SOME REACTIONS AND PROPERTIES OF TETRALITHIUM PEROXYDIPHOSPHATE

Thesis for the Degree of Ph. D.
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Clyde Hok Heen Chong

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This is to certify that the

thesis entitled

SOME REACTIONS AND PROPERTIES OF
TETRALITHIUM PEROXYDIPHOSPHATE

presented by

CLYDE HOK HEEN CHONG

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of the requirements for

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Elmer Leininger
Major professor

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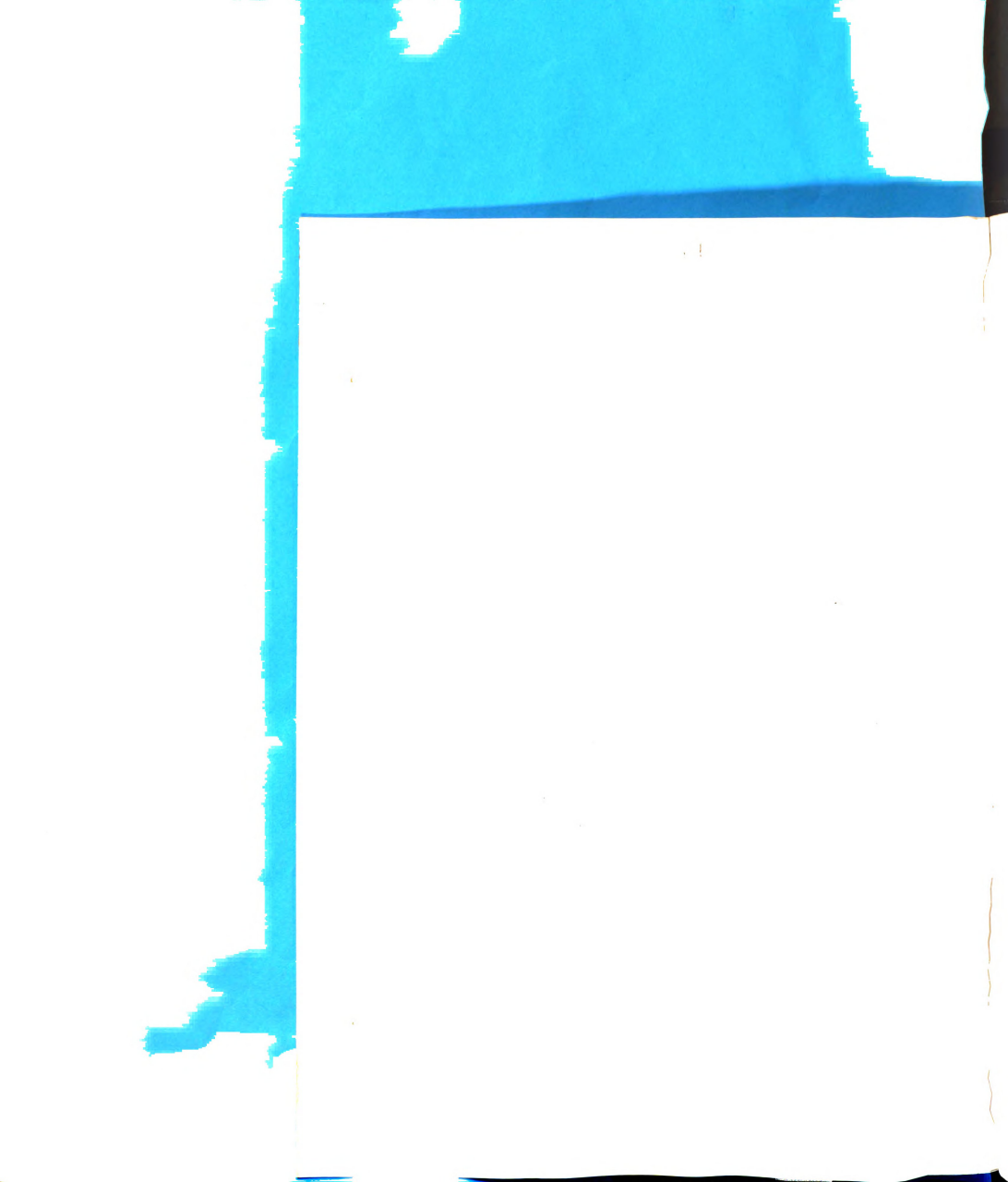

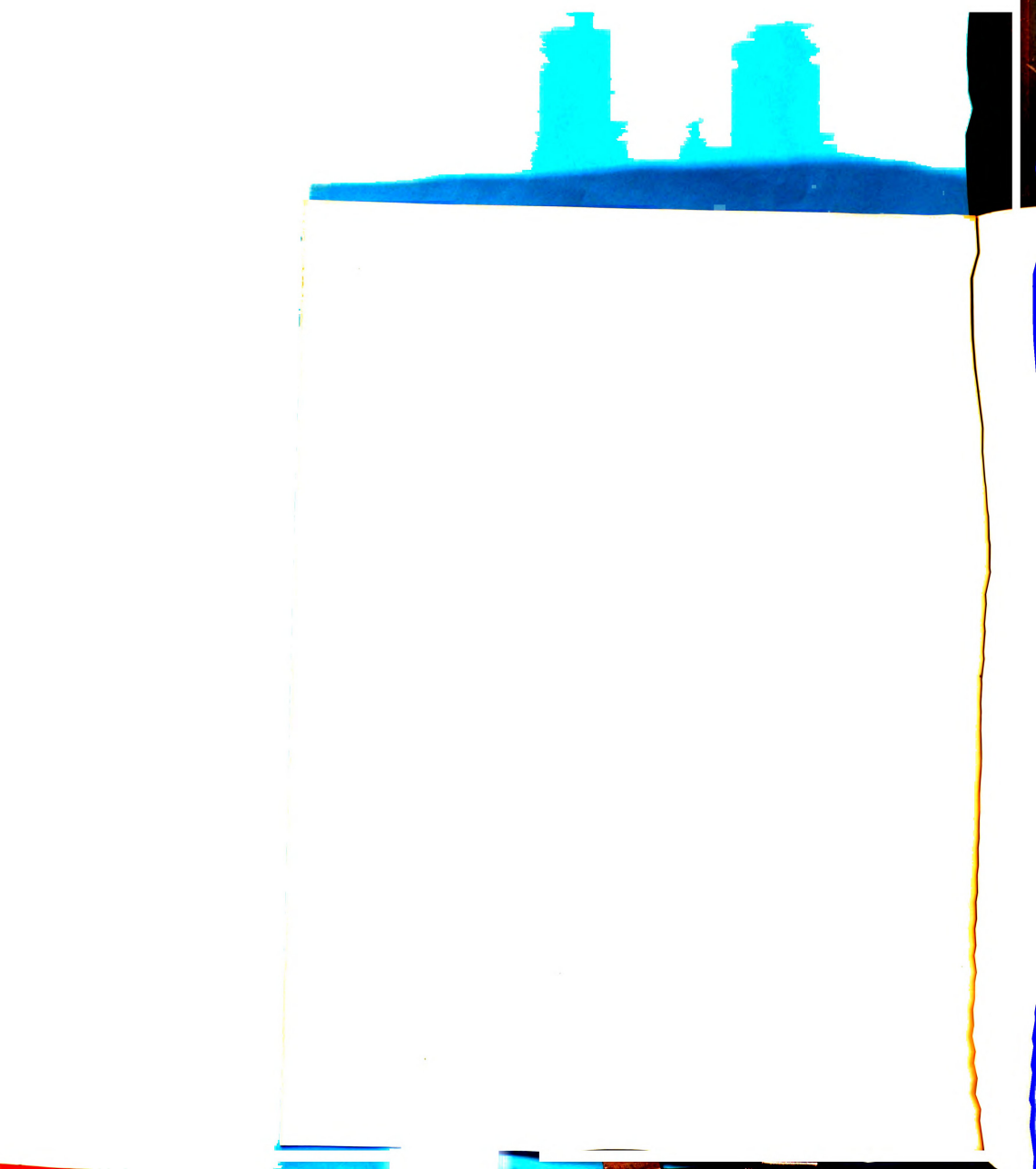

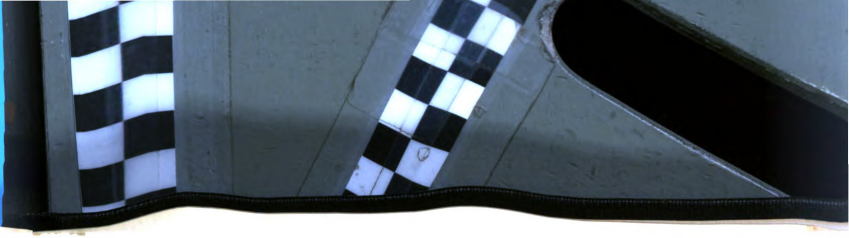

SOME REACTIONS AND PROPERTIES OF TETRALITHIUM PEROXYDIPHOSPHATE

By

Clyde Hok Heen Chong

A THESIS

Submitted to the School for Advanced Graduate Studies
of Michigan State University of Agriculture and
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VITA

Name: Clyde H. H. Chong

Born: March 6, 1933 in Honolulu, Territory of Hawaii

Academic Career: Western Military Academy, Alton, Illinois
1945-1950

Wabash College, Crawfordsville, Indiana
1950-1954

Michigan State University, East Lansing, Michigan
1954-1958

Degrees Held: A. B., Wabash College, 1954

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AN ABSTRACT

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ABSTRACT

Tetrapotassium peroxydiphosphate was prepared by electrolysis of an alkaline phosphate solution and converted to the lithium salt by the method of Chulski (1). This method was modified to increase the yield to 69 per cent from 38 per cent based on the amount of phosphate originally taken.

It was found that basic or neutral peroxydiphosphate solutions exposed to diffuse light for 12 hours at room temperature or heated at 100°C. for 30 to 60 seconds showed no appreciable loss in oxidizing power.

A method was developed for the determination of manganese based upon the oxidation of manganous ion to manganese dioxide by means of an excess of peroxydiphosphate. The time required for the oxidation of 5 to 50 mg. of manganese was approximately 12 hours at room temperature, four hours at 50-55°C. and 30 to 60 seconds at 100°C.

Two methods were used to complete the determination.

(a) The excess peroxydiphosphate in the filtrate, after removing the manganese dioxide, was determined by reaction with ferrous ion (1).

(b) The manganese dioxide was dissolved in excess ferrous ammonium sulfate and the excess ferrous ion determined by means of potassium dichromate. This method required the use of a correction factor of 1.01.

Despite their interference with the analysis of the filtrates, mercuric, chromic, arsenic(III), chloride and ammonium ions were found to give no adverse effects when the precipitates were analyzed for manganese. Tungstate, thallous, cobaltous, ferric, aluminum, silver, barium, lead, zinc, and nitrate ions interfered in either modification.

The mechanism of the peroxydiphosphate reaction is believed to involve the oxidation of manganous ion to a higher valent species, probably permanganate, which then reacts with manganous ion to form manganese dioxide.

A spectrophotometric method for determining peroxydiphosphate in the ultraviolet region was developed. No definite absorption peaks were obtained, only characteristic curves dependent on concentration and pH. These curves were found to adhere to Beer's Law at 240 mμ and at a pH of 6.0. The method was used for the determination of excess peroxydiphosphate in the filtrate following oxidation of divalent manganese and removal of the precipitate formed.

Individual oxidation of thallous, chromic, and cobaltous ions as well as selenious acid was attempted under various conditions. Although oxidation occurred to some extent, none of these reactions were found suitable for quantitative use. In the presence of a known amount of manganous ions, it was possible to effect quantitative oxidation of thallous and chromic ions. In these reactions, the oxidation of the manganese appears to induce the oxidation of the

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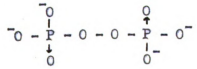
thallium or the chromium.

The structure of peroxydiphosphate was investigated. It was shown that decomposition of peroxydiphosphate resulted in the formation of orthophosphate, but no pyrophosphate was detected. Potentiometric titration of peroxydiphosphoric acid revealed that there was one strong hydrogen per phosphorus atom. This was further verified by a conductometric titration.

A nuclear magnetic resonance spectrum revealed only one peak shifted -7.4 parts per million relative to 85 per cent orthophosphoric acid which suggested the symmetrical structure.

The foregoing series of investigations indicated that the structure of peroxydiphosphate must be



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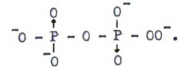

REFERENCE

1. Chulski, T., Doctoral Dissertation, Michigan State College, East Lansing, Michigan (1953).

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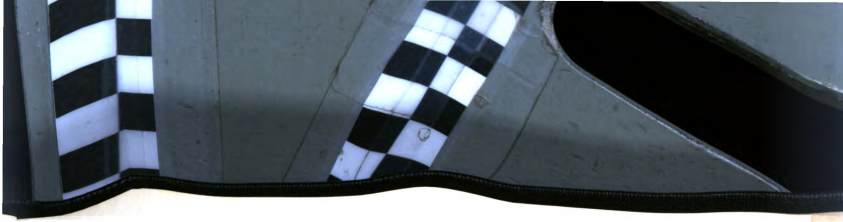


LIST OF FIGURES

I. INTRODUCTION

Little use of peroxydiphosphate as an oxidizing agent has been made. Despite methods for the successful preparation (12,16,17,18,35) and determination of peroxydiphosphate (11), no analytical applications have been made of peroxydiphosphoric acid, $H_4P_2O_8$, or its salts in analytical chemistry.

It was the purpose of this work, therefore, to undertake a more extensive investigation on the possible analytical use of peroxydiphosphate as an oxidizing agent and to extend the studies, initiated primarily by Chulski (11), on the characterization of peroxydiphosphate.

The problem was undertaken by preparing the stable tetralithium peroxydiphosphate tetrahydrate, $Li_4P_2O_8 \cdot 4H_2O$, and using this peroxy salt as the original starting material throughout the course of the work.

II. HISTORICAL

A considerable amount of work has been done on peroxydiphosphates prior to 1953. Chulski (11) has included a complete bibliography of the work on both peroxymono- and peroxydiphosphate reported through 1953. The preparations, reactions and properties of peroxyphosphates were considered.

Survey of the literature from 1953 up to and including 1957 indicated no additional studies have been made with peroxyphosphates except perhaps for the amine-peroxide reaction of Schoenemann (33,36). The reaction involved the detection of organophosphorus compounds. An alkaline peroxide solution containing an oxidizable primary amine such as o-dianisidine reacted with the organophosphorus compound forming a peroxyphosphate which then reacted with the primary amine to form a highly colored azo dye. The amine-peroxide reaction was stated to be applicable to all quinquevalent phosphorus containing compounds having a residual positive charge on the phosphorus atom allowing nucleophilic displacement of a labile anionic group by the perhydroxyl ion.

III. PREPARATION OF TETRALITHIUM PEROXYDIPHOSPHATE TETRAHYDRATE

Chulski (11) was able to prepare pure tetralithium peroxydiphosphate, $Li_4P_2O_8$, by adding lithium perchlorate to a cold solution of tetrapotassium peroxydiphosphate. The latter was prepared by the method of Fichter and Gutzwiller (16). This consisted of electrolyzing a monopotassium phosphate solution containing potassium hydroxide, potassium fluoride, and potassium chromate. The potassium perchlorate, lithium phosphate and lithium fluoride formed upon the addition of lithium perchlorate were not very soluble in water and were filtered off. The lithium peroxydiphosphate was then removed from the filtrate by the addition of methanol.

The recommended procedure as suggested and outlined by Chulski for preparing hydrated lithium peroxydiphosphate was followed.

Sixty grams monopotassium phosphate, 40 g. potassium hydroxide, 24 g. potassium fluoride dihydrate and 0.07 g. potassium chromate were dissolved in 150 ml. of water. Cooling was necessary as considerable heat was evolved. After cooling the solution, it was filtered through a number two Whatman filter paper on a Buechner funnel and then diluted to 200 ml.

The solution was transferred to a 210 ml. volume platinum dish. The solution was cooled in an ice bath during the electrolysis; the temperature of this bath was maintained at 0-3°C. The platinum dish served as the anode and a rapidly rotating bent platinum wire was used

as the cathode. A current of 1.9-2.2 amperes was obtained by applying 5.2 volts across the electrodes. The electrolysis was carried out for approximately 6.5 hours using a Sargent-Slomin electro-analyzer. Since the sharp odor of ozone was detected in the course of the electrolysis, the preparation of the peroxydiphosphate was carried out in a well ventilated hood.

Following the stated electrolysis period the platinum dish was covered with a watch glass and the electrolyte allowed to stand in the dish at room temperature for at least 12 hours. Longer standing was not detrimental since it was found that the peroxydiphosphate in this solution was stable for months.

Electrolysis was carried out a second time for another 6.5 hours. Following this electrolysis period the electrolyte was transferred to a rubber stoppered 300 ml. Erlenmeyer flask. The platinum dish was used for the next run without rinsing.

After standing for at least 12 hours the electrolyte was heated to 50-55°C. Sixty grams of potassium hydroxide was then added to this warm solution. The flask was stoppered and shaken until all the potassium hydroxide dissolved.

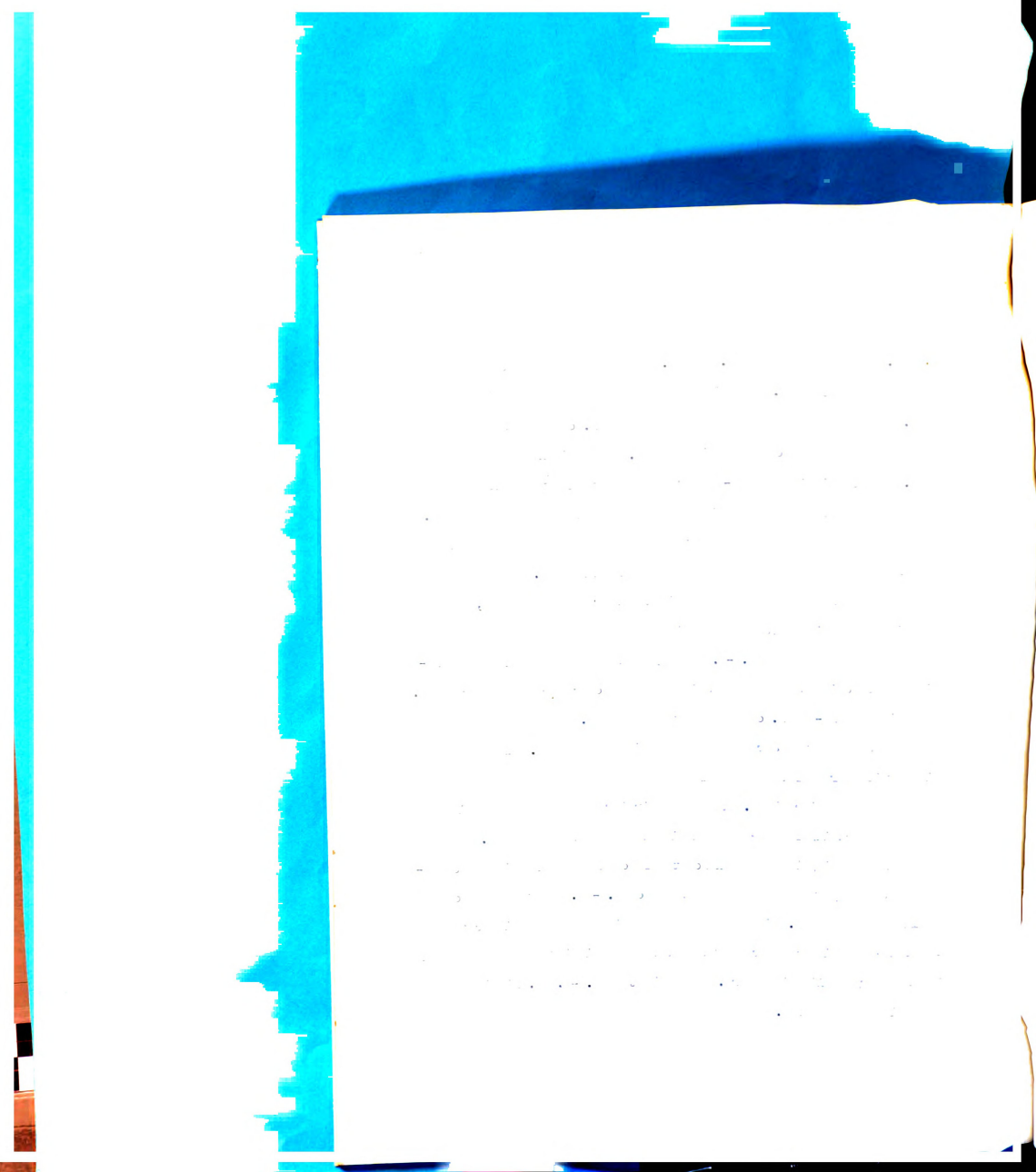
After standing overnight or for a longer period of time, the supernatant liquid was decanted off and the microcrystalline impure tetrapotassium peroxydiphosphate filtered on a medium porosity sintered glass filter funnel. In this method the mother liquor was then discarded.

The crude tetrapotassium peroxydiphosphate was then dissolved in 200 ml. of water in a 600 ml. beaker. The solution was cooled in an ice bath while 140 ml. of a lithium perchlorate solution containing 54 g. lithium perchlorate trihydrate per 100 ml. of solution was added in a dropwise rate from a dropping funnel. Mechanical stirring was used. After stirring for 15-20 minutes the material was filtered through a number two Whatman filter paper employing a Buechner funnel. Completeness of the precipitation was tested by the addition of a little more lithium perchlorate solution to the cold filtrate.

Since qualitative tests showed that carbonate was present, the solution of lithium peroxydiphosphate was freed from carbonate by acidifying it to a pH of 6.0-6.5 with 35 per cent perchloric acid solution and removing the carbon dioxide by aeration under reduced pressure. Approximately 10-15 ml. of the acid was required.

The solution was aerated by placing it in a 500 ml. filtering flask fitted with a rubber stopper bearing a capillary tube which extended to the bottom of the flask. A water aspirator was used to draw air through the capillary tube and solution for about five minutes.

Before adding the methanol for the removal of the lithium peroxydiphosphate the pH was adjusted to a value of 9.5-10.0 by the addition of lithium hydroxide. It was observed that if the pH was higher or lower than the indicated range the material precipitated by the methanol was less crystalline in nature. Approximately 0.5-0.8 g. lithium hydroxide was required.



After the pH was adjusted to 9.5-10.0 the solution was cooled to 0-5°C. in an ice bath. Any additional potassium perchlorate that precipitated was removed by filtration and the solution transferred to a 600 ml. beaker.

It was found that oftentimes a viscous material was obtained when the methanol was added at room temperature. Precipitation at ice bath temperatures always produced the viscous material. However, when the precipitation was carried out at 40-45°C. the formation of the viscous material was avoided. Moreover, by carrying out the precipitation with methanol at the specified temperature range, a smaller volume of the alcohol was required than when precipitation was done at room temperature.

As a result of the above findings the solution containing the lithium peroxydiphosphate was heated to 40-45°C. and placed in a water bath at the same temperature. While the solution was stirred mechanically 70 ml. methanol was poured in from a graduated cylinder. No precipitate was obtained immediately but after five minutes of stirring a precipitate formed. Then 30 additional ml. of methanol was added at a rapid dropwise rate from a dropping funnel. The solution was stirred for a total of 15 minutes.

The lithium peroxydiphosphate was filtered on a Buechner funnel using a number two Whatman filter paper and sucked as dry as possible. The residual chromate was removed by washing the precipitate with 1:1 water-methanol mixture at 40-45°C. until the wash liquor came through colorless; generally four or five 20 ml. portions of the wash solution

were sufficient. The absence of chromate in the peroxydiphosphate was checked by the use of s-diphenylcarbazide (38) as well as spectrophotometrically.

The compound was air dried until free flowing. It was shown by Chulski that the material was tetralithium peroxydiphosphate tetrahydrate. The yields obtained from this method of preparation averaged 24.4 g. Based on the amount of phosphate taken this would correspond to a 38 per cent yield; based on the conversion of the potassium peroxydiphosphate to the lithium salt this would correspond to a 52 per cent yield. The possibility for improving the yield of tetralithium peroxydiphosphate was investigated.

It had been shown previously that prolonged electrolysis for total periods of time greater than 12 hours resulted in no material increase in the amount of phosphate which was converted to the peroxydiphosphate form (11). It was claimed a 73 per cent conversion was usually obtained. This would immediately imply that complete recovery of the tetrapotassium peroxydiphosphate from the electrolyte was not achieved in the previous work. The consistently low yields of tetralithium peroxydiphosphate tetrahydrate can be attributed mainly to this factor.

The following modification was made in the conversion and recovery procedure for tetralithium peroxydiphosphate tetrahydrate. It essentially consisted of a resaturation of the mother liquor. The filtrate following the removal of tetrapotassium peroxydiphosphate was returned to the 300 ml. rubber stoppered Erlenmeyer flask and left overnight at room temperature. Following this period of standing the solution was

reheated to 50-55°C. and an additional 60 g. of solid potassium hydroxide was added to the warm solution. The flask was restoppered and shaken until all the potassium hydroxide dissolved. A precipitate formed shortly thereafter. Had the resaturation been carried out immediately after removal of the original precipitate, no appreciable precipitation of tetrapotassium peroxydiphosphate would have occurred.

The precipitate of tetrapotassium peroxydiphosphate was filtered off after an overnight standing period and the subsequent treatment previously described for the preparation of the lithium salt from tetrapotassium peroxydiphosphate was followed. Resaturation with potassium hydroxide in the manner described ultimately resulted in an average total yield of 44 g. tetralithium peroxydiphosphate tetrahydrate. Based on the amount of phosphate taken the yield was increased to 69 per cent or based on the amount of tetrapotassium peroxydiphosphate used, the yield was 95 per cent.

The oxidizing power of the peroxydiphosphate from each of the two fractions obtained was determined by the ferrous ammonium sulfate-potassium dichromate method (11). From several representative preparations a series of approximately 0.09 N lithium peroxydiphosphate solutions was prepared from each fraction by dissolving approximately 1.600 g. tetralithium peroxydiphosphate tetrahydrate in water and diluting to 100 ml. Twenty milliliter portions of the peroxydiphosphate solutions were pipetted into 250 ml. iodine flasks containing 30 ml. water. The concentration of the peroxydiphosphate was calculated from the amount of ferrous ion that had not reacted attributing all the

oxidizing properties of the solution to the peroxydiphosphate. Triplicate determinations were made with a precision of two parts per thousand. The concentrations of the peroxydiphosphate samples were expressed in terms of normality and all were calculated to the same relative sample weight of 1.600 g. The results are tabulated in Table I.

TABLE I

COMPARISON OF THE OXIDIZING POWER OF PEROXYDIPHOSPHATE FROM RECOVERED FRACTIONS

Run	Fraction	Normality $Li_4P_2O_8$*
3	a	0.0883
	b	0.0849
6	a	0.0850
	b	0.0849
10	a	0.0868
	b	0.0863

*Calculated to the same sample weight of 1.600 g.; 1.600 g. = 0.0883 N

The above data show that there is no appreciable loss in oxidizing power in the second fraction obtained by saturating the filtrate again with solid potassium hydroxide.

VI. EXPERIMENTAL

A. Reagents and Chemicals

All the chemicals which were used in the course of this work were of sufficient purity to meet the specifications of the American Chemical Society for reagent chemicals.

An approximately 0.1 N tetralithium peroxydiphosphate solution was prepared by dissolving 16 g. of tetralithium peroxydiphosphate tetrahydrate, which was made by the method previously described, in water and diluting to one liter. Other concentrations of peroxydiphosphate solutions were prepared by taking the appropriate quantity of lithium salt and diluting with water. Preparation of peroxydiphosphate solutions made in this manner were basic in nature and stable for a considerable period of time (11).

Ferrous ammonium sulfate solution approximately 0.2 N and 0.15 M in sulfuric acid was prepared by dissolving 80 g. of ferrous ammonium sulfate hexahydrate in 600 ml. of water acidified with 18 ml. of concentrated sulfuric acid and diluting to one liter.

Potassium dichromate solution, 0.1000 N, was prepared by weighing out 4.9352 g. Mallinckrodt reagent grade potassium dichromate, dissolving it in water, and diluting quantitatively to one liter. The potassium dichromate was dried at 110°C. for two hours before it was weighed out.

The ferrous ammonium sulfate solution was standardized each day it was used by titrating it in the following manner with the 0.1000 N potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Twenty milliliters of the ferrous ammonium sulfate solution was pipetted into a 250 ml. Erlenmeyer flask followed by the addition of 30 ml. water and 6 ml. 6 N sulfuric acid. Then 3 ml. of 85 per cent phosphoric acid was added for each 50 ml. of volume expected at the end. Three-tenths milliliter, six drops, of 0.01 M diphenylamine sodium sulfonate solution was added as indicator. Potassium dichromate solution was added until the first tinge of purple or violet-blue color appeared.

The concentration of the lithium peroxydiphosphate solution was found by determining the total equivalent weight of oxidizing material present and attributing all the oxidizing properties of the solution to peroxydiphosphate. The amount of oxidizing material present was determined by adding a measured excess of standardized ferrous ammonium sulfate solution to a known volume of the acidified solution of peroxydiphosphate. After standing for a minute the excess ferrous ion was back titrated with 0.1000N potassium dichromate solution using diphenylamine sodium sulfonate as indicator. The difference between the volume of 0.1000N potassium dichromate solution used in the standardization of a given volume of ferrous ammonium sulfate solution and the volume of potassium dichromate solution used in the back titration of excess unreacted ferrous ion following reaction with peroxydiphosphate

solution represented the amount of ferrous ion which reacted with the peroxydiphosphate. The same volume of ferrous ammonium sulfate was used in both cases. The concentration of the peroxydiphosphate was calculated from this difference obtained. The concentration of peroxydiphosphate was expressed in terms of normality. Triplicate determinations agreed to three parts per thousand.

A manganous sulfate solution containing approximately 10 mg. manganese per ml. was prepared by dissolving 32.60 g. Baker's manganous sulfate monohydrate in 100 ml. water and diluting to one liter.

Approximately 0.04M potassium permanganate solution was prepared and standardized against pure sodium oxalate by the usual procedure (19). Some of the solution was also standardized against ferrous ammonium sulfate solution. The ferrous ammonium sulfate was previously standardized against 0.1000N potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Standardization of the permanganate solution by the ferrous ammonium sulfate method gave an average value of 0.0412M for three determinations with a deviation of three parts per thousand; by the oxalate method an average value of 0.0411M was obtained for three determinations with a deviation also of three parts per thousand.

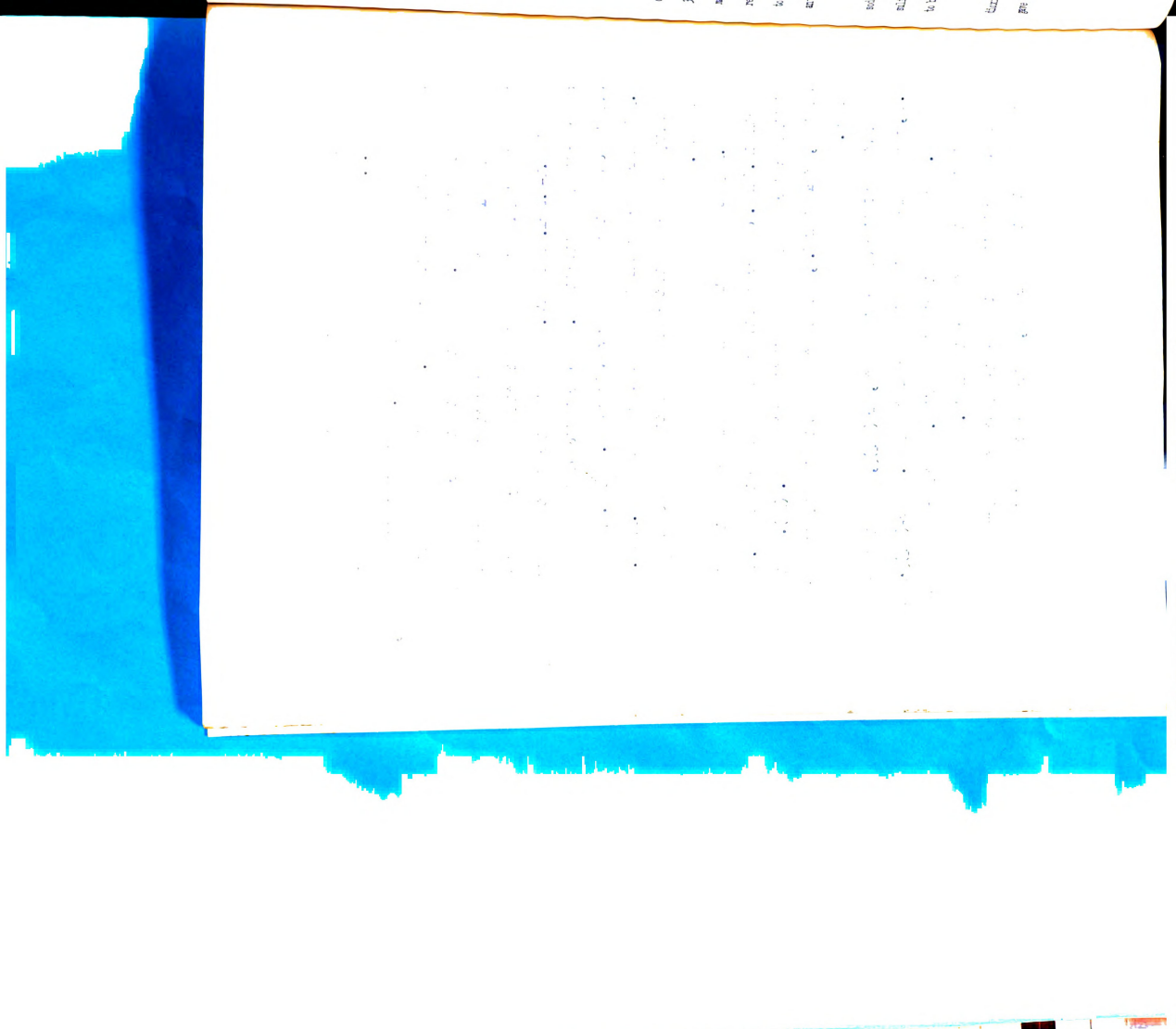
The potentiometric titration method of Lingane and Karplus (26) was used to standardize the manganous sulfate stock solution. Twenty milliliters of the manganous sulfate was pipetted into a 400 ml. beaker followed by 150 ml. of saturated sodium pyrophosphate solution.

Two milliliters of 6N sulfuric acid was added to give a solution with a pH of 6.7. A Beckman saturated calomel electrode was placed in the solution to serve as a reference electrode. As the indicating electrode, a Beckman platinum electrode was used. The titration was carried out with a Fisher titrimeter. Standardized potassium permanganate solution was added from a burette bearing an offset tip in one milliliter increments until a rapid change in potential was noted; then it was added in 0.1-0.2 ml. increments. During the titration the solution was stirred with a magnetic stirrer. Standardization of the manganous sulfate solution in this manner gave values of 0.3746; 0.3759 and 0.3769N for three determinations or an average value of 0.3758N. The normality was expressed in terms of an oxidation change of two for manganese.

A 0.1003N thallous sulfate solution was prepared by dissolving exactly 12.621 g. of recrystallized thallous sulfate in 200 ml. of distilled water and diluting quantitatively to 500 ml. (34). This stock solution, at a pH of 6.4, was used throughout the investigations to follow.

A stock solution of chromic sulfate, $Cr_2(SO_4)_3$, approximately 0.1M, was prepared by dissolving approximately 35 g. of $Cr_2(SO_4)_3 \cdot 18H_2O$ in 500 ml. of water and diluting to one liter. Heating was necessary to effect dissolution of the chromic sulfate.

The standardization of the chromic sulfate stock solution was effected by oxidation to chromate, followed by the addition of a



measured excess of ferrous ammonium sulfate solution and titration with standard potassium dichromate (23). The oxidation was carried out in acid solution with ammonium persulfate in the presence of silver nitrate (43). Upon standardization of the chromic sulfate stock solution in this manner, the normality was found to be 0.4227.

An approximately 0.1N vanadyl sulfate solution was prepared by dissolving 8.0 g. of vanadyl sulfate, $VOSO_4 \cdot xH_2O$, in 200 ml. of water and diluting to 500 ml. The dark blue vanadium solution was standardized with potassium permanganate (37). The average of four determinations gave a value of 3.62 ± 0.001 mg. vanadium per ml.

An approximately 0.05M solution of sodium nitrite was prepared by dissolving 1.777 g. Mallinckrodt analytical reagent sodium nitrite in 300 ml. of water and diluting to 500 ml. The solution prepared in this manner gave a pH of 9.1. Similarly, 3.15 g. Mallinckrodt analytical reagent sodium sulfite was dissolved in 300 ml. of water and diluted to 500 ml. to give an approximately 0.05M sulfite solution. The resultant solution was at a pH of 10.1.

A 0.1N sodium sulfide solution was prepared by dissolving 1.78 g. sodium sulfide in 500 ml. of water. Standardization of the sodium sulfide solution was made with iodine (37). The solution was found to be 0.0887N as determined by this procedure.

A selenious acid solution was prepared by adding 5.6 g. of selenium dioxide to 500 ml. of water and diluting to one liter. The solution gave a pH of 2.3. The selenious acid solution was standardized by the

addition of a measured excess of standardized potassium permanganate and back titrating with standard ferrous ammonium sulfate (44). The solution prepared and standardized in this manner was 0.0718N.

A cobaltous sulfate solution was prepared by dissolving 7.030 g. of Mallinckrodt analytical reagent cobalt sulfate heptahydrate, $CoSO_4 \cdot 7H_2O$, in 100 ml. of water and diluting to 250 ml. The solution was standardized by an electrodeposition method (37) and was found to contain 6.092 mg. cobalt per ml.

Other solutions and reagents were prepared whenever necessary. These are described more fully at appropriate placed in the work carried out.

B. Apparatus

A Beckman Model H-2 pH Meter, equipped with a glass electrode and a sleeve type saturated calomel electrode pair, was used in adjusting solutions to the required pH values.

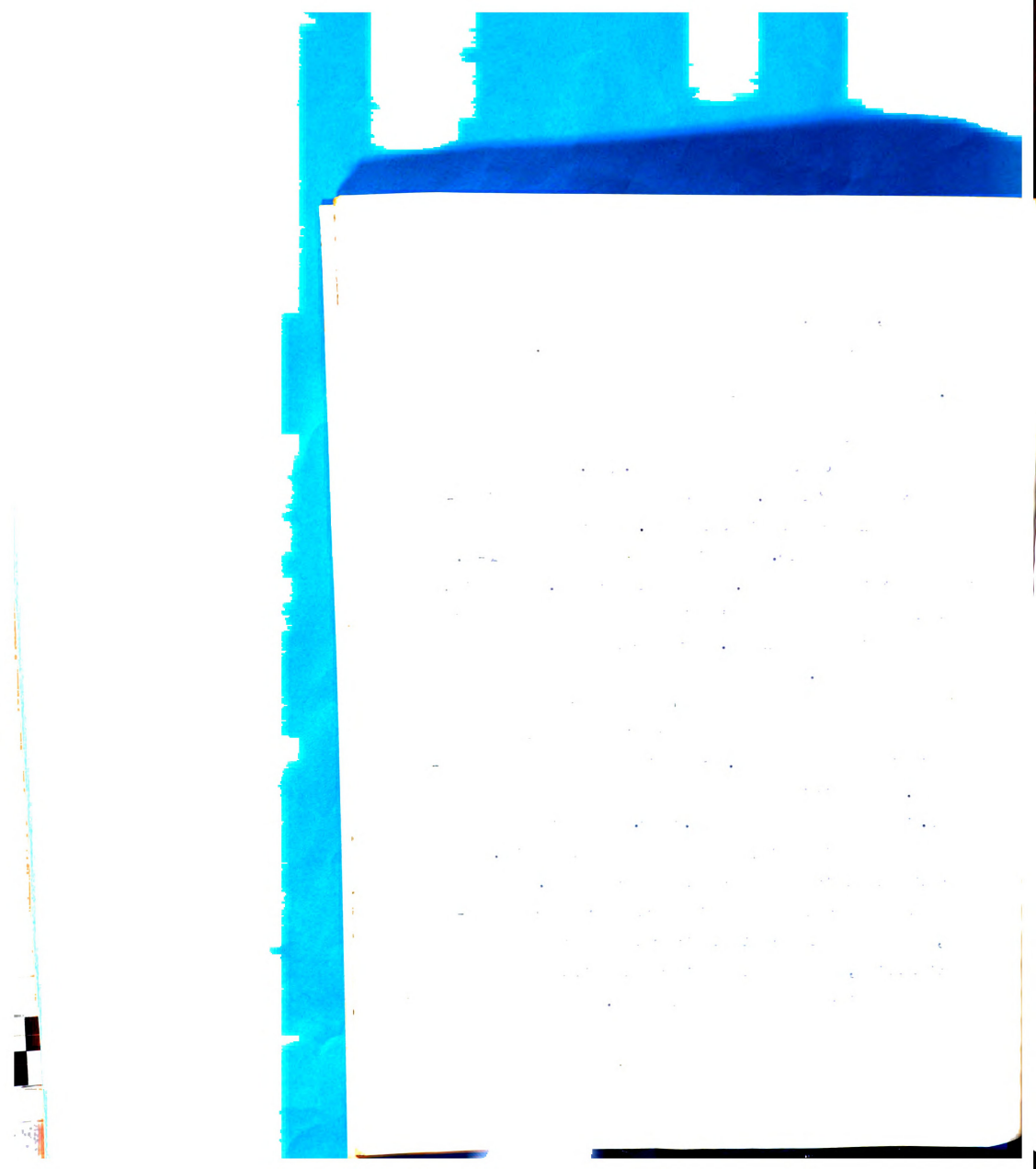
Spectrophotometric measurements were made with a Beckman Model DU quartz spectrophotometer equipped with a photomultiplier attachment and hydrogen discharge lamp. Preliminary absorbance and per cent transmittancy measurements were made with a Beckman Model DK-2 Ratio Recording Spectrophotometer. Generally the Beckman DK-2 Spectrophotometer was used primarily for rapid scanning of the spectrum and for qualitative work; the Beckman DU Spectrophotometer was used for quantitative work. Matched 1-cm. Corex and silica cells were used in the visible and ultraviolet regions of the spectrum respectively.

Weights, burettes, pipettes and other glassware were calibrated before use and corrections were applied wherever necessary.

C. Stability Studies of Tetralithium Peroxydiphosphate Solutions

Some stability studies have been carried out for peroxydiphosphate solutions both at room temperature and at 50°C. (11). It was found that at room temperature a 0.1N solution of tetralithium peroxydiphosphate was stable for 49 days in basic medium. At lower pH values the solutions were less stable. Peroxydiphosphate solutions of pH 2.0-10.2 were found to be stable at 50°C. for at least four hours. In addition, it was found that the effect of light increased the rate of decomposition of the peroxydiphosphate solution. It was desired to study the extent of this decomposition.

Peroxydiphosphate solutions of various pH values were prepared and exposed to strong sunlight as well as to diffused artificial light approximating working conditions. Twenty milliliter portions of approximately 0.05N tetralithium peroxydiphosphate solution were pipetted into 250 ml. iodine flasks containing 25 ml. water. The desired pH was adjusted by the addition of 17 per cent phosphoric acid solution. Four pairs of solutions at various pH values were prepared. One pair was exposed to extremely bright sunlight for 12 hours at room temperature, another pair was placed in an actual working laboratory containing artificial light, and the remaining pairs were left in the dark for the same period of time as those exposed to the light.



After the requisite period of exposure to light, the normality of each solution was determined. The original normality of the peroxydiphosphate stock solution was used as the basis of comparison and as a measure of the extent of decomposition of the other peroxydiphosphate solutions. The results are shown in Table II.

TABLE II

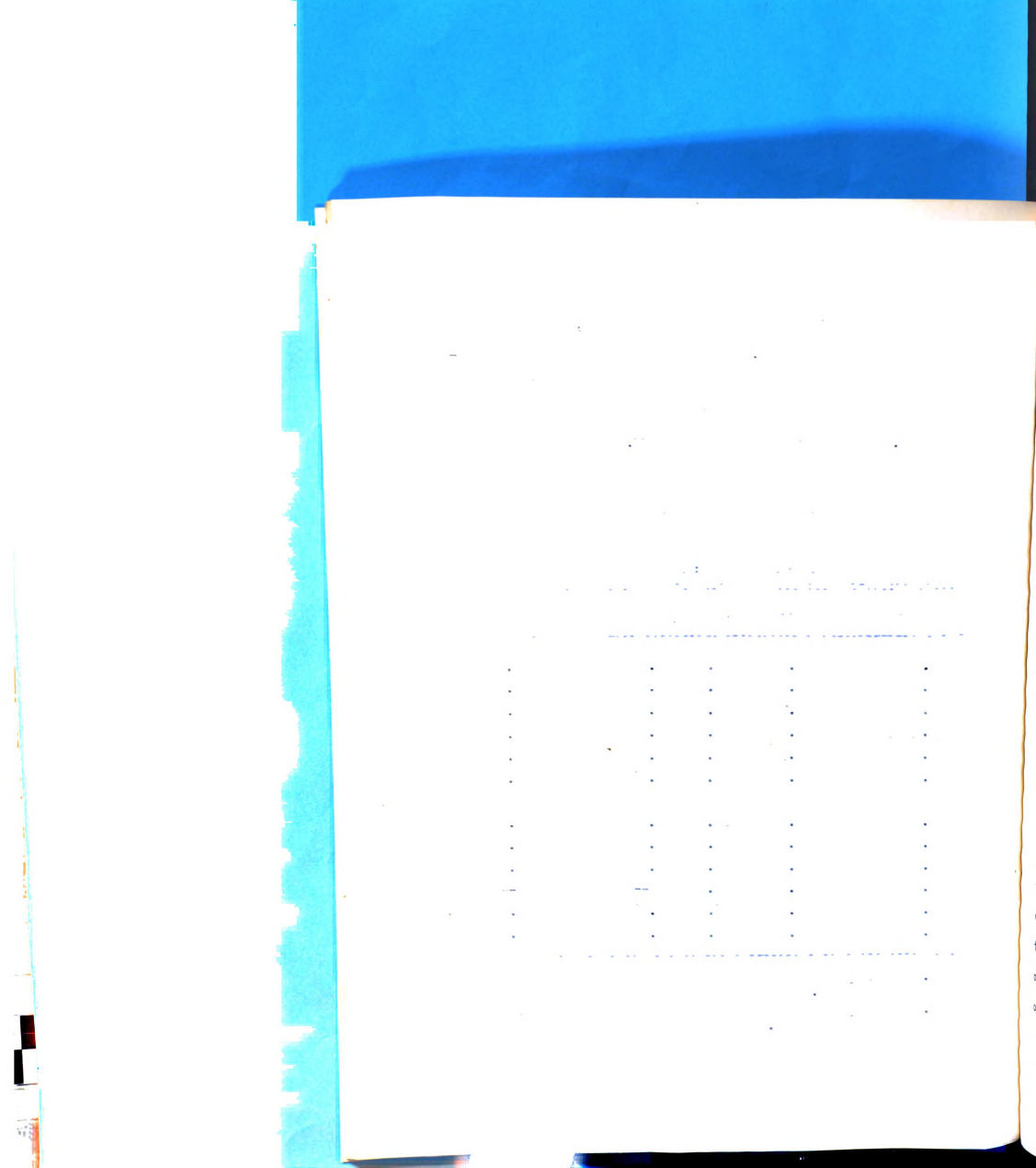
INFLUENCE OF LIGHT ON THE DECOMPOSITION OF TETRALITHIUM PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES AT ROOM TEMPERATURE

Time of Exposure: 12 Hours

Normality of $Li_4P_2O_8$	Deviation Parts/Thousand	pH	Normality of $Li_4P_2O_8$ in the Dark	Deviation Parts/Thousand
In bright sunlight				
0.06180	22.2	11.0	0.06455[a]	0.0
0.05895	86.8	8.0	0.06465	1.6
0.05902	85.7	7.5	0.06455	0.0
0.05895	86.8	7.0	0.06458	0.5
0.05747	109.7	4.0	0.06458	0.5
0.05640	126.3	3.0	0.06415	6.2
In diffused light				
0.06210	0.0	10.0	0.06210[b]	0.0
0.06198	2.2	8.5	0.06202	1.3
0.06198	2.2	7.0	0.06195	2.5
0.06198	2.2	6.5	--	--
0.06190	3.2	6.0	0.06192	2.9
0.06165	7.4	4.0	0.06195	2.5

[a] 0.06455N $Li_4P_2O_8$ taken as the standard of comparison in the sunlight studies.

[b] 0.06210N $Li_4P_2O_8$ taken as the standard of comparison in the diffused light studies.



The data in Table II clearly show that tetralithium peroxydiphosphate solutions are unstable when exposed to very bright sunlight. Decomposition of the peroxydiphosphate solutions occurred over the pH range 3.0 to 11.0 increasing markedly with decrease in pH. Peroxydiphosphate solutions left in the dark are also included in the table for comparative purposes. These solutions appeared to be essentially stable over the entire pH range studied except in strongly acid solution of pH 3.0 where decomposition occurred.

Table II also indicates exposure of peroxydiphosphate solutions to diffused light results in no appreciable loss in relative oxidizing power. Maximum decomposition occurred at a pH of 4.0 where a deviation of seven parts per thousand was obtained when compared with the original concentration of peroxydiphosphate stock solution. Thus, when compared with samples of the same pH that had been left in the dark, it can be seen that peroxydiphosphate solutions at various pH values can be left in diffused light for some time before any measurable decomposition occurred, provided a neutral or basic medium was maintained.

Studies have been made on the stability of peroxydiphosphate solutions at 50°C. It was believed advantageous to try even higher temperatures. Preliminary qualitative investigations revealed that boiling of peroxydiphosphate solutions for periods of time greater than two to three minutes resulted in rapid decomposition. However, shorter periods of boiling were apparently without effect. Peroxydiphosphate solutions of various pH values and at different concentrations were prepared in

a manner previously described. These solutions were then heated to 100°C. for five seconds, cooled for one hour and subsequently the amount of peroxydiphosphate was determined following dilution with water back to its original volume. Triplicate determinations were made and the precision obtained was one part per thousand. The amount of peroxydiphosphate was expressed in terms of normality. The results are given in Table III along with the normality of the original peroxydiphosphate stock solution used as a means of comparison.

TABLE III

STABILITY OF 0.1N TETRALITHIUM PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES WHEN BOILED FOR FIVE SECONDS

Temperature	Normality of $Li_4P_2O_8$			
	pH of Solution			
	9.9	7.0	6.0	4.0
22°C	0.1055	0.0863	0.1058	0.0946
100°C	0.1055	0.0862	0.1057	0.0942

The data in Table III show that peroxydiphosphate solutions of pH 4.0 to 9.9 are stable at 100°C. when heated for five seconds. There apparently is no loss in oxidizing power. This suggests the strong possibility of carrying out reactions with tetralithium peroxydiphosphate at 100°C. without fear of appreciable loss in oxidizing power of the solution.

The results obtained by increasing the time of heating at 100°C. are compiled in Table IV. Heating was maintained at 100°C. for a

a manner previously described. These solutions were then heated to 100°C. for five seconds, cooled for one hour and subsequently the amount of peroxydiphosphate was determined following dilution with water back to the original volume. Triplicate determinations were made and the precision obtained was one part per thousand. The amount of peroxydiphosphate was expressed in terms of normality. The results are given in Table III along with the normality of the original peroxydiphosphate stock solution used as a means of comparison.

TABLE III

STABILITY OF 0.1N TETRAETHYLTIN PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES WHEN HOLDED FOR FIVE SECONDS

Temperature	Normality of $Li_4P_2O_8$ pH of Solution			
	5.9	7.0	8.0	9.0
22°C	0.1059	0.0863	0.1058	0.0942
100°C	0.1057	0.0852	0.1057	0.0902

The data in Table III show that peroxydiphosphate solutions of pH 5.0 to 9.0 are stable at 100°C. when heated for five seconds. There apparently is no loss in oxidizing power. This suggests the strong possibility of carrying out reactions with tetraethyltin peroxydiphosphate at 100°C. without fear of appreciable loss in oxidizing power of the solution.

The results obtained by increasing the time of heating at 100°C. are compiled in Table IV. Heating was maintained at 100°C. for a

TABLE IV

STABILITY OF 0.1N TETRALITHIUM PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES WHEN BOILED FOR SIXTY SECONDS

Temperature	Normality of $Li_4P_2O_8$				
	pH of Solution				
	3.0	6.0	6.8	7.3	9.5
23°C	0.0867	0.0939	0.0877	0.0819	0.1163
100°C	0.0854	0.0930	0.0876	0.0819	0.1164

maximum period of 60 seconds. Under these conditions of relatively excessive heating the stability of the peroxydiphosphate solution again decreased with decreasing pH. Decomposition of the solution became evident immediately in the acid region. At pH 6.0 the deviation was eight parts per thousand while at pH 3.0 decomposition increased to 15 parts per thousand when compared with their respective peroxydiphosphate stock solutions. Solutions in basic medium showed no decomposition upon heating to boiling. These solutions were stable.

D. An Analytical Study of the Reaction Between Peroxydiphosphate and Manganese(II)

1. Introduction

Numerous analytical methods for the precipitation of manganese as the dioxide and the volumetric determination of this compound with a standard reducing agent have been proposed in the literature. From the practical point of view the most important procedures are those in which the precipitation of the dioxide takes place in acid medium;

oxidation in neutral or alkaline medium by means of bromine, hypobromite, chlorine, hypochlorite or ferricyanide is unsatisfactory, in general, when iron is present, and even in the absence of iron results tend to be variable. Manganese may also be precipitated by ammonium persulfate in an ammoniacal solution, or by potassium chlorate in the presence of zinc chloride in a neutral solution (32).

In acid solution manganese is oxidized to the dioxide by boiling with ammonium or potassium persulfate. Von Knorre (42) has based a determination on this particular reaction. The precipitated manganese dioxide is collected by filtration, washed, and dissolved in standard ferrous sulfate or hydrogen peroxide and the excess ferrous ion or peroxide is titrated with standard potassium permanganate. The method does not give theoretical values; an empirical factor must be applied. The method has also been applied by Lüdert and others (20,27,31) with some slight modifications.

A method that has enjoyed considerably greater popularity than that of von Knorre is the procedure based on the precipitation of manganese dioxide by long boiling with potassium chlorate in strong nitric acid solution. Beilstein and Jawein (2) first made use of this method of precipitation for a gravimetric determination of the element; Hampe (22) and others based a volumetric estimation on the same reaction. Hampe found that potassium bromate could be used in place of the chlorate but preferred the chlorate. Kolthoff and Sandell (25) recommended the use of potassium bromate as the reagent for the oxidation

of manganese to the dioxide claiming reproducible results were obtained when an empirical factor was employed.

In every case cited above a considerable excess of the oxidizing agent is used to effect the oxidation of divalent manganese to the dioxide. The results are based on the precipitate formed; the excess oxidizing agent is not determined. The excess chlorate or bromate added to effect the oxidation can not be determined following the reaction because of destructive loss of much of the excess chlorate or bromate in the method used. The bromine or chlorine in excess of that needed to oxidize the manganese in an ammoniacal solution oxidized part of the ammonia to nitrogen and therefore can not be used as a suitable means of determination (44). Excess persulfate can not be determined because under the conditions used, decomposition occurred. Similar results are encountered with other oxidizing agents.

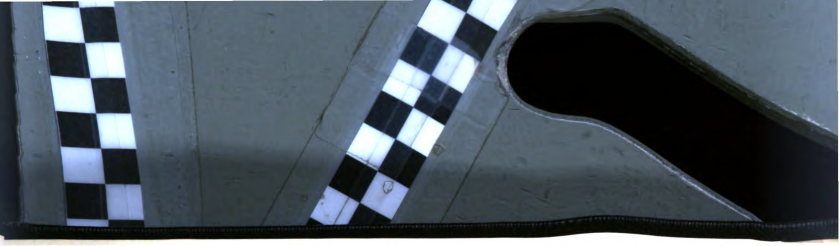
The Volhard method (41) is based on the principle that when potassium permanganate is added to a hot, neutral solution of manganous salt, the latter is oxidized to manganese dioxide and the permanganate reduced to the same form. The complete oxidation of the divalent manganese is evident by the pink color of permanganate persisting in solution. Since acid is formed in the reaction, zinc oxide is added in order to keep the solution neutral.

Fichter and Bladergroen (14) have shown that when peroxydiphosphoric acid is added to a dilute manganous sulfate solution, a violet color is produced. Schmidlin and Massini (35) interpret this as the formation

of permanganic acid, $HMnO_4$. Fichter and Bladergroen conclude that the color is due to the formation of the very stable manganic phosphate (15) as the five characteristic absorption bands of permanganic acid are never observed in a spectrometer; only a uniform darkening from green to violet is observed.

From the work cited so far it becomes quite evident that either the manganese dioxide formed or the amount of oxidizing agent required to effect the oxidation of divalent manganese was determined but not both. There has been no case found in the literature where both the amount of oxidizing agent used and the manganese dioxide formed as a result of the oxidation of divalent manganese are determined in a given solution.

It was found that when excess slightly basic tetralithium peroxydiphosphate solution was added to a slightly acidic manganous sulfate solution at room temperature, oxidation of the divalent manganese occurred in the resultant near neutral solution. Evidence for such a reaction taking place was indicated by the immediate appearance of a pale pink color imparted to the solution which became more intense upon standing, ultimately leading to the formation of a brown-black precipitate believed to be manganese dioxide. In addition, it was also observed that in the presence of sufficient excess of peroxydiphosphate a drop of 1.1-1.3 pH units accompanied the oxidation. It was found possible to remove the precipitate and determine the amount of unreacted peroxydiphosphate using an excess of standard ferrous ammonium sulfate solution and back titrating the excess ferrous ion with 0.1000N potassium dichromate solution.



The possibility of using this reaction as a quantitative method for determining manganese was investigated.

2. Identification of the Precipitate Formed

As the first step in the study of the oxidation of divalent manganese the identity of the precipitate formed in the near neutral solution was made. It was strongly suspected to be manganese dioxide. Five milliliters 0.0972N manganous sulfate solution (with respect to an oxidation change of two) corresponding to 13.35 mg. manganese was pipetted into a 250 ml. iodine flask containing 25 ml. of water. Twenty milliliters of approximately 0.09N tetralithium peroxydiphosphate was added and the flask stoppered. Initial pH of the solution was 7.5. An immediate flesh pink color developed in the solution increasing in depth to a deep red then to a dark brown and ultimately ending in the formation of a dense brown-black precipitate. Four such samples were prepared in this manner as well as four blanks.

After an overnight period of standing in the dark at room temperature, the pH of the solutions dropped to 6.4-6.5. The precipitates formed were removed by filtration through Gooch crucibles with suction. The precipitates were readily filterable and each was washed thoroughly with 150 ml. of water in 20 ml. increments. Completeness of washing was tested on the last 50 ml. portion of wash for the presence of any orthophosphate by the addition of ammonium molybdate reagent (36) in a nitric acid medium. No yellow precipitate of ammonium phosphomolybdate was found.

Addition of nitric acid did not dissolve the precipitate. Hydrochloric acid, however, did dissolve the precipitate with the evolution of chlorine gas. Acidic ferrous ammonium sulfate solution dissolved the precipitate forming a nearly colorless solution. The precipitate, after dissolving with ferrous ammonium sulfate solution, was found to contain no phosphorus in the form of orthophosphate when treated with ammonium molybdate.

The oxidation state of the manganese precipitate was determined by means of an indirect titration procedure in the following manner. The precipitate was dissolved in 19.98 ml. 0.1032N ferrous ammonium sulfate solution. Nine milliliters 6N sulfuric acid was added and the solution was diluted to a total volume of 150 ml. with water in a 400 ml. beaker. A magnetic stirrer was used to aid in a more rapid dissolution of the precipitate. After complete reaction, as evidenced by the absence of any particles in solution, the excess ferrous ion was titrated with 0.1000N potassium dichromate solution in the presence of 9 ml. 85 per cent phosphoric acid using diphenylamine sodium sulfonate as indicator. The back titration of the excess ferrous ion contained in two samples required 15.83 ml. and 15.87 ml. of the standard potassium dichromate solution.

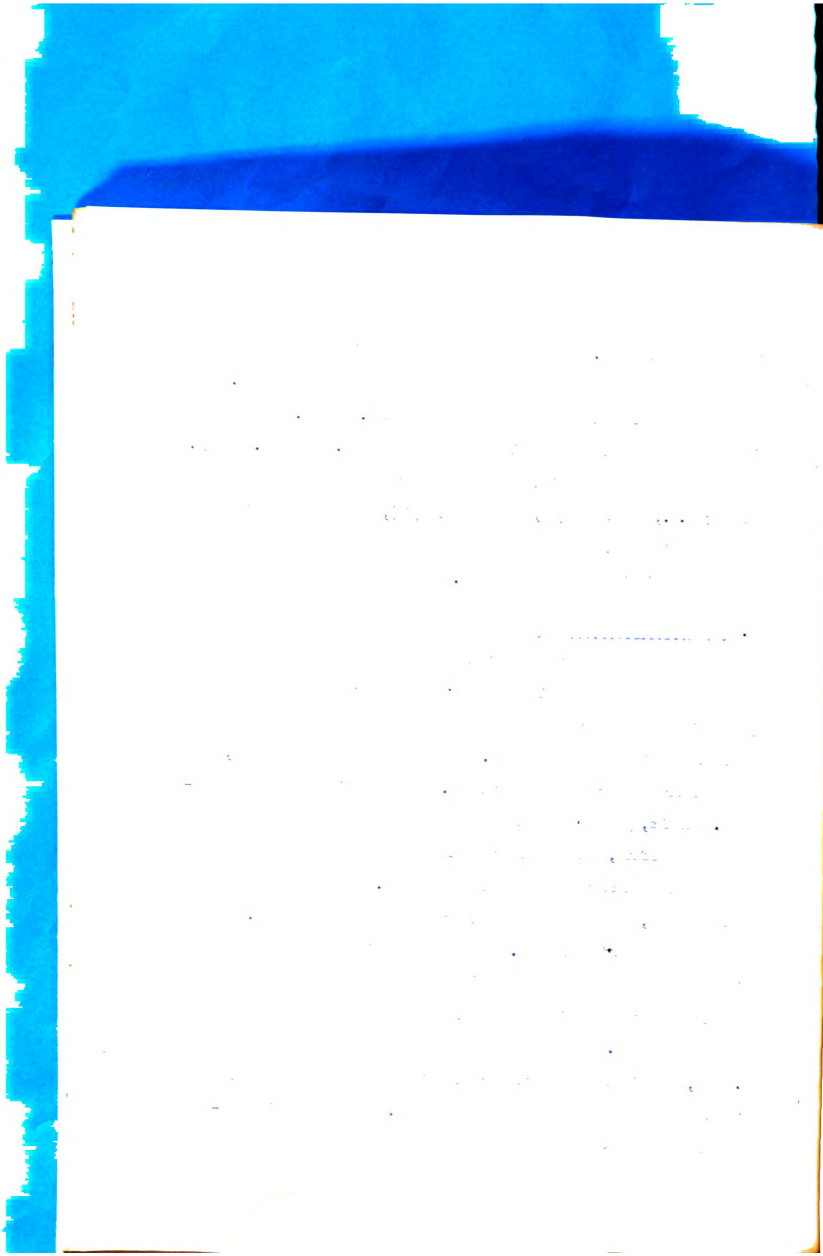
The number of milliequivalents of ferrous iron used to reduce the precipitate to a soluble form was obtained from the difference between the number of milliequivalents of ferrous iron originally added and the number of milliequivalents of ferrous iron found after reaction

7

with the precipitate. This difference in milliequivalents would also correspond to the number of milliequivalents of manganese present. The average of two determinations revealed that 0.479 meq. of ferrous iron was used to effect reduction of the precipitate. Since 0.486 meq. of manganese was taken initially with respect to an oxidation change of two; i.e., manganese (II) to manganese (IV), the results indicated that the original assumption of having manganese dioxide formed as the product of oxidation was indeed valid.

3. Titration of the Filtrate

The filtrates plus washings which were retained following the removal of the manganese dioxide were analyzed for excess unreacted peroxydiphosphate by the addition of a measured excess of standard ferrous ammonium sulfate solution. After standing for one minute, the excess ferrous ion was titrated with 0.1000N potassium dichromate solution. Blanks, prepared in exactly the same manner as those containing manganous sulfate, were treated with the same amount of ferrous ammonium sulfate solution as those used for the samples. After a standing period of one minute, the excess ferrous ion was back titrated with 0.1000N potassium dichromate solution. The difference in volume of potassium dichromate used in the back titration of the excess ferrous ion in the actual sample and that in the blank represented the milliliters of peroxydiphosphate. Since the dichromate solution used was exactly 0.1000N, the milliequivalents of peroxydiphosphate required for oxidation of divalent manganese was readily determined. The number of milliequivalents of peroxydiphosphate used in the oxidation would also



correspond to the number of milliequivalents of divalent manganese oxidized. Any unreacted divalent manganese present in the filtrate did not interfere with the titration. Triplicate determinations were made.

The results on the amount of peroxydiphosphate required to effect the oxidation of a known quantity of divalent manganese to some higher oxidation state are shown in Table V.

TABLE V

MILLIEQUIVALENTS TETRALITHIUM PEROXYDIPHOSPHATE REQUIRED TO OXIDIZE 13.35 MILLIGRAMS MANGANESE

Meq. $Li_4P_2O_8$ Added	Meq. $Li_4P_2O_8$ Found	Meq. $Li_4P_2O_8$ Used	Meq. Mn Present	Meq. Mn Calculated for Mn(II) → Mn(III)	Meq. Mn Calculated for Mn(II) → Mn(IV)
1.421	0.938	0.483	0.483		
1.421	0.934	0.487	0.487	0.243	0.486
1.421	0.936	0.485	0.485		
Av.	0.936	0.485	0.485		

The results indicate that, from an average of three analyses, 0.485 meq. of peroxydiphosphate was required to effect oxidation of the divalent manganese present in solution. This value compared favorably with the theoretical amount of 0.486 meq. manganese originally added in which the assumption was made that an oxidation change of two occurred resulting in the oxidation to manganese dioxide. The results also substantiated the previous findings for the precipitates.

Measurement of the filtrate for excess peroxydiphosphate provided a satisfactory method for determining the amount of divalent manganese

oxidized. Analysis of the manganese dioxide formed also provided a satisfactory method of determining the extent of oxidation. Utilization of both methods were employed as checks against one another in the studies to follow.

4. Effect of pH on the Rate of Formation of Manganese Dioxide

Preliminary investigation revealed that both the rate of oxidation of divalent manganese by tetralithium peroxydiphosphate and the character of the precipitate formed were greatly influenced by the initial pH of the solution. A series of experiments was conducted to determine the effect of pH on the time required for precipitation to occur.

Five milliliter portions of 0.0970N manganous sulfate solution were pipetted into 125 ml. iodine flasks containing 25 ml. water. To each was added 19.98 ml. of 0.0742N tetralithium peroxydiphosphate solution and the various pH values were obtained by the addition of the required amount of 1N sulfuric acid. Solutions from pH 1.5-7.7 were prepared in this manner. The length of time required for the appearance of a brown-black precipitate following the addition of the oxidizing agent was measured. The results of pH influence on the manganese oxidation at room temperature, 23°C., at 50°C. and at 100°C. are contained in Table VI.

The data in Table VI reveal that appearance of a precipitate was immediate in the pH range 5.3-7.7 under all temperature conditions studied accompanied by a drop in pH. The precipitates formed in this indicated pH range were dense in nature, settled relatively fast and

[redacted]

TABLE VI

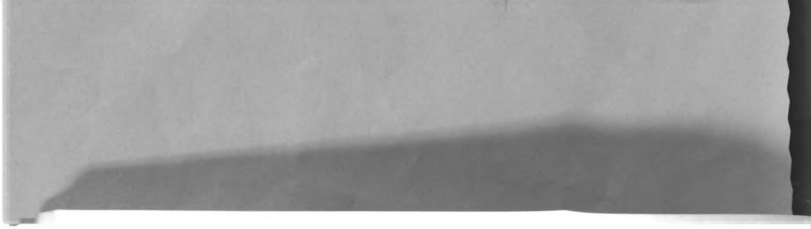
EFFECT OF pH ON THE OXIDATION OF DIVALENT MANGANESE BY TETRALITHIUM PEROXYDIPHOSPHATE

pH	Time Required for the Formation of an Observable Precipitate (Minutes)		
	Room Temperature, 23°C.	50-55°C.	100°C.
1.5		360	10
2.0	210	120	< 5
3.1	60	40	immediate
4.5	30	< 5	immediate
5.3	< 5	immediate	immediate
6.0	immediate	immediate	immediate
7.2	immediate	immediate	immediate
7.5	immediate	immediate	immediate
7.7	immediate	immediate	immediate

Above pH 5.3 precipitates dense and settled rapidly; easily filtered.
Below pH 5.3 precipitates finely divided and colloidal in character.

were easily filtered, particularly those that had been heated. However, decreasing the pH below 5.3 at room temperature progressively, resulted in correspondingly longer periods of time before the formation of precipitates were observed. In conjunction with this work, it was found that various shades of color were obtained prior to the ultimate formation of a precipitate. The precipitates formed in this region were finely divided making for difficult filtration.

By selecting experimental conditions in the acid range it was possible to follow the formation of the precipitate more closely. Addition of variable amounts of peroxydiphosphate to fixed amounts of



manganese were also studied qualitatively. A faint pink appeared in the initially colorless solution deepening in color and intensity with standing to a dark red, then brown and ultimately resulting in precipitation of manganese dioxide.

No studies were made at pH values greater than 7.7 because brown colloidal manganese hydroxide formed at these higher values. Addition of peroxydiphosphate resulted in an increased darkening of the solution brought about by the partial formation of manganese dioxide. These precipitates were gelatinous in character; apparently incomplete oxidation existed.

Furthermore, the continual decrease in pH until a constant value was reached in the oxidation of manganese can be explained by the reaction

$$Li_4P_2O_8 + MnSO_4 + 2H_2O \longrightarrow Li_2SO_4 + MnO_2 + 2LiH_2PO_4$$

in which the acidic character of the solution was increased by the formation of manganese dioxide.

5. Proposed Mechanism of Oxidation

When manganous sulfate was treated with excess tetralithium peroxydiphosphate solution in an acidic medium at room temperature, the formation of a precipitate resulted after standing for one to two hours. In the time interval from the preparation of the sample solution to the appearance of a precipitate, a series of color changes occurred. By adding an insufficient quantity of peroxydiphosphate solution to a

fixed amount of divalent manganese, it was possible to retard the color changes somewhat, particularly in the pink-red region.

A sample containing 25.59 mg. divalent manganese, 10 ml. 0.1628N tetralithium peroxydiphosphate solution, 30 ml. water and 2 ml. 6N sulfuric acid was prepared. The sample prepared in such a manner gave a pH of 1.6 and under these conditions a faint pink color, suggestive of permanganate, was observed in the solution approximately 1.5 hours after preparation. It was found that chromate-free tetralithium peroxydiphosphate solution did not absorb in the 500- to 800-mμ region of the spectrum. The possibility of obtaining a spectrum for the pink-red color which could then be used as a possible aid in characterizing the mechanism of oxidation was investigated.

A sample containing 13.24 mg. manganese, 25 ml. water, 2 ml. 6N sulfuric acid and 19.98 ml. 0.1036N tetralithium peroxydiphosphate solution was prepared. The solution prepared in this manner gave a pH of 1.5. After a 50 minute waiting period at room temperature, the development of faint pink color was observed in the previously colorless solution. Using the Beckman DK-2 a per cent transmittancy spectrum in the 350- to 800-mμ region was obtained with a portion of the colored solution ten minutes after color development occurred. Other spectra were made at five minute intervals until the formation of manganese dioxide resulted. A total of eight spectra was obtained (Figure 1).

Examination of the series of spectra obtained revealed absorption characteristics in the region approximating that of permanganate.

characteristics in the region approximating that of permanganate.

Examination of the series of spectra obtained revealed absorption
bands at 525 and 545 mμ. A total of eight spectra was obtained (Figure 1).
Measurements were made at five minute intervals until the formation of manganese
dioxide resulted. A total of eight spectra was obtained (Figure 1).
solution ten minutes after color development occurred. Other spectra
the 350- to 800-mμ region was obtained with a portion of the colored
solution. Using the Beckman DK-2 a per cent transmittancy spectrum in
development of faint pink color was observed in the previously colorless
of 1.5. After a 30 minute waiting period at room temperature, the
solution was prepared. The solution prepared in this manner gave a pH
sulfuric acid and 10.98 ml. 0.1039M tetrasilthium peroxydiphosphate

A sample containing 17.81 mg. manganese, 25 ml. water, 2 ml. 6N
sulfuric acid and 10.98 ml. 0.1039M tetrasilthium peroxydiphosphate
solution was prepared. The solution prepared in this manner gave a pH
of 1.6 and under these conditions a faint pink color, suggestive
of permanganate, was observed in the solution approximately 1.5 hours
after preparation. It was found that chromate-free tetrasilthium peroxy-
diphosphate solution did not absorb in the 520- to 600-mμ region of the
spectrum. The possibility of obtaining a spectrum for the pink-red
color which could then be used as a possible aid in characterizing the
reactions of oxidation was investigated.

A sample containing 17.81 mg. manganese, 25 ml. water, 2 ml. 6N
sulfuric acid and 10.98 ml. 0.1039M tetrasilthium peroxydiphosphate
solution was prepared. The solution prepared in this manner gave a pH
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diphosphate solution did not absorb in the 520- to 600-mμ region of the
spectrum. The possibility of obtaining a spectrum for the pink-red
color which could then be used as a possible aid in characterizing the
reactions of oxidation was investigated.

A sample containing 25.39 mg. manganese, 10 ml. 0.1039M
tetrasilthium peroxydiphosphate solution, 30 ml. water and 2 ml. 6N
sulfuric acid was prepared. The sample prepared in much a manner gave
a pH of 1.6 and under these conditions a faint pink color, suggestive
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solution. Using the Beckman DK-2 a per cent transmittancy spectrum in
the 350- to 800-mμ region was obtained with a portion of the colored
solution ten minutes after color development occurred. Other spectra
were made at five minute intervals until the formation of manganese
dioxide resulted. A total of eight spectra was obtained (Figure 1).

Examination of the series of spectra obtained revealed absorption
bands at 525 and 545 mμ. A total of eight spectra was obtained (Figure 1).
characteristics in the region approximating that of permanganate.

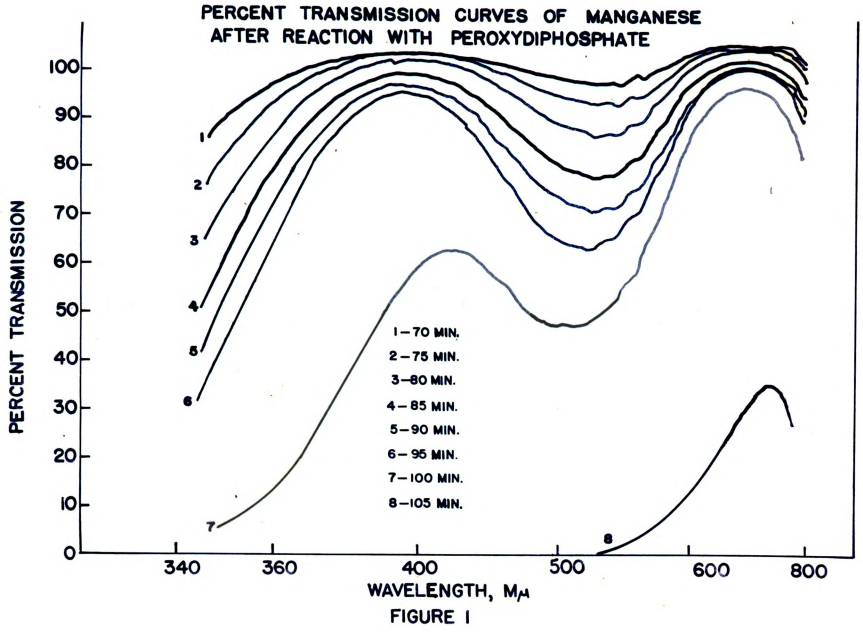
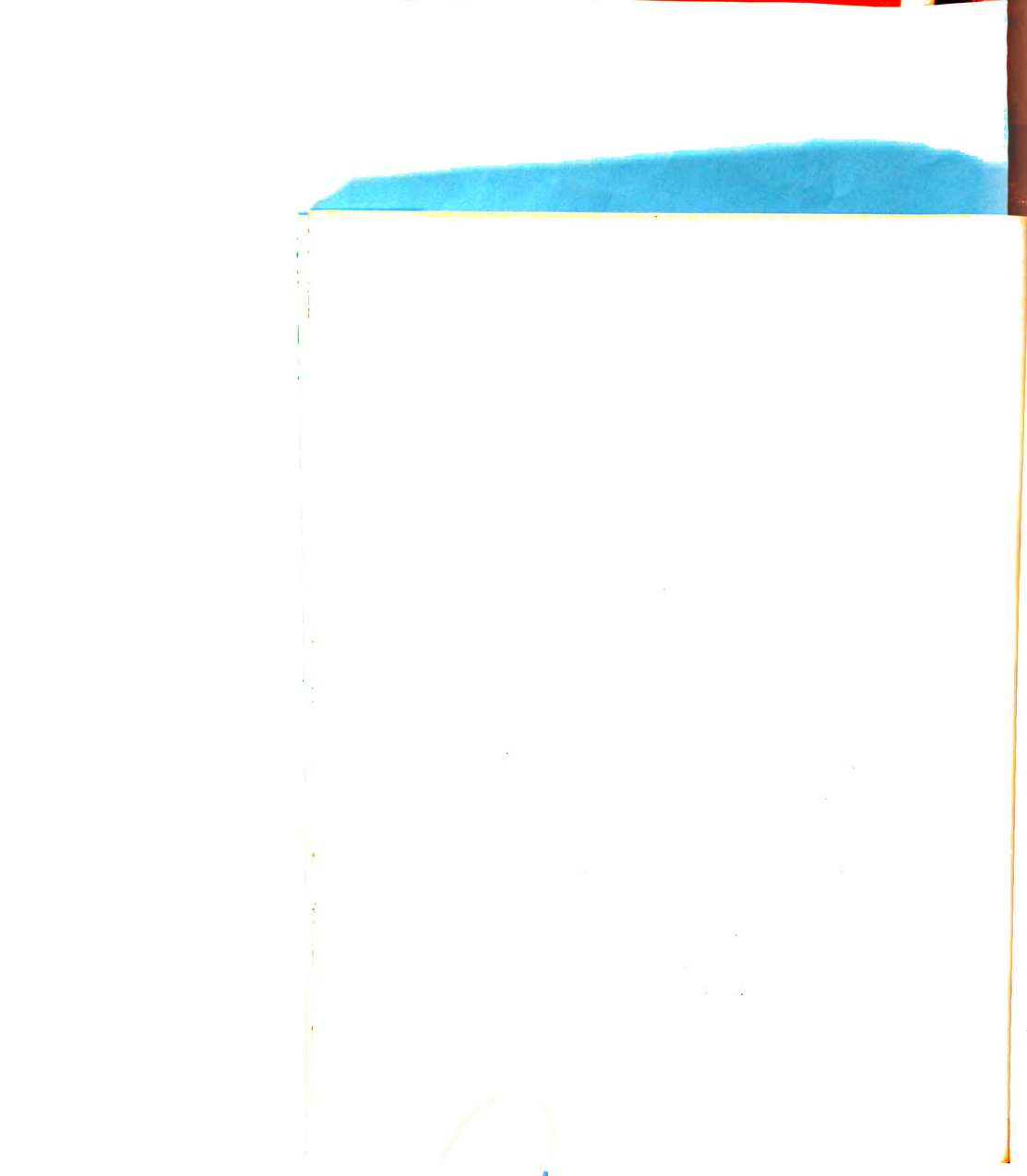

PERCENT TRANSMISSION CURVES OF MANGANESE
AFTER REACTION WITH PEROXYDIPHOSPHATE
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
340
360
400
500
600
800
WAVELENGTH, Mμ
1
2
3
4
5
6
7
8
1 – 70 MIN.
2 – 75 MIN.
3 – 80 MIN.
4 – 85 MIN.
5 – 90 MIN.
6 – 95 MIN.
7 – 100 MIN.
8 – 105 MIN.

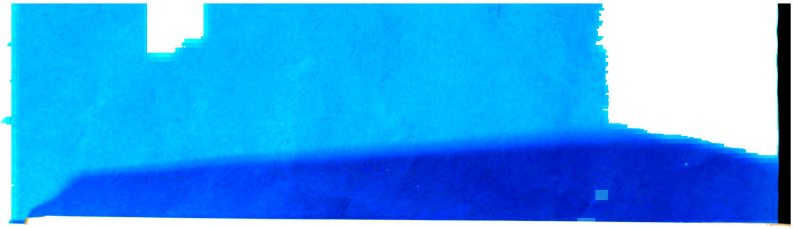
FIGURE 1



However, no definite, well-defined peaks at 525- or 540-mμ were obtained; merely indications of such breaks were observed. The spectrum was shown not to be due to manganic absorption by comparing it with a manganic pyrophosphate spectrum. The manganic spectrum did not show absorption peaks in the same spectral region as the sample. The continual increase in the color intensity with time may be partially responsible for the poor spectrum recorded together with some possible interference from trivalent manganese.

It was possible to follow the increase in color intensity with time as shown in Figure 1. This would suggest that if permanganate were present and thus responsible for the color observed, it formed initially as a very small concentration which increased with increase in time to some maximum concentration. Failure to observe whether there was a decrease in the concentration, if a maximum concentration value was once reached, must be attributed to the formation of manganese dioxide which obscured the absorption of the solution thereafter.

Apparently what must be occurring in a solution of divalent manganese and peroxydiphosphate can be postulated in the following manner. Divalent manganese reacts with the peroxydiphosphate to give permanganate followed by the permanganate reacting with the divalent manganese to yield a precipitate of manganese dioxide. The reaction probably involves a rate determining step evident by the persistent pink-red color prior to the formation of a precipitate. It appears the concentration of permanganate must first reach a definite maximum concentration before

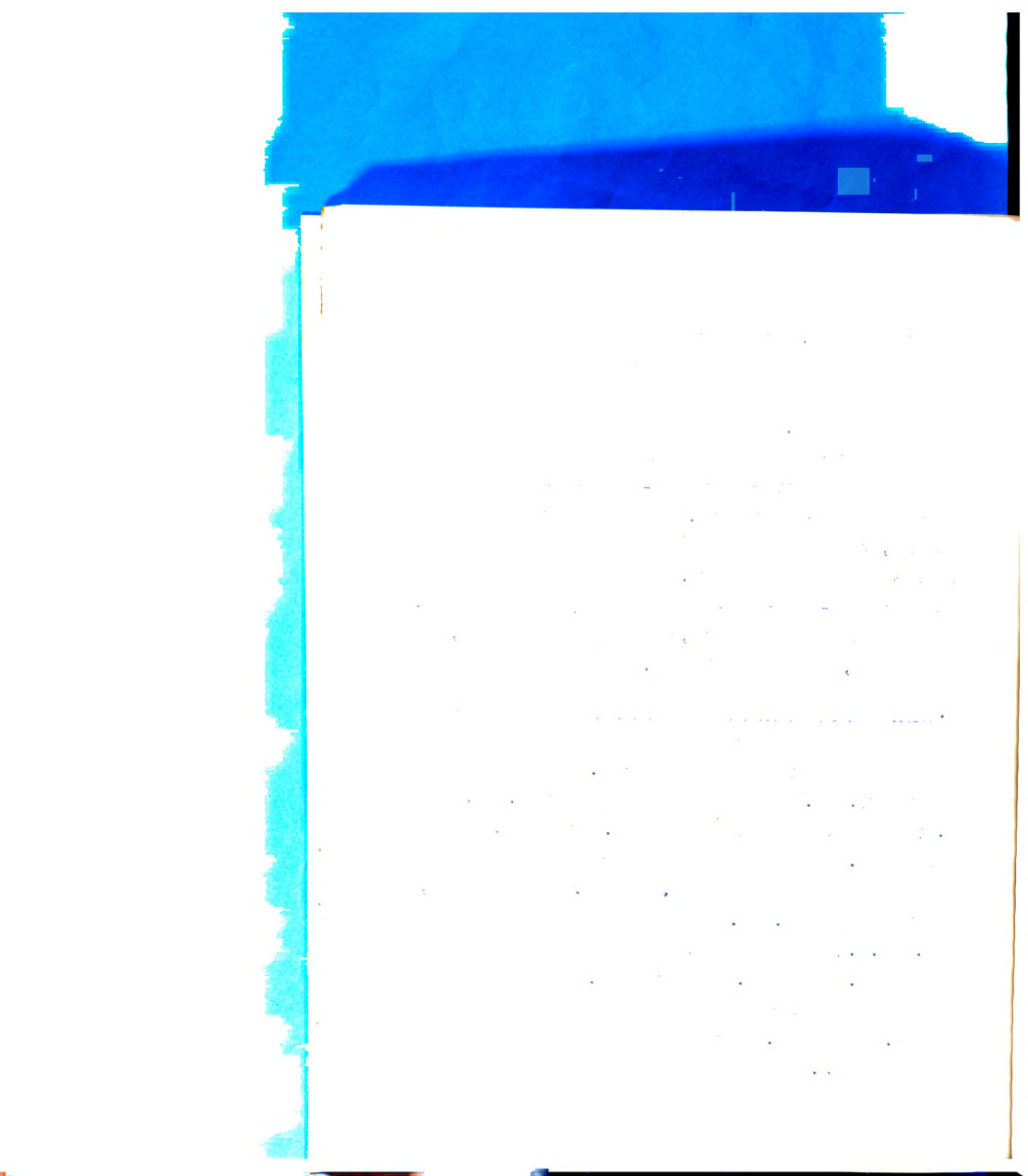


precipitation occurs. This was evident in the studies conducted previously where various amounts of peroxydiphosphate were added to a fixed quantity of manganese and the time required for the formation of a precipitate recorded.

These studies on the appearance of a possible permanganate color were made in acid solution where the pink-red color persisted for a short but measurable period of time. In neutral and slightly basic solutions, divalent manganese oxidized by peroxydiphosphate yielded a light brown color almost immediately. This color development probably obscured the pink-red permanganate color which may have formed initially. As was indicated in previous studies, the rate of reaction depended, to a great extent, on the pH of the solution.

6. Time Required to Effect Oxidation at Room Temperature

A series of experiments was designed for studying the time required to effect complete oxidation at room temperature. Six pairs of samples containing 13.24 mg. manganese were prepared by pipetting 4.97 ml. 0.0970N manganous sulfate solution into 250 ml. iodine flasks. Twenty milliliters 0.0860N peroxydiphosphate solution was added to each flask and diluted to a total volume of 50 ml. with water. In similar fashion, solutions containing 10.23 mg. manganese were prepared by the addition of 1.00 ml. 0.3726N standard manganous sulfate solution to each of twelve 125 ml. iodine flasks. Ten milliliters 0.1022N peroxydiphosphate solution was added followed by sufficient water to give a total volume of 50 ml. to each sample. A pair of blanks was also prepared for each set at a pH of 5.9.



The samples and blanks were stoppered and stored in the dark at room temperature for varying lengths of time to effect oxidation. Temperature was not maintained at a particular value since it was not critical in this region. The solutions possessed initial pH values ranging from 7.2 to 7.5. Formation of manganese dioxide occurred shortly after the addition of excess oxidizing agent passing through the color changes noted and described previously. At various times after preparation, pairs of samples containing the precipitate of manganese dioxide and excess peroxydiphosphate were analyzed for completeness of oxidation. The precipitate was removed by filtration through a Gooch crucible with suction and washed thoroughly with distilled water. Both the combined filtrate and washings and the precipitate were analyzed. The results of the analysis at various time intervals denoting the quantity of divalent manganese oxidized are shown in Table VII.

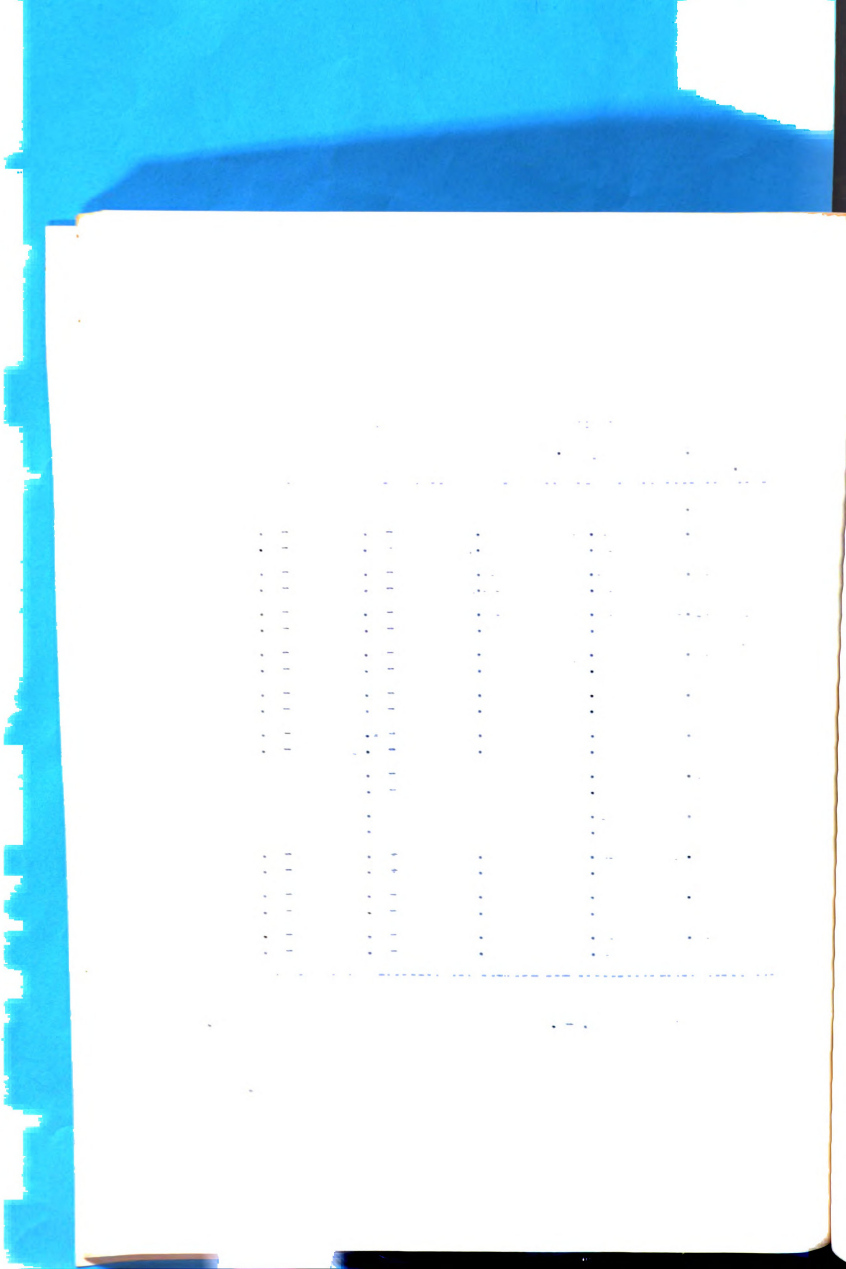
The data presented show that, as expected, increased periods of time gave progressively better results. After ten hours complete oxidation of the manganese was effected as indicated in Table VII. The average of the last six determinations for the 10.23 mg. manganese samples in the time interval 12-24 hours resulted in values of 10.21 mg. and 10.13 mg. for the filtrate and precipitate respectively. The average of these six precipitates was approximately one per cent below the theoretical value, strongly suggesting that an empirical factor be applied to the precipitates (25). Incomplete oxidation was observed visually by the faint brown imparted to the filtrate following removal of the precipitate. The absence of any color imparted to the filtrate and the

TABLE VII

TIME STUDY ON THE OXIDATION OF DIVALENT MANGANESE AT ROOM TEMPERATURE

Time Hrs.	Mg. Mn Added	Mg. Mn Found		Per Cent Error	
		Filtrate	Precipitate	Filtrate	Precipitate
1	13.24		incomplete		
2	13.24	11.62	10.82	-12.24	-18.28
		11.59	10.78	-12.46	-18.58
4	13.24	12.22	11.40	- 7.70	-13.89
		12.16	11.34	- 8.16	-14.35
5	13.24	12.71	11.70	- 4.00	-11.56
		12.77	11.75	- 3.55	-11.25
6	10.23	9.88	9.34	- 3.42	- 8.70
		9.86	9.28	- 3.61	- 9.29
8	10.23	9.94	9.61	- 2.83	- 6.06
		9.94	9.64	- 2.83	- 5.77
9	10.23	10.00	9.69	- 2.25	- 5.26
		9.94	9.89	- 2.83	- 3.32
10	13.26	13.24		- 0.15	
		13.18		- 0.60	
12	13.26	13.26		0.00	
		13.21		0.38	
	10.23	10.24	10.16	+ 0.09	- 0.68
		10.24	10.11	+ 0.09	- 1.17
15	10.23	10.19	10.14	- 0.39	- 0.88
		10.16	10.10	- 0.68	- 1.27
24	10.23	10.22	10.13	- 0.09	- 0.98
		10.22	10.16	- 0.09	- 0.68

constant pH values of 6.0-6.3 indicated complete reaction had occurred. Duplicate determinations were therefore run under a rigid time schedule to minimize continued oxidation of the manganese left in solution.



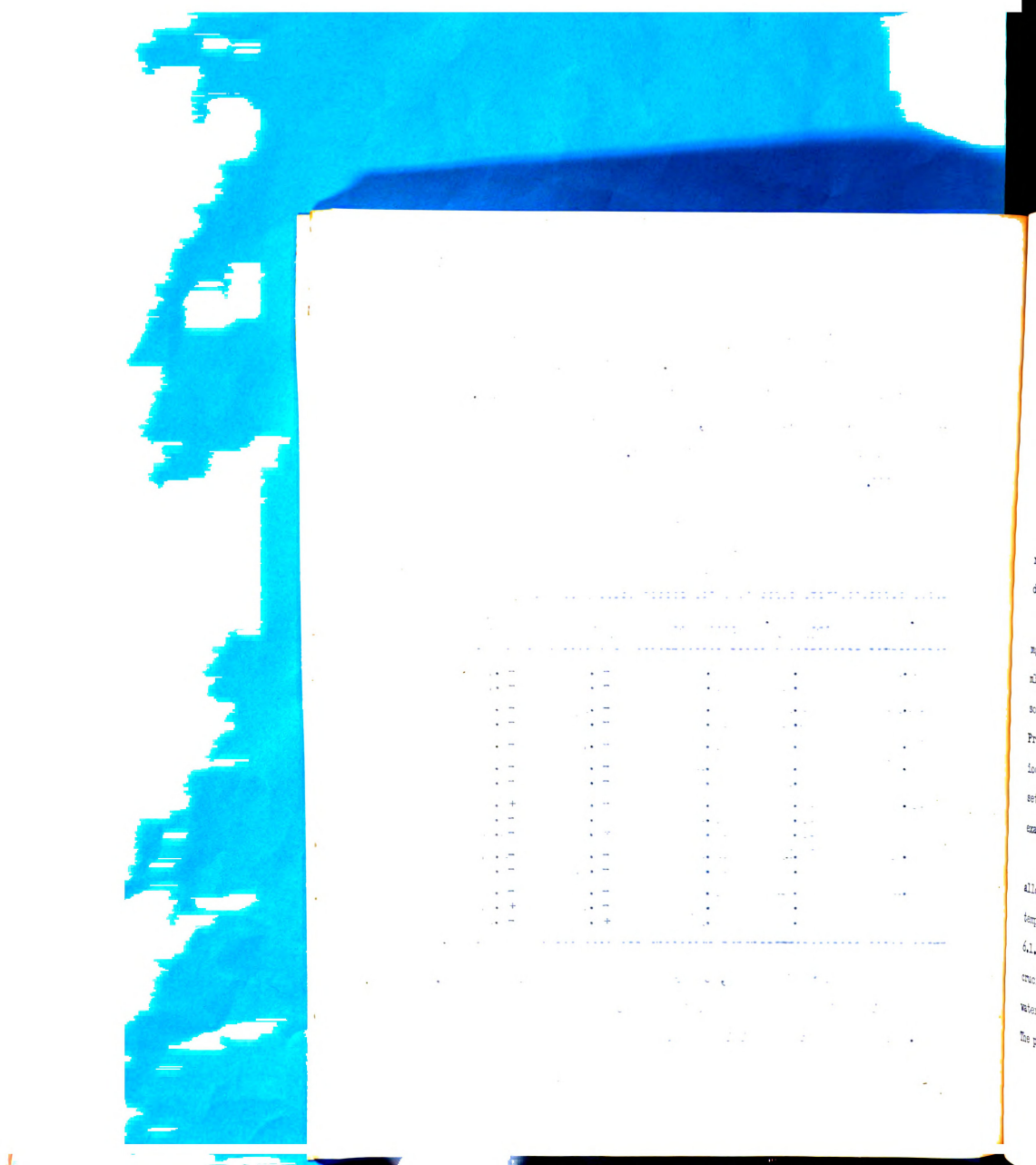
The same procedure as above was employed for various concentrations of manganese up to approximately 50 mg. A period of 12 hours was arbitrarily selected as the time required for complete oxidation. For larger sizes samples of manganese, the time of standing to effect complete reaction was increased to 14 hours. Results are given in Table VIII.

TABLE VIII

OXIDATION OF VARYING QUANTITIES OF MANGANESE AT ROOM TEMPERATURE FOR TWELVE HOURS

Mg. Mn Added	Mg. Mn Found		Per Cent Error	
	Filtrate	Precipitate	Filtrate	Precipitate
51.38	50.38	49.98	-1.98	-2.72
	50.53	49.98	-1.64	-2.72
41.52	41.38	40.56	-0.34	-2.31
	41.33	30.50	-0.46	-2.46
25.68	25.49	25.22	-0.74	-1.79
20.46	20.32	20.10	-0.68	-1.76
	20.35	20.19	-0.54	-1.32
13.24	13.13	13.25	-0.83	+0.08
	13.24	13.18	0.00	-0.45
	13.29	13.08	+0.45	-1.21
10.23	10.19	10.10	-0.39	-1.27
	10.13	10.02	-0.97	-2.05
5.12	5.11	5.08	-0.19	-0.78
	5.08	5.20	-0.78	+1.57
	5.14	4.96	+0.39	-3.12

As evident from the table, the results obtained were fairly good. Quantitative oxidation was not obtained for the largest size sample used. The form of the precipitates in the larger samples was more



finely divided in nature resulting in extremely prolonged periods of time for effective removal of the precipitate. Increased time of standing did not materially improve the results obtained. The long period of standing required to effect the complete oxidation suggested that a search be made for a more rapid method of oxidation.

7. Time Required to Effect Oxidation at 50-55°C.

Chulski (11) suggested the possibility of carrying out oxidation reactions at 50-55°C. with peroxydiphosphate. The quantitative oxidation of manganese was studied in this temperature range.

Six 4.97 ml. portions of 0.070N manganous sulfate solution (13.23 mg. manganese) were pipetted into 250 ml. iodine flasks containing 25 ml. water. Twenty milliliters of 0.1421N tetralithium peroxydiphosphate solution and 0.05 ml. 1N sulfuric acid were added to each flask. Preparation in this manner gave solutions with pH values of 6.6. The iodine flasks were stoppered and placed in a constant temperature oven set at 50° ± 5°C. Six blanks at a pH of 6.0 were also prepared in exactly the same manner as the samples.

After an hour at 50°C., two samples and blanks were removed and allowed to cool to room temperature. Thirty minutes cooling at room temperature was sufficient. At this point the samples were at a pH of 6.1. The manganese dioxide precipitates were filtered through Gooch crucibles with suction. The precipitates were washed with 150 ml. of water in 30 ml. portions. Both the filtrate and washings were retained. The precipitates were analyzed by the ferrous ammonium sulfate-potassium

finely divided in nature resulting in extremely prolonged periods of time for effective removal of the precipitate. Increased time of standing did not materially improve the results obtained. The long period of standing required to effect the complete oxidation suggested that a search be made for a more rapid method of oxidation.

7. Time Required to Effect Oxidation at 50-55°C.

Cmulski (11) suggested the possibility of carrying out oxidation reactions at 50-55°C. with peroxydiphosphate. The quantitative oxidation of manganese was studied in this temperature range.

Six 4.97 ml. portions of 0.0704M manganous sulfate solution (13.23 mg. manganese) were pipetted into 250 ml. iodine flasks containing 25 ml. water. Twenty milliliters of 0.1421M tetralithium peroxydiphosphate solution and 0.05 ml. 1N sulfuric acid were added to each flask. Preparation in this manner gave solutions with pH values of 6.6. The iodine flasks were stoppered and placed in a constant temperature oven set at 50° ± 5°C. Six blanks at a pH of 6.0 were also prepared in exactly the same manner as the samples.

After an hour at 50°C., two samples and blanks were removed and allowed to cool to room temperature. Thirty minutes cooling at room temperature was sufficient. At this point the samples were at a pH of 6.1. The manganese dioxide precipitates were filtered through Gooch crucibles with suction. The precipitates were washed with 150 ml. of water in 30 ml. portions. Both the filtrate and washings were retained. The precipitates were analyzed by the ferrous ammonium sulfate-potassium

dichromate method described earlier. Similarly, the filtrate and washings were determined for the amount of peroxydiphosphate used in the oxidation from which the amount of manganese could then be calculated.

The same procedure was carried out after two hours at 50°C. with another set of samples and blanks. The precipitates that had formed were much more voluminous. The solutions were at a pH of 5.8. Both the precipitate, which was recovered, and the filtrate and washings were analyzed in the usual manner for the amount of manganese which had been oxidized.

The third set of samples and blanks were removed from the constant temperature oven after four hours. The cooled solutions gave a pH value of 5.6. Both the combined filtrate and washings and the precipitate of each sample were analyzed for manganese in the usual manner. The results of the six samples analyzed at the above prescribed time intervals are contained in Table IX.

TABLE IX

OXIDATION OF MANGANESE AT 50-55°C. FOR VARIOUS PERIODS OF TIME

Time Hrs.	Mg. Mn Present	Mg. Mn Found		Per Cent Error	
		Filtrate	Precipitate	Filtrate	Precipitate
1	13.24	12.06	12.01	-8.91	-9.29
		12.11	12.06	-8.53	-8.91
2	13.24	12.47	12.32	-5.82	-6.95
		12.41	12.41	-6.25	-6.25
4	13.24	13.21	13.13	-0.15	-0.83
		13.23	13.15	-0.08	-0.68

Examination of the data reveal that oxidation was not complete after two hours at 50°C. but that quantitative oxidations were obtained for samples maintained at 50°C. for four hours. The progressive decrease in pH with time was also taken as an indication of incomplete oxidation. The results show that treatment for four hours at 50°C. was adequate for complete oxidation of the manganese samples.

A series of additional runs containing varying quantities of manganese and sufficient excess peroxydiphosphate solution were prepared and allowed to remain at a constant temperature of 50°C. for four hours. The solutions were within a pH range of 6.8-7.2 initially. Both filtrate and precipitate were analyzed for manganese in the same manner as previously described. The results of 11 runs containing various amounts of manganese are compiled in Table X.

From the numerous samples of manganese which have been run both at room temperature and at 50°C., the amounts of manganese in the precipitates were found to be all approximately one per cent low, strongly indicative of the need for an empirical factor. Utilization of a factor equal to 1.01 was made on the precipitates to bring them more in line with the values found for the filtrate. This was done for the results in Table X where the corrected values of the manganese obtained in the precipitates are shown together with the actual values obtained from the precipitates. The latter was included primarily for comparative purposes. It is readily seen that application of the empirical factor on the precipitates results in good agreement with the theoretical. The factor was used hereafter in all the work to follow.

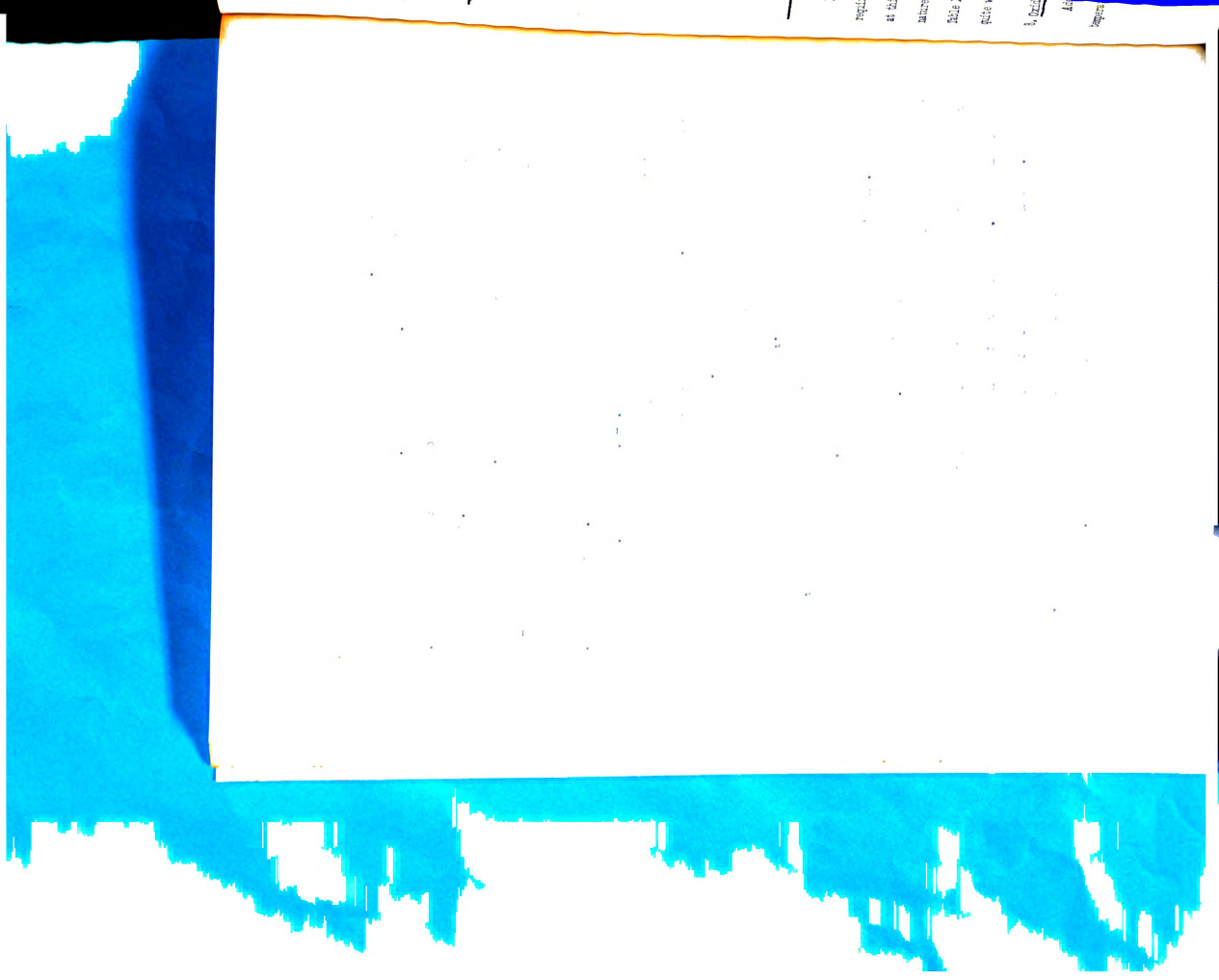


TABLE X

OXIDATION OF MANGANESE AT 50°C. FOR FOUR HOURS

Mg. Mn Present		Mg. Mn Found		
		Filtrate	Precipitate	Precipitate with Factor = 1.01
10.23		10.16	10.08	10.18
		10.16	10.16	10.26
		10.24	10.00	10.10
		10.13	10.13	10.23
		10.13	10.08	10.18
		10.27	10.10	10.20
		---	10.13	10.23
	Av.	10.19	10.10	10.21
13.24		13.24	13.11	13.24
		13.18	13.07	13.20
	Av.	13.21	13.09	13.22
20.46		20.51	20.25	20.45
		20.40	20.20	20.40
		20.38	20.22	20.42
	Av.	20.43	20.22	20.42

By maintaining a temperature of 50°C. for four hours, the time required for oxidation was materially reduced. The precipitates formed at this elevated temperature were observed to be much more dense in nature and subsequently found to be readily filterable. As seen from Table X the results on the filtrate and precipitate for manganese agreed quite well with the theoretical value.

8. Oxidation at Elevated Temperatures

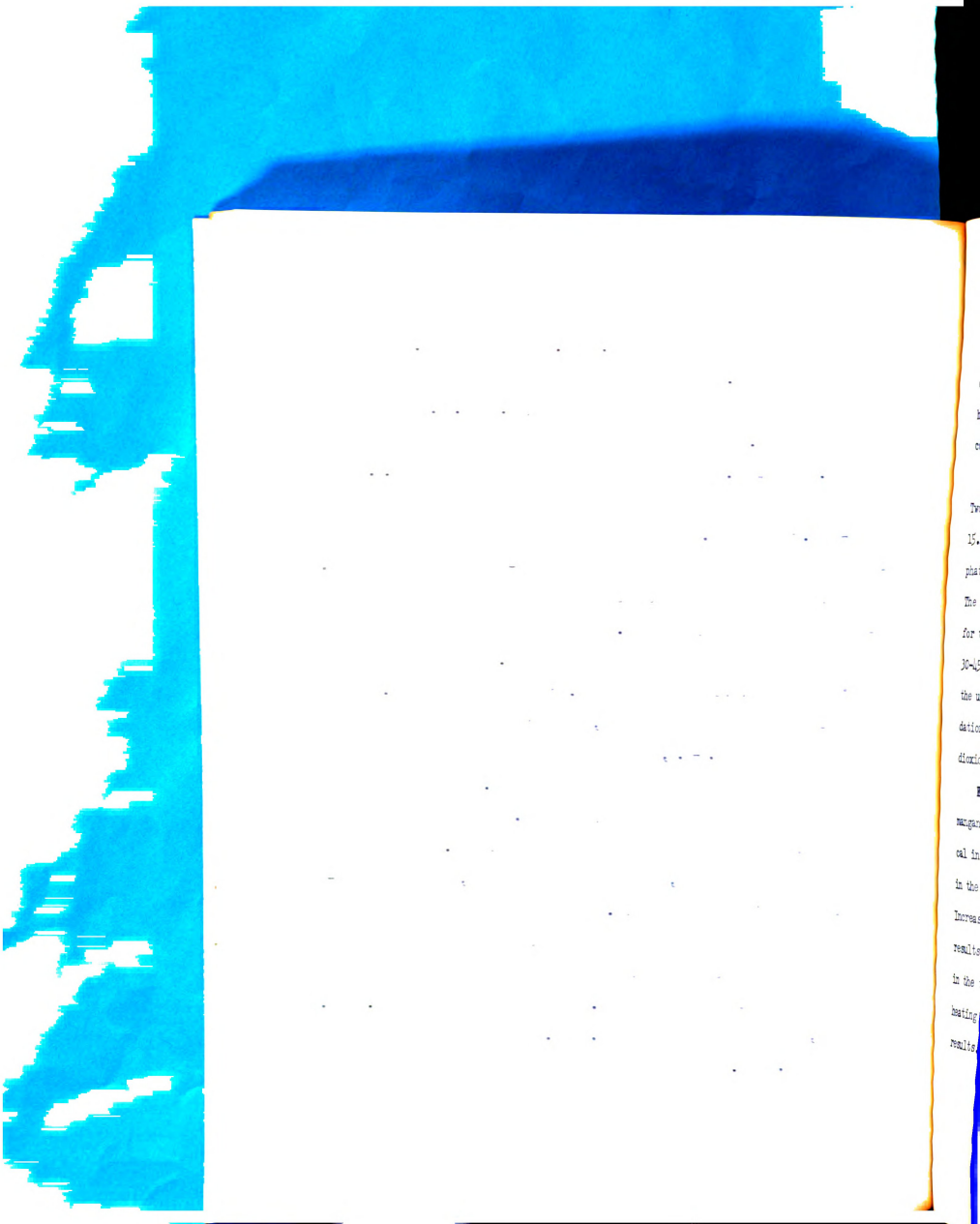
Additional studies were made on the oxidation of manganese at temperatures of 80-85°C. Six 1.00 ml. portions of the standard manganous

[redacted]

sulfate stock solution containing 10.23 mg. manganese per ml. were pipetted into 250 ml. iodine flasks followed by sufficient excess peroxydiphosphate solution to effect oxidation; 9.97 ml. 0.1041N was deemed sufficient. The total volume of each sample was then made up to 50 ml. with water. The solutions were initially at a pH of 6.8. The samples were then heated over Tirrill burners until a temperature of 80-85°C. was reached. Treatment of the samples in this manner resulted in the immediate formation of the brown-black manganese dioxide. The samples were allowed to cool to room temperature for a period of time ranging from 20 to 30 minutes. Blanks were also prepared and treated in exactly the same manner as the samples. The blanks were adjusted to an approximate pH value of 6.0 with 1N sulfuric acid.

Following this period of cooling, during which time the pH of the solutions dropped to 5.4-5.6, the precipitates were filtered with suction on Gooch crucibles and thoroughly washed with water. The time required for this operation was usually 25 to 30 minutes. The total quantity of water used for each precipitate was approximately 100 ml. The procedure of analysis on the filtrate, supplemented by the blank, and the precipitate have been discussed previously.

In similar fashion a series of samples containing different amounts of manganese were also prepared and treated with sufficient excess peroxydiphosphate to effect oxidation. Five samples containing 20.46 mg. manganese, four samples containing 30.70 mg. manganese and four samples containing 41.24 mg. manganese were studied in exactly the same manner



as previously described for the 10.23 mg. manganese samples except the cooling time after heating to 80-85°C. was increased to 1.0 to 1.5 hours. The results found for all these samples of different manganese concentrations are compiled in Table XI.

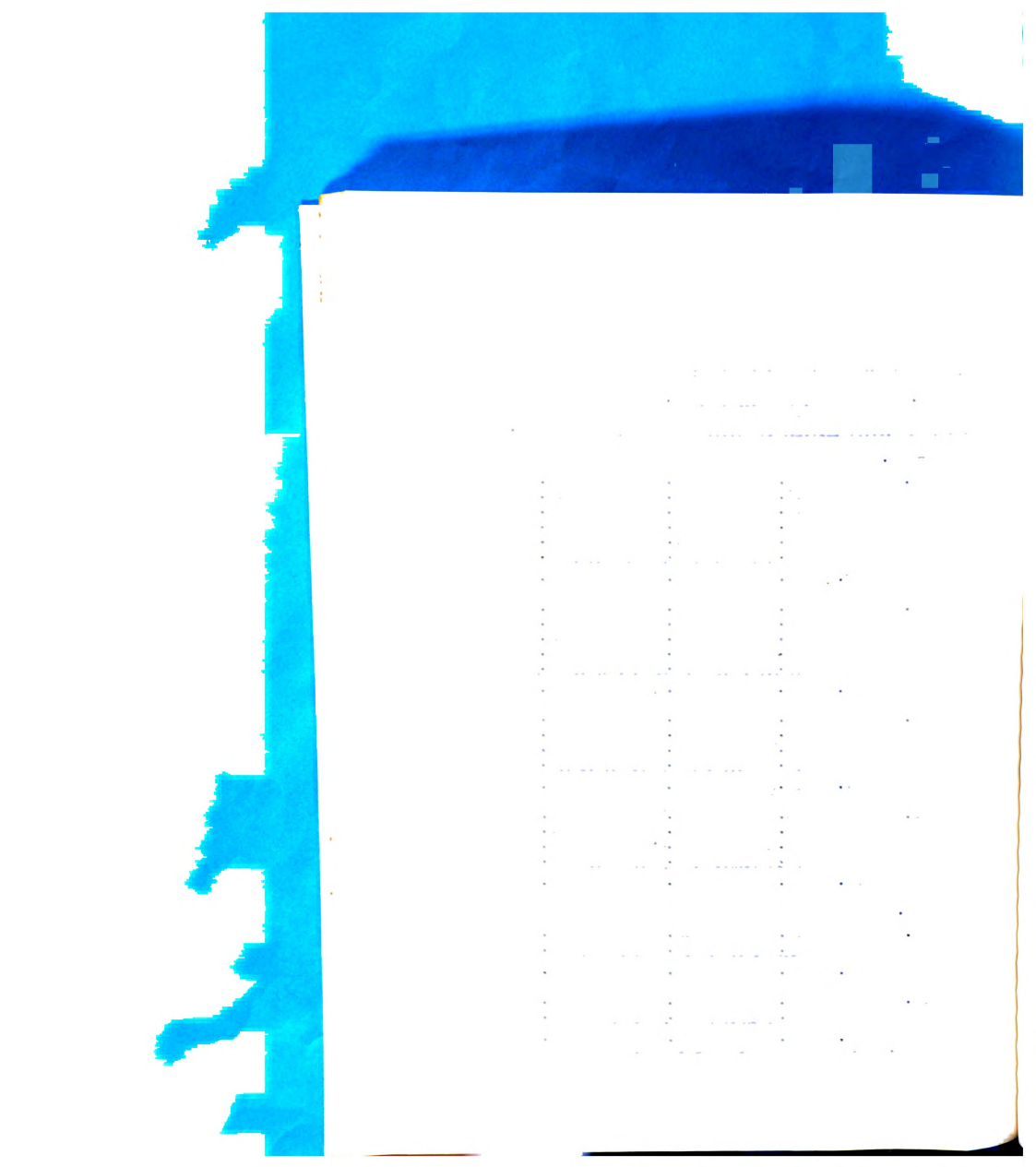
Similar studies were made at a slightly increased temperature. Two samples containing 10.23 mg. manganese and two samples containing 15.40 mg. manganese were treated with 19.98 ml. 0.0876N peroxydiphosphate solution and were diluted to a total volume of 50 ml. with water. The samples were heated to 100°C. and were maintained at that temperature for ten seconds. The solutions were cooled to room temperature for 30-45 minutes. Both the filtrates and precipitates were determined in the usual manner for the amount of peroxydiphosphate used in the oxidation of manganese and the quantity of manganese present as manganese dioxide respectively. The results are also included in Table XI.

Examination of the data in Table XI revealed that the amount of manganese found from the filtrates compared favorably with the theoretical in all cases studied. This also proved to be true for the manganese in the precipitates following an appropriate correction factor. Increased length of standing at room temperature did not affect the results obtained on the filtrates nor on the precipitates. The data in the table also reveal that there was little to be gained by increased heating to 100°C., heating to 80-85°C. was adequate for quantitative results.

TABLE XI

OXIDATION OF MANGANESE AT ELEVATED TEMPERATURES

Mg. Mn Added		Mg. Mn Found		
		Filtrate	Precipitate	Precipitate with Factor 1.01
At 80-85°C.				
10.23		10.24	10.13	10.23
		10.19	10.16	10.26
		10.24	10.16	10.26
		10.19	10.16	10.26
		10.19	10.10	10.20
		10.27	10.10	10.20
	Av.	10.22	10.14	10.24
20.46		20.46	20.26	20.46
		20.43	20.24	20.44
		20.48	20.32	20.52
		20.43	20.30	20.50
		20.46	20.26	20.46
	Av.	20.45	20.27	20.47
30.70		30.62	30.54	30.84
		30.70	30.54	30.84
		30.73	30.56	30.86
		30.73	30.28	30.58
	Av.	30.70	30.48	30.78
41.24		41.24	40.70	41.10
		41.35	40.80	41.21
		41.13	40.83	41.24
		41.24	40.86	41.27
	Av.	41.24	40.80	41.20_5
At 100°C.				
10.23		10.24	10.16	10.26
		10.27	10.13	10.23
	Av.	10.26	10.15	10.24_5
15.40		15.43	15.24	15.39
		15.40	15.30	15.45
	Av.	15.41_5	15.27	15.42



9. Recommended Volumetric Procedure

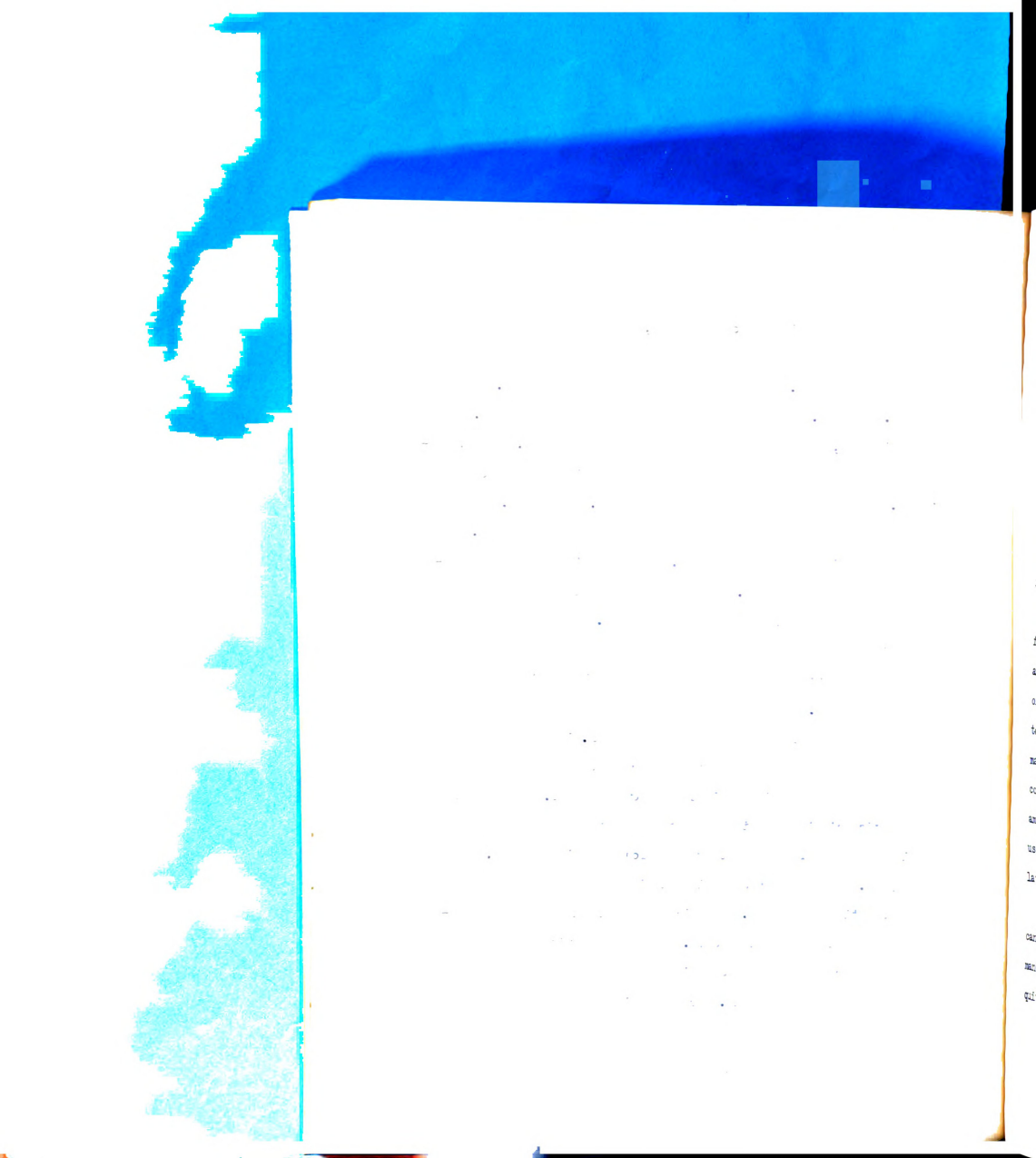
The results of all these preceding experiments provided sufficient background data for the development of a suitable volumetric determination of manganese following oxidation of divalent manganese with excess tetralithium peroxydiphosphate solution.

The recommended procedure for the determination of manganese is as follows.

The requisite volume of solution containing divalent manganese, in the form of the sulfate and acidified to a pH of 3-4, is added to a 250 ml. iodine flask. Convenient quantities for the determination range from 5 to 50 mg. of manganese. A 2.5-to 3.0-fold excess tetralithium peroxydiphosphate solution is then added to effect the oxidation of the manganese to manganese dioxide followed by the addition of sufficient distilled water to give a total volume of 50 ml. Addition of the oxidizing agent results in a faint pink color imparted to the solution, turning progressively darker with time. The solution sample oxidized in this manner should have an initial pH in the range 7.0 to 7.5. Heating over a Tirrill burner is then carried out until the first sign of boiling occurs. At this elevated temperature the immediate formation of a hydrous brown-black precipitate of manganese dioxide was obtained. Blanks, containing the same quantity of peroxydiphosphate as added in the sample, are also prepared and diluted to the same total volume of 50 ml. These blanks are adjusted to a pH of 6.0 with 1N sulfuric acid and carried through the entire procedure in the same manner as the samples.

Following a 45 minute cooling period, the precipitate is filtered on a Gooch crucible previously washed with dilute sulfuric acid and thoroughly with water. The precipitate is washed with 150 ml. of water in 30 ml. portions. Both the filtrate and washings are retained. The precipitate, after washing, is transferred to a 400 ml. beaker, dissolved in a known quantity of excess ferrous ammonium sulfate followed by 9 ml. 18N sulfuric acid and diluted to 200 ml. with water. Magnetic stirring is used in hastening the dissolution of the precipitate. The excess ferrous ion is titrated with 0.1000N potassium dichromate solution in the presence of 9 ml. 85 per cent phosphoric acid and using diphenylamine sodium sulfonate as the indicator. The weight of manganese present in the precipitate can readily be found from the difference required to titrate the same volume of ferrous solution in the absence of the precipitate.

The combined filtrate and washings of 200 ml. is analyzed for the amount of peroxydiphosphate remaining after the oxidation of divalent manganese to manganese dioxide in the following manner. Nine milliliters 18N sulfuric acid is added to the filtrate and washings followed immediately by a measured quantity of ferrous ammonium sulfate. After a minute 9 ml. 85 per cent phosphoric acid is added and the excess ferrous ion is back titrated with 0.1000N dichromate solution using diphenylamine sodium sulfonate as indicator. The blank is titrated in exactly the same manner following the addition of the same quantity of ferrous solution as used in the sample. From the difference in volumes of



0.1000N potassium dichromate used in the blank and the sample the amount of manganese can be calculated.

10. Effect of Foreign Ions

It was desired to study the effect of other ions on the manganese oxidation. The solutions used in studying the effect of various ions on the manganese oxidation were prepared from reagent grade salts which were essentially free from manganese. The solutions generally contained 1 or 2.5 mg. of the desired ion per ml. Wherever possible salts containing sulfate as the anion were used.

Solutions containing a fixed amount of manganese in the divalent form, a measured volume of the standard solution of the foreign ion and sufficient excess tetralithium peroxydiphosphate to effect oxidation of the manganese, were diluted to 50 ml. These solutions were adjusted to pH values of 6 or 7. These series of solutions prepared in such a manner were heated to boiling for five seconds and then allowed to cool for 45 minutes. The precipitate formed was filtered off and the amount of manganese was determined. From the amount of peroxydiphosphate used to effect oxidation of the manganese, the manganese could be calculated from the filtrate. The results are tabulated in Table XII.

The data in Table XII indicate that the determination of manganese can be made in the presence of quite a number of ions. The amount of manganese found in the presence of these various individual ions agreed quite closely with the theoretical quantity added initially.

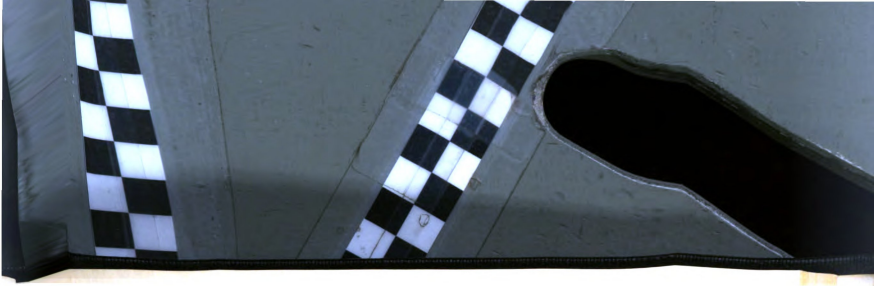


TABLE XII

DETERMINATION OF MANGANESE IN THE PRESENCE OF OTHER ELEMENTS

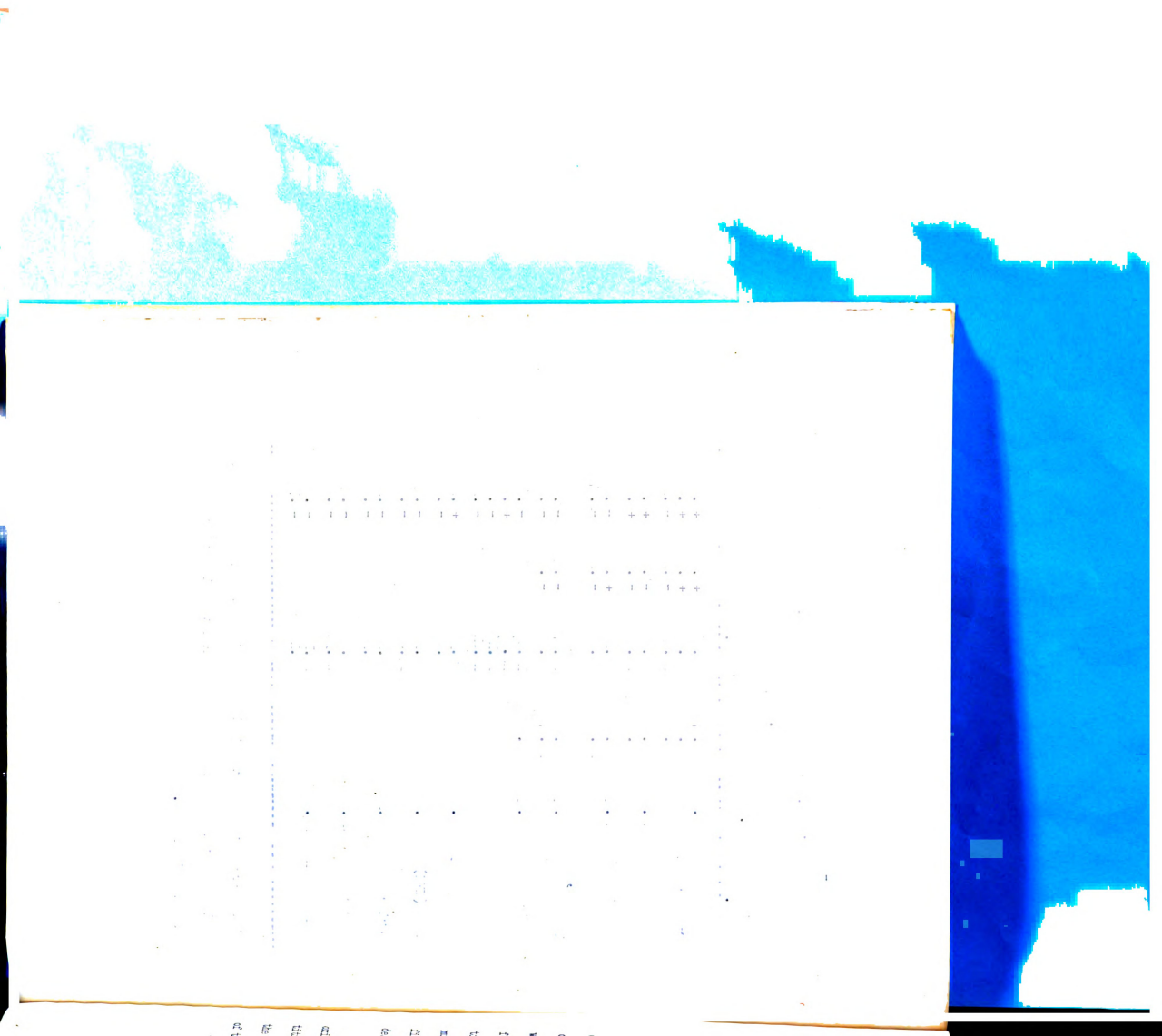
Foreign Ion Ion	Mg. Added	Mg. Mn Present	Mg. Mn Found Filtrate	Mg. Mn Found Precipitate with Factor 1.01	Per Cent Error Filtrate	Per Cent Error Precipitate
Vanadium(V)	1	10.23	10.22	10.26	-0.09	+0.29
			10.27	10.22	+0.39	-0.09
	1	15.35	15.32	15.32	-0.19	-0.19
			15.32	15.17	-0.19	-1.18
			15.34	15.51	-0.07	+1.04
	1	25.59	25.57	25.59	-0.08	0.00
			25.59	25.57	0.00	-0.08
			25.59	25.54	0.00	-0.19
Vanadyl	4	10.23	10.16	10.24	-0.68	+0.09
			10.22	10.10	-0.09	-1.27
			10.16	10.23	-0.68	0.00
			10.24	10.21	+0.09	-0.19
	40	10.23	10.16	10.24	-0.68	+0.59
			10.19	10.23	-0.39	0.00
Cupric	10	10.23	10.24	10.18	+0.09	-0.49
			10.30	10.23	+0.69	0.00
			10.21	10.15	-0.19	-0.78
Calcium	10	10.23	10.27	10.20	+0.39	-0.29
			10.21	10.23	-0.19	0.00
Cadmium	10	10.23	10.27	10.23	+0.39	0.00
			10.21	10.23	-0.19	0.00
			10.24	10.29	+0.09	+0.59
			10.27	10.26	+0.39	+0.29
	20	10.23	10.27	10.26	+0.39	+0.29
			10.21	10.23	-0.19	0.00
	30	10.23	10.21	10.26	-0.19	+0.29
			10.26	10.26	+0.29	+0.29
Nickelous	5	10.23	10.08	10.15	-1.47	-0.78
			10.27	10.10	+0.39	-1.27
	10	20.18	20.16	20.10	-0.09	-0.39
			20.29	20.02	+0.54	-0.79

Continued

TABLE XII - Continued

Foreign Ion		Mg. Mn Present	Mg. Mn Found		Per Cent Error	
Ion	Mg. Added		Filtrate	Precipitate with Factor 1.01	Filtrate	Precipitate
Sodium	20	10.23	10.27	10.26	+0.39	+0.29
Potassium	10		10.32	10.29	+0.88	+0.59
			10.21	10.21	-0.19	-0.19
Zinc	2	10.23	10.22	10.26	-0.09	+0.29
			10.20	10.24	-0.29	+0.09
Molybdate	6	10.23	10.26	10.19	+0.29	-0.39
			10.21	10.11	-0.19	-1.17
Phosphate, dihydrogen	50	10.23	10.19	10.17	-0.39	-0.59
			10.17	10.20	-0.59	-0.29
Chromic	4	10.23		10.16		-0.68
				10.26		+0.29
				10.16		-0.68
				10.21		-0.19
	5	20.26		20.30		+0.22
				20.21		-0.25
Arsenic(III)	25	20.18		20.10		-0.39
				19.88		-1.48
Chloride	25	20.18		20.15		-0.15
				20.11		-0.35
Mercuric	25	20.26		20.32		-0.29
				20.32		-0.29
Ammonium	10	10.23		10.18		-0.49
				10.15		-0.78

No interference was observed in the determination of manganese based on the filtrate or the precipitate when the following ions were added in the amounts indicated.



vanadium (V)	1 mg.	calcium	10 mg.
cadmium	40 mg.	sodium and potassium	20 mg. + 10 mg.
vanadyl	40 mg.	zinc	2 mg.
cupric	10 mg.	molybdate	6 mg.
nickelous	10 mg.	phosphate, dihydrogen	50 mg.

Proportionally larger quantities of the foreign ions resulted in incomplete oxidation evident by colloidal precipitates formed in most cases and erratic and irregular titration data. High concentrations of copper and cadmium, 50 and 100 mg. respectively, resulted in highly colored filtrates following removal of the precipitates. These colors were bright red suggestive of permanganate. All the ions which interfere with the ferrous ammonium sulfate-potassium dichromate back titration in the analysis for peroxydiphosphate used in the oxidation must be absent. It was this apparent limitation on the analysis on the filtrate that led to spectrophotometric methods of analysis to be described in the next section.

In cases where no analysis was possible on the filtrate due to oxidation of the foreign ion or interference of the ion with the back titration procedure, the precipitate provided a means for determining the amount of manganese oxidized. Ions which interfered in the analysis of the filtrate but not in the precipitate included:

mercuric	25 mg.	arsenic(III)	25 mg.
chromic	5 mg.	chloride	25 mg.
		ammonium	10 mg.

The ions which definitely interfered in the oxidation and hence, effected both the filtrate and precipitate were: tungstate, thallous, cobaltous, ferric, aluminum, silver, barium, and nitrate. Tungstate, ferric, and aluminum ions actually retarded oxidation. In these cases no definite precipitations occurred; only a persistent red color was observed in solution marked by an apparent colloidal suspension of undetermined nature.

Lead, barium, silver and zinc ions formed insoluble peroxydiphosphates (16) which would effectively reduce the amount of peroxydiphosphate in solution. Furthermore, the insoluble peroxydiphosphate salts would be carried over in the manganese dioxide precipitate resulting in large positive errors when the precipitates were determined for manganese. It was found, however, that zinc in small quantities, 1-3 mg., did not interfere.

E. Spectrophotometric Determination of Peroxydiphosphate

It was noted that solutions of peroxydiphosphate absorbed in the ultraviolet region. This opened up the possibility of a spectrophotometric method for determining the excess peroxydiphosphate in solution following a given reaction. This would be particularly true of the manganese oxidation where the manganese dioxide could be filtered off and the excess peroxydiphosphate in the filtrate determined spectrophotometrically.

Preliminary absorbance and per cent transmittancy measurements were made with a Beckman DK-2 Spectrophotometer. Lithium peroxydiphosphate

solutions at various concentrations were prepared and absorbance measurements made in the ultraviolet region from 220- to 340-mμ using water as the reference standard. No definite absorption peaks were obtained in this region of the spectrum, merely a strong dependence on concentration. Figure 2 shows the characteristic type of curve obtained.

The following sets of experiments were carried out to establish definitely that the curves obtained in Figure 2 were truly due to the peroxydiphosphate and not to the decomposition products. Spectra of monohydrogen phosphate, dihydrogen phosphate, pyrophosphate and phosphoric acid were obtained in the 220- to 340-mμ range. The different phosphates and pyrophosphate used were in the form of sodium salts. The solutions on which such measurements were made contained approximately 8-10 mg. phosphate ion in its various forms and 1.7 mg. pyrophosphate ion per ml. at pH values ranging from 8.1 to 8.3. These solutions of anions were transparent throughout the spectral range studied in agreement with the work of Buck and co-workers (6). Furthermore, the deliberate addition of phosphate or pyrophosphate to a peroxydiphosphate solution caused no change in the characteristic shape of the absorption curve. The phosphate was added in this instance either as the disodium or monosodium phosphate.

The fact that no absorption peaks were found in the ultraviolet region for peroxydiphosphate made it necessary to arbitrarily select a suitable wavelength for the spectrophotometric determination. The selection of a suitable wavelength was achieved by preparing a series

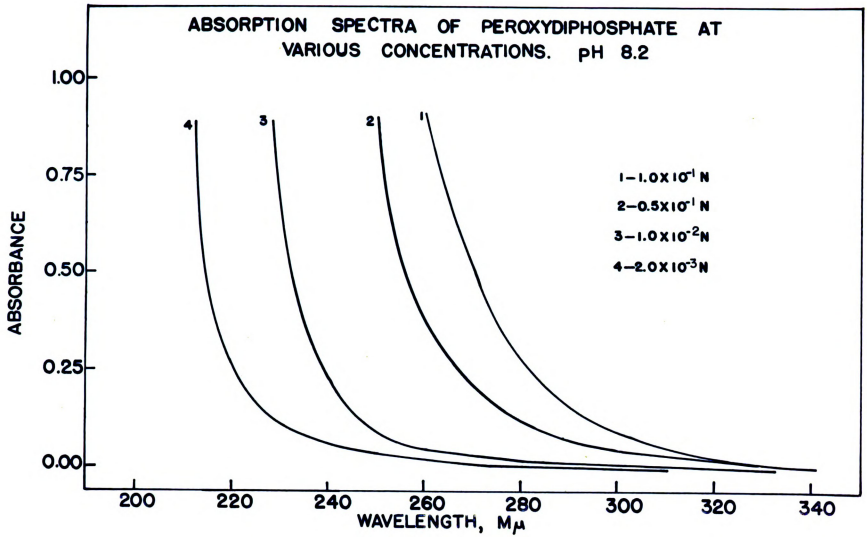
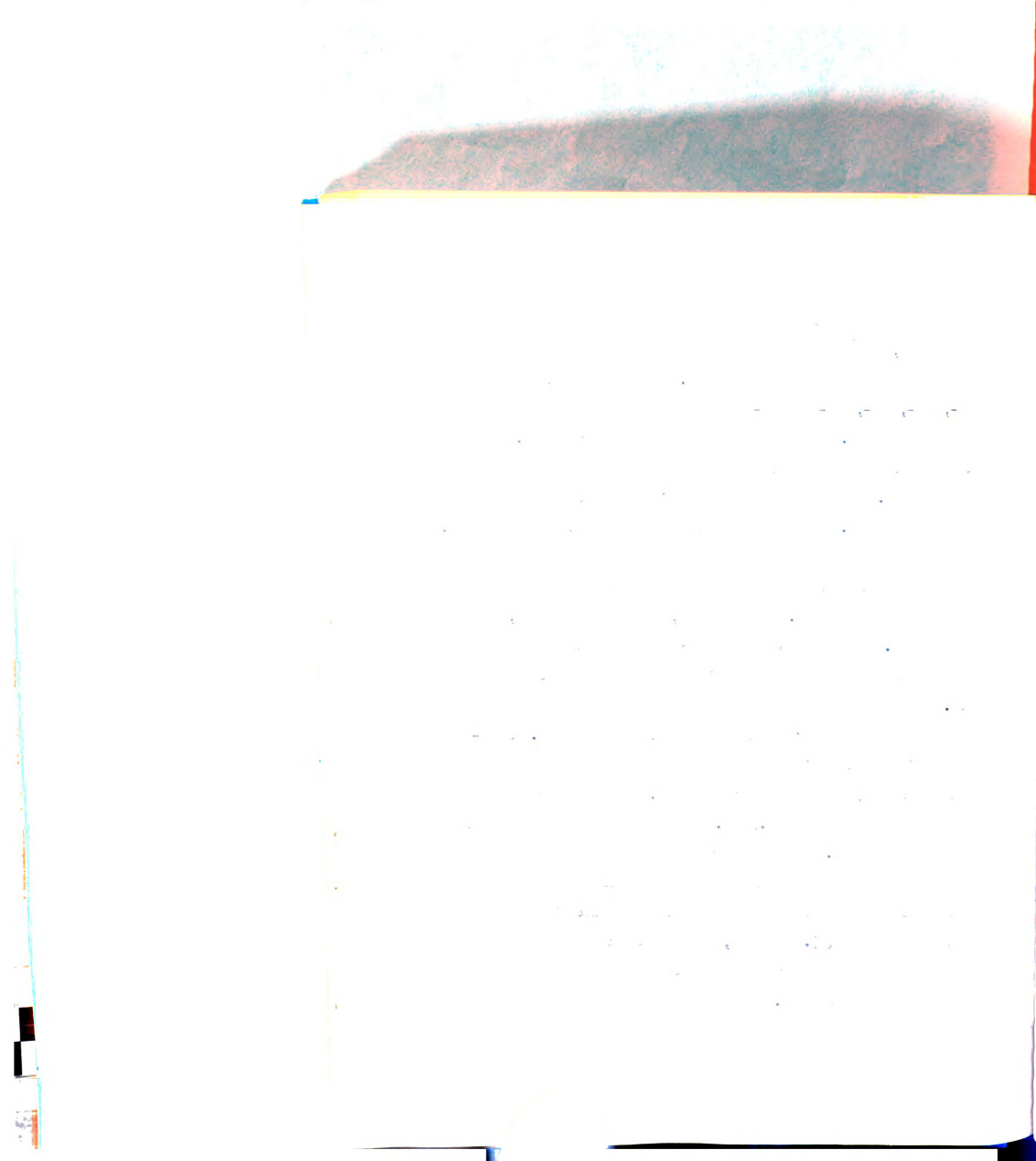

ABSORPTION SPECTRA OF PEROXYDIPHOSPHATE AT VARIOUS CONCENTRATIONS. pH 8.2
ABSORBANCE
1.00
0.75
0.50
0.25
0.00
200
220
240
260
280
300
320
340
WAVELENGTH, Mμ
1
2
3
4
1—1.0X10⁻¹ N
2—0.5X10⁻¹ N
3—1.0X10⁻² N
4—2.0X10⁻³ N

FIGURE 2

of peroxydiphosphate solutions of various concentrations at fixed pH values of 4, 6 and 7 and obtaining absorbance measurements for these solutions at various wavelength settings. The settings chosen were 230-, 240-, 250-, 260- and 270-mμ with appropriate slit widths to obtain maximum absorbance. The Beckman DU Spectrophotometer was used. The data for the peroxydiphosphate solutions at pH 6 are plotted in Figure 3 as absorbance vs. concentration of peroxydiphosphate at constant pH and wavelength setting. The results are also tabulated in the Data Appendix. Solutions of peroxydiphosphate at various concentrations at pH 4 and 7 gave curves similar to those obtained for the solutions at pH 6 except for differences in slopes. These results, in the form of plots, are not included. This effect of pH on the spectrophotometric determination of peroxydiphosphate has been investigated in a later portion of this work.

The data in Figure 3 reveal that plots of absorbance vs. concentration give straight lines at all wavelength settings with greater positive slope(s) at the shorter wavelengths. The wavelength setting of 240 mμ and slit width of 0.70 mm. was selected for the determination of peroxydiphosphate. This setting was chosen for the method not only because it provided a reasonable sensitivity but also because it would be in the region where relatively few interferences from inorganic ions are likely to occur (6). Moreover, the range of concentration covered by this wavelength setting was adequate for the work to be done with peroxydiphosphate solutions.



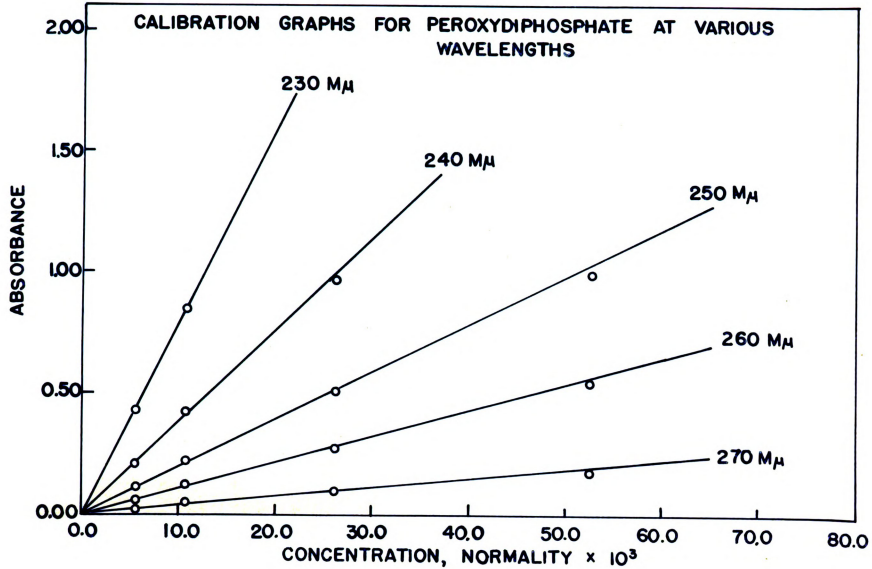

CALIBRATION GRAPHS FOR PEROXYDIPHOSPHATE AT VARIOUS WAVELENGTHS
230 Mμ
240 Mμ
250 Mμ
260 Mμ
270 Mμ
ABSORBANCE
2.00
1.50
1.00
0.50
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
CONCENTRATION, NORMALITY x 10^3

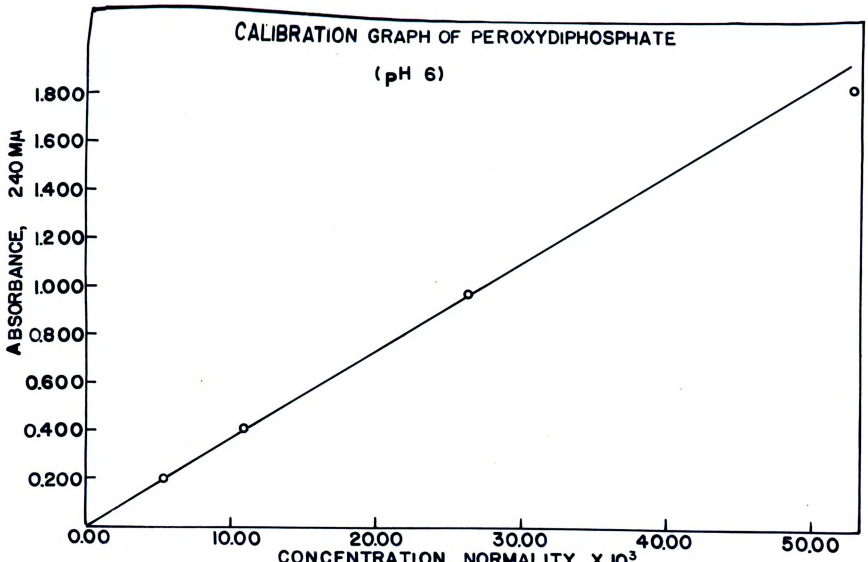
FIGURE 3

In conjunction with the above work, it was found that these solutions of varying concentrations adhered to Beer's Law in every instance. Since many of the reactions with peroxydiphosphate were to be carried out under near neutral conditions (pH between 5.5-7.5) a working calibration curve was prepared at a pH of 6 at 240 mμ and at a slit width of 0.70 mm. (Figure 4). The concentration region covered by this plot was from 0.000 to 0.034N, sufficient for the method of determination of peroxydiphosphate. The peroxydiphosphate solutions, previously standardized by the ferrous ammonium sulfate method, were heated to boiling for five seconds, cooled for 45 minutes and 20 minutes after adjustment to pH 6.0 the measurements were made. Water at a pH of 6.0 was used as the reference blank.

It was qualitatively observed that decreasing the pH to lower values resulted in absorbance measurements which varied appreciably as evidenced by the change in slope of the spectra obtained. This was mentioned previously in connection with the work involved in selecting a suitable working wavelength. Further studies were made to determine the effect of pH on the spectrophotometric analysis of peroxydiphosphate.

A solution of lithium peroxydiphosphate was prepared by dissolving approximately 4 g. of tetralithium peroxydiphosphate tetrahydrate in water and diluting to 250 ml. The pH of the solution prepared in this manner was 9.6. The solution was standardized by the ferrous ammonium sulfate method and found to be 0.1245N.

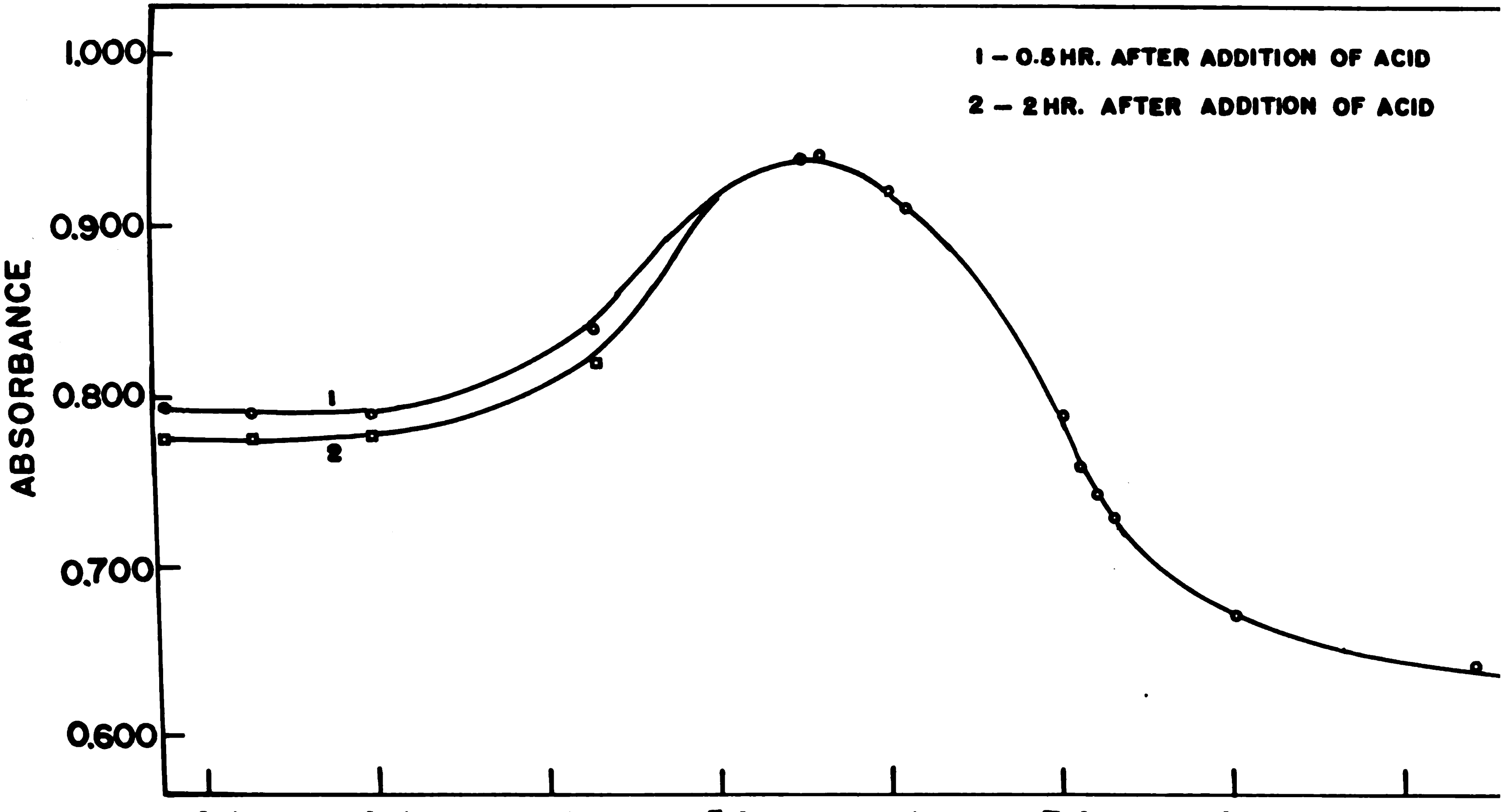
Solutions with various pH values were prepared by adding various amounts of 17 per cent phosphoric acid to 10 ml. portions of this above

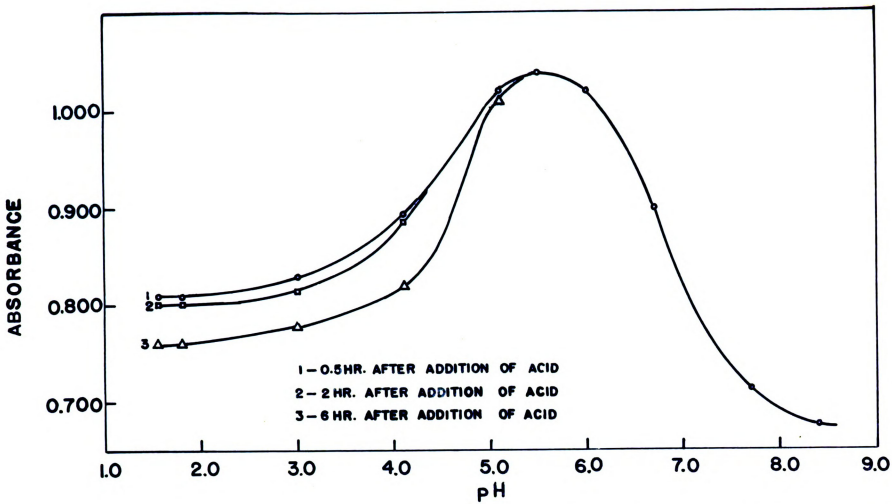

CALIBRATION GRAPH OF PEROXYDIPHOSPHATE
(pH 6)
ABSORBANCE, 240 MμA
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.00
10.00
20.00
30.00
40.00
50.00
CONCENTRATION, NORMALITY X 10³
FIGURE 4

peroxydiphosphate solution and diluting to 50 ml. with water. The concentration of these solutions was thus 0.02090N. Absorbance measurements at 240 mμ were then obtained for these solutions at room temperature employing the Beckman Model DU Spectrophotometer an hour after adjustment of pH. The absorbance of these solutions were also remeasured and compared with the original values obtained. The data are shown graphically in Figure 5 and tabulated in the Data Appendix.

A similar set of experiments was performed except 3N sulfuric acid was used to adjust the pH of the various solutions. The concentration of these individual solutions was 0.02644N. Absorbance measurements at 240 mμ were taken a half hour, an hour and six hours after addition of the acid. The data are shown graphically in Figure 6 and tabulated in the Data Appendix.

It is seen from Figures 5 and 6 that the plots of absorbance vs. pH at constant concentration underwent a maximum at a pH of 5.5. This would strongly suggest some type of active species present in solution with a maximum concentration at pH 5.5 under the conditions employed. Furthermore, the stability studies made at various time intervals show a progressive decrease in absorbance in acid medium. This was particularly evident after the attainment of the maximum. In basic medium no apparent change in absorbance was observed. These results, coupled with the facts previously found (11), provided another means of verifying the instability of peroxydiphosphate in acid medium with time.


1 – 0.5 HR. AFTER ADDITION OF ACID
2 – 2 HR. AFTER ADDITION OF ACID
ABSORBANCE
1.000
0.900
0.800
0.700
0.600
1
2



ABSORBANCE OF PEROXYDIPHOSPHATE AS A FUNCTION OF pH
ACIDIFYING AGENT: SULFURIC ACID
FIGURE 6

1. Determination of Excess Peroxydiphosphate in the Manganese Oxidation

The excess peroxydiphosphate following the reaction between lithium peroxydiphosphate and divalent manganese was determined spectrophotometrically. This involved the addition of a measured excess of standard peroxydiphosphate solution to a fixed quantity of manganous sulfate, heating at 100°C. for five seconds and then allowing to cool to room temperature for 30 minutes. Following the removal of the manganese dioxide formed by the reaction using either a 60F fritted funnel or a 60M fritted funnel covered with asbestos, the filtrate was diluted to a known volume, generally 200 ml., such that the absorbance obtained would fall somewhere in the calibrated portion of the previously prepared graph (Figure 4). The diluted filtrate was adjusted to a pH of 6.0 and, after a 20 minute period of standing, the absorbance was measured. Subtraction of the peroxydiphosphate found in this manner from the quantity of peroxydiphosphate originally added to the reaction gave the amount of manganese which had been oxidized. Samples containing from 10 to 100 mg. manganese were oxidized with excess peroxydiphosphate. The results, corrected in the manner described above, are contained in Table XIII along with the method used to effect the removal of the precipitates formed following the oxidations.

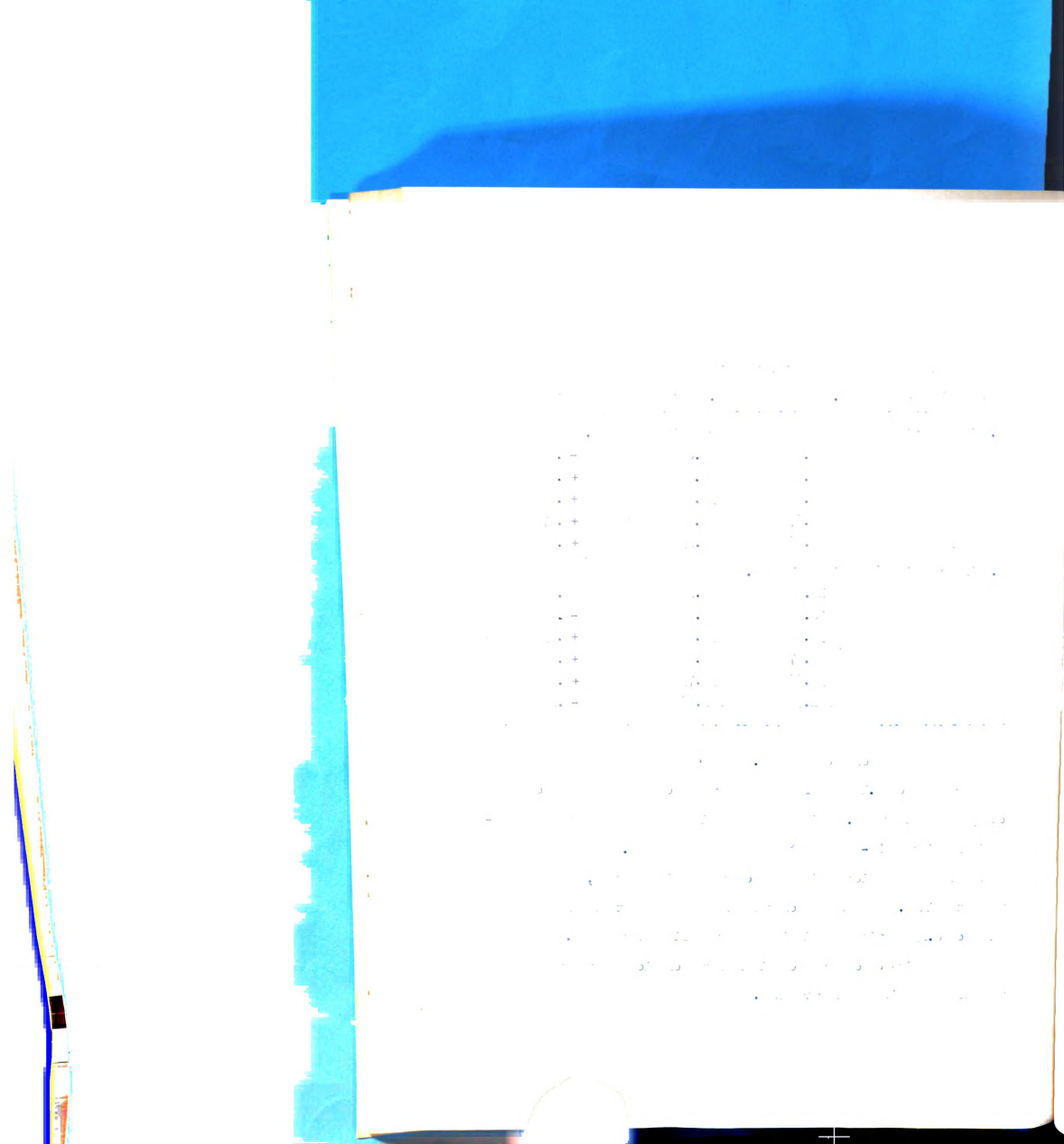
The original peroxydiphosphate solution used in the above work was standardized by the ferrous ammonium sulfate method and also spectrophotometrically by the standard calibration curve. Comparison of the two methods showed no appreciable difference. Standardization of a

TABLE XIII

INDIRECT DETERMINATION OF MANGANESE SPECTROPHOTOMETRICALLY

Determinations	Mg. Mn Added	Mg. Mn Found	Per Cent Error
A. Filtered with 60M Fritted Funnel Covered with Asbestos.			
4	10.10_5	10.08	-0.25
4	20.18	20.30	+0.54
2	30.48	30.54	+0.19
3	40.67	40.94	+0.67
3	50.66	51.13	+0.93
B. Filtered with 60F Fritted Funnel.			
4	10.10_5	10.10_5	0.00
4	20.18	20.14	-0.19
4	30.48	30.55	+0.23
6	40.67	40.91	+0.59
2	50.66	50.73	+0.14
2	101.74	101.56	-0.18

peroxydiphosphate solution of pH 6.0 by the chemical method gave an average value of 0.1914N for three determinations with a deviation of one part per thousand. This same peroxydiphosphate solution was quantitatively diluted 10-fold and the absorbance measured. From the standard curve prepared previously in terms of the chemical method, the normality was determined. The average of three such measurements resulted in a value of 0.1910N with a deviation of four parts per thousand. Comparison of the normality of other peroxydiphosphate solutions by the two methods were found to give similar results.



The removal of precipitates by filtration through asbestos covered 60M fritted funnels or through 60F fritted funnels did not effect the results obtained. This was shown in Table XIII where the calculated per cent error of various amounts of manganese taken for oxidation studies ranged for -0.25 to +0.93. As generally expected, increasing the amount of manganese for oxidation gave progressively poorer results.

The indirect determination of peroxydiphosphate used in the reaction provided a means for estimating the amount of manganese oxidized. The results were satisfactory.

To further verify the fact that the results were reproducible, a series of peroxydiphosphate solutions was prepared and determined spectrophotometrically under exactly the same experimental conditions as the manganese-peroxydiphosphate samples. In addition, the effect of temperature on the absorbance readings of the individual samples was simultaneously studied.

Ten milliliters portions of 0.1056N lithium peroxydiphosphate standardized by chemical methods were pipetted into 50.00 ml. volumetric flasks and diluted quantitatively to mark. The pH of each sample was adjusted to 6.0 by the addition of 1 ml. 17 per cent phosphoric acid. The samples were heated at 100°C. for 10 seconds and then allowed to cool for 30 minutes. The peroxydiphosphate content was determined at the preselected wavelength of 240 mμ and slit width of 0.70 mm. The solutions were read 1.5 hours after preparation. The results are tabulated in Table XIV at a temperature of 23° ± 3°C.

It is seen from the table that the results of 10 determinations

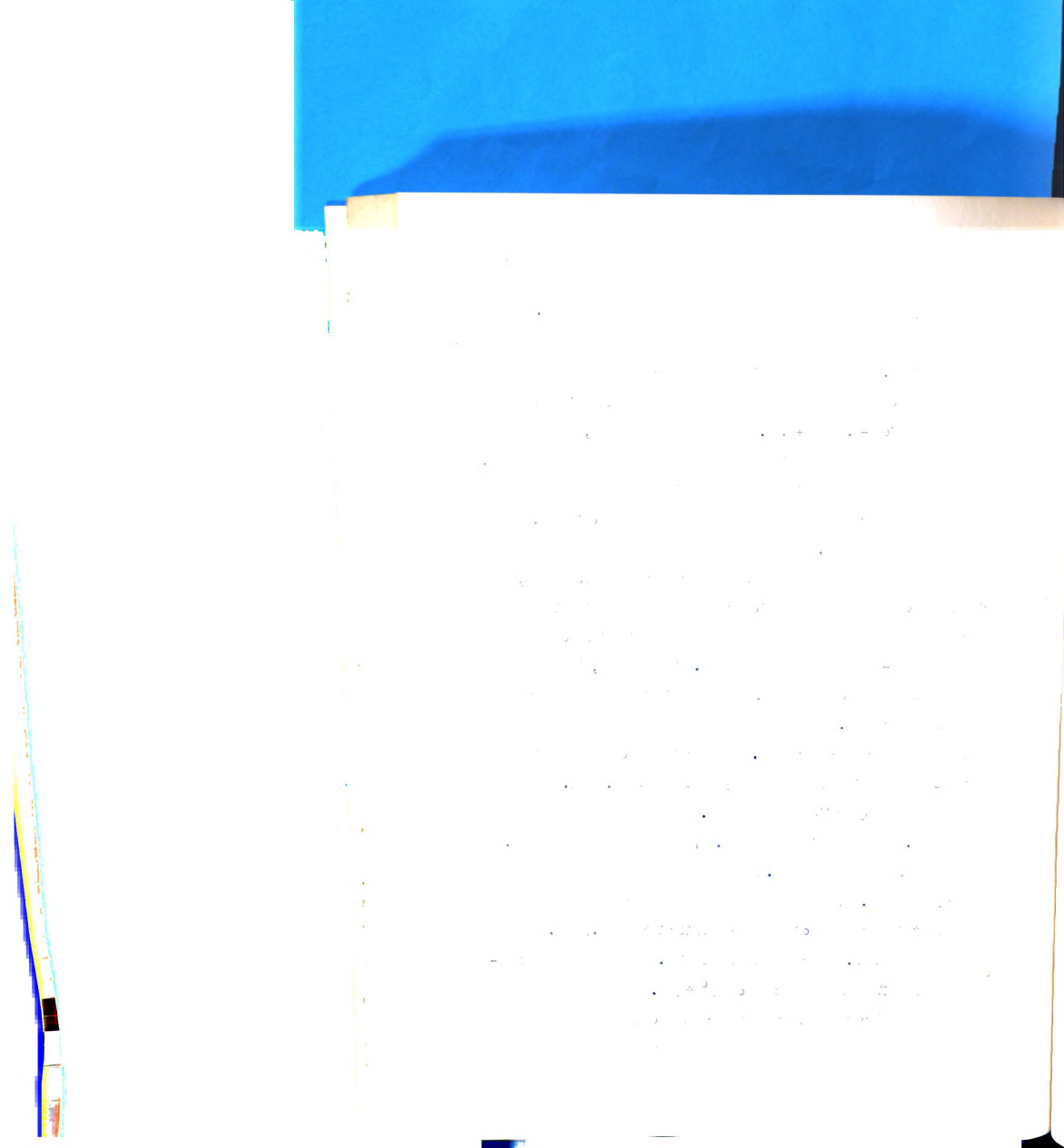


TABLE XIV

REPRODUCIBILITY OF DETERMINATION OF PEROXYDIPHOSPHATE SOLUTIONS

Absorbance	Normality $Li_4P_2O_8$ Found[a]	Meq. $Li_4P_2O_8$ Found (Corrected)	Difference Meq. $Li_4P_2O_8$ (Found - Taken)
0.852	0.02132	1.062	+0.006
0.838	0.02097	1.046	-0.010
0.832	0.02082	1.041	-0.015
0.840	0.02102	1.051	-0.005
0.839	0.02100	1.046	-0.010
0.840	0.02102	1.050	-0.006
0.840	0.02102	1.050	-0.006
0.838	0.02097	1.047	-0.009
0.840	0.02102	1.048	-0.008
0.841	0.02105	1.048	-0.008
		Av. 1.048	Av. dif. 0.008
			σ 0.005[b]

[a] Normality $Li_4P_2O_8$ taken: 0.02112N
Meq. $Li_4P_2O_8$ taken: 1.056

[b] $\sigma = \sqrt{\frac{(\text{average-found})^2}{n}}$

with no regard to temperature gave an average value of 0.1048 meq. for lithium peroxydiphosphate. The average difference between the samples was only 0.008 meq. and the standard deviation was 0.005 meq.

The series of determinations indicated that temperature variance was of no appreciable consequence in the absorbance measurements.

The successful determination of manganese by the indirect method of spectral analysis was accomplished in the absence of any interfering ions. Several ions were studied for possible interference. It was possible to immediately eliminate the study of ions which absorbed at 240 mμ (6). Moreover, ions that normally interfered with the manganese oxidation were not studied except for those which showed negligible effect when present in small amounts. As a result of these considerations, the following ions were studied as major constituents; nickelous, zinc, cobaltous and magnesium. Both cadmium and tungsten ions were considered as minor constituents. The ions were added as the metallic sulfates except tungsten which was added as sodium tungstate.

Solutions used in the interference studies were prepared by adding the diverse ion or a combination of ions to a solution containing approximately 10 mg. manganese. The solutions were oxidized in the same manner as before with excess peroxydiphosphate. Filtration was effected using medium porosity fritted funnels covered with asbestos. Absorbance measurements were made at 240 mμ 20 minutes after adjustment of the pH to 6.0 with 17 per cent phosphoric acid. Blanks containing peroxydiphosphate and the foreign ion or ions were also prepared and carried out in similar fashion. Data for these determinations of manganese are given in Table XV. Duplicate determinations were made.

The data in Table XV show that the indirect determination of manganese spectrophotometrically yielded good results despite the presence of the foreign ion or ions listed. The manganese dioxide formed in all

TABLE XV

INDIRECT DETERMINATION OF MANGANESE SPECTROPHOTOMETRICALLY IN THE PRESENCE OF FOREIGN IONS. 10.10_5 MILLIGRAM MANGANESE ADDED

Foreign Ion Added	Mg. Foreign Ion	Mg. Mn Found
Tungstate	0.08	10.24
Zinc	5.0	10.13
Nickelous	5.0	10.16
Magnesium	5.0	10.11
Cobaltous	5.0	----
Cadmium	0.08	10.18
a		10.13
b		10.06
c		10.08
d		10.01

[a] 0.08 mg. each of Cd(II) and tungstate.

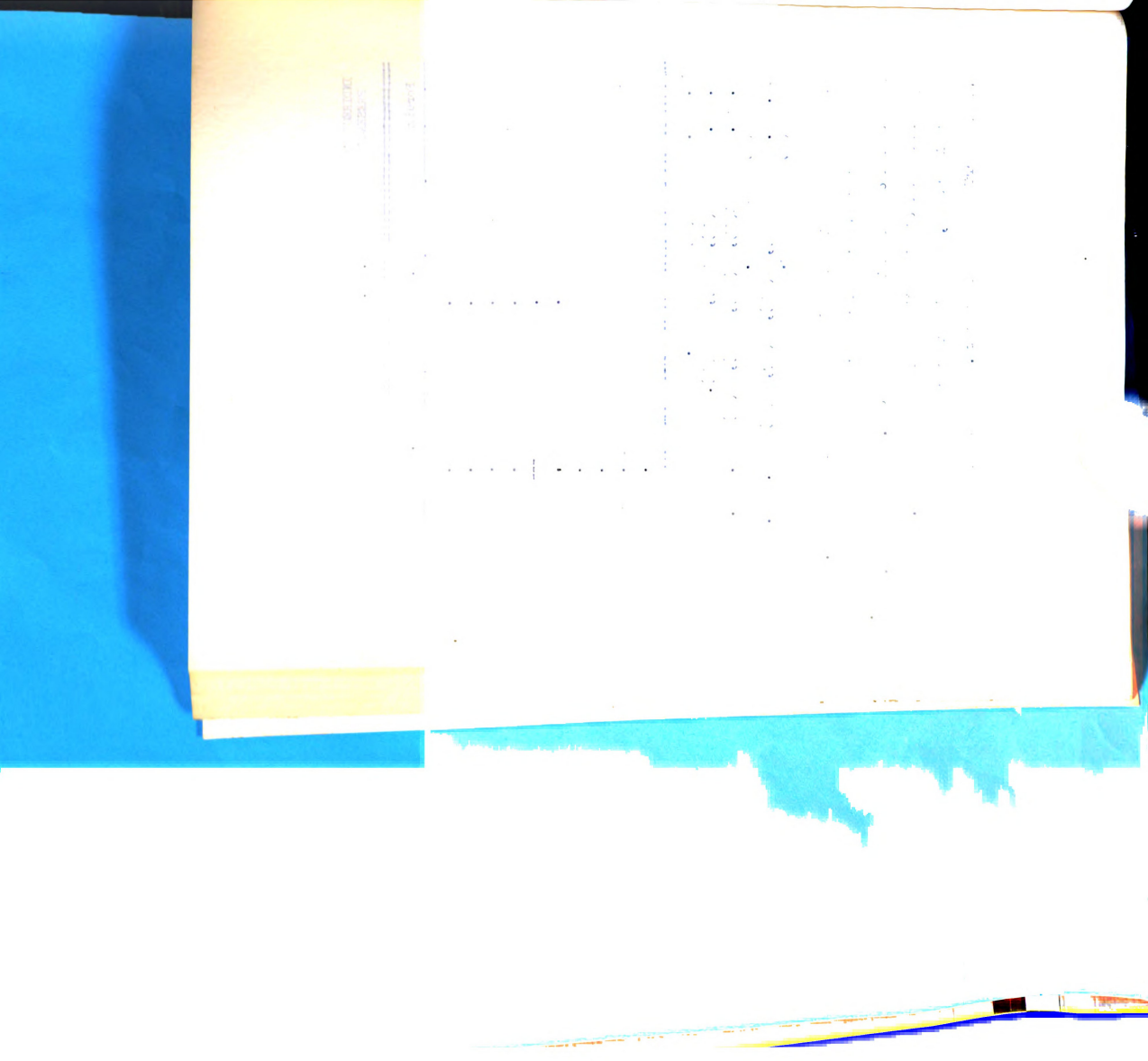
[b] 5.0 mg. each of Zn(II), Ni(II), and Mg(II).

[c] 5.0 mg. each of Ni(II), Al(III), Zn(II), Mg(II) and 0.08 mg. each of Cd(II) and tungstate.

[d] 12.5 mg. each of Ni(II), Al(III), Zn(II), Mg(II) and 0.20 mg. each of Cd(II) and tungstate.

cases was dense and easily filterable except when cobalt was present. The manganese dioxide precipitate formed in the presence of cobalt was gelatinous and too finely divided to effect removal. As a consequence, no suitable analysis of this particular filtrate could be made.

In samples c and d, the precipitates were also determined by the previously described method for manganese. The amount of manganese in



these individual precipitates was found to agree quite well with that found in their corresponding filtrates from the spectral analysis work.

F. Attempts at Oxidation of Other Ions

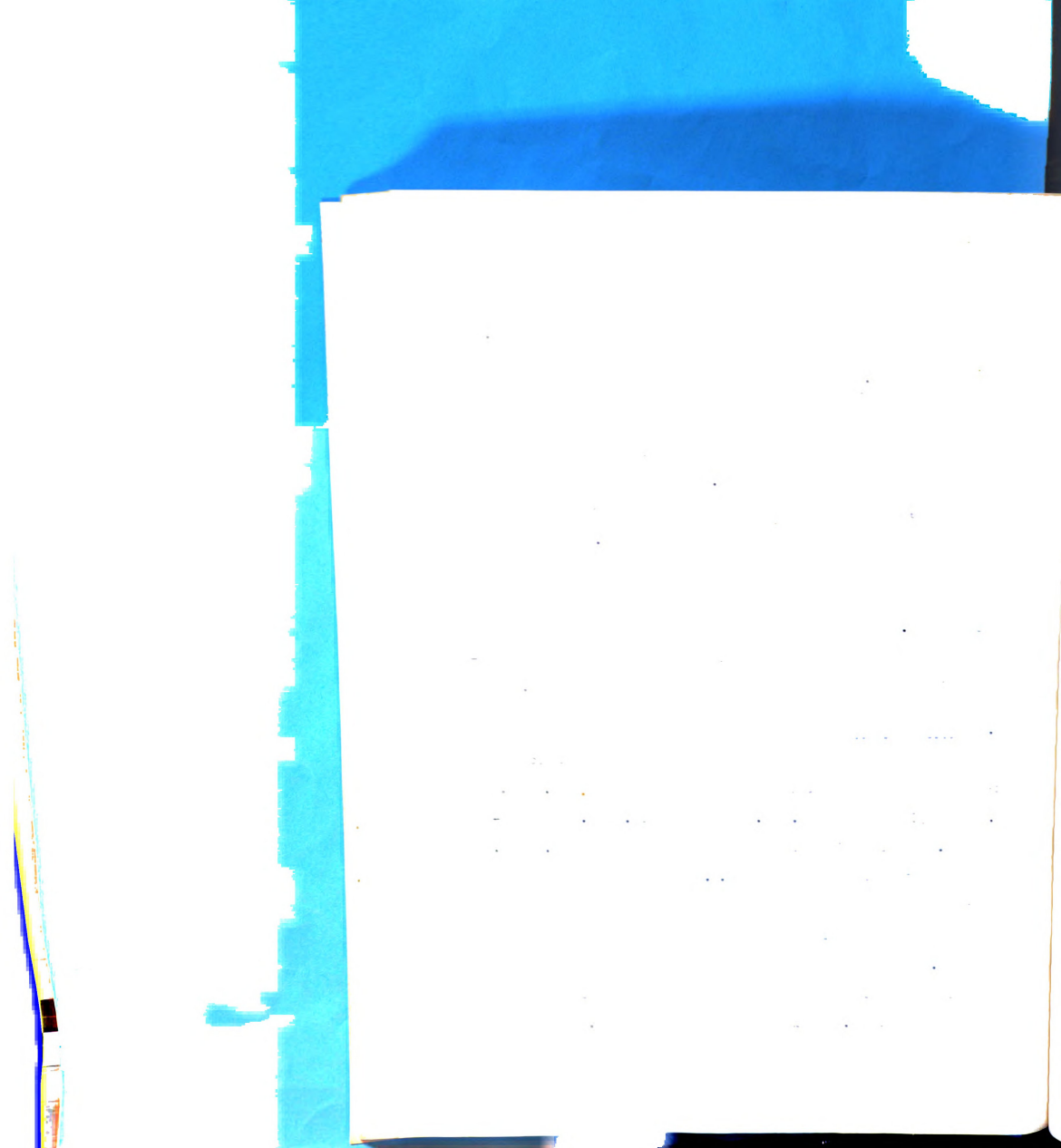
It was noted in the course of investigating the interferences associated with the manganous oxidation that thallous as well as chromic ions were oxidized by peroxydiphosphate. In the case where chromic ions were present, a yellow color characteristic of chromate was evident in solution following removal of the manganese precipitate. Correspondingly, the results on the determination of the manganese precipitate and the excess peroxydiphosphate in solution were erratic in the presence of thallous ions.

An investigation was carried out to study the possibility of oxidizing thallous and chromic ions individually with peroxydiphosphate.

1. Oxidation of Thallium(I)

The time required for the appearance of a precipitate at room temperature indicative of oxidation in a solution containing 4.97 ml. 0.1003N thallous sulfate (51.1 mg. thallium) and 19.98 ml. of approximately 0.08N tetralithium peroxydiphosphate was greater than 4.5 days. The solution was at an initial pH of 8.4. Increasing the amount of peroxydiphosphate and also increasing the acidity with dilute sulfuric acid did not materially reduce the time required for precipitate formation.

Solutions of thallium and peroxydiphosphate were also heated at elevated temperatures. Samples were heated at 50° ± 5°C. for four



hours and also at 100°C. for 30 seconds. As normally would be expected with an increase in temperature, the time required for the appearance of a precipitate was reduced somewhat. The time required for the appearance of a precipitate when a sample was heated at 50°C. for four hours and then allowed to stand at room temperature was 24 hours. And for a sample heated at 100°C. for 30 seconds and allowed to stand at room temperature, the time required for a precipitate to form was eight hours.

In no instance was complete oxidation of thallium made. That this was true was readily seen by the removal of the precipitates after a 12 hour period following the initial appearance of the precipitates and allowing the filtrates to stand whereupon additional precipitation occurred.

Attempts at dissolving the brown precipitates with 6N sulfuric or hydrochloric acid were without success. Addition of excess reducing agent, ferrous ammonium sulfate, caused the immediate dissolution of the thallium precipitates. It was further shown that the precipitates did not contain any orthophosphate by qualitative testing with ammonium molybdate solution. The conclusion was drawn that the brown precipitate was thallic oxide, Tl_2O_3.

The preliminary work described above indicated that the reaction between peroxydiphosphate and thallium(I) proceeded very slowly. However, it was found that the reaction was greatly accelerated by the simultaneous occurrence of the reaction between manganese(II) and peroxydiphosphate. The possibility of achieving rapid and complete

oxidation of thallium(I) in the presence of manganese(II) was further investigated.

A series of samples containing measured quantities of thallous sulfate and manganous sulfate was taken from their respective stock solutions in various milliequivalent ratios and treated with a 3.0- to 3.5-fold excess of peroxydiphosphate solution to effect oxidation. Blanks containing the same amount of manganese and peroxydiphosphate were also prepared. The method of preparation, temperature conditions, period of standing and pH were essentially those used in the manganese-peroxydiphosphate oxidation procedure. The oxidations were studied at room temperature, at $50^{\circ} \pm 5^{\circ}$C. for four hours and at boiling for approximately 30 seconds. Removal of the precipitates formed in all cases was achieved by employing asbestos covered Gooch crucibles with suction. Thorough washing of the precipitates was made with water. The individual filtrates and washings were retained and subsequently were analyzed for excess unreacted peroxydiphosphate. The manganese-peroxydiphosphate blanks were treated similarly.

The precipitates were dissolved in a measured excess of ferrous ammonium sulfate solution approximately 0.1M in sulfuric acid and the excess subsequently back titrated with 0.1000N potassium dichromate solution. The difference between the milliequivalents of standard dichromate required to oxidize an equivalent quantity of ferrous ammonium sulfate and the milliequivalents used in the back titration represented the milliequivalents of manganese and thallium which had

been present in the precipitate. Under the conditions used, complete oxidation of manganese was assumed in the reaction. Hence, subtraction of the milliequivalents of manganese originally added to the sample from the milliequivalents found gave the milliequivalents of thallium which had been oxidized. The results, compiled in this manner, for the oxidation of thallium with peroxydiphosphate in the presence of manganese are contained in Table XVI.

The filtrate and washings from the individual samples and blanks were analyzed for excess peroxydiphosphate by the ferrous ammonium sulfate-potassium dichromate method. The difference in milliequivalents between the sample and blank represented the milliequivalents of thallium oxidized. The results on the amount of thallium oxidized by this indirect method of determination are also contained in Table XVI.

It is readily seen from the table that the presence of manganese exerted a pronounced influence on the rate of oxidation of thallium. Approximately an equivalent amount of manganese(II) was needed to effect the oxidation of thallium(I). Ratios of milliequivalents of manganese(II) to milliequivalents thallium(I) less than one caused incomplete oxidation. More important, however, was the effect of temperature and the manner in which heating and cooling was carried out. As expected, an increase in temperature resulted in an increase in the amount of thallium(I) oxidized.

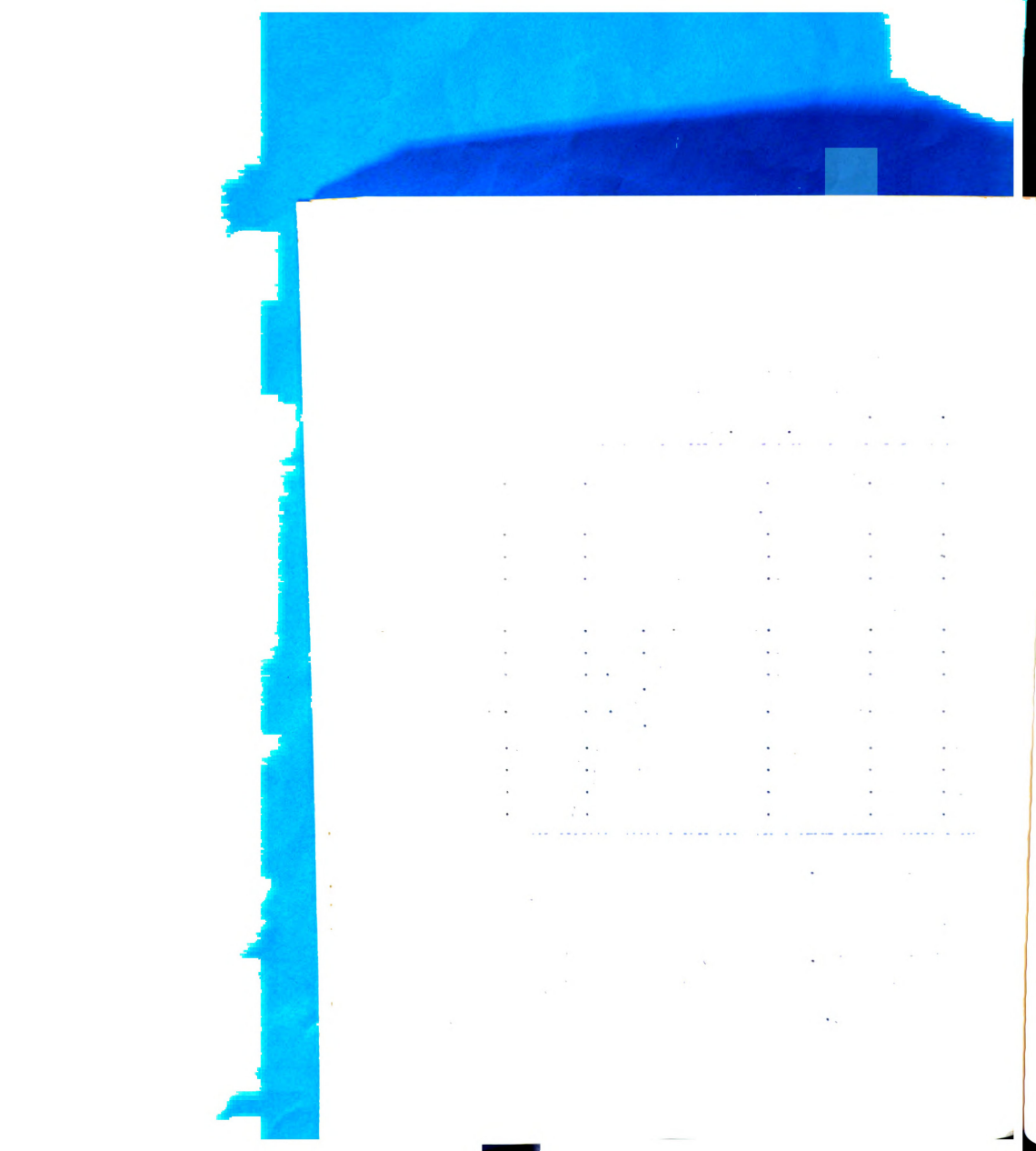
In light of the studies made in the presence of manganese(II), the mechanism of the thallium(I) oxidation with peroxydiphosphate can be

TABLE XVI

THALLIUM(I) OXIDATION WITH PEROXYDIPHOSPHATE IN THE PRESENCE OF MANGANESE(II) AT VARIOUS TEMPERATURES

Mg. Tl Added	Mg. Mn Added	Meq. Mn/Meq. Tl	Time of Standing	Per Cent Tl Oxidized Filtrate	Precipitate
Room temperature					
20.24	0.66	0.12	12 hours	45.95	48.96
Heated for four hours at 50°C.					
20.24	0.66	0.12	1 hour	79.25	77.27
20.24	4.60	0.84	1 hour	95.72	94.42
20.24	5.54	1.01	1 hour	95.96	97.31
Boiled for 30 seconds					
20.24	5.54	1.01	30 min.	85.82	83.40
20.24	5.54	1.01	45 min.	92.95	92.14
20.24	5.54	1.01	Cooled to 50°C. 30 min.	98.70	98.46
20.24	5.54	1.01	Cooled to 60°C. 30 min.	99.20	100.98
20.24	5.54	1.01	2 hours	99.84	99.72
20.24	5.54	1.01	2 hours	97.64	96.65
30.46	6.90	0.84	2 hours	96.29	94.00
50.90	4.15	0.30	2 hours	84.87	85.76

tentatively postulated. The immediate appearance of a pink color in the original sample solution followed by the subsequent brown-black precipitate characteristic of manganese dioxide was indicative that a reaction was occurring. Manganese(II) was probably oxidized to a higher valent species which reacted not only with the manganese(II) but also with the thallium(I). Indications pointed to the fact that manganese(II)



was oxidized to permanganate and it was this latter species or some intermediate which effected the oxidation of the thallous ion. This would necessarily imply a couple type reaction (28). The peroxydiphosphate was the actor since it acted on both the other two constituents; manganese(II) was the inductor and thallium(I) was the acceptor. The reaction between peroxydiphosphate and manganese(II) was the primary reaction and that between peroxydiphosphate and thallium(I) was the induced reaction.

2. Oxidation of Chromium(III)

Preliminary investigations had shown that attempts at oxidizing green chromium(III) with peroxydiphosphate in near neutral solutions at room temperature did not result in a visual color change to yellow. It was virtually impossible to distinguish visually whether a slight color change to yellow occurred in the green solution. Varying the temperature, pH, concentrations, and periods of standing also gave inconclusive results. However, boiling a chromic sulfate solution with excess peroxydiphosphate for 10 minutes and cooling for 30 minutes resulted in the appearance of a yellowish cast to the solution. The initial pH of this solution was 4.1 and after two hours dropped to 3.6. The yellow color did not increase in intensity with increased time of standing.

It became obvious that oxidation of chromium(III) with peroxydiphosphate was too slow for a suitable quantitative procedure. It was found that the amount of chromium(III) oxidized by peroxydiphosphate

to chromium(VI) was materially increased in the presence of manganous sulfate. A more thorough study of this reaction was made.

Two milliliters of the chromic sulfate stock solution was pipetted into a 125 ml. iodine flask followed by 1.98 ml. 0.371_8N manganous sulfate solution. Twenty milliliters of 0.1027N peroxydiphosphate solution was added and the entire solution diluted to a total volume of 50 ml. with distilled water. The solution was then boiled for approximately three minutes whereupon the appearance of a yellow color developed simultaneously with the formation of a brown-black manganese dioxide precipitate. After cooling for three hours, the precipitate was removed by filtering through an asbestos covered 60M fritted funnel. The yellow colored filtrate was retained for further study.

A spectrophotometric method of analysis for determining the presence of chromium in the hexavalent form was used. This procedure was used because there is essentially no other way of determining chromate or dichromate in the presence of excess peroxydiphosphate. Both gravimetric and volumetric methods of analysis for hexavalent chromium would fail for this particular situation.

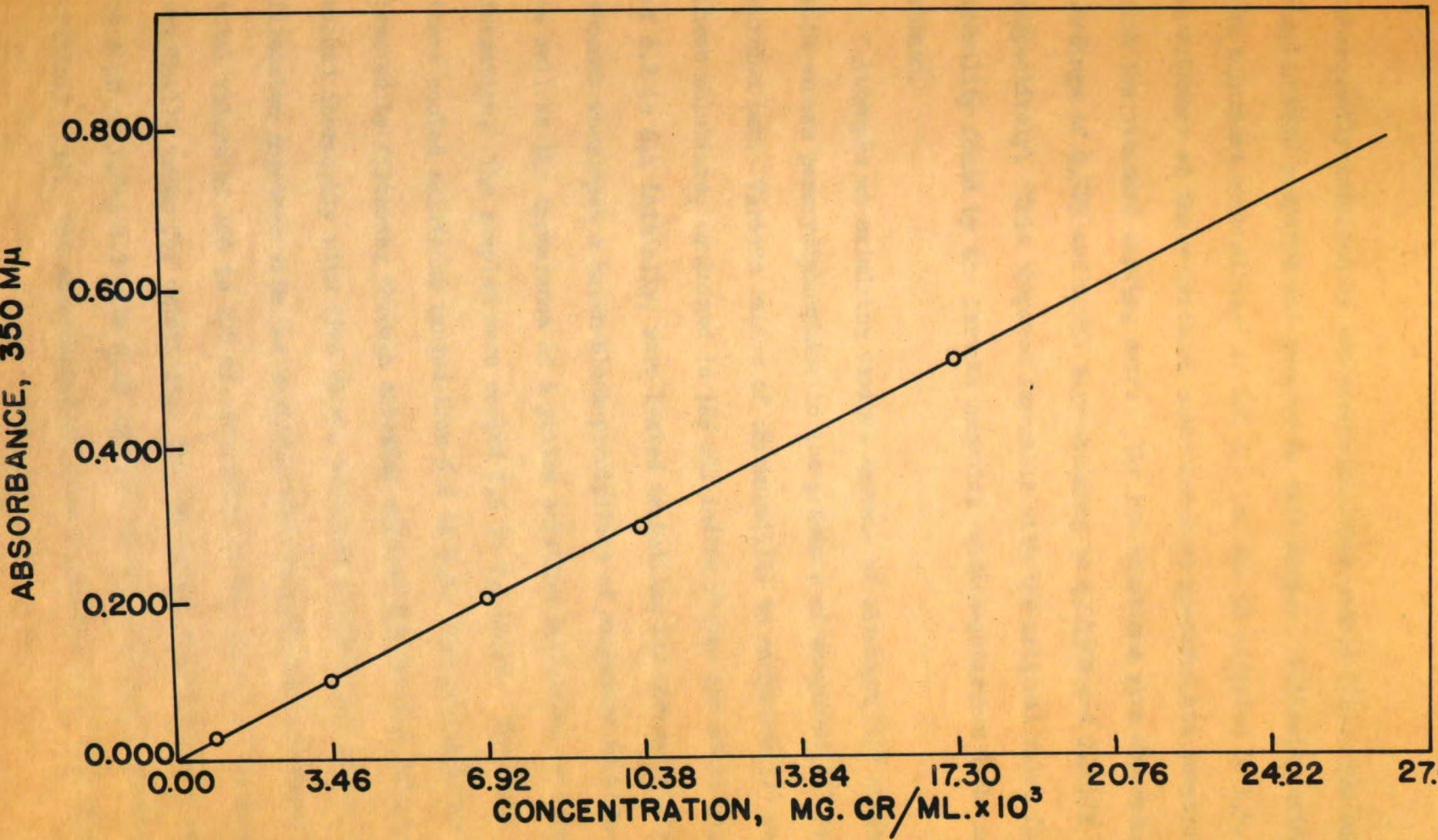
In addition, other factors influenced the selection of a spectrometric method of analysis. In acid solution dichromate has two absorption maxima, one at 257.5 mμ and the other at 350 mμ, which are well defined (13). It was found that peroxydiphosphate did not absorb at 350 mμ in strong acid solution and other ions such as phosphate, sulfate, chromic and divalent manganese were transparent in the ultraviolet region (6). Convenience of the method was also an advantage.

A complete absorption curve can be obtained in a matter of minutes and compared with a standard working curve prepared under exactly the same manner as the samples.

In order to have some reference source as a means of estimating the extent of chromic oxidation in the presence of manganous sulfate, it was necessary to prepare a suitable working curve, i.e., a Beer's Law plot of absorbance as a function of concentration. A 0.1000N potassium dichromate solution was prepared by dissolving 4.9352 g. of Baker's analytical reagent grade potassium dichromate in 300 ml. of water, adjusting the pH to 1.5 by the addition of 0.1N sulfuric acid, and diluting quantitatively to exactly one liter. A series of solutions at various concentrations was prepared by taking aliquots of the standard dichromate solution and diluting with water to the desired concentrations. Dichromate solutions containing 0.88×10^{-3}, 3.46×10^{-3}, 6.92×10^{-3}, 8.68×10^{-3} and 17.30×10^{-3} mg. chromium(III) per ml. were prepared in such a manner. These solutions were all adjusted to a pH of 1.5 with dilute sulfuric acid.

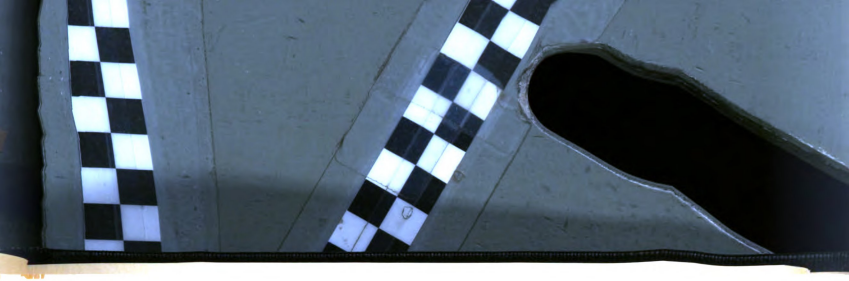
The absorbances of the individual solutions were measured at 350 mμ at a constant slit width of 0.40 mm. using a Beckman DU Spectrophotometer. The reference cell was a matched 1-cm. silica cell containing water which had been adjusted with dilute sulfuric acid to a pH of 1.5. A plot (Figure 7) of absorbance vs. milligrams of chromium resulted in a straight line from 0.000 to 0.0173 mg. chromium per ml.

As a check on the validity of the working curve, 1.98 ml. 0.1055N chromic sulfate stock solution was pipetted into a 250 ml. beaker and



BEER'S LAW PLOT OF ABSORBANCE vs CONCENTRATION OF CHROMIUM (VI)

FIGURE 7



subsequently oxidized by the peroxydisulfate method (72). Two such samples were prepared and treated in this manner. Following oxidation, the solutions were diluted to 200 ml. and the pH adjusted to 1.5. The absorbances of these oxidized solutions were measured and compared with the standard working curve. The two solutions gave absorbance readings of 0.525 and 0.531 corresponding to 0.1030N and 0.1041N respectively. This compared favorably with the original value for the normality found by the ferrous ammonium sulfate-potassium dichromate method.

Attempts at oxidizing various amounts of chromium(III) quantitatively with excess peroxydiphosphate in the presence of manganese(II) were carried out. Various ratios of chromium(III) to manganese(II) were taken. These solutions, contained in 125 ml. iodine flasks and at pH values of 6.2 to 6.4 initially, were heated to boiling for approximately 60 seconds whereupon a brown-black precipitate of manganese dioxide formed as well as the appearance of a yellow solution indicative of chromium(VI) formation. The samples were cooled 0.5 to 2.5 hours. The final pH of these cooled solutions ranged from 5.2 to 5.5. The precipitates were removed by filtering through asbestos covered 6CM fritted funnels and washed thoroughly with five 20 ml. portions of distilled water. The filtrates together with the washings were diluted quantitatively to a total volume of 100 to 200 ml. depending on the amount of chromium(III) originally taken for oxidation. The individual filtrates were adjusted to a pH of 1.5 ± 0.3 with 0.1N sulfuric acid. Rigid pH control was not critical (13). The absorbances of these solutions were then measured

on the Beckman DU Spectrophotometer for the amount of chromium(VI) formed following the same procedure used in the construction of the working calibration curve.

The results of the chromium(III) oxidation with peroxydiphosphate in the presence of manganese(II) are contained in Table XVII. Only the hexavalent form of chromium was measured; no attempts were made to determine the amount of unoxidized trivalent chromium which may have still been present.

The results in Table XVII indicated that complete oxidation of trivalent chromium to the hexavalent form was possible provided an appreciable excess of divalent manganese was present. As seen from the table, increasing the amount of divalent manganese apparently resulted in a proportionally larger percentage of trivalent chromium being oxidized. The excess of manganese required to effect the oxidation of trivalent chromium was unduly large. In short, trivalent chromium can be looked upon as a definite interference in the determination of manganese.

The necessity for the presence of large amounts of divalent manganese to effect oxidation of trivalent chromium precluded a catalytic type of reaction since manganese itself was oxidized to manganese dioxide. Rather an induced type of reaction is suggested similar to that encountered with thallium. It was readily possible to distinguish between the actor, acceptor, and inductor and from the nature of the reactions carried out determine that the chromium-manganese oxidation with peroxydiphosphate involved a couple type reaction; i.e., electron transfer

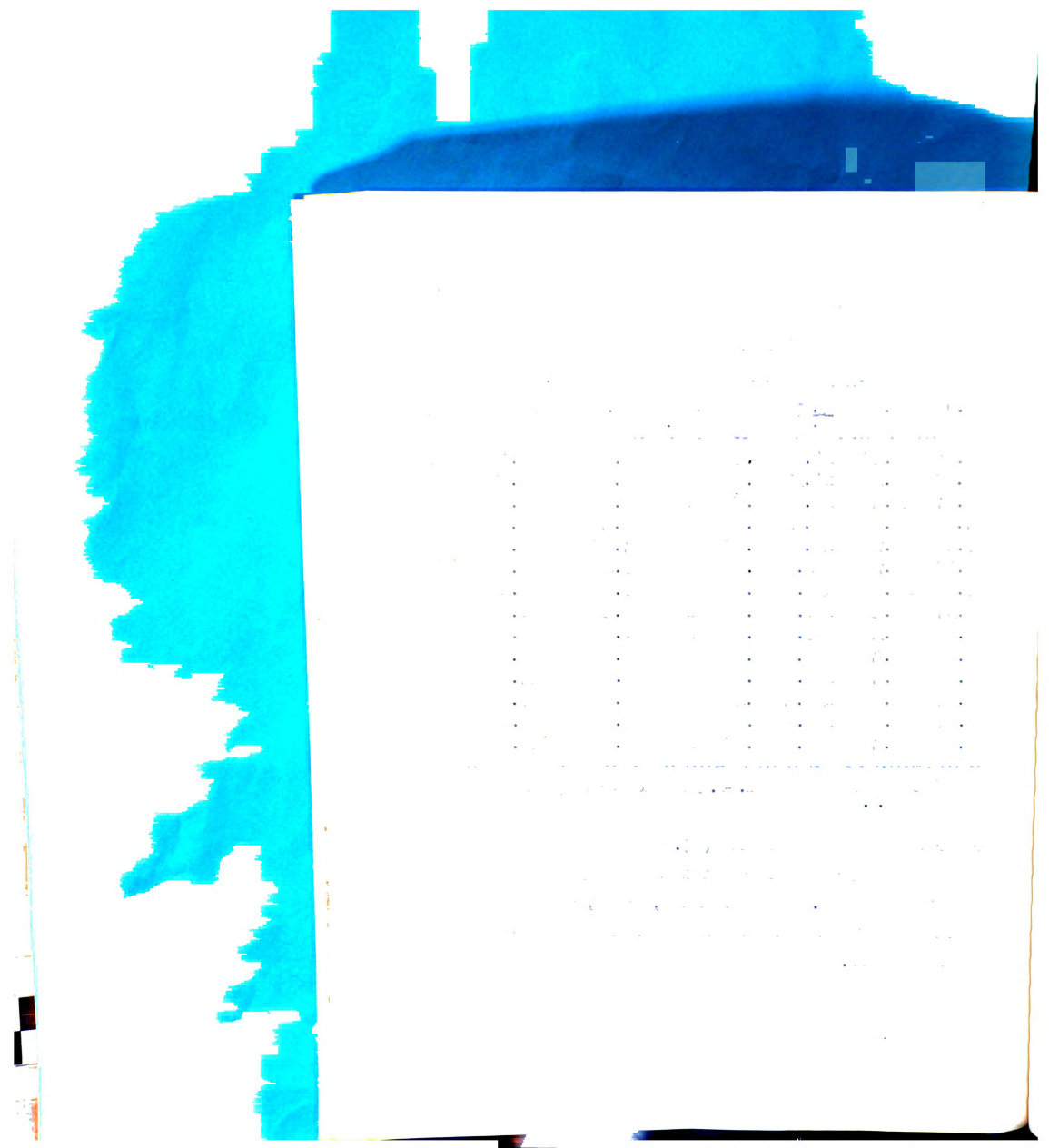
TABLE XVII

OXIDATION OF CHROMIUM(III) WITH PEROXYDIPHOSPHATE IN THE PRESENCE OF MANGANESE(II)

Mg. Cr Added	Mg. Mn Added	Mg. Cr / Mg. Mn	A_S 350	Volume Ml.	Mg. Cr Found	Per Cent Cr Oxidized
5.457	5.036	1/0.92	0.530	200	3.606	66.08
3.626	20.18	1/5.56	0.445	200	3.030	83.56
5.457	30.37	1/5.56	0.662	200	4.504	82.54
7.288	40.64	1/5.57	0.892	200	6.076	83.37
9.412	50.74	1/5.29	0.446	500	7.586	80.60
3.626	50.74	1/14.00	0.458	200	3.114	85.88
3.626	101.8	1/28.08	0.480	200	3.260	89.91
0.907	19.83	1/21.86	0.244	100	0.830	91.51
0.907	30.37	1/33.48	0.250	100	0.848	93.50
0.907	40.67	1/44.84	0.132	200	0.902	99.45
0.907	40.67	1/44.84	0.130	200	0.880	97.02
0.907	45.69	1/50.37	0.130	200	0.902	99.45
0.907	50.47	1/55.64	0.134	200	0.904	99.67
0.907	50.47	1/55.64	0.266	100	0.898	99.01

Determination made at pH 1.3-1.8; reaction carried out initially at pH 6.4.

rather than a chain type of reaction (28). The actor in this study was peroxydiphosphate; the inductor was divalent manganese; and the acceptor was trivalent chromium. It was not possible, however, to determine the coupling index since insufficient data had been collected to warrant such an evaluation.



The mechanism of the reaction appeared to be very similar to that observed in the thallium(I) oxidation where divalent manganese was oxidized to some higher valent species, presumably permanganate, which was then responsible for the actual oxidation.

3. Oxidation of Vanadium(IV)

When neutral tetralithium peroxydiphosphate solution was added to a vanadium(IV) solution, the disappearance of the blue color was observed and a light yellow color appeared shortly thereafter. The possibility of using this reaction analytically was investigated.

A sample containing 18.03 mg. of vanadium was treated with 20 ml. of 0.0995N tetralithium peroxydiphosphate solution. The solution was then diluted to a total volume of 50 ml. with distilled water. The initial pH of the solution was 5.5. A change in color from light blue to yellow was observed after standing for 3.5 hours at room temperature. The pH of the solution accordingly dropped to 5.0 after this period of time.

Attempts at decreasing the time required for oxidation were made. Oxidation of vanadium(IV) was carried out in the same manner as above except various heating periods were used. Two samples of vanadium(IV) were placed in a constant temperature oven at $50^{\circ} \pm 5^{\circ}$C.; two more were boiled for 30 seconds. The results indicated that heating accelerated the oxidation. Samples of vanadium(IV) required less than 45 minutes to effect a color change at 50°C., while the change from light blue vanadium(IV) to the yellow color of vanadium(V) at 100°C. occurred in less than five minutes when an appreciable excess of peroxydiphosphate had been used.

Decreasing the pH of the reaction to 1.5 by the addition of dilute sulfuric acid was also found to increase the rate of oxidation of vanadium(IV). Samples of vanadium(IV) were prepared in the same manner as above with excess peroxydiphosphate as the oxidizing agent. The pH of the solutions was adjusted to 1.5. The addition of 1.0 ml. 0.1N sulfuric acid was sufficient to obtain the desired pH value. The rate of vanadium(IV) oxidation at this pH value was increased considerably as was evidenced by the time required for the appearance of the oxidized vanadium(V) species. At room temperature the time required for the color change was found to be two hours; less than 30 minutes at 50°C. and immediately at 100°C.

The completeness of oxidation was tested by titrating the vanadium solution with potassium permanganate. In every case studied, one drop of 0.2097N permanganate was sufficient to cause the immediate appearance of the pink color thereby suggesting the absence of any vanadium(IV) in solution. These determinations were made in strongly acid solution and heating was used to effect sharper endpoints. Six milliliters of 6N sulfuric acid was used to obtain the high acidity.

Direct titration of vanadium(IV) with peroxydiphosphate was attempted. Heated samples of vanadium(IV) were titrated with 0.0990N peroxydiphosphate solution. The samples were heated to a temperature of approximately 80°C., acidified with 6 ml. 6N sulfuric acid and immediately titrated with peroxydiphosphate solution. The initial light blue colored vanadium solution was titrated until a yellow color was observed. Unfortunately,

the change in color was not sharp unless an appreciable excess of titrant was used. However, it was impossible to determine the excess peroxydiphosphate by the ferrous ammonium sulfate method since this would also result in the reduction of the oxidized vanadium. The conclusion was reached, therefore, that a suitable titration procedure was not possible.

4. Oxidation of Cobalt(II)

When divalent cobalt was treated with peroxydiphosphate, qualitative studies indicated some sort of reaction occurred as evidenced by the formation of a black precipitate in basic as well as in near neutral solution. The initial red color associated with the cobaltous ion was no longer evident.

Ten milliliters of the cobalt stock solution (60.92 mg. cobalt) were pipetted into a 250 ml. iodine flask followed by 25 ml. of distilled water and 30 ml. of 6N ammonium hydroxide solution. Twenty-five milliliters of approximately 0.1N peroxydiphosphate solution was then added to the solution and the flask immediately stoppered. Under these conditions a black precipitate developed, gelatinous in nature, after a three hour standing period at room temperature. Acidifying a portion of this solution with dilute sulfuric acid caused the dissolution of the precipitate. Removal of the precipitate from solution was virtually impossible because of its gelatinous character. Further studies of the reaction in neutral and slightly acidic media did not improve the character of the precipitate found even after boiling for 30 to 60 seconds.

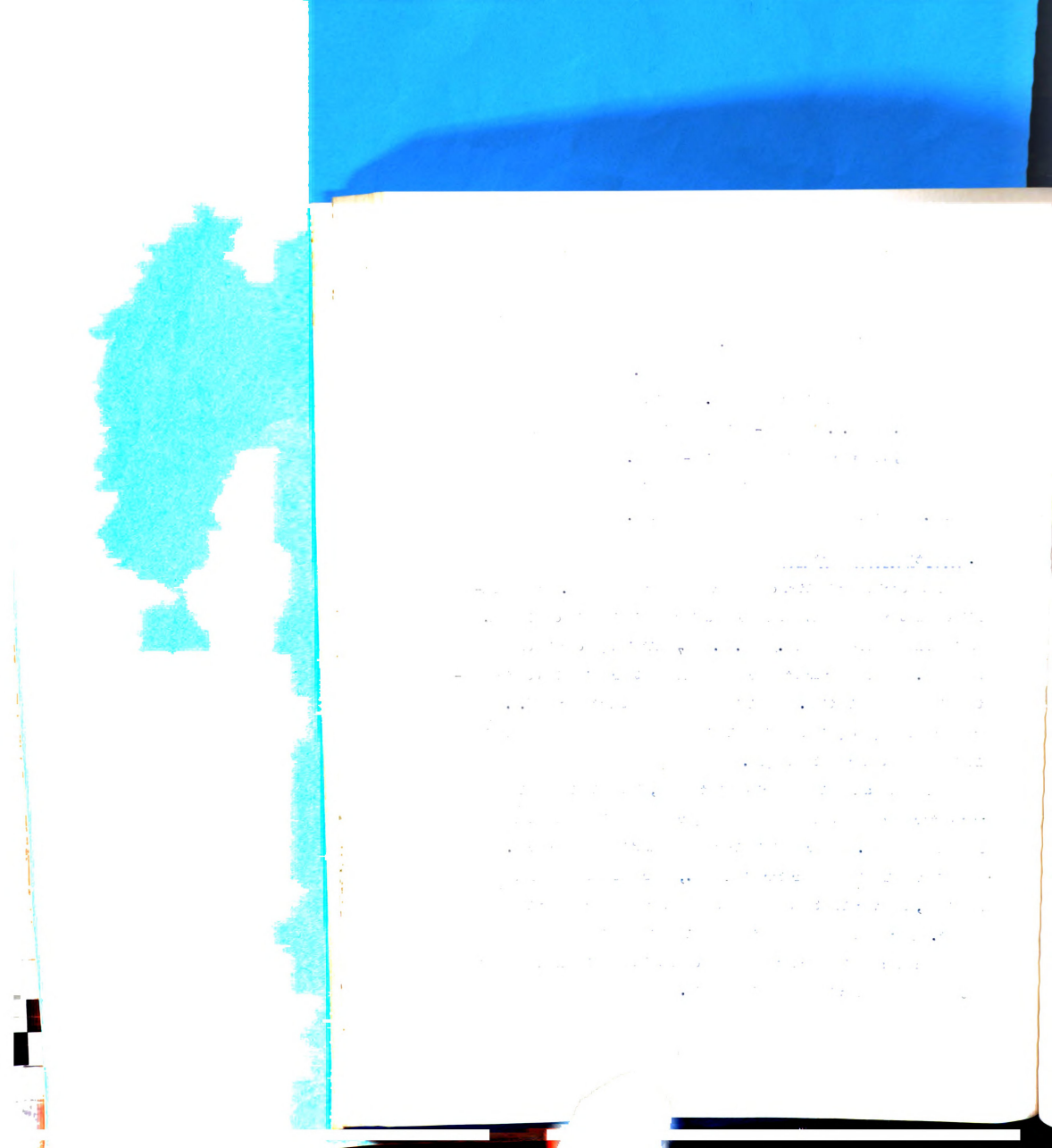
Attempts at obtaining better formed precipitates by having divalent manganese present were investigated. The same quantities were employed as above except no ammonium hydroxide was added. Various amounts of manganous sulfate solution were added. Solutions prepared were at pH values of 6.5 to 6.8. No well-defined precipitates were obtained even when heated; all were gelatinous and ill-defined. It was apparent that the physical state of the precipitate was not improved by the manganese dioxide. The work was subsequently discontinued.

5. Oxidation of Selenite Ion

The possible oxidation of selenious acid was studied. Ten milliliters of the standardized selenious acid was pipetted into a 125 ml. iodine flask followed by 19.98 ml. 0.0905 N lithium peroxydiphosphate solution. The flask was stoppered and allowed to remain at room temperature to effect oxidation. The initial pH of the solution was 6.4. Two blanks of peroxydiphosphate solution were also prepared and treated in the same manner as the sample.

Following a 15 minute period of standing, the extent of oxidation was determined by measuring the excess peroxydiphosphate with ferrous ammonium sulfate. The result indicated no oxidation had occurred.

Increasing the temperature to 100°C., decreasing the pH of the solution, and varying the amount of oxidizing agent were all without effect. It was concluded from these series of experiments that the oxidation of selenious acid was much too slow for a suitable volumetric method of analysis with peroxydiphosphate.



G. Oxidation in Basic Medium

The stability of peroxydiphosphate in basic medium suggested the possibility of its use as a basic oxidant since relatively few oxidizing agents are known which can be used in this manner. An investigation was initiated to determine if it was possible to effect such an oxidation with various ions.

The first attempt at working out a suitable analytical procedure concerned the oxidation of nitrite ion with tetralithium peroxydiphosphate in basic medium. A measured excess of peroxydiphosphate was used. Following appropriate periods of standing at room temperature ranging from five minutes to seven hours, examination of the nitrite samples for completeness of oxidation was made by measuring the excess peroxydiphosphate. Unfortunately, the requirement that an acidified medium be used in the procedure for determining the excess peroxydiphosphate immediately invalidated the method.

Other variables which would perhaps increase or influence the rate of oxidation were studied. The factors included variation of the nitrite and peroxydiphosphate concentrations, application of heat to the samples at 50-55°C., and the addition of basic catalysts. None of these changes resulted in an appreciable oxidation of the nitrite samples. Acidifying with dilute sulfuric acid resulted in the immediate evolution of oxides of nitrogen.

The possibility of oxidizing the sulfite ion to sulfate in basic medium was also investigated. Solutions containing sodium sulfite and

a measured excess of peroxydiphosphate were prepared and allowed to stand at room temperature to effect oxidation. At various intervals of time, ranging from ten minutes to 12 hours, the sulfite samples were measured for completeness of oxidation by determining the excess peroxydiphosphate. Unfortunately, upon addition of ferrous ammonium sulfate and acidification of the sample with 6N sulfuric acid, the evolution of sulfur dioxide was detected invalidating any suitable method of analysis almost immediately. Varying the amount of peroxydiphosphate, increasing the temperature and the use of basic catalysts were all without effect on increasing the rate of oxidation of the sulfite.

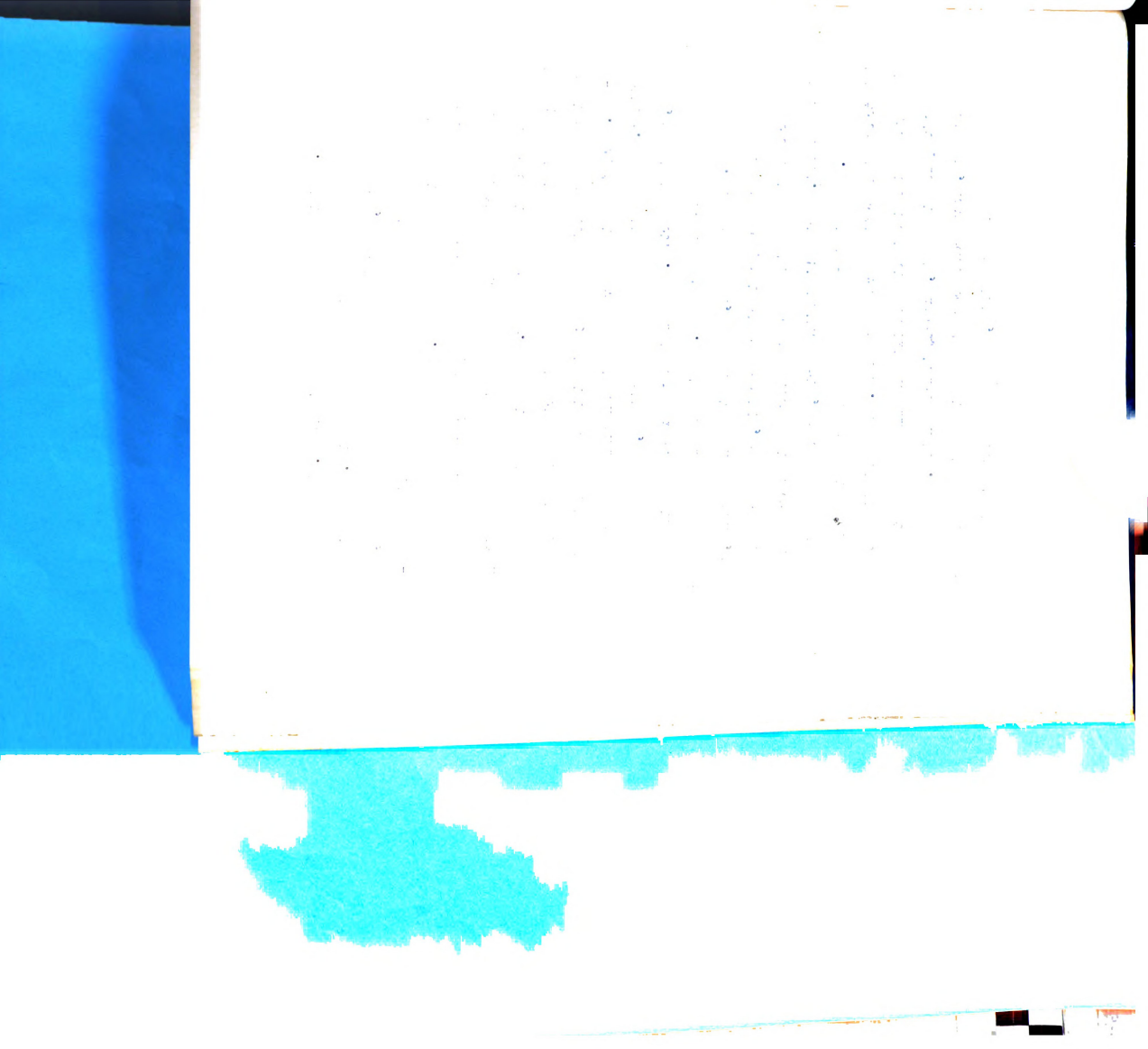
An attempt to qualitatively determine whether oxidation did occur was made. A barium chloride solution was added to a sample of sodium sulfite and peroxydiphosphate which had been kept at 60°C. for two hours and cooled for two hours. A white precipitate was formed but because of the insolubility of barium sulfite, it was not possible to distinguish whether sulfate was also present. Moreover, barium peroxydiphosphate is insoluble (16) but soluble in hydrochloric acid; both barium sulfate and barium sulfite are insoluble in hydrochloric acid. As a result no means of detecting sulfate was possible.

Similar difficulties were encountered when sodium sulfide was treated with peroxydiphosphate in basic medium. As expected, the attempt at determining the excess peroxydiphosphate by the volumetric method with ferrous ammonium sulfate proved to be unsatisfactory. Potentiometric titration with ferrous ammonium sulfate as the titrant was also

unsuccessful. Acidification of the samples with 10 ml. 6N sulfuric acid resulted in the immediate evolution of hydrogen sulfide. Increasing the time of standing, varying the amount of peroxydiphosphate used, heating and using basic catalysts did not materially result in any increase in the oxidation of the sulfide.

It was observed that the addition of 6N sulfuric acid resulted in not only the evolution of hydrogen sulfide but also caused the initially clear sulfide solution to turn cloudy. Increasing the time of standing in stoppered iodine flasks for an overnight period resulted in a large quantity of yellow particles to form; maintaining the temperature at 50-55°C. for 5 to 10 minutes gave a proportionally larger amount of particles. The formation of these yellow particles, believed to be free sulfur, was studied further. The particles were removed by filtration and washed thoroughly with warm water. Whatman number 42 ashless filter paper was used. The filter paper, containing the yellow particles, was then placed in a previously weighed Vycor crucible, the paper charred and the residue ignited until none of the yellow particles originally present was left. During this ignition period, fumes of sulfur dioxide were detected. The gain in weight of the crucible was slight following this treatment indicating no residue was left. The qualitative data strongly suggest that oxidation of sulfide to sulfur can occur to some extent with peroxydiphosphate, but only in acid solution.

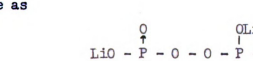
In summary, it was concluded that peroxydiphosphate in basic medium reacted much too slowly with sulfite, sulfide or nitrite ions to be of



any analytical value. This slowness of oxidation was also reflected in the inability to use conventional methods of analysis where acidification of the sample solution was required.

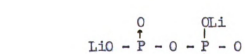
H. Structure of Tetralithium Peroxydiphosphate

Although peroxydiphosphate either in the form of the acid or as a salt has been known for nearly 50 years (35), there has actually been no definite attempt at a full characterization of its structure. In the absence of such data, the structure of the peroxydiphosphate has been considered analogous to peroxydisulfuric acid, $H_2S_2O_8$ (30). This would immediately suggest that the structure of anhydrous tetralithium peroxydiphosphate as



(I)

However, there is also the possibility of a structure of the type



(II)

which can not be overlooked.

Characterization of the structure of peroxydiphosphate was undertaken in order that a better understanding of its reactions, could be made. This particular problem was approached by both chemical and physical means.

1. Chemical Methods

In contact with water at ordinary temperatures and in basic medium, tetralithium peroxydiphosphate is quite resistant to hydrolysis (11,30). Decreasing the pH results in an increase in the hydrolysis rate. Assuming cleavage at the -O-O- site upon hydrolysis for both of the proposed structures of peroxydiphosphate, structure I should give orthophosphate and peroxymonophosphate initially, followed by further hydrolysis of the latter to orthophosphate and hydrogen peroxide while structure II should result in pyrophosphate and hydrogen peroxide. The pyrophosphate can further hydrolyze slowly to orthophosphate (30). A series of experiments were devised to determine the products of hydrolysis.

a. Presence of Orthophosphate

A magnesia mixture was prepared by dissolving 55 g. of magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$, in 200 ml. of water. To this was added 140 g. of ammonium chloride and 350 ml. of ammonia (sp. gr. 0.90); the solution was then diluted to one liter with distilled water. The solution was allowed to stand overnight and then filtered into a one liter glass stoppered bottle.

Approximately 8.0 g. of tetralithium peroxydiphosphate tetrahydrate was dissolved in 200 ml. of water and diluted to 500 ml. The pH of the solution prepared in such a manner was 9.5. This stock solution was used in the following series of studies.

Fichter and Gutzwiller (16) indicated that peroxydiphosphate did not form a precipitate with magnesia mixture, i.e., the magnesium salt

of peroxydiphosphate was soluble. A separation from phosphate was suggested but no experimental work was recorded. In order to substantiate their work, 10 ml. of magnesia mixture was added to 50 ml. of the freshly prepared peroxydiphosphate solution. No precipitate was initially observed in this basic medium. However, after approximately 24 hours, the formation of a white precipitate, characteristic of magnesium ammonium phosphate was found to develop; the amount increasing proportionally with time.

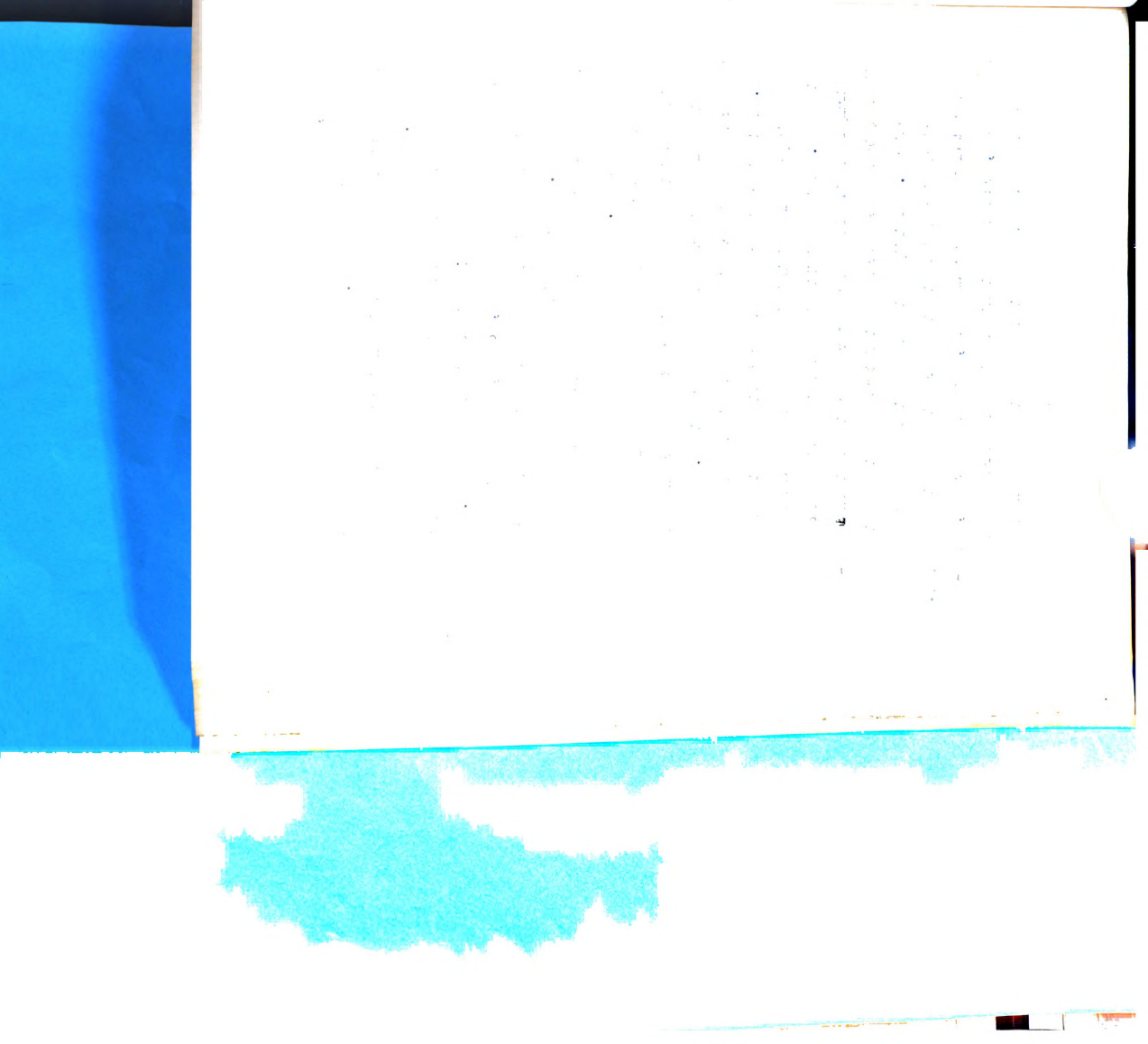
An acidified solution of peroxydiphosphate was also treated with magnesia mixture. Fifty milliliters of the freshly prepared peroxydiphosphate solution was acidified with 3N sulfuric acid to a pH of 4.0. To this solution was added 10 ml. of magnesia mixture in a dropwise fashion. In this acidified medium, a white precipitate developed in approximately 16 hours. Acidifying a peroxydiphosphate solution to a pH of 2.0 gave similar results when treated with the magnesia reagent. The development of a precipitate occurred in less than eight hours.

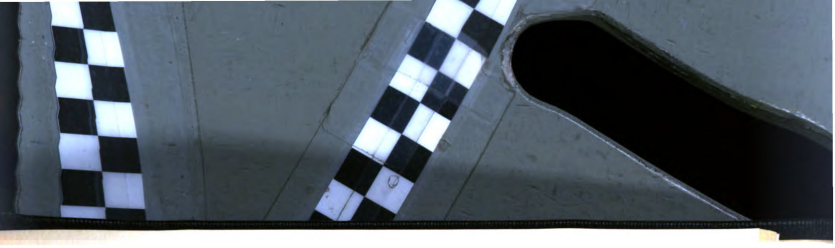
Fifty milliliter portions of the peroxydiphosphate stock solution at pH values of 9.5, 4.0 and 2.0 which had been kept for 18 days in stoppered 125 ml. iodine flasks at room temperature were also treated with magnesia mixture. Addition of 10 ml. of the reagent to the basic peroxydiphosphate solution resulted in the formation of a precipitate after a 10 minute standing period. The addition of 10 ml. magnesia reagent to the peroxydiphosphate solutions at pH 4.0 and 2.0 resulted in the immediate formation of precipitates. The more acidic solutions,

moreover, yielded a considerable larger amount of precipitate than observed for the basic solution. These tests show definitely that orthophosphate ion is present in acid solutions which have stood for some time.

It had been mentioned previously that peroxydiphosphate solutions were stable for a considerable period of time in basic medium. The above results with magnesia mixture, however, would indicate that decomposition of peroxydiphosphate may be occurring in basic as well as in acidic medium. Several possible explanations can be presented for the observed results encountered when peroxydiphosphate was treated with magnesia mixture.

The reagent which contains both ammonium and chloride ions could possibly be oxidized by the peroxydiphosphate thereby resulting in the formation of a magnesium ammonium phosphate precipitate. It has been shown previously that peroxydiphosphate can oxidize ammonium and chloride ions. That this reaction would be slow was evidenced by the time required to produce a precipitate in a freshly prepared solution in basic medium. Or the possibility that peroxydiphosphate solutions were not truly stable in basic medium but were undergoing continual decomposition may be the reason for the precipitates of magnesium ammonium phosphate formed. Stability studies on peroxydiphosphate solutions involved attributing all the oxidizing power to the peroxydiphosphate (11). As a result of this arbitrary assumption, any hydrogen peroxide, peroxymonophosphate, or any other oxidizing agent capable of reacting with ferrous ion that may have formed in the peroxydiphosphate solution would





be considered as part of the total oxidizing power of peroxydiphosphate. Increasing the acidity of the solutions decreased the stability of peroxydiphosphate and, as would be expected, an increased amount of the products would be formed. This would partially explain the immediate precipitate formed when magnesia mixture was added to an acidified solution of peroxydiphosphate that had been kept for an extended period of time.

Further, the formation of magnesium ammonium phosphate indicated that orthophosphate was at least present in solution. Whether pyrophosphate was also involved in the peroxydiphosphate solution could not be evaluated from this series of studies.

b. Absence of Pyrophosphate

Numerous analytical methods and modifications have been devised for both the qualitative and quantitative determination of pyrophosphate in the presence of orthophosphate. The zinc titration (3) can not be used because of the partial insolubility of zinc peroxydiphosphate in water (16). The method of Gerber and Miles (21) which consisted essentially of a pH titration lacked precision and sensitivity at pyrophosphate content below five per cent. The chromatographic method (24) has good precision and is free of interference from other phosphates, but requires too much time for the purposes desired. A fast and sensitive colorimetric method proposed by Chess and Bernhart (10) for the determination of small amounts of pyrophosphate in soluble orthophosphates was chosen for the detection and estimation of any pyrophosphate in peroxydiphosphate. In this method pyrophosphate present in less than one

per cent concentration in orthophosphate could be determined by the complexing effect of pyrophosphate on iron utilizing 1, 10 phenanthroline to follow the concentration of ferrous ion.

A calibration curve of absorbance vs. concentration of tetrasodium pyrophosphate (time held constant) was prepared following the outline suggested by Chess and Bernhart. A sample of tetralithium peroxydiphosphate equal to the amount of orthophosphate present in the calibration curve was then taken and the procedure repeated in exactly the same manner as was done in the preparation of the calibration curve. Unfortunately, the conditions employed in the method of Chess and Bernhart were unsatisfactory for a successful color development in the peroxydiphosphate samples.

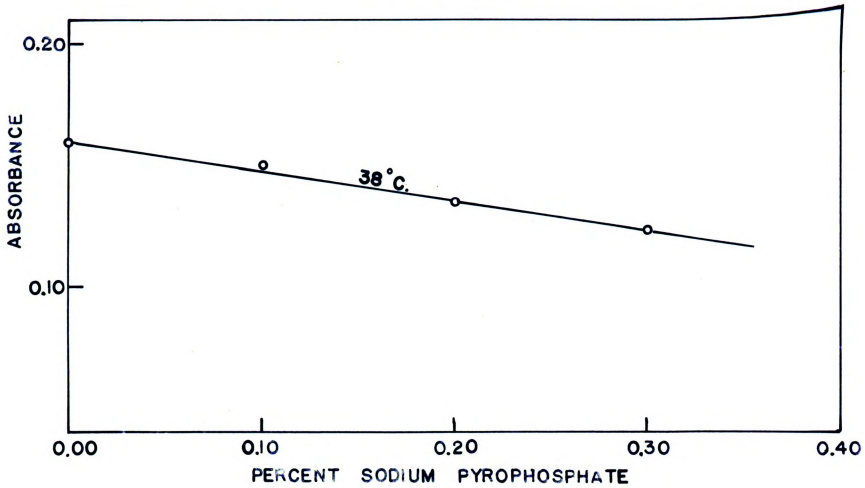
The failure of a color development was traced to the insufficient addition of 1, 10 phenanthroline reagent and hydroxylamine hydrochloride solution. The latter was found to be strongly influenced by the amount of iron stock solution used. These factors were considered and the conditions were modified in order that the attainment of the phenanthroline color with iron was possible.

The procedure was modified in the following manner. All reagents used were those suggested by Chess and Bernhart. A calibration curve was prepared by adding two milliliters of disodium phosphate (200 mg.) to each of eight 50 ml. Nessler tubes. The tubes were marked in pairs, one of each being the blank. One milliliter of pyrophosphate solution (1.000 g. tetrasodium pyrophosphate in 500 ml. of water) was added to each tube of the second pair, two milliliters to each of the third pair,

and three milliliters to the fourth pair (equivalent to 0.00 mg., 0-20 mg., 0.40 mg. and 0.60 mg. pyrophosphate). To one tube of each pair was added five milliliters (0.04 mg.) of standard iron solution and mixed well.

Ten milliliters of 10% hydroxylamine hydrochloride solution and three milliliters of glacial acetic acid were added to each tube and diluted to 40 ml. with water and mixed. The pH of these solutions were approximately 3.5. The tubes were then placed in a water bath at 38° ± 0.5°C. and the tubes allowed to reach the temperature of the bath (45 minutes). Then, to the first blank was added 8.0 ml. of 0.1% 1, 10 phenanthroline solution, diluted to 50 ml. with water and timed for 2.5 minutes before being placed in a Beckman B colorimeter. The colorimeter was set to read zero absorbance at 515 mμ with the blank. The procedure was repeated with the other tube of the pair containing the iron and the absorbance of the solution read when the approximate time had elapsed (60 seconds). In similar fashion, the procedure was repeated with each pair of tubes. A plot of absorbance vs. concentration of tetrasodium pyrophosphate, using the absorbance values obtained, was then made. The standard curve is shown in Figure 8.

A freshly prepared solution of tetralithium peroxydiphosphate at a pH of 8.6, a solution of the peroxydiphosphate that had been prepared 10 days ago with a pH of 7.1 and an acidified solution at pH 3.8 were used to determine if any pyrophosphate was present in these solutions. Two milliliters of the peroxydiphosphate solution (equivalent to 198 mg. disodium phosphate) was taken and treated in exactly the same manner as



RELATION OF SODIUM PYROPHOSPHATE CONCENTRATION TO ABSORBANCE AT 515 Mμ

FIGURE 8

had been done in the preparation of the standard curve. Duplicate determinations on each of the above solutions were made along with their corresponding blanks. The results taken from the calibration curve are shown in Table XVIII. The absorbance readings of the two determinations for each solution agreed with each other. The values found indicated that there was essentially no pyrophosphate present in any of the peroxydiphosphate solutions used. The amount present was too small to be of any measurable consequence and may be attributed to experimental errors.

TABLE XVIII

DETERMINATION OF PYROPHOSPHATE IN TETRALITHIUM PEROXYDIPHOSPHATE

Sample	Initial pH	Absorbance Reading	Per Cent Pyrophosphate Present
10 day old solution	7.1	0.160	0.00
10 day old solution	7.1	0.162	0.00
Freshly prepared solution	8.6	0.158	0.016
Freshly prepared solution	8.6	0.160	0.00
Three day old solution	3.8	0.159	< 0.012
Three day old solution	3.8	0.157	< 0.027

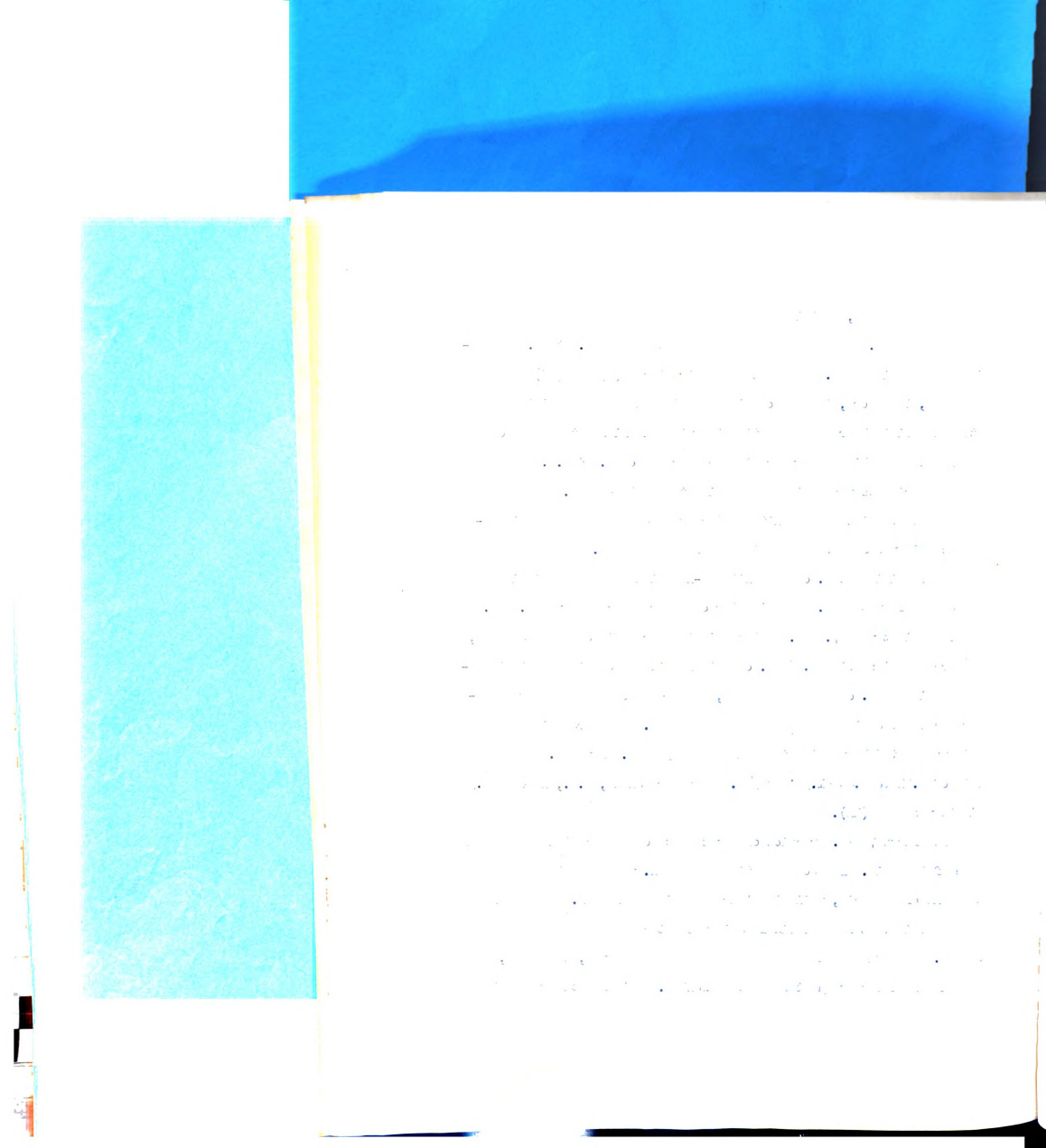
c. Titration of Peroxydiphosphoric Acid and Its Salt

Van Wazer and Holst (40) have shown by titrations of various phosphoric acids with alkali that all the phosphoric acids, regardless of

their compositions, contained one strongly acidic hydrogen atom per phosphorus atom. This hydrogen was neutralized at pH 3.8 to 4.2 depending on the acid taken. Examination of structures (I) and (II) would indicate, therefore, that peroxydiphosphoric acid should exhibit two strongly acidic hydrogens when titrated with alkali and these hydrogens should be neutralized somewhere in the pH range of 4.0 ± 0.2. A series of pH experiments was designed to verify these statements.

The conversion of tetralithium peroxydiphosphate to peroxydiphosphoric acid was achieved by an ion exchange procedure. An ion exchange column containing 52 g. of Amberlite IR-100H ion exchange resin in the hydrogen form was used. The diameter of the resin column was 5.0 cm. and the height was 27.0 cm. A tetralithium peroxydiphosphate solution, prepared by dissolving 0.569 g. of tetralithium peroxydiphosphate tetrahydrate in 50 ml. of distilled water, was placed on the resin by allowing the solution to flow into the resin column. The peroxydiphosphoric acid was eluted by washing the column with 300 ml. of water. A flow rate of 0.01 to 0.05 ml./minute/ml. exchanger column, i.e., 1 to 5 ml./minute was used (11).

The first 70 ml. fraction of eluate was found to contain essentially none of the acid. A second fraction of 200 ml. was found to contain the bulk of the acid, while the third fraction of 150 ml. was much like the first in that no appreciable acid was detected when treated with alkali. Selection of the second fraction of eluate was, therefore, used in all the subsequent studies to follow. This fraction was retained



following titration with alkali to determine the number of milliequivalents of acid present in the sample solution titrated. Duplicate phosphorus determinations were made by reducing the peroxydiphosphate with warm 1:1 hydrochloric acid and precipitating the phosphate as magnesium ammonium phosphate. To insure that all the phosphorus was in the orthophosphate form the solution was evaporated to near dryness on a steam bath in the presence of nitric acid prior to the precipitation of the magnesium ammonium phosphate. The magnesium ammonium phosphate was reprecipitated, ignited to magnesium pyrophosphate, and weighed as such. The average value of the two determinations for phosphorus indicated 1.33_6 millimoles peroxydiphosphate had been converted to the acid form. This would correspond to approximately 65 per cent of the total peroxydiphosphate originally taken which was present in the second fraction.

The eluate containing the bulk of the acid was titrated with 0.1183N potassium hydroxide. The change in pH upon the addition of alkali was measured with a Beckman model H-2 pH meter equipped with a glass electrode. The potassium hydroxide solution was added in one milliliter increments until a measurable change in pH occurred, then in smaller increments. Magnetic stirring was used during the titration. It was found that no adverse effects were experienced in the readings provided slow stirring was used. The data are plotted in Figure 9 and tabulated in the Data Appendix.

The initial pH of the acid solution was 2.0. Four breaks in the titration curve were obtained. From the appearance of the titration

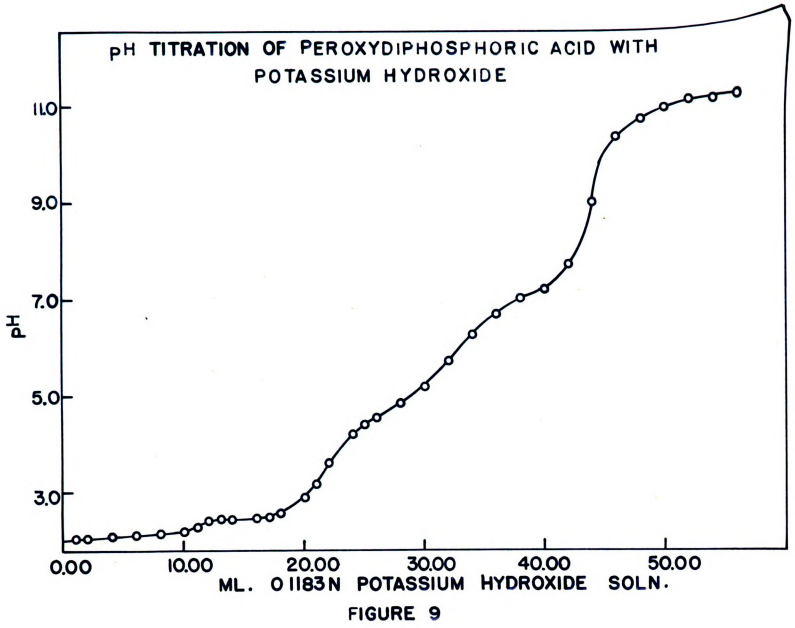
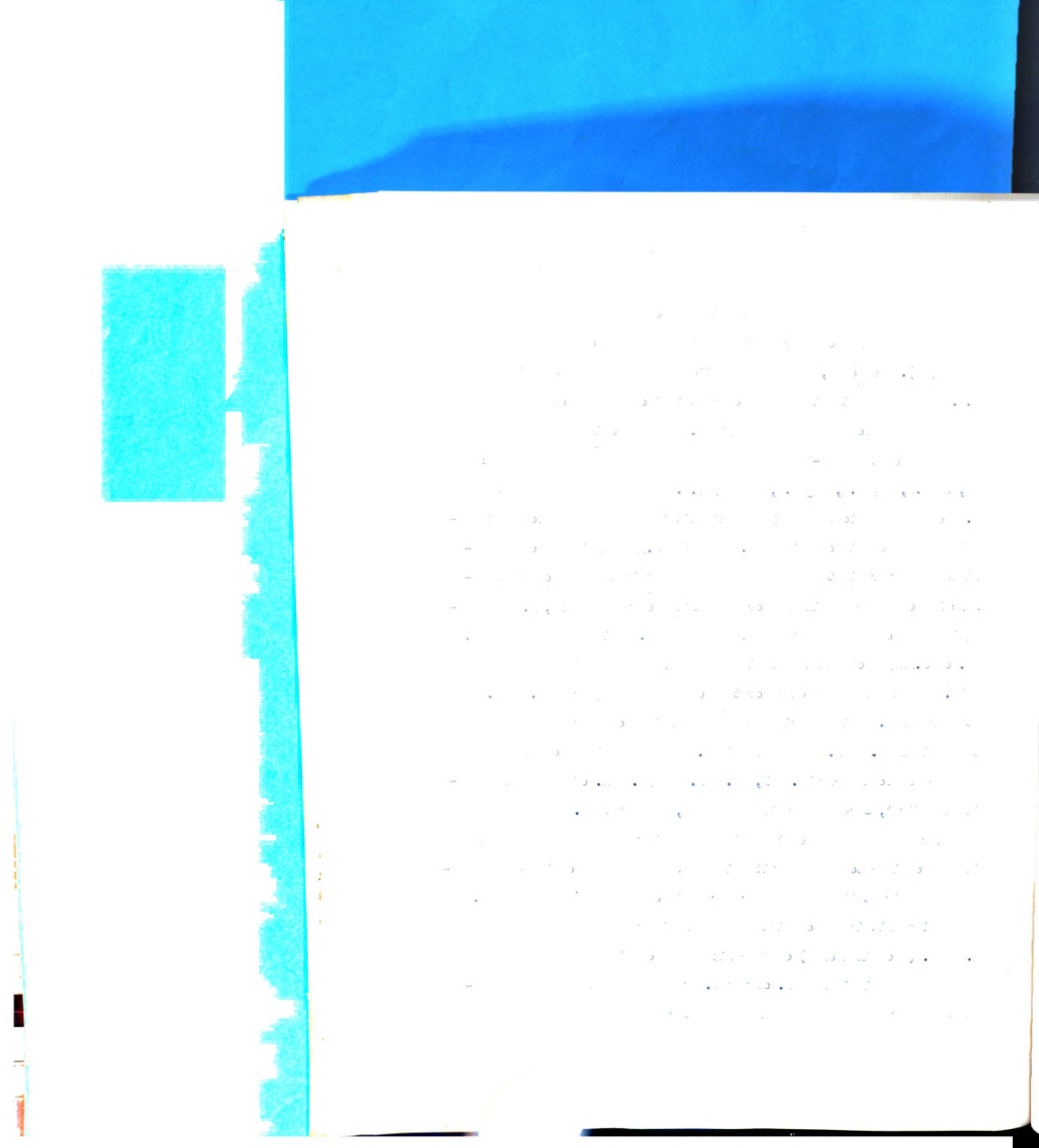

pH TITRATION OF PEROXYDIPHOSPHORIC ACID WITH POTASSIUM HYDROXIDE
11.0
9.0
7.0
5.0
3.0
pH
0.00
10.00
20.00
30.00
40.00
50.00
ML. 0 1183 N POTASSIUM HYDROXIDE SOLN.

FIGURE 9

curve it can be seen that the first two hydrogens were nearly of equal strength in fairly good agreement with the statement of Van Wazer and Holst (40). Moreover, the neutralization occurred at approximately pH 3.6. As expected the third and fourth titration breaks corresponded to much weaker hydrogens being neutralized. The approximate pK values obtained from the half-titration points of the individual breaks are: pK_1 of 2.1, pK_2 2.5, pK_3 4.2, and pK_4 7.0. The equivalence point at pH 9.0 corresponded to the complete neutralization of the acid to the tetrapotassium peroxydiphosphate salt. Assuming 1.33_6 millimoles of peroxydiphosphate were in the sample that had been titrated and four replaceable hydrogens are available for neutralization with alkali, 5.34_6 milliequivalents of the acid must have been present. This would require 45.11 ml. of 0.1183N potassium hydroxide for complete neutralization of the acid. The equivalence point for the fourth break required 45.00 ml. of standard base. This experimental value was in good agreement with the theoretical 45.11 ml. of base required. The other titration breaks required approximately 11.0 ml, 21.6 ml. and 32.0 ml. of base to neutralize the first, second and third hydrogens, respectively.

A replacement type of titration with acid was performed to see if it was possible to obtain a titration curve the reverse of the one obtained by the direct titration of the peroxydiphosphoric acid with alkali.

A tetralithium peroxydiphosphate solution was prepared by taking 0.579 g. (two millimoles) of tetralithium peroxydiphosphate tetrahydrate and dissolving it in 150 ml. of water. The pH titration of the peroxydiphosphate was made immediately thereafter in much the same manner as



described above for the acid. Standardized sulfuric acid, 0.1007N, was used as titrant. The data are plotted in Figure 10 and tabulated in the Data Appendix.

The initial pH of the tetralithium peroxydiphosphate solution was 8.40 which corresponded fairly well with the pH of 9.0 found for the complete neutralization of the acid in the previous work. Only one break in the titration curve was obtained. This break, at 20.16 ml., did not correspond to any one of the breaks obtained in the direct titration of the acid with base. No conclusions pertaining to the relative strengths of the peroxydiphosphoric acid and its acid salts can be deduced from the information revealed by this titration.

From the appearance of the titration curve in Figure 9, it is apparent that the first and third breaks are rather poorly developed. It was decided to establish with certainty whether these two were actual breaks by employing a conductometric method of titration.

A peroxydiphosphoric acid sample, prepared in the same manner as previously described in the pH titration, was titrated conductometrically with base. A Serfass Conductivity Bridge Model RC M15 equipped with platinized platinum electrodes was used for the measurements. The cell constant was 0.10. Potassium hydroxide, 0.1183N, was added in one milliliter increments to the sample containing the peroxydiphosphoric acid. The conductance was expressed in terms of micromhos/cm. specific conductance. Magnetic stirring was employed during the titration. The results are plotted graphically in Figure 11 and tabulated in the Data Appendix.

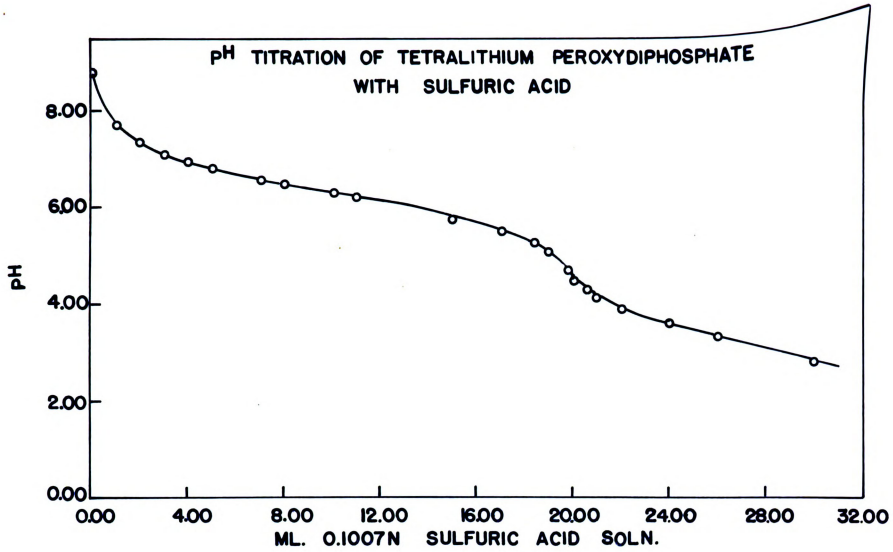

pH TITRATION OF TETRALITHIUM PEROXYDIPHOSPHATE
WITH SULFURIC ACID
pH
8.00
6.00
4.00
2.00
0.00
0.00
4.00
8.00
12.00
16.00
20.00
24.00
28.00
32.00
ML. 0.1007N SULFURIC ACID SOLN.

FIGURE 10

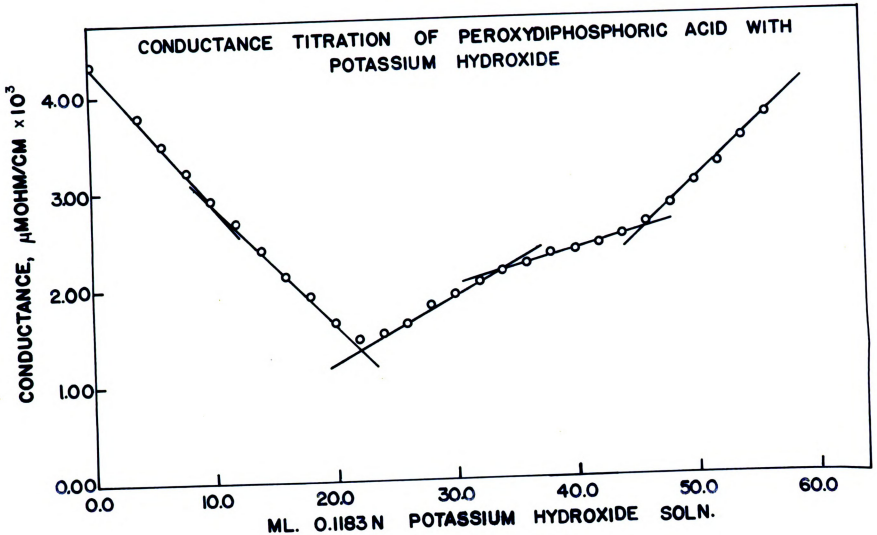

CONDUCTANCE TITRATION OF PEROXYDIPHOSPHORIC ACID WITH POTASSIUM HYDROXIDE
CONDUCTANCE, μMOHM/CM x 10³
4.00
3.00
2.00
1.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
ML. 0.1183 N POTASSIUM HYDROXIDE SOLN.

FIGURE 11

Four breaks in the conductance titration curve were obtained, the first one was poorly developed while the next three were sharp and well defined. It was found that 10.60 ml., 22.15 ml., 32.90 ml. and 45.00 ml. of 0.1183N potassium hydroxide were required to effect the neutralization of the first, second, third and fourth hydrogens, respectively. Comparison of Figures 9 and 10 revealed almost identical neutralization points for approximately the same size sample of acid taken. The conductance titration essentially substantiated the work done previously with the pH titration. The curves obtained indicated all four breaks are present and that the first two hydrogens are of approximately equal strength.

In summary, titration of peroxydiphosphoric acid with alkali revealed neutralization of all four hydrogens was possible, two of which were approximately of equal strength substantiating the statement of Van Wazer and Holst (40), the third and fourth were much weaker. Attempts at a displacement type titration with the salt of peroxydiphosphate were made. No satisfactory results were obtained when the salt was treated in this manner. Additional evidence for the work on the pH titration of the acid was obtained. A conductometric titration of the acid substantiated the previous statement of two equivalent hydrogens in peroxydiphosphoric acid.

The investigation strongly suggested the presence of a -P-O-O-P- type structure rather than a -P-O-P- type where nonequivalent hydrogens would be much more evident.

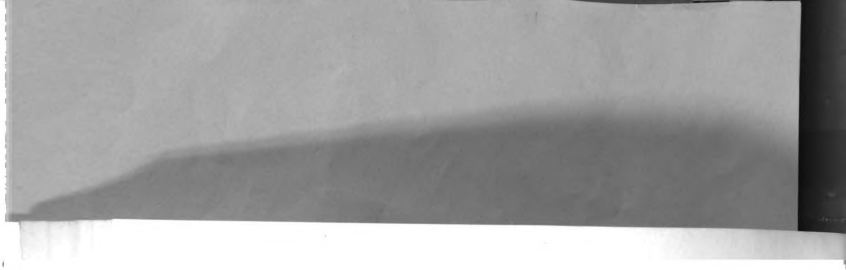
2. Physical Methods

a. Structural Proof by Infrared

The infrared spectra have been recorded for many inorganic compounds most of which are salts containing polyatomic ions (29). No graphical spectrum in the infrared region has been made for tetralithium peroxydiphosphate tetrahydrate. It was believed that such a spectrum would serve as an aid in distinguishing whether the peroxy group, -O-O-, was linked between two phosphorus atoms (structure I) or between a phosphorus and a lithium atom (structure II). The latter would result in a pyrophosphate type structure, -P-O-P, which has indeed been observed and recorded tentatively in the literature (4,5).

The infrared spectrum was obtained with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer equipped with a sodium chloride prism. The sample was prepared by milling a small portion (approximately 0.3 gm.) with liquid petrolatum (Nujol) and placing the mull paste between sodium chloride plates. The spectrum of the sample so prepared was recorded from 2.0 to 14.5 microns, using air as the reference. The spectrum of tetralithium peroxydiphosphate tetrahydrate is shown in Figure 10 together with the conditions used.

The marked influence of the cation (lithium) as well as the hydrated water present is noticeable when compared with other phosphate containing compounds (29). It can readily be seen from Figure 10 that an ill-defined spectrum of peroxydiphosphate was obtained. The reason for this was not clear, but it may be due to lack of a single well-ordered crystal



structure (29). The absence of sharp clearly defined peaks in both the 930-970 cm^{-1} and 2560-2700 cm^{-1} (regions of symmetric and asymmetric -P-O-P type structure and -P-O-H structure respectively) portions of the spectrum in Figure 12 made the evaluation of any characteristic type linkage or molecular groups for peroxydiphosphate virtually impossible. That is, the lack of spectral data on reference compounds such as those structures with the type -P-O-O-H and -P-O-O-P, and the inadequacy of information concerning characteristic frequencies of molecular groups containing phosphorus made it impossible to reach a conclusion on the structure of the peroxydiphosphate from infrared studies.

b. Structural Proof by Nuclear Magnetic Resonance

It has been shown that correct structural formulas for phosphorus compounds can be ascertained by nuclear magnetic resonance measurements (8,39). Interaction of a nucleus with its electronic environment, especially the valence electrons, influences the magnetic resonance absorption of the nucleus (1). At resonance, a change in the electronic environment within the atom so as to reduce the magnetic field at the nucleus necessitates an increase in the applied magnetic field. This increase is called a positive chemical shift. These shifts, which may be positive or negative, are generally measured in parts per million (p.p.m.) of the applied magnetic field relative to a chemical compound of the element arbitrarily chosen as a reference. Since the only naturally occurring isotope of phosphorus, P^{31}, has a spin of one-half and a high magnetic moment (9), this tool would be especially appropriate for investigating phosphorus compounds.

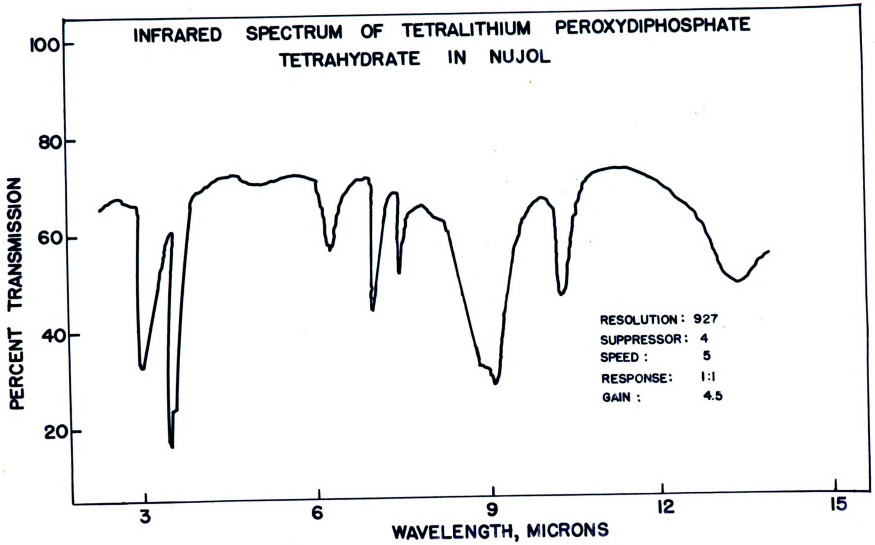

INFRARED SPECTRUM OF TETRALITHIUM PEROXYDIPHOSPHATE TETRAHYDRATE IN NUJOL
PERCENT TRANSMISSION
100
80
60
40
20
3
6
9
12
15
WAVELENGTH, MICRONS
RESOLUTION: 927
SUPPRESSOR: 4
SPEED: 5
RESPONSE: 1:1
GAIN: 4.5

FIGURE 12

If structure I correctly represented the peroxydiphosphate containing the two phosphorus atoms in which the nuclei have the same electronic environments and hence are chemically equivalent, there should be only one resonance peak in its nuclear magnetic spectrum. If the material were structure II containing the two phosphorus atoms in which the nuclei have different electronic environments, the spectrum of the material should exhibit several resonance peaks corresponding to a different electronic environment of the nucleus. A nuclear magnetic resonance spectrum should, therefore, provide a powerful means for proving whether the structure of peroxydiphosphate was structure I or structure II by the number of resonance peaks obtained.

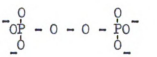
However, the lack of enough experience with the effect of the -O-O- linkage on the chemical shift to definitely distinguish by shift alone between I and the structure

III

would provide a serious drawback if the latter species were present in solution. But the relative instability of peroxymonophosphate in aqueous solution would preclude its existence. A spectrum of peroxymonophosphate would be helpful for identification and comparison purposes in conjunction with this work.

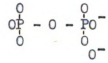
Through the courtesy of Dr. C. F. Callis of Monsanto Chemical Company, St. Louis, Missouri, a nuclear magnetic resonance spectrum

of tetralithium peroxydiphosphate was prepared (Figure 13) together with the conditions used. The latter has been included in the Data Appendix. It was significant that there was only one peak shifted -7.4 parts per million of the applied field relative to 85 per cent orthophosphoric acid. Because of this shift value, it was concluded that the compound was not a phosphate structure of any kind (7). Further, the solution contained only one kind of phosphorus and from the evidence derived in the pH titrations previously where it was shown that the species in solution was not that of a monophosphorus molecule, the nuclear magnetic spectrum indicates the structure must be



I

and not



II

The species in solution can definitely not be II above, since II would give rise to more than one nuclear magnetic resonance peak.

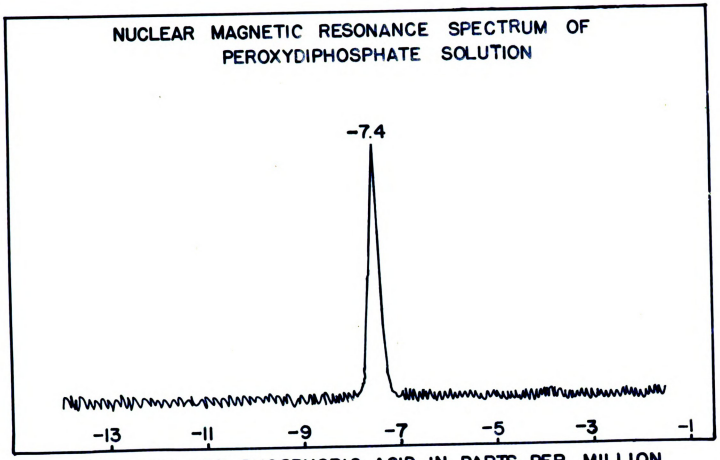

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF
PEROXYDIPHOSPHATE SOLUTION
-7.4
-13
-11
-9
-7
-5
-3
-1
SHIFT FROM 85% PHOSPHORIC ACID IN PARTS PER MILLION

FIGURE 13

V. SUMMARY

Tetralithium peroxydiphosphate tetrahydrate was prepared by the electrolytic method outlined by Chulski (11). It was possible to increase the yield of final product by approximately 50 per cent from that previously obtained by a resaturation of the electrolyte with additional solid potassium hydroxide followed by the subsequent conversion and recovery of the lithium salt. No measurable loss in oxidizing power was obtained as evidenced when an equivalent amount of this second batch was compared with the first.

Stability studies on peroxydiphosphate solutions at different pH values were made. Exposure to strong sunlight for 12 hours at room temperature resulted in rapid decomposition of the solutions particularly those at relatively high acidity. Basic or neutral peroxydiphosphate solutions exposed to diffused light for 12 hours at room temperature showed no appreciable loss in oxidizing power. Heating of basic or neutral peroxydiphosphate solutions at 100°C. for 30 to 60 seconds caused no appreciable loss in oxidizing power.

The oxidation of divalent manganese was successfully achieved when the reaction was carried out in the pH range 5.8-7.5 as evidenced by the formation of a brown-black precipitate. Excess peroxydiphosphate was required to effect the oxidation. It was possible to quantitatively analyze both the precipitate, which was shown to be manganese dioxide, as well as the filtrate for excess peroxydiphosphate by the volumetric

ferrous ammonium sulfate method. It was necessary, however, to use a correction factor of 1.01 for the precipitate in order to obtain quantitative results. The time required to effect complete oxidation of the manganese was approximately 12 hours at room temperature, four hours at 50-55°C. and 30 to 60 seconds at 100°C. The amount of manganese taken for study varied from approximately 5 to 50 mg.

It was shown that quantitative results for manganese could be obtained in the presence of the following ions: vanadium(V), vanadyl, cupric, cadmium, nickelous, calcium, zinc, molybdate, sodium, potassium and dihydrogen phosphate. Despite their interference with the analysis of the filtrates, mercuric, chromic, arsenic(III), chloride and ammonium ions were found to give no adverse effects when the precipitates were analyzed for manganese. Tungstate, thallous, cobaltous, ferric, aluminum, silver, barium, lead, zinc and nitrate ions interfered with the oxidation.

A possible mechanism for the oxidation was also investigated. It was believed the divalent manganese was oxidized to some higher valent species by the peroxydiphosphate, presumably to permanganate, which then reacted with the manganous ion present to form manganese dioxide.

A spectrophotometric method for determining peroxydiphosphate was developed. Peroxydiphosphate solutions absorbed in the ultraviolet region resulting in no definite peaks but giving characteristic curves which were dependent on concentration and pH. Moreover, it was shown that this absorbance adhered to Beer's Law and as a consequence a plot

of absorbance as a function of concentration was prepared at a wavelength of 240 mμ. The excess peroxydiphosphate in the filtrate following oxidation of manganese and removal of the precipitate formed was determined by this method.

Individual oxidation of thallous, chromic and cobaltous ions as well as selenious acid were attempted under various conditions. Although oxidation occurred to some extent, none was found suitable for use as possible quantitative procedures. The gelatinous character of the precipitate in the cobalt oxidation made it impossible to determine the excess peroxydiphosphate. In the presence of a known amount of manganous ions, it was possible to effect the oxidation of thallous and chromic ions. The thallium oxidation was determined volumetrically by the ferrous ammonium sulfate method; the chromate formed was analyzed spectrophotometrically. The possibility of the manganese acting as an inducer was suggested.

Individual attempts on the oxidation of nitrite, sulfite and sulfide were made in basic medium with excess peroxydiphosphate. It was found, however, that the amount of unused peroxydiphosphate could not be determined.

The structure of peroxydiphosphate was investigated. It was shown that decomposition of peroxydiphosphate occurred in acid medium resulting in the formation of orthophosphate as one of the products. Treatment of basic solutions of peroxydiphosphate with magnesia mixture resulted in the formation of white precipitates but only after a period

of standing. Two possibilities for this orthophosphate formation in basic medium were proposed. Attempts at detecting the presence of pyrophosphate in peroxydiphosphate solutions were also made. Colorimetric tests indicated that there was no pyrophosphate present.

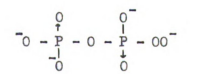
The pH titration of peroxydiphosphoric acid revealed that there was one strong hydrogen per phosphorus atom while the other two hydrogens were much weaker. This was further verified by a conductometric titration. Attempts at a displacement type titration with the lithium salt of peroxydiphosphate were made. No satisfactory results were obtained when the salt was treated in this manner.

Two physical methods were also used in an attempt to elucidate the structure. An infrared spectrum of tetralithium peroxydiphosphate tetrahydrate in Nujol mull was made. However, no additional or helpful information of any consequence was gained from this spectrum.

The other physical method involved the use of nuclear magnetic resonance. The nuclear magnetic resonance spectrum for tetralithium peroxydiphosphate revealed only one peak shifted -7.4 parts per million relative to 85 per cent phosphoric acid which suggested the symmetrical structure.

The foregoing series of structural investigations strongly indicate that the structure of peroxydiphosphate must be

and not



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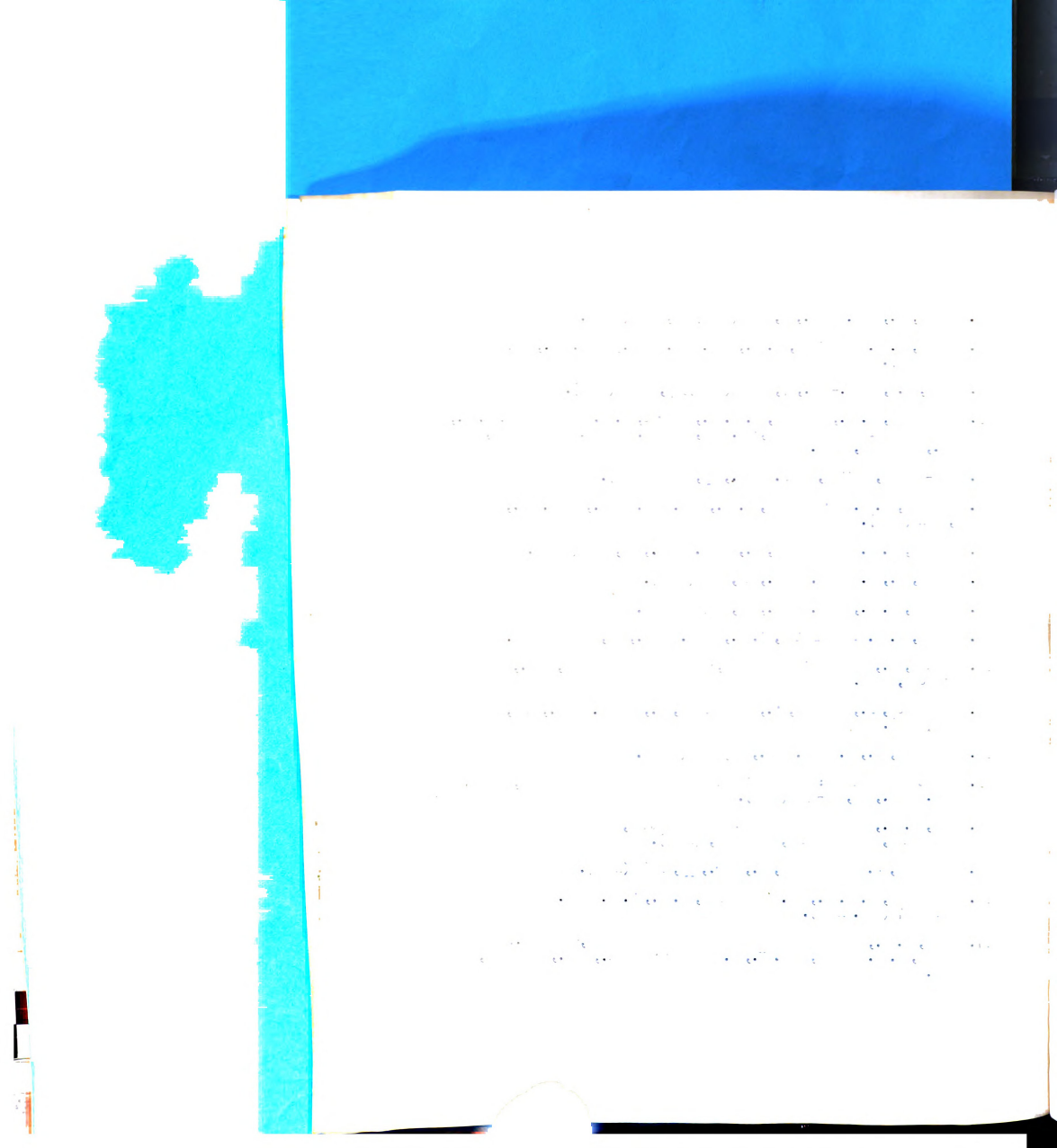

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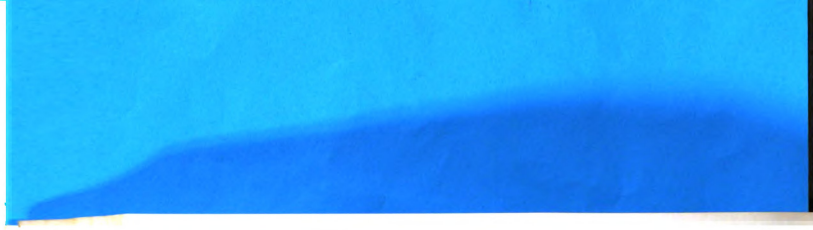


DATA APPENDIX

The data plotted in Figure 3 are contained in Table XIX.

TABLE XIX

ABSORBANCE AT VARIOUS WAVELENGTH SETTINGS OF DIFFERENT CONCENTRATIONS OF TETRALITHIUM PEROXYDIPHOSPHATE SOLUTIONS

pH Constant at 6.0

		Absorbance					
Concentration, N x 10^3	Slit Width, mm.	λ_{230} 0.80	λ_{236} 0.76	λ_{240} 0.70	λ_{250} 0.64	λ_{260} 0.60	λ_{270} 0.54
105.4		--	--	--	1.81	1.04	0.609
52.7		--	--	1.82	0.99	0.545	0.312
26.35		2.00	1.31	0.984	0.511	0.284	0.163
10.54		0.850	0.554	0.420	0.220	0.124	0.072
5.27		0.430	0.275	0.208	0.115	0.066	0.039

DATA APPENDIX

The data plotted in Figure 5 are contained in Table XX.

TABLE XX

EFFECT OF pH ON THE SPECTROPHOTOMETRIC DETERMINATION OF PEROXYDIPHOSPHATE

Addition of 17 per cent phosphoric acid

Concentration of peroxydiphosphate solutions = 0.02090N*

pH	Absorbance at 240 mμ, Slit Width of 0.70 mm.	
	1 Hour	2 Hours
9.6	0.635	0.635
9.4	0.642	0.642
8.0	0.670	0.670
7.3	0.729	0.729
7.2	0.744	0.744
7.1	0.760	0.760
7.0	0.790	0.790
6.1	0.910	0.910
6.0	0.920	0.920
5.6	0.940	0.938
5.5	0.938	0.936
4.3	0.840	0.820
3.0	0.790	0.778
2.3	0.790	0.776
1.8	0.795	0.775

*By the ferrous ammonium sulfate method.

DATA APPENDIX

The data plotted in Figure 6 are contained in Table XXI.

TABLE XXI

EFFECT OF pH ON THE SPECTROPHOTOMETRIC DETERMINATION OF PEROXYDIPHOSPHATE

Addition of 3N sulfuric acid

Concentration of perosydiphosphate solutions = 0.02644N*

pH	Absorbance at 240 mμ at Slit Width of 0.70 mm.		
	0.5 Hour	1 Hour	2 Hours
8.4	0.680	0.678	0.678
7.7	0.715	0.712	0.711
6.7	0.900	0.900	0.900
6.1	1.02	1.02	1.02
5.25	1.02	1.01	1.00
5.1	1.04	1.04	1.01
4.1	0.895	0.885	0.810
3.0	0.830	0.812	0.778
1.8	0.810	0.800	0.760
1.55	0.810	0.800	
1.55	0.809	0.798	0.760

*By the ferrous ammonium sulfate method.

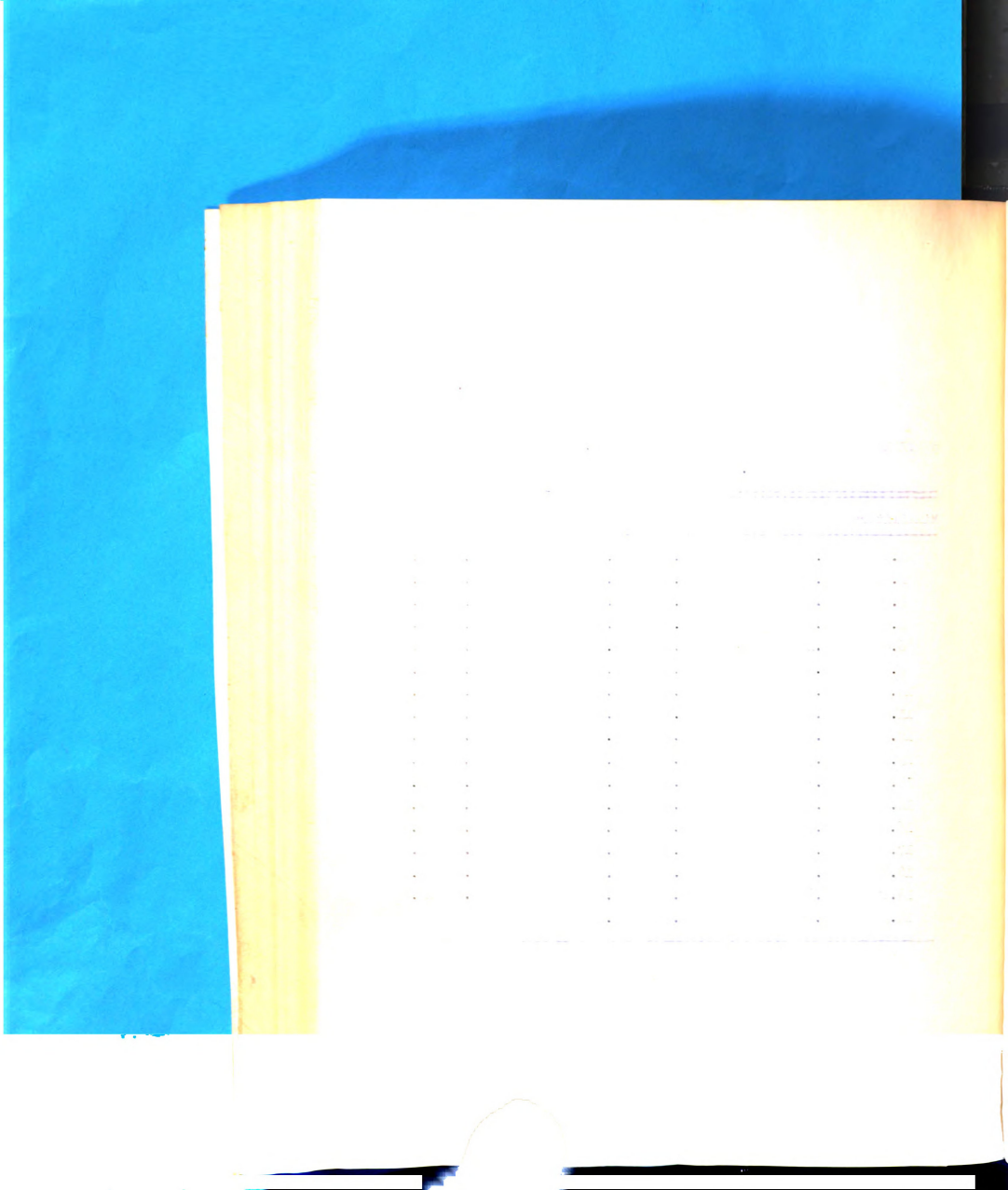
DATA APPENDIX

The data plotted in Figure 9 are tabulated in Table XXII.

TABLE XXII

pH TITRATION OF PEROXYDIPHOSPHORIC ACID WITH 0.1183N POTASSIUM HYDROXIDE
(200 ml. Fraction From Ion Exchange)

Milliliters	pH	Milliliters	pH	Milliliters	pH
0.00	2.01	20.00	2.89	32.00	5.71
1.00	2.04	21.00	3.15	34.00	6.25
2.00	2.05	21.20	3.21	36.00	6.68
4.00	2.09	21.40	3.30	38.00	7.00
6.00	2.11	21.60	3.40	39.00	7.11
8.00	2.15	21.80	3.49	39.50	7.16
10.00	2.20	22.00	3.60	40.00	7.20
11.00	2.30	23.00	3.99	41.00	7.48
12.00	2.42	23.60	4.08	42.00	7.70
13.00	2.45	24.00	4.20	44.00	8.99
14.00	2.45	24.40	4.28	46.00	10.35
14.50	2.47	24.60	4.30	48.00	10.70
16.00	2.49	24.80	4.34	50.00	10.95
17.00	2.51	25.00	4.39	52.00	11.10
18.00	2.59	26.00	4.52	54.00	11.12
18.20	2.60	28.00	4.85	56.00	11.21
18.80	2.69	30.00	5.19		



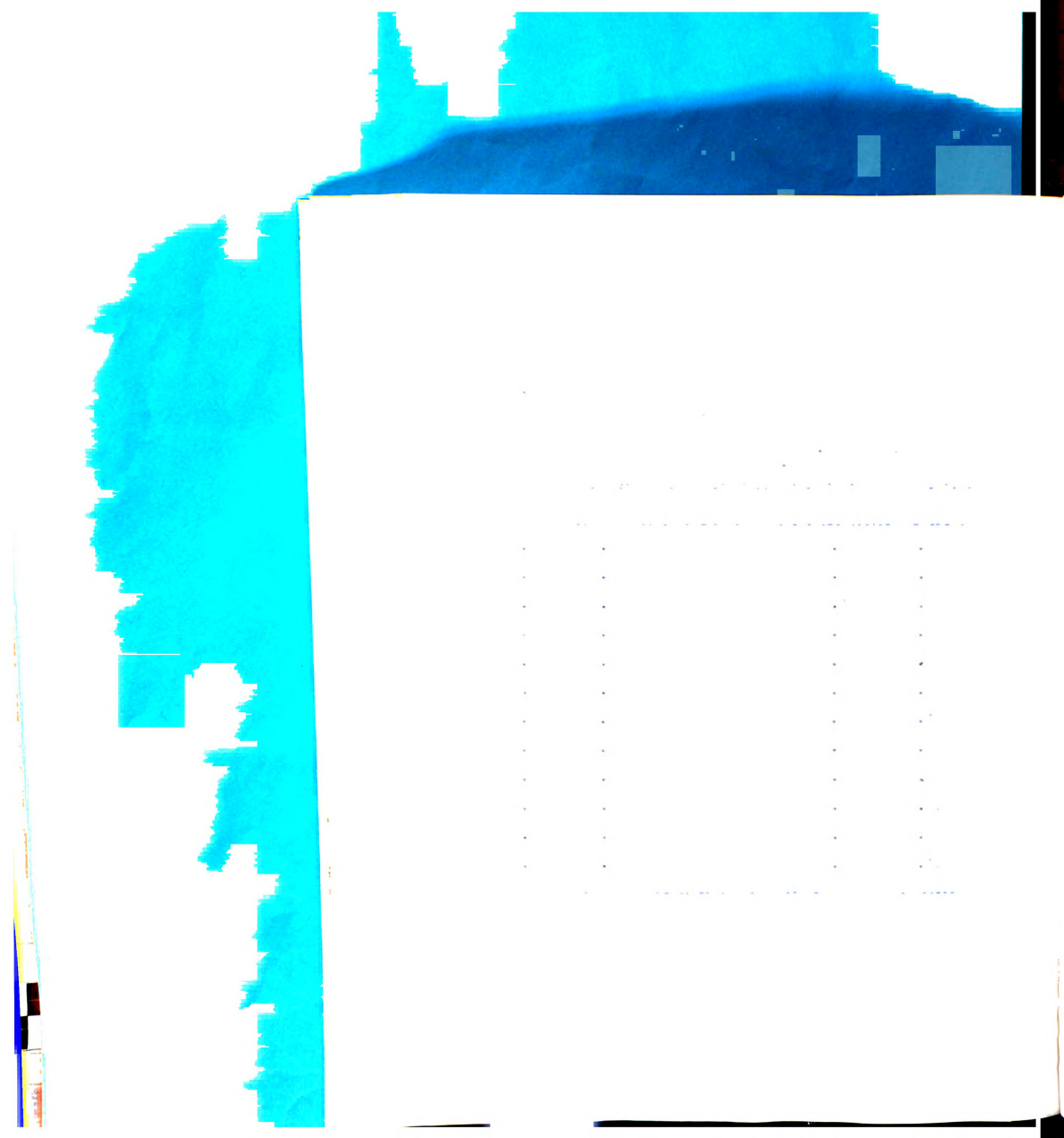
DATA APPENDIX

The data plotted in Figure 10 are contained in Table XXIII.

TABLE XXIII

pH TITRATION OF 0.579 GRAM TETRALITHIUM PEROXYDIPHOSPHATE WITH 0.1007N SULFURIC ACID

Milliliters	pH	Milliliters	pH
0.00	8.40	18.50	5.24
1.00	7.70	19.00	5.05
2.00	7.35	19.80	4.75
3.00	7.10	20.00	4.50
4.00	6.96	20.30	4.30
5.00	6.80	21.00	4.15
7.00	6.58	22.00	3.90
8.00	6.48	24.00	3.60
10.00	6.30	26.00	3.30
11.00	6.20	30.00	2.80
15.00	5.75	35.00	2.38
17.00	5.49	36.01	2.16



DATA APPENDIX

The data plotted in Figure 11 are contained in Table XXIV.

TABLE XXIV

CONDUCTOMETRIC TITRATION OF PEROXYDIPHOSPHORIC ACID WITH 0.1183N KOH FOLLOWING CONVERSION OF THE LITHIUM SALT BY ION-EXCHANGE 0.589 GRAM TETRALITHIUM PEROXYDIPHOSPHATE TAKEN

Milliliters	$\Lambda - 10^3$ umhos/cm.	Milliliters	$\Lambda - 10^3$ umhos/cm.
0.00	4.38	21.50	1.49
1.00	4.21	21.80	1.45
2.00	4.09	22.00	1.44
3.00	3.92	23.00	1.44
4.00	3.78	24.00	1.50
5.00	3.62	25.00	1.58
6.00	3.50	26.00	1.61
7.00	3.34	27.00	1.70
8.00	3.19	28.00	1.78
9.00	3.05	29.00	1.82
9.60	2.98	30.00	1.89
10.00	2.90	31.00	1.95
10.60	2.82	31.50	2.00
10.80	2.80	32.00	2.01
11.00	2.78	32.40	2.03
11.20	2.70	32.80	2.09
12.00	2.68	33.00	2.10
12.40	2.65	33.50	2.11
12.80	2.59	34.00	2.13
13.00	2.58	36.00	2.21
14.00	2.41	38.00	2.29
15.00	2.30	40.00	2.33
16.00	2.12	42.00	2.40
17.00	2.00	43.00	2.42
18.00	1.89	44.00	2.48
18.60	1.80	46.00	2.59
19.00	1.75	48.00	2.80
19.50	1.69	50.00	3.01
20.00	1.62	52.00	3.20
20.51	1.59	54.00	3.46
21.00	1.51	56.00	3.64

DATA APPENDIX

The data plotted in Figure 12 are contained in Table XXIV.

TABLE XXIV

CONDUCTOMETRIC TITRATION OF PHOSPHOTUNGSTIC ACID WITH ~~[illegible]~~
REFLUXING CONVERSION OF THE ETHYLENE DATE BY DIN-TEC ACID
0.250 GRAM THERMOLYSIS PHOSPHOTUNGSTIC ACID

Millilitres (~ 10⁻³ mhos/cm.	Millilitres (~ 10⁻³ mhos/cm.	
0.00	7.38	23.50
1.00	8.21	24.40
2.00	8.89	25.00
3.00	9.45	25.00
4.00	9.98	25.00
5.00	10.45	25.00
6.00	10.86	26.00
7.00	11.24	27.00
8.00	11.59	28.00
9.00	11.92	29.00
9.50	12.08	30.00
10.00	12.20	31.00
10.50	12.32	32.00
10.90	12.40	33.00
11.00	12.48	34.00
11.50	12.60	35.00
12.00	12.68	36.00
12.40	12.76	37.00
12.80	12.84	38.00
13.00	12.89	39.00
13.60	12.96	40.00
14.00	13.02	41.00
14.60	13.08	42.00
15.00	13.15	43.00
15.60	13.20	44.00
16.00	13.25	45.00
16.60	13.30	46.00
17.00	13.35	47.00
17.60	13.40	48.00
18.00	13.45	49.00
18.60	13.50	50.00
19.00	13.55	51.00
19.50	13.60	52.00
20.00	13.65	53.00
20.50	13.70	54.00
21.00	13.75	55.00

DATA APPENDIX

The nuclear magnetic resonance spectrum in Figure 13 was obtained using the following operational conditions:

RF Frequency 16.2 Mc. Nuclei P^{31}

Reference: zero H_3PO_4

Resolu: H

Instrument **data:**

RF atten: 18db

RF current: 40ua

Sw. Freq.: 1C 6F

Sw. Field: 1C 3F

Attenuation 2X

Ch. Sp. 5mm/sec.

Probe Insert 15 mm

Peak	cps
A	-119
or	-7.4 ppm