I. COULOMETRIC AND AMPEROMETRIC METHODS OF ANALYSIS

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III. DETERMINATION OF CARBON BY WET COMBUSTION

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ABSTRACT

The conditions under which electrolytically generated chlorine can be used for secondary coulometric titrations with an amperometric end point have been investigated. A procedure is described by which tripositive arsenic has been titrated in quantities of from 30 to 800 micrograms with an average error without regard to sign of less than 0.5 micrograms.

The method proposed by Wooster (30) for calculating corrections for the coulometric titration of iodide in hydrochloric acid has been studied. Data are presented to show that improved methods of calculation give more accurate results.

For the coulometric titration of iodide by means of electrolytically generated bromine perchloric acid may be substituted for hydrochloric acid. The perchloric acid requires no purification and the titrations are just as accurate as those made with hydrochloric acid.

A metallic bismuth micro-reductor has proven satisfactory for quantitative reduction of ferric iron. Samples containing 234 micrograms of iron have been reduced and titrated with electrolytically generated chlorine to an accuracy of better than 1%. Iodine monochloride has also been used for the oxidation of ferrous iron. Recommendations are made for further investigation.

A combination of coulometric and amperometric techniques

has been used to determine a dissociation constant for iodine monobromide and a constant for the oxidation-reduction equilibrium involving cupric copper and bromide ions. For the iodine-iodine monobromide half-cell, data from this investigation yield a potential value of -0.92 volt as compared with a value of -0.88 volt obtained from the literature. On the other hand, a potential value for the cupric-cuprous bromide half-cell calculated from this experimental data differed by 0.06 volt from data found in the literature.

A study of the indicator currents caused by various oxidation states of vanadium established the fact that tripositive and quadrapositive vanadium give rise to an indicator current. Also, it was observed that a reducing agent capable of replacing hydrogen ion would probably be partially oxidized by the indicator circuit; a special method would be required for the coulometric titration of such a substance.

The equilibrium constant for the formation of the monobromo complex of copper (II) was determined by means of a spectrophotometric method. In solutions of unit ionic strength the constant was found to be 2.1 ± 0.25.

For the determination of carbon in organic solids and relatively nonvolatile liquids, a scheme has been devised to use the Van Slyke-Folch combustion solution. An apparatus is described for situations where a Van Slyke manometric apparatus cannot be provided. The results are accurate to ± 0.05 mg of carbon.

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I. COULOMETRIC AND AMPEROMETRIC METHODS OF ANALYSIS

Introduction

A coulometric titration may be defined as an electrolytic process in which a reaction is effected quantitatively with known electrical efficiency and the number of equivalents is determined by measuring the amount of electricity consumed. As discussed by Szebelledy and Somogyi (28) there are two types of coulometric processes: the primary or direct process in which the desired reaction takes place at a suitable electrode, and the secondary or indirect process in which an intermediate half-cell reaction is caused to take place at the electrode and the electrolytic product then causes the desired reaction.

Lingane (14) has described examples of the primary process in which certain metal ions were reduced at a mercury cathode. Inasmuch as the cathode voltage was controlled, selective reductions could be accomplished. However, the current decreased exponentially during the titration, and the titration time was therefore prolonged.

Examples of the secondary process have been described by Szebelledy and Somogyi (29). In these procedures the intermediate half-cell reaction was the electrolytic oxidation of bromide to bromine; the bromine then oxidized such substances as thiocyanate, hydrazine and hydroxylamine. Since these reducing agents are not susceptible to stoichiometric anodic oxidation, it is apparent that the secondary process can be used to extend the range of application of coulometric methods. Furthermore, the presence of a high concentration of the intermediate substance (bromide, for example) provides two additional advantages:

1. A constant electrolysis current can be maintained with assurance that the electrode efficiency is known. This permits the use of the relatively simple constant current-time method for determining the amount of electricity used in a titration. In comparison with the cathode-voltage controlled process the titration is more rapid.
2. Accurate micro titrations are possible because the current and current efficiency remain constant regardless of the concentration of the substance to be determined.

Recently, electrolytically generated bromine has been used for the titration of thiodiglycol (23), tripositive arsenic (20), tripositive antimony (1), and iodide (34). All of this work differed from that of Szebelledy and Somogyi in three major respects: the constant current-time method was substituted for the chemical coulometer, an amperometric end point was used in place of visual indicators, and the quantity of material to be determined was reduced to the micro scale. With similar apparatus cuprous copper (19) and iodine (21) have been used as intermediate substances.

The amperometric end point consists of detecting an excess of the intermediate by means of a diffusion current set up between two polarized platinum electrodes in a stirred solution. In the case of reversible half-cell reactions the diffusion current is linearly proportional to the concentration of the substance which is present in low concentration. In addition, this quantitative feature of the amperometric method has proven useful in the study of aqueous dissociation equilibria, and the results of such investigations are described below.

I-1. THE USE OF ELECTROLYTICALLY GENERATED CHLORINE IN COULOMETRIC TITRATIONS

Until the present work only three intermediate half-cell reactions had proven satisfactory for coulometric determinations. For the titration of reducing agents, bromine has been employed rather extensively (1, 20, 23, 29, 34) and recently Ramsey, Farrington, and Swift (21) have shown that iodine can be used for the titration of arsenic. Cuprous copper has been used for the coulometric titration of certain oxidizing agents (19).

In order to increase the number of substances which could be titrated by such processes, a stronger oxidizing intermediate than bromine was sought. Since the halogen half-cells are so readily reversible at electrodes, chlorine seemed to be the logical choice for investigation. Wooster, Farrington, and Swift (34) used chlorine as an intermediate in the coulometric titration of iodide in 2 formal hydrochloric acid and observed positive errors of from 0.5 to 1%. Since these errors may have arisen from the iodine monochloride formed in those titrations a study has been made of the oxidation of tripositive arsenic by electrolytically generated chlorine and the results are presented below.

Experimental

Reagents. All chemicals used were "Reagent Grade."

One volume formal sodium chloride solutions, prepared from the salt, were found to contain no extraneous oxidizing or reducing agents.

Sulfuric acid (2.5 formal) was purified by bubbling chlorine gas through the solution for 2-3 minutes. After boiling the acid for one hour, no excess chlorine remained in solution and only a very small amount of reducing material was detected.

The reducing material present in hydrochloric acid was determined by coulometric titration with chlorine. The stoichiometric amount of potassium chlorate was then added to 8 F hydrochloric acid. After one day essentially all of the chlorate had reacted and the acid was ready for use.

Standard solutions of tripositive arsenic were prepared in the following way: Bureau of Standards arsenious oxide was dried for two hours at 110-115° C. A 0.5 gm sample of the oxide was accurately weighed out and dissolved in 10 ml of water containing 1 gm of sodium hydroxide. The resulting solution was neutralized with 8 ml of 2.5 F sulfuric acid and about 180 ml of boiled distilled water were added, then the total weight of the stock solution was determined. Weighed samples of the stock solutions were diluted to appropriate volumes to provide standard solutions for analysis. Stock solutions were discarded after 5 days: dilute standard solutions were used only on the day of preparation.

Laboratory distilled water was boiled 15-20 minutes to remove a small amount of oxidizing agent, presumably chlorine.

Apparatus. The apparatus described by Meier, Myers, and Swift (19) was used with the following changes: The generator cathode instead of the generator anode was enclosed in a shield. In order to improve current regulation, the laboratory D.C. supply was replaced by a simple voltage-regulated rectifier. The indicator electrodes were made the same size, 2 x 2.5 cm. The same basic apparatus was used for all coulometric investigations; only the modifications will be noted in subsequent sections.

Preliminary Adjustment. The current of the generation circuit was determined by measuring the voltage drop across a standardized resistance through which the generation current was passing. All voltage measurements were referred to a cell which had been checked against a bank of cells obtained from the Bureau of Standards. Generation rates of about 10^{-8} and 10^{-7} equivalent per second were used.

When not in use the indicator electrodes were shorted together and stored in a solution 0.5 F in sulfuric acid and 0.2 F in sodium chloride. Before each series of titrations both indicator electrodes were connected to the generator anode and chlorine was generated at the high rate for about 30 seconds. To maintain the sensitivity of the electrodes they were given the same treatment for 10 seconds after each blank and every titration.

Titration Procedure. All solutions had a total volume of 45 ml and were 0.5 formal in sulfuric acid and 0.2 formal in sodium chloride; the initial indicator potential was set at 0.30 volt. The considerations influencing the selection of the various conditions of the procedure are discussed later. A correction for reducing material in the reagents was made by generating in a blank solution of the composition given above for short intervals of time and recording the values of the indicator current. A plot of indicator current vs. generation time was constructed and the linear curve was extrapolated to zero time; the intercept on the time axis was designated as the "blank time."

When the apparatus had not been in use for several hours the first one or two "blank time" values were usually erratic and were not included in the average "blank time" value. At least three consistent values were used in obtaining the average "blank time."

To make a titration the proper amount of sulfuric acid and sodium chloride solution were mixed in a titration cell with sufficient water to make the volume either 35 or 20 ml. A 10 or 25-ml portion of standard arsenite solution was pipetted into the cell and the total volume was then 45 ml. As soon as the titration cell was attached to the stirring apparatus, generation was started. By means of the built-in potentiometer the generating current could be checked during the course of the titration and the current was held constant by making small adjustments. Near the end-point the indicator current underwent a momentary reversal, and at this point generation was stopped immediately. After a few seconds the indicator current rose slowly and reached a steady value of less than 10 microamperes. Generation was continued for short intervals and values of the indicator current and time were recorded. The linear curve of indicator current vs time was extrapolated to the time axis, and the point of intersection was taken as the "titration time" inasmuch as the chlorine excess is assumed to be zero at the extrapolated zero indicator current. By subtracting the average "blank time" from the "titration time" a corrected titration time was obtained. The weight of arsenic was calculated from the values of the corrected titration time and the rate of generation.

Discussion

Potential Difference Applied Across the Indicator Electrodes. Chlorine was generated in a blank solution until the indicator current was 25 microamperes with an applied potential difference between the indicator electrodes of 500 mv. The indicator potential was then varied between values from 50 to 1000 mv and values of the indicator current were recorded. Before each change of indicator potential the current was adjusted to 25 microamperes at 500 mv by the generation of chlorine. The data thus obtained are presented in Table I. When these data were plotted, the curve of indicator current vs indicator potential was similar in form to the one obtained by Ramsey for iodine (21) except that the flattest portion of the curve was from 400 to 600 mv. Although it would have been desirable to use an indicator

TABLE I

Values of Indicator Current and Indicator Potential for a Solution Containing Chloride [a] and Chlorine [b]

Potential (Millivolts)	Current (Microamperes)	Potential (Millivolts)	Current (Microamperes)
60	4.0	553	26.1
106	7.5	617	27.5
175	12.2	696	29.0
217	14.2	755	30.5
286	18.0	798	32.1
319	19.2	848	33.2
362	20.7	935	37[c]
417	23.0	1042	43[c]
500	25.0		

[a] Sodium Chloride 0.2 F.

[b] Chlorine was generated until indicator current was 25.0 microamperes at an indicator potential of 500 millivolts. The chlorine concentration was approximately 2×10^{-6} F.

[c] The indicator current was changing rapidly so that these values are uncertain.

potential which lay on this flat portion of the curve, this was not practicable because high initial indicator currents (that is, before beginning generation) were obtained in blank solutions. In order to reduce this initial value of the indicator current to 1 microampere or less, it was necessary to use a potential of 300 mv. This potential proved to be satisfactory for the titrations; linear curves of indicator current vs time were obtained for blank titrations, and the electrode sensitivity was good.

<u>The Effect of pH on Indicator Current</u>. Inasmuch as chlorine tends to hydrolyze even in slightly acid solutions, it was desirable to determine the maximum pH at which a stable indicator current could be obtained when the chloride was 0.2 F. In a solution buffered to a pH of 3 with phosphoric acid and dihydrogen-phosphate no indicator current could be observed when the low rate of generation was used. For a solution in which the pH was 2 an indicator current was obtained but it decreased at the rate of 1 microampere in 4 seconds as soon as generation was stopped; this is not adequate stability for quantitative measurements. A stable indicator current was obtained in 0.05 F H_2SO_4; however, to include a factor of safety, solutions 0.5 F in H_2SO_4 were used in the titrations.

<u>Indicator Current Phenomena</u>. The indicator current response was slower for chlorine than for bromine or iodine. When either a blank chloride solution or such a solution containing arsenic was placed in the cell and a potential was applied between the

indicator electrodes, the indicator current surged to a high value then decreased slowly. In either case several minutes elapsed before the current reached a steady value of about 0.2 microampere. In practice, generation was started in a blank solution as soon as the indicator current dropped to 1 microampere instead of waiting until 0.2 microampere was reached; no difference in blank time was observed. When arsenic was titrated, generation was begun immediately after closing the indicator circuit because the indicator current always dropped rapidly and underwent a reversal near the end point and the value of the indicator current during the titration had no significance.

After the first period of generation in a blank solution and after the current reversal at the end of a titration, the indicator current rose so slowly that a period of 1 to 3 minutes was necessary for steady state to be attained. For all other readings of indicator current a steady state was reached in 10 to 15 seconds.

The current reversal near the titration end point is similar to the one observed by Myers and Swift (20); however, with the present apparatus no hydrogen enters the solution from the generator cathode. When the potential is first applied to the indicator electrodes, the current surges to a high value (more than 50 microamperes) then decreases. During the passage of this current a small quantity of hydrogen or possibly arsenic is probably being produced on the indicator cathode. Near the titration end point the concentration of chlorine increases rapidly and there is a transition of indicator electrode potentials and reactions. If there is a significant lag in removing adsorbed hydrogen (or possibly arsenic) from the indicator cathode, a cell would be established in opposition to the applied potential and a current would flow in the reverse direction.

The Effect of Chloride and Acid on the Coulometric Titration.

In view of the positive errors obtained by Wooster in the titration of iodide with chlorine in 2 F hydrochloric acid (34), it seemed advisable to use the lowest practicable chloride and hydrogen ion concentrations. As discussed above 0.5 F H_2SO_4 was taken as a safe minimum acid concentration. With a chloride ion concentration of 0.05 F there was evidence that the generator anode efficiency was slightly less than 100%, while 0.1 F chloride ion seemed perfectly satisfactory. Confirmatory titrations were made using the chloride and acid concentrations given in the procedure above, and the results are listed in Table II. To investigate the effects of varying acid and chloride concentrations, titrations were made according to the conditions listed in Table III. It should be noted that each stock solution was titrated by the regular procedure, so that the data in Table III may be directly compared with the data for the corresponding stock solution in Table II. The arsenic found when titrating in 0.05 F sodium chloride solution was about 0.2% greater than the value obtained in 0.2 F sodium chloride solution; this indicates that the current efficiency may not have been 100% in the 0.05

formal chloride solution. Considering that chlorine would be expected to oxidize the platinum anode in the presence of such high chloride concentrations, it is surprising that significant positive errors were obtained only in the titrations in 6 F hydrochloric acid.

Conclusions

Chlorine can be used as the intermediate for a secondary coulometric process in which use is made of platinum electrodes and an amperometric end point. The acid concentration should not be lower than 0.1 volume formal, and the chloride concentration should be between 0.1 and 2 formal. In the coulometric titration of arsenic by this method an accuracy of ± 0.2% was obtained for 300 to 800 microgram quantities of arsenic; 30 to 100 microgram quantities were titrated with an average error of less than 1%.

The material presented in this section has been accepted for publication by Analytical Chemistry (3).

TABLE II

Coulometric Titrations of Tripositive Arsenic By Means of Electrolytically Generated Chlorine

	Arsenic (micrograms)			
Number[a]	Taken	Found	Error	% Error
I	29.8	30.2	0.4	1.34
		29.9	0.1	0.33
		29.9	0.1	0.33
		29.9	0.1	0.33
I	82.4	83.1	0.7	0.85
		82.7	0.3	0.36
		82.6	0.2	0.24
		82.6	0.2	0.24
I	321.9	321.9	0.0	0.0
		321.9	0.0	0.0
		322.3	0.4	0.13
		321.9	0.0	0.0
I	802.5	802.2	-0.3	-0.04
		801.8	-0.7	-0.09
		803.5	0.5	0.06
		802.6	0.1	0.01
II	819.1	818.6	-0.5	-0.06
		817.8	-1.3	-0.16
		817.9	-1.2	-0.15
		817.8	-1.3	-0.16
		817.8	-1.3	-0.16
III	795.6	796.1	0.5	0.06
		794.8	-0.8	-0.10
		794.5	-1.1	-0.14
		796.1	0.5	0.06
		795.3	-0.3	-0.04

[a] Roman numerals indicate stock solution used.

TABLE III

Effect of Acid and Chloride Ion Concentrations on Titrations of Tripositive Arsenic

Number[a]	Solution	Arsenic (micrograms) Taken	Arsenic (micrograms) Found	% Error
II	0.5 F H_2SO_4	819.1	819.4	0.04
			819.4	0.04
	0.05 F NaCl		819.0	-0.01
			819.8	0.09
II	0.5 F H_2SO_4	819.1	817.4	-0.21
			817.4	-0.21
	3.0 F NaCl		817.4	-0.21
II	0.5 F H_2SO_4	819.1	817.9	-0.15
			817.9	-0.15
	Saturated NaCl		817.8	-0.16
III	2 F HCl	795.6	794.9	-0.09
			794.9	-0.09
			796.4	0.10
			795.7	0.01
III	6 F HCl	795.6	798.4	0.35
			800.5	0.62
			799.2	0.45

[a] Roman numerals indicate stock solutions used.

I-2. COULOMETRIC TITRATIONS

A. The Coulometric Titration of Iodide in Hydrochloric Acid

The coulometric titration of iodide in hydrochloric acid by means of electrolytically generated bromine and an amperometric end point was first investigated by Wooster (30). In Figure 1 it can be seen that the indicator current at the beginning of an iodide titration may be significant. This initial indicator current introduces a correction in addition to those described in Part I-1. Although Wooster obtained good results, his method of calculating corrections involved several approximations. It appeared that a more rigorous method of calculating corrections might improve the accuracy of the titrations. Furthermore, Wooster stated (32) that positive errors were obtained if the indicator current was allowed to flow during the titration. In order to clarify these points the experiments described below were undertaken.

Experimental

Reagents. Six formal hydrochloric acid solutions were prepared from reagent grade concentrated acid. The acid available commercially was found to contain as much as 3.5×10^{-8} equivalent of reducing agent per milliliter. The amount of reducing agent present was determined by electrolytic oxidation and was removed

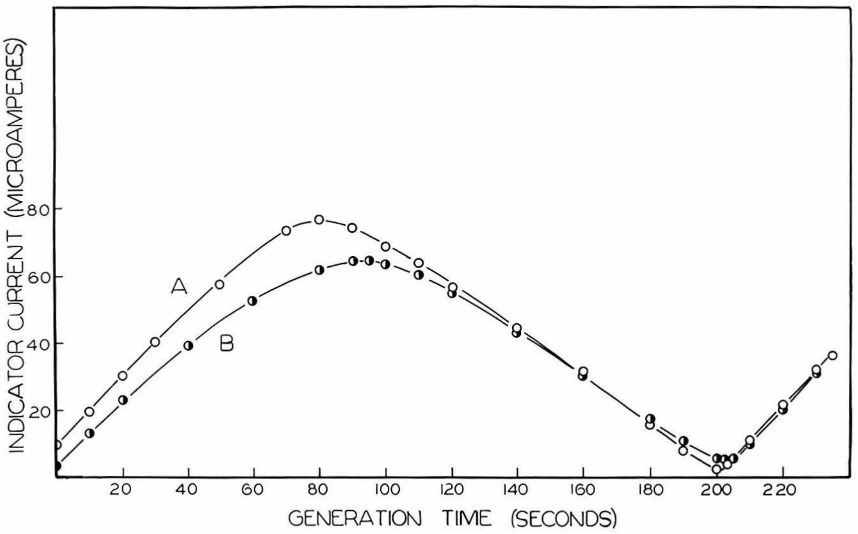

Figure 1. Behavior of Indicator Current during Titrations in Hydrochloric Acid Solutions.

A. No bromide present B. Bromide present by boiling the 6 F acid with the calculated amount of 3% hydrogen peroxide. Excess peroxide was destroyed by boiling the acid for about 15 minutes.

One formal sodium bromide solutions were prepared from reagent grade salt. These solutions, when tested, were found to contain no extraneous oxidizing or reducing agents.

Stock 0.1 F solutions of potassium iodide were made up by weight from reagent grade salt which had been dried for 1 hour at 110° C. The potassium iodide used was found to contain no iodate. The solutions were made 0.01 F in sodium carbonate to minimize air oxidation. Dilutions of the stock solutions, 0.005 F in sodium carbonate, were used directly for titrations.

Apparatus. The apparatus was the same as in Part I-1 except that the indicator anode was 1.5 by 1.5 cm and the indicator cathode was 2 by 2.5 cm.

Preliminary Adjustment. When not in use the electrodes were stored in a solution 2 F in hydrochloric acid and 0.1 F in sodium bromide. Before use the indicator electrodes which were shorted together during storage, were made the generator anode, and then bromine was generated on their surfaces for a period of about 10 seconds on the high rate (10 milliamperes). The electrodes were given the same treatment after each blank and every titration.

Titration Procedure. The indicator potential was set at 138 millivolts as suggested by Wooster (31). The solutions for titration were 2 F in hydrochloric acid and 0.1 F in sodium bromide with a total volume of 50 ml. Before each series of titrations several blank solutions were titrated in order to determine the blank time.

For a titration, the acid, bromide and water were mixed in a titration cell. Upon the addition of a sample of dilute iodide solution, the initial indicator current was recorded, the generation current was adjusted and generation was started. Readings of the indicator current were made at short intervals of generation to establish the initial slope of the indicator current curve. By means of the built-in potentiometer the generating current was checked throughout the course of the titrations, and adjustment was made whenever necessary to hold the current at a constant value. In general the indicator circuit was left open until the equivalence-point was nearly reached; variations from this procedure are noted in Table IV. As the current began to rise after the minimum point, readings of indicator current were recorded after several short intervals of generation.

Discussion

Corrections for Initial Current, Solution Blank, and End Point.

Two methods were used for obtaining these corrections.

Method A (Wooster), approximate in nature, consisted of generating in a solution, prepared as was that to be used for the titration but containing no iodide, until a suitable indicator current reading was obtained, usually from 25 to 40 microamperes. This current value divided by the generation time in seconds gave a factor, by which subsequent indicator current readings could be converted into equivalent generation times. These measurements were repeated until the reproducibility indicated that the desired constancy of electrode sensitivity was being obtained. In the subsequent iodide titrations, the initial current was recorded, then generation was continued until the indicator current had gone through the minimum, and had increased to values of the same magnitude as those obtained for the blank solutions. The initial current and the final current reading were then converted to equivalent times by application of the above factor. The time equivalent to the initial current was added, and the time equivalent to the final current was subtracted from the total generation time.

In Method B (Farrington), the correction for the initial current was made by recording values of the indicator current during the initial rise, then extrapolating to zero current the linear curve obtained by plotting these values against time. Time equivalent to the distance from zero time to the intercept of this curve was added to the generation time. When generation was started with blank solutions there was a short time interval before the current began to rise, indicating the presence of a small quantity of some substance capable of reducing bromine. A correction was made for this material by continuing generation until the plot of indicator current versus time was linear, then extrapolating this curve to zero current. The time equivalent to the distance from this intercept to zero time was subtracted from the generation time. The end point of the titration was obtained by continuing generation, after the indicator current minimum, until the plot of indicator current versus generation time was linear, then extrapolating this curve to zero current.

Titration values obtained by these two methods are tabulated in Table IV. It can be seen that the theoretical titration value is more closely approached by using Method B. When titrating iodide in hydrochloric acid in the absence of bromide, Wooster (33) reported large positive errors (up to 8%); such errors appear to be largely due to the method of calculation (A) and actually are more nearly on the order of 0.5%.

The occurrence of positive errors when the indicator current was allowed to flow during the titration was not confirmed.

The experiments described in this section have been included in a recent publication (34).

TABLE IV

Comparison of Methods A and B For Calculating The End Points of Iodide Titrations

	Iodide, Micrograms			
			Found	
Series	Taken		Method A	Method B
I (indicator current off)	134.4		134.7	134.1
			134.7	134.1
			136.0	134.4
		Av.	135.1	134.2
II (indicator current off)	134.4		135.6	134.9
			135.5	134.3
			135.2	133.9
		Av.	135.4	134.4
III (indicator current on for half of titration) (indicator current on continuously)	134.3		133.6	133.8
			134.7	134.1
			135.6	134.3
		Av.	134.6	134.1
IV (indicator current on through minimum point only)	134.3		133.3	133.8
			133.4	134.2
			134.6	134.7
		Av.	133.8	134.2
V (indicator current off)	134.3		134.1	133.9
			134.2	134.0
		Av.	134.1	133.9

I-2B. The Coulometric Titration of Iodide in Perchloric Acid

The coulometric titration of iodide in perchloric acid is essentially the same as the titration described in the preceding section (I-2A), and it was studied only as a supplement to the investigation of the iodine monobromide equilibrium.

Experimental

Reagents. The 60% perchloric acid required no special purification.

Potassium iodide containing no iodate, was dried for 1-2 hours at 100° C. Stock solutions were made up by weight to contain approximately 10^{-4} formula weight of iodide per gram of solution, and were made 0.01 F in sodium carbonate to minimize air oxidation. The iodide concentrations varied less than 0.1% from values obtained by titration to the iodine monochloride end-point with a standard iodate solution. Portions of the stock solutions were delivered from weight burets and diluted with 0.005 F sodium carbonate. Only freshly prepared dilute solutions were used for titrations.

Apparatus. The apparatus used in Part I-2A was also used for this investigation.

Procedure. A total volume of 45 ml was used and the solutions were 0.2 F in sodium bromide and 2 F in perchloric acid. In all other respects the titrations were performed exactly as in Part I-2A.

Calculation of the amount of iodide found was made exactly as in Method B of the preceding section. The results of confirmatory titrations are presented in Table V.

Discussion

The most important advantage of using perchloric acid instead of hydrochloric acid lies in the purity of the former. Reagent grade perchloric acid contains so little reducing material that it may be used without special treatment, while untreated hydrochloric acid causes excessive blank time (See Part I-2A). In addition, the platinum electrodes are less subject to oxidation in perchloric acid solution because there is no complexing effect.

If titrations require more than 200-250 seconds, low results will be obtained, probably because of loss of iodine.

There is some evidence that low results will be obtained if the solution is above 25° C during titration. For best results it is recommended that the temperature of the solution be 18-23° C.

TABLE V

The Titration of Iodide in Perchloric Acid by Means of Electrolytically Generated Bromine

Iodide (micrograms)	
Taken	Found
45.4	45.3
	45.9
	45.4
113.2	113.3
	113.2
	113.4
134.4	134.0
	134.5
	134.5
482.7	482.8
	484.8
	482.1
	484.1
	484.1
	484.1
1203.6	1201.2
	1204.6
	1203.9
	1203.9
	1201.9
	1203.9

I-2C. The Coulometric Titration of Iron

Many investigators have recommended procedures for the determination of iron; however, very accurate methods for determing microgram quantities of iron are somewhat limited. For example, Cooke, Hazel and McNabb (2) find errors up to 2% when titrating less than 0.5 mg of ferric iron with chromous chloride; this is typical of many volumetric procedures. On the other hand Mehlig and Shepherd (16) describe a spectrophotometric procedure which can be used to determine small quantities of iron with an accuracy of 0.2%.

In studying the composition and properties of blood, investigators at the California Institute have sought a convenient method for determining iron in small amounts. To them the available volumetric and colorimetric techniques did not appear to be satisfactory. In an effort to develop a rapid and accurate method for the titration of micro quantities of iron the application of a secondary coulometric process to such a titration was investigated. Inasmuch as no intermediate has yet been developed which will quantitatively reduce ferric iron, methods of oxidizing ferrous iron were considered. The titration of ferrous iron by means of electrolytically generated chlorine has been studied, and further development of this procedure is recommended. A new approach to the problem involved the use of iodine monochloride as the oxidizing agent. A small amount of iodide was oxidized to iodine monochloride by the generation of chlorine, then ferrous iron was added to the titration cell. The iodine monochloride end point was restored by the generation of chlorine and the time required for that operation was taken as the titration time. Further investigation of this system should be profitable.

Experimental

Apparatus. The apparatus was the same as that used in Part I-2A.

Preliminary Experiments.

1. To a 40 x 80 mm titration cell containing 15 ml of 6 F HCl in 40 ml of solution was added 5 ml of 0.005 F $FeSO_4$. Chlorine was then generated in the cell at the rate of 10^{-7} equivalent per second, and, if the ferrous iron reacted stoichiometrically, no chlorine excess should be indicated before 240 seconds of generation. After about 10 seconds of generation the indicator current was greater than 50 microamperes. When generation was stopped, the indicator current decreased fairly rapidly indicating that an excess of chlorine had been generated before the equivalence point and that the ferrous iron was reacting at a measurable rate with the chlorine. An accurate titration would be impossible under such conditions.

2. To a titration cell containing 15 ml of 6 F HCl in 40 ml of solution was added 1.5 x 10^{-5} moles of KI. Chlorine was generated until the iodide had been converted to iodine monochloride and the indicator current was at the minimum point of

2 microamperes (See Fig. 1). Upon the addition of 5 ml of 0.005 F $FeSO_4$ the indicator current increased to a high value. When chlorine was generated the indicator current decreased but passed through a minimum current of 20 microamperes before 200 seconds of generation. Again there are indications of a slow rate of reaction with ferrous iron and a successful titration is impossible under these conditions.

3. To a titration cell containing 15 ml of 6 F HCl and 10 ml of 85% H_3PO_4 was added 7.5 x 10^{-6} moles of KI, and chlorine was generated until a minimum indicator current of 3 microamperes was attained. Upon the addition of 5 ml of 0.005 F $FeSO_4$ the indicator current increased to a high value (off scale). When chlorine was generated, the indicator current decreased steadily and reached a stable value of 3 microamperes after 241 seconds of titration. Three successive titrations by this procedure used 241.2, 241.9, and 241.3 seconds of generation respectively. These conditions have definite possibilities.

4. Experiment 3 was repeated with only 5 ml of 85% H_3PO_4. As the equivalence point was approached, instability of the indicator current with time gave evidence that the oxidation of the remaining ferrous iron was not instantaneous. Evidently the concentration of phosphoric acid (or H_3PO_4) is critical.

5. To a titration cell containing 15 ml of 6 F HCl and 10 ml of 85% H_3PO_4 was added about 2 ml of a dilute solution of $FeSO_4$. Chlorine was generated, and the oxidation of ferrous iron appeared to proceed smoothly. The indicator current in-

creased as for a normal end point, and the good stability of the indicator current gave evidence that, under these conditions, there was no measurable rate of reaction between chlorine and ferrous iron.

6. In order to provide for the addition of 10 to 15 ml of solution from a reductor a 125 ml titration vessel was used. To the titration cell containing 25 ml of 2 F HCl and 20 ml of 85% H_3PO_4 was added 2.5×10^{-6} equivalent of KI, and the total volume was 60 ml. After oxidizing the iodide to iodine monochloride, several milliliters of dilute $FeSO_4$ solution were added. No difficulty was experienced in titrating to the iodine monochloride end point; evidently the reagent proportions are correct for these volumes.

7. Experiment 6 was repeated with only 15 ml of 85% H_3PO_4. Inasmuch as a measurable reaction rate was observed near the end point, the 20 ml of H_3PO_4 can be considered the minimum requirement for approximately 75 ml of solution.

8. To a titration cell containing 20 ml of 85% H_3PO_4 and 9 ml of 1 F NaBr was added a small crystal of $FeSO_4$. Bromine was generated and almost immediately the indicator current began to increase. Whenever generation was stopped, the indicator current decreased rapidly: evidently the ferrous iron and bromine were reacting at a measurable rate even though the H_3PO_4 was present.

<u>Investigation of Micro Reductors</u>. In order to avoid large

volumes of wash solution, reductors of small size were prepared. Unless otherwise specified the column of reducing material was about 7 to 8 cm high and 6 mm in diameter. The titration procedure described in preliminary experiment 6 was used because an inert atmosphere was unnecessary and the accuracy of that procedure appeared to be sufficiently good to test reductors. Instead of using the minimum indicator current as a reference point, a value of the indicator current on the iodine side of the minimum point was taken because of the greater meter response for each second of generation in that region. A dilute solution of iron, 1 F in HCl, was prepared by dissolving a weighed sample of pure iron wire.

1. Silver Reductor. Finely divided metallic silver was prepared by reducing silver ion with copper in a solution slightly acidified with HNO_3. A 5 ml portion of the dilute iron solution was passed through the reductor and into the iodine monochloride solution in about 3 minutes. Ten milliliters of 0.5 F HCl were used to wash the reductor. Successive titrations required progressively shorter titration times, indicating that the small silver reductor was probably being rapidly exhausted by the formation of a surface coating of silver chloride. Efforts were made to maintain a fresh silver surface by inserting an anode in the solution above the silver column and applying a potential between the silver column and the positive electrode. When a platinum anode was used, considerable hydrogen was evolved from the silver column. When a silver wire anode was used, the anode

surface appeared to be polarized after one or two samples had passed through the reductor. In such small size the silver reductor was unsatisfactory.

2. Zinc Reductor. A surface coating of amalgam was applied to 30 mesh zinc by pouring the zinc into a very dilute solution of $HgCl_2$. One reductor was made from a section of a 50 ml buret (zinc column about 7 cm high) and another of the size indicated above. With both reductors the titrations varied by several percent. Inasmuch as hydrogen bubbles appeared in the column, it is probable that portions of the column were blocked.

3. Cadmium Reductor. A 20% cadmium amalgam was prepared as directed by Helger (7): the amalgam is solid when cool and can be granulated. When the cadmium reductor was used, the titrations were more consistent than with the silver or zinc reductors; however, the titration values still varied about 3%. Hydrogen was formed in small amount and may account for the variation. Perhaps a lower hydrogen ion concentration in the iron solution would give better results with the cadmium reductor.

4. Bismuth Reductor. Although Someya (24) used a bismuth amalgam to reduce ferric iron, no references have been found in which metallic bismuth has been used as a reducing agent.

Finely divided metallic bismuth (black) was prepared by immersing a strip of zinc in an acid solution of $BiCl_3$. About 8 cm of this bismuth in a section of a 50 ml buret constituted the first trial reductor. In a series of four titrations using this reductor the maximum variation in titration time was only a little over 1%. Similar results were obtained with a reductor 6 mm in diameter. The bismuth reductor appears to be the best of the reductors studied.

Reduction of Iron by Bismuth and Titration with Electrolytically Generated Chlorine. In order to more thoroughly test the bismuth reduction of iron and to try a more straightforward type of titration, the chlorine titration of iron was investigated.

Apparatus. The apparatus was the same as that used in Part I-2A.

Reagents. The material in 8 F HCl which was reducing to chlorine was oxidized by the addition of $KClO_3$ as described in Part I-2A.

Phosphoric acid (85%) was freed of material reducing to chlorine by adding an excess of chlorine, allowing the acid to stand for several days, and then boiling the acid vigorously to remove excess chlorine.

A stock solution 0.1050 F in ferric iron was prepared by dissolving $FeCl_3 \cdot 6H_2O$ in 1 F HCl. A test for ferrous iron with ferricyanide was negative. Standardization of the ferric solution was carried out by the iodometric procedure suggested by Swift (25). Sodium thiosulfate for the titration was standardized against KIO_3 using the starch end point. Dilutions of the stock ferric solution, 1 F in HCl, were used for coulometric titrations.

Procedure. The usual process of shorting the indicator electrodes and generating intermediate on their surfaces for several seconds was carried out after each blank and titration.

For these titrations an intermediate rate of generation, 4.131 x 10^{-8} equivalent per second, was used. The indicator potential was 300 millivolts.

To a 40 x 80 mm titration cell was added 20 ml of 85% H_3PO_4, 3.0 ml of 8 F HCl, and 7 ml of water. After placing the cell in position on the stirring apparatus, tank nitrogen was bubbled through the solution for 4 to 5 minutes. The glass nitrogen inlet tube was then withdrawn to the upper part of the cell, and a constant flow of nitrogen into the cell was maintained for the duration of the titration. A 5-ml sample of dilute ferric chloride solution was pipetted into the reductor which had been filled with freshly precipitated bismuth (bismuth column 8 cm high, 6 mm in diameter). By means of a stopcock the flow through the reductor was regulated so that 2 to 3 minutes were required for the sample to flow into the titration cell. Ten milliliters of 0.5 F HCl were used to wash the reductor; the total volume in the titration cell was then 45 ml.

The indicator circuit was closed, and chlorine was generated until the indicator current reversed to a negative value. At that point generation was stopped and the indicator current increased to a positive value in about 30 seconds. Readings of indicator current values were then recorded after 5-second intervals of generation.

Reagent blanks were prepared and swept out with nitrogen. A 5 ml portion of the HCl used in the sample was passed through the reductor, followed by 10 ml of 0.5 F HCl. Chlorine was then generated for 5-second intervals and the corresponding values of the indicator current were recorded. The linear curves of indicator current vs. time were extrapolated to the time axis. Tor the titration curve the intersection was taken as the "titration time." The intersection in the case of a blank was designated the "blank time." By subtracting the average "blank time" from the "titration time" a corrected titration time was obtained.

Discussion

The results obtained by the above procedure were accurate to about 1% and indicate that further investigation should be profitable. With samples containing 233.7 micrograms of iron titration values of 233.0, 230.7 and 234.8 micrograms were found.

The bismuth micro reductor appears to be quite satisfactory for this application. If allowed to stand in acid solution exposed to the air, the bismuth will dissolve fairly rapidly. After the reductor has been allowed to stand for about two days, the bismuth column seems to be more tightly packed: replacement with freshly precipitated bismuth is recommended. The purity of the metallic bismuth has not been checked. In particular, iron should not be present; therefore, a sample of the precipitated and acid washed bismuth should be dissolved and a test made for iron and perhaps copper.

The amount of H_3PO_4 used in the above procedure significantly increases the solution viscosity and decreases the indicator electrode sensitivity.

After the addition of ferrous solution from the reductor, there was an indicator current of about 30 microamperes. This current decreased during the titration and current reversal occurred near the end point as mentioned in the procedure. Perhaps some hydrogen was being produced in the reductor; reduction of the acid concentration in both iron solution and wash solution should be tried.

Suggestions for Further Investigation

Chlorine Titration

1. Reduce the acidity of the titrated solution with the possibility of reducing the H_3PO_4 requirement.

2. Use NaH_2PO_4 plus $HClO_4$ in place of H_3PO_4; there may be less reducing material present.

3. Use the maximum permissible pH (about 1.5), and try fluoride as a substitute for H_3PO_4.

Iodine Monochloride Titration

1. As a reference point take an indicator current value on the chlorine side of the minimum point; the meter sensitivity is greatest in that region.

2. In order to shorten the period during which iodine and iodine monochloride are in contact with the platinum electrodes, two possibilities appear for reducing the iron and then running it rapidly into the titration solution:

a). Reduce the sample in a small bulb, flushed with N_2 or CO_2, by adding finely divided bismuth and swirling for a few minutes. By means of a stopcock, drain the sample rapidly through a plug of glass wool and into the titration cell.

b). Construct a reduction column with a 20 to 25-ml chamber placed below the column stopcock. Flush the chamber with inert gas, and collect the sample and washings in the chamber. Through a second stopcock quickly run the sample and washings into the titration cell.

I-3. EQUILIBRIUM STUDIES

A. Equilibria in Iodine Monobromide Solutions

During an iodide titration the indicator current passes through a minimum value in the region of the iodine monobromide equivalence point (See Fig. 1). Since the indicator current is limited by the iodine concentration before the minimum point and by the bromine concentration afterward, it appears that the value of the minimum current is related to the concentrations of the halogens in equilibrium with iodine monobromide. A mathematical correlation of the minimum indicator current with the cupric bromide equilibrium has been made by Meier (17); Kolthoff and Lingane (8) present calculations for the silver iodate equilibrium in which only cathode reactions are involved. In order to simplify study of the iodine monobromide equilibrium interhalogen chloride complexes were eliminated by using perchloric acid in place of hydrochloric acid.

Experimental

Reagents. The reagents described in Part I-2B were used for these experiments.

-p. 6

Apparatus. The instrument described in Part I-1 was used with two modifications:

a). For the iodine monobromide equilibrium studies the microammeter was replaced by a Leeds and Northrup box-type, reflecting galvanometer. A shunt resistance of approximately one ohm made the galvanometer sensitivity one microampere per scale division. As a result the potential drop across the galvanometer was always much less than one millivolt, and the potential applied to the indicator electrodes was held constant without adjustment.

b). In order to study the mechanism of the indicator diffusion currents, two titration cells were connected by a glass bridge containing 2 formal perchloric acid. A sintered glass disk in the bridge retarded flow between the cells. Both cells were equipped with platinum electrodes and constant speed stirrers. It was then possible to separate two indicator electrodes and to determine which pairs of ionic or molecular species would carry indicator currents.

Procedures and Results. The data for Figure 2 were obtained by recording indicator current as a function of applied potential for a solution which was 2 F in perchloric acid and 0.1 F in sodium bromide and which contained 1.62×10^{-5} mole of iodide titrated to the point of minimum current. Since the flattest portion of the indicator current-voltage curve lies in the range 40-70 millivolts, an indicator potential of 65 millivolts was chosen for the study of the iodine monobromide equilibrium.

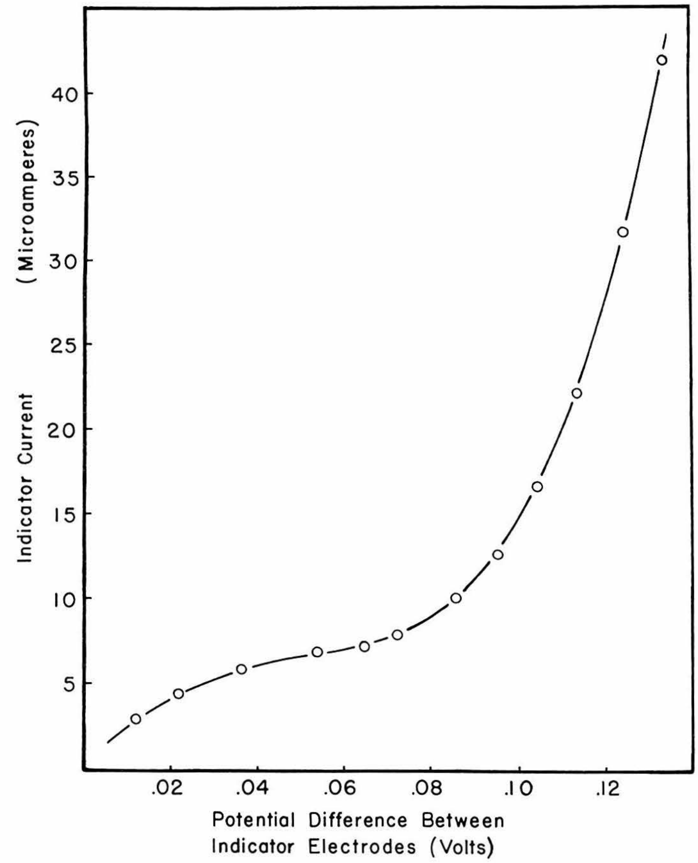

Figure 2. Variation of Indicator Current with Potential Difference Between Indicator Electrodes for a Solution Containing 1.62 x 10^{-5} Mole of Iodine Monobromide.

Data for equilibrium calculations were taken in solutions 2 F in perchloric acid and either 0.1 F or 0.3 F in sodium bromide. About 98% of the known amount of iodide in each solution was oxidized to iodine monobromide by the addition of saturated bromine water. By generating at the constant rate of 1.039 x 10^{-8} equivalent per second for short intervals of time oxidation of the iodine was completed, and the value of the indicator current was observed during this process. A typical set of data taken in the region of the iodine monobromide equivalence point is shown in Figure 3. When 6 x 10^{-8} mole of iodide was titrated, a small current (0.3 to 0.6 microampere) was noted at the minimum point. With this quantity of iodine monobromide present the minimum indicator current should have been essentially zero; consequently, this observed indicator current was considered to be a residual current which should not be attributed to halogens in equilibrium with iodine monobromide.

The two-cell arrangement described in the fourth paragraph of apparatus was used with several pairs of solutions. With a solution in each cell, a platinum electrode in one cell was connected as an indicator anode and an electrode in the other cell was made an indicator cathode. Since the circuit was completed by the acid-filled bridge, current passing through the electrodes was governed by the nature and concentration of the halogen complexes present in the solutions. This indicator current is therefore similar to the diffusion currents obtained when the electrodes are contained in one cell. In Table VI are presented

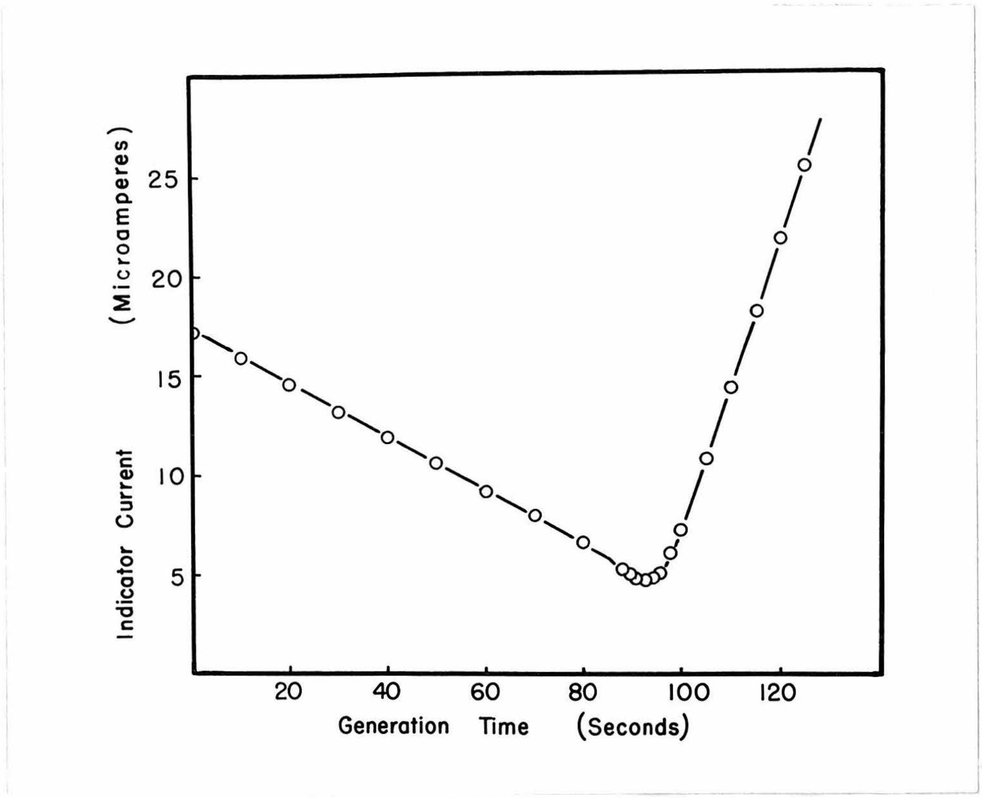

Figure 3. Behavior of Indicator Current in the Region of the Minimum Point.

Iodine Monobromide 5.60 x 10^{-4} formal.

the results of a series of experiments in which all solutions were 2 F in perchloric acid and 0.1 F in sodium bromide. The potential difference between the electrodes was 65 mv.

Experiments 1 and 2 show that iodine, in the presence of bromide, will react at both anode and cathode to give an indicator current. Such a mechanism had been proposed (33) as the explanation of the indicator current maximum near the iodine equivalence point.

Since many substances do not react readily on electrodes, it is of interest to determine whether IBr_2^- undergoes reduction at the indicator cathode. Under the conditions of experiment 4 the concentration of iodine and the concentration of bromine are each about 1×10^{-7} F in the cathode cell. Consideration of the indicator currents and the halogen concentrations of experiments 2, 3, and 4 leads to the conclusion that IBr_2^- does react at the cathode.

Calculation of Iodine Monobromide Equilibrium Constant. It has been observed that before the minimum point is reached the indicator current is linearly proportional to the iodine concentration. After passing through the minimum, the current becomes linearly proportional to the bromine concentration. Therefore, in the vicinity of the minimum point, it seems reasonable to represent the indicator current by the expression,

$$i = k_1(I_2^*) + k_2(Br_2^*), \qquad (1)$$

in which a starred quantity indicates the total concentration of

TABLE VI

Diffusion Currents Between Two Isolated Electrodes

No.	Anode Solution Active Constituent[a]	Anode Solution Formal Concentration	Cathode Solution Active Constituent[a]	Cathode Solution Formal Concentration	Indicator Current (Microamperes)
1	- - -	- - -	I_2	5.8×10^{-4}	0
2	I_2	1.08×10^{-5}	I_2	5.8×10^{-4}	9
3	I_2	1.08×10^{-5}	Br_2	5.80×10^{-7}	8
4	I_2	1.08×10^{-5}	IBr	5.66×10^{-4}	25

[a] In these solutions the iodine, bromine, and iodine monobromide exist primarily as the ions I_2Br^-, Br_3^-, and IBr_2^- respectively. All solutions were 2 F in perchloric acid and 0.1 F in sodium bromide, and the potential difference between the electrodes was 65 millivolts.

all species which contain that halogen in the oxidation state indicated by the formula.

From the equilibrium expression,

$$\frac{(I_2^*)(Br_2^*)}{(IBr^*)^2} = K^*,$$

substitution in equation (1) gives

$$i = k_1(I_2^*) + k_2\,\frac{K^*(IBr)^2}{(I_2^*)} \quad .$$

Since the concentration of iodine monobromide is large with respect to the iodine and bromine concentrations, it is essentially constant for these studies and may be represented by C_o; then,

$$i = k_1(I_2^*) + k_2\,\frac{K^*C_o^2}{(I_2^*)} \quad . \qquad (2)$$

Differentiating with respect to time of generation,

$$\frac{di}{dt} = k_1\,\frac{d(I_2^*)}{dt} - k_2\,\frac{K^*C_o^2}{(I_2^*)^2}\,\frac{d(I_2^*)}{dt} = \left[k_1 - \frac{k_2K^*C_o^2}{(I_2^*)^2}\right]\frac{d(I_2^*)}{dt} \quad .$$

At the point of minimum current

$$\frac{di}{dt} = 0 \text{ , but } \frac{d(I_2^*)}{dt} \neq 0 \quad .$$

Therefore, at the minimum point

$$k_1 - K_2 \frac{K^*C_o^2}{(I_2^*)^2} = 0$$

and

$$(I_2^*)_m = \sqrt{\frac{k_2K^*C_o^2}{k_1}} \quad . \qquad (3)$$

Substitution in equation (2) and collection of terms gives as the relation for the minimum point current, i_m,

$$i_m = 2C_o\sqrt{k_1k_2K^*} \quad .$$

The value of the equilibrium constant is then given by the expression,

$$K^* = \frac{(i_m)^2}{4k_1k_2C_o^2} \quad . \qquad (4)$$

Differentiation of equation (1) with respect to time gives

$$\frac{di}{dt} = k_1 \frac{d(I_2^*)}{dt} + k_2 \frac{d(Br_2^*)}{dt} \quad .$$

Before the minimum point in the region where the bromine concentration is very small compared to the iodine concentration, $\frac{d(Br_2^*)}{dt}$ is negligible and

$$\frac{di}{dt} = k_1 \frac{d(I_2^*)}{dt} \quad .$$

Denoting the generation rate as K_g (1.039×10^{-8} equivalent per second) and the volume of solution as V (liters)

$$\frac{d(I_2^*)}{dt} = - \frac{2K_g}{V}$$

and

$$k_1 = - \frac{(di/dt)V}{2K_g} .$$

The value of $\frac{di}{dt}$ may be determined graphically by measuring the slope of the linear portion to the left of the minimum point of the indicator current-time curve (See Figure 3). In a similar manner k_2 can be calculated from the generator constant and the slope of the linear portion of the indicator current curve after the minimum point.

Data for the evaluation of k_1, k_2, and i_m were obtained as described above. The values of C_o were calculated from the initial amounts of iodide added, assuming complete conversion to iodine monobromide. Values of K^* calculated from equation (4) are presented in Table VII.

Since iodine, bromine, and iodine monobromide all form complexes with bromide ion, the equilibrium,

$$\frac{(I_2Br^-)(Br_3^-)}{(IBr_2^-)^2} = K ,$$

should be considered. Under conditions approaching those of the present work the dissociation constants of I_2Br^- and Br_3^- may be taken as 0.068 (22) and 0.055 (6) respectively. A more recent value of the I_2Br^- constant has been obtained (9), but the equilibrium was studied in neutral rather than acid solutions. Faull (4) states a value of 2.7×10^{-3} for the dissociation constant of IBr_2^-. With the aid of these dissociation constants values of K were calculated from values of K* and the results are given in Table VII.

Forbes and Faull (5) determined the value of K* to be 2.06×10^{-8} in 0.974 F HBr and 3.00×10^{-8} in 4.725 F HBr, and the corresponding values of K are 1.82×10^{-8} and 2.92×10^{-8}. Using these values of K one calculates potential values of -0.87 and -0.88 volt for the half-cell,

$$I_2\ (s) + 4Br^- = 2IBr_2^- + 2e^-,$$

as compared with a value of -0.92 v which was calculated from the average value of K in Table VII. For these calculations the potential of the bromide-tribromide half-cell was taken as -1.05 v (10), and 1.34×10^{-3} M was accepted as the solubility of iodine (26).

Since the agreement between the present work and that of Forbes and Faull is not particularly good, the experimental technique was altered somewhat in an effort to check the order of magnitude of the equilibrium constant. In the titration cell was placed a second indicator anode which had a sensitivity of one-half and two-thirds that of the regular anode when the concentrations of the ion reacting at the cathode were about 0.1 F and 10^{-5} F respectively. For an iodine monobromide solution at the point of minimum indicator current, the indicator current was observed when each of the anodes was in the circuit. Since iodine is the only current limiting substance being oxidized at the indicator anode, the decrease in indicator current, Δi_m, observed on switching from large to small anode is about one-third, or at most one-half, of the indicator current carried by iodine at the large anode.

From equations (2) and (3) it can be shown that the indicator current carried by iodine at the minimum point is given by the relation,

$$(i_{I_2}*)_m = \sqrt{k_1 k_2 K^* C_o^{\,2}} \quad ;$$

therefore,

$$K^* = \frac{(i_{I_2}*)_m}{k_1 k_2 C_o^{\,2}} \quad .$$

The highest possible ratio of $\frac{\Delta i_m}{(i_{I_2}*)_m}$ will give a minimum value for K^*; therefore, since Δi is at most one-half of $i_{I_2}*$,

$$K^*_{min} = \frac{(2\ \Delta i_m)^2}{k_1 k_2 C_o^{\,2}} \quad .$$

A series of six determinations of Δi_m with three different iodine monobromide concentrations and two different bromide concentrations gave an average value of 4.4×10^{-7} for K^*_{min}. Because of the relatively small values of Δi_m, these calculations are less precise than the ones involving i_m. However, these experiments do serve as a check on the assumption that the minimum indicator current is determined primarily by the iodine and bromine which are present at that point.

TABLE VII

Dissociation Constant of Iodine Monobromide

k_1 (ua/10^{-6}F)	k_2 (ua/10^{-6}F)	i_m^* (microamperes)	IBr (F)	Br^- (F)	$K^* \times 10^6$	$K \times 10^7$
2.38	8.39	6.7	5.60×10^{-4}	0.100	1.80	7.10
1.16	6.30	4.3	5.60×10^{-4}	0.100	2.03	8.00
3.20	7.98	12.9	1.12×10^{-3}	0.100	1.31	5.16
2.62	6.76	24.7	2.24×10^{-3}	0.100	1.72	6.78
2.08	8.75	4.6	5.60×10^{-4}	0.300	0.945	6.51
2.01	8.02	9.4	1.12×10^{-3}	0.300	1.10	7.59
2.46	7.75	17.7	2.24×10^{-3}	0.300	0.816	5.64

* corrected for residual current

$$K^* = \frac{(I_2^*)(Br_2^*)}{(IBr^*)^2} \qquad K = \frac{(I_2Br^-)(Br_3^-)}{(IBr_2^-)^2}$$

B. Oxidation - Reduction Equilibria In Cupric Bromide Solutions

While studying coulometric titrations in solutions containing cupric copper (0.005 F) and bromide (0.4 F) Meier (18) observed that the indicator current never decreased to zero but always had an appreciable minimum value. He derived a relationship between the minimum indicator current and the constant for the equilibrium,

$$2Cu^{++} + 7Br^{-} \rightleftharpoons 2CuBr_2^{-} + Br_3^{-} .$$

Assuming that the potential value for the bromide-tribromide half-cell was well established, Meier then calculated a molal potential for the half-cell,

$$CuBr_2^{-} = Cu^{++} + 2Br^{-} + e^{-} .$$

Although Meier's potential value for above copper half cell was within 26 millivolts of the value which he calculated from data given by Latimer (12,13), the bromide complexes of cupric copper had not been taken into account. When the data presented in Part II of this thesis were available, corrections for the presence of $CuBr^{+}$ and $CuBr_2$ were applied to Meier's data. These corrections increased the divergence between the potential calculated from amperometric data and that calculated from Latimer's data. A complete recheck of calculations then appeared to be in order.

On page 171 of Oxidation Potentials (12) a value $E_o = -0.05$ is given for the half-cell, $2\ Br^- + Cu = CuBr_2^- + e^-$; this is on of the values which Meier used in calculating a reference cuprous bromide - cupric copper half-cell potential which he compared with his experimentally determined value. However, if one combines the following data which have been checked to the original sources given by Latimer (11,12)

$$Cu = Cu^+ + e^- \qquad E_o = -0.522$$

$$CuBr_2^- = Cu^+ + 2Br^- \qquad K = 1.2 \times 10^{-6}$$

then a value $E_o = -0.173$ is obtained for the half-cell

$$2Br^- + Cu = CuBr_2^- + e^- .$$

For the half-cell

$$CuBr_2^- = Cu^{++} + 2Br^- + e^-$$

one then obtains the value $E_o = -0.52$ which is considerably different from the -0.64 with which Meier compared his experimental value of -0.666. An examination of Meier's experimental conditions was made. Inasmuch as the value of the indicator potential was found to be of considerable significance in the study of the iodine monobromide equilibrium, an investigation was undertaken to determine the effect of indicator potential upon minimum indicator current.

Experimental

Reagents. A stock solution of 1.01 F $CuSO_4$ was prepared from reagent grade $CuSO_4 \cdot 5H_2O$. A ten fold dilution of the stock solution was standardized iodometrically as directed by Swift (27). The sodium thiosulfate solution was standardized against dried potassium iodate.

Stock solutions of 1.00 F and 6.0 F NaBr were prepared by weight from the reagent grade salt which had been dried at least 2 hours at 120° C.

Reagent grade concentrated H_2SO_4 was diluted to give 3 F acid.

Apparatus. Except for the microammeter the apparatus was the same as that used in Part I-2A. The microammeter was replaced by a shunted galvanometer as described in Part I-3A. The sensitivity of the galvanometer was about 3 divisions per microampere.

Determination of the Proper Potential for Studying the Cupric Bromide Equilibrium. A solution containing 5 ml of 1.01 F $CuSO_4$, 5 ml of 3 F H_2SO_4, and 7.5 ml of 6 F NaBr was made up to a volume of 45 ml with water. With an applied indicator potential of 100 millivolts the indicator current was carefully adjusted to its minimum value. The indicator potential was then varied and corresponding values of the indicator current were recorded. A plot of indicator current vs indicator potential is presented in Figure 4. Inspection of Figure 4 shows that an indicator potential of about 60 millivolts is most suitable for this equilibrium study.

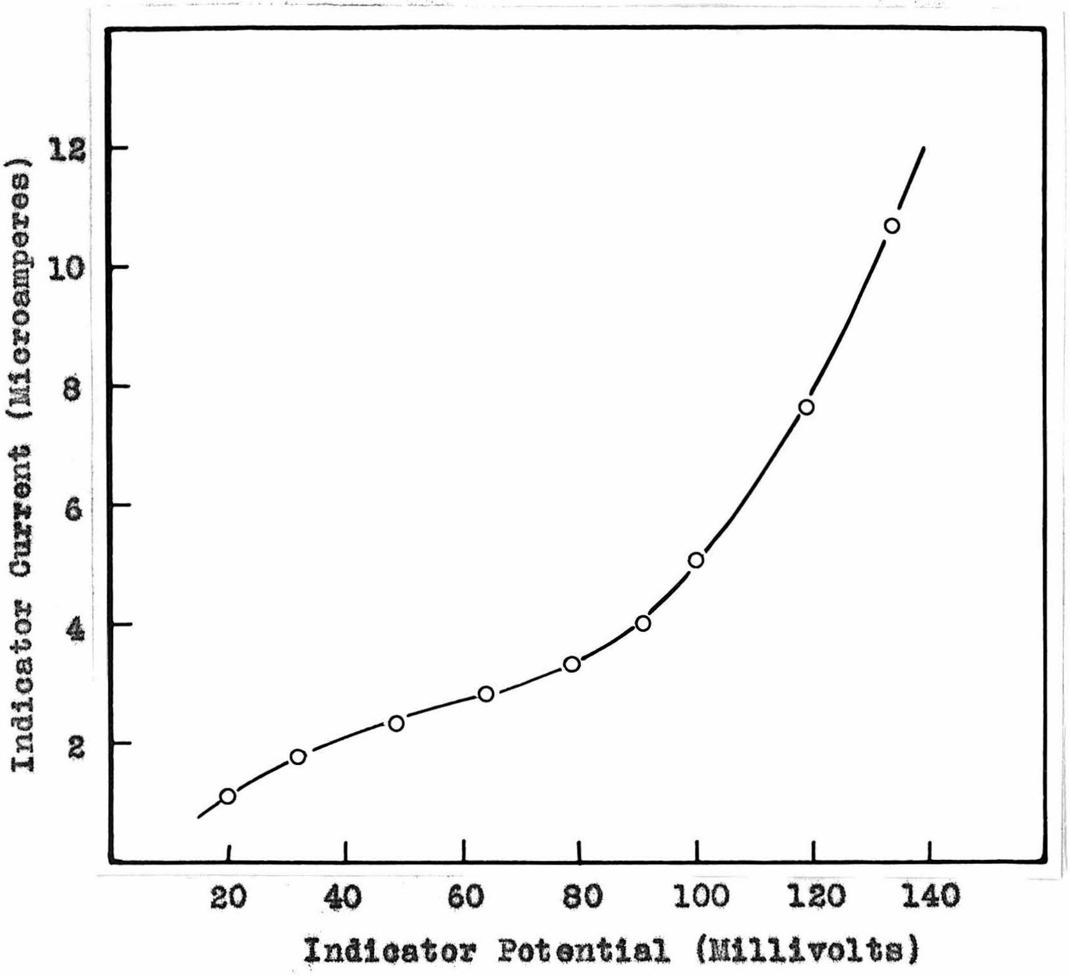

Figure 4. Variation of Indicator Current with Potential Difference Between Indicator Electrodes for a Solution Adjusted to the Point of Minimum Indicator Current at 100 Millivolts.

Solution 0.112 F in $CuSO_4$ and 1.00 F in NaBr.

Procedure for Obtaining Equilibrium Data. In view of the above experiment, the indicator potential was set at 60 millivolts. Data for equilibrium calculations were taken in solutions 0.33 F in H_2SO_4 and with a total volume of 45 ml. By means of pipets $CuSO_4$ and NaBr stock solutions were added to a titration cell (See Table VIII for experimental concentrations). Bromine was generated in the cell, and values of indicator current were recorded after each second of generation. Polarity of the generating electrodes was then reversed, and generation was continued until the indicator current had passed through the minimum point. When excess cuprous copper was being generated, values of the indicator current were recorded after each 2-4 seconds of generation. The value of the minimum indicator current was determined by passing very slowly back and forth through the minimum point until a reproducible reading was obtained.

Calculation of Cupric Bromide Equilibrium Constant. Meier (17) has derived an expression for the equilibrium constant, $K_1 = (CuBr_2^-)^2\ (Br_3^-)$, in terms of the minimum indicator current and the indicator sensitivities on each side of the minimum point. Inasmuch as that derivation is quite similar to the one in Part I-3A of this thesis, a detailed treatment will not be presented here. The calculations are based on the assumption that the indicator current is a linear function of the cuprous copper and bromine concentrations:

$$i = k_1(CuBr_2^-) + k_2(Br_2) + k_3(Br_3^-)$$

or

$$i = k_1(CuBr_2^-) + k_4(Br_3^-)$$

because at constant bromide concentration the ratio of bromine to tribromide is a constant. The cuprous copper exists primarily as $CuBr_2^-$ at the bromide concentrations used.

If $K_1 = (CuBr_2^-)^2(Br_3^-)$,

Meier has shown (17) that

$$K_1 = \frac{4(i_m)^3}{27k_1^2k_4} \qquad (A)$$

in which i_m = minimum indicator current,

$$k_1 = \frac{(di/dt)V}{K_g} ,$$

V = 0.45 liter

K_g = rate of generation (1.039×10^{-8} equivalent per second)

and

$$k_4 = \frac{(di/dt)V}{2K_g}\left[\frac{1 + 17(Br^-)}{17(Br^-)}\right] .$$

If

$$K_2 = (Cu^{++})^2(Br^-)^7 ,$$

then

$$K = \frac{K_1}{K_2} = \frac{(CuBr_2^-)^2(Br_3^-)}{(Cu^{++})^2(Br^-)^7} .$$

Values of K_1 were calculated by substituting into equation (A). The minimum current was a direct experimental measurement. Values of k_1 and k_4 were obtained by graphical estimation of the indicator current slope and substitution of that value into the proper equation. In order to calculate values of K_2 it was necessary to correct for the bromide complexes of cupric copper. From part II of this thesis the value of $K_{c_1} = 2.1$ was taken for the equilibrium,

$$Cu^{++} + Br^{-} = CuBr^{+} \quad ,$$

As an approximation for the formation of the dibromide complex,

$$CuBr^{+} + Br^{-} = CuBr_2 \quad ,$$

it was assumed that the constants for the bromide complexes would have the same ratio as the constants for the chloride complexes. From the work of McConnell and Davidson (15) one finds a value of 5.65 for the ratio of the monochloride constant to the dichloride constant. By applying this ratio the approximate value of $K_{c_2} = 0.37$ was obtained for the dibromide equilibrium given above. Higher bromide complexes of copper were assumed to be negligible in their effect on the cupric or bromide ion concentrations. In Table VIII both the formal and molal concentrations are listed for cupric and bromide ions. These molal concentrations were calculated by accounting for the cupric bromide complexes described above. Values of K_2 calculated from the molal cupric and bromide ion concentrations are presented in Table VIII.

For the equilibrium,

$$K = \frac{(CuBr_2^-)^2(Br_3)}{(Cu^{++})^2(Br^-)^7} ,$$

values of K for various cupric and bromide ion concentrations will be found in Table VIII. From the average value $K \cong 1.32 \times 10^{-16}$ the value of $E_o = -.468$ is obtained for the cell reaction given above. If the value $E_o = -1.05$ is taken (10) for the half-cell,

$$3Br^- = Br_3^- + 2e^- ,$$

then one calculated $E_o = -0.58$
for the half-cell,

$$CuBr_2^- = Cu^{++} + 2Br^- + e^- .$$

As mentioned earlier in this section the data in Latimer (11,12) yield a value of $E_o = -0.52$ for this half-cell.

The source of greatest error appears to be an indicator current which may be given by the following electrode reactions:

Indicator anode $3Br^- = Br_3^- + 2e^-$

Indicator cathode $2Cu^{++} + 4Br^- + 2e^- = 2\ CuBr_2^-$.

Inasmuch as indicator current due to this decomposition augments the indicator current due to cuprous copper and bromine, an indeterminate error is introduced because it appears to be impossible to separate the two currents. Of course the decomposition current varies with the concentration of cupric copper and bromide; therefore, it is difficult to make an estimate of the effect.

Activity coefficients have not been taken into account in all these calculations. The agreement between this work and the literature would probably not be improved by considering activities.

TABLE VIII

Constant for Cupric Bromide Oxidation - Reduction Equilibrium

No.	k_1 (Div/10^{-6} F)	k_4 (Div/10^{-7} F)	i_m (Div.)*	(Cu^{++}) (F)	(Br^-) (F)
1	9.10	5.10	7.5	0.112	1.00
2	9.95	5.45	9.8	0.0561	1.00
3	5.40	5.20	10.6	0.404	1.00
4	6.16	5.45	3.6	0.0561	0.70
5	8.65	6.75	5.1	0.0224	1.00
6	8.41	6.75	4.3	0.0561	0.70
7	6.16	4.41	8.6	0.0561	1.00

No.	(Cu^{++}) (M)	(Br^-) (M)	$K_1 \times 10^{20}$	$K_2 \times 10^4$	$K \times 10^{16}$
1	0.0318	0.90	1.39	4.84	0.287
2	0.0152	0.95	2.42	1.61	1.50
3	0.143	0.69	10.7	15.3	0.699
4	0.0206	0.66	0.306	0.232	1.32
5	0.0059	0.98	0.366	0.304	1.20
6	0.0206	0.66	0.226	0.232	0.974
7	0.0152	0.95	5.29	1.61	3.28
				Av	1.32

$$K_1 = \frac{4(i_m)^3}{27{k_1}^2 k_4} \qquad K = \frac{(CuBr_2^-)^2(Br_3^-)}{(Cu^{++})^2(Br^-)^7}$$

$$K_2 = (Cu^{++})^2(Br^-)^7$$

* 1 scale division = 0.33 microamperes

4. Study of the Successive Oxidation States of Vanadium

During a coulometric titration of tripositive arsenic (20) no change of indicator current is observed until the equivalence point is reached. Some substances such as iodine cause an indicator current during the course of the titration (see Figure 1). Professor Swift suggested that the oxidation of vanadium through several oxidation states might give rise to a series of indicator current peaks. A possible application of such phenomena would be the development of differential titrations.

Experimental

Reagents. A solution of $NaVO_3$ had been prepared and standardized by Dale Meier. The solution was said to contain $NaVO_3$ (0.152 F) and Na_2CO_3 (0.2 F). This stock vanadate solution was diluted exactly ten-fold, and sufficient HCl was included to neutralize the Na_2CO_3 and give a final acid concentration of 0.1 F.

The hydrochloric acid (8 F) described in Part I-1 was used here.

For the reductor 30-mesh zinc was given a light coat of mercury by reduction of $HgCl_2$. A small Jones reductor was prepared with a zinc column 8 cm high and about 7 mm in diameter.

Apparatus. The instrument described in Part I-1 was used for this investigation. A generation rate of 1.054 x 10^{-7} equivalent per second was used for all experiments.

Use of Small Jones Reductor and Observation of Indicator Currents.

1. A 1-ml portion of the dilute $NaVO_3$ was equivalent to about 150 seconds of generation for each electron change of the vanadium.

About 30 ml of a solution 0.1 F in HCl and 0.2 F in NaCl were added to a titration cell and the cell was flushed out with nitrogen. For all succeeding operations an atmosphere of nitrogen was maintained in the cell. One milliliter of the dilute $NaVO_3$ solution was pipetted into the reductor and was allowed to pass into the cell at the rate of one drop about every 10 seconds. Several milliliters of solution (0.1 F HCl and 0.2 F NaCl) were passed through the reductor to wash out the sample. With the indicator potential set at 200 millivolts the indicator current was very high and could only be followed by using a microammeter fitted with a variable shunt. When generation of chlorine was started, the indicator current decreased steadily for about 40 seconds; then, the indicator current remained at a low value (about 3 microamperes) for about 140 seconds while generation continued. After a total of 180 seconds of generation, the indicator current increased rapidly and did not again return to a low value, even after

330 seconds of generation. Similar results were obtained upon repetition of this procedure.

Inasmuch as Meier, Myers, and Swift (20) observed no indicator current for hydrochloric acid solutions containing V^{+4} and V^{+5}, the above experiments might be interpreted as follows:

> Roughly 30% of the vanadium was reduced to the plus three state and 40 seconds were required to oxidize that V^{+3} to V^{+4}. During the next 140 seconds the V^{+4} was oxidized to V^{+5}, then a chlorine end point was obtained. However, before it can be definitely stated that V^{+3} and V^{+4} support an indicator current, it must be shown that in the above experiments the indicator current is not caused by hydrogen from the reductor.

2. To a titration cell was added 35-40 ml of 0.3 F HCl, then the cell was flushed out with CO_2. After passing 1 ml of the dilute $NaVO_3$ solution through the reductor, CO_2 was bubbled through the solution and the indicator current (potential 300 millivolts) was observed but no chlorine was generated. The indicator current decreased slowly and reached 10 microamperes in about 3 minutes.

The same operations were performed with no vanadium in the solution going through the reductor. The initial current in the solution was a great deal less than with vanadium present. Upon passing CO_2 through the solution, the indicator current decreased rapidly to 2 microamperes in about 20 seconds.

3. Experiment 2 was repeated with a vanadium sample and purified nitrogen was used in place of CO_2. The nitrogen was bubbled through a gas washing bottle filled with 3 F NaOH saturated with $Na_2S_2O_4$: this process was supposed to remove oxygen. After the sample had been in the cell for five minutes, the indicator current had decreased somewhat but remained at a high (off scale) value.

In view of the results of experiments 2 and 3 it seems reasonable to conclude that an indicator current has been observed which is caused by V^{+3} and V^{+4}.

4. In previous experiments no evidence had been obtained regarding the presence of V^{++}. Because of the dilute solutions used it was not possible to identify the oxidation state by color.

About 3 ml of the stock 0.152 F $NaVO_3$ were acidified with HCl and placed in a small flask. The flask was flushed with CO_2, then granular zinc was added and the flask was stoppered. After swirling the contents of the flask for 20-30 seconds, the solution turned purple. To a cell containing 0.2 F HCl and flushed with nitrogen 3 drops of the purple solution were transferred. The initial indicator current decreased as chlorine was generated but there was no region of low indicator current (below 20 microamperes) prior to the final current rise. Also, there was no additional indicator current maximum or minimum which might be expected during the oxidation of V^{++} to V^{+3}.

A partial explanation of the above experiment is that V^{++} was oxidized at the indicator anode while hydrogen was being produced at the indicator cathode. However, the presence of hydrogen does not seem to account for the absence of a low indicator current during the oxidation of V^{+4}.

Use of Potentiometric Indicating System. For these experiments 0.0152 F $NaVO_3$ solution was reduced by granular zinc in a stoppered flask; the flask was filled with CO_2. One-milliliter portions of the reduced solution were transferred to the titration cell when needed.

A Beckman No. 270-6 calomel electrode was used as a reference electrode. A short length of platinum wire and two pieces of platinum foil (1 cm^2 and 5 cm^2) were tried as electrodes in the titrated solution. The potential difference between the calomel electrode and a platinum electrode in the cell was measured by a Beckman millivoltmeter.

In preliminary tests, stable potential readings were obtained when iodide was oxidized in a solution of sodium bromide. However, during a titration of tripositive arsenic with chlorine, potential values fluctuated 20-30 millivolts when readings were taken.

Several experiments were made by introducing reduced vanadium solution into a titration cell containing 0.2 F HCl. An atmosphere of nitrogen was maintained in the cell. Chlorine was generated for short intervals of time and potential readings were recorded. In no case was it possible to get a set of good potential values for a titration. The potential values either drifted or fluctuated. No one of the three platinum electrodes mentioned above improved the results.

A large calomel half-cell was prepared and connected to the titration cell by means of an agar-agar salt bridge. The potential between this calomel half-cell and a platinum wire electrode in the cell was measured by means of a "Queen" potentiometer. Stable potential values could not be obtained with this arrangement.

Conclusions

Inasmuch as vanadium can be determined coulometrically by electrolytically generated cuprous copper (20), further investigation did not appear to be profitable at this time.

Two conclusions can be drawn from the experiments using the amperometric circuit.

1. In a hydrochloric acid solution tripositive and quadrapositive vanadium cause an indicator current.
2. If a good reducing agent such as dipositive vanadium is placed in a titration cell and the indicator circuit is closed, a significant amount of the reducing agent may be oxidized by the indicator anode while hydrogen is being produced at the indicator cathode. For the coulometric titration of such substances a special method will be required.

References

1. Brown, R. A. and Swift, E. H., J. Am. Chem. Soc., 71, 2717 (1949).

2. Cooke, W. O., Hazel, F., and McNabb, W. M., Anal. Chem., 21, 1011 (1949).

3. Farrington, P. S. and Swift, E. H., Anal. Chem., 22, (1950). In Press.

4. Faull, J. H., J. Am. Chem. Soc., 56, 522 (1934).

5. Forbes, G. S. and Faull, J. H., J. Am. Chem. Soc., 55, 1820 (1933).

6. Griffith, R. O., McKeown, A., and Winn, A. G., Trans. Faraday Soc., 28, 101 (1932).

7. Helger, B., Chemical Abstracts, 43, 5688 (1949).

8. Kolthoff and Lingane, Polarography, Interscience, New York, 1946, P. 455-458.

9. Korenman, I. M., J. Gen. Chem. (USSR) 17, 1608 (1947).

10. Latimer, The Oxidation States of the Elements, Prentice-Hall, New York, 1938. Page 53.

11. Ibid, Page 169.

12. Ibid, Page 171.

13. Ibid, Page 173.

14. Lingane, J. J., J. Am. Chem. Soc., 67, 1916 (1945).

15. McConnell, H. and Davidson, N., ibid, 72 (1950). In Press.

16. Mehlig, J. P. and Shepherd, M. J., Anal. Chem., 21, 642 (1949).

17. Meier, D. J., M.S. Thesis, C.I.T. (1948). Part IV.

18. Ibid, Page 38.

19. Meier, D. J., Myers, R. J., and Swift, E. H., J. Am. Chem. Soc., 71, 2340 (1949).

References (Continued)

20. Myers, R. J. and Swift, E. H., ibid., 70, 1047 (1948).

21. Ramsey, W. J., Farrington, P. S., and Swift, E. H., Anal. Chem., 22, 332 (1950).

22. Ray, P., and Sarker, P. V., J. Chem. Soc., 121, 1449 (1922).

23. Sease, J. W., Niemann, C., and Swift, E. H., Anal. Chem., 19, 197 (1947).

24. Someya, K., Z. Amorg. Algem. Chem., 152, 368 (1926).

25. Swift, E. H., J. Am. Chem. Soc., 51, 2682 (1929).

26. Swift, E. H., A System of Chemical Analysis, Prentice-Hall, New York, 1939. Page 69.

27. Ibid, Page 245.

28. Szebelledy, L. and Somogyi, Z., Z. Anal. Chem., 112, 313 (1938).

29. Szebelledy, L. and Somogyi, Z., ibid., 112, 385, 391, and 400 (1938).

30. Wooster, W. S., M.S. Thesis, C.I.T. (1947).

31. Ibid, Page 10.

32. Ibid, Page 11.

33. Ibid, Page 12

34. Wooster, W. S., Farrington, P. S., and Swift, E. H., Anal. Chem., 21, 1457 (1949).

II. SPECTROPHOTOMETRIC INVESTIGATION OF THE COPPER (II) MONOBROMO COMPLEX

In Part I-3B of this thesis the calculations required information concerning the bromide complexes of cupric copper. For many years it has been known that cupric copper in concentrated bromide solutions (above 3.5 formal HBr) produces a reddish-brown to purple color; however, no one seems to have published an equilibrium constant for any of the bromide complexes. McConnell and Davidson (1) have determined equilibrium constants for both the monochloro and dichloro complexes of cupric copper: the spectrophotometric method which they used is relatively uncomplicated for determination of a monohalide complex and it was adopted for this investigation. All solutions used for these measurements were adjusted to an ionic strength of unity.

Experimental

Reagents. A solution of $Cu(ClO_4)_2$ had been prepared by Harden McConnell by dissolving $CuCO_3 \cdot Cu(OH)_2$ in $HClO_4$: the excess $HClO_4$ was reported to be very small. A solution of $Na_2S_2O_3$ was prepared and standardized against KIO_3. The $Cu(ClO_4)_2$ solution was then standardized iodometrically as directed by Swift (2), and the copper concentration was found to be 1.342 F.

A stock solution of NaBr (0.100 F) was prepared by dissolving a weighed portion of the reagent grade salt in chloride-free water and diluting to the mark in a volumetric flask. The NaBr had been dried for 1.5 hours at 120° C. Solutions 0.0050 F and 0.0250 F in NaBr were prepared by accurate dilution of the stock solution.

A standard solution of $HClO_4$ (2.673 F) was prepared by diluting 60% acid. Standardization of the acid was accomplished by the iodate method outlined by Swift (3).

Apparatus. A Beckman Model DU Spectrophotometer with hydrogen lamp was used for measurements of optical density. The rectangular right prism quartz cells were of 1.00 cm path length.

Preliminary Experiments.

1. Portions of the above solutions were pipetted into a 50 ml volumetric flask so that the final solution was 0.250 F in $Cu(ClO_4)_2$, 0.00100 F in NaBr, and 0.249 F in $HClO_4$. Before the addition of NaBr, the volumetric flask was flushed out with CO_2. After the solution in the flask was thoroughly mixed, a portion of the solution was transferred to a spectrophotometer cell and a cell cover was placed in position with a thin film of grease to exclude air.

A blank solution 0.249 F in $HClO_4$ was used to balance the spectrophotometer at each wave length. A copper comparison solution was made up to be 0.250 F in $Cu(ClO_4)_2$ and 0.249 F in $HClO_4$.

At a given wave length the spectrophotometer was balanced at zero optical density when a blank solution was in the light path. The copper comparison solution was then placed in the light path and the optical density was determined. Immediately, the copper solution containing bromide was placed in the light path and the optical density was measured. Thirteen wave lengths from 255 to 300 millimicrons were used. The wave length intervals varied from 1 to 10 millimicrons depending upon the change in optical density.

Below 260 millimicrons the optical densities of both copper solutions were high (above 0.6) and the difference in optical densities was not large enough to permit accurate calculations (see Discussion). The copper complex appeared to absorb most strongly about 280 millimicrons; however, the optical density of the copper complex solution in that region was too low (about 0.1) for accurate work.

2. A solution 0.250 F in $Cu(ClO_4)_2$, 0.005 F in NaBr, and 0.245 F in $HClO_4$ was prepared as in experiment 1. Optical densities were measured (as in exp. 1) at every 5-millimicron interval from 260 to 300 millimicrons. The results of this experiment indicated that 0.005 F NaBr was a suitable concentration for subsequent experiments.

3. The optical density of a solution 0.485 F in $HClO_4$ and 0.005 F in NaBr was measured using 0.485 F $HClO_4$ as the blank solution. Over the range 270 to 295 millimicrons the optical density of the bromide solution varied from 0.002 to 0.004.

Procedure. All solutions were prepared by pipetting standard solutions into 50 ml volumetric flasks and diluting to the marks. Flasks to contain bromide were flushed with CO_2 just before the addition of bromide solution. The $Cu(ClO_4)_2$ concentrations were 0.250 F, 0.210 F, 0.170 F, 0.135 F, and 0.100 F. The NaBr concentration was always 0.005 F, and sufficient $HClO_4$ was added in each case to bring the ionic strength to unity. Each blank solution contained the amount of $HClO_4$ used in the corresponding copper complex solution: each copper comparison solution contained the same amount of $Cu(ClO_4)_2$ and $HClO_4$ as the corresponding copper complex solution.

The operation of transferring the copper complex solution to a spectrophotometer cell was performed in a large beaker into which a stream of CO_2 was passed. That cell was then closed with a rubber stopper which had been trimmed to fit the square top of the cell.

The spectrophotometer was balanced with the blank solution at each wavelength, then the optical densities of a copper complex solution and the corresponding copper comparison solution were measured. Readings were taken at 5-millimicron intervals from 260 to 300 millimicrons. To check possible drifting of the readings, optical densities of each set of solutions were remeasured at several wavelengths about 15 minutes after the first determination.

Discussion

For solutions of the same ionic strength it is a reasonably good assumption that the activity coefficients of the ions of interest are constant even though the composition of the solutions is varied. As shown by preliminary experiment 1, very dilute solutions cannot be used because there would be insufficient complex to give easily measurable absorption. In consideration of these facts a constant ionic strength of unity was chosen for this investigation.

In the equilibrium,

$$Cu^{++} + Br^{-} \rightleftharpoons CuBr^{+}$$

let $(CuBr^{+}) = x$,

then $(Cu^{++}) = a - x$ and $(Br^{-}) = b - x$.

For the equilibrium constant, K, one obtains the relation

$$\frac{x}{(a-x)(b-x)} = K.$$

If $a \gg b$ and $a \gg x$,

as a first approximation

$$\frac{x}{b-x} = Ka$$

or

$$\frac{x}{b} = \frac{Ka}{1+Ka} \qquad (1)$$

By definition,

$$D_0 = \epsilon_0 a \quad \text{and} \quad D_1 = \epsilon_1 x$$

in which D_0 and D_1 are the optical densities of solutions (a) and (x) formal in Cu^{++} and $CuBr^{+}$ respectively and with a total ionic strength of 1.00. The quantities ϵ_0 and ϵ_1 are the molar extinction coefficients of Cu^{++} and $CuBr^{+}$ respectively. If D_{o_1} is the optical density of a solution (a) formal in copper perchlorate, (b) formal in sodium bromide and with sufficient perchloric acid to bring the ionic strength to unity, further use of the fact that $a \gg x$ yields the approximation

$$D_{o_1} = \epsilon_1 x + \epsilon_o a ;$$

then

$$D_1 = \epsilon_1 x = D_{o_1} - D_o \quad .$$

Substituting in equation (1)

$$\frac{D_1}{b} = \frac{Ka\,\epsilon_1}{1 + Ka}$$

and

$$\frac{D_{o_1} - D_1}{b} = \frac{Ka\,\epsilon_1}{1 + Ka} \quad .$$

Inversion of this equation yields the relation,

$$\frac{b}{D_{o_1} - D_o} = \left(\frac{1}{K\epsilon_1}\right) \frac{1}{a} + \frac{1}{\epsilon_1} \quad . \qquad (2)$$

If $CuBr^{+}$ is the only complex formed in significant quantity, then a plot of $\frac{b}{D_{o_1} - D_o}$ against $\frac{1}{a}$ should be a straight line. When the experimental data were plotted on such a graph, the points were somewhat scattered but no smooth curve other than a straight line could be passed through the points. In equation (2) it can be seen that the equilibrium constant, K, is obtained from the ratio of intercept to slope.

Instead of evaluating K graphically, the method of least squares was used to correlate the data. Although optical densities had been measured at nine wave lengths, the data used for the calculation of K was that which was taken in the region of maximum absorption by $CuBr^+$. After obtaining values of K, a check was made on the change of Cu^{++} concentration by complex formation: the numerical approximations made in deriving equation (2) are within experimental errors.

Values of K calculated from data at five wave lengths are presented in Table IX. By means of standard formulas the probable error was calculated for each of the five slopes and intercepts. From an average value of the slopes, intercepts, and probable errors in those values, a probable error was calculated for the average value of K: this probable error was found to be 0.249.

For each of the five solutions used in this investigation (x), the concentration of $CuBr^+$, was calculated using the average value of K. From the approximation mentioned above,

$$D_1 = D_{o_1} - D_o \quad ,$$

then
$$\epsilon_1 = \frac{D_1}{x} = \frac{D_{o_1} - D_o}{x}$$

Values of the molar extinction coefficient of $CuBr^+$, ϵ_1, were calculated for each of the five solutions, and the average value of ϵ_1 was found for each of the nine wave lengths. Figure 5 shows the curve obtained by plotting $\log_{10} \epsilon_1$, against wave length.

Summary

An equilibrium constant for the formation of the monobromo complex of copper (II) in solutions of unit ionic strength has been determined by a spectrophotometric method. At 22 ± 2° C the average value for that equilibrium constant was found to be 2.1 ± 0.25.

The molar extinction coefficient of $CuBr^+$, ϵ_1, been determined over the range 260 to 300 millimicrons, and ϵ_1 is reported graphically as a function of wave length.

TABLE IX

Equilibrium Constant for the Copper (II) Monobromo Complex in Solutions of Unit Ionic Strength

Wave Length (Millimicrons)	K[a] (liter/mole)
275	2.06
280	2.04
285	1.87
290	2.20
295	2.25
Av.	2.08

[a] $K = \dfrac{(CuBr^{+})}{(Cu^{++})(Br^{-})}$

References

1. McConnell, H. and Davidson, N., J. Am. Chem. Soc., 72, (1950) In Press.

2. Swift, E. H., A System of Chemical Analysis, Prentice-Hall, New York (1938). Page 245.

3. Ibid, Page 526.

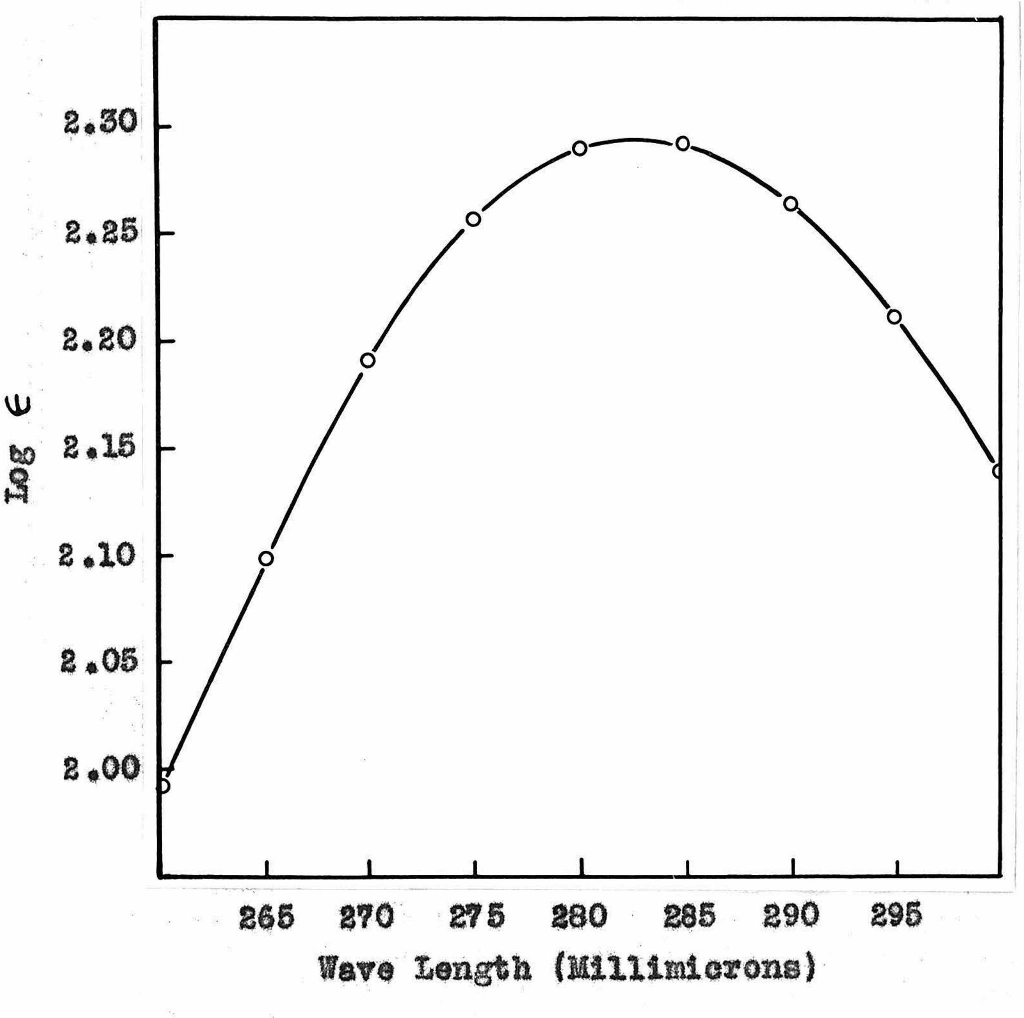

Figure 5. Molar Extinction Coefficient of $CuBr^+$ in Solutions of Unit Ionic Strength.

III. Determination of Carbon by Wet Combustion *

Equipment recommended for use by a Chemical Warfare Service Mobile Unit was subject to the following special requirements:

a). The apparatus should require a minimum of space when packed and when assembled for use.

b). When packed, the apparatus must withstand heavy shocks in transport.

The Van Slyke manometric apparatus was designed to use the Van Slyke-Folch (4) combustion mixture for the determination of carbon in organic compounds. However, the Van Slyke apparatus is bulky and fragile and does not meet the above requirements. It appeared possible to design a less expensive apparatus which could be assembled easily in a small space. With these objectives in view this investigation was undertaken.

Briefly, the procedure is as follows: A sample of 10 to 12 mg is heated with an anhydrous sulfuric, phosphoric, chromic, and iodic acid mixture in a stream of carbon dioxide - free air, and the carbon dioxide evolved is absorbed in sodium hydroxide. The carbonate thus formed is precipitated as barium carbonate and determined acidimetrically. The Van Slyke-Folch combustion

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* Based upon work done for the Office of Scientific Research and Development under Contract OEMsr-325 with the California Institute of Technology.

solution has been used in other procedures (2,3), but in these the carbon dioxide has been determined gravimetrically.

Experimental

Reagents. Preparation of the combustion solution. Pour 60 ml of 30% fuming H_2SO_4 into a flask containing 40 ml of 85% phosphoric acid and add 10 gm of CrO_3 and 1 gm of KIO_3. Heat to $140-150^\circ$ C and swirl or stir for 1-2 minutes. Cool and store in small glass-stoppered bottles. As an alternative to using fuming sulfuric acid, use 20 gm of P_2O_5, 85 ml of 95% H_2SO_4, and 15 ml of 85% H_3PO_4 with the stated quantities of CrO_3 and KIO_3.

Sodium Hydroxide (0.5 F). Dissolve 5 gm of NaOH in 20 ml of water, add 1 ml of 1 F $BaCl_2$ solution and centrifuge. Dilute the centrifugate to 250 ml and store in a siphon bottle protected by a soda lime tube.

Barium Chloride Reagent, 1 F in $BaCl_2$ and 0.001 F in HCl.

Preliminary Experiments. The following seventeen experiments are presented to outline the developments leading to the final procedure and the apparatus shown in Figures 6 and 7 (page 91).

1. The first rather crude apparatus consisted of a drying tower, filled with pellets of NaOH, and two 15-ml centrifuge tubes connected in series as are tubes A, M, and G in Figure 6 (Page 91). The tube corresponding to combustion tube M was closed with a rubber stopper, the CO_2 was admitted into ab-

sorption tube G by means of glass tubing drawn to a fine tip, and a solution of $Ba(OH)_2$ was used in tube G.

A sample of 3, 5 dinitrobenzoic acid was weighed into the combustion tube. By means of a water aspirator air was drawn through the apparatus for several minutes, CO_2 being absorbed by the NaOH in the drying tower. To the combustion tube were added 2 ml of combustion solution, and 2 ml of saturated $Ba(OH)_2$ and 3 ml of water were added to the absorption tube. While a stream of air was drawn through the apparatus, the combustion solution was heated to boiling for 6-8 minutes. The absorption tube was then disconnected, and the $BaCO_3$ precipitate was washed with two 3-ml portions of water then titrated with 0.0462 F HCl to a methyl orange end point in hot solution.

The result was about 25% high and indicated that the precipitate should be washed more efficiently. A tendency for solid $BaCO_3$ to clog the tip of the inlet tube in the absorption chamber was troublesome.

2. Experiment 1 was repeated to the washing of the precipitate. After the precipitate was drained of excess $Ba(OH)_2$ solution, 1 ml of water and 1 drop of 0.1% phenolphthalein indicator were added to the precipitate. Very dilute HCl (about 0.04 F) was added dropwise with stirring until the solution was just decolorized. A faint pink color on the precipitate indicated that the acid was not present in excess. The mixture was centrifuged, and the precipitate was washed with 2 ml of water. The carbonate was titrated to a methyl orange end point

in hot solution with 0.1932 F HCl.

The result was about 30% low indicating that absorption was incomplete; perhaps the combustion progressed too rapidly. Some of the solid $BaCO_3$ was carried up on bubbles and deposited on the upper wall of the tube and on the stopper. After washing the precipitate and centrifuging, the centrifugates were turbid; a small loss here but not enough to account for the large error.

3. Repeated experiment 2 with the following changes:
   a. The $Ba(OH)_2$ was replaced with 0.5 F NaOH.
   b. The combustion solution was heated slowly.
   c. One milliliter of 1 F $BaCl_2$ reagent was added to the absorption tube to precipitate the carbonate.
   d. After the base adsorbed on the precipitate was neutralized with dilute HCl as described in experiment 2, 2 drops of 2% Braunsol wetting agent were added before centrifuging.

The results of three runs were 97, 101, and 94% of the amount of carbon thought to be present. The above modification appeared to correct the major difficulties; however, there is a tendency toward low results.

4. The drying tower filled with NaOH pellets was replaced by two bubblers made from test tubes; the first was filled with 50% NaOH and the second with 0.5 F NaOH. In earlier experiments combustion tube M had been an ordinary 15-ml centrifuge tube closed by a rubber stopper. A special head was made on a male standard taper ground-joint (14/20): inlet and outlet tubes

were provided in the sides of the head for gas flow, and an inlet tube for introducing combustion solution was sealed in the top. The female 14/20 joint was sealed on a 15-ml centrifuge tube and this combustion tube (M) was fitted to the head, using H_3PO_4 as a lubricant and air seal. Modifications of the procedure were as follows:

a. After most of the excess base on the precipitate had been neutralized and the mixture had been centrifuged as described in experiment 2, the remaining adsorbed base was neutralized in similar fashion instead of washing with water.

b. The carbonate was determined by adding an excess of standard HCl and backtitrating with standard NaOH.

The average of several runs was still low by about 2%. Blank runs averaged 0.016 mg of carbon which was about 0.5% for most of the samples used.

5. Rate of flow of the gas stream through the absorption tube G was varied in a series of three experiments. The results were consistently low indicating that the recovery of CO_2 in the absorption tube might not have been 100% efficient.

6. Anhydrous Na_2CO_3 was prepared by heating $NaHCO_3$ at 270-300° C to constant weight. Three samples of the Na_2CO_3 were weighed out and treated by the procedure of experiment 4; H_2SO_4 was used to decompose the carbonate.

The average result was 97% of the calculated value giving additional evidence that the CO_2 was not completely absorbed.

7. The precipitation and titration procedures were checked with weighed samples of the freshly prepared Na_2CO_3 (experiment 6). Each carbonate sample was dissolved in a small amount of water, then 0.5 F NaOH was added and the precipitation, washing, and titration were performed as in experiment 4.

The results of three tests averaged about 0.5% high showing that there was no loss involved in the above operations.

8. A second absorption tube was placed in series with the usual absorber. The only alteration of procedure was to add 5 drops of 1 F $BaCl_2$ to the first washing of the $BaCO_3$ precipitate and 3 drops to the second washing.

One sample of Na_2CO_3 was treated as in experiment 6 and the result was 98.3% of the calculated value: no $BaCO_3$ was obtained in the second absorption tube. For a second sample of Na_2CO_3 the result was only 94.7% of the calculated value: a significant quantity of $BaCO_3$ was obtained in the second tube and the precipitate was estimated to be about 0.1 mg of carbon.

Obviously a more efficient absorption system was needed. It was desirable to absorb the CO_2 in a centrifuge tube so that precipitation and centrifugation could be effected with a minimum of exposure to the air. No sintered glass units would fit into a 15-ml centrifuge tube; however, a small porous dispersing unit became available commercially and one of those was ordered.

9. While the dispersing unit was on order, a different type of apparatus was tried. Two 15-ml centrifuge tubes, fitted

with ground glass joints, were connected together by means of a glass tube which carried two male ground-joints. Sealed into the bridge directly above each of the tubes was an inlet tube, each of which was closed by a stopcock. A sample was weighed into one of the tubes and the joint of that tube was lubricated with syrupy H_3PO_4. Through one of the inlet tubes the assembly was evacuated with a water aspirator. About 5 ml of 0.5 F NaOH were admitted to the empty tube, and 5 ml of combustion solution was admitted to the tube containing the sample. The combustion solution was then heated to decompose the sample, and the assembly was shaken to aid in absorbing the CO_2 into the base. Precipitation and determination of the carbonate was done as in experiment 8.

Many experiments were performed and several minor variations of the apparatus were used. In almost all cases the results were low. The excess CrO_3 decomposes at elevated temperatures producing oxygen which destroys the vacuum in the apparatus and hinders the transfer of CO_2 to the base. For this reason these experiments were discontinued and further detail is omitted from this report.

10. A dispersing unit, stated to be a 50-micron disperser, was obtained from Wilkens-Anderson Co. The unit was constructed from a 2.5-cm length of 6-mm o.d., 4-mm i.d. Alfrax tubing (Carborundum Co.) which was cemented to a section of 4-mm glass tubing; the opposite end of the porous tube was closed with a white cement. This disperser served as the gas inlet in

absorbing tube G. The only changes of procedure were the following:

a. Because of the large area involved, the inside of the disperser was rinsed as well as the outside. The washings were added to the solution in tube G.

b. After the addition of the $BaCl_2$ to precipitate the carbonate, the 15-ml centrifuge tube (G) was stoppered with a rubber stopper fitted with a short section of glass capillary tubing. The tube was then placed in a bath of boiling water for 2-3 minutes to allow coagulation of the precipitate.

Eight samples of adipic acid (recrystallized) were tested and the results were consistently 1 to 2% high. The absorption of CO_2 was evidently satisfactory but the efficiency of the scrubbers for incoming air was questionable. Heating the $BaCO_3$ precipitate before centrifugation was definitely an improvement and the centrifugates were clear.

11. To serve as a compact and efficient CO_2 scrubber, a Kraissl tube packed with Ascarite was placed in the position shown in Figure 6 (page 91). After the combustion tube M had been heated sufficiently long (5-6 minutes) to decompose the sample and the excess CrO_3, the combustion tube was nearly filled with concentrated H_2SO_4. With less dead space in tube M a shorter period of air flow would be necessary to sweep over all the CO_2.

Four analyses of adipic acid gave results less than 1%

(about 0.05 mg of carbon) high. A blank run produced no visible $BaCO_3$ precipitate in the absorption tube.

12. Inasmuch as the $BaCO_3$ precipitate was washed for the last time in a solution which had been adjusted to the phenolphthalein transition point, the final back titration with standard NaOH was made to the phenolphthalein end point for several samples which had been titrated to the methyl orange end point. The average difference in the two titrations amounted to about 0.01 mg of carbon.

13. A 10-ml portion of water which had been used for washing the dispersers and the walls of the centrifuge tube was tested with $BaCl_2$ and a precipitate was obtained. The precipitate was estimated to correspond to 0.01 mg of carbon; therefore, freshly boiled distilled water should be used for washing.

14. When several milligrams of NaF were placed in the combustion tube with a sample, the disperser became clogged during the process of running a determination. Small pieces of porous porcelain were placed in the rubber tubing connecting the combustion and absorption tubes; however, after samples containing fluoride were run, etching was visible on the upper portion of the disperser inlet tube. With a plug of moist glass wool in the connecting tube, no signs of HF attack were visible beyond the glass wool.

Four samples of sodium oxalate with added NaF were analyzed. One pair of samples was tested when 0.05 F HCl was placed on the glass wool, and the results were 0.05 to 0.11 mg of carbon high.

The other two samples were analyzed with distilled water on the glass wool and the results were only 0.02 mg of carbon high: similar results were obtained with samples containing no fluoride and with distilled water on the glass wool.

15. The cement on the dispersing unit deteriorated rapidly because of the basic solution in which it was immersed and it was not possible to make a glass seal between the Alfrax and glass tubing. After a lengthy correspondence with the Carborundum Company, a sample of porous Zircofrax tubing was obtained. This tubing was 6-mm o.d. and 4-mm i.d. and could be sealed to Pyrex glass. A small dispersing unit was then constructed from a 3-mm length of Zircofrax tubing which was sealed to a 3-mm Pyrex inlet tube and the opposite end was closed with a glass plug. This disperser was very satisfactory in all respects.

16. The vacuum siphon shown in Figure 7 (page 91) was developed to minimize absorption of CO_2 while the excess NaOH was removed from the $BaCO_3$ precipitate. Tests showed that small positive errors were not materially reduced by the use of the vacuum siphon; however, its use should eliminate positive errors which might arise if the time required to make the determination were unduly prolonged.

17. The combustion-tube head D was designed to have the minimum number of ring seals: earlier models required 3 ring seals.

Final Procedure

The procedure given below and the apparatus shown in Figures 6 and 7 (page 91) are the results of the experiments described above and some observations which were not included there.

Assembly of the Apparatus. Assemble the apparatus as shown in Figure 6 (page 91). Clean, dry and reserve a glass-stoppered 15-ml centrifuge tube (Tube M) (Note 1). Pack the Kraissl absorption tube A on both sides with 20-30 mesh Ascarite or soda lime (Note 2). Add sufficient concentrated H_2SO_4 to the bubble counter B to immerse the inlet tube about 2 mm.

Connect micro stopcock C (Note 3) to tube A and head D with short lengths of clean, dry rubber tubing; leave stopcock C in the open position. Lubricate stopcock E with concentrated H_3PO_4 and leave it in the closed position. (Note 4). Connect tube F to the outlet of head D with a 2 to 3-inch length of rubber tubing. Fill tube F with glass wool moistened with 3-4 drops of distilled water (Note 5).

Bore three holes in a No. 1 rubber stopper. Through one hole, pass a short length of 4-mm glass tubing which has a 1-mm tip. Connect this tube to the delivery tube of the storage bottle H (which contains sodium hydroxide-barium chloride reagent, 0.5 F in NaOH and 0.004 F in $BaCl_2$), and attach pinch clamp J to the connecting tube. By applying a slight pressure through the soda-lime tube of bottle H, force solution from H until it fills the delivery tube, then close clamp J. Moisten

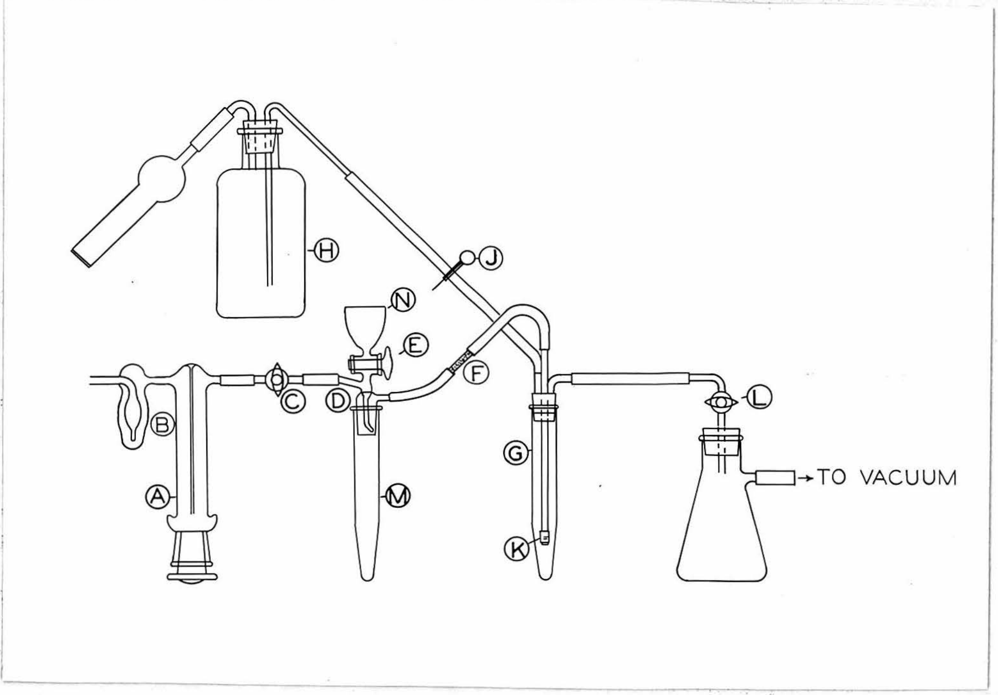

Figure 6. Apparatus for Determination of Carbon.

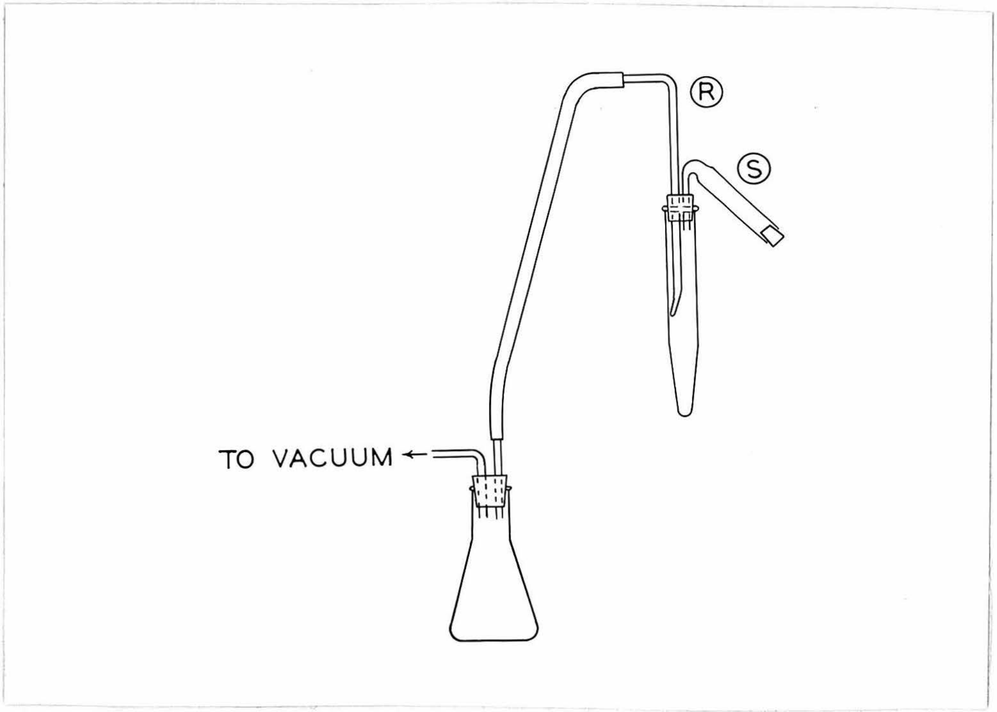

Figure 7. Vacuum Siphon.

the glass tubing which carries the disperser K (Note 6) with a drop of glycerine and insert the tubing in the rubber stopper (Note 7); connect the disperser inlet tube to tube F with a 4 to 5-inch length of rubber tubing. Insert in the third hole of the stopper a 4-mm glass outlet tube and connect it to micro stopcock L (Note 3) with clean, dry rubber tubing (Note 8). Pass the other arm of the stopcock (L) through a No. 3 rubber stopper, then fit the stopper into a 125-ml suction flask and connect the side arm of the suction flask to a water aspirator. Just before attaching the 15-ml centrifuge tube (G) to the 3-hole stopper assembly, open clamp J and allow 2 to 3 ml of the $NaOH-BaCl_2$ reagent to flush out the connecting tube.

Finally, assemble the vacuum siphon (Figure 7, page 91). Place tube R (Note 9) and special soda-lime tube (Note 10) in a two-hole No. 1 rubber stopper. Connect tube R to the 50-ml flask with about 2 feet of rubber tubing. When the vacuum siphon is used, disconnect the rubber tubing from the outlet of tube G and connect that tubing to the outlet of the 50-ml flask.

Notes.

1. The tube, which receives the sample, should be cleaned with hot $CrO_3-H_2SO_4$ solution, rinsed, dried, and protected from dust by inverting in a clean beaker or by stoppering with a glass stopper.

2. Place a plug of glass wool in each compartment of the Kraissl tube to protect the inlet and outlet tubes. Another

plug of glass wool should be placed between the filling and the stopper.

3. Stopcocks C and L should be lubricated with a thin film of grease.

4. The stopcock should turn easily. Do not force the stopper as it may lock.

5. If it is known that the sample does not contain fluorine, tube F may be omitted from the apparatus. This tube is inserted to remove HF which would attack the inside of the disperser and so clog the pores that the disperser could not be flushed out.

A clean tube and filling should be used for each run because the acid produced by the absorption of SO_3 lowers the efficiency of HF absorption.

6. The disperser can be made by closing, with a piece of glass, one end of a short length of Zircofrax tubing, 12-7P.89, 1/4 x 1/8, and joining the other end to a length of standard wall Pyrex tubing. The joints are glass.

7. Since the disperser is moved in the stopper during each run, the inlet tube should be kept movable in the stopper. The disperser should be rinsed out with dilute HCl and water and should be dried before being used.

8. Solid or liquid which may have been deposited in the connecting tube by spray from previous runs should be washed out and the tube should be dried.

9. Tube R is made from 4-mm tubing drawn to a 1-mm tip at

one end. Allow a 15-cm length from the tip, then make a right angle bend which will aid in moving the tube in the stopper.

10. Special soda-lime tube S consists of a 3-inch length of 10-mm tubing attached to 2 inches of 4-mm tubing bent as shown in Figure 7 (page 91). The 4-mm tubing can be sealed to 10-mm tubing or a section of the 10-mm tubing can be collapsed and drawn to 4-mm diameter.

Place a plug of glass wool at the narrowed end of the 10-mm section and fill the tube with Ascarite or soda lime. Cap the tube with a plug of glass wool and a cork which has been grooved on the side with a file.

Procedure for the Analysis of Solid Substances

Weighing the Sample. Carefully weigh (Note 11) a 10 to 12-mg sample of the substance for analysis into a clean, dry 15-ml glass-stoppered centrifuge tube (M).

Moisten the ground surface on head D with concentrated H_3PO_4; then attach tube M, turning the tube until a firm seal is obtained.

Flushing and Filling the Apparatus. Turn on the water aspirator and slowly open stopcock L until the rate of air flow through bubble counter B is 3-4 bubbles per second. After 4-5 minutes, carefully open clamp J and admit NaOH to tube G to within 3 to 4 cm of the top of the tube. Do not admit the NaOH so rapidly as to cause liquid to back up into the disperser tube. Pour 5 to 6 ml of combustion solution into cup N, and adjust the rate of air flow to 1 to 2 bubbles per second. Close stopcock C (Note 12) and immediately open stopcock E. When most of the liquid has entered tube M close stopcock E (Note 13) and immediately open stopcock C.

Combustion of the Sample and Absorption of Carbon Dioxide. By means of stopcock L adjust the rate of air flow through counter B (Note 14) to 3 to 4 bubbles per second. Watch the action of bubble counter B (Note 15) and first warm the upper portion of the combustion mixture with a micro burner, then the lower part. When gas is evolved, control the heating so that bubble counter B indicates positive flow or is at equilibrium (Note 16). If liquid starts to back up in B (Note 17), quickly close stopcock C and cease heating for a few seconds until the evolution subsides. Open stopcock C and continue to boil the combustion mixture. Heat the mixture so as to obtain vigorous gas evolution (Note 18).

After 5 to 6 minutes of heating (Note 19), remove the flame and fill cup N with concentrated H_2SO_4. Close stopcock C and open stopcock E. When the liquid level in tube M is 2 to 3 mm below the inlet tube of head D, close stopcock E (Note 13) and open stopcock C. Ascertain that the rate of air flow through B is still about 3 bubbles per second.

Removal of the Absorbing Tube. When 3 to 4 minutes have elapsed since filling tube M with acid, slide the disperser inlet tube up through the stopper until the disperser is 1 cm or more above the solution. Close stopcock L, then disconnect the rubber tubing from the disperser inlet tube. By means of a long capillary dropper fill the disperser inlet tube with CO_2-free distilled water (Note 20). Carefully open stopcock L and draw the water through the disperser. (Do not draw air through the disperser.) Close L and remove the stopper from the centrifuge tube (Note 21). Rinse off the bottom of the stopper and the disperser with a few drops of CO_2-free water, then rinse down the walls of tube G with a few drops of the water.

Precipitation of the Carbonate. With a dropper or pipet add 1-1.5 ml of barium chloride reagent (1 F in $BaCl_2$, and 0.001 F in HCl) (Note 22) to tube B and immediately stopper the tube with a No. 1, one-hole rubber stopper which is fitted with a short piece of 0.5-mm capillary tubing. Place the centrifuge tube in a bath of boiling water for 2 to 3 minutes. Replace the rubber stopper with a rubber centrifuge tube cap, then centrifuge until the solution is clear.

Washing the Precipitate. Mount the centrifuge tube (G) firmly in a buret clamp. Moisten tube R in the vacuum siphon apparatus so that it moves freely through the rubber stopper. Adjust tube R so that the tip projects only 3 to 4 cm below the rubber stopper. Remove the cap from the centrifuge tube and immediately insert the rubber stopper. Carefully open stopcock L until solution is drawn slowly out through R. With a twisting motion push R down as the solution level recedes until the tip of R is just above the precipitate (Note 23); no precipitate should pass into R. Remove the stopper from the centrifuge tube and rinse down the walls of the tube with 1 to 2 ml of CO_2-free water.

Add 1 drop of 0.2% phenolphthalein to the mixture and stir up the precipitate. By means of a dropper, add 0.05 F HCl, stirring the mixture intermittently to break up the precipitate (Note 24), until the phenolphthalein color becomes light pink; then add 8 to 10 drops of 1 F $BaCl_2$ (Note 25) and 1 drop of 1% Aerosol OT solution. While stirring, add 0.05 F HCl dropwise until the mixture is white, then add just 1 drop of the acid in excess. Rinse any precipitate from the stirring rod into the centrifuge tube. Centrifuge until the solution is clear, and remove and discard the solution with a dropper.

Titration of the Carbonate. Rinse down the walls of the tube with 1 to 2 ml of boiled water. Add 1 drop of 0.2% phenolphthalein and 3 to 4 drops of 1 F $BaCl_2$ and then stir up the precipitate (Note 26). If necessary add 0.05 F HCl dropwise with stirring, until the mixture is white, then add 1 drop of 0.1% methyl orange. From a microburet, add standard 0.2 F HCl and stir intermittently until the solution is pink. Place the tube in a bath of boiling water for about 1 minute, stirring to aid evolution of CO_2. If necessary add more standard acid until the pink color remains, then add about 0.1 ml of the standard acid in excess. Transfer the solution to a 50-ml conical flask and rinse the centrifuge tube with 2 to 3 ml of CO_2-free water. While swirling the flask continuously, boil the solution gently for about 1 minute. Cool the solution to room temperature and titrate with standard 0.05 F NaOH. After the methyl orange becomes yellow, continue the titration (2 to 3 drops) until the pink of the phenolphthalein produces a light orange color; this last color is the end-point of the titration. From the amounts of acid and base used, calculate the percent of carbon in the compound.

Notes.

11. Solids should be handled in weighing tubes. Hold the combustion tube A in a horizontal position and insert the weighing tube inside it so that the sample is delivered into the tip of the combustion tube. Do not scatter particles of the sample along the combustion tube as the weighing tube is withdrawn. Since the combustion fluid occupies only a third of tube A, particles of sample in the upper part of the tube may not be decomposed.

The weighings should be estimated to 0.02 mg. In order to obtain this accuracy, the sensitivity of the balance should be 8 to 10 divisions per milligram.

Although this procedure has been designed primarily for solids, β,β' dichloroethyl sulfide (mustard gas) has been satisfactorily analyzed. Liquids of similar or lower volatility may be analyzed by this procedure, using a pycnometer for weighing out the sample. In order to decrease the possibility of loss by evaporation, the sample should be delivered into the very tip of the combustion tube.

12. Stopcock C must be closed during the admission of

liquid into tube M; otherwise bubbles of the viscous combustion mixture will be formed in the head (D) and combustion fluid will be blown up into the outlet tube.

13. Cut off the flow of liquids before the last few drops reach the stopcock; no air should be admitted to the apparatus.

14. The rate of gas flow through disperser K should be watched in making the rate adjustment as the main objective of the flow regulation is to keep the bubbles from K relatively small. It may be necessary to adjust the rate of flow occasionally if the flow through K is seen to vary appreciably.

15. When liquid backs up in bubble counter, B, gas is passing from tube M to tube A. This should be prevented since any CO_2 which reaches tube A will be absorbed and cause error; for this reason it is necessary to observe counter B at all times.

16. Tube M should not be heated in one spot as the oxidation reaction may proceed suddenly and force CO_2 back into tube A. Although it is satisfactory to operate the system so that there is no actual positive flow through B, there must be <u>no reverse flow</u> through B.

17. When the temperature of the combustion mixture is well over 150° C, the chromic acid decomposes to give off oxygen. The oxygen evolution is not smooth or easily controlled; therefore, the heat should be applied carefully.

18. Actual boiling of the mixture is needed to completely sweep out the CO_2. Occasional heating at the tip of tube M is

desirable because the bubbles formed there will sweep through the entire solution.

19. If the solution in tube M has not turned green by this time, because of the decomposition of chromic acid to chromic ion, the mixture has not been heated sufficiently.

20. All distilled water used for rinsing or washing in this determination should be boiled before being used in order to eliminate the error due to dissolved CO_2. Boil the water for several minutes and store it in a glass-stoppered Pyrex bottle from which portions may be removed to dropping bottles.

21. To prevent absorption of CO_2, avoid breathing into the open centrifuge tube.

22. Since diffusion in the solution may be slow, the $BaCl_2$ reagent should be squirted in instead of being added dropwise. Stirring is not necessary if the reagent is injected forcefully.

23. Avoid jarring the apparatus during the removal of solution; otherwise particles of precipitate may be freed and drawn out.

24. Expecially in the case of large amounts of precipitate, as much as 3 to 4 ml of the 0.05 F HCl may be required. Therefore, do not start by adding the acid dropwise but deliver it in jets through the surface of the solution by means of a fine-tipped dropper. Use a dropwise addition when the base is nearly neutralized. It is necessary to keep the time of washing

down to 3 to 4 minutes to avoid absorbing an appreciable amount of CO_2. On the other hand, large local excesses of acid must be avoided, expecially on the surface of the solution.

25. Because of the acid in the $BaCl_2$ reagent, the mixture may turn white after adding the $BaCl_2$. In that case do not add any more 0.05 F HCl but proceed directly to the centrifugation. An excess of barium is provided to prevent solution of the precipitate during the addition of acid.

26. All precipitate adhering to the walls must be scraped off and thoroughly stirred up.

Discussion

This procedure was designed primarily for the analysis of solid compounds, especially Chemical Warfare agents and their derivatives. The apparatus is less complicated and can be assembled much more rapidly than the dry combustion train: in addition, single analyses can be made much more quickly with the apparatus described here. However, this method has not been tested on the wide variety of compounds which the dry combustion method is known to handle; therefore, difficulty may be encountered with some compounds. For example, some compounds containing a CN group have given off HCN when treated with the combustion mixture; hence, quantitative carbon values for such compounds could not be expected if this method is used. Halogens, nitrogen, and sulfur do not interfere.

β,β' Dichloroethyl sulfide has been satisfactorily analyzed by this procedure by weighing the liquid from a pycnometer into the combustion tube. Although it seems reasonable that other liquids of similar or lower volatilities can be satisfactorily analyzed by this method, the maximum volatility of substances which can be adequately handled by this procedure has not been determined. Compounds more volatile than β,β' dichloroethyl sulfide can probably be analyzed by cooling the combustion tube and sample during the flushing operation.

Combustions performed with ammonium chloride and with biuret proceeded smoothly and produced no unusual or sudden gas evolution.

Blank analyses gave less than 0.01 mg of carbon.

Some typical analytical results are given in Table X. It is apparent that the method is accurate to ± 0.05 mg of carbon. A determination requires about 45 minutes.

A brief summary of this work has been published in Analytical Chemistry (1).

TABLE X

Results of Carbon Analysis by Wet Combustion Method

	Milligrams of Carbon	
	Present	Found
Sodium oxalate	2.92	2.95
	2.15	2.16
	1.87	1.84
	1.86	1.88
	1.69	1.68
	1.88	1.92
Potassium hydrophthalate	4.51	4.54
	6.29	6.26
	5.33	5.33
	5.61	5.61
β, β'-Dichloroethyl sulfide	2.73	2.76
Adipic acid	5.84	5.85
	5.38	5.43
	5.20	5.20
	5.47	5.51

References

1. Farrington, P. S., Niemann, C., and Swift, E. H., Anal. Chem., 21, 1423 (1949).

2. Lindenbaum, A., Schubert, J., and Armstrong, W. D., Anal. Chem., 20, 1120 (1948).

3. McCready, R. M., and Hassid, W. Z., Ind. Eng. Chem., Anal. Ed., 14, 525 (1942).

4. Van Slyke, D. D., and Folch, J., J. Biol. Chem., 136, 509 (1940).

Propositions Submitted by Paul S. Farrington

1. (a). Ethers have been used almost exclusively for the extraction of complex metal acids (for example, $HFeCl_4$) from aqueous solution (1,2). It is suggested that benzotrifluoride ($CF_3C_6H_5$), trifluoromethyl-cyclohexane ($CF_3C_6H_{11}$) or other fluorinated compounds be substituted for ethers.

(a). The use of HF in place of HCl should be considered for the extraction of complex metal acids.

2. Salts of alginic acid have received little attention as stabilizing colloids for volumetric precipitation procedures; investigation of their applicability is recommended.

3. Substances which reduce hydrogen ion cannot be titrated coulometrically by the ordinary oxidation procedures (3). The use of ICl or $CuCl_2$ solutions is suggested for such titrations.

4. An amperometric method for determining halogen or halide concentrations in a turbulently flowing stream should be useful for studying the transfer of material under such conditions.

5. A method for the determination of micro quantities of water might be developed by using a modified Karl Fischer reagent and electrolytically generated iodine.

6. The design of water treatment equipment based on the lime-soda process has been largely empirical and often has been made

on the assumption that supersaturation effects (4) were the most important aspect of the problem. Recently it has been noted that the following rate equation is important (5):

$$\frac{d(Ca^{++})}{dt} = k(Ca^{++})(HCO_3^-)(OH^-)$$

No thorough study of the effect on reaction rate of $CaCO_3$ or other surfaces has been made. Such an investigation with data showing the effects of temperature should provide a more sound basis for the design of lime-soda units.

7. Ion exchange materials have been used as catalysts for acid catalyzed organic reactions (6). Exchange materials which are resistant to chemical attack should be considered as possible catalysts for oxidation-reduction reactions; for example, acid washed alumina (7) might catalyze the oxidation of hypophosphorous acid by halogens.

8. Industrial specifications of density and viscosity are often given as functions of the particular apparatus used to determine the physical property. Calculations involving those physical properties would be simplified if specifications were in terms of absolute units.

9. (a). Methanol is suggested as a solvent for the determination of unsaturation by means of electrolytically generated bromine.

(b). Coulometric and amperometric methods can be used to provide useful information concerning rates of addition and substitution when the halogens react with organic compounds.

10. (a). The number of physical education classes required of senior students should be reduced to two per week.

(b). Senior students should receive more encouragement to consult with the faculty of the Chemistry Department concerning graduate study.

References

1. Mylius and Huttner, Ber. 44, 1315 (1911).
2. Swift, E. H., J. Am. Chem. Soc., 46, 2375 (1924).
3. Thesis, page 66.
4. Behrman and Green, Ind. Eng. Chem., 31, 128 (1939).
5. Stumper R. and Clasen F., Compt. Rend., 228, 83 (1949).
6. Sussman, S., Ind. Eng. Chem., 38, 1228 (1946).
7. Kubli, H., Helv. Chim. Acta, 30, 453 (1947).