. No determinations have been made with chromic sulfate, however, in which the pH has been controlled.

It was found after a great number of poor results that the pH of the solution must be rather carefully controlled if hydrogen is not to be evolved. The hydrogen overvoltage on mercury changes considerably with hydrogen ion concentration and theoretically it would seem best to make the determinations in solutions of higher pH. There are practical limitations on this, however, since ferric hydroxide precipitates at a pH of around 4. In order to determine the maximum pH which could be used, a solution of the chrome alum and ferric sulfate was prepared as it was to be used in the actual electrolysis, then the electrodes of a pH meter were placed in this solution. The pH was found to be about 1.4. Small increments of 4N sodium hydroxide were then added until precipitation resulted. It was decided that a pH of 3.5 was as high as could be safely used. Each time a new solution of sodium hydroxide or potassium chrome alum was prepared, the quantity of sodium hydroxide necessary to produce the above pH was determined. The base was added from a graduated pipette and this quantity of base was used as long as these stock solutions were available.

After a large number of determinations had been made, it was found that the voltage readings obtained were becoming somewhat erratic. This was the cause of considerable consternation until it was suggested by Dr. Paul Arthur that perhaps the calomel cell was not functioning properly. On close examination of the cell, a slight green coloration was noted on the surface of the mercurous chloride. When the cell was remade, the voltage readings were found to be greatly improved. It was decided that due to prolonged contact with the chromium

No [illegible]

solution, chromic ions had diffused through the agar plug into the cell. From this point on, a new side arm was prepared every week or two. It was found, however, that after several weeks the readings would again become erratic and it was decided to make a new side arm every day. Since the agar solution was prepared in a large quantity, it was necessary only to heat the flask and, by means of a short piece of rubber tubing, draw the solution into a previously prepared glass tube which served as the side arm.

It will be noted later that runs were made using various concentrations of the chromium solution. It was thought that at lower concentrations of chromium, hydrogen would be evolved. This, however, was not found to be the case. The factor which seems to limit the concentration of chromium used is the time involved for the indicator electrode to reach equilibrium and produce a steady voltage reading. One run using 40 ml. of the solution diluted to 100 ml. was made and though the error in the determination was reasonably small, the time required for the voltage readings to become constant was far too great to make this low concentration feasible. It would appear then, that time, and not hydrogen evolution is the limiting factor insofar as chromium ion concentration is concerned.

[illegible]

It was thought possible that the potassium chrome alum solution might contain enough iron or other reducible impurity to cause a significant error. This was indeed found to be

No analysis to determine this was made by the author.

true. For the different solutions used, the blank time ranged from 50 to 70 seconds for 100 ml. of the solution. In the tables of results, this blank time has been subtracted from the total run time in calculating the quantities of iron.

In Mr. Donahue's work with titanium, a stream of carbon dioxide was passed over the solution during the electrolysis. This procedure was followed throughout this problem, and in the process of eliminating possible errors in the method, the gas was also passed through the solution for a short period before performing the electrolysis. This was found to reduce the error by an appreciable amount and so was continued through the rest of the experimental work. The carbon dioxide was used without purification. At one point when it was thought that perhaps the CO_2 which was being used (from a new tank) contained an appreciable amount of oxygen, nitrogen was substituted. The nitrogen was purified by passing it through concentrated sulfuric acid, alkaline pyrogallol, and finally distilled water.

Although nitrogen provided an inert atmosphere above the solution and thus prevented oxidation of the reduced iron by air, it is perhaps not as effective as carbon dioxide due to the lower density of the nitrogen and its consequently less efficient blanketing action.

In the construction of the cell, a fritted glass disk of medium porosity was used to separate the anode from the cathode. When tests were made it was found that the sulfuric acid from the anode chamber was flowing through the plug into the cathode chamber more rapidly than was desirable. In order to decrease this seepage, very finely powdered pyrex glass was drawn through the frit to partially clog the pores of the disk. This proved to be satisfactory, though the process had to be repeated occasionally. It should be pointed out that diffusion was caused by the difference in the levels of the two chambers. It was necessary to keep the level of the anolyte somewhat above that of the catholyte to prevent seepage or diffusion of the iron out of the cathode compartment which would cause an error in the determination.

PROCEDURE AND RESULTS

In performing a typical determination, the batteries were allowed to discharge through the by-pass circuit for at least 30 minutes at a current comparable to that to be used in the determination. In the meantime, the cell was thoroughly washed and rinsed with distilled water and securely clamped in position. Mercury was poured into the cathode chamber until a pool of the proper size was formed. For the sake of consistency, a line was marked on the outer surface of the cathode chamber and the mercury level was adjusted to this line each time.

Next, the desired volume of potassium chrome alum solution was measured into the cathode chamber. If less than 100 ml. of the chromium solution was used, enough water was added to make the final volume 100 ml. Immediately, the anode compartment was filled with 1N sulfuric acid solution to a level about 3 mm. above that of the chrome alum. A 2 ml. sample of the iron solution was next pipetted into the cathode. The iron solution was previously standardized by the well-known permanganate method, 2-ml. samples measured from this same pipette being found to contain 0.1102 grams of iron.

The rubber stopper containing the stirrer and indicator electrode was placed in the top of the cathode and the stirrer connected to a variable speed motor by means of a chuck mounted on the shaft of the motor. The stirrer was started and while the iron and chromium solutions were being mixed, the required amount of sodium hydroxide was drawn into a pipette. The stopper was then raised just enough to permit the entry of the pipette and the base was added slowly to prevent a large concentration accumulating at any one point in the solution. When the base was well mixed with the rest of the solution, the stirrer was stopped and a tube which was connected to either a carbon dioxide or nitrogen supply was placed in the solution. The gas was allowed to bubble through the solution for 15 minutes.

While the solution was being degassed, the flask containing the ammonium nitrate-agar gel was placed in boiling water until most of the gel had melted. A short piece of rubber tubing was attached to an L-shaped glass tube, 7 mm. in diameter (which served as a detachable salt bridge to the calomel electrode), and the liquid gel was drawn into the tube until it was filled. The side arm of the calomel cell thus prepared was held under cold water until the gel had hardened. The side arm was then connected to the saturated calomel electrode by means of a short section of rubber tubing.

When the solution had been degassed for 15 minutes, the bubbling tube was removed from the solution, held above the surface, and washed with distilled water so that the wash water would go into the solution. The gas supply was then connected to the cell by the glass tube (E) provided for that purpose and the gas (Co_2 or N_2) immediately turned on. The stopper was pressed tightly into place and the stirrer again started.

The timers were both checked and set at zero. The platinum anode was placed in the anode compartment and both it and the platinum wire leading to the mercury cathode were connected into the electrolysis circuit. The side-arm from the saturated calomel electride and the platinum indicator electrode were inserted into the cell and connected to the potentiometer. When all connections were made, and the timers set, the by-pass circuit was opened and the electrolysis circuit closed. The milliammeter was immediately tapped and the current adjusted to the proper value by means of the variable resistors.

The electrolysis was permitted to procede for five minutes and at the end of this period the circuit was opened and a reading taken of the potential difference between the indicator electrode and the S. C. E. The potentiometer was always standardized against the Eppley cell during the electrolysis. The voltage reading and the time to the nearest second, as read from the Precision Timer, were then recorded. The electrolysis circuit was again closed, the ammeter tapped and the current adjusted if necessary.

Voltage readings were taken at 15, 25, 30 and 31 minutes when 0.1 amp was used. After the 31 minute reading, voltages were taken as often as seemed necessary in order to determine the end point.

When a large drop in potential indicated that the electrolysis was completed, the by-pass circuit was closed and the cell was removed and emptied. The cell was thoroughly washed and rinsed as before and set up for the next run.

The end point for each of the determinations was found by plotting time, in seconds, against voltage (See Figure 3). The mid-point of the steepest portion of the curve was taken as the end point. Although care was used in plotting these curves, it was frequently found that the best end point could not be located more closely than to plus or minus two seconds--and occasionally the possible error was greater. This, fortunately, did not happen very often.

No attempt was made to use a dead-stop end point, i.e. to electrolyze to a pre-determined potential. Very recently, however, when several curves were plotted on the same piece of graph paper, it was found that perhaps 0.12 volts would serve as a dead-stop end point for runs performed under the conditions described for line on in Table 6. It is the belief of the author, however, that more trustworthy results are generally obtained by the curve plotting method, for sluggish electrode behavior or other troublesome factors show up better this way and give warning of possible error.

To calculate iron, in grams, from the electrolysis time, the following equation may be used:

$$\text{Grams of iron} = \frac{(55.84)\ (I)\ (t)}{96{,}500}$$

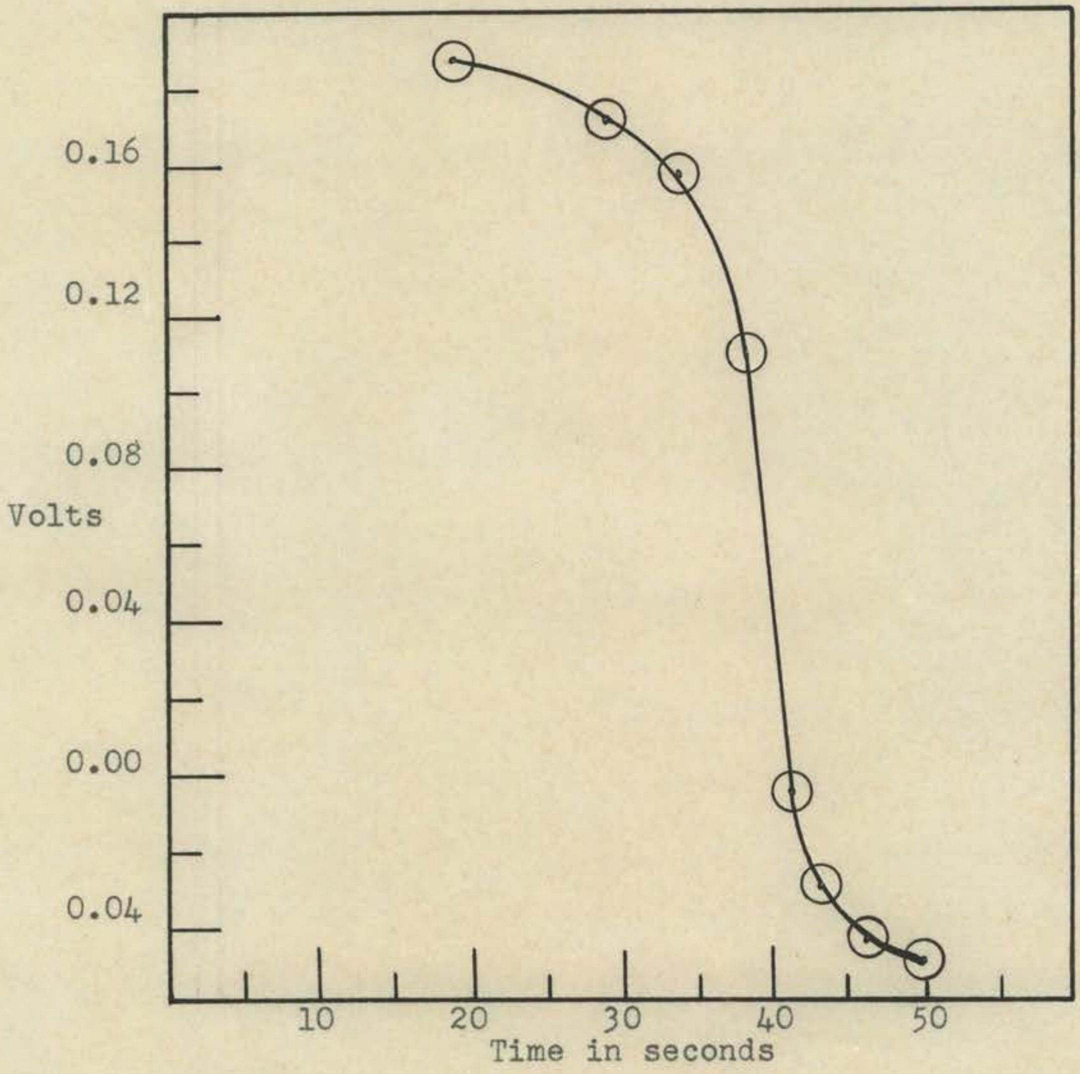

Figure 3

where 55.84 is the equivalent weight of iron, I is the current in amperes, t is the time in seconds corrected for blank time, and 96,500 is Faraday's constant.

To calculate the amount of iron when using, e.g., 0.1 amp. (actually 0.1019 amp. by calibration), the constants may be combined and the following logarithmic function derived:

$$\log \text{gm. iron} = \log \text{time} + \bar{5}.77059$$

This equation was used in making calculations of the results shown in Table I.

The same type of calculation may be used for 0.05 and 0.2 amp. (or accurately, 0.0491 and 0.1910 amp., respectively). The constant must, of course, be changed accordingly.

In the tables which follow it will be noted that three different concentrations of potassium chrome alum solution were used (Tables 1, 2 and 3). The purpose of this was to investigate any effect changes in concentration of chromic ion might have on the results obtained. As mentioned before, the only limitation on concentration seems to be the time involved in making a determination. Two other tables (Tables 4 and 5) have been prepared showing data obtained from runs using 100 ml. of the chromic ion solution at currents of 0.05 and 0.2 amp., respectively.

It will be noted that all of the 0.05 amp. determinations were somewhat short of the theoretical (assuming that the standardization of the iron was accurate). This may be due to reduction of some of the iron by the mercury itself in the presence of large quantities of sulfate ion.

This explanation may immediately be questioned when one notes that chromous ion is used as a reducing agent for mercurous sulfate. It would seem then that the explanation could be valid only if there were a rate process involved, i.e., if the mercurous sulfate is not reduced as fast as the mercury is oxidized. Since at no time does more than minute concentrations of Cr^{+2} form in the solution and since a long period of time is required before the iron is all reduced, such a slow heterogeneous reaction between Cr^{+2} and solid mercurous sulfate is quite possible. In order to test this theory, one run was made in the following manner: 100 ml. of the chromium solution, 2 ml. of the ferric sulfate, and the required amount of base were placed in the cell. The solution was degassed but then, instead of the electrolysis being started immediately, the solution was allowed to stand, with stirring, for 35 minutes. The solution was then electrolyzed at 0.1 amp. In this manner the total time of contact between the solution and the mercury was approximately the same as that required for the whole analysis at 0.05 amp. When results were calculated, it was found that the actual end point occured 26 seconds before the theoretical. *This would indicate therefore, that time of contact, and probably reduction of iron by mercury, was the direct cause of error.

In Table 5 are shown the results of five runs using 0.2 amp. The time required for the electrolysis is, in each case, greater than the theoretical time. At least part of the reason for this error was obvious for, at this higher current, hydrogen was observed to be evolved at the cathode; thus not all of the current was used to reduce the iron as should be the case. It is believed that little can be done to alleviate this situation. The pH of the solution has been adjusted as high as is believed reasonable and unless different cell and electrode dimensions were used, it would seem that currents not far in excess of 0.1 amp. should be used. On the other hand, if conditions are held constant it is possible that a percentage correction could be applied and the accuracy thus be made quite acceptable, for the precision of the determination is good.

Table 6 was prepared to show the comparison between the results obtained using the various methods described above.

Table 1

Results With 0.26M Potassium Chrome Alum at 0.1 ampere

Time*	Grams of Iron	Deviation
31' 06"	0.1100	−0.0001
31' 00"	0.1097	−0.0004
31' 11"	0.1103	+0.0002
31' 04"	0.1099	−0.0002
31' 04"	0.1099	−0.0002
31' 17"	0.1107	+0.0006
31' 11"	0.1103	+0.0002
31' 05"	0.1100	−0.0001
31' 11"	0.1103	+0.0002
31' 06"	0.1100	−0.0001

Average = 0.1101 g.

Average deviation = 0.0002 g. = 0.20%

Actual weight of iron = 0.1102 g.

Error = 0.0001 g. = 0.09%

---

* Times given here are values after the blank run is subtracted.

Table 2

Results With 0.21M Potassium Chrome Alum at 0.1 ampere

Time*	Grams of Iron	Deviation
31' 11"	0.1103	+0.0001
31' 02"	0.1098	−0.0004
31' 10"	0.1103	+0.0001
31' 13"	0.1105	+0.0003
31' 06"	0.1100	−0.0002

Average = 0.1102 g.

Average deviation = 0.0002 = 0.18%

Actual weight of iron = 0.1102 g.

Error = 0.0000 g. = 0.00%

---

* Times given here are values after the blank run is subtracted.

Table 3

Results With 0.16M Potassium Chrome Alum at 0.1 ampere

Time*	Grams of Iron	Deviation
31' 11"	0.1103	+0.0001
31' 11"	0.1103	+0.0001
31' 10"	0.1103	+0.0001
31' 04"	0.1099	−0.0003
31' 11"	0.1103	+0.0001

Average = 0.1102 g.

Average deviation = 0.0001 g. = 0.13%

Actual weight of iron = 0.1102 g.

Error = 0.0000 g. = 0.00%

---

* Times given here are values after the blank run is subtracted.

Table 4

Results With 0.26M Potassium Chrome Alum at 0.05 ampere

Time*	Grams of Iron	Deviation
63' 30"	0.1083	−0.0008
63' 56"	0.1090	−0.0001
64' 02"	0.1092	+0.0001
64' 11"	0.1094	+0.0003
64' 10"	0.1094	+0.0003

Average = 0.1091 g.

Average deviation = 0.0003 = 0.27%

Actual weight of iron = 0.1102 g.

Error = 0.0011 g. = 0.99%

---

* Times given here are values after the blank run is subtracted.

Table 5

Results With 0.26M Potassium Chrome Alum at 0.2 ampere

Time*	Grams of Iron	Deviation
16' 56"	0.1123	+0.0001
17' 02"	0.1129	+0.0007
16' 52"	0.1118	−0.0004
16' 52"	0.1118	−0.0004

Average = 0.1122 g.

Average deviation = 0.0004 g. = 0.36%

Actual weight of iron = 0.1102 g.

Error = 0.0020 g. = 1.81%

---

* Times given here are values after the blank run is subtracted.

Table 6

Statistical Summary of Results

			Iron				
Molarity Cr soln.	No. of runs	Current (amps.)	Ave. Gms.	Ave. Dev. Gms.	Ave. Dev. Percent	Max. Dev.	Percent Error
0.26	10	0.1	0.1101	0.0002	0.20	+0.0006	0.09
0.21	5	0.1	0.1102	0.0002	0.19	−0.0004	0.00
0.16	5	0.1	0.1102	0.0001	0.13	−0.0003	0.00
0.26	5	0.05	0.1091	0.0003	0.28	−0.0008	0.99
0.26	4	0.2	0.1122	0.0004	0.36	+0.0007	1.81

CONCLUSION

The chromic-chromous couple has been shown, by the results obtained in this research, to be effective as an intermediate in coulometric analysis. This couple, while only tested for the reduction of iron, might well be applied to the analysis of other substances capable of being reduced by chromous ion. Certainly work along this line should be carried out.

While this problem was not directed primarily toward the development of a new method of analysis for iron, the results indicate that it might well be so applied. The time involved is, of course, somewhat prohibitive. If an electronically-controlled current source, such as the one suggested by Reilley, Cooke and Furman (15) could be substituted for the storage batteries and variable resistances, an operator would be required only near the end point. With several cells in operation at the same time, the average time for an analysis [illegible] could be made as short as that required for standard volumetric or gravimetric procedures.

While this aspect was not investigated, it seems probable that the determination of several samples of iron with one sample of the intermediate is a definite possibility. This would reduce the cost of the analysis considerably and eliminate the necessity of emptying and washing the cell after each run. A dead-stop end point would probably be necessary if this procedure was to be followed.

While the field of coulometric analysis is yet comparatively new, it appears that in the future it will definitely take its place as an acceptable method of instrumental analysis.

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Biography

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