

TITANIC CHLORIDE AS AN INTERMEDIATE IN COULOMETRIC

ANALYSIS

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By

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Introduction

Coulometric analysis is a method of quantitative determination based upon Faraday's Laws of electrolysis in which the amount of substance in question may be determined by measuring the quantity of electricity required to oxidize or reduce the substance.

Szebelledy and Somogyi (11) have pointed out that there are two types of coulometric processes; those in which the desired reaction takes place directly at the electrode, and those in which an intermediate half-cell reaction takes place at the electrode and the product of this reaction reacts quantitatively with the substance being analyzed. From the standpoint of coulometric analysis it is necessary to further classify these as anodic-- i.e., oxidations -- or cathodic --i.e., reductions -- for the problems encountered may differ greatly in many respects. For purposes of this research it was decided to limit the problem to cathodic reactions in which an intermediate half-cell reaction is employed.

Although some work of this type has been done (8) (1) the most powerful reducing couple employed was the cupric-cuprous chloride and the method was applied to the analysis of only such powerful oxidizing agents as chromates, vanadates, and ceric salts. In addition, most of this work was done with micro or semimicro samples. In this research it was proposed to extend the range of substances that may be analyzed by this method by using more powerful reducing substances, and in addition to determine the feasibility of using larger currents and macro samples. Consideration was given to the titanous-titanic couple,



and the chromous-chromic couple,



Standard solutions of titanous chloride and chromous chloride have been used in quantitative analysis as reducing agents, but have always presented the problem of air oxidation both while being stored and during the titration. Coulometric analysis presents a way of producing these reagents and letting them react immediately with minimum interference from air oxidation; also the need for standardization is then eliminated. Since efficient and quantitative reduction of these ions would require an electrode of high hydrogen overvoltage, various electrode materials were to be tested.

Instead of trying a strong oxidizing agent, it was decided to try to analyze iron in the ferric state by reducing it to the ferrous state with titanous or chromous ions produced at the cathode by electrolysis.



Since it was desired to develop a method that would permit the analysis of as many substances as possible, it was decided to use potentiometric methods for determining the endpoint.

Chemical endpoints are limited to those reactions that will give sharp color changes at the end of the titration or for which a suitable indicator has been developed. Amperometric endpoints cannot be used with generating currents larger than 10 milliamperes because these currents cause induced parasitic currents in the indicator circuit which obliterate the endpoint. In addition this endpoint cannot be used in titrations of long duration; consequently samples are limited to micro quantities.

Historical

The relationship between the amount of electricity passing through an electrolyte and the amount of material liberated at the electrodes was first discovered by Faraday. His findings have been resolved into two laws of electrolysis which bear his name. These are:

- (1) The mass of a substance liberated in an electrolytic cell is proportional to the quantity of electricity passing through the cell.
- (2) When the same quantity of electricity is passed through different electrolytic cells the masses of the substances liberated are proportional to their chemical equivalents.

Various methods of quantitative determinations have been developed utilizing these laws. Szebelledy and Somogyi, two European workers, were among the first to perfect one of these so-called "Coulometric" analyses. They determined the amount of thiocyanate in a solution by allowing electrolytically generated bromine to oxidize the thiocyanate, then titrating the excess bromine with sodium thiosulfate and a starch-iodide indicator. The potential was maintained at a set value throughout the titration and the amount of electricity used in generating the bromine was measured by means of a silvercoulometer (16). They also determined hydrazine (12) and hydroxylamine (14) in this manner with good results.

In a cell made up of a silver anode and a platinum cathode, Szebelledy and Somogyi determined hydrochloric and sulfuric acid by electrolyzing them in a solution to which potassium chloride had been added, using bromo cresol green to recognize the endpoint (13)(15).

In this country Lingane and Furman have contributed to coulometric determinations, and Swift and his colleagues working at the California Institute of Technology have done extensive work in the field.

Six or eight years ago Lingane showed by experiments conducted on electrolytic reduction of metal ions and some compounds (5) that one hundred percent current efficiency could readily be obtained by use of a mercury cathode, the e.m.f. of which was precisely controlled as the electrolysis proceeded. Results of the experiment suggested a means of determining the concentration of ions in solution by measuring the quantity of electricity used in the electrolysis or needed to carry out the quantitative reaction at one of the electrodes.

This idea resulted in the development of a method of coulometric analysis for the metal ions of Cu, Bi, and Pb (6). The accuracy of these determinations compared favorably with the gravimetric analysis of these cations.

Recently Lingane applied these principles to the determination of halide ions (7) and developed a very satisfactory method for their analysis. A halide solution is electrolyzed in a cell containing a silver anode and a platinum cathode. Then by appropriate adjustment of the e.m.f. the potential of the silver anode will remain constant at such a value that the reaction, $Ag + Cl^- = AgCl + e^-$, will proceed quantitatively and with one hundred percent current efficiency. Under these conditions the current decreases exponentially with time, finally dropping virtually to zero when the electrolysis is complete. The quantity of halide ion reacting is then computed by using Faraday's Laws of electrolysis, from the quantity of

electricity passed as measured by a coulometer in series with the cell. Such a determination takes about fifteen minutes. Using this method of analysis the three halide ions may be determined separately or as a mixture.

In each of the methods discussed thus far, the voltage was maintained at a constant value and the current allowed to decrease. The number of coulombs of electricity used was measured by means of coulometers. Furman and Swift and his co-workers, on the other hand, used constant current methods and calculated results from the current and the time. Furman (1) determined the concentration of chromate and ceric ions by allowing them to oxidize electrically generated ferrous ion. He used a potentiometric endpoint and the results obtained were satisfactory. Swift and his colleagues (10) analyzed thiodiglycol (1), this substance being oxidized by electrically generated bromine. The endpoint was determined amperometrically. A small potential was applied to the indicator circuit and no current flowed as long as there was no free bromine in solution, but upon completion of the titration, the appearance of free bromine was indicated by a current flowing through the indicator circuit.

Swift and Meyers (9) investigated this type of analysis further by making a study of the arsenous acid determination. It was carried out in the same manner as the previous determination, except that the cathode was shielded from the rest of the cell by a piece of glass tubing so that the hydrogen produced there would not mingle with the rest of the solution. Later Swift also studied the effects of electrically generated iodine (4) and chlorine (2) on the coulometric determination of arsenic.

In addition to the analysis of the above reducing agents, Swift (8) has developed a method for the titration of solutions of chromate and vanadate

by reducing them with electrically generated cuprous ion in a cupric sulfate-hydrochloric acid solution. Again he used an amperometric endpoint. The results obtained were very good.

Up to this time Swift studied only the analysis of those compounds which gave no reversible reactions. He now made a determination of a substance that would give a reversible reaction, choosing the iodide ion (3), letting it be oxidized to iodine by electrically generated bromine. He separated the cathode from the rest of the solution by a glass tube, the bottom of which was closed by a sintered glass disk. The results obtained here for micro determinations were much better than those obtained by other methods.

Swift's work was done on a micro scale and his current ranged about 10 milliamperes. His runs were of short duration, never being more than approximately five minutes.

Reagents

All reagents used were of the "Chemically Pure" or "Analytical Reagent" variety. Solutions of these were prepared as follows:

Ferric Sulfate 0.1M (0.2N Fe^{3+}) solution, 1N in sulfuric acid .

11.168 gm of No. 38, standardizing quality iron wire, were placed in a liter beaker and 100 ml of concentrated hydrochloric acid and 100 ml of water were added. The solution was kept warm until all the iron was dissolved. Then 25 ml of concentrated nitric acid were added and the solution was evaporated under a hood to half of the original volume. Sixty ml of concentrated sulfuric acid were added and the solution was carefully evaporated until sulfur trioxide fumes appeared. It was cooled, diluted with 500 ml of water, and transferred quantitatively from the beaker to a liter volumetric flask where enough water was added to bring the solution up to full volume. It was then poured into a labeled glass stoppered bottle.

Sulfuric Acid (1N solution). One liter was prepared from 88 ml of 98% C.P. reagent.

Hydrochloric Acid. C.P. reagent, concentrated.

Hydrochloric Acid (1N solution). One liter was prepared from 83 ml of C.P. reagent.

Hydrochloric Acid (3N solution). One liter was prepared from 250 ml of C.P. reagent.

Nitric Acid. C.P. reagent, concentrated.

Ammonium Hydroxide (50% solution). Prepared as needed from equal volumes of water and C.P. reagent.

Chromic Sulfate (0.1M solution, 4N in Sulfuric Acid). One liter was prepared by dissolving 39.22 gm of C.P. material in a liter of 4N sulfuric acid.

Potassium Dichromate (0.1N solution). Prepared by dissolving 4.93 gm of C.P. salt in water, and diluting to 1 liter.

Cupric Chloride (0.1M solution, 1N in Hydrochloric acid). Prepared by dissolving 13.44 gm of anhydrous C.P. cupric chloride in 1N hydrochloric acid, and diluting with 1N hydrochloric acid to 1 liter.

Potassium Hydroxide (1N solution). Prepared by dissolving 56 gm of technical grade material in 1 liter of water.

Sodium Hydroxide (0.1016N solution). Prepared by dissolving 4 gm of the C.P. pellets in water and standardizing with potassium acid phthalate.

Potassium Cyanide. Technical grade material.

Gold Chloride. Merck.

Titanic Chloride (solution). Prepared by adding water to 200 ml of titanium tetrachloride until the hydrolysis ceased. An excess of water was then added to make the total volume 500 ml. The resulting solution was analyzed for titanium by hydrolyzing a sample and igniting to titanic oxide, and by titrating a second sample with standard sodium hydroxide solution to the phenolphthalein endpoint. Results showed the solution to be 3.6M with titanium, while the acidity corresponded to 7.4N hydrochloric acid.

Some difficulty was encountered in obtaining a solution of a titanium compound. First, titanium sulfate was tried by adding it to both hot and cold water, but the compound would not dissolve in either. Concentrated sulfuric acid dissolved only a very small quantity of the substance and the solubility was not increased by heating the mixture for a day at 90° C. A 9N solution of sulfuric acid was tried both hot and cold, but there was no evidence of a significant increase of solubility.

Since, at that time, there was no other titanous compound on hand, it was decided to try to oxidize a solution of titanium trichloride with oxygen or chlorine. Oxygen did not effect an oxidation of the titanous chloride, but chlorine did; however, this method was abandoned as impractical because it was extremely difficult to tell when there was neither chlorine nor titanous chloride left in solution, and such solutions gave considerable quantities of precipitates on standing. An electrolysis of the solution was tried but the results were unsatisfactory.

Last of all some titanium tetrachloride was obtained and its solubility tested in hydrochloric acid. Acid solutions from 0.01N to 6N were prepared and a volume of 10 ml of each solution was used. Small portions of titanium tetrachloride were added to each acid solution, and precipitates formed in all solutions less than 1N. The 1N acid solution precipitated in three days.

Using the 3N acid, a solution of titanium tetrachloride was prepared so that the titanium tetrachloride was approximately 0.2M. The solution was made by adding 22 ml of titanium tetrachloride to a liter of 3N hydrochloric acid. This solution proved to be unsatisfactory in the electrolysis because hydrogen was liberated. A suitable method for the dissolving of titanium tetrachloride was finally discovered and prepared as described at the beginning of this section. Ten ml of this solution were taken and diluted to 100 ml with water and used for the electrolysis.

Of all the solutions made up only ferric sulfate, potassium dichromate and sodium hydroxide needed to be accurate. All the rest needed to be only approximate.

Apparatus and Experimental

For this research problem a direct current source was supplied by a 6-volt lead storage battery. A radio potentiometer regulated the voltage output from the battery to the electrolysis circuit. Weston's multirange direct current voltmeter (Model No. 430) and milliammeter (Model No. 430) were used to indicate voltage and amperage, respectively; and a single-pole single-throw switch opened and closed the circuit. A Gra Lab Universal Timer, operated independently of the electrolysis circuit, was used to determine the time on each run.

In the course of time it was found that the single 6-volt storage battery was not a suitable constant current source. However, it was used until enough progress was made so as to indicate that the problem might be successful to some degree.

After this, a bank of seven 6-volt storage batteries connected in series and delivering 42 volts was substituted for the single storage battery, and a resistance box was substituted for the radio potentiometer. At the voltage and current used, approximately 420 ohms of resistance in series with the batteries and cell were required; consequently small variations in cell resistance during an electrolysis caused only negligible variations in the current.

The resistance box incorporated connections for the voltmeter and the milliammeter. It consisted of two variable resistances of 500 ohms and 50 watts for coarse adjustment and a variable resistance of 10 ohms and 25 watts for fine adjustments, all connected in series. A double pole single throw switch S_1 (see Fig. 1) controlled the electrolysis circuit

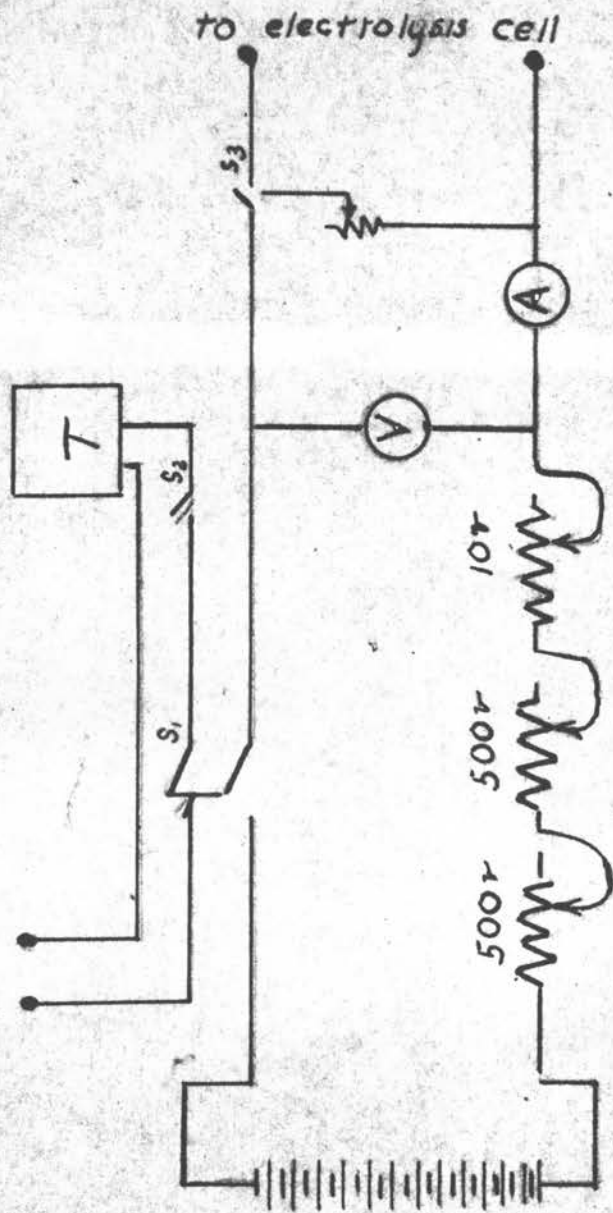


Figure 1
Schematic Wiring Diagram

and the timer so that they operated simultaneously. A single pole single throw switch S_2 (see Fig. 1) allowed the electrolysis circuit to be closed without operating the timer. A fourth variable resistance was short circuited across the electrolysis circuit and controlled by a single pole double throw switch S_3 (see Fig. 1) so that the current would flow through the resistance without flowing through the cell. This arrangement allowed for the voltage change that takes place when the circuit is first closed to level off before the electrolysis was started.

The endpoint was determined potentiometrically, using a platinum wire as the indicator electrode and a saturated calomel half-cell for the reference electrode. A Leeds and Northrup Student Potentiometer was used first to determine voltage changes, but later this was replaced by a built-in unit made from a Central Scientific Company instrument. A Weston standard cell was used to calibrate the potentiometer.

Many difficult problems were encountered in the construction and use of the cell. The cell used in the initial phases of the investigation was of 400 ml capacity and thus required large volumes of reactant. For this reason a smaller cell having a capacity of 150 ml was substituted.

The anode of the cell was a platinum wire gauze anode taken from an ordinary set of electrodes used in electrolytic deposition. Swift's work (8) showed that the anode should be shielded from the rest of the solution as otherwise any reduction at the cathode would be partially offset by oxidation at the anode. Swift showed also that the electrolyte in the compartment must be on a slightly higher level than the electrolyte in the cathode portion of the cell to prevent loss of substance to be analyzed from the cathode compartment. The shield was necessary to prevent the oxygen from mingling with the reduced portions and reoxidizing them.

A porous plate served as the bottom of the anode compartment, keeping the solutions separated and yet allowing free flow of current. Since the electrolyte in the anode compartment was kept at a higher level than the outer electrolyte there was no loss of material being analyzed.

The first anode compartment was made by fitting a porcelain, porous bottom crucible into a glass tube 40 x 130 mm and cementing them together with silver chloride cement. The bottom of the crucible was covered, using suction, with a mat of acid-washed asbestos as a means of lessening the flow of the electrolyte, but the mat proved to be inadequate. Powdered glass washed into the pores of the plate gave better results, but even this was not entirely satisfactory. Another type of compartment was made by cementing a round piece of porous plate to the same kind of a glass tube, but this did not work well. Later on when the construction of the cell was revised a glass tube with a sintered glass disk 20mm in diameter and of medium porosity was used after powdered glass had been drawn into the pores. It was very satisfactory. One N sulfuric acid was used as the anode electrolyte.

Cathodes and the results of their use will be taken up as the discussion of the experiment proceeds. However, it was recognized that a suitable cathode should have certain characteristics to be useful in the work.

It should have a fairly high hydrogen overvoltage. Platinum's low hydrogen overvoltage eliminated its use in the final results. The electrode should have a smooth even surface. Often when electrolytic deposition of metal takes place, the deposited metal is rough. Such roughness causes reduction in the hydrogen overvoltage of the metal and, for purposes such as those described here, lead to poor results.

The electrode should not be attacked by the reagents of the solution into which it is dipped, and the surface should be easily preserved over a long period of time. Copper was eliminated on this basis for it was attacked by some of the reagents and its surface was found to change with use.

Efficient stirring was essential in order to minimize polarization. This was first done by a glass paddle driven by a variable speed electric motor. The motor proved to be quite cumbersome; so when the cell was rebuilt the motor was replaced by a magnetic stirrer.

A quantity of 0.1M chromic sulfate was electrolyzed at various current ranges up to 0.1 ampere. Runs were made with three electrodes, platinum gauze, copper plated on platinum gauze, and copper amalgam plated on platinum gauze.

The deposition of copper was carried out in a cupric sulfate acid bath; the electrolysis never gave a completely smooth surface. Copper on the copper amalgam electrode was prepared in the same way as described previously and the mercury was deposited by electrolyzing mercuric chloride solution.

During the determination the solution was stirred continuously. On each run large quantities of hydrogen were liberated indicating that, at the acidity and with the electrodes used, the chromic-chromous ion couple was not suitable as an intermediate for quantitative determinations. Although it was recognized that further work might yield better results, this couple was set aside to permit the investigation of more promising couples.

Since at this point in the problem, difficulties were being met in dissolving titanium compound, it was decided to try Swift's method(8) of

using the cupric-cuprous ion couple to analyze an iron solution and test the amalgam electrode. No hydrogen was produced when several runs were made with 0.1M cupric chloride 1N in hydrochloric acid at 0.1 ampere. The solution turned brown when the electrolysis was allowed to proceed for any length of time. Next the electrolysis container was filled with 350 ml of cupric chloride-hydrochloric acid solution and from a buret 9.29 ml of 0.2N iron solution was added -- this being enough to complete the reaction in thirty minutes. Carbon dioxide was bubbled through the solution for ten minutes before electrolysis to remove any oxygen. A current of 0.1 ampere was used, the electrolysis was allowed to run for fifty minutes, being stopped at intervals for voltage readings on the potentiometer. A curve of voltage against electrolysis time was plotted to determine the endpoint. A good break in the curve was not obtained. The curve was compared with one obtained from the same solution titrated with cuprous chloride when the runs were made on the Fisher Titrimeter; neither curve showed sharp drops in potential. This work was stopped when some titanium tetrachloride was obtained. Sufficient data was not available to draw any conclusions about the copper amalgam cathode.

Titanium tetrachloride was dissolved as previously described. The 0.2M titanium tetrachloride in 3M acid was diluted 1:1 and experiments were begun on its use.

First a platinum cathode was placed in the cell containing titanium solution. Some runs were made with currents ranging up to 0.1 ampere. Large quantities of hydrogen were evolved on each run. The same runs made using a copper-plated platinum electrode gave no visible evidences of hydrogen liberation. Samples were taken at intervals during this electrolysis and tested with potassium ferrocyanide for the presence of reduced

titanium. All tests were positive.

A cell was then made up using a pure copper cathode in a titanium tetrachloride solution and fifteen minutes runs were made with 18.65 ml of 0.1N dichromate and 9.32 ml of 0.2N iron solution. The electrolysis was stopped at intervals and readings of the voltage change were taken. These were plotted against the time to determine the endpoint and an excellent curve was obtained for the chromate solution. However, the copper was badly corroded after the run and there were other definite evidences that the copper electrode was being attacked by the oxidizing agents; consequently, it was decided to work the problem out with iron, although the iron did not give as good a curve.

At this point in the problem the cell was completely rebuilt (see Fig. 2). The old one, as previously stated, was much too large and consumed too much reagent. The new cell container was a 150 ml beaker. The glass paddle was replaced by a magnetic stirrer and the new anode compartment was a glass tube with a sintered glass disk on the bottom for separating the electrodes. A cap 13 inches in diameter was made for the cell from a piece of half-inch plywood. It was hollowed out on the under side so it would fit down over the cell container. In the cap, holes of various sizes were drilled to accommodate the electrodes which were fastened securely but so that each could readily be removed if it was so desired. Snaps were used to make circuit connections.

Since a new electrode of some material less easily attacked than copper was needed to carry on the work and it was found in the literature (17) that gold had a high hydrogen overvoltage (0.588 volts at 100 milliamperes per square centimeter current density, in 2N sulfuric acid), it was decided that

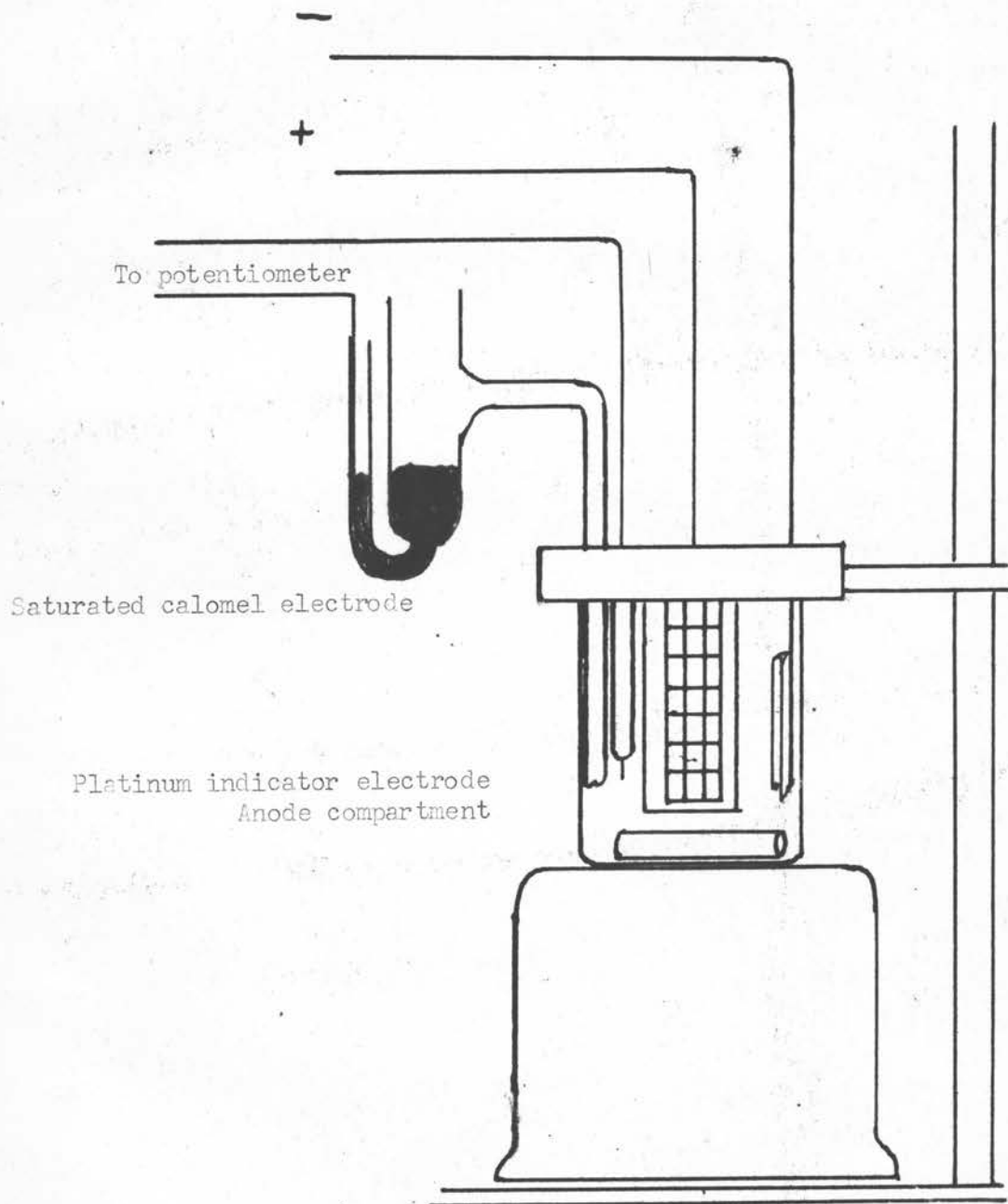


Figure 2

Electrolysis Apparatus

gold should be tried. No gold sheet was available; consequently, it was necessary to gold-plate a platinum electrode. A piece of sheet platinum was obtained, approximately one inch square, and a platinum wire stem was welded to it. A gold-plating solution was prepared from gold chloride, potassium cyanide, and potassium hydroxide. About 3 gm of gold chloride was added to 150 ml. of 0.1 N potassium hydroxide; then potassium cyanide was added until electrolyzed oxygen stopped forming on the gold anode. The platinum cathode was put into the above mentioned bath along with a gold wire anode. The electrolysis was then carried out at a little above 50 milliamperes.

Every half hour the electrolysis was stopped. The cathode was removed from the cell and polished with a cloth and some sodium bicarbonate or calcium sulfate. This was necessary to assure a smooth even surface on the electrode. The gold cathode was allowed to stand in concentrated nitric acid for about fifteen minutes after polishing. After about two hours, there was a sufficient amount of gold on the electrode.

The gold electrode gave off hydrogen sporadically when a number of tests were made with it. First, it was thought that due to pores and flaking some of the platinum might be exposed; so the electrode was heat treated. This undoubtedly helped in the long run, especially in preventing the flaking; but some hydrogen was still coming off so the 0.2M titanous chloride solution was increased in concentration considerably by the addition of more titanous chloride; this was then diluted 1:10 with water. Visible evidences of hydrogen evolution disappeared. The information these results provided led to the experiments (described earlier) with varying acid and titanium concentrations and to the development of the solution described under "Reagents".

It was still found necessary however, to deposit more gold on the electrode from time to time. The ideal solution to this problem is probably the use of gold sheet as the electrode material.

Procedure and Results

In a typical run, the storage batteries were connected in series and a knife switch which was used as a safety switch was closed. Switch S_3 was closed and the rheostat adjusted to allow 100 (or 50 milliamperes, whichever was to be used) to flow. This was done about half an hour before any runs were made and the voltage was allowed to stabilize itself. The anode compartment was filled with 1N sulfuric acid. Ten ml of titanium tetrachloride solution diluted to a volume of 100 ml with water was poured into the cell container. A measured portion of the substance to be analyzed was pipeted into the titanium solution and the container was placed on the magnetic stirrer, and stirring was started immediately. The stirrer was rotated at a speed such that no air bubbles were drawn into the solution nor any appreciable cone formed. The carbon dioxide was turned on and allowed to pass across the surface of the solution during the entire time of the electrolysis. Not enough evidence was accumulated to show definitely whether or not the carbon dioxide was needed; however, four successive runs which were made without this protection gave bad results, and although there may have been other causes for these failures, the coincidence is suggestive. The carbon dioxide was used here as a precautionary measure since there were enough troublesome variables without permitting possible air oxidation of the sample being analyzed.

When stabilization was completed, switch S_3 was opened. The timer was turned on as to read zero, the calibration of the potentiometer checked against the Weston Standard Cell, then the potentiometer was switched to connect it to the indicator electrode-calomel half cell combination. Since the dead stop method was used, the potentiometer was set at a

voltage obtained from experimentally determined curves. In most cases, 0.2 volt was used. Once again all switches and the timer were checked to make sure each was in the right position. Then switch S_1 was closed and the electrolysis and timer started. As the electrolysis approached the endpoint, the tap key on the potentiometer was closed for an instant every few seconds and when the galvanometer needle no longer moved the electrolysis was stopped by opening switch S_1 . The time and current setting were then recorded. The container was removed from the cell, its contents poured out; then it was rinsed, filled with water and replaced in the cell. The magnetic stirrer was turned on and the electrode was rinsed.

During the course of the titrations sometimes it was found necessary to adjust the resistance once or twice due to a slight drop in the current.

To determine the full extent of this drop and to determine whether or not there might be other current fluctuations, a Brown Recording Potentiometer with a 10 millivolt full scale deflection and a $4\frac{1}{2}$ second movement was connected across a 0.1 ohm resistance which was in series with the electrolysis cell. When the current curves were run there were no significant fluctuations observed. The drop of the current during the analysis was found to be less than 0.1 milliamperes — and that of only short duration.

The results of experiments with electrodes other than gold, with intermediate reactants other than titanium, and with various solutions of titanium have already been discussed in connection with the description of apparatus and reagents. Little quantitative work was attempted with these since it was obvious that hydrogen evolution or electrode corrosion must cause poor results.

With the titanium solution which was finally developed and the gold electrode, much better results could be expected. Consequently a large number of runs of various types were made, using iron as described in the paragraphs above.

Quantitative determinations of iron were carried out at currents of 0.1 ampere and 0.05 ampere. The milliammeter was calibrated with a standard 1-ohm resistance. When set at 0.1 ampere (meter reading) the actual current was found to be 0.1024 ampere and when set at 0.05 ampere the actual current was found to be 0.0499 ampere.

Two pipets, one 10 ml and the other 5 ml, were used to deliver the iron samples. The amount of iron in the solution which each would deliver was determined gravimetrically. The 10 ml pipet delivered 0.1100 gm and the 5 ml pipet delivered 0.05585 gm of iron.

Tests were run to determine the endpoint for the titrations. Voltage differences were read on the potentiometer at intervals and plotted against time. At first the runs were allowed to proceed uninterrupted in these tests; but when this procedure was used, a sharp break in the curve could not be obtained although the magnitude of the break proved to be large. So instead, the electrolysis was stopped at intervals and readings were taken. With this procedure, much better breaks were obtained. A comparison of these breaks may be observed in the figures (see Figs. 3, 4, 5). This lag is believed to be due to a certain amount of time required for the indicator electrode reaction to reach equilibrium and probably could be corrected by allowing the solution to stand a short time just before the final endpoint was reached. The dead stop method was used for the quantitative determinations and 0.2 volts seemed to serve well as an endpoint setting in most cases.

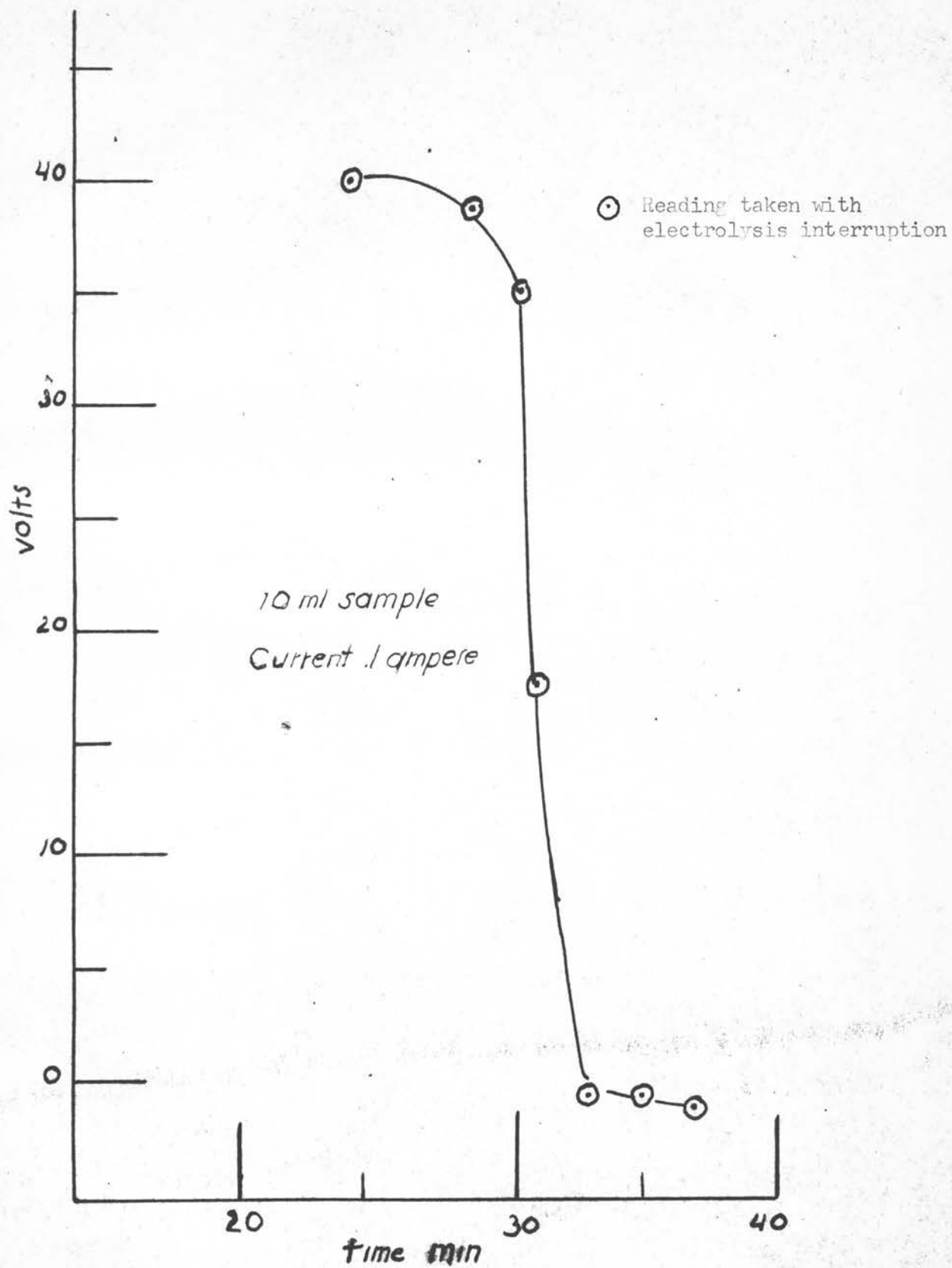


Figure 3

Voltage Time Curve

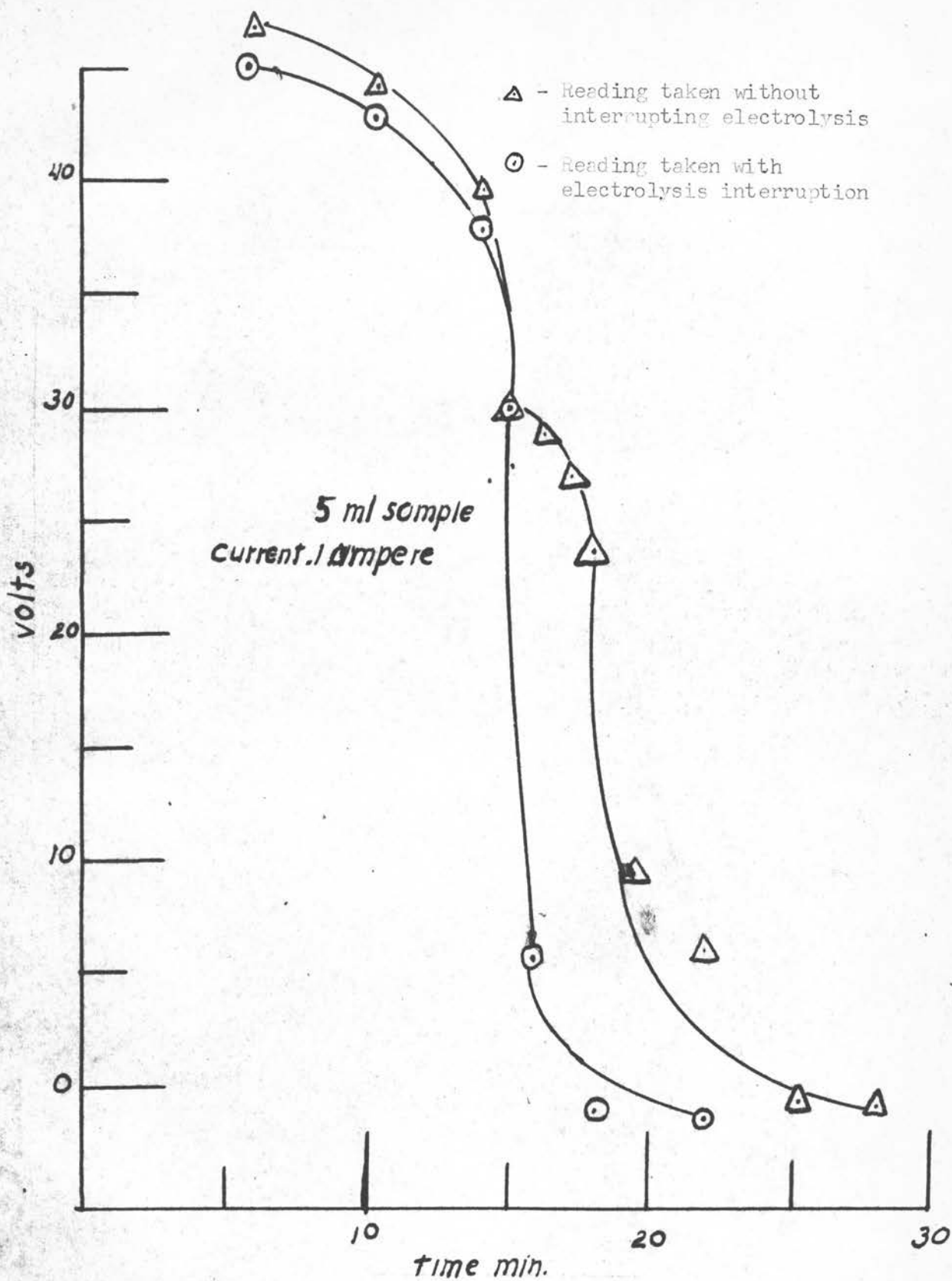


Figure 4

Voltage Time Curve

Voltage Time Curve

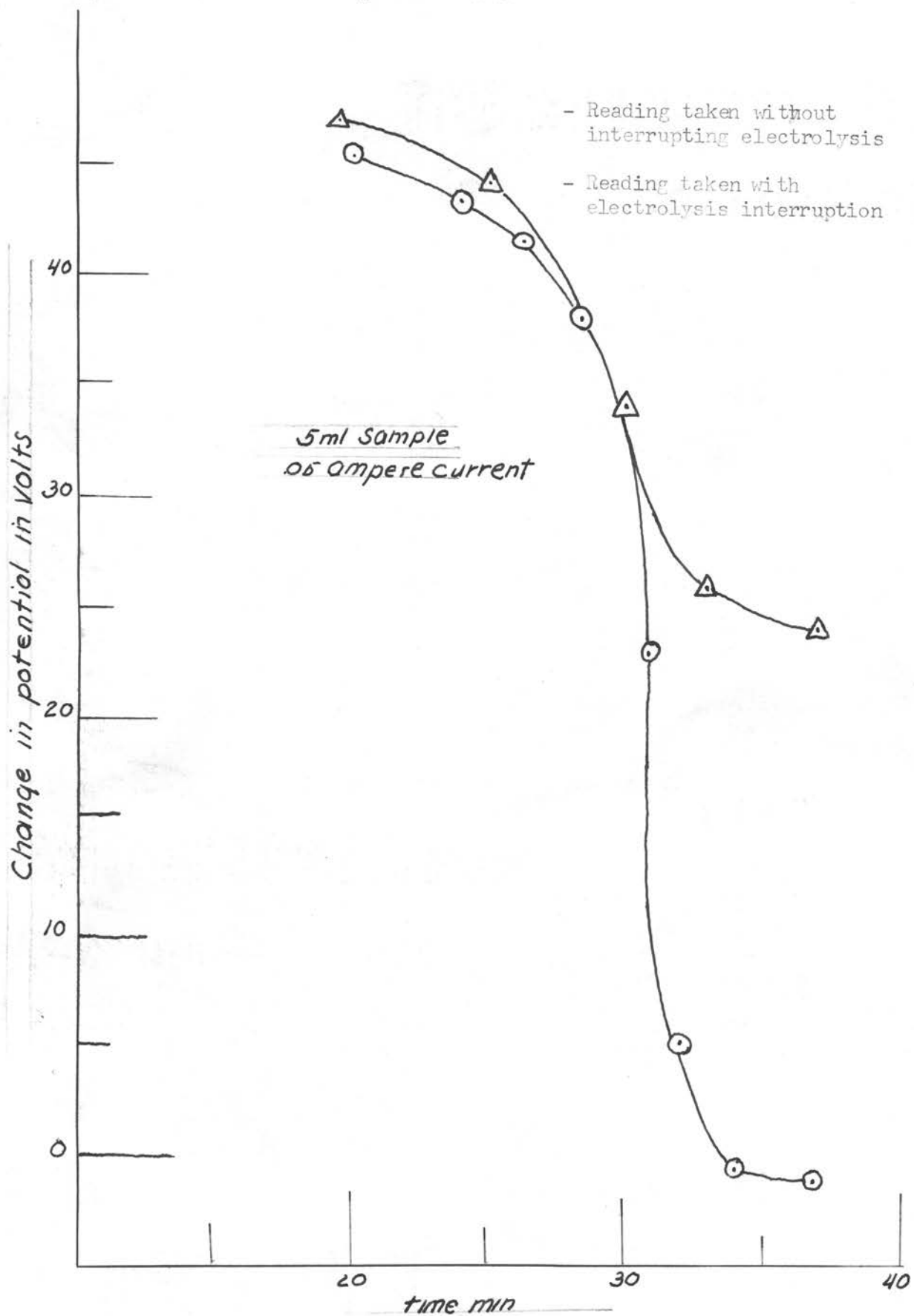


Figure 5

In the following tables the results of three sets of determinations are recorded. In Table 1 are given the time, amount of electricity, calculated quantity of iron, and average deviation for several 10 ml samples, as determined using an electrolysis current of 0.1 ampere. Tables 2 and 3 contain the same data as above when 5 ml were used with electrolysis currents of 0.1 ampere and 0.05 ampere, respectively.

Table 1

10 ml sample

Current 0.1 amp.

Dead Stop Setting = .2 volt

1 Faraday = 96,500 coulombs

Time	Coulombs	Grams of Fe	Deviation
32'	196.6	.1138	.003
30' 57"	190.3	.1100	.0008
31'	190.4	.1102	.0006
31'	190.4	.1102	.0006
31'	190.4	.1102	.0006
30' 48"	189.5	.1098	.0010
31' 21"	192.6	.1115	.0007
31' 10"	191.2	.1109	.0001
30' 45"	189.0	.1093	.0015
31' 31"	193.0	.1120	.0012

Average (in grams) = .1108 g.

Average Deviation = .0010 g. = 0.91%

Grams of Iron (determined by standard gravimetric methods) = 0.1100 g.

Table 2

5 ml sample

Current 0.1 amp.

Dead Stop Setting = .3 volt

1 Faraday = 96,500 coulombs

Time	Coulombs	Grams of Fe	Deviation
15' 40"	96.25	.05571	0.00032
15' 48"	96.65	.05606	0.00003
15' 50"	97.30	.05628	0.00025
15' 48	96.65	.05606	0.00003
15' 48"	96.65	.05606	0.00003

Average (in grams) = .05603 g.

Average Deviation = 0.00015 = 0.27%

Grams of Iron (determined by standard gravimetric methods) = 0.05585 g.

Table 3

5 ml sample

Current 0.05 amp.

Dead Stop Setting = .2 volt

1 Faraday = 96,500 coulombs

Time	Coulombs	Grams of Fe	Deviation
32' 5"	96.05	.05553	.00024
32' 15"	96.54	.05588	.00011
32' 4"	96.01	.05552	.00025
32' 10"	96.32	.05575	.00002
32' 25"	97.05	.05617	.00040

Average (in grams) = .05575 g.

Average Deviation = 0.00020 g. = 0.35%

Grams of Iron (determined by standard gravimetric methods = 0.05585 g.)

Conclusion

The problem, as far as it was carried, has shown only that the method is workable. It is believed that if properly perfected it will give a thoroughly acceptable quantitative technique of coulometric analysis. The results that were obtained, although better than expected for the first trial, could be considerably improved by eliminating some of the difficulties. Time did not permit the solution of these difficulties.

No effort was made to determine the minimum concentration of the titanium tetrachloride which is needed, although the facts that low acidity is needed, and that the acidity and titanium concentration are interdependent, were clearly shown. Determination could be improved probably by degasing with an inert gas before electrolysis in order to remove the dissolved oxygen from the solution. The distilled water probably should be boiled before use to remove chlorine. There were no systematic determinations made with the specific idea of studying the effect of removing chlorine and oxygen. Such studies would have been little more than indicative until proper electrodes were available and unfortunately the purchase of these seemed unwarranted until too late in the research.

The ideal answer to the present electrode situation is a substitution of pure gold sheet for the gold-plated platinum electrode. Other electrodes could be studied more thoroughly. The amalgam electrode or a mercury pool electrode, in particular, might prove to be valuable because of the high hydrogen overvoltage of mercury.

The end point break needs to be corrected, but this can be solved most likely by allowing a time lapse, just before the end point is reached

with the current turned off to allow the indicator electrode to reach equilibrium. The dead-stop method, with this precaution, should be quite generally acceptable for many determinations.

The analysis of iron is just one of the many determinations that have possibilities. Besides the strong oxidizing agents that were tried, such substances as copper and arsenic might be possibilities. Organic compounds might present interesting problems with this particular type of coulometric analysis, for titanous chloride is a recognized reagent for titrating a number of such compounds.

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Biography

John F. Donahue was born May 2, 1921 in Albert Lea, Minnesota. He graduated from Albert Lea High School in 1937 and received his bachelor of science from Creighton University of Omaha in 1944.

He served in the Army in Germany as an infantry rifleman and after being discharged from the service, he taught school at Waukon, Iowa. The following year he enrolled in the Graduate School at Oklahoma A. and M. College.

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