PART I

Iodometric Determination of Copper

SECTION I

The Use of Thiocyanate

SECTION II

The Use of Sulfate-Hydrogen Sulfate Buffers

PART II

The Use of Iodine Monochloride End-Point for the Titration of Antimony Using Ceric Sulfate, Potassium Permanganate and Potassium Iodate Solutions

PART III

The Use of Iodine Monochloride as an Indicator in the Titration of Thiocyanate with Permanganate, Iodate and Ceric Sulfate

PART IV

The Distribution of Thallium Between Isopropyl Ether and Hydrochloric Acid

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This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT REPORT

PART I

This part of the thesis reports a study of some of the limitations encountered in the iodometric determination of copper. The sulfate-hydrogen sulfate buffer was introduced for this determination. The permissible pH range for this buffer was found to be from about 0.5 to 3. It was found that the "oxygen error" was not noticeable even at the lower limits of this range and the end-points were stable enough for a normal titration. Chlorides and nitrates do not cause serious errors. The procedure using the sulfate buffers and thiocyanate was tested against pure copper and copper alloys which contain interfering constituents. The results show that the percentage difference from the theoretical is less than one part per thousand.

The effect of adding thiocyanate at various points during the titration, the amount required, and the necessity of using pure thiocyanate were studied and reported. A study of the difference of the iodide and thiocyanate end-points was made. It was observed that a small excess of thiosulfate could be back titrated. Several wetting agents as well as shellac were tried in an attempt to protect the cuprous iodide during this back titration.

PART II

A study has been made of the titration of antimony with permanganate, ceric sulfate, and iodate solutions, using the iodine monochloride as the indicator. The oxidizing solutions were standardized against Bureau of Standards arsenious oxide by two methods which agreed within one part per thousand. In the analysis of an antimony ore, the amount of antimony found was about three parts per thousand too high of that present.

ABSTRACT REPORT (CONTINUED)

PART III

A study of the titration of thiocyanate has been made in which permanganate, iodate and ceric sulfate were used as the oxidizing agents, and iodine monochloride used as the indicator. Results show that iodate titration gives results within one part per thousand, the permanganate titration within three parts per thousand, and ceric sulfate titration was not satisfactory. Potassium thiocyanate can be used as a primary standard.

PART IV

This report is a progress report on the study of the distribution of thallium between isopropyl ether and hydrochloric acid solution. The method for purifying the ether and the method of the analyzing the ether and water layers is given. There is not sufficient data to draw any definite conclusions as to the distribution curve nor the extracted species. PART I

Iodometric Determination of Copper

ACKNOWLEDGMENT

The author desires to express his great appreciation to Professor E. H. Swift. This research project was under the guidance of Professor Swift. He was most generous with his professional advice and experience. The author expresses his indebtedness to Professor Swift for his untiring patience, encouragement and humanism. The author also wishes to express his appreciation to Professor Richard Eadger for supplying the wetting agents used in this study, and to Professor Howard Lucas for his helpful suggestions in the purification of isopropyl ether. Mr. John Gryder was most helpful with his suggestions during this study. Acknowledgment is made to Mr. David Beavan for the use of his unpublished report on "<u>The</u> <u>Determination of Thiocyanate</u>", and to Mr. Thomas Lee for his report on <u>The Distribution of Thallium Between Hydrochloric Acid and Isopropyl Ether</u>.

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SECTION I

The Use of Thiocyanate

INTRODUCTION

The iodometric determination of copper is widely used; this method consists of treating a solution of cupric salt with a soluble iodide which precipitates the copper as slightly soluble cuprous iodide, and titrating the tri-iodide with a standard thiosulfate solution. This is a very simple and quick method, however, it has had certain limitations which have limited the accuracy of the method.

The object of Section I of this thesis is to report a study of some of these limitations and of the conditions under which quantitative results can be obtained. A study of the factors listed below has been made including the use of sulfate-hydrogen sulfate buffers. Such buffers have a good efficiency in pH range of 2.0 to 2.5 and are effective over a pH range of about 0.5 to about 3. Thus experiments have shown that at a pH of 2.0 the sulfate to hydrogen sulfate ratio is 3; while at a pH of 2.5 the ratio is approximately 9.5.

The various limitations and conditions which have been studied are as follows:

1. The addition of a soluble thiocyanate at various times during the course of the titration of the tri-iodide with thiosulfate, including variations in amounts of potassium thiocyanate added, the effect of having ammonium ion present at various pH values, and the effect of impurities in the thiocyanate.

2. The absorption of iodine by the cuprous iodide precipitate in a potassium iodide solution with a pH of about 2.2 to 2.5 and the effect of the presence of starch, and of certain wetting agents.

3. The effect of a change of the pH in sulfate buffers upon the end-points with and without thiocyanate, hereafter called the iodide and thiocyanate end-points respectively.

4. The application of the sulfate buffers to the analysis of pure copper and copper alloys, with and without the presence of interfering constituents.

5. Certain other factors involved in the method or in the experimental study such as: the removal of nitric acid from solutions by fuming with sulfuric acid. The effect of the presence of nitrates and chlorides during the titration with thiosulfate. The absence of the oxygen error in the sulfate buffers over a pH range of about 0.5 to 2.5.

PART I

SECTION I

The Use of Thiocyanate

INTRODUCTION

The use of thiocyanate near the end of the thiosulfate titration as suggested by Foote and Vance (6) has been widely recommended. Foote and Vance stated that when thiocyanate was used the additional thiosulfate required was about 0.15 ml of a 0.1 N solution. They stated that the error in the absence of thiocyanate is "due partly to absorption of iodine by cuprous iodide", and that "cuprous thiocyanate is more insoluble than cuprous iodide, thus tending to make the reaction more complete". No experimental evidence was given to indicate the relative importance of these two effects; nor is there a complete statement of the conditions under which the difference of 0.15 ml was observed. The experiments reported in this thesis were made as a part of an investigation of these effects and of other factors involved in the method.

In these experiments the solutions were buffered to pH values of from 2.0 to 2.5 by means of sulfate and hydrogen sulfate. The sulfatehydrogen sulfate system was used because the complex-ion formation observed by Crowell (3) in other systems was largely eliminated and because, as will be shown in another part of this thesis, the sulfate buffer system can be used to maintain pH values at which neither hydrolysis of the cupric ion nor oxygen error cause serious variations.

EXPERIMENTAL

The sodium thiosulfate solutions were prepared and stored

according to the instructions given by Swift (13). These solutions were standardized, before and after each series of experiments, against Bureau of Standards potassium dichromate; the procedure of Bray and Miller (1) was used. Three determinations were made, and the maximum deviation was less than one part per thousand; volume burets were used exclusively. Some of the solutions were used over a period of 30 to 60 days, but in no case was a change in normality as much as one part per thousand observed.

The copper sulfate solutions, approximately 0.1 formal, were prepared by dissolving cupric sulfate pentahydrate in water or be treating Bureau of Standards copper. Sample No. 45 A having a melting point of 1083° C, with just enough dilute nitric acid to cause complete solution and then fuming with sulfuric acid; the sulfuric acid was then neutralized with standard ammonium hydroxide, and additional ammonium sulfate was added when necessary. These solutions were made approximately 1.8 formal in ammonium sulfate; this concentration was selected because in 50 ml of the solution the sulfate present would be equivalent to that formed by neutralizing 5 ml of 18 formal sulfuric acid with ammonium hydroxide; this volume of sulfuric acid is frequently recommended for the removal of the nitric acid used in dissolving copper ores or alloys. The pH values of the cupric sulfate-ammonium sulfate solutions were approximately 3.6 at 20° C. The pH of the solution to be titrated was adjusted by addition of sulfuric acid or ammonium hydroxide. The pH measurements were made with a Beckman glass electrode pH meter.

Various brands of reagent grade potassium thiocyanate were used. Since in some cases this material showed evidence of decomposition and

required a significant correction because of reaction with iodine, recrystallized material was used in the later experiments.

All other chemicals used were of reagent grade; they were tested for reaction with iodine and iodide and appropriate corrections were made when necessary.

TITRATION PROCEDURE

A portion of the copper sulfate solution, usually 50 ml, was pipetted into a 200 ml conical flask and sulfuric acid or ammonium hydroxide added to give the desired initial pH. Three grams of potassium iodide, iodate and iodine free, were added in 5 ml of water, then while swirling the mixture thiosulfate was added until the tri-iodide color became indistinct. Five ml of starch solution were added and the titration was continued until the starch-iodine color disappeared. This endpoint was recorded and will be designated the iodide end-point. Four grams of potassium thiocyanate were added and the titration continued until the color was again bleached. This end-point will be designated as the thiocyanate end-point.

The addition of solid potassium thiocyanate at or near the iodide end-point imparts a blue purple color to the mixture, this is not the characteristic starch color, furthermore this color will form in the absence of the starch upon adding thiocyanate at the equivalence-point. If the thiocyanate is added at the iodide end-point, in the presence of starch, approximately 0.15 ml of 0.1 N thiosulfate will be required to remove the color. If added at the equivalence-point, without starch, the color will form and will last for from about 30 to 40 seconds; if added at the iodide end-point, without starch, the color will be less intense and will last from about 10 to 15 seconds, if starch is added at this point the ordinary color will appear.

This color will form in the presence of bromide and (or) chloride as well as with iodide. It is possible to form this color in the complete absence of halides.

It is well known that the thiocyanate can not be added early in the titration and Foote and Vance (6) recommended that the thiocyanate be added near the end of the titration. Experiments were made in which the thiocyanate was added at various points during the titration and the results are recorded in Table I. The end-points were accurately determined by the general procedure and then the same solutions were used for these experiments. The iodide end-point was found to be 45.08, and the thiocyanate was 45.18 ml of 0.1 N thiosulfate solution.

TABLE I

ADDITION OF POTASSIUM THIOCYANATE AT VARIOUS POINTS

Expt.	Thiocyanate added at ml of thiosulfate	Thiocyanate end-point
l	31.00	44.91
2	35.00	45.12
3	40.00	45.15
4	45.00	45.18
5	45.05	45.18
6	45.18	45.21
7	45.20	45.20

In experiment 7, Table I, when the thiocyanate was added a definite color appeared and lasted about one minute. The results in Table I show

that the thiocyanate should not be added too early during the titration, however, it can be added as early as 5 ml before reaching the iodide endpoint without serious trouble. The results seem to indicate a trend to over run the equivalence-point if the thiocyanate is added much beyond the iodide end-point.

Foote and Vance (5) recommended that four grams of potassium thiocyanate be used but gave no basis for this amount. The following experiments were made in which the amounts of potassium thiocyanate varied from 0.5 to 8 grams. The results are recorded in Table II. The results show a definite trend toward low values for the thiocyanate end-point below 2 grams of thiocyanate, above this amount the end-points were all the same. The end-points, using four grams of thiocyanate, were accurately determined by the general procedure, the iodide was found to be 44.95 and the thiocyanate was 45.08 ml of 0.1 N thiosulfate solution.

TABLE II

Expt.	Thiocyanate grams	End Iodide	l-Points Thiocyanate	Delta
1.	8	44.95	45.08	0.13
2.	4	44.95	45.08	0.13
3.	2	44.95	45.08	0.13
4.	l	44.95	45.06	0.11
5.	0.5	44.95	45.01	0.06

ADDITION OF VARIOUS AMOUNTS OF POTASSIUM THIOCYANATE

Each volume represents the average of three determinations in which the maximum deviation from their mean was 0.02 ml. The term "delta" in this

thesis refers to the difference in ml of the iodide and thiocyanate endpoints, this difference will be called delta hereafter in this thesis.

Since it was observed that the difference in the end-point s changed from one brand of thiocyanate to another the purity of the thiocyanate was investigated. It was observed that in some cases the thiocyanate reacted with a tri-iodide solution when the two were mixed together. Experiments were made in which four grams of the thiocyanate, that was to be tested, were added to standard tri-iodide solution, then the excess triiodide was titrated with 0.1 N thiosulfate solution. These experiments were made in water solutions and in solution 1.8 formal in ammonium sulfate and with sufficient sulfuric acid to have a pH value of about 2.5. This solution is called "B" solution.

TABLE III a

REACTION OF THIOCYANATE AND TRI-IODIDE

Water Solution

"B" Solution

	ml of tri-iodide solution	ml o thio rea	of O.l N osulfate quired	ml of tri-iodide solution	ml th r	of O.l N iosulfate equired
Expt.		with KCNS	without KCNS		with KCNS	without KCNS
1.	12.50	1.76	2.18	12.50	2.06	2.18
2.	11.24	1.58	1.96	17.90	2.98	3.15
3.	10.00	1.33	1.74	12.50	2.05	2.20
4.	12.70	1.78	2,22			

<u>Water Solution</u>				"B" Solution			
Expt.	KCNS & KI	with KCNS	without KCNS	KCNS & KI	with KCNS	without KCNS	
1.	0.10	2.75	0.05	0.04	1.89	0.04	
2.	0.10	2.50	0.05	0.04	2.00	0.04	
3.	0.11	2.40	0.04	0.04	1.97	0.04	

TABLE III b

VOLUME OF TRI-IODIDE REQUIRED TO GIVE STARCH-IODINE COLOR

The experiments in Table III a, a portion of tri-iodide solution was taken and to one was added four grams of the thiocyanate that was to be tested and the solution was titrated with O.1 N thiosulfate solution, using starch as indicator. The tri-iodide was approximately 0.01 N in iodine. The results show that without thiocyanate, 1 ml of the tri-iodide solution was equivalent to 0.133 ml of 0.1 N thiosulfate solution, both in the water and buffered solutions. The experiments in Table III b show the volume of the 0.01 N tri-iodide solution required to give the starch-iodide color in water and buffered solutions. The results show that the solutions without thiocyanate required less tri-iodide solution than those with the thiocyanate presence. The addition of three grams of potassium iodide seems to stabilize the reaction between the tri-iodide and thiocyanate in the water solutions but had no effect in the buffered solutions. It is to be noted that the buffered solutions seem to stabilize the reaction between the tri-iodide and the thiocyanate. The results indicate clearly that this thiocyanate reacted with the tri-iodide solution. The thiocyanate was recrystallized from hot water and dried at 110° C and stored in a glass stoppered bottle in a dark place; this product did not react with the above

tri-iodide solution. Experiments were made with the recrystallized and stock thiocyanate and it was observed that the differences in the endpoints were in agreement with the amount of tri-iodide that reacted with the stock thiocyanate.

Experiments were made to prepare an ammonium free system and then to add the ammonium ion at various points during the titration. This system was prepared by dissolving sufficient copper sulfate pentahydrate, sodium hydroxide and sulfuric acid to give a solution, 0.1 formal in cupric sulfate, 1.3 formal in sodium sulfate and a pH value of about 2.5. The ammonium ions were added as ammonium iodide. The results of these experiments are recorded in Table IV. Experiments 1 through 6 were ammonium free system; 7 through 12 were those where equivalent amount of ammonium iodide was used in place of three grams of potassium iodide. These values are the results of two determinations of which the maximum deviation was of the order of 1 part per thousand. The results show that the presence of ammonium ion effect the difference in the iodide and thiocyanate end-points. The ammonium free system is not recommended because of the solubility of sodium sulfate in the sulfate buffers and the end-points are not as sharp due to the colloidal nature of the solution.

Expt.	pH	Iodide end-point	Thiocyanate end-point	Delta Difference in end-points
1.	4.7	37.35	38.40	1.05
2.	4.0	44.45	44.49	0.04
3.	3.0	44.47	44.047	0.00
4.	2.1	44.50	44.53	0.03
5.	1.5	44.50	44.55	0.05
6.	0.5	44.49	44.51	0.02
7.	4.7	No rea	al end-point	
8.	4.0	43.70	44.00	0.30
9.	3.5	44.38	44.48	0.10
10.	3.0	44.40	44.50	0110
11.	2.0	44.40	44.50	0.10
12.	1.0	44.47	44.53	0.06

TABLE IV

THE EFFECT OF AMMONIUM IONS ON THE DIFFERENCE IN END-POINTS

It seems logical to assume that the equilibrium for the reaction of cupric copper in the presence of excess iodide should be well to the right since the tri-iodide that is formed is reduced by titration with thiosulfate to iodide, and furthermore the cuprous iodide is precipitated from the solution. It has been found that the over-all reaction in the iodometric determination of copper does not go to completion to the extent that the triiodide which is titrated against thiosulfate is not quantitatively equal to the copper originally present in the solution. This difference has been the object of numerous investigations. For a more complete discussion and list of investigators see Swift (14). It has been observed that the titration should be made in a solution with sufficient hydrogen ion concentration to prevent or repress the hydrolysis of the cupric ion.

As is shown in this thesis there are factors that effect the difference in the iodide and thiocyanate end-points. The following have been studied and are reported here.

1. The absorbed iodine on the cuprous iodide is not completely removed by the thiosulfate in the presence of excess iodide and starch.

2. There is not complete reduction of the cupric copper by the iodide. Some of the cupric copper may be tied up as a complex-ion or mechanically entrapped by the cuprous iodide. Experiments to determine the ratio of cupric copper to cuprous copper in the precipitate by the method of Walker and Dover (10) were not successful.

3. At or near the upper limits of the pH range some of the cupric copper may be hydrolyzed; results show that the difference in end-point are larger than in the lower part of the pH range. It has also been pointed out that the presence of ammonium ions will effect this difference.

4. The formation of the starch-iodine complex and the absorption of this complex on the cuprous iodide. This factor is of a lesser degree of importance but as results will show it is a detectable factor with a fair degree of consistency.

The evidence most frequently used for the support of the theory that iodine is absorbed on the cuprous iodide is the color of the precipitate at the iodide end-point. Experiments were made in which 1.9 grams of cuprous iodide, known to contain iodine, was dissolved in potassium iodide, the iodine was titrated with thiosulfate using starch as an outside

indicator, then a slight excess of thiosulfate, one drop of 0.1 N, was added and the cuprous iodide was precipitated by adding water. The precipitate was not white but a gray-brown in color. The precipitate was separated from the solution, washed with water, ethyl alcohol and finally with diethyl ether. The precipitate was again dissolved in fresh potassium iodide solution, negative iodine test with starch. This data seems to indicate that the cuprous iodide is not white although it does not give a starch-iodine color when dissolved in a potassium iodide solution. This seems to indicate that the cuprous iodide is not white although it does not give a starch-iodine color when dissolved in potassium iodide solution.

In a series of experiments the cuprous iodide was separated from the titrated solutions at the iodide end-point and points in which an excess of thiosulfate had been added. The mixture was centrifuged until the filtrate was clear then the filtrate was decanted, the precipitate was washed with about 5 ml of the sulfate buffer, this washing was added to the filtrate. The precipitate was dissolved in potassium iodide solution, the liberated iodine was titrated with 0.1 N thiosulfate; the filtrate was titrated with standard tri-iodide solution. The results are recorded in Table V. In experiments 1 through 9 the starch was added at the normal time, experiments 10 and 11, the starch was added after the precipitate had been separated from the filtrate and dissolved in the potassium iodide solution. The iodide end-point was found to be 44.55 and the thiocyanate was 44.68 ml of 0.1 N thiosulfate.

The results seem to indicate that if starch is present when the cuprous iodide is separated from the filtrate some absorbed iodine is carried

along with the precipitate. The results show that the precipitate does contain iodine or cupric copper at the iodide end-point. The experiments gave no indication as to whether the difference was due to iodine or cupric copper or both.

TO A TOT TO	17
TABLE	V

TITRATION OF CUPROUS IODIDE IN POTASSIUM IODIDE SOLUTION

THIOSULFATE

FILTRATE

Expt.	Titrating solution	Excess	Cuprous iodide	Tri-iodide solution	thiosulfate equivalent
1.	44.55	0.0	0.15	0.00	0.00
2.	44.77	0.22	0.13	0.20	0.09
3.	44.83	0.28	0.12	0.39	0.17
4.	44.95	0.40	0.08	0.79	0.34
5.	45.05	0.50	0.03	0.90	0.38
6.	45.10	0.55	0.05	1.10	0.47
7.	45.20	0.65	0.08	1.45	0.62
8.	45.30	0.75	0.05	1.53	0.65
9.	45.50	0.95	0.05	2.00	0.95
10.	45.05	0.50	0.00	0.85	
11.	45.30	0.75	0.00	1.50	

It was observed that a small excess of thiosulfate could be added to the titrated solution, the cuprous iodide removed from the mixture and the excess thiosulfate could be titrated with a standard tri-iodide solution. It is true, as the data in Table VI show, only if an excess of less than one ml of thiosulfate is added in the sulfate buffers. In these experiments the iodide end-point was accurately determined by the general procedure, then the same solutions were used for all other experiments in this series. The iodide end-point was 49.85 ml of 0.1 N thiosulfate solution. The data in Table VI show that below one ml of excess thiosulfate the final end-point is in good agreement with the thiosyanate end-point. When one ml of 0.1 N thiosulfate was added the thiosulfate showed a tendency to decompose. The time for the titration was from about 2 to 5 minutes.

TABLE VI

BACK TITRATION OF EXCESS THIOSULFATE IN A SULFATE BUFFER

	THIOSULFATE	SOLUTION	TRI-IODIDE S	OLUTION
Expt.	Total Vol.	Excess	With Cul present	Without CuI
l	49,85	0.00	0.13	0.05
2	49.95	0.10	0.23	0.10
3	50.10	0,25	0.35	0.25
4	50.35	0.50	0.63	0.50
5	50,85	1.00	1.17	1.07

These values are from the average of two determinations in which the deviation of each was of the order of one part per thousand. The triiodide was standardized against the thiosulfate solution and the normality adjusted so one ml of thiosulfate would be just equal to one ml of the triiodide solution.

It had been reported by Caldwell (2) that a small amount of shellac in an alcoholic solution would give a sharper iodide end-point and prevent the coprecipitation of the starch-iodine complex along with the cuprous iodide. Experiments were studied in which several wetting agents were used as well as "Siller Pure Shellac" to determine the effect of these agents upon the iodide end-point. The shellac was added at the iodide end-point, 2 ml before reaching the iodide end-point and before adding the potassium iodide. The end-point was determined by the general procedure. The results are recorded in Table VII. The iodide end-point was 43.83; the thiocyanate 44.03 ml of 0.1 N thiosulfate.

TABLE VII

THE EFFECT OF ALCOHOLIC SHELLAC ON THE IODIDE END-POINT

End-points	Without Shellac	Shellac added before KI	Shellac added at iodide e-p	Shellac added 2 ml before iodide e-p
Iodide	43.83	43.85	43.80	43.80
Thiocyanate	44.03	44.03	44.05	44.05
Delta	0.20	0.18	0.25	0.25

It is the opinion of this experimenter that the iodide end-point is not as sharp with the shellac as without it. Floating material, may be shellac, interfered with sharpness of the end-point. Some of the solutions were centrifuged in an attempt to clear the solutions. The addition of thiocyanate to the mixture gave the ordinary color at the iodide end-point and as the results show the end-points agree with or without the shellac. The results were taken from three determinations. The agreement with the shellac is not as good as without the shellac. The thiocyanate end-points are sharp and stable for about 10 to 15 minutes. It was observed that the shellac particles absorbed iodine as little blue streamers were observed coming from them upon standing 3 to 5 minutes. The shellac is definitely not recommended for the sulfate buffers. The shellac causes a film to form on the glassware which was very troublesome.

In another attempt to find a suitable agent to protect the cuprous iodide so it would not be necessary to remove it from the mixture during the back titration; several wetting agents were employed without success. The results show that if excess thiosulfate is added and back-titrated with standard tri-iodide solution the final end-point agrees more closely to the iodide end-point than to the thiocyanate end-point. The agents were added at various points during the titration, the results were averaged and recorded in Table VIII. The iodide end-point was previously determined and was found to be 44.95 ml of 0.1 N thiosulfate.

TABLE VIII

	THE EFFECT ()F WETTING	AGENTS ON THE	IODIDE EN	D-POINT	
	THIOSULFAT	Έ	BACI	K-TITRATIC	N	
No.	Total S203	Excess	I3	S203	Agents	
1.	46.07	1.12	1.25	1.20	Tween 20	
2.	45.65	0.70	0.75	0.71	Tween 20	
3.	45.65	0.70	0.55	0.52	Morpholin	e
4.	45.50	0.55	no real e	end-point,	pH 6.5 tet pen	ra-ethylene ta-amine
5.	44.95	0.00	0.00	0.00	polyvinyl	alcohol
6.	45.50	0.55	0.55	0.52	polyvinyl	alcohol

These agents were most difficult to work with in these highly concentrated salt solutions, in most cases the agents precipitated out of

solution and they would be in some cases colored with absorbed iodide. Two ml of 10% solutions were used in all cases where the wetting agents were employed.

SUMMARY

A study of the use of thiocyanate has been made. It has been found that the addition of 2 grams of potassium thiocyanate at the iodide end-point will give a volume of thiosulfate which is within one part per thousand of the correct volume. The thiocyanate should be tested for purity; this can be done by the absence of reaction with tri-iodide, or by using freshly recrystallized thiocyanate. The addition of thiocyanate at the equivalence-point imparts a color to the mixture which disappears without the addition of thiosulfate. A small excess of thiosulfate can be backtitrated with standard tri-iodide solution if the cuprous iodide is removed from the mixture. Several wetting agents as well as alcoholic shellac were used without success in an attempt to protect the cuprous iodide during the back-titration. It was observed that the presence of ammonium ion affected the iodide end-point. In an ammonium free system the iodide end-point was essentially the same as the thiocyanate end-point. This system is not recommended because of the solubility of sodium sulfate in the sulfate buffers and the collodial nature of the solution at the end-points.

SECTION II

The Use of Sulfate-Hydrogen Sulfate Buffers

PART I

SECTION II

The Use of Sulfate-Hydrogen Sulfate Buffers

INTRODUCTION

The pH range within which the iodometric determination of copper can be made, and the buffer system employed for maintaining this range, have been the subject of numerous investigators (3,4,5,6,11,14). There seems to be general agreement that in the absence of interfering elements, such as arsenic, the minimum pH limit is determined by an increasing "oxygen error". There does not seem to be agreement as to the minimum value of this pH limit, since procedures are to be found in which it varies from 3.7, established by acetate buffer, to whatever value is obtained by the use of not more than 2 ml of concentrated mineral acid in a volume of 50 ml. As regards to the maximum limit there seems to be uncertainty both as to the value of the limit and the factors establishing it. The statement is made in a recent text (12) that the reaction between cupric and iodide ions is "catalyzed by hydrogen ions and the assumption that equilibrium conditions obtained during the titration is justified only if the pH is below 4.5". Both Park (11) and Crowell (3) have shown that the maximum limit is influenced by the buffer system used when that system contains constituents which may cause a precipitate or form unionized compounds, and Crowell has found evidence of the latter with the anions of the organic acids commonly used as buffer agents for this titration.

Since sulfuric acid is commonly used to displace the nitric acid used in dissolving copper ores or alloys, and since there is no evidence of

cupric complexes in sulfate solution, it seems worth while, first, to establish the minimum and maximum pH limits permissible in such solutions and, secondly, to determine the effectiveness with which these limits could be maintained by the use of a sulfate-hydrogen sulfate system.

There are presented below the experimental studies of the pH limits in sulfate solutions, the magnitude of the resulting errors on exceeding these limits, the effect of the presence of certain anions, and test analysis with certain alloys.

TABLE I

THE EFFECTIVE pH RANGE IN SULFATE BUFFERS

EXPT.	H2S04		pH VALUES			THIOSULFATE			
	mi added 6 N	Initial	Iodide e-p	Thiocyanate e-p	Iodide e-p	Thiocyanate e-p	Delta	Maximum deviation	
la	0.00	3.60		6.15	44.59	44.97	0.38	0.05	
2a	0.30	2.45		2.56	45.03	45.17	0.14	0.01	
3a	0.50	2.13		2.30	45.05	45.18	0,13	0.00	
4a	1.0	1.80		2.10	45.06	45.20	0.14	0.02	
5a.	2.5	1.45		1.60	45.09	45.20	0.11	0.00	
6a	6.0	1.00		1.15	45.09	45.20	0.11	0.02	
7a	15.0	0.49		0.69	45.10	45.20	0.10	0.00	
lb	0.00	3.62	6.05	6.05	43.60	43.95	0.35	aaa aaa	
2ъ	0.05	3.15	3.41	3.37	43.80	44.05	0.25	0.00	
3b	0.10	2.91	3.11	3.08	43.83	44.05	0.22	0.02	
4b	6.0	1.00	1.27	1.20	43.90	44.03	0.13	0.00	
5b	15.0	0.50	0.77	0.70	43.95	44.05	0.10	0.05	
6ъ	4.15(18F)) 0.0	esté dita	0.37	43.90	44.03	0.13		
7b	5.0 "		etta esti-		43.95	44.10	0.15		
85	25.0 "	sco. erañ	970 G19	600 een	44.10	Decomp.		905 685	
9Ъ	30.0 "	9000 6000			44.60	12		6559 GLGD	

THE PERMISSIBLE pH RANGE

The data collected in Table I show the effect of making the titration at various pH values. This data has been selected from over ninety titrations. Duplicate, in many cases triplicate and more were made except for the

last four experiments shown in Table I. The maximum deviations of such titrations are shown in the last column of the table. Although the concentrations of the copper sulfate solutions used in these experiments were not established exactly it is believed, as the results of the experiments cited below, that the volumes obtained at the thiocyanate end-point when the initial pH value lie between 3.15 and 0.5 are within one part per thousand of the correct volume of thiosulfate. The extreme drop in hydrogen ion concentration in the absence of added acid in experiments la and lb is probably due to two causes: first, the thiosulfate solution was stabilized by the addition of 0.1 gram of sodium carbonate per liter as recommended by Kilpatrick and Kilpatrick (8), and secondly, the removal of the acidity contributed by the hydrolysis of the cupric ion. This latter effect was confirmed by experiments in which it was found that a pure cupric sulfate solution. approximately 0.1 formal, had a pH of 4.06, but that after addition of potassium iodide and titration with thiosulfate without the added carbonate the pH at the iodide end-point was 5.35.

The experiments indicate that the maximum initial pH limit with the sulfate system is approximately three (3.0) since above that value so little acid is present that inadequate buffering action is obtained. The results with the experiments at low pH values are surprising in that they indicate that so long as a significant amount of sulfate is present no significant deviations are observed. For example, in experiment 6b, where 4.15 ml of 18 formal sulfuric acid were added, the calculated ratio of hydrogen sulfate to sulfate is 10 to 1 yet the volume of thiosulfate is the same as at the higher pH values; with 5 ml of 18 formal sulfuric acid, experiment 7b, which should

represent a solution of hydrogen sulfate with no excess sulfate, the thiosulfate used for the thiocyanate end-point indicates an upward trend. With larger excess of 18 formal sulfuric acid decomposition of thiocyanate occurred. The abnormally high hydrogen ion activity of these solutions is attributed to the high ionic strength of the solutions and is in agreement with the trend observed with sulfate-hydrogen sulfate by Jaffreys and Swift (7).

OXYGEN ERROR

In the general procedure no effort was made to use air or oxygen free solutions, yet in the time required for a normal titration, 2 to 5 minutes, no appreciable oxygen error is indicated, only after 5 ml of 18 formal sulfuric acid have been added are deviations observed. On stoppering the flasks containing the titrated solutions and allowing them to stand a marked difference was observed in the time required for a return of the starchiodine color. With no added acid and an initial pH of 3.6, no return of color was observed even after 24 hours; with initial values of 1 to 2 the thiocyanate end-point was stable for from 5 to 10 minutes. In all cases where the pH value was below 3.6, the time required for the return of the starch-iodine color was directly proportional to the pH value. It is to be noted that the difference between the iodide end-point and the thiocyanate end-point decrease as the pH is decreased to the value of about 1.5 to 1.0, therefore if one is not to use thiocyanate more accurate values are obtained nearer the lower limit. The results of a study of the causes of the difference between the two end-points have been presented in another section of this thesis. In some of the experiments the solutions were saturated with carbon dioxide, the containers "swept out" with carbon dioxide and then titrated, the results were the same as those with air saturated solutions.

CONFIRMATORY ANALYSIS OF PURE COPPER

The data in Table II was obtained by the analysis of weighed samples of Bureau of Standards copper, sample No. 45 A. Although this is a melting point standard it was assumed to be pure copper since the melting point (1083° C) agrees with that given in the International Critical Tables for pure copper, and since six electrolytic determinations gave 100.06% copper with and average deviation from the mean of 0.02%. The samples were dissolved in a minimum amount of diluted nitric acid, 5.5 ml of 18 formal sulfuric acid added, the mixture fumed, diluted to 30 ml, boiled, 15 formal ammonium hydroxide added until the first perceptible blue, then 1 ml of 6 normal sulfuric acid added and then diluted to 50 ml. The pH of this solution was approximately 2.2. The solution was titrated as outlined in the general procedure. The results obtained indicate that under the conditions of this procedure the volume of thiosulfate found at the thiocyanate end-point can be used without a correction factor and that pure copper is a satisfactory primary standard for thiosulfate solutions. The iodide end-point gave results which, while having an average deviation from their mean of only 0.05%, averaged 0.34% low. If the iodide end-point is to be used for the standardization of the thiosulfate solutions a correction factor should be used or the solution should be used only for the titration of copper solutions. These conclusions are in agreement with those reached by Crowell (3).

TABLE II

ANALYSIS OF PURE COPPER USING SULFATE BUFFERS

EXPT. <u>THIOSULFATE</u>				COPPER			DEVIATION	
	Iodide end-pt	Thiocyanate end-point	<u>Taken</u>	Fc Iodide	Thio- cyanate end-pt.	-Iodide end-point values	Thiocyanate end-point values	
l	47.40	47.51	0.3115	0.3108	0.3117	-0,23	0,00	
2	47.55	47.70	0.3128	0.3118	0.3127	-0.32	-0.03	
3	47.30	47.45	0.3114	0.3101	0.3111	-0.42	-0.10	
4	425 add	47.60	0.3120	uce cms	0.3121	com exter	0.03	
5	which earths	47.30	0.3111	and alley	0.3110	0607 MBN	-0.03	
6	45.37	45.52	0.2902	0,2891	0,2900	-0,38	-0.07	
7	45.38	45.52	0.2901	0.2892	0.2900	-0.31	-0.03	
8	45.45	45.60	0.2906	0,2896	0.2906	-0.34	-0.00	
9	45.55	45.70	0.2913	0,2902	0.2913	-0.38	0.00	
Normality of thiosulfate, Expt. 1 to 5,					Average	-0.3/	-0.02	
0.10	314: Expt.	6 to 9. 0.1002	my or age	0.14	-0.0~			

THE EFFECT OF CERTAIN CONSTITUENTS

There has been some uncertainty as to the effect of chloride ion on this titration. Moser (9) claimed it to be undesirable, while Kolthoff (8) found that a slight concentration of hydrochloric acid was not troublesome; he attributed the effect of high concentration to the formation of the cupricchloride complexes. The experiments in Table II indicate that up to 5 grams of sodium chloride can be added to the sulfate buffers without serious errors in the end-points.

TABLE III

Expt.		NaCl Added grams	THI Iodide end-point	IOSULFATE Thiocyanate end-point	Delta
	a	0	44.55	44.70	0.15
I	b		44.52	44.68	0.16
	с		44.55	44.70	0.15
	a	1.0	44.53	44.70	0.17
II	Ъ		44.52	44.68	. 0.16
	С		44.55	44.68	0.13
	a	2.0	44.51	44.70	0.19
III	b		44.51	44.70	0.19
	с		44.51	44.70	0.19
VI	a	5.0	44.50	44.70	0.20
	b		44.52	44.68	0.16
	с		44.55	44.70	0.15

THE EFFECT OF CHLORIDE IONS

The effect of adding sodium chloride, as shown by the data in Table III has no effect on the sulfate buffers up to 5 grams of sodium chloride in 50 ml of solution; this being the limiting factor which is due to the solubility of the salts.

The effect of certain metallic elements in the sulfate buffers is considered since such elements may be found in small amounts in copper alloys and ores and which their higher oxidation states may oxidize iodide to iodine. These elements are, iron, arsenic and antimony. In order to ascertain their effect in sulfate buffers the experiments were made and the results recorded in Table IV. The initial pH value was approximately 2.4, this value was obtained by the use of 90 millimoles of ammonium sulfate and 1 millimole of sulfuric acid. An increase of about 0.1 ml of 0.1 N thiosulfate was observed when 6 mg of iron was added as ferric chloride, this was with or without phosphate being present. However, if the titrated solutions were allowed to stand much less iodine formed in the solution containing the phosphoric acid. Antimony and arsenic caused no significant effect in the amounts used which were larger than those likely to be present in copper alloys.

TABLE IV

THE EFFECT OF CERTAIN METALLIC ELEMENTS

EXI	ρΤ.	ELEMENT	AMOUNT OF	THI	OSULFAT E Thiocvanate	-	THIOCYANA END-POIN	ATE VT
			ADDED mg	End-point	end-point	After 5 min	After 10 min	After 75 min
	a		0.00	48.85	49.00	49.05	49.05	49.05
I	b	Fe	0.6 mg	48.85	49.00	49.15	49.15	49.15
	с	Fe	6.0	48.90	49.10	49.65	49.95	50.15
	d	Fe	60.0	58.40	59.25	64.25	67.50	69.45
	a	Fe	0.6	48.85	49.00	49.07	49.07	
II b c	Ъ	H3P04	6.0	48.90	49.10	49.07	49.07	
	с		60.0	58.40	59.25	59.50	59.50	
	a	Sb ^v	0.6	43.98	44.12			
III	b	Sb ^v	6.0	43.98	44.11			
	с	Sb ^v	60.0	44.00	44.10			
	a	As	0.00	44.00	44.12			
778	b	As ^v	0.6	43.98	44.11			
ΤV	с	As ^v	6.0	43.98	44.12			
	d		60.0	44.00	44.12			

In the early phases of this study it was observed that the presence of small amounts of nitrates did not cause an error in the iodometric determination of copper using the sulfate buffers. It was observed that 2 ml of freshly boiled nitric acid could be added to the solution just before titrating without noticeable error. An investigation of this seems worth while since nitric acid is widely used for the dissolving of copper ores and alloys and to investigate the possibility of determining copper without the sulfuric acid fuming. The sulfuric acid fuming is considered to be a good source of error due to the spattering of the copper sulfate. The procedure consisted of treating weighed samples of pure copper, Bureau of Standards Sample 45 A, with just enough nitric acid to cause complete solution and then boiling until the volume in about 2 ml. This was diluted to about 30 ml, 10 grams of ammonium sulfate added and then boiled, cooled to room temperature and diluted to 50 ml. This solution was then titrated by the general procedure. The results are recorded in Table V. As the results indicate the presence of nitric acid does not interfere with the determination of pure copper. Experiments 4 through 12, in Table V, are alloys that contain about 10% tin, 10% lead, 0.5% iron and traces of arsenic and antimony. Although the results are not as good as those of pure copper they are comparable to those observed by the fuming method. Since a heavy white precipitate formed when the alloy was heated with nitric acid, 5 ml of concentrated hydrochloric acid were added to experiments 7, 8, and 9, and the volume concentrated to about 3 ml. Experiments 10, 11, and 12 were treated with two 5 ml portions of concentrated hydrochloric acid. The results show that the addition of the hydrochloric acid had little effect on the thiocyanate end-point.

TABLE V

DETERMINATION OF COEPER IN A NITRIC ACID SOLUTION

EXPT.	COPP	ER	THIO	SYLFATE	DELTA	pH	% DIF.
	Taken	Found	lodide end-point	end-point			
1.	0.2804	0.2803	44.18	44.40	0.22	1.72	-0.05
2.	0,2818	0.2816	44.40	44.61	0.21	1.50	-0.05
3.	0.2789	0.2788	43.94	44.16	0.22	1.65	-0.03
4.	0.4007	77.78%	49.10	49.36	0.25	1.51	-0.30
5.	0.4002	77.93	49.20	49.40	0.20	1.72	-0.16
6.	0.3998	77.86	49.06	49.31	0.25	1.83	-0.25
7.	0.4006	77.86	49.15	49.40	0.15	1.80	-0.25
8.	0.4007	77.80	49.05	49.33	0.28	1.87	-0.32
9.	0.4008	77.75	49.20	49.35	0.15	1.85	-0.38
10.	0.3998	77.91	49.15	49.34	0.19	1.50	-0.18
11.	0.3997	77.84	49.10	49.28	0.18	1.52	-0.27
12.	0.4000	77.84	49.10	49.32	0.22	1.55	-0.27

Samples 1 through 6 were treated with nitric acid only, 7 through 9 were treated with nitric and 5 ml of concentrated hydrochloric acid, the last three were treated with two 5 ml portions of concentrated hydrochloric acid.

The final phase of this part of the thesis deals with the analysis of copper alloys that contain interfering constituents; Bureau of Standards samples 63 and 37 D were selected with this in view. Sample 63 contains about 10% lead, 10% tin, 0.5% iron and traces of antimony and arsenic. Sample 37 D contains only traces of iron. The results are recorded in Table VI. The results show that even in the presence of tin and lead the sulfate buffers give results just a little more than one part per thousand.

TABLE VI

THE ANALYSIS OF COPPER ALLOYS

Expt.	SAMPLE Weight gram	COPPER Found %	THIOS Iodide end-point	SULFATE Thiocyanate end-point	Delta	% Dif.
1.	0.4408	70.79	44.45	44.58	0.13	0.01
2.	0.4019	70.74	44.53	44.67	0.14	-0.05
3.	0.4003	70.77	44.38	44.51	0.13	-0.01
4.	0.4010	70.80	44.45	44.50	0.05	0.03
5.	0.3998	70.73	44.30	44.43	0.13	-0.07
6.	0.3501	77.79	42.25	42.37	0.12	-0.10
7.	0.3510	77.93	42.40	42.51	0.11	-0.16
8.	0.3502	77.96	42.25	42.43	0.18	-0.11
9.	0.3503	77.96	42.30	42.44	0.14	-0.11

SUMMARY

A study of the effect of a change in pH value upon the iodide and thiocyanate end-points in the sulfate buffers has been made. The introduction of the sulfate-hydrogen sulfate buffer has been introduced into this determination. The permissible pH range using the sulfate buffers has been found to be from about 0.5 to 3.0. The thiocyanate end-points are stable in this range, at the lower limit the time required for a return of the starch-iodide color is about 5 minutes. The so-called "oxygen error" was not noticeable in this pH range using the sulfate buffers.

The determination of copper using the sulfate buffers and a pH value

of about 2.2 to 2.5 was tested against pure copper. Results average about 0.02% low, and about 0.05% low for alloys containing traces of interfering constituents. With alloys containing 10% tin, 10% lead and traces of iron, antimony and arsenic, the results were about 0.12% low. The presence of antimony and arsenic and a small amount (6 mg) of iron did not cause noticeable error. The presence of nitrates and chlorides did not show noticeable errors. Pure copper was determined in a nitric solution using the sulfate buffer and a pH of about 1.8 with average results of about 0.04% low. The alloy contain tin and lead showed results that were about 0.3% low.

REFERENCES CITED

- 1. Bray and Miller, J. Am. Chem. Soc. 46, 2204 (1924).
- 2. Caldwell, ibid, 57, 96 (1935).
- 3. Crowell, Ind. Eng. Chem. Anal, Ed. 11, 159 (1939).
- 4. Crowell, et al., ibid, 8, 9 (1936).
- 5. Foote and Vance, ibid, 8, 119 (1936).
- 6. Foote and Vance, J. Am. Chem. Soc. 57, 845 (1935).
- 7. Jeffreys and Swift, ibid, 54, 3220 (1932).
- 8. Kilpatrick and Kilpatrick, ibid, 45, 2132 (1923).
- 9. Kolthoff, Volumetric Analysis, Vol. II, page 429, (1929), John Wiley.
- 10. Moser, Z. Analyt. Chem. 45, 597 (1907).
- 11. Park, Ind. Eng. Chem. Anal. Ed. 3, 77 (1931).
- 12. Rieman, Neuss and Neiman, Quantitative Analysis, 2nd Ed. pp. 226 (1942) McGraw-Hill.
- 13. Swift, A System of Chemical Analysis, pp. 80 (1940), Prentice-Hall.
- 14. Swift, ibid, pp. 242.
- 15. Walker and Dover, J. Chem. Soc. Lon. 87, 1584 (1905).

PART II

The Use of Iodine Monochloride End-Point for the Titration of Antimony Using Ceric Sulfate, Potassium Permanganate and Potassium Iodate Solutions

PART II

The Use of Iodine Monochloride End-Point for the Titration of Antimony Using Ceric Sulfate, Potassium Permanganate and Potassium Iodate Solutions

INTRODUCTION

The object of this part of this thesis is to report a study of the use of the iodine monochloride end-point in the titration of antimony with the following oxidizing agents being used: ceric sulfate, potassium permanganate and potassium iodate.

Lang (4) reported that in the reaction of permanganate with tripositive arsenic the addition of a small amount of potassium iodate or iodide acted as a catalyst. Bright (1) reported that permanganate could be standardized against arsenious oxide with results that are within one part per three thousands of the Bureau of Standards sodium oxalate method if a small amount of either potassium iodate or iodide was added. Kolthoff, Laitinen and Lingane (3) reported that the normality of permanganate solution could be determined within 0.03% of the potentiometric titration of potassium iodide and potassium permanganate. It was later found by Metzler, Myers and Swift (7) that the oxidation state of the added iodine did not effect the efficiency of the catalyst. They added iodine monochloride as the catalyst and ortho-phenanthroline ferrous complex as the indicator in the standardization of permanganate against arsenious oxide. This method consists of two main steps. They are as follows:

1. The arsenious acid is quickly oxidized by the iodine monochloride in the presence of a strong hydrochloric acid, the iodine monochloride is reduced to iodine. 2. The liberated iodine is rapidly oxidized back to iodine monochloride by the standard oxidizing agent in hydrochloric acid solution that is at least 4 formal for iodate solution, and about 3.5 for permanganate and ceric sulfate.

The reaction for the above method can be expressed by the following equations:

2 ICl + H_3AsO + H_2O = I_2 + H_3AsO + 2 HCl I_2 + (0) + 2 HCl = 2 ICl + H_2O

As part of this thesis, a study of these reactions was made in which the oxidizing substance (0) represents iodate, permanganate, and ceric sulfate, and the arsenic was replaced by antimony.

Swift and Gregory (9) in a study of the iodine monochloride endpoint with some of the standard oxidizing agents suggested the use of iodine monochloride as an indicator for the standardization of permanganate and ceric sulfate against arsenious oxide. The results show that the iodine monochloride end-point would be within quantitative limitations if the hydrochloric acid concentration is at least 2 formal, better if between 3 and 4 formal at the end-point for permanganate, and at least 4 formal at the endpoint for ceric sulfate.

EXPERIMENTAL METHODS AND RESULTS

The permanganate solution was prepared by dissolving sufficient amount of reagent grade potassium permanganate to make a solution approximately 0.1 N in permanganate. The solution was boiled and allowed to stand as recommended by Swift (8). The solution was then filtered and stored in a glass stoppered bottle with a black outer coating. The solution was

standardized against Bureau of Standards arsenious oxide by the method of Metzler, Myers and Swift (6). The results are recorded in Table I. Three determinations were made for each standardization. Two standardizations were made against separate arsenious oxide solutions. The results show a maximum deviation of 0.03 ml of approximately 0.1 N solution.

The iodate solution was prepared by dissolving sufficient amount of reagent grade potassium iodate in water to give a solution approximately 0.1 N in iodate. This solution was standardized against Bureau of Standards arsenious oxide using the iodine monochloride end-point by the method of Swift and Gregory (8). The results are recorded in Table I. Three determinations were made for each standardization. Two standardizations were made against separate arsenious oxide solutions. The results show a maximum deviation of 0.03 ml of approximately 0.1 N solution. The normalities agree within one part per thousand of each other.

The ceric sulfate solution was prepared by dissolving sufficient ceric ammonium sulfate dihydrate and sulfuric acid to make a solution approximately 0.1 N in ceric sulfate and 0.5 formal in sulfuric acid. The solution was allowed to stand, sufficiently long to allow the cloudy precipitate which formed during the preparation to settle. The solution was filtered and stored in a glass stoppered bottle. This solution was standardized against Bureau of Standards arsenious oxide by the method of Swift and Gregory (9). The results are recorded in Table I.

The iodine monochloride solution was prepared by the method of Jamieson (2). The concentration of iodine monochloride was more concentrated than that prepared by Jamieson. This concentrated solution was diluted with 6 N hydrochloric acid to the desired concentration. In this study 5 ml of

0.025 formal in iodine monochloride and 6 formal in hydrochloric acid were used as an indicator.

Three determinations were made for each standardization and two standardizations were made against separate arsenious oxide solutions using different indicators. The results show a maximum deviation of 0.03 ml for the iodine monochloride and 0.05 ml when ortho-phenanthroline ferrous complex was used. The normalities agree within less than one part per thousand.

In order to save time in drying and weighing individual samples arsenious oxide solutions were prepared by precisely weighing sufficient amount of dried Bureau of Standards arsenious oxide to make a solution approximately 0.1 N in arsenite. The weighed sample was dissolved in dilute sodium hydroxide then transferred to a volumetric flask and diluted with water to the calibrated mark. This solution was used immediately since alkaline arsenite solutions are slowly oxidized. Whenever it became necessary to check the normality of one of the oxidizing solutions a fresh arsenite solution was prepared.

In testing the method to be used in the determination of antimony a solution of antimonious chloride solution was used. This solution was prepared by dissolving sufficient antimonious chloride and hydrochloric acid to make a solution approximately 0.1 N in antimony and 3 formal in hydrochloric acid. The normality of this solution was determined by the above oxidizing agents, using the iodine monochloride end-point for all determinations. The normality was checked against permanganate using the permanganate color as the indicator and against ceric sulfate using methyl orange as the indicator.

The results are recorded in Table II. Three determinations were made for each standardization with a maximum deviation of 0.05 ml of approximately 0.1 N ceric sulfate solution when methyl orange was used as the indicator, the others show maximum deviation of 0.03 ml of 0.1 N solution. The normalities show a maximum deviation of less than one part per thousand from their mean.

An antimony ore which contained 27.85%* antimony and a small amount of arsenic was analyzed by the method outlined below. The ore was made into a solution and aliquot portions of this solution were used. The sample was precisely weighed, transferred to a 300 ml conical flask, 20 ml of dilute hydrochloric acid added, warmed slowly, then 100 ml of 12 formal hydrochloric acid was added. The flask was equipped with a test tube condenser in order to prevent volatilization of the antimony. The solution was boiled until the volume had been reduced by about one third or the solution was equivalent to a constant boiling hydrochloric acid solution. The solution was diluted with an equal volume of water and transferred to a volumetric flask and diluted with 3 formal hydrochloric acid to the calibrated mark. Portions of this solution were then pipetted into an iodine flask, then sufficient hydrochloric acid added to have a concentration at the end-point of at least 4 formal for iodate and ceric sulfate and between 3 and 4 formal of permanganate. Five ml of carbon tetrachloride, free of oxidizing and reducing agents, and 5 ml of 0.025 formal iodine monochloride added. The solution was titrated with the oxidizing agent to point where the iodine color in the organic layer was indistinct. The results of these titrations are recorded in Table II. Three determinations were made with each oxidizing agent. The results show that the maximum deviation was

* 27.85 2 0.1 absolute percentage

0.03 ml of 0.1 N solution. The normality of the solution agrees within one part per thousand of their mean.

TABLE I

STANDARDIZATION OF OXIDIZING AGENTS AGAINST ARSENIOUS OXIDE

	PERM	ANGANATE	IC	DATE	CERIC	SULFATE
Expt.	Volume	Normality	Volume	Normality	Volume	Normality
la	41.75		43.45		48.05	
2a	41.78		43.48		48.07	
3a	41.78		43.45		48.08	
Ave.	41.77	0.1061	43.46	0.1019	48.07	0.09245
Normali ^{As} 2 ⁰ 3 indic	ity 3 sator -	0.08854 o-phen		0.08854 ICl		0.08881 IC1
lb	41.81		43.55		48.80	
2Ъ	41.80		43.53		48.85	
3Ъ	41.83		43.53		48.80	
Ave.	41.81	0.1061	43.54	0.1020	48.81	0.09240
Normali As ₂ 03 Indic	ity 3 2ator	0.08881 0-phen		0.08881 IC1		0.08895 o-phen

Volume of arsenious oxide solution was 50.07 ml for all determinations.

STANDARDIZATION OF ANTIMONIOUS CHLORIDE SOLUTION

	PERM	ANGANATE	IO	DATE	CERIC S	SULFATE	
Expt.	Volume	Normality	Volume	Normality	Volume	Normality	
la	41.43		43.15		47.57		
2a	41.42		43.17		47.58	×	
3a	41.43		43.15		47.57		
Ave.	41.43	0.08784	43.16	0.08790	47.57	0.08780	
Normal: oxidize	ity er	0.1061		0.1020		0.09245	
Indica	tor	MinO-4		ICL		ICI	
lb	41.39		diffe upon anot		47.59		
2Ъ	41.43		NOT AND AN		47.57		
3b	41.43		4000 MIG		47.62		
Ave.	41.41	0.08780	4007 KIDS Auga	with cash gain	47.59	0.08884	
Normal: oxidize	ity er	0.1061		653 69 5 mg		0.09245	
Indica	tor	ICL		And were still?		Methyl orange	Э

Volume of arsenious oxide solution was 50.07 ml for all determinations.

TABLE III

ANALYSIS OF ANTIMONY ORE

PERMANGANATE		NGANATE	IODATE		CERIC	SULFATE
Expt.	Volume	Normality	Volume	Normality	Volume	Normality
1.	43.30	0.1061	45.10	0.1020	49.75	0.09245
2.	43.33		45.12		49.76	
3.	43.30		45.12		49.75	
Ave.	43.32		45.11		49.75	
Percent Antimony	27.95		27.96		27.97	

The volume of the antimony solution was 50.07 for all determinations. The solution used in the permanganate titration contained 19.998 grams of ore per liter. The solutions used in the iodate and ceric sulfate titrations contained 20.002 grams per liter.

The results in Table II. show that antimony can be determined by this method. The results also show that the agent can be standardized against arsenious oxide. The results in Table III show that the percent antimony found was high by about three parts per thousand of the antimony present. This might have been due to the presence of arsenic as an impurity in the ore.

DISCUSSION

A solution of antimony chloride was used as a test solution for testing the possibility of determining antimony by the method outlined above. It was observed that the antimony found was within one part per thousand of the antimony present. In the standardization of the antimony solution against permanganate the method as recommended by McNabb and Wagner (5) with aslight

modification was used. The modification was used since the results without it gave results that were lower than those obtained by the iodate and ceric sulfate determinations. The method used in this study consisted of having a titration solution approximately 2 formal in hydrochloric acid at the end-point and cool the solution below 5° C. The results obtained with this method agreed within one part per thousand of the other determinations. The end-point was sharp and clear and the color lasted for from 30 to 40 seconds.

The iodine monochloride end-point was sharp and gave results that were within 0.03 ml of 0.1 N solution in the standardization and determination. Smith (7) has introduced dyestuff which can be used as indicators in the determination of antimony and thiocyanate with iodate as the oxidizing agent. None of these indicators were used in this study.

SUMMARY

A study has been made of the possibility of determining antimony in ore or as chlorides by using permanganate, ceric sulfate and iodate solutions as oxidizing agents. The iodine monochloride was used as the indicator. The results are within one part per thousand of each other and the antimony found is within this limit of that present. The oxidizing agents were standardized against Bureau of Standards arsenious oxide.

REFERENCES CITED

1.	Bright, Ind: Eng. Chem. Anal. Ed. 9, 577 (1937).
2.	Jamieson, Volumetric Iodate Methods, Chemical Catalog Co. (1926).
3.	Kolthoff, Laitinen and Lingane, J. Am. Chem. Soc. 59, 429 (1927).
4.	Lang, Z. Anal. Chem. 152, 197 (1926).
5.	McNabb and Wagner, Ind. Eng. Chem. Anal. Ed. 2, 251 (1930).
6.	Metzler, Myers & Swift, ibid, 16, 625 (1944).
7.	Smith, Ind. Eng. Chem. Anal. Ed. 13, 460 (1941); 14, 49 (1942).
8.	Swift, A System of Chemical Analysis, pp 293, Prentice-Hall (1940).
9.	Swift and Gregory, J. Am. Chem. Soc. 52, 901 (1930).

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PART III

The Use of Iodine Monochloride as an Indicator in the Titration of Thiocyanate with Permanganate, Iodate and Ceric Sulfate

PART III

The Use of Iodine Monochloride as an Indicator in the Titration of Thiocyanate with Permanganate, Iodate and Ceric Sulfate

INTRODUCTION

The object of this part of this thesis is to report a study of the conditions and limitations in the use of iodine monochloride as an indicator in the titration of thiocyanate with permanganate, iodate and ceric sulfate. The preparation and use of potassium thiocyanate as a primary standard was also investigated.

Kolthoff and Lingane (2) reported that potassium thiocyanate can be used as a primary standard if it is first recrystallized from water, dried to constant weight in a vacuum dessicator with phosphorous pentoxide, heated in a drying oven at 150° C for 2 hours, fused for 10 minutes at 170° to 200°C and finally cooled to room temperature in a dessicator. This potassium thiocyanate must be stored in moisture proof bottle as it will absorb moisture very quickly in air with humidity greater than 50%. These statements have been confirmed.

Some of the preliminary experiments for this study were made by Beavon (1). The method he used consisted chiefly of the oxidation of the thiocyanate with iodine monochloride in a solution of low concentration of hydrochloric acid. The liberated iodine was oxidized back to iodine monochloride with one of the standard oxidizing solutions in a high concentration of hydrochloric acid. The disappearance of the iodine color in the carbon tetrachloride layer was taken as the end-point. The equations for this method are as follows:

6 ICl + CNS + 4H₂0 = HCN + HSO + 3I₂ + 6H + 6 Cl
2 I₂ + IO₃ + 6H + 5 Cl = 5ICl + 3H₂0

$$\frac{de_{4}v^{ec}}{de_{4}v^{ec}}$$

It was observed that the course of the reaction depended upon the hydrochloric acid concentration of the solution during the oxidation of the thiocyanate by iodine monochloride. It was also observed that the amount of iodine monochloride must be at least equivalent to the thiocyanate present in the original solution. Stokes and Cain (3) reported that in concentrated acid thiocyanates form polmers such as $H_2C_2N_2S_2$ and $H_2C_2N_2S_3$. These polmers are slow to react with an oxidizing solution. It was observed that the presence of more than one equivalent of iodine monochloride did not cause a noticeable effect with iodate titrations but did effect those with permanganate. The time of standing during the oxidation of the thiocyanate with iodine monochloride had no real effect upon the determination if the acid concentration was 1 formal or less.

EXPERIMENTAL METHODS AND RESULTS

The preparation and standardization of the oxidizing solutions used in this study were described in Part II of this thesis.

The potassium thiocyanate solution was prepared from recrystallized potassium thiocyanate as recommended by Kolthoff and Lingane (2). Sufficient amount of this potassium thiocyanate was precisely weighed into a weighing bottle, the sample was heated for 5 minutes at 180° C, cooled to room temperature in a dessicator and the weight checked, (if not to constant weight the process should be repeated). The weighing bottle with the sample was placed in a long stem funnel, the stem of the funnel extending into the neck of a volumetric flask. Water was added to the sample until it was completely dissolved, the funnel and weighing bottle were carefully washed and removed from the flask. The solution was diluted with water to the calibration mark. This solution was standardized against a standard silver nitrate solution. Three determinations were made and the results show a maximum deviation of 0.06 ml or less than one part per thousand. The normality by this determination agreed with the gravimetry method by less than one part per thousand. Results show that 24.95 ml of thiocyanate solution required 163.12 ml of 0.1 N silver nitrate solution. The normality of the thiocyanate was found to be 0.09177.

The concentrated iodine monochloride solution described in Part II was used in this study. This solution was 0.5 formal in iodine monochloride and 6 formal in hydrochloric acid. This solution was tested before each experiment to ascertain the presence of any oxidizing material or any free iodine. The oxidizing materials were removed by adding potassium iodide solution and the free iodine was removed by adding iodate solution. The endpoint was taken when the carbon tetrachloride layer had a very slight pink color.

The procedure for the determination of thiocyanate consisted of the following method. A portion of the thiocyanate solution was pipetted into an iodine flask. To this was added 15 ml of carbon tetrachloride, free of oxidizing and reducing agents. This mixture was cooled in an ice bath until the temperature of the mixture was below 10° C. To this mixture was added an equivalent amount of iodine monochloride which had been cooled to 10° C or below. The flask was stoppered and the mixture was shaken until all the liberated iodine had dissolved in the carbon tetrachloride. Then to the mixture was added sufficient concentrated hydrochloride acid to give the

proper concentration of hydrochloric acid at the end-point. The acid was added to the neck of the flask before opening the flask so the acid would wash back into the flask any iodine or solution that might be on the stopper or neck of the flask. The flask was again stoppered and shaken. The solution was immediately titrated with the standard oxidizing solution. The end-point was taken when the color of the iodine in the carbon tetrachloride was just indistinct. No end-point correction was made. The hydrochloric acid concentration was 3.5 formal for the iodate and permanganate end-points, and varied for the ceric sulfate. The end-point for the iodate determination was sharp and rapid, only a fraction of a drop of 0.1 N iodide solution would give a color to the carbon tetrachloride layer. The results are recorded in Table I.

TABLE I

	PERM	1ANGANATE	IC	DDATE	CERIC	SULFATE
Expt.	Volume	Normality Thiocyanate	Volume	Normality Thiocyanate	Volume	Normality Thiocyanate
1.	43.11		45.00		49.50	
2.	43.10		45.00		49.35	
3.	43.12		45.02		49.21	
Ave.	43.11	0.09141	45.01	0.09174	49.35	0.09077

DETERMINATION OF THIOCYANATE USING IODINE MONO-CHLORIDE AS THE INDICATOR

The normality of the thiocyanate solution as determined by the standardization with silver was found to be 0.09177, and by gravimetric to be 0.09173. The results in Table 1 show that the iodate determination gives

results within the limits of quantitative requirements. The permanganate values are in good agreement of each other but they are consistently low by about three parts per thousand. The permanganate solutions were allowed to stand for about 2 hours. During this time an iodine color formed in the carbon tetrachloride and required an average of 0.31 ml of permanganate to remove the color, this gave a total volume of 43.41 ml of permanganate with a maximum deviation of 0.02 ml of solution. The normality of the thiocyanate using this volume was 0.09204 or about two parts per thousand too high. The iodine monochloride added was equivalent to the thiocyanate present in all determinations. This deviation in normality was not due to the presence of manganous chloride since the addition of an equivalent amount of this salt to the iodate determination had no noticeable effect upon the end-point. The effect of the cyanide and sulfate ions was eliminated by titrating a potassium iodide solution containing equivalent amounts of cyanide and sulfate. The results are recorded in Table II.

TABLE II

TITRATION OF POTASSIUM IODIDE IN PRESENCE OF CYANIDE AND SULFATE IONS

	POTASSI	JM IODIDE	PERMANGANATE		
Expt.	Weight taken	Weight found	Volume	Normality	
1.	0.3881	0.3880	44.05	0.1061	
2.	0.3879	0.3880	44.03	0.1061	
3.	0.3862	0.3863	44.85	0.1061	
4.	0.3883	0.3882	44.07	0.1061	
5.	0.3891	0.3892	44.18	0.1061	

The potassium iodide used in these experiments was Baker's C P Special Grade. The results show that the presence of cyanide and sulfate ions does not affect the iodine monochloride end-point.

It was observed that the presence of excess iodine monochloride did not affect the end-point in the iodate but definitely did affect the permanganate and possibly the ceric sulfate determinations.

Experiments were made in which the volume of the iodine monochloride was varied from zero to 20 ml of 0.5 formal iodine monochloride. The results are recorded in Table III.

TABLE III

		PERMANG	ANATE	IODATI	2	CERIC SU	LFATE
Expt.	Ml of ICl	with sulfate & cyanide	without added ions	with sulfate & cyanide	without added ions	with sulfate & cyanide	without added ions
1.	0	47.34	47.33	49.25	49.30	56.02	azzo-duto etait
2.		100 -co 005	47.35	49.30	608 600 ang	600 orga res	56.05
3.	10	46.95	46.96	49.30	49.32	ana ana ana	1000 (IIII) 1000
4.		46.95	weath 45552 e-555	ಕಾರಾ ವರ್ಷ ಮನ	49.30	ang mga ang	600 mark (100
5.	20	46.57	46.55	49.30	49.30	57.00	59.10

The ceric sulfate end-points were not stable, after standing over night the solutions required from 1.00 to 3.50 ml of 0.1 N potassium iodide solution to restore the iodine color to the carbon tetrachloride.

Experiments were made in the ceric sulfate determination in which the hydrochloric acid concentration was varied from 3.0 to 4.3 formal in hydrochloric acid. Two experiments were made in which the solution contained

3.5 formal in sodium chloride and 1.0 formal in sulfuric acid at the end-point. The amount of iodine monochloride was equivalent to the thiocyanate present. The results are recorded in Table IV.

TABLE IV

DETERMINATION OF THIOCYANATE WITH CERIC SULFATE WITH VARYING ACID CONCENTRATION

Hydroc ac:	hloric id	3.0 Formal	4.0 formal	4.3 formal	3.5 Nacl 1.0 H ₂ SO ₄
Expt.	1	44.60	49.57	49.50	49.80
	2	44.54	49.52	49.35	49.75
	3	44.60	49.42	49.21	1000 and 1000 -

The time required for the end-point varied from about 5 minutes for the 4.3 formal solution to 1 hour for the solution containing the sodium chloride and sulfuric. The results are all lower than one part per thousand except the last column, which required one hour for the titration.

SUMMARY

A study has been made of the titration of thiocyanate with various oxidizing agents using the iodine monochloride as an indicator. The results obtained are within one part per thousand when iodate is used; low results were obtained with permanganate and unsatisfactory results with ceric sulfate. It was shown that potassium thiocyanate can be used as a primary standard. The method used involved the oxidation of the thiocyanate in solutions from 0.5 to 1.0 formal in hydrochloric acid, and oxidation of the iodine that was liberated to iodine monochloride in solutions of from 4.0 to 6.0 formal in hydrochloric acid. The solutions were cooled in order to prevent the loss of iodine when the concentrated hydrochloric acid was added.

REFERENCES CITED

- 1. Beavon, Mr. David Beavon unpublished report was invaluable in this study.
- 2. Kolthoff and Langane, J. Am. Chem. Soc. 57, 2126 (1935).
- 3. Stokes and Cain, Bulletin of Bureau of Standards, 3, 157 (1907).

PART IV

The Distribution of Thallium Between Isopropyl Ether and Hydrochloric Acid

PART IV

The Distribution of Thallium Between Isopropyl Ether and Hydrochloric Acid

INTRODUCTION

The final part of this thesis consists of a progress report on the study of the distribution of thallic chloride between isopropyl ether and hydrochloric solutions.

Diethyl ether has been used widely in the extraction of certain elements, notably iron. Dodson, Forney and Swift (2) introduced the use of isopropyl ether as an extraction medium. It has the advantage of not involving the fire hazard of diethyl ether. One disadvantage of the present day isopropyl ether is the presence of peroxides or peroxide inhibitors. Dodson, Forney and Swift (2) have shown that iron is extracted as the undisassociated molecule HFeCl_4 at the optium hydrochloric acid concentration. Their method will be used in this study for the extraction of thallic thallium with isopropyl ether.

EXPERIMENTAL METHODS

Solutions of potassium iodate, silver nitrate, potassium thiocyanate, sodium hydroxide and hydrochloric acid were prepared and standardized by conventional methods. The hydrochloric acid was also standardized against iodate by the method of Kolthoff and Furman (3).

The isopropyl ether was purified by treating equal volume of ether with dilute hydrochloric acid and allowing the mixture to stand for from 24 to 36 hours with constant stirring. The phases were separated and the ether portion was treated with a mixture of anhydrous calcium oxide and sodium hydroxide, approximately 25 grams of this mixture per liter of ether was used. The ether was distilled from this mixture and found to be free of peroxides but was stable for about 4 to 6 hours. It was found that be treating the freshly distilled ether with 5 grams of hydroquinone (1) per liter the ether would stay free of peroxides for several weeks. The ether was distilled from the hydroquinone as needed.

The distribution experiments consist of mixing equal volumes of ether and thallic thallium solution, approximately 0.1 formal in thallic chloride and varying concentration of hydrochloric acid. The mixture was allowed to come to equilibrium in a thermostatic bath, regulated to 25.0 ± 0.05° C. The layers were separated and each layer was analyzed for thallium, hydrochloric acid and total chlorides. The thallium was determined by reducing the thallic to thallous by saturating the solution with sulfur dioxide and allowing the solution to stand over night. The excess sulfur dioxide was removed by boiling the solution until the volume had been reduced by about one third. The thallous was determined by the method of Swift and Garner (4) using iodate as the oxidizing agent. The hydrochloric acid was determined by the method of Kolthoff and Furman (3) which consisted of adding a volume of standard iodate solution to a portion of solution to be analyzed, excess potassium iodide was added, excess thiosulfate was added and the solution was filtered. The precipitated was washed with water and discarded. The filtrate and washings were titrated with a standard hydrochloric acid solution using methyl red as the indicator; an end-point correction was made. The total chlorides were determined by the Volhard method.

The thallic species and hydrochloric acid were extracted from the ether layer by adding water and 0.1 formal hydrochloric acid solution. The acid solution was used to prevent the precipitation of thallic hydroxide. The solution was then analyzed for thallium, hydrochloric acid and total chlorides by the method given above.

Blank forms are shown to indicate the procedure and methods of calculation for the analysis of the two layers. There is not sufficient data at present time to draw any definite conclusions on the distribution nor the species found in the ether layer.

REFERENCES CITED

1. This suggestion was made by Mr. Rollie Myers.

2. Dodson, Forney and Swift, J. Am. Chem. Soc. 58, 2573 (1936).

3. Kolthoff and Furman, Volumetric Analysis, Vol. II pp 389, John Wiley.

4. Swift and Garner, J. Am. Chem. Soc. 58, 113 (1936).

DATA	ON	SOLUTIONS	SOLUTION	NO.	
					CONTRACTOR DESCRIPTION OF THE OWNER OWNER OF THE OWNER

ORIGINAL SOLUTION

Volume of water	solution	enda Latuara angla minanakana anglas	(V ₀)		
Volume of ether	solution	17 <u>1729</u>	(V _e)		
	Formality	of solution			
HClF					
Tl***F					
Cl F					
	AT EQUI	LIBRIUM	TIME	HRS.	
Volume of water	phase	(v _l))		
Volume of ether	phase	(V ₂))		
Formality of Solutions					
ETHER PHASE		WATER PHASE		TOT AL	
HCl F'		HClI	ភ្វះ ខ	HCl	FILI
Tl***F'		Tl***	ក្ខ៖	Tl ***	F
ClF'		C1	ក្ខា	C1 ⁻	FIL

RATIO
R =
$$F^{\dagger}V_2/FV_2(100)$$

HCl Tl^{***} Cl⁻
R____% R____% R____%

Volume of hydrochloric acid used in extraction ______

HC1 DETERMINATION

SOLUTION NO

ANALYSIS OF SOLUTIONS

WATER PHASE		
10 ml of Aq. Soln.	65457-705	(V ₁)
H_2O_2 to 100 ml	digitationalas - Barthoudayada.	(v_t)
10 ml of soln.		(V ₂)
50 ml of KIO3 Soln.		(v _o)
2 g of KI 5 g of $\text{Na}_2\text{S}_2\text{O}_3$ filte	er	
filtrate M.R. 2 drops St'd HCl Soln.		(V _s)

Vol. of sq. soln. ____(V])

Normality of soln. ____(N]

Dilution volume ____(V_t)

Vol. of dil. soln. ____(V_2)

Normality of soln. ____(N2)

Vol. of KIO soln. ____(V_)

Normality of soln. ____(N_)

Vol. of HCl soln. (V_s)

Normality of soln. ____(N_s)

 $N_1 = V_t / V_1 V_2 (V_0 N_0 - V_s N_s)$

N₁ _____

F _____

ETHER PHASE
25 ml of eth. soln. (V_1)
H O for ext. dil(v_t) to 250 ml
50 ml of soln. (V_2)
50 ml of KIO_3 soln(V_0)
2 g of KI 5 g of Na ₂ S ₂ O ₃ filter
filtrate M. R. 2 drops St'd HCl soln(V _s)

RECORD

Vol. of ether soln.	(V)
Normality of soln.	(N_1)
Dilution volume	(V_t)
Vol. of dil. Soln.	(V_2)
Normality of soln.	(N_2)
Vol. of KIO soln.	(V_)
Normality of soln.	(N_)
Vol. of HCl soln.	(V_s)
Normality of soln.	(N _s)

$$N_1 = V_t / V_1 V_2 (V_0 N_0 - V_s N_s)$$



SOLUTION NO THALLIUM DETERMINATION ANALYSIS OF SOLUTIONS WATER PHASE 25 ml of aq. soln. ____(V1) H₂O to 100 ml H₂O for ext. 100 ml SO₂ saturate, stand SO2 saturate, stand CCl₄ 5 ml CCl₄ 5 ml

St'd KIO3 soln. ____(Vo)

10 ml burette

ETHER PHASE 25 ml of eth. soln. (V_1)

St'd KIO3 soln. ____(Vo)

RECORD

Vol. of aq. soln.	(V _l)
Normality of soln.	(N ₁)
Dilution volume	$_$ (V _t)
Volume of dil. soln.	(V ₂)
Normality of soln.	(N ₂)
Vol. of KIO3 soln.	(V_o)
Normality of soln.	(N _o)

 $N_1 = V_t / V_1 V_2 (V_0 N_0)$

if $V_t - V_2$

- $N_1 = V_0 N_0 / V_1$
- N_1 ------F _____

Vol. of ether soln.	(V ₁)
Normality of soln.	(N_1)
Dilution volume	(V _t)
Vol. of Dil. soln.	(V ₂)
Normality of soln.	(N ₂)
Vol. of KIO soln.	(V ₀)
Normality of soln.	(N _o)

 $N_1 = V_t / V_1 V_2 (V_o N_o)$

$$N_{1} = V_{0}N_{0}/V_{1}$$

$$N_{1} = F$$

TOTAL CHLORIDES

SOLUTION NO.

ANALYSIS OF SOLUTIONS

WATER	PHASE	
W ALLING	TIMOL	

10 ml of aq. soln. 10 ml of 6 N NaOH	(v ₁)
Heat, filter H ₂ 0 to 250 ml	(V _t)
10 ml of soln.	(v ₂)
50 ml of AgNo ₃ 2 ml nitrobenzene 5 ml Fe(NO ₃) ₃	(V)
St'd KCNS soln.	(V _s)

ETHER PHASE

25 ml of eth. soln. H_2O for ext.	(V ₁)
5 to 10 ml 6 N NaOH Heat, filter	
H_20 to 250 ml	(V _t)
50 ml of soln.	(v ₂)
50 ml of AgNo ₃ 2 ml nitrobenzene 5 ml Fe(NO ₃) ₃	(v _o)
St'd KCNS soln.	(V_s)

RECORD

Vol. of aq. soln.	(V _l)
Normality of soln.	(N _l)
Dilution volume	(V _t)
Vol. of dil. soln.	(V ₂)
Normality of soln.	(N ₂)
Vol. of AgNO3	(V _o)
Normality of soln.	(N _o)
Vol. of KCNS	(V _s)
Normality of soln.	(N _s)

$$N_{1} = v_{t} / v_{1} v_{2} (v_{0} N_{0} - v_{s} N_{s})$$

N₁ -----

Vol. of ether soln.	(V ₁)
Normality of soln.	(N _l)
Dilution volume	(V _t)
Vol. of dil. soln.	(V ₂)
Normality of soln.	(N ₂)
Vol. of AgNO3	(V _o)
Normality of soln.	(N _o)
Volume of KCNS	(V _s)
Normality of soln.	(N _s)

$$N_{1} = V_{t} / V_{1} V_{2} (V_{o} N_{o} - V_{s} N_{s})$$

