THE VOLUMETRIC DETERMINATION OF PEROXYDIPHOSPHATE

By

Thomas Chulski

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
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Department of Chemistry

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ABSTRACT

Tetrapotassium peroxydiphosphate was prepared by the method of Fichter and Gutzwiller (1) by electrolyzing a solution containing 302.2 g. monopotassium orthophosphate, 198 g. potassium hydroxide, 120 g. potassium fluoride, and 0.355 g. potassium chromate per liter using platinum electrodes. Their findings were substantiated except for the claim that the final product was pure white. The tetrapotassium peroxydiphosphate always contained some chromate. No method of crystallization could be found that would remove the chromate.

Tetrapotassium peroxydiphosphate was precipitated from the electrolyte of Fichter and Gutzwiller by adding solid potassium hydroxide. The product also contained chromate but the precipitation served as an efficient method for the preparation of a rather impure chromate containing tetrapotassium peroxydiphosphate which was found to be suitable as a starting material for the preparation of tetralithium peroxydiphosphate tetrahydrate.

A solution of lithium peroxydiphosphate was prepared from a solution of the crude tetrapotassium peroxydiphosphate by precipitating the potassium, phosphate, and fluoride by adding a lithium perchlorate solution. The peroxydiphosphate was precipitated from the solution as tetralithium peroxydiphosphate tetrahydrate by the addition of methanol. The material was chromate free.

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A 0.1 normal solution of the tetralithium peroxydiphosphate tetrahydrate had a pH of 10.2. It decomposed to the extent of five parts per thousand in 49 days. At lower pH values the solution was less stable.

Peroxydiphosphate was determined by adding excess ferrous ions to a solution of peroxydiphosphate and back titrating the excess with potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Reaction mixtures 0.25 to 1.0 molar in sulfuric acid and 0.25 to 2.0 molar in perchloric acid were found to give satisfactory results. In 1.0 to 2.0 molar hydrochloric acid solutions plausible results were obtained. The amount of excess ferrous ion was not critical. The determination could be carried out in the presence of phosphate.

The direct potentiometer titration of peroxydiphosphate with a ferrous ammonium sulfate solution was accomplished. Satisfactory results were obtained when the reactio mixture was 0.25 to 0.50 molar in sulfuric acid or 0.50 molar in phosphoric acid.

The equivalence point in the titration of peroxydiphosphate with a ferrous ammonium sulfate solution was successfully determined by means of the dead stop end point technique. Satisfactory results were obtained if the peroxydiphosphate solution was 0.25 to 1.0 molar in sulfuric acid, 0.50 to 1.0 molar in phosphoric acid, or 0.25 to 0.50 molar in perchloric acid.

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An iodometric determination of peroxydiphosphate was achieved. The rate of reaction between peroxydiphosphate and iodide ions was found to be influenced profoundly by the acidity of the reaction mixture; a small increase in acidity greatly increased the rate of reaction. The determination was successful both in the absence and presence of phosphate when the reaction mixture was 1.0 molar in sulfuric acid.

(1) Fichter, F. and Gutzwiller, E., Helv. Chim. Acta., 11, 323 (1928).

DEDICATION

The author wishes to dedicate this thesis to all those people who made his education possible. Special mention is made of Dr. Elmer Leininger under whose kind and efficient direction this work was done.

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I. INTRODUCTION

Phosphorus forms two peroxy acids: peroxymonophosphoric acid, H_3PO_5, and peroxydiphosphoric acid, $H_4P_2O_8$. Peroxymonophosphoric acid has been used as a reagent for the detection of manganese (23). No use has been made of peroxydiphosphoric acid or its salts in analytical chemistry. Before applications of either can be made more information is needed on their characteristic reactions as there is but little information on them in the literature.

Hence the purpose of this work was twofold: to work out methods for the determination of peroxydiphosphate, and to characterize it more fully.

II. HISTORICAL

Petrenko (15) reported the preparation of a sodium peroxyphosphate by treating sodium phosphate with hydrogen peroxide.

Pinerva-Alvarez (16) claimed to have isolated a compound having the formula $NaPO_4$ but Rudenko (20) showed that it was an indefinite mixture of sodium phosphate and sodium peroxide. Rudenko also showed that the material reported by Petrenko was sodium phosphate containing hydrogen peroxide of crystallization.

In 1910 Schmidlin and Massini (23) prepared peroxymonophosphoric acid by treating phosphorus pentoxide at a low temperature with hydrogen peroxide of thirty per cent strength or greater. They represented the reaction as

$$P_2O_5+2H_2O_2+H_2O=2H_3PO_5.$$

The concentrated solution decomposed to the extent of about thirty per cent in two days but diluted solutions retained their activity much longer. Acid solutions were much more stable than neutral or alkaline solutions.

The diluted reaction mixture had strong oxidizing properties. It liberated iodine instantly from iodides. Aniline was oxidized first to nitrosobenzene and then to nitrobenzene. Manganous ion was oxidized, presumably to permanganate, even at room temperature. Heavy metal salts such as silver, iron, and manganese did not precipitate peroxymonophosphates in acid solution but did so in neutral or alkaline solution. Decomposition started immediately with the formation of orthophosphate and oxygen with ozone being formed in some cases.

By treating syrupy pyrophosphoric acid with 30 per cent hydrogen peroxide Schmidlin and Massini obtained the formation of both peroxydiphosphoric, $H_4P_2O_8$, and peroxymonophosphoric acids. The peroxymonophosphoric acid was determined by titrating the iodine liberated immediately from the iodide ion with thiosulfate solution; the peroxydiphosphoric acid by the additional iodine liberated after standing for 24 hours. Before the addition of the potassium iodide the excess hydrogen peroxide was determined by titrating it with potassium permanganate solution.

Schmidlin and Massini used the solution of peroxymonophosphoric acid to detect manganese. In this application hydrogen peroxide would interfere; hence it was destroyed electrolytically. A clay cathode chamber filled with dilute phosphoric acid was used. Electrolysis was carried out until the anolyte no longer decolorized potassium permanganate solution.

Schmidlin and Massini stated that the electrolysis of a dilute phosphoric acid solution with hydrogen peroxide present formed peroxymonophosphoric acid at the anode. No experimental conditions were given.

With the exception of the unstable heavy metal peroxymonophosphates Schmidlin and Massini did not attempt to prepare the salts of either peroxy acid.

D'Ans and Friedrich (1) claimed that they independently did the same work as Schmidlin and Massini (23) but that the latter published first. D'Ans and Friedrich stated that their results were the same as those of Schmidlin and Massini.

Siebald (24) claimed to have formed a peroxyphosphoric acid by the action of 30 per cent hydrogen peroxide on phosphorus oxychloride and that a true peroxyphosphate was formed by neutralizing the solution with alcoholic sodium hydroxide. However Husain and Partington (10) were not able to obtain peroxyphosphoric acid by this method.

Fichter and Müller (6) developed a method for the simultaneous preparation of peroxymonophosphate and peroxydiphosphate by the electrolysis of a solution two molar in respect to dipotassium hydrogen phosphate, four molar in potassium fluoride and containing 0.32 g. potassium chromate per liter.

Fichter and Müller studied the influence of temperature and found that the current efficiency increased with decreasing temperature. The range of temperature from 25 to 0° C. was studied.

The current efficiency decreased with increasing current density in the range from 1.06 to 0.01 ampere per square centimeter. A current density of 0.03 ampere per square centimeter was taken as a practical optimum current density. Platinum electrodes were used and in this connection they stated that the surface condition of the platinum anode had a great effect on the current efficiency but in an unexplainable manner.

Prolonged electrolysis favored the formation of peroxymonophosphate.

Ammonium phosphate solutions containing ammonium fluoride and ammonium chromate were employed; both peroxydiphosphate and peroxymonophosphate were formed. The same result was obtained using rubidium salts. Sodium phosphate was not soluble enough to be employed.

Fichter and Müller stated that if a phosphoric acid solution containing hydrofluoric acid and a little monopotassium hydrogen phosphate were electrolyzed the solution gave a pronounced reaction with manganous ion. No experimental conditions were given.

In all cases the peroxymonophosphate was determined by titrating the iodine liberated immediately from acidified potassium iodide solution, the peroxydiphosphate plus the peroxymonophosphate by the iodine liberated upon standing for 24 hours. No attempt was made to prepare solid peroxyphosphates.

Fichter and Rius y Mirò (7) studied the electrolysis further. They repeated much of the work of Fichter and Müller and obtained essentially the same results. They recommended a solution 2.2 molar in respect to fluoride ion, and containing 0.60 g. potassium chromate per liter. The practical optimum current density at 5° C. was 0.03 ampere per square centimeter. Decreasing the concentrations decreased the yield.

It was shown that a high cathode density prevented the cathodic reduction of peroxydized material and that the chromate served as a cathodic depolarizer. A compartmental cell did not work as efficiently as having chromate present.

The mole ratio of potassium to phosphate ions before the addition of the potassium fluoride was varied from 1.67 $K^+:PO_4^{-3}$ to 4 $K^+:PO_4^{-3}$. With a ratio of 3.5 $K^+:PO_4^{-3}$ and higher there was no yield at all of peroxydized material. The maximum yield of peroxydized product occurred at a ratio of 2.5 - 2.6 $K^+:PO_4^{-3}$. The yield of peroxydiphosphate went through a maximum at that point while the yield of peroxymonophosphate decreased steadily with increasing amounts of potassium.

The function of the potassium fluoride in solutions having a potassium to phosphate ration of 2.5 - 2.6 : 1.0 was to increase the potential on the anode. Oxidation occurred without fluoride being present but the efficiency was only one half of that obtained with fluoride present. It was claimed that in alkali poor solutions the potassium fluoride also served to suppress the ionization of the monopotassium phosphate thereby increasing the yield.

Fichter and Rius y Mirò were able to prepare pure tetrapotassium peroxydiphosphate, $K_4P_2O_8$. A solution containing 30.22 g. potassium dihydrogen phosphate, 19.8 g. potassium hydroxide, 12 g. potassium fluoride, and 0.0355 g. potassium chromate in 100 ml. solution was electrolyzed in a large platinum crucible which served as the anode. A current density of 0.02 to 0.03 ampere per square centimeter was used. The electrolyte was cooled to 0° C. in an ice bath. The solution was stirred mechanically during electrolysis. Electrolysis was carried on until 1.0 ml. of the electrolyte required 18 - 19 ml. of 0.1 normal sodium thiosulfate for the iodine liberated from acidified potassium iodide solution. (Note: for 100 per cent conversion of the phosphate to peroxydiphosphate and with no loss of water during electrolysis 21.7 ml. would be required.) This high content of peroxydiphosphate was attained at the expense of good current efficiency.

The electrolyzed solution was evaporated with constant stirring on a water bath. The first crystals to come down were largely unchanged phosphate. After further evaporation the bulk of the peroxydiphosphate precipitated as fine crystals. Two recrystallizations in this manner gave a white product which, when analyzed for phosphorus, potassium, and active oxygen, gave the empirical formula $K_4P_2O_8$. Further recrystallization was not advised because decomposition to phosphate and oxygen occurred.

A solution of the purified product in water was not stable. A 50 per cent decomposition occurred in five days.

When the purified material was dissolved in potassium iodide solution, iodine was not liberated. Acidification with acetic acid did not cause the liberation of iodine. However when sulfuric acid was used iodine was liberated immediately. It was stated that an alkaline solution of tetrapotassium peroxydiphosphate precipitated the higher oxides of cobalt, nickel, and lead. Aniline was oxidized to nitro or nitrosobenzene followed by a brown color. Indigo was decolorized. Fichter and Rius y Mirò further showed that their product did not contain hydrogen peroxide of constitution but was the salt of a true peroxy acid by its failure to give typical hydrogen peroxide reactions with chromic, permanganic, or titanic acid.

The tetrapotassium peroxydiphosphate did not form a precipitate with magnesia mixture.

In strong phosphoric acid solution the following disproportionation reaction took place:

$$H_4P_2O_8+H_2O = H_3PO_5+H_3PO_4.$$

This reaction was suggested as a method for preparing a solution of peroxymonophosphoric acid to be used in testing for manganous ion.

The electrolysis was believed to take place in two steps as follows:

$$2K_2HPO_4 = K_4P_2O_7+H_2O$$

$$K_4P_2O_7+O = K_4P_2O_8$$

The fact that peroxydiphosphate was formed when a solution of potassium pyrophosphate was electrolyzed was taken as verification of the above reactions.

Rius y Mirò published the information in reference (7) above independent of Fichter in a journal of limited circulation (17). In further work (18) he showed that peroxymonophosphoric acid reacts with hydrogen peroxide to form oxygen and orthophosphate.

Fichter and Bladergroen (4) prepared a solution of peroxymonophosphoric acid by treating a 5 molar solution of orthophosphoric acid with fluorine. When the solution of peroxymonophosphoric acid prepared in this manner was added to a dilute manganous sulfate solution a violet color was produced. Schmidlin and Massini (23) interpreted this as the formation of permanganic acid. Fichter and Bladergroen concluded that the color was due to the formation of the very stable manganic phosphate as the five characteristic absorption bands of permanganic acid were never observed in a spectrometer; only a uniform darkening from green to violet was observed.

Fichter and Bladergroen suggested that the peroxymonophosphate was formed as the result of two successive reactions. The first yielded peroxydiphosphoric acid by the removal of hydrogen: $2H_3PO_4 + F_2 = H_4P_2O_8 + 2HF$. The peroxydiphosphoric acid then hydrolyzed immediately to peroxymonophosphoric acid because of the high acid concentration (17): $H_4P_2O_8 + H_2O = H_3PO_5 + H_3PO_4$.

No solid compounds containing peroxidized phosphorus were obtained.

Fichter and Gutzwiller (5) improved the method of Fichter and Rius y Mirò (7) for preparing tetrapotassium peroxydiphosphate. The composition of the electrolyte and the conditions of electrolysis were essentially the same as those of Fichter and Rius y Mirò. However the electrolysis was carried out at three intervals so that any peroxymonophosphate formed decomposed in the alkaline solution.

The electrolyte contained 302.2 g. monopotassium orthophosphate, 198 g. potassium hydroxide, 120 g. potassium fluoride and 0.355 g. potassium chromate per liter of solution. Two hundred fifteen milliliters of this solution was electrolyzed in a platinum crucible. The crucible served as the anode and a bent rapidly rotating platinum wire served as the cathode. The temperature was kept below 14° C. by external cooling. The anode current density was 0.023 ampere per square centimeter, but neither the total current nor the total anode surface area was mentioned. After three hours the electrolysis was interrupted and the electrolyte allowed to stand quietly overnight at room temperature. The peroxymonophosphate formed during the electrolysis decomposed in the alkaline solution to orthophosphate, oxygen, and some peroxydiphosphate. The amount of peroxydiphosphate in solution was determined by treating an aliquot with potassium iodide solution acidified with two normal sulfuric acid, heating gently, and titrating the liberated iodine with 0.1 normal sodium thiosulfate solution. A 45.53 per cent conversion of the phosphate to peroxydiphosphate was obtained. After a second electrolysis of two hours duration the resulting solution was allowed to stand overnight. The percentage conversion was 72.45. A third electrolysis of one hour duration followed by standing overnight increased the per cent converted to 79.65. By further electrolysis a greater conversion could be obtained but only with a disproportionately large expenditure of current; maximum conversion was stated to be about eighty five per cent.

After the third electrolysis the solution was evaporated in a porcelain vessel on a water bath. Mechanical stirring was used. A current of air was blown across the surface so that the temperature of the solution did not exceed 80° C. After cooling the mother liquor was removed from the crystals by centrifugation in a porcelain centrifuge.

Crystallizing three times in this manner yielded a product 96.4 to 99.8 per cent pure. No analytical data were given.

Barium peroxydiphosphate tetrahydrate was prepared by adding a solution of the tetrapotassium peroxydiphosphate to an aqueous solution of barium chloride. It was insoluble in water, but soluble in acetic, hydrochloric, and nitric acids. The concentrations of the acids in which the barium peroxydiphosphate dissolved were not stated.

Zinc peroxydiphosphate tetrahydrate was formed by the interaction of potassium peroxydiphosphate and zinc sulfate solutions. It was described as being somewhat soluble in water.

Anhydrous lead peroxydiphosphate was precipitated from a lead nitrate solution in the same manner. The lead peroxydiphosphate dissolved in warm dilute nitric acid.

Analytical data were given for the above salts of peroxydiphosphoric acid. In all cases the experimental values were close to the calculated ones.

Fichter and Gutzwiller also prepared rubidium peroxydiphosphate. It was prepared by electrolyzing a rubidium phosphate solution containing fluoride and chromate. The electrolyte was concentrated under vacuum. Unchanged rubidium phosphate precipitated first, then rubidium peroxydiphosphate. It was stated that rubidium peroxydiphosphate was too soluble to prepare easily. No analytical data were given.

Ammonium peroxydiphosphate was obtained in solution by the electrolysis of an ammonium phosphate solution containing fluoride and chromate. The solution of the ammonium salt was not stable, apparently due to the oxidation of the ammonium ion as nitrite and nitrate could be detected in the solution.

Peroxydiphosphate did not form a precipitate with magnesia mixture. A separation from phosphate was suggested but no experimental work was recorded.

Rius y Mirò (19) showed that peroxymonosulfuric acid could be titrated potentiometrically with a standard solution of ferrous sulfate. A well defined break occurred in the potential curve if manganous ion was present. Peroxydisulfuric acid did not interfere unless its concentration was high. Rius y Mirò stated that peroxymonophosphoric acid behaved in a manner entirely analogous to peroxymonosulfuric acid but gave no data.

Rius y Mirò also titrated peroxymonosulfuric acid potentiometrically in the presence of peroxydisulfuric acid with a sodium sulfite solution containing five per cent of 95 per cent ethanol. He stated that peroxymonophosphoric acid could be determined in the same manner but gave no data.

The peroxymonophosphoric acid was prepared by the hydrolysis of tetrapotassium peroxydiphosphate in 50 per cent phosphoric acid.

Husain and Partington (10) studied the action of hydrogen peroxide upon lithium, sodium, potassium, rubidium, cesium, calcium, strontium, barium, and thallium phosphates. In all cases no peroxy compound was formed; only phosphates containing hydrogen peroxide of crystallization were obtained. As criteria for phosphates containing hydrogen peroxide of crystallization the following were used: (1) the compounds did not oxidize acidified manganous ion to permanganate ion; (2) acidified aniline solution was not oxidized to nitrosobenzene and nitrobenzene, e.g., a color change from green to brown did not take place; (3) silver nitrate did not give a yellow precipitate which soon turned brown (except when ammonium ion was present); (4) the compound gave the reactions characteristic of hydrogen peroxide, (A) decomposition of permanganic acid, (B) blue color with chromic acid and ether, (C) yellow color with titanic acid.

Phosphorus oxychloride with hydrogen peroxide gave no peroxidized material.

The electrolysis of lithium, sodium, or thallium phosphate solution having present fluoride and chromate gave no peroxyphosphate. When rubidium, cesium, or ammonium phosphate was used peroxyphosphate was formed.

A detailed study of the electrolysis of a secondary ammonium phosphate solution containing ammonium fluoride and ammonium chromate was made. The influence of anodic current density, duration of electrolysis, temperature, and the concentrations of ammonium phosphate, fluoride, and chromate was studied. The most favorable condition for the formation of ammonium peroxydiphosphate was found to be the electrolysis of a four molar secondary ammonium phosphate solution three molar in ammonium fluoride and containing 0.32 g. ammonium chromate per liter. The optimum current density was 0.0146 ampere per square centimeter at 0° C. The longer the electrolysis the greater the yield.

The peroxymonophosphate plus the peroxydiphosphate content of the electrolyte was determined by adding an aliquot immediately after the cessation of the electrolysis to an acidified potassium iodide solution and after standing titrating the liberated iodine with standard sodium thiosulfate solution. The peroxydiphosphate was determined by treating an aliquot similarly after the electrolyte had stood overnight. The acid used to acidify the potassium iodide solution and its concentration in the reaction mixture was not stated, neither was the time of standing.

Husain and Partington attempted to prepare pure ammonium peroxydiphosphate by evaporating the electrolyzed solution of secondary ammonium phosphate at room temperature in vacuum over anhydrous calcium chloride and over sodium hydroxide. Even the fourth crop of crystals was chiefly ammonium phosphate. The residual mother liquor was evaporated to dryness. The solid material so obtained contained peroxydiphosphate. No analytical data were given.

Saturating the electrolyzed solution with secondary ammonium phosphate did not deposit crystals of ammonium peroxydiphosphate.

When freshly electrolyzed solution was treated with 95 per cent ethanol and silver nitrate a precipitate was formed which contained both the phosphate and the peroxyphosphates.

No precipitate was obtained when the electrolyte was acidified with dilute or glacial acetic acid.

Barium carbonate did not precipitate the phosphate.

Barium hydroxide precipitated phosphate, fluoride, and chromate; the filtrate contained active oxygen. The filtrate was freed of ammonia by a current of air under reduced pressure over concentrated sulfuric acid. The excess barium was precipitated by passing in carbon dioxide. Husain and Partington concluded that "the perphosphate probably decomposed during the lengthy process."

The electrolysis of a concentrated solution of secondary rubidium phosphate or secondary cesium phosphate with chromate present gave both peroxymonophosphate and peroxydiphosphate even without fluoride being present. By evaporating the electrolyzed solution at ordinary temperature and reduced pressure over sulfuric acid a solid product containing active oxygen was obtained. Neither pure rubidium nor cesium peroxydiphosphate could be prepared in a pure condition because of their extreme solubilities.

Toennies (27) suspended phosphorus pentoxide in acetonitrile and to the suspension added a solution of hydrogen peroxide and water in acetonitrile. An energetic reaction took place; peroxymonophosphoric acid being formed. External cooling was necessary to keep the reaction mixture from exceeding room temperature.

Rather small quantities of material were used. In one instance 5.55 millimoles of phosphorus pentoxide was suspended in 1.5 ml. of acetonitrile. To the suspension was added 12.94 millimoles of hydrogen peroxide (80 to 90 per cent hydrogen peroxide was used) and 4.03 millimoles of water in 1.40 ml. of acetonitrile.

No attempt to isolate the peroxymonophosphate from the reaction mixture was made.

Phosphorus pentoxide and hydrogen peroxide did not react in ether or isoamyl alcohol.

Schenk and Rehaag (22) prepared the anhydride, P_2O_6, of peroxydiphosphoric acid. By heating phosphorus pentoxide in a stream of oxygen at approximately 190° C. and eight millimeters of mercury pressure a violet solid sublimed to the cooler portion of the apparatus. A solution of the violet colored material did not form a color with titanic sulfate solution. It liberated iodine from potassium iodide solution. Aniline in acid solution was oxidized in the cold to nitrosobenzene and nitrobenzene. With manganous sulfate solution a violet color was formed.

It was noted that the peroxydiphosphoric anhydride was insoluble in chloroform but that phosphoric anhydride was soluble.

Maxted (13) studied the detoxification of platinum hydrogenation catalysts in the hydrogenation of crotonic acid in acetic acid solution. Toxifying agents used were cysteine, thionaphthol, and thiophene. Detoxicating agents studied were potassium persulfate, perchromic acid, and peroxymonophosphoric acid. The peroxymonophosphoric acid was the most efficient detoxifier with all three of the toxifying agents studied.

The peroxymonophosphoric acid was made by treating phosphoric pentoxide with 30 per cent hydrogen peroxide. The entire reaction mixture was added to the hydrogenation pipette.

In further work (14) Maxted showed that the double bond of crotonic acid was not attacked by the peroxymonophosphoric acid under the conditions used.

Machu (12) credits Degussa (2) with the preparation of pure ammonium peroxydiphosphate, $(NH_4)_4P_2O_8 \cdot 2H_2O$. A hot saturated solution of ammonium chlorate was added to a cold saturated solution of potassium peroxydiphosphate. The potassium chlorate was filtered off and the ammonium peroxyphosphate precipitated from the filtrate by the addition of methyl alcohol.

Degussa (3) also prepared ammonium peroxydiphosphate by the electrolysis of a triammonium phosphate solution containing a small amount of chromate. By evaporating in vacuum or by cooling below 0° C. pure ammonium peroxydiphosphate was obtained.

III. PREPARATION OF PEROXYDIPHOSPHATE IN SOLUTION

Fichter and Gutzwiller (5) electrolyzed 215 ml. of a solution containing 302.2 g. monopotassium orthophosphate, 198 g. potassium hydroxide, 120 g. potassium fluoride, and 0.355 g. potassium chromate per liter in a platinum dish. The platinum dish served as the anode and a rapidly rotating bent platinum wire served as the cathode. An anode current density of 0.023 ampere per square centimeter was used. They did not specify the anode area, the total current, nor the voltage applied across the electrodes.

In duplicating their work 200 ml. of solution of the above composition was electrolyzed in a platinum dish of approximately 210 ml. capacity and 143 square centimeter inner surface area. The platinum dish served as the anode and a rapidly rotating bent platinum wire was used as the cathode. A voltage of 7.5 volts across the electrodes gave a current density of 0.015 ampere per square centimeter at the anode. During electrolysis the electrolyte was cooled in an ice bath.

Since Fichter and Müller (6) stated that the surface condition of the anode had a marked effect on the efficiency of the electrolytic oxidation but did not explain how the anode should be conditioned to obtain maximum efficiency work was done on the effect of various treatments of the anode in connection with the interruption technique of Fichter and Gutzwiller (5).

In the run designated herein as run number 1 the platinum dish was conditioned by polishing it with sea sand and then with a cerium oxide optical polish. Immediately before it was used it was heated to a dull red heat over a Fisher burner. Electrolysis was carried out for three hours using the conditions described above. Upon cessation of the electrolysis the electrolyte was allowed to stand quietly in the platinum dish at room temperature for overnight.

The next day a two ml. aliquot of the electrolyte was pipetted into an iodine flask. It was diluted with 50 ml. of water; then three grams of potassium iodide, one gram boric acid, and five milliliters of six normal sulfuric acid were added. After standing for at least 12 hours the liberated iodine was titrated with 0.1 normal standardized sodium thiosulfate solution. The amount of tetrapotassium peroxydiphosphate in solution was calculated from the amount of iodine liberated. Electrolysis was carried out again but for only two hours. The electrolyte was allowed to stand overnight as before.

The tetrapotassium peroxydiphosphate in a two ml. aliquot of the solution that had been electrolyzed for five hours was determined as above. Electrolysis was carried out again for one hour.

The data are given in Table I.

In run 2 the platinum dish was conditioned by polishing it again with the cerium oxide optical polish followed by ignition at a bright red temperature. Two hundred milliliters of the electrolyte was processed in the same manner as in run 1.

In run 3 the platinum dish was conditioned by polishing it with the optical polish. The nitric acid was boiled in the dish.

In run 4 the platinum dish was conditioned by boiling concentrated hydrochloric acid in it.

In runs 5 and 6 the platinum dish was conditioned by filling it with concentrated hydrochloric acid and allowing it to stand at room temperature for three days before using it.

TABLE I

EFFECT OF VARIOUS TREATMENTS OF THE ANODE UPON THE AMOUNT OF PHOSPHATE OXIDIZED TO PEROXYDIPHOSPHATE

Run Number	% KH_2PO_4 Oxidized to $K_4P_2O_8$ Hours Electrolysis 3	5	6
1	22.3	40.8	48.5
2	27.9	41.7	51.2
3	15.1	25.3	32.7
4	24.7	38.2	46.3
5	39.7	57.9	67.3
6	24.3	37.7	46.1

For anode treatment, see text.

The data in Table I cannot be compared directly to that of Fichter and Gutzwiller as they did not specify the total current or voltage used. However platinum dishes of approximately the same volume of necessity must have approximately the same inner surface area. If the percentages of phosphate converted to peroxydiphosphate as listed in Table I were to be multiplied by the factor, current density used by Fichter and Gutzwiller: current density used herein, about the same yield of peroxydiphosphate in solution would be indicated as that obtained by Fichter and Gutzwiller except for runs 3 and 5. See Table II.

TABLE II

AMOUNT OF PHOSPHATE OXIDIZED TO PEROXYDIPHOSPHATE AFTER SIX HOURS ELECTROLYSIS WHEN CALCULATED TO THE CURRENT DENSITY USED BY FICHTER AND GUTZWILLER (5)

Run Number	% KH_2PO_4 Oxidized to $K_4P_2O_8$
1	72.8
2	76.8
3	49.1
4	69.5
5	100.0
6	69.2

For anode treatment, see text.

It is seen from the data in Table I that conditioning the surface with hot nitric acid lowered the yield of peroxydiphosphate in solution. However of all the other procedures tried none was significantly better than the others. As a matter of convenience the hydrochloric acid treatment was taken as the procedure to be followed in the immediate subsequent work.

The separation of pure potassium peroxydiphosphate from the electrolyte would be facilitated by having present only a small amount of phosphate. Hence an attempt was made to convert all the phosphate to peroxydiphosphate.

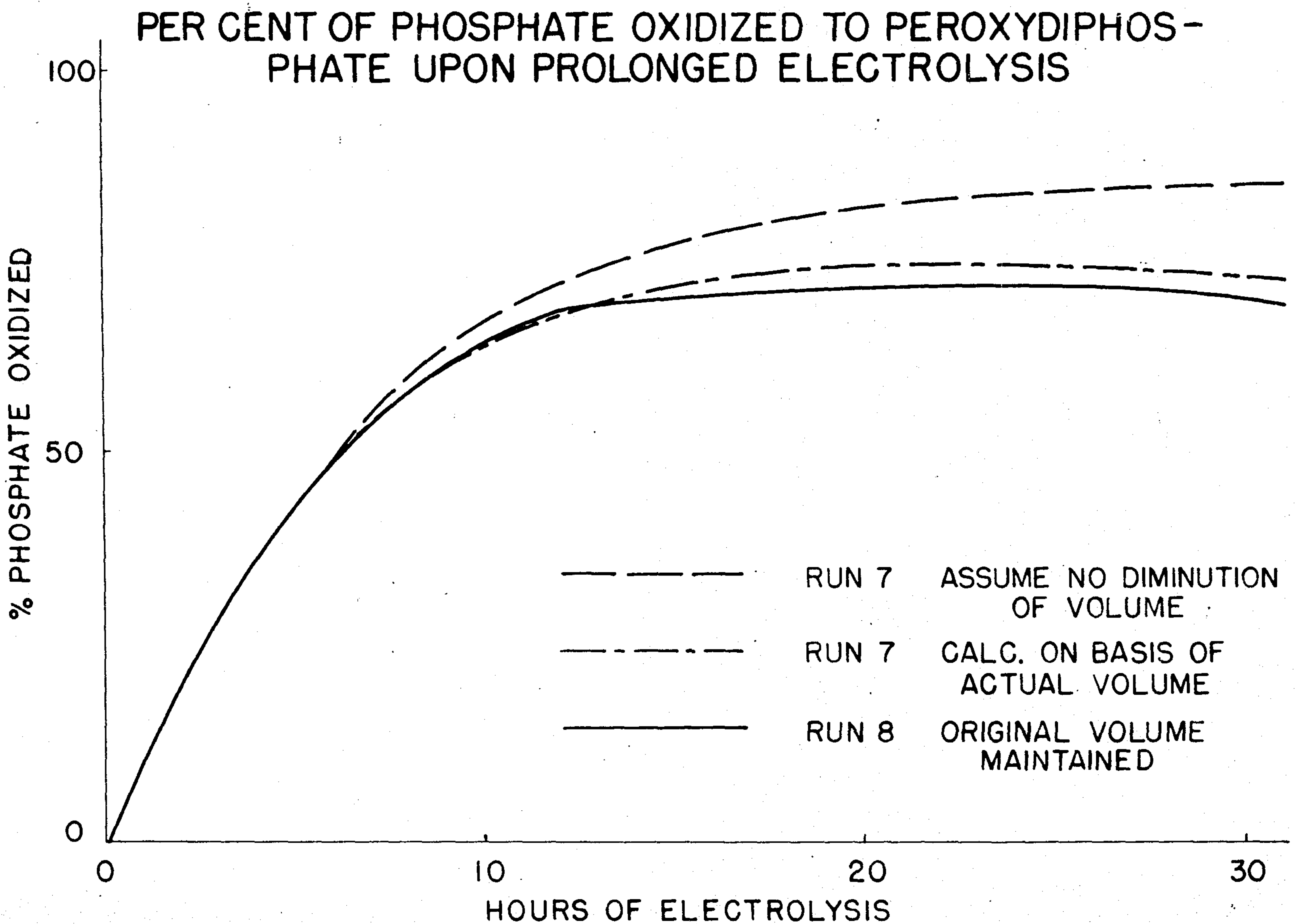
The platinum dish described above was used. It was conditioned by filling it with concentrated hydrochloric acid and allowing it to stand for three days before being used.

In run 7, 200 ml. of solution of the above composition was electrolyzed for six hours. During electrolysis the solution was cooled in an ice bath. A potential of 7.5 volts across the electrodes gave a current of 2.2 amperes. Upon cessation of the electrolysis the electrolyte was allowed to stand quietly at room temperature in the platinum dish for overnight.

The next day a two milliliter aliquot was pipetted into an iodine flask. Twenty-five milliliters of water and six milliliters six normal sulfuric acid were added. Immediately after the addition of the sulfuric acid 50 ml. of standardized 0.1 normal ferrous ammonium sulfate solution was added by pipette. After standing for five minutes the excess ferrous ion was titrated with 0.1000 normal potassium dichromate solution using diphenylamine sodium sulfonate as indicator. The amount of peroxydiphosphate in solution was calculated from the amount of ferrous ion oxidized by the two milliliter aliquot of the electrolyte. The percentage of the phosphate oxidized was calculated assuming no diminution in volume. The volume of the electrolyte was then measured in a graduated cylinder. Assuming that there had been no mechanical loss of solution and that the diminution in volume was due to the electrolysis of water the percentage of phosphate oxidized to peroxydiphosphate was calculated on the basis of the measured volume of the electrolyte.

Electrolysis was carried out again for six hours.

This procedure was repeated a number of times. The data are presented graphically in Figure 1.



PER CENT OF PHOSPHATE OXIDIZED TO PEROXYDIPHOSPHATE UPON PROLONGED ELECTROLYSIS

FIGURE I

Run 8 was a parallel experiment but the volume of the electrolyte was measured after each six hour period of the electrolysis and the loss in volume made up by adding water before sampling. The data are presented graphically in Figure 1 and tabulated in the data appendix.

Duplicates of runs 8 and 9 verified the results obtained.

Fichter and Rius y Mirò (7) and Fichter and Gutzwiller (5) claimed that the electrolytic oxidation of the phosphate to peroxydiphosphate could be made nearly complete. Figure 1 suggests that their data were in error inasmuch as they did not consider the diminution in volume during the electrolysis.

From Figure 1 it is seen that the optimum time of electrolysis is 12 hours.

Information was sought to explain why more than 70 per cent of the phosphate could not be oxidized.

The apparent pH of the solution before electrolysis and during electrolysis was determined with a Beckman pH meter, model G. The initial pH was 11.1 and it did not change during the electrolysis.

The potential on the anode was followed during electrolysis by using a saturated calomel electrode as a reference electrode. A potentiometer was used to measure the potential existing between the calomel electrode and the platinum dish. It was found that the measured potential varied with the position of the calomel electrode. However when the calomel electrode was placed very near the platinum dish reproducible readings were obtained.

Starting with a fresh portion of electrolyte the measured potential increased gradually from 1.91 volts to 2.07 volts in six hours. After standing overnight the electrolysis was continued. The initial potential was 1.89 and increased gradually to 2.07 volts in six hours. Decreasing the applied voltage so as to get the original potential on the anode did not increase the yield of tetrapotassium peroxydiphosphate in solution.

An attempt was made to decrease the potential on the anode by adding dipotassium phosphate, potassium hydroxide, and phosphoric acid. All increased the anode potential. The yield of peroxydiphosphate was not increased.

With the above information in mind the effect of various prior treatments of the anode on the efficiency of the electrolytic oxidation was studied further.

In runs 10, 11, 12, 13, and 14, 200 ml. of solution of the composition used previously was electrolyzed for six hours in the platinum dish as above. After the electrolysis the volume of the electrolyte was determined by means of a graduated cylinder whereupon the electrolyte was transferred to a Pyrex flask. Enough water, five to ten milliliters, to bring the volume of the electrolyte to the original volume was used to rinse the platinum dish. The rinsings were added to the electrolyte in the Pyrex flask. The platinum dish was thoroughly rinsed with distilled water and filled with concentrated hydrochloric acid.

The next day the platinum dish was thoroughly rinsed with distilled water and the electrolysis carried out again for six hours. The data are given in Table III.

Between runs the platinum dish was kept filled with concentrated hydrochloric acid.

Runs 15, 16, 17, and 18 were the same as runs 10 through 14 except for the treatment of the anode. In these runs the anode was thoroughly rinsed with distilled water after being used and stored inverted in a clean drawer.

Runs 19, 20, 21, 22, and 23 were the same as runs 10 through 14 and 15 through 18 except that the dish was not rinsed after being used. The electrolyte was poured out after the cessation of the electrolysis and the platinum dish kept in a clean drawer.

The data in Table III indicate that the three anode treatments tried are of comparable value. Storing the platinum dish without rinsing it apparently is beneficial to a slight extent and is the recommended anode treatment.

No peroxydiphosphate was formed when a lead dioxide anode was used.

TABLE III

EFFECT OF VARIOUS TREATMENTS OF THE ANODE UPON THE AMOUNT OF PHOSPHATE OXIDIZED TO PEROXYDIPHOSPHATE

Run Number	% KH_2PO_4 Oxidized to $K_4P_2O_8$	Anode Treatment
10	70.4	Filled with conc. hydrochloric acid except when in use.
11	69.1	
12	68.8	
13	66.5	
14	69.5	
15	67.0	Rinsed with distilled water and stored dry.
16	70.9	
17	71.6	
18	71.2	
19	74.6	Electrolyte poured out and dish stored with residual electrolyte in it.
20	72.1	
21	72.8	
22	74.4	
23	70.2	

IV. PREPARATION OF TETRAPOTASSIUM PEROXYDIPHOSPHATE

A. By the Method of Fichter and Gutzwiller

Fichter and Gutzwiller (5) prepared pure tetrapotassium peroxydiphosphate, $K_4P_2O_8$, by electrolyzing a potassium phosphate solution containing potassium fluoride and potassium chromate and evaporating the electrolyte. The potassium peroxydiphosphate concentrated in the material that separated first. Two recrystallizations in the same manner gave 96.4 to 99.8 per cent pure tetrapotassium peroxydiphosphate.

In duplicating their work the following procedure was used.

Two hundred milliliters of solution containing 302.2 g. monopotassium phosphate, 198 g. potassium hydroxide, 120 g. potassium fluoride, and 0.355 g. potassium chromate per liter was electrolized in the platinum dish described previously. The platinum dish served as the anode and a rapidly rotating bent platinum wire as the cathode. The temperature of the electrolyte was kept between 8 and 12° C. by cooling in an ice bath.

Electrolysis was carried out for three hours. After standing overnight at room temperature the solution was electrolyzed again for two hours. The third day the electrolysis was carried out for one hour.

Approximately 60 per cent of the phosphate was converted to peroxydiphosphate.

The electrolyte was evaporated in a porcelain evaporating dish on a steam bath. The solution was stirred mechanically so that the temperature never exceeded 80° C. Evaporation was continued until a considerable amount of crystals was obtained. The material was filtered on a Buechner funnel through a number two Whatman filter paper. Filtration was slow. The volume of the mother liquor was 47 ml.

The yellow colored crystals were hygroscopic and could not be air dried. They were dissolved in 70 ml. of water and recrystallized in the same manner.

The second batch of crystals contained nearly all the chromate of the first crystals. The volume of the mother liquor was 23 ml.

A second recrystallization was carried out. The crystals obtained again contained nearly all the chromate; i.e., the crystallization did not remove chromate efficiently. After drying in vacuo over anhydrous calcium chloride the crystals weighed 20 g. The volume of the mother liquor was 9 ml.

Based on the amount of potassium phosphate taken the yield was 27 per cent. Based upon the amount of potassium peroxydiphosphate in solution the yield was 44 per cent.

The material was analyzed for active oxygen by titrating the iodine liberated by weighed samples from potassium iodide solution 0.6 normal in sulfuric acid upon 12 hours of standing using sodium thiosulfate solution. The total phosphorus was determined 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 data are tabulated below.

	Found		Calc. for $K_4P_2O_8$
% P_2O_5	39.45	39.48	40.99
% Active Oxygen	4.568	4.568	4.619

$$\frac{\text{\% Active Oxygen Found}}{\text{\% Active Oxygen Calc. for } K_4P_2O_8} \times 100 = 98.90 \text{ \% pure}$$

The amount of chromate in the purified potassium peroxydiphosphate was not determined. However by a visual comparison it was estimated that half of the chromate originally taken was contained in the potassium peroxydiphosphate. The amount of chromate present was not accurately determined as the yellow color of the chromate present was sufficient evidence that the material contained too much chromate to be suitable for elucidating the analytical chemistry of peroxydiphosphate. Further work was done to obtain a material that was chromate free.

Evaporation of the electrolyte under reduced pressure yielded a yellow crystalline material that stuck to the walls of the porcelain evaporating dish. The mother liquor was colorless indicating that the chromate was also precipitated.

Attempts to recrystallize the potassium peroxydiphosphate from dilute methanol or ethanol always led to two liquid phases. The addition of either alcohol to the electrolyzed electrolyte also produced two liquid phases. The non aqueous layers did not contain active oxygen.

B. By Precipitation with Potassium Hydroxide

It was discovered that the addition of a considerable quantity of solid potassium hydroxide to the electrolyzed solution (see Section III) caused the precipitation of a microcrystalline material that contained active oxygen. When a 50 per cent solution of potassium hydroxide was added no crystals were formed.

The addition of less than 12 g. potassium hydroxide per 100 ml. of electrolyte did not cause the formation of a precipitate. The addition of increasing amounts of potassium hydroxide brought down more and more material. However after 30 g. potassium hydroxide had been added per 100 ml. electrolyte the further addition of potassium hydroxide removed very little additional peroxydiphosphate from the solution.

When the potassium hydroxide was added to the electrolyte at room temperature the material, presumably tetrapotassium peroxydiphosphate, did not settle or filter very well. Cooling was not beneficial. By heating the electrolyte to 50-55° C. and adding the solid potassium hydroxide all at once the settling and filtering properties of the precipitate were greatly improved. However even with this improvement standing overnight before filtering was necessary.

When the precipitation was carried out in an open beaker carbonate was coprecipitated. If the precipitation was carried out in an Erlenmeyer flask stoppered with a rubber stopper the amount of carbonate coprecipitated was minimized.

In all cases most of the chromate present in the electrolyte was coprecipitated.

The procedure used for the preparation of tetrapotassium peroxydiphosphate by this method was as follows.

The solution described in Section III was electrolyzed for six hours on each of two successive days. The day after the second period of electrolysis the electrolyte was transferred to a 300 ml. Erlenmeyer flask and heated to 50-55° C. Sixty grams potassium hydroxide pellets were added as rapidly as possible. The flask was stoppered with a rubber stopper and shaken until all the potassium hydroxide was dissolved. Considerable heat was evolved as the temperature rose to 70-75° C.

After standing for at least 12 hours at room temperature the supernatant solution was decanted and the crystals collected on an all glass Buechner funnel which had a medium porosity glass frit as the filtering medium.

After drying in vacuo over anhydrous calcium chloride until it was free flowing the material weighed 36 g. The active oxygen in it was determined by adding excess standardized ferrous ammonium sulfate to a weighed portion dissolved in one normal sulfuric acid and back titrating the excess ferrous ion with 0.1000 normal potassium dichromate solution using diphenylamine sodium sulfonate as indicator. The total phosphorus was determined as above. The data are given below.

	Found		Calc. for $K_4P_2O_8$
% P_2O_5	36.42	36.42	40.99
% Active Oxygen	4.054	4.053	4.619

$$\frac{\text{\% Active Oxygen Found}}{\text{\% Active Oxygen Calc. for } K_4P_2O_8} \times 100 = 87.77 \text{ \% pure}$$

The yield of tetrapotassium peroxydiphosphate based on the amount of phosphate taken was 42 per cent. Based upon the amount of potassium peroxydiphosphate in solution the yield was 72 per cent.

Recrystallization in the same manner gave a material that contained only a slightly greater percentage of active oxygen and nearly all of the chromate present in the original crystals. Since a chromate free material was desired no further crystallizations were carried out.

V. PREPARATION OF TETRALITHIUM PEROXYDIPHOSPHATE TETRAHYDRATE

The purification of tetrapotassium peroxydiphosphate was greatly hampered by its high solubility in water. As previously mentioned attempts to recrystallize it from dilute methanol or ethanol always led to two liquid phases.

The possibility that lithium peroxydiphosphate would have solubility characteristics more suitable was investigated.

It appeared that a lithium peroxydiphosphate solution containing but little potassium, phosphate, and fluoride could be obtained by adding lithium perchlorate to a solution of the tetrapotassium peroxydiphosphate obtained in Section IV-B inasmuch as potassium perchlorate, lithium phosphate, and lithium fluoride are not very soluble in water. The idea was investigated as follows.

The damp crude tetrapotassium peroxydiphosphate obtained by adding 60 g. potassium hydroxide to 200 ml. of the electrolyte as described above was dissolved in 200 ml. water. The pH of the solution as determined by a glass electrode was 11.5. To the solution of the tetrapotassium peroxydiphosphate was added at a dropwise rate 140 ml. of a lithium perchlorate solution which contained 54 g. lithium perchlorate trihydrate per 100 ml. of solution. Mechanical stirring and external cooling in an ice bath was used. A thick slurry was obtained. It filtered rapidly through a number two Whatman filter paper on a Buechner funnel. Additional lithium perchlorate solution was added to the filtrate until the further addition caused no further precipitation, approximately 10 ml. being required. The additional precipitate was collected on a Buechner funnel as before. Then 350 ml. methanol was added at a dropwise rate while the solution was stirred mechanically. A white crystalline material containing active oxygen, presumably lithium peroxydiphosphate, was obtained.

The material was not pure white. However if the crystals were washed on the filter with 1:1 water-methanol solution at 40-45° C. a pure white material was obtained.

Qualitative tests showed that carbonate was present. The solution of lithium peroxydiphosphate was freed of carbonate by acidifying it to a pH of 6.0 to 6.5 with a 35 per cent perchloric acid solution and removing carbon dioxide by aeration under reduced pressure. Before adding the methanol the pH was adjusted to a pH of 9.5 - 10.0 by adding solid lithium hydroxide. It was observed that if the pH of the solution was either lower or higher than the indicated range the material precipitated by the methanol was less crystalline in nature.

Often times 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.

By carrying out the precipitation with methanol at 40-45° C. a smaller volume of methanol was required than when the precipitation was carried out at room temperature. It was found that adding more than 100 ml. methanol did not materially increase the yield of precipitated material.

Microscopic examination showed that it was impossible to air dry the material without some dehydration of the crystals occurring. Dehydration occurred even when the material was dried under conditions of very high humidity and limited air circulation. Drying over partially dehydrated material proceeded too slowly to be practical. After 14 weeks of drying in this manner the crystals were still damp.

The crystals which had been dried under conditions of high humidity and limited circulation were analyzed for phosphorus pentoxide, active oxygen, lithium oxide, potassium oxide, water, and chromate as follows.

Approximately four grams of the air dried crystals were weighed out by difference, dissolved in water, and diluted quantitatively to 500 ml. All determinations except the determination of water were carried out using aliquots of this stock solution.

Immediately after preparing the stock solution the active oxygen was determined by adding an excess of standard ferrous ammonium sulfate solution to 25 ml. aliquots acidified with sulfuric acid and back titrating the excess ferrous ion according to the procedure developed in Section VIII.

The lithium and potassium were separated from the peroxydiphosphate by means of an ion exchange column using the method of Helrich and Rieman (9) for separating calcium and phosphate. An ion exchange column containing 19 g. Amberlite IR-100H ion exchange resin in the hydrogen form was used. The diameter of the resin column was 2.5 cm. and the height was 15 cm. Ten milliliters of the stock lithium peroxydiphosphate solution was diluted to 30 ml. The lithium and potassium ions were placed on the resin by allowing the solution to flow into the resin column. The peroxydiphosphate ion was eluted by washing the column with 500 ml. water. A flow rate of 0.01 to 0.05 ml./minute/ml. exchanger column (11); i.e., 1 to 5 ml./minute was used. The last 250 ml. of eluate was neutral to litmus paper. The lithium and potassium ions were then eluted by passing 500 ml. of 1.2 normal hydrochloric acid through the column using the same flow rate as when the peroxydiphosphate was eluted.

The eluate containing the lithium and potassium was evaporated to near dryness on a steam bath and then transferred quantitatively to a tared platinum dish. A drop of concentrated sulfuric acid was added and the solution evaporated in a Hillebrand evaporator to fumes of sulfur trioxide followed by ignition at 500° C. for 30 minutes in a muffle furnace. After cooling in a desicator over anhydrous calcium chloride the material was weighed as lithium plus potassium sulfate.

In order to separate the lithium from the potassium it was necessary to convert back to mixed chlorides. This was done by precipitating the sulfate with barium chloride and removing the excess barium ion with ammonium carbonate. The ammonium ion was destroyed by adding nitric acid to the final filtrate and evaporating to dryness on a steam bath. The salts were dissolved in water and transferred to a porcelain casserole. One milliliter concentrated hydrochloric acid was added and the solution again evaporated to dryness. To ensure the complete removal of ammonium salts the material was ignited at 400° C. for 30 minutes. The potassium in the mixed chlorides was precipitated as the chloroplatinate (28) and weighed as such. The lithium content was then calculated by difference from the weight of the mixed sulfates.

The amount of water in the prepared material was determined by igniting a weighed sample in a stream of oxygen at 500° C. and weighing the liberated water in a Pregl type absorption tube filled with Dehydrite.

The stock solution of lithium peroxydiphosphate was tested qualitatively for chromate with s-diphenylcarbazide (25). The test indicated that there was no chromate present. That the test was valid in the presence of peroxydiphosphate was determined by adding a small amount of chromate to the solution being tested and observing that the pink color characteristic of the test developed.

The analytical data are collected in Table IV.

It is shown that the material is tetralithium peroxydiphosphate tetrahydrate. As previously stated microscopic examination of the crystals revealed some dehydration had occurred. Yet the analyses show more water to be present than that required for the formation of a tetrahydrate. These facts are not considered incompatible; it merely means that the material was heterogenous. That is, some crystals dehydrated before others were fully dry. Drying over partially dehydrated material was shown to be too slow to be practical.

The variable water content greatly influences the calculated formula as shown by the data in Table V which are the same data as in Table IV but calculated to an anhydrous basis.

The recommended procedure for preparing hydrated tetralithium peroxydiphosphate is as follows.

Sixty grams monopotassium phosphate, 40 g. potassium hydroxide, 24 g. potassium fluoride dihydrate, and 0.07 g. potassium chromate are dissolved

TABLE IV

ANALYSIS OF LITHIUM PEROXYDIPHOSPHATE PRECIPITATED BY ADDING METHANOL TO A LITHIUM PEROXYDIPHOSPHATE SOLUTION

Per cent	Run 42		Run 43		Calculated for	
					$Li_4P_2O_8 \cdot 4H_2O$	$Li_4P_2O_8 \cdot 5H_2O$
P_2O_5	48.86	48.86	47.79	47.66	48.98	46.10
Active Oxygen	5.36	5.36	5.35	5.35	5.52	5.20
Li_2O	20.37	20.67	20.27	20.11	20.62	19.42
K_2O	0.66	0.44	1.67	1.81		
H_2O	27.17	26.88	25.91	25.99	24.88	29.27
Purity*	100.2	99.79	98.26	98.26		
Summation	102.42	102.21	100.99	100.92		

$$^{*}\ \frac{\text{Active oxygen found calc. to anhydrous basis}}{\text{Active oxygen calc. for } Li_4P_2O_8} \times 100 = \%\ \text{purity}$$

TABLE V

ANALYSIS OF THE LITHIUM PEROXYDIPHOSPHATE PRECIPITATED BY ADDING METHANOL TO A LITHIUM PEROXYDIPHOSPHATE SOLUTION, CALCULATED TO AN ANHYDROUS BASIS

Per cent	Run 42		Run 43		Calculated for $Li_4P_2O_8$	Calculated for Li_3PO_4
P_2O_5	67.09	66.82	64.50	64.34	65.63	61.30
Active oxygen	7.36	7.33	7.22	7.22	7.35	
Li_2O	27.97	27.62	27.36	27.15	27.44	38.70
K_2O	0.91	0.60	2.25	2.44		
Purity*	100.2	99.79	98.26	98.26		
Summation	103.3	102.3	101.3	101.2		

$$^{*}\frac{\text{Active oxygen found}}{\text{Active oxygen calc. for } Li_4P_2O_8} \times 100 = \%\ \text{purity}$$

in 150 ml. water. Considerable heat is evolved. After cooling the solution, it is filtered through a number two Whatman paper on a Buechner funnel and then diluted to 200 ml. The filtration step is necessary to remove the paraffin introduced by the potassium fluoride. Potassium fluoride is commonly obtained in paraffin lined glass bottles and invariably it is contaminated by the paraffin.

The solution is transferred to a 210 ml. volume platinum dish. The solution is cooled in an ice bath during electrolysis. The platinum dish serves as the anode and a rapidly rotating bent platinum wire is used as the cathode. A current of 2.2 amperes is obtained by applying 7.5 volts across the electrodes. Electrolysis is carried out for six hours. A Sargent-Slomin electrolytic analyzer is ideal for this electrolysis.

Upon cessation of the electrolysis the platinum dish is covered with a watch glass and the electrolyte allowed to stand in the dish at room temperature for at least overnight. Longer standing is not detrimental as the peroxydiphosphate in this solution is stable for months.

Electrolysis is carried out for a second time for six hours. This time the electrolyte is transferred to a rubber stoppered 300 ml. Erlenmeyer flask. The dish is used for the next run without rinsing.

After standing for at least overnight the electrolyte is heated to 50-55° C. Sixty grams potassium hydroxide is added. The flask is stoppered and shaken until all the potassium hydroxide dissolves.

After standing overnight (longer standing is not detrimental) the supernatant is decanted off and the microcrystalline impure tetrapotassium peroxydiphosphate filtered on a medium porosity sintered glass filter. The mother liquor is discarded.

The crude tetrapotassium peroxydiphosphate is dissolved in 200 ml. water in a 500 ml. beaker. The solution of crude tetrapotassium peroxydiphosphate is cooled in an ice bath while 140 ml. of a lithium perchlorate solution containing 54 g. lithium perchlorate trihydrate per 100 ml. of solution is added at a dropwise rate from a dropping funnel. Mechanical stirring is used. After stirring for 15 minutes the material is filtered through a number two Whatman filter paper on a Buechner funnel.

A lithium perchlorate solution of the specified concentration can be prepared by slurrying 52 g. lithium carbonate in 100 ml. water and neutralizing it with 240 ml. of 35 per cent perchloric acid. It is necessary to remove carbon dioxide by aerating under reduced pressure.

After filtration the completeness of precipitation is tested for by adding a little more lithium perchlorate solution. Additional lithium perchlorate solution is added if necessary. Rarely is more than 15 ml. required.

The pH of the solution is adjusted to 6.0-6.5 by the addition of 35 per cent perchloric acid. A pH meter is used to determine the pH of the solution. Approximately 10 ml. of the acid is required.

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

The pH of the solution is adjusted to 9.5-10.0 by adding solid hydrated lithium hydroxide. Approximately 0.5 g. is required.

After adjusting the pH to 9.5-10.0 the solution is cooled to 0-5° C. in an ice bath. Any additional potassium perchlorate that precipitates is removed by filtration.

The solution is transferred to a 600 ml. beaker. It is heated to 40-45° C. and placed in a water bath at the same temperature. While the solution is stirred mechamically 70 ml. methanol is poured in from a graduated cylinder. No precipitate forms immediately but after stirring for five minutes a considerable quantity of crystals is obtained. Then 30 additional ml. of methanol is added at a rapid dropwise rate from a dropping funnel. The solution is stirred for a total of 15 minutes.

The lithium peroxydiphosphate is filtered on a Buechner funnel using a number two Whatman filter paper and sucked as dry as possible. The residual chromate is removed from the crystals by washing them on the filter with 1:1 water-methanol mixture at 40-45° C. until the wash liquor comes through colorless. Four or five 20 ml. portions of the wash solution are usually sufficient.

The crystals are air dried until free flowing. Drying in an atmosphere of high relative humidity is recommended as the material is easily dehydrated. The yield is 27.0 g.

The percentage yield of pure product based on the amount of phosphate taken is 42 per cent. Based on a 65 per cent conversion of the phosphate to peroxydiphosphate by the electrolytic oxidation the percentage yield is 64 per cent.

Additional but less pure product can be obtained by combining the mother liquor and the methanol-water wash liquor. Sufficient methanol is added to bring the methanol concentration to 50 per cent by volume. While mechanically stirred the temperature of the solution is maintained at 50-55° C. for 30 minutes. About three grams of material is obtained.

All the chemicals used should be of sufficient purity to meet the specifications of the American Chemical Society for reagent chemicals.

VI. STABILITY OF PEROXYDIPHOSPHATE SOLUTIONS

A. Tetrapotassium Peroxydiphosphate

The only information recorded in the literature on the stability of peroxydiphosphate is that of Fichter and Rius y Mirò (7). They stated that a solution of purified tetrapotassium peroxydiphosphate decomposed to the extent of 50 per cent in five days. Yet both Fichter and Rius y Mirò (7) and Fichter and Gutzwiller (5) were able to crystallize tetrapotassium peroxydiphosphate from aqueous solution.

More exact information on the stability of tetrapotassium peroxydiphosphate solution was desired.

For this work the tetrapotassium peroxydiphosphate prepared by the method of Fichter and Gutzwiller (5) was used even though it was colored yellow by the presence of chromate. Six grams of it was weighed out, dissolved in water, and diluted to 250 ml. to give a 0.05 molar solution. Since there is one atom of active oxygen per molecule of peroxydiphosphate a 0.05 molar solution is 0.10 normal in a redox reaction. The pH of the solution was 7.5 as determined by the glass electrode.

The concentration of the peroxydiphosphate was determined periodically by determining the total equivalent weights 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 two milliliters of three molar sulfuric acid to a 10 ml. aliquot followed immediately by 20 ml. of standardized 0.1 normal ferrous ammonium sulfate solution which was 0.1 molar in respect to sulfuric acid. After standing for five minutes the excess ferrous ion was back titrated with 0.1000 normal potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Details of this titration are given in Section VII. A 10 ml. burette was used. The number of milliequivalent weights of oxidizing material present in the 10 ml. aliquot was determined by calculating the amount of ferrous ion that had disappeared. Duplicate determinations gave a precision of two parts per thousand.

The data are tabulated in Table VI.

TABLE VI

STABILITY OF 0.1 NORMAL POTASSIUM PEROXYDIPHOSPHATE SOLUTION AT pH 7.5 AT ROOM TEMPERATURE

Days Standing	Normality of $K_4P_2O_8$
0	0.1227
1	0.1222
2	0.1221
7	0.1222
17	0.1215

The data in Table VI show that the solution of tetrapotassium peroxydiphosphate did not decompose to a 50 per cent extent in five days as claimed by Fichter and Rius y Mirò (7). In fact it is perfectly stable for seven days if the decomposition occurring during the first day is disregarded. Over a 16 day period the peroxydiphosphate concentration decreased only 0.6 per cent.

The pH of the solution did not change during the 17 day period.

Fichter and Rius y Mirò did not state the concentration of the tetrapotassium peroxydiphosphate solution that decomposed to such a large extent in five days. Perhaps a more concentrated solution would be less stable but a 50 per cent decomposition of a concentrated solution in five days seems unlikely. In this connection it is worthy to note that in the concentrated alkaline solutions of potassium peroxydiphosphate obtained by electrolysis as described in Section III, the concentration of oxidizing material did not decrease even after standing for six weeks at extreme summer temperatures.

Inasmuch as the material prepared by the method of Fichter and Gutzwiller contained too much chromate to be useful in the study of the reactions of peroxydiphosphate of analytical importance the stability of solutions of various pH's was not studied.

B. Tetralithium Peroxydiphosphate Tetrahydrate

In the study of the reactions of a particular substance it is desirable to have information on the stability of solutions of the material under various conditions. Since the tetralithium peroxydiphosphate prepared in Section V was to be used in elucidating the analytical chemistry of peroxydiphosphate the stability of solutions of it under various conditions was studied.

A liter of 0.1 normal tetralithium peroxydiphosphate solution was made by dissolving 16.5 g. of tetralithium peroxydiphosphate tetrahydrate prepared as described in Section V in water and diluting to one liter. The pH of the solution was 10.2 as determined by the glass electrode. The solution was stored in a glass stoppered Pyrex bottle at room temperature in the dark.

Solutions with various pH values were prepared by adding various amounts of 85 per cent phosphoric acid to solutions prepared in the above manner. The addition of one milliliter of phosphoric acid gave a pH of 7.0; eight milliliters gave a pH of 4.0; and 16 ml. gave a pH of 2.0. A solution 0.45 molar in respect to phosphoric acid was prepared by adding 30 ml. of the 85 per cent phosphoric acid to the liter of solution; the pH of the solution acidified in this manner was 1.5.

The concentration of the peroxydiphosphate was determined periodically by determining the total number of equivalent weights of oxidizing materials present and attributing all the oxidizing properties of the solution to peroxydiphosphate as was done with the tetrapotassium peroxydiphosphate solution above. A 25 ml. aliquot was taken. It was acidified with six milliliters of three molar sulfuric acid immediately before adding 50 ml. of standard ferrous ammonium sulfate solution. The excess ferrous ion was back titrated with 0.1000 normal potassium dichromate solution. Duplicate determination gave a precision of two parts per thousand.

The data are given in Table VII.

TABLE VII

STABILITY OF 0.1 NORMAL LITHIUM PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES AT ROOM TEMPERATURE

Days of Standing	Normality of $Li_4P_2O_8$				
	pH of the solution				
	10.2	7.0	4.0	2.0	0.45 molar H_3PO_4
0	0.1123	0.1072	0.1090	0.1160	0.1183
1	0.1120	0.1069	0.1086	0.1156	0.1178
2	0.1115	0.1067	0.1084	0.1156	0.1174
3	0.1117	0.1068	0.1086	0.1156	0.1166
4	0.1121	0.1068	0.1088	0.1154	0.1159
5	0.1117	0.1067	0.1086	0.1149	0.1153
8	0.1116	0.1068	0.1084	0.1148	0.1141
14	0.1118	0.1067	0.1084	0.1142	0.1117
21	0.1120	0.1069	0.1084	0.1129	0.1092
28	0.1119	0.1068	0.1082	0.1118	0.1068
35	0.1118	0.1066	0.1077	0.1102	0.1041
49	0.1118	0.1065	0.1071		

Examination of the data shows that the solutions are stable over the pH range 10.2 to 2.0 for a number of days. At pH 10.2 the concentration of peroxydiphosphate in the solution did not change in 49 days. At pH 7.0 the solution was stable for 28 days and in 49 days decomposed only four parts per thousand. Since the experimental procedure used was precise to two parts per thousand for all practical purposes the solution of tetralithium peroxydiphosphate at pH 7.0 was stable for 49 days. At pH 4.0 the solution was stable for 21 days and in 49 days decomposed five parts per thousand. At pH 2.0 the solution was stable for four days and in 35 days decomposed 53.4 parts per thousand; i.e., 5.34 per cent. The solution of tetralithium peroxydiphosphate which was 0.45 molar in respect to phosphoric acid was not stable at all. In four days it decomposed 19 parts per thousand and in 35 days it decomposed 120 parts per thousand; i.e., 12 per cent.

The pH of each solution remained constant during the period of standing.

Thus it is seen that no special procedures or precautions are necessary to obtain a stable 0.1 normal solution of lithium peroxydiphosphate. Merely dissolving the tetralithium peroxydiphosphate tetrahydrate in the requisite quantity of water gives a solution that is perfectly stable.

Although a solution of peroxydiphosphate in 0.45 molar phosphoric acid annot be considered stable it is stable enough to carry out reactions in such a medium involving a few hours of standing.

The stability of these same solutions was determined at 50° C. Twenty-five milliliter aliquots were pipetted into 250 ml. iodine flasks and placed in an oven at 50° C. for various periods of time. After cooling the concentration of the peroxydiphosphate ion was determined as above. The data are given in Table VIII.

The data in Table VIII shows that tetralithium peroxydiphosphate solutions of pH 10.2 to 2.0 are stable at 50° C. for at least four hours. This points out the possibility of carrying out reactions with peroxydiphosphate at 50° C.

TABLE VIII

STABILITY OF 0.1 NORMAL LITHIUM PEROXYDIPHOSPHATE SOLUTIONS OF VARIOUS pH VALUES AT 50° C.

Hours at 50° C.	Normality $Li_4P_2O_8 \cdot 4H_2O$ pH of the solution 10.2	7.0	4.0	2.0	0.45 molar H_3PO_4
0	0.1119	0.1068	0.1082	0.1142	0.1117
1	0.1121	0.1068	0.1080	0.1140	0.1106
2	0.1120	0.1064	0.1077	0.1138	0.1093
4	0.1118	0.1066	0.1080	0.1140	0.1097

VII. AN ANALYTICAL STUDY OF THE REACTION BETWEEN PEROXYDIPHOSPHATE AND FERROUS IONS

When a ferrous ammonium sulfate solution was added to an acidified chromate free tetralithium peroxydiphosphate solution the color of the ferric ion appeared immediately. The possibility of using this reaction analytically was investigated by making a systematic study of the more important variables.

An approximately 0.1 normal tetralithium peroxydiphosphate solution was prepared by dissolving 30 g. of tetralithium peroxydiphosphate tetrahydrate, which was made by the method described in Section V, in water and diluting to two liters.

Ferrous ammonium sulfate solution approximately 0.08 normal and 0.12 molar in respect to sulfuric acid was prepared by dissolving 32 g. of ferrous ammonium sulfate hexahydrate in 300 ml. water acidified with seven milliliters concentrated sulfuric acid and diluting to one liter with water.

Potassium dichromate solution 0.1000 normal was prepared by weighing out 9.8704 g. Mallinckrodt reagent grade potassium dichromate, dissolving it in water, and diluting the solution quantitatively to two liters. The potassium dichromate used had been compared to Bureau of Standards standard sample number 136 and found to be the same as the standard sample. The potassium dichromate was dried for one hour at 110° C. before it was weighed out. All the chemicals used met the American Chemical Society's specifications for reagent chemicals.

The ferrous ammonium sulfate solution was standardized each time it was used by titrating it in the following manner with the 0.1000 normal potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Twenty-five milliliters of the ferrous ammonium sulfate solution was pipetted into a 250 ml. iodine flask. Twenty-five milliliters water and 10 ml. three molar sulfuric acid were added. Then three milliliters of 85 per cent phosphoric acid was added for each 50 ml. of volume expected at the end point. Sarver and Kolthoff (21) have shown that the presence of the phosphoric acid is necessary to obtain a satisfactory end point but that the amount present is not critical. Hence even though the expected amount of ferrous ion were not present a satisfactory end point would be obtained. Three tenths of a milliliter, six drops, of 0.01 molar diphenylamine sodium sulfonate solution was used as indicator. The potassium dichromate solution was added until the first tinge of purple or violet-blue color appeared. As an indicator blank, 0.05 ml. was subtracted from the volume of dichromate solution used (21).

The burettes and pipettes were Kimble Normax grade and were calibrated before use. Corrections were applied wherever necessary.

As the first variable studied in the reaction between peroxydiphosphate and ferrous ions it was decided to determine the effect of carrying out the reaction in sulfuric acid of various concentrations. To do so would necessitate the arbitrary standardization of the amount of excess ferrous ion in the reaction mixture as no information was available on the amount of excess ferrous ion necessary to drive the reaction to completion. Consequently the effect of having present various amounts of excess ferrous ion was combined with the study of the reaction in sulfuric acid of various concentrations. This was carried out in the following manner.

In one series of determinations five milliliter portions of the lithium peroxydiphosphate solution were pipetted into five different 250 ml. iodine flasks. Sufficient nine molar sulfuric acid to give final sulfuric acid concentrations of 0.25, 0.50, 1.0, 2.0, and 3.0 molar was added from a burette. Immediately 50 ml. standardized 0.08 normal ferrous ammonium sulfate solution 0.12 molar in respect to sulfuric acid was added by means of a pipette. After standing for at least five minutes but for no more than 25 minutes the excess ferrous ion was back titrated with 0.1000 normal potassium dichromate solution using diphenylamine sodium sulfonate as indicator. The concentration of the peroxydiphosphate was calculated from the amount of ferrous ion that had disappeared attributing all the oxidizing properties of the solution to peroxydiphosphate. Duplicate determinations gave a precision of two parts per thousand.

In a second series of experiments the amount of peroxydiphosphate solution was increased to 10 ml. Sufficient nine molar sulfuric acid was added to give the designated acid concentrations. Fifty milliliters of ferrous ammonium sulfate solution was again added so that the ratio of peroxydiphosphate ion to ferrous ion was halved.

The procedure was repeated using 20 and 40 ml. of the lithium peroxydiphosphate solution.

The data are tabulated in Table IX.

TABLE IX

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN SULFURIC ACID SOLUTION

Ml. $Li_4P_2O_8$	Mole ratio $\frac{P_2O_8^{-4}}{Fe^{+2}}$	Normality $Li_4P_2O_8$				
		Molarity of H_2SO_4 of the Reaction Mixture				
		0.25	0.50	1.0	2.0	3.0
5	1.0:17.6	0.1018	0.1000	0.1006	0.1004	0.1004
10	1.0:8.8	0.1023	0.1012	0.1014	0.1014	0.1011
20	1.0:4.4	0.1016	0.1015	0.1013	0.1010	0.1010
40	1.0:2.2	0.1014	0.1015	0.1014	0.1010	0.1008

To arrive at the concentration of peroxydiphosphate in the solution it is obvious that the 20 different determinations reported in Table IX should not be averaged. The results obtained with reaction mixtures 2.0 and 3.0 molar in sulfuric acid are lower than the rest of the determinations. This is attributed to decomposition of the peroxydiphosphate in the strong acid solution even though the ferrous ammonium sulfate solution was pipetted in immediately after the addition of the acid.

The results obtained using five milliliters of sample are not as accurate as the others as in a determination involving the back titration of a large excess of reagent the constituent being determined is obtained by subtracting a large volume from a second somewhat larger volume. Hence a small percentage of error in the two large volumes is reflected in the determination as a proportionately larger error.

The anomalous results obtained with the 10 ml. sample at 0.25 molar sulfuric acid cannot be explained. Additional determinations gave a normality of 0.1023, 0.1023, 0.1025, and 0.1020. An error due to faulty calibrations of the volumetric ware would be reflected in the other determinations involving the ten milliliter samples.

In the above work the factor of time of standing was not rigidly controlled. Inasmuch as there are no discrepancies in the data of Table IX it can be concluded that the time of standing is not critical. However to determine unequivocally whether the time of standing is a critical factor or not an experiment was designed for that expressed purpose as follows.

Twenty milliliters of the lithium perosydiphosphate solution was pipetted into a 250 ml. iodine flask. Sufficient 9 molar sulfuric acid was added to give a final sulfuric acid concentration of 0.25 molar followed immediately by 50 ml. ferrous ammonium sulfate solution added by means of a pipette. The excess ferrous ion was back titrated as expeditiously as possible with potassium dichromate solution. Although there was a short time interval before all the excess ferrous ion was titrated this procedure by definition was designated as zero time of standing. The procedure was repeated but the reaction mixture was allowed to stand for various times before back titrating the excess ferrous ion. Timing was started when the pipette containing the ferrous ammonium sulfate solution was half empty and stopped when the first drop of potassium dichromate solution was added. The data are given in Table X.

The data in Table X substantiates the conclusion made before that the time of standing before the excess ferrous ion is back titrated is not critical; at least up to 60 minutes.

TABLE X

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN 0.25 MOLAR SULFURIC ACID AS A FUNCTION OF TIME

Minutes of Standing	Normality $Li_4P_2O_8$
0	0.1018
10	0.1018
20	0.1018
40	0.1018
60	0.1017

Mole ratio $P_2O_8^{-4}:Fe^{+2} = 1.0:4.4$

The effect of substituting hydrochloric acid for the sulfuric acid was studied. The procedure used was the same as was used when the reaction mixtures were acidified with sulfuric acid. Twelve molar hydrochloric acid was added to give the desired acid concentration in the reaction mixtures. The data are given in Table XI.

The data in Table XI were gathered without rigid time control. As when sulfuric acid was used it was desirable to determine whether the time of standing was a factor or not. In addition more information was sought on the reaction in 0.25 molar hydrochloric acid. The procedure was the same as above except 25 ml. of the lithium peroxydiphosphate solution was used. The data are given in Table XII.

The low results with the reaction media 0.25 and 0.50 molar in hydrochloric acid can be explained by the reaction between peroxydiphosphate

TABLE XI

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN HYDROCHLORIC ACID SOLUTION

Ml. $Li_4P_2O_8$	Mole ratio $\frac{P_2O_8^{-4}}{Fe^{+2}}$	Normality $Li_4P_2O_8$			
		Molarity of HCl of the Reaction Mixture			
		0.25	0.50	1.0	2.0
5	1.0:17.6	0.1028	0.1020	0.1030	0.1028
10	1.0:8.8	0.1019	0.1020	0.1017	0.1019
20	1.0:4.4	0.1011	0.1018	0.1019	0.1020
40	1.0:2.2	0.09985	0.1011	0.1018	0.1019

TABLE XII

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN HYDROCHLORIC ACID AS A FUNCTION OF TIME

Minutes Standing	Normality $Li_4P_2O_8$	
	0.25 M HCl	1.0 M HCl
0	0.1008	0.1015
5	0.1012	0.1016
10	0.1012	0.1014
20	0.1012	0.1015
40	0.1012	0.1014
60	0.1013	0.1012

Mole ratio $P_2O_8^{-4}:Fe^{+2} = 1.0:4.4$

and ferrous ions being sluggish under such conditions. There is no apparent explanation for the somewhat high and erratic results with the higher acid concentrations. In all cases the end point of the titration was sharp and permanent.

The reaction between ferrous and peroxydiphosphate ions was carried out in a medium acidified with perchloric acid. The procedure used was the same as was used previously when the reaction media were acidified with sulfuric and hydrochloric acids. The perchloric acid was added as a 35 per cent solution. The data are given in Tables XIII and XIV.

TABLE XIII

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN PERCHLORIC ACID SOLUTION

		Normality $Li_4P_2O_8$			
	Mole ratio	Molarity of $HClO_4$ in the Reaction Mixture			
Ml. $Li_4P_2O_8$	$\frac{P_2O_8^{-4}}{Fe^{+2}}$	0.25	0.50	1.0	2.0
5	1.0:17.6	0.1002*	0.1016	0.1016	0.1014
10	1.0:8.8	0.1009*	0.1016	0.1016	0.1015
20	1.0:4.4	0.1015	0.1015	0.1015	0.1016
40	1.0:2.2	0.1016	0.1016	0.1016	0.1015

* End point not distinct.

The data show that peroxydiphosphate is quantitatively reduced by an excess of ferrous ion in perchloric acid media and that the time interval between adding the excess ferrous ion and the back titration of the excess is not a factor up to 60 minutes of standing.

TABLE XIV

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN 0.50 MOLAR PERCHLORIC ACID AS A FUNCTION OF TIME

Minutes Standing	Normality $Li_4P_2O_8$
0	0.1015
10	0.1017
20	0.1014
40	0.1014
60	0.1017

Mole ratio $P_2O_8^{-4}:Fe^{+2} = 1.0:4.4$

The results obtained using 40 ml. samples of the peroxydiphosphate are compiled in Table XV. It is seen that approximately the same normality was obtained with reaction media 0.25, 0.50, and 1.0 molar in sulfuric acid as was obtained with reaction media 0.25, 0.50, 1.0, and 2.0 molar in perchloric acid. Sufficient data were not gathered for a statistical treatment. However the average normality of the cited determinations is 0.1015.

The recommended acidities for carrying out the determination are 0.25 to 1.0 molar sulfuric acid solutions or 0.25 to 2.0 molar perchloric acid solutions. The use of hydrochloric acid is not recommended.

The reaction between ferrous and peroxydiphosphate ions was carried out in phosphoric acid solutions of various concentrations. The same solution of lithium peroxydiphosphate was used as was used for the work

TABLE XV

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN SOLUTIONS OF SULFURIC, HYDROCHLORIC, AND PERCHLORIC ACIDS

Reaction Medium	Normality $Li_4P_2O_8$
0.25 M H_2SO_4	0.1014
0.50 M H_2SO_4	0.1015
1.0 M H_2SO_4	0.1014
2.0 M H_2SO_4	0.1010
3.0 M H_2SO_4	0.1008
0.25 M HCl	0.09985
0.50 M HCl	0.1011
1.0 M HCl	0.1018
2.0 M HCl	0.1019
0.25 M $HClO_4$	0.1016
0.50 M $HClO_4$	0.1016
1.0 M $HClO_4$	0.1016
2.0 M $HClO_4$	0.1015

Sample size, 40.00 ml.

Mole ratio $P_2O_8^{-4}:Fe^{+2} = 1.0:2.2$

with reaction mixtures containing sulfuric, hydrochloric, and perchloric acids. The procedure employed was identical to that used previously. The phosphoric acid was added as an 85 per cent solution. The data are given in Table XVI.

TABLE XVI

DETERMINATION OF PEROXYDIPHOSPHATE WITH FERROUS ION IN PHOSPHORIC ACID SOLUTION

Ml. $Li_4P_2O_8$	Mole ratio $\frac{P_2O_8^{-4}}{Fe^{+2}}$	Normality $Li_4P_2O_8$		
		Molarity of H_3PO_4		
		0.5	1.0	2.0
5	1.0:17.6	0.1038	0.1052	0.1054
10	1.0:8.8	0.1027	0.1035	0.1047
20	1.0:4.4	0.1014	0.1022	0.1027
40	1.0:2.2	0.1017	0.1016	0.1019

The data show that the reaction between peroxydiphosphate and ferrous ion is not as suited for analytical purposes when carried out in the described manner in a phosphoric acid solution as when carried out in sulfuric, hydrochloric, or perchloric acid solution. Since the back titration of an excess of a reagent was carried out the high results tabulated in Table XVI indicate a consumption of ferrous ion in addition to that required by the peroxydiphosphate. This could be attributed to the fact that ferrous ion is a stronger reducing agent in phosphoric acid than in the other acids employed (21) thereby accelerating air oxidation. The data verifies this hypothesis inasmuch as the solutions containing the most phosphoric acid gave the highest results when the amount of excess ferrous ion was kept constant. In addition with solutions containing the same amount of phosphoric acid but different amounts of excess ferrous ion the solution containing the greatest excess gave the highest results.

Various experiments were designed to further verify the hypothesis that the air oxidation of the ferrous ion was responsible for the high results reported in Table XVI.

Twenty-five milliliter portions of approximately 0.08 normal ferrous ammonium sulfate solution which was 0.12 molar in respect to sulfuric acid were pipetted into 250 ml. iodine flasks. Sufficient 85 per cent phosphoric acid was added to give the desired phosphoric acid concentrations. After standing for 15 minutes in diffused daylight six milliliters of three molar sulfuric acid was added and the concentration of the ferrous ion determined by titration with 0.1000 normal potassium dichromate solution as above. The data are given in Table XVII. The deviations tabulated are based upon the results obtained with aliquots treated similarly but having no phosphoric acid present prior to the actual titration with the potassium dichromate solution. The determinations were carried out in duplicate. A precision of one part per thousand was attained.

TABLE XVII

DECOMPOSITION OF FERROUS AMMONIUM SULFATE SOLUTIONS CONTAINING VARIOUS AMOUNTS OF PHOSPHORIC ACID

Molarity H_3PO_4	Normality Fe^{+2}	Deviation Parts/Thousand
0.0	0.08812	---
0.5	0.08792	2
1.0	0.08780	4
2.0	0.08748	8

Time of standing, 15 minutes

The data show that ferrous ammonium sulfate solution containing phosphoric acid is not stable.

The effect of varying the time of standing was studied by pipetting 25 ml. portions of the ferrous ammonium sulfate solution into 250 ml. iodine flasks, adding 1.7 ml. 85 per cent phosphoric acid to make the solution 1.0 molar in phosphoric acid, and titrating the ferrous ion present with 0.1000 normal potassium dichromate solution after various times of standing. Timing was started when the phosphoric acid was added and stopped when the first drop of potassium dichromate solution had been added. Hence the designation zero time of standing is somewhat in error as there was necessarily a few minutes of time between the addition of the phosphoric acid and the completion of the titration with the potassium dichromate solution. The data are given in Table XVIII.

TABLE XVIII

DECOMPOSITION OF FERROUS AMMONIUM SULFATE SOLUTIONS 1.0 MOLAR IN PHOSPHORIC ACID DURING VARIOUS TIME INTERVALS

Minutes Standing	Normality Fe^{+2}	Deviation Parts/Thousand
0	0.08856	---
5	0.08860	0
10	0.08840	2
20	0.08824	4
30	0.08820	4

The data show that the air oxidation of ferrous ion in phosphoric acid solution is not instantaneous. Also the rate of reaction is apparently greatly decreased after 20 minutes.

The effect of having present both phosphoric acid and lithium ion was studied. Twenty-five milliliter aliquots of the ferrous ammonium sulfate solution were pipetted into 250 ml. iodine flasks. To each was added 10 ml. of 0.1 molar lithium hydroxide solution followed immediately by the requisite amount of 85 per cent phosphoric acid. After standing for 20 minutes the concentration of the ferrous ion was determined as before. The data are given in Table XIX.

TABLE XIX

DECOMPOSITION OF FERROUS AMMONIUM SULFATE SOLUTIONS 0.025 MOLAR IN LITHIUM ION CONTAINING VARIOUS AMOUNTS OF PHOSPHORIC ACID

Molarity H_3PO_4	Normality Fe^{+2}	Deviation Parts/Thousand
0.0	0.08884	---
0.5	0.08860	3
1.0	0.08824	8
2.0	0.08808	10

Time of standing, 20 minutes

Comparison of the data in Table XIX with that of Table XVII wherein no lithium ion was present indicates that the presence of lithium ion, in the concentration used, does not have a marked effect on the stability of ferrous ammonium sulfate solutions containing phosphoric acids.

The stability of ferrous ammonium sulfate solutions containing lithium ions, ferric ions, and various amounts of phosphoric acid was studied. The procedure was the same as employed above. To the 25 ml. of ferrous ammonium sulfate solution was added an equal volume of 0.1 molar ferric sulfate solution which was 0.2 molar in lithium sulfate. The requisite amount of 85 per cent phosphoric acid was added immediately. The data are given in Table XX.

TABLE XX

DECOMPOSITION OF FERROUS AMMONIUM SULFATE SOLUTIONS 0.05 MOLAR IN FERRIC ION AND 0.1 MOLAR IN LITHIUM ION CONTAINING VARIOUS AMOUNTS OF PHOSPHORIC ACID

Molarity H_3PO_4	Normality Fe^{+2}	Deviation Parts/Thousand
0.0	0.09008	---
0.5	0.08996	1
1.0	0.08980	3
2.0	0.08944	7

Time of standing, 20 minutes

The data in Table XX indicate that the presence of lithium and ferric ions in the concentration used does not render a ferrous ammonium sulfate solution containing phosphoric acid less stable than when they are absent.

The data of Tables XVII, XVIII, XIX and XX support the hypothesis that the determination of peroxydiphosphate in a phosphoric acid medium by the addition of excess ferrous ion and the back titration of the excess gives high results because of the air oxidation of the ferrous ion. The use of phosphoric acid in the determination as described is not recommended.

The determination of peroxydiphosphate by means of the reaction between it and ferrous ion was carried out in the presence of various amounts of phosphate. The reaction media were acidified with sulfuric, hydrochloric, and perchloric acid. The procedure used was as follows.

Twenty milliliters of the same lithium peroxydiphosphate used previously was pipetted into a 250 ml. iodine flask. To it was added 50 ml. of 2.0 molar monopotassium phosphate solution. A final solution 0.5 molar in respect to sulfuric acid was desired so 9.4 ml. of nine molar sulfuric acid was added. Immediately after the addition of the acid 50 ml. of standardized ferrous ammonium sulfate solution was added by means of a pipette. The excess ferrous ion was back titrated as before.

The 20 ml. of 0.05 molar lithium peroxydiphosphate solution contained 1.0 millimole of peroxydiphosphate. The total amount of phosphate added was 100 millimoles. Hence the peroxydiphosphate to phosphate ratio was 1:100. That is to say the reaction mixture so prepared was comparable to the solution of a sample of phosphate material containing one mole per cent of peroxydiphosphate.

The amount of ferrous ammonium sulfate solution added represented a 2.2 fold excess.

Solutions containing smaller amounts of phosphate were prepared by adding smaller amounts of the 2.0 molar monopotassium phosphate solutions.

In each case enough water was added to bring the volume to 79 ml. The data are given in Table XXI.

The effect of phosphate upon the reaction between peroxydiphosphate and ferrous ions in hydrochloric acid media was also determined. The procedure used was the same as that above except that 6.4 ml. of 12 molar hydrochloric acid was added to make the reaction mixture 1.0 molar in respect to hydrochloric acid. The data are also given in Table XXI.

With another series of samples 14 ml. of six molar perchloric acid was added to each sample.

TABLE XXI

DETERMINATION OF PEROXYDIPHOSPHATE IN THE PRESENCE OF PHOSPHATE

Reaction Medium	Normality $Li_4P_2O_8$ Mole ratio $P_2O_8^{-4}:PO_4^{-3}$ 1.0:0.0	 1.0:20	 1.0:40	 1.0:80	 1.0:100
0.50 M H_2SO_4	0.1010	0.1012	0.1012	0.1012	0.1017
1.0 M HCl	0.1012	0.1010	0.1009	0.1009	0.1013
1.0 M $HClO_4$	0.1010	0.1011	0.1014	0.1014	0.1014

Mole ratio $P_2O_8^{-4}:Fe^{+2} = 1.0:4.4$

The determination of peroxydiphosphate in the presence of potassium phosphate cannot be compared directly to the determination in reaction media acidified with phosphoric acid by comparing the data of Tables XVI and XXI. In Table XVI the concentration of the phosphate is stated but the ratio between the phosphate and peroxydiphosphate is not. In Table XXI the converse is true. However in Table XXII both the molar concentration of the phosphate in the reaction mixture and the ratio existing between the peroxydiphosphate and the phosphate are given. Data was taken from Table XVI which utilized a mole ratio of peroxydiphosphate ion to ferrous ion of 1.0 to 4.4 and from Table XXI which utilized reaction media 0.50 molar in sulfuric acid.

TABLE XXII

DETERMINATION OF PEROXYDIPHOSPHATE IN THE PRESENCE OF PHOSPHATE

Conc. PO_4^{-3}	Mole ratio $P_2O_8^{-4}:PO_4^{-3}$	Acid Conc.	Normality $Li_4P_2O_8$
0.00 M	1.0:0.00	0.5 M H_2SO_4	0.1010
0.15	1.0:20	0.5 M H_2SO_4	0.1012
0.31	1.0:37	0.5 M H_3PO_4	0.1012
0.50	1.0:40	0.5 M H_2SO_4	0.1014
0.62	1.0:80	0.5 M H_2SO_4	0.1012
0.77	1.0:100	0.5 M H_2SO_4	0.1014
1.0	1.0:75	1.0 M H_3PO_4	0.1022
2.0	1.0:162	2.0 M H_3PO_4	0.1027

Mole ratio $P_2O_8^{-4}:Fe^{+2}$ = 1.0:4.4

It is seen that the concentration of phosphate in the reaction mixture has a greater influence than the value of the ratio between the peroxydiphosphate and phosphate. Hence in the determination of peroxydiphosphate in the presence of phosphate the reaction mixtures should be diluted until the phosphate concentration is 0.5 molar or less.

The data of Table XXI was obtained without rigid control of time. Hence a series of determinations were made in which the time of standing before the back titration of the excess ferrous ion was the variable studied.

Twenty milliliters of the lithium peroxydiphosphate solution was pipetted into a 250 ml. iodine flask. Twenty-five milliliters of 2.0 molar monopotassium phosphate, 25 ml. water, and 9.4 ml. of nine molar sulfuric acid were added in the order named. Then 50 ml. of standardized ferrous ammonium sulfate solution was added by means of a pipette. For zero time of standing the excess ferrous ion was back titrated as expeditiously as possible. In the other cases timing was started when the pipette containing the ferrous ammonium sulfate solution was half empty and stopped when the first drop of potassium dichromate had been added. The data are given in Table XXIII.

The procedure was repeated acidifying with 12 molar hydrochloric acid and six molar perchloric acid instead of the sulfuric acid. The data are also given in Table XXIII.

It is seen from the data of Table XXIII that the time of standing after the addition of the ferrous ammonium sulfate solution is not critical except when the reaction medium is 1.0 molar in hydrochloric acid. With a reaction medium 1.0 molar in hydrochloric acid it is necessary to wait five minutes before back titrating the excess ferrous ion.

TABLE XXIII

DETERMINATION OF PEROXYDIPHOSPHATE IN THE PRESENCE OF PHOSPHATE AS A FUNCTION OF TIME

Reaction Medium	Normality $Li_4P_2O_8$ Minutes Standing 0	10	20	40	60
0.5 M H_2SO_4	0.1010	0.1010	0.1010	0.1010	0.1012
1.0 M HCl	*	0.1007	0.1010	0.1010	0.1005
1.0 M $HClO_4$	0.1008	0.1011	0.1010	0.1014	0.1013

Mole ratio $P_2O_8^{-4}:PO_4^{-3}$ = 1.0:40

Mole ratio $P_2O_8^{-4}:Fe^{+2}$ = 1.0:4.4

* No end point obtainable. Five minutes of standing gave 0.1005 normal.

The above work shows that the reaction between peroxydiphosphate and ferrous ions is rapid. This fact suggested the direct potentiometric titration of peroxydiphosphate with standardized ferrous ammonium sulfate solution.

Twenty-five milliliters of approximately 0.1 normal lithium peroxydiphosphate solution was pipetted into a 150 ml. beaker. Seven tenths of a milliliter of nine molar sulfuric acid was added to make the solution 0.5 molar in respect to sulfuric acid. 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 calomel electrode was connected to the negative binding post of a Sargent potentiometer. The potential existing between the two electrodes was determined by means of the potentiometer. After adding one milliliter of standardized 0.1 normal ferrous ammonium sulfate solution 0.12 molar in sulfuric acid from an Exax quality burette bearing an offset tip, the potential was again determined. The ferrous ammonium sulfate solution was added in one milliliter increments until a rapid change in potential was noted; then it was added in one tenth milliliter increments. During the titration the solution was stirred with a magnetic stirrer. It was found that the magnetic stirrer did not affect the potentiometer readings. The data are shown graphically in Figure 2 and tabulated in the Data Appendix.

The titration was repeated except that the ferrous ammonium sulfate solution was added as rapidly as possible to the acidified lithium peroxydiphosphate solution to within one milliliter of the predetermined end point. It was then added in one tenth milliliter increments. The data are shown graphically in Figure 2 and tabulated in the Data Appendix.

The equivalence point in the titration was taken as the volume of 0.1000 normal ferrous ammonium sulfate solution required to reduce the peroxydiphosphate in a 25 ml. aliquot of the solution when an excess of the reducing agent was added and the excess back titrated with potassium dichromate solution using diphenylamine sodium sulfonate as indicator. The reaction medium was 0.50 molar in respect to sulfuric acid. It was found that 25.00 ml. of the lithium peroxydiphosphate solution required 27.75 ml. of 0.1000 normal ferrous ammonium sulfate solution.

A different platinum electrode was used and the potentiometric titration carried out again by adding the ferrous ammonium sulfate solution in one milliliter increments. The data are shown graphically in Figure 2.

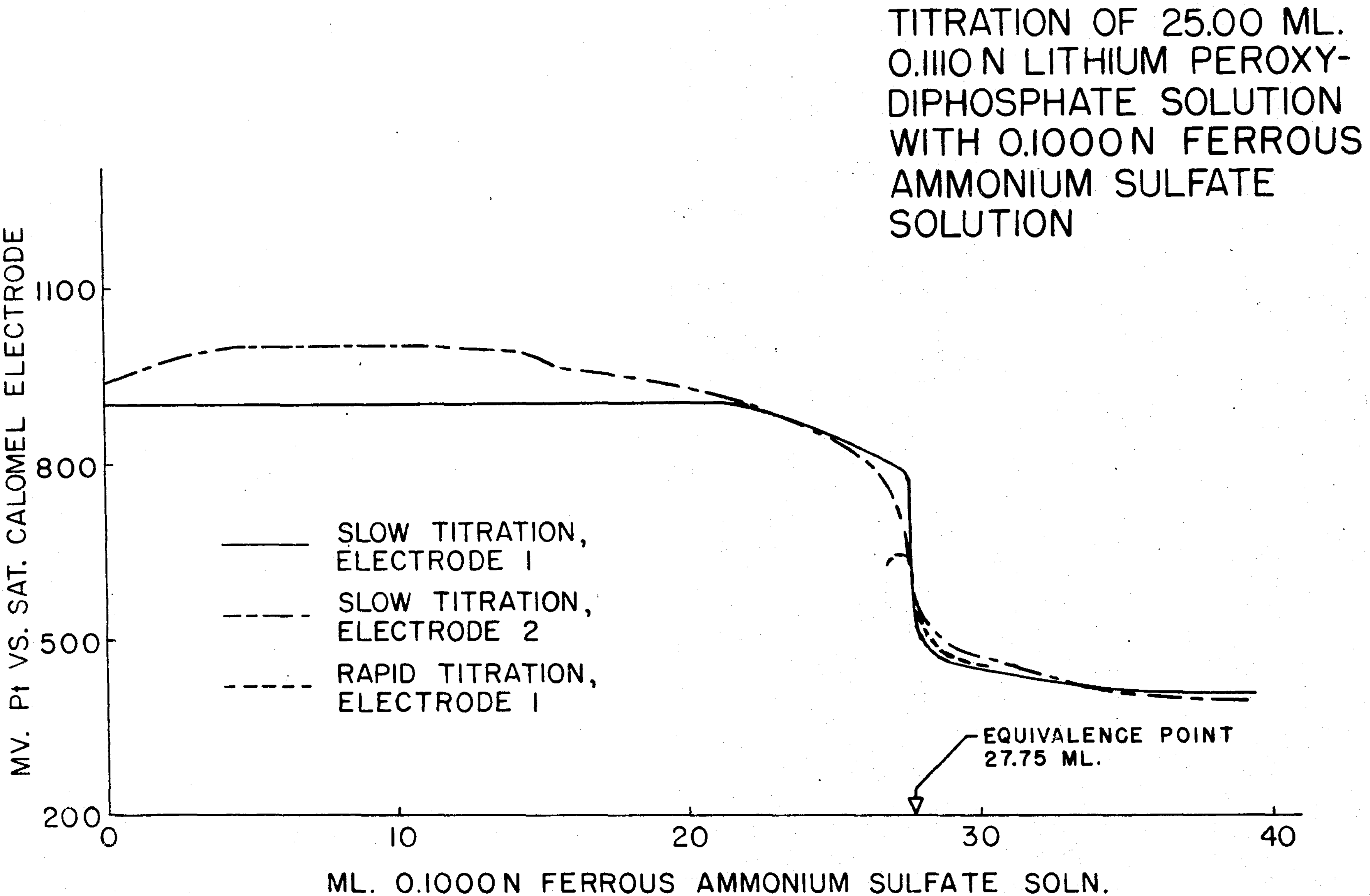

TITRATION OF 25.00 ML. 0.1110 N LITHIUM PEROXYDIPHOSPHATE SOLUTION WITH 0.1000 N FERROUS AMMONIUM SULFATE SOLUTION

FIGURE 2

It is seen from Figure 2 that the shape of the curve depends upon external factors. The reaction between peroxydiphosphate and ferrous ions would be expected to be irreversible which is borne out by the data plotted in Figure 2. That is, the curve results from the combination of two half cell reactions; (1) the irreversible reduction of peroxydiphosphate and (2) the reversible oxidation of ferrous ion and as such would be expected to be nonreproducible.

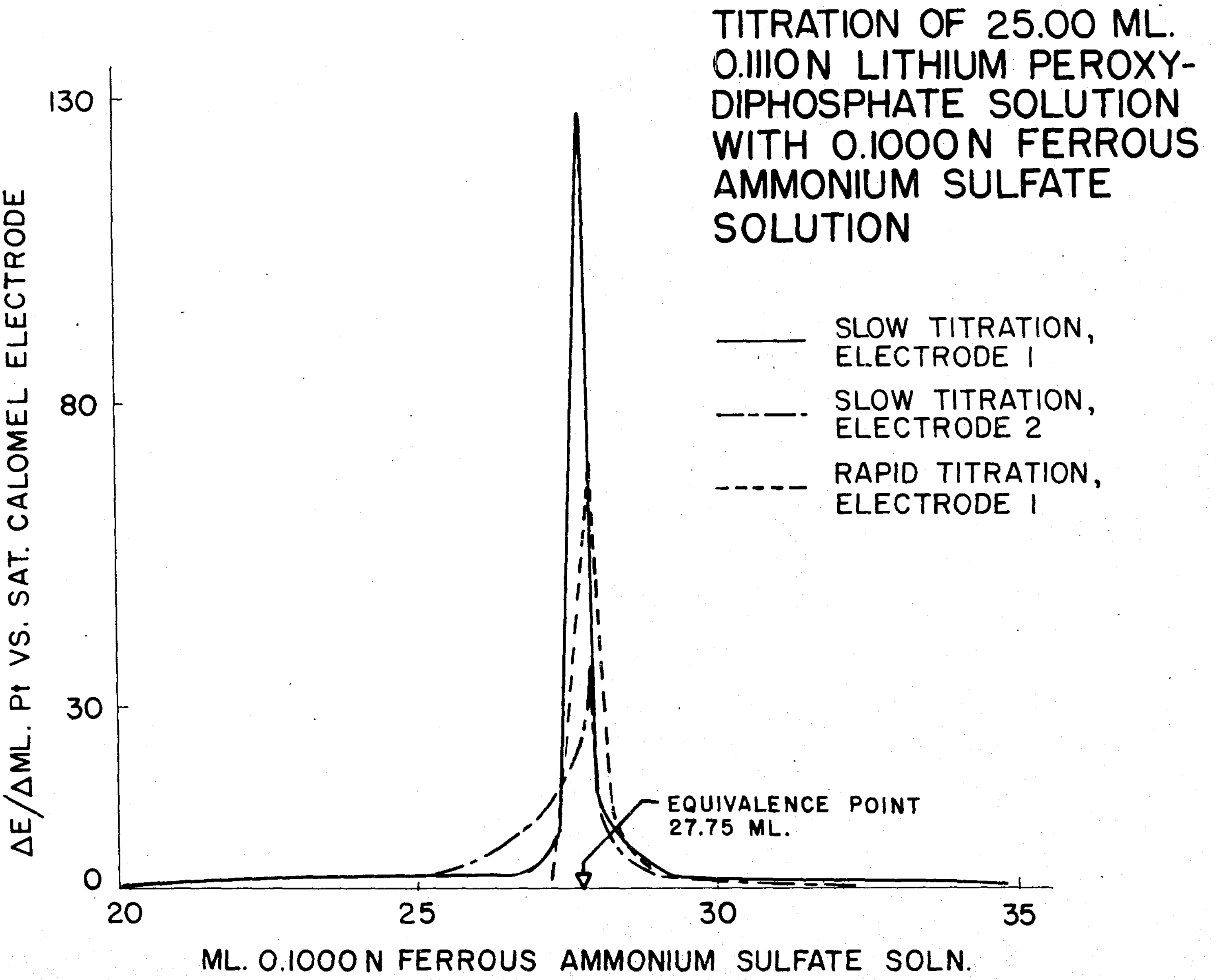
However if the change in potential per one tenth of a milliliter of ferrous ammonium sulfate solution, $\Delta E/\Delta$ ml., is plotted against total volume of ferrous ammonium sulfate solution the end point can be readily obtained as shown by Figure 3. The precision was ± 0.05 ml.

The titration was repeated with reaction media of 0.50, 1.0, 2.0, and 3.0 molar sulfuric acid. Both the slow, i.e., adding the ferrous ammonium sulfate solution in one milliliter increments, and the rapid titration were carried out at each acidity. The data are given in Table XXIV.

In no case was exactly 0.1000 normal ferrous ammonium sulfate solution used. Since a solution of ferrous ammonium sulfate is not stable all volumes were calculated to equivalent volumes of exactly 0.1000 normal solution. Thus the data are readily compared.

Reaction media of phosphoric, hydrochloric, and perchloric acid were tried. When hydrochloric acid was used the odor of chlorine was detected. The data are also given in Table XXIV.

If the volume of ferrous ammonium sulfate solution required to react with 25.00 ml. of the lithium peroxydiphosphate solution determined by



TITRATION OF 25.00 ML. 0.1110 N LITHIUM PEROXYDIPHOSPHATE SOLUTION WITH 0.1000 N FERROUS AMMONIUM SULFATE SOLUTION

FIGURE 3

TABLE XXIV

POTENTIOMETRIC DETERMINATION OF THE END POINT IN THE TITRATION OF 25.00 ML. OF LITHIUM PEROXYDIPHOSPHATE SOLUTION WITH 0.1000N FERROUS AMMONIUM SULFATE SOLUTION

Reaction Medium	Ml. 0.1000 N Ferrous Ammonium Sulfate Solution to Reach the End Point			
	Slow titration		Rapid titration	
0.25 M H_2SO_4	27.75	27.70	27.80	
0.50 M H_2SO_4	27.70	27.65	27.90	
1.0 M H_2SO_4	27.15		27.80	
2.0 M H_2SO_4	26.55		27.80	
3.0 M H_2SO_4	25.75		27.45	
0.50 M H_3PO_4	27.75	27.75	27.75	27.85
1.0 M H_3PO_4	27.85	27.85	27.85	27.85
2.0 M H_3PO_4	27.85	27.85	27.85	27.95
0.25 M HCl*	25.95		26.30	
0.50 M HCl*	25.40		26.10	
0.25 M $HClO_4$	17.40			
0.50 M $HClO_4$	27.65		27.85	
1.0 M $HClO_4$	27.55		27.85	
2.0 M $HClO_4$	27.10		27.55	

Equivalence point at 27.75 milliliters

* Odor of chlorine detected

adding an excess of the reducing agent and back titrating the excess with potassium dichromate solution is taken as the volume required to reach the equivalence point the data show that in the potentiometric titration the sulfuric acid concentration should be between 0.25 and 0.50 molar for results that check to within three parts per thousand of the designated standard. However, if the amount of peroxydiphosphate present is approximately known, sulfuric acid concentrations up to 2.0 molar can be used by adding the ferrous ammonium sulfate solution rapidly until the end point is nearly reached and then finishing the titration slowly. With acid concentrations greater than 0.50 molar with the slow titration and greater than 2.0 molar with the fast titration low results are obtained, presumably due to the decomposition of the peroxydiphosphate because of the high acidity.

If the criterion described above is applied to the titrations utilizing phosphoric acid satisfactory results are obtained only when the phosphoric acid concentration is 0.5 molar. Greater acid concentrations give high results.

When hydrochloric acid is used low results are obtained because of the oxidation of the chloride ion.

When the reaction media acidified with perchloric acid are used, satisfactory results are not obtained with acid concentrations from 0.25 to 2.0 molar.

In summary the end point in the titration of peroxydiphosphate with ferrous ammonium sulfate solution can be satisfactorily determined potentiometrically if the peroxydiphosphate solution is 0.25 to 0.50 molar in sulfuric acid or 0.50 molar in phosphoric acid. If the amount of peroxydiphosphate is approximately known sulfuric acid concentrations up to 2.0 molar can be used.

When a solution of peroxydiphosphate is titrated with ferrous ammonium sulfate there are essentially no ferrous ions in the solution being titrated until after the equivalence point has been reached. The possibility of detecting the appearance of ferrous ions by means of the dead stop end point technique (26) was investigated as follows.

Platinum electrodes identical to those used by Stone and Scholten (26) were employed. Also a Fisher Elecdropode was used to apply the potential across the electrodes and to observe the current flowing in the electrode circuit.

Twenty-five milliliters of lithium peroxydiphosphate solution was pipetted into a 150 ml. beaker. The platinum electrodes were introduced and a potential of fifty millivolts was applied across the electrodes. The sensitivity control of the Elecdropode was set at IX. The peroxydiphosphate solution was made 0.25 molar in sulfuric acid by adding 0.7 ml. of nine molar sulfuric acid. Standardized 0.1 normal ferrous ammonium sulfate solution was added at a rapid rate until the galvanometer indicated that a current was flowing in the electrode circuit. The addition of the ferrous ammonium sulfate solution was then ceased until the system reached equilibrium which was indicated by the galvanometer reading being the same as before the titration was started. The titration was carried out in this manner until a permanent deflection of the galvanometer was obtained. As the end point was approached smaller and smaller volumes of the ferrous ammonium sulfate solution caused a temporary deflection of the galvanometer. However even when very close to the end point equilibrium was attained rapidly.

During the titration the solution was stirred by a motor stirrer. Stirring with a magnetic stirrer caused a deflection of the galvanometer which was proportional to the speed of the stirrer. The motor stirrer did not affect the galvanometer.

As before the equivalence point in the titration was taken as the volume of 0.1000 normal ferrous ammonium sulfate solution required to reduce the peroxydiphosphate in a 25 ml. aliquot of the solution when an excess of the reducing agent was added and the excess back titrated with potassium dichromate solution. It was found that 25.00 ml. of the lithium peroxydiphosphate solution required 26.95 ml. of 0.1000 normal ferrous ammonium sulfate solution.

The titration was repeated with the reaction media acidified with various amounts of sulfuric, phosphoric, and perchloric acid. The data are given in Table XXV. In all cases the end point was determined without recourse to graphical methods. The sharpness of the end point is shown by the data in Table XXVI.

If the equivalence point is taken as 26.95 ml. of 0.1000 normal ferrous ammonium sulfate solution the determination of the end point by the dead stop technique is satisfactory for sulfuric and solutions ranging from 0.25 to 1.0 molar. The criterion taken for satisfactory results is that the end point in the titration does not differ by more than three parts per thousand from the equivalence point. On the same basis reaction media 0.50 to 1.0 molar in phosphoric acid and 0.25 to 0.50 molar in perchloric acid are satisfactory.

TABLE XXV

DETERMINATION OF THE END POINT IN THE TITRATION OF LITHIUM PEROXYDIPHOSPHATE WITH FERROUS AMMONIUM SULFATE SOLUTION BY MEANS OF THE DEAD STOP END POINT

Titration Medium	Ml. of 0.1000 N Ferrous Ammonium Sulfate Solution Required for 25 ml. $Li_4P_2O_8$	
0.25 M H_2SO_4	26.90	26.90
0.50 M H_2SO_4	26.88	26.86
1.0 M H_2SO_4	26.86	
2.0 M H_2SO_4	26.84	
3.0 M H_2SO_4	26.67	
0.50 M H_3PO_4	26.97	26.94
1.0 M H_3PO_4	26.97	
2.0 M H_3PO_4	27.05	27.03
0.25 M $HClO_4$	26.91	26.87
0.50 M $HClO_4$	26.90	26.83
1.0 M $HClO_4$	26.84	
2.0 M $HClO_4$	26.66	

Equivalence point at 26.95 milliliters.

As with the direct potentiometric determination of the end point higher concentrations of sulfuric or perchloric acid gave low results which substantiates the hypothesis that decomposition of the peroxydiphosphate occurred.

TABLE XXVI

SHARPNESS OF THE DEAD STOP END POINT IN THE TITRATION OF LITHIUM PEROXYDIPHOSPHATE WITH FERROUS AMMONIUM SULFATE

Titration Medium	Ml. 0.1000 Fe^{+2} Solution	Galvanometer Reading
0.25 M H_2SO_4	26.85	3
	26.90	70
1.0 M H_2SO_4	26.85	6
	26.87	42
0.50 M H_3PO_4	26.95	3
	26.97	27
1.0 M H_3PO_4	26.97	3
	27.03	12
0.25 M $HClO_4$	26.87	5
	26.90	81
2.0 M $HClO_4$	26.64	5
	26.66	100

Examination of the data in Tables XXIV and XXV reveals that when reaction mixtures containing phosphoric acid gave unsatisfactory results it was because too much of the ferrous ammonium sulfate solution was used to reach the end point, i.e., additional ferrous ion was oxidized. The phenomenon can be explained by the ferrous ion being a stronger reducing agent in the presence of phosphoric acid than in sulfuric or perchloric acids thereby accelerating the air oxidation of the ferrous ion during the titration. This hypothesis is substantiated by the fact that the titration was satisfactory when the concentration of phosphoric acid was low (21).

Although much the same results were obtained with the potentiometric determination of the end point as with the dead stop technique, the dead stop technique is recommended as equilibration of the electrode system was attained much more rapidly. In addition the dead stop technique gives the end point directly; graphical methods are not necessary.

VIII. AN ANALYTICAL STUDY OF THE REACTION BETWEEN PEROXYDIPHOSPHATE AND IODIDE IONS IN ACID SOLUTION

The liberation of iodine by peroxydiphosphate from acidified potassium iodide solution was used by previous workers for the estimation of peroxydiphosphate. However an analytical study of the reaction had never been made.

Fichter and Gutzwiller (5), used two normal sulfuric acid to acidify the reaction mixture but did not state how much acid was used. None of the other authors even stated what acid they used to acidify the solution. The time of standing necessary to complete the reaction had never been studied. With the exception of Fichter and Gutzwiller (5) previous workers allowed the reaction mixture to stand overnight without ascertaining if a shorter period of time would be sufficient. Instead of allowing the reaction mixture to stand overnight Fichter and Gutzwiller gently warmed the reaction mixture and then titrated the liberated iodine. Their procedure cannot be considered good analytical practice because of the probability of losing iodine by reason of its high vapor pressure. Also none of the previous workers considered the possibility of the formation of iodine by air oxidation of the iodide.

All of these factors have been considered in this study. The reaction mixture was acidified with various amounts of various acids and allowed to stand for various periods of time before titrating the liberated iodine.

It was desirable to be able to relate the results obtained by determining peroxydiphosphate by the titration of the iodine liberated by it from acidified iodide solution to the results obtained by the reduction with ferrous ion as described in Section VII. In order to better relate the results obtained by the two methods the sodium thiosulfate and sodium arsenite solution used to titrate the liberated iodine were standardized with the same potassium dichromate as was used in Section VII.

Approximately 0.1 normal sodium thiosulfate solution was made by dissolving 24.85 g. sodium thiosulfate pentahydrate in 100 ml. water containing 0.1 g. sodium carbonate and diluting this solution to one liter.

Approximately 0.1 normal sodium arsenite solution was prepared by dissolving 4.9460 g. arsenious oxide previously dried at 110° C. for one hour in a solution composed of three grams sodium hydroxide dissolved in 10 ml. water (8). The solution was diluted to 400 ml. Three drops of phenolphthalein solution was added and the alkali neutralized by adding three molar sulfuric acid until the indicator was decolorized. Twenty-five grams sodium bicarbonate was added and the solution diluted quantitatively to one liter.

Approximately 0.1 normal iodine solution was prepared by dissolving 6.5 g. iodine in a solution of 10 g. potassium iodide in 20 ml. water and diluting with water to 500 ml.

All the chemicals used met the American Chemical Society's specifications for reagent chemicals.

The sodium thiosulfate solution was standardized by means of the potassium dichromate solution as follows. Twenty-five milliliters of the dichromate solution was introduced into a 250 ml. iodine flask by means of a pipette. Two grams potassium iodide and four milliliters 1:1

hydrochloric acid was added. The flask was stoppered and a freshly prepared concentrated potassium iodide solution was placed in the gutter of the flask. The flask was allowed to stand in the dark at room temperature for one hour. After the period of standing the potassium iodide solution in the gutter was allowed to run into the flask. After diluting with 100 ml. water the iodine was titrated with the sodium thiosulfate solution using three milliliters of a 0.5 per cent soluble starch solution as indicator (29). Triplicate standardizations agreed to one part per thousand.

The iodine solution was standardized by titrating 25 ml. aliquots acidified with two milliliters 1:1 hydrochloric acid with the sodium thiosulfate solution using starch solution as indicator. The sodium arsenite solution was then standardized by titrating 25 ml. aliquots of the iodine solution in the presence of sodium bicarbonate with the arsenite solution. After the sodium arsenite was standardized a 25 ml. aliquot of the iodine solution was titrated with the sodium thiosulfate solution to insure that there had been no change in the concentration of the iodine solution. By this method the normality of the sodium arsenite solution was found to be 0.09905.

The same sodium thiosulfate and sodium arsenite solutions were used throughout.

In studying a reaction as a function of time it is always desirable to be able to quench the reaction at will. The reaction between peroxydiphosphate and iodide ions could be quenched merely by neutralizing the acid present provided that the peroxydiphosphate would not liberate iodine from a neutral potassium iodide solution. Hence it was necessary to determine if peroxydiphosphate and iodide ions would react in a neutral solution.

A neutral solution containing peroxydiphosphate and iodide ions was prepared as follows. Ten milliliters of 0.1 normal tetrapotassium peroxydiphosphate solution was pipetted into a 250 ml. iodine flask. Three grams sodium bicarbonate, 10 ml. water, one milliliter three molar sulfuric acid, and three grams potassium iodide were added in the order named. The flask was stoppered and a freshly prepared concentrated potassium iodide solution was placed in the gutter of the flask. After standing for four hours in the dark the potassium iodide solution in the gutter was allowed to run into the flask. Three milliliters of a 0.5 per cent starch solution was added. A very faint blue color was observed. The color was too faint to warrant titration of the iodine present. The experiment was repeated but the time of standing was increased to 24 hours. In this instance the color of the starch-iodine complex was much deeper. One tenth of a milliliter of 0.1000 normal arsenite solution was required to discharge the color.

At the most 10 minutes is required for the titration of iodine with arsenite solution using starch solution as indicator. Since peroxydiphosphate does not liberate an appreciable amount of iodine from a neutral potassium iodide solution in 10 minutes the extent of reaction between the two ions in acid solution for a given period of time can be determined by neutralizing the solution with sodium bicarbonate and titrating the liberated iodine with neutral arsenite solution provided that peroxydiphosphate and arsenite do not react to an appreciable extent in 10 minutes in a neutral solution.

Experiments were carried out to determine if peroxydiphosphate and arsenite react in a neutral solution.

Ten milliliters 0.1 normal tetrapotassium peroxydiphosphate solution was pipetted into a 250 ml. iodine flask. Three grams solid sodium bicarbonate was added and 20 ml. of 0.09905 normal sodium arsenite solution 0.06 molar in respect to sulfuric acid was added by means of a pipette. A blank was prepared by replacing the peroxydiphosphate solution with 10 ml. water. After standing for one hour the amount of arsenite remaining was determined by titrating with 0.1 normal iodine solution using a 0.5 per cent starch solution as indicator. The blank and the solution containing the peroxydiphosphate required the same volume of iodine solution indicating that no reaction had taken place between the arsenite and peroxydiphosphate. The experiment was repeated with the time of standing increased to 24 hours. In 24 hours one per cent of the peroxydiphosphate was reduced by the arsenite.

Thus it is seen that the extent of the reaction between peroxydiphosphate and iodide ions in an acidified potassium iodide solution for various times of standing can be determined by neutralizing the reaction mixture with sodium bicarbonate after the period of standing and titrating the liberated iodine with neutral arsenite solution.

The reaction between peroxydiphosphate and potassium iodide was studied in reaction mixtures acidified with sulfuric, phosphoric, and perchloric acids. The reaction was not studied in the presence of hydrochloric acid because of the oxidation of the chloride ion by the peroxydiphosphate as previously noted. Also the effect of having phosphate present was studied.

The effect of varying the time of reaction and the concentration of sulfuric acid was ascertained as follows.

Twenty-five milliliters of lithium peroxydiphosphate solution approximately 0.1 normal was pipetted into a 250 ml. iodine flask. Three grams potassium iodide was added followed by sufficient nine molar sulfuric acid to give the requisite concentration of acid in the reaction mixture. The flask was immediately stoppered and a freshly prepared concentrated potassium iodide solution was placed in the gutter of the iodine flask to guard against the loss of iodine. After standing at room temperature in the dark for the designated time the potassium iodide solution in the gutter was allowed to run into the flask. Excess sodium bicarbonate was added and the iodine present was titrated with standardized approximately 0.1 normal neutral sodium arsenite solution using starch solution as indicator.

Timing was started upon the addition of the sulfuric acid and stopped when the sodium bicarbonate was added.

Blanks were prepared by omitting the lithium peroxydiphosphate solution and substituting an equal volume of water. In all cases only a small amount of iodine was liberated; e.g., in all cases 0.02 ml. of 0.1 normal neutral arsenite solution was sufficient to discharge the blue starch-iodine color.

The data for various concentrations of sulfuric acid and for various times of reaction are given in Table XXVII.

The concentration of tetralithium peroxydiphosphate in the solution being used was determined by adding excess ferrous ammonium sulfate solution

TABLE XXVII

DETERMINATION OF PEROXYDIPHOSPHATE BY THE TITRATION OF THE IODINE LIBERATED FROM POTASSIUM IODIDE SOLUTION ACIDIFIED WITH SULFURIC ACID AS A FUNCTION OF TIME

Reaction Time	Normality $Li_4P_2O_8$* Acidity		
	0.25 M	0.50 M	1.0 M
5 min.		0.1012	0.1078
10 min.		0.1073	0.1078
15 min.	0.09422	0.1079	0.1078
30 min.	0.1037	0.1079	0.1079
45 min.	0.1067	0.1079	0.1080
60 min.	0.1073	0.1080	0.1080
2 hours	0.1077		
3 hours	0.1077		
5 hours	0.1077		
7 hours	0.1079		
8 hours	0.1077		

*By the ferrous ammonium sulfate procedure, 0.1078.

to a measured volume of the peroxydiphosphate solution acidified to 0.50 molar with sulfuric acid and back titrating the excess reducing agent with 0.1000 normal potassium dichromate solution as previously described. The concentration of the lithium peroxydiphosphate solution determined in this manner was 0.1078 normal.

The data show that the rate of reaction between peroxydiphosphate and iodide ions is markedly affected by the concentration of sulfuric acid in the reaction mixture. With the reaction mixture 0.25 molar in sulfuric acid a reaction period of 120 minutes is required. When the acidity is 0.50 molar a reaction period of 15 minutes is sufficient; when 1.0 molar, a five minute period is adequate.

Thus it is seen that if previous workers carried out the reaction between peroxydiphosphate and iodide ions in a medium acidified with sulfuric acid it was not necessary to allow the solution to stand overnight for the reaction to go to completion if the reaction mixture was 0.25 molar or greater in sulfuric acid.

The determination was attempted without a period of standing; e.g., the liberated iodine was titrated with standardized sodium thiosulfate solution immediately after the addition of the sulfuric acid. A reaction mixture 1.0 molar in sulfuric acid was used. Approximately two milliliters from the equivalence point a false end point was obtained. After five false end points were obtained without obtaining a true end point the titration was terminated as it was deemed that a determination carried out in such a manner had no advantage over allowing a five minute reaction period prior to the titration and then titrating to a true end point with no complications arising from false end points. Adding three drops of 0.25 per cent osmium tetroxide solution was not beneficial.

The reaction between peroxydiphosphate and iodide ions was studied as a function of time with solutions acidified with six molar perchloric acid.

The procedure employed was the same as when sulfuric acid was used. The data are listed in Table XXVIII.

TABLE XXVIII

DETERMINATION OF PEROXYDIPHOSPHATE BY THE TITRATION OF THE IODINE LIBERATED FROM POTASSIUM IODIDE SOLUTION ACIDIFIED WITH PERCHLORIC ACID AS A FUNCTION OF TIME

Reaction Time	Normality $Li_4P_2O_8$*	
	Acidity	
	0.50 M	1.0 M
5 Min.	0.09418	0.1078
10 Min.	0.1041	0.1079
15 Min.	0.1041	0.1077
30	0.1078	0.1080
45	0.1078	0.1082
60	0.1078	0.1083

* By the ferrous ammonium sulfate procedure, 0.1078.

The data of Table XXVIII again show the pronounced influence of acidity on the reaction between peroxydiphosphate and iodide ions. Also with the greater acid concentration the reaction time should not be longer than 30 minutes.

The determination was attempted without a period of standing. A reaction mixture 1.0 molar in acid was used. Once again the procedure was not considered feasible because of the occurrence of false end points. The addition of three drops of 0.25 per cent osmium tetroxide solution was not beneficial.

The effect of having present various amounts of lithium peroxydiphosphate was studied in reaction mixtures acidified with sulfuric and perchloric acid. The procedure used was the same as above except that the liberated iodine was titrated with standardized sodium thiosulfate solution after the period of standing. The timing was started when the acid was added and stopped with the first addition of the sodium thiosulfate solution.

The data are given in Table XXIX.

TABLE XXIX

DETERMINATION OF PEROXYDIPHOSPHATE BY THE TITRATION OF THE IODINE LIBERATED FROM POTASSIUM IODIDE SOLUTION

Ml. $Li_4P_2O_8$ Taken	Normality $Li_4P_2O_8$* Acidity 0.25 M H_2SO_4 [a]	1.0 M H_2SO_4 [b]	1.0 M $HClO_4$ [b]
5	0.1089	0.1081	0.1086
10	0.1078	0.1080	0.1078
20	0.1077	0.1080	0.1078
25	0.1075	0.1078	0.1078
40	0.1081	0.1077	0.1077

* By the ferrous ammonium sulfate procedure, 0.1078

a 60 minute reaction time

b Five minute reaction time

The data of Table XXIX indicate that the determination of peroxydiphosphate by the titration of the iodine liberated from a potassium iodide solution 0.25 molar in sulfuric acid is satisfactory when the iodine is titrated with sodium thiosulfate solution after 60 minutes of standing. When the reaction mixture is 1.0 molar in sulfuric acid or 1.0 molar in perchloric acid satisfactory results are obtained with a reaction time of five minutes.

The reaction between peroxydiphosphate and iodide ions in 0.50 and 1.0 molar phosphoric acid was studied as a function of time. The procedure used was the same as the determinations wherein sulfuric and perchloric acids were used. The data are listed in Table XXX.

TABLE XXX

DETERMINATION OF PEROXYDIPHOSPHATE BY THE TITRATION OF THE IODINE LIBERATED FROM POTASSIUM IODIDE SOLUTION ACIDIFIED WITH PHOSPHORIC ACID AS A FUNCTION OF TIME

Reaction Time	Normality $Li_4P_2O_8$* Acidity 0.50 M	Normality $Li_4P_2O_8$* Acidity 1.0 M
0.25 Hr.	0.04706	0.05301
0.50	0.07219	0.1019
0.75	0.07761	0.1058
1.0	0.08846	0.1049
2.0	0.1014	0.1073
3.0	0.1055	0.1072
5.0	0.1078	0.1078

*By the ferrous Ammonium Sulfate procedure, 0.1078.

The sluggishness of the reaction between peroxydiphosphate and iodide ions in the solutions acidified with phosphoric acid is attributed to the fact that phosphoric acid is a weaker acid than sulfuric or perchloric acid. This hypothesis was substantiated by carrying out the reaction in a 10 per cent acetic acid solution. In a reaction time of one hour 45 per cent of the peroxydiphosphate reacted as determined by the amount of iodine liberated and in a three hour reaction time 74 per cent of the peroxydiphosphate reacted. That is, in a reaction medium acidified with an acid weaker than phosphoric acid the extent of the reaction was less than in media acidified with phosphoric acid.

The reaction between peroxydiphosphate and iodide in the presence of phosphate in solutions acidified with sulfuric and perchloric acid was studied as follows.

Twenty milliliters of the lithium peroxydiphosphate solution was pipetted into a 250 ml. iodine flask. Fifty milliliters of 2.0 molar monopotassium phosphate solution was added. This amount of phosphate gave a molar ratio of 1:100 between the peroxydiphosphate and the orthophosphate. After the addition of three grams potassium iodide, 8.3 ml. of nine molar sulfuric acid was added to give a reaction mixture 1.0 molar in sulfuric acid. A freshly prepared concentrated potassium iodide solution was placed in the gutter. After standing for five minutes the liberated iodine was titrated with 0.1032 normal sodium thiosulfate solution using starch solution as indicator. In all cases a well defined end point was obtained.

Smaller volumes of the potassium phosphate solution were used to give different peroxydiphosphate to phosphate ratios. The volume of the reaction mixture was kept constant by the addition of water.

The data are given in Table XXXI.

The procedure was repeated with the time of standing increased to 15 minutes. The reaction was also carried out in solutions acidified with perchloric acid.

TABLE XXXI

DETERMINATION OF PEROXYDIPHOSPHATE IN THE PRESENCE OF PHOSPHATE BY THE TITRATION OF THE IODIDE LIBERATED FROM POTASSIUM IODIDE SOLUTION

Mole ratio $P_2O_8^{-4}:PO_4^{-3}$	Normality $Li_4P_2O_8$* Acidity		
	1.0 M [a] H_2SO_4	1.0 M [b] H_2SO_4	1.0 M [b] HCl_4
1.0:0.0	0.1078	0.1079	0.1083
1.0:20	0.1078	0.1081	0.1080
1.0:40	0.1078	0.1078	0.1078
1.0:80	0.1053	0.1068	0.08069
1.0:100	0.09728	0.1057	0.07751

* By the ferrous ammonium sulfate procedure, 0.1078.
a Five minute reaction time.
b 15 minute reaction time.

The data of Table XXXI again illustrates the profound influence that the acidity has upon the reaction between peroxydiphosphate and iodide. That is, a large amount of phosphate decreases the acidity of the medium by the formation of phosphoric acid. This is shown more clearly by Table XXXII which contains the same data as Table XXXI but expressed as indicated.

TABLE XXXII

EXTENT OF REACTION BETWEEN PEROXYDIPHOSPHATE AND IODIDE IN THE PRESENCE OF VARIOUS AMOUNTS OF PHOSPHATE

	% $Li_4P_2O_8$ Reacted	
Mole ratio	in 5 minutes	in 15 minutes
$H_2SO_4:KH_2PO_4$ [a]		
1.0:0.00	100.0	100.1
1.0:026	100.0	100.2
1.0:0.52	100.0	100.0
1.0:1.0	97.68	99.30
1.0:1.3	90.24	98.05
$HI:KH_2PO_4$ [b]		
1.0:0.00		100.3
1.0:0.26		100.1
1.0:0.52		100.0
1.0:1.0		74.85
1.0:1.3		71.90

[a] Acidity 1.0 molar H_2SO_4
[b] Acidity 1.0 molar HCl_4

The data presented show that the reaction between peroxydiphosphate and iodide is greatly influenced by the acidity of the reaction medium. Even in the presence of phosphoric acid a small change in the concentration of the acid exerts a large influence on the rate of reaction. The dependence of the rate of reaction between peroxydiphosphate and iodide upon the acid concentration is an important consideration in the determination of peroxydiphosphate by the iodometric procedure, especially in the presence of phosphate. The recommended acidity in the absence of phosphate is 1.0 molar in sulfuric acid or perchloric acid. The minimum recommended reaction time is five minutes. A reaction time of up to 60 minutes is not detrimental when sulfuric acid is used. When perchloric acid is used the maximum reaction time is 30 minutes. In the presence of phosphate the acid concentration should be 1.0 molar in sulfuric acid. When less than 2.5 mole per cent of peroxydiphosphate is present the minimum reaction time should be increased to 15 minutes.

Since a primary standard quality peroxydiphosphate compound could not be prepared the iodometric determination must be compared to the results obtained by the ferrous ammonium sulfate procedure. Sufficient data were not gathered for a statistical treatment of the iodometric determination. However it is worthy of note that the average concentration of the lithium peroxydiphosphate in Table XXVII obtained by titrating the iodine liberated from reaction mixtures 1.0 molar in sulfuric acid was 0.1079 while the normality determined by the method involving the back titration of an excess of ferrous ion gave a value of 0.1078. With the reaction mixture acidified with perchloric acid to the extent of 1.0 molar the average normality of the lithium peroxydiphosphate solution was found to be 0.1079. Although not on a statistical basis it can be said that the ferrous ammonium sulfate procedure gives results that differ from the results obtained iodometrically by one part per thousand.

IX. SUMMARY

Tetrapotassium peroxydiphosphate was prepared by the method of Fichter and Gutzwiller (5). Their findings were substantiated except for the claim that the final product was pure white. The tetrapotassium peroxydiphosphate always contained some chromate. No method of crystallization could be found that would remove the chromate.

Tetrapotassium peroxydiphosphate was precipitated from the electrolyte of Fichter and Gutzwiller by adding solid potassium hydroxide. The product also contained chromate but the precipitation served as an efficient method for the preparation of a rather impure chromate containing tetrapotassium peroxydiphosphate which was found to be suitable as a starting material for the preparation of tetralithium peroxydiphosphate tetrahydrate.

A solution of lithium peroxydiphosphate was prepared from a solution of the crude tetrapotassium peroxydiphosphate by precipitating the potassium, phosphate, and fluoride by adding a lithium perchlorate solution. The peroxydiphosphate was precipitated from the solution as tetralithium peroxydiphosphate tetrahydrate by the addition of methanol. The material was chromate free.

A 0.1 normal solution of the tetralithium peroxydiphosphate tetrahydrate had a pH of 10.2. It decomposed to the extent of five parts per thousand in 49 days. At lower pH values the solution was less stable.

Peroxydiphosphate was determined by adding excess ferrous ions to a solution of peroxydiphosphate and back titrating the excess with potassium dichromate solution using diphenylamine sodium sulfonate as indicator. Reaction mixtures 0.25 to 1.0 molar in sulfuric acid and 0.25 to 2.0 molar in perchloric acid were found to give satisfactory results. Higher acid concentrations gave low results. When reaction mixtures containing hydrochloric acid were used somewhat erratic results were obtained. In 1.0 to 2.0 molar hydrochloric acid solutions plausible results were obtained. No time of standing was necessary. The amount of excess ferrous ion was not critical. The determination could be carried out in the presence of phosphate. When phosphoric acid was used to acidity the reaction mixture high results were obtained. In this instance the higher acid concentrations gave higher results. With reaction mixtures 0.5 to 2.0 molar in phosphoric acid the results were a function of the amount of excess ferrous ion present. The largest excess gave the highest results.

The direct potentiometric titration of peroxydiphosphate with a ferrous ammonium sulfate solution was accomplished. Satisfactory results were obtained when the reaction mixture was 0.25 to 0.50 molar in sulfuric acid or 0.50 molar in phosphoric acid. Higher sulfuric acid concentrations gave low results while higher phosphoric acid concentrations gave high results. Reaction mixtures 0.25 to 2.0 molar in perchloric acid gave low results. The use of hydrochloric acid gave low results because of oxidation of the chloride ion.

The equivalence point in the titration of peroxydiphosphate with a ferrous ammonium sulfate solution was successfully determined by means of the dead stop end point technique. Satisfactory results were obtained if the peroxydiphosphate solution was 0.25 to 1.0 molar in sulfuric acid, 0.50 to 1.0 molar in phosphoric acid, or 0.25 to 0.50 molar in perchloric acid. Higher concentrations of sulfuric or perchloric acid gave low results. Higher concentrations of phosphoric acid gave high results.

An iodometric determination of peroxydiphosphate was achieved. The rate of reaction between peroxydiphosphate and iodide ions was found to be influenced profoundly by the acidity of the reaction mixture; a small increase in acidity greatly increased the rate of reaction. In the absence of phosphate the reaction between peroxydiphosphate and iodide in 1.0 molar sulfuric acid or 1.0 molar perchloric acid was complete in five minutes. The determination was successful in the presence of phosphate. However when less than 2.5 mole per cent of peroxydiphosphate was present only the 1.0 molar sulfuric acid medium was satisfactory and a 15 minute period of standing was necessary.

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APPENDIX

The data plotted in Figure 1 are tabulated in Table XXXIII.

TABLE XXXIII

PER CENT OF PHOSPHATE OXIDIZED TO PEROXYDIPHOSPHATE UPON PROLONGED ELECTROLYSIS

	% Phosphate Oxidized to Peroxydiphosphate	
Hours Electrolysis	Calc. on Basis of Actual Volume	Assume No Diminution of Volume
	Run 7	
5	43	43
11	67	71
18	73	80
24	75	85
30	73	86
	Run 8*	
6	49	
12	70	
16	70	
22	72	
28	73	
30	71	

* Original volume maintained by adding water.

The data plotted in Figure 2 are tabulated in Table XXXIV.

TABLE XXXIV

TITRATION OF 25.00 ML. 0.1110 N LITHIUM PEROXYDIPHOSPHATE SOLUTION WITH 0.1000 N FERROUS AMMONIUM SULFATE SOLUTION

Slow Titration, Electrode 1		Slow Titration, Electrode 2		Rapid Titration, Electrode 1	
Milliliters	Millivolts	Milliliters	Millivolts	Milliliters	Millivolts
0.0	901	0.0	943	26.9	634
1.1	901	1.1	975	27.0	640
2.2	901	2.2	983	27.1	647
3.4	901	3.3	998	27.2	647
4.5	901	4.4	998	27.3	649
5.6	901	5.6	1005	27.4	649
6.7	901	6.7	1005	27.6	648
7.8	905	7.8	1005	27.7	645
9.0	905	8.9	1000	27.8	642
10.1	905	10.0	1000	27.9	572
11.2	905	11.1	1000	28.0	524
12.3	905	12.2	999	28.1	511
13.4	905	13.3	995	28.2	496
14.6	905	14.4	986	28.3	492
15.7	905	15.5	969	28.6	482
16.8	905	16.7	957	29.1	466
17.9	905	17.8	952		
19.0	905	18.9	940		
20.2	905	20.0	927		
21.3	905	21.1	910		
22.4	888	22.2	904		
23.5	880	23.3	873		
24.6	861	24.4	860		
25.8	835	25.5	822		
26.9	813	26.6	789		
27.0	810	27.0	740		
27.2	810	27.2	727		
27.3	802	27.3	711		
27.5	795	27.4	697		
27.6	795	27.5	691		
27.7	668	27.6	593		
27.8	543	27.8	563		
27.9	515	27.9	527		
28.0	501	28.1	518		

(Continued next page)

TABLE XXXIV - Continued

Slow Titration, Electrode 1		Slow Titration, Electrode 2		Rapid Titration, Electrode 1	
Milliliters	Millivolts	Milliliters	Millivolts	Milliliters	Millivolts
28.6	475	28.2	510		
29.1	462	28.4	497		
30.2	449	28.9	482		
31.4	437	30.0	463		
32.5	427	31.1	452		
33.7	422	33.3	419		
34.8	420	38.9	401		
35.9	415				
37.0	415				
38.2	410				
39.3	407				

The data plotted in Figure 3 are tabulated in Table XXXV.

TABLE XXXV

TITRATION OF 25.00 ML. 0.1110 N LITHIUM PEROXYDIPHOSPHATE SOLUTION WITH 0.1000 N FERROUS AMMONIUM SULFATE SOLUTION

Slow Titration Electrode 1		Slow Titration Electrode 2		Rapid Titration Electrode 1	
Milliliters	El./ml.	Milliliters	El./ml.	Milliliters	E/ml.
20.8	0	20.6	0.2	27.0	6
21.9	1.7	21.7	0.1	27.1	7
23.0	0.8	22.8	2.0	27.2	0
24.1	1.9	23.9	1.0	27.3	2
25.2	2.6	25.0	3.8	27.4	0
26.3	2.3	26.1	3.3	27.6	1
27.0	3.0	26.8	12.0	27.7	3
27.3	8.0	27.1	13.0	27.8	3
27.6	0.0	27.3	16.0	27.9	70
27.7	127	27.4	14.0	28.0	48
27.8	125	27.5	6.0	28.1	13
27.9	28	27.6	2.0	28.2	14
28.0	14	27.8	30.0	28.3	4
28.3	9	27.9	36.0	28.5	3
29.4	1.3	28.1	9.0	28.9	3
29.7	1.3	28.2	8.0		
30.8	1.2	28.3	6.0		
31.9	1.0	28.7	1.6		
33.2	0.5	29.5	2.0		
34.3	0.2	30.6	1.0		