

COULOMETRIC ANALYSIS
IN ANHYDROUS ACETIC ACID

by

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Signed:

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CHAPTER I

INTRODUCTION

Coulometric analysis is the quantitative determination of a substance by measurement of the coulombs of electricity necessary to cause a certain electron exchange involving the substance. The number of coulombs can then be related to the number of chemical equivalents of the substance by Faraday's law, which states that the passage of one Faraday of electricity (96,500 coulombs) through a solution causes one equivalent of reaction to take place at the electrode.

The main advantage of coulometric analysis over gravimetric and volumetric analyses is the time saved. As a general rule these two methods are rather long and involve many steps. A gravimetric analysis requires weighing and solution of the sample, precipitation, filtration, washing and drying or igniting, and often several of these steps must be repeated. Volumetric analysis requires the preparation, standardization, and storage of a solution of accurately known composition, in addition to the preparation of the sample. Coulometric analysis does not require time consuming operations. After the initial apparatus set-up has been made, only the weighing and solution of

the sample and a period of electrolysis remains for the analysis.

In a coulometric titration either the substance to be determined or an intermediate substance can be reacted at the electrode. In the former case the unknown is directly oxidized or reduced by coming in contact with the electrode, while in the latter the intermediate is oxidized or reduced at the electrode and this subsequently reacts with the unknown. The second method, in which an excess of the intermediate is added, is to be preferred, for the electrode is continually supplied with excess reagent which, after being oxidized or reduced, can circulate throughout the solution and react with the limited amount of unknown.

The anode and cathode must be separated so that the oxidized or reduced reagent will not be swept against the opposite electrode and the reverse reaction take place. This is usually done by trapping the electrode which has the undesired reaction, so that it makes electrical contact through a sintered-glass disk which retards the passage of ions.

Several methods of end point detection can be used; among the more widely used are the colorimetric, potentiometric and amperometric methods. The colorimetric method utilizes the color change due to either an added indicator or an excess of reagent. The potentiometric

method utilizes the change in electrical potential across a pair of sensing electrodes in the solution. The amperometric method utilizes the change in current flowing between two sensing electrodes.

The number of coulombs of electricity passed through the solution to bring about the desired reaction can be measured directly on a coulometer, or it can be taken as the product of the time and the amperage.

Although experimental work had been done prior to that of Sease, Niemann and Swift, it is of no consequence to this paper. In 1947 an article was published by these three men in which they describe a rapid and accurate coulometric titration utilizing a constant current supply and amperometric detection of the end point.²³ They quantitatively determined microgram quantities of thiodiglycol with electricity generated bromine. The end point was detected by the increase in current between two additional platinum electrodes when excess bromine was generated. The sensing electrodes were on a separate circuit, and approximately 0.3 volt was impressed across them. Their work offered the first simple, rapid and accurate procedure for running a coulometric titration.

Since coulometric analysis utilizes electrical currents it can be easily adapted for use in automatic titrimeters. In 1949 an article appeared in which Austin, Turner and Percy developed an instrument for the continuous

automatic titration of sulfur compounds with electrically generated bromine.² The gas or other flowing sample is mixed with the reagent in a fixed proportion and continually titrated to a fixed potential.

The scope of coulometric analysis was further broadened by Deford, Pitts and Johns when they devised the idea of generating their reagents externally by a constant electrolysis current and delivering the reagent to the solution through a small capillary tube.³ They successfully titrated acids, bases and arsenic by this method using potentiometric detection of the end point. They incorporated this procedure in the construction of an automatic titrimeter for acidimetry and alkalimetry.⁴ This procedure eliminated any secondary reactions at the electrodes; however, it had the disadvantages of diluting the solution and of a time lag, while the reagent was being swept down the capillary.

In 1953 an automatic titrimeter was constructed in which photometric detection of the equivalence point was used.²⁶ This eliminated the troubles associated with the sensing electrodes.

In the same year the use of "dual intermediates" was also reported. In a solution of cupric copper and bromide ion it was possible to electrolytically generate a known excess of bromine and then reduce this with electrolytically generated cuprous copper by reversing the polarity of the

generating electrode. This demonstrated the possibility of making coulometric back-titrations where an excess of reagent was required because of the slowness of the main reaction.

Chlorides, bromides,¹⁷ and iodides,^{15,17} have been successfully titrated by electrically generated silver ion. In these determinations the silver ion is oxidized directly from a silver anode placed in the titration vessel.

In late 1954 an article was published which described an automatic titrimeter for the determinations of mercaptans on a micro scale.¹⁶ The mercaptans are reacted with electrically generated silver ions and the equivalence point is detected amperometrically. This procedure is of considerable importance for it is one of the first ones in which a purely non-aqueous solvent is utilized; a mixture consisting of two parts of ethyl alcohol to one part of benzene serves as the solvent.

No reference could be found in the literature in which acetic acid was used as a solvent in a coulometric titration. Its primary use as a solvent has been for the volumetric titration of salts of organic bases,^{6,19} inorganic salts,^{6,11,12,13,14,18,20} and weak organic bases.^{6,8,19,21} A considerable amount of work has been done on the amines,¹⁸ and methods have been devised to titrate mixtures of primary, secondary and tertiary amines,⁶ amine hydrochlorides,⁶ and numerous acid salts.^{14,20}

Since acetic acid is an acid solvent, it tends to bring out the basic characteristics of the weaker bases and raises them all to the same level of basicity; this very important phenomena is termed "leveling effect", and the acetic acid would be the leveling solvent.⁶ It is this effect of acetic acid that makes possible its use as a solvent for titrations of weak bases. A diverse effect is noted on acids in that their acidic strengths are lessened. Considerable work has been done on comparative strengths of inorganic acids in acetic acid, and on the basis of conductivity measurements, the following list has been prepared in order of decreasing strength: perchloric, hydrobromic, sulfuric, hydrochloric, and nitric.^{1,6} On the basis of this experimental data, perchloric acid is usually chosen as the titrant for weak bases in acetic acid. The preparation of the titrant involves removal of the water introduced by the addition of the perchloric acid using acetic anhydride,^{6,19} and the standardization of the acid solution.²²

Added indicators,^{6,18,19,22} and electrode systems^{6,10,19,25} have both been discussed considerably in the literature. One main disadvantage to the use of visual indicators is their wide range of color change. The correct color change for any particular system being titrated can be determined by running the titration

using both the indicator and an electrode system.²²

Several other interferences to end point detection have been discussed.^{6,7,8,10,19,22} Of particular importance is the adverse effect water has on the detection of end points. It greatly reduces the sharpness of color changes of visual indicators and of potential changes across sensing electrodes. This interference is generally removed by the addition of a slight excess of acetic anhydride, which reacts with the water to form acetic acid. When primary and secondary amines are titrated, however, this cannot be done, for the acetic anhydride will react with these amines as well as with the water.

Besides a pure acetic acid solvent, considerable use has been made of mixtures of acetic acid and other organic solvents.^{7,8,21}

CHAPTER II

DISCUSSION OF THE PROBLEM

The problem of performing coulometric titrations in anhydrous acetic acid can be divided into several parts. They are (1) acquiring a truly anhydrous system, (2) finding a suitable electrolyte, (3) finding a suitable reagent, and (4) affecting the proper use and measurement of a suitable current supply.

In numerous earlier articles,^{8,10} the deleterious effect of water on the detection of end points was pointed out. In most of these articles the water was removed by the addition of either a calculated amount of acetic anhydride or an excess amount, if the excess caused no interfering reaction. These calculations, however, were generally quite rough, and as a safety precaution usually only 90 per cent of the theoretical amount of the anhydride was added to the solution; no attempts were made to obtain a pure, 100 per cent acetic acid solvent.

Some work has been done on solubilities of various inorganic and a few organic salts in acetic acid, and these results have been tabulated.¹ These tables are by no means complete and in some cases give only a rough

estimate of solubility. The solubility of a salt is by no means an indication of its properties as an electrolyte or of its ability to carry a current. It must be remembered that the solvent is acetic acid, not water, and that the rules of solubility, mobility, and dissociation which pertain to aqueous solutions are not applicable here. Several incomplete lists have been prepared giving the equivalent conductances,¹ and the comparative degrees of dissociation,^{13,14} of numerous cations and anions. There is, however, no work reported on electrolytes which would give satisfactory reactions at both the cathode and anode during an electrical generation of a reagent in acetic acid.

For a suitable oxidation a reagent must be found that can be oxidized by the anode and will then react quantitatively with the constituent to be determined; the reagent in its oxidized state must be stable in the acid solution. Unlike the solvent water, acetic acid cannot give up an oxygen atom which complexes with certain cations and thus stabilizes their oxidized states. The reagent in its oxidized form must either remain as a free ion or complex with the acetate radical.

The problems arising from affecting the proper use and measurement of a suitable current supply do not differ appreciably from those of coulometric titrations in aqueous

media, except that the cell resistances are usually higher in non-aqueous media. Two types of current supply are available for use, one using essentially constant voltage from dry cell or wet cell batteries, or both, the other using constant current from a current-regulated electronic supply. There are two methods for measuring the number of coulombs of electricity passed through the solution. The first utilizes a coulometer, the accuracy of this method depending on the accuracy of the instrument itself. In the second method the number of coulombs is calculated as the product of the current and the time. The accuracy of this method depends on the accuracy of the ammeter and the timing device, as well as the ability with which the initiation of current-flow and time can be synchronized. Proper use of the current is essentially obtaining 100 per cent current efficiency of the desired reaction. To obtain quantitative results in any coulometric titration, the applied current must bring about an electron transfer on the reagent or the constituent being determined only; there can be no side reactions, secondary reactions, or electron changes at the generating electrode involving any other constituent in the solution.

Coulometric analysis in anhydrous acetic acid utilizes the advantages of both a coulometric method and an acid solvent. The coulometric advantages are, briefly,

simplicity, rapidity, and adaptability to automatic instrumentation; the advantage of an acid solvent is its ability to increase the basicity of weak bases.

CHAPTER III

EXPERIMENTAL

A Non-aqueous Solvent

The water in glacial acetic acid was removed with acetic anhydride by means of the following reaction:



All acetic acid used in these tests was Baker's Glacial Acetic Acid, C. P., with a minimum purity of 99.8 per cent. Tests for either excess water or excess acetic anhydride were made by conductivity measurements on a Model RC 16B Conductivity Bridge of Industrial Instruments Inc. Due to the high resistance of the acetic acid solutions a 2.2 megohm resistance was connected across the terminals of the conductivity bridge in parallel with the conductivity cell. The resistance could then be calculated from the following equation:

$$\frac{1}{\text{bridge resistance}} = \frac{1}{2.2} + \frac{1}{\text{cell resistance}}.$$

Knowing the cell constant the specific resistance could then be calculated,

$$\text{specific resistance} = \text{cell resistance} \times \text{cell constant}.$$

In the following section all resistances are given directly

as the bridge resistance, for only the comparative values are of interest.

The reaction between acetic anhydride and water to form acetic acid is a rather slow reaction when the reactants are present only in small amounts. A solution containing an excess of acetic anhydride will exhibit a steady decrease in resistance when the vessel is left open to atmospheric moisture. This phenomena was evidenced in solutions containing three, five, and fifty per cent acetic anhydride, as well as in pure acetic acid.

Several titrations were run on acetic acid solutions in an attempt to find a point of maximum resistance, which would be the point where the concentration of the water was a minimum. The solution being titrated contained an equilibrium mixture of three per cent acetic anhydride and acetic acid. The data in Table I is a typical titration. The titrant consisted of a ten per cent solution of water in acetic acid. The titrations were followed by conductivity measurements with the end point being the point of maximum resistance; readings were taken every two minutes. A closed system was used, and a constant temperature was maintained. As can be seen from the data no point of maximum resistance was found.

Further tests for obtaining an anhydrous system were made by adding varying amounts of Baker's 98.3 per cent

Acetic Anhydride to glacial acetic acid and by storing various solutions over a sulfuric acid dessicant. The results are tabulated in Table II. Solution A is pure acetic acid taken directly from the bottle; solution B is pure acetic acid stored over sulfuric acid for several days; solution C contains an equilibrium mixture of five per cent acetic anhydride; solution D is a five per cent mixture of acetic anhydride stored over sulfuric acid for several days; solution E is a five per cent mixture of acetic anhydride whose resistance was taken immediately after mixing. The solution containing zero per cent of acetic anhydride differs from solution A in the fact that it received the same handling and mixing as did the other solutions of the anhydride. Table III gives the resistances of the same solutions as those in Table II after the solutions had been standing overnight.

TABLE I - Titration Data of Acetic Anhydride

<u>Resistance in megohms</u>	<u>Ml. of titrant</u>
1.93	1
1.90	2
1.86	3
1.82	4
1.80	5
1.76	6
1.74	7
1.70	8
1.65	9
1.63	10
1.61	11
1.57	12
1.57	13
1.51	14
1.48	15
1.45	16
1.42	17
1.41	18
1.36	19
1.34	20
1.32	21
1.30	22
1.26	23
1.23	24
1.30	25
1.18	26
1.17	27
1.14	28
1.11	29
1.09	30

TABLE II - Resistances of Various Solutions of Acetic Acid.
(Listed percentages are of acetic anhydride.)

<u>Solution</u>	<u>Resistance in megohms</u>
A	2.05
B	1.90
C	1.96
D	1.92
E	1.90
0%	2.00
0.08%	2.01
0.12%	2.04
0.16%	2.03
0.20%	2.02

TABLE III - Resistances of Various Solutions of Acetic Acid

<u>Solution</u>	<u>Resistance in megohms</u>
0%	1.99
0.08%	2.01
0.12%	2.05
0.16%	2.04
0.20%	2.04

The data listed in these two tables are averages of values taken from numerous experiments.

Although the resistance of the pure acetic acid cannot be exceeded, an optimum amount of acetic anhydride must be added to maintain this level of resistance while working with the acid. It must also be remembered that the maximum limit of water in the acetic acid used in these experiments was 0.2 per cent.

Electrolytes

For coulometric titrations in which neither the constituent to be determined nor the reagent can react appreciably at the non-generating electrode, or when their mobility in the solution is low, an electrolyte must be added to make the solution conductive to an electrical current. Several inorganic salts were tried. In some cases it was necessary to reflux the solution for an hour or more in order to get either a saturated solution of the salt or at least a solution of appreciable concentration. All resistances in this section are specific resistances of the respective solutions.

Potassium bromide A saturated solution of this salt had a resistance of 75,250 ohms. This solution was prepared by refluxing. A solution that was prepared by allowing it to stand in contact with an excess of the salt without refluxing gave a resistance of 220,000 ohms.

Sodium bromide A saturated solution prepared by refluxing had a resistance of 39,500 ohms.

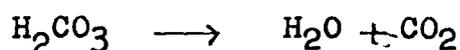
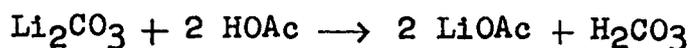
Calcium chloride This salt was quite soluble and did not have to be refluxed; a 0.4 N solution had a resistance of 3,090 ohms.

Barium iodide A 0.4 N solution of this salt had a resistance of 2,550 ohms. The salt is quite soluble and the solution did not have to be refluxed. The solution

became very dark after several minutes due to the formation of free iodine. When a current was passed through the solution, free iodine was liberated at the anode.

Zinc chloride The solution of this salt was approximately 0.6 N and gave a resistance of 1,350 ohms. When a current was passed through this solution metallic zinc was deposited on the cathode, the deposited zinc then slowly reacted with the acetic acid to liberate hydrogen gas.

Lithium nitrate A solution of this salt in excess of one normal gave a resistance of 175 ohms. When an acid-base indicator (considering pure acetic acid as essentially neutral) was added to this solution, the initial color was that of a neutral solution; however, after standing a short time, the indicator changed to a basic color. A solution of lithium nitrate was also prepared by titrating, volumetrically, a solution of lithium acetate to neutrality with an acetic acid solution of nitric acid of known concentration. The lithium acetate was formed by adding lithium carbonate to pure acetic acid, then warming the solution to drive off the carbon dioxide that was formed.



Acetic anhydride was then added to remove the water formed. During the titration the solution was extremely slow to

reach equilibrium; when the end point was finally reached, the neutral color of the indicator did not remain but changed gradually to an acid color. Resistances obtained on the basis of this procedure were completely inconsistent with the concentrations, and in several cases a more concentrated solution would have the higher resistance. The indicator used for these titrations was methyl violet.

Ammonium nitrate A saturated solution of this salt had a resistance of 11,000 ohms.

Ammonium perchlorate A solution of this salt was prepared by titrating an acetic acid solution of ammonium acetate with one molar perchloric acid in acetic acid; the solution was titrated to a neutral indicator color. A precipitate formed during the titration, consequently the solution was saturated; the resistance was 70,000 ohms.

Potassium perchlorate A saturated solution was prepared by titrating potassium acetate with perchloric acid. Potassium hydroxide was dissolved in acetic acid to form the potassium acetate. The water which formed was then removed by reaction with acetic anhydride. The resistance was 39,000 ohms.

Magnesium perchlorate This salt was fairly soluble and a saturated solution was prepared without refluxing; the resistance was 1,365 ohms.

Lithium chloride Resistances of lithium chloride solutions of varying concentrations are given Table IV. When a current was passed through a solution of this salt, hydrogen gas was given off at the cathode and chlorine at the anode. The chlorine did not bubble out

TABLE IV - Resistances of Solutions of Lithium Chloride of Varying Concentrations.

<u>Normality</u>	<u>Specific Resistance inches</u>
0.0100	95,000
0.0300	38,000
0.0600	16,800
0.1000	7,750
0.1500	3,555
0.2000	2,025
0.2500	1,285
0.4000	775
0.5000	360
0.7000	209
0.9805	136

of the solution, but dissolved in the acetic acid. A solution of lithium chloride was slightly acid but could easily be titrated to neutrality with an acetic acid solution of sodium acetate. Lithium chloride was readily soluble in acetic acid and the solutions did not have to be refluxed. Once the solution had been neutralized with sodium acetate, it maintained the same level of acidity and the indicator color remained unchanged over a period of time. The neutralized solution was very responsive to any slight addition of acid or base, and there was a sharp change in the indicator color.

The advantages of using lithium chloride as an electrolyte are its solubility, its greater electrical conductivity for solutions of the same concentration, stability of the solutions, and the sensitivity of the solutions to changes in acidity.

Coulometric Titration of the Hydrogen Ion

In the following experiments perchloric acid was titrated coulometrically by reducing the hydrogen ion at the cathode. The results are given in Table V. The electrolyte used in these experiments was lithium chloride. In the first experiment the solution was 0.25 N in the electrolyte, and in all others it was approximately 0.45 N.

In the first two experiments, the source of current was a series of wet cell batteries producing 104 volts; in the third and fourth experiments four forty-five volt R. C. A. Industrial B Batteries were connected in series with the wet cell batteries to produce approximately 280 volts. The current was averaged over specified lengths of

TABLE V - Coulometric Titration of Perchloric Acid
(All results are given in milliequivalents.)

<u>Acid added</u>	<u>Acid found</u>
0.2873	0.1895
0.1915	0.0957
0.3830	0.3920
0.3830	0.1877
0.2873	0.1740
0.2873	0.3080

time; the product of the average current and the time increments gave the number of coulombs per time increment, and by summing the number of coulombs for each time increment, the milliequivalents of acid could be calculated. In the last two experiments a constant current source similar to one reported in earlier literature²⁶, was used. The total number of coulombs in these cases was the product of the total time and the current.

The generating electrodes used were corrugated platinum foil, the cathode being twelve by forty-five millimeters and the anode thirteen by thirteen millimeters. In the first experiment the anode was trapped in a single glass tube containing a sintered-glass bottom, the tube being immersed directly in the titration vessel. In the remainder of the experiments the anode was trapped in two such tubes, a smaller one fitting inside the larger one used in the first experiment.

Two types of titrations vessels were used, a 250 milliliter Griffin beaker and a 200 milliliter electrolytic beaker.

Both colorimetric and potentiometric methods of end point detection were used. The indicators were methyl violet in an alcohol solution and crystal violet in an acetic acid solution. A Beckman model H-2 pH Meter was used for the potentiometric detection of the end point. The sensing electrodes used were a glass indicating

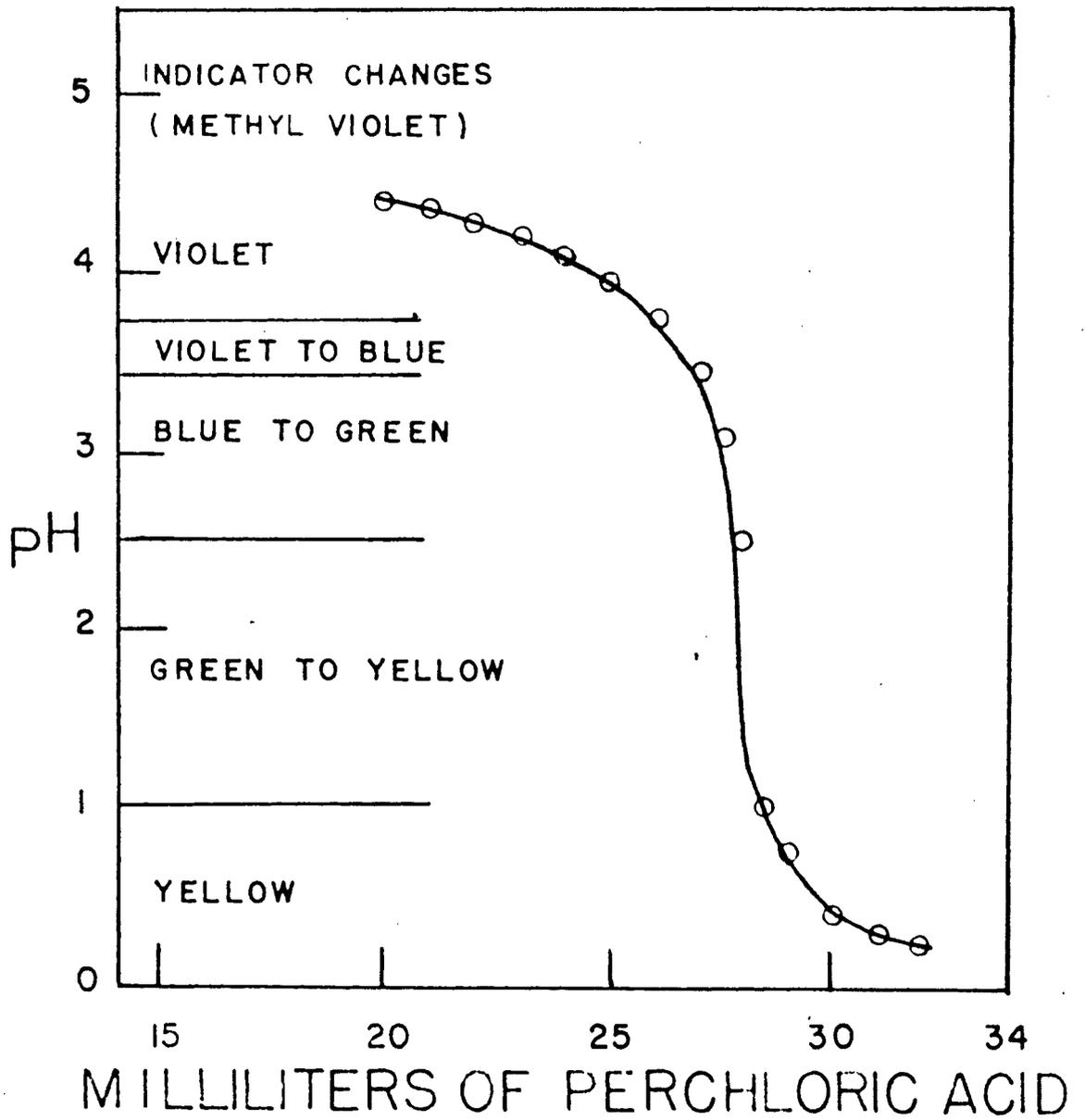
electrode and a silver-silver chloride reference electrode; they were immersed directly in the titration vessel.

Since an acetic acid solution of lithium chloride gave an acid color with the indicators used, in order to establish a reference point to which the titration could be run, the solution was titrated to a neutral green color with an acetic acid solution of sodium acetate. It was found in earlier experimental work that this green color came at the center of a break in the emf curve for a titration of lithium acetate with perchloric acid as shown in Figure I. Once the green color had been established, a known amount of perchloric acid was added, and the current was started. The acid was titrated by reducing the hydrogen ion at the cathode, and the titration was continued until the neutral green color of the indicator had been obtained. The color change was rather gradual and not too sharp; it was necessary to retain a portion of the neutralized lithium chloride solution in order to determine the end point by comparison. In all of the experiments the change in potential given by the sensing electrodes was too gradual to afford a means of detecting the end point. In all cases the generating current had to be interrupted to take emf readings on the pH meter.

In many of these titrations it was impossible to determine an end point by either a colorimetric or potentiometric method; in these cases either the indicator color

faded or else the original green color was never obtained. The fading of the indicator was due partly to the bleaching effect of the chlorine which was generated in the anode compartment. This was corrected somewhat by trapping the anode inside two sintered-glass bottom tubes instead of just one.

FIGURE I - Potentiometric Titration of Lithium
Acetate with Perchloric Acid.



Oxidation of Hydroquinone and Metol with
Electrically Generated Ceric Ion

Hydroquinone and metol are weak organic reducing agents and are used extensively in photographic developer solutions. In a coulometric titration they can be oxidized either directly at the anode or an intermediate reagent can be oxidized at the anode which then oxidizes the hydroquinone and metol. Hydroquinone is readily soluble in acetic acid, the metol only slightly; however, neither will carry a current to any appreciable extent.

Cerous perchlorate was found to be readily soluble in acetic acid and carried a current extremely well. Test samples of unknown amounts of hydroquinone and metol were readily oxidized with the generated ceric ion, giving a sharp change in the emf when excess ceric ion was generated. The emf changes were detected by means of a platinum indicating electrode and a silver-silver chloride reference electrode.

The use of several redox indicators was investigated and their color changes and solubilities were determined; the results are tabulated in Table VI. All of the indicators were found to change color just prior to the break in the emf curve for coulometric titrations of hydroquinone, the diphenylamine changing somewhat earlier than the others. These color changes came at no specific emf but over a range of from 250 to 450 millivolts.

The apparatus used for the coulometric titration of

TABLE VI - Oxidation-reduction Indicators

<u>Indicator</u>	<u>Color change</u>	<u>Remarks</u>
Erio-green	yellow to orange	reversible and soluble
Erio-glaucine	yellow-green to salmon pink	reversible and soluble
N-Phenanthranilic acid	colorless to red-violet	reversible and soluble
Sodium diphenylamine sulfonate	colorless to violet	reversible and soluble
Diphenylamine	colorless to violet	reversible and soluble
Sodium diphenylbenzidine sulfonate	colorless to violet	irreversible and slightly soluble

TABLE VII - Coulometric Titration of Hydroquinone in Acetic Acid Solution of Cerous Perchlorate

<u>Milliequivalents added</u>	<u>Milliequivalents found</u>
0.1377	0.1506
0.2775	0.4173
0.2775	0.3381
0.1159	0.1258

TABLE VIII - Coulometric Titration Data of Hydroquinone in an Acetic Acid Solution of Cerous Perchlorate and Cerous Acetate

<u>Milliequivalents added</u>	<u>Milliequivalents found</u>	<u>Per cent error</u>
0.1159	0.1145	-1.21
0.1190	0.1161	-2.44
0.1388	0.1330	-4.18
0.05551	0.05584	-0.59

hydroquinone in acetic acid was very similar to that used for the determination of perchloric acid; both batteries and a current supply were used to furnish the electrical current, and both singly and doubly trapped electrodes were used. Cerous perchlorate was the electrolyte and electrically generated ceric ion was the oxidizing reagent in all of the titrations. Data of typical titrations are given in Table VII. There were no coulometric titrations of metal made; it was so slightly soluble that only a very small amount (too small to be of any practical value for a quantitative determination) could be put into solution even after several hours of refluxing.

It can be seen from the data that the titrations were far from quantitative. To determine if the ceric ion reacted quantitatively with the hydroquinone, standard solutions of ceric ion were prepared by generating ceric ion from a solution of cerous perchlorate with a constant current for a specified length of time. These prepared solutions were then used to titrate, volumetrically, known samples of hydroquinone. In several cases the standard solutions of ceric ion became considerably lighter before the titration could be run, and after several more minutes they became colorless. The results of these titrations were by no means quantitative. The ceric ion had been spontaneously reduced back to the cerous ion. Two factors

were found that affected the rate of this reaction; they were temperature and concentration of acetic anhydride. When the temperature was kept below thirty degrees centigrade and the concentration of acetic anhydride was kept at a minimum, the rate of the reaction of ceric ion to cerous ion was greatly reduced, but the reaction was not stopped.

Further experimental work in which a small amount of cerous carbonate was added to the acetic acid solution of cerous perchlorate yielded results shown in Table VIII. The cerous carbonate reacted with the acetic acid to give cerous acetate, water and carbon dioxide which bubbled out of the solution; acetic anhydride was added to remove the water that formed. The exact effect of this cerous acetate is not known. Cerous acetate does contain the solvent anion, and therefore reduces the acidity of the acetic acid solution, just as cerous hydroxide reduces the acidity of an aqueous solution. Although the cerous-ceric system is not affected directly by the hydrogen ion concentration, it may have some indirect effect, or it may affect the hydroquinone-quinone system. Systems containing only the cerous acetate and no cerous perchlorate are not capable of carrying enough current with which to perform a coulometric titration. Solutions containing approximately eight grams of cerous perchlorate and approximately one half gram of cerous carbonate per 100 milliliters of acetic acid are used.

Coulometric Titration of Hydroquinone and Metol in
Photographic Developer Solutions

For the coulometric titration of hydroquinone and metol in photographic developer solutions, the same apparatus and set-up was used as the one described above. Since there was no reducing agent generated at the cathode which could reduce a drop of ceric perchlorate solution when it was added to the solution in the cathode cell, a singly trapped cathode was used; this lowered the resistance across the cell and a less concentrated solution of cerous perchlorate could be used in the titrations.

Sodium sulfite, which is used as a preservative in photographic developer solutions, could not be determined by coulometric titration, but it did interfere with the determination of metol and hydroquinone. In a titration of a sample of hydroquinone in which there was sodium sulfite, there was no sharp change in the emf but rather a gradual rise in the emf through the titration.

To avoid the deleterious affect of the sodium sulfite, samples of hydroquinone were extracted from an Eastman D-72 photographic developer by means of the following procedure.²⁴

- (1) Pipette 25 ml. of developer into 150-ml. extraction funnel.
- (2) Add a few drops of 0.04 per cent thymol blue solution.

- (3) Add 1:1 sulfuric acid until the solution is red, then 1 ml. in excess.
- (4) Add 50 ml. of ethyl acetate and shake for one minute.
- (5) Remove water layer to second extraction funnel and repeat step 4.
- (6) Remove water layer and save for metal determination.
- (7) Mix two ethyl acetate portions and add 25 ml. of SO_2 wash solution.
- (8) Shake for a few moments and remove and discard water layer.

Coulometric titrations were then run on the hydroquinone by adding specified aliquots of the ethyl acetate extract to the acetic acid solution of cerous perchlorate and cerous acetate; typical results are given in Table IX.

The metal was extracted by the following procedure.²⁴

- (9) Place sample from hydroquinone step 6 in 150-ml. extraction funnel.
- (10) Add a few drops of 0.04 per cent thymol blue solution.
- (11) Add 2.0 N NaOH until solution turns blue.
- (12) Add 25 ml. of ethyl acetate and shake for one minute.

TABLE IX - Data for Coulometric Titration of Hydroquinone
Extracted from Eastman D-72 Developer.

<u>Milliequivalents added</u>	<u>Milliequivalents found</u>	<u>Percent error</u>
0.05414	0.05395	- 0.35
0.05414	0.05408	- 0.11
0.05414	0.05240	- 3.22
0.05414	0.05148	- 4.92
0.05414	0.05471	/ 1.05
0.05414	0.05415	/ 0.02
0.05414	0.05391	- 0.43
0.05414	0.05395	- 0.35
0.05414	0.05409	- 0.09
0.05414	0.05411	- 0.06
0.05414	0.05347	- 1.24
0.05414	0.05181	- 4.31
0.05414	0.05347	- 1.24
0.05414	0.05440	/ 0.66
0.05414	0.05440	/ 0.66
0.05414	0.05382	- 0.59
0.05414	0.05400	- 0.26
0.05414	0.05436	/ 0.41
0.05414	0.05604	/ 3.60
0.05414	0.05444	/ 0.55
0.05414	0.05392	- 0.41
0.05414	0.05414	0.00
0.05414	0.05374	- 0.74

TABLE X - Data for Coulometric Titration of Metol Extracted
from Eastman D-72 Developer

<u>Milliequivalents added</u>	<u>Milliequivalents found</u>	<u>Percent error</u>
0.04321	0.04041	- 6.48
0.04321	0.04166	- 3.58
0.04321	0.04228	- 2.14
0.04321	0.03800	-12.1
0.04321	0.03818	-11.6
0.04321	0.04040	- 6.50
0.04321	0.03962	- 8.30
0.04321	0.03738	-13.5
0.04321	0.03740	-13.5

- (13) Remove water layer to another 150-ml. extraction funnel and repeat step 12 using 15 ml. of ethyl acetate.
- (14) Remove water layer to extraction funnel and repeat step 12 using 10 ml. of ethyl acetate.
- (15) Discard water layer and mix three portions of ethyl acetate extract.

This extract was then diluted with ethyl acetate to 100 milliliters in a volumetric flask and coulometric titrations were run on aliquot portions of this. The ethyl acetate used for the dilution was previously shaken with an aqueous solution of sodium hydroxide. When the pure acidic and anhydrous ethyl acetate was used, the metal precipitated from the solution. Many of the ethyl acetate solutions of metal became brown and yielded results with as much as forty per cent error. In all cases the aqueous layer in the extraction became at least faintly brown due to the oxidation product of metal caused by the continued shaking with atmospheric oxygen. Typical results are given in Table X. The two extractions for hydroquinone remove only 99.36 per cent, and the three extractions for metal remove only 99.20 per cent.²⁴ The theoretical amounts of hydroquinone and metal added were corrected according to these values. Each division in the tables gives the data for one extraction. Before any titration was run an unknown amount of either

hydroquinone or metol was added to the titration vessel, and ceric ion was generated until the emf corresponding to the value at the center of the break in the emf curve had been reached, approximately 650 millivolts. The known sample was then added and the titration was run until the emf had again reached 650 millivolts. The rate of increase of the emf near the end point was not consistent; in some cases the generation of current for two or three seconds caused considerable rise in the emf, while in other cases the effect was much less pronounced. Numerous samples could be run in the same acetic acid solution by titrating back to the same emf each time.

The timer used on these titrations was a Model S-10 of the Standard Electric Time Company. The timer and constant current supply were wired so as to start and stop simultaneously.

Titrations run on aqueous samples of the developer that had been acidified and boiled to remove the interfering sulfur dioxide yielded very poor results. There was no sharp break in the emf curve but rather a gradual rise in the emf.

In addition to the ceric ion two other reagents were investigated as possible oxidizing agents. Iodide ion could be oxidized to free iodine at the anode from a solution of barium iodide with the iodine remaining in solution. As was noted in an earlier section, however, the barium iodide reacted spontaneously to form free iodine upon dissolving

the salt in acetic acid. This spontaneous reaction took place almost as fast as iodine could be generated at the anode.

Chromic acetate was quite soluble in acetic acid and carried a current fairly well. When a current was put through a solution of the salt to oxidize the chromic ion, an immediate rise in the emf between two sensing electrodes in the solution was noted. This rise in the emf was not steady, and within a very few minutes it had drifted back to its initial value. It must be remembered that in aqueous solutions chromium, in its higher oxidative states, complexes with oxygen atoms to form the chromate and dichromate ions. Solutions of chromic acetate in acetic acid have a very dark green color.

CHAPTER IV

CONCLUSIONS

1. It was not possible to increase the resistance of acetic acid by the addition of acetic anhydride above that of commercial glacial acetic acid, C. P., the minimum purity of which was 99.8 per cent. The addition of the anhydride was necessary, however, to maintain this high resistance while working with the acid.

2. Lithium chloride is a suitable electrolyte for coulometric titrations of acids in glacial acetic acid. For solutions of the same strength it is more electrically conductive than the other salts tried. It is readily soluble in acetic acid and does not decompose when dissolved in the acid. Solutions are quite stable and are sensitive to changes in acidity.

3. It was not possible to quantitatively titrate an acid in acetic acid by direct oxidation of the hydrogen ion to hydrogen gas at the cathode. The results were not consistent, and both positive and negative errors of considerable magnitude were obtained.

4. Ceric ion, electrically generated from an acetic acid solution of cerous perchlorate and cerous acetate, is a satisfactory oxidizing agent for hydroquinone and metol.

For coulometric titrations of hydroquinone in acetic acid, the solution of electrolyte and reagent must contain cerous acetate in addition to the cerous perchlorate. Although the results obtained were not consistently quantitative, the percentage of error was considerably less than for titrations run in a solution containing only cerous perchlorate.

5. Consistent quantitative results for the coulometric titrations of hydroquinone and metol extracted from photographic developer solutions with ethyl acetate could not be obtained. Part of the error in the metol determinations was due to the air oxidation of the metol during the extraction procedure. It was not possible to determine the sodium sulfite by means of a coulometric titration, but the sulfite did interfere with the determinations of hydroquinone and metol.

CHAPTER V

SUGGESTIONS FOR FUTURE WORK

The possibilities for future work arising from this paper are numerous. The need for future work for the coulometric titration of acids using a lithium chloride electrolyte is self evident from the experimental data. Better results could undoubtedly be obtained if some intermediate reagent were found that could be reduced at the cathode and subsequently reduce the hydrogen ion. On the basis of previous work, however, the possibilities for coulometric titrations of weak bases in acetic acid would appear to be of more practical value. This would probably entail finding a suitable reagent which could be oxidized at the anode and then in turn neutralize the base. If the reagent itself was not a suitable conductor, an electrolyte would also have to be found to facilitate the passage of current through the solution.

As mentioned earlier, the exact effect of the cerous acetate in the coulometric titrations of hydroquinone and metol is not known, but the cerous acetate does reduce the acidity which might indirectly affect the stability of the cerous-ceric system. It was definitely found that increased temperature and excess acetic anhydride hasten the rate at

which the ceric ion is reduced to cerous ion, but these are not necessarily the direct causes of the reaction.

More research might well be conducted on the extraction of hydroquinone and metol from photographic developer solutions, and the coulometric titrations of reducing agents in these extractions. One appreciable error is the inability to extract the metol without oxidizing it. This undesirable effect might possibly be overcome by the use of an inert atmosphere.

Another field in which considerable work needs to be done is that of end point detection. The redox indicators mentioned in this paper all changed color at too low an emf (250 to 450 millivolts) to be of any value for the quantitative determinations of hydroquinone and metol; they served only to give a warning that the end point was approaching. For the cerous-ceric system an indicator is needed that changes in the 600 to 700 millivolt region.

As mentioned earlier in this paper the change in the emf near the end point was not consistent during a coulometric titration of hydroquinone or metol. In some cases the generation of a slight excess of ceric ion had a very marked effect on the emf, and in other cases there was only a slight effect. Perhaps a different reference electrode could be found to alleviate this difficulty.

Other methods of end point detection have been used

successfully for coulometric titrations in aqueous media and for volumetric titrations in acetic acid. Amperometric detection of the end point has been used quite extensively for coulometric titrations in aqueous media and in some cases in benzene and alcohol mediums. Another possibility which has been used successfully for volumetric titrations in acetic acid is that of high frequency detection of end points.

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