OXIDATION METHODS FOR THE VOLUMETRIC DETERMINATION OF HYPOPHOSPHATE, PHOSPHITE, AND HYPOPHOSPHITE

Bу

Stanley J. Carlyon

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

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THESIS ABSTRACT

Volumetric oxidation methods were developed for the determination of hypophosphate, phosphite, and hypophosphite using standard solutions of sodium hypochlorite, potassium dichromate, and ceric ammonium sulfate under suitable conditions. The compounds used for the analyses were disodium dihydrogen hypophosphate hexahydrate which was prepared by the method of Leininger and Chulski,¹ reagent grade phosphorous acid, and purified sodium hypophosphite. The compositions of the phosphorous acid and sodium hypophosphite were established by a gravimetric procedure in which the compounds were oxidized to orthophosphate by repeated evaporations with aqua regia and the orthophosphate converted to magnesium pyrophosphate.

Hypophosphate, phosphite, and hypophosphite were quantitatively oxidized to phosphate by an excess of standard potassium dichromate in 12 normal sulfuric acid at the temperature of a boiling water bath. The oxidations were complete in one hour. The excess dichromate was determined iodometrically after adjusting the sulfuric acid concentration to approximately three normal by the addition of sodium hydroxide solution. The excess dichromate was also determined by adding an excess of standard ferrous annonium sulfate solution and backtitrating the excess ferrous ion with standard dichromate. It was found that there was a loss of 0.01 to 0.03 ml. of 0.1 normal dichromate during the oxidations and corrections were applied to compensate for this loss.

Leininger, E., and Chulski, T., J. Am. Chem. Soc., <u>71</u>, 2385 (1949).

Hypophosphate, phosphite, and hypophosphite were quantitatively oxidized to phosphate under suitable conditions by an excess of standard sodium hypochlorite. Hypophosphate was determined with an excess of standard sodium hypochlorite in a solution made neutral with sodium bicarbonate. The excess hypochlorite was determined after 30 minutes by adding an excess of standard sodium arsenite and backtitrating the excess arsenite with standard sodium hypochlorite using Bordeaux as indicator. The excess hypochlorite was also determined by titrations with standard arsenite in which the endpoint was determined either potentiometrically or by the deadstop technique. The iodometric determination of hypochlorite in the presence of bicarbonate or buffers gave unsatisfactory results.

Phosphite was determined by a slight excess of standard sodium hypochlorite in a solution containing bicarbonate and bromide, or essentially by hypobromite. The oxidation was sufficiently rapid under these conditions that a direct titration of the phosphite with hypochlorite was possible if the equivalence point in the titration was determined by the deadstop technique. The use of Bordeaux as indicator in this titration was not satisfactory.

Hypophosphite was only very slowly oxidized by an excess of sodium hypochlorite in neutral solution but was quantitatively oxidized to phosphate by excess hypochlorite in one normal sulfuric acid in ten hours.

Phosphite and hypophosphite were quantitatively oxidized to phosphate by an excess of standard ceric ammonium sulfate in dilute sulfuric

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acid solution in one hour at boiling temperature. Hypophosphate was incompletely oxidized under these conditions. A small loss of ceric sulfate during the oxidations required the use of blank corrections.

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TABLE OF CONTENTS

		EGE
I.	INTRODUCTION	1
II.	HISTORICAL	3
III.	REAGENTS AND STANDARD SOLUTIONS	16
	A. Preparation of Standard Solutions B. Standardization of Solutions C. Indicators	16 18 19
IV.	DETERMINATION OF HYPOPHOSPHATE	21
	 A. Oxidation of Hypophosphate by Excess Potassium Dichromate in Sulfuric Acid Solution B. Oxidation of Hypophosphate By Excess Sodium 	21
	C. Oxidation of Hypophosphate With Sodium Hypochlorite	17
	D. Oxidation of Hypophosphate by Excess Ceric Sulfate in Sulfuric Acid Solution	52 55
V.	DETERMINATION OF PHOSPHITE	57
	 A. Oxidation of Phosphite By Excess Potassium Dichrom- ate in Sulfuric Acid Solution B. Oxidation of Phosphite by Excess Hypochlorite in the Presence of Bromide C. Oxidation of Phosphite with Sodium Hypochlorite D. Oxidation of Phosphite By Excess Ceric Sulfate in Sulfuric Acid Solution	60 64 69 78 80
VI.	DETERMINATION OF HYPOPHOSPHITE	82
	 A. Oxidation of Hypophosphite by Excess Dichromate in Sulfuric Acid Solution B. Oxidation of Hypophosphite by Excess Sodium Hypochlorite in a Bicarbonate Medium C. Oxidation of Hypophosphite by Excess Hypochlorite in the Presence of Bromide D. Oxidation of Hypophosphite by Excess Hypochlorite 	85 87 87 88

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TABLE OF CONTENTS - Continued

	E. Oxidation of Hypophosphite by Excess Ceric Sulfate in Nitric Acid Solution F. Oxidation of Hypophosphite By Excess Ceric Sulfate	91
	in Sulfuric Acid Solution	93
	Summary of Volumetric Methods for the Determination of Hypophosphite	97
VII.	DISCUSSION	99
VIII.	SUMMARY	106
LITERA	TURE CITED	108

I. INTRODUCTION

1

Phosphorus forms a series of oxy acids and salts of these acids. The first three members of this series include hypophosphorous ...i, phosphorous acid, and hypophosphoric acid in which the oxidation numbers of phosphorus are positive one, positive three, and positive four respectively. Some of the properties of these acids and their salts such as their physical properties, molecular structure, stability, acid strength, and preparation have been fairly well established but accurate rapid methods for their determination are not available. Better analytical methods for the determination of the members of this series would assist greatly in further studies made of the series.

Theoretically, phosphorous and hypophosphorous acids and their salts are powerful reducing agents; however, reactions of these acids and their salts with even the strongest oxidants are slow and in many cases require several hours for completion. The slow oxidation of hypophosphate by strong oxidants has been explained by the presence of P-P bonds in its structure and in some cases by the time required for its hydrolysis to phosphite and phosphate before the oxidation can proceed. An equilibrium between tautomeric forms of the compound has been suggested as the reason for the slow oxidation of phosphite and hypophosphite.

An appreciable amount of work has been done on the development of enalytical methods for hypophosphite largely because of its use in medicine. The literature describes the work of several investigators

who proposed methods for the determination of phosphite but very little has been published on the determination of hypophosphate. Much of what has been written on the determination of these acids, especially on the first two members of the series, is often misleading and has been subjected to criticism by other investigators. There has been much disagreement concerning the experimental conditions for carrying out many of the methods which have been proposed. Some of the methods have been based on materials which were considered to be primary standards and in many cases it is very doubtful that the material could be considered as a pure compound with a definite composition.

Chulski (12) made a limited study of the oxidation of hypophosphate to phosphate by sodium hypochlorite and by potassium dichromate in sulfuric acid solution. The results indicated that the oxidations may be made quantitative under the proper conditions.

It was considered that the use of these oxidants might be extended to the determination of the other reducing acids of phosphorus.

The purpose of this work is to develop new volumetric methods for the determination of hypophosphate, phosphite, and hypophosphite with emphasis on the use of potassium dichromate and sodium hypochlorite.

II. HISTORICAL

In aqueous solution hypophosphoric acid, $H_4P_2O_6$, is tetrabasic. The most common salts are of the type $MH_2P_2O_6$, but salts in which the other hydrogens are replaced by metals are known. The thorium salt, ThP_2O_6 , and normal silver salt, $Ag_4P_2O_6$, are practically insoluble, the former even in strong mineral acids. The disodium salt is sparingly soluble and is the usual form in which hypophosphate is separated from other phosphorus salts. Aqueous solutions of the acid and its acidified salts disproportionate according to the following equation:

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

That hypophosphoric acid is a dimer rather than the monomer, H_2PO_3 , follows from cryoscopic data on the acid and its salts, the diamagnetic properties of a number of its salts, and the crystal structure of the ammonium salt (41). Indications that the structure involves a P-P bond include the fact that the acid and its salts are formed only from materials containing this bond, and the remarkable resistance of hypophosphate to oxidation.

Their chemical behavior characterizes hypophosphates as intermediate between phosphites and phosphates; they reduce only the strongest oxidizing agents but not the salts of the noble metals. They are not oxidized by halogens but are oxidized by permanganate and dichromate and by these probably only as the acid is hydrolyzed to phosphorous and phosphoric acids (59).

The couples (41)

 $H_4 P_2 O_6 + 2H_2 O \rightleftharpoons 2H_3 PO_4 + 2H^+ + 2e^-; E^\circ = ca. 0.8 V$ and $2H_3 PO_3 \rightleftharpoons H_4 P_2 O_6 + 2H^+ + 2e^-; E^\circ = ca. - 0.4 V$

emphasize the fact that even powerful reducing agents do not convert phosphoric acid to hypophosphoric acid and that treatment of phosphorous acid with an oxidizing agent sufficiently strong to give hypophosphoric acid will give phosphoric acid instead.

Yost and Russell (72) state that hypophosphate is not oxidized by boiling dichromate. However, this may mean that hypophosphate itself is not oxidized by hot dichromate but that in acid solution it is oxidized to phosphate through hydrolysis and oxidation of the phosphorous acid.

Solutions of the salts of hypophosphoric acid are much more stable to decomposition than are those of the acid, and the rate of decomposition of the acid alone is too slow to be measured at room temperature (72). Solutions of the acid and its salts are unstable at higher temperature.

Methods have been proposed for the determination of hypophosphate based on oxidation to phosphate or on precipitation of slightly soluble salts.

Salzer (53) determined hypophosphate by direct titration with permanganate at boiling temperature but satisfactory results could be obtained only if the permanganate solution was standardized against pure disodium dihydrogen hypophosphate.

Wolf and Jung (70) determined hypophosphate in the presence of phosphite and phosphate by precipitating silver hypophosphate from a solution adjusted to a pH of one to two. The excess silver was determined in the filtrate after the precipitate was removed. Probst (47) dissolved the precipitated silver salt in ammonium hydroxide and converted it to silver chloride.

Treadwell and Schwarzenbach (66) precipitated hypophosphate as uranous hypophosphate, UP_2O_6 , with a standard uranous sulfate solution in an atmosphere of carbon dioxide. The endpoint was determined electrometrically.

Wolf and co-workers (71) made a direct titration of hypophosphate with silver nitrate in a solution buffered with disodium phosphate. Exclusion of air was not necessary. Grundmann and Hellmich (20) stated that the indirect determination of hypophosphoric acid as the silver salt is unsatisfactory in the presence of phosphate but can be determined in the presence of phosphate and phosphite by a potentiometric titration in a solution buffered with sodium acetate using a silver iodide indicator electrode.

Van Name and Huff (67) hydrolyzed hypophosphoric acid to phosphorous and phosphoric acids by repeated evaporations with hydrochloric acid and determined the phosphorous acid with excess iodine in a solution buffered with disodium phosphate.

Blaser and Halpern (5) found that sodium hypophosphate was oxidized to pyrophosphate by bromine:

 $Na_4P_2O_6 + Br_2 + H_2O \longrightarrow Na_2H_2P_2O_7 + 2NaBr$

The oxidation was rapid and quantitative at a pH of 8, while outside the limits of pH 5 to 11 the reaction was scarcely detectable.

Moeller and Quinty (42) oxidized hypophosphate to phosphate with excess ceric ammonium nitrate. The cerium phosphates were kept in solution by boiling in nitric acid. The excess cerium was determined by a potentiometric titration with arsenite. They found that no blanks were necessary and also that the disodium dihydrogen hypophosphate hexahydrate prepared by the method of Leininger and Chulski (37) was a primary standard.

Meta and pyro phosphorous acids and their salts are obtainable but the ortho acid is the only one which is important. The meta and pyro acids hydrate rapidly to the ortho acid in aqueous solution (41). The ortho acid behaves as a dibasic acid, which suggests that one hydrogen atom is covalently bonded to the phosphorus atom. Only two series of salts are known, MH_2PO_3 and H_2HPO_3 , but two series of esters with structures $P(OR)_3$ and $RPO(OR)_2$ suggest the tautomeric equilibrium:

$$P(OH)_3 \longrightarrow HPO(OH)_2$$

Mitchell (μ 0) assumed the above tautomeric forms of phosphorous acid in proposing a mechanism for the oxidation of the acid by iodine.

The couples (41)

 $H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H^+ + 2e^-; E^O = 0.20 V$ in acidic solution, and

 $HPO_3^{-2} + 30H^- \implies PO_4^{-3} + 2H_2O + 2e^-; E^0 = 1.05 V$ in alkaline solution, indicate that phosphorous acid and phosphites are

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strong reducing agents. However, reactions with oxidizing agents are often slow, particularly at ordinary temperature, for example those with the halogens (40) and dichromate. Phosphoric acid or phosphate is the oxidation product.

Hypophosphorous acid, H_3PO_2 , behaves as a monobasic acid in aqueous solution and this suggests that only one hydrogen atom is attached to an oxygen atom. In aqueous solution the acid is moderately strong (72). The solutions decompose above 140° C. Jenkens and Jones (23) found that a 0.05 molar solution of C.P. sodium hypophosphite stored at room temperature at a pH of five decomposed to the extent of 85 per cent in one year and 0.8 per cent in one year at a pH of 1.5.

As shown by the couples (41)

 $H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2H^+ + 2e^-; E^0 = 0.59 V$ and

 $P + 2H_2O \rightleftharpoons H_3PO_2 + H^+ + e^-$; $E^O = 0.29 V$ in acidic solution, and the couples

 $H_2PO_2 + 30H \longrightarrow HPO_3^2 + 2H_2O + 2e; E^O = 1.65 V$ and

 $P + 20H \rightarrow H_2PO_2 + e^-; E^\circ = 1.82 V$

in alkaline solution, hypophosphorous acid and its salts are strong reducing agents. However, as in the case of phosphites, oxidation by many oxidizing agents is very slow. The reactions with the halogens proceed at a measurable rate (39,19). Because of the reducing power of phosphorous acid, strong oxidants convert hypophosphites to phosphates rather than to phosphites.

Methods have been proposed for the determination of phosphorous and hypophosphorous acids and their salts based on their oxidation to higher oxidation states. Two gravimetric methods (65) which have been used are (a) oxidizing to orthophosphate by repeated evaporations with nitric acid and determining the phosphate as magnesium pyrophosphate and (b) oxidizing to phosphate by excess mercuric chloride and weighing the mercurous chloride formed. Sandri (54), and Schwicker (57) modified the mercuric chloride procedure by determining the mercurous chloride formed with a standard potassium bromate solution using methyl orange as indicator. Bond (6) stated that the mercuric chloride method gave results which were only 80 per cent of theoretical but that the determination as magnesium pyrophosphate is satisfactory.

Rosenheim and Pinsker (50) determined phosphite and hypophosphite by excess potassium permanganate in the presence of sulfuric acid heated to 80 to 90° C. Zivy (74) recommended the addition of the phosphite or hypophosphite sample to a mixture of sulfuric acid, manganous sulfate and excess standard permanganate. The mixture was then refluxed for 25 minutes, an excess of standard oxalic acid added, and the excess oxalate backtitrated with permanganate. Kolthoff (28) pointed out the errors from the instability of permanganate in hot solution and proposed oxidation in cold sulfuric acid solution with blank experiments to compensate for permanganate decomposition. He recommended 24 hours standing for the oxidation of hypophosphite (28), and two hours standing for phosphite (27). Koszegi (36) has indicated that errors exceeding one to four per cent are possible in this method when used for hypophosphite. He recommended (35) the use of permanganate in neutral solution

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at boiling temperature followed by an iodometric determination of the excess permanganate after filtering.

Schweicker (57) used an excess permanganate in sulfuric acid solution and a 30 minute heating period. He stated that the rate of oxidation is greatly increased by the addition of a few drops of a five per cent ammonium molybdate solution.

Pound (46) reported that the oxidation of hypophosphite in neutral or acid solution by direct titration with permanganate is impossible and that even after several days standing with excess permanganate in acid solution oxidation does not exceed 96 per cent. He stated that a small amount of potassium bromide has a catalytic effect, possibly due to the formation of free bromine, and that the oxidation is complete in a few hours at room temperature if the bromide is present.

Gall and Ditt (16) determined phosphite and hypophosphite with an excess of standard manganete solution at elevated temperature in alkaline solution.

Stamm (63) suggested the use of an excess of alkaline permanganate for the oxidation of phosphite and hypophosphite. The permanganate was reduced to manganate and precipitated by barium ion. The oxidation was reported to be complete in five minutes.

The quantitative oxidation of phosphite and hypophosphite by the halogens under different conditions has been proposed by many investigators. Rupp and Finck (51) appear to be the first to suggest the use of iodine for the determination of phosphite. The oxidation was carried out in a bicarbonate medium and the excess iodine titrated with sodium

thiosulfate after the mixture had been standing for two hours. Boyer and Bauzil (8) used a similar procedure for phosphite and determined hypophosphite by oxidizing it to phosphite by excess iodine in sulfuric acid solution. The oxidation was completed to phosphate by excess iodine in neutral solution. The procedure required eight to ten hours.

Wolf and Jung (70) pointed out inconsistencies in the method of Rupp and Finck (51) and developed a method of determining phosphite and hypophosphite separately or in the presence of each other. They determined phosphite by an excess of standard iodine solution in a bicarbonate medium saturated with carbon dioxide. The excess iodine was determined by a titration with standard sodium arsenite after 45 minutes. Hypophosphite was determined by treating it with an excess of standard iodine solution in dilute sulfuric acid. After 10 to 12 hours the solution was made neutral with sodium bicarbonate and the oxidation completed to phosphate. Raquet and Pinte (48) used a warm borax solution in place of the bicarbonate. Bond (7) stated that this method gave results for hypophosphite which were 20 per cent low. Schwicker (56) recommended a solution of ammonium borate for the buffer.

Kamecki (25) found that the rate of the oxidation of hypophosphite to phosphite by excess iodine was increased by increasing sulfuric acid concentration but was practically constant for one to four normal acid. He recommended the oxidation of hypophosphite by iodine in one to two normal sulfuric acid, and that the excess iodine be determined after three hours. He claimed that phosphite did not interfere.

Jones and Swift (24) modified the method of Wolf and Jung (70) and proposed a method for the determination of hypophosphorous acid and phosphorous acid alone or in the presence of each other. They pointed out that the data of Wolf and Jung showed results for the determination of hypophosphite which were 0.4 per cent lower than the corresponding gravimetric results and also that phosphite interferes in the method proposed by Kamecki. They developed the method on the assumptions that (a) phosphorous acid can be oxidized quantitatively by excess iodine in a neutral solution in one hour and that the oxidation of hypophosphorous acid under these conditions is negligible and (b) hypophosphorous acid can be oxidized quantitatively by excess iodine in one to two normal hydrochloric acid. They found the assumptions to be valid if the oxidation of the phosphorous acid was carried out in a solution buffered to a pH of approximately 7.3 by a phosphate buffer and if the oxidation of hypophosphorous to phosphorous acid was carried out in about 1.5 molar hydrochloric acid. The results compared favorably with analyses made from neutralization titrations on the acids using a glass electrode pH meter.

Vermeil (68) suggested a micro determination of phosphite by excess iodine in ammonium borate buffer, and determined the excess iodine spectrophotometrically.

Manchot and Steinhauser (38) determined phosphite with an excess of standard bromine solution in a bicarbonate medium. Hypophosphite was determined in a similar manner using sodium acetate in place of the bicarbonate and heating the mixture. Brukl and Behr (10) determined phosphite and hypophosphite by oxidation to phosphate with an excess of standard iodic acid solution. The procedure was completed by boiling off the iodine which was liberated in the oxidations and determining the excess iodic acid. An alternate procedure was carried out by collecting the iodine which was distilled off and determining it.

Rupp and Kroll (52), and Schwicker (57) recommended the use of an excess standard bromate-bromide solution for the determination of hypophosphite.

Komarowski and co-workers (34) used an excess chloramine-T in dilute sulfuric acid for the oxidation of hypophosphite to phosphite. The oxidation required 24 hours and the results were somewhat lower than the results obtained by the method of Rupp and Finck (51).

Benrath and Ruland (3) reported that hypophosphorous acid is oxidized to phosphorous acid at boiling temperature when titrated with ceric sulfate. No other conditions and no data were given.

Cocking and Kettle (13) separated phosphite from hypophosphite by removing the former with lead acetate and determined the hypophosphite on an aliquot portion of the supernatant solution with excess one normal potassium dichromate in approximately five normal sulfuric acid. The oxidation with dichromate was carried out by heating the mixture in a water bath for one hour. The excess dichromate was determined iodometrically. Pelizza and Risso (43) used an excess of 0.1 normal dichromate in a similar procedure carried out in five to six normal sulfuric acid in which the mixture was refluxed for one hour. This procedure

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and the one described by Cocking and Kettle are somewhat limited in that only very small samples of the hypophosphite solution were used.

Kirson (26) found that the oxidation of phosphorous acid to phosphoric acid by chromate ion is about twice as fast in the presence of perchloric acid as in the presence of sulfuric acid and that the reaction is faster with increasing acidity.

Kolthoff (27) determined phosphite with excess standard hypobromite in bicarbonate medium. The mixture was allowed to stand for one-half to one hour and the excess hypobromite determined iodometrically.

Schwicker (57) oxidized phosphite by an excess of standard sodium hypochlorite in a solution made neutral with sodium bicarbonate. After the mixture had been standing for ten minutes, an excess of sodium bicarbonate was added and the excess hypochlorite determined by a titration with standard potassium iodide solution.

Sodium hypochlorite is a highly reactive substance but many investigators have found that hypochlorite solutions are quite stable if they are properly stored. It has many advantages as a titrimetric reagent but its use has been somewhat limited in comparison to many of the standard oxidants. Jellinek and Kresteff (21) described the use of a sodium hypochlorite solution as a valuable volumetric aid. They found that a 0.1351 normal solution changed to 0.1330 normal in 17 days. They attributed this loss to the fact that they made no attempt to shield the solution from sunlight. Jellinek and Kuhn (22) prepared a standard sodium hypochlorite solution and found that its concentration remained practically constant for several weeks.

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Belcher (1) found that a sodium hypochlorite solution prepared from commercial sodium hypochlorite was stable for a week. Goldstone and Jacobs (18) recommended the use of Clorox for the preparation of a standard sodium hypochlorite solution. They added sufficient sodium hydroxide to the solution to bring the pH to about 12.5, the pH of greatest stability. They found that a 0.005000 normal solution stored in a brown bottle at room temperature changed to 0.004977 normal in 56 days.

Chapin (11) studied the effect of hydrogen ion concentration on the decomposition of hypohalites and concluded that aside from notable stability in strongly acid solution in the absence of halide ions the stability of dilute sodium hypochlorite solutions was greatest at a pH of 13.1 and least at a pH of 6.7. Chopin also found that the decomposition of sodium hypochlorite solutions, at least over certain ranges of pH, was notably accelerated by acetate, borate, and carbonate and that even phosphate seemed to exert some effect.

It seems to be well established that the stability of hypochlorite solutions is greater if they are stored away from sunlight (1,17,14).

Kolthoff and Stenger (33) proposed the use of a calcium hypochlorite solution as a standard oxidizing agent and found that the solution could be kept in dark bottles for a long time without appreciable change in titer. A disadvantage in the use of calcium hypochlorite as compared to sodium hypochlorite is the formation of a turbidity on standing as the result of the precipitation of calcium carbonate.

In many cases hypobromite reacts faster than hypochlorite but hypobromite solutions are less stable. A hypobromite solution of known concentration can be prepared extemporaneously by adding an excess of alkali bromide to a standard hypochlorite solution:

 $OCl + Br \rightarrow OBr + Cl$

The reagent is particularly useful for oxidations which require a neutral or alkaline medium.

III. REAGENTS AND STANDARD SOLUTIONS

All reagents used in this work were, unless otherwise stated, analytical reagent grade.

The volumetric equipment used was calibrated Kimble Normax and corrections were applied where necessary. All standard solutions which were prepared from weighed amounts of reagents were adjusted to volume in a Kimble Normax volumetric flask which was certified by the National Bureau of Standards.

All weighings were made with calibrated weights.

A. Preparation of Standard Solutions

Potassium dichromate, 0.1000 normal, was prepared from Mallinckrodt, Primary Standard Analytical Reagent which had been dried at 160° C. for three hours. The solution contained 4.9035 grams of the reagent per liter of solution. It was found to be equivalent to a 0.1000 normal solution prepared from National Bureau of Standards reagent (N.B.S. number 136) in a titration of a ferrous ammonium sulfate solution.

Sodium arsenite, 0.1000 normal, was prepared from Baker and Adamson, Primary Standard Analytical Reagent arsenious oxide which had been dried at 110° C. for two hours. To 4.9455 grams of the dry reagent was added approximately eight grams of sodium hydroxide pellets and 20 ml. of water. When the mixture was dissolved it was diluted with water to 100 ml., made slightly acid to litmus with sulfuric acid, approximately

three grams of sodium bicarbonate added, and diluted to one liter. It was found to be equivalent to a 0.1000 normal solution prepared from National Bureau of Standards reagent arsenious oxide.

17

Sodium hypochlorite, 0.1 normal, was prepared by diluting approximately 65 ml. of Clorox (Clorox Chemical Company), 5.25 per cent sodium hypochlorite by weight, to one liter. The solution was stored in an amber bottle and kept out of direct light as much as possible.

Ceric ammonium sulfate, O.l normal, was prepared by dissolving 70 grams of reagent grade ammonium tetrasulfato cerate (G. Frederick Smith Chemical Company) in 400 milliliters of water containing 28 ml. of concentrated sulfuric acid and slowly diluting the solution to one liter. The solution was allowed to stand for at least 24 hours and was filtered with a sintered glass crucible before it was standardized.

Iodine solution, 0.1 normal, was prepared by dissolving 6.5 grams of reagent grade iodine and 20 grams of reagent grade potassium iodide in 30 ml. of water and diluting to one liter.

Sodium thiosulfate, 0.1 normal, was prepared by dissolving 25 grams of reagent grade sodium thiosulfate pentahydrate and 0.5 gram of sodium carbonate in water and diluting to one liter. The solution was allowed to stand for at least 24 hours before it was standardized.

Ferrous ammonium sulfate, 0.1 normal, was prepared by dissolving 39 grams of reagent grade ferrous ammonium sulfate hexahydrate in 200 ml. of water containing 40 ml. of six normal sulfuric acid and diluting to one liter.

B. Standardization of Solutions

The solutions used in the experimental work described in this thesis were standardized according to the following procedures unless the procedure was changed for a specific purpose in which case the procedure is described in the section where the solution was used.

Sodium thiosulfate, 0.1 normal, was standardized by the following procedure (hh). To 25.00 ml. of 0.1000 normal potassium dichromate solution in a 500 ml. Erlenmeyer flask was added 100 ml. of two normal sulfuric acid. Approximately two grams of powdered sodium carbonate was added in small portions with constant swirling, and then about six grams of potassium iodide dissolved in ten ml. of water was added. The flask was stoppered, allowed to stand for about eight minutes, the contents diluted to about 350 ml., and the liberated iodine titrated with the sodium thiosulfate solution. Four ml. of 0.5 per cent freshly prepared starch solution was added near the equivalence point.

Ferrous ammonium sulfate, 0.1 normal, was standardized by the following procedure (30). To 25.00 ml. of the ferrous ammonium sulfate solution in a 500 ml. Erlenmeyer flask were added 20 ml. of 1:5 sulfuric acid, five ml. of 85 per cent phosphoric acid, and six drops of 0.01 molar sodium diphenylamine sulfonate indicator. The solution was titrated with 0.1000 normal potassium dichromate to the appearance of the first tinge of purple or violet-blue. In indicator blank of 0.05 ml. of 0.1000 normal potassium dichromate was subtracted from the volume of dichromate used (55).

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Ceric anmonium sulfate, 0.1 normal, was standardized by the following procedure (62). To 25.00 ml. of 0.1000 normal sodium arsenite solution in a 300 ml. Erlenmeyer flask were added 65 ml. of water, 20 ml. of six normal sulfuric acid, one drop of ferroin indicator, and three drops of 0.01 molar osmium tetroxide. The solution was titrated at room temperature with the ceric ammonium sulfate solution to the elimination of the red tint.

Sodium hypochlorite, 0.1 normal, was standardized against sodium ersenite by the following procedure (32). To 25.00 ml. of 0.1000 normal sodium arsenite solution in a 200 ml. Erlenmeyer flask were added one gram of potassium bromide and 0.5 gram of sodium bicarbonate. The solution was titrated with the sodium hypochlorite solution until within a few ml. of the expected endpoint, one drop of Bordeaux indicator added, and the titration continued until the red color of the indicator faded. One more drop of indicator was added and the titration continued dropwise until the color of the solution flashed from pink to colorless or light yellow green. An indicator blank of 0.03 ml. of 0.1 normal sodium hypochlorite was subtracted from the volume of hypochlorite used.

C. Indicators

Bordeaux. A 0.2 per cent aqueous solution was prepared from Bordeaux, British Color Index 88, G. Frederick Smith Chemical Company.

Diphenylamine sodium sulfonate, 0.01 molar, was prepared (69) by dissolving 0.32 gram of diphenylamine barium sulfonate in 100 ml. of water and adding 0.5 gram of sodium sulfate. After standing over night

the clear solution was decanted from the precipitated barium sulfate.

Ferroin. A prepared solution obtained from the G. Frederick Smith Chemical Company was used.

Quinoline Yellow. A C.2 per cent aqueous solution was prepared from quinoline yellow, technical, British Color Index 801, Eastman Kodak Company.

Tartrazine. A 0.05 per cent aqueous solution was prepared from tartrazine, practical, British Color Index 640, Eastman Kodak Company.

<u>Cresyl violet</u>. A 0.2 per cent aqueous solution was prepared from cresyl violet, Allied Chemical and Dye Corporation.

Starch. A 0.5 per cent aqueous solution of soluble starch, freshly prepared.

IV. DETERMINATION OF HYPOPHOSPHATE

It was desirable to use as a basis for a study of methods for the determination of hypophosphate a hypophosphate which is a primary standard, reasonably stable in solution, and one which does not contain cations which may interfere in the methods used. Disodium dihydrogen hypophosphate hexahydrate prepared by the method of Leininger and Chulski (37) meets these requirements (37,12,42).

Disodium hypophosphate was prepared by the method of Leininger and Chulski. The product was recrystallized twice from water; the crystals were allowed to form at room temperature. They were finally washed five times with five ml. of ice-cold water and air dried at room temperature until they tumbled freely when stirred. They were stored in a tightly stoppered bottle.

Standard 0.02500 molar solutions of the preparation were made by dissolving 7.8514 grams of the crystals in 400 ml. of warm water and diluting to one liter after adjusting to temperature.

A. Oxidation of Hypophosphate by Excess Potassium Dichromate in Sulfuric Acid Solution

Determination of excess dichromate with ferrous ion. Chulski (12) found that disodium dihydrogen hypophosphate is oxidized by an excess of potassium dichromate in sulfuric acid solution. He found that the excess potassium dichromate could be determined by adding an excess of ferrous ion and titrating the excess with potassium dichromate. This titration could be done in much stronger acid than recommended (55) if there was present three ml. of 85 per cent phosphoric acid for each 50 ml. volume of solution. The volume of phosphoric acid present had to be equal to at least one half the volume of concentrated sulfuric acid present. The reverse titration of potassium dichromate with ferrous ion was not possible.

To measured samples of 0.05000 normal disodium phosphate in 500 al. Erlenmeyer flasks which had been thoroughly cleaned with hot chromic acid cleaning solution and thoroughly rinsed with water were added a measured excess of 0.1000 normal potassium dichromate and sufficient concentrated sulfuric acid to make the resulting mixture 12 normal in scid. The flasks were covered with small beakers and heated in a boiling water bath. The contents of the flasks were cooled to room temperature, diluted with water to 250 ml., 15 ml. of 65 per cent phosphoric acid added, and then a measured excess of standard ferrous emmonium sulfate solution. The excess ferrous ammonium sulfate was immediately titrated with the standard dichromate using six drops of diphenylamine sodium sulfonate as indicator. An indicator blank of 0.05 ml. of 0.1 normal dichromate was subtracted from the volume of dichromate used. Blanks were determined in the same manner, substituting water for the hypophosphate solution. A minimum of ferrous ion was added before the backtitration to keep the chromic ion concentration low and provide a sharper endpoint. The results are shown in Table I.

TABLE I

DETERMINATION OF HYPOPHOSPHATE WITH EXCESS POTASSIUM DICHROMATE (BACKTITRATION WITH FERROUS ION)

H1. 0.05 N	Ml. O.l N	Meg.	NazHzPzC	6 Found	
Na ₂ H ₂ P ₂ O ₆	K ₂ Cr ₂ O ₇	Na ₂ H ₂ P ₂ O ₆ Taken	Meq.	Percent	
9.99 19.98 49.98 5.00 9.99 9.99 19.98 19.98 19.98 25.00 25.00 25.00 25.00 49.98 49.98 49.98 0.0 0.0	25.00 25.00 49.98 5.00 9.99 25.00 19.98 19.98 19.98 19.98 25.00 25.00 25.00 49.98 49.98 25.00 25.00 25.00	0.500 0.999 2.499 0.250 0.500 0.500 0.999 0.999 0.999 1.250 1.250 1.250 1.250 2.499 2.499	0.494 0.995 2.475 0.251 0.503 0.506 0.999 1.001 1.002 1.252 1.250 1.248 2.487 2.494	99.8 99.6 99.0 100.4 100.6 101.2 100.0 100.1 100.2 100.2 100.2 100.2 100.2 100.2 100.0 99.8 99.5 99.8 99.5 99.6 0.09* 0.05*	(a) (a) (a)
0.0	25.00			0.02 ((a)

Conditions: 12 N Sulfuric Acid, Heating Time One Hour

^{*} Ml. 0.1 N K₂Cr₂O₇ lost (a) heated 40 minutes.

An indicator blank of 0.05 ml. of dichromate was used in the calculations of the results in Table I but the blanks resulting from the small loss of dichromate were disregarded.

The data in Table I show that heating for 40 minutes in 12 normal sulfuric acid at the temperature of a boiling water bath is not quite

long enough to complete the oxidation. Hypophosphate hydrolyzes to phosphite and phosphate in the hot acid solution. It is quite possible that the rate of the oxidation of hypophosphate by dichromate is determined by the rate of the hydrolysis and that the phosphite, rather than the hypophosphate, is oxidized. However, the reacting ratio is the same if hydrolysis does or does not take place. In both cases the equivalent weight of the disodium dihydrogen hypophosphate is one-half of the molecular weight and the equivalent weight of the potassium dichromate is one-sixth of the molecular weight.

The accuracy of the method using a hot acid solution of potassium dichromate depends upon the stability of potassium dichromate in hot acid solution and upon the accuracy of the procedure used to determine the excess dichromate. In order to study the stability of the dichromate in hot acid solution and determine the accuracy of the procedure used to determine the excess dichromate a series of blanks was determined by the method used for the determination of hypophosphate substituting water for the hypophosphate solution. Each blank contained sufficient sulfuric acid to make the resulting mixture 12 normal in acid and all were heated for one hour in a boiling water bath. A slight excess of standard ferrous ammonium sulfate was added to each sample before backtitration with standard dichromate.

Table II shows that potassium dichromate is stable in 12 normal sulfuric acid at the temperature of a boiling water bath. The small loss of dichromate may result from the oxidation of small quantities of reducing substances in the sulfuric acid. If the blanks are to be kept

Ml.O.l N K ₂ Cr ₂ O7	Ml. Concentrated H_2SO_4	Ml. Water	Ml. O.l N K ₂ Cr ₂ O ₇ Lost
25° M	った	<u> </u>	0.02
25.00	25	2) 05	0.02
25.00	25	25	0.03
25.00	25	25	0.02
25.00	25	25	0.01
9.99	10	10	0.00
9.99	10	10	0.00
9,99	10	10	0.01
9.99	10	10	0.00

TABLE II

STABILITY OF POTASSIUM DICHROMATE IN HOT SULFURIC ACID SOLUTION

small, great care must be taken to use flasks which are thoroughly cleaned because of the drastic oxidizing conditions used.

In order to determine the effect of making the calculations on the basis of blanks, a series of hypophosphate samples was determined by the same procedure as used in the previous determination of hypophosphate by excess dichromate with the exception that the results were calculated on the basis of blanks determined in the same manner as the samples.

The data in Table III show that slightly better results are obtained if the small blanks are taken into consideration in the calculations.

The best results are obtained if the volume of hypophosphate solution taken for analysis is limited to 20 to 30 ml. If the volume of sample taken is very large, a large amount of sulfuric acid is required and this makes the endpoint in the back-titration less sharp. Also, the

TABLE III

M1.0.05 N	Ml. O.1 N	Meq. Na ₂ H ₂ P ₂ O ₆	Na-H-P-	D _e Found
Ra2H2P206	K ₂ Cr ₂ O ₇	Taken	Meq.	Percent
70.00	متر 0 0	0.000	0.000	
19.90	25.00	0.999	0.990	99.9
19.98	25.00	0.999	1.001	100.2
19.98	25.00	0.999	0.998	99.9
19.98	25.00	0.999	0,999	100.0
25.00	25.00	1.250	1.246	99.7
25.00	25.00	1.250	1.249	99.9
25.00	25.00	1.250	1.249	99.9
25.00	25.00	1.250	1.247	99.8 🏒
0.0	25.00			0.04
0.0	25.00			0.02**

DETERMINATION OF HYPOPHOSPHATE WITH EXCESS DICHROMATE MAKING CALCULATIONS ON THE BASTS OF BLANKS

* Ml. O.1 N K2Cr207 lost.

amount of excess ferrous ion added should be kept at a minimum in order that a smaller amount of chromic ion will be present at the endpoint. The color of a high concentration of chromic ion makes the endpoint less sharp.

If the oxidation of hypophosphate by excess dichromate is to be complete in approximately one hour, it must be carried out in at least 12 normal sulfuric acid.

In order to determine the effect of added phosphate on the determination of hypophosphate with excess potassium dichromate in sulfuric acid solution, samples and blanks were determined by the procedure described with the exception that phosphate was added before the heating period. The phosphate was added in the form of reagent grade phosphoric acid and monopotassium phosphate.



It was found that a small amount of dichromate was used by the phosphate. However, the amount of dichromate used was not constant for a constant amount of added phosphate and varied with the source of the phosphate. It even varied with the same amount of phosphoric acid taken from different bottles of the reagent grade phosphoric acid. The amount of dichromate used was smaller for the same amount of phosphate added in the form of potassium phosphate than in the form of phosphoric acid.

The phosphoric acid used was marked as meeting A.C.S. specifications which means that its reducing properties are such that ten ml. of the 85 per cent acid should not decolorize 0.20 ml. of 0.1 normal potassium permanganate (49). It was found that the addition of ten ml. of the phosphoric acid resulted in a blank of approximately 0.13 ml. of 0.1 normal dichromate which corresponds to a reducing property which is well within the A.C.S. specifications.

It was concluded that phosphate has no effect on the determination of hypophosphate with potassium dichromate in hot sulfuric acid solution except the effect due to reducing substances present in the added phosphate.

Determination of the excess potassium dichromate iodometrically. Because dichromate liberates iodine from an acid solution of potassium iodide it should be convenient to determine an excess potassium dichromate iodometrically. However, the acid concentration present in the determination of hypophosphate by excess dichromate in 12 normal sulfuric acid is much higher than the acid concentration recommended for the iodometric determination of dichromate (31,45).

than recommended on the iodometric determination of dichromate a series of dichromate samples was determined iodometrically in solutions of different sulfuric acid concentration.

To 19.98 ml. samples of 0,1000 normal potassium dichromate in 500 ml. Erlenmeyer flasks were added various amounts of water and sulfuric acid so that the total volume of the solution was 100 ml. To each flask was slowly added two grams of powdered sodium carbonate and six grams of potassium iodide dissolved in 15 ml. of water. After standing for eight minutes the contents of the flasks were diluted with water to about 350 ml. and the liberated iodine was titrated with a sodium thiosulfate solution. The results are shown in Table IV.

TABLE IV

Sample	App roximat é	Concentration	Ml. 0.1 N
No.	of	Acid	Na ₂ S ₂ O ₃
1	2	N	19.91
2	2	N	19.92
3	3	6 N	19.97
4	7	2 N	20.03

EFFECT OF ACID CONCENTRATION ON THE IODOMETRIC DETERMINATION OF POTASSIUM DICHROMATE

* Recommended concentration.

In order to determine the effect of a much stronger acid solution
Samples 1 and 2 in Table IV were determined by the recommended procedure for the iodometric determination of dichromate. The data in Table IV show that a larger volume of thiosulfate is used when the acid concentration is higher than recommended. The larger amount of thiosulfate used in a solution of high acidity is probably due to air oxidation of the iodide.

In order to study the effect of determining the excess dichromate iodometrically in the 12 normal acid used in the determination of hypophosphate, a series of hypophosphate samples was oxidized by excess potassium dichromate in 12 normal sulfuric acid by the procedure previously described and the excess dichromate was determined iodometrically in the 12 normal acid. The volume of each solution was adjusted so that each flask contained about 75 ml. of 12 normal sulfuric acid during the oxidation. All samples were heated for one hour. The results are shown in Table V.

TABLE V

DETERMINATION OF HYPOPHOSPHATE BY EXCESS POTASSIUM DICHROMATE, BACKTITRATING THE EXCESS DICHROMATE IODOMETRICALLY IN STRONG ACID SOLUTION

Ml. 0.05 N	Ml. O.lN	Meq. Na ₂ H ₂ P ₂ O ₆	<u>Na₂H₂P₂(</u>	D ₆ Found
Na ₂ H ₂ P ₂ O ₆	K ₂ Cr ₂ O7	Taken	Meq.	Percent
9.99	9.99	0.500	0.470	94.0
19.98	19.98	0.999	0.968	96.9
19.98	19.98	0.999	0.965	96.6
25.00	25.00	1.250	1.201	96.1

Table V shows that low results would be obtained if the excess dichromate were determined iodometrically in the 12 normal sulfuric acid.

It seemed reasonable to expect that dichromate could be accurately determined iodometrically in a highly acid solution if part of the acid were first neutralized so that the acidity was the same as required by the recommended procedure. In order to determine if such were the case, a series of dichromate samples was treated with water and concentrated sulfuric acid so that the resulting mixtures each had a volume of approximately 75 ml. and were 12 normal in sulfuric acid concentration. The mixtures were cooled in an ice water bath and different weighed amounts of sodium hydroxide dissolved in a constant volume of water added. The mixtures were cooled to remove the heat given off in the neutralization. After the addition of two grams of sodium carbonate to sach mixture, the dichromate was determined iodometrically. The results obtained were compared to results obtained by the recommended procedure.

Table VI shows that potassium dichromate can be determined iodometrically in 12 normal sulfuric acid if the acid is partially neutralized so that the determination is completed in two to three normal acid. If the determination is carried out in this manner, the results obtained agree with the results obtained by the recommended procedure. The data in Table VI also indicate that it should be possible to carry out an iodometric determination of the excess dichromate in an oxidation using excess dichromate in 12 normal sulfuric acid. This procedure was used to determine the excess dichromate in the oxidation of hypophosphate with dichromate.



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TABLE VI

Ml. 0.1 N K ₂ Cr ₂ O ₇	Ml. Conc. H ₂ SO ₄	Grems NaOH Added	Approximate Acid Concentration [*]	Ml. Na ₂ S ₂ O ₃
25.00 25.00 25.00 25.00 25.00 25.00 25.00	(a) (a) 25 25 25 25 25 25	0 0 26 20 20 17 17	2 N 2 N 1.6 N 2.5 N 2.5 N 3 N 3 N	24.23 24.24 24.18 24.21 24.23 24.25 24.23

IODOMETRIC DETERMINATION OF DICHROMATE IN HIGHLY ACID SOLUTION BY NEUTRALIZING PART OF THE ACID

Measured samples of hypophosphate were treated with sulfuric acid and a measured excess of standard potassium dichromate. After heating for one hour in a boiling water bath the samples were cooled in ice water and sodium hydroxide solution added until the resulting mixtures had a volume of approximately 100 ml. and were two to three normal in sulfuric acid concentration. The excess dichromate was then determined iodometrically using a standard sodium thiosulfate solution.

Table VII shows that the excess dichromate in the oxidation of hypophosphate with dichromate can be determined iodometrically. The results obtained are essentially the same as the results obtained when the excess dichromate was determined with a ferrous ammonium sulfate solution. Table VII also shows that increasing the time of heating to one and one-half hours has no effect on the results.

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TABLE VII

DETERMINATION OF HYPOPHOSPHATE BY EXCESS DICHROMATE IN 12 N SULFURIC ACID DETERMINING THE EXCESS DICHROMATE IODOMETRICALLY AFTER NEUTRALIZING PART OF THE ACID (Heating Time One Hour)

M1. 0.05 N	Ml. O.l N	Meq. Na ₂ H ₂ P ₂ O ₆	Na ₂ H ₂ P ₂ O	Found (a)
Na ₂ H ₂ P ₂ O ₆	K ₂ Cr ₂ O ₇	Taken	Meg.	Percent
9.99 9.99 19.98 19.98 19.98 19.98 19.98 25.00 25.00 25.00 25.00 25.00	9.99 9.99 19.98 19.98 19.98 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	0.500 0.500 0.999 0.999 0.999 0.999 0.999 1.250 1.250 1.250 1.250 1.250 1.250 1.250 1.250	0.498 0.500 1.003 0.996 0.999 0.995 0.996 1.247 1.250 1.246 1.248 1.248 1.248 1.247 2.496	99.6 100.0* 100.4 99.7 100.0 99.6 99.7 99.8 100.0 99.7 99.8 100.0 99.7 99.8 100.0 99.7 99.8 99.8 99.8 99.8
49.98	49.98	2.499	2.496	99.9

[#] Heated for one and one-half hours. (a) Calculated on the basis of blanks.

The iodometric determination of the excess dichromate has no particular advantage over the procedure using a ferrous ammonium sulfate solution except that the former is a direct determination.

B. Oxidation of Hypophosphate By Excess Sodium Hypochlorite

Chulski (12) made a limited study of the oxidation of hypophosphate by sodium hypochlorite and concluded that hypophosphate is oxidized by excess sodium hypochlorite in approximately neutral solution. He determined the excess hypochlorite iodometrically in the presence of buffers and the results obtained were somewhat irregular in that better results were obtained if calculations were made on the basis of a direct standardization of the hypochlorite solution than if blanks, treated in the same manner as the hypophosphate samples, were used as the basis for the calculations.

The same irregularities in the iodometric determination of hypochlorite were experienced during the investigation described in this thesis. This is described more fully in the section of this thesis dealing with the determination of phosphite with hypochlorite.

Arsenite reacts rapidly with hypochlorite in a bicarbonate solution. However, no indicator is available for determining the equivalence point in a titration of hypochlorite with arsenite because the indicators usually employed in oxidation-reduction systems are destroyed by hypochlorite. It seemed reasonable to expect that hypochlorite could be determined by adding to it an excess of standard arsenite solution and titrating the excess arsenite with a standard oxidant. Arsenite can be titrated with hypochlorite in bicarbonate solution using Bordeaux indicator to determine the endpoint (32). It is necessary to have bromide present at the endpoint because Bordeaux is not decolorized by a slight excess of hypochlorite but it is decolorized by a slight excess of hypobromite. The hypobromite is formed by the reaction between the bromide and hypochlorite.

Determination of hypophosphate with excess hypochlorite, determining the excess with excess arsenite. To measured samples of 0.05000 normal hypophosphate in 250 ml. iodine flasks were added approximately

one gram of sodium bicarbonate and a measured excess of standard sodium hypochlorite solution. The flasks were allowed to stand in the dark for various time intervals, a measured excess of standard sodium arsenite added, and then approximately one gram of potassium bromide. The excess sodium arsenite was titrated with the standard sodium hypochlorite solution using Bordeaux indicator as in the procedure for the standardization of hypochlorite against sodium arsenite. An indicator blank of 0.03 ml. of 0.1 normal hypochlorite was subtracted from the volume of hypochlorite used. Blanks were determined in the same manner, substituting water for the hypophosphate solution. The hypophosphate is oxidized to phosphate:

 $HaClO + Na_2H_2P_2O_6 + H_2O \longrightarrow 2NaH_2PO_4 + NaCl$

The data in Table VIII show that hypophosphate is oxidized completely by excess sodium hypochlorite in bicarbonate medium. The data also show that the oxidation is complete in 30 minutes, incomplete in 15 minutes, and that increasing the standing time up to two hours has no effect on the results. The blanks due to the loss of hypochlorite during the standing are negligibly small.

Several series of hypophosphate samples were determined by excess sodium hypochlorite using the same procedure. The results of the analysis of a typical series in which the hypophosphate samples were allowed to stand with excess standard hypochlorite for various time intervals from 30 to 90 minutes are shown in Table IX.

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TABLE VIII

Ml. 0.05 N NeH ₂ P ₂ O ₆	Ml. O.l N NaClO Added With Sample	Meq. Na ₂ H ₂ P ₂ O ₆ Taken	Standing Time Min.	<u>NezHzPz</u> Meq.	0 ₆ Found Percent
25.00 25.00 25.00 25.00 25.00 0.0	19.98 19.98 19.98 19.98 19.98 19.98 19.98	1.250 1.250 1.250 1.250 1.250 1.250	15 30 45 60 120 30 60	1.240 1.250 1.252 1.248 1.251	99.2 100.0 100.2 99.8 100.1 0.01** 0.00**

DEPERMINATION OF HYPOPHOSPHATE WITH EXCESS SODIUM HYPOCHLORITE AS A FUNCTION OF TIME

* Ml. 0.1 N hypochlorite lost.

Table IX shows that the amount of excess hypochlorite used can be varied from two to four times the amount required for the oxidation of the hypophosphate with no effect on the results.

TABLE IX

DETERMINATION OF HYPOPHOSPHATE WITH EXCESS HYPOCHLORITE (ARSENTTE-HYPOCHLORITE MODIFICATION)

M1. 0.05 N	Ml. O.1 N NaClO Added With	Meq. Na ₂ H ₂ P ₂ O ₆	NazHzPz	0 ₆ Found
Na ₂ H ₂ P ₂ O ₆	Sample	Taken	Meq.	Percent
9.99 9.99 9.99 19.98 19.98 25.00 25.00 25.00	19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 25.00	0.500 0.500 0.500 0.999 0.999 1.250 1.250 1.250 1.250	0.497 0.501 0.499 0.999 1.000 1.251 1.249 1.250	99.4 100.2 99.8 100.0 100.1 100.1 99.9 100.0

Determination of excess hypochlorite by a potentiometric titration with standard sodium arsenite. Preliminary experiments were carried out to determine if it were feasible to determine the excess hypochlorite by a direct potentiometric titration with standard sodium arsenite rather than using an excess arsenite. Potentiometric titrations of hypochlorite with arsenite and of arsenite with hypochlorite were made and the results compared with the results of titrations of arsenite with hypochlorite using Bordeaux indicator. Previous oxidetions using hypochlorite had been carried out in stoppered iodine flasks. Because it would be inconvenient to carry out potentiometric titrations in flasks, it would be necessary to use beakers. It was then necessary to determine if there was a measurable loss of hypochlorite from a covered beaker during the time required for the oxidation of hypophosphate with excess hypochlorite. In order to determine this, hypophosphate samples were determined by excess hypochlorite in beakers which were covered with a watch glass, and in stoppered iodine flasks. The standing time varied from 30 to 60 minutes. The excess hypochlorite was determined by adding an excess of standard arsenite and titrating the excess arsenite with hypochlorite using Bordeaux indicator. The results are shown in Table X.

The data in Table X show that there is no measurable loss of hypochlorite from a covered beaker during the time required to carry out the oxidation of hypophosphate with excess hypochlorite.

In order to compare potentiometric titrations of arsenite with hypochlorite with titrations using Bordeaux indicator, a 0.1000 normal sodium arsenite solution was titrated with a hypochlorite solution

TABLE X

Sample [*]	Meg. Na ₂ H ₂ P ₂ O ₆ Taken	Meq. Na ₂ H ₂ P ₂ O ₆ Found
Fı Bı Fz Ba Ba	1.250 1.250 1.250 1.250 1.250 1.250	1.250 1.249 1.250 1.250 1.250 1.249

DETERMINATION OF HYPOPHOSPHATE IN BEAKERS AS COMPARED TO DETERMINATION IN IODINE FLASKS

* B refers to determination made in beaker, F in flask;

listed in order of stending time.

using Bordeaux indicator and it was found that 19.96 ml. of the arsenite solution required 19.26 and 19.26 ml. of the hypochlorite solution in two titrations with no correction for the indicator blank. The arsenite solution was then titrated with the hypochlorite solution and the equivalence point determined potentiometrically by the following procedure. To 19.98 ml. samples of the arsenite solution in 150 ml. beakers were added 35 ml. of water, 0.5 gram of sodium bicarbonate, and one gram of potassium bromide. The solution was titrated with the hypochlorite solution and the equivalence point determined with a Sargent potentiometer with platinum and saturated calomel electrodes. Data for a typical titration are shown in Table XI.

Other 19.98 ml. samples of the sodium arsenite solution titrated potentiometrically in the same manner required 19.24 and 19.25 ml. of the hypochlorite solution. A 19.98 ml. sample of the arsenite solution

TABLE XI

Ml. O.l N	E	∆ E	∆V	$\Delta E / \Delta V$	V
NaClO	Volts	Volts	Ml.		Ml.
18.57 18.66 18.76 18.63 19.17 19.19 19.23 19.26 19.27 19.29 19.32 End poi	0.132 0.139 0.145 0.150 0.157 0.159 0.309 0.661 0.737 0.753 0.758 nt 19.25 m	0.007 0.006 0.005 0.007 0.002 0.150 0.352 0.076 0.016 0.005	0.09 0.10 0.07 0.34 0.02 0.04 0.03 0.01 0.02 0.03	0.078 0.060 0.071 0.021 0.10 3.8 11.8 7.6 0.80 0.17	18.62 18.71 18.60 19.00 19.18 19.21 19.25 19.28 19.28 19.28 19.32

POTENTIOMETRIC TITRATION OF ARSENITE WITH HYPOCHLORITE IN THE PRESENCE OF BROMIDE

was titrated with the hypochlorite by the same procedure except that no potassium bromide was added to the arsenite sample. The results are shown in Table XII.

The data in Tables XI and XII show that sodium arsenite solution in sodium bicarbonate medium can be titrated with sodium hypochlorite and the equivalence point determined potentiometrically. The data also show that the presence of bromide does not influence the equivalence point in the titration. The average volume of hypochlorite required to oxidize 19.98 ml. of the arsenite solution was found to be 19.28 ml. (before the indicator correction) in two titrations using Bordeaux as indicator. The average volume of hypochlorite required by 19.98 ml. of the arsenite in four potentiometric titrations was found to be 19.25 ml.

TABLE XII

Ml. O.l N NaClO	E Volts	∆ ≟ Volts	∆v Ml.	$\Delta E / \Delta V$	V Ml.
19.05	0.176				
19.15	0.182	0.006	0.10	0.60	19.10
19.22	0,220	0.038	0.07	0.54	19.19
19.23	0.330	0.110	0.01	11.0	19.23
19.24	0.478	0.148	0.01	14.8	19.2L
19.26	0.652	0.174	0.02	8.7	19.25
19.27	0.661	0.009	0.01	0,90	19.27
19.32	0.695	0.034	0.05	0.68	19.30
19.41	0.715	0.020	0.09	0,22	19.37

POTENTIONETRIC TITRATION OF ARSENITE WITH HYPOCHLORITE

The 0.03 ml. indicator blank used in titrations using Bordeaux indicator is therefore well substantiated.

Experiments were carried out to compare the results obtained by potentiometric titrations of hypochlorite with arsenite with the results obtained by titrations of arsenite with hypochlorite using Bordeaux as indicator. The normality of the hypochlorite was found to be 0.09789 and 0.09769 by two titrations using Bordeaux as indicator; the normality was calculated on the basis of the normality of the standard arsenite solution. The normality of the hypochlorite was also determined potentiometrically. To 19.98 ml. samples of the hypochlorite solution in 150 ml. beakers were added 35 ml. of water and 0.5 gram of sodium bicarbonate. The solution was titrated with the standard arsenite solution and the equivalence point determined by means of a Fisher Titrimeter with platinum and saturated calomel electrodes. The instrument was adjusted to a null point at 0.00 volts. Data obtained in a typical titration are shown in Table XIII.

TABLE XIII

POTENTIOMETRIC	TITRATION	\mathbf{OF}	HYPOCHLORITE	WITH	ARSENITE
----------------	-----------	---------------	--------------	------	----------

Ml. O.l N	E	∆E	∆V	$\Delta E / \Delta V$	V
Arsenite	Volts	Volts	Ml.		Ml.
19.45 19.46 19.48 19.51 19.53 19.54 19.55 19.57 19.65	0.703 0.691 0.669 0.645 0.550 0.231 0.130 0.121 0.104	0.012 0.022 0.024 0.095 0.319 0.101 0.009 0.017	0.01 0.02 0.03 0.02 0.01 0.01 0.02 0.08	1.2 1.1 0.80 4.8 32.0 10.0 0.45 0.20	19.46 19.47 19.50 19.52 19.54 19.55 19.56 19.61

Other 19.98 ml. samples of the hypochlorite solution determined by a potentiometric titration with the standard arsenite using the same procedure, required 19.55, 19.54 and 19.55 ml. of the 0.1000 normal arsenite. The average normality of the hypochlorite on the basis of the potentiometric titrations was then calculated to be 0.09785, which agrees well with the normality of 0.09789 found by the method using Bordeaux as indicator.

The preliminary experiments indicated that the excess hypochlorite in the determination of hypophosphate by excess hypochlorite could be determined by a direct potentiometric titration with standard sodium

arsenite. This procedure was used to determine a series of hypophosphate samples. A Fisher Titrimeter was used to determine the end point in the arsenite titration. The hypochlorite solution was standardized against standard sodium arsenite using Bordeaux as indicator. The hypophosphate samples were allowed to stand with excess hypochlorite for 35 to 90 minutes before the determination of the excess hypochlorite. The results are shown in Table XIV.

TABLE XIV

DETERMINATION OF HYPOPHOSPHATE WITH EXCESS HYPOCHLORITE, DETERMINING THE EXCESS HYPOCHLORITE BY A POTENTIOMETRIC TITRATION WITH STANDARD SODIUM ARSENITE

Ml. 0.05 N Ma ₂ H ₂ P ₂ O ₆	Ml. O.1 N NaClO Added With Sample	Meg. NazHzPzO ₆ Taken	NazHzPz Meg.	D _e Found Percent
25.00 25.00 25.00 25.00 19.98 19.98	19.98 19.98 19.98 19.98 19.98 19.98 19.98	1.250 1.250 1.250 1.250 0.999 0.999	1.249 1.250 1.252 1.250 0.999 1.001	99.9 100.0 100.2 100.0 100.0 100.2

Determination of excess hypochlorite by a titration with arsenite using the dead stop endpoint. The dead stop endpoint is often a convenient means of detecting the equivalence point in a titration, and is especially valuable if a good indicator for the titration is not available. Experiments were carried out to determine if the equivalence point in the titration of hypochlorite with arsenite could be detected by the dead stop technique. It was found by experiment that if a small



potential was applied across platinum electrodes immersed in a hypochlorite solution containing bicarbonate a current flowed between the electrodes. Also, if arsenite was added to this solution, the current decreased to zero and then increased as the volume of arsenite added was increased.

Experiments were also carried out with measured volumes of hypochlorite and arsenite. A sodium hypochlorite solution was standardized against a standard sodium arsenite solution by the procedure in which Bordeaux is used as the indicator. The normality of the hypochlorite solution was found to be 0.1054; this value was the average of four determinations. The normality of the hypochlorite was also determined by the dead stop procedure. To 19.98 ml. samples of the hypochlorite solution were added 35 ml. of water and 0.5 gram of sodium bicarbonate. Platinum electrodes were immersed in the solution and connected to a Fisher Elecdropode. A potential of 450 millivolts was applied to the electrodes. The standard arsenite solution was added from a burette until close to the equivalence point and current readings taken as the ersenite solution was added in small increments. The solution was stirred with a magnetic stirrer. The equivalence point was taken as the point where the current was at a minimum. Data for a typical titration are shown in Table XV.

Table XV shows that there is a large change in current before and after the equivalence point and the end point is easily detected. Other 19.98 ml. samples of the hypochlorite solution were titrated with the 0.1000 normal arsenite solution by the same procedure. The average of

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M1. 0.1000 N Arsenite	Current Reading
20.74	305
20.87	220
20.98	124
21.00	102
21.02	78
21.03	54
21.05	18
21.07	2
21.08	21
21.11	51
End po:	int 21.07 ml.

TABLE XV

DEADSTOP TITRATION OF SODIUM HYPOCHLORITE WITH SODIUM ARSENITE

six titrations was 21.07 ml. of 0.1000 normal arsenite used for a 19.98 ml. sample of arsenite with a maximum deviation of 0.03 ml. of arsenite. The normality of the hypochlorite solution was then calculated to be 0.1055 normal which agrees well with the normality of 0.1054 determined by titrations using Bordeaux as indicator. The results indicated that in an oxidation using excess hypochlorite, the excess can be determined by a titration with standard sodium arsenite, detecting the endpoint with the deadstop technique unless some other component in the mixture interferes.

Samples of hypophosphate were determined by excess hypochlorite in sodium bicarbonate medium and the excess hypochlorite determined by a titration with standard arsenite determining the endpoint by the deadstop procedure. The samples were allowed to stand for 35 to 80 minutes. A voltage of 450 millivolts was applied to the electrodes in the deadstop backtitration. The results are shown in Table XVI.

TABLE XVI

DETERMINATION OF HYPOPHOSPHATE BY EXCESS HYPOCHLORITE AND DEADSTOP BACKTITRATION WITH ARSENITE

M1.0.05 N	Ml. O.lN	Meq. Na ₂ H ₂ P ₂ O ₆	NazHzPz	0 ₆ Found
Ha2H2P206	NaClO	Taken	Meq.	Percent
9.99 9.99 9.99 19.98 19.98 19.98 19.98 19.98 19.98 25.00 25.00	19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98	0.500 0.500 0.500 0.999 0.999 0.999 0.999 0.999 0.999 1.250 1.250	0.501 0.501 0.502 0.999 1.001 0.999 0.999 1.000 1.249 1.250	100.2 100.2 100.4 100.0 100.2 100.0 100.0 100.1 99.9 100.0
25.00	19.98	1.250	1.249	99.9

Table XVI shows that the excess hypochlorite in the oxidation of hypophosphate can be determined by a dead-stop titration with standard ersenite.

It would be very convenient if an indicator were available which could be used in a titration of hypochlorite with arsenite. Indicators have been proposed for the titration of arsenite with hypochlorite. Some of these indicators have been reported to be somewhat reversible in that if the indicator is bleached by hypochlorite the addition of ersenite will restore the color of the indicator. These indicators were investigated to determine if any were sufficiently reversible to

use in a titration of hypochlorite with arsenite and to determine if any of them were more convenient to use than Bordeaux in the reverse titration.

Sinn (60) recommended the use of a 0.2 per cent aqueous solution of quinoline yellow for detecting the equivalence point in titrations of arsenite with hypochlorite. The arsenite solution contained potassium bromide. Young and Gupta (73) used quinoline yellow for titrations of hypochlorite with arsenite but did not state that bromide was present. Belcher (2) reviewed the use of this indicator and found that it was slightly reversible in the presence of bromide.

A 0.2 per cent aqueous solution of quinoline yellow was prepared. Titrations of arsenite with hypochlorite and the reverse titrations were tried using this indicator with and without bromide present. It was found that several drops of 0.1 normal hypochlorite were required to decolorize the indicator if bromide was not present, but the color was bleached from yellow to colorless by a trace of hypochlorite in the presence of bromide. The indicator was found to be slightly reversible, but when the color was bleached by a small amount of hypochlorite in the presence of bromide and an excess of arsenite was added the return of the color required about one minute. The indicator could not be used for a titration of hypochlorite with arsenite.

Sheentsis (58) recommended the use of cresyl violet for titrations of arsenite with hypochlorite and claimed that the results for the determination of available chlorine agreed with those determined iodometrically.



Experiments showed that the red color of cresyl violet was bleached to colorless by a trace of hypochlorite without bromide present but the indicator was found to be completely irreversible. It was found to be somewhat more sensitive to local excesses of hypochlorite than is Bordeaux and its use does not present any advantage over the use of Bordeaux in titrations of arsenite with hypochlorite except that the presence of bromide is not required when cresyl violet is used.

Belcher (1) used an aqueous solution of tartrazine as indicator in titrations of arsenite with hypochlorite in the presence of bromide. Studies on the use of this indicator showed that the yellow color of the indicator is decolorized only by a large excess of hypochlorite if bromide is not present but is decolorized by a trace of hypochlorite in the presence of bromide. The indicator was found to be slightly reversible but the return of the color upon addition of excess arsenite was not rapid enough that the indicator could be used for titrations of hypochlorite with arsenite even if the indicator was added close to the equivalence point.

It was found that none of the indicators studied is better than Bordeaux for detecting the endpoint in titrations of arsenite with hypochlorite and none was sufficiently reversible to be used for titrations of hypochlorite with arsenite.

C. Oxidation of Hypophosphate With Sodium Hypochlorite in a Solution Containing Bromide

It was found by experiment that phosphite is rapidly oxidized by a slight excess of hypochlorite in a solution containing sodium bicarbonate and potassium bromide. This is discussed more fully in the section of this thesis dealing with the determination of phosphite by hypochlorite in a bromide solution. An attempt was made to oxidize hypophosphate under the same conditions. It was found that the reaction between hypophosphate and hypochlorite in the presence of bromide, or essentially the reaction between hypophosphate and hypobromite, is much slower than the reaction of phosphite with hypobromite. The reaction is so slow that the yellow color indicating and excess hypochlorite appeared on the first addition of hypochlorite to a solution containing hypophosphate and bromide and disappeared very slowly especially near the equivalence point. It was therefore not possible to determine hypophosphate by a slight excess of hypochlorite in a bromide solution as was done in the case of phosphite, because the slow reaction did not readily allow the detection of a slight excess of hypochlorite.

An attempt was made to determine hypophosphate in the presence of bromide by a measured excess of hypochlorite. To a series of 0.05000 normal hypophosphate samples were added one gram of sodium bicarbonate and one gram of potassium bromide. Measured amounts of standard sodium hypochlorite were added from a burette. The samples were allowed to stand for various time intervals, an excess of standard sodium arsenite solution added, and the excess arsenite titrated with hypochlorite from

the same burette using Bordeaux to determine the endpoint. Blanks were determined in the same manner, substituting water for the hypophosphate solution. The results are shown in Table XVII.

TABLE XVII

DETERMINATION OF HYPOPHOSPHATE WITH EXCESS HYPOCHLORITE IN THE PRESENCE OF BROMIDE AS A FUNCTION OF TIME OF STANDING AND EXCESS HYPOCHLORITE

Ml. 0.05 N Ne ₂ H ₂ P ₂ O ₆	Approx. Ml. O.IN NaClO Before Standing	lieg. Na _z H _z P ₂ O ₆ Taken	Standing Time Min.	NagHgPg Meg.	0 ₆ Found Percent
19.98 19.98 19.98 19.98 19.98 19.98 19.98 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	11 (a) 11 (a) 12 (a) 14 16 17 18 13 13 18 20 20 20 10 10	0.999 0.999 0.999 0.999 0.999 0.999 0.999 1.250 1.250 1.250 1.250 1.250 1.250	10 3 3 3 1 5 5 3 9 5 1 2 8	0.996 0.995 0.999 1.004 1.007 1.007 0.998 1.240 1.229 1.248 1.229 1.248 1.250 1.254	99.7 99.6 100.0 100.5 100.8 100.8 99.9 99.2 98.3 99.0 100.0 101.4 100.3 0.16* 0.28*

* Ml. O.1 N NaClO lost.

(a) The hypochlorite was added slowly with constant swirling until a yellow color persisted then allowed to stand the time indicated.

The data in Table XVII show that hypophosphate is oxidized by excess hypochlorite in bromide solution. The data also shows that a large excess of hypobromite in the presence of bromide is unstable, or forms products on standing which do not react with arsenite in

<u>1</u>8

bicarbonate medium. This accounts for the large loss of hypochlorite when blanks were determined. Quantitative results for the determination of hypophosphate were not obtained, for the results depend on the amount of excess hypochlorite used and on the time of standing.

Farkas and Lewin (15) made a study of the reaction between sodium hypochlorite and potassium bromide and found that the rate of the re-

(1) ClO⁻ + Br⁻ ---> BrO⁻ + Cl⁻ decreases with increasing pH. At lower pH values other reactions take place:

(2)	2 C 10	+	Br0	·>	201	+	Br03	3	
(3)	C10 ⁻	÷	2HC10	>	2H ⁺	+	201	+	ClO ₃
(4)	Br0	+	2HC10	>	Br0 ₃	•• ·	+ 2H ⁺	+	201

and the rate of these reactions increases with decreasing pH. They found that in the pH range of 9.0 to 9.4 an excess of hypochlorite quantitatively oxidized bromide ion according to equation (1), and that the oxidation was complete in five minutes. If the reaction were allowed to proceed for a longer time, the effect of the other reactions was apparent and loss of hypochlorite occurred.

Because the results of the determination of hypophosphate by excess hypochlorite in a solution containing bromide and bicarbonate were erratic, the determination was tried in a solution buffered to a pH of approximately 9.2. It was considered that under these conditions the oxidation of the hypophosphate might be confined to a reaction between hypophosphate and hypobromite without loss of hypochlorite due to the formation of bromate and chlorate.

A buffer of pH 9.4 was prepared from boric acid and sodium hydroxide. The pH of a mixture of 25.00 ml. of 0.05000 normal hypophosphate, 19.98 ml. of 0.1 normal sodium hypochlorite, one gram of potassium bromide, and 50 ml. of the buffer of pH 9.4 was found to be 9.2 as determined with a Beckman Hodel H-2 pH meter. To measured samples of hypophosphate were added one gram of potassium bromide and 50 ml. of the pH 9.4 buffer. A measured excess of hypochlorite was added from a burette, the mixture allowed to stand for 15 minutes, an excess of standard arsenite added, and the excess arsenite titrated with standard hypochlorite from the same burette using Bordeaux indicator. The hypochlorite was standardized against the standard ersenite solution in the presence of 50 ml. of the pH 9.4 buffer and it was found that the results obtained were the same as those found when bicarbonate was used in place of the buffer.

Table XVIII shows that the oxidation of hypophosphate by excess hypochlorite in the presence of bromide at a pH of approximately 9.2 is complete in 15 minutes if the excess hypochlorite is 60 per cent or above. However, the results obtained are slightly high indicating some loss of hypochlorite but are not as erratic as the results found in a bicarbonate medium (Table XVII).

The determination was repeated using approximately 60 per cent excess hypochlorite and varying the time of standing. The results are shown in Table XIX.

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TABLE XVIII

DETERMINATION OF HYPOPHOSPHATE BY EXCESS HYPOCHLORITE IN THE PRESENCE OF BROMIDE AT A pH OF APPROXIMATELY 9.2 AS A FUNCTION OF EXCESS HYPOCHLORITE

Ml. 0.05 N Na ₂ H ₂ P ₂ O ₆	Approx. Ml. O.l N NaClO	Meq. NaH ₂ P ₂ O ₆ Taken	Approx. Percent Excess NaClO	<u>NazHzPz</u> Meq.	0 ₆ Found Percent
9.99 19.98 9.99 19.98 25.00 25.00 19.98 19.98 29.97 25.00 19.98 39.96 25.00	20 25 10 20 25 25 18.5 17.5 20 15 25 15	0.500 0.999 0.500 0.999 1.250 1.250 0.999 0.999 1.499 1.250 0.999 1.998 1.250	300 150 100 100 100 100 85 75 66 60 50 25 20	0.502 1.004 0.501 1.003 1.252 1.254 0.996 1.505 1.252 0.992 1.996 1.227	100.4 100.5 100.2 100.4 100.2 100.3 99.7 99.7 100.4 100.2 99.3 99.9 98.2

Table XIX shows that if a 60 per cent excess hypochlorite is used, the oxidation of hypophosphate is complete in ten minutes and that a longer standing period up to 30 minutes has no appreciable effect on the results. The method using hypochlorite in the presence of bromide has no particular advantage over the method using hypochlorite without bromide except that the oxidation of hypophosphate is complete in a shorter time if bromide is present. This advantage is minimized by the necessity of using a buffer and a critical excess of approximately 60 percent hypochlorite when bromide is present. The latter requirement makes the method somewhat empirical.

TABLE XIX

Ml. 0.05 N Na ₂ H ₂ P ₂ O ₆	MI. O.I N Nacio	Meq. Na ₂ H ₂ P ₂ O ₆ Taken	Standing Time Min.	Na ₂ H ₂ P Meq.	20 ₆ Found Percent
25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98	1.250 1.250 1.250 1.250 1.250 1.250 1.250 1.250 1.250	5 8 10 10 12 15 20 30	1.245 1.246 1.251 1.249 1.249 1.249 1.248 1.251 1.251 1.252	99.6 99.7 100.1 99.9 99.9 99.8 100.1 100.2

DETERMINATION OF HYPOPHOSPHATE BY EXCESS HYPOCHLORITE IN THE PRESENCE OF BROMIDE AT A pH OF APPROXIMATELY 9.2 AS A FUNCTION OF TIME OF STANDING

D. Oxidation of Hypophosphate by Excess Ceric Sulfate in Sulfuric Acid Solution

It was found by experiment that hypophosphite is completely oxidized by excess ceric sulfate in sulfuric acid solution at boiling temperature. It was also found that the excess ceric sulfate could be determined by a titration with a standard ferrous ammonium sulfate solution or with a standard arsenite solution. A small amount of ceric sulfate was lost during the boiling period and it was necessary to apply corrections for this loss. Determinations by excess ceric sulfate are discussed more fully in the section of this thesis dealing with the determination of hypophosphite with ceric sulfate. Experiments were carried out to determine if hypophosphate could be determined by excess ceric sulfate in sulfuric acid solution.



To measured samples of 0.05000 normal hypophosphate were added a measured excess of standard ceric ammonium sulfate and ten ml. of concentrated sulfuric acid. The mixtures were refluxed for various time intervals in 500 ml. flasks attached by glass joints to watercooled condensers. The precipitate of cerium hypophosphate which formed when the ceric sulfate was added to the hypophosphate dissolved when the flask was heated and remained in solution during the determination. Each condenser was rinsed with about 30 ml. of water which drained into the attached flask. The contents of the flasks were cooled to room temperature. two drops of ferroin added, and the excess ceric sulfate titrated with a standard ferrous ammonium sulfate solu-The excess ceric sulfate in some of the samples was determined. tion. by adding two drops of ferroin. three drops of osmium tetroxide solution and titrating with a standard arsenite solution. Blanks were also determined in the same manner, substituting water for the hypophosphate solution. The results were calculated on the basis of the blanks and are shown in Table XX.

Table XX shows that hypophosphate is not completely oxidized to phosphate by excess ceric sulfate in approximately six normal sulfuric acid in one hour at boiling temperature. The oxidation is fairly rapid when the reacting mixture is first heated but increasing the heating time from 45 to 60 minutes has little effect on the oxidation. It is quite possible that the oxidation takes place through a hydrolysis of the hypophosphate and oxidation of the phosphite formed and that in the relatively low concentration of acid used the hydrolysis is not completed

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TABLE XX

DETERMINATION OF HYPOPHOSPHATE BY EXCESS CERIC SULFATE IN SULFURIC ACID SOLUTION AS A FUNCTION OF TIME OF HEATING Note: Excess ceric sulfate determined with standard ferrous ammonium sulfate except where indicated.

Ml. 0.05 N	Ml. O.1 N	Meq. Na ₂ H ₂ P ₂ O ₆	Refluxing Time	Na _z H _z P	206 Found
Na2H2P206	Ceric Sulfate	Taken	Min.	Meg.	Percent
25.00 25.00 19.98 19.98 19.98 25.00 25.00 25.00 25.00 25.00 25.00	25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	1.250 1.250 0.999 0.999 0.999 1.250 1.250 1.250 1.250 1.250	15 25 30 45 50 50 60 60 60 60	1.220 1.229 0.984 0.985 0.983 1.233 1.236 1.234 1.233 1.232 1.232	97.6 98.3 98.5 98.6 98.4 98.7 98.9 98.7 98.6 98.6 98.6 (2)
25.00	25.00	1.250	60	1.234	98.7 (a)
0.0	25.00 25.00		60 60		0.07 # 0.09 *

* Ml. 0.1 N ceric sulfate lost.

(a) Excess ceric sulfate determined with arsenite.

in one hour. Also, it was found in another part of this work that phosphite is not readily oxidized by ceric sulfate and this may be a factor in the oxidation of the hypophosphate.

The oxidation of hypophosphate may possibly be completed if carried out in stronger acid solution or if heated for a period longer than one hour, but the investigation was discontinued because other methods for the determination of hypophosphate developed during this work are much more satisfactory. Summary of Results of Hypophosphate Determination

The average results obtained by the methods developed for the determination of hypophosphate are as follows:

Method	Average Percent Na ₂ H ₂ P ₂ O ₆	
<pre>Excess Dichromate, Ferrous Sulfate Procedure (No blank corrections)</pre>	100.1 ± 0.2 99.9 \pm 0.1 99.8 \pm 0.2 100.0 \pm 0.1 100.0 \pm 0.1 100.0 \pm 0.1	

The results listed are the average results of analyses made on samples containing from 10 to 50 ml. of 0.05 normal hypophosphate solution. The average deviations are also given. The data show that the method in which an excess of hypochlorite is used is the most accurate and precise and that the procedure used to determine the excess hypochlorite has no influence on the results. The hypochlorite method is much better than the dichromate method for several reasons: it is more accurate and precise, it is faster and carried out at room temperature, no blank other than an indicator blank is required, and the oxidant is less expensive. The hypochlorite method is well adapted to the determination of a large number of hypophosphate samples for the standing time and amount of excess hypochlorite can be varied within wide limits.

Several methods of equal accuracy and precision are available for determining the excess hypochlorite. If the amount of excess hypochlorite is approximately known it can be determined quite rapidly by a deadstop titration with standard arsenite for current readings need to be taken only near the endpoint. Plotting the changes in current is unnecessary even if the approximate endpoint is not known because the current changes before and after the endpoint are very pronounced.

The dichromate method is more difficult to use because of the heating required. It is not well adapted to samples of large volume. It may be used to advantage for the determination of hypophosphates which are insoluble in the bicarbonate medium used in the hypochlorite method but which are soluble in acid solution. For routine determinations the blanks can be disregarded if precautions are taken to eliminate any extraneous reducing material from the reaction flask.

The methods which have been developed for the determination are far superior to the gravimetric procedures which are commonly used, at least as far as the time required for the analysis is concerned.

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V. DETERMINATION OF PHOSPHITE

A phosphite was required as a basis for the comparison of several methods for its determination. A survey of the literature indicated that a primary standard phosphite had not been prepared. Therefore, it was necessary to prepare a phosphite which could be made homogeneous and contain no substance which would interfere with the methods used for the determination of phosphite. For this purpose approximately 50 grams of reagent grade phosphorous acid was ground in a morter and placed in a desiccator over phosphorus pentoxide. The grinding and crying process was repeated several times until the small crystals could be poured freely. The phosphorous acid was weighed in a closed weighing bottle and allowed to stand in the open weighing bottle over phosphorus pentoxide for a week. The 50 grams lost about 16 milligrams and it was considered that further drying was not necessary. The weighing bottle was then closed, the acid mixed thoroughly by shaking, and the closed bottle kept in a desiccator over phosphorus pentoxide.

Samples of the phosphorous acid were weighed as required to make sample solutions by pouring approximately the required amount into a small dry weighing bottle which had been previously weighed, and weighing again to find the weight of the phosphorous acid. The transfer was made with as little exposure to the air as possible, for the acid was very hygroscopic. The weighed samples were dissolved in water and diluted to one liter to make solutions of approximately 0.025 molar or

0.05 normal in terms of oxidation of the phosphite to phosphate.

The purity of the phosphorous acid was established by oxidizing the acid to orthophosphate and determining the phosphate as magnesium pyrophosphate, a method which has been used by others to check volumetric results. One hundred ml. samples of a phosphorous acid solution containing 2.2421 grams of the acid per liter were evaporated to dryness three times with 30 ml. of concentrated hydrochloric acid and ten ml. of concentrated nitric acid after adding to each sample sufficient magnesium chloride equivalent to the formation of magnesium orthophosphate. The residue was dissolved in water, diluted to 100 ml., magnesia mixture added, and magnesium ammonium phosphate slowly precipitated with ammonium hydroxide. The precipitate was allowed to stand overnight, filtered, washed with cold ten per cent ammonium hydroxide, dissolved in hydrochloric acid and reprecipitated. After standing overnight the precipitate was filtered by means of a sintered porcelain crucible, washed with cold ten per cent ammonium hydroxide and ignited to magnesium pyrophosphate at 1000° C. in a muffle furnace to constant The per cent purity of the phosphorous acid was calculated from weight. the weight of pyrophosphate obtained. The per cent purity was found to be 99.57, 99.51, 99.48, 99.51 for four samples; the average was then calculated to be 99.52 per cent. It was assumed that the remainder of the phosphorous acid was water for it was not dried to an anhydrous state. Tests for other substances were not made. All results for the determination of phosphite reported in this thesis are expressed on the basis of the average of the gravimetric results. In each table,

the milliequivalents of H_3PO_3 taken are the milliequivalents of H_3PO_3 which were present in the sample taken for analysis.

The composition of the phosphorous acid was further established by the method of Wolf and Jung (70). This method was reviewed by Jones and Swift (24) who stated that it is accurate for the determination of phosphite.

To measured samples of approximately 0.05 normal phosphorous acid in 250 ml. iodine flasks was added 50 ml. of 0.2 molar sodium bicarbonate solution which was saturated with carbon dioxide. A measured excess of at least ten ml. of 0.1 normal iodine solution was added to each flask. The flasks were allowed to stand in the dark for 45 to 60 minutes, and the excess iodine titrated with standard sodium arsenite solution. The results were calculated on the basis of blanks determined in the same manner as the samples, substituting water for the phosphorous acid solution. The results are shown in Table XXI.

TABLE XXI

DETERMINATION OF PHOSPHITE BY METHOD OF WOLF AND JUNG

M1. 0.05 N	Ml. O.l N	Meg. H ₃ PO3	H ₃ PO	3 Found
H ₃ PO ₃	Iodine	Taken	Meg.	Percent
	<u>, </u>			
25,00	25 .0 0	1.360	1.359	99.9
25.00	25.00	1.360	1.360	100.0
25.00	25 00	1.360	1.360	100.0
25 00	25 00	1,360	1,359	99.9
25 00	25.00	1,360	1.359	99.9
27.00	-2.44	.		// •/

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The average per cent found was calculated as 99.9 per cent from the data in Table XXI. The results by the Wolf and Jung method therefore agree well with the results of the gravimetric method.

A. Oxidation of Phosphite By Excess Potassium Dichromate in Sulfuric Acid Solution

Preliminary experiments were conducted to determine if phosphorous scid is oxidized by excess potassium dichromate in sulfuric acid solution and to determine the effects of time of heating and concentration of sulfuric acid. A solution of approximately 0.025 molar phosphorous acid was prepared from reagent grade crystals of the acid which were not dried and which were moist on the surface. The undried reagent was used only in these preliminary experiments; the dried reagent was used in all other procedures dealing with the determination of phosphite. Measured samples (19.98 ml.) of the 0.025 molar solution were treated with 19.98 ml. of 0.1 normal potassium dichromate and sufficient concentrated sulfuric acid to make the resulting mixture 12 normal in sulfuric acid. The mixtures were heated in a boiling water bath and the excess dichromate determined iodometrically after neutralizing part of the acid as previously described in the section of this thesis dealing with the determination of hypophosphate by excess dichromate. The results are shown in Table XXII.

The procedure was repeated using different concentrations of sulfuric acid and various heating times. Each sample contained 19.98 ml. of the 0.025 molar phosphorous acid and 19.98 ml. of 0.1 normal dichromate. The results are shown in Table XXIII.

TABLE XXII

OXIDATION OF PHOSPHITE BY EXCESS DICHROMATE IN 12 NORMAL SULFURIC ACID AS A FUNCTION OF TIME OF HEATING

Time of Heating Min.	Meq. H ₃ PO ₃ Found
5	0.913
10	0.968
15	0.984
30	0.985
60	0.986
90	. 0.986
120	0.986

TABLE XXIII

OXIDATION OF PHOSPHITE BY EXCESS DICHROMATE AS A FUNCTION OF SULFURIC ACID CONCENTRATION AND TIME OF HEATING

Approximate Normality H ₂ SO ₄	Time Heating Hours	Meq. H ₃ PO ₃ Found	
12 12 6 6 3.6 3.6	1 1 0.5 1 1.5 0.5 1	0.985 0.989 0.841 0.946 0.980 0.614 0.846	

Tables XXII and XXIII indicate that phosphorous acid is completely oxidized by excess dichromate in 12 normal sulfuric acid in 30 to 45 minutes and that if the oxidation is to be complete in one hour, the sulfuric acid concentration must be at least above six normal. The preliminary experiments were carried out to determine the conditions necessary to oxidize phosphorous acid with excess dichromate. The composition of the phosphorous acid was not accurately known, but it was assumed that the oxidation was complete if no further oxidation took place with a longer heating period using the same acid concentration.

62

Solutions of phosphorous acid were prepared from the dried acid. To measured samples of the solutions were added a measured excess of standard potassium dichromate and sufficient sulfuric acid to make the resulting mixture 12 normal in sulfuric acid. The mixtures were heated for one hour in a boiling water bath and the excess dichromate was determined by a standard ferrous ammonium sulfate solution as previously described in the section of this thesis dealing with the determination of hypophosphate with excess dichromate.

Table XXIV shows that if the blanks are taken into consideration, the results are in better agreement with the gravimetric results than if the blanks are neglected.

The determination was repeated by the same procedure except that the excess dichromate was determined iodometrically after neutralizing part of the sulfuric acid as described in the section of this thesis dealing with the determination of hypophosphate with dichromate. The results are shown in Table XXV.

Table XXV shows that phosphite is completely oxidized by excess dichromate in 12 normal sulfuric acid in 45 minutes at the temperature of a boiling water bath.

TABLE XXIV

DETERMINATION OF PHOSPHITE BY EXCESS DICHROMATE IN 12 NORMAL SULFURIC ACID (Ferrous Sulfate Backtitration)

	Conditions:	Time of Heating	One Hour	
Ml. 0.05 N	Ml. O.1 N	Heg. H ₃ PO ₃	H ₃ PO ₃	Found
MaPOa	K ₂ Cr ₂ O7	Taken	Meq.	Percent
19.98	19.98	1.171	1.172	100.1**
19.98	19.98	1.171	1.171	100.0**
19.98	19.98	1.171	1.171	100.0**
25.00	25.00	1.376	1.380	100.2
25.00	25.00	1.376	1.381	100.3
25.00	25.00	1.376	1.377	100.2
25.00	25.00	1.376	1.377	100.2

* Results calculated on the basis of blanks.

TABLE XXV

DETERMINATION OF PHOSPHITE BY EXCESS DICHROMATE IN 12 NORMAL SULFURIC ACID (lodometric Backtitration /fter Neutralizing Part of The Acid)

-	Conditions:	Time of Heating	45 Minutes	
Ml. 0.05 N H ₃ PO ₃	Ml. 0.1 N K ₂ Cr ₂ O7	Meg. H ₃ PO ₃ Taken	H ₃ PO ₃ B Meq.	Found (a) Percent
25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	1.376 1.376 1.376 1.376 1.376 1.360 1.360 1.360 1.360 1.360 1.360	1.377 1.378 1.373 1.377 1.375 1.361 1.360 1.361 1.360 1.357	100.1 100.1 99.8 100.1 99.9 100.1 100.0 100.1 100.0 99.8

* Heated one hour.

(a) Correction for blanks.

B. Oxidation of Phosphite by Excess Hypochlorite in The Presence of Bromide

Nitrite and arsenite are oxidized rapidly by hypochlorite in a solution containing bromide and bicarbonate (29). It seemed reasonable to expect that phosphite may be oxidized under the same conditions.

To measured samples of 0.05 normal phosphorous acid in 200 ml. Erlenmeyer flasks were added one gram of sodium bicarbonate and one gram of potassium bromide. Standard sodium hypochlorite was added from a burette until a slight yellow color appeared, indicating a slight excess of hypochlorite. The hypochlorite could be added to the solution as rapidly as the burette would deliver it, and the yellow color would not persist until there was an excess of hypochlorite. The flasks were allowed to stand for two to three minutes, a small measured excess of standard arsenite added, and the excess arsenite titrated with the standard hypochlorite from the same burette using Bordeaux as indicator. The volume of the solution was adjusted to 50 to 75 ml. at the endpoint. An indicator blank of 0.03 ml. of 0.1 normal hypochlorite was subtracted from the volume of hypochlorite used. An excess of about 0.5 ml. of 0.1 normal hypochlorite was used with each sample.

The data in Table XXVI were obtained using two different phosphorous acid solutions of slightly different concentration but prepared from the same reagent. Table XXVI shows that phosphite is completely oxidized by a slight excess of hypochlorite in the presence of bromide and the results obtained agree fairly well with the results obtained by the gravimetric and Wolf and Jung methods. The data also show that

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Ml. 0.05 N	Meq. H ₃ PO ₃	H ₃ PO ₃ 1	Found
H ₃ FO ₃	Taken	Meq.	Percent
9.99 9.99 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 25.00 25.00 49.98 49.98	0.616 0.616 1.231 1.231 1.231 1.168 1.168 1.168 1.168 1.168 1.168 1.168 1.540 1.540 3.080 3.080	0.617 0.616 1.230 1.230 1.229 1.168 1.168 1.142 1.168 1.155 1.538 1.538 3.076 3.076	100.1 100.0 99.9 99.9 99.8 (a) 100.0 100.0 97.8 (b) 100.0 (c) 98.9 (d) 99.8 99.8 99.8 99.9 99.9

TABLE XXVI

DETERMINATION OF PHOSPHITE BY A SMALL EXCESS OF HYPOCHLORITE IN A SOLUTION CONTAINING BROMIDE AND BICARBONATE

(a) Allowed to stand 10 min. before adding arsenite.

(b) Direct titration, endpoint indefinite.
(c) 30 ml. buffer pH 7.4 used in place of bicarbonate.
(d) KBr added after arsenite instead of with sample.

phosphite is not completely oxidized in two to three minutes by a small excess of hypochlorite unless bromide is present.

In order to determine the stability of the phosphorous acid used for this work, the acid was determined by the hypochlorite-bromide method after the acid had been standing for four months in a closed weighing bottle which was kept in a desiccator over phosphorus pentoxide. The results are shown in Table XXVII.

TABLE XXVII

M1.0.05 N	Meq. H ₃ PO ₃	H ₃ PO	Found	
H ₃ PO ₃	Taken	Meq.	Percent	
25.00 25.00 25.00 25.00 25.00	1.376 1.376 1.376 1.376 1.376 1.376	1.374 1.376 1.376 1.375 1.375	99.9 100.0 100.0 99.9 99.9	

DETERMINATION OF STABILITY OF PHOSPHOROUS ACID ON STANDING, USING HYPOCHLORITE-BROMIDE METHOD OF ANALYSIS

Table XXVII shows that there was no apparent change in the composition of the phosphorous acid during four months, for the results agree with the results in Table XXVI which were obtained four months earlier.

<u>Direct titration of phosphite in a bromide-bicarbonate medium with</u> <u>hypochlorite</u>. Attempts were made to titrate phosphite directly in a solution containing sodium bicarbonate and potassium bromide using a solution of Bordeaux to determine the endpoint. The reaction near the equivalence point is so slow that the indicator was destroyed before a true endpoint was reached. Several drops of indicator were added and decolorized before an excess of hypochlorite could be detected. If a reversible indicator were available for titrations with hypochlorite a direct titration may be possible.

The possibility of using the deadstop technique to determine the endpoint in a direct titration of phosphite in a bromide-bicarbonate medium with hypochlorite was investigated. It was found that when a small potential was applied to platinum electrodes immersed in a phosphorous acid solution containing sodium bicarbonate and potassium bromide, no current flowed as determined by a Fisher Elecdropode. However, one drop of 0.1 normal sodium hypochlorite in a bicarbonatebromide medium, produced a current under the same conditions. It was then considered that a very slight excess of hypochlorite may be detected by the deadstop procedure.

To measured samples of 0.05 normal phosphorous acid in 150 ml. beakers were added one gram of sodium bicarbonate and one gram of potassium bromide. Platinum electrodes were immersed in the solution and a potential of 450 millivolts applied by means of a Fisher Elecdropode. The solution was stirred with a magnetic stirrer. Upon the addition of standard sodium hypochlorite from a burette, a current flowed which decreased to zero in a few seconds. Near the equivalence point in the titration the addition of a drop of hypochlorite produced a large increase in current which rapidly decreased to zero when the addition of hypochlorite was stopped. The titration was continued until a fraction of a drop of hypochlorite caused a steady current to flow. This point was taken as the equivalence point. If the hypochlorite was added until within 0.5 ml. of the endpoint, the titration could be completed in two to three minutes. The full sensitivity of the instrument was used near the endpoint. The hypochlorite solution was standardized against standard sodium arsenite using Bordeaux as indicator.

Table XXVIII shows that phosphite can be determined by a direct titration with hypochlorite in a solution containing bromide and bicarbonate.

TABLE XXVIII

M1. 0.05 N	Meq. H _a PO _a	H ₃ PO3	H ₃ PO ₃ Found	
H ₃ PO ₃	Taken	Meg.	Percent	
19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98	1.101 1.101 1.101 1.101 1.101 1.101 1.101 1.101	1.099 1.097 1.100 1.099 1.099 1.100 1.100	99.8 99.6 99.9 99.8 99.8 99.8 99.9 99.9	
17.7 0	1.101		27•1	

DIRECT TITRATION OF PHOSPHITE WITH HYPOCHLORITE IN A SOLUTION CONTAINING BROMIDE USING A DEADSTOP ENDPOINT

In order to have a deadstop endpoint in which a current flows between the electrodes before and after the endpoint with zero current at the endpoint it is necessary that there be a system capable of undergoing electrolysis before and after the endpoint (64). The current changes observed on the addition of sodium arsenite to sodium hypochlorite are typical of this type of endpoint. Sufficient information is not available to predict just what the electrolysis before the endpoint involves because of the variable oxidation states of chlorine but after the endpoint the electrolysis presumably involves the arseniteersenate system.

Another type of deadstop endpoint, such as that encountered in the titration of phosphite with hypochlorite in the presence of bromide, is characterized by no current flowing between the electrodes before the endpoint and a current after the endpoint. The requirements for this type of endpoint are that a system incapable of electrolysis under the conditions used must be present before the endpoint and one which can be electrolyzed after the endpoint. The phosphite and phosphate do not undergo electrolysis, and as soon as there is a permanent slight excess of hypochlorite present, a system is available for electrolysis and a current flows. The electrolysis after the endpoint may involve oxidation states of bromine because of the hypobromite present from the reaction of the first trace of excess hypochlorite with the bromide present.

C. Oxidation of Phosphite with Sodium Hypochlorite

In order to determine if there is an optimum pH at which phosphite is oxidized by hypochlorite, a series of buffers was prepared and the oxidation carried out with excess hypochlorite in the presence of each buffer. The pH of each buffer was determined with a Beckman Model H-2 pH meter. Because in some cases the pH of the mixture of the buffer and the other components of the reacting mixture was slightly different than the pH of the buffer itself, the pH of each reacting mixture was also measured.

To 19.98 ml. samples of 0.05 normal phosphorous acid solution in 250 ml. iodine flasks were added 50 ml. of buffer solution and 25.00 ml. of 0.1 normal sodium hypochlorite. The gutters were filled with saturated potassium iodide solution and the flasks were allowed to stand in the dark for 20 minutes. The potassium iodide solution was then allowed to flow into the flask, 20 ml. of glacial acetic acid

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added, and the liberated iodine titrated with standard sodium thiosulfate after about one minute. The hypochlorite solution was standardized against the standard thiosulfate in two ways. In one, a measured volume of the hypochlorite was added to 50 ml. of water, 10 ml. of saturated potassium iodide solution added, and then 20 ml. of glacial acetic acid. After about one minute the liberated iodine was titrated with thiosulfate. In the other method, 50 ml. of buffer of pH 7.0 was used in place of the 50 ml. of water. The comparison of the hypochlorite with the thiosulfate was made several times using different buffers and in every case the amount of thiosulfate required for a certain volume of hypochlorite solution was smaller when a buffer was used than was the case for a comparison made without the buffer. Also, if the hypochlorite was allowed to stand with a certain volume of buffer, the time of standing had no measurable effect on the volume of thiosulfate required.

Table XXIX shows that the oxidation is more complete in the pH range of 7.0 to 7.8 and that the oxidation takes place only to a very small extent at a pH above 12. It also shows the large difference in results obtained if the hypochlorite is standardized by the different methods discussed. It would be expected that better results would be obtained if the comparison of the hypochlorite and thiosulfate was made in the presence of a buffer as in the determination of the excess hypochlorite used with the phosphite samples, or in other words, by a blank.

TABLE XXIX

EFFECT OF pH ON THE OXIDATION OF PHOSPHITE BY EXCESS HYPOCHLORITE

Conditions: 20 minute standing, 150% excess NaClO

pH *	Fercent Oxidized (a)	Percent Oxidized (b)
5.9	100.2	99.4
6.1	100.0	99.2
6.6	100.1	99.2
7.0	100.6	99.7
7.3	100.5	99.7
7.6	100.5	99.7
7.8	100.6	99.7
8.9	56.7	55.9
9.2	37.2	36.4

Buffers of pH range 5.9 to 6.6 were prepared from NaH₂PO₄ and Na₂HPO₄, pH 7.0 to 8.9 from KH₂PO₄ and NaOH, pH 9.2 from H₃BO₃ and NaOH, and pH 12.1 from NaOH and acetic acid.
(a) Besis of standardization of NaClO in the absence of a buffer.
(b) Besis of a standardization of NaClO in buffer pH 7.0

(b) Basis of standardization of NaClO in buffer pH 7.0.

In order to determine more closely the optimum pH at which phosphite is oxidized by hypochlorite, another series of buffers was prepared and the determinations repeated by the same procedure. The results are shown in Table XXX.

Table XXX shows that the oxidation of phosphite by excess hypochlorite is most complete over a pH range of 7.3 to 7.8. The results in this table correspond more closely to the results obtained by the gravimetric method if they are calculated on the basis of the normality

TABLE XXX

EFFECT OF pH ON THE OXIDATION OF PHOSPHITE BY EXCESS HYPOCHLORITE

рН	Percent Oxidized (a)	Percent Oxidized (b)
6.9	99.6	99.0
7.3	100.0	99.4
7.5	100.0	99.4
7.8	100.0	99.4
8 _. l	96 . 0	95.4

Conditions: Time of stending 20 min., 150% excess hypochlorite.

* Buffer pH 6.9 was prepared from NaH_2PO_4 and Na_2HPO_4 , pH

7.3 to 8.1 from NaH2PO4 and NaOH.

(a) Basis of standardization of NaClO in the absence of a buffer.

(b) Basis of standardization of MaClO in buffer pH 7.5.

of the hypochlorite determined in the absence of a buffer whereas the opposite was true in Table XXIX. The only difference was in the reagents from which the buffers were prepared. A series of phosphite samples was determined by the same procedure using buffer 7.8; it was the same buffer that was used for the data in Table XXIX. The results obtained agreed with the results in Table XXIX, that is, better results were obtained on the basis of the normality of the hypochlorite determined in the presence of the buffer than in the absence of the buffer. This would seem to indicate that the extent of the oxidation depends not only on the pH of the solution but also on the buffer used.

The accuracy of the method depends upon an accurate iodometric determination of hypochlorite in the presence of a buffer. The hypochlorite

used cannot be considered as a solution of a pure compound for it may contain variable amounts of chlorate and chlorite depending on the age of the solution and on the age of the Clorox from which the solution was prepared. Hypochlorite and chlorite are determined iodometrically in acetic acid solution however Kolthoff and Sandell (30) state that chlorite liberates iodine from an iodide solution slowly in acetic acid solution. Chlorate liberates iodine from iodide only from a solution made highly acidic with a strong acid. In a determination of available chlorine in a bleaching solution using arsenite in a bicarbonate medium, there is no interference from chlorite or chlorate and only the chlorine from the hypochlorite is determined.

The iodometric determination of available chlorine was carried out under various conditions. It was found that the volume of thiosulfate solution used for the same volume of hypochlorite varied with the acid used to acidify the potassium iodide solution. A smaller volume of thiosulfate was used with acetic acid than with sulfuric acid and if the concentration of sulfuric acid was increased, a slightly larger volume of thiosulfate was used.

The effect of the presence of buffers on the iodometric determination of hypochlorite was determined. It was found that the volume of thiosulfate solution required for a constant volume of hypochlorite was smaller if a buffer of pH 5.7 to 8.5 was present than if it was not present. This effect was found if the solution was acidified with either acetic acid or sulfuric acid before the liberation of the iodine.

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The effect of buffers is shown by the following. A solution of three grams of sodium bicarbonate in 50 ml. of water was added to each of several iodine flasks. Different weighed amounts of reagent grade monopotassium phosphate were added followed by 19.98 ml. of 0.1 normal hypochlorite. Ten ml. of saturated potassium iodide solution was added to each flask and then 25 ml. of glacial acetic acid carefully added. The liberated iodine was titrated with 0.1 normal sodium thiosulfate solution. The results are shown in Table XXXI.

TABLE XXXI

EFFECT OF BUFFERS ON THE IODOMETRIC DETERMINATION OF HYPOCHLORITE

Grams KH ₂ PO ₄	Ml. O.l N Na ₂ S ₂ O ₃	
0	20,82	
l	20.82	
2	20.80	
3	20,79	
· 24	20.75	
24	20.75	

Table XXXI shows that smaller amounts of iodine are liberated from a potassium iodide solution by a constant amount of hypochlorite in a bicarbonate medium if increasing amounts of monopotassium phosphate are added. It means that the buffer either interferes with the liberation of iodine or affects the titration of iodine with thiosulfate. The results are opposite to what would be expected as the pH of the solution

decreases with increasing amounts of the phosphate and if the effect is one of pH only, it would not be expected that a smaller amount of iodine would be liberated at a lower pH. *I* possible explanation of the effect is that the carbon dioxide in solution from the reaction between the bicarbonate and phosphate liberates hypochlorous acid which decomposes.

Hypochlorite was determined iodometrically in the presence of increasing amounts of NaH_2PO_4 and it was found that the amount of phosphate present, at least up to four grams, had no measurable effect on the results. The same was found to be the case when increasing amounts of K_2HPO_4 or Na_2HPO_4 were used. However, when a buffer prepared from mono and disodium phosphates was used, the amount of iodine liberated was less than was the case if the buffer were not present. This suggests that the amount of iodine liberated depends upon the pH of the solution.

The effect of using different acids in the iodometric determination of hypochlorite was determined. To 50 ml. of various buffers were added 19.98 ml. of a freshly prepared 0.1 normal hypochlorite solution, two grams of potassium iodide, and 20 ml. of either glacial acetic acid or six normal sulfuric acid. The liberated iodine was then titrated with a thiosulfate solution. In one sample 50 ml. of water was used in place of the buffer. The results are shown in Table XXXII.

Table XXXII shows that when the iodometric determination of hypochlorite is carried out in the presence of a buffer a smaller amount of thiosulfate is used than if the buffer is not present and also that when a buffer is present the type of acid used has little effect on the results.

TABLE XXXII

pH of Buffer	Acidified <u>With Acetic Acid</u> Ml. Na ₂ S ₂ O ₃	Acidified <u>With Sulfuric Acid</u> Ml. Na ₂ S ₂ O ₃
Water	18.80	18.84
5.7	18.70	18.70
6.6	18.71	18.70
8.5	18.72	18.69

EFFECT OF ACID USED ON IODOMETRIC DETERMINATION OF HYPOCHLORITE IN THE PRESENCE OF BUFFERS

It also shows that when a buffer is not present, a larger amount of thiosulfate is used when the solution is acidified with sulfuric acid rather than acetic acid.

Because of the erratic results found in the determination of phosphite by excess hypochlorite in the presence of buffers, the determination was attempted in a bicarbonate medium. The results in bicarbonate medium were not as erratic as the results found using buffers but the presence of the bicarbonate had an effect on the iodometric determination of hypochlorite similar to that found when a buffer was present. The results for the determination of phosphite were in better agreement with the results obtained by other methods if the comparison of the hypochlorite and thiosulfate solutions was made in the absence of bicarbonate.

Experiments were conducted to study the oxidation of phosphite by hypochlorite with no buffer or bicarbonate present. To measured samples of 0.05 normal phosphorous acid solution in 250 ml. iodine flasks was added a measured excess of standard sodium hypochlorite. The flasks were allowed to stand in the dark for various time intervals, ten ml. of saturated potassium iodide solution and 20 ml. of glacial acetic acid added and the liberated iodine titrated with a standard sodium thiosulfate solution. Blanks were determined in the same manner substituting water for the phosphorous acid solution and calculations were made on the basis of the blanks. The results are shown in Table XXXIII.

TABLE XXXIII

DETERMINATION OF PHOSPHITE BY EXCESS HYPOCHLORITE IN AN UNBUFFERED SOLUTION

Ml. 0.05 N H ₃ PO ₃	Ml. O.l M NaClO	Meq. H ₃ PO ₃ Taken	Meq. H ₃ PO ₃ Found	Time Standing Min.	Percent Oxidized
19.98 19.98 19.98 19.98 19.98	25.00 25.00 25.00 25.00	1.177 1.177 1.177 1.177 1.177	1.174 1.176 1.175 1.175	3 5 10 40	99.7 99.9 99.8 99.9

Table XXXIII shows that phosphite is rapidly oxidized by sodium hypochlorite in an unbuffered solution. These data also support the conclusion that the iodometric determination of hypochlorite in the presence of buffers is erratic. A large number of phosphite samples were determined by excess hypochlorite in the presence of buffers and sodium bicarbonate and the results were inconsistent. Chulski (12) experienced the same irregularities in determining the excess hypochlorite used in oxidations of hypophosphate in the presence of buffers and sodium bicarbonate.

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The determination of hypochlorite by a comparison against standard sodium arsenite gave consistent results if the determination was made in the presence of bicarbonate or buffers of pH approximately six to ten, and gave results which agreed with the iodometric determination made without a buffer present and acidified with acetic acid. For this reason, during this work, an excess hypochlorite was determined by the arsenite method rather than by the iodometric method. The iodometric determination of hypochlorite in the presence of buffers requires more study.

The determination of phosphite by excess hypochlorite has no advantage over the determination using a slight excess of hypochlorite in the presence of bromide. The method in which bromide is used is somewhat shorter and is easier to carry out.

D. Oxidation of Phosphite By Excess Ceric Sulfate in Sulfuric Acid Solution

The details of oxidations using excess ceric sulfate in sulfuric acid solution are more fully discussed in the section of this thesis dealing with the determination of hypophosphite by ceric sulfate.

Experiments were conducted to determine if phosphite were oxidized by excess ceric sulfate in sulfuric acid solution. To measured samples of 0.05 normal phosphorous acid were added a measured excess of 0.1 normal ceric sulfate and ten ml. of concentrated sulfuric acid. The mixtures were heated under reflux for one hour and the excess ceric sulfate determined by a titration with standard ferrous ammonium sulfate

es described in the section dealing with the determination of hypophosphite by ceric sulfate. Blanks were determined by the same procedure, substituting water for the phosphorous acid solution, and calculations made on the basis of the blanks. The results are shown in Table XXXIV.

TABLE XXXIV

DETERMINATION OF PHOSPHITE WITH EXCESS CERIC SULFATE IN SULFURIC ACID SOLUTION

	Conditions: 6 N H	A ₂ SO ₄ , boiling	one hour.	
Ml. 0.05 N	Ml. O.l N	Meq. H ₃ PO ₃	H ₃ PO ₃	Found
H ₃ PO ₃	Ceric Sulfate	Taken	Meg.	Percent
19.98	25.00	1.101	1.095	99.6
19.98	25.00	1.101	1.099	99.9
19.98	25.00	1.101	1.092	99.5
19.98	25.00	1.376	1.096	99.6
25.00	25.00	1.376	1.376	100.0 *
25.00	25.00	1.376	1.372	99.7 *
25.00	25.00	1.376	1.374	99.9 *
25.00	25.00	1.376	1.367	99.3 *

3 normal sulfuric acid used.

Table XXXIV shows that phosphite is oxidized by excess ceric sulfate in sulfuric acid solution, but as a quantitative method, the results are slightly lower and less precise than the results obtained by other methods for the determination of phosphite. Preliminary experiments showed that the oxidation requires at least one hour at boiling temperature in six normal sulfuric acid. It is possible that the oxidation



would be faster and more complete in a stronger acid solution than six normal but the data in Table XXXIV show that there is little change in results on increasing the sulfuric acid concentration from three normal to six normal. The method offers no advantage over the method using an excess hypochlorite in the presence of bromide and is much more inconvenient to use.

Summary of Volumetric Methods For The Determination of Phosphite

In Table XXXV is shown a summary of results obtained by the volumetric methods developed for the determination of phosphite. The results are based on the gravimetric procedure in which the phosphite is determined as magnesium pyrophosphate. Results obtained by the method of Wolf and Jung are shown in the same table so that the volumetric methods developed may be compared with a reported volumetric method. The average results listed are averages of results obtained using the methods on several different solutions of phosphorous acid prepared from the same reagent. The average deviation for each method is also shown in Table XXXV.

Table XXXV shows that the results obtained by the volumetric methods are in slightly better agreement with the results obtained by the Wolf and Jung method than with the results of the gravimetric method and are in general slightly lower than the results of the gravimetric method. The reason for this may be that the phosphorous acid contained a small emount of phosphate. Table XXXV shows that for accurate results, the

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TABLE XXXV

SUMMARY OF RESULTS OF VOLUMETRIC METHODS FOR THE DETERMINATION OF PHOSPHITE

Method	Average Percent H _a PO ₃
Wolf and Jung	99.9 ± 0.1
Excess Dichromate, Ferrous Sulfate Backtitration (No Blank Corrections)	100.2 ± 0.1
Excess Dichromate, Ferrous Sulfate Backtitration (Blank Corrections)	100.0 ± 0.1
(Blank Corrections)	100.0 + 0.1
Slight Excess NaClO in Presence of Bromide Direct Titration with NaClO, Deadstop Endpoint	99.9 ± 0.1 99.8 ± 0.1
Excess Ceric Sulfate in H ₂ SO ₄ Solution (Blank corrections)	99.7 ± 0.2

blanks should be taken into consideration in the dichromate method. The results obtained by the ceric sulfate method are lower and less precise than the results by other methods. As in the determination of hypophosphate, the use of a standard hypochlorite solution is most convenient for the determination of phosphite. The oxidation of phosphite by hypochlorite in the presence of bromide, or essentially by hypobromite, is rapid and quantitative. The Wolf and Jung method for determining phosphite appears to be accurate and precise but the method is not as convenient to use as the hypochlorite-bromide method.



VI. DETERMINATION OF HYPOPHOSPHITE

A hypophosphite was required as a basis for the comparison of several methods for its determination. A survey of the literature indicated that a primary standard hypophosphite has not been prepared. Therefore it was necessary to use a hypophosphite which could be made homogeneous and contain no substance which would interfere with the methods used for its determination.

Sodium hypophosphite monohydrate, NaH₂PO₂·H₂O, was used for this purpose. The reagent was prepared by recrystallizing the C.P. reagent three times from redistilled ethyl alcohol and air drying the product. The purified reagent was stored in a tightly stoppered bottle. Brooks (9) found that the reagent prepared in this manner did not contain phosphite and that it could not be completely changed to the anhydrous salt without decomposition by oven drying. Standard solutions of the purified reagent were prepared by dissolving weighed amounts of the salt in freshly boiled water and diluting to one liter with the boiled water.

The composition of the sodium hypophosphite was established by oxidizing aliquots of a solution of the hypophosphite to orthophosphate by repeated evaporations to dryness with aqua regia. The orthophosphate was then precipitated twice as magnesium ammonium phosphate and ignited to magnesium pyrophosphate as outlined in the procedure for the gravimetric determination of phosphite. The composition of the sodium hypophosphite was determined from the weight of pyrophosphate obtained. The results are shown in Table XXXVI.

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TABLE XXXVI

	Sample Number			
	1	2	3	4
Grams Hypophosphite Taken Grams Mg ₂ P ₂ O ₇ Found Per cent NaH ₂ PO ₂ Per cent NaH ₂ PO ₂ ·H ₂ O	0.3000 0.3225 85.00 102.4	0.3000 0.3226 85.03 102.4	0.3000 0.3222 84.92 102.3	0.3000 0.3221 84.89 102.3

GRAVIMETRIC DETERMINATION OF HYPOPHOSPHITE

Table XXXVI shows that the sodium hypophosphite was partially dehydrated and could not be considered as a monohydrate. The average per cent NaH₂PO₂ was calculated from the data in Table XXXVI to be 84.96%, and the average per cent NaH₂FO₂·H₂O was 102.4\%. Data for the volumetric determination of hypophosphite listed in the following tables are based on the average of the gravimetric results. In each table the milliequivalents of NaH₂PO₂ taken are the milliequivalents of NaH₂PO₂ which were present in the sample taken for analysis.

The gravimetric results were compared with those obtained by the method of Wolf and Jung (70). This method was recently reviewed by Jones and Swift (24) who pointed out that the method, as used by Wolf and Jung, gave results which were 0.4 per cent lower than the corresponding gravimetric results. The data of Wolf and Jung show that the oxidation of hypophosphite to phosphite in the first part of the determination is very slow and that it is impossible to find the time in which oxidation is complete to phosphite because of the simultaneous oxidation of the phosphite to phosphate. The sodium hypophosphite was determined according to the procedure described by Wolf and Jung. To measured samples of 0.07 normal hypophosphite in 250 ml. iodine flasks were added ten ml. of six normal sulfuric acid and a measured excess of at least ten ml. of 0.1 normal iodine solution. The flasks were tightly stoppered, the gutters filled with water, and the flasks allowed to stand for 12 hours. The flasks were then opened and a slurry of sodium bicarbonate carefully added until the evolution of carbon dioxide ceased. Fifty ml. of 0.2 molar sodium bicarbonate solution saturated with carbon dioxide was added to each flask, the flasks tightly stoppered and allowed to stand for one hour. The excess iodine was then titrated with standard sodium arsenite using freshly prepared starch solution as indicator. Calculations were made on the basis of blanks treated in the same manner as the samples, substituting water for the hypophosphite solution.

Table XXXVII shows that the results obtained by the method of Wolf and Jung are approximately 1.3 per cent lower than the results of the gravimetric method. A disadvantage of the Wolf and Jung method is the loss of iodine when the acid solution of iodine is treated with sodium bicarbonate. This loss depends on the amount of iodine present and on the temperature. The only way that the method could be used accurately would be to have the same amount of iodine present in the blanks that would be present in the sample after the oxidation of the hypophosphite to phosphite. For an unknown sample, this would be rather difficult to arrange.

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TABLE XXXVII

DETERMINATION OF HYPOPHOSPHITE BY THE METHOD OF WOLF AND JUNG

Ml. 0.07 N	Ml.O.l N	Meq. NaH2PO2	NaH2PO2 Found	
NaH ₂ PO ₂	Iodine	Taken	Meq.	Percent
19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98	25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	1.545 1.545 1.545 1.545 1.545 1.545 1.545 1.545	1.530 1.524 1.528 1.525 1.525 1.525 1.522 1.524	99.0 98.6 98.9 98.7 98.7 98.7 98.5 98.6

Volumetric methods for the determination of hypophosphite developed during this work and described in the following pages of this thesis support the conclusion that the Wolf and Jung method for determining hypophosphite gives low results.

A. Oxidation of Hypophosphite by Excess Dichromate In Sulfuric Acid Solution

Experiments were conducted to determine if hypophosphite is oxidized by excess potassium dichromete and to determine the time required to complete the oxidation in 12 normal sulfuric acid at the temperature of a boiling water bath.

To measured samples of 0.05 normal sodium hypophosphite were added a measured excess of standard potassium dichromate and sufficient concentrated sulfuric acid to make the resulting mixture 12 normal in acid. The mixtures were heated in a boiling water bath for various time

intervals and the excess dichromate determined iodometrically after neutralizing part of the sulfuric acid present as described in the section of this thesis dealing with the determination of hypophosphate by excess dichromate. Blanks were determined in the same manner, substituting water for the hypophosphite solution. The results are shown in Table XXXVIII.

TABLE XXXVIII

DETERMINATION OF HYPOPHOSPHITE BY EXCESS DICHROMATE IN 12 NORMAL SULFURIC ACID AS A FUNCTION OF TIME OF HEATING

Ml. 0.05 N	Ml. O.l N	Meq, NaH ₂ PO ₂	Heating Time	NəH₂P	0 ₂ Found
NaH ₂ PO ₂ (a)	K ₂ Cr ₂ O ₇	Taken	Min.	Meq.	Percent
25.00 25.00 25.00 25.00 25.00 25.00	25.00 25.00 25.00 25.00 25.00 25.00	1.282 1.282 1.282 1.282 1.282 1.282	10 15 25 40 70	1.140 1.269 1.281 1.278 1.283	88.9 99.0 99.9 99.6 100.1
19.98 19.98 19.98 19.98	25.00 25.00 25.00 25.00	1.545 1.545 1.545 1.545	60 60 60	1.541 1.543 1.542 1.543	99.7 (b) 99.9 (b) 99.7 (b) 99.9 (b)

(a) The 19.98 ml. samples were from a different hypophosphite solution than the 25.00 ml. samples; the solutions were prepared from the same salt.

(b) Calculations made on the basis of blanks.

Table XXXVIII shows that hypophosphite is completely oxidized by excess dichromate in one hour at the temperature of a boiling water bath and that the oxidation is not complete in 15 minutes.

B. Oxidation of Hypophosphite by Excess Sodium Hypochlorite in a Bicarbonate Medium

87

Schwicker (57) found that phosphite could be oxidized to phosphate in a bicarbonate medium with no interference from hypophosphite.

To measured samples of a sodium hypophosphite solution were added one gram of sodium bicarbonate and a measured excess of sodium hypochlorite solution. After standing for different time intervals an excess of standard sodium arsenite was added, and then one gram of potassium bromide. The excess arsenite was titrated with the standard hypochlorite solution using Bordeaux indicator.

It was found that after two and one-half hours the hypophosphite was oxidized about 10 per cent and after 13 hours about 50 per cent assuming that it was oxidized to phosphate. It may be possible to determine phosphite with excess hypochlorite in the presence of a small amount of hypophosphite with little interference from the latter, but it seems unlikely that the determination could be made in the presence of a large amount of hypophosphite.

C. Oxidation of Hypophosphite by Excess Hypochlorite in the Presence of Bromide

Experiments were carried out to study the oxidation of hypophosphite by a slight excess of hypochlorite in a solution containing potassium bromide and souium bicarbonate. It was found that like hypophosphate, but unlike phosphite, the oxidation was very slow and the procedure used for the determination of phosphite was not successful.

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The oxidation was found to be more rapid when a large excess of hypochlorite was used in the presence of bromide, but the large loss of hypochlorite under these conditions made the method unreliable.

D. Oxidation of Hypophosphite by Excess Hypochlorite in Sulfuric Acid Solution

In order to use hypochlorite in a sulfuric acid solution, it was first necessary to determine the stability, or change in oxidizing capacity, of hypochlorite in an acid solution. To 19.98 ml. samples of O.1 normal sodium hypochlorite in 250 ml. iodine flasks were added 25 ml. of water and 10 ml. of six normal sulfuric acid. The flasks were tightly stoppered, the gutters filled with saturated potassium iodide solution, and the flasks allowed to stand in the dark for various time intervals. The flasks were then cooled in ice-water to reduce the pressure in the flasks in order that when they were carefully opened the potassium iodide solution was drawn into the flasks. The flasks were allowed to stand for about one minute and the liberated iodine titrated with standard sodium thiosulfate. The results are shown in Table XXXIX.

Table XXXIX shows that there is a loss of approximately 0.05 ml. of 0.1 normal hypochlorite in approximately two hours in one normal sulfuric acid. This does not necessarily mean that the hypochlorite remains as hypochlorite, or as hypochlorous acid, but that its oxidizing capacity toward potassium iodide in acid solution is only slightly



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TABLE XXXIX

Standing Time	Ml. O.l N
Minutes	Ne ₂ S ₂ O ₃
0 0 30 45 60 90 125	20.29 20.27 20.29 20.27 20.26 20.26 20.26 20.24 20.24 20.23

OXIDIZING CAPACITY OF SODIUM HYPOCHLORITE IN ONE NORMAL SULFURIC ACID

changed on standing. Its decomposition products probably liberate iodine under the same conditions.

Experiments were conducted to determine the extent of the oxidation of hypophosphite by excess sodium hypochlorite in dilute sulfuric acid solution. To measured samples of 0.06 normal hypophosphite in 250 ml. iodine flasks were added a measured excess of standard sodium hypochlorite and ten ml. of six normal sulfuric acid. The flasks were tightly stoppered and the gutters filled with saturated potassium iodide solution. After standing in the dark for various time intervals, the flasks were cooled in ice water to reduce the pressure which had built up in the flasks during the reaction. The flasks were then carefully opened and the potassium iodide solution was drawn into the flasks by the reduced pressure. The flasks were allowed to remain stoppered for about one minute and the liberated iodine titrated with standard sodium thiosulfate solution. Blanks were determined in the same manner, substituting water for the hypophosphite solution, and calculations made on the basis of the blanks. The blanks were allowed to stand for approximately the same time as the samples.

The hypochlorite solution was standardized iodometrically against the standard thiosulfate solution by pipetting 25.00 ml. of the hypochlorite solution into an iodine flask, adding 20 ml. of water, 10 ml. of six normal sulfuric acid, and 10 ml. of saturated potassium iodide solution. The liberated iodine was then titrated with the standard thiosulfate solution.

Table XL shows that hypophosphite is not completely oxidized to phosphate in six hours by excess sodium hypochlorite in approximately one normal sulfuric acid solution. The data show that the oxidation is complete in ten hours, and that there is no appreciable change in the results if the time of standing is increased to 19 hours. The data also show that the oxidation is somewhat slower in hydrochloric acid than it is in sulfuric acid of the same concentration.

The use of hypochlorite in acid solution for the determination of hypophosphite gives fairly accurate and precise results as compared to the gravimetric procedure, but the long time required for the oxidation makes the method inconvenient to use. Also, the flasks must be opened very carefully after the oxidation because of the pressure built up during the reaction. Even with the tightly fitting stoppers of the iodine flasks, a few of the samples showed evidence of leakage during

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TABLE XL

Ml. 0.06 N	Ml. O.l N	Meg. NaH ₂ PO ₂	Standing	NaH ₂ PO ₂	Found (b)
NaH ₂ PO ₂ (a)	NaClO	Taken	Time	Meq.	Percent
19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 19.98 25.00 25.00	19.98 19.98 19.98 25.00 19.98 25.00 19.98 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00 25.00	1.026 1.319 1.026 1.026 1.319 1.026 1.545 1.026 1.545 1.169 1.169 1.169 1.169 1.169 1.169 1.463 1.463	50 min. 60 min. 70 min. 80 min. 90 min. 100 min. 10 hr. 10 hr. 10 hr. 10 hr. 10 hr. 10 hr. 14 hr. 17 hr. 17.5 hr. 18 hr. 18 5 hr. 19 hr. 19 hr.	0.954 1.215 0.977 0.979 1.238 0.942 1.523 1.027 1.025 1.535 1.169 1.166 1.168 1.464 1.464 1.461	93.0 92.1 95.2 95.4 93.8 91.8 (c) 98.5 100.1 99.9 (c) 99.3 100.0 99.7 99.9 99.7 100.1 99.9

DETERMINATION OF HYPOPHOSPHITE WITH EXCESS HYPOCHLORITE IN DILUTE SULFURIC ACID AS A FUNCTION OF TIME OF STANDING

(a) Several solutions prepared from the same salt were used.

(b) Calculated on the basis of blanks which amounted to a loss of 0.04 to 0.07 ml. of 0.1 N NaClO.

(c) 10 ml. of 6 N HCl used in place of 10 ml. of 6 N H_2SO_4 .

standing as indicated by coloration of the potassium iodide solution in the gutters of the flasks; these samples were discarded.

E. Oxidation of Hypophosphite by Excess Ceric Sulfate in Nitric Acid Solution

Moeller and Quinty (42) determined hypophosphate by excess ceric nitrate in nitric acid solution at boiling temperature. The excess

ceric nitrate was determined by a potentiometric titration with standard arsenite.

Experiments were conducted to determine if hypophosphite could be determined with excess ceric sulfate in nitric acid solution. To measured samples of 0.05 normal hypophosphite in 150 ml. beakers were added a measured excess of standard ceric ammonium sulfate and ten ml. of concentrated nitric acid. The beakers were allowed to stand for various time intervals and heated to boiling for various times. The excess ceric sulfate was determined by a potentiometric titration with a standard sodium arsenite solution.

It was found that the oxidation to phosphate was approximately 50 per cent completed in one hour and 60 per cent completed in 12 hours at room temperature. The oxidation was found to be more rapid when the mixture was boiled; the per cent oxidized varied from 99 to 101 per cent when the boiling time was varied from five to 20 minutes. Much difficulty was experienced in heating the samples because of the bumping which resulted in some loss of solution. When the volume of concentrated nitric acid added was increased from ten ml. to 20 ml., the per cent oxidized increased to 102 per cent. Because of the erratic results which were found, the procedure could not be considered as a quantitative method for determining hypophosphite.

F. Oxidation of Hypophosphite By Excess Ceric Sulfate in Sulfuric Acid Solution

It has been shown that solutions of hexanitrato ammonium cerate are more stable in hot sulfuric acid than in hot nitric acid (61). It was considered that ceric ammonium sulfate may also be more stable in hot sulfuric acid solution than in hot nitric acid solution. For this reason, it was considered that hypophosphite might be determined in sulfuric acid solution with excess ceric sulfate with more consistent results.

In order to overcome the difficulty of the bumping encountered in heating nitric acid solutions of hypophosphite and ceric sulfate, 250 ml. Erlenmeyer flasks with ground glass joints which could be attached to condensers were used for heating the sulfuric acid solutions. It was found by experiment that a ceric sulfate solution standardized against a standard arsenite solution by the recommended procedure using ferroin as indicator could be standardized by the reverse procedure in which the ceric sulfate was titrated with the standard arsenite solution. It was also found that a ceric sulfate solution could be standardized by a titration in which the ceric sulfate was titrated with a standard ferrous ammonium sulfate solution. The results indicated that it was possible to determine an excess ceric sulfate in sulfuric acid solution by a titration with either standard arsenite or standard ferrous ammonium sulfate using ferroin as indicator.

Preliminary experiments in which hypophosphite was determined with excess ceric sulfate in sulfuric acid solution gave results of slightly over 100 per cent hypophosphite when blanks were not taken into consideration, indicating a loss of ceric sulfate. It was also found that the oxidation to phosphate required from 45 to 60 minutes at boiling temperature for its completion.

Determination of hypophosphite by excess ceric sulfate in sulfuric acid solution determining the excess by a titration with standard sodium arsenite. To measured samples of 0.06 normal hypophosphite in flasks which could be attached to water-cooled condensers were added a measured excess of standard ceric sulfate and seven ml. of concentrated sulfuric acid. The mixtures were refluxed for one hour and the condensers washed with about 30 ml. of water; the washings were collected in the attached flasks. Three drops of osmium tetroxide solution and two drops of ferroin indicator were added to each flask and the excess ceric sulfate titrated with a standard sodium ersenite solution. Blanks were determined in the same manner, substituting water for the hypophosphite solution, and calculations were made on the basis of the blanks. The results are shown in Table XLI.

Table XLI shows that hypophosphite is completely oxidized by excess ceric sulfate in dilute sulfuric acid solution at boiling temperature in one hour. It also shows that the blanks are sufficiently large that they must be taken into consideration. Blanks were determined by the same procedure during this work and the volume of 0.1 normal ceric sulfate lost under the same conditions of time of boiling and acid concentration varied from 0.03 to 0.08 ml. The blanks were constant for a particular ceric sulfate solution but varied slightly in solutions



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TABLE XLI

DETERMINATION OF HYPOPHOSPHITE WITH EXCESS CERIC SULFATE (Backtitration with Arsenite)

M1. 0.06 N	Ml. O.l N	Meg. NaH ₂ PO ₂	N əH ₂ F	0 ₂ Found
NaH ₂ PO2	Ceric Sulfate	Taken	Meq.	Percent
25 00	25 00	7).63	1 461	99 9
25.00	25.00	1.463	1.460	99.8
25.00	25.00	1.463	1.462	99.9
25.00	25.00	1.463	1.460	99.8
19.98	25.00	1.545	1.545	100.0
19.98	25.00	1.545	1.545	100.0
19 .9 8	25.00	1.545	1.544	99.9
19.98	25.00	1.545	1.544	99.9
0.0	25.00			0.04 (a
0.0	25.00		-	0.04 (a
0.0	25.00			0.05 (a
0.0	25.00			0 . 05 (a

Conditions: 4.5 N H₂SO₄, boiling time one hour.

* Two different solutions prepared from the same salt were used. (a) Ml. O.l N ceric sulfate lost.

prepared from the same bottle of reagent grade ceric ammonium sulfate. This indicates that the reagent was not completely homogeneous and that it contains a small amount of substance which is oxidized at boiling temperature in sulfuric acid solution.

Determination of hypophosphite by excess ceric sulfate in sulfuric acid solution, determining the excess by a titration with a standard ferrous ammonium sulfate. Measured samples of a 0.05 normal hypophosphite solution were treated with a measured excess of standard ceric sulfate and five ml. of concentrated sulfuric acid. The mixtures were

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heated for one hour under reflux. The flasks were cooled to room temperature, two drops of ferroin added, and the excess ceric sulfate titrated with standard ferrous ammonium sulfate solution. The ferrous ammonium sulfate solution was standardized against the standard ceric sulfate solution. The endpoint in the titration of the ceric sulfate with the ferrous solution was marked by a sharp change in color from light green to reddish orange. Blanks were determined in the same manner, substituting water for the hypophosphite solution, and calculations were made on the basis of the blanks. The results are shown in Table XLII.

Table XLII shows that hypophosphite can be determined with excess ceric sulfate and the excess determined by a titration with standard ferrous ammonium sulfate. It also shows that the amount of excess ceric sulfate used is not critical if the amount of excess is at least 70 per cent of the amount required. The minimum excess required was not determined.

The procedure in which the excess ceric sulfate is determined with ferrous ammonium sulfate is somewhat easier to use than the procedure in which arsenite is used because the endpoint in the former is somewhat sharper and gives very good warning of its approach. However, this advantage is somewhat minimized by the necessity of keeping a standard ferrous ammonium sulfate solution which is unstable to air oxidations.



TABLE XLII

DETERMINATION OF HYPOPHOSPHITE WITH EXCESS CERIC SULFATE IN SULFURIC ACID SOLUTION (Backtitration With Ferrous Ion)

M1.0.06 N	Ml. O.l N	Meq. NaH ₂ PO ₂	NaHzP	0 ₂ Found
NaH ₂ PO ₂ *	Ceric Sulfate	Taken	Meq.	Percent
9.99	25.00	0,579	0.576	99.5
9.99	25.00	0.579	0.579	100.0
9.99	25.00	0.579	0.578	. 99.8
19.98	25.00	1.158	1,157	99.9
25.00	25.00	1.449	1.448	99.9
25.00	25.00	1.449	1.448	99.9
25.00	25.00	1.449	1.449	100.0
25.00	25.00	1.463	1.461	99.9
25.00	25.00	1.463	1.460	99.8
25.00	25.00	1.463	1.462	99.9
0.0	25.00			0.04 (a
0.0	25.00	The Arch		0.04 (a
0.0	25.00	-		0.03 (;

Conditions: $3.5 \text{ N} \text{ H}_2 \text{SO}_4$, boiling time one hour.

* Different solutions prepared from the same salt were used. (a) Ml. O.l N ceric sulfate lost.

Summary of Volumetric Methods For The Determination of Hypophosphite

In Table XLIII is shown a summary of the results, and the average deviations obtained by the methods developed for the determination of hypophosphite based on the gravimetric procedure in which the hypophosphite is determined as magnesium pyrophosphate. The average results listed are averages of results obtained using the methods on several different solutions of the sodium hypophosphite prepared from the same salt. The results obtained by the method of Wolf and Jung are included in the table as a comparison with the volumetric methods developed during this work.

TABLE XLIII

SUMMARY OF VOLUMETRIC METHODS FOR THE DETERMINATION OF HYPOPHOSPHITE

Method	Average Percent NaH ₂ PO ₂
Excess Dichromate (Blank correction)	99.8 ± 0.1
Excess NaClO in H ₂ SO ₄ Solution	99.8 ± 0.2
Excess Ceric Sulfate in H ₂ SO ₄ Solution	99.9 ± 0.1
Wolf and Jung	98.7 ± 0.1

Table XLIII shows that the results obtained by the volumetric methods were slightly lower than the results obtained by the gravimetric method. The reason for this may possibly be due to the presence of a small amount of phosphate in the hypophosphite or a slight air oxidation of the hypophosphite solution. The method in which hypochlorite is used in a sulfuric acid solution is not as precise as the other methods because of the difficulty in making an accurate determination of the excess hypochlorite and its decomposition products. The data in Table XLIII show that the Wolf and Jung method for the determination of hypophosphite gives low results.

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VII. DISCUSSION

The volumetric methods developed during this work for the determination of hypophosphate, phosphite, and hypophosphite made use of standard solutions of sodium hypochlorite, potassium dichromate, and ceric sulfate.

The oxidation of hypophosphoric, phosphorous, and hypophosphorous acids to phosphoric acid by excess potassium dichromate in 12 normal sulfuric acid is complete in one hour at the temperature of a boiling water bath; the minimum times required to complete the oxidations are approximately 50, 25, and 40 minutes respectively. Heating for periods longer than one hour has no apparent effect on the results. The facts that the oxidation of phosphorous acid is more rapid than the oxidation of hypophosphoric acid, and that the oxidation of the latter is faster in stronger acid suggest that the rate of oxidation of the hypophosphoric acid is controlled by its hydrolysis. The dichromate method is limited to the determination of each acid alone, and other reducing substances must not be present.

Because of the drastic oxidizing conditions used in the dichromate method, the flasks used for the determination must be thoroughly cleaned before use, preferably with hot chromic acid cleaning solution, and thoroughly rinsed. For the same reason, samples should not be delivered from a burette as a slight contamination with stopcock lubricant may result. If these precautions are taken the blanks are small but should



be taken into consideration for accurate results. It is possible that the small blanks may result from a small amount of reducing substance in the sulfuric acid. The minimum amount of excess dichromate required for the oxidations was not determined, but the oxidations were complete using a 100 per cent excess and if the excess was increased to 200 per cent there was no apparent change in the results.

The excess dichromate can be determined either by adding a measured excess of ferrous ion and titrating this excess with standard potassium dichromate, or by an iodometric determination after adjusting the sulfuric acid concentration to approximately three normal. The iodometric method is somewhat more inconvenient because with samples containing a large amount of sulfuric acid, part of the acid must be neutralized which requires some care to prevent loss of solution due to spattering. This disadvantage is somewhat minimized in that it involves a direct titration of the excess dichromate by means of the iodine liberated by the dichromate and all solutions used are stable to air oxidation.

For best results the volume of the sample taken for analysis should not exceed 30 to 40 ml. because larger volumes require a larger amount of sulfuric acid which is an inconvenience in determining the excess dichromate.

Hypophosphate, phosphite, and hypophosphite can be determined under suitable conditions with a standard solution of sodium hypochlorite. Hypophosphate is quantitatively oxidized to phosphate by an excess of sodium hypochlorite in a sodium bicarbonate medium in 30 minutes.

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Longer periods of standing up to two hours have no apparent effect on the results. The minimum excess of hypochlorite required was not determined, but consistent results were obtained when the amount of excess hypochlorite was varied between 60 and 300 per cent of the amount required for the oxidation. The excess hypochlorite can be accurately determined by adding an excess of standard sodium arsenite solution and titrating this excess with a standard sodium hypochlorite solution using Bordeaux to detect the equivalence point. The endpoint can also be determined potentiometrically or by the deadstop procedure. The excess hypochlorite can also be determined by means of a titration with standard sodium arsenite in which the equivalence point is determined either potentiometrically or by the deadstop technique. The electrometric methods. especially the potentiometric method, require more time. The iodometric method of determining hypochlorite in the presence of a buffer does not give satisfactory results, and the irregularities found in the method require more study. This is discussed more fully in the section of this thesis dealing with the determination of phosphite with hypochlorite.

Phosphite can be quantitatively oxidized to phosphate by an excess of sodium hypochlorite but the oxidation is much more rapid in a solution containing bromide and made neutral with sodium bicarbonate. The use of a large excess of hypochlorite in the presence of bromide should be avoided because of side reactions between hypochlorite and bromide which produce ions other than hypobromite. The oxidation of phosphite by hypochlorite in the presence of bromide is not fast enough to allow

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a direct titration using an irreversible indicator such as Bordeaux, but the direct titration can be made if the endpoint is detected by means of the deadstop technique which acts in a manner similar to a highly reversible indicator.

Hypophosphite is not quantitatively oxidized by excess hypochlorite in a neutral solution in 12 hours, but the oxidation proceeds sufficiently that the presence of hypophosphite in appreciable amounts may interfere with the hypochlorite determination of hypophosphate and phosphite, with less interference in the case of the latter. Hypophosphite is oxidized by an excess of hypochlorite in a solution containing bromide and bicarbonate, but the oxidation is much slower than the oxidation of phosphite under these conditions. A large excess of hypochlorite is required which causes erratic results.

Hypophosphite is quantitatively oxidized to phosphate by an excess of sodium hypochlorite in dilute sulfuric acid solution but the oxidation requires a minimum of about ten hours for completion. The excess hypochlorite can be accurately determined iodometrically because no buffer is present. The time required for the method and the care which must be taken in using it make the method impractical, especially since shorter methods for the determination of hypophosphite have been developed, for example, the dichromate and ceric sulfate methods

The optimum pH range for quantitative oxidation of hypophosphate (12) and phosphite by sodium hypochlorite is between seven and eight but in this pH range hypophosphite is oxidized only very slowly.

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Phosphorous and hypophosphorous acids are quantitatively oxidized to phosphoric acid in dilute sulfuric acid solution by an excess of ceric sulfate at boiling temperature in one hour. The excess ceric sulfate can be accurately determined by a titration with either standard ferrous ammonium sulfate or standard sodium arsenite using ferroin as indicator. The use of ferrous ammonium sulfate provides an endpoint that is somewhat sharper and more easily determined than the use of arsenite. It is necessary to run blanks along with the samples and make the celculations on the basis of the blanks or high results will be found. Hypophosphoric acid is not completely oxidized to phosphoric acid by an excess of ceric sulfate in dilute sulfuric acid solution in one hour at boiling temperature and it was considered to be impractical to reflux the mixture for a longer time since accurate shorter methods for the determination of hypophosphate have been developed. The oxidation may proceed by hydrolysis which is slower in dilute sulfuric acid solution than in the 12 normal acid used in the dichromate method.

Some basis must be available for determining if an analytical procedure is accurate. Several studies have shown that the disodium dihydrogen hypophosphate hexahydrate prepared by the method of Leininger and Chulski is a primary standard (12,37,42). The results found in this work substantiate this. Because no primary standard phosphite or hypophosphite is available, preparations which were not primary standards were used. The volumetric results were compared with the results obtained by the gravimetric procedure in which the phosphite and hypophosphite were determined as magnesium pyrophosphate, a procedure which

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has been used by others as a basis for an evaluation of volumetric methods.

In addition to accuracy, other factors which must be considered in making an evaluation of volumetric methods include precision, the time required for the analysis, whether or not the method is empirical, the number of steps in the procedure, and the stability of the standard solutions.

The hypochlorite method for the determination of hypophosphate gave accurate and precise results and the method is reasonably rapid. The method is not empirical and blanks are negligibly small. The standard hypochlorite solution is reasonably stable.^{*} The dichromate method gave results which were accurate and precise but the method is not as convenient to use as the hypochlorite method especially since it requires heating and takes longer.

The best procedure for the determination of phosphite is the method in which hypochlorite is used in the presence of bromide. It gave results which agreed with the method of Wolf and Jung and which were one to two parts per thousand lower than the gravimetric results. The Wolf and Jung method takes much longer to carry out and it has the disadvantage that it requires the use of a standard iodine solution which is subject to change in titer due to the volatility of iodine. The dichromate and ceric sulfate methods can be used for the determination of phosphite but the results using ceric sulfate were not as

^{*} For example, it was found during this work that the normality of a sodium hypochlorite solution changed from 0.1108 to 0.1106 in 16 days when stored in a brown bottle at room temperature.



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precise as the results found by the other volumetric methods. The ceric sulfate and dichromate methods for the determination of phosphite have no advantage over the other methods developed.

The ceric sulfate and dichromate methods for the determination of hypophosphite gave equally accurate and precise results. Each method requires about the same time but it is somewhat easier to determine an excess of ceric sulfate than an excess of dichromate because the former can be titrated directly in the more dilute sulfuric acid solution. However, the blanks are larger in the ceric sulfate method and must be taken into consideration whereas they may be neglected in the dichromate method unless very accurate analyses are required. The Wolf and Jung method for determining hypophosphite gave results which were about 1.3 per cent lower than the results of the gravimetric and other volumetric methods used.

The method for determining hypophosphite using an excess of hypochlorite in sulfuric acid solution is too time-consuming to be practical especially since accurate shorter methods have been developed.

VIII. SUMMARY

New volumetric methods were developed for the determination of hypophosphate, phosphite, and hypophosphite.

Hypophosphate was determined with an excess of standard sodium hypochlorite in a bicarbonate medium. The excess hypochlorite was determined with standard sodium arsenite.

It was found that phosphite, in the presence of bromide and bicarbonate, was quantitatively oxidized to phosphate by a slight excess of hypochlorite. The oxidation was found to be sufficiently rapid that the phosphite could be determined by a direct titration with standard hypochlorite. The equivalence point in the titration was detected by the deadstop technique; the use of Bordeaux as indicator in this titration was not satisfactory.

It was found that hypochlorite in a buffered medium could be determined either by adding a measured excess of standard arsenite and titrating this excess with standard hypochlorite using Bordeaux as indicator or by titrating the hypochlorite with standard arsenite, determining the endpoint either potentiometrically or by the deadstop procedure. It was found that the iodometric determination of hypochlorite in a buffered solution was unsatisfactory and gave erratic results.

Hypophosphite and phosphite were determined by an excess of standard ceric sulfate in dilute sulfuric acid at boiling temperature and the excess ceric sulfate was determined by a titration with either standard ferrous ammonium sulfate or standard sodium arsenite. Hypophosphate, phosphite, and hypophosphite were quantitatively oxidized to phosphate by an excess of standard potassium dichromate in 12 normal sulfuric acid at the temperature of a boiling water bath. The excess dichromate was determined either iodometrically after neutralizing part of the sulfuric acid, or by means of a standard ferrous ammonium sulfate solution.

The volumetric methods which were developed for the determination of hypophosphate show that the disodium dihydrogen hypophosphate prepared by the method of Leininger and Chulski (37) is a primary standard. The volumetric methods developed for the determination of phosphite and hypophosphite gave results which agreed within two parts per thousand with the results obtained by the gravimetric method in which the phosphite and hypophosphite are determined as magnesium pyrophosphate.

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